RHEOLOGICAL AND CURING CHARACTERISTICS OF THERMOSETTING PLASTICS AS RELATED TO INJECTION MOULDING

K.T. PAUL B.Sc. APRI

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Summary

This thesis discusses the measurement of the flow characteristics of thermosetting plastics relevant to injection moulding. Three basic techniques have been used, a capillary viscometer, a variable torque rheometer and an oscillating disc rheometer.

The capillary viscometer measured the shear stress/shear rate characteristics of a compounded melt prepared in the injection barrel and the results correlated well with those of a capillary viscometer fitted in place of the nozzle of the injection machine. Phenolic, urea and melamine formaldehyde materials show a power law relationship between shear stress and apparant shear rate up to shear ratesof $10^3 \mathrm{sec}^{-1}$. At very low shear rates, phenolic and melamine materials show Bingham flow behaviour merging into laminar flow. At high shear rates, the phenolic shows plug flow as the melt emerges from the injection nozzle and mould gate. The capillary viscometer gave different results when used with granular (i.e. non-worked) materials and only gave a general indication of the material viscosity.

The variable torque rheometer gave an empirical measure of the duration of fluidity of a thermosetting material which correlated well with results obtained during injection moulding trials.

Only the oscillating disc rheometer viscosity recorded changes throughout the complete crosslinking reaction. The dynamic torque measurement is different to the continuous shear viscosity measurements made with the capillary and torque rheometers. There is a general correlation between their measurements but more important is the possibility of correlating the oscillating torque value (after separation into elastic and viscous components) with the crosslinking process and the chemical reactions involved during the material formation and moulding processes. The oscillating disc rheometer enables the cure rate of a material to be determined as well as the chemical kinetic reaction constants. An Arrhenius type relationship exists between the temperature, and gelation and cure time.

The thesis shows how the results of each of the three techniques correlate well with the injection moulding process that the three techniques form a necessary, complementary combination of data and which are not mutually replaceable.

These techniques enable the injection moulding behaviour of materials to be predicted, although injection moulding results show that the process itself involves a complex interaction between machine, mould and material and that none of the proposed or current techniques will provide a precise measure of 'injection mouldability'. The proposed technique does however, provide a better foundation on which to base material control and evaluation studies.

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Chapter 1 Introduction to Thermosetting Plastics and Processing

It is well known that plastics materials may be divided into two groups, thermoplastics and thermosetting plastics. The behaviour of these materials both during the forming of useful articles from the plastics and also during their service life are quite different.

A thermoplastic material often consists mainly of polymer and its properties are largely determined during the process of polymer formation. However, other materials are sometimes added during a later compounding operation and in such cases the properties of the material are determined by both the polymerisation and the compounding processes. When a thermoplastic material is moulded to produce an article, it's properties do not change greatly and this stability makes it possible to use a variety of physico-chemical or mechanical tests to study the state of the material at any stage of the process.

Thermosetting moulding materials on the other hand are quite different. They frequently contain a major proportion of non-polymeric material as a reinforcement or filler and the polymer itself may be present in the form of a low molecular weight precursor (or indeed of non-polymeric chemicals) which reacts during the forming process to give polymer which is irreversibly crosslinked and is incapable of melting or "plasticizing". This makes it very difficult to measure the properties of such a material as these properties are changing irreversibly while the measurement is being made.

For many years thermosetting materials were processed only by compression moulding. In this process the cold or sometimes preheated material is placed in a heated mould which is closed under considerable pressure causing the material to melt and flow within the confines of the mould. In such circumstances, the properties of the moulding material could vary over quite a wide range without causing serious problems, especially if the mould was of a relatively simple shape.

Later, transfer moulding was developed in which the material was preheated in a separate part of the mould and then forced through an orifice or runner into the mould proper. The requirements for a transfer moulding material were a little different to those required for compression moulding but could still vary somewhat without causing problems.

Most recent developments are concerned with the injection moulding process (which was originally developed for and is largely used with thermoplastics). In this process, the material is both conveyed and melted by the rotation of an Archimedian screw in a heated cylinder. The melt is then forced via a series of runners into the mould under pressure by the now, non-rotating screw acting as a ram. The material may change substantially during these processes and the final crosslinking or curing of the material takes place in the mould. In the case of injection moulding, the way in which the material properties change over the range of temperatures and shear rates used is highly important to the operation of the injection moulding process which is essentially a continuous process.

There is a limited amount of information available concerning the effect of time and temperature on the changes in properties of thermosetting moulding materials (often referred to by the jargon used in industry as "thermosets) but this is not well correlated and does not always have special reference to the injection moulding process. There is a need therefore to study the ways of measuring such transient properties to obtain either fundamental scientific data or at least reliable and sound empirical data which can be related to the behaviour of thermosetting moulding materials during the injection moulding process. These data would be of considerable help to the thermosetting moulding industry as they will result in a cost saving by reducing wastage of material and production time. Material wastage has been estimated as 11% and time wastage as 19% for thermoplastics injection moulding (1). Similar figures can be expected with the injection moulding of thermosetting materials but unlike thermoplastics, waste materials e.g. substandard mouldings, sprues and runners cannot be re-used since the material has irreversibly cross-linked.

Chapter 2 Literature Survey

2.1 Properties of Thermosetting Moulding Materials

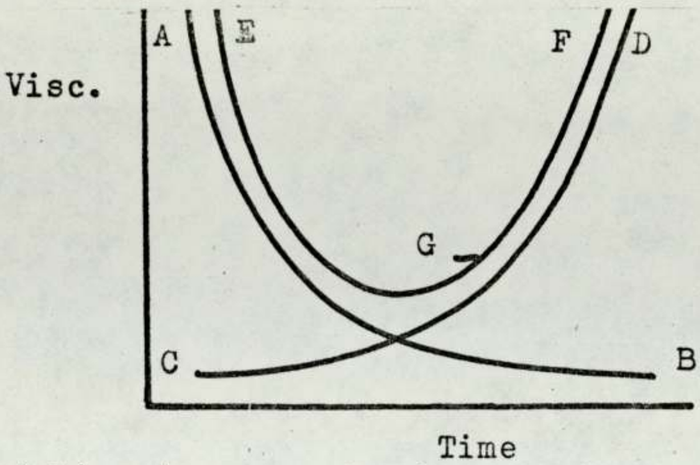


Fig.1 Schematic representation of viscosity changes during the moulding of thermosetting materials.

When a thermosetting material is heated to say 150°C, two competing processes occur and these are illustrated in Fig.1. Firstly the viscosity of the material decreases i.e. it becomes plastic due to the resin melting or to a considerable reduction of the resin viscosity (AB). Secondly a chemical reaction takes place which causes the degree of polymerization and hence the viscosity of the polymer to increase (CD). The resultant viscosity/time curve is therefore U-shaped and represents the change from a solid to a viscous fluid to the final thermo set solid state (EF).

In industrial jargon, the minimum viscosity is frequently referred to as the plasticity or flow of a material, the time at which the viscosity has increased significantly (G) as the flow life of the material or the onset of precuring, and the more rapid increase in viscosity and crosslinking (GF)as the curing time. When the viscosity can no longer increase, ie.the crosslinking reaction is largely complete, the material is said to be cured. Both the rate of softening and the rate of crosslinking are dependent on the temperature and cross linking reactions are exothermic.

In addition to this, many thermosetting materials contain water or liberate water of condensation or other products which can act as plasticizers and thus increase the fluidity of the material. (2).

In a moulding process, the way in which the material flows is affected by two factors, the viscous flow of the material and the adhesion of the viscous melt to the mould surface. The relative contribution of these two components can vary with increasing crosslinking (3) and the viscosity of the melt can also be affected by the presence of unfused particles of the moulding material.

Measurement of Cure

When a thermosetting material has crosslinked to the required degree, the moulding is said to be cured and it is then ejected from the mould. The industrial jargon "cured material" is difficult to quantify since it is usually expressed as "that degree of crosslinking at which a moulding has attained it's required properties" Different properties of cured mouldings attain maximal or minimal values at different degrees of crosslinking (4) and thus no single definition of cure is possible in terms of physical property measurements.

The degree of cure is determined by a wide variety of methods and these may be divided into the following categories:-

a) Solvent extraction. A widely used example of solvent extraction involves the measurement of the acetone soluble fraction of a powdered, phenolic moulding which is refluxed with acetone.

b) Solvent or chemical attack. Urea formaldehyde mouldings are boiled in water and the resultant surface damage is used to indicate the degree of cure. Sometimes a dye (Rhodamine B) is used to accentuate the damage while melamine formaldehyde mouldings are boiled in sulphuric acid.

(c) Measurement of physical properties. Several techniques have been used including the measurement of flexural strength or modulus particularly at elevated temperatures, the resistance to penetration by a heated needle, and, more frequently by the formation of a glossy, blister free surface to the moulding.

(d) Measurement of residual chemical reactivity using techniques such as differential scanning calorimetry.

(e) Measurement of chemical composition and residual chemical groups using a wide range of techniques including infra red spectroscopy.

For moulding production, methods a, b and c are commonly used while methods d and e are largely limited to use in the research laboratory. In addition, the moulding must be suitable for its intended use i.e. it must have adequate strength, its surface must be free from blisters and it must be dimensionally stable.

2.2 Processing of Thermosetting Materials

The moulding processes and the conditions used in these processes are illustrated in Fig.2 and Table 1. There is no need to examine the compression, or transfer moulding processes here but the injection moulding process is germane to this project and must be examined in detail. Certain thermosetting materials e.g. phenolics and polyester based dough moulding materials can be extruded but the process is not used to any significant extent commercially. Laminating resembles the compression moulding process but involves the use of continuous sheets of reinforcement impregnated with a thermosetting resin. Other laminating techniques using liquid resins are frequently encountered in the polyester and epoxy industries but use a wide variety of manual or semiautomated techniques and can be ignored since they are not relevant to this project.

Certain thermosetting plastics e.g. polyester based dough moulding compounds can be injection moulded using the older type of ram injection machine but most injection moulding materials are processed with screw injection moulding machines and it is this process that must be discussed in detail.

Injection Moulding of Thermosetting Material

In the injection moulding process, a rotating Archimedian screw conveys material from the hopper along a heated barrel where it is melted or plasticized partly by conduction of heat from the heated barrel and partly by frictional heat developed by the rotation of the screw. The rate of frictional heating is determined by the viscosity of the material, the rate at which the material is sheared i.e. the screw rotation speed, and the adhesion of the melt to the adjacent metal surfaces.

TABLE 1 Conditions of Processes for Moulding Thermosetting Materials

Moulding Process	Typical Temperature	Typical Shear Rate	Effect
Compression	140-180°C	$1-10\ sec^{-1}$	Limited particle breakdown. High bulk materials may be regarded as resin matrix binding the filler or reinforcement
Transfer	140-180°C	Intermediate, less than inj. moulding	Degree of particle breakdown depends on mould design
Injection Barrel	80-100°C	$10-10^{2}\ sec^{-1}$	Material is partly plasticised by mechanical working
Nozzle	100-110°C	$10^{2}-10^{4}\ sec^{-1}$	–
Runners/ gate	100-140°C	$10^{2}-10^{4}\ sec^{-1}$	High frictional heating reduces cure time and aids flow
Mould	150-190°C	Low	Material is static and remains in mould until cured
Laminating	130-190°C	Low	Can effectively be regarded as 100% resin since little movement of the reinforcement occurs

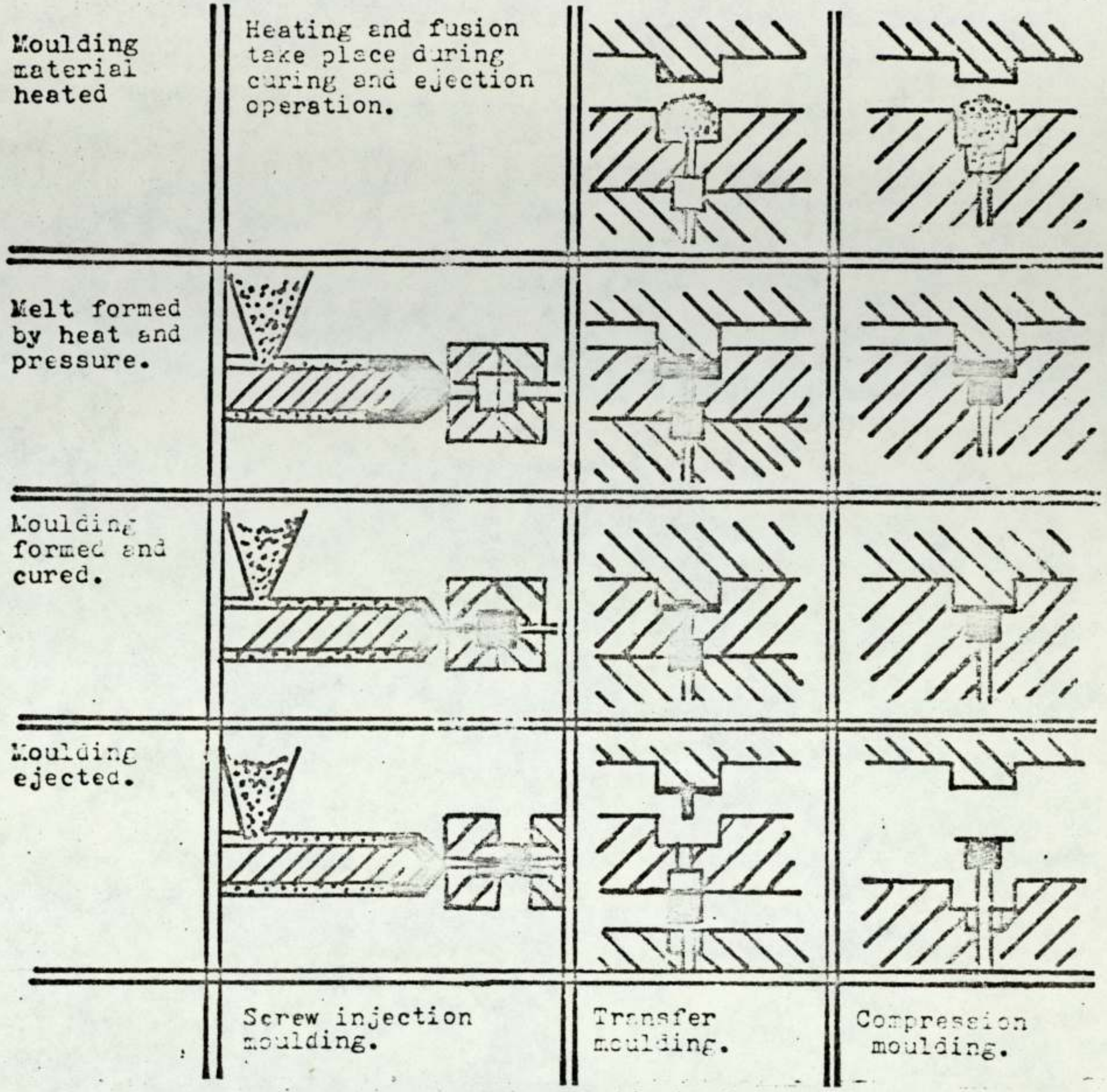


Fig. 2. Schematic representation of moulding processes used with thermosetting plastics materials.

Current developments also include screw pre-heaters which resemble the injection moulding barrel but the melt is injected into a cool (90 - 100 °C) mould to form a pellet which is then transferred manually or automatically to a transfer or compression moulding process. It is claimed to be superior to high frequency or conductive preheating and if adopted could mean that many of the complexities of injection moulding will occur in compression and transfer moulding areas.(6,7).

Thermosetting Injection Moulding Materials

Thermosetting moulding materials are not simple compounds but are based on thermosetting resins and contain large quantities of additives such as fillers, reinforcements as well as catalysts, lubricants, pigments etc.

Resins which crosslink by condensation reactions are largely composed of the formaldehyde based materials and include phenol, urea and melamine formaldehyde and phenol - melamine formaldehyde. Epoxies undergo a step wise reaction similar to condensation but polyester materials which cross-link by a condensation reaction, (glyptals) have been replaced and the modern polyester resin is crosslinked by an addition reaction.

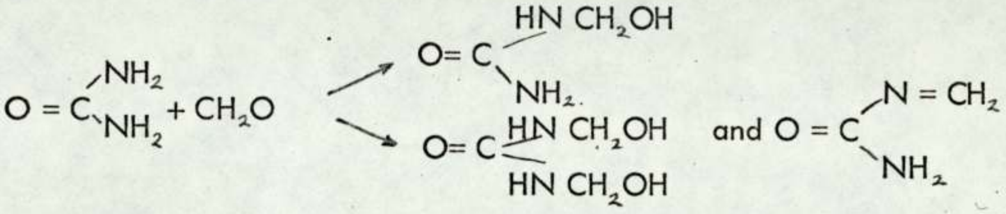
Thermosetting resins which crosslink by an addition reaction are based on resins such as alkyds, 1.2 polybutadiene (1.4 polybutadiene is a rubber) and di-allyl phthalates. Unlike condensation crosslinked materials which are acid or base catalysed, addition reactions are normally initiated by free radicals and careful selection of the free radical producer can give a material which is essentially thermoplastic in the injection moulding barrel and will only crosslink at mould temperatures.

Typical formulations for thermosetting moulding materials are given in table 2 and a simplified reaction mechanism for the crosslinking reactions involved in curing a urea formaldehyde resin (4) is shown in Fig.3.

TABLE 2. Typical formulations of thermosetting moulding materials (4)

Component	Condensation Materials		Addition Materials	
	Phenolic	parts	Polyester	parts
Base Resin	Novolac	100	Polyester Resin	100
Crosslinking Agent	Hexamine	12.5	Styrene	49
Catalyst/Promoter	Magnesium Oxide	3	Benzoyl Peroxide	1.5
Lubricant	Stearic Acid	2	Calcium Stearate	3
Pigment	as required	4	as required	3
Reinforcement/Filler	Wood Flour	100	Glass Fibre	30
			Calcium carbonate	360

Fig.3. Simplified Reactions in formation of Urea Formaldehyde material (7)



Initial Reactions

$>N - CH_2 - OH + H - \overset{|}{N} - CH_2OH \longrightarrow >N - CH_2 - \overset{|}{N} - CH_2OH + H_2O$

$>N - CH_2 - OH + H - OCH_2 - N< \longrightarrow >N - CH_2 - O - CH_2 - N< + H_2O$

$>N - CH_2 - OH + HO\,CH_2 - N< \longrightarrow >N - CH_2 - N< + H_2O + CH_2O$

Subsequent crosslinking reactions.

2.3 Characterization of Thermosetting Moulding Materials

The processing of thermosetting plastics involves complex and frequently interacting reactions which create considerable problems for the material manufacturer and moulder. The maintenance of a consistent product demands test methods which easily determine variations in the properties of the material.

The material is partly sintered during its passage along the screw and much of the mechanical work occurs at the nozzle end of the screw, where the material is smeared against the melt accumulated in the nozzle end of the barrel. As more material is plasticized, the screw is forced towards the hopper end of the barrel. The plasticized material is held at relatively low temperatures (e.g.90 - 100°C) until the now stationary screw moves forward as a ram forcing the melt through a series of runners and gates at high shear rates (10^2- 10^4 sec^{-1}). Frictional heating increases the melt temperature to about 130 - 150°C. Once in the mould the material is heated by conduction under static conditions until the desired degree of cure is obtained when the mould is opened and the moulding ejected. During the period when the moulding is curing the screw rotates to plasticize further material and the process is therefore of a continuous cyclic nature.

There are thus several distinctly different parts of the injection process each of which must be related to each other and to the properties of the material in order to achieve satisfactory control of the injection moulding process. For example, excessively high frictional heating results in premature crosslinking or precuring of the melt in the barrel and the melt will no longer flow into the mould. A similar effect is caused by a material of insufficient melt stability. The melt is required to cure rapidly in the mould and while this is aided by the use of high mould temperatures and catalysts, it is essential to use fast curing materials and also to heat the melt rapidly by frictional heating during its passage through the runners. The last two requirements are contrary to the factors which promote good melt stability in the barrel and the properties of injection moulding materials are thus a compromise of conflicting requirements.

The injection moulding process usually gives a moulding with a sprue and runners. Recently warm runner moulding (5) has been developed in which the melt is injected into a slightly open mould which is then closed giving mouldings with more randomly orientated filler particles and without the gate and runner mouldings. The material in the sprue and runners is held in the molten state. The warm runner technique results in cost and material savings but demands greater control of the material properties.

The thermosetting injection moulding process involves changes in both chemical composition, material temperature and flow velocity or shear rate. Detailed rheological and kinetic data would be required to analyse the process theoretically and even then only the more simple mould geometries could be analysed. These conditions have led to the growth of many empirical flow tests (8).

Early test methods were based on compression or transfer moulding techniques and each invariably measured a single parameter e.g. a time, a pressure or a flow distance under specified conditions. Some of these tests have been subsequently modified to incorporate electronic measuring systems e.g. the instrumented spiral flow (9), while test techniques are being developed which simulate more closely the conditions of the injection moulding process as well as producing time related data. However, the single point test is still widely used in industry especially for quality control purposes.

Methods of Characterizing Thermosetting Plastics

The methods used to characterize thermosetting moulding materials have been the subject of a detailed literature survey by the present author and this report (RAPRA Report B441) is summarized in the following pages. The references quoted for each heading refer to the relevant section in the literature survey and a copy of Report B441 is included at the end of this thesis.

Compression Techniques (B 441, 2.1)

Two basic compression techniques are currently used to characterize thermosetting moulding materials. These are the cup flow and disc flow tests. The cup flow is an open flask beaker mould. Fig.4.

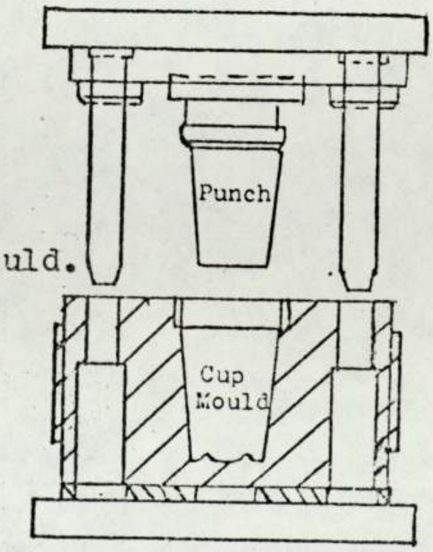


Fig. 4. Cup flow mould.

The test material (30-40grams) is placed into the heated mould and the punch lowered, a timer is started when the pressure starts to rise and stopped when the mould has closed. The plasticity of the material is expressed as the duration of the flow in seconds. The use of this basic test is extended to determine the cure time of the material (i.e. the time required to produce a blister-free moulding,) as well as to assess properties such as gloss, colour dispersion etc.

This basic test is currently used with different sized beakers having various wall sections, and it is used as a standard test by many countries.

The cup flow test is most useful with high viscosity compression moulding materials but is of less use with transfer moulding materials and is considered tobe of little value with low viscosity injection moulding materials. (8,10,11,12)

One variation of the cup flow mould is to cut two slots in the upper part of the cup mould and to overcharge the mould using the test in a similar manner to the orifice test described in the next section. (98)

The disc flow test is essentially two parallel press platens which compress a specified volume of material to produce a thin,moulded disc. The flow of the material is determined by measuring the thickness of the disc or more occasionally it's diameter. Tonogai (13) has used the disc flow test to determine chemical curing reaction kinetics.

Other compression tests include the multi-cavity test in which the flow of a material is expressed as the number of complete mouldings produced under specific conditions, and the compaction test in which a small pellet moulding is made and the flow of the material is expressed by the rate of mould closure. The latter test is also used at low temperatures (90°- 100°C) as a pelleting test.

Compression tests are in general simple to operate but are unsuitable for obtaining fundamental data and are essentially empirical in nature. A more detailed discussion of these techniques will be found in RAPRA B441, Section 2.1

Capillary Techniques (B441/2.2)

The essential feature of the capillary flow test is that fused material is forced under pressure through a circular runner or die. The rate of flow under specified conditions is used to calculate the material viscosity. In the orifice test the capillary runner or die is very short; it's length being considerably less than its diameter e.g. a typical orifice has a length to diameter ratio (L:D) of about 0.3:1. In contrast capillary viscometer dies have L:D ratios of greater than 5:1 and capillaries of up to 100:1 have been used with thermally stable materials.

Many variations of the orifice and capillary tests have been reported in the literature. They have been used to measure the relationship between pressure, temperature, time and material viscosity as well as to produce simple, single measurements of flow.

Fig. 5 & 6 shows a typical orifice flow test mould and fig.7 published orifice flow results obtained with this test for typical thermosetting plastics.

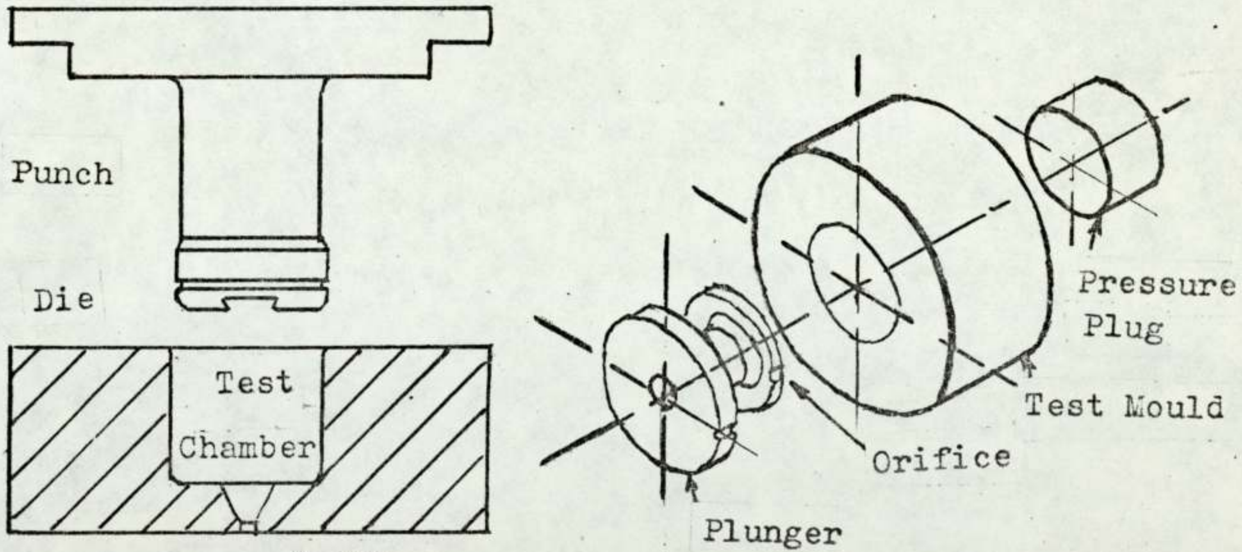


Fig. 5

Fig. 6

Fig. 5 & 6. Typical orifice flow test moulds.

An important aspect of the capillary or orifice flow test is that it can be operated at the very high shear rates encountered in injection moulding.

As the melt enters the capillary flow channel it's velocity changes profile in a manner which is equivalent to increasing the length of the capillary channel. This increase in effective length can be calculated and using well established theories and the results from a capillary flow test can be expressed in fundamental units.

Dujardin (15 & 112)has published a theoretical interpretation of the orifice test but other sources suggest that the results of the orifice test are more empirical in nature.

The capillary viscometer should ideally be used with a thermally stable material since it requires a continuous stable flow in order to produce accurate data. This has limited its use with thermosetting plastics in that actual measurements must be made at the period of minimum viscosity. Heyd (16) has used the rate of increase of flow pressure to measure the initial cure rate of the material (Fig.8.) while various workers use the relationship between the heating period and the material flow rate (Fig.7) to assess the flow stability of the material. (14) (17).

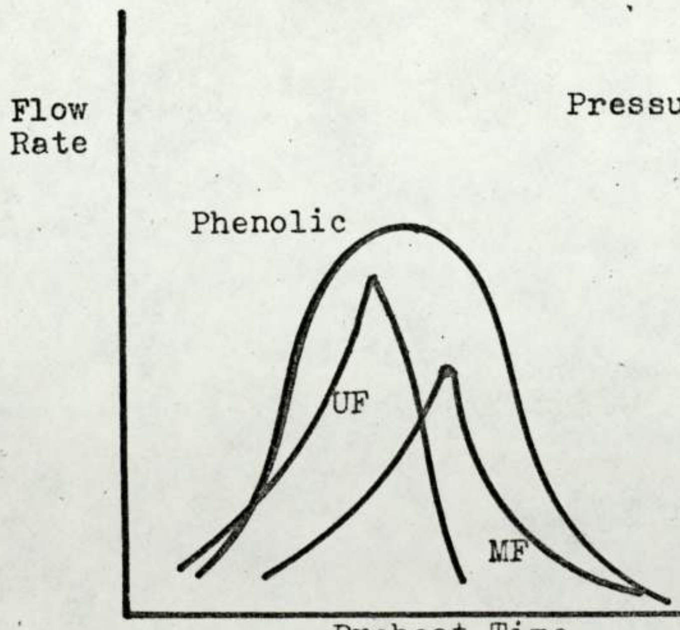


Fig. 7.Flow rate/time curves for orifice test.

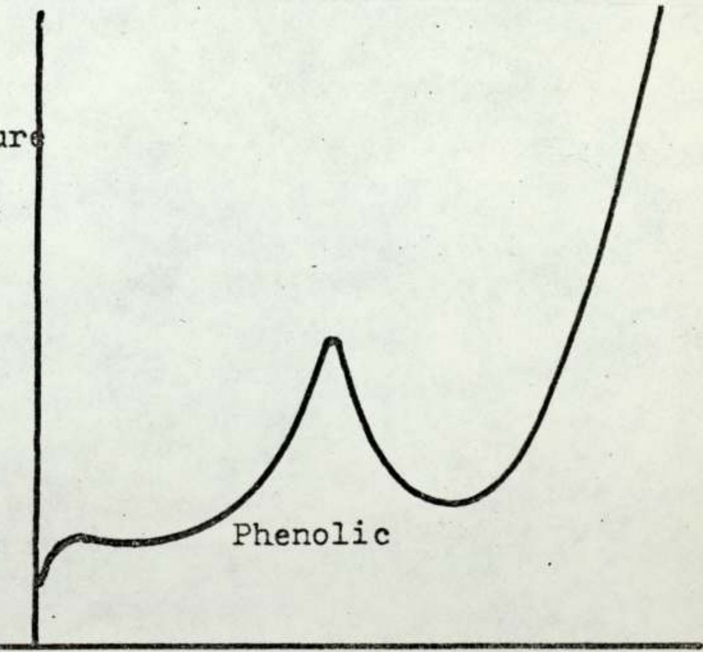


Fig. 8.Pressure/time curve for capillary viscometer.

Most capillary viscometers use a die of circular cross-section but other sections can be used, although the analysis is complicated by the presence of two dimensional flow paths. The various different types of orifice and capillary flow test are discussed in RAPRA B441 but are summarised in Table 3.

Type of Instrument	Reference
Single orifice, bottom exit (Fig. 5)	Ferridoy (14)
Single orifice, side exit	Morita (17)
Double orifice, punch edge (Fig 6)	(Dujardin (15) (112) (Kerr & Dontje (18)
Constant pressure capillary flow test	Goulbourne (19)
Constant extrusion rate capillary flow test	Heyd (16)

TABLE 3 Types of Capillary viscometer

These methods test a melt generated by a compression moulding process but the injection moulding barrel has been used to generate the melt which is forced through the injection nozzle acting as a simple orifice flow test or with an extended nozzle fitted with pressure and temperature sensors as a capillary viscometer. (20)(21)

The orifice and capillary techniques described above require that the melt passes through the die. A series of capillary flow tests were developed in which the melt flows in a long capillary and its viscosity increases and flow ceases within the confine of the capillary. The Rossi Peakes flow test (2,22) is probably the best known of this type of test and employs a straight capillary while in the spiral flow test the capillary is replaced by a spiral flow channel.

The Rossi Peakes flow test (Fig.9) consists of a small heated chamber into which the test material is placed. After a specified time weights are placed on the platform and the force is transmitted to the material via a series of strings and pulleys. The melt flows up the capillary and its progress is recorded as a function of time using a recorder connected to the small weight placed in the capillary. This represents the original (1934) and intended method of operation but the test is more usually used to measure the pressure required to cause the melt to flow a specified distance in a specified time.

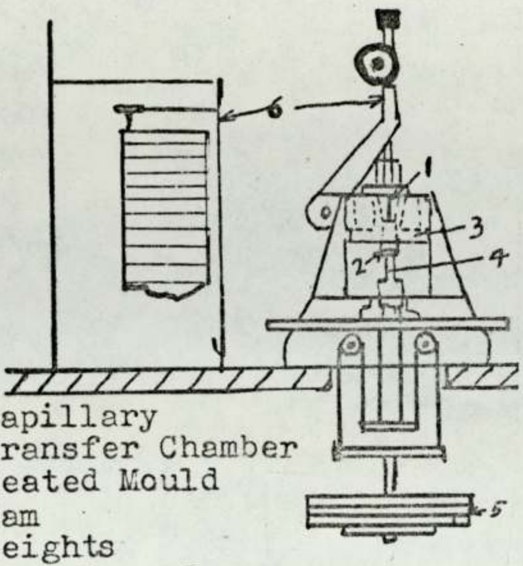


Fig. 9a

Fig. 9a. Rossi Peakes Flow Test.

Fig. 9b. Section through test chamber.

Fig. 9c. Distance/time and flow length/pressure curves.

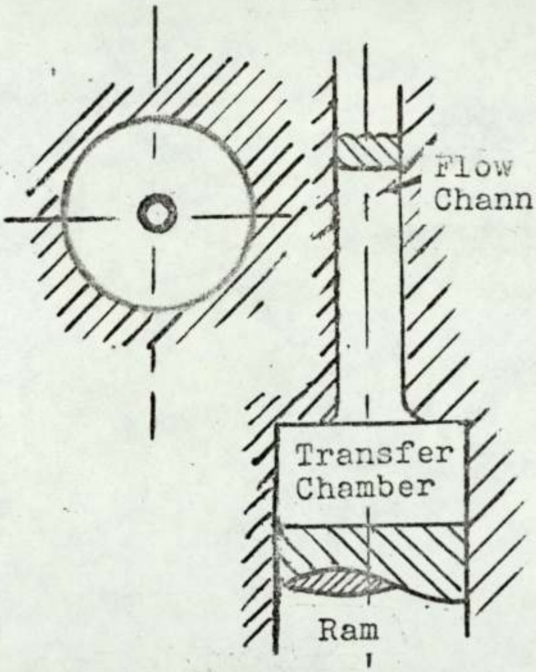


Fig. 9b

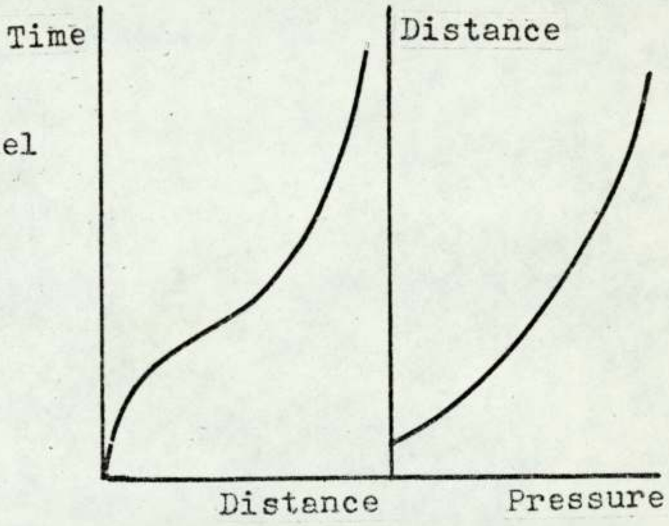


Fig. 9c

Published work shows the pressure, temperature and flow length characteristics of various thermosetting materials. Goulbourne (19) claimed to use the Rossi Peakes test to obtain fundamental viscosity data by recording the pressure and the flow rate over $\frac{1}{4}$ second intervals. This technique ignores the fact that the shear rate is varying throughout the test and that the viscosity of thermosetting plastics changes with shear rate.

A series of test methods have been developed from the original Rossi Peakes test. These are summarised in Table 4 and are discussed in more detail in RAPRA B441. These tests are essentially the same in principle but vary in shape and/or section of the capillary or in the manner of measuring the flow properties.

Test	Capillary Shape		Reference
	Section	Profile	
Rossi Peakes	Circular	Parallel	2, 22
Olsen	Circular	Parallel	23
Rashig	Rectangular	Parallel	24
Krahl	Rectangular	Tapered	25
Hessen	Cylindrical	Tapered anulus	24
Erickson-Rashig	Circular	Tapered	27,24
Zwick	Rectangular	Parallel	28,26
	Large Sample		
Burns	Circular	Parallel	29
	Several capillaries of different diameter		
Spiral Flow Test			
MESA	Trapezoidal	Parallel	10
IBMA EMMI	Half round	Parallel	10,30

TABLE 4 Examples of Capillary Flow test developed from Rossi Peakes and Spiral Flow Tests.

The spiral flow test is similar in principle to the Rossi Peakes test but the capillary is wound into a spiral. Two basic types of spiral exist (of trapezoidal or half-round section) and its results have been interpreted in a similar manner to those of the straight capillary. Recent developments include the measurement of both the position and velocity of the ram as a function of time in an effort to improve the sensitivity of the instrument and to produce pressure, temperature, flow rate data for thermosetting materials. (8,9)

Transfer Moulding Techniques

The transfer flow test uses a simple transfer flow mould (usually of an impact test piece) and measures the relationship between the transfer pressure and the mould filling rate under specified temperature conditions . (8) (11) (32) (96)

Rotational Techniques B441/2.3

Two types of rotational viscometer are described in the literature for use with thermosetting plastics, a simple rotational viscometer of the type originally developed by Kanavets and a small instrumented internal mixer typified by the Brabender Plastograph.

The Kanavets Plastimeter was developed in 1956 by Kanavets (33) and consists of a heated cylinder with a hemispherical top which forms the compression ram Fig.10. The outer part rotates and the load transmitted to the central mandrel is recorded as a function of time. Kanavets selected a speed of rotation of 3 revs per hour to eliminate the effect of excessive velocity gradients. Both the outer cylinder and the inner mandrel are splined to prevent the melt slipping at the melt/metal interface.

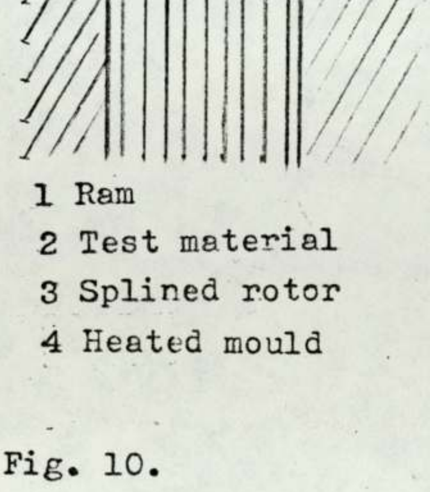


Fig. 10.
Kanavets Plastimeter.

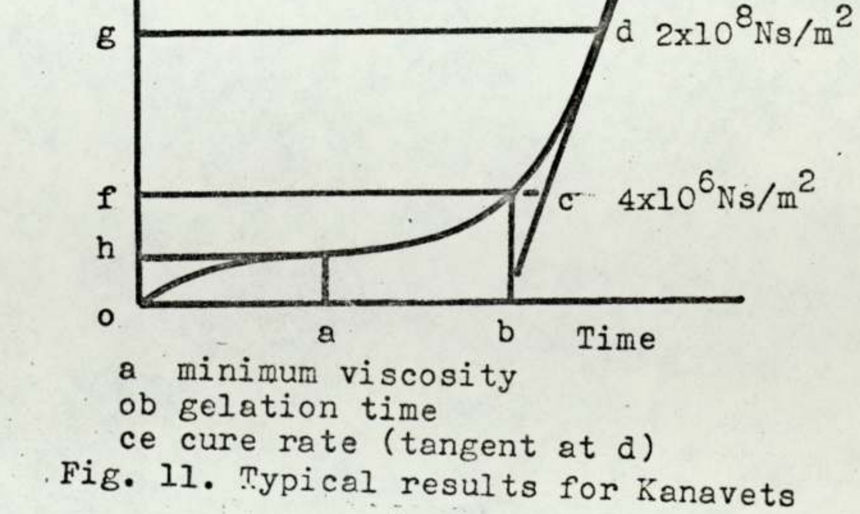


Fig. 11. Typical results for Kanavets Plastimeter

Materials in pellet form are placed in the upper chamber, fused and forced by the compression ram into the measuring chamber when the rotation of the mandrel commences. The material thus undergoes a compression moulding process before the measurement of the viscosity commences. A typical trace is shown in Fig.11. together with the interpretation of the result as described by Kanavets (33,40) and Ehrentraut (34,35). The values of shear stress used to determine the time of gelation and cure times are given for an injection moulding phenolic although different values are used to specify these points for amino materials.(36)

The basic plastimeter has been modified by several workers whose work is summarised in Table 5.

Main Authors	Summary of Work	References
Kanavets Sokolov	Use with transfer chamber to determine the effects of high shear and mechanico-chemical degradation on viscosity time characteristics of phenolics.	38,39 41
Danilkin Kanavets	Use over shear rates of 10^{-2} - 10^{2} sec^{-1} to determine viscosity/shear rate characteristics of phenolics. Frictional heating allowed for using viscosity/temperature curve obtained at 0.016 sec^{-1}.	43,44
Dalhoff Ehrentraut	Complete redesign to produce Durocorder which accepts melt from injection machine nozzle. Used to measure viscosity/time effects at low shear rate (0.016 sec^{-1}) and to determine effects of injection machine variables on material curing characteristics.	3,45,46

TABLE 5 Modifications to rotational viscometer developed by Kanavets.

The basic Plastimeter is available in more sophisticated forms e.g. Durograph and PPR - 1 and the method has been adapted as a Russian Standard (GOST - 15882 - 70). Several papers illustrate the use of the Kanavets Plastimeter for general material evaluation, and for quality control applications. (42,37,136). A more detailed discussion of this work will be found in RAPRA B441. Examples of the industrial use of the plastimeter will be found in references (34,37,47,48,49) Ulbricht (50) and Meyer (51) consider that the Plastimeter is too complex and less satisfactory for quality control use than conventional tests.

Instrumental Extruder

Small Instrumented extruders have been used to measure the plasticity of thermosetting materials (52,53). This technique is claimed to simulate the injection machine barrel but cannot be used to measure the change of viscosity with time and can only be used over a limited range of temperatures.

Variable Torque Rheometer

The variable torque rheometer comprises two contra- rotating rotors in a double-cylindrical chamber (Fig. 12). The rotors rotate at different speeds and the chamber is heated. The torque required to rotate the rotors at a constant velocity and the melt temperature are recorded as a function of time.

It is a feature of the torque rheometer that different types of material give different but characteristic shaped torque traces. The situation is complicated and different interpretations of the curves and in particular in the extent of crosslinking which occurs during the latter stages of each test are described in the literature (e.g. Fig 13).

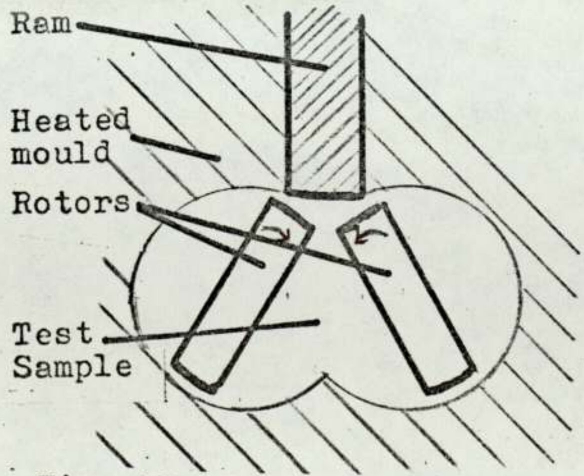


Fig. 12. Crossection through variable torque rheometer (Hampden TR-1)

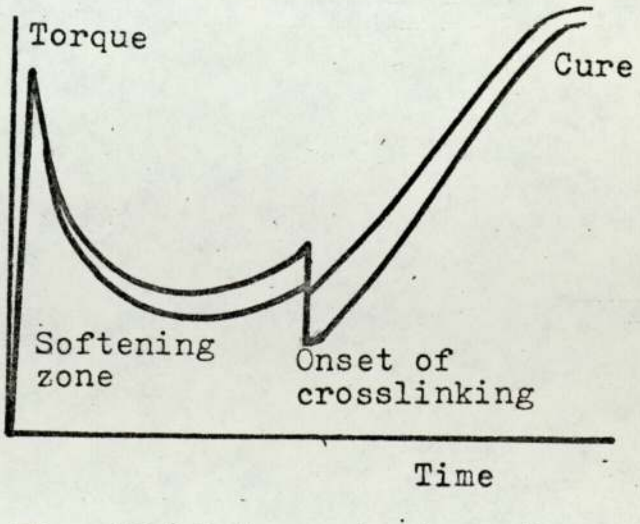


Fig. 13. Interpretation of torque rheometer results.

Many examples exist of the use of the variable torque rheometer with thermosetting materials details of which will be found in RAPRA B441. The most useful and informative papers include those by Ehrentraut and Dalhoff (118), Schreiber (52) and Scholtis(54).

Several rheological analyses have been published for the Brabender Plastograph, a commercial variable torque rheometer, but these are based on assumptions that the variable torque rheometer is analogous to two concentric cylinder viscometers, that the rotors approximate to cylinders and that an average shear rate and shear stress exist in the two cylinders. The theories were originally published by Goodrich and Porter (55) and developed by Blyler and Daane (56) and Lee and Purdon (57). Norman (58) considers their theories suspect and that the flow behaviour is too complex to permit a theoretical interpretation of the results and consequently the results are only semi- empirical.

The variable torque rheometer has one important feature in that it is capable of monitoring the changes which take place as the material is fused under dynamic heating conditions, a feature which distinguishes this instrument from the majority of other testing techniques.

Simple rotational viscometers can be used to produce fundamental data but have a number of disadvantages which were summarised by Batchelor (59) as follows:-

a) Unknown flow conditions at the cylinder ends.
b) Unstable flow conditions at shear rates greater than 10 sec^{-1}.
c) Frictional heating effects are significant.

Oscillating Disc Rheometers B441/2.4

Oscillating disc and probe rheometers have been used to measure the consistency of thermosetting materials as a function of time. Because the overall deformation of the sample is relatively small, these techniques can be used to monitor the crosslinking reaction until the material has cured.

Three basic types of oscillating rheometers have been reportedly used with thermosetting materials, an oscillating probe, a cone and plate and a biconical disc rheometer.

a) The Oscillating Probe Rheometer (The Wallace Shawbury Curometer) has been successfully used with thermosetting resins but is unsuitable for use with thermosetting moulding materials. (60).

b) The Cone and Plate Rheometer has also been used with thermosetting resins by several workers (61,62,63,64,65) but few references exist to it s use with thermosetting moulding materials. Sieglaff and Evans (66) have used an oscillating disc rheometer to measure the elastic modulus of polyester based dough moulding materials and conclude that it offers considerable advantages over the standard type of test. Although the cone and plate rheometer can be used with thermosetting moulding materials, problems arise because of the poor adhesion between the rotor and the material under test. (i.e. slippage can occur) while at higher shear rates (>1 sec^{-1}) the material tends to come out of the gap between the rotor and stator (59). The cone and plate rheometer can be used to measure the normal force of the materials i.e. the force that is generated in viscoelastic fluids at right angles to the direction of the applied shear.

c) The Biconical Disc Rheometer is essentially two cone and plate rheometers mounted back to back to give a biconical disc mounted in an enclosed chamber or mould (Fig. 14). Many variations of this instrument exist (as curemeters in the rubber industry) but only the Monsanto Rheometer has been reportedly used with thermosetting plastics materials. Figs. 14 and 15 show a diagramatic representation of the instrument together with a typical trace of torque against time.

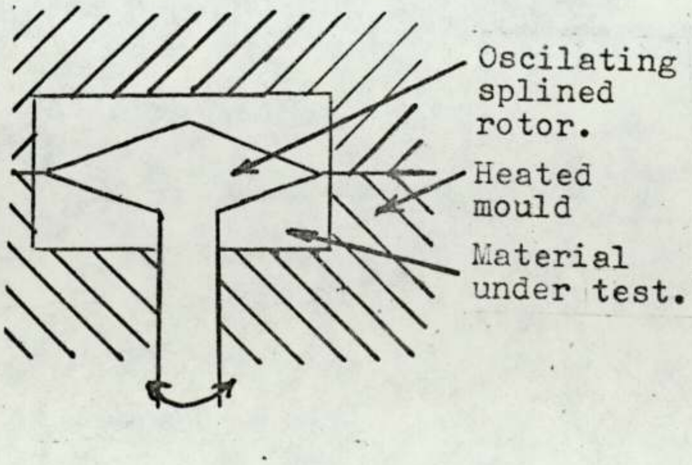


Fig. 14. Monsanto Rheometer.

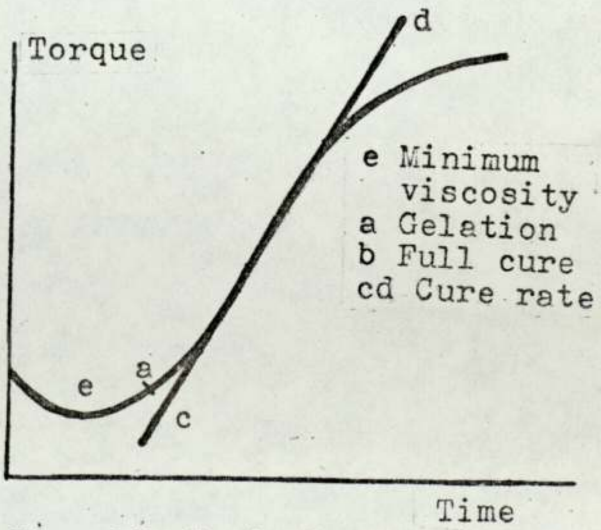


Fig. 15. Typical results for Monsanto Rheometer.

Brodbeck and Hartzel (67) used the instrument to compare glass fibre reinforced diallyl phathalate moulding materials. They concluded that the torque/time trace was more sensitive to material variations than the cup flow test normally used with their materials. Talwar and Ashlock (68) used the instrument with similar materials based on diallyl isophthalate resins and statistically correlated their results with the injection moulding properties of the materials. Beck and Golovy (69) also used an oscillating disc rheometer to monitor the curing characteristics of phenolic materials.

The biconical rheometer can be used to measure the rheological properties of materials and its results can be interpreted in terms of the elastic, viscous and complex ~~dynamic~~ modulus of the material and these properties can be determined over the complete curing cycle of a thermosetting material (Fig.15). Their use, however, is limited to relatively low shear rates.

Considerable work has been published concerning the correlation of the results of the oscillating disc rheometer with the degree of crosslinking of the test material with chemical reaction kinetics and with the mechanical properties of the material but this information relates predominantly to thermosetting rubbers.

Other Methods

Recent years have seen a considerable increase in the study of the curing kinetics of thermosetting materials. The methods used include those listed in table 6 and measure the changes which take place during the crosslinking reaction and do not actually measure the viscosity changes of the material.

Differential Thermal Analysis	70,71
Differential Scanning Calorimetry	71,72,73,74,80.
Ultrasonic measurements	75,76
Nuclear magnetic resonance	77,78
Dielectric measurements	79,80
Infra red spectroscopy	80,81

TABLE 6. Methods of monitoring the thermosetting crosslinking process

Many of these techniques have been used to evaluate raw materials or to determine the degree of cure of mouldings prepared with different cure times. Most of the work had been carried out with epoxy resins but the techniques could doubtless be applied to other materials.

Attempts by the present author to use differential scanning calorimetry measurements to compare phenolic and amino moulding materials and to determine the degree of cure of phenolic mouldings proved to be unsuccessful because of poor reproducibility from an inhomogenous sample. This was probably due to the necessity of using a very small sample (50 milligrams) and to the nature of the material. Ultrasonic measurements were also made but these also proved to be unsuccessful because of a lack of sensitivity to variations in cure time. (Results differed by only 10% for a slightly blistered phenolic moulding cured for one minute at 150°C and an over cured moulding cured for 8 minutes at 150°C. Similar poor results were obtained with urea formaldehyde materials.)

Dielectric sensors (79) and ultrasonic measurements (76) have been used to monitor and thence control the curing of compression moulding laminates by inserting the sensor in the press paten while ultrasonic sensors have been used to monitor the viscosity of thermoplastics melt during injection moulding. (82).

The most common method of measuring the curing of a thermosetting plastic is to prepare a series of mouldings of different cure times and to measure the properties of these mouldings. Typical test systems are described in Chapter 2.1 but other physical properties e.g. volume resistivity can also be used. A commonly used technique for phenolic and amino materials is to measure the time required to produce a blister free moulding using the cup flow mould.

The use of the injection moulding process as a test method.

It is frequently suggested that only the injection moulding process is sufficiently sensitive to detect small variations in injection moulding materials (84), and the machine has been used to determine flow data as well as for quality control purposes. This approach, which uses a typical but non- standard injection mould has some obvious advantages but also some disadvantages. (see Table 7)

TABLE 7: Use of Injection Moulding Machine as Test Procedure

Advantages	Disadvantages
1. Materials are tested under actual injection moulding conditions.	1. The testing procedure is relatively lengthy.
2. The initial powder is worked mechanically to produce a melt containing few, if any, unfused particles.	2. Fairly large quantities of material may be required.
3. The results may be directly related to injection moulding, although possibly to one type of machine.	3. The test ' ties-up' an expensive and, from the processors point of view a potential profit making machine.
	4. It is arguable that the test results are only relevant to the machine on which the material was tested, because of differences between machines.
	5. The injection moulding process is a non-reproduc~~i~~eable process showing some shot to shot variations as well as long term drift. This has been shown for thermoplastic injection moulding and it is reasonable to assume that the comment applies to thermosetting materials. (31).

The injection moulding process has also been used to determine the flow properties of thermosetting moulding materials. Two approaches have been used; to measure the pressure at the injection nozzle during the moulding process and to measure the pressure drop across the gate.(85,86,87,88). The injection barrel has also been used as a viscometer using an extended nozzle as a capillary viscometer (20,21). The results obtained by these techniques vary from fundamental data to empirical flow curves and the results show that phenolic materials are pseudo-plastic and may show Bingham flow behaviour.

Characterization of Thermosetting Rubbers

There is some analogy between rubbers and thermosetting plastics in that thermosetting rubbers are compression, transfer and injection moulded using similar equipment to that used for thermosetting plastics. A review of the techniques used in the rubber industry is therefore relevant to this project.

Gengrinovich (89) has published a major review of flow measuring techniques while Emil(90), Adamski(91) and Pearson(92) have discussed the use of oscillating rheometers. This review is largely based on these papers.

The rubber industry divides the viscosity-time curve of a thermosetting rubber into several sections and usually measures each section under different conditions of shear rate and temperature. Many of the techniques record the flow of a rubber as a function of time and the rubber industry makes little use of single point measurements.

The plasticity or minimum viscosity of a thermosetting rubber is usually measured at 100°C using a rotational viscometer (Mooney viscometer with a constant speed of 2 rpm) but can also be measured using a parallel plate test. Capillary viscometers are sometimes used to measure flow properties at high shear rates.

The elastic component of a viscoelastic material is usually measured by the techniques used to measure plasticity.

The scorch time of a rubber is the time a rubber can be maintained at processing temperatures before prevulcanisation has reached such a stage that the unvulcanised rubber can no longer be satisfactorily processed (BS 1673). Scorch testing is usually carried out at 121°C using the rotational (Mooney) viscometer or by the oscillating techniques described below. In practice, the scorch time is determined by the time required for the consistency of the rubber to rise an arbitrary number of units (e.g.1, 2½, 5 or 30) above its minimum value.

The curing properties of rubber mix are measured by monitoring the change in its properties as a function of time. This is usually carried out at 140 - 180°C and typical instruments include the oscillating biconical disc rheometer, e.g. Monsanto Rheometer, the oscillating dished platen curelastomer (Japanese Synthetic Rubber) the oscillating probe curometer e.g. the Wallace-Shawbury Curometer and the plunger or CEPAR technique.

These techniques can be used to measure the minimum plasticity, scorch time, cure time as well as the chemical kinetic induction time and reaction rate.

All of these test techniques have obvious applications to thermosetting plastics but the majority of the instruments used are, in themselves, unsuitable for use with thermosetting plastics materials.

Discussion of testing techniques for thermosetting plastics.

A summary of the various test techniques is given in Fig.16.

Early plastics test methods were based on compression or transfer moulding techniques and invariably measured a single point e.g. a time, a pressure or a flow distance under specified conditions. Since the tests were carried out in moulds of different shapes and sizes, the shear rates and the degree of crosslinking at which the material ceases to flow varied between tests and consequently different methods gave different relative results and often could not be correlated with each other or with a production mould. Examples of this are quoted in Table 8 by Wainwright(93) Fina (94) and Brooks(95) while table 9 shows examples from the writers personal experience; also in the materials section, Chapter 13, Section 1.

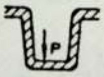
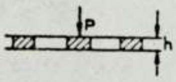
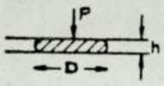
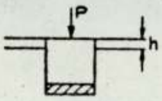
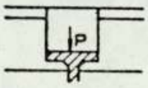
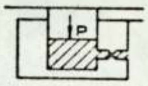
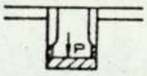
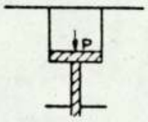
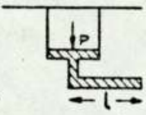
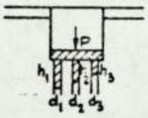
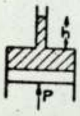
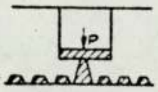
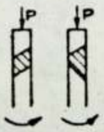
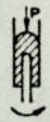
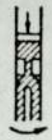
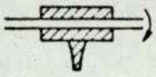
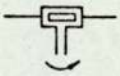
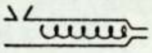
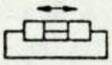
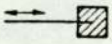
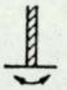
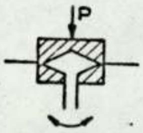
Test Method	**Diagram**	**Type of Measurement**	**Parameters Measured**	**Conditions of Test Specified Parameters**
Compression Techniques				
Flow Cup		Flow Path Flow/Cure Combination	$P = f(t)$ $h = f(t)$ P Ti Ti	h, Te P, Te h, Te, h P Te h P Te h
Multi Cavity Mould		Flow/Cure Combination	No. of cavities filled	P Te h
Disc Flow		Flow/Cure Combination	D and/or h	P,. Te
Compaction Test		Compaction Flow Path	$P = f(h)$	Te
Capillary Type				
Orifice Flow		Flow/Cure Combination " Flow Path	q t p	P Te Ti (residence) q Ti e P h Te
			$q = f(t)$	P Te
			t, q	P Te
Capillary Viscometer		Flow Rate Flow Path	q $P = f(t)$	P Te q
Long Capillary (Straight Type)				
Flow Mould		Flow/Cure Combination	t	P Te
Multi Capillary		Flow/Cure Combination	$h_1h_2h_3$ etc.	P Te $d_1d_2d_3$ etc.
Rossi Peakes/Zwick		Flow/Cure Combination Flow Path " "	h $h = f(t)$ $h = f(t)$ P	P Te P Te P Te h Ti Te capillary can be conical
Long Capillary Spiral Type				
Spiral Flow		Flow/Cure Combination Flow Path	l $h = f(Ti)$	P Te P Te Ti (residence)

Fig. 16. Diagramatic representation of test methods used to measure flow properties of thermosetting plastics.

Fig. 16 continued.

<u>Rotational Type</u>				
Rotational Plunger		Flow Path	Rotor Speed = f(t)	P Te Torque
Kananvec Plastimeter Durograph		Flow Path	Torque = f(t)	P Te Rotor Speed
Modified Kanavec Plastimeter		Flow Path	Torque = f(t)	P Te Rotor Speed
Durocorder		Flow Path	Torque = f(t)	Fed by injection m/c
Variable Torque Rheometer		Flow Path	Torque = f(t)	P Te
Mooney Viscometer		Flow Path	Torque = f(t)	Te Rotor Speed
Extruder		Flow/Cure Combination	Torque	Te Screw Speed
<u>Oscillating Types</u>				
Oscillating Capillary		Flow Path	Osc Ti	Te P
Oscillating Probe		Flow Path	Osc Ti	Te Rate of Osc
Torsional Pendulum		Flow Path	Osc = f(t)	Te
Oscillating Disc		Flow Path	Torque = f(t)	P Te Osc
Rheometer Monsanto Farol Weissenburg Rheogoniometer			Torque = f(t) P	Te Osc

Key:-	
P	Pressure
H	Thickness
l	Length
D	Diameter
Te	Temperature
Ti, t	Time
q	quantity (e.g. output of die)
Osc Ti	Period of Oscillation
f	function (e.g. P = f(t). Pressure as a function of time)

TABLE 8 Comparison of Phenolic Materials using different test methods

Test Method	Materials					
Cup Flow (secs)	12	12	12	12	12	
Extrusion test (length mm,)	38	32	31	18	3.8	
Extrusion test (press. for 25 mm) MN/m^2	4.3	4.0	4.5	6.2	8.2	
Disc thickness (mm)	56	61	81	94	89	
Minimum Moulding Pressure ($Kg \times 10^3$)	3.56	3.05	5.6	4.07	5.09	
(These figures relate to materials of different composition)						
Flow Length mm	12.7	19.1	19.1	21.6	17.8	17.8
Plasticity Index	22.3	26.4	26.4	21.1	23.3	-
Tube Base (Cup Flow Type)	22	14	10*	15*	16*	15*
* Pressure reduced for these results						

Material	Test Specification	Description of Material
Amino	Two batches of material of similar specification.	The second material had a higher viscosity and was slower curing than the first.
Phenolic	Similar flow/cure values by standard tests.	Six batches, the last of which required modified machine settings to produce adequate mouldings
Urea Formaldehyde	Two batches from the same manufacturing process	Material of one batch set up in injection barrel.
Epoxy	-	Burnt areas due to bad mixing of additive.

TABLE 9 Moulding properties of materials

This lack of correlation resulted in companies modifying the basic test and consquently produced a further increase in the number of tests in use (94, 96). The complexity of moulding thermosetting plastics undoubtedly prevented any simple understanding of the process since it involves changes in temperature, velocity and composition. Detailed rheological and kinetics data would be needed to analyse the process theoretically and even if available it would probably only apply to simple mould geometries. (8).

The inadequacies of many early test methods were recognised many years ago (93) and serious doubts exist concerning their relevance to injection moulding (94,97, 83). Peakes (2,22,99) realised the necessity of measuring 'flow' as a function of time and Forrer (100) recognised the need to test material at the same shear rate as that found in the moulding process. In 1939 Schwittman (101) recognised the need to obtain viscosity/time/temperature data and modified the cup flow test (98).

Several of the older types of test are still in use. These have sometimes been developed by the use of sophisticated recording equipment but many of the original objections to the test still exist. Indeed in the case of the Rossi Peakes test, it is now frequently used as a single point test rather than in its original form when it measured the flow length/time relationship.

Considerable success has been claimed for the capillary viscometer but while it is the only instrument capable of operating at very high shear rates, it is not suitable for measuring time dependent effects.

More recently, limited application has been made of the rotational viscometer (in the form of the variable torque rheometer) and the Kanavets rotational viscometer and of the oscillating disc rheometer to measure the duration of plasticity and the viscosity/time curve of thermosetting plastics. Of these techniques only the Kanavets Plastimeter has received the status of a standard test method and specification and is used for quality control purposes. (In USSR).

Conversely, considerable success has been obtained by the widespread use of rotational and oscillating disc rheometers in the thermosetting rubber industry.

As recently as 1969 it was reported that many present day methods of characterizing thermosetting materials are less sensitive than the injection moulding process. The author states that much of the difficulty experienced in injection moulding is due to the lack of relevant viscosity time data.(102).

"What is still lacking at the present time is a standard test method. The test in question must be simple and speedy, to answer the requirements of industry........ The conditions of moulding must be approached as nearly as possible especially as regards the time used for deformation, if this time is longer and is to do with polymerizable material the result will be distorted by the premature curing of the material. It is necessary to agree on the temperatures at which the plasticity is measured and also on the speed of application of pressure........ Lastly it is necessary to express plasticity in figures. The figures may be arbitrary but it is necessary that everyone adopts the same scale." These words were originally written by M.Forrer in 1933 (100) and are still relevant today although it would be better if the specification of plasticity referred to by Forrer was extended to include the change of plasticity with time.

Opinions of Industry and Current Procedures

In order to obtain more up-to-date background information for this work, the opinions of thermosetting material and machinery manufacturers and moulders were obtained during a series of discussions. These discussions resulted in an industry sponsored project at RAPRA and are summarized below.

The moulding industry is particularly concerned with batch to batch variation of materials which are particularly noticeable during the injection moulding of large mouldings, and occur mainly in the barrel, nozzle and runner sections. It is generally felt that many of the current test procedures were insufficiently sensitive and it is interesting to note that none of the manufacturers used the same test procedures and that all tested occasional batches of material with an injection moulding machine.

All companies stressed the need to test materials at relevant temperatures, shear rates and at similar flow times to those involved in the injection moulding process, and agreed that while it was desirable to produce fundamental results, it was essential to produce reliable empirical data. Any new test proce~~e~~dure must be practical and of direct relevance to the moulder.

A further problem exists in quantifying the state of melt at the nozzle which is necessary to produce satisfactory mouldings. This is currently set by an experienced tool setter using the system of trial, and error, and experience. While this technique can give excellent results it has two inherent weaknesses; it relies on a competent and consistent operator and can be time consuming. It was considered that a means of quantifying the ideal melt state at the injection nozzle would be of considerable value to industry as a means of machine setting process monitoring as well as providing a better understanding of the melt itself.

Chapter 3. Problems and Requirements of Thermosetting Plastics Characterization Methods.

The general aims of this project are to investigate the flow properties of thermosetting materials in order to relate them to behaviour during moulding. This chapter deals with the factors which have been shown to be relevant and speculates on the type of information needed and the experimental work necessary to validate it.

3.1 Relevant Factors in Injection Moulding of Thermosetting Materials

The thermosetting plastics injection moulder is concerned with the aspects of material flow which directly affect the moulding process. These include the conditions within the barrel, runners and mould. Typical values for pressure, temperature and shear rate normally used are shown in Table 1. From this information it can be inferred that an evaluation procedure should be capable of operating over a wide range of conditions, i.e. temperatures of 80 - 190°C, and shear rates of zero to 10^4sec^{-1}. The pressures also vary considerably but these largely depend on the material being moulded and on the mould used. A major requirement of an evaluation procedure is that the consistency of the material should be recorded as a function of time and should ideally allow the prediction of processing behaviour under variable conditions. The latter requirement means that the results should be expressed in fundamental units or if this is impractical then in reliable semi-empirical terms.

Difficulties and Disadvantages with existing test methods

Flow Measurements

a) Compression Instruments. These instruments are simple to operate but the flow pattern is extremely complex and compression instruments are unsuitable for measuring fundamental flow properties. Their use is largely restricted to measuring single point, empirical data and to low shear rates. For these reasons they have not been considered in this investigation.

b) Rotational Viscometers Rotational viscometers are subject to unknown end flow effects but their results are capable of fundamental interpretation. In their simple form they are unsuitable for use with thermosetting plastics. The variable torque rheometer is basically a rotational viscometer comprising two rotors in two connected chambers. This instrument will record the fusion and flow process and unlike most instruments does not require a melt before rheological measurements can be made. Rheological analyses have been published for the variable torque rheometer.

c) Capillary Viscometers. Capillary viscometers are the only instruments capable of operating at the high shear rates ($>10^4$ sec^{-1})encountered in injection moulding. These instruments ideally require a stable melt since they rely on a continuous steady flow through the capillary to produce satisfactory results. Care must be taken to avoid the material curing in the die, and capillaries of short land length are frequently used to avoid this effect. The material is usually heated by a conduction process, a lengthy operation which can lead to premature crosslinking before the test is carried out.

The rheological theory for flow in capillaries is well established and capillary viscometer results can be easily obtained in fundamental terms.

d) Oscillating Disc Rheometers. Rheological measurements can only be obtained under steady state conditions, i.e. during the period of minimum viscosity when the material viscosity is approximately constant. Changes which take place after this period are of interest and must be measured. Mechanical methods of following viscosity changes are limited to those which cause a limited distortion of the test sample. This is because the onset of crosslinking prevents the material flowing and thus any gross distortion of the material will cause its mechanical comminution. The two methods which have been used are a slow speed rotational viscometer and an oscillating disc rheometer. The former e.g. the Kanavets Plastimeter, operates at very low shear rates (0.016 sec^{-1}) which eliminates frictional heating effects, while the oscillating disc rheometer is widely used for thermosetting rubbers.

3.2. Objectives of the investigation

In the light of what has been discussed in the preceeding section, the hypothesis is suggested that no single or simple test method will characterize a thermosetting material for injection moulding but that a combination of three methods are required. The three methods are listed in Table 10. In order to correlate these results with the injection moulding process, it is proposed to use an instrumented injection moulding machine. Judicious application of the three methods will enable thermosetting moulding materials to be correlated to the compression and transfer moulding processes.

TABLE 10 Suggested correlation between test method and moulding process

Test Procedure	Corresponding Section of Moulding Process		
	Injection	Transfer	Compression
Variable Torque Rheometer	Injection machine barrel	-	-
Capillary Viscometer	Nozzle, runners, gates	runners gates	-
Oscillating Disc Rheometer	Mould	Mould	Mould

Materials to be examined

a) It is proposed to use current commercial moulding materials whenever possible. This approach has the advantage of providing materials having similar properties and variations of properties found in industry. It also means that their composition will be largely unknown and that the materials will be defined in the rather vague manner used by industry, e.g. general purpose, wood-filled, phenolic with an easy flow, good flow stability and disc flow .75 mm and cup cure of 55sec.

The base resin of PF5 and UF6 was confirmed by infra-red pyrolisate spectra analysis.

b) The injection moulding process would be used to characterize the materials as required.

c) Occasional materials would be prepared in the laboratory to demonstrate the effect of certain aspects. e.g. catalyst concentration.

d) Most thermosetting materials have a limited storage life and it will be necessary to employ more than one batch of a given material especially as the practical work will be spread over several years.

About 90% of thermosetting plastics which are injection moulded are phenolic based and urea formaldehyde materials constitute the second largest type. This work will therefore concentrate on phenolic and urea materials with other formaldehyde based thermosetting materials, listed in Table 11 and described in detail in the appendix.

TABLE IIa Classification of Materials considered.

Material	Purpose and use of materials
Feasibility Test Materials Melamine - Phenolic	Four materials used for feasibility tests and to ensure that the proposed technique is capable of differentiating between materials of known different behaviour. Materials represent compression, transfer and injection process.
Primary Materials General purpose phenolic and urea materials.	Main evaluation materials to investigate instrument variables and to determine the flow properties of materials at different shear rates and temperatures.
Secondary Materials General Purpose phenolic and amino materials	Similar to primary materials but includes small series of materials differing in a single property barrel life or cure rate, etc.
Tertiary Materials Phenolic and Amino Materials	Typical commercial production materials, laboratory prepared materials etc.

TABLE 11b: Thermosetting Moulding Materials

Material Type	Code*	Description
Feasibility Test Materials		
Melamine Phenolic	1*	Stiff flow compression moulding grade.
Wood filled	2	Stiff flow transfer grade.
	3	Easy flow transfer grade.
	4	Very easy flow injection moulding grade.
Primary Evaluation Materials		
Phenolic, wood filled	5	Injection moulding grade.
Urea formaldehyde cellulose filled	6	Injection moulding grade.
Secondary Evaluation Materials		
Phenolic, wood filled	7	Increasing resin precure.
Urea formaldehyde cellulose filled	8	Increasing resin precure.
Phenolic, wood filled	9	Increasing barrel life.
" " "	10	Increasing cure time.
" " "	11	Increasing flow pressure.
Modified phenolics+	12	Increasing accelerator addition.
Tertiary or Back-up Materials		
Phenolic	13	Various batches of injection moulding grade.
"	14	" " " " "
"	15	Injection moulding grades from various manufacturers.
"	16	Based on PF5 but with addition of lubricants and flow promotors.
"	17	Fibre reinforced phenolic materials.
"	18	Various batches of compression moulding materials.
"	19	Laboratory prepared materials.
Modified Phenolic+	20	Typical materials.
Urea Formaldehyde	21	Injection, transfer and compression moulding grades.
" "	22	Similar to above.
Dicyandiamide-Formaldehyde	23	Typical materials.
Melamine Formaldehyde	24	Injection and compression grades.

* where a particular category includes more than a single material, the material will be coded with a letter, e.g. 1A, 1B etc.

+ materials based on phenol but modified to give good high temperature properties.

Equipment Considerations.

The following equipment was available at RAPRA and was used for the work described in this thesis.

Variable Torque Rheometer	RAPRA/Hampden TRI described in Chapter 5
Capillary Viscometer	Designed at RAPRA and built as a single unit by BIP Engineering Ltd and described in Chapter 4
Oscillating Disc Rheometer	Monsanto Rheometer MPV, micro dies, described in Chapter 6

Injection Moulding Machines

Instrumented injection moulding machines and moulds were to be used to determine the behaviour of materials during the moulding process and to provide information to correlate with the results of the three test techniques.

Some of the work described in this thesis was carried out as part of a sponsored project using a Bipel machine and mould hired for the duration of the project only, and subsequent work had to be carried out using the RAPRA Turner machine. ERDE offered the use of a highly instrumented mould in their Ankerwerke machine for the comparison of a limited number of materials and consequently three injection machines were used in this work.

These were:-

1) Turner CTA - 2 - TS fitted with 60g or 120g barrels
2) BIP Bipel 60/26, 90g shot weight.
3) Ankerwerke V17/65 120g shot weight.

Chapter 4 Investigation of the rheological characteristics of thermosetting plastics using capillary viscometers

4.1 Introduction

The capillary viscometer used in this work was designed and made specifically for use with thermosetting plastics and with granular materials as well as with melt plasticized in the injection moulding machine barrel.

4.2 Theoretical Interpretation of Shear Flow in Capillaries

The theory of flow of fluids through capillaries is well established. It can be readily found in standard literature and in the technical press. Therefore it is not proposed to review the theory in detail. (104,105,106).

The theoretical analysis assumes that the flow is laminar, that time dependent effects do not occur, that the relationship between shear stress and shear rate is independent of die dimensions and that slippage between the melt and the die wall does not occur.

The theory shows that the shear stress at the die wall is equal to $\Delta P.D/4L$ and the apparent shear rate is $\frac{32Q}{\pi D^3}$ where ΔP is the pressure drop, D and L the diameter and length of the die and Q the volumetric flow rate. For many materials the relationship between these parameters is given by the equation $\frac{\Delta P.D}{4L} = K(\frac{32Q}{\pi D^3})^n$ where K and n are referred to as consistency indices. If the value of n is constant, the fluid is said to obey the Power Law. Viscosity is simply the ratio of shear stress to shear rate.

A Bingham plastic is a material where value of n can alter, representing a change due to the final breaking down of the structure of the material. (Fig.17). This is discussed by Kanavets and Sokolov (87,103) who showed that:-

$$\eta_1 = \frac{\tau - P_{K_1}}{\gamma}, \qquad \eta_2 = \frac{\tau - P_{K_2}}{\gamma}$$

where η = effective viscosity

τ = shear stress

γ = apparent shear rate

P_{K_1} = lower limit } of shear stress for Bingham flow behaviour

P_{K}. = upper limit }

Fig.17. Relationship between shear stress and shear rate for Bingham material (87,103)

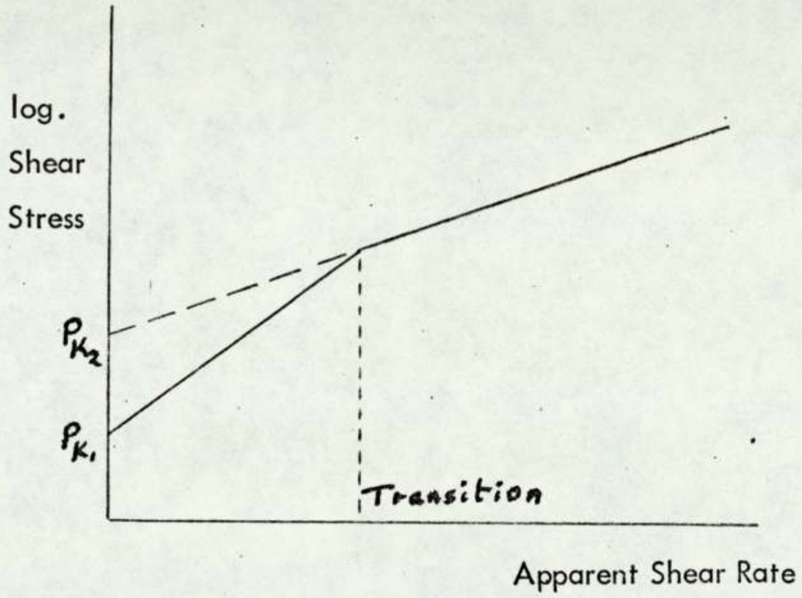


Fig.17 Shear stress/apparent shear rate curve for Bingham fluid.

Beck (20,21) reported that the pressure/flow rate relationship for a thermosetting plastic was similar to that of a Bingham Plastic and that the material flowed as a central plug surrounded by a thin layer of liquid at the wall of the flow channel. The equation used to describe this flow condition was

$$Q = \frac{R^4 . \Delta P.}{8 \eta . L} \left(1 - \frac{4x}{3} + \frac{x^4}{3}\right)$$

where Q = extrusion rate

η = viscosity of liquid layer

ΔP = pressure drop over nozzle length .

R = nozzle radius

L = length of nozzle

x = ratio of central plug to radius R (approx 0.3 for phenolics)

In certain materials the melt does not wet the capillary walls and the flow distribution is essentially plug flow. The flow process is then controlled primarily by the friction between the melt and the die and not by the viscous properties of the material.

Dujardin (15,112) analysed the flow process which takes place in an orifice test (a capillary in which the die length is considerably less than its diameter) and showed that the average flow rate can be related to the mean effective viscosity of the material under test.

$$\bar{\eta}_o = \frac{Q_o \, \Delta P \, t_u}{Q_u}$$

where $\bar{\eta}_o$ = mean effective viscosity

Q_o = initial amount of material in test mould

Q_u = amount of material flowing from orifice

t_u = flow time

ΔP = pressure drop

Heat Flow Calculations

Temperature calculations concerning static (as opposed to dynamic or shear heating) have been carried out using the method described by Hands (115) which uses standard graphical solutions to Fouriers equations. These give the relationship between several dimensionless groups ϕ, M, ε and Y where

$$\phi = \frac{\alpha t^2}{a^2}, \quad M = \frac{K}{ah}, \quad \varepsilon = \frac{r}{a}, \quad Y = \frac{\theta_1 - \theta}{\theta_1 - \theta_a}$$

The master graphs are given (115) for an infinite slab, an infinite cylinder and a sphere. Y is plotted against ε and each graph represents a different value of M. Separate curves are given (115) for various values of Q.

where α = thermal diffusivity
t = time
a = semi-thickness of slab or radius of cylinder of sphere
K = thermal conductivity
h = heat tranfer coefficient across material/vessel interface
r = semi dimension in normal direction to thickness
θ_1 = temperature of heating or cooling medium
θ = temperature of sample at $t = 0$
θ_a = initial uniform temperature

4.3 Use of Capillary Viscometer with Compounded Melt

The capillary viscometer consisted of three detachable parts; a melt transfer chamber and hydraulically operated ram, an instrumented bolster and a nozzle tip illustrated in Fig.18,19. Hydraulic oil pressure was transmitted to the ram through connections to the hydraulic oil system on the injection machine, its plunging action being automatically operated from the machine control by the ejector circuit. The transfer chamber was jacketed and hot water or oil circulated to maintain the melt temperature in the chamber at the approximate temperature of ejection of the melt from the nozzle of the machine. The volume of the transfer chamber was arranged to accept the full swept volume of the barrel of the injection machine. The bolster contained a pressure transducer and a melt thermocouple both situated flush with the internal wall.

A linear potentio-meter measured the ram displacement. The measurements were recorded on a UV oscillograph. A number of nozzle tips were constructed of differing capillary diameters and length/diameter ratios.

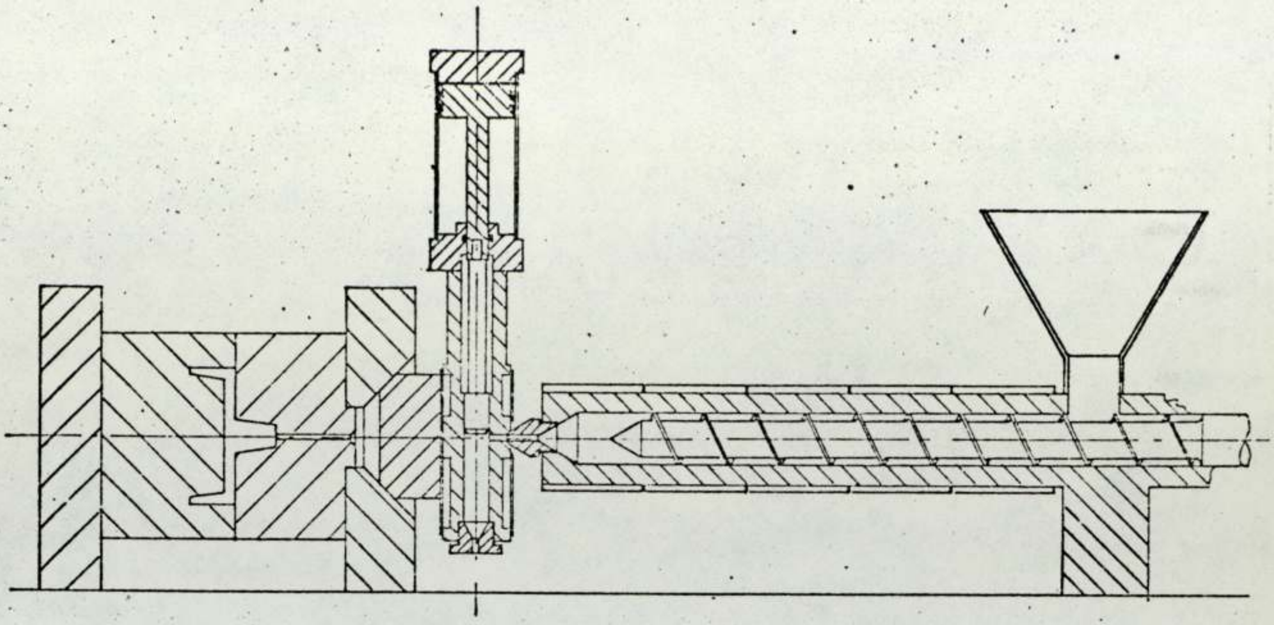


Fig. 18 Capillary Viscometer with Injection Moulding Machine showing method of clamping.

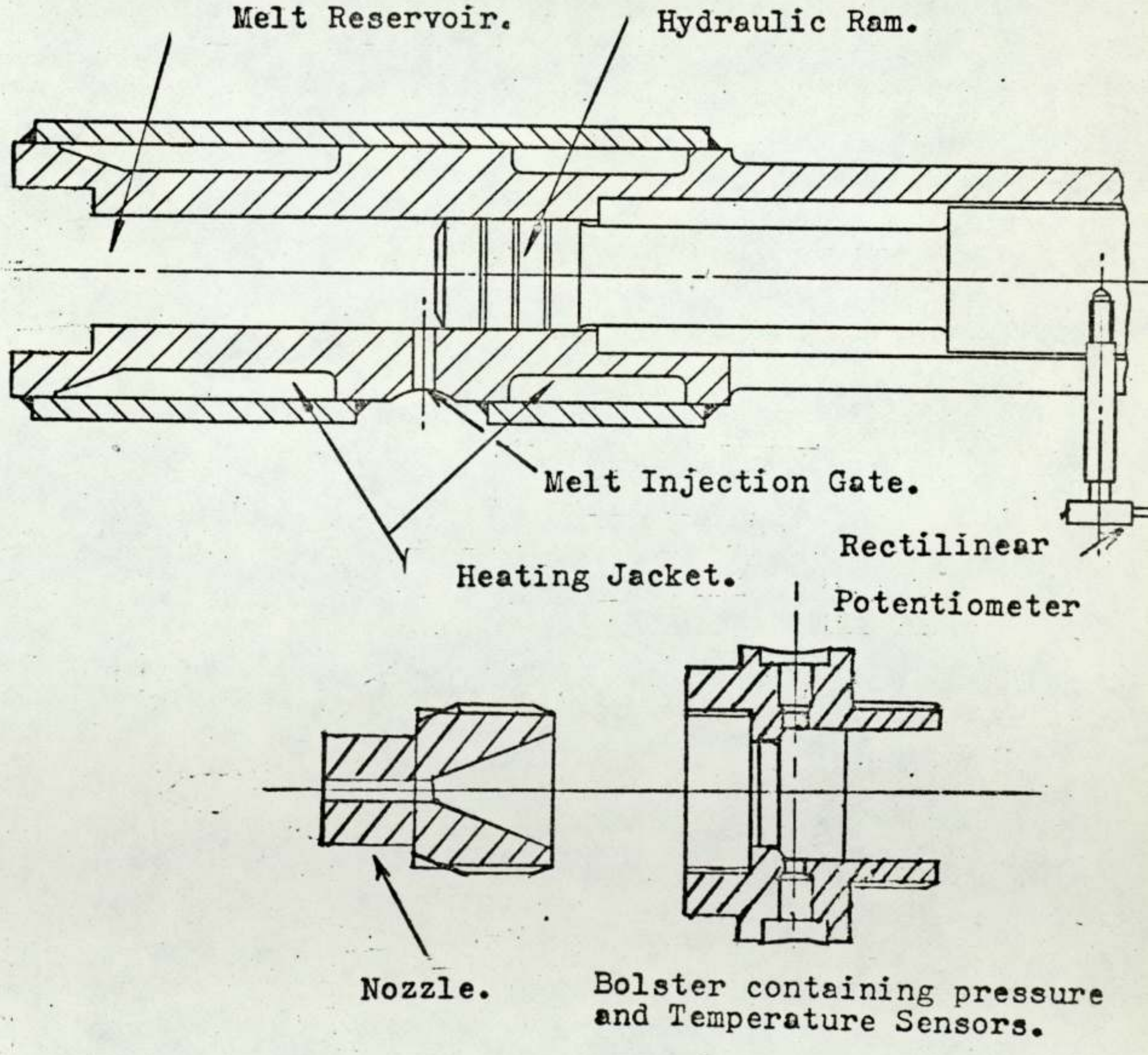


Fig. 19 Section through Capillary Viscometer.

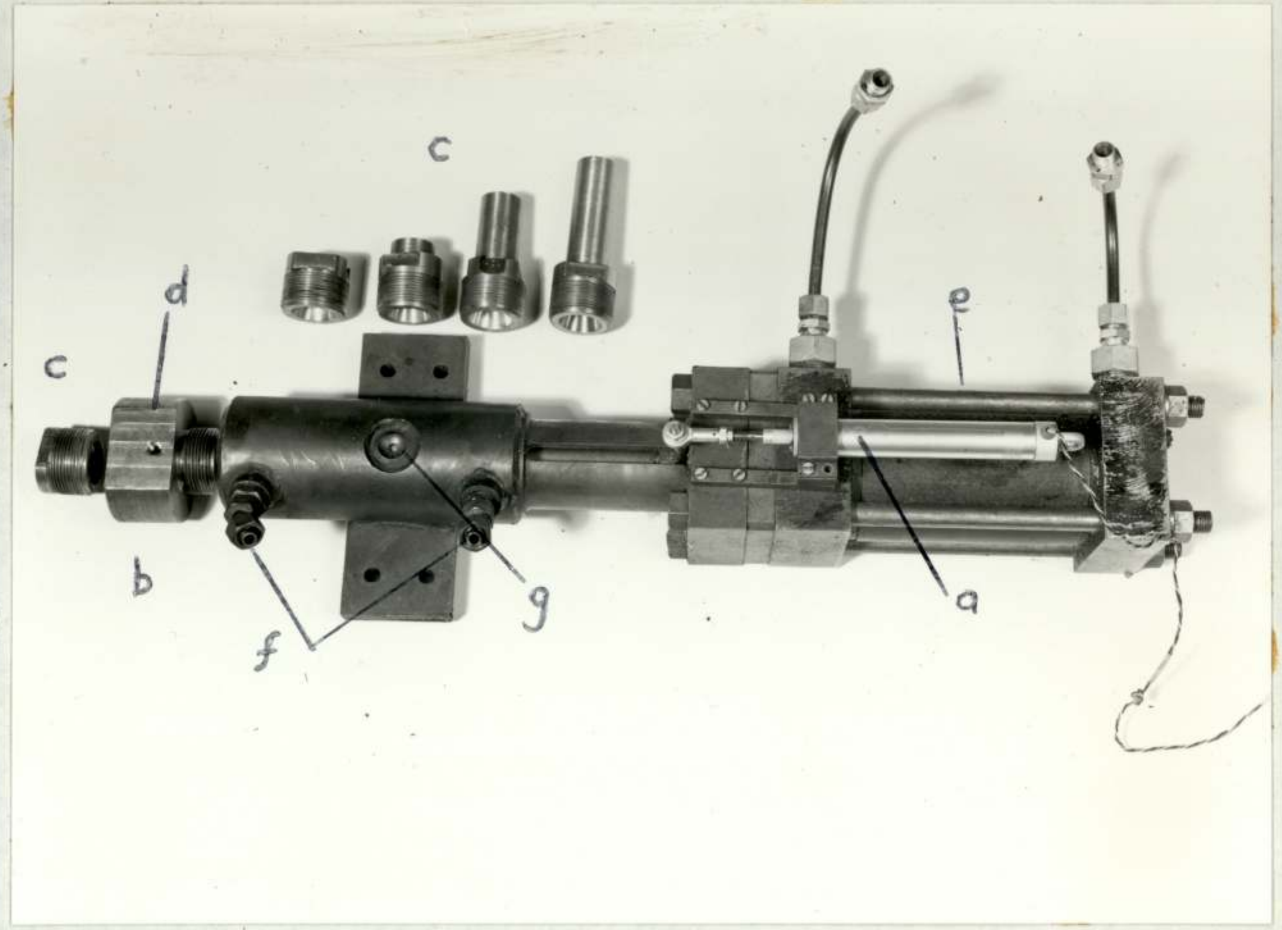


Plate 1. Capillary Viscometer.

a	Linear potentiometer.
b	Bolster for temperature and pressure sensors.
c	Nozzles of different diameter and L/D ratio.
d	Melt reservoir.
e	Hydraulic operating cylinder.
f	Heating oil supply pipes.
g	Melt injection point.

Length/diameter (L/D) ratios of 5:1, 10:1 and 15:1 were used to obtain extrusion rate vrs. pressure data. In operation, the capillary viscometer was recessed into the fixed platen of the injection machine so that the nozzle of the machine seated into aperture in the wall of the viscometer transfer chamber Fig. 18. The machine was set on automatic cycle approximating to practical production conditions. Plasticized compound was injected from the barrel of the machine into the viscometer transfer chamber and immediately after the chamber was filled it was ejected by the transfer ram through the capillary nozzle. The period for ejection was that normally taken for the material to cure in the mould. The apparatus was operated as a screw plasticizing/ram transfer machine. After discarding the first 5 sequential shots (to allow the system to reach equilibrium), the next ten shots were measured for each pressure setting and the results averaged.

A typical pressure/time curve obtained with the capillary viscometer is shown in Fig. 20 and shows several of the drawbacks which existed with the equipment. The initial high pressure was due to a cold slug in the die. The construction of the ram and transfer chamber did not allow the total swept volume of material to be ejected through the capillary nozzle, and residual material was not forced out until the next stroke of the ram. Material ejected by the viscometer therefore consisted of residual compound followed by freshly transferred compound which differed in their melt history and may account for the 2-stage pressure curve. Superimposed on the pressure traces were gross variations as well as smaller, transient fluctuations. The former variations were large for some machine settings, while the latter could vary from ± 1½% to ± 20% and occured within 0.3 seconds. The rapid fluctuations indicated a probable stick/slip effect of material in the capillary die. The larger pressure fluctuations were most noticeable at high extrusion rates and followed variations in the hydraulic pressure (monitored by a pressure sensor fitted in the hydraulic circuit). Because of these fluctuations, the measurements obtained from the traces were only approximations. Only the 5:1 and 10:1 L/D ratio nozzles having a 6.3mm orifice could be used with confidence. The slow extrusion rate through a nozzle of 15: 1 L/D ratio caused partial curing of the material in the capillary. Further nozzles of 5.7 mm orifice diameter and L/D ratios of 5:1 and 10:1 and dies of 3mm diameter 1:1 and 5:1 were also used. At lower rates of extrusion the ram distance/time curve was essentially linear but at higher rates of extrusion, a distinct change in the gradient was noted which corresponded to the change in the pressure levels recorded.

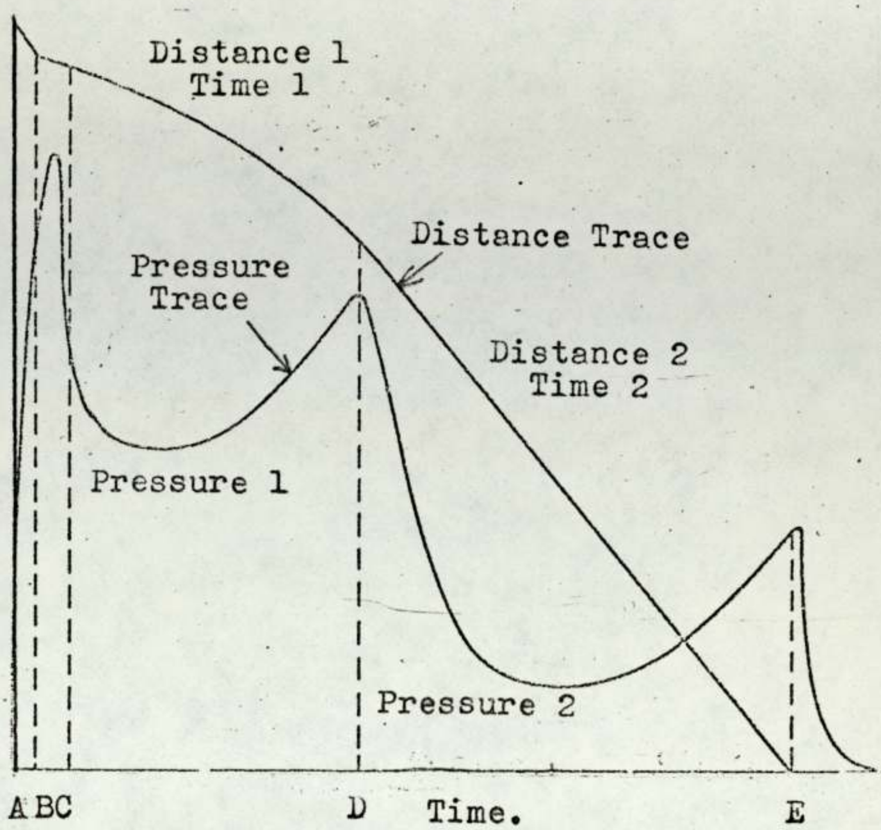
The melt temperature also increased by 4 to 8°C.

It was observed that at very high flow rates the flow of the material through the die was made up of a central plug and an outer layer of melt. This is discussed later in this chapter.

In order to calculate suitable values for the shear stress and apparent shear rate, a number of factors affecting the results have had to be ignored. It had to be assumed that time dependent effects such as thixotropy and premature condensation did not occur to any significant extent and that steady state conditions existed during the experiments. In practice, partial condensation of the material did occur, particularly at the higher back pressures and barrel temperatures used. This is shown by the considerable difference in the melt pressures and extrusion rates shown by the two sections of Fig.20. Detailed measurements are reported in the appendix but a reduction in pressure of 20% between the two parts of the curve corresponded to an increase in extrusion rate of about 230%. This difference in indicated viscosity occurred over a time period of only 45 - 50 seconds and illustrates the rate at which the melt is changing during its stay in the viscometer. It also had to be assumed that slippage did not occur between the melt and the capillary wall, although the rapid pressure fluctuations observed indicated that this was not strictly true. Furthermore, the experimental results used to calculate viscosity data were an estimated mean of variations of pressure and temperature.

Calculation of Shear Stress/Apparent Shear Rate Results

The recorded values of pressure, ram displacement distance and time for each of the two sections of the curve shown in Fig.20 are tabulated in the appendix, together with the extrudate weight.



A-B Slack in system.
B-C Peak pressure due to ejection of cold slug.
C-D High pressure/slow flow rate from previous shot.
D-E Low pressure/fast flow rate from current shot.

Fig. 20. Typical Pressure/Time and Distance/Time trace for capillary viscometer.

The volume extrusion rate for each section of the curve was calculated as follows:-

$$Q_1 = \frac{w}{\rho} \times \frac{d_1}{d} \times \frac{1}{t_1}, \qquad Q_2 = \frac{w}{\rho} \times \frac{d_2}{d} \times \frac{1}{t_2}$$

where Q_1 = Volumetric extrusion rate, first section

Q_2 = Volumetric extrusion rate, second section

d_1 = Ram displacement, first section

d_2 = Ram displacement, second section

d = Total ram displacement

t_1 = Ram displacement time, first section

t_2 = Ram displacement time, second section

w = Extrudate weight.

ρ = Specific gravity of melt assumedto be 1.3 for phenolic and 1.5 for urea materials.

As a melt flows from a wide to a narrow capillary, the velocity profile changes and this change results in a pressure loss which can be expressed either as a pressure or as an apparent increase in the length of the capillary. These factors can be measured as the intercepts with the y and x axes of a plot of pressure against capillary L/D ratio for specific extrusion rates. (Fig. 21b)

Alternatively, graphs of extrusion rate against pressure can be plotted for each capillary and the pressure required for several output rates determined (Fig 21a) These pressure values can then plot against the capillary L/D ratio for each output rate, (Fig21b). The gradient of each graph is then measured $\frac{\Delta P}{L/D}$.
The values of the apparent shear stress $\frac{\Delta P.D}{4L}$ and apparent shear rate were then calculated.

Example of Calculations of Results

Results after averaging and converting to SI units, and calculated volume flow rate for 3mm die.

TABLE 12a Experimental Results

PRESSURE (2) MN/m^2	DISTANCE (2)	Total	TIME(2) secs	SHOT WEIGHT Kg x 10 -3	VOLUME FLOW Rate cm^3/sec
		5:1 L:D			
25.5	2.5	5.61	2.33	60.3	8.8
33.0	2.29	5.75	0.84	61.8	22.5
34.1	1.84	5.75	0.54	61.6	28.1
37.0	1.85	5.75	0.6	61.7	33.1
		10:1 L:D			
42.0	2.73	6.1	3.17	60.5	6.8
48.3	2.75	6.09	1.46	61.3	14.6
50.1	2.86	6.1	1.32	62.5	17.1
51.5	3.05	6.1	1.27	63.3	19.2

Fig 21a Shows a plot of P against Q. Values of P for selected values of Q are shown below.

TABLE 12b Pressures for specific flow rates

Pressure MN/m^2		Volumetric flow rate cm^3/sec
Capillary 5:1	10:1	
23.0	41.0	5
26.0	45.0	10
29.0	48.5	15
31.5	52.0	20
34.5	55.5	25

Fig. 21b shows plot of P against L/D ratio for specific values of Q. and shows readings of die entry pressure loss to be made (intercept of line on pressure axis) and of values of $\Delta P/L/D$ (gradient of line).

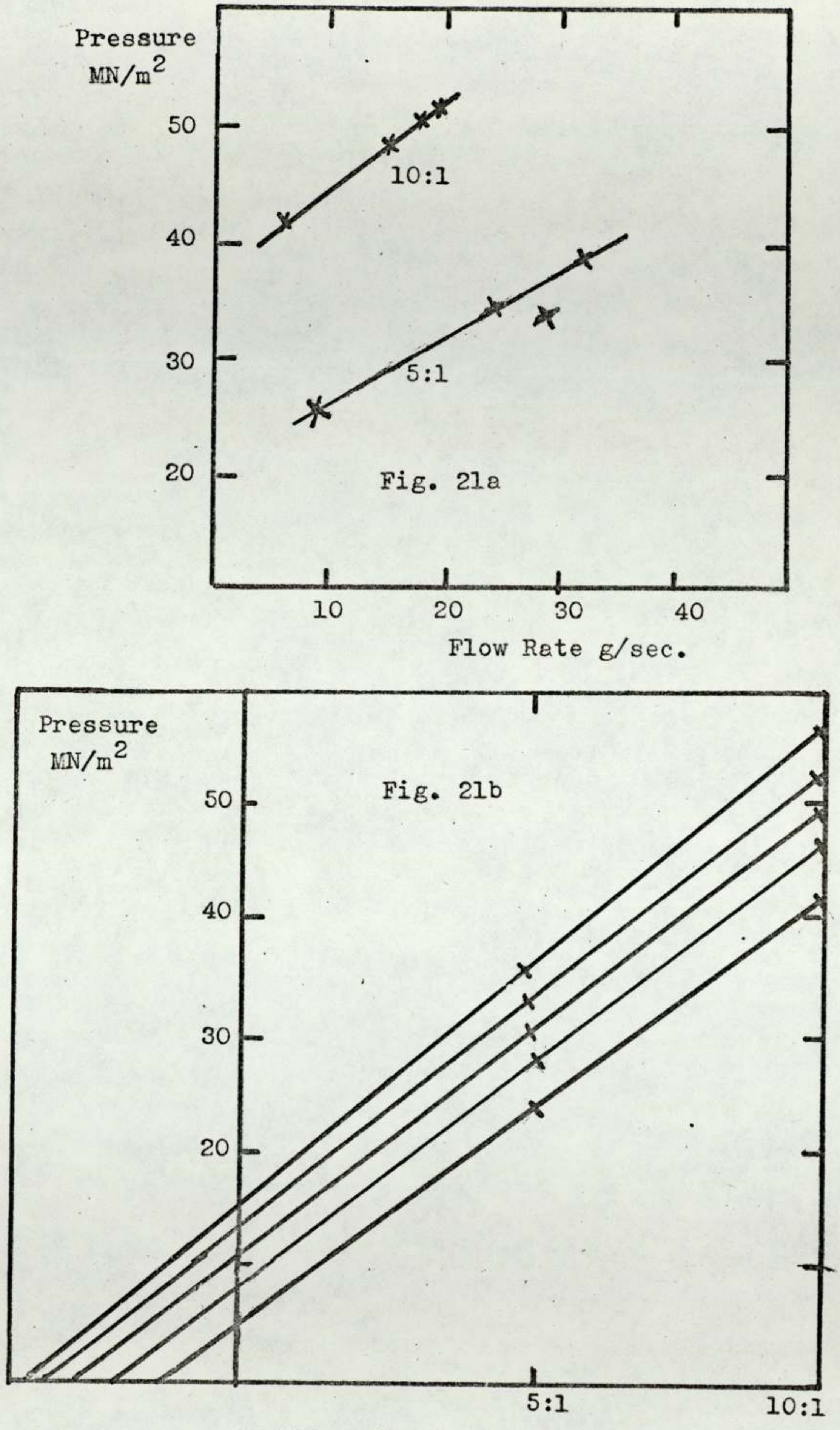


Fig. 21. Typical diagrams used in the calculation of viscosity results.

TABLE 12c Die entry pressure for specific flow rates (from Fig 21b)

Selected flow rate cm^3/sec	Die entry pressure MN/m^2	Gradient of graphs P/L:D
5	5.0	3.6
10	8.0	3.8
15	11.5	3.9
20	13.5	4.1
25	15.5	4.2

These results permitted the values of shear stress and apparent shear rate to be calculated.

TABLE 12d Results of calculations

Shear Stress $\frac{\Delta P.D}{4L}$ MN/m^2	Apparent Shear Rate $\frac{32Q}{\pi D^3}$ sec^{-1}
0.9	203
0.95	407
0.97	610
1.03	814
1.05	1017

The relationship between shear stress and apparent shear rate for phenolic material is shown in Fig. 22. Two curves are plotted for the phenolic material corresponding to the two sections of the pressure/time curve shown.

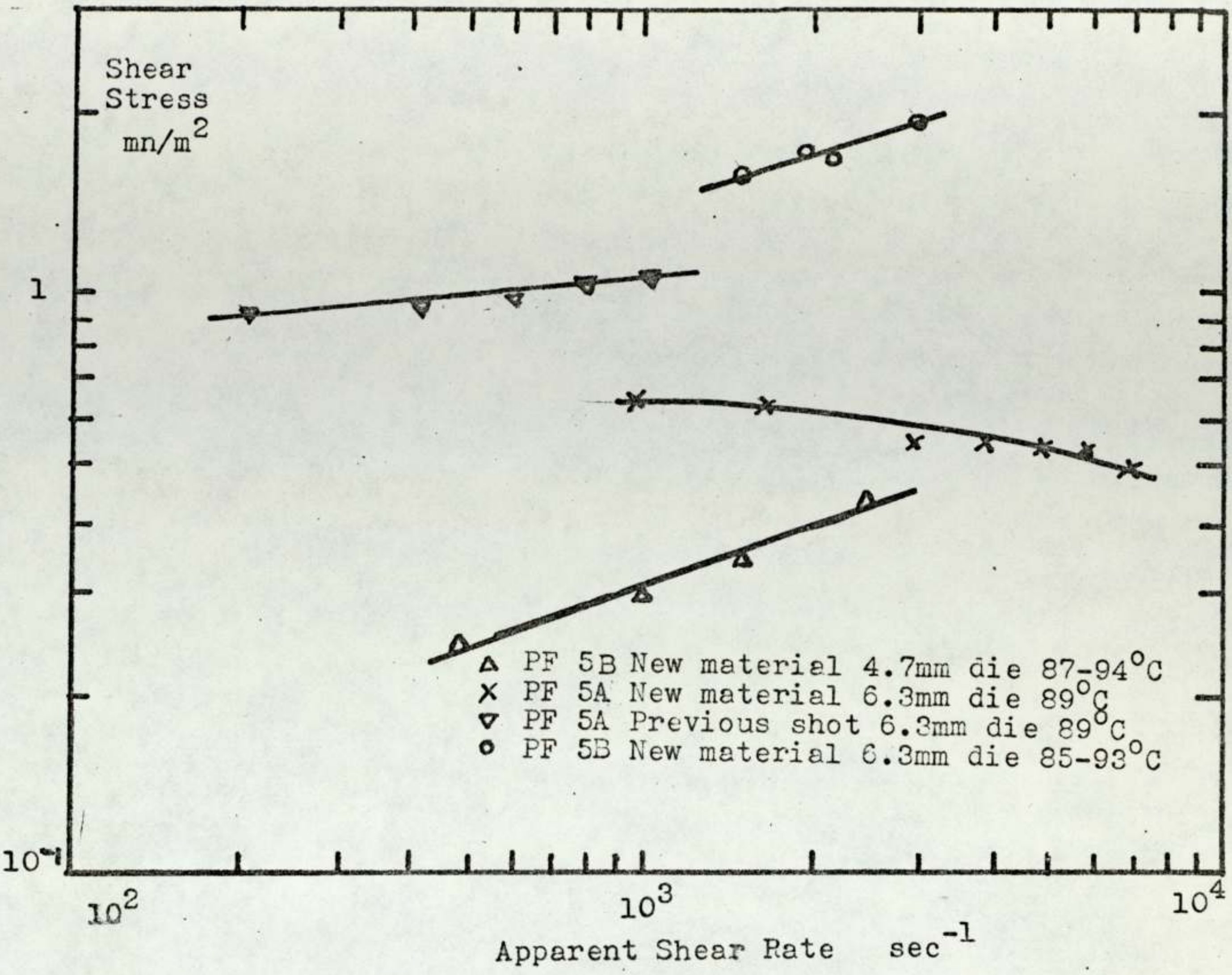


Fig. 22 Relationship between shear stress and apparent shear rate for Phenolic material determined in the melt capillary viscometer.

Attempts to use the capillary viscometer with urea formaldehyde materials failed since this material would not flow consistently through dies of less than 4.7mm diameter 1:1 L/D, or through dies of 6.3 mm and 5:1 L/D at medium pressures.

Results obtained with a urea formaldehyde material showed the two section type of pressure curve previously described for phenolic materials. Typical results are given in Table 13.

TABLE 13. Typical Results for Viscometer Trace

Measurement	Phenolic (PF5)		Urea (UF6)	
	1st Section	2nd Section	1st Section	2nd Section
Pressure MN/m^2	88 - 97	75 - 85	38 - 43	30 - 32
Temperature °C	77.5 - 87.0		90.5 - 92.8	
Flow rate g/sec	7.2 - 14.0	14.4 - 27.2	0.1 - 0.17	0.37 - 0.44

All subsequent work carried out with the capillary viscometer was performed with the 2mm dia. nozzle at the maximum pressure having an L/D ratio of 0.4 : 1 which corresponded to typical injection moulding machine nozzles. The viscometer was operated at a single pressure to give simple flow rate data.

Effect of machine variables on material flow properties

The results for phenolics Table 14a, showed that the more severe the process conditions (e.g. increased back pressure, screw speed, injection speed, injection pressure) the higher the melt temperature and flow rate for a lower recorded pressure. At very high machine settings*, reduced flow rates were recorded and the melt partially cured in the viscometer. Flow data could not be obtained at a barrel temperature of 95°C because the material partly cured in the viscometer.

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* 'high machine settings' refers to high back pressures, fast injection speeds and fast screw rotation speeds.

TABLE 14a: Effect of injection moulding machine settings on melt flow properties pressure, temperature and mass flow rate of Phenolic PF5. Figures in brackets give actual results, other figures were predicted using a multi variable regression analysis. (120).

PARAMETER Capillary Flow Pressure MN/m^2		BACK PRESSURE								
		0.41 MN/m^2			0.82 MN/m^2			1.24 MN/m^2		
INJECTION	INJECTION	SCREW SPEED			SCREW SPEED			SCREW SPEED		
PRESSURE	SPEED	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}
4.82 MN/m^2	2.5	(75) 76	70	63	75	70	(60) 63	69	(67) 65	59
	3.5	73	(70) 72	70	(73) 70	67	67	60	61	(68) 60
	4.3	70	71	(72) 70	66	(66) 67	67	(53) 56	58	59
6.89 MN/m^2	2.5	72	67	(63) 63	71	(66) 67	60	(64) 64	61	56
	3.5	(71) 71	70	68	67	67	(64) 66	58	(59) 59	58
	4.3	69	(69) 70	68	(64) 64	66	65	54	57	(57) 57
8.96 MN/m^2	2.5	68	(61) 62	54	(66) 66	61	55	59	56	(51) 50
	3.5	68	68	(62) 65	63	(66) 64	63	(53) 54	56	49
	4.3	(67) 66	67	66	61	63	(64) 63	51	(54) 54	54

PARAMETER Capillary Melt Temp °C		BACK PRESSURE								
		0.41 MN/m^2			0.82 MN/m^2			1.24 MN/m^2		
INJECTION	INJECTION	SCREW SPEED			SCREW SPEED			SCREW SPEED		
PRESSURE	SPEED	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}
4.82 MN/m^2	2.5	(84.4) 83.2	81.9	79.8	92.9	91.4	(86.0) 89.1	95.1	(94.6) 93.4	90.9
	3.5	80.7	(85.8) 83.0	84.5	(87.1) 90.5	92.6	93.9	92.8	94.7	(97.5) 98.8
	4.3	77.4	08.7	(84.8) 83.1	87.3	(86.7) 90.3	92.6	(91.0) 89.6	92.4	94.5
6.89 MN/m^2	2.5	88.7	87.1	(83.6) 84.0	97.5	(98.0) 95.7	93.2	(98.3) 98.7	96.8	94.1
	3.5	(85.3) 86.1	88.2	89.5	95.0	96.9	(102.8) 98.0	96.4	(97.6) 98.0	98.9
	4.3	82.9	(83.0) 85.9	88.1	(97.1) 91.8	94.6	96.6	93.1	95.8	(94.0) 97.6
8.96 MN/m^2	2.5	91.6	(90.9) 89.8	87.2	(98.0) 99.5	97.5	94.7	99.8	97.6	(95.3) 94.7
	3.5	89.1	90.9	(91.1) 91.9	97.0	(98.0) 98.6	(97.9) 99.6	(96.0) 97.4	(97.8) 98.9	99.5
	4.3	(87.4) 87.8	88.5	90.5	93.8	96.3	(97.9) 98.1	94.2	(97.8) 96.6	98.2

PARAMETER Capillary Flow Rate grams/sec.		BACK PRESSURE								
		0.41 MN/m^2			0.82 MN/m^2			1.24 MN/m^2		
INJECTION	INJECTION	SCREW SPEED			SCREW SPEED			SCREW SPEED		
PRESSURE	SPEED	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}	1 s^{-1}	1.66 s^{-1}	2.3 s^{-1}
4.82 MN/m^2	2.5	(19.8) 23.3	23.1	23.2	23.7	26.0	(24.3) 25.7	25.8	(25.4) 27.7	27.0
	3.5	21.9	(26.0) 25.7	26.8	(24.9) 24.1	27.5	28.2	25.1	28.1	(31.4) 28.4
	4.3	22.8	25.7	(27.9) 28.3	24.8	(29.4) 28.4	29.4	(23.2) 25.5	28.7	29.3
6.89 MN/m^2	2.5	25.8	26.9	(29.4) 28.3	26.7	(29.5) 29.4	29.5	(29.2) 26.3	28.3	29.3
	3.5	(27.2) 27.2	31.3	32.8	27.0	30.7	(29.4) 31.8	25.5	(30.9) 28.8	29.5
	4.3	28.1	(31.9) 32.5	34.4	(28.8) 27.6	31.6	32.9	25.9	29.4	(26.8) 30.3
8.96 MN/m^2	2.5	28.6	(34.4) 32.1	32.9	(24.3) 27.0	30.1	30.5	24.1	26.8	(26.5) 26.8
	3.5	29.7	34.2	(34.7) 36.1	27.1	(28.2) 31.1	32.6	(23.4) 23.1	26.3	27.8
	4.3	(30.7) 30.6	35.4	37.5	27.6	32.0	(38.2) 33.7	23.4	(27.4) 27.3	28.6

Machine Conditions

Bipel 60g machine

Barrel temp 88°C

Nozzle Capillary Viscometer

Capillary Temp. 90°C

Cycle Time 45 secs.

At a fixed barrel temperature of 88°C and a cycle time of 45 - 50 seconds, the intermediate machine settings produced a minimum melt viscosity (i.e. Back pressures of 0.82 MN/m^2, screw speeds of 100 - 140 rpm, injection speed settings of 2.9 - 2.35 and injection pressures of 6.9 - 9.0 MN/m^2). Excessively high machine settings resulted in a decrease in flow rate.

The flow properties of the urea resin material did not vary significantly with variations of process settings as reported in Table 14b.

The significance of these results in injection moulding were determined by an investigation into the effects of process settings on the quality(appearance and physical properties) of mouldings reported separately but summarized in the enclosed articles in the appendix.

The capillary viscometer was also used to compare a series of injection moulding phenolic materials, see Table 15.

TABLE 14b

Flow Characteristics of Urea Formaldehyde Material determined with the Instrumented Nozzle and Capillary Viscometer

Machine Variable		Instrumented Nozzle			Capillary Viscometer				
Variable	Level	Nozzle Pressure MN/m^2	Nozzle Temp °C	Inj. Time secs	Pressure 1 MN/m^2	Flow Rate 1 g/sec	Pressure 2 MN/m^2	Flow Rate 2 g/sec	Temp °C
Barrel Temp.	80°C	85	89.5	2.2	42	12	32	41	90.5
	90°C	82	90.5	1.8	43	10	32	37	90.5
	98°C	79	98.2	1.4	44	13	31	44	91.5
Cycle Time	-	-	-	-	-	-	-	-	-
	35 secs	82	90.5	1.8	43	10	32	37	90.5
	45 secs	80	94.3	1.6	39	11	32	37	92.5
Back Press.	0.2 MN/m^2	77	94.5	2.1	42	15	32	29	92.3
	0.48 MN/m^2	74	89.5	2.1	41	13	31	25	92.3
	0.82 MN/m^2	72	96.5	1.8	40	12	31	31	91.5
Screw Speed	1.0 sec^{-1}	72	97.0	2.0	40	12	32	31	91.5
	1.66 sec^{-1}	74	89.6	2.1	41	13	31	30	92.3
	2.33 sec^{-1}	72	97.1	1.9	38	13	31	30	91.5
Inj. Speed	2.5	70	96.8	2.1	38	13	31	30	91.7
	3.5	74	89.5	2.1	41	13	31	30	92.3
	4.3	74	97.0	1.9	38	15	32	27	91.5
Inj. Pressure	5.5 MN/m^2	55	96.2	5.1	40	17	32	24	91.5
	7.6 MN/m^2	74	89.5	2.1	47	13	31	25	92.3
	9.5 MN/m^2	89	98.5	1.7	42	16	31	28	91.5

Nozzle 1:1 L:D 6.3 mm DIA.

Unless otherwise stated, the following machine conditions were used:
Barrel Temp 90°C, cycle time 35 secs, Back Press. 0.48 MN/m^2
Screw Speed 1.66 sec^{-1}

TABLE 15 Comparison of Injection Moulding Materials

Material	Capillary Viscometer							
Phenolic	Pressure 1st section	Pressure 2nd section	Temp.	Screw Displ 1	Screw Displ 2	Inj Time 1	Inj Time 2	Shot
PF13	MN/m^2	MN/m^2	C°	cm	cm	secs	secs	weight grams
A	96.6	75.5	86.1	4.1	3.3	3.5	1.13	95.3
B	91.2	75.6	86.3	4.1	3.4	2.6	1.08	96.6
C	97.2	80.5	83.5	4.3	2.9	4.1	1.29	94.2
D	97.8	77.3	85.5	4.2	2.6	3.8	0.94	91.8
E	91.2	75.6	86.3	4.1	3.4	2.6	1.08	96.6
F	95.1	76.3	84.0	3.9	3.5	3.5	1.36	95.3

4.4. Use of the capillary viscometer with granular materials

When used as a normal capillary viscometer with granular materials, the instrument was inverted, powder was poured into the barrel and the nozzle screwed in place. The material was heated for a specified time and then extruded. The extrusion rate was measured using a linear potentiometer attached to the ram. It had originally been intended to use pressure and temperature sensors in the capillary bolster but this proved impracticable because of the relationship between the swept volume of the viscometer and the bulk density of the material.

Initial feasibility studies were carried out at 90°C and 150°C at 1.06 and 10.6MN/m^2 and used capillaries of 0.4:1 and 5:1, L/D. The results showed that capillaries of 5:1 L/D ratio could not be used at the lower temperatures. At 150°C, the total flow time is approximately 1 second and this obviously limited the usefulness of the results since the measuring equipment is only capable of measuring to ± 0.1 second. Similarly a variation of only ± 15 seconds on a residence time of 210 seconds was sufficient to alter the mean recorded flow rate from 24.7 to 28g/sec. Fig.23. Thus measurements made at higher temperatures are of limited value since the errors involved are greater than the differences between some materials. Most work has therefore been carried out at lower temperatures (90° - 98°C). High pressures have been used in order to produce high shear rates. (For phenolic materials 10.6 MN/m^2 gives a shear rate of 3.5×10^2 to 7.3×10^3 sec^{-1}) (Table 17).

TABLE 16 Comparison of Material Flow Rates through dies of 5:1 and 1:1 L/D

Material PF 11	Flow rate g/sec	
	Capillary 6.3m.m die, 150°C	10.6 MN/m^2
	5:1 L:D	1:1 L:D
A	40	25.3
B	39.2	25.9
C	30.2	32.0
D	25.8	22.5
E	27.3	22.5
F	31.0	35.0

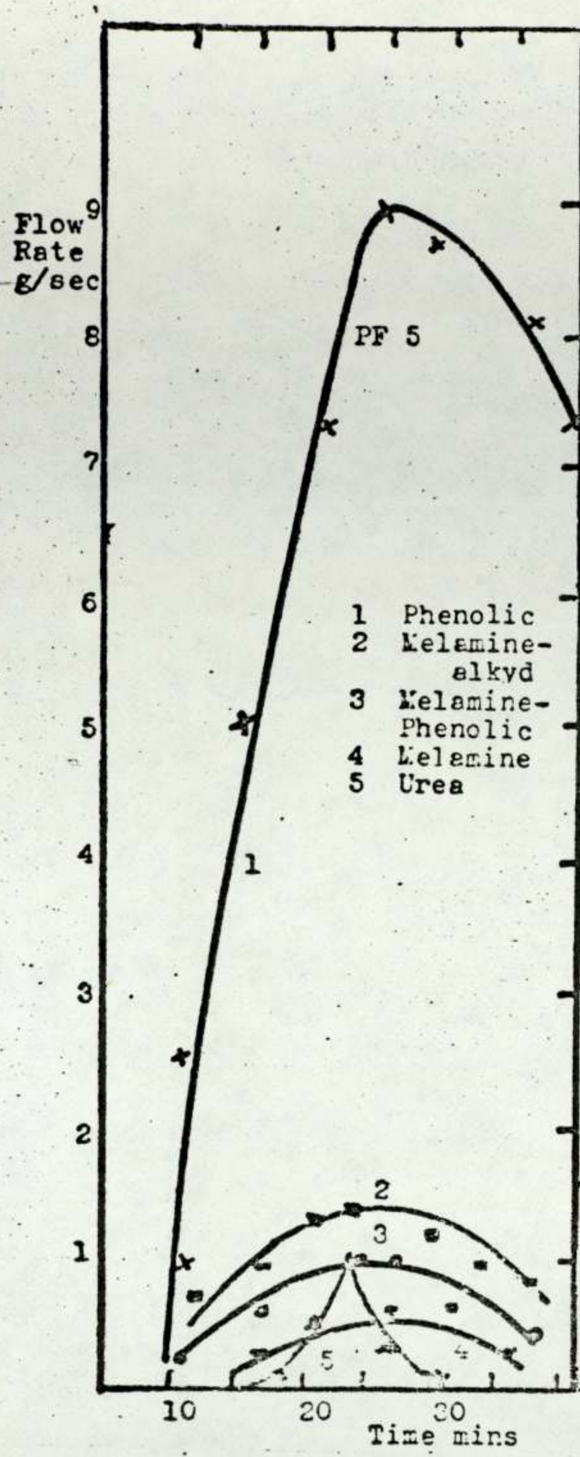


Fig. 23. Flow rate/chamber residence time curves for capillary viscometer. Granular materials at 98°C, 10.6 MN/m^2 pressure 2mm die

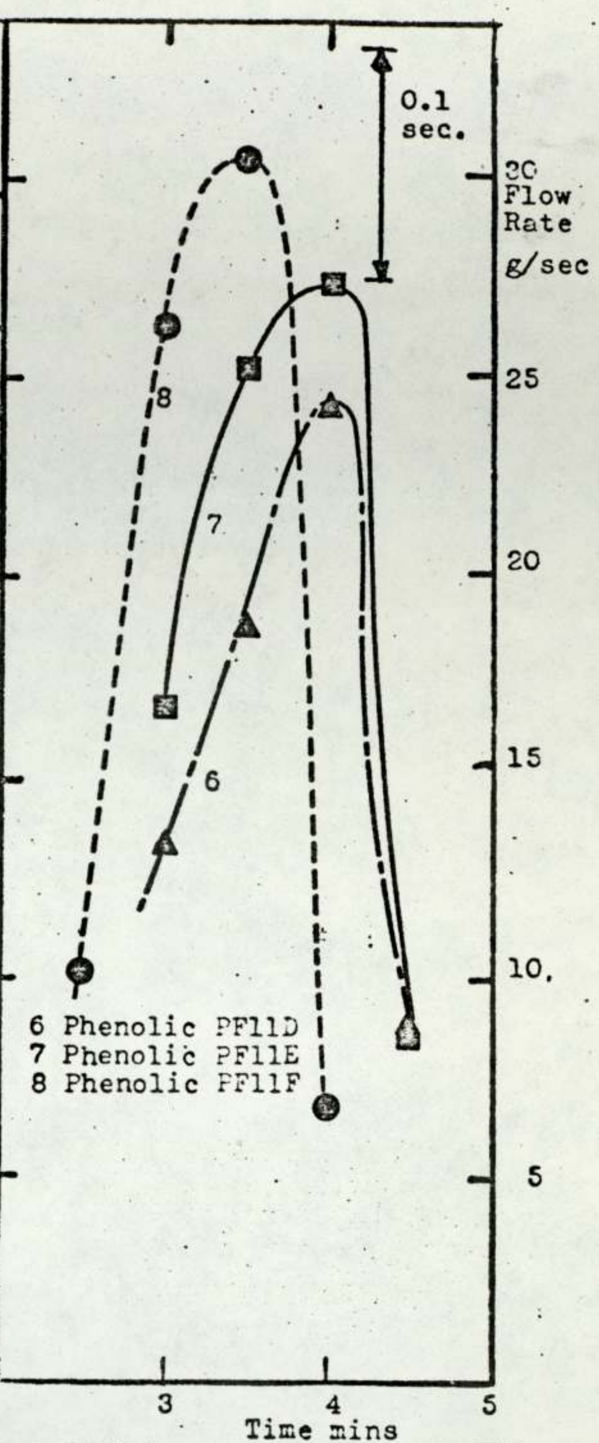


Fig. 24. Flow rate/chamber residense time curves for capillary viscometer. Granular materials at 150°C 10.6 MN/m^2 pressure 2.6mm die.

A criticism of using a single extrusion pressure is that it measures the volumetric flow rate of a material, at a fixed shear stress. Thus low viscosity materials will flow more rapidly and therefore at higher shear rates than a material of higher viscosity. For the comparison of dissimilar materials this is of limited use since the viscosity of many materials is shear dependent, but this disadvantage can be overcome by measuring the flow rate over a range of pressures, see Fig.25. A comparison of the flow rate of materials at constant pressure is shown in Table 17.

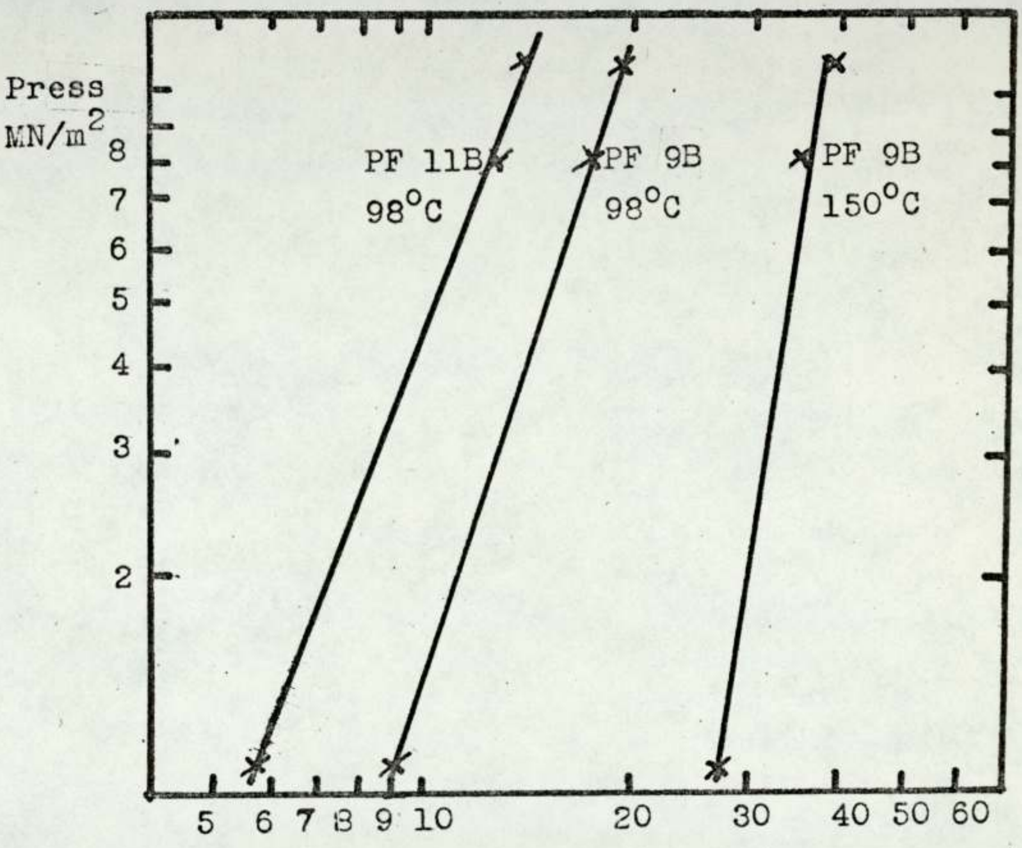


Fig. 25. Relation between pressure and flow rate for capillary viscometer with granular (unplasticised) materials.

For most materials the ratio of extruded material to the original charge weight is approximately constant showing that cessation of flow was not due to precure of the material. The results relate to the period of maximum plasticity and are not affected significantly by variations in material performance e.g. cure rate, barrel life etc. (Fig 26).

TABLE 17: Mean Effective Viscosity of Materials using Orifice Flow Meter with Sintered Powder

Material	Mean Effective Viscosity $N s/m^2 \times 10^6$	Apparent Shear Rate $sec^1 \times 10^2$	Flow Rate g/sec	Flow Retention %
	Die 2 mm Dia. 98°C			
PMF 4	13.1	7.4	.6	41
PF 5	.3	117	9.3	41
UF 6	12.8	3.6	.6	41.1
PF 7A	.8	120	9.3	40.0
" 7B	1.6	63	5.0	41.2
" 7C	7.8	12	1.0	37
" 7D	916	-	.01	9.3
UF 8A	10.9	3.2	.71	39.5
" 8B	83	0.9	.09	41
" 8C	1410	0.07	.01	22.5
PF 9A	.72	137	10.9	35.1
" 9B	.68	144	11.5	36.0
" 9C	.47	207	16.5	35.2
PF 13	.8	118	8.6	38
	.9	108	8.5	-
PF 14A	1.5	66	13.2	38.2
" 14B	1.5	67	13.3	38.9
" 14C	1.8	54	10.9	38.2
" 14D	.9	58	5.5	38.0
" 14E	1.5	67	13.4	38.4
" 14F	1.2	33	16.5	37.5
PF 15F	5.6	56	4.4	40.5
PF 18A	13.9	29	.55	43
" 18B	11.4	24	.68	-
18C	460	2.5	.01	16
UF 22B	305	0.3	.02	17.9
" 22C	4670	<.01	.01	-
" 22D	16.3	6.0	.5	29.2
" 22E	9.1	11	.85	28.2
" 22F	6.2	1.6	1.3	13.3
DIDI 23B	6.1	1.6	1.3	13.3
MF 24C	90 .4	0.5	.88	31

Material	Mean Effective Viscosity $N s/m^2 \times 10^6$	Apparent Shear Rate $sec^1 \times 10^2$	Flow Rate g/sec
	Die 0:8:1	2.6 mm	Dia. 98°C
PF 9A	.43	116	18.0
" B	.39	128	20.0
" C	.36	139	21.7
PF 11 A	.6	79	12.3
" B	.6	88	13.8
" C	1.8	28	3.3
" D	.5	105	16.4
" E	.9	56	8.6
" F	.69	72	11.3
PF 15 E	2.1	24	3.6
	Die 0:8:1	2.6 mm	Dia. 150°C
PF 9A	.2	27	39.2
" B	.19	28	40.2
" C	.2	27	39.2
PF 11A	.19	264	40.0
" B	.2	257	39.1
" C	.26	192	29.2
" D	.31	165	25.0
" E	.29	176	26.7
" F	.26	198	30.0
PF 15E	.77	71	10.2

A comparison of materials differing in various properties is given in Fig.26. The results show that the capillary technique measures considerable differences in the viscosity of these various materials but that it does not readily show differences in properties such as flow life, cure rate etc. The relationship between the duration of fluidity of a material and it's barrel life can be obtained (Fig 26a) but this is an extremely lengthy process which involves heating a static powder. The results in Chapter 5 show that a better correlation is obtained by measurments made under dynamic heating conditions.

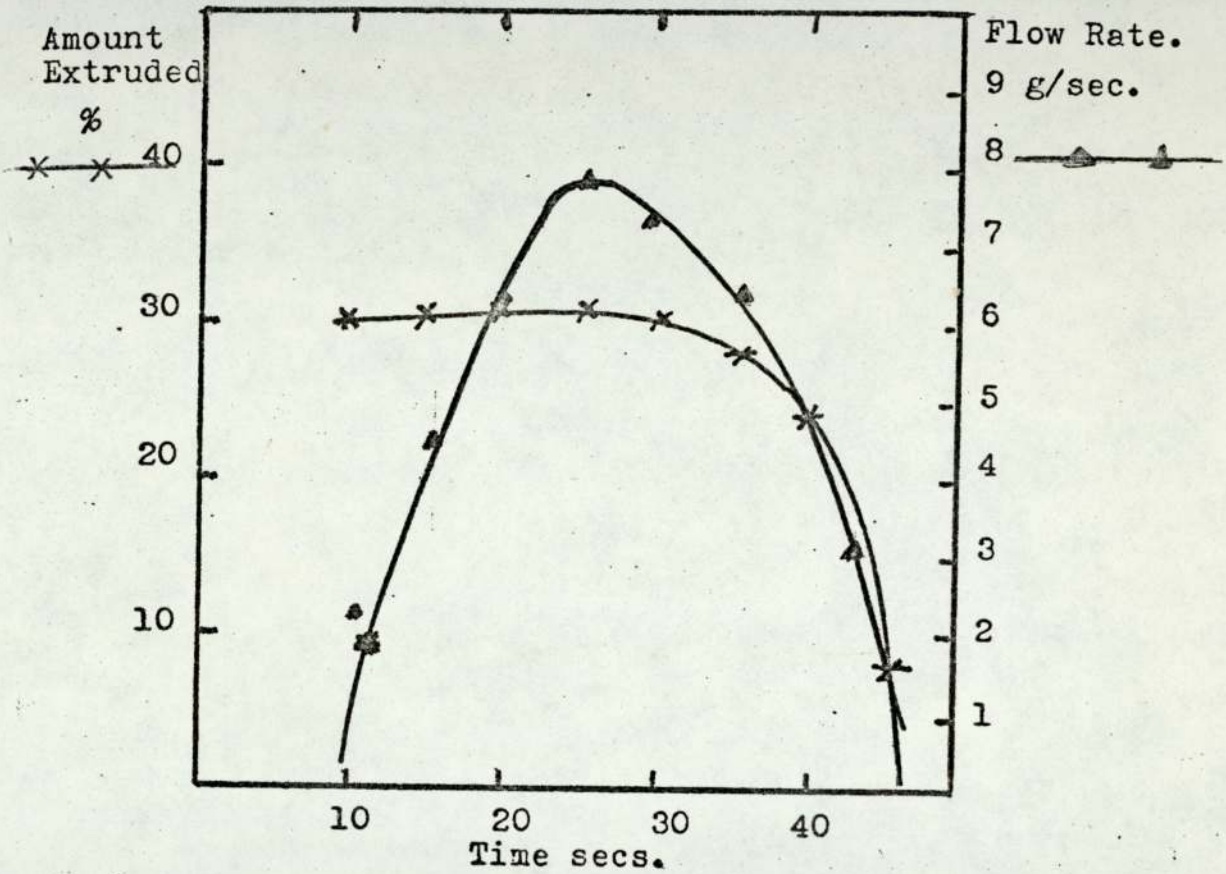


Fig. 26a. Correlation between chamber residence time, material flow rate and the amount of material extruded. Phenolic PF 5.
Pressure 10./6 MN/m^2
Temperature 98°C
Die 2mm dia. 0.8:1, L/D ratio.

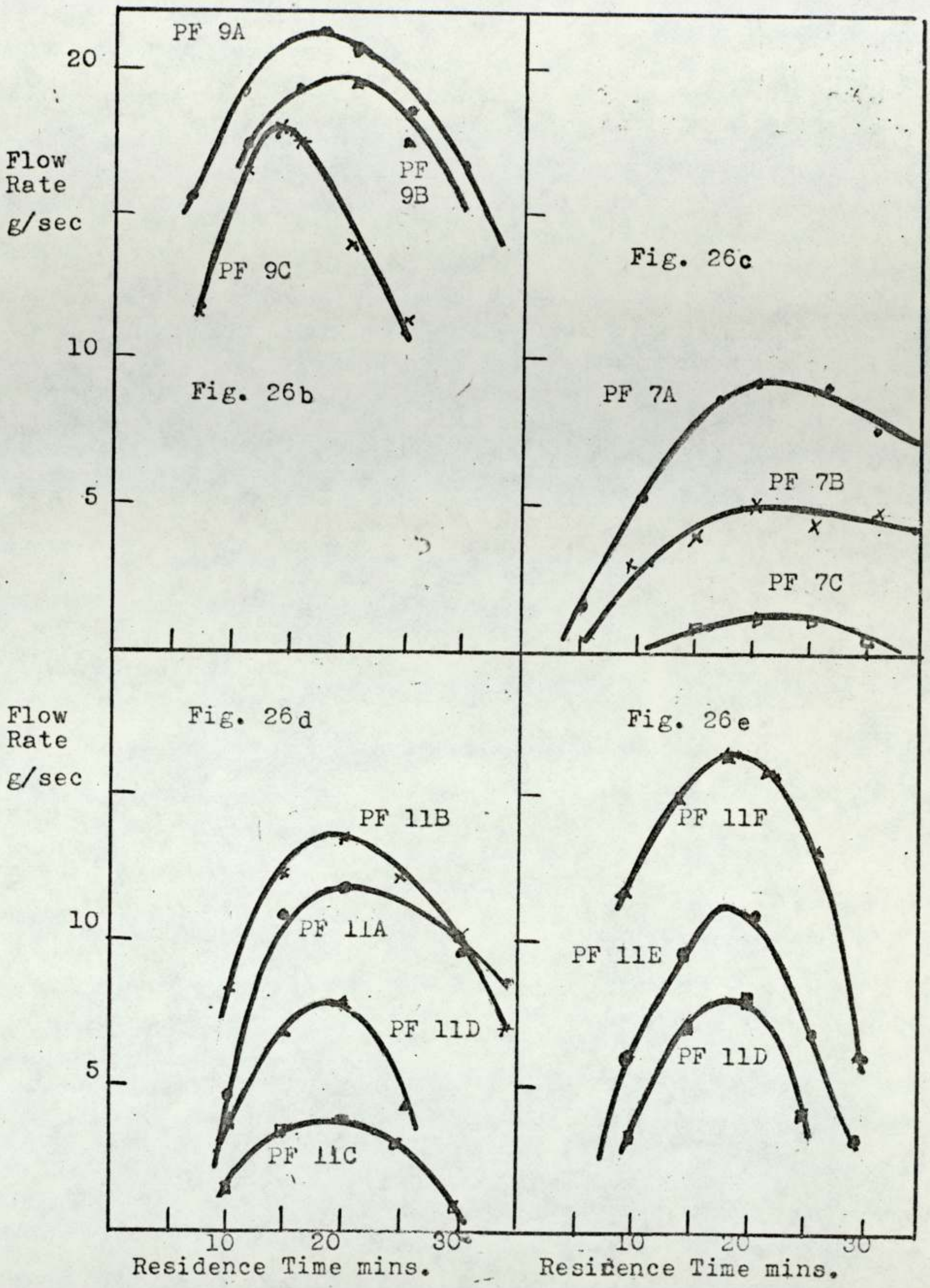


Fig. 26. Relationship between viscometer residence time and flow rate for Phenolic materials of different barrel life (26b), resin precure (26c), flow pressure (26d), and cure rate (26e).

4.5 Use of Injection Machine Nozzle as a capillary viscometer.

A nozzle adaptor was constructed to take a pressure transducer and a melt thermocouple, both instruments being located flush with the internal bore of the adaptor. Fig.27. The adaptor had a threaded end onto which the nozzle tip was screwed. Nozzle tips of varying L/D ratios were made. A rectilinear potentiometer, measured the screw displacement and all parameters were recorded using a UV oscillograph. Two Turner machines (60g and 120g) and a Bipel machine (90g) were fitted with this instrumentation. Process conditions used on each machine were arranged to be as near as practicable to production settings previously determined using a plaque tool. Hydraulic pressure was varied to several different levels for each of the nozzles examined which differed in L/D ratio and orifice diameter. Machines were arranged to eject the full swept volume of the barrel into air on automatic cycle, the ejected material being collected and weighed.

Approximately 40-50 shots were taken at each pressure setting and the initial 5-10 shots were discarded to allow the machine to reach equilibrium after resetting. Monitored information typical of the Turner machines and the Bipel is illustrated in Fig.28. At lower set hydraulic pressures a fairly constant screw displacement rate was obtained but at the higher pressures it increased towards the end of the screw stroke. The results showed that, in general, high hydraulic pressures gave shorter extrusion times and screw strokes, and higher shot weights. Longer nozzle tips resulted in longer extrusion times and lower shot weights (Fig.29). Above a certain hydraulic pressure (7 to 8 MN/m^2) these relationships remained unaltered. In general, changes in nozzle pressure showed similar changes to those occuring in the hydraulic pressure. Distinct differences can be seen between the monitored pressures from the Turner machine and the Bipel machine. As with the Turner, the Bipel gave shorter extrusion times and higher shot weights at higher pressure settings and longer extrusion times and lower shot weights with the longer nozzles. The pressure curves obtained from the Bipel were similar to those obtained when the capillary viscometer was used on the same machine and it is probable that differences in the monitored data between the two machines are due to differences in the two hydraulic systems. The reproducibility of these results is shown in Table 18.

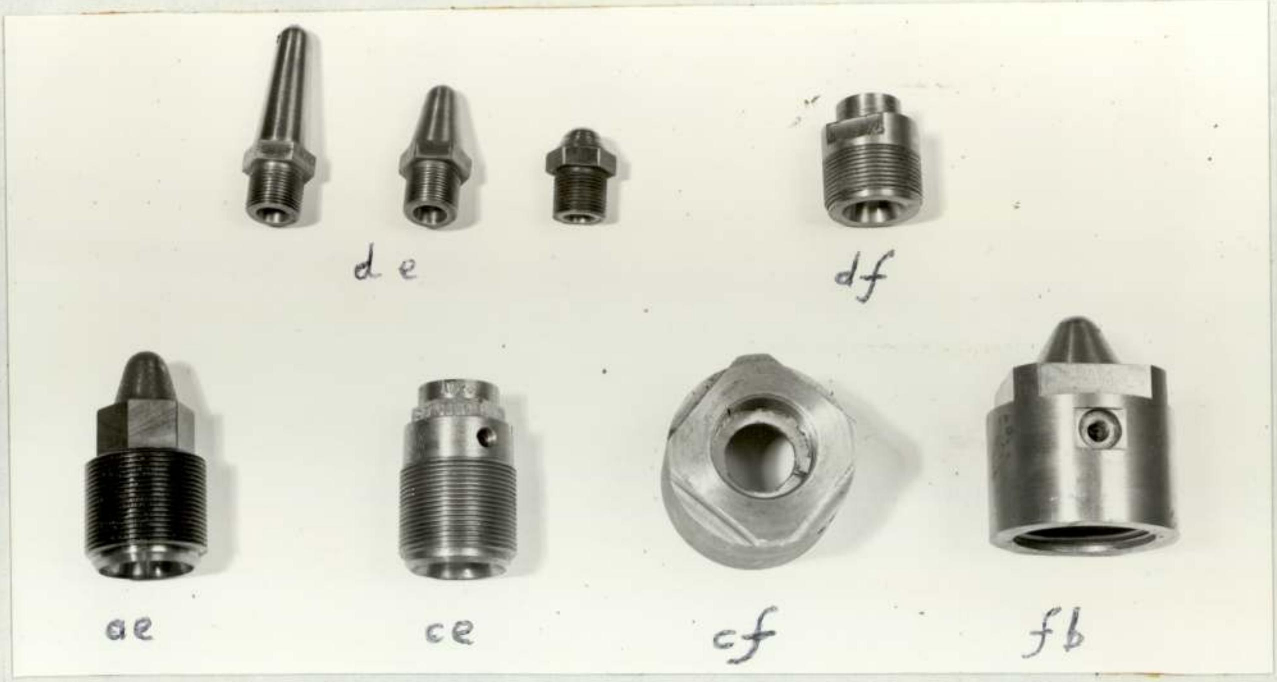


Plate 2. Injection moulding machine nozzles.

a Standard nozzle. d Nozzle tips.
b Instrumented nozzle. e For Turner 60g m/c.
c Instrumented bolster. f For Bipel 90g m/c.

Plate 3. Instrumented nozzle fitted to Turner 60g m/c showing temperature (tip and melt) and pressure sensors and screw displacement potentiometer.

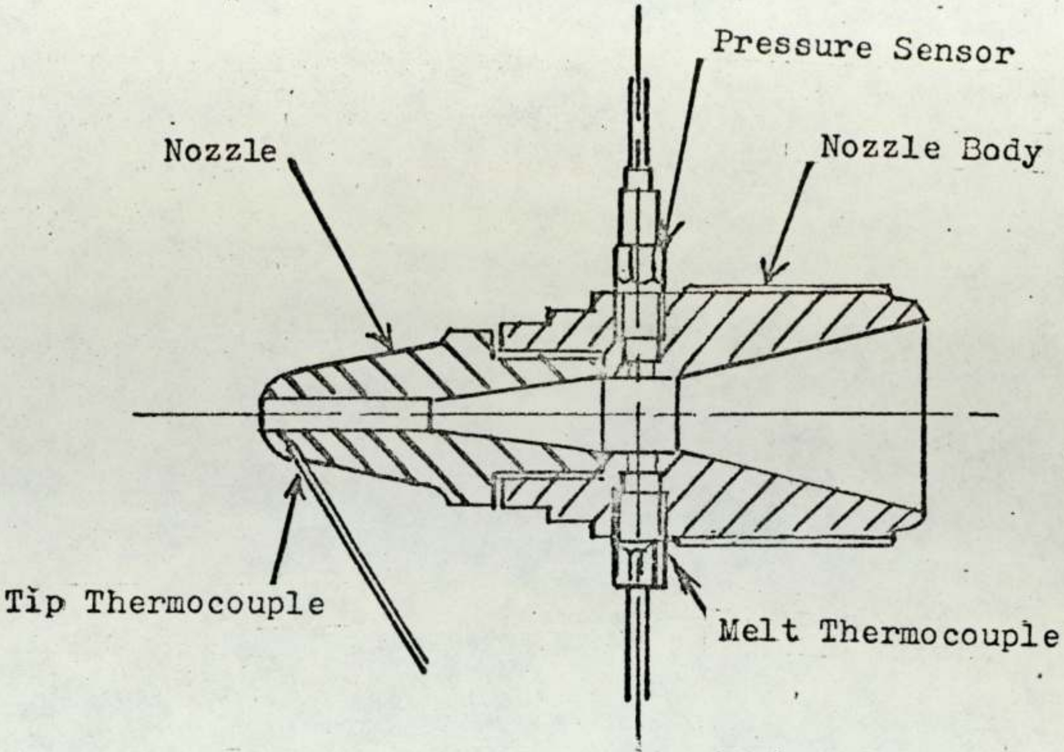


Fig. 27 . Section through instrumented nozzle.

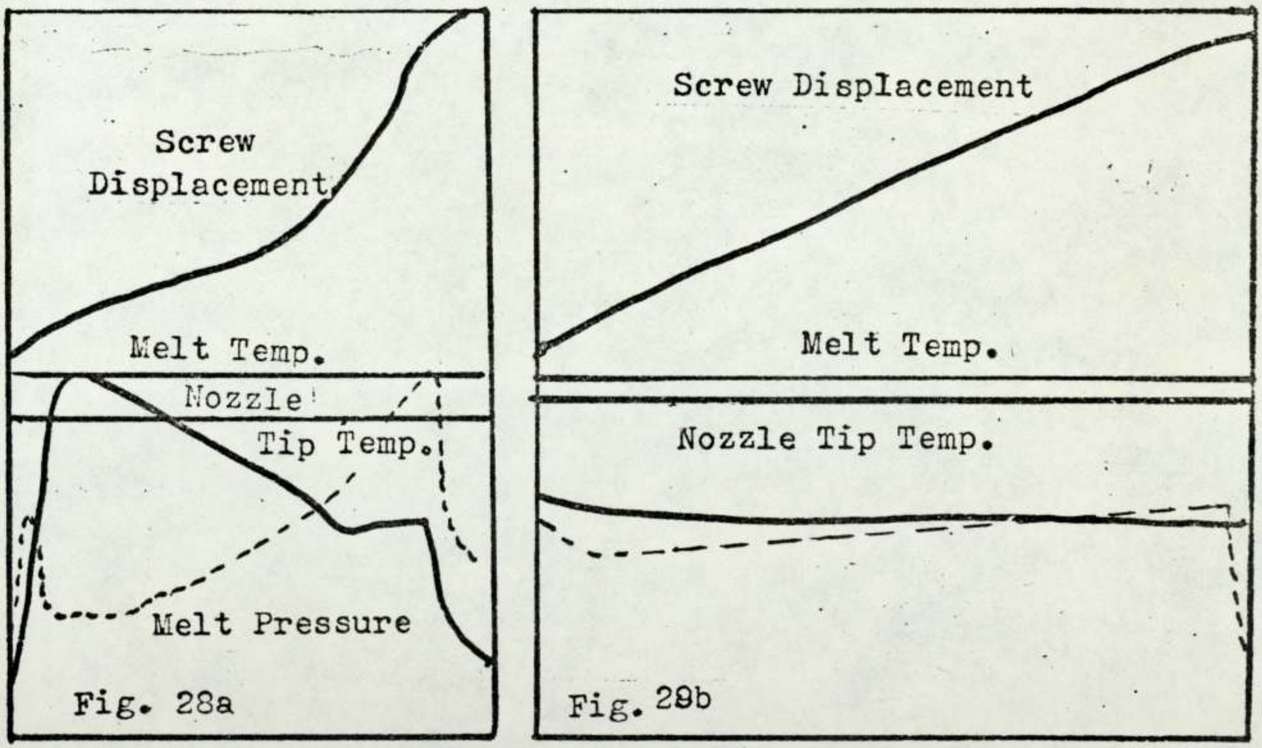


Fig. 28 . Typical traces for screw displacement, melt temperature, nozzle tip temperature and melt pressure for high (Fig.28a) and low (Fig. 28b) hydraulic pressures.

—— Turner machines ---- Bipel machine.

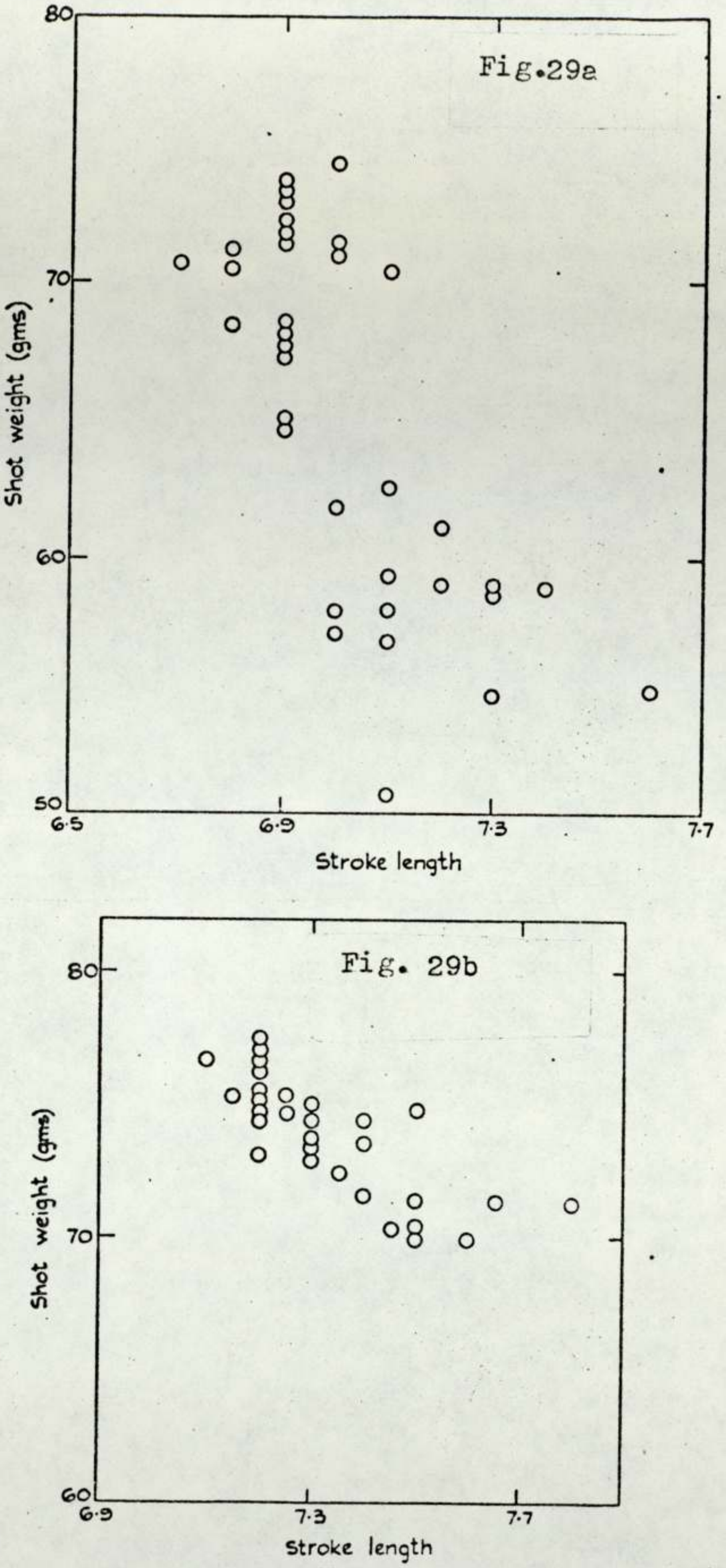


Fig. 29 . Relationship between shot weight and stroke length for nozzles of 1:1,L:D (Fig. 29a) and of 10:1,L:D (Fig. 29b).

TABLE 18 Coefficients of Variance for air shot measurements Turner 60g machine

Nozzle	Shot Weight	Pressure	Melt Temp	Nozzle Tip Temp
1:1	1.5 - 0.84	2.5 - 1.2	0.4 - 1.7	0.32 - 1.1
5:1	5.7 - 1.4	3.1 - 1.1	0.3 - 0.7	0.31 - 0.9
10:1	4.8 - 1.5	2.8 - 1.5	0.2 - 0.8	0.3 - 0.7

The screw was observed to turn slightly at the start of the injection stroke and this, coupled with the slippage of the melt over the screw flights means that the screw displacement cannot be used as an accurate measure of extrusion rate and that for analysis purposes, the average extrusion rate obtained by dividing shot weight by extrusion time was used. It is difficult to determine the effective pressure during a shot but for convenience the mean values have been used. It is, however, recognised that this may not represent the true mean pressure except for the lower hydraulic pressures. Measured melt temperatures were fairly constant but the temperature of the nozzle tip is raised by about 4°C during each shot. This effect has been ignored. Nozzles of identical diameter but of different lengths were used. The shortest nozzle has an L/D ratio of 1:1 and while this approximates to a production nozzle, it is inadequate for viscosity determinations. The other nozzles have L/D ratios of 5:1, 10:1 and 15:1 and are barely adequate. The latter nozzle gave erratic results due to material precuring in the nozzle.

Fig 30a shows the relationship between the nozzle pressure and material flow rate for a phenolic material when tested in the Turner machines using nozzles of different L:D ratios. These graphs are approximately linear and can be used to calculate the shear stress/apparent shear rate relationships.

Fig.30b shows the pressure/flow rate for the Bipel 90g machine. Nozzles of 10:1 and 5:1 are similar to those obtained with the Turner machines and the shear stress/apparent shear rate relationship calculated from these results are in good agreement with those of the Turner machines. Fig 31.

At high shear rates and especially with short capillaries, the appearance of the melt surface was different to that which occurred at low shear rates. The change corresponded to the maximum pressure value observed in the pressure/flow rate relationship shown in Fig.30b.

Plug flow occurs above material flow rates of 50-80g/sec with phenolic PF5 in the Bipel 90g machine, (fig 30b), but does not occur until 150-200 g/sec in the Turner 60g machine, fig 32. The reason for this difference is not fully understood but the results in fig 79 and table 45 show that the Bipel imparts more energy to the melt than the Turner machine when both machines are set to nominally the same settings and this may result in a greater degree of particle structure breakdown. The peak value shown in fig 30b is similar to that shown in the shear stress/apparent shear rate curve shown in fig 22. Bassow (133) also obtained a similar shaped curve.

A more detailed examination was undertaken using glass fibre reinforced materials to determine the flow characteristics of the material as it passes through the die. (See plates). This shows the surface appearance of the extrudate and the internal structure of the melt; the reinforcement indicating the flow pattern of the melt. Pressure/flow rate curves for various materials are shown in Fig 30a, 30b and 32. At very low flow rates only the outer annulus is orientated in the direction of flow but this annulus increases in size with increasing flow rate until the complete melt becomes orientated in the direction of flow. At very high shear rates the flow pattern again changed as small sections regularly peeled away from the central plug as the melt emerged from the nozzle.

The experiments indicated that the transition between the random orientated central section with a laminar flow outer annulus (Bingham Flow) occurred between 8 and 20 g/sec and that the transition between laminar and plug flow occurred at about 160g/sec. Similar experiments with a glass reinforced melamine material indicated a transition from Bingham to laminar flow at about 40g/sec but that plug flow was not observed up to 140g/sec.

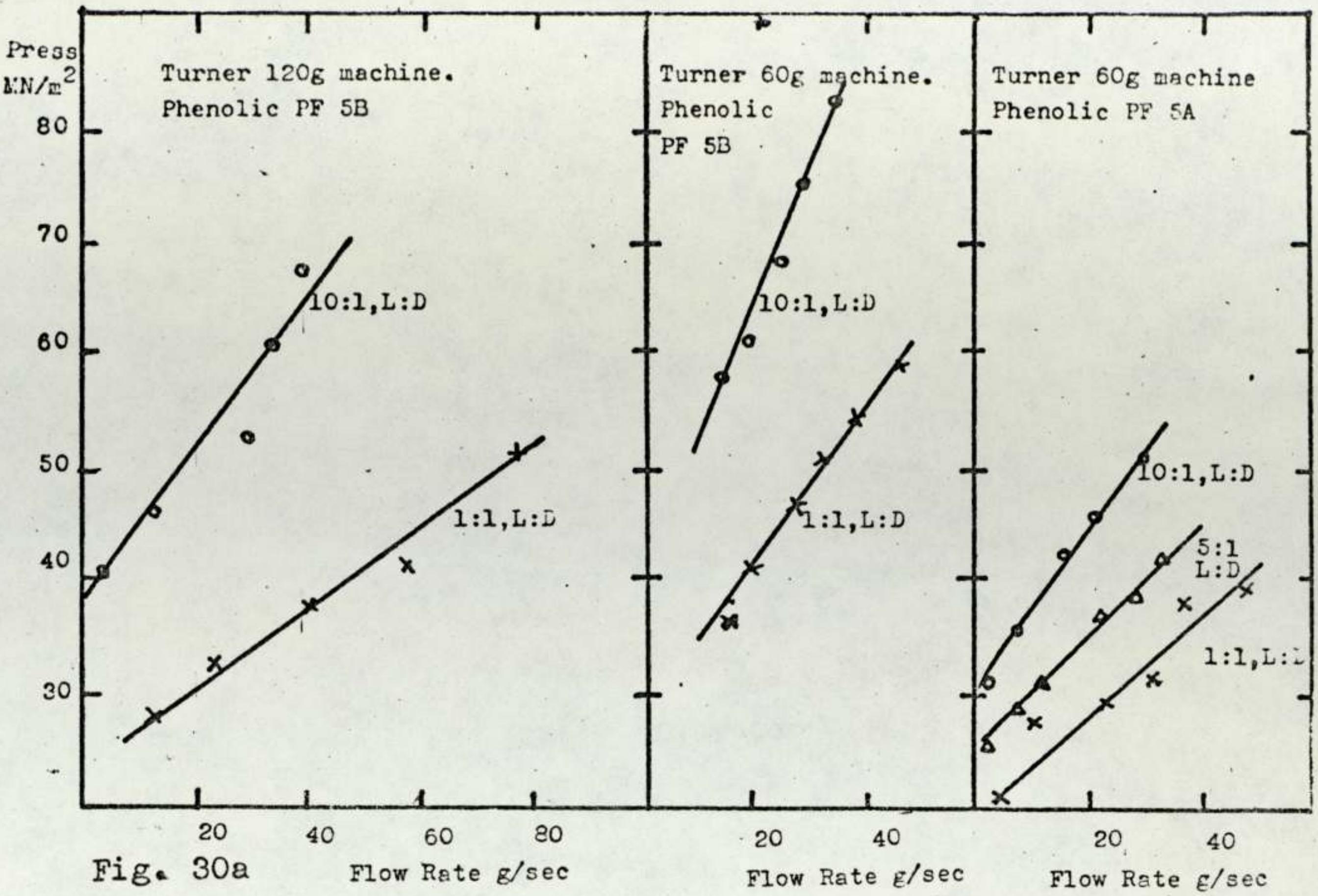


Fig. 30a

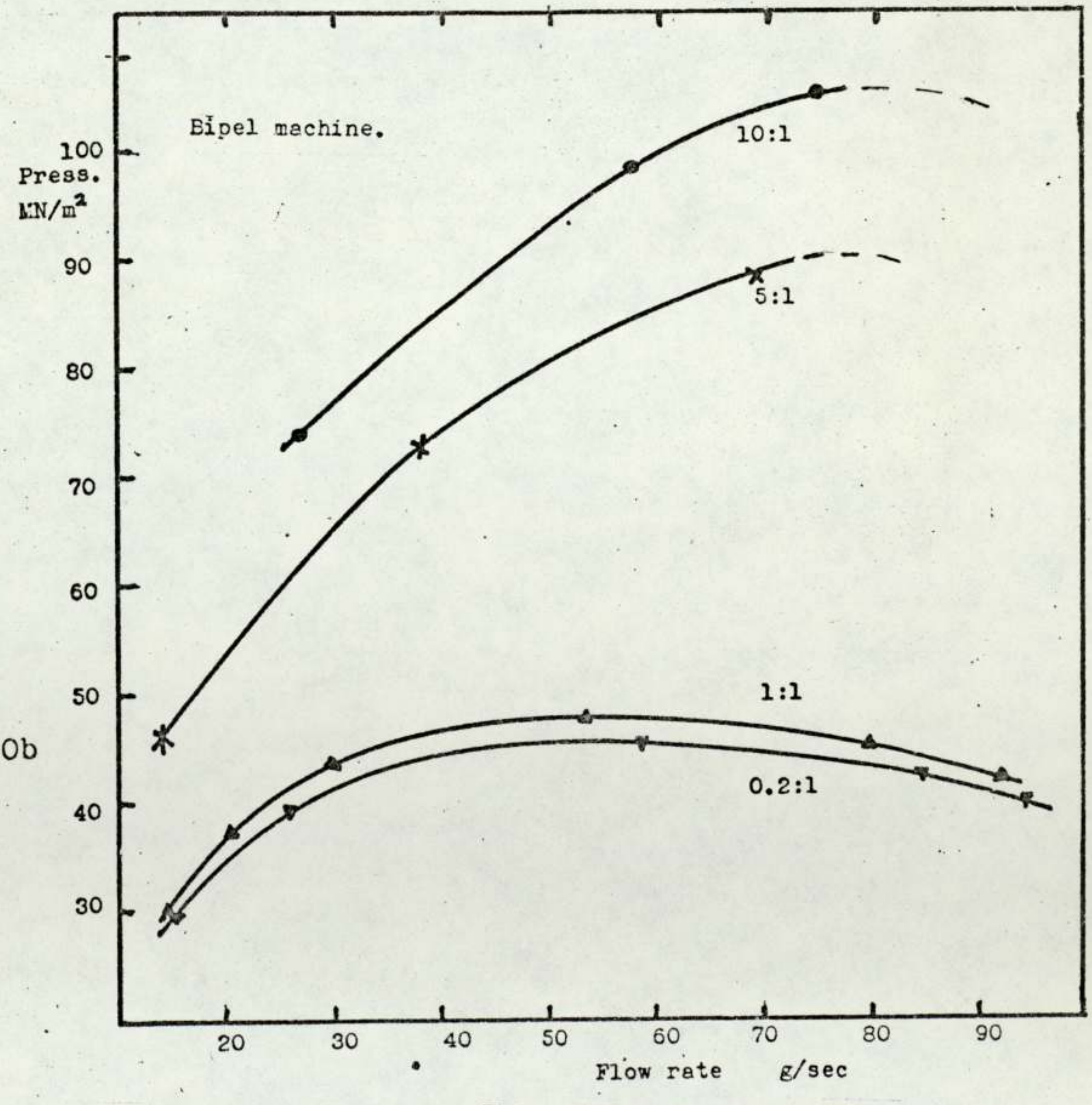


Fig. 30b

Fig. 30 Effect of nozzle length on pressure/flow rate curves for Phenolic PF 5.

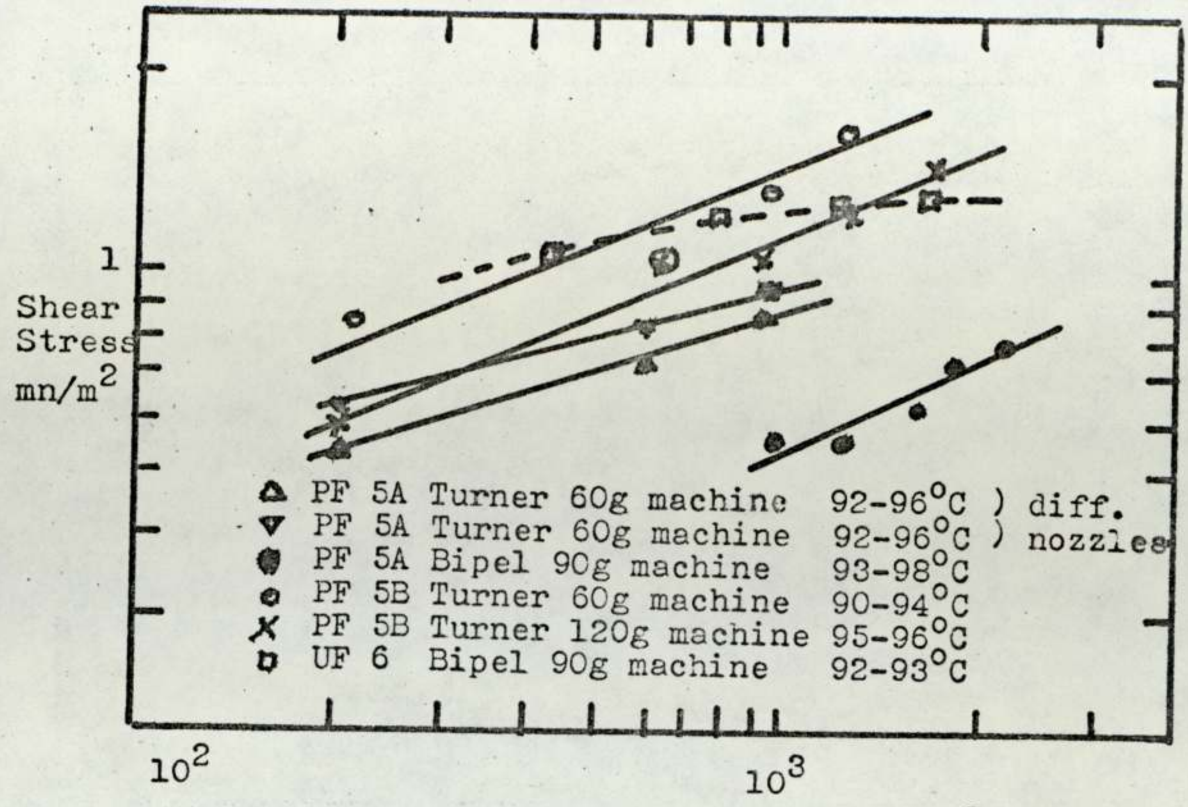


Fig. 31. Relationship between shear stress and app apparent shear rate determined with the nozzle capillary viscometer.

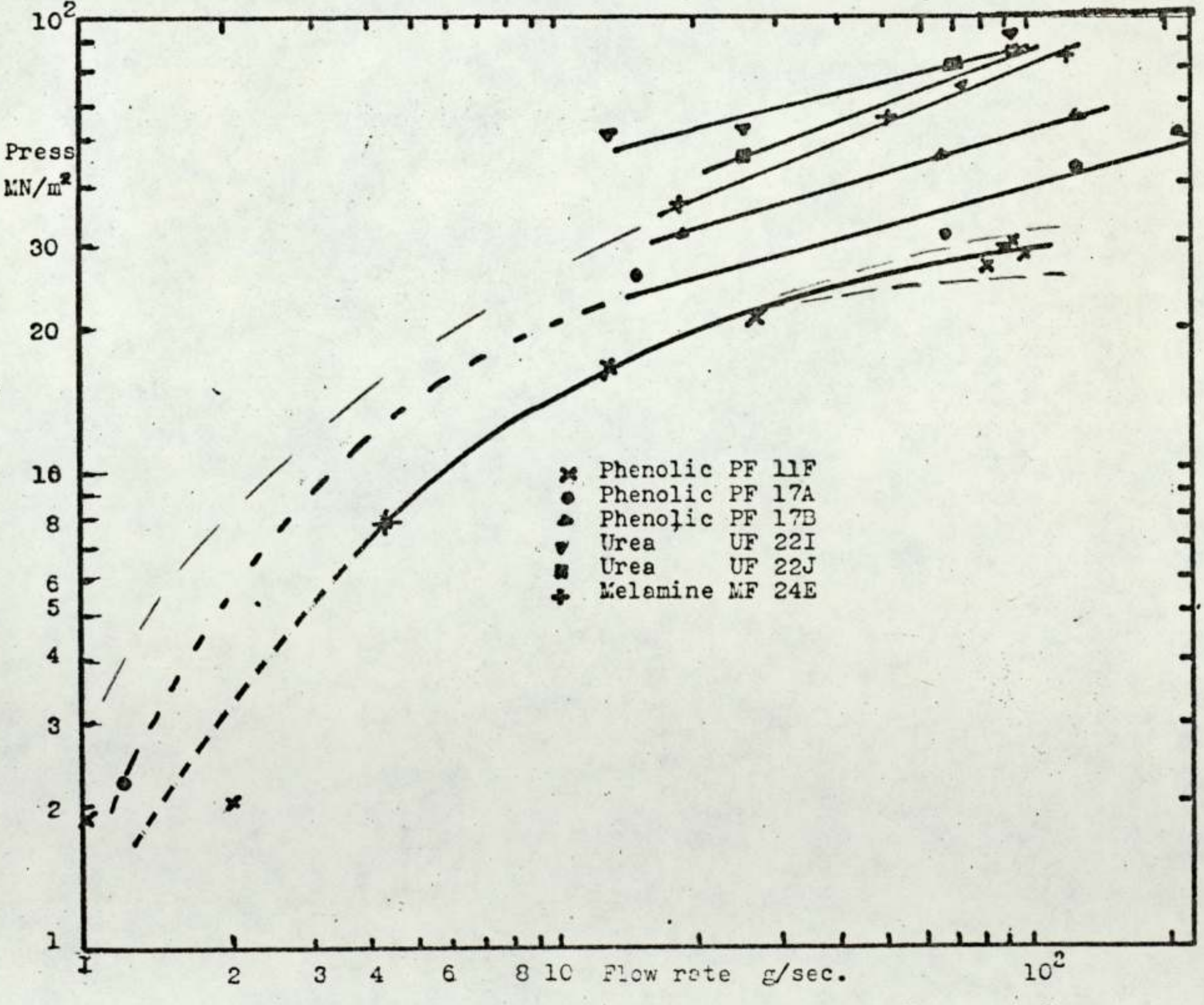


Fig. 32 Relationship between nozzle pressure and flow rate for various materials, Turner 60g machine.

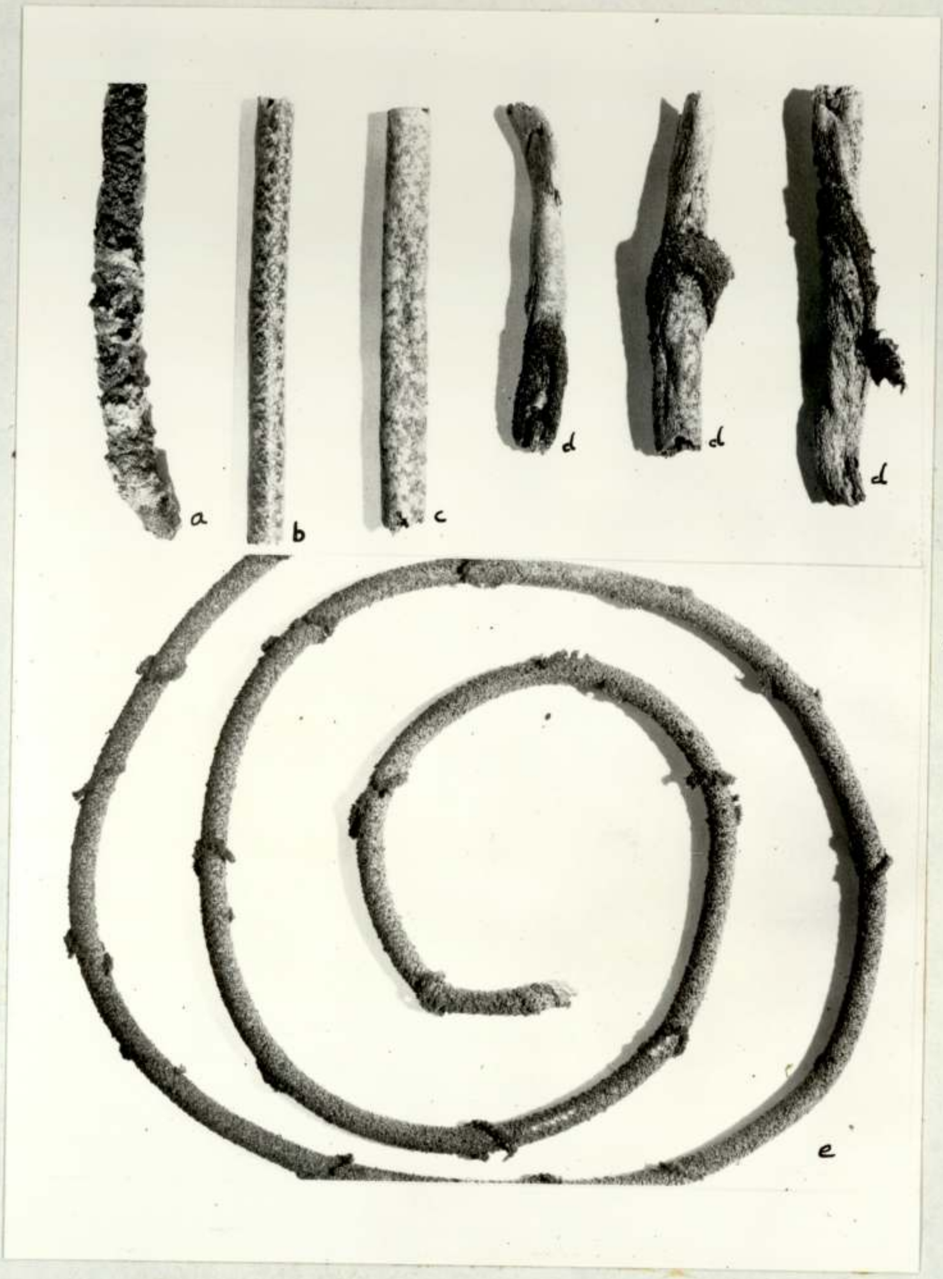
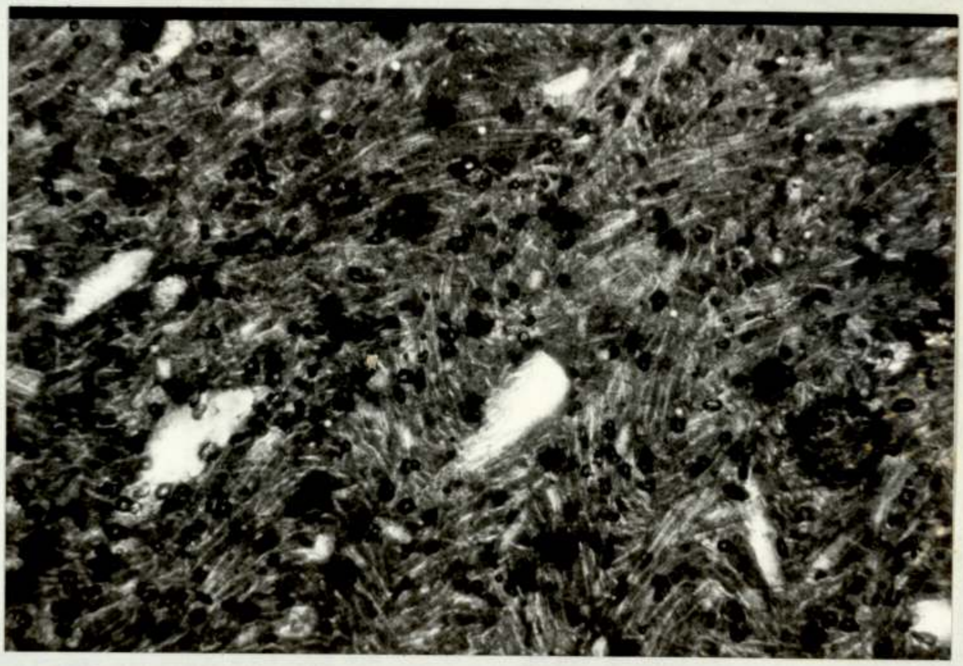


Plate 4. Effect of increasing flow rate on the surface of the extrudate. Phenolic PF 17A.

- a Slow rate, outer skin sticks and splits exposing central core. 1.3g/sec, 41 sec^{-1}.
- b Slow rate, smooth outer with compacted inner, 15g/sec, 470 sec^{-1}.
- c Fast rate, smooth outer with slightly porous inner, 145g/sec, 2100 sec^{-1}.
- d Fast rate, outer skin peels away from porous inner, 219g/sec, 6900 sec^{-1}.
- e As d showing regularity with outer skin peels away from inner.

O a



I a

Plate 5A. Effect of increasing flow rate showing increase in filler orientation, Phenolic PF 17A, (PF 17B similar)

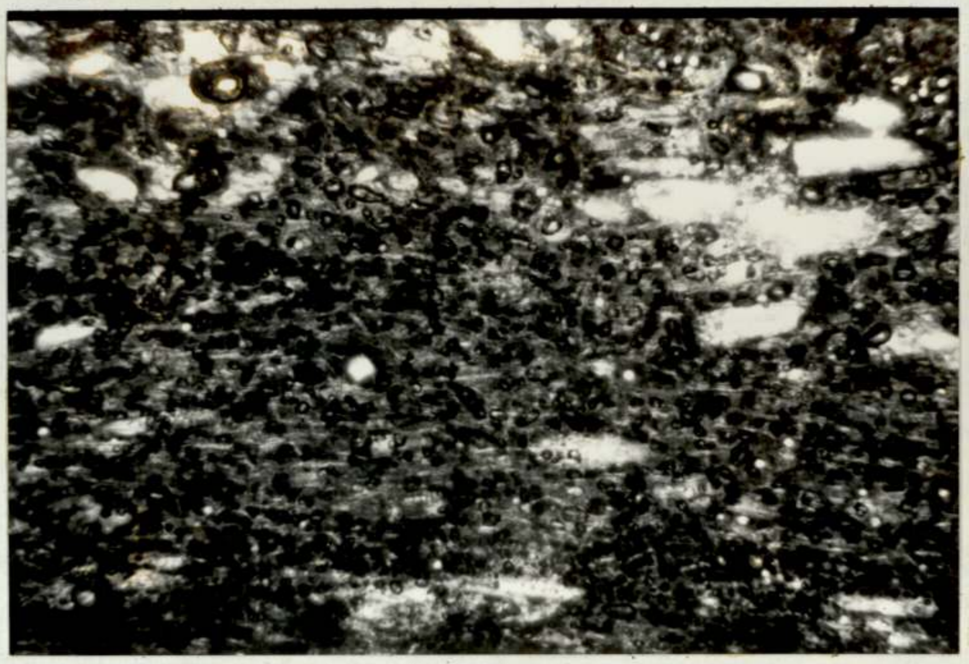
⟶ Direction of flow.

O Section through extrudate outer.

I Section through extrudate inner.

Magnification 100 times.

Key to letters as for plate 4.



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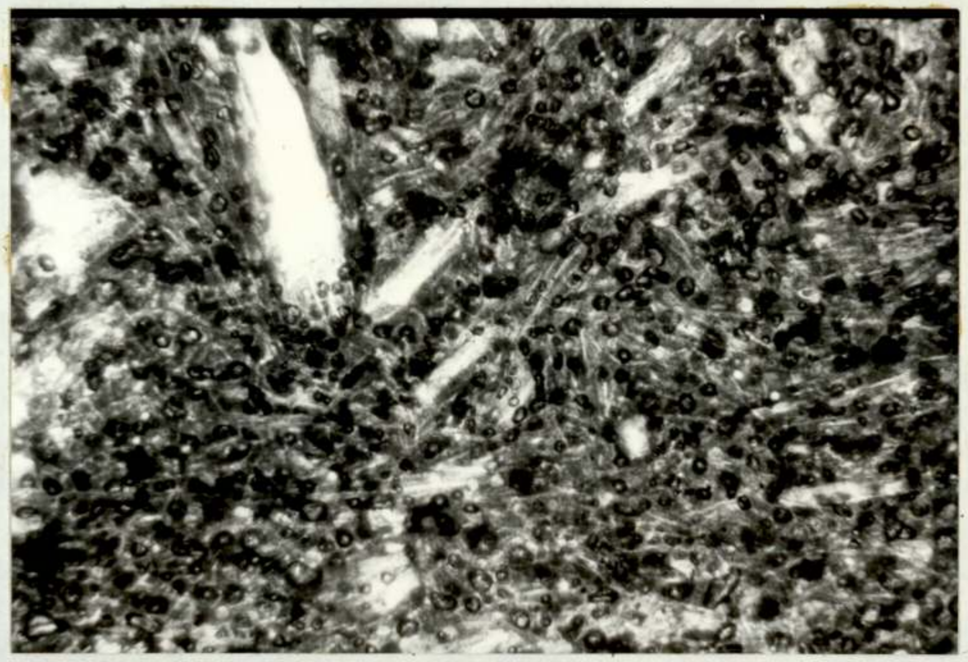


Ib

Plate 5A. Effect of increasing flow rate showing increase in filler orientation, Phenolic PF 17A, (PF 17B similar

→ Direction of flow.

O Section through extrudate outer.

I Section through extrudate inner.

Magnification 100 times.

Key to letters as for plate 4.

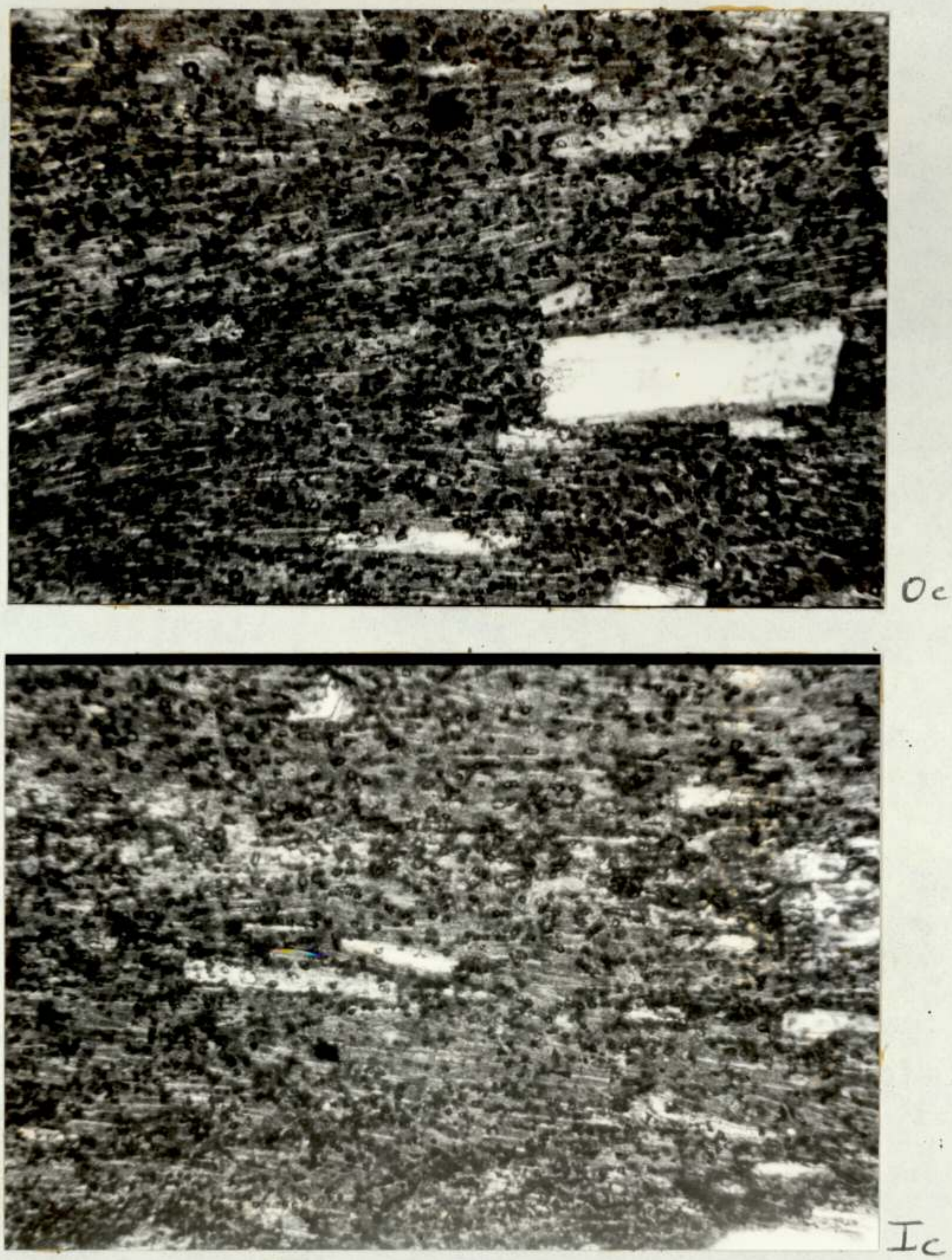


Plate 5B. Effect of increasing flow rate showing increase in filler orientation, Phenolic PF 17A, (PF 17B similar)

→ Direction of flow.
O Section through extrudate outer.
I Section through extrudate inner.
Magnification 100 times.
Key to letters as for plate 4.


Od


Id

Plate 5B. Effect of increasing flow rate showing increase in filler orientation, Phenolic PF 17A,(PF 17B similar)

⟶ Direction of flow.
O Section through extrudate outer.
I Section through extrudate inner.
Magnification 100 times.
Key to letters as for plate 4.

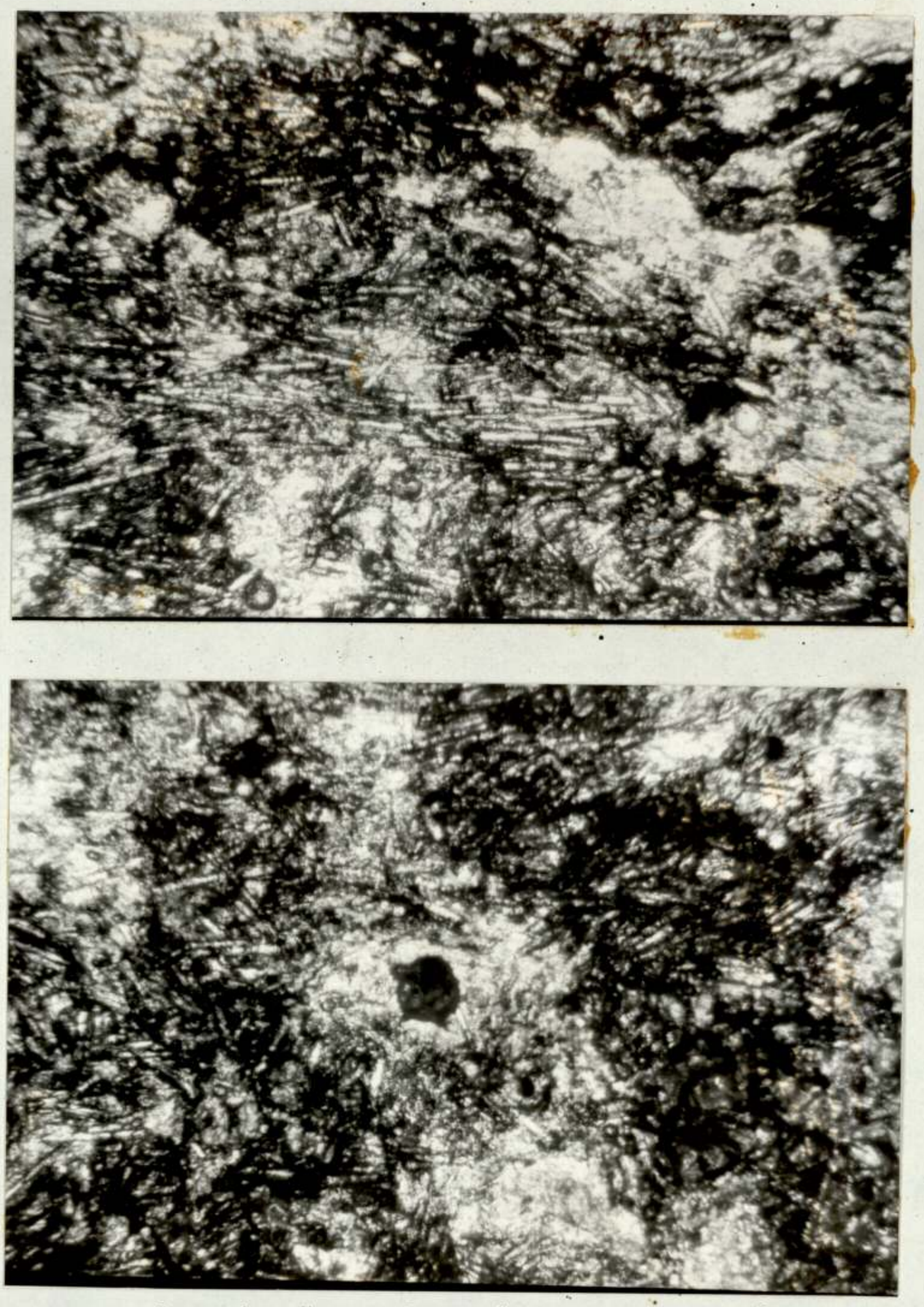


Plate 6A. Effect of increasing flow rate showing increase in filler orientation, Melamine MF 24E.
a   Slow rate, 1.5 g/sec, 106 sec^{-1}.

→ Direction of flow.
O   Section through outer.
I   Section through inner.
Magnification 100 times.

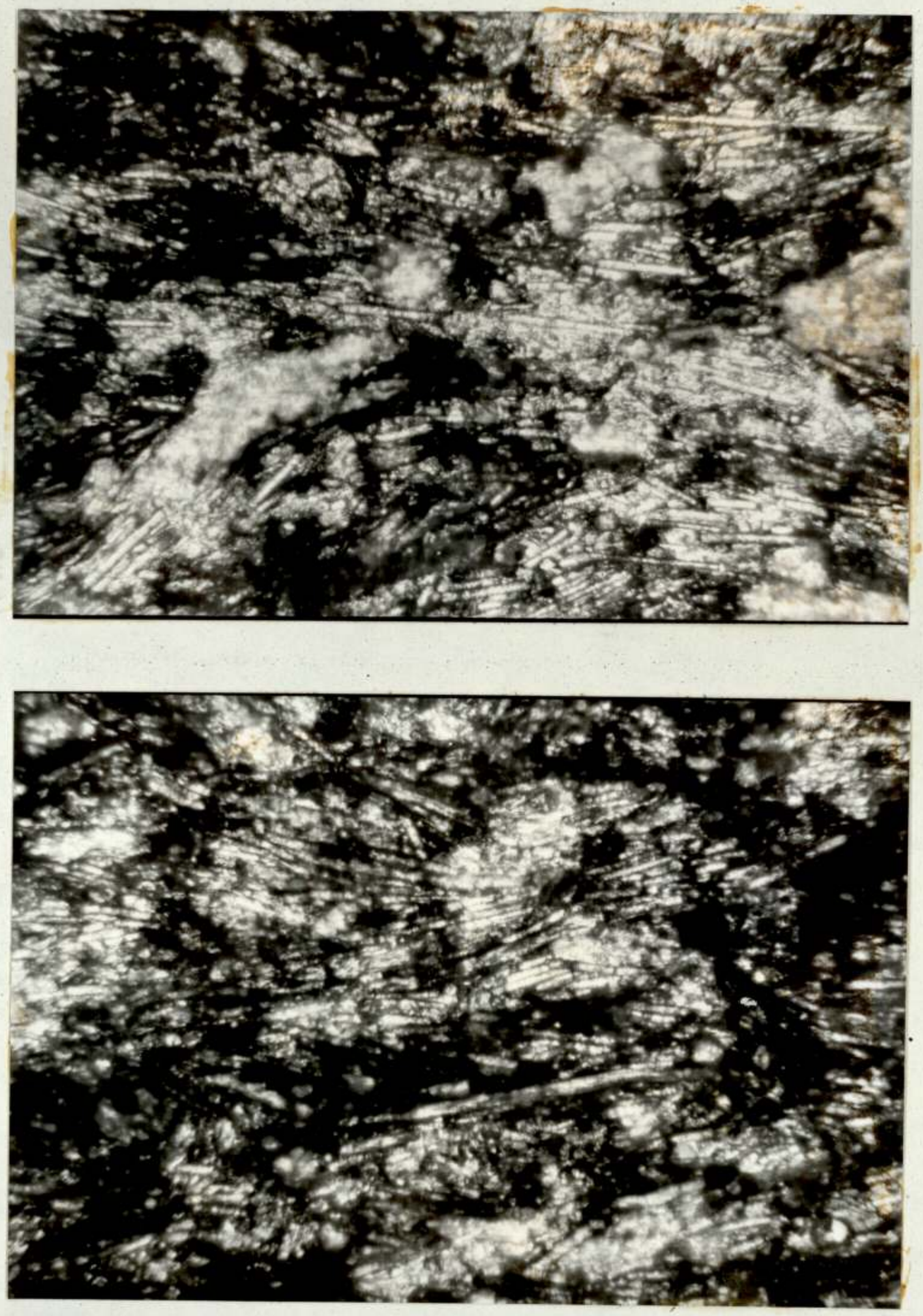


Plate 6A. Effect of increasing flow rate showing increase in filler orientation, Melamine MF 24E.

? b Slow rate, 18.0g/sec,1300 sec^{-1}.

⟶ Direction of flow.
O Section through outer.
I Section through inner.
Magnification 100 times.

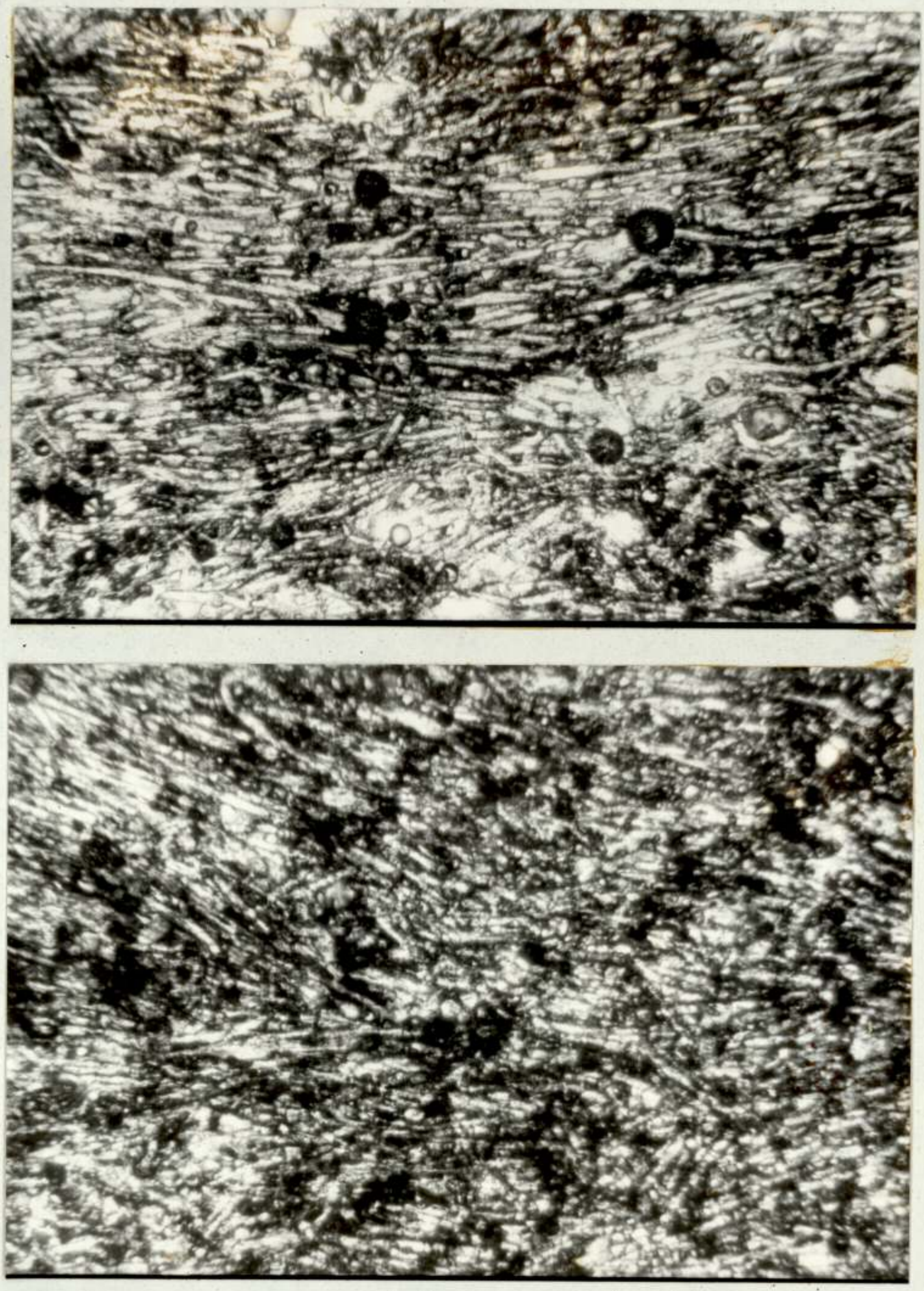


Plate 6B. Effect of increasing flow rate showing increase in filler orientation, Melamine MF 24E.

c Med rate, 52g/sec, 3700 sec^{-1}.

⟶ Direction of flow.
O Section through outer.
I Section through inner.
Magnification 100 times.

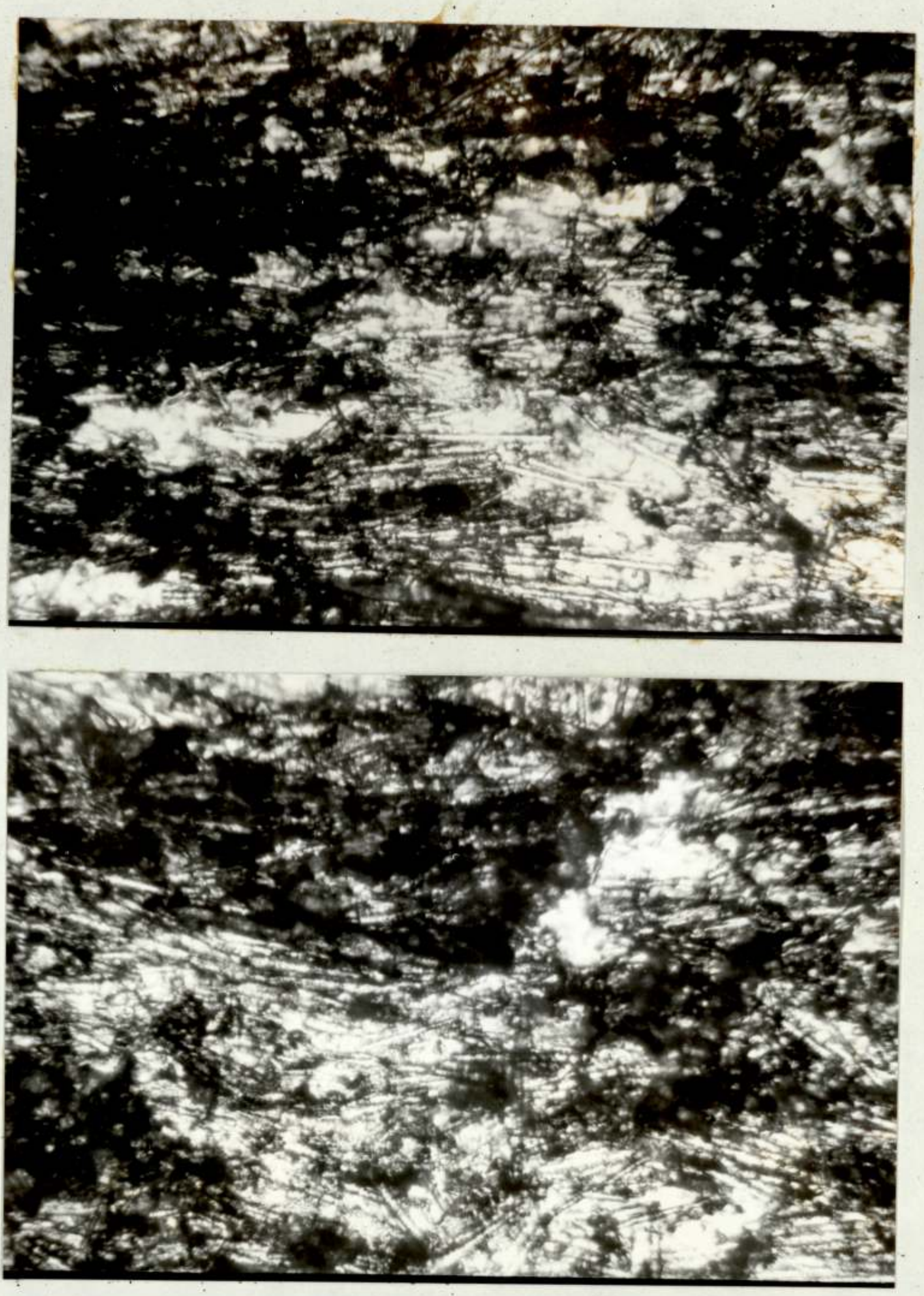


Plate 6B. Effect of increasing flow rate showing increase in filler orientation, Melamine MF 24E.
d Fast rate, 125g/sec, 8900sec^{-1}.

→ Direction of flow.
O Section through outer.
I Section through inner.
Magnification 100 times.

The position with urea formaldehyde materials is difficult to determine since fibre reinforced materials are not available and material blends of two colours did not adequately show the flow pattern. The transition to plug flow was observed at about 100g/sec. This effect is probably due to precuring since, while the phenolic extrudate was still essentially thermoplastic, the urea formaldehyde material had significantly precured.

A detailed comparison of phenolic materials is shown in Table 19.

TABLE 19a: Comparison of Phenolics using Instrumented Nozzle Technique

Set Hydraulic Pressure MN/m^2	Pressure MN/m^2	Nozzle Temp °C	Average Output Rate Grams/Sec
Material PF13A			
30	58.1	90.0	21.4
50	89.8	92.4	71.0
70	101.1	94.0	145.5
90	107.6	95.5	175.0
Material PF13B			
30	54.9	88.5	18.8
50	88.5	90.0	62.7
70	93.3	92.30	135.0
90	110.6	93.5	173.8
Material PF13C			
30	58.0	88.75	21.9
50	90.4	93.80	68.7
70	106.8	96.72	137.5
90	90.0	98.75	172.5
Material PF13D			
30	55.4	90.75	29.4
50	85.2	90.0	78.0
70	103.2	91.5	137.2
90	106.3	92.0	163.5
Material PF13E			
30	51.3	96.0	22.5
50	86.2	92.72	28.5
70	106.3	9.35	157.0
90	109.6	93.5	168.0
Material PF13F			
30	53.3	94.9	19.6
50	90.5	95.0	68.5
70	108.5	96.5	143.5
90	109.9	97.5	179.0

TABLE 19b Detailed Comparison of two batches of Phenolic PF5

Material	Batch A			Batch B		
Set hydraulic pressure MN/m^2	6.3	9.65	11.03	6.3	9.65	11.03
Shot Weight g	83.45	82.0	81.19	82.6	83.12	82.59
Melt pressure						
peak MN/m^2	40.0	42.4	43.1	49.4	51.9	53.0
min MN/m^2	15.5	15.2	14.6	16.2	16.9	16.3
Hydraulic pressure						
peak MN/m^2	7.44	8.27	8.48	7.49	8.41	8.55
min MN/m^2	4.06	4.06	4.06	4.31	4.31	4.31
Stroke duration (secs)	1.01	0.95	0.95	1.1	1.0	1.0
Melt Temp.						
Initial °C	93.2	92.7	93.4	94.5	94.0	94.5
Final °C	93.2	92.7	93.4	94.5	94.0	94.5
Nozzle Tip temp.						
Initial °C	80.35	79.5	79.0	82.5	82.0	82.5
Final °C	80.35	79.7	79.7	83.0	82.0	82.5

Use of extended nozzle with pressure sensors in capillary

Fluctuations in the pressure curves obtained with the capillary viscometer described earlier in this chapter and the uncertainty of the end corrections due to the low L/D ratios of the capillaries used led to the development of a viscometer in which the pressure was measured at two points in the capillary itself. This enabled the pressure drop to be measured directly and should enable viscosity data to be calculated more accurately. The viscometer was fitted to the instrumented nozzle of the Turner machine and was heated by an electrical band heater (Fig.33). Unfortunately a square section capillary was required to enable the pressure sensors to be fitted and this made the calculations of shear rates uncertain. Various authors have calculated the shear rate for a slit capillary as $\frac{6Q}{Wh^2}$ where Q is the volumetric flow, W the width of the slit and h it's depth, but this calculation is only theoretically valid when W is 10 times greater than h.

Typical pressure traces are shown in Fig.34 for a phenolic (PF11F) and a urea material (UF221). The difference between the measurements of capillary pressure is not constant but varies considerably less than the pressure itself. The pressure curves for the phenolic are relatively smooth but the pressure curves for the urea material fluctuate rapidly indicating a slip-stick effect in the capillary . This may be due to precuring of the extrudate surface which had a rather glossy surface.

Fig 35 shows the relationship between the three pressure measurements and the material flow rate. The relationship between the shear stress and apparent shear rate is shown in Fig.36. The latter shows a greater curvature than that shown elsewhere in this thesis but the reasons for this are not fully understood and are discussed later.

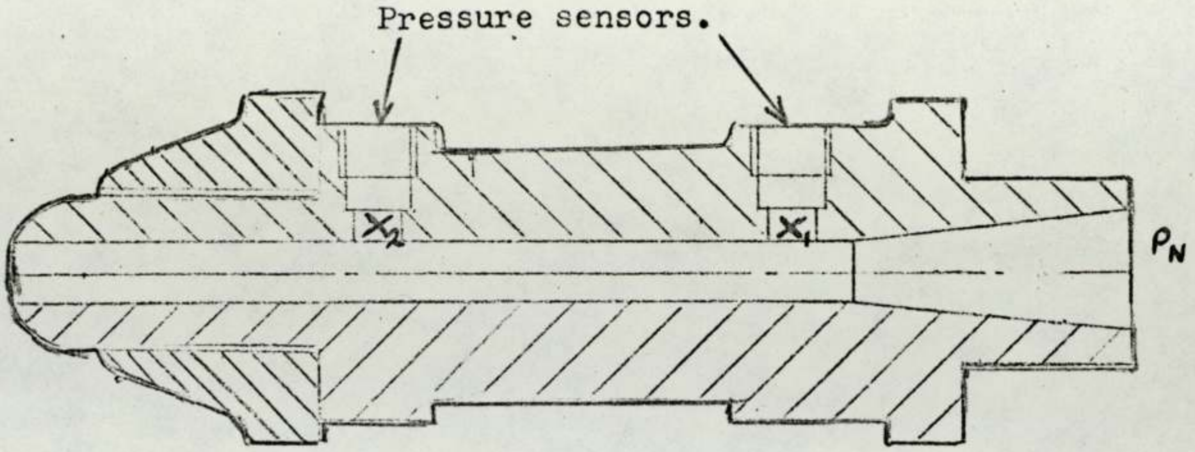


Fig. 33. Section through extended capillary nozzle showing position of pressure sensors.(X).

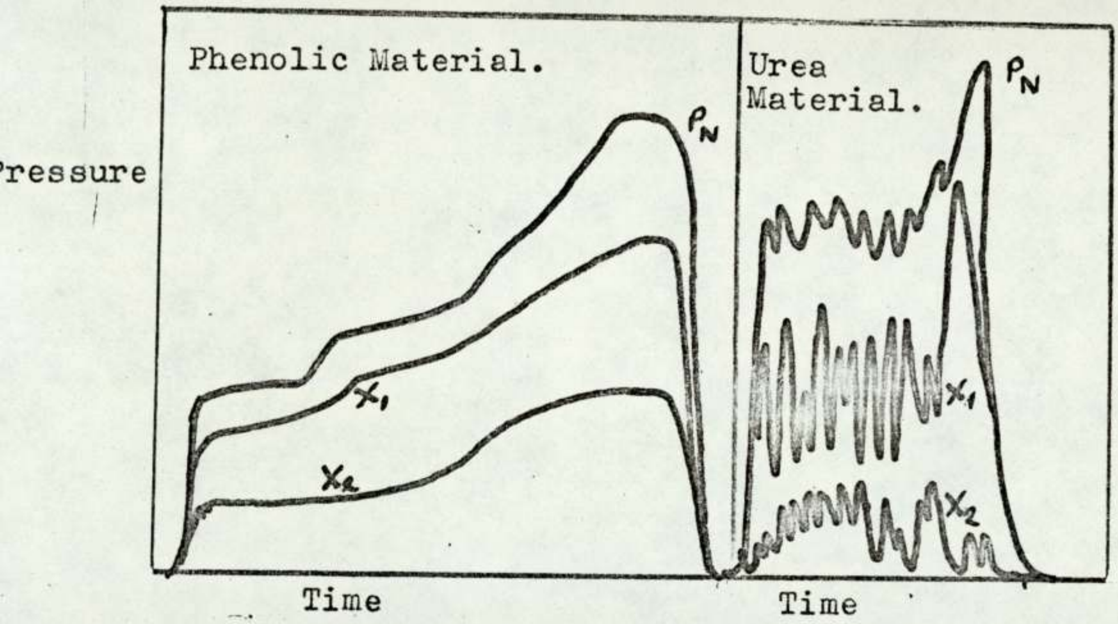


Fig. 34 Pressure/time traces recorded using the extended nozzle capillary viscometer.

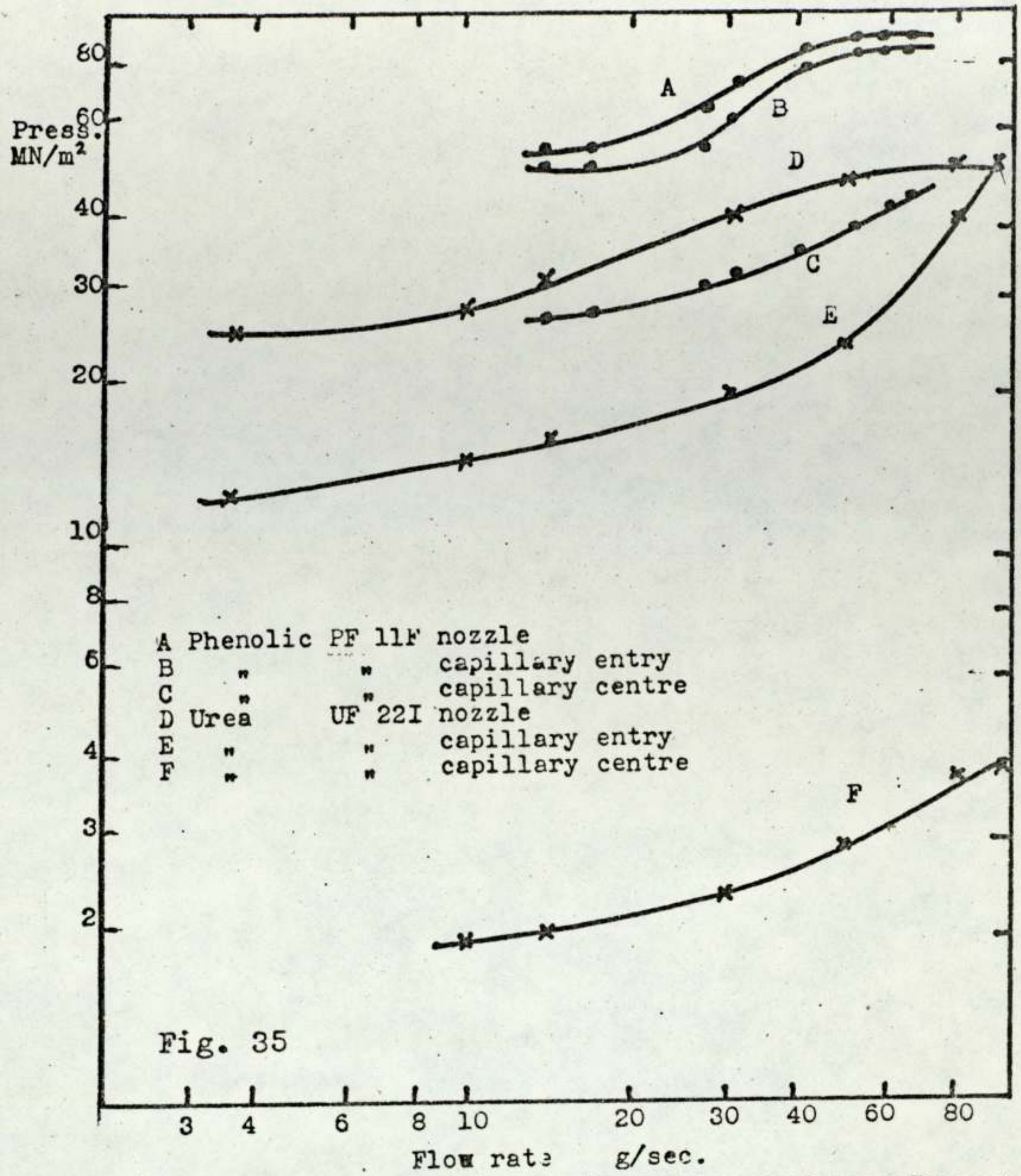


Fig. 35

Fig. 36

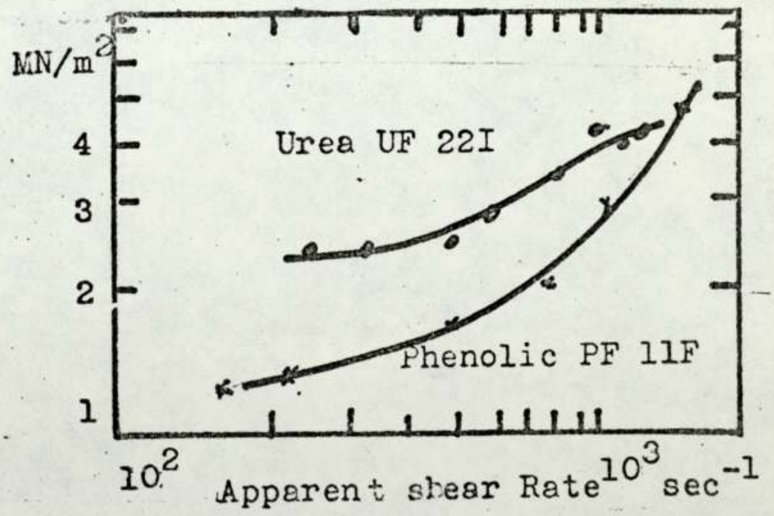


Fig. 35 Relationship between pressure and material flow rate for extended nozzle capillary with pressure sensors in capillary.

Fig. 36 Shear stress/apparent shear rate curves calculated from results of extended nozzle capillary.

4.6 Discussion of capillary viscometer results.

The results obtained with the capillary viscometer fitted to the injection moulding barrel (Fig.22) show that phenolic materials are pseudo-plastic, and that the relationship between the shear stress and apparent shear rate approximates to the power law equation. At high shear rates, the gradient of the graph of log shear stress against log apparent shear rate decreases.(133). The results also show that the phenolic melt prepared under the conditions encountered in the injection moulding process is unstable and that its viscosity increases rapidly with time. In practice steady state conditions do not occur and in consequence the results given in Fig.22 can only approximate to the true values. It has also been shown that the injection machine settings also affect the temperature and flow rate of the materials (Table 14).

The lack of melt stability meant that it was impossible to obtain viscosity data with urea formaldehyde (UF6) or to evaluate the phenolic material (PF5) at set barrel temperatures greater than 88°C(producing melt temperatures of 90 - 95°C). It is possible to link the results obtained from the capillaries of 6.3 and 4.7mm diameter (Fig.22) to give a single curve similar in shape to that obtained from the instrumented nozzle (Fig.32). The resultant curve would be of a similar shape to that reported for phenolic materials by several authors (87,103,104) Fig 17 who state it is indicative of Bingham flow behaviour. Bernhardt (105) suggests that Bingham flow is simply a modification of pseudoplastic flow. There is no report in the literature of a similar piece of equipment to the melt capillary viscometer which is capable of measuring the viscosity of a compounded melt at high shear rates. In 1970 Dalhoff (45,46) fitted a rotational viscometer in place of the mould of an injection moulding machine. Although designed primarily as a curemeter, the instrument recorded viscosity values of 17.32 Ns/m^2 at an apparent shear rate of 0.014 sec^{-1}. The only other comparable data has been obtained using instrumented injection moulding machines and this is discussed below. Table 20 gives typical values of viscosity for thermosetting materials, although it must be emphasised that each source refers to a different material, and that they are only similar in very broad terms.

TABLE 20: Comparison of Shear Stress/Apparent Shear Rate results with typical values from the literature

Shear Stress MN/m^2	Apparent Shear Rate Sec^{-1}	Temperature °C	Measuring Technique	Reference
	Phenolic Materials			
$5\times10^2-2\times10^3$	$5\times10^3-2\times10^4$	76 - 98	Orifice (granular)	Table 18
0.2 - 2·0	$5\times10 - 10^3$	95	Capillary (melt)	Fig 22
0.3 - 2·0	$2\times10^2-2\times10^3$	92 - 96	Nozzle Viscometer	Fig 31
0.2	$2\times10 - 2\times10^2$	88 - 94	Torque Rheometer	Fig 46
0.1 - 0.2	$10 - 10^2$	100	" "	133
1.0 - 2.5	$10^3 - 10^4$	90 - 110	Capillary	41
2.6 - 3.0	$3\times10^2-10^3$	110	Capillary	85
0.1 - 0.2	$10 - 10^2$	120	Torque Rheometer	133
0.3 - 0.6	$25 - 10^2$	120	Rotational	43
0.3 - 0.5	$10^2 - 10^3$	130	Capillary	109
$2-5\times10^2$	$1-6\times10^3$	120 - 130	Runner/mould	Fig 75
1.4 - 1.8	$0.2-1\times10^4$	150	Capillary	103
0.3 - 0.4	$10^2\times10^3$	150	"	109
	$2.7\times10^4-2.7\times10^5$	150	Orifice	Table 18
0.9 - 2.0	$1-12\times10^3$	150	Mould	87
0.08 - 0.09	$10 - 10^2$	150	Torque Rheometer	133
1.1-1.8	$10^2 - 10^3$	150 - 160	Mould/gate	Table 42
Urea Materials				
0.3 - 1.6	$3-6.2\times10^2$	76 - 98	Orifice	Table 18
1.3 - 1.4	$8\times10^2-2\times10^3$	93	Nozzle Viscometer	Fig 31
10	$10 - 10^2$	88 - 94	Torque Rheometer	Fig 46
4 - 7	$7\times10^2-2.5\times10^3$	120 - 130	Runner Capillary	Fig 75

It is convenient to next discuss the results of the capillary adaptors fitted to the injection machine nozzle since these results are in general agreement with those obtained from the capillary viscometer. It should be noted that similar results were obtained with both the Bipel and the Turner machines. (Fig.31).

The pressure/flow rate curves appear to show a maximum value and to show two different shear rate values for the same value of shear stress. The general shape of the curve is similar to that obtained from shear stress/apparent shear rate curves from typical injection nozzles. It is possible to obtain two distinctly different flow rates for the same recorded pressure (Fig.30).

Pearson (106) states that the flow characteristics of a material can change with increasing shear rate and can give a maximum and minimum value to the shear stress/shear rate curve, an effect which appears as melt fracture in extrusion. It is also possible to obtain two different mould filling rates for the same pressure in thermoplastics injection moulding. Norfleet (85) reported two different shear stress/ shear rate curves for the same phenolic material when injection moulded under the same conditions but offered no explanation for this.

It is suggested that the flow pattern of phenolic materials changes from Bingham flow to laminar flow and finally to a plug flow state. Similar changes may occur with the urea materials but plug flow has not been observed with the melamine material.

The change to plug flow may be linked to lubrication effects since an excess of lubricant will result in a change to multi-layered structure in injection mouldings and it has been qualitively shown that the adhesion of a phenolic melt to the chamber walls decreases with increasing condensation (Chapter 5). It may be linked to melt instability since it is most noticeable with dies of low L/D ratio.

Beck also used an extended instrumented injection nozzle to study the flow characteristics of phenolic materials. (20)

His results indicated that phenolics show Bingham flow behaviour. Beck also studied the orientation pattern of the reinforcing fibres in the extruded melt and showed that the ratio of the diameter of the central plug to the die diameter and also the ratio of the nozzle pressure to the volume flow rate was a constant. This is not shown by the results in this thesis (see plates and Table 21). Beck did not encounter the wide fluctuations in pressure which are reported here (Fig.28) but he used injection times of 12 seconds. The work described in this thesis was carried out using injection times of 1-6 seconds which corresponds to typical moulding times. Although more regular traces were obtained at longer injection times, it was decided to accept the irregularities in the pressure traces in order to obtain data directly comparable to industrial moulding practice. Beck and Golovy also showed the existance of Bingham flow with Phenolic materials (69)

TABLE 21: Ratio of Pressure to Flow Rate for Phenolic Materials

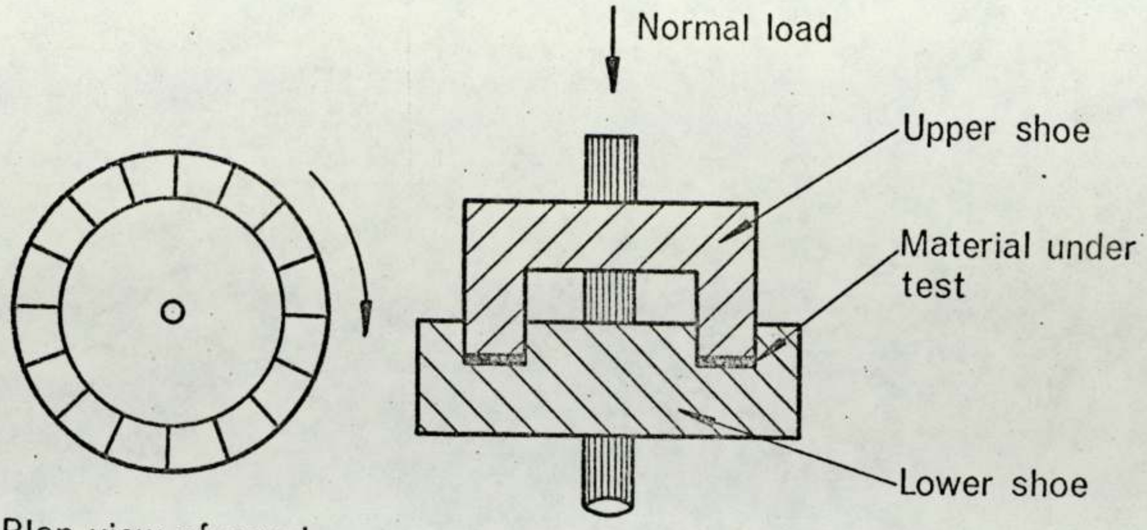
Set Hydraulic Pressure MN/m^2	Nozzle L:D	1:1	Nozzle L:D	10:1
	P/Q p^{1+}	P/Q p^2	P/Q p^1	P/Q p^2
	MN sec/m^2			
	Turner 120g barrel			
5.55	1.72	1.53	-	-
6.89	1.21	0.91	9.79	7.65
8.27	0.76	0.54	2.69	2.17
9.65	0.56	0.4	1.68	1.33
11.03	0.53	0.35	1.37	0.99
12.41	0.53	0.32	1.35	0.95
	Turner 60g barrel			
5.55	1.87	1.39	-	-
6.89	1.63	1.19	3.58	2.68
8.27	1.36	0.99	2.62	1.98
9.65	1.17	0.89	2.33	1.68
11.03	1.11	0.75	2.09	1.44
12.41	1.04	0.69	1.97	1.35
	Bipel 90g barrel			
2.94	6.96	5.72	-	-
4.90	1.33	0.91	2.66 (3.57)*	2.00 (7.80)*
6.86	0.97	0.65	1.25 (1.77)*	0.90 (4.48)*
8.82	0.97	0.68	1.02 (1.11)*	0.74 (2.24)*

p^{1+} = maximum recorded pressure at nozzle.
p^{2+} = mean recorded pressure at nozzle.
* = UF material (UF6).

The results (Fig. 36) obtained with the extended nozzle containing two pressure sensors differ from those of the other nozzle adaptors in that both the shape of the graph of log pressure against log flow rate and the relative positions of the curves for the phenolic and urea material are altered (Fig.31).

It is considered that the phenolic melt adhered to the die wall over it's full length giving a die of length to width ratio of about 12:1. The pressure traces obtained with the urea material showed wide pressure fluctuations especially with the pressure sensors in the capillary itself and indicated that the melt was slipping considerably at the die wall. The very low pressure values recorded near the nozzle exit indicate that the effective length of the nozzle may only be about 7:1 (Fig.35). This could possibly explain the differences between the two sets of results but other possible reasons may be linked with the nature of the pressure measurement and with the coefficient of friction of these materials. Gerohkovich (107) has shown that the radial pressure in a capillary die is a function of the flow pressure but that this relationship depends on the material tested. Lodge (137) suggests that normal forces have a greater effect in small capillaries. Eswaren (108) showed that the pressure measured in a slit viscometer is different from that measured in the entry region of a capillary viscometer but did not offer a proper explanation. Experience using an annular shear cell showed that at temperatures of 80° - 120°C, the coefficient of friction between a phenolic material and a steel surface, increased considerably while that of the urea material decreased (Fig.37).

The results obtained when the capillary viscometer is used with powdered materials show reasonable general agreement with the injection nozzle results when both techniques are used to compare materials having widely different flow characteristics (Fig.38). However, when used to compare similar materials, the capillary viscometer results are less useful. The gradient of the graph of log (pressure) against log (flow rate) for powder materials (Fig.25) is considerably greater than that obtained with the injection nozzle or with the capillary viscometer used with compounded melt. The reasons for this difference are not completely understood but are probably connected with the fact that the powder in the capillary viscometer is sintered and not compounded or sheared. Fig 70 indicates that the degree of compounding can affect the gradient of the graphical relationship. The degree of compounding will also affect the material temperature and it has been shown that a capillary barrel wall temperature of 98°C will give a temperature of 76°C in the centre of the powdered material. (Attempts to use higher barrel temperatures of 120°C lead to precuring of the material).

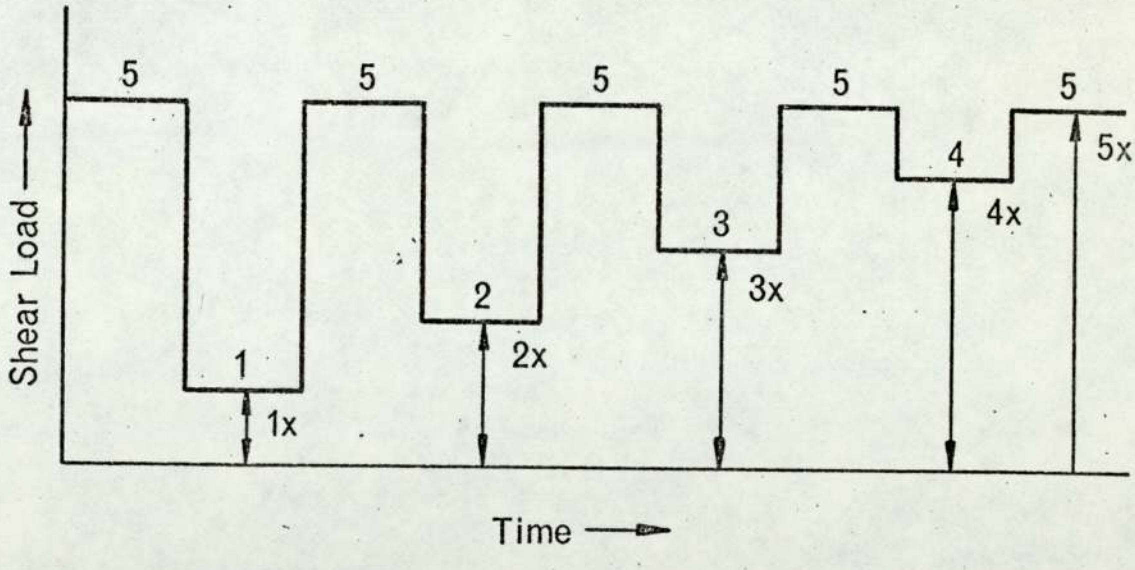


Plan view of powder shoe showing keys

Section of annular shear cell

Section through annular shear cell.

Typical trace of shear load against time for various normal loads (1-5). Note that the powder is compacted with the full normal load between each measurement.



Annular shear cell, interpretation of data.

Coefficient of friction is given by ratio of shear force to the normal force.

Fig. 37a Measurement of coefficient of friction of granular materials. Powder shoe is shown, smooth metal shoe is used for measureing powder to metal friction.

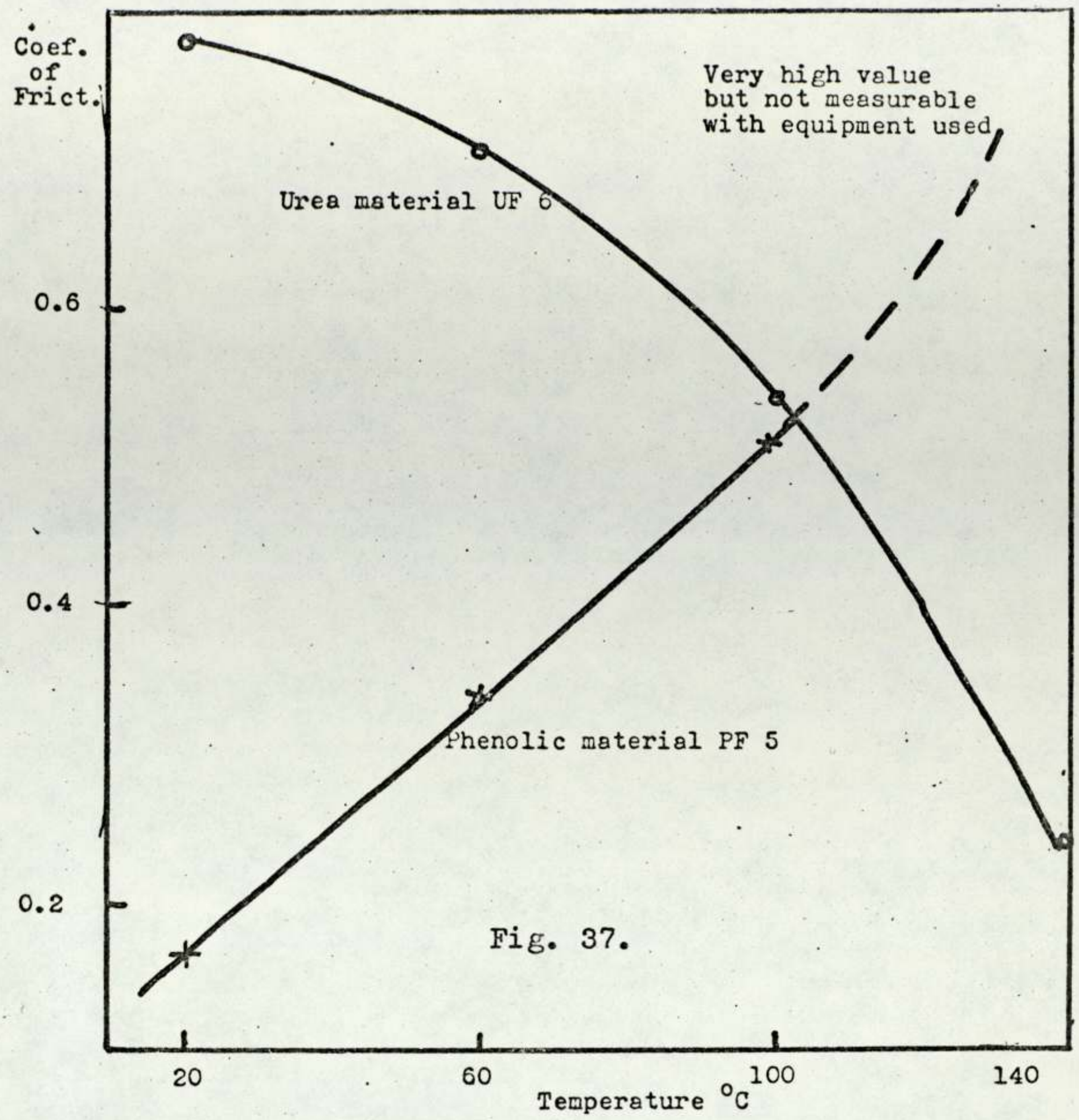


Fig. 37.

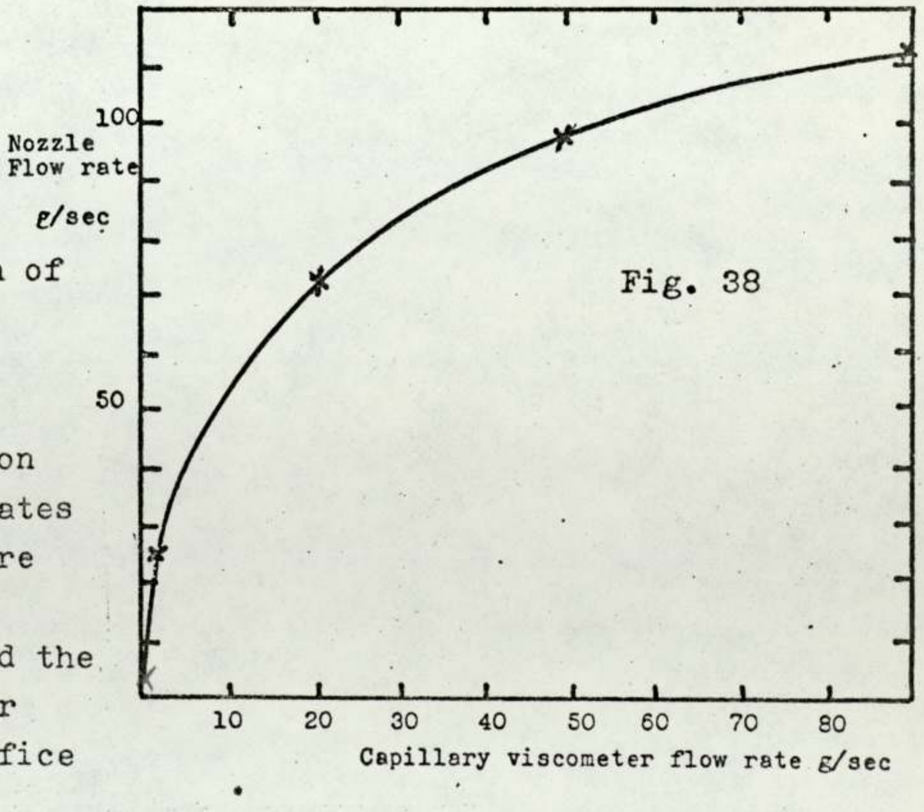


Fig. 38

Fig. 37b Variation of of friction with temperature.

Fig. 38. Correlation of material flow rates at constant pressure through standard injection nozzle and the capillary viscometer fitted with the orifice die.

The temperature profile also produces a viscosity profile across the capillary barrel whereas the nozzle and melt capillary experiments, used a material of fairly uniform temperature. However, Bortnikov and Shamgunov (109) have shown that the gradient of the log plot of shear stress against apparent shear rate is approximately constant over a temperature range of 40°C, and consequently the change of gradient referred to above is unlikely to be due solely to temperature effects. (see also fig 25).

Kanavets and Sokolov suggest that the minimum viscosity is due to the complete dispersion of structure forming systems (41) and the inference is that the flow properties of a material are partly dependent on the degree of compounding i.e. on its shear history. It has been reported that the physical properties of the final moulding depend partly on the breakdown of the initial powder structure (110). It is known that the presence of solid particles in a melt will affect its viscosity characteristics (111).

Between November 1971 and 1974 Norfleet and various co-workers (85,86) published a series of papers describing an investigation of the rheology of thermosetting plastics. Their results confirm the results in this thesis in general but the viscosity of phenolics is reported as $4\text{-}7 \times 10^2$ Ns/m^2 at 10^3 sec^{-1} and 110°C which differs from the results of Dujardin who publishes viscosity figures of 3.8×10^9 Ns/m^2 at 110°C and 1.6×10^{10} Ns/m^2 at 100°C (15,112). The dimensions of Dujardin's instrument have not been published in detail but a sketch shows that it comprises two wedge shaped orifices at the edge of the punch of a closed transfer chamber.

The results in Table 17 are intermediate between those reported by Dujardin and Norfleet, all results referring to materials of the general classification of "general purpose injection moulding phenolics". The difference between these results indicates that the viscosity figures obtained from a sintered melt are partly dependent on the capillary geometry, that the analysis may be of only limited value and the results can only really be used for comparison purposes. A limited amount of work Table 17, Fig 26, has measured the flow rates of materials at 95-100°C since this corresponds to the nozzle/runner section of the injection process.

The results have been measured at a constant pressure and although it is rheologically preferable to use a constant rate of extrusion it is more practical to use this approach which corresponds to the way in which the injection process is set up. It is also the basis on which thermoplastics materials are currently characterized by the Melt Flow Index.(113).

Other workers (Table 20) confirm these results in general. Perevertov et al (114) developed a capillary viscometer which measured the viscosity of thermosetting materials during the early stages of cure.

Results for phenolics may be of doubtful accuracy. The time during which a phenolic can be heated in the capillary barrel without the viscosity increasing due to premature crosslinking is typically 3-5 minutes at 150°C (Fig 24) and 25 - 30 minutes at 98°C (Fig 23, 26). These figures are similar to those published by Heyd (16) who lists values of 5 minutes at 125°C, 1 minute at 150°C and 10 seconds at 175°C. These figures for the duration of fluidity are considerably greater than those which have been reported for the capillary viscometer when used with a plasticised melt (Fig.22) and there appears to be a difference between sintered melt and a plasticised melt which may not be completely explained by temperature effects.

Because of the apparent differences between static sintering and dynamic heating, it is concluded that other test techniques e.g. the variable torque rheometer, are more suited to measuring properties to be correlated with dynamic process. Similar situations can be found in the assessment of antioxidants, stabilisers etc. in the evaluation of thermoplastics materials.

The orifice test results differ from published results in one important aspect. The literature reports that the effect of chamber residence time on flow rate varies with different materials (Fig.7.) and that it is possible to determine the flow life with this technique (14,17). The results described in this report have been limited to injection moulding materials but show that the maximum flow rate occurs between 22½ and 25 minutes and that the results do not adequately distinguish between materials of different flow (barrel) life (Fig.26). It is suggested that because of the cylinder geometry the temperature distribution is more uniform than that found in the instruments described in the literature.

Details of a typical industrial orifice flow test mould are given by Ferriday(14). Using the method described by Hands (115) who published graphical solutions to Fouriers equations it is possible to calculate the temperatures inside the capillary barrel and to show that considerable differences exist in the temperatures within the two types of capillary barrel. (Table 22).

TABLE 22: Comparison of Orifice flow test as used by Ferriday (14) with capillary viscometer (Fig 19) fitted with orifice die.

Property	Orifice/ Capillary Viscometer	Typical Commercial Orifice Meter
Diameter cm	3.2	4.4
Stroke length cm	10.4	4.5
Optimum Heating Time mins	22.5	14
Chamber temperature	98°C	100°C
Calculated Temperature		
at centre	74°C +	38°C
at centre of area	84°C	67°C

+ Confirmed by experiment

Heyd (16) used the capillary viscometer as a curemeter and measured the change in material flow rate as a function of chamber residence time. He obtained the typical u-shaped viscosity/time curve of a thermosetting material and measured the minimum viscosity and the flow life of a material. An attempt by the writer to use this technique with a gas driven viscometer showed the feasibility of the technique but practical difficulties prevented its use for this work.

4.7 Correlation of Capillary Viscometer results with Injection Moulding

A fairly good correlation exists between the relative positions and gradients of the graphs of log shear stress against log apparent shear rate and of log pressure against log flow rate for a range of injection moulding materials compared using the instrumented injection nozzle (Fig. 32), the instrumented nozzle with the injection moulding process (Fig.72) and the injection mould runner viscometer (Fig.75).

However, the difference between these materials is greater than those that are expected to occur between production batches. Six batches of a phenolic material (PF14) differing slightly in their flow properties (as measured by standard tests) were compared in the injection moulding process and by the various capillary techniques used in this thesis. For convenience these results are shown graphically in Fig.38a & b together with the standard test results.(Fig.39c). There is no clear cut correlation between the injection moulding results and the test results, or indeed with the standard test results. All the materials could be satisfactorily injection moulded using the same set conditions.

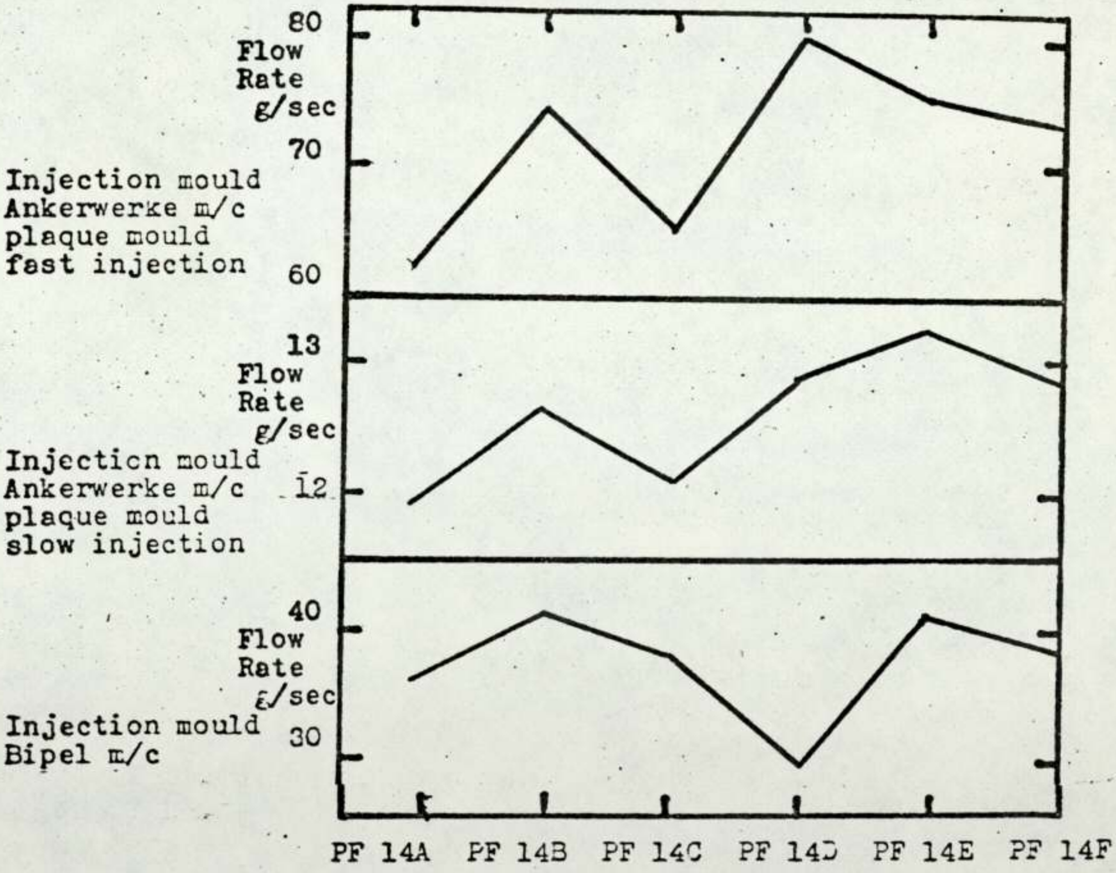


Fig. 39a. Material flow rates at constant pressure for a series of Phenolic materials (PF 14A-F) measured with injection moulding experiments with the Ankerwerke machine and the disc mould (fast and slow injection) and with the Bipel machine fitted with the capillary viscometer.

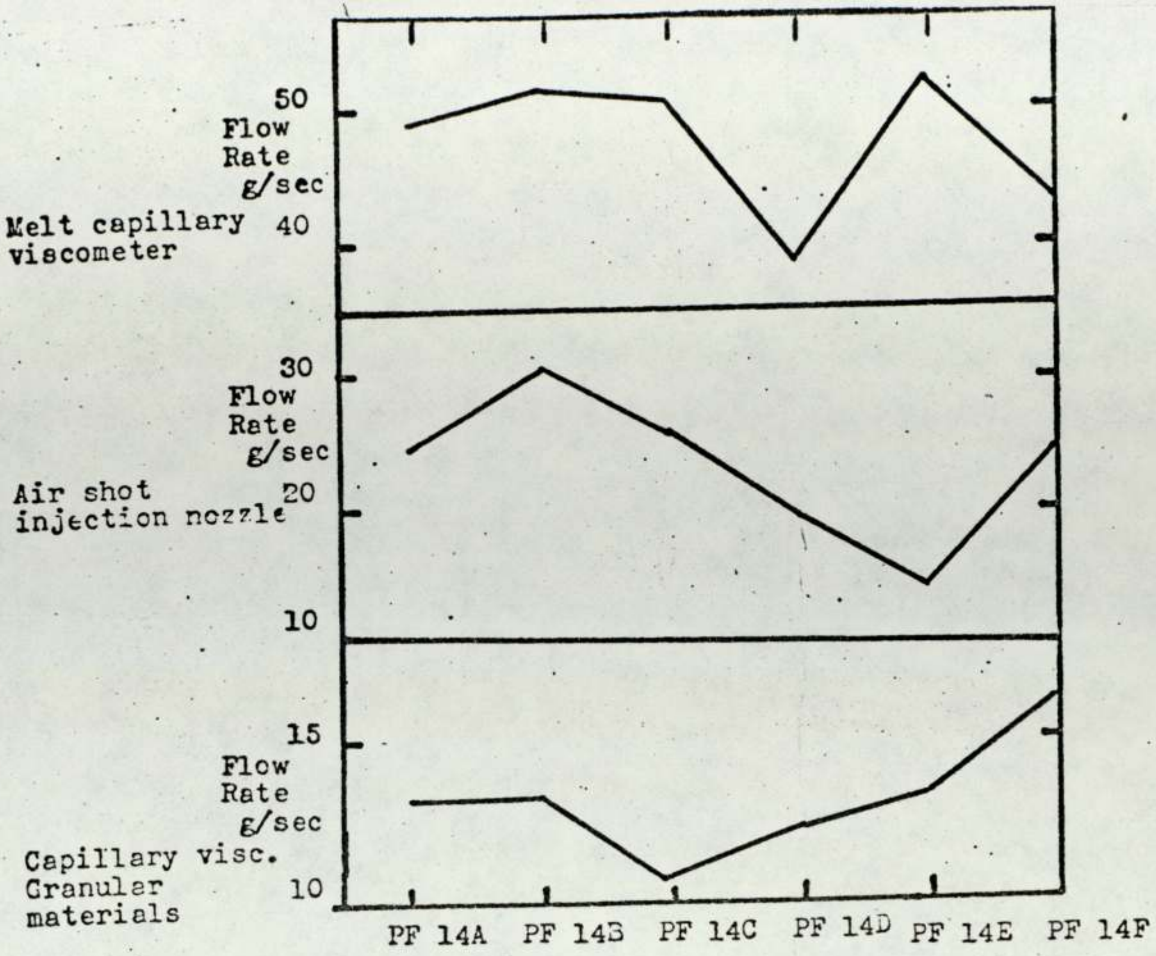


Fig. 39b. Material flow rates at constant pressure for a series of Phenolic materials (PF 14A-F) measured with the melt capillary viscometer, the capillary viscometer with granular materials and with the Bipel injection moulding machine set to produce air shots.

It is concluded that while a capillary viscometer is essential to measure the flow characteristics of a material, at high shear rates, it will only indicate its suitability as an injection moulding material and will not, on its own, provide sufficient assurance as to the "injection mouldability" of the material.

Of the various capillary techniques investigated the capillary viscometer fitted to the injection nozzle is probably the most useful and convenient to use. However, further modification of the runner viscometer (Chapter 7) would provide a better answer especially if small transducers suitable for fitting into a circular runner were used. The runner should be open ended (no mould cavity). This technique would enable materials to be compounded as in the injection process and would enable their flow properties to be measured at elevated temperatures. The problems of material curing in the capillary barrel and die encountered in this work would be eliminated by the opening of the capillary die and by the injection of the cured melt. This would also enable results to be obtained using large capacity machines and would only involve the manufacture of a relatively simple test tool which could be used with any injection machine.

The transition of laminar to the plug type of flow behaviour seen as the melt emerges at high speed from a capillary die has also been observed when the melt passes from a tab gate into the injection mould and is reflected in the mould filling pattern. (Fig 71).

The results also show that the optimum quality mouldings are produced by the melt having the minimum viscosity and minimum pressure/flow rate gradient.

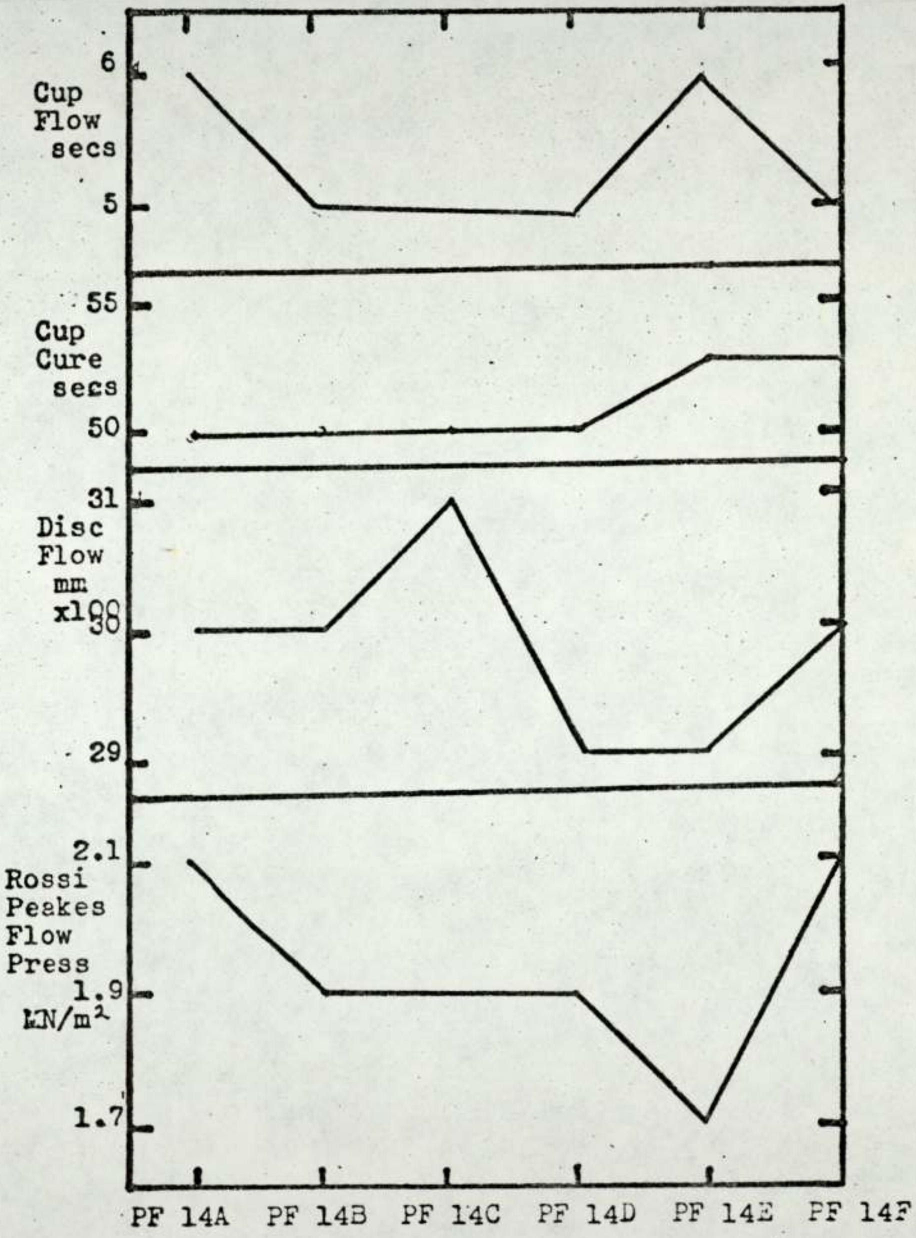


Fig. 39c. Results of current, standard flow tests for a series of Phenolic materials (PF 14A-F) used to produce the graphs in Figs. 39a & b.

Chapter 5

Assessment of the rheological properties of thermosetting plastics using the Variable Torque Rheometer.

5.1 Introduction

The variable torque rheometer is a small instrumented, internal mixer in which the torque required to rotate the rotors at constant speed and the melt temperature are recorded as a function of time.

Variations in torque are caused by changes in the consistency of the material and the torque variations may be used to indicate changes such as melting, solidification or any other process which may occur to the material when it is heated and sheared. It is therefore possible to record changes in the consistency of a polymeric material due to fusion, degradation, gelation, cross-linking etc. Changes in temperatures due to frictional heating and exothermic reactions are recorded.

5.2 Theoretical Analysis of the Variable Torque Rheometer

Several rheological analyses have been published for the Brabender Plastograph (a variable torque rheometer) and show that this type of instrument may be used to determine the fundamental rheological properties of materials.

McCabe (116) plotted log rotor speed against log torque for various rubbers and showed that the result was a straight line similar to the Ostwalde-de-Wade Relationship.

The analysis published by Goodrich and Porter (55) is based on the assumption that a torque rheometer is analogous to a concentric cylinder viscometer and states that the equations describing the relation between shear stress and shear rate, viscosity and between the thermal activation energy and temperature will apply. For non-Newtonian liquids the viscosity is dependent on the shear rate and Goodrich and Porter claim that a factor (determined with a capillary viscometer) can be introduced to allow for this.

They conclude that the torque rheometer can be used to determine approximate rheological parameters but has the added advantage of measuring side reactions such as degradation and crosslinking.

The analysis given above is criticized by Blyler and Daane(56) who point out that it does not take into account the range of shear stresses and shear rates which occur within each part of the rheometer chambers. They define a distribution function for shear rates within the rheometer chambers and relate this to the amount of shear stress acting on the rotors attritutable to the incremental range of shear rates. Blyler and Daane integrate the relationship and conclude that the gradient of a log log plot of torque against rotor speed at constant temperature is the same as for the log log plot of shear stress against shear rate obtained with a capillary viscometer. The flow activation energy obtained from the torque rheometer and the capillary viscometer are also identical. Blyler and Daane confirm this theory using both branched and linear polyethylenes.

Lee and Purdon (57) extend the analysis of Blyer and Daane and use the analogy of Goodrich and Porter to relate the theoretical constants to two experimentally determinable constants. Lee and Purdon state that the total force over an imaginary cylinder of total area equivalent to the existing cylinder contact area is equivalent to a torque M at a rotor speed of N. They assume that the motion of the material in the rheometer is laminar, that the equation developed is of the form that applies for both Newtonian and non-Newtonian fluids, that a constant can be used to allow for the fact that the concentric cylinder viscometers are interconnected, that the shear stress and shear rate referred to occurs at the surface of the imaginary cylinder and that the material shows a straight line relationship between log shear stress and log shear rate. The shear stress is given by the equation.

$$\text{Shear Stress} = 0.1745\ a\ N/n\ (1 - R_e/R_c)^{2}/n)$$

and the relationship between torque and rotor speed is given by

$$M = \frac{Re^2}{1.978 \times 10^3} \times \left(\frac{0.1745a}{n(1-(R_e / 1.975)2/n} \right)^{n} K N^{n}$$

where N = Rotor speed
a = Instrument Constant
n = Power Law Index
R = Chamber diameter(fixed)
M = Torque
Re = Diameter of equivalent cylinder

This equation has the basic form of equation $M = C(n)KN^n$

Lee and Purdon claim that this analysis confirms that of Blyler and Daane and that knowing the value of C(n) (from a log log plot of torque against rotor speed) and the material constants n and K it is possible to calculate R_e and a. Lee and Purdon substantiated their analysis for various thermoplastics materials. However, Norman (58) considers that the flow pattern in the variable torque rheometer is too complex to be analysed in this manner and that the results given by these analyses can only be semi-fundamental.

The significant point which arises from the various analyses is that the torque/rotor speed curve is similar to the shear stress/apparent shear rate curve. Although frictional heating cannot be eliminated, its presence does indicate the significance of this property with various materials and corresponds to processing conditions.

Use of torque rheometer with thermosetting materials

Torque rheometer results for thermosetting materials show a characteristic U-shaped torque curve and the correlation of the results with capillary viscometer flow data is therefore limited to the minimum torque value where the material momentarily corresponds to the steady state.

The interpretation of the torque/time trace for thermosetting plastics is discussed in the literature but the situation is confusing since widely differing opinions are given.

For example, several papers state that the data can only be used to measure the minimum viscosity, flow life and frictional heating properties of a material (52,117,118). Other authors state that the material completely cures in the rheometer chamber and that cure rates and cure times can be measured(18,119).

5.3 Equipment used for the assessment of flow properties

The variable torque rheometer used for this work was developed at RAPRA and is marketed by Hampden Test Equipment. It is essentially a small internal mixer in which the torque of the rotors is measured by a load cell. A thermocouple is inserted into the chamber and both torque and temperatures are recorded during mixing as a function of time on a rectilinear twin-trace recorder. The mixer is fitted with an oil jacket so that it's temperature can be controlled. A variable speed motor is used to drive the mixer head and loading of the rheometer chamber is by means of a pneumatic ram. The chamber volume is approximately 45 cm^3.

5.4. Experimental Results

Fig 40 shows the torque curves for the range of melamine phenolic materials and indicates that the variable torque rheometer will distinguish between materials of different moulding behaviour. Different materials were then tested in the variable torque rheometer and the results showed that the actual shape of the torque trace and in particular its detail is affected by the test conditions (rotor speed, temperature, ram pressure, sample weight and chamber geometry) and by the type of material tested. An optimum sample weight and ram pressure exist for each material since they affect the reproducibility of the results. The temperature, rotor speed and material are the variables used for evaluation purposes. Typical effects of these parameters are shown in Fig. 41.

Fig. 42a shows a typical torque trace for an injection moulding grade of phenolic moulding material. The curve shows the expected peak as the material is forced into the chamber followed by a minimum and then a final peak as the material crosslinks. Closer inspection of the curve indicates that not only do two small sub-peaks occur but a significant change in the trace width is also present.

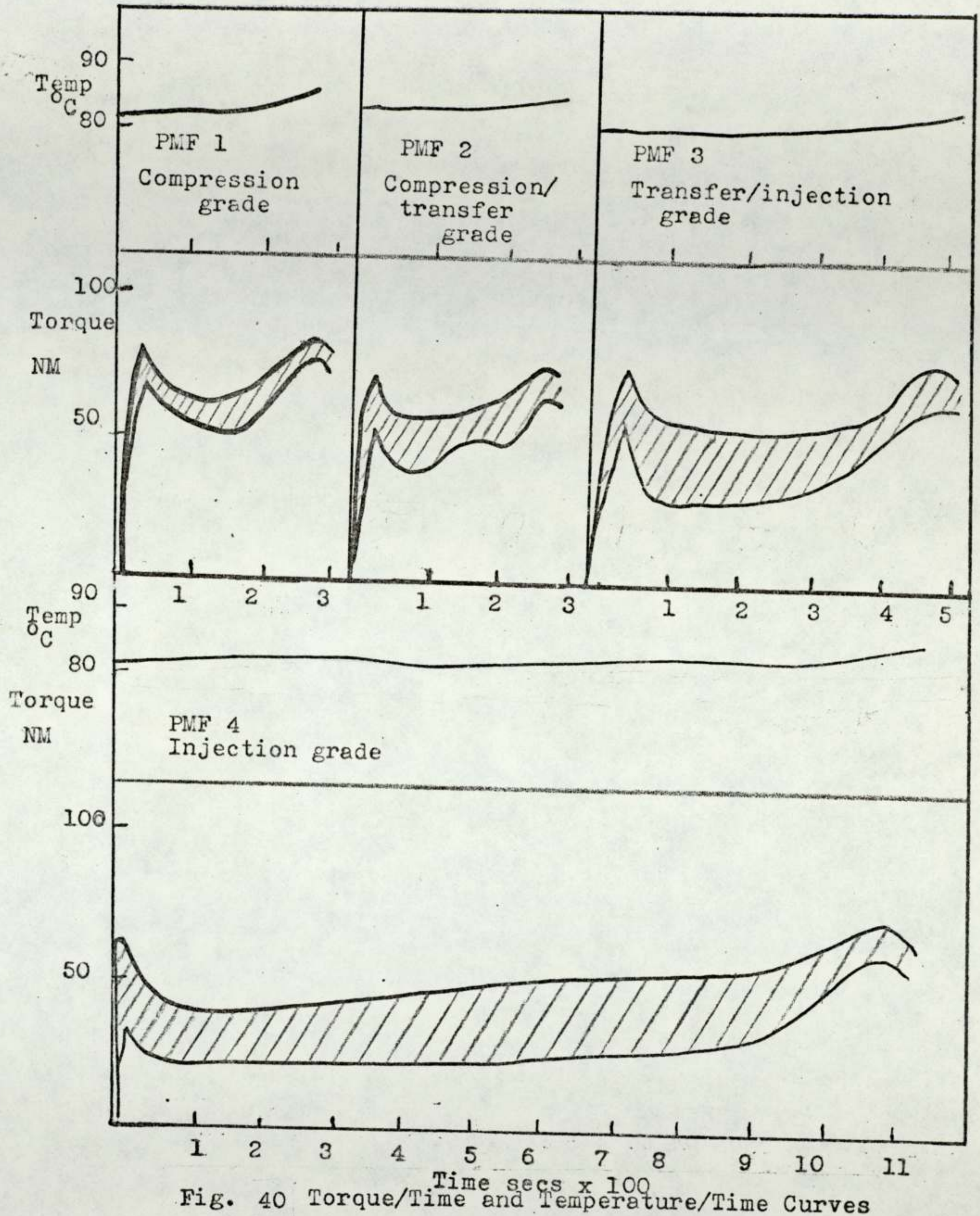


Fig. 40 Torque/Time and Temperature/Time Curves for Melamine Phenolic Test Materials.

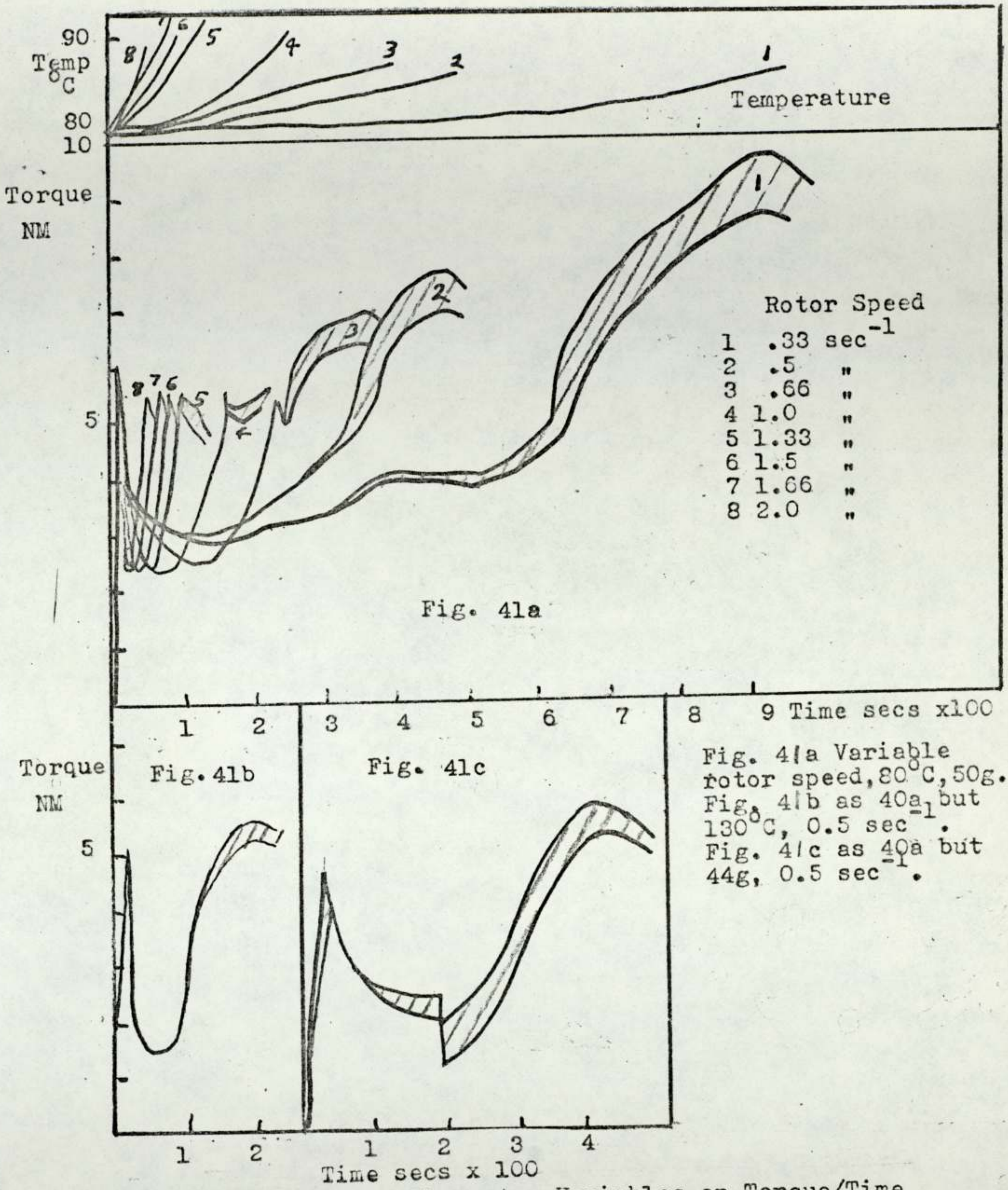
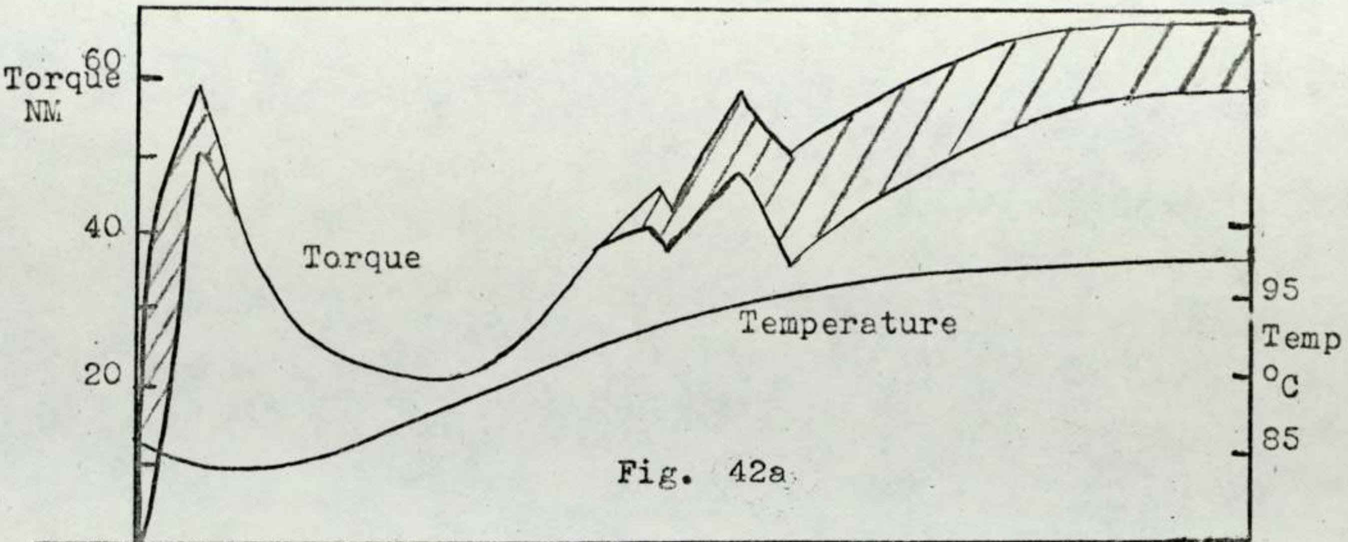


Fig. 41a Variable rotor speed, 80°C, 50g. Fig. 41b as 40a but 130°C, 0.5 sec^{-1}. Fig. 41c as 40a but 44g, 0.5 sec^{-1}.

Fig. 41. Effect of Rheometer Variables on Torque/Time and Temperature/Time Trace.



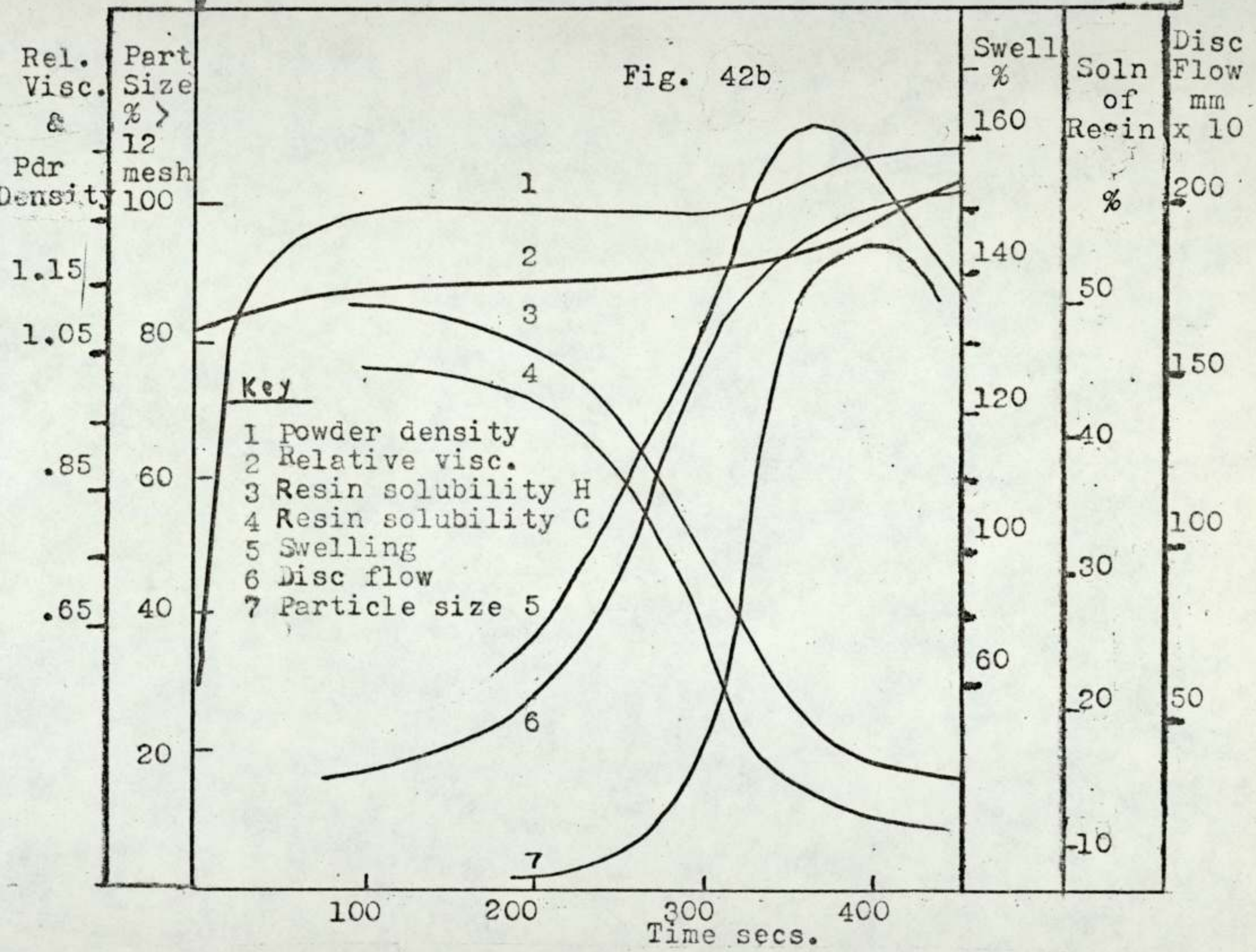


Fig. 42a. Typical Torque/Time & Temperature/Time Curve for Phenolic (PF 5).

Fig. 42b. Properties of Material from Torque Rheometer Chamber.

In order to understand this rather complex curve, the properties of material removed from the rheometer chamber were measured and the results are plotted as a function of chamber residence time in Fig. 42b. Visual examination of material removed from the chamber shows that it is first compressed, mixed and air is forced out until it forms a putty-like material which adheres to the chamber wall. This occurs shortly before the minimum torque value. The original particulate structure is also broken down during this process. The material consistency increases with increasing residence time until it becomes fairly rigid, and does not adhere to the rheometer. Before the sub-peaks the material is very soluble and readily breaks up into small pieces. The solubility of the resin decreases with increasing residence time while immersing the material in acetone for 24 hours causes considerable swelling. At the point of maximum swelling, the material is essentially a single large piece but beyond this point the swelling becomes less and an increasing number of smaller pieces of material are produced. (The swelling technique is widely used in the rubber to measure gelation).

These results indicate that the significant trace features are the small sub-peaks which denote the gelation of the material and mark the end of its useful flow life under conditions in the rheometer chamber. Beyond this point, the material continues to crosslink but it is mechanically cominuted by the action of the rotors.

This information refers to phenolic materials tested at relatively low temperatures (80 - 100°C). At higher temperatures the sub-peaks do not occur, the torque/time curve forming a U-shape. The final peak does not represent full cure, but represents a much higher degree of crosslinking than that represented by the peak at low temperatures However, the duration of flow is very short at higher temperatures and is difficult to determine accurately because small variations in loading time become significant. Different phenolics give different, but reproducible trace characteristics. e.g. they may not show the minor peaks but the trace may merely broaden.

A torque curve for a urea formaldehyde material is shown in Fig. 43a, 43b. The trace does not show the small peaks of the phenolic but does show a widening of the trace corresponding to the initial increase in torque value which is followed by the peak value.

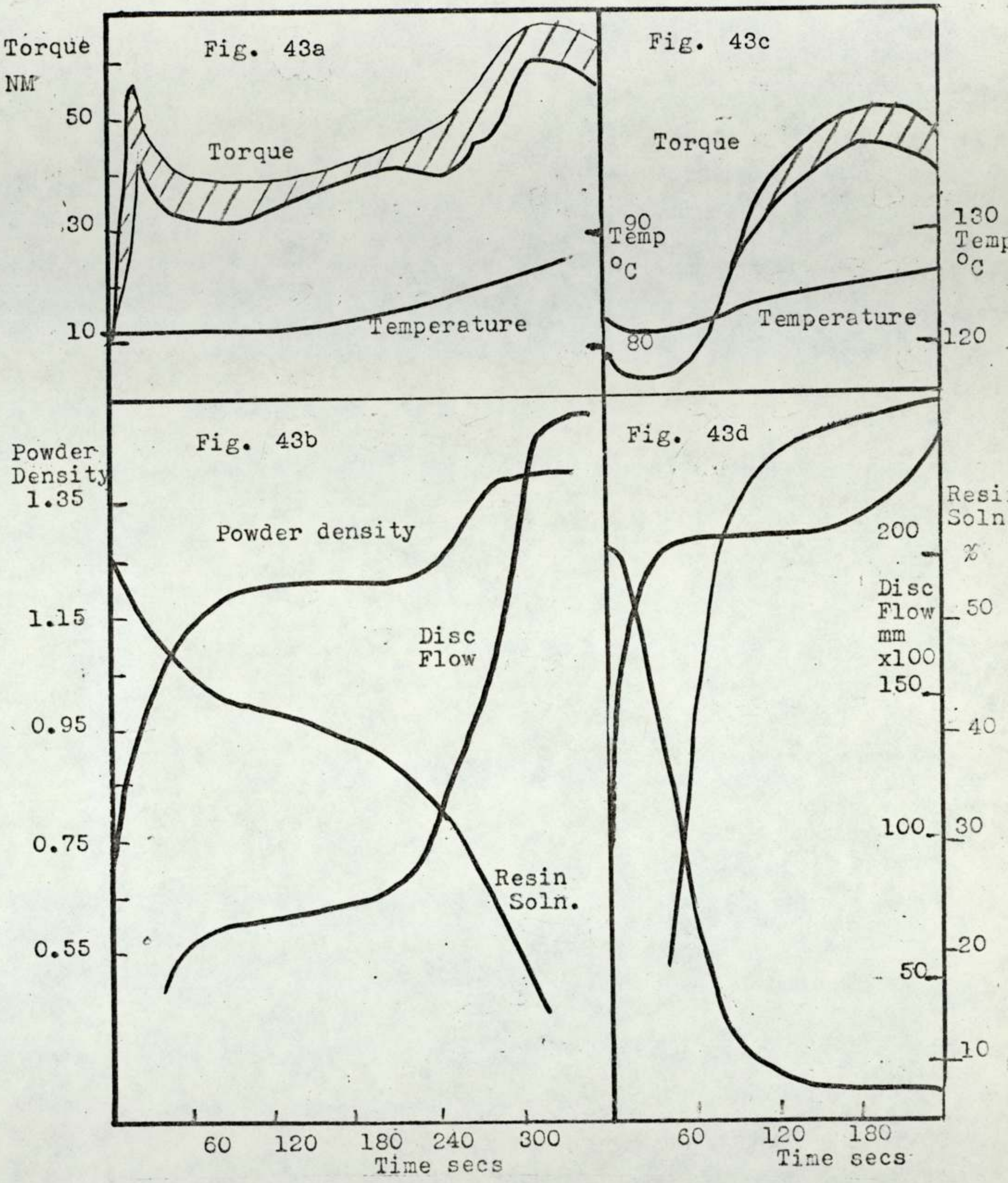


Fig. 43. Torque/Time and Temperature/Time trace for Urea Formaldehyde Material (UF 6) at 80°C (43a) and 120°C (43c) and relationship with properties of material in rheometer chamber (43b) and (43d).

Examination of material taken from the rheometer chamber at different times shows that most of the material is initially ground to a powder before being compacted to form a putty-like material, the consistency of which increases until it becomes a solid when it is ground to powder. In contrast to the phenolic material , the urea formaldehyde material does not adhere to the chamber walls. At higher temperatures, urea materials show similar torque traces to those of phenolic materials. It is interesting to note that at 120 - 130°C both urea and phenolic materials have similar coefficients of friction (fig 37).

Other formaldehyde based thermosetting materials (melamines, melamine phenolics, and dicyandiamide formaldehyde materials) show similar torque traces to those of urea materials. Since these materials do not show the gelation peaks of the phenolic material, the duration of fluidity is measured by the time to the final peak torque value. The relationship between the time to the gelation peak and to the final peak torque for a phenolic material is shown in Fig.44.

Once the material has gelled it is mechanically degraded, but this does not occur with the modified phenolic materials until the later stages of the crosslinking reaction and the torque rheometer results may be used to measure the initial cure rate of these materials.(Fig 45).

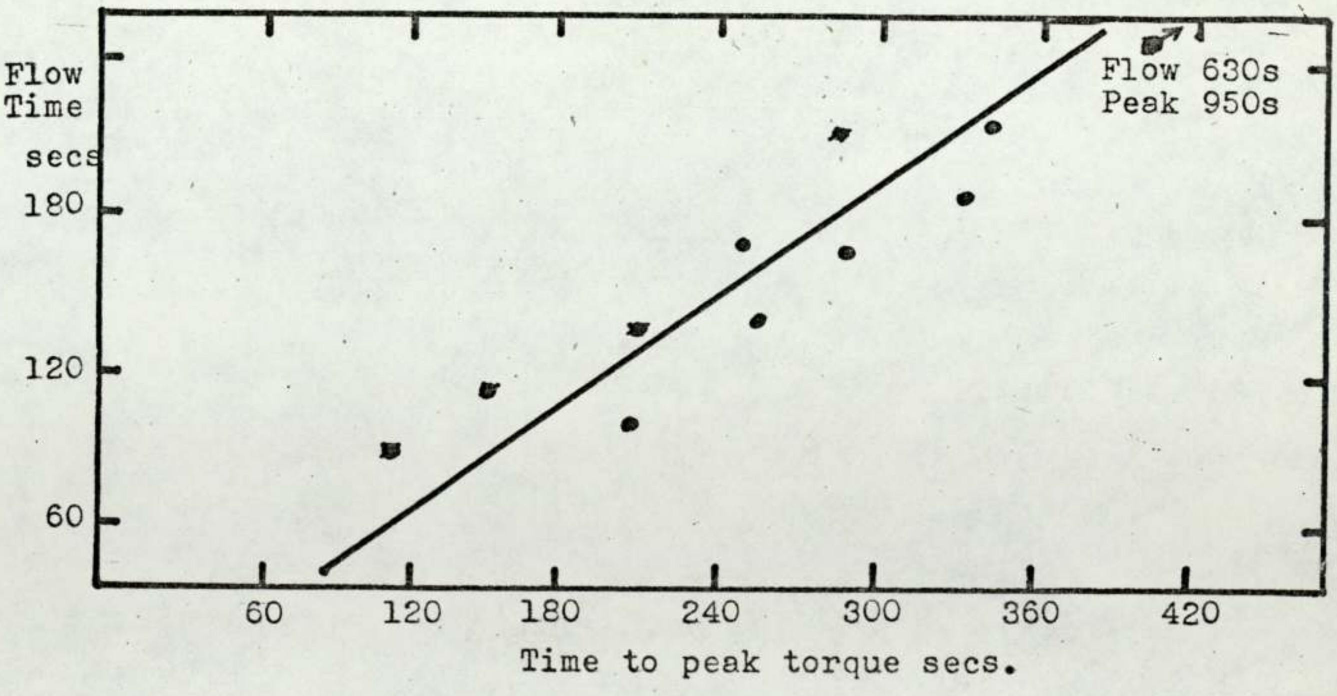


Fig. 44, Relation between flow time (torque trace change point) and time to peak torque value.

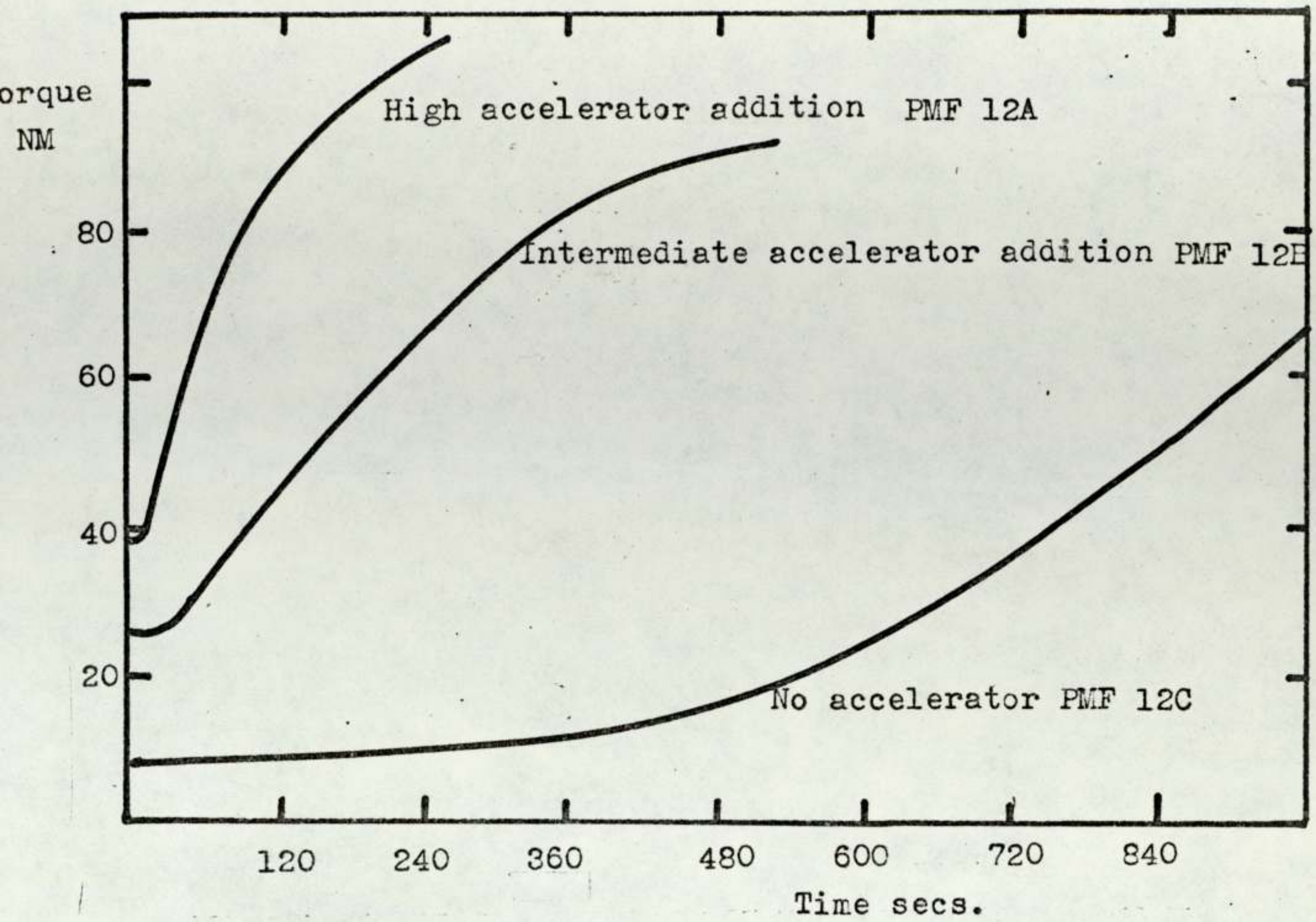


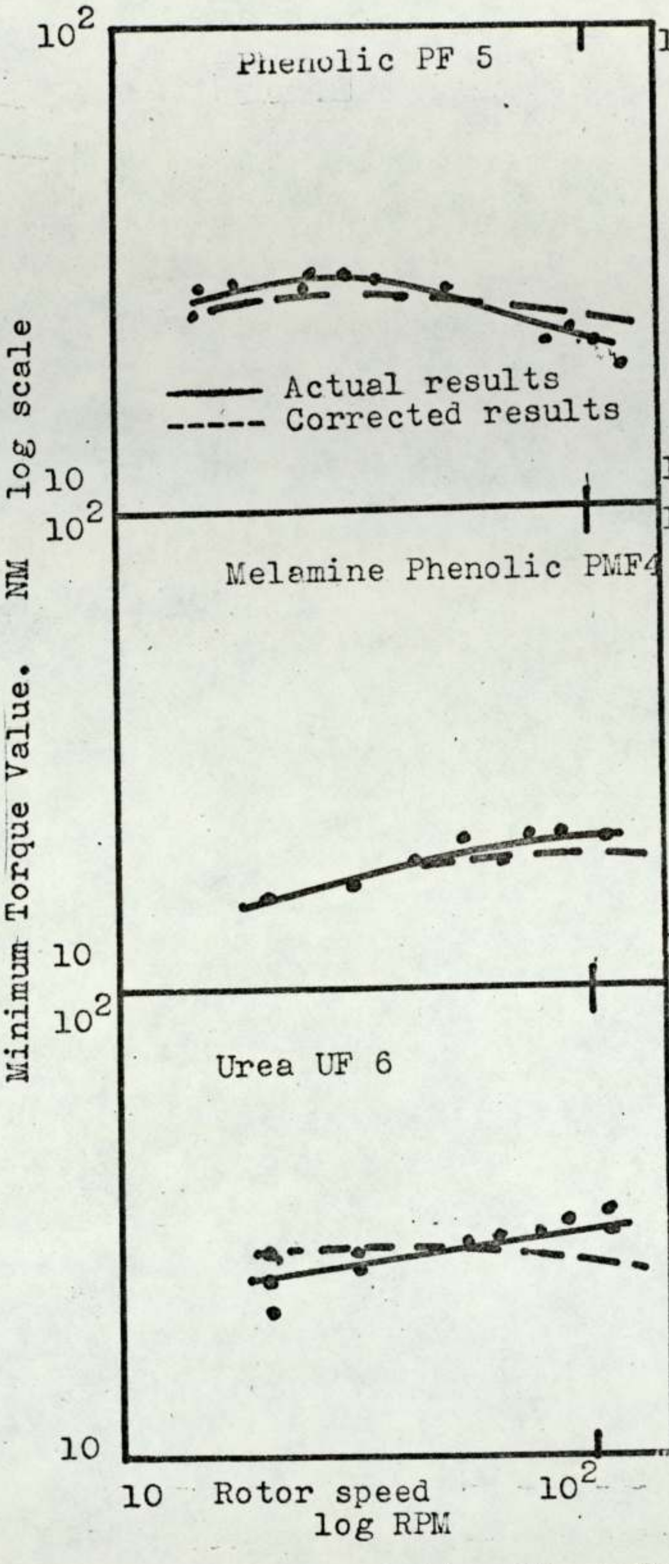
Fig. 45. Torque/time curves for modified Phenolic materials having different accelerator addition.

Reproducibility of Results

Typical values of the coefficients of variance for the minimum torque value range from 2.0 - 7.0 (average 4.3) for the minimum torque value and 2.4 - 14.0 (average 7.5) for the gel time.

Evaluation of Materials

The effect of rotor speed on the rheometer torque is given as a log log plot in Fig.46 for typical injection moulding materials. Two curves are given, one for the actual results and a second curve for which the results have been corrected to constant temperature using the torque/temperature curve in Fig.48.



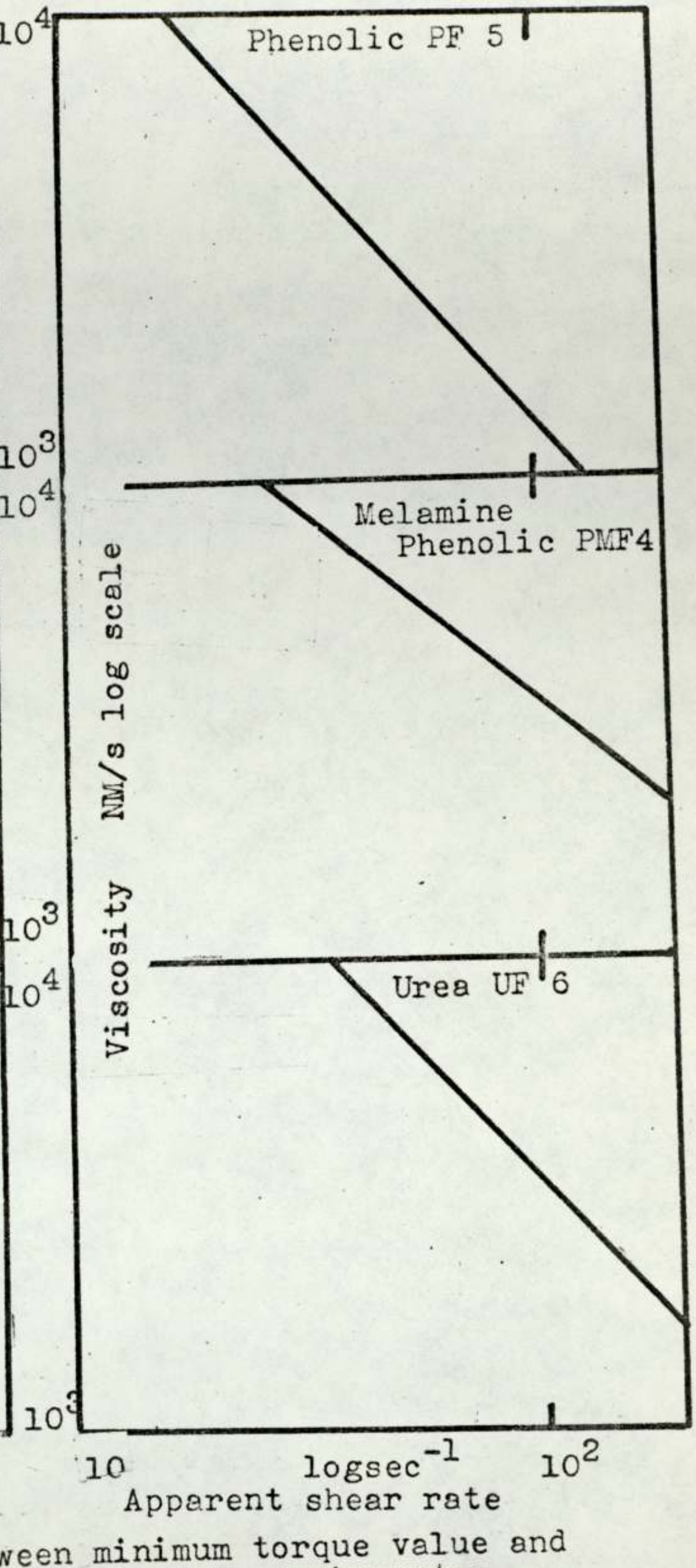


Fig. 46 Relationship between minimum torque value and rotor speed for variable torque rheometer.

Fig. 47' Viscosity/apparent shear rate curves calculated from torque results.

TABLE 23

Interpretation of Torque Rheometer Data

Coefficient of equations in section 5.2	Phenolic PF5	Material Urea Formaldehyde UF6	Melamine Phenolic MPF 4
Analysis by Goodrich and Porter(55) and Lee and Purdon (57)			
Radius of Equivalent Cylinder cm (Re)	1.83	1.86	1.87
Ratio of Rotor speed to Shear Rate	11.6	4.0	2.4
Instrument Constant	7.8×10^{-4}	4.7×10^{-4}	4.2×10^{-4}
Power Law Index (n)	0.02	0.7	1.2
Power Law Constant(cn)K	2.6	1.8	0.54

The results in Fig.46 have been interpreted by the analysis of Goodrich and Porter (55) and Lee and Purdon (57). The results in Fig.46 were used to calculate experimental constants and the radius of a cylinder equivalent to the rheometer rotors, and this was then used to calculate the viscosity/shear rate curve, Fig.47, for these materials using the equations and constants in Table 23.

In view of the assumptions made in the theory, it is unwise to pursue the theoretical interpretation of the torque rheometer results (since they can only be semi-empirical) and to use the torque rheometer to produce empirical results.

Increases in rotor speed give a reduction in flow time (see Fig. 48 a). This is partly because the frictional heating reduces the flow life and partly because the higher shear rate means that the torque value is more sensitive to the onset of cross linking.

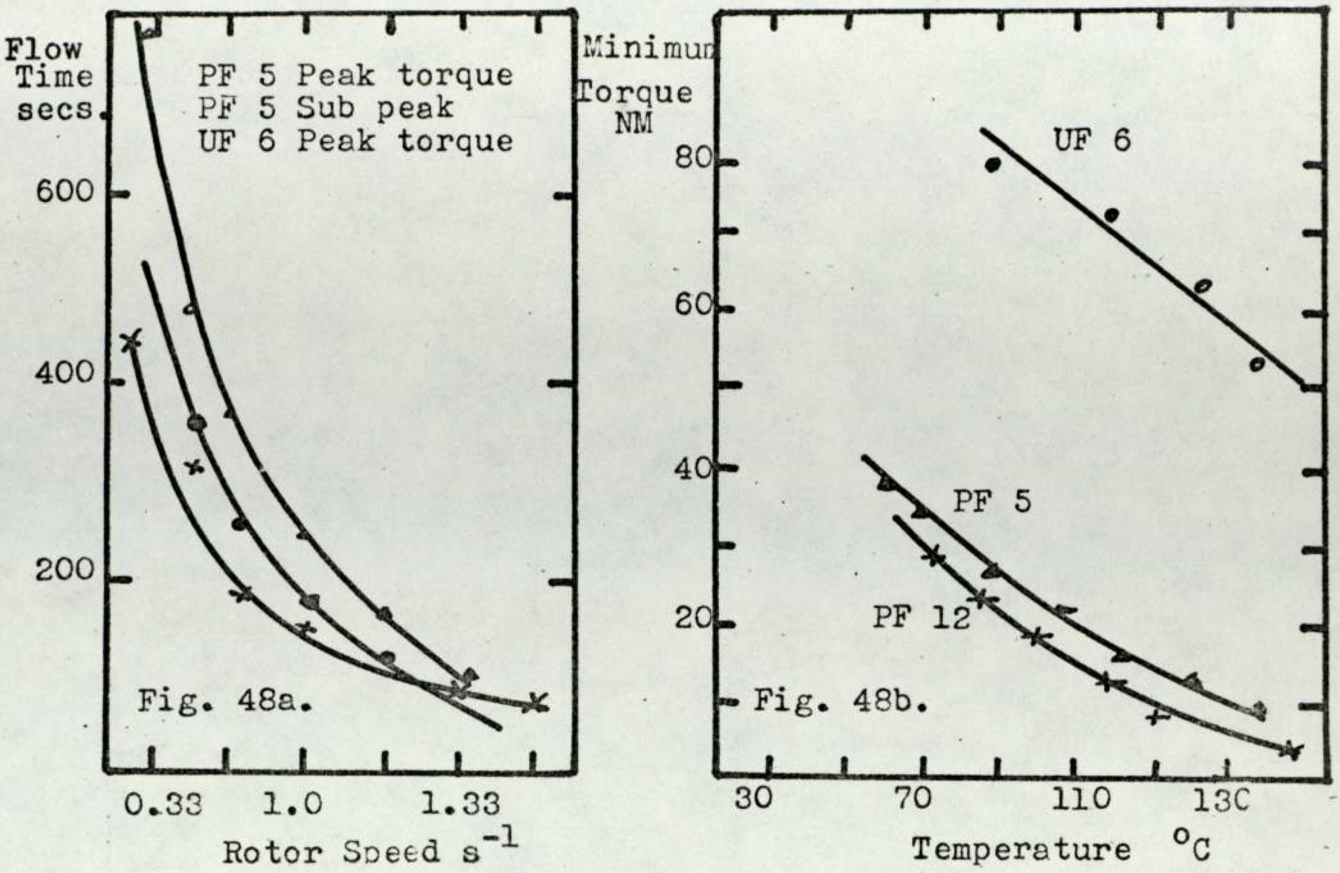


Fig. 48. Correlation of the duration of fluidity with rotor speed and the minimum torque value with temperature.

The Arrhenius equation relates the rates of chemical reactions to the temperature of the process. It can be used to calculate the Thermal Activation Energy of a process using the equation (given below).

$$K = Ae^{-\frac{E}{RT}}$$

$$\text{or} \quad \log_{10} t = \frac{E}{2.3026R}\left(\frac{1}{T}\right)$$

Where t = Time (or other measured property)

E = Thermal activation constant

R = Universal Gas Constant

T = Absolute temperature

A, K, = Constants

The plot of log reaction time against the reciprocal of the absolute temperature should be a straight line. The variable torque rheometer results can be approximated to a straight line over the temperature range of 70 - 120°C. Above these temperatures the gradient of the line changes indicating a change in mechanism. Fig 49.

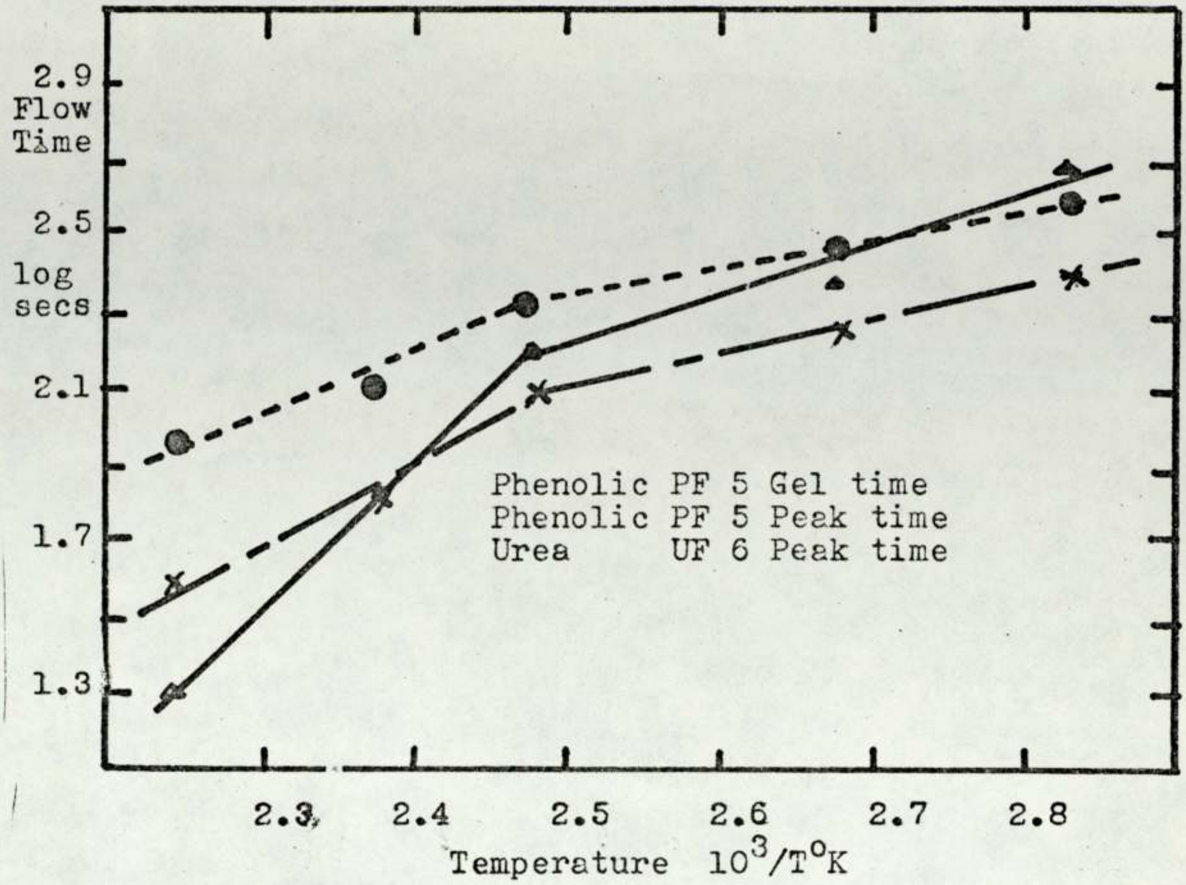


Fig. 49a Arrhenius relationship between temperature and flow time as determined in the variable torque rheometer.

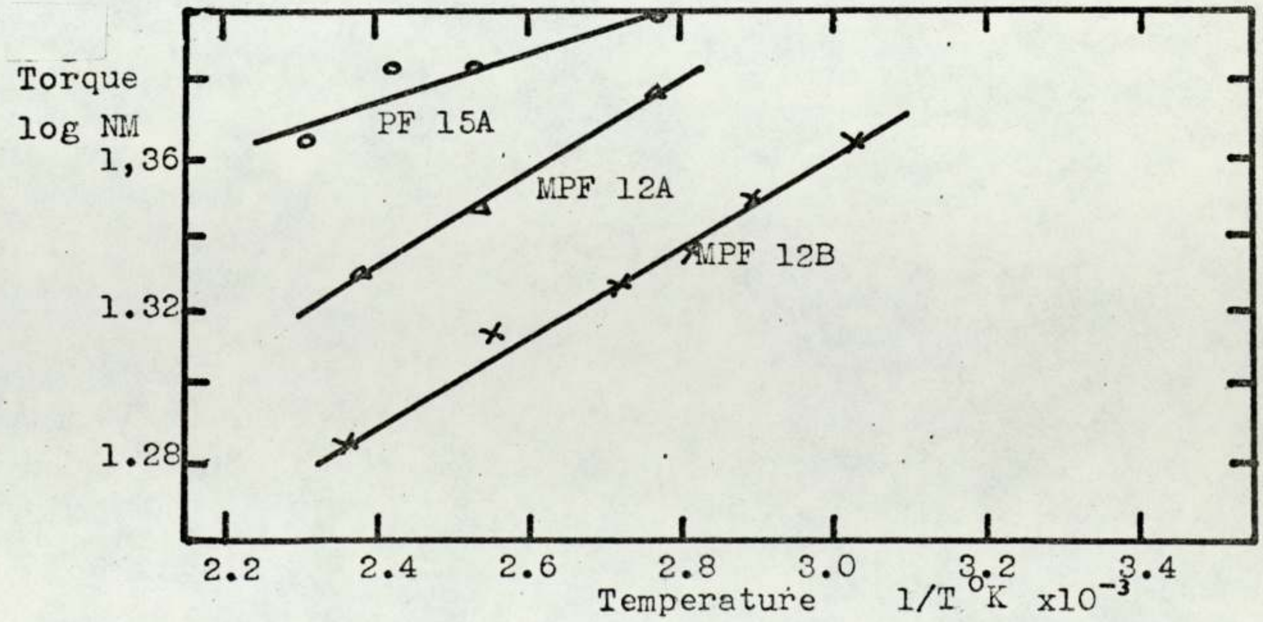


Fig. 49b. Arrhenius plot of torque as a function of temperature.

Typical thermal activation energies for the duration of fluidity for various materials are given in Table 24, which shows that the activation energy of a material decreases as the cure rate of the material is increased.

TABLE24. Thermal Activation Energy for the duration of fluidity of thermosetting materials

Material Code		Flow Energy KJ/mol	Material Code	Flow Energy KJ/mol
Phenolic	9A	20.3	Urea Formaldehyde	
	9B	20.3	Injection Grade 6	26.2
	9C	19.1	Compression Grade 22H	36.1
	10A	25.8		
	10B	19.9	Modified Phenolic 20A	41.0
	10C	18.0		
	19A	38.2		
	19B	17.4		
	19C	15.3		
	19D	11.9		

It is tempting to measure the torque as a material is slowly heated at a constant rate. The resultant torque/temperature graph is shown in Fig. 50 and shows the softening temperature, the temperature of maximum plasticity and the temperature at which the material starts to crosslink rapidly. However, it can easily be shown that the shape of the curve and the temperatures referred to depend on the rate at which the sample is heated.

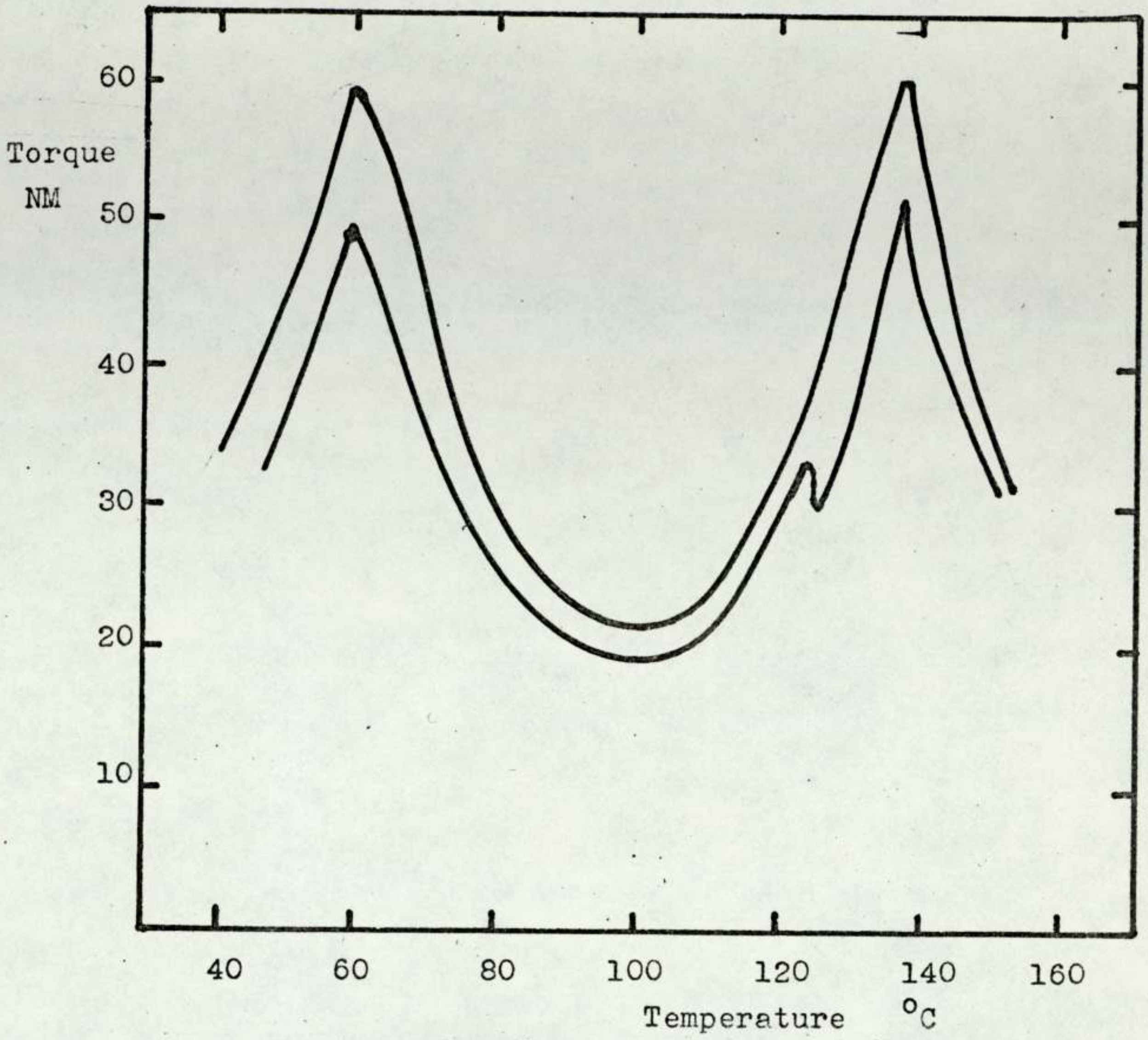


Fig. 50. Torque/temperature curve obtained by plotting torque against temperature measurements made as the material was heated at a constant rate in the variable torque rheometer chamber.

A considerable difference exists in the flow life as measured by the variable torque rheometer (Fig.44) and that indicated by the results in the previous chapter.(Fig.26). A limited number of experiments were carried out to compare the effects of static and dynamic heating. These experiments were carried out in the variable torque rheometer and the 'flow' of the material removed from the chamber determined by the disc flow test. (Table 25a).

TABLE 25a : Changes in the flow of a phenolic material held in the torque rheometer chamber under static and dynamic heating conditions.

Chamber Residence Time secs.	Temperature °C	Disc Flow mm	Comments
360	80 increasing to 90°	230	Typical run
360	80	75	Rotors stationary
360	90	55	"
0	-	45	Virgin Material
720	80 increasing to 90°	250	Material plasticized and then held for 360 secs with rotors stationary, rotors started and normal run completed

TABLE 25b :

Run No.	Plasticizing Period secs	Static Period secs	Alternating Dynamic Periods	Flow Life secs	Total Residence Time secs
1	–	0	-	339	339
2	160	40	-	310	350
3	160	90	-	300	390
4	160	110	-	290	400
5	100	30	60	285	380

A similar experiment was conducted using a phenolic material to investigate the effect of increasing the ration of static to dynamic periods. (Runs 1 to 4, Table 25b)

5.5. Discussion of Results of variable torque rheometer

The variable torque rheometer may be used to measure the minimum consistency and the duration of fluidity of a material. It may also be used to determine the effect of temperature and shear rate (rotor speed) on the properties of a material as well as being used as a mixer. It is best used at lower temperatures (70 - 110°C) and a summary of the important trace data is shown in Fig.51.

The results obtained with the variable torque rheometer provide an approximation of the viscosity shear rate characteristics of the material (Fig.47) and a good correlation of the duration of the melt fluidity with the barrel life of a material (Fig.54). It is also possible to estimate the initial rate of cure of some materials (Fig.4 as well as the extent of frictional heating. These conclusions are in general agreement with those of Mandler(117) and Schreiber (52) but conflict with other workers who claim that the material actually cures in the rheometer and that it is possible to measure the cure time of the material with the variable torque rheometer. e.g. Kerr and Dontje (18) and Varodhochary (119). The work described in this thesis concerning the interpretation of the rheometer results is in general agreement with the work of Ehrentraut and Dalhoff (118) and Schreiber.(52).

The torque/time traces of different materials obtained under different temperature and shear rates show different but reproducible characteristics (Fig.41). The interpretation of the trace is consequently semi-empirical and it is often possible to estimate the type of polymer in a moulding material by the shape of the torque/time trace. Changes in the rheometer torque value may be caused by physical as well as chemical affects and it is essential to identify any novel or new trace features since failure to do so accurately can lead to erroneous or misleading conclusions. (This statement applies equally well to other materials e.g.PVC) It is this difficulty of obtaining accurate and fundamental interpretation of the variable torque rheometer results which probably accounts for the confusion which exists in the literature concerning the interpretation of torque rheometer data and even concerning the usefulness of this type of instrument.

Fig. 51. Interpretation of Torque Rheometer Results.

Fig. 51a. Rheometer trace, Phenolic PF 5.

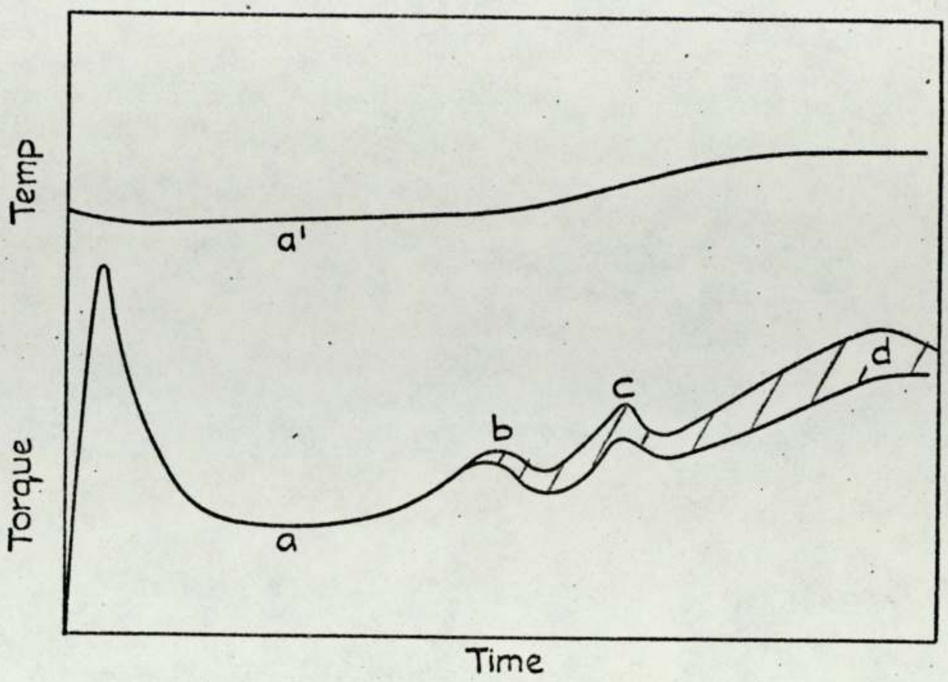
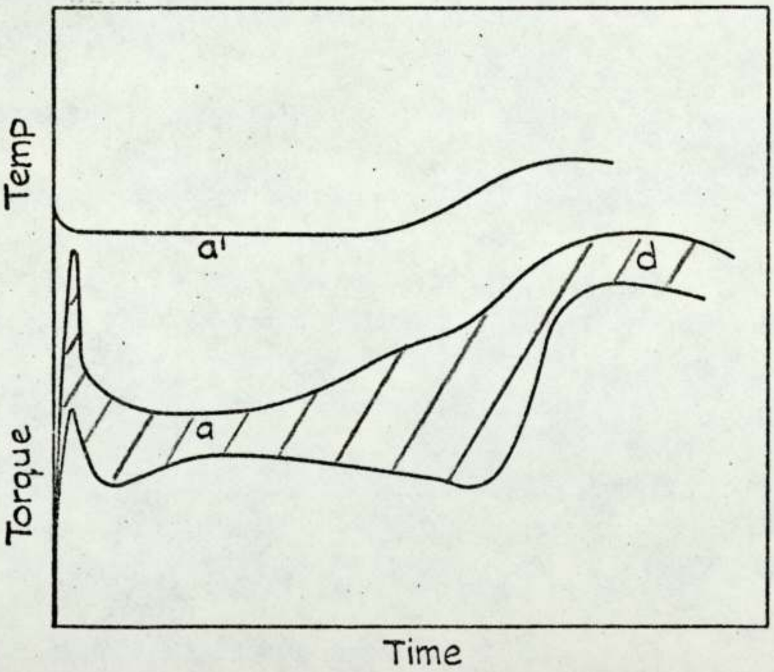


Fig. 51b. Rheometer trace, Urea formaldehyde UF 6.



Key.

a Minimum torque value at temperature a'
b,c Gel time for phenolic materials
d Time to peak torque, used as gel time for
many materials including UF's, MF's & PMF's.

Frictional heating effects occur and the effect of this is that high viscosity materials show a shorter relative flow life than they would under isothermal conditions. This effect was also noted by Schreiber (52).

Visual inspection of the material in the torque rheometer chamber shows that considerable differences exist between phenolic materials and amino materials. Phenolic materials adhere strongly to the walls of the chamber although the adhesive forces decrease with increasing resin condensation and the material may be ejected quite easily when gelled. In contrast, amino materials do not adhere to the chamber walls. Thus, the rheometer can yield qualitative information concerning the friction properties of materials.

A considerable difference is observed in the duration of fluidity of materials as measured in the capillary viscometer and the variable torque rheometer under what are nominally the same temperature conditions. Thus the flow life of an injection moulding phenolic in the capillary viscometer is 30 minutes (see fig.26) while that in the variable torque rheometer is about 6 minutes (see fig.54). The viscosity of a material changes little in the rheometer chamber under static conditions. The most probable explanation to this is that of temperature difference. Although the chamber temperatures of the capillary viscometer and the variable torque rheometer are nominally the same, it can be shown that in the capillary viscometer the powder temperature is considerably less than the wall temperature. In a dynamic situation, heat is generated which is proportional to the product of shear stress and shear rate. As the condensation reaction of a thermosetting material proceeds, so the shear stress increases and with it frictional heating. Curing reactions are also exothermic. A temperature increase of 8 - 15°C is observed in the torque rheometer but this reading is taken near the chamber wall and the true temperature is probably considerably higher, and temperatures measured in the centre of the melt are typically 5-8°C higher than the recorded temperature. This increase in temperature may cause a reduction in viscosity which will offset the increase in viscosity caused by the condensation reaction thus producing a pseudo-steady state.

The relative difference between the duration of fluidity of plasticised and unplasticised, heated powder quoted above for the variable torque rheometer and capillary melts (1:5) at 95-98°C coincides closely with similar figures (1:6) published by König (121). König evaluated injection moulding phenolics and measured these effects in the injection moulding machine barrel.

The results in Fig.22, 76, Table 43, show that the melt in the injection moulding barrel is changing rapidly and that a delay of a few seconds in the moulding cycle or an increase of 10°C in the barrel temperature is sufficient to cause the viscosity of the material to increase to the extent that it would not mould satisfactorily (Fig.78). This evidence confirms the value of the torque rheometer as a means of assessing the duration of fluidity under similar dynamic conditions encountered in the injection barrel, since the capillary viscometer will not give this type of information.

The variable torque rheometer records the consistency of thermosetting materials during the fusion, flow and early states of cure but its results are only semi-fundamental and require practical experience in interpretation of its results. It is, however, one of the few instruments capable of measuring these changes and its results correlate well with the injection moulding barrel. Fig. 54.

Evaluation of Additives and material formulations

A comparison of materials of increasing condensation shows three basic features (see Fig 52.). As the degree of precure is increased so the minimum torque increases, the flow time decreases and in the final two curves, the trace width increases. A widening of this trace may be due to various causes but subsequent solubility and flow measurements showed that the final material had partially gelled.

It follows that this technique could be used to measure the changes brought about by compounding. This technique has been described elsewhere by the writer (120). It is interesting to note that materials showing a wide torque trace (PF7D&E) would not injection mould satisfactorily. (Table 30).

The effect of additives on the flow properties of a material can also be determined using the torque rheometer. Figs.53 a, b, c, d, e, were obtained using a powdered proprietary material (PF5) to which various ingredients were added. Figs.53 f, g, used specially prepared moulding materials. The rheometer was used purely as a mixer at low temperatures to mix resin solution with fillers catalysts, lubricants, etc. When mixed, the material was removed from the rheometer, dried to a constant weight and finally tested at 80 - 88°C.

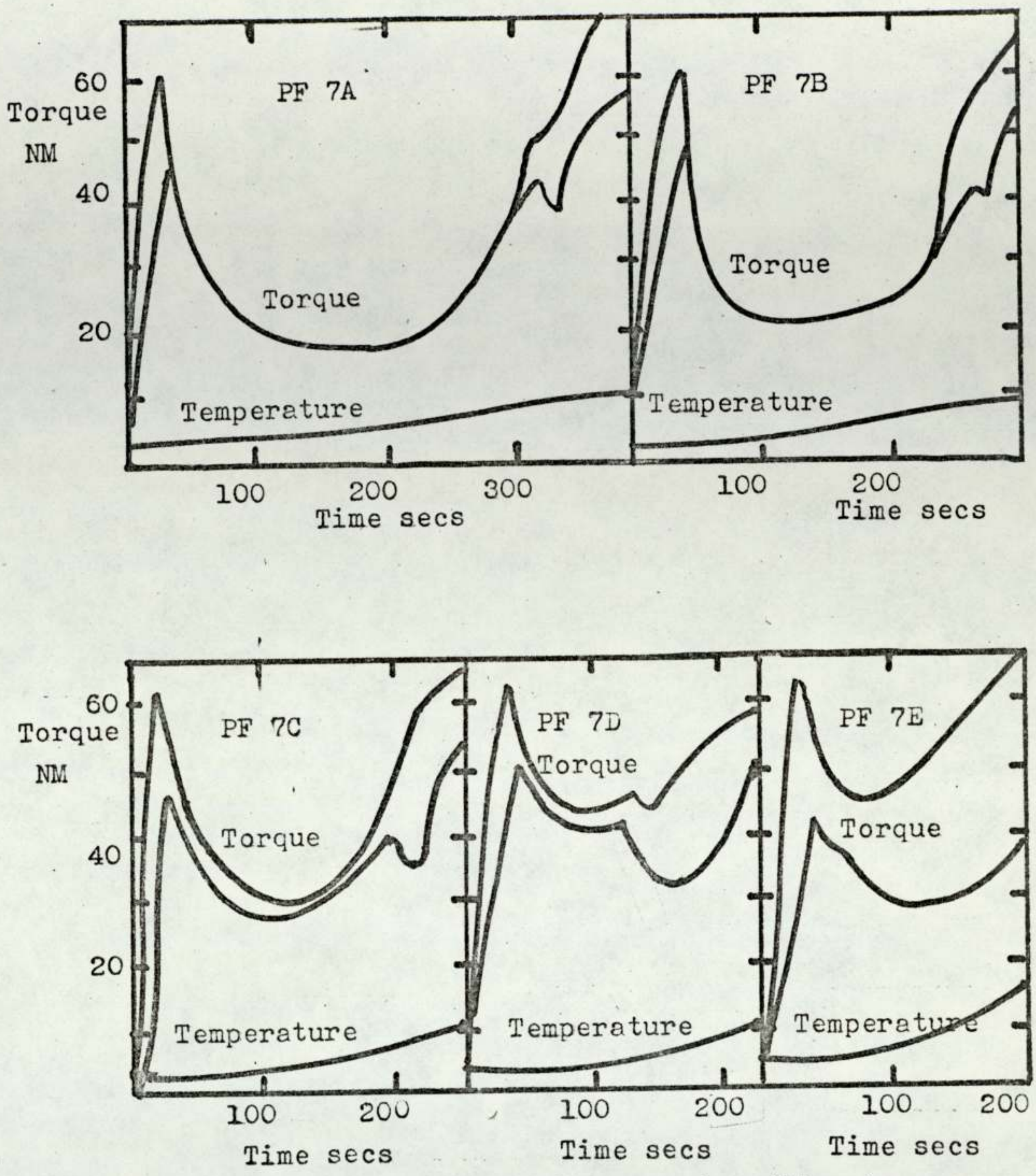


Fig. 52. Torque/time and temperature/time traces for Phenolic materials of increasing resin precure.

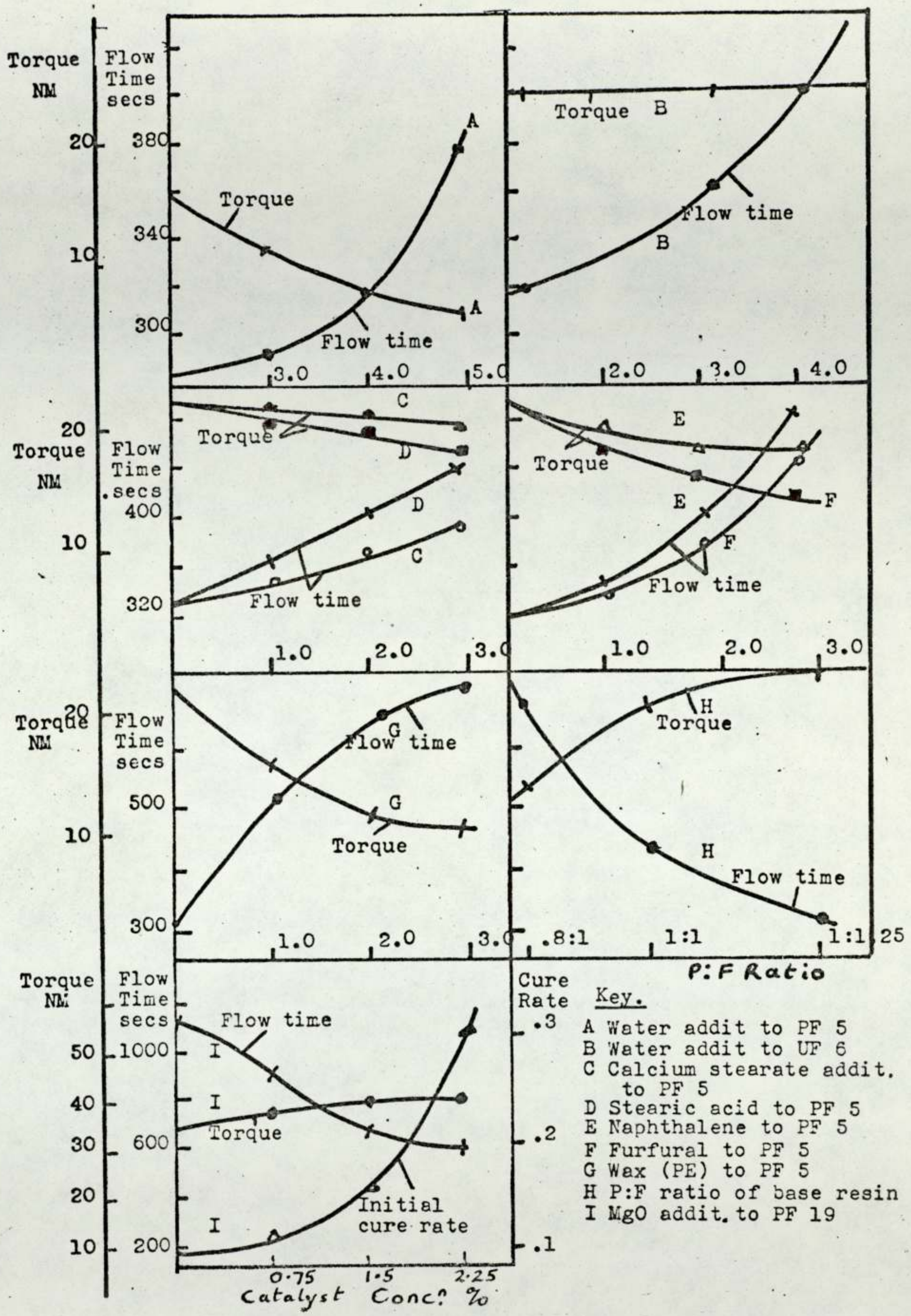


Fig. 53. Effect of formulation variables of thermosetting moulding materials as determined in the variable torque rheometer.

5.6 Correlation of Variable Torque Rheometer Results with Injection Moulding

A correlation is shown in Fig 54a between the minimum torque value as measured in the variable torque rheometer and the rate of flow of the material through the injection nozzle. The poor correlation is probably due to the large differences in the shear rates involved, the shear rate in the variable torque rheometer being $10\text{-}10^2\text{sec}^{-1}$ and that at the injection nozzle of the order of $5\times10^2\text{-}10^4\ \text{sec}^{-1}$.

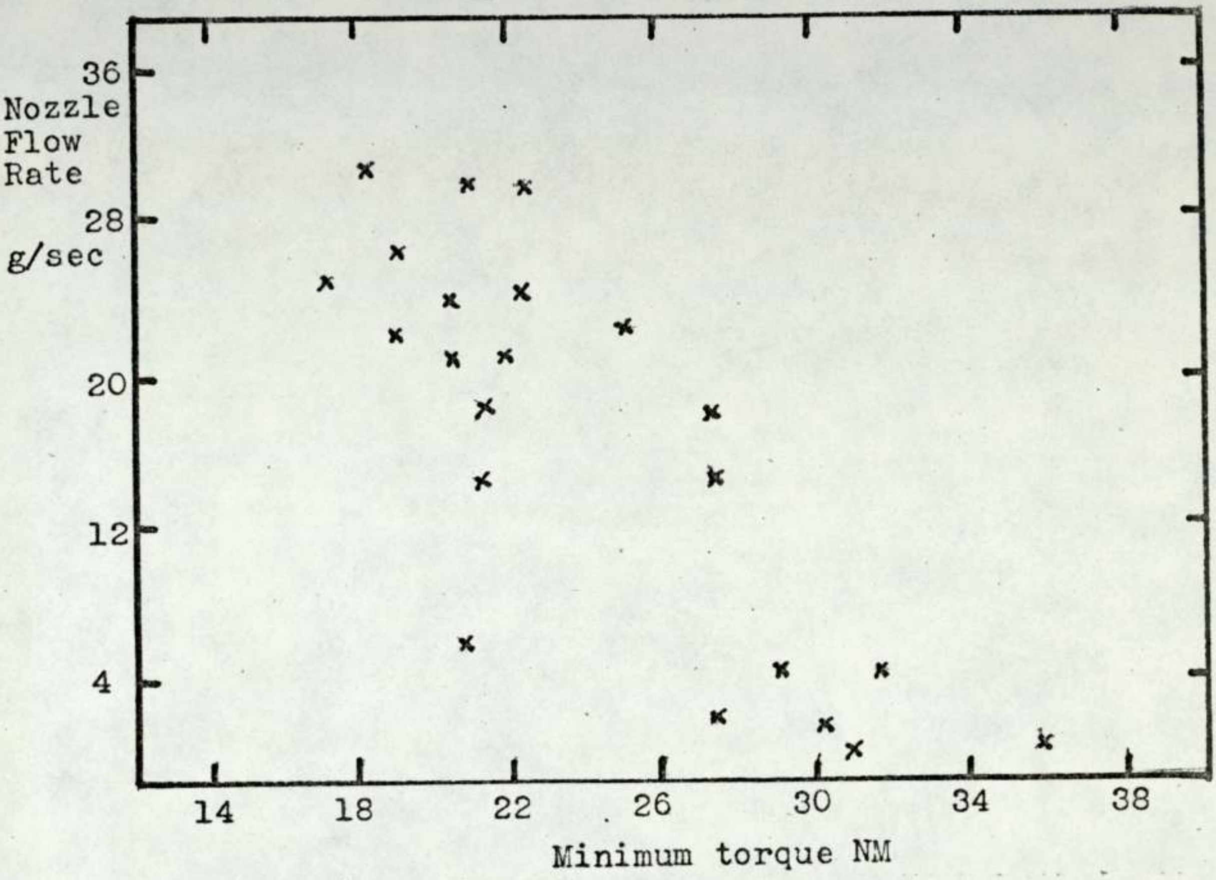


Fig. 54a. Relationship between minimum torque value as determined in variable torque rheometer and injection nozzle flow rate.

The correlation between duration of fluidity of a thermosetting moulding material as determined in the variable torque rheometer and in the injection moulding barrel or barrel life is shown in Fig.54b. These graphs show that a good correlation is obtained with phenolic and urea materials and this is confirmed by the qualitative information given in Table 26. The qualitative statements of flow stability are those given by the material manufacturers and it is most important to compare the flow stability results for each group of materials and not to compare materials from different groups. A similar correlation is shown for urea formaldehyde materials.

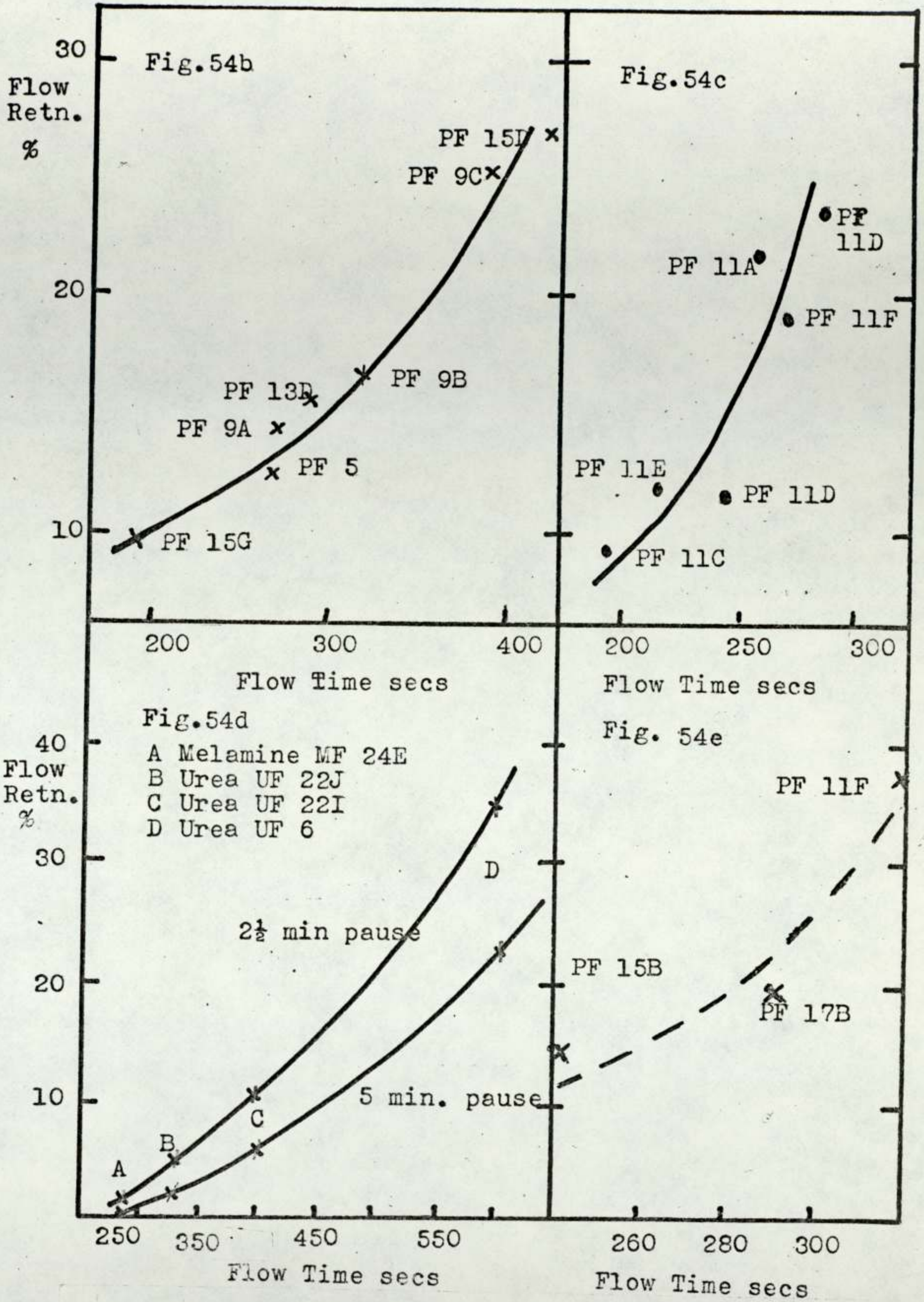


Fig. 54. Correlation between flow retention as determined in injection machine and flow life as determined in variable torque rheometer. Fig 54b&c in Bipel machine, Fig 54d&e in Turner 60g machine.

TABLE 26: Correlation between flow properties of materials

Material	Manufacturers Designation		Torque Rheometer	Data
Barrel life	Flow	Flow Life	Min Torque NM	Flow Time secs
Phenolic 15 A	Easy	Good	32	220
B	"	Fair	44	160
C	"	Good	38	260
D	"	Good	24	215
E	"	V. Good	18	350
F	"	Good	28	280
9A	"	Good	26	374
9B	"	Medium	22	313
9C	"	Poor	22	290
Urea 21J	Very Easy	Very long	31	540
21E	Easy	Long	46	347
21F	Stiff	Short	50	164
21G	Stiff	Long	54	241
21H	Stiff	Medium	57	197
21I	Easy	Long	42	331

Chapter 6.

Investigation of the oscillating disc rheometer with thermosetting plastics.

6.1. Introduction

The oscillating disc rheometer has an important advantage when compared to the other instruments used in this thesis in that it imparts a very small strain to the sample. This means that it is capable of recording the consistency of a thermosetting material throughout its complete cure cycle. The other techniques cannot be used beyond the point where viscous shear flow ceases since at that point the material flow cannot be measured (capillary viscometer) or the material will be mechanically degraded (variable torque rheometer).

6.2 Theoretical Analysis of Oscillating Disc Rheometer Data

The rheometer records the torque of the oscillating rotor as a function of time and produces a trace indicative of the changes which occur within the material. The theory of sinusoidal deformation of visco-elastic materials is described in detail by Scott and Payne,(122) and by Monsanto (123) and consequently only a brief description is given here.

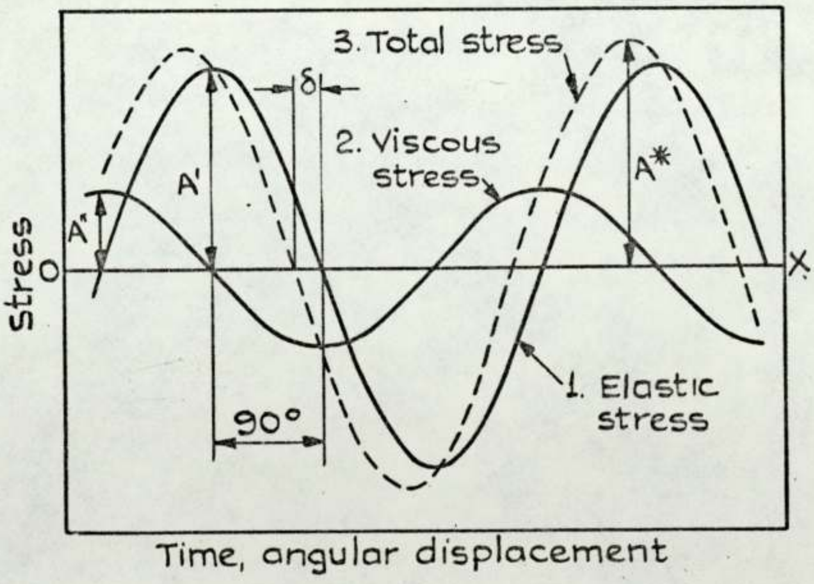


Fig.55. Relationship between the total(complex) stress the elastic and viscous components and the loss angle.

When a sinusoidal strain is applied to a material, it produces a stress which is out of phase with the applied strain. (see Fig.55). This stress (referred to as the total or complex stress) can be resolved into two parts; a component which is in phase with applied strain, (the elastic stress (σ')) and a component which is 90° out of phase with the applied strain, (the viscous stress σ'')).
The loss angle(δ) is the phase angle between the complex and elastic stresses.

When stress and strain are plotted against each other, the resultant curve is an ellipse, the area of which is proportional to the frictional heat build-up in the material and is the resultant of the energy losses in oscillatory systems.

The oscillating rheometer will record the changes in the torque throughout the complete crosslinking reaction and various workers have used it as a means determining the chemical reaction kinetics of rubbers. The theory was developed by Coran (125)(126) for rubber materials and the rheometer results have been subsequently correlated with measurements of crosslink density measurements for rubbers (127, 128).

The theory assumed that crosslink formation is a first order reaction after the induction period t_i. It was shown that the crosslink density after time (t) was directly proportional to the torque (R_t). Coran's equation becomes:-

$$\log_{10} (R_{max} - R_t) = \log_{10} R_{max} \frac{+ k(t - t_i)}{2.303}$$

Where the t is the time, t_i the induction time, and k the first order constant. R_t and R_{max} can be directly read from the rheometer curve (Fig.56).

The crosslinking reaction thus may be characterised by three parameters.

t = the time necessary for the reaction to become first order i.e. the time for the formation of an activated crosslinking intermediate.

k = the overall first-order rate constant.

R_{max} = the maximun torque developed during the crosslinking process which is a measure of the crosslink density.

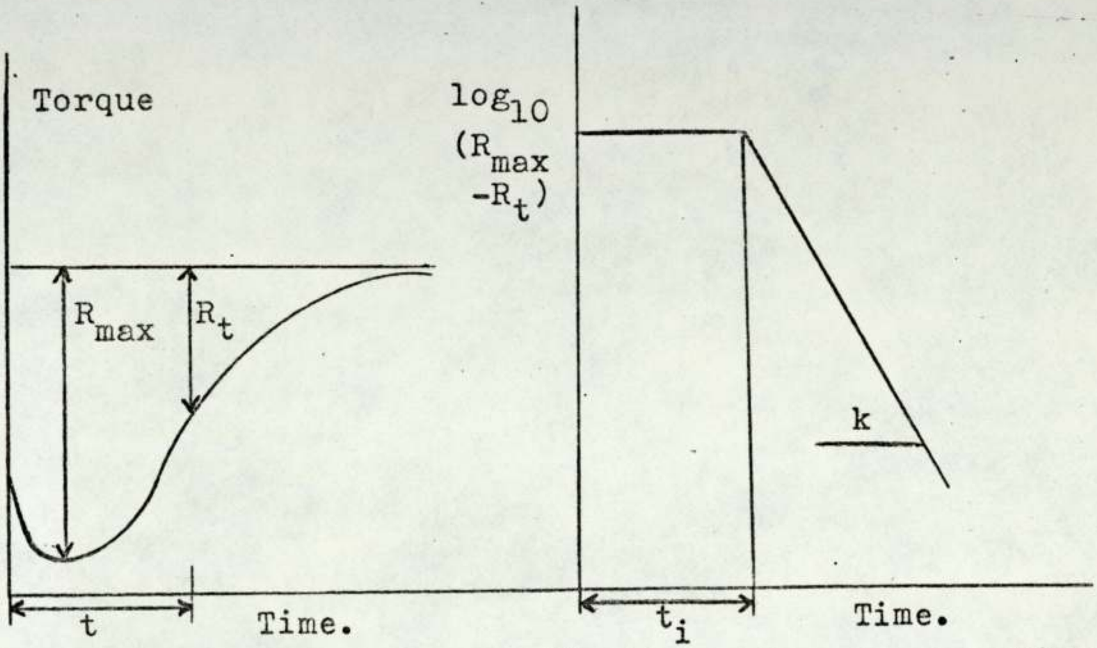


Fig. 56. Determination of kinetics of curing reaction using oscillating disc rheometer.

Thermal Activation Energy of Cross-linking reactions.

Rheometer data obtained over a range of temperatures can be used to calculate the thermal activation energy of the crosslinking process by using the Arrhenius equation discussed in the previous chapter.

Several activation energies may be calculated for a process depending on the value of t. It is thus possible to obtain thermal activation energies for gel time, cure time and viscous flow.

6.3. Equipment Used

The oscillating disc rheometer used for this work was the Monsanto Rheometer Model MPV fitted with the circular micro dies and a biconical rotor.

The rheometer platens are electrically heated and maintained at a preset temperature and the rotor can be oscillated over different arcs and at different rates. The torque required to oscillate the rotor at a constant rate is recorded as a function of time. At low rates of oscillation (0.016 - 0.25 sec^{-1}), the maximum torque is recorded while at intermediate rates of oscillation (0.16-2.5 sec^{-1}) the torque is measured when the strain is a maximum. At the highest rate of oscillation, (12.5 sec^{-1}) both torque values can be measured.

The micro dies form a small, (12grm change weight) circular, open flash mould which contains the biconical rotor. The rotor is designed to give an approximately equal shear rate throughout the dies and both the die faces and the rotor are splined to minimise any slippage of the material. The upper die is hollow (Fig.57) and is designed to distort slightly as the dies close around the test material. The test material will shrink as it crosslinks and the distorted upper die will gradually revert to its original shape thereby minimising the effects of cure shrinkage.

As the upper die is lowered onto the test material, the material flows throughout the mould cavity.

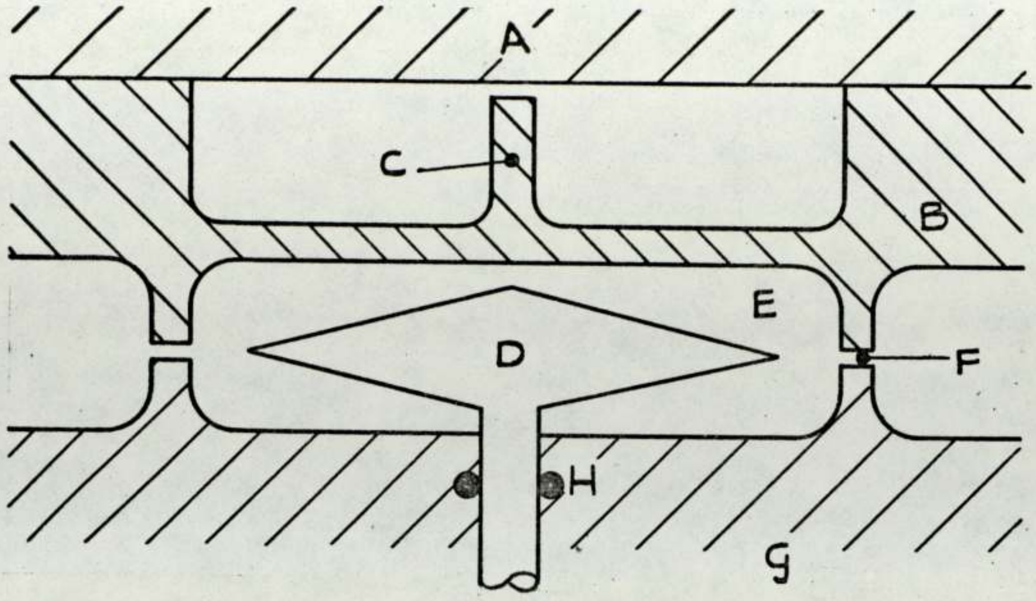


Fig. 57, Section through rheometer chamber.

A Top platen back plate.
B Hollow platen.
C Central plug to limit platen distortion.
D Biconical rotor.
E Mould cavity.
F Flash line.
G Lower platen.
H Seal.

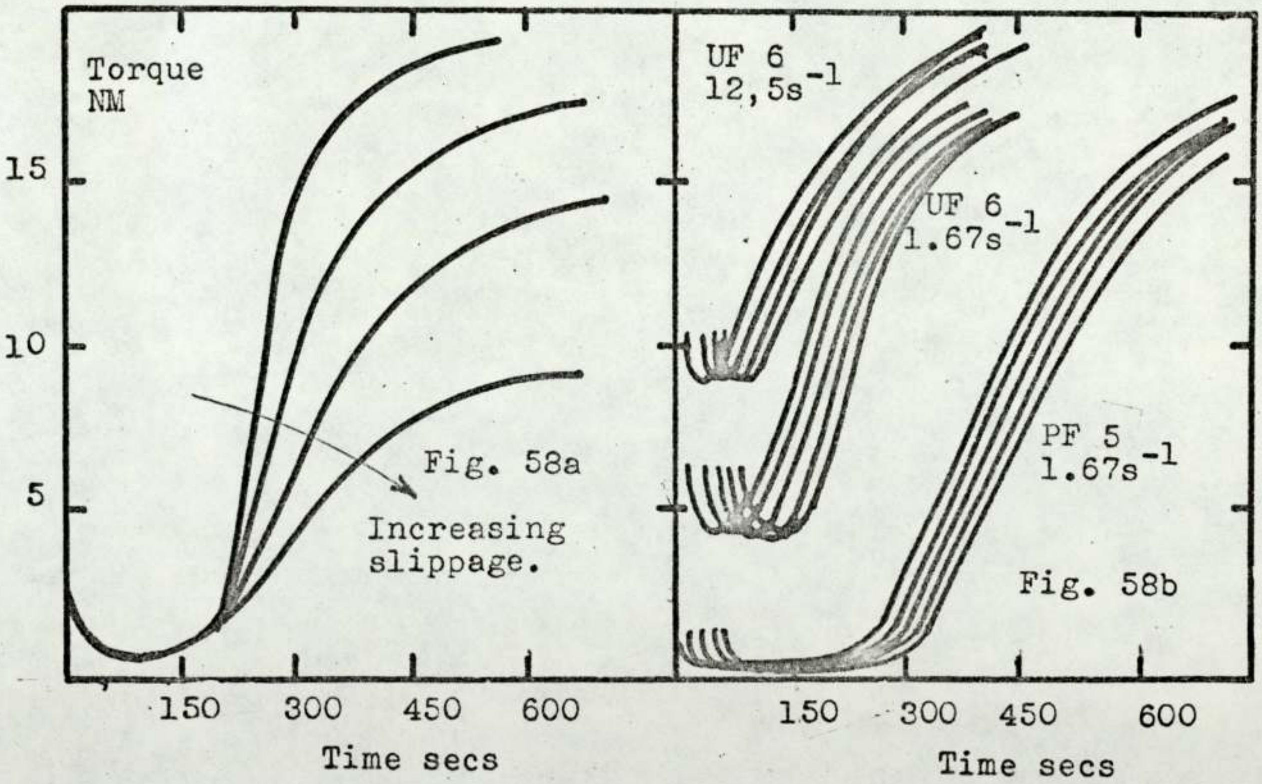


Fig. 58. Reproducibility of torque/time trace for oscillating disc rheometer.

Fig. 58a Poor results due to spray-on lubricants.

Fig. 58b Examples of good reproducibility.

When the mould dies are closed, a preset timer (20 seconds) is started which activates the rotor clamping system, starts the oscillation of the rotor and starts the recorder.

6.4. Use of the Oscillating Disc Rheometer with thermosetting plastics

Initial feasibility studies concerning the use of the Monsanto Rheometer MPV with thermosetting plastics revealed the need to modify the equipment and also to limit its operating variables. Many of these modifications resulted from the fact that the instrument was designed for use with rubbers whereas thermosetting plastics are much harder and stiffer in both the uncured and cured states. The arc of oscillation must be limited to 1°, claimed to reduce slippage (124). The upper platen must be reinforced (a carefully made steel block was used) and in this form it will no longer distort to take up cure shrinkage. It is essential to use release films between the dies and the material but even so the material must be removed from the die cavity and from around the rotor using a mallet, a lever, and a series of drifts. The rotor and die face splines require frequent cleaning. The use of spray-on lubricants leads to very bad reproducibility(Fig.58a). Practical limitations also arise because materials such as phenolic and amino plastics do not form a satisfactory melt at low temperatures ($<110^{\circ}$C) while slippage increases at the higher temperatures (150-160°C).

It has been previously stated that the Monsanto Rheometer MPV records the torque in phase with the applied strain and the maximum torque. At two rates of oscillation,(12.5 and 0.16 sec.^{-1}) it is possible to record both torque values and using the theoretical interpretation of the results discussed previously, it is possible to calculate the three moduli and the loss angle. This approach suffers from several disadvantages in that it assumes that the torque measured at the maximum strain position is the in-phrase torque i.e. that there is no slack in the measuring system. The method of computation involves calculating the difference of two squares which tends to amplify the errors which are implicit in the use of two separate electronic measuring systems.

An alternative and better approach is to measure the stress/strain relationship directly by attaching a linear potentiometer to the rheometer.

This permitted more accurate values of the torque component and the loss angle to be calculated directly although in practice, lack of adequate calibrating facilities caused the results to be in arbitary units. The technique of measuring stress/strain curves directly could only be used at low rates of oscillation. (<0.4 sec^{-1})

None of the authors of the three papers (67, 68, 69) which deal with the use of the rheometer with thermosetting plastics discuss the interpretation of the trace and a limited amount of work has therefore been carried out to correlate the curing rate of a thermosetting moulding material in a simple plaque tool with the rheometer torque trace.

These results (Fig. 59 and Table 27) show that the rheometer torque trace approximately follows the rate of stiffening of a plaque moulding and that the 90% cure time as determined by the rheometer lies between the blister free time and the cure time of the moulding, (assessed as the time for the moulding to attain 90% of its maximum flexural strength).

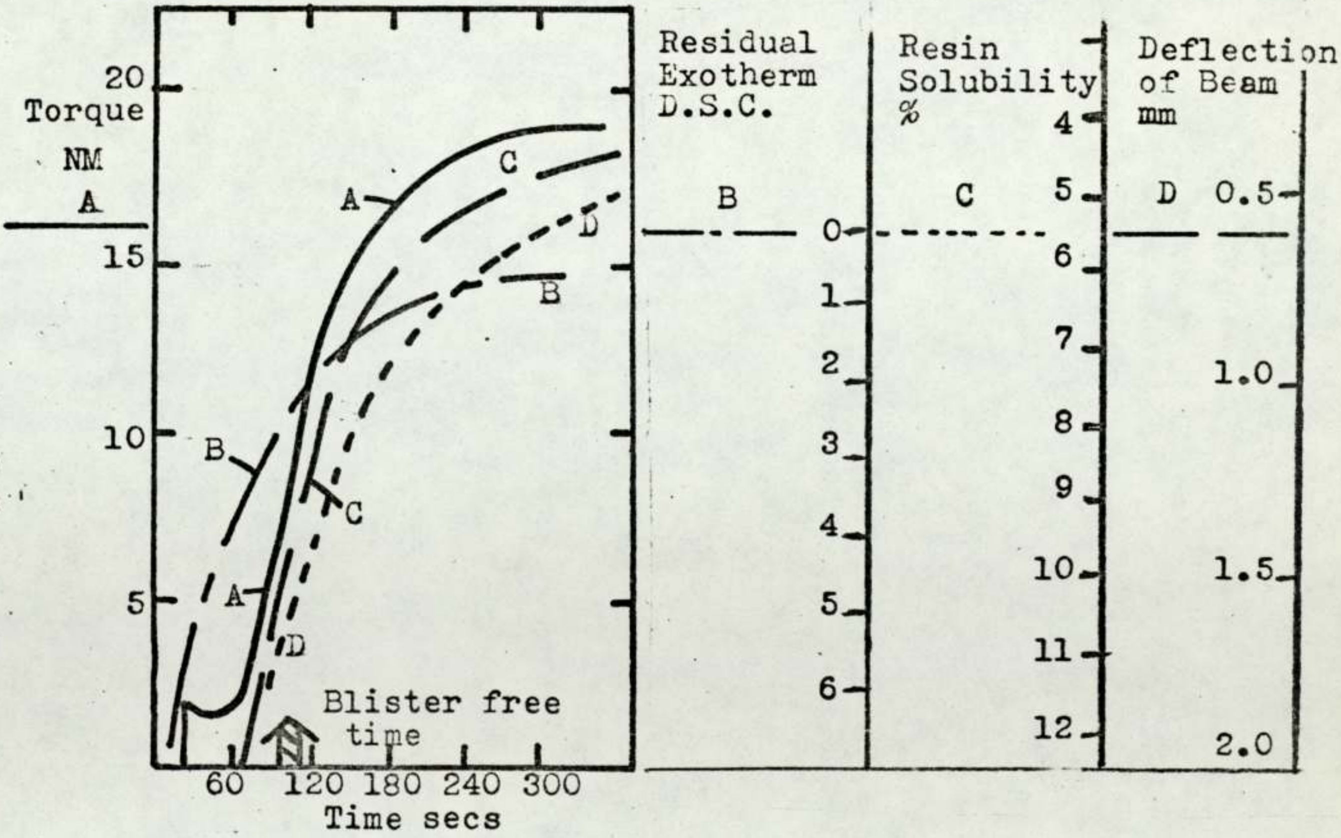


Fig. 59 Correlation of disc rheometer trace with properties of material.

TABLE 27: Cure times determined by various techniques

terial	Temperature	Assessment of Cure Time (secs)			
		Blister Free Time		Deflection of Plaque	Rheometer Time to 90% max Torque Value
		Cup Cure Mould	Plaque Mould		
ea rmaldehyde aterial UF6	150°C	35 - 40	30 - 45	60	50
enolic aterial PF5	150 - 157°C	50 - 55	60 - 90	150	90 - 150

Because of the hardness of a pellet of a thermosetting material, the time required for the die to close at the beginning of a test is quite long and a linear potentiometer was fitted to the rheometer to record the initial mould closure and the initial compression moulding process. (Fig.60)

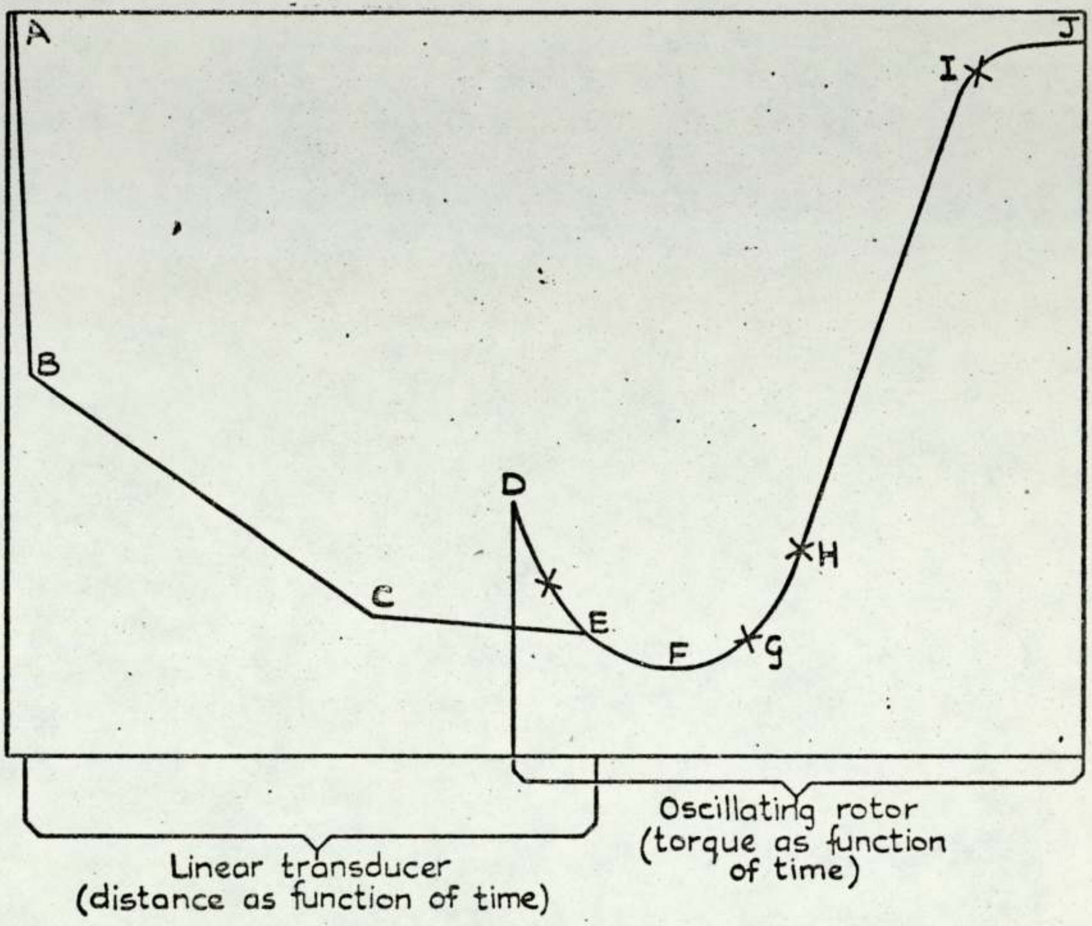
The reproducibility of the oscillating disc rheometer when used with thermosetting plastics is shown in Table 28 and Fig.58b.

TABLE 28: Reproducibility of Results

Coefficient of Variance. $\frac{\text{(Standard deviation x 100)}}{\text{mean}}$					
Material	Min Torque	Gel time	Cure Rate	Time to 90% Max. Torque	Max Torque Value
UF6 (12.5c/s)	2.1	3.0	4.2	8.3	1.8
UF6 (1.66c/s)	1.4	5.8	1.8	9.2	1.4
PF5 (1.66c/s)	6.7*	2.9	2.5	7.3	1.5

*6 readings between 1.5 and 1.9. Initial die close rate, 9.1%

Fig. 60 Operating cycle of modified Monsanto Rheometer.



Key to operating diagram

AB	Ram is lowered and pellet crushed.
BC	Pellet flows.
C	Mould effectively closed, timer starts.
CE	Mould continues to close, upper platen stationary at E.
D	Rotor starts to oscillate.
F	Minimum torque (viscosity).
G	Material gels (scorch time for rubber materials is measured at minimum torque + 2 units).
H	Induction time
I	90% of full cure value (J).
GHIJ	Cure rate, (initial cure rate can be obtained from torque /time curve, reaction Kinetics and final cure rates from log plot
J	Modulus of cured material.

6.5 Experimental Results of Assessment of Thermosetting Materials using Oscillating Disc Rheometer

The oscillating disc rheometer results show considerable difference between the various feasibility test materials (Figs. 61a & b)

Mould Closing Rate

The rate of softening or initial flow of a material as shown by the linear transducer is dependent on several material and experimental factors and a comparison of the mould close rate and the minimum torque value is shown in Fig.62. Where a straight forward comparison of similar materials is required, e.g. quality control work, the torque/time data alone will characterise the material. However, the necessity of including the initial part of the flow curve in the calculation of material properties is highlighted in Table 29.

TABLE 29 Flow times of moulding materials determined in oscillating disc rheometer

Material	Temp.	Flow Time secs.		
		Time to close die	Torque Trace	Total
Phenolic 5	120	14	22	36
	140	11	20	31
	150	8	22	30
18D	120	19	27	46
	140	14	26	40
	150	9	26	35
Modified Phenolic 12A	120	27	24	51
	140	9	23	32
	150	7	18	25
Urea 6	120	13	23	36
	140	4	23	27
	150	4	21	25

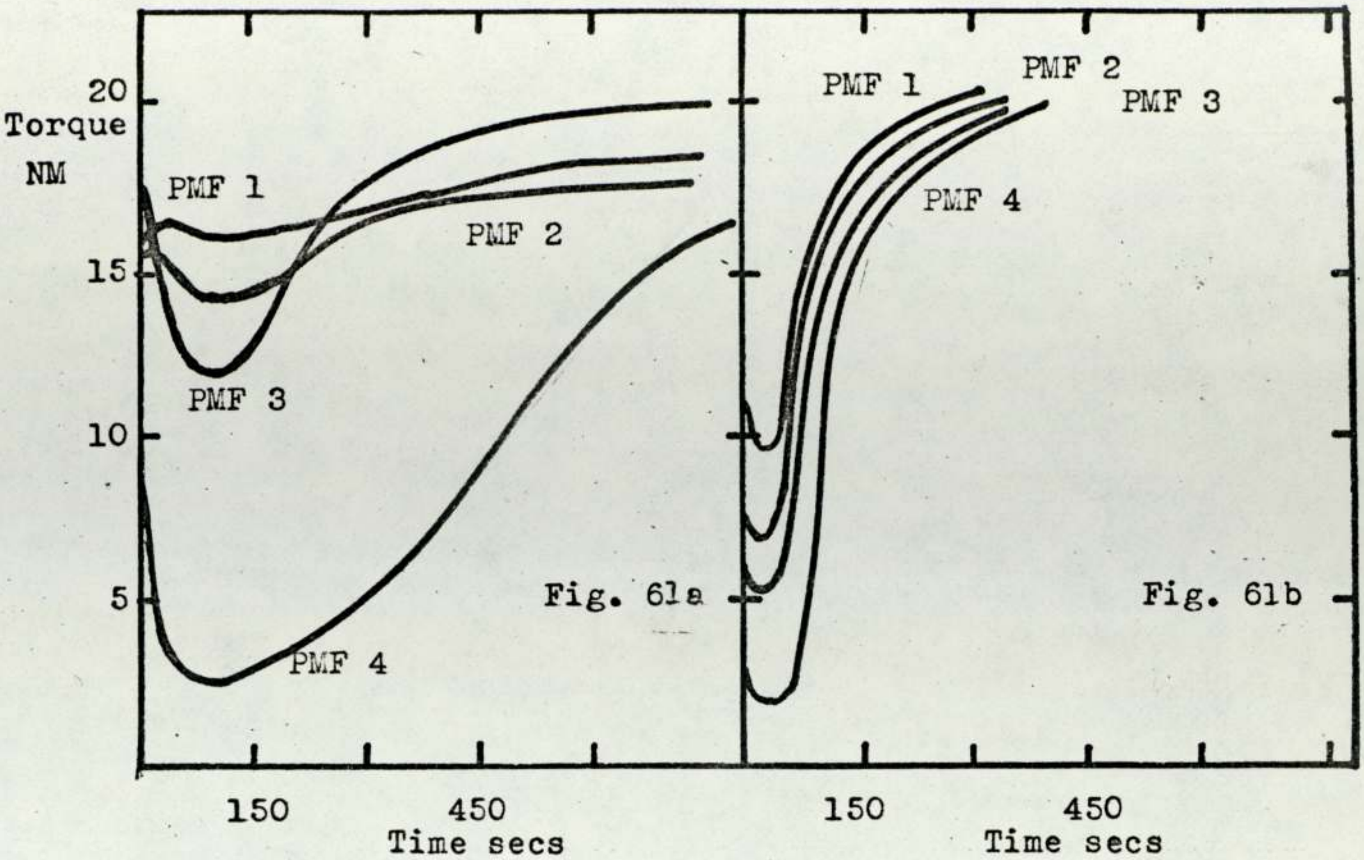


Fig. 61. Torque/time curves for oscillating disc rheometer at 120°C (Fig. 61a) and at 140°C (Fig. 61b).

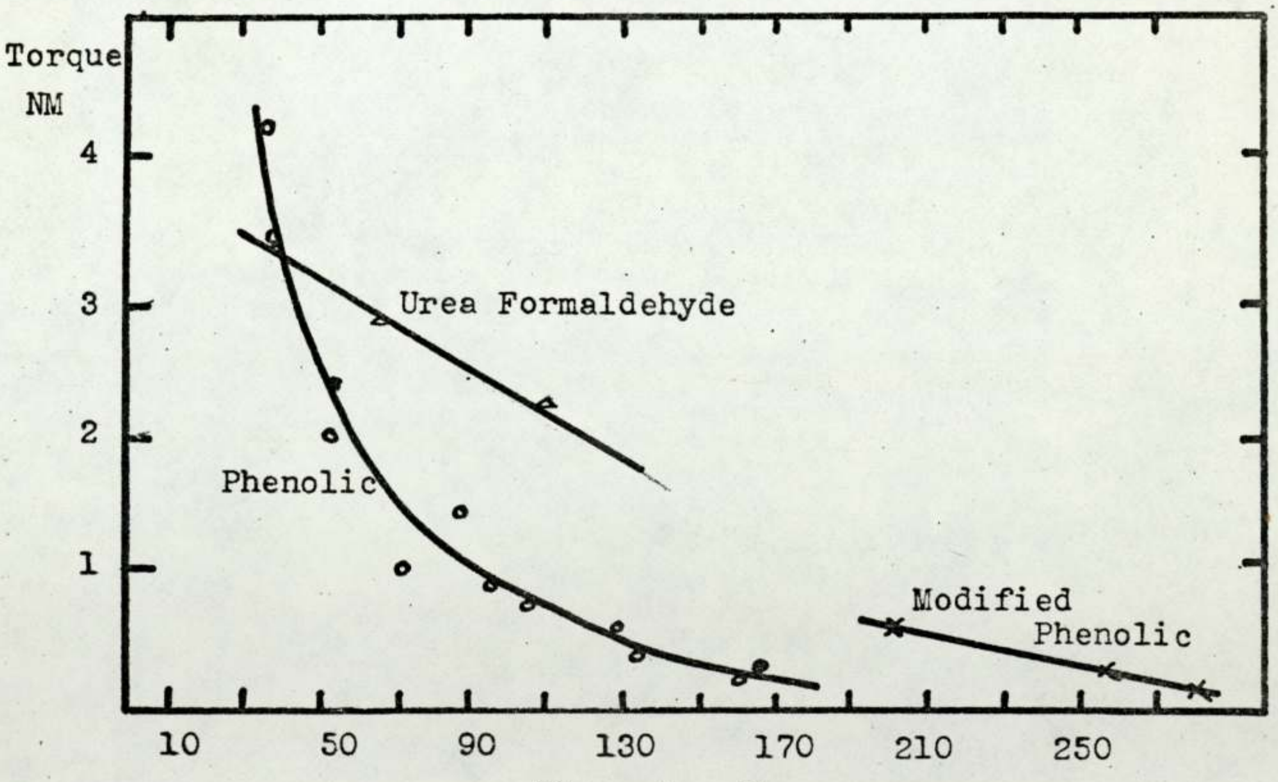


Fig. 62. Correlation between minimum torque value and rheometer close rate.

Determination of Viscosity

The viscosity measurments previously reported in this thesis are the continuous shear viscosities whereas an oscillating rheometer measures the dynamic torque or modulus of a material. It has previously been explained that the dynamic measurement can be analysed into an elastic and a viscous component. The relationship between the two types of measurement has not been satisfactorily determined but the literature (129) indicates that the continuous shear viscosity may be related to the viscous component of the dynamic measurement for viscoelastic and pseudo-plastic materials for very low shear rates and low rates of oscillation.

The stress/strain relationships have been measured at frequent time intervals throughout the crosslinking reaction of various thermosetting materials and these results have been used to calculate the complex, elastic and viscous components and the loss angle shown in Table 30a. Similar relationships are also shown in Table 30c and graphically in Fig. 63. The latter relationships were calculated from measurements of the maximum and the in-phase torque made directly from the oscillating disc rheometer results. The results for PF5 at 0.16 sec^{-1} were obtained by both technique (Table 30b) and show reasonable agreement with each other.

TABLE 30 Comparison of complex and tan values at minimum torque values for moulding materials and relationship to mouldability

Material	Code	Reinforcement	Complex torque	tan δ	Mouldability	
					Injection	Compression
TABLE 30a Measurements from stress/strain curves				$\dot{\gamma} = 0{\cdot}1s^{-1}$		
Phenolic	5	Wood Flour	0.5	0.9	Good	Good
	11D	Wood Flour	0.5	1.0	Good	Good
	11E	Wood Flour	0.45	0.95	Good	Good
	11F	Wood Flour	0.55	1.05	Good	Good
	17A	Asbestos	0.85	0.7	Good	Good
	17B	Glass	0.4	0.62	Good	Good
Urea	22I	α Cellulose	2.4	0.72	Good	Good
	8B	α Cellulose	9.1	0.08	Not Mouldable	Poor
Melamine	24E	Glass	3.3	0.73	Good	Good
TABLE 30b Measurements from Max & in phase torque				$\dot{\gamma} = 0{\cdot}1s^{-1}$		
Phenolic	5	Wood Flour	0.6	0.87	Good	Good
TABLE 30c Measurements from Max & in phase torque				$\dot{\gamma} = 10{\cdot}2s^{-1}$		
Phenolic	7A	Wood Flour	1.2	1.1	Good	Good
	B	Wood Flour	1.6	1.25	Good	Good
	C	Wood Flour	2.85	1.1	Good	Good
	D	Wood Flour	5.25	0.85	Very Poor	Fair
	E	Wood Flour	8.4	0.56	Not Mouldable	Very Poor
Urea	8A	α Cellulose	8.5	0.46	Good	Good
	8B	α Cellulose	18.1	<0.01	Not Mouldable	Very Poor
Urea	22H	α Cellulose	20.1	0.2	Compression Grade	Good

The results show that considerable differences occur between the materials tested and in particular between the values of the complex torque and the loss tangent.

Fig 63 shows the relationship between torque and shear rate.

The relationship between the various torque components and temperature is shown in Fig.64 while Fig.65 shows the relationship between the complex torque value and temperature and the Arrhenius relationship between the log of the torque value and the reciprocal of the absolute temperature.

The high torque values of UF6 at temperatures greater than 140°C are due to the fact that the material has started to react before it has reached the rheometer temperature.

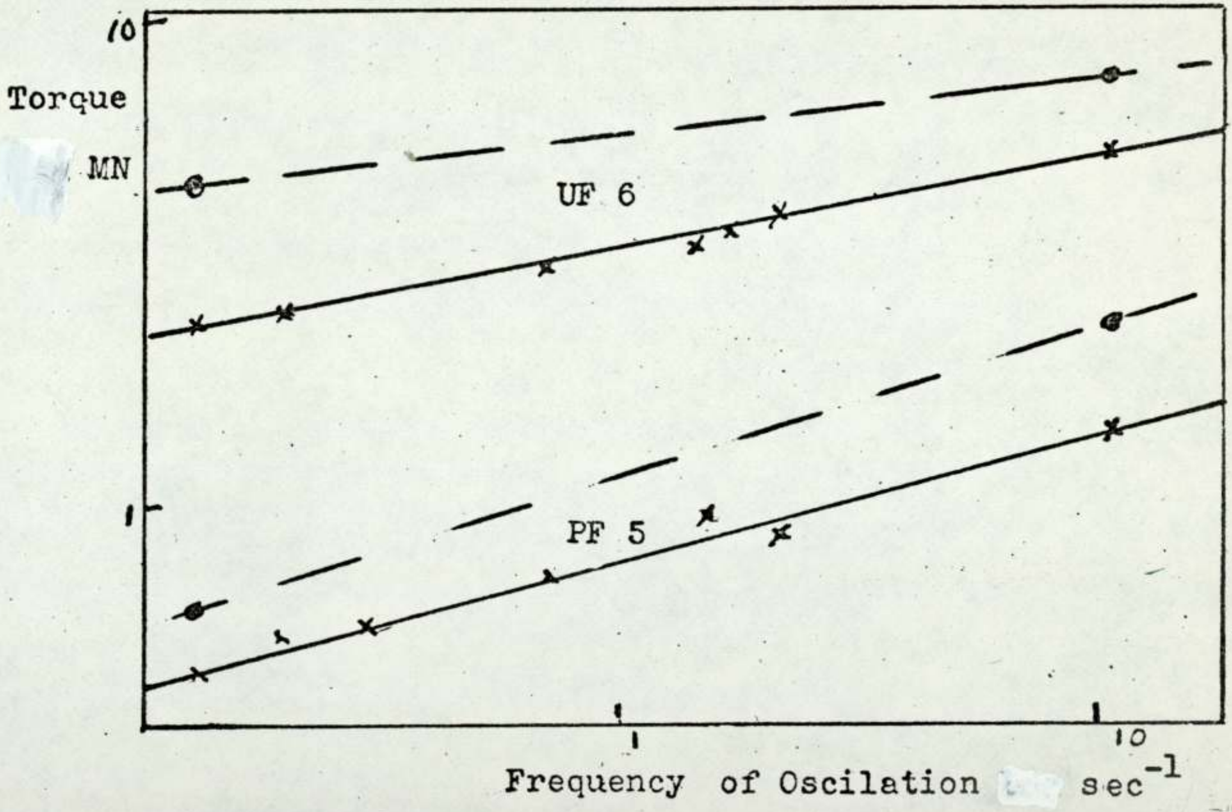


Fig. 63, Relationship between the frequency of oscillation of the rotor and the Complex (---) and Elastic (——) torque.

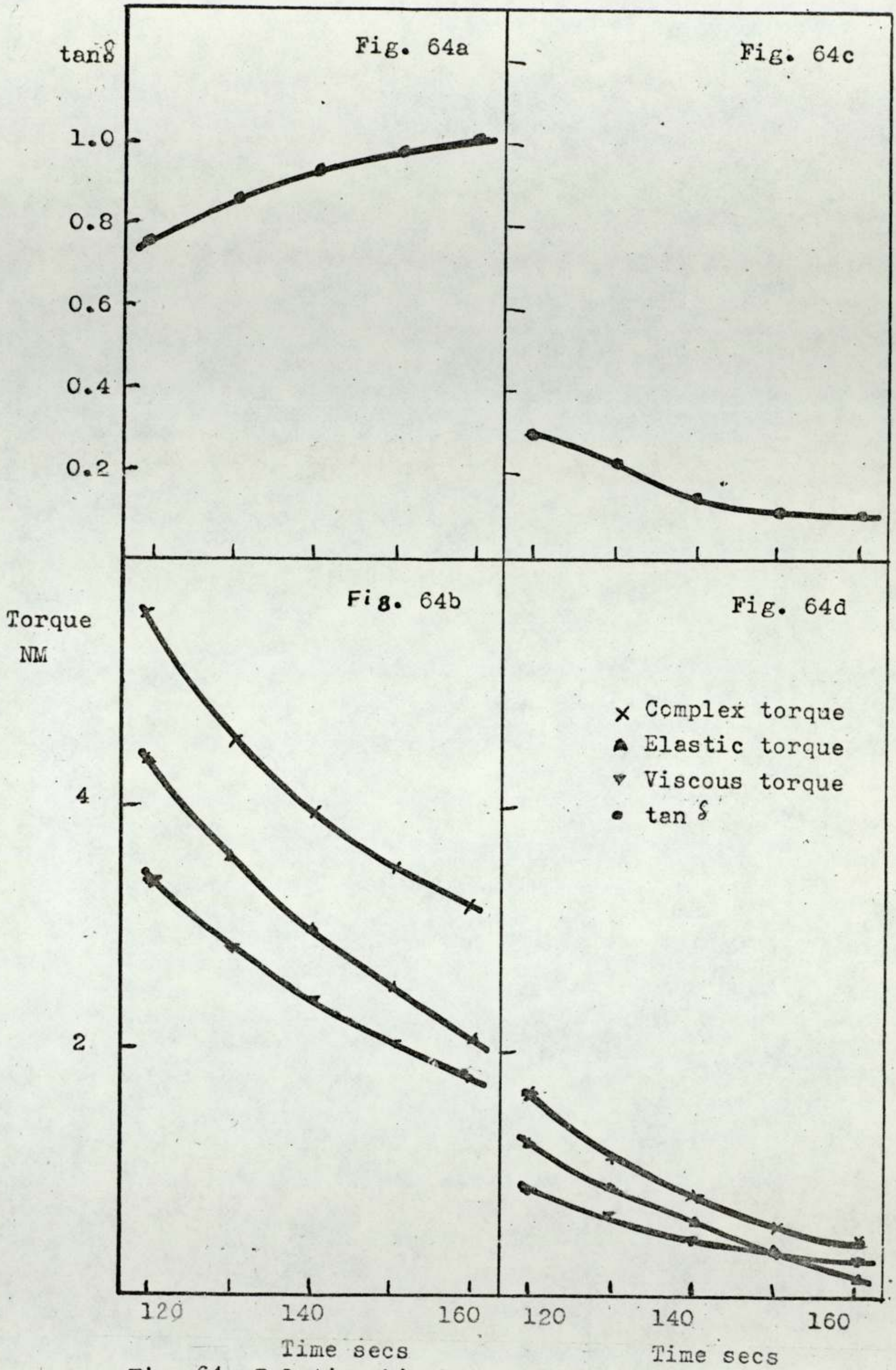


Fig. 64. Relationship between temperature and the complex, elastic, viscous component and tan δ. for Phenolic PF 5 (64c&d), and Urea UF 6 (64a&b).

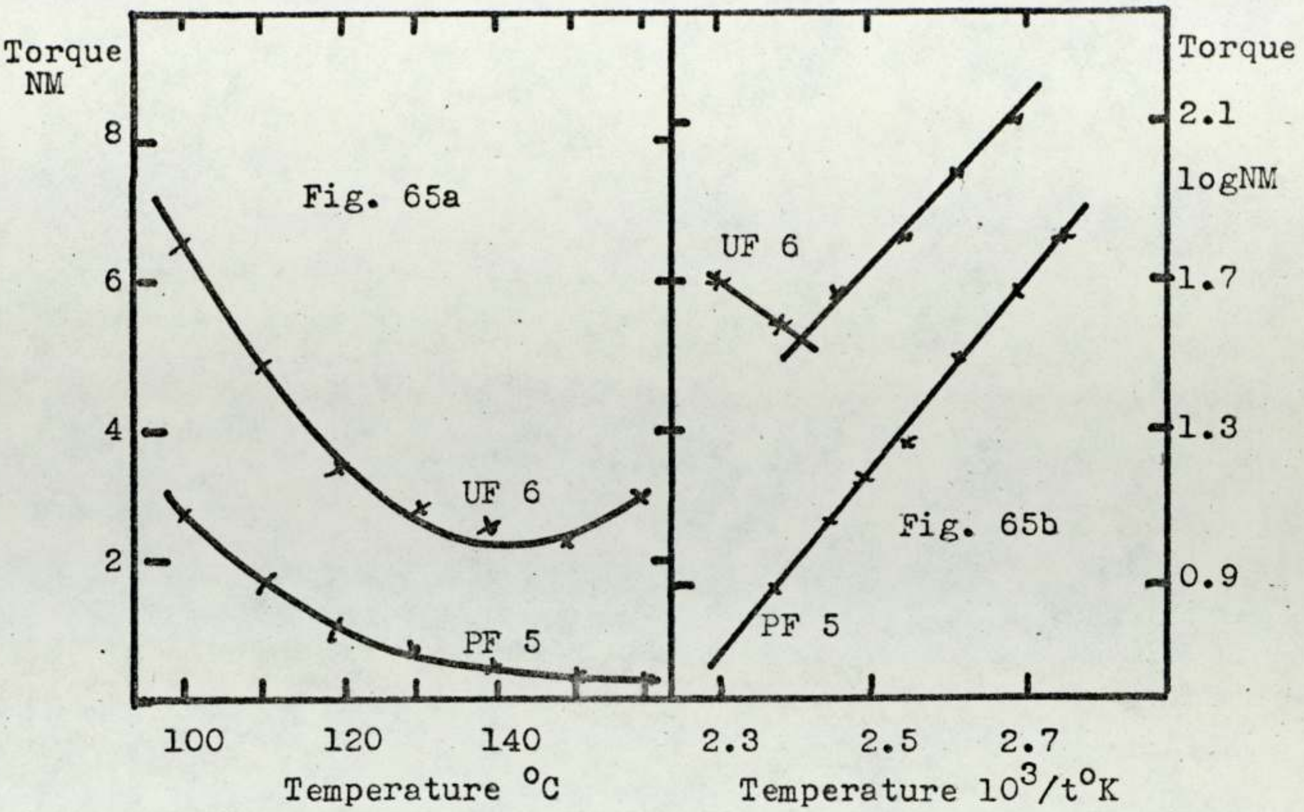
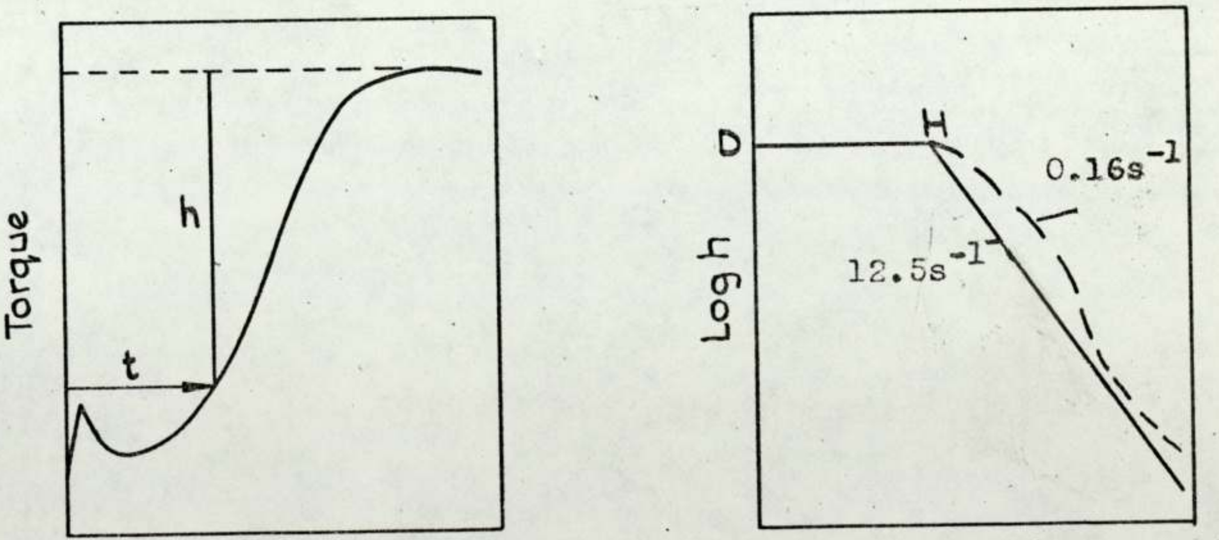


Fig. 65 Torque/temperature relationship for injection moulding materials.

Measurement of reaction kinetics, flow time and cure rates.

The theory published by Coran assumed that the materials tested have first order reaction rates. Thermosetting plastics involve several consecutive reactions and the rheometer only measures their overall effect. However, many thermosetting plastics give pseudo-first order reactions and approximate to the straight line relationship shown in Fig.66.



Rheometer trace

Plot of log h against t

Fig. 66. Interpretation of the oscillating disc rheometer torque trace.

Induction times and cure rates have been measured for various phenolic materials and typical results are given in Table 31a. This value was obtained at 120°C using the maximum rate of oscillation. (12.5 cs/sec).

TABLE 31a Cure Kinetics for Phenolic Materials Oscillating Disc Rheometer

Phenolic Material		Induction Time Secs.	Cure Rate Nm/s
Increasing Precure	8A	275	.29
	8B	202	.27
	8C	206	.29
	8D	186	.25
	8E	151	.24
Increasing Barrel Life	9A	223	.11
	9B	249	.15
	9C	258	.17
Increasing Cure Rate	10A	165	.36
	10B	199	.20
	10C	333	.09

From a practical point of view, it is relatively simple to measure the gradient of the torque/time curve directly from the rheometer trace while determination of the kinetic cure rate involves considerable computation. The relationship between these two figures is shown in Table 31b. For similar compounds, it is probably sufficient to use their torque trace for comparison purposes. A disadvantage of calculating the kinetic gradient of the log/linear plot is that it is dependent to some extent on the upper reaches of the torque curve, a section in which the reproducibility is less than that of the lower part of the curve.

Material	Rate of Osc. at 120°C sec^{-1}	Reaction Rate	
		ex Torque Trace Nm/s	Kinetic Plot Nm/s
Phenolic Material PF 5	12.5	.79	.24
	2.5	.50	.18
	1.6	.42	.16
	0.83	.37	.13
	0.25	.27	.115
Urea Material UF 6	12.5	.69	.41
	2.5	.56	.26
	1.60	.54	.27
	0.83	.53	.245
	0.25	.53	.22

TABLE 31b Correlation between kinetic cure rate and gradient of torque curve

These results show that the cure rate varied with the frequency of oscillation of the rotor. Frictional heating was suspected as the cause and was investigated using a spacer containing a thermocouple inserted between the upper and lower platens of the micro die. The results showed that increasing the frequency of oscillation gave a more rapid heating rate and that there was a good correlation between the frequency of oscillation and the observed curing rate. (Table 32).

These results are different from those reported elsewhere in this thesis for the same materials since the insertion of the thermo-couple decreases the shear rate because the dies are further apart. A similar reduction in torque was reported by Kaye and Johnson (130) for continuously rotating systems but this may be mere coincidence.

A significant point concerning these results is the variation of temperature during each test. Indeed, fast reacting materials may be partly crosslinked before they attain the required temperature. High frequencies of oscillation give high frictional heating and are preferred partly for this reason and partly because they give a closer approximation to a pseudo first order reaction rate. This consequently simplifies the interpretation and calculation of results.

The temperature lag represents a problem which can be largely alleviated by the use of dielectric preheating. A brief feasibility study showed that it is possible to raise the temperature of a pellet by 100°C in 12-14 seconds.

Typical Arrhenius plots are shown in Fig. 67 and the thermal activation energies for the gel and cure time in Table 34. The method of calculating the activation energy reported in the literature is to measure time values directly from the torque/time trace (131) but this technique effectively ignores the initial stages of the flow process.

Considerable differences occur between the activation energies calculated by the two techniques but the difference is much less for activation energies relating to the cure time. Indeed for many materials this difference may only be a few per cent because the initial flow time is small compared to the cure time but is quite large compared to the gel time. See Table 34.

TABLE 32 Effect of frequency of oscillation on Rheometer Data, Modified Chamber with thermocouple

Frequency sec^{-1}	Torque Nm.	Temp. °C	Gel time secs.	Temp. °C	Cure time secs.	Temp. °C	Cure Rate NM/sec	Max. Torque Nm.	Temp. °C
Phenolic Material PF 5									
12.5	1.24	122	135	122.5	690	123	.24	6.21	124
2.5	.79	120.5	225	122	678	122	.18	5.64	122.5
1.67	.67	120	240	121.5	780	122	.16	5.64	122
0.83	.56	120	249	121	-	-	.13	-	121.5
0.17	.45	119	261	120	-	-	.12	-	120.5
0.09	.38	118	261	119.5	-	-	-	-	119.5
Urea Formaldehyde Materials UF 6									
12.5	3.61	121	90	122	225	125	.41	5.87	126.5
2.5	2.25	117	79.2	120	-	-	.28	5.42	125
1.67	2.03	114	75	118		124	.26	5.08	125
0.83	1.8	112	75	117	270	124	.27	4.51	125
0.17	1.92	109	82.8	115	-	-	.25	-	124
0.09	1.58	106	111.0	120	-	-	.2		122.5

TABLE 33 Effect of Temperature on Results of Oscillating Disc Rheometer

Property	Temperature °C					
	100	120	130	140	150	160
Phenolic Material PF 5						
Trace Readings						
Gel time secs	300	105	78	45	27	22
Cure time secs	1540	390	250	142	54	36
Cure rate Nm/sec	.048	.40	1.1	2.5	2.9	5.5
Kinetic Values						
Induct. time secs	1800	210	143	47	37	35
Cure rate	0.019	0.16	0.21	0.33	0.42	0.59
Urea Formaldehyde Material UF6						
Trace Readings						
Gel time secs	150	52	60	34	21	-
Cure time secs	340	360	120	78	48	-
Cure rate NM/sec	.15	.44	.9	2.50	4.00	-
Kinetic Values						
Induct. time secs	273	96	60	48	30	-
Cure rate	0.02	0.12	0.26	0.39	0.64	-

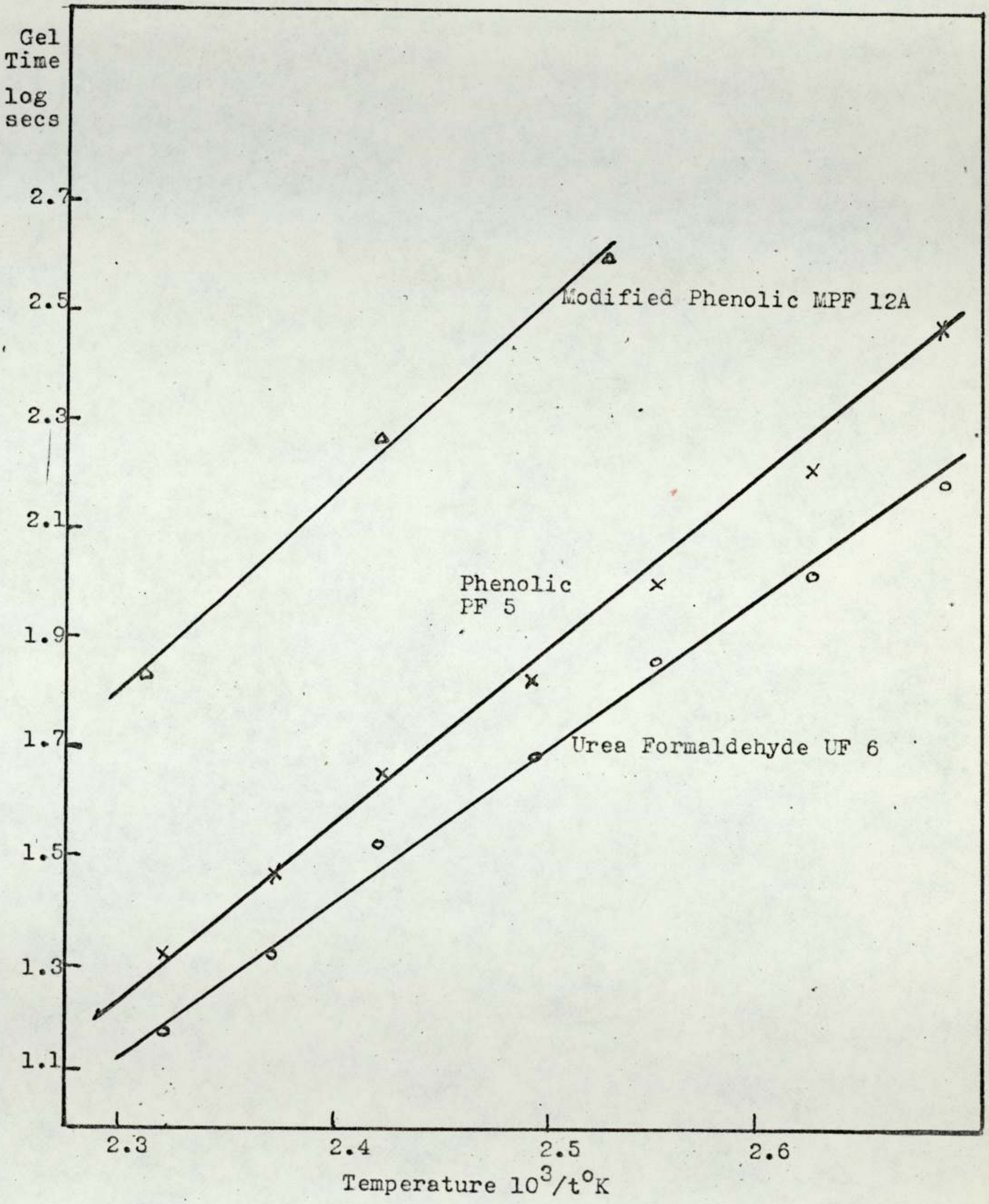


Fig. 67. Arrhenius relationship between gel time and reciprocal of temperature.

TABLE 34 Activation Energy of Gel Time Determination

Material Type		Activation Energy					
		Gel Time			Cure Time		
		Total trace A_t	Torque trace A_o	% Diff. $\frac{(A_t - A_o)}{A_t} \times 100$	Total trace A_t	Torque trace A_t	% Diff. $\frac{(A_t - A_o)}{A_t} \times 100$
Phenolic	PF5	40	59.5	33	66	68	2.9
	PF18D	55	66.5	17.5	25.6	26.2	2.3
	PF17A	75	116	32.5	69	75	8.0
Modified Phenolic	MPF12A	73	92.5	21.3	70.5	75	6.0
Melamine/Phenolic	PMF 4	60	72.5	17.2	82.	88	6.8
	PMF 1	48	85	43	45.2	53	14.2
Melamine	MF 24B	49.5	79.6	37.9	72.5	77	8.4
	MF 24C	47.2	70	32.4	54.2	56	3.2
Dicy.	DIDI 23B	53	105	49.2	43.5	47	7.4
Urea	UF6	44	64	31.5	68	71	4.2
	UF 22H	45	53	34	32	38.5	16.2

The importance of a straight line Arrhenius relationship is that it permits materials to be compared at lower temperatures then those used in moulding practice and to thereby obtain greater differentiation between materials. However, this relationship of some materials shows a distinct change of gradient at a specific temperature which indicates a change in the reaction mechanism and which will limit the temperature range over which the Arrhenius relationship may be used.

Comparison of Thermosetting Materials using the Oscillating Disc Rheometer

The results quoted so far have been largely restricted to the particular property under discussion. e.g. viscosity, cure rate etc. In this section the complete torque/time curves are compared for materials differing in a particular property.

Reference has already been made to the differences between the values of minimum torque and tan δ for different materials. The various torque components and tanδ vary with time and are shown in Fig.68 and are discussed in the next section.

Fig.69 shows the torque/time relationship for injection moulding materials differing in various ways. A more specific comparison is made in Table 35 which compares the properties of materials of known formulation.

Material PF	19D	19E	19F	19G	19I
Phenol: Formaldehyde	0.8:1	0.8:1	0.8:1	1:1	1:1
Resin	20pbw	20pbw	20pbw	20pbw	20.5pbw
Hexamine	2.31"	2.31"	2.31"	2.7"	2.31"
Wood Flour	20 "	20 "	20 "	20 "	20 "
Calcium Stearate	0.68"	0.68"	0.68"	0.68"	0.68"
Magnesium Oxide	0.99"	-	-	-	-
Calcium Oxide	-	0.66"	-	-	-
Oxalic Acid	-	-	0.66"	-	-
Temperature	120°C				
Torque Nm	1.46	1.63	2.37	2.14	5.33
Gel Time secs	203	204	132	188	120
Cure Time secs	542	552	434	485	530
Cure Rate Nm/sec	.78	.86	.94	.92	.51
Max Torque Nm	20.3	20.6	20.3	20.3	16.3
Temperature	150°C				
Torque Nm	1.29	1.41	2.2	1.2	10.4
Gel Time secs	45	37.5	32	54	54
Cure Time secs	105	94	84	120	256
Cure Rate Nm/sec	61	70	84	56	292
Max Torque Nm	20.1	20.1	19.0	19.3	17.4

TABLE 35: Comparison of moulding materials of known formulation

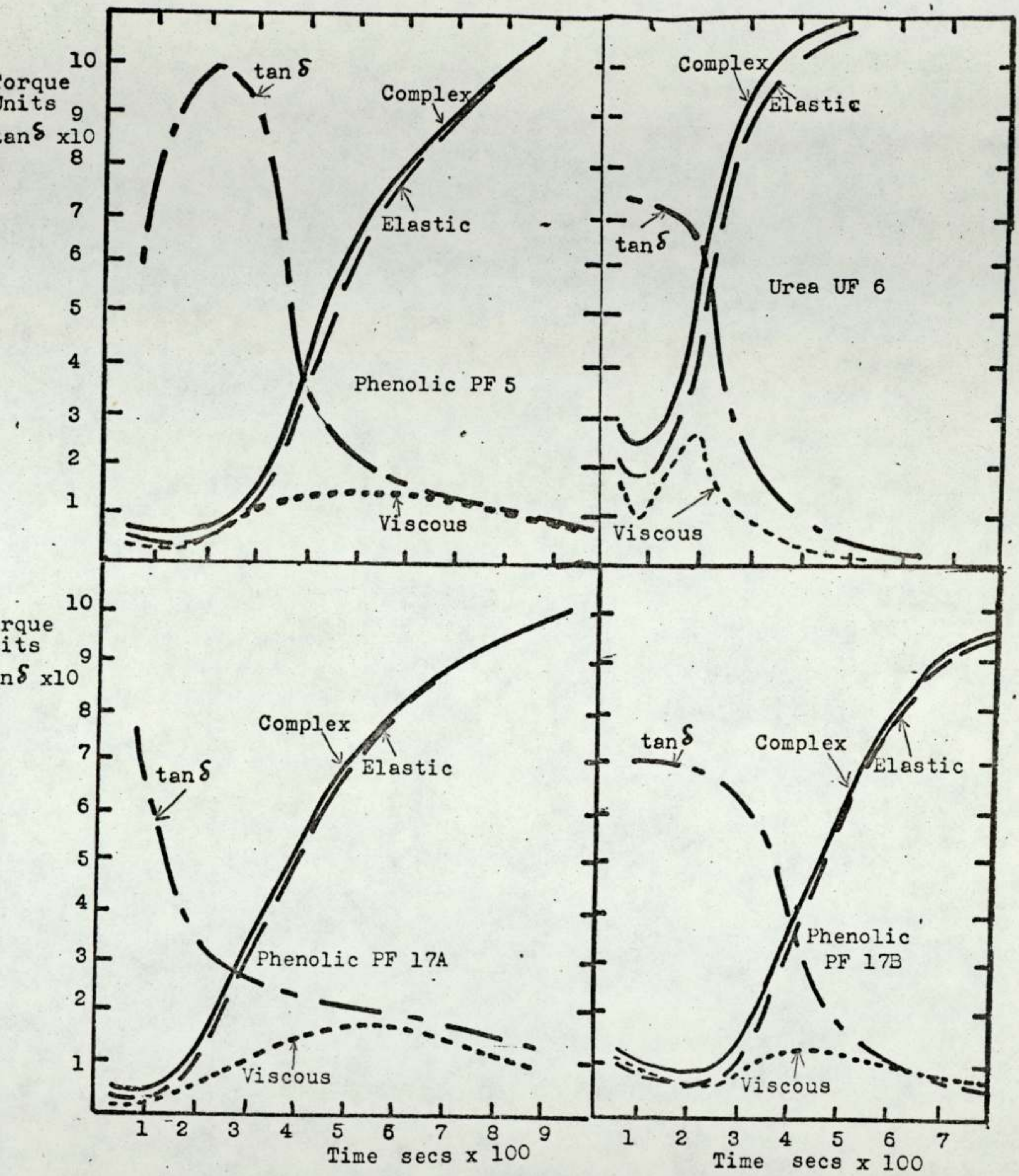


Fig. 68. Relationship between the torque and loss angle curves with residense time as determined in the oscillating disc rheometer.

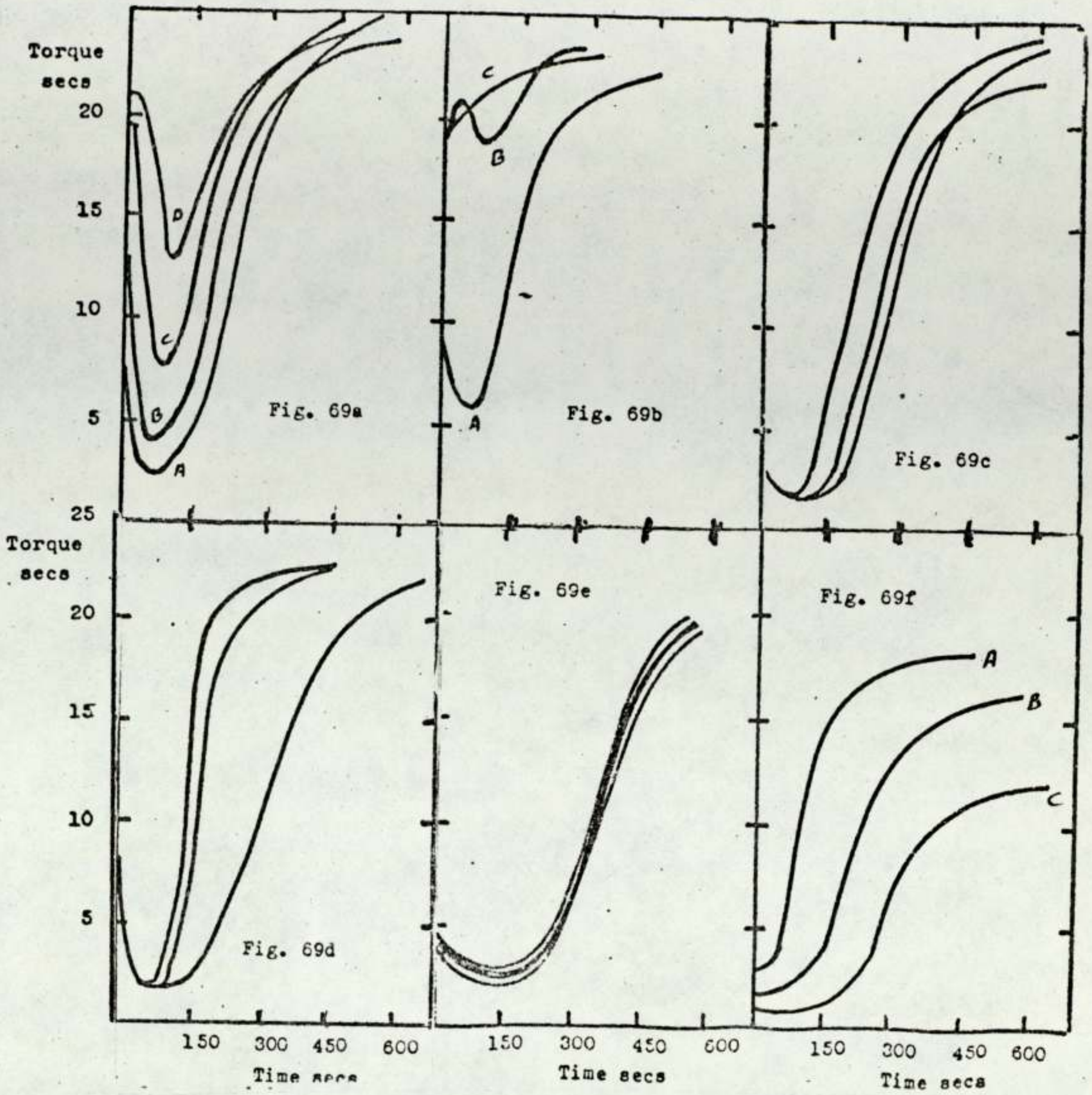


Fig. 69. Torque/residence time curves for thermosetting materials of different rheological properties.

a) Increasing resin precure PF 7A-D.
b) Increasing resin precure UF 8A-C.
c) Increasing barrel life PF 9A-C.
d) Increasing cure rate PF 10A-C.
e) Different Rossi Peakes flow pressure PF 11A-D.
f) Increasing accelerator addition PMF 12A-C.

6.6. Discussion of Results of Oscillating Disc Rheometer

The modified Monsanto Rheometer can be used to record the changes in the consistency of a thermosetting material which take place during the crosslinking process and unlike the other test procedures previously described, the oscillating disc rheometer will record these changes throughout the complete cure process.

The results of the modified rheometer will give useful information concerning the elastic and viscous components of the minimum complex torque value. The results indicate that both the complex torque and the value of tan δ are important in determining moulding properties of a material. Table 30. (It should be noted that it is possible to obtain materials of similar complex torque value but having vastly different values of the viscous and elastic components, the ratio of which is given by tanδ) Thus, UF 8A can be compression and injection moulded but UF22 A&E can only be compression moulded. UF 8B&C cannot be satisfactorily compression moulded and although the complex torque value is less than that of UF22 A&E, its value of tan δ is less. Similar trends are shown by phenolic materials PF 7A, D and E. Although both the glass and wood filled phenolics can be easily moulded under similar injection machine conditions, their values of tan δ differ considerably. The complex torque value of the glass filled material is less than that of the wood filled material although its continuous shear flow rate is much less than that of the wood filled material under similar conditions. (See Fig.32.)

It is suggested that both the complex torque value and the value of tan δ are important and that a maximum torque value and a minimum value of tan δ may exist for a satisfactory moulding material.

Uri(132) has shown that the oscillating rheometer is much more sensitive to crosslinking reactions than viscosity measurements made with a rotational viscometer. He related the reactions of linear chain extending and crosslinking liquid rubbers to their behaviour in oscillatory and rotational viscometers.

The writer has been unable to obtain confirmation of these results because of the lack of relevant information in the literature but the results in Table 30 show differences between materials which are not shown by other test methods and which probably relate the chemistry of the resin and crosslinking reactions.

Mussatti and Macosko (65) use an oscillating disc rheometer to measure the components of the dynamic torque for epoxy and phenolic resins. They extrapolate the elastic cure curve to zero modulus to obtain the gel time and use the modulus curves to calculate the chemical kinetic data. Sieglaff and Evans (66) also consider that measurement of the change of the elastic modulus with time is useful in monitoring the properties of polyester based sheet moulding materials.

An Arrhenius type relationship exists between the minimum rheometer torque the duration of fluidity and the cure time of thermosetting materials, and the temperature. Although there is a considerable spread in the thermal activation energies so obtained, the values are of a similar order to those obtained by the ball and plate rheometer (133). Values of 40-73 KJ/m are quoted in Table 24, while the literature values are 34-93 for "general purpose, wood filled, phenolic injection materials".

6.7 Correlation of Oscillating Disc Rheometer Results with Injection Moulding

Correlation of the minimum torque value with the continuous shear viscosity measured by the other techniques discussed in this thesis is complicated since the relationship between these two types of measurement (ie. oscillatory and continuous shear) has not been satisfactorily determined. Although the literature indicates that the continuous shear viscosity may relate to the viscous component of the dynamic measurement for viscoelastic and pseudo-plastic materials, at low shear rates and frequencies of oscillation, (129) it is unwise to correlate these two measurements in anything other than in a cursory manner. A general correlation exists between the minimum torque value and the flow rate of a material at the injection nozzle (Table 36) but the correlation does not show small differences between similar materials. However, the shear rates involved in these two measurements differ by several orders (oscillating rheometer $< 10\ sec^{-1}$; injection nozzle $10^2-10^3\ sec^{-1}$) and complications exist because of the basic differences in the two measurements (discussed above).

The oscillating rheometer also measures the duration of fluidity (Table 37) although the results do not show the same degree of difference between materials as found in the injection moulding machine. The duration of fluidity is partly dependent on the shear rate Fig. 41a, 48 Table 32, and the difference in shear rate between the rheometer and the injection moulding barrel may be responsible for the lack of sensitivity.

ABLE 36: Comparison of flow measurements Phenolic injection moulding materials

Material	Comparison of Flow Measurements		Material	Comparison of flow measurements of production batches	
	Torque (Rheometer) Nm	Flow Rate (injection nozzle) g/sec.		Torque (Rheometer) Nm	Flow Rate (injection nozzle) g/sec.
7A	1.12	110	PF13 A	1.52	146
7B	1.86	100	PF13 B	1.63	135
7C	3.22	71	PF13 C	1.63	138
7D	5.87	24	PF13 D	1.41	137
7E	10.1	21	PF13 E	1.46	157
			PF13 F	1.70	145

Table 37. Comparions of Flow Life of Injection Materials

Material	Gel Time secs	Cure Time secs	Barrel Life (Table 43) Flow retention %
PF 9A	105	204	14.5
PF 9B	107	225	17.2
PF 9C	120	295	25.2

The oscillating rheometer will also measure the rate of increase of crosslinking of a thermosetting material and the chemical kinetic reaction constants although the latter assumes the reaction to be first order. This is not strictly accurate but many thermosetting plastics do show a pseudo- first order reaction, particularly at the higher frequencies of oscillation. The rheometer can also be used to determine the cure time of a material (Table 38) and is more sensitive than the more usual methods of measuring cure time used in industry.

Table 38. Comparison of Cure Rate of Injection Phenolics

Phenolic	Gel Time secs	Cure Time secs	Cure Rate Nm/sec	Cup Cure secs
PF10A	90	555	.54	55
PF10B	83	207	1.02	50
PF10C	75	178	1.57	45
PF9A	105	204	.68	53 +
PF9B	107	225	.54	62 +
PF9C	120	295	.70	68 +

+ Injection mould cure time

However, the importance of the oscillating disc rheometer is that it is capable of monitoring the viscosity of a thermosetting material throughout its complete curing cycle and as such is able to identify differences between materials which are not shown by the more usual type of flow/cure test. Table 39.

TABLE 39a Comparison of injection moulding modified phenolics

Standard Test Methods	Test Results		
Material MPF	12B	20A	20B
Cup Flow secs.	3.2	3.6	2.8
Cup Cure secs.	75-80	65-70	65-70
Disc Flow mm x 10^2	110	83	100
Monsanto Rheometer			
Min Torque Nm	1.92	6.0	4.23
Gel time secs.	120	94	165
Cure time secs.	1460	352	750
Cure Rate	0.1	0.59	0.26
Max. Torque Nm.	16.9	21.5	19.5

TABLE 39b: Comparison of flow/cure properties of compression grade phenolics

Property	Method of Measurement		Material PF18				
			A	B	C	D	E
Flow	Cup Flow	secs	9.9	9.1	10.0	9.8	10.0
	Disc Flow	mm	1·21	1·25	1·31	1·30	1·25
Cure	Cup Cure	secs	50-55	50-55	50-55	50-55	50-55
Modified Monsanto Rheometer							
Flow Rate	Linear Transducer	mm/sec	0.42	0.48	0.39	0.37	0.42
Flow Time	Linear Transducer	sec	5.3	4.3	4.6	4.5	4.06
	Monsanto Rheometer	sec	96	84	114	102	90
	Total	secs	132	122	155	142	126
Min. Viscosity	Monsanto Rheometer	Nm	47	51	45	42	43
Cure Rate	Monsanto Rheometer	Nm/sec	.38	.39	.31	.35	.54
Cure Time*	Linear) Transducer) Monsanto) Rheometer)	secs	510	590	600	540	560

*Time to 90% max torque value

The published work concerning the use of the oscillating disc rheometer with thermosetting injection moulding materials is largely of an empirical nature. Brodbeck and Hartzel (67) concluded that the torque/time trace is more sensitive to material variations than the cup flow test and that it could be correlated with the compression moulding process. Talwar and Ashlock (68) statistically correlated the oscillating rheometer results with the injection moulding process while Beck and Golovy (69) merely used the instrument to measure the effect of temperature on the duration of fluidity and cure rate of their materials. The results quoted by these authors are of a similar order to the results reported in this thesis.

The thermal activation energies calculated from typical industrial methods of determining cure are shown in Table 40, together with the activation energies determined from the rheometer data.

TABLE 40

Activation Energies for Phenolic Materials

Mould	Property used to determine cure point	Act.Energy KJ/mol
Monsanto[1]	Gel time (total trace)	40
Rheometer	Gel time (torque tace only)	59.5
	Cure time[3] (total trace)	66
	(torque trace only)	68
3mm thick plaque[2]	Blister free time	37.2
3mm thick plaque[2]	time to 90% of max rigidity	72

1 Temperature range used 120 - 150 °C

2 Temperature range used 130 - 190°C

3 Time to reach 90% of max. torque value

These results show good agreement between the activation energy calculated for the gel time and the blister free time and also between the cure time (time to 90% of the maximum torque value) and the time for the moulding to attain 90% of its maximum stiffness at elevated temperatures. (Table 40) It is interesting to compare this data with that given in Fig. 59 which shows that the blister free time for a moulding is slightly greater than the rheometer gel time and that the cure time as assessed by the deflection test and acetone extraction is approximately the same as the rheometer cure time.

Chapter 7

Injection Moulding Experiments

7.1 Introduction

A series of injection moulding experiments were carried out to determine the flow characteristics of thermosetting plastics during the actual moulding process. The work may be subdivided into several sections as follows:

1) Viscosity and flow measurements during moulding experiments.
2) Measurement of Duration of Fluidity.
3) Reproducibility of Injection Moulding Process.
4) Comparison of Injection Moulding Machines Used.

7.2 Equipment Used for injection moulding experiments

Three injection moulding machines were used for this work (see Chapter 3) and the machines were fitted with simple but different plaque moulds. The machines and moulds used were as follows:-

1) Turner CTA - 2 - TS

This machine was fitted with a 60g shot weight barrel but for a limited amount of work the machine was fitted with a 120g shot weight barrel. The 60g barrel was used with a tab gated plaque mould.

2) BIP Bipel 60/26,90g.shot weight.

This machine was initially fitted with a tab gated plaque mould for phenolic tests but this was replaced by a submarine gated plaque mould.

3) Ankerwerke V17/65, 120g shot weight. A circular tab gated mould was fitted to this machine.

7.3 Viscosity and flow rate measurements

Three sets of pressure sensors were used in different experiments. In each series of tests, the injection moulding machine was set to produce satisfactory mouldings and the injection pressure varied to enable a pressure/flow rate curve to be obtained.

a) Instrumented Nozzle

This work was part of a larger programme of work carried out to determine the effect of injection machine settings on the flow properties of the material and on the physical properties and dimension of mouldings. The results were reported by RAPRA (120) and are summarized in the publications enclosed with this thesis.

The flow properties of thermosetting materials were monitored by using pressure and temperature sensors fitted in the injection nozzle and measuring the screw displacement rate, and by using the capillary viscometer described in Chapter 4 at constant pressure to produce simple flow rate information.

A log log plot (Fig.70) of pressure against material flow rate for various moulding runs shows that machine conditions exist such that the gradient of this line is a minimum for phenolic materials. This condition refers to medium screw back pressures and screw speeds and corresponds roughly to the conditions necessary to produce the minimum viscosity of the melt. At this stage the material shows maximum flow rate at a given pressure but is also more susceptible to variations in pressure. This minimum gradient is not shown with urea or melamine materials where an increase in the severity of machine conditions slightly increases the pressure/flow rate gradient. It should be noted that the slope and position of the pressure/flow rate graph is affected by the mould/runner system as well as the machine mould conditions.

A computerised multi-linear regression analysis was used to analyse the results of the moulding study and to correlate properties of mouldings with machine conditions.

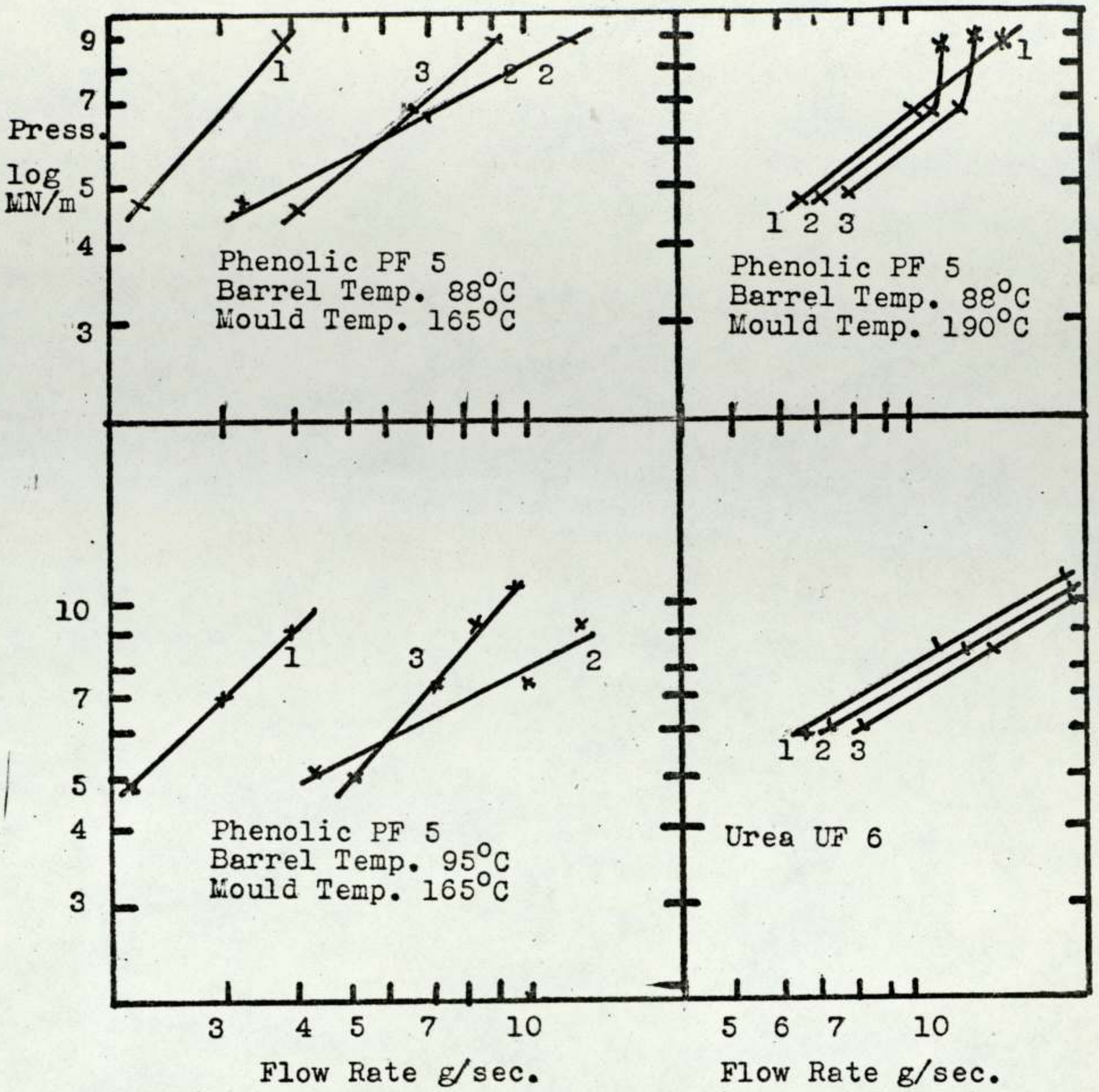


Fig. 70. Pressure/flow rate curves for injection moulding experiments, Bipel machine.

Curves 1, Low screw speed, inj. speed, back press
Curves 2, Med. screw speed, inj. speed, back press
Curves 3, High screw speed, inj. press, back press.

The results showed that few of the mouldings produced from the range of machine settings used gave mouldings having a good gloss without any flow marks or distortion. The greatest improvement in gloss and reduction in flow marks was obtained by the use of intermediate machine settings of back pressure, screw speed and injection speed. Low machine settings gave a layered effect opposite the gate (see Fig,71) while high machine settings gave mouldings having a rough surface in the form of an anchor shape opposite the gate. Tests using short mouldings confirmed that the melt entered the mould cavity as a single rod which formed the layered pattern before being compacted. High injection speeds resulted in the melt initially hitting the mould wall opposite the gate while the outer parts of the melt peeled away at the gate forming a porous swirl pattern (Fig.71c). A similar pattern has been observed as the melt emerges from the injection nozzle. The use of a submarine gate eliminates these effects by changing the mould filling pattern.

The importance of these results is that the machine settings which give the better quality mouldings are close to those which give the maximum flow or plasticity to the material. This, and the minimum slope to the pressure/flow rate curve, showed the importance of obtaining a properly compounded melt and the usefulness of the instrumentation used to monitor its properties.

A comparison of similar materials is shown in Table 41 and Fig. 72.

TABLE 41. Comparison of materials during injection moulding. Pressure/flow rate measurements with instrumented nozzle.

Material Phenolic PF 14	Instrumented Nozzle			Instrumented Nozzle fast injection			Instrumented nozzle slow injection		
	Pressure	Temp.	Flow Time	Pressure	Temp.	Flow time	Pressure	Temp.	Flow time
	MN/m^2	°C	secs	MN/m^2	°C	secs	MN/m^2	°C	secs
A	28.6	89.0	2.65	52.4 29.3	95.7	0.73	27.3 29.0	93.8	2.3
B	28.2	87.8	2.39	50.3 29.0	94.8	0.61	26.9 29.0	93.6	1.9
C	26.0	87.0	2.53	51.0 30.3	95.0	0.70	28.6 28.3	93.7	2.5
D	30.7	86.7	3.16	47.6 26.9	95.3	0.57	26.6 29.0	93.5	1.8
E	28.2	87.8	2.39	46.9 31.0	95.4	0.60	26.2 27.6	93.4	1.9
F	28.4	83.6	2.46	48.0 31.0	95.2	0.62	27.2 21.1	93.5	2.3
G	-	-	-	48.3 30.2	95.2	0.7	27.6 26.2	92.0	3.9
7A	-	-	-	-	-	-	26.9 29.0	92.2	3.4
Mould	Capillary Viscometer Bipel Injection Machine			Disc Mould Ankerwerke Injection Machine					

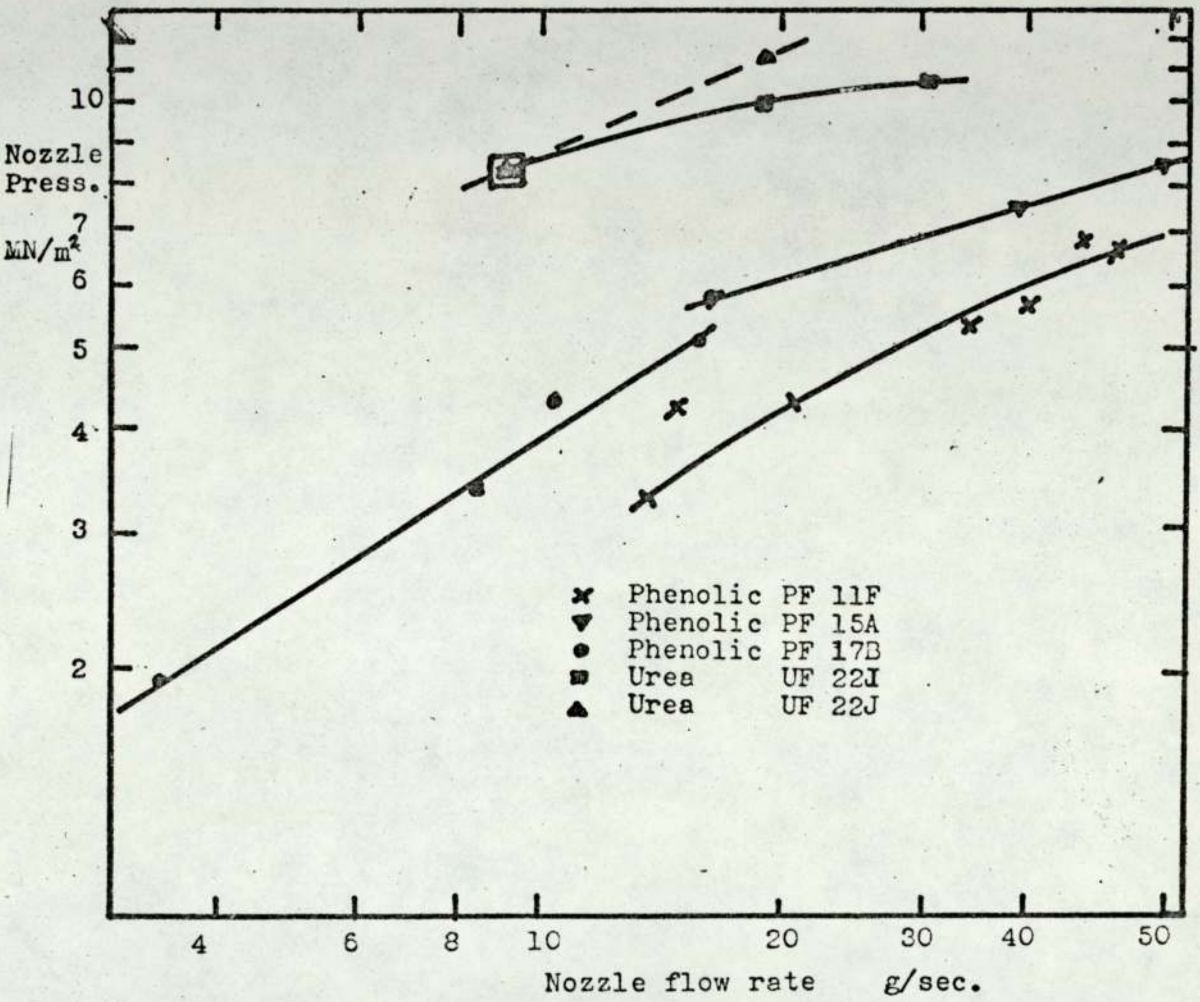


Fig. 72 Nozzle pressure/flow rate curves for injection moulding, runner capillary with plaque mould.

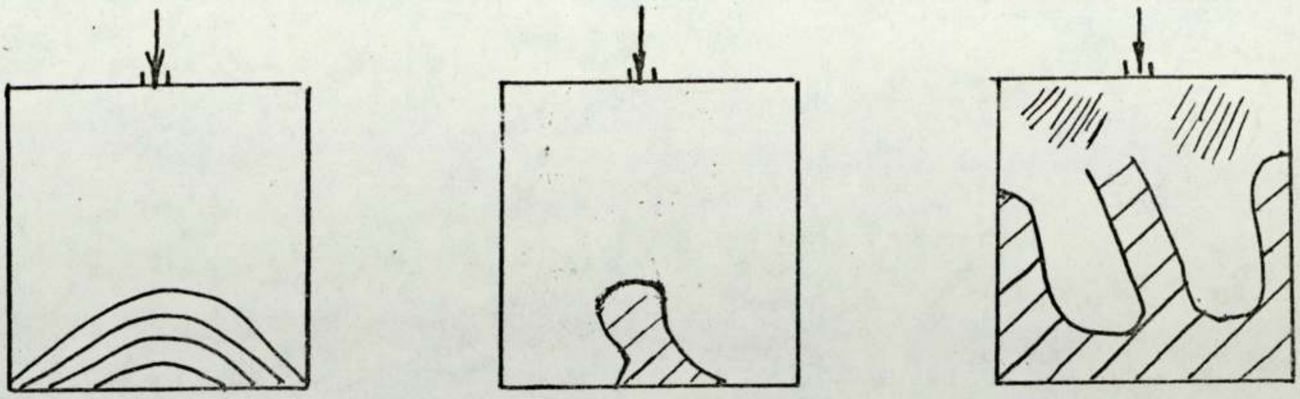


Fig. 71a Fig. 71b Fig. 71c

Fig. 71 Flow lines on mouldings prepared with a tab gate. Note effect of increasing severity of injection machine settings. Figs. 71a→71b→71c.

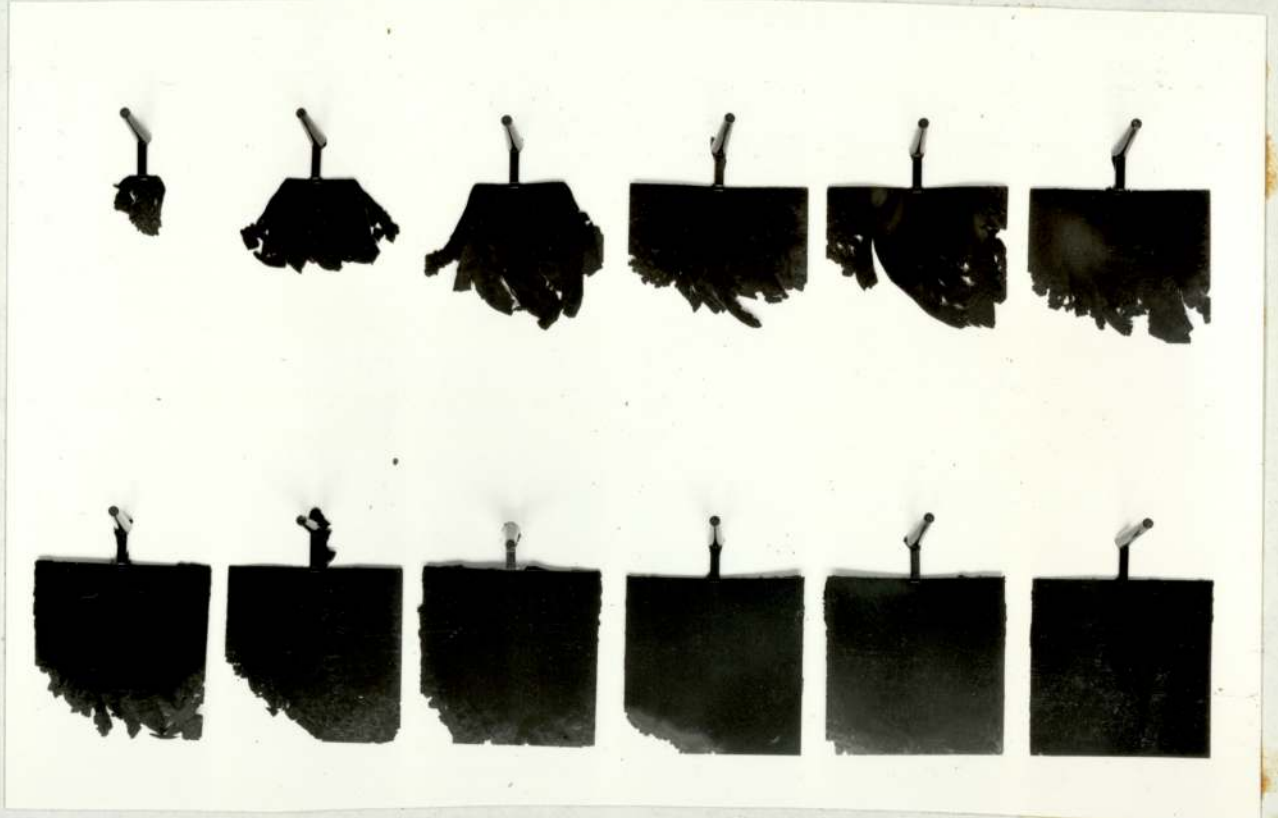


Plate 7A. Mould filling pattern of plaque mould with submarine gate. Phenolic PF 5.

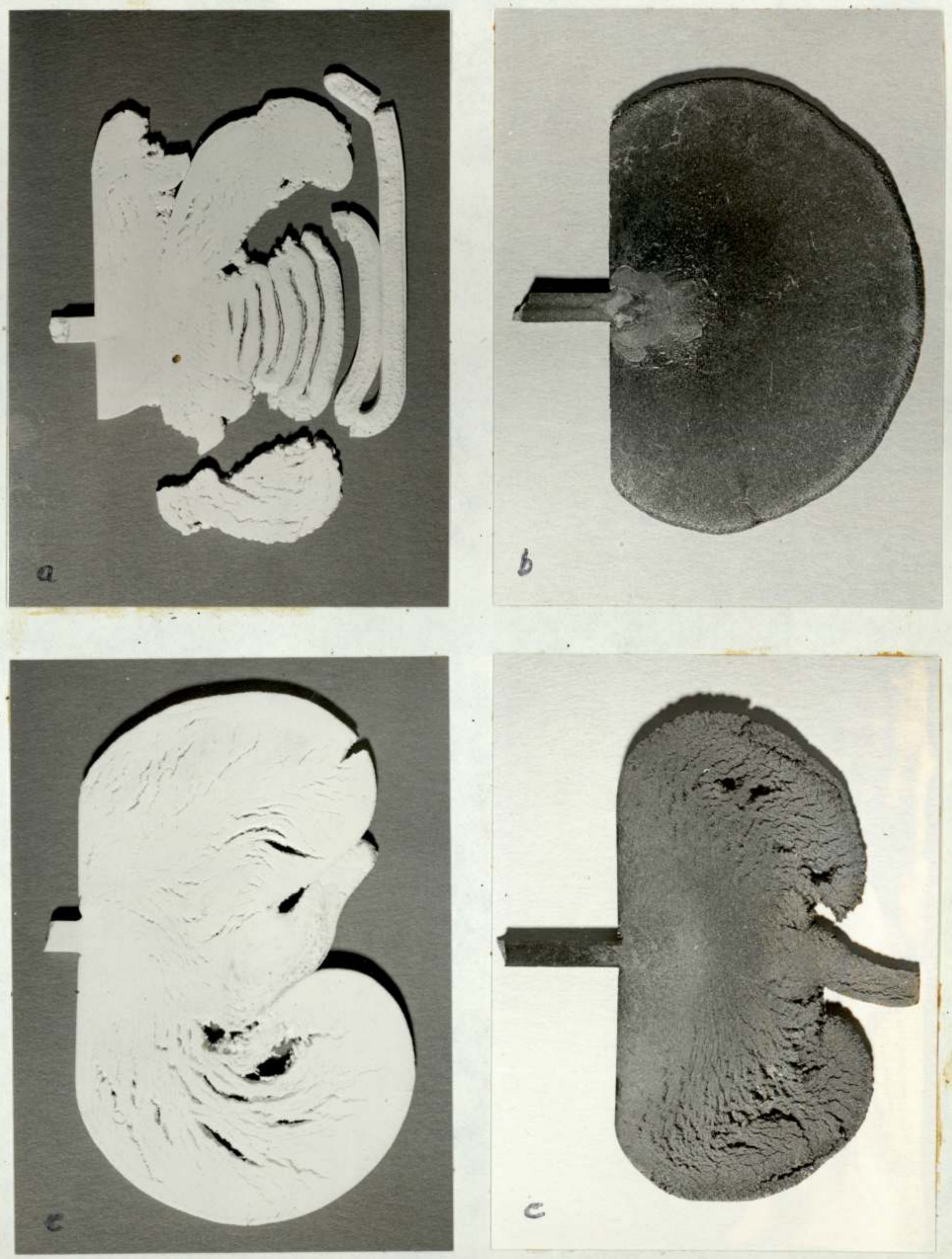


Plate 7B. Mould filling pattern showing effect of increasing screw back pressure, screw speed, injection speed, and injection pressure.

a Low machine parameter settings.
b Mediun machine parameter settings.
c High machine parameter settings.

a & c observed with Phenolics (PF 5,11F, 17B), Urea (UF 22I) and Melamine (MF 24E).
b observed with Phenolic PF 17B only.

b) Instrumented Nozzle and Mould

This work involved the comparison of phenolic materials using pressure and temperatures sensors fitted to the injection nozzle and pressure sensors immediately before and after the mould gate and in the mould opposite the gate. The practical work was carried out for the writer by Dr.D. Simms of ERDE who used a tab gated disc mould fitted to an Ankerwerke injection moulding machine. Pressure, temperature and material flow rate readings were taken at high and low injection speeds. Simms (134) used di-allyl phthalate material for his work.

A typical series of traces is shown in Fig.73 Frizelle and Paulson (135) used the pressure difference across the mould gate to calculate the shear stress rate values of their phenolic materials, and their technique has been used to calculate the viscosity values for the range of phenolic materials given in Table 42. However, the values are of doubtful accuracy because of the variable geometry of the gate which is of limited length and has a convergent entry and a divergent exit.

TABLE 42: Material viscosity as measured by pressure drop across mould gate

	Fast Injection Speed				Slow Injection Speed			
Material	Shear Stress MN/m^2	App. Shear Rate sec^{-1}	Apparent Viscosity $Ms/m^2 \times 10^{-2}$	Temp. Increase °C	Shear Stress MN/m^2	App. Shear Rate sec^{-1}	Apparent Viscosity $Ms/m^2 \times 10^{-2}$	Temp. Increase °C
PF 9A	1.7	170	10	2.1	-	-	-	-
PF14A	1.4	800	1.8	5.7	1.4	152	9.3	2.3
PF14B	1.8	950	1.9	4.8	1.4	161	9.0	1.9
PF14C	1.5	830	1.8	5.0	1.2	157	8.3	2.5
PF14D	1.1	1,020	1.1	5.0	1.5	167	9.0	1.8
PF14E	1.2	970	1.2	5.3	1.2	170	7.0	1.9
PF14F	1.7	940	1.8	5.4	1.1	167	6.3	2.3
PF14G	1.6	830	1.9	5.2	1.3	149	8.6	2.0

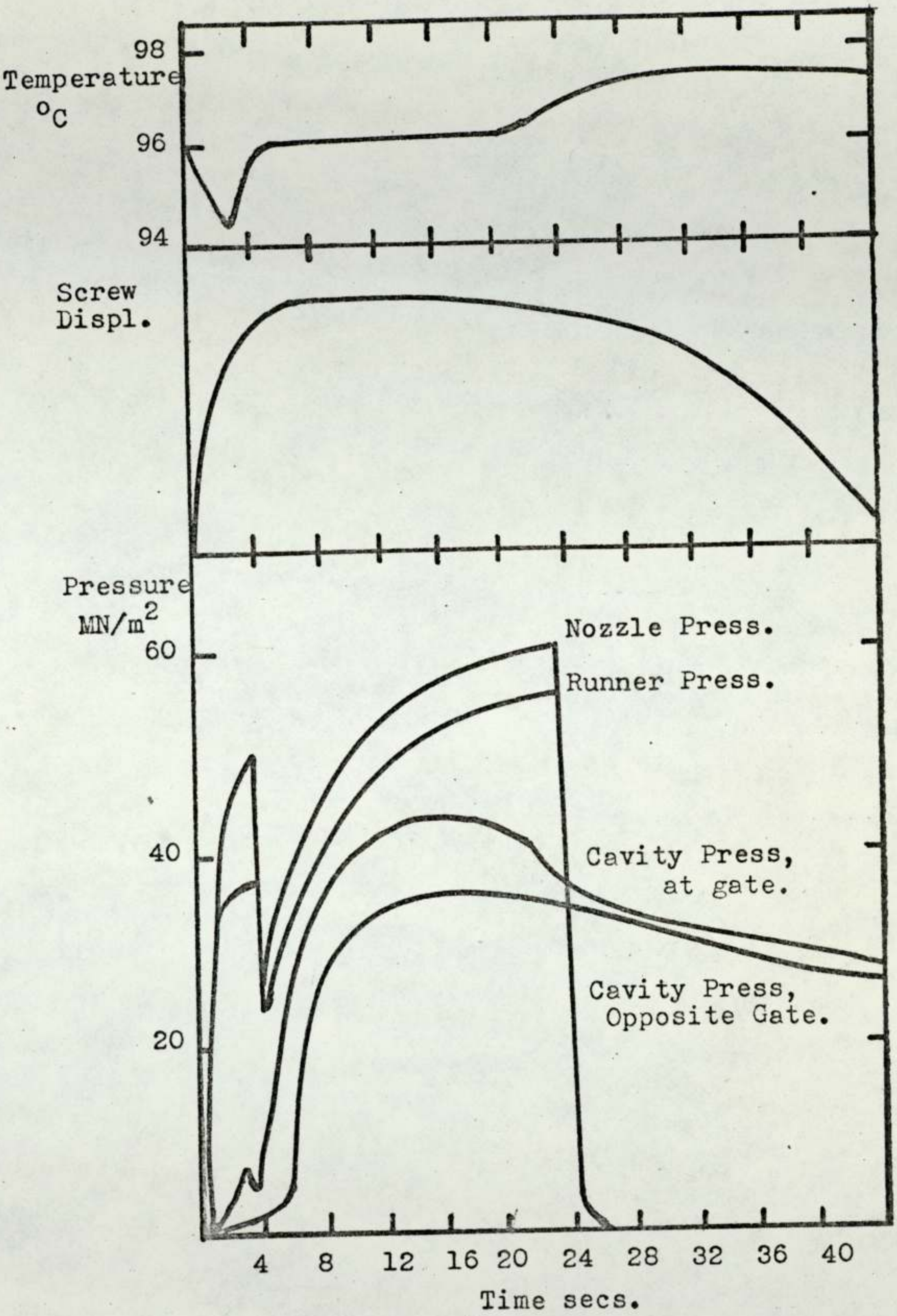


Fig. 73. Typical traces from Ankerwerke machine, Injection moulding experiments. PF 14A.

c) Instrumented Runner

A tab gated plaque mould was modified to permit two pressure sensors to be fitted in a long parallel section of the mould runner. This effectively produced a capillary viscometer since the pressure drop between the two pressure sensors may be used to calculate the shear stress and the pressure traces can be used to calculate the apparent shear rate. The instrumented nozzle was used in conjunction with this mould.

Although the pressure/time curves obtained from the runner sensors fluctuated, the fluctuations were smaller than those shown by the nozzle sensor. The overall variation in the pressure difference between the two sensors was also smaller than the variation in pressure at the injection nozzle.(Fig.74). The relationship between the shear stress and apparent shear rate for a limited number of materials is shown in Fig.75. It is difficult to determine the effective temperature of the melt as it passes through the runner since it is here that the melt which was at 88 –100°C at the nozzle is in contact with the mould surface at 165°C.

Thermocouple measurements indicate that the melt temperature is approximately 125 - 135°C as it passes through the runner.

Plate 8. Moulding from runner viscometer/plaque mould.

Positions of pressure sensors marked X.

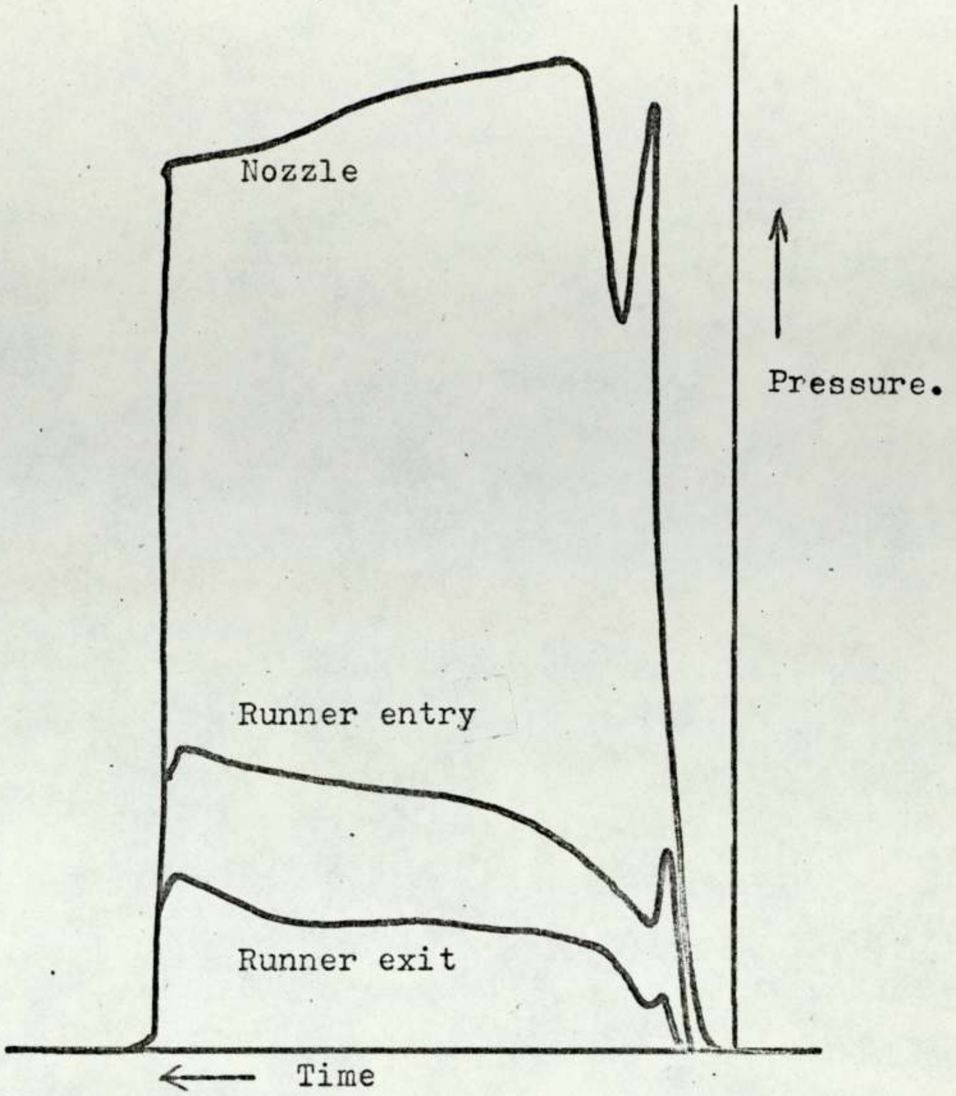


Fig. 74 Typical pressure/time traces for runner capillary.

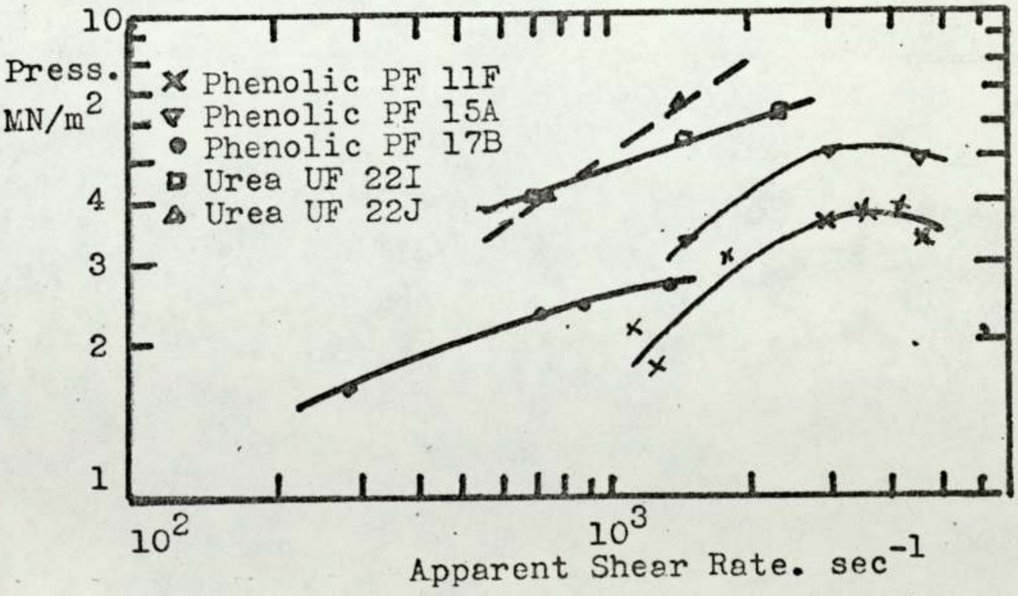


Fig. 75. Pressure/apparent shear rate relationship for runner viscometer during injection moulding experiments.

7.4 Duration of Fluidity

The duration of fluidity of a thermosetting melt in an injection moulding machine barrel may be expressed in several ways but most methods essentially relate the flow properties of a melt held in the injection barrel for a specified period to the flow properties of the material under normal production conditions. Typical methods of expressing the 'barrel life' of a material include:-

a) The number of cycles required to produce a good moulding.

b) The simple ratio of the two flow rates expressed as a percentage.

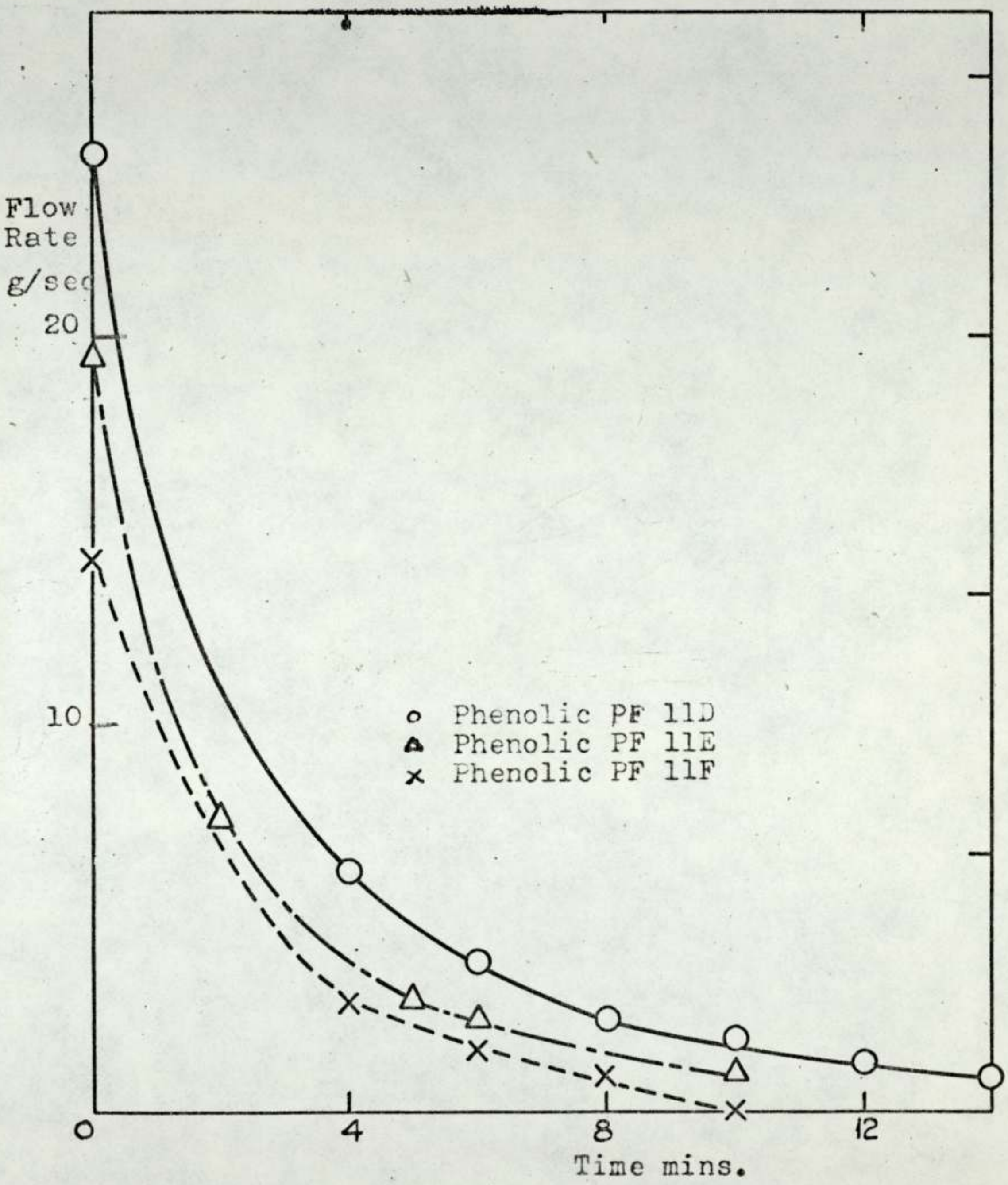
c) The time for the material flow rate to decrease to a specified value.

For this work, the second definition has been used and typical results are given in Table 43. The relationship between the material flow rate under constant conditions and the cycle delay time is shown in Fig.76.

TABLE 43 Duration of Fluidity of Injection Moulding Materials

Material	Residual Flow Rate*	Material Residual	Flow Rate %*
BIPEL 90g Machine (1)		BIPEL 90g Machine 2	
Phenolic PF11A	22.2	Phenolic PF5	12.7
11B	24.2	9A	14.5
11C	9.5	9B	17.2
11D	12.0	9C	25.2
11E	12.2	13D	15.7
11F	12.7	15D	27.7
		15G	9.7
TURNER 60g Machine		TURNER 60g Machine	
Phenolic PF11F	39.6	2½ minute pause	
15A	18.0		
17B	15.7	Urea UF6	35.0
Urea UF6	23.0	UF22I	4.0
UF22I	1.0	UF22J	10.5
UF22J	5.0	Melamine MF24E	1.0
Melamine MF24E	<0.5		

* Flow rate after 5 minute pause in moulding cycle expressed as a percentage of flow rate during normal automatic cycle.



Injection Barrel Residence Time.

Fig. 76. Relationship between material flow rate and injection barrel residence time.

7.5 Reproducibility of Injection Moulding Process

The injection machine was set out to produce satisfactory mouldings and approximately 1 in every 10 mouldings was monitored by measuring the melt pressure and temperature at the nozzle, the screw displacement rate and the moulding weight.

The results are shown graphically in Fig. 77. It can be seen that random variations occur about a mean value which can change gradually during the simulated production run. The resultant variations in the moulding are quite small but Fig. 77 shows that the injection moulding process is not perfectly reproducible.

The large variations which occur after moulding number 250 are due to variations in the cycle time deliberately introduced to determine the sensitivity of the moulding process to such changes. Subsequent tests using a series of different cure times (Fig. 78) showed that the maximum material flow rate of material results from optimum machine settings. Even a small delay in the machine operating cycle will result in a decrease in the flow rate of the material and which emphasises the non-steady state conditions which exist in a thermosetting melt.

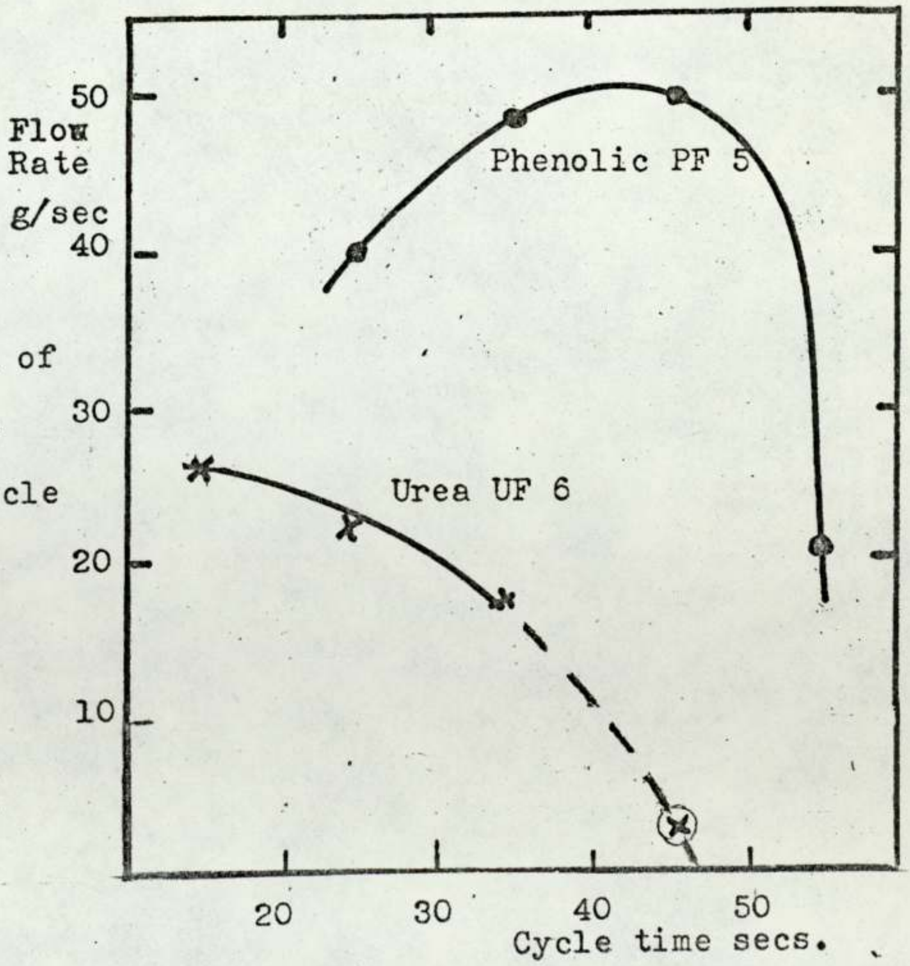


Fig. 78. Variation of material flow rate with increasing cycle time.

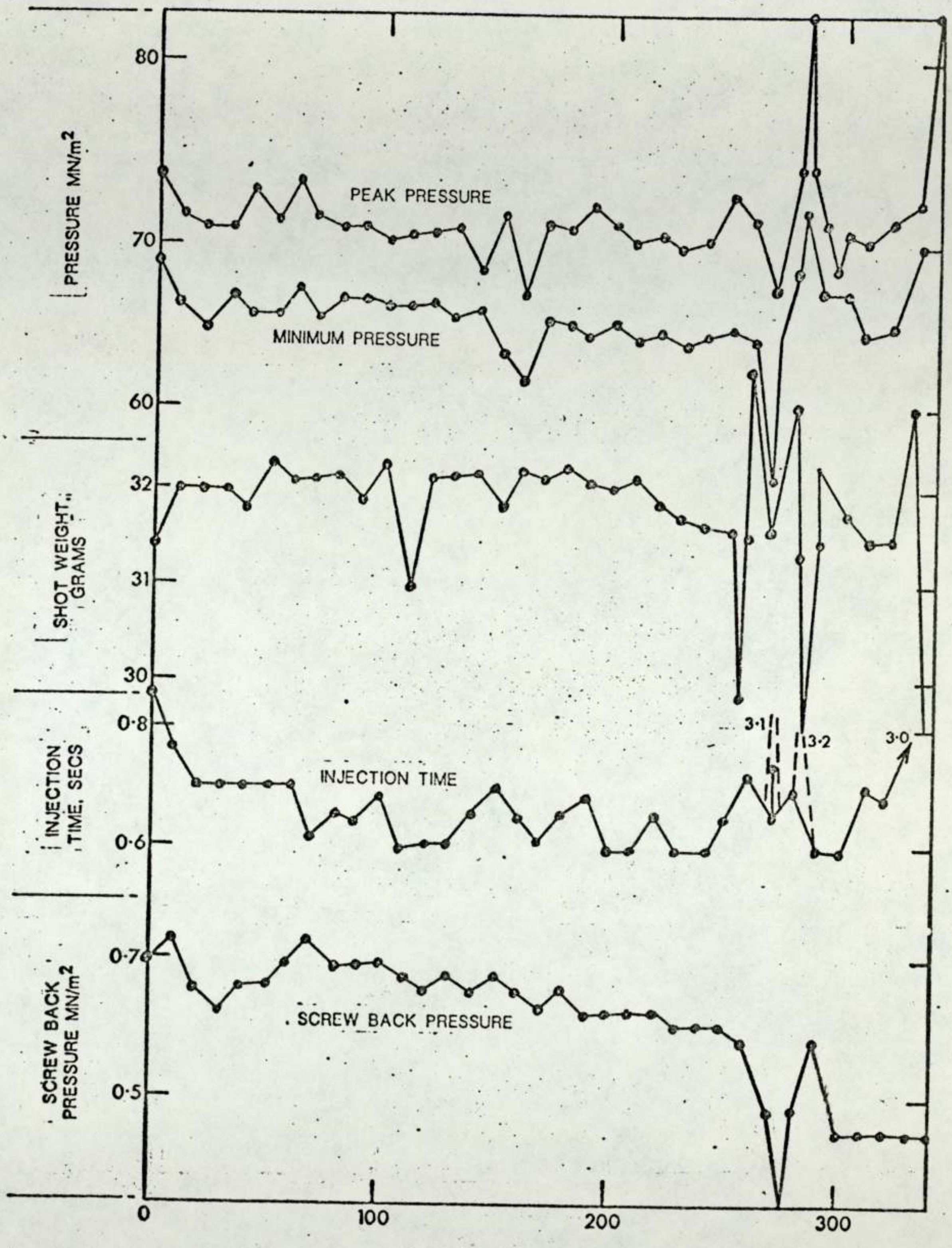


Fig. 77. Variation of melt measurements with time during a long injection moulding run, (7½ hrs)

7.6 Comparison of Injection Moulding Machines

It was necessary to use three injection moulding machines for various parts of the work described in this thesis(see Table 44).

TABLE 44 Measurements made using different injection machines

Material	Type of Measurement	Technique	Machine
Phenolic	Shear Stress/shear rate	Capillary Viscometer	Bipel
	" " " "	Nozzle Viscometer	Bipel, Turner
	" " " "	Runner Viscometer	Turner
	" " " "	Mould Gate	Ankerwerke
	Pressure/flow rate	Injection nozzle	Bipel, Turner
	" "	Injection mould	Bipel, Ankerwerke
Urea	Shear Stress/shear rate	Nozzle viscometer	Bipel
	" " " "	Runner Viscometer	Turner
	Pressure/flow rate	Injection nozzle	Bipel, Turner
	" "	Injection mould	Bipel
Melamine	Pressure/flow rate	Injection nozzle	Turner
		Injection mould	Turner

These machines differed with respect to their size as well as to their mechanical design. In order to establish whether the machines differed in their effect on the material, air shots were made with a phenolic material using each machine set to similar conditions of screw speed, back pressure,temperature etc. and the flow properties of the cooled air shots were compared using the variable torque rheometer and the oscillating disc rheometer. The results showed that for standard machine settings, the Turner machine imparted less energy to the melt than the Bipel which in turn imparted less energy to the melt than the Ankerwerke. These results (Fig.79) show the changes which can take place during screw compounding operations. The changes largely occur as the plasticized melt is gradually cooled since rapidly cooling the melt in liquid nitrogen gives materials showing little change from the uncompounded virgin material. (Table 45).

TABLE 45 Effect of different compounding conditions on the flow-cure properties of a material

Machine Settings*	Phenolic PF5		Urea UF6	
	Min Torque	GelTime	MinTorque	GelTime
Virgin Material	Nm 25.5	secs 540	Nm 30.4	secs 530
Liquid nitrogen cooled melt				
1111	27.0	510	33.3	420
2222	27.9	515	30.8	420
3333	28.4	480	34.3	420
Air cooled melt				
1111	29.4	372	36.3	348
2222	29.4	312	38.2	240
3333	30.4	240	40.2	180

*

1111 Low screw back pressure, screw speed, injection speed and pressure.

2222 Intermediate screw back pressure, screw speed, injection speed and pressure.

3333 High screw back pressure, screw speed, injection speed and pressure.

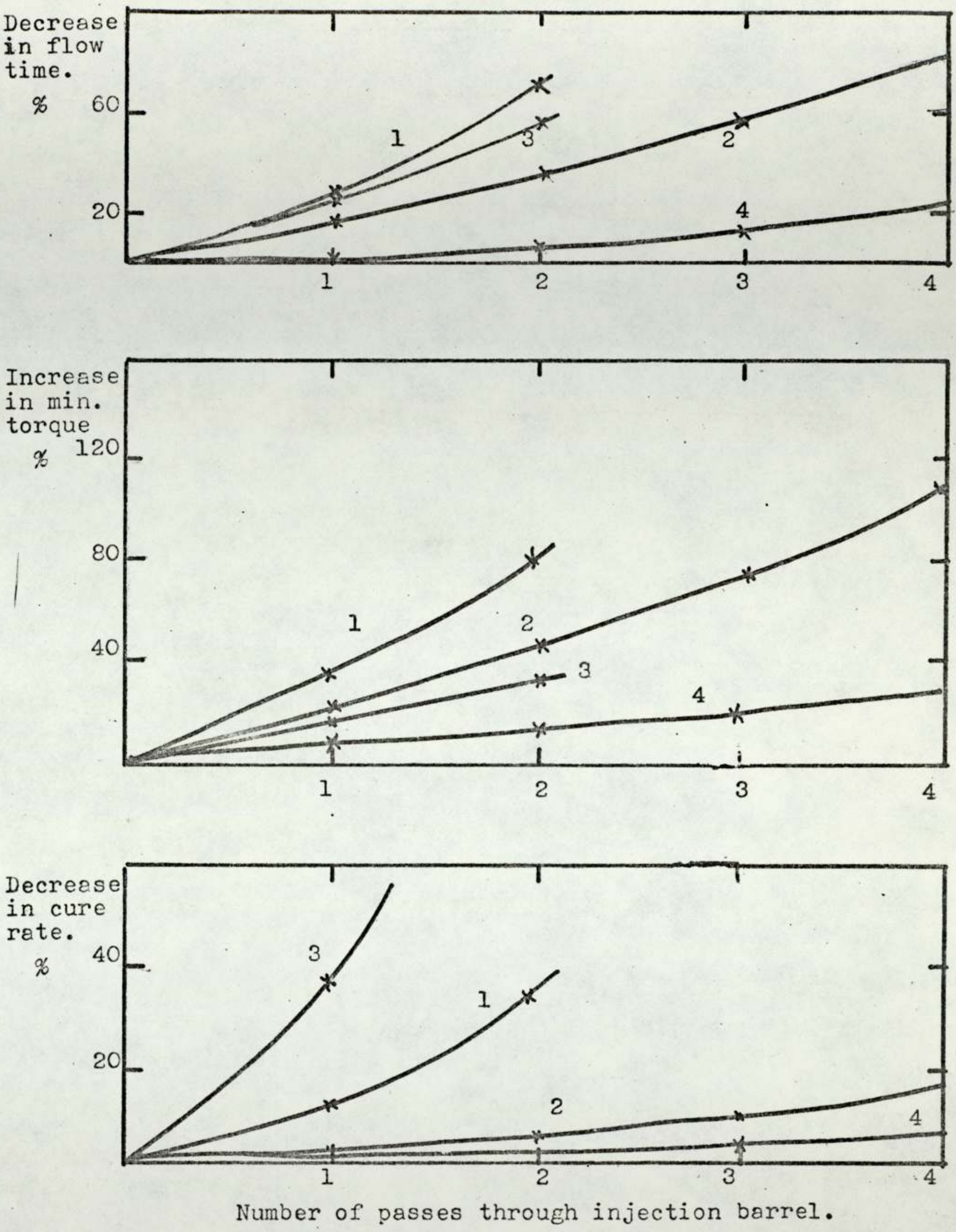


Fig. 79. Effect of different injection machines on the viscosity/time characteristics of thermosetting materials.

1 PF 5, Ankerwerke m/c. 2 PF 5, Bipel m/c.
3 UF 6, Bipel m/c. 4 PF 5, Turner m/c, 60g.

Chapter 8

Discussion of Results

8.1 Introduction

The purpose of this chapter is to bring together the results which have already been described in detail in the preceeding chapters, to comment on the various preferred methods and to recommend how they may be used to assist the moulder in the control of thermosetting moulding materials for injection moulding and in the control of the process itself. Comparison of the results of the work described in this thesis with those related in the literature has already been made at the end of each chapter describing the practical work.

A thermosetting material is thermally unstable and as a consquence its viscosity changes with time. The rate of change can be quite marked under processing conditions and thus the steady state condition required for the determination of rheological properties does not exist except possibly for relatively short periods. The viscosity data quoted in this thesis are therefore only approximate.

The hypothesis stated that no single test procedure could adequately measure the variation of viscosity with time over the full range of temperature and shear conditions encountered in the thermosetting injection moulding process. These are listed in Chapter 3 and are reproduced here for convenience. (Table 46).

TABLE 46 Conditions of Thermoset Injection Moulding Process

Moulding Process	Typical Temperature	Typical Shear Rate	Effect
Injection Barrel	80-100°C	$10\text{-}10^2$ sec^{-1}	Material is partly plasticised by mechanical working
Nozzle	100-110°C	$10^2\text{-}10^4$ sec^{-1}	
Runners/ gate	100-140°C	$10^2\text{-}10^4$ sec^{-1}	High frictional heating reduces cure time and aids flow
Mould	150-190°C	Low	Material is static and remains in mould until cured.

8.2 The use of the Capillary Viscometer with Thermosetting Plastics

Three basic types of capillary viscometers were used to measure the shear stress/ shear rate characteristics of thermosetting materials over the shear rate range of 10- 10^4 sec^{-1}. Practical reasons limited the use of all three viscometry techniques to the rather low temperatures of 90 - 100°C. The results of the capillary viscometer with a compounded melt were in fairly good agreement with those of the nozzle capillary viscometer. Fig. 22, Fig.31).

The results showed that phenolic, melamine and urea materials have a linear relationship between log shear stress and log shear rate but that at high shear rates ($>10^3 sec^{-1}$) the flow pattern can change to a plug flow system. At very low shear rates, phenolics and melamines show a Bingham type of flow behaviour i.e. the outer annulus of material surrounds a central non-orientated plug of melt. (See Plates)

The melt capillary viscometer proved rather unwieldy to use in practice and its only advantage over the nozzle viscometer was that it exerted a constant displacement rate onto the melt.

The nozzle viscometer proved satisfactory in use but the material slipped along the screw slightly during the ejection stroke. This was indicated by the initial 1/8 - 1/4 turn of the screw at the start of the ejection stroke, and also by the relationship between the stroke length (related to swept volume) and the shot weight, fig 29. However, the duration of the ejection stroke can easily be measured from the pressure/ time trace. (fig. 28).

Marked pressure variations occured in the pressure traces of both the capillary melt viscometer and the nozzle viscometer fig. 28. The shear stress/shear rate results fig 22,31 quoted in this thesis are therefore only approximate. The pressure variations were considerably reduced in the runner capillary viscometer fig 74 which, because it opened along the capillary length, could also be used at elevated temperatures. It is a necessary part of the operation of capillary viscometers using compounded melt, that the viscometer shall be capable of operating with consecutive injection shots. To do this the melt must either be stable in the capillary die, or it must be ejected. The alternative to this procedure is to test a single shot from the injection barrel - a procedure that was examined but rejected as impractical because of the size and unwielding nature of the viscometer used (fig 18).

The runner viscometer could easily be developed for use with larger machines. This is an important point since the indications are that thermosetting injection moulding problems are aggravated by the use of larger machines. The mould capillary technique would also permit the effect of injection machine settings on the melt viscosity to be studied, an aspect which the injection moulding results in Chapter 7 show to be important.

However, the shape of the graph of log pressure against log flow rate,fig. 32, is similar to that of the graph of log shear stress against log apparent shear rate and for many practical purposes it is probably sufficient as well as simpler to measure simply the pressure/flow rate behaviour of materials fig 31. It is necessary to use an instrumented nozzle having a heated nozzle tip of the L/D ratio of at least 5:1.

Of the three capillary viscometery techniques used for this work, the capillary viscometer used with sintered powder (as distinct from the compounded melt discussed above) was probably the least useful technique. Its results correlated roughly with those of the other capillary techniques only for materials differing widely in their viscosities,fig. 38. The gradient of the log pressure/log flow rate curve (fig 25) differed markedly from graphs of the same properties measured by the other techniques fig. 32,72,75. This is probably because of the lack of shear work in the capillary barrel which will result in a poor dispersion of moulding powder granules. Kanavets and Sokolov (40,41) suggested that the minimum viscosity occurs when there is a complete dispersion of structure forming systems. The presence of solid particles in a melt will significantly affect the viscous properties of the melt (111) while the presence of some powder structure has been established in compression moulded test pieces (110). The formation of the melt in the capillary viscometer barrel with powder materials is also a simple compression moulding process.

The use of the capillary viscometer with powder material was limited by the relatively low extrusion pressure (11MN/m^2) which required the use of dies of less than 1:1 L/D ratio.

The capillary viscometer is not itself capable of measuring the duration of fluidity since it is an essential part of its mode of operation that the melt flows through the capillary die, section 4.2. The capillary viscometer, either as a viscometer, an instrumented nozzle, or as a mould runner, permitted the shear stress/shear rate relationships of thermosetting materials to be measured over the full range of shear rates found in the injection moulding process and enabled fundamental viscosity data to be calculated, fig 22,31. The use of a capillary viscometer with uncompounded powder is probably useful to obtain an approximate indication of the viscosity of a material but its applicability is limited by lack of shear.

8.3 Variable Torque Rheometer

The correlation of the minimum torque value and the material viscosity as determined with the capillary viscometer and with the injection process was poor, fig 54a, and was probably due to the large difference in the shear rates involved. Although the variable torque rheometer results were used to calculate viscosity data, fig 47, the results are probably only semi-empirical because of the assumptions made in the theoretical interpretation of the rheometer and because of the extremely complex flow pattern involved. (Section 5.2).

The variable torque rheometer also measures the fluidity and duration of fluidity of a thermosetting material heated under dynamic shear conditions fig 40,41,42. However, the way in which the duration of fluidity is determined from the rheometer torque trace is dependent on the particular material and thus the results can only be used to compare similar materials, fig 51.

The variable torque rheometer can be operated over a range of temperatures although its results at elevated temperatures are subject to some error.
It is best used at 80 - 120°C, temperatures which correspond closely with the temperatures used for the injection barrel, fig 43.
The variable torque rheometer will give a limited indication of the initial cure rate of some types of materials. Fig 45.

8.4 Oscillating Disc Rheometer

The oscillating disc rheometer differs from the capillary viscometer and the variable torque rheometer in three important aspects. Firstly, it imparts a small strain to the test sample, secondly both the rotor and the die walls are splined and thirdly it operates in an oscillatory manner. The first factor means that the rheometer will record the viscosity of the material throughout its complete curing cycle (Fig. 60) and the second factor means that the recorded changes occur within the material itself since the splines eliminate slippage between the chamber wall and the melt thereby minimizing lubricant effects. The third factor means that the viscosity measurements made are of a dynamic nature which are not the same as the continuous shear measurements made with the capillary viscometer and the variable torque rheometer. The torque values recorded by the rheometer can be analysed into two components, a viscous torque and an elastic torque. The ratio between these two measurements is the loss angle (tan δ). (Table 30). Fig 55.

Uri (132) related the viscosity increase in crosslinking and chain extending liquid rubber systems to their different elastic properties determined in an oscillating probe viscometer. The results in Table 30 indicate that the complex or total torque value and the loss angle as determined in an oscillating disc rheometer may both play an important role in determining the moulding properties of a material. It is suggested that the measurement of these values may indicate the significance of chain extending and crosslinking reactions in the initial resin and moulding material production processes. This approach has not been used industrially where relatively simple flow tests predominate but the simple tests can fail to distinguish between materials of similar formulation having different injection moulding properties. This situation is known to occur with materials of different heat and shear histories. As in the case of the variable torque rheometer, the oscillating disc rheometer, Table 36, will distinguish between materials of widely different viscosities but not between materials having small differences. The oscillating disc rheometer results can be expressed in fundamental units and it is capable of being used over a wide range of temperatures.

The oscillatory disc rheometer will follow the viscosity changes of a material throughout its complete curing cycle, fig 59. It is therefore possible to measure a simple cure time and cure rate from the torque/time curve as well as to determine the induction time and kinetic reaction rate constants. For many materials an Arrhrenius type relationship exists between the log of the reaction time and the reciprocal of the absolute temperature, fig 65. This means that materials may be tested at lower temperatures than that used in industrial moulding thereby enabling greater differention to be made between materials.

8.5 Correlation of results with injection moulding process

The various test proceedures described in this thesis have already been correlated with the injection moulding process at the end of each chapter, e.g. capillary viscometry 4.7, variable torque rheometer 5.6 and oscillating disc rheometer 6.7. It is now necessary to bring each of these sections together and to discuss how the test proceedures listed in the original hypothysis correlate overall with the injection process.

The examination of the injection moulding process described in Chapter 7 shows that the injection moulding process is extremely complex and that the process itself is subject ot small random variations as well as more gradual changes in machine performance (fig 77). These effects have been studied by Whisson (31) in the thermoplastic moulding process and are found with all types of materials, moulds and machines. It is also important to realise that while it is possible to set injection machine parameters such as back pressure, screw speed etc, these variables will interact with each other and will have a combined effect on the flow properties of the melt, (Table 14a,b, Fig 70), and also on the mould filling pattern (Fig 71 and Plates). It has also been shown that variations can occur between similar materials which result in slightly different mould filling rates and that different materials can react differently with different moulds and machines (Fig 39). The production of good quality, commercially acceptable mouldings is therefore dependant on the interaction between the injection machine, the mould and the material and that in this context, it is extremely difficult to devise a test proceedure which will adequately describe the injection moulding properties of a material.

Because of this complexity, the writer, in conjunction with Whisson, explored the use of injection nozzle pressure and temperature sensors with measurements of screw displacement to produce an empirical diagram of the required melt/machine conditions necessary to produce commercially acceptable mouldings from a given material, mould and machine. This technique, (reported in part 2 of reference 120), proved to be successful in that it enabled machine conditions to be established and to be reset which would produce good quality mouldings and which would allow for minor variations between different batches of the same material. It also permitted the moulding production and machine performance to be monitored. A similar approach is advocated by Norfleet and coworkers (86) but this technique is essentially an "in-house" operation for the moulder and does not aid the material manufacturer nor provide a better understanding of the rheological properties of his materials.

As previously stated, the injection moulding machine consists of three basic parts, the barrel, the runners and the mould. The results in fig 70, Table 14 indicate that the rheological properties of the melt depend partly on the mechanical working it receives in the injection barrel. A capillary viscometer is essential to measure the rheological properties at high shear rates. It is necessary to generate the melt in an injection barrel or to use a specially developed piece of equipment (see Chapter 10), since in the typical type of capillary viscometer, the material is merely sintered. This has been discussed in section 4.6 and the more usual type of instrument is thus only capable of providing a limited assessment of the shear stress/shear rate properties (compare fig 25 with figs 22,31,70) The separate melt capillary viscometer described in section 4.3 is rather unwieldy and can only be used over a very limited temperature range. The most suitable capillary instrument used in this investigation is the nozzle viscometer fig 31,32. It gives similar results to those observed in injection moulding (figs 72 , 75) but has several major disadvantages in that it can only be used over a limited range of temperatures and cannot be used with the higher back pressures and/or screw speeds occasionally encountered in industrial injection moulding. (Under these conditions, the injection barrel merely acts as an extruder. This cannot happen during the injection moulding process where the cured sprue prevents material emerging from the nozzle during the screw back period). These difficulties may be overcome by modifying and developing the capillary runner viscometer (described in Chapter 7) and discussed in Chapter 10.

The instrumented nozzle viscometer is capable of operating over the range of shear rates encountered in injection moulding (fig 31) although it is essential to use a nozzle of sufficient length if the problems of melt instability are to be avoided (fig 32). Unfortunately nozzles of 15:1, L/D ratio result in precuring of the material. In practice the shear stress/apparent shear rate curves (fig 31) so obtained are similar to the pressure/flow rate curves obtained by a simple extended nozzle (fig 30a,b,32) and also during the injection moulding process (fig 72,75).

It is probably sufficient to measure pressure/flow rate data at different temperatures for material quality control purposes.

Both the variable torque rheometer and the oscillating disc rheometer are, in principle, capable of measuring the viscosity of a thermosetting melt. The variable torque rheometer will only give semi-empirical data, will only operate over a limited range of shear rates (fig 47), and does not distinguish adequately between injection materials with large differences in viscosity at high shear rates (fig 54). Table 47 shows the limited differences shown between injection and compression grades.

TABLE 47 Comparison of Injection and Compression Grade Materials in the Variable Torque Rheometer and Capillary Viscometer (Granular Material)

Material	Variable Torque Rheometer Torque Nm	Capillary Viscometer Flow rate g/sec
Injection Grade		
PF5	20	9.3
PF7A	19	9.3
PF9C	22	16.5
UF6	38	0.6
UF8	35	0.7
UF22I	32	1.3
Compression Grade		
PF18A	66	0.55
PF18B	61	0.68
PF18C	59	0.01
UF22B	34	0.02
UF22C	99	0.01
UF22D	34	0.5

The torque/time trace of a phenolic material will widen as the material gels (fig 42) indicating an increase in the stiffness of the material. It is interesting to note that phenolic materials showing the wide torque trace characteristic at the minimum torque value cannot be injection moulded (fig 52, table 30).

The differences between the viscosity measurements made under continuous shear and under dynamic conditions have already been discussed (Section 6.2). A further complication which exists when comparing viscosity measurements made in the oscillating disc rheometer with the injection moulding process is the large difference in the shear rates involved. Table 30 shows that the oscillating disc rheometer will determine differences between materials which are not shown by the capillary viscometer (fig 32). They may be qualitatively indicated by the broadening torque trace of the variable torque rheometer (fig 42) for phenolic materials. The results in Table 30 indicate that the "flow" properties of a material depend on both the elastic and the viscous component of the torque although further work needs to be carried out to correlate these observations with the injection moulding process. Indications are that the oscillating disc rheometer may provide a link between the basic chemistry of resin formation and crosslinking, and the moulding properties of the material (section 6.6). The simple correlation of minimum torque values as determined in the oscillating disc rheometer and the injection moulding process (table 36) shows that the simple measurement of torque is not particularly useful.

The duration of fluidity or melt stability of a material in the injection barrel is of paramount importance since many industrial injection moulding machines are required to operate continuously. Changes in the injection cycle time of only a few seconds can cause reject mouldings (fig 77,78) and it follows that variations in the melt stability of a material will also lead to similar difficulties. The variable torque rheometer will measure the duration of fluidity of thermosetting materials (discussed in section 5.6) and the results correlate very well with the injection moulding process (fig 54, table 26). Unfortunately, the method of determining the duration of fluidity is semi-empirical (see fig 42, 43,44) and must be limited to the comparison of similar materials. This is an obvious disadvantage but the variable torque rheometer is the only instrument currently available which is capable of recording the changes in the material consistency which take place over the range of temperatures and shear rates which occur in the injection barrel. The use of the variable torque rheometer with thermosetting materials is limited to 80 - 120°C (fig 41b,43c) but it is essential to interpret the torque trace correctly to avoid erroneous conclusions. This is discussed in section 5.4.

Although the capillary viscometer can be used to measure the time dependance of material flow rate and the amount of material extruded (fig 26a), the capillary viscometer results do not adequately distinguish between materials of known different melt stability (fig 26, fig 76, table 43). The results of the capillary viscometer used with a compounded melt show that the thermosetting melt is changing rapidly but the instrument is not suitable for quantitatively determining the rate of change (fig 22). The literature indicates that capillary and orifice meters can be used to determine time dependant effects but significant differences are to be seen between the capillary viscometer used in this work and the instruments described in the literature (table 22) but this is discussed in section 4.6. In view of the desirability of mechanically working the melt before determining its rheological properties (see above) some doubt must be expressed concerning the validity of the results obtained from sintered powder.

The oscillating disc rheometer is capable of measuring the duration of fluidity of a thermosetting material (table 37) but will only do this at very low shear rates (1 - 10 sec^{-1}). These measurements do not correlate well with the injection moulding process although two papers (65,66) state that the elastic modulus or torque as measured by an oscillating disc rheometer is more sensitive to crosslink formation than the more usual type of measurement. However, the duration of fluidity varies with the rate of shear (fig 41a) and the large differences in shear rates between the measurements in the oscillating disc rheometer and the injection barrel may account for the apparent lack of sensitivity of the oscillating disc rheometer in respect of the duration of fluidity.

The most significant advantage of the oscillating disc rheometer is that it will record the change of viscosity throughout the complete curing process (fig 60) and consequently will measure the cure rate as well as the reaction kinetic constants (Table 31a,31b, 34). This is of limited immediate value to the injection moulder except possibly to predict or adjust cure time but it is of obvious value to material control and production. The results of the oscillating disc rheometer can be directly related to the physical strength development of the moulding (fig 59), a fact which is of relevance in determining the point at which a moulding can be ejected. The variable torque rheometer can give limited information concerning the cure rate of certain materials (fig 45), but this information cannot be obtained from the capillary viscometer (fig 26c) and only the oscillating disc rheometer is satisfactory in this respect.

It has been shown that no single test method will adequately measure the rheological properties of thermosetting plastics over the range of temperatures and shear rates encountered in the injection moulding process. The results included in this thesis have shown that only a capillary viscometer will measure the viscosity of materials at high shear rates and that the variable torque rheometer gives the better measurement of duration of fluidity. Of the instruments used in this thesis, only the oscillating disc rheometer is capable of recording the complete cure process. The three techniques are therefore complimentary and not mutually exclusive.

It is interesting to compare the three test techniques used in this study to characterize the rheological properties of injection moulding materials with the published material evaluation schemes of other workers. In August, 1972 Bassow et at (133) considered it necessary to use a ball (? cf cone) and plate viscometer, a rotational viscometer and a capillary viscometer fitted in place of the injection machine nozzle to measure the shear stress/shear rate characteristics of phenolic moulding materials over the range of shear rates of 10^{-3}-10^{4} sec^{-1} and 100-180°C. Bassow overcomes problems of precuring in the equipment by omitting the catalyst from his materials, an approach which permits the measurement of viscosity but not viscosity/time effects.

In May 1973 Slysh et al (72) described the use of the spiral flow test to measure the flow of a material, a variable torque rheometer to measure the duration of fluidity or processing time and differential scanning calorimetry to measure the curing characteristics of diallyl phthalate injection moulding materials. The combination of the three tests to measure the three aspects of the injection moulding process is interesting but the spiral flow is inherently unsuitable for measuring fundamental flow properties. Differential scanning calorimetry has been widely used with liquid resins but the present author experienced considerable difficulties during attempts to use it with phenolic and urea moulding materials.

The papers by Bassow (133) and Slysh (72) represent an interesting and novel approach to the problems of material characterization. Most current proceedures rely on a combination of the older test methods eg: cup flow, disc flow and cup cure, tests which correspond best to the compression moulding process and not to the injection moulding process. The necessity of combining several, relevant test proceedures has already been discussed in chapters 2 and 3 and has been demonstrated by the practical work described in this thesis,

Chapter 9

Conclusions

The following conclusions may be drawn from the work described in this thesis.

1 Injection grade phenolic materials behave as power law fluids up to apparent shear rates of about $10^3 sec^{-1}$ at 90 - 100°C. Within this region the flow pattern changes from the Bingham type, i.e. a central plug surrounded by an annulus of laminar flow to an overall laminar flow pattern. Above $10^3 sec^{-1}$, the flow pattern may change to plug flow and is particularly noticeable at the exit of short dies or mould gates. The adhesion of the phenolic melt to the die wall decreases with increasing resin condensation.

Urea and melamine based materials show similar trends to the phenolic materials but the amino melt does not adhere to the die walls as well as the phenolic. Plug flow was not observed with melamine materials at apparent shear rates of $1.3 \times 10^3 sec^{-1}$.

2 The capillary viscometer results obtained with the compounded melt correlate with the material flow rate observed in injection moulding. Practical difficulties prevented the equipment being used at temperatures of greater than 100°C. The use of the capillary viscometer with uncompounded material is unsatisfactory since its results differ markedly from those of injection moulding.

3 Simple pressure/flow rate information obtained from an extended injection nozzle (preferably greater than 5:1, L/D ratio) correlated fairly well with the injection process and provides an acceptable test procedure.

4 Measurements of the duration of fluidity with the variable torque rheometer correlate well with similar measurements made with the injection machine.

5 The oscillating disc rheometer records the viscosity change throughout the complete cure process. Its results provide a simple assessment of the curing behaviour of the material as well as the chemical kinetic constants of the curing reaction. The oscillating disc rheometer offers considerable promise as a means of investigating the various flow components and of possibly relating the chemical reaction of materials to their flow properties.

6 Of the three techniques investigated, only the variable torque rheometer is satisfactory for immediate use. The nozzle viscometer can be easily made for any injection machine while the runner viscometer would need some development work. The oscillating disc rheometer, even when modified as described in this thesis, is hardly adequate for industrial use with thermosetting plastics and requires major redesign and development.

7 This thesis has shown that the proceedure shown in Table 48 will give results that correlate well with the injection moulding process. The proceedure has been tested with small numbers of materials but needs to be proved industrially with material and moulding production plants. While this procedure is superior to many of the current techniques, it is doubtful if any test procedure will be completely satisfactory since the injection moulding performance of a material depends on the complex interaction between material, machine and mould.

TABLE 48 Test Procedure

Technique	Measurement	Injection Moulding
Capillary Viscometer Capillary nozzle	Viscosity/shear rate	Fundamental viscosity data and testing of 'flow'
Capillary nozzle	Pressure/flow rate	Empirical quality control
Variable Torque Rheometer	Duration of fluidity	Empirical measure of barrel life
Oscillating disc Rheometer	Dynamic torque, loss angle with time	Cure rate, fundamental properties, Reaction kinetics

Chapter 10 Suggestions for future work.

The results of the investigations described in this thesis lead to the following suggested projects for future work.

a) The work in Chapter 6 has suggested that the relative degrees of linearity and cross-linking of a thermosetting material may be as important as its overall consistency, and that measurement of the individual component should enable a better characterisation of the material to be made.

Thermosetting moulding materials will have to be prepared from carefully formulated and charactised resins which will have a predetermined or known relationship between polymer extension and cross-linking reactions. These moulding materials will be evaluated in an oscillating disc rheometer designed to measure stress/strain relationships and thence the complex and elastic moduli and loss angle. These measurements will be correlated with the chemical behaviour of the resins.

The moulding materials will then be injection moulded using an instrumented machine and mould, and the observed moulding properties correlated with the rheological information obtained from the oscillating disc rheometer.

When these results have been satisfactorily correlated, samples of current moulding materials of known performance will be evaluated and, if successful, the work will be widened to involve the monitoring of commercial materials. It is intended to establish a liaison with material manufacturers and moulders to substantiate the technique by mutual trials.

This project is currently being progressed at RAPRA and is jointly supported by RAPRA and the Department of Trade and Industry Engineering Requirements Board.

b). The work described in this thesis has demonstrated the need for a capillary viscometer to measure the viscosity/shear rate characteristics of a compounded thermosetting melt over a range of temperatures up to the temperature of the mould. The capillary viscometers described in this thesis are inadequate in several ways and it is recommended that the runner technique described in chapter 7 should be developed as a viscometer, by the insertion of further pressure and temperature sensors in the runner, and by the removal of the mould cavity to produce an open ended capillary. The developed viscometer would then be operated in place of the mould of the usual injection moulding process and would offer the following advantages:-

a. It could be used over a wide range of temperatures and shear rates.

b. The melt would be compounded in the injection barrel and the presence of the sprue would permit the full range of back pressures, screw speeds etc. to be employed.

c. The residual melt in the capillary will be ejected at the end of each shot (the capillary length is along the mould split line) and problems of precuring at the end of each cycle will thus be eliminated.

d. The use of a series of pressure sensors would enable end corrections to be eliminated and would enable flow data to be obtained directly.

e. The capillary runner viscometer could be easily used with machines of different types and sizes.

f. The flow relationships of a material would be determined over a number of shots to minimize errors.

The viscometer should be used to investigate the rheological properties of thermosetting materials using capillaries of different section. The rheological analysis of continuous shear flow in channels of circular cross-section is well established but the majority of runners used in industrial moulding practice are of trapezoidal or rectangular cross-section.

A disadvantage of the proposed viscometer is that it relies on the screw to provide the displacement force for the material and this will lead to errors since material can slip along the screw. It should be possible to allow for this by using a series of pressure sensors to indicate the rate of flow or by calculating the slippage from the ratio of shot volume to swept volume in the barrel. The alternative is to use a viscometer similar to that described in chapter 4 but to arrange for it to split along the barrel to eject any precured melt. While the latter would probably provide the best solution, it would be difficult to design it to function correctly.

c). It has been shown that it is necessary to mechanically work a melt before measuring its rheological properties. Both in this thesis and in (b) above, this has been carried out in an injection machine barrel, a process which "ties up" a potential profit making machine and necessitates the use of considerable quantities of material. It is desirable to develope a small compounder (possibly based on a high shear version of the Kanavets Plastimeter) in which the granular material is heated and sheared before being forced through a capillary viscometer.

d). This thesis describes the use of three basic techniques (capillary viscometer, variable torque rheometer and oscillating disc rheometer) and shows how the rheological properties they measure may be correlated with the injection moulding process. The injection moulding machine instrumentation has also been used to establish and to reset an injection process as well as to monitor actual production. It is recommended that these techniques should be applied to the shop floor as quality control proceedures for material and moulding production. Such a project would require the co-operation of a number of companies but should aid the productivity of such companies. N.B. Since the practical work described in this thesis was carried out, the use of the variable torque rheometer (with moulding materials) and an oscillating probe curemeter (with thermosetting resins) in laboratories has increased although lack of a really suitable commercial oscillating disc rheometer and capillary viscometer has impeded their use by the thermosetting industry. The last few years has also seen a considerable increase in the use of pressure/temperature and displacement sensors for production monitoring particularly for thermoplastics injection moulding although examples exist in the compression and injection moulding of thermosetting plastics.

e). The Monsanto Rheometer model MPV was specially designed for use with rubbers and as such it is not really suitable for use with thermosetting plastics. An oscillating disc rheometer suitable for use with thermosetting plastics is required. It is suggested that a suitable instrument should have the following features:

a) The biconical rotor driven from the top to eliminate resin leaking into the drive unit.

b) Vertical flash mould to permit the use of granular materials.

c) Three plate stripper mould to eject cured material.

d) Mould splines to be fewer in number and to be designed in conjunction with ejector pins to aid ejection.

e) Rotor splines to be reduced in number and to be capable of easy cleaning.

f) RF heaters to be incorporated into the platens to increase heating rate.

Chapter 11 Bibliography

Publications by the author of relevance to this thesis

1. Applications of the Variable Torque Rheometer. K.T. Paul. RAPRA Bulletin 2. 1972 p29 - 35.

2. RAPRA Variable Torque Rheometer, Use with thermosetting rubbers. K.T. Paul. RAPRA Members Journal. 3. 1973 p61 - 65.

3. Thermoset Injection Moulding
   R.R. Whisson, K.T. Paul, RAPRA Members Journal.
   Part 1 12. 1973 P 308 - 311
   Part 2 3. 1974 P 64 - 67*
   Part 3 5. 1974 P 121 - 125*

4. Oscillating Disc Rheometer - Use with thermosetting plastics. K.T. Paul. RAPRA Members Journal. 5. 1974 P 126 - 133.

5. Characterization of Thermosetting Materials for Moulding.
   K.T. Paul.
   Proceedings of Polymer Rheology and Plastics Processing Conference, British Soc. Rheol. and Plastics Institute Conference.
   1975. P 49 - 64+

RAPRA Confidential Reports.

6. B441. A review of the methods of characterizing the flow/cure properties of thermosetting plastics materials.
   K.T. Paul. RAPRA 3. 1971*

7. B477. Thermoset injection moulding; characterization of the process and materials.
   K.A. Scott, R.R. Whisson, K.T. Paul. RAPRA. 8. 1972.

* Enclosed with thesis.

\+ Lecture and publication.

Publications referred to in the thesis

1. Europlastics Monthly, 4, 1972 P 59, RAPRA, RR 133, 1964.
2. G.L. Peakes, Brit. Plast. 2 1934 P421 - 6.
3. G. Menges, W. Dalhoff, Kunstst. 9. 1969 P584 - 92.
4. J.A. Brydson, Plastics Materials, Iliffe, 1969.
5. F.J. Parker, Nat. Coll. Rubb. Tech. Symposium, 4. 1974.
6. Penwalt/Stokes Triscrew Publication 1973.
7. H.L. Kleinbaum, Plast. Mod. Elast. 12. 1971 P123-7.
8. D.W. Sundstrom, et al SPE 26th ANTEC 1968 P561 - 8.
9. P.J. Heinle, M.A. Rogers, SPE RETEC 12 1968.
10. L. Spiwak, Plastics Technol. 5, 1965 P 41 - 2.
11. F.C. Karas, Mod. Plast. 1. 1963 P140 - 2.
12. A. Schwittmann, Kunstst. 3. 1946 P49 - 52.
13. S. Tonogai, SPE32nd ANTEC 5 1974 P568 - 572.
14. J.E. Ferriday, Plastics 9, 1968, P1010 - 1011.
15. G.J. Dujardin, Kunstst. 3, 1971, P177 - 182.
16. J.W. Heyd, et al, J. Polym. Sci. 1965, Part A Vol. 3, P 1911 - 39.
17. Y. Morita, SPE 22nd ANTEC. 3 1966 Session VIII - 5.
18. D.L. Kerr, A.J. Donje, SPE 22nd ANTEC 1966 Paper XXIV-I
19. G.H. Goulbourne, Brit. Soc. Rheol. Conf. 1970.
20. R.H. Beck, Confidential Report, Ford Motor Company 1970.
21. R.H. Beck, SPEJ. 5.1971 P 43 - 48.
22. G.L. Peakes, Brit. Plast. 3 1934 P 475 - 81, 4, 1934, P 516 - 19.
23. L.M. Debing, S.H. Silbarkraus, Ind. Eng. Chem. 8. 1941, P 973 - 5.
24. R. Thater, Plaste u. Kaut 1 1963 P 35 - 39.
25. M. Krahl, Brit. Plast. 11, 1934 P 235 - 240.
26. C.M. von Meysonbug, ASTM Special Technical Papers, 2 47, P 155 - 68, 1958.
27. W. Woebcken, et al, Kunstst. 12, 1967 P974 - 83.
28. R. Thater, K. Ulbricht, Plaste u Kaut, 4, 1965 P224 - 8.
29. R. Burns, Proc. Am. Soc. Testing Materials 1940, 40, P1283.
30. EMMI - 66 - 1.
31. R.R. Whisson, RAPRA, RR 170, 1968, RR 188 1971.
32. M.S. Akutin, Sov Plast. 6, 1973 P 62 - 5.

33. I.F. Kanavets, ITEIN ANSSR. No. 1 - 56 - 66 1956.
34. P. Ehrentraut, Kunstst. 10 1966 P 695 - 707.
35. P. Ehrentraut, Rheol. Act a 1. 1968 P 64 - 74.
36. S.A. Kolesvikova, et al Sov. Plast. 3 1969 P 36 - 9.
37. O. Gottefert, Plast. Verarbeiter. 8 1968 P 609 - 615.
38. I.F. Kanavets, L.G. Batalova DANSSR, 1957, 5, 114.
39. V.A. Kargin, T.I. Sogolova, DANSSR, 1956, 4, 108.
40. I.F. Kanavets, A.D. Sokolov, Sov. Plast. 5, 1965, P 30 - 35.
41. I.F. Kanavets, A.D. Sokolov, Sov. Plast. 6, 1965, P 24 - 28.
42. N.N. Danilkin, I.F. Kanavets, Sov. Plast. 5, 1969, P 58.
43. N.N. Danilkin, I.F. Kanavets, Sov. Plast. 11, 1969, P 27 - 9.
44. N.N. Danilkin, I.F. Kanavets, Sov. Plast. 1, 1970 P27 - 30.
45. G. Menges, P. Ehrentraut, W. Dalhoff, Kunstst. 12, 1967, P 957-64.
46. W. Dalhoff, Kunstst. Technik, 10, 1970 P 365 - 369.
47. V.K. Maryashin, et al Sov. Plast, 2, 1971, P 15-19.
48. A.S. Perevertov, et al Sov. Plast, 5, 1969 P 26.
49. A.S. Pereventov, et al Sov. Plast, 9, 1972 P 9 - 12.
50. K. Ulbricht, Plaste u Kaut, 12, 1972 P 912-918.
51. G. Meyer, Plaste u Kaut, 11, 1966 P 660-663.
52. B. Schreiber, Kunstst, 6, 1969 P 362 - 67.
53. A. Rothenpieler, L. Schone, Plast. Inst. Conf. London 9, 1973 paper 11.
54. K. Scholtis, et al, Kunstst 8, 1967 P 635 - 7.
55. J.E. Goodrich, R.S. Porter, Polym Eng Sci, 1, 1967 P 45 - 51.
56. L.L. Blyler, J.H. Doane, Polym, Eng Sci, 3, 1967 P 178 - 182.
57. G.C.N. Lee, J.R. Purdon, Polym, Eng. Sci. 9, 1969, P 360 - 5.
58. R.H. Norman, Private Communication, RAPRA 1975.
59. J. Batchelor, RAPRA Report B 437, 1970.
60. A.L. Soden, RAPRA Internal Report 1960.
61. J.L. Henson, A.J. Lovatt, G.S. Learmonth, J. Appl. Polym. Sci.
Voll II, 1967 P 2543 - 52.
62. P.P. Stricos, Diss. Abs. 25.3, 9, 1963, P 1526
63. R.P. White, Polym. Eng. Sci. 1 1974 P 50 - 7.
64. C. Macosko, J.M. Starita, SPEJ II, 1971 P 38 - 42.
65. F.G. Mussatti, C. Macosko, ANTEC 1974 P 73 - 80.
66. C.L. Sieglaff, T.R. Evans, Plast. Des. & Proc. II, 1972, P 16 - 18.

67. R.M. Brodbeck, L.W. Hartzel, Rubb. & Plast. Age 9 1969 P 651 - 5.
68. B.L. Talwar, L.T. Ashlock, SPEJ, 10 1970 P 42 - 6.
69. R.H. Beck, A. Golovy, SPE 30th ANTEC, 10, 1972, P 87 - 93.
70. R.B. Prime, SPE 31st ANTEC, 5, 1973 P 205 - 9.
71. W. Knappe, et al, Kunstst, 7 - 1972 P 455 - 459.
72. R. Slysh, et al SPE 31st ANTEC 5, 1973, P 210 - 5.
73. P.E. Willard, SPEJ, 7, 1973 P 38 - 42.
74. L.W. Crane, et al, J. Polym. Sci. Lett. Ed. 11, 8, 1973 P 533 - 40.
75. J.H. Speake, et al, J. Phys. D7 No. 3, 2, 1974 P 412 - 24.
76. P. Plowiec, Polym-Tworz Wielk, 18, 12, 1973 P 620 - 3.
77. K. Bergmann, K. Demmler, Koll. ZZ Polym. 252, 3, 1974. P 193 - 206.
78. D.W. Larson, J.H. Strange, J. Polym Sci Polym Phys. 7, 1973 P 1453 - 9.
79. R.W. Meyer, SPI 29th Conf. 1974 9E P 1 - 6.
80. P. Eyerer, J Appl. Polym. Sci. 18, 4, 1974 P 975 - 92.
81. P.V. Sidyakin, V.Y.S. Soed. 14A No. 5 1972 P 979 - 88.
82. G. Menges, M. Meissever, Kunstst. 2, 1972 P 120.
83. A. Rothenpieler, R. Hess, Kunstst. 4, 1972 P 215 - 8.
84. J. Kestler, Mod. Plast. 8, 1969 P 58 - 9.
85. J.S. Norfleet, W.G. Frizelle, SPEJ, II. 1971 P 44 - 9.
86. J.S. Norfleet, C.D. Boone SPE 31st ANTEC 1973 P 532 - 7.
87. A.D. Sokolov, I.F. Kanavets, Sov. Plast. 12, 1964 P 23 - 9.
88. R.J. Groleau, SPE RETEC 10, 1972.
89. B.I. Gengrinovich, Inst. Shin. Prom. 1960, 567, P 91 - 100.
90. G. Emil, Rev. Gen. Caout. Plast. 2, 1968 P 172 - 82.
91. T. Adamski, MSc. Thesis, Univ of Lancaster 10, 1971.
92. J.R.A. Pearson, Rubb. Chem. Technol 2, 1968 P 23 - 46.
93. C. Wainwright, IPI Trans, 6, 1937 P 7 - 28.
94. P. Fina, Plast. Technol, 2, 1966 P 27 - 9.
95. P.H. Brooks, Rubb. & Plast. Age 12, 1966 P 1285 - 8.
96. D.W. Sundstrom, et al, SPE 28th ANTEC 1970 P 174 - 77.
97. A. Rothenpieler, Kunstst u. Gummi 3, 1966 P 79 - 86.
98. A. Schwittmann, Plastics 9, 1944 P 426 - 32.
99. G.L. Peakes, Mod. Plast. 6 1937 P 39 - 41.
100. M. Forrer, Brit. Plast. Year Book 1933 P 68 - 92.
101. A. Schwittmann, Kunstst. 7, 1939 P 190 - 4.
102. L.D. Fishbert, D.C. Longstreet, Mod, Plast. 6, 1969. P 92 - 103.

103. A.D. Sokolov, I.F. Kanavets, Sov. Plast, 3, 1966 P 22 - 6.

104. Van Wazer, et al, Viscosity and Flow Measurement, Interscience, New York, 1963.

105. E.C. Bernhardt, Processing of Thermoplastics Materials. Reinhold Publishing Corporation, 1959.

106. J.R.A. Pearson, Mechanical Principles of Polymer Melt Processing, Pergammon, 1966.

107. B.M. Gershkovich, Sov. Plast. 4, 1971. P 58 - 60.

108. R. Eswaran, et al, Rheol Acta, 12. 1963. P 83 - 91.

109. V.G. Bortinkov, D.R. Shamgunov Sov. Plast. 8, 1971 P 23 - 4.

110. A.S. Perevertoy, et al Sov. Plast. 6, 1970 P 30 - 3.

111. A. Karnis, et al J. Coll & Interface, Sci 22, 1966 P 531 - 55.

112. G.J.P. Dujardin, Kunstst, 6, 1973 P 387 - 390.

113. BS2782, 105C.

114. A.S. Perevertov, et al Sov. Plast. I, 1969 P 68 - 72.

115. D. Hands, RAPRA Tech., Review 60.

116. C.C. McCabe, Soc. of Rheol. Lehigh Univ. 11, 1969.

117. H. Mandler, Plast. Verarbeiter, II, 1970 P 959 - 962.

118. P. Ehrentraut, W. Dalhoff, Kunstst. 6, 1967 P 439 - 446.

119. S.N. Varadhochary, SPEJ 6, 1967 P 99 - 103.

120. K.A. Scott, R.R. Whisson, K.T. Paul, RAPRA B 477,8, 1972.

121. K. König, Plaste u Kaut, 11 1970 P 831 - 836.

122. A.R. Payne, J.R. Scott, Eng. Des. with Rubber, MacLaren.

123. Oscillating Disc Rheometer, Tech. Report, Monsanto 1964.

124. J.R. Dunn, H.R. Bennett, Rubber Age, 10, 1972 P 51 - 54.

125. A.Y. Coran, Rubb, Chem, Tech, 3, 1964 P 689 - 97.

126. A.Y. Coran, Rubb, Chem. Tech, 1, 1965 P 1 - 14.

127. D.A. Hills, Rubb. Journal, 9 1968 P 26 - 34.

128. J.E. Stuckey, M.S. Downing, Rubb. Journal 1, 1969, P 48-55

129. J.D. Ferry, Viscoelastic props, of polym, J, Wiley & Sons Inc. N.Y. 1970.

130. A. Kaye, R. Jackson, Brit. J of Appl Phys, Vol 17, 1966, P 1355 - 60.

131. L.R. Barber, JIRI 6, 1973 P 121 - 123.

132. N. Uri, Brit. Polym. J. 5, 1971 P 138 - 44.

133. N.E. Bassow, et al, Plaste u Kaut, 7, 1972 P 507 - 10.

134. D. Simms, Plastics and Polymers, 12, 1974 P 254 - 259.

135. W.G. Frizelle, D.C. Paulson, Mod. Plast. 8, 1968, P 124.

136. A.S. Perevertov, et al, Sov. Plast. 2, 1971 P 15 - 18.

137. A.S. Lodge, Elastic Liquids, Academic Press, 1964.

Chapter 12

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Chapter 13 Appendix of materials and results.

The detailed experimental results are sub-divided into sections.

1. Materials, a general description of the materials used and the results of standard flow tests (cup flow cure, disc flow and Rossi Peakes flow pressure).
2. Capillary Viscometer.
3. Variable Torque Rheometer.
4. Oscillating Disc Rheometer.
5. Injection Moulding.

1 Materials

The work described in this thesis was carried out over a period of several years and it was necessary to employ different batches of similar materials. The materials used are listed below together with their flow/cure properties determined by standard test methods at 150°C. The main materials were as follows.

Material	Code	Suppliers
Melamine Phenolics	PMF1-4	Resart Gesellschaft MPV Type 182
Phenolic	PF5	Bakelite Xylonite Ltd. X19465/45
Urea Formaldehyde	UF6	BIP Beetle INJX 8255

Many of the secondary evaluation materials were supplied by Bakelite Xylonite Ltd. Material X19471/45 is (PF14) similar to X19465 (PF5, PF13) and both grades are similar to X41/45 (PF11). A series of these materials were obtained in various grades and effectively constitute the bulk of the secondary materials coded PF7, 10, 11, 12, 13, 14, 16 and 17. The tertiary or back-up materials are not identified in detail since they have only been used as general materials.

In order to obtain materials of similar composition but having different degrees of resin precure, standard materials were compounded in the injection machine barrel and air cooled. They were then granulated and the process repeated to give a series of materials of different resin condensation. (PF7A-7E and UF8A-8C).

Specially Prepared Materials PF19

A series of materials were specially prepared with different resin/catalyst systems.

Material PF19	A	B	C	D	E	F	G	H	I	J	K
Resin Type	Novolac						Novolac				Resole
P:F Ratio in Resin	0.8:1						1:1				1:1.5
Parts by Weight											
Resin	20	20	20	20	20	20	20	20.5	20.5	20.5	23.0
Hexamine	2.31	2.31	2.31	2.31	2.31	2.31	2.7	1.92	2.31	2.7	-
Wood Flour	20	20	20	20	20	20	20	20	20	20	20
Calcium Stearate	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
Magnesium Oxide	-	0.33	0.66	0.99	-	-	-	-	-	-	-
Calcium Oxide	-	-	-	-	0.66	-	-	-	-	-	-
Oxalic Acid	-	-	-	-	-	0.66	-	-	-	-	-

Additives dry mixed in small blade mixer (actually the variable torque rheometer). Resin dissolved in IMS to produce 50% solids solution. Resin solution added to mixer and mixed for 15 minutes. Moulding materials dried at room temperature till constant weight. Moulding materials were then stored for 2 months before testing in variable torque rheometer and oscillating disc rheometer.

Material Type	Code	Reinforcement	Cup Flow secs	Cup Cure secs	Disc Flow in x 10^{-3}	Flow Pressure psi	Grade	Notes
Melamine Phenolic	1	Wood Flour	4	21	87	-	Compression)	General purpose materials representing the range of flow properties used for compression, transfer and injection moulding
	2		6-8	50	91	-	Compression/)	
	3		7	60	77	-	Transfer)	
	4		4	90	56	-	Transfer/) Injection) Injection)	
Phenolic	5	Wood Flour	6	50-55	27	300	Injection	Typical general purpose phenolic injection moulding material
Urea Formaldehyde	6	α cellulose	5.2	35-40	135	-	Injection	Typical general purpose urea formaldehyde injection moulding material
Phenolic	7A	Wood Flour				-	Injection)	A range of materials prepared in laboratory by screw compounding a commercial material similar to PF5 to give a range of materials of increasing resin precure.
	B					-	-)	
	C					-	-)	
	D					-	-)	
	E					-	-)	
Urea Formaldehyde	8A	α cellulose				-	Injection)	Similar to above but based on material similar to UF6
	B					-	-)	
	C					-	-)	
Phenolic	9A	Wood Flour	-	45	-	375	Injection)	Materials generally similar to PF5 but differing in having different barrel lives
	B		-	50	-	325	Injection)	
	C		-	53	-	250	Injection)	
	10A	Wood Flour	7	55	28	-	-)	Development materials having a difference in cure rate.
	B		6	50	24	-	-)	
	C		5	45	30	-	-)	
	11A	Wood Flour	8	45	30	250	Injection)	Materials similar to PF5 but having different flow pressures
	B		8	45	31	275	Injection)	
	C		9	45	36	300	Injection)	
	D		9	45	38.5	375	Injection)	Materials similar to PF 11A-D but with different cure rates and flow pressure
	E		9	40	35	375	Injection)	
	F		8	50	32	300	Injection)	
Modified Phenolics	12A	Wood Flour	3.8	45-50	135	-	Injection)	Development materials having a different accelerator addition
	B		3.2	78-80	110	-	Injection)	
	C		3.4	105-110	78	-	Injection)	
Phenolic	13A	Wood Flour	7	50	30	-	Injection)	A series of production batches of the same grade similar to PF5 and representing the scatter of production materials
	B		7	50-55	28	325	Injection)	
	C		7	45-50	30	-	Injection)	
	D		7	50-55	27	225	Injection)	
	E		6	50-55	27	-	Injection)	
	F		6	50	26	300	Injection)	
	G		5	50	27	250	Injection)	
	H		6	50	25	250	Injection)	
	I		6	50	26	250	Injection)	
Phenolic	14A	Wood Flour	6	50	30	300	Injection)	A second series similar to above
	B		5	50	30	275	Injection)	
	C		5	50	31	275	Injection)	
	D		5	50	29	275	Injection)	
	E		6	50-55	29	250	Injection)	
	F		5	50-55	30	300	Injection)	

Material Type	Code	Reinforcement	Cup Flow secs	Cup Cure secs	Disc Flow in x 10^{-3}	Flow Pressure psi	Grade	Notes
Phenolic	15A	Wood Flour	8	-	51	-	Injection	General purpose material similar to PF 5 but from a different supplier.
	B		11	-	65	-	Injection	As above but stiff with reduced flow life.
	C		8	-	47	-	Injection	As above but stiff with extended flow life.
	D		4	-	56	-	Injection	As 15A but different supplier.
	E		11	50	65	-	Injection	As 15A but different supplier, easy flow with a long flow life.
	F		8	50	51	-	Injection	As above but with a shorter flow life and faster cure.
	G		10	45-50	110	-	Injection	As above but stiffer flow
Phenolic	16	Wood Flour	-	-	-	-	-	Material PF5 ball milled and blended with various lubricants etc.
Phenolic	17A	Asbestos	8	55-60	37	-	Injection	Asbestos fibre
	B	Glass	9	55-60	26	-	Injection	Glass fibre/mineral filled
Phenolic	18A	Wood/Mica	9.9	50-55	121		Compression)	Production batches of commercial materials, general purpose/electrical grade.
	B		9.1	50-55	125		)	
	C		10.0	50-55	131		)	
	D		9.8	50-55	130		)	
	E		10.0	50-55	125		)	
Phenolic*	19	Wood Flour	-	-	-	-	-	Laboratory prepared materials
Modified Phenolic	20A	Wood Flour	3.2	75-80	110		-)	Development materials
	B		3.6	65-70	83		-)	
	C		2.8	65-70	100		-)	
Urea Formaldehyde	21A		5	-	130		Compression)	Various examples of commercial materials from various suppliers.
	B	Wood Flour	6	-	109		Compression)	
	C	Wood Flour	9	-	175		Compression)	
	D	α cellulose	12	-	185		Compression)	
	E	α cellulose	-	29	61		Injection))	Low injection pressure and long flow life
	F		-	17	88		Injection/) Transfer)	Similar to above but stiffer with shorter flow life.
	G		-	34	110		Injection)	Long flow life with good flowability
	H		-	22	85		Injection/) Transfer)	Stiff medium flow life
	I		-	-	-		)	
	J		-	-	61		Injection)	
	K		-	-	68		Injection)	
Urea Formaldehyde	22A	α cellulose					Compression)	Various examples of commercial materials from various suppliers
	B	" "	6.1	30-32	166		Injection/) Transfer)	
	C	" "	6.9	25-30	185		Compression)	
	D	" "	71.1	45-50	141		)	
	E	" "	7.5	30-35	165		Injection)	
	F	" "	5.2	35-40	135		)	
	G	" "	7.0	35-40	135		Injection)	
	H	" "	-	-	-		Compression)	
	I	α cellulose	10.0	55-60	44	-	Injection	General purpose
	J	α cellulose	-	55-60	47	-	Injection	General purpose
Diayandiamide Formaldehyde	23A	Wood Flour	9	-	90	-	Injection	
	23B	" "	-	-	87	-	Injection	
Melamine Formaldehyde	24A	α cellulose	9.8	60-65	95	-	Injection	
	B	" "	6.3	77-80	94	-	" /Transfer	
	C	Wood Flour	-	-	82	-	Injection	
	D	α cellulose	9.9	70	66	-	Injection	
	E	Glass	10.0	60	75	-	Injection	

2 Capillary Viscometer

The results given in this section were obtained using the capillary viscometer with plasticized material from the injection moulding barrel, the capillary viscometer with heated, sintered powder and with the instrumented injection moulding machine set to produce air shots and mouldings.

Three injection moulding machines were used for this work. Details of the machines and machine conditions used will be found in the section dealing with injection moulding. (Chapter 7).

The capillary viscometer used for this work was built specifically for the purpose and is described in Chapter 4.

Viscosity Measurements, Capillary Viscometer
Phenolic Material PF5

Set Pressure	Mean Pressure psi	Distance	Time secs	Total Distance	Shot Weight grms.	Temp. °C
Nozzle Diameter 1/8" 5:1 L:D						
25%	9,960	6.06	5.83	10.2	104.1	86.5
50%	11,015	4.23	2.12	10.2	104.9	92.9
75%	10,940	4.27	1.89	10.2	104.8	93.5
100%	10,875	4.37	2.16	10.2	104.7	93.7
Nozzle Diameter 3/16" 5:1 L:D						
25%	10,600	5.0	4.76	10.2	105.1	87.2
50%	10,800	6.4	2.07	10.2	105.3	88.9
75%	11,500	5.53	1.41	10.2	105.2	90.1
100%	11,680	5.38	1.41	10.2	105.3	91.2
Nozzle Diameter ¼" 5:1 L:D						
25%	6,450	5.41	4.87	10.18	105.3	81.1
50%	8,170	5.30	1.66	10.15	105.2	85.2
75%	8,420	5.59	1.04	10.15	105.2	88.1
100%	8,590	5.76	1.13	10.15	105.2	89.0
Nozzle Diameter 3/16" 10:1 L:D						
25%	10,510	5.32	2.33	10.15	103.2	88.9
50%	11,700	4.05	2.2	10.15	104.3	91.5
75%	11,800	4.32	2.25	10.15	104.9	92.9
100%	11,070	3.84	3.98	10.15	105.0	94.2
Nozzle Diameter ¼" 10:1 L:D						
25%	12,125	5.14	5.21	10.2	104.4	87.5
50%	12,743	5.45	2.25	10.2	104.8	91.2
75%	13,077	5.23	1.84	10.2	104.9	92.3
100%	13,080	5.00	1.54	10.2	104.9	93.0
Nozzle Diameter ¼" 15:1 L:D						
25%	11,500	6.4	5.9	8.9	95.8	93.5
50%	11,900	5.9	2.4	8.8	97.5	93.5
75%	12,300	5.5	3.1	8.75	97.2	92.5
100%	12,400	6.7	3.9	8.85	97.0	92.0

Viscosity Measurements CAPILLARY VISCOMETER Phenolic Material PF5

Results of Two Plateau Traces

PRESSURE psi			DISTANCE cms			TIME secs			SHOT	
PEAK	1ST *	2ND *	1ST *	2ND *	TOTAL	1ST*	2ND*	TOTAL	WEIGHT grams.	Temp. °C
12,200 13,505 14,700	4,200 4,831 5,700	3,600 3,694 4,250	0.45 0.51 0.65	2.40 2.50 3.15	5.61 5.61 5.61	0.45 0.58 0.70	1.05 2.33 3.05	5.4 5.56 5.6	59.560 60.529 60.700	89.2°C
12,600 14,045 14,800	4,900 5,675 5,800	4,600 4,785 4,800	0.35 0.54 0.85	2.15 2.29 2.40	5.75 5.75 5.75	0.25 0.27 0.35	0.82 0.84 0.90	2.02 2.03 2.08	61.42 61.759 64.42	89.2°C
13,500 14,685 15,300	5,700 6,275 7,000	4,300 5,230 5,400	0.25 0.41 0.45	1.75 1.84 1.85	5.75 5.75 5.75	0.10 0.19 0.25	0.50 0.54 0.58	1.10 1.28 1.30	61.59 61.624 61.740	89.2°C
13,900 14,835 15,400	5,900 6,385 6,700	5,300 5,490 5,600	0.35 0.36 0.45	1.85 1.85 1.85	5.75 5.73 5.75	0.17 0.23 0.39	0.47 0.60 0.64	1.30 1.31 1.40	61.900 61.727 61.120	89.2°C
15,400 15,030 14,800	6,450 6,665 7,100	5,650 6,085 6,400	1.00 1.08 1.15	2.80 2.73 3.05	6.0 6,10 6.15	1.20 1.60 2.02	2.85 3.17 3.70	6.05 6.33 6.60	60.240 60.544 60.806	89.2°C
14,900 15,140 15,300	7,400 7,600 8,400	6,550 7,000 7,200	0.80 0.88 1.00	2.65 2.75 3.00	5.95 6.09 6.10	0.72 0.83 1.00	1.35 1.46 1.75	2.45 2.58 2.77	61.208 61.307 61.820	89.2°C
15,100 15,295 15,400	7,550 7,800 8,300	7,300 7,345 7,650	0.55 0.64 0.70	2.50 2.86 3.05	6.10 6.10 6.10	0.75 0.63 0.55	1.22 1.32 1.57	2.12 2.25 2.45	62.043 62.456 62.705	89.2°C
15.450 15,260 15,400	7.800 8,175 8,500	7.100 7,465 7,600	0.45 0.64 0.75	3.00 3.05 3.15	6.10 6.10 6.10	0.45 0.56 0.55	1.17 1.27 1.37	2.07 2.15 2.25	63.040 63.287 63.987	89.2°C

* See Fig. 36

Comparison of Injection Moulding Materials Phenolics

Material Phenolic PF13	Instrumented Nozzle			Capillary Viscometer							
	Pressure	Temp.	Flow Time	Pressure 1	Pressure 2	Temp.	Screw Displ.		Inj. Time		Shot Weight
							1	2	1	2	
	psi	°C	secs	psi	psi	°C	cm	cm	secs	secs	grams
A	4,145	89.0	2.65	14,000	10,950	86.1	4.1	3.3	3.5	1.13	95.3
B	4,085	87.8	2.39	13,220	10,960	86.3	4.1	3.4	2.6	1.08	96,6
C	3,765	87.0	2.53	14,095	11,675	83.5	4.3	2.9	4.1	1.29	94.2
D	4,456	86.7	3.16	14,178	11,214	85.5	4.2	2.6	3.8	0.94	91.8
E	4,085	87.8	2.39	13,220	10,960	86.3	4.1	3.4	2.6	1.08	96.6
F	4,115	83.6	2.46	13,795	11,060	84.0	3.9	3.5	3.5	1.36	95.3

Results of air shot flow experiments with Phenolic material in Turner 60g and 120g machines.

Set Hydraulic Pressure	Stroke Efficiency	Recorded Hydraulic Pressure		Stroke Length	Stroke Time	Melt Temp.		Tip Temp.		Shot Weight	Injection Pressure	
psi	%	psi		cm	secs.	°C		°C		grams	psi	
		Max.	Min.			Max.	Min.	Max.	Min.		Max.	Min.
						Turner 4oz Machine Nozzle L:D 1:1						
800	79.0	1060 1060	900 900	5.045 4.95	7.05 7.5	96.2 97.0	95.6 96.0	95.8 96.0	92.0 93.0	82.58 86.12	3970 4100	2105 2130
		1060	900	5.10	6.3	95.5	94.5	95.5	91.0	80.78	3750	2100
1000	78.7	1270 1270	1000 1000	5.13 5.05	4.06 4.5	96.9 97.0	96.2 96.5	95.3 96.5	91.2 91.5	83.24 84.56	4685 4900	2300 2400
		1270	1000	5.20	3.7	96.5	96.0	95.0	90.0	81.66	4200	2200
1200	81.5	1430 1430	1110 1110	5.1 5.25	2.24 2.3	96.6 97.0	96.0 96.5	94.8 96.0	90.8 92.0	85.21 86.89	5440 5500	2450 2500
		1430	1110	5.10	2.1	96.0	95.5	94.0	91.0	82.87	5350	2300
1400	78.0	1640 1640	1220 1220	5.24 5.30	1.5 2.0	95.5 96.0	95.1 96.0	93.5 94.5	90.0 90.5	84.70 85.37	5985 6200	2465 2550
		1640	1220	5.20	1.3	94.5	94.5	93.0	89.5	83.67	5700	2350
1600	77.0	1750 1750	1160 1160	5.29 5.35	1.27 1.3	94.5 94.5	94.5 94.5	90.9 91.5	88.6 89.5	84.18 85.60	6660 6750	2310 2500
		1750	1160	5.25	1.2	94.5	94.5	90.5	88.0	83.31	6600	2250
1800	77.0	1960 1961	1110 1110	5.27 5.30	1.06 1.1	94.5 94.5	94.5 94.5	90.5 90.5	88.1 88.5	83.53 84.71	7380 7450	2315 2450
		1960	1110	5.25	1.0	94.5	94.5	90.5	88.0	82.36	7200	2200
						Turner 4oz Machine Nozzle L:D 10:1						
1000	55,2	1210 1210	1110 1110	5.35 5.40	18.9 23.0	93.6 94.0	93.2 94.5	93.3 95.0	90.4 92.5	61.25 64.74	6020 6200	3930 4800
		1210	1110	5.35	14.2	92.5	93.0	91.5	87.0	58.38	5900	2600
1200	65.2	1380 1380	1210 1210	5.38 5.40	5.58 8.4	95.0 95.0	94.8 95.0	95.1 95.5	91.6 93.0	73.06 77.05	6600 6900	4235 4350
		1380	1210	5.35	4.3	95.0	94.5	93.0	91.0	65.96	6250	4215
1400	68.5	1590 1590	1310 1310	5.40 5.40	3.13 3.5	95.0 95.0	95.0 95.0	94.4 94.5	91.1 91.5	76.97 79.28	7550 7600	4080 4150
		1590	1310	5.35	2.8	95.0	95.0	93.5	90.5	75.16	6900	4000
1600	64.9	1900 1900	1450 1450	5.41 5.45	2.19 2.4	95.0 95.0	95.0 95.0	92.8 94.0	89.4 90.3	74.94 77.79	8865 9600	3990 4100
		1900	1450	5.40	2.0	95.0	95.0	92.0	88.0	68.46	8450	3750
1800	66.7	2020 2020	1430 1430	5.42 5.35	1.93 2.1	95.0 95.0	95.0 95.0	90.5 92.5	87.2 88.5	74.60 77.75	9800 10100	3820 3900
		2020	1430	5.45	1.8	95.0	95.0	90.0	86.5	71.69	8600	3700
						Turner 2oz Machine Nozzle L:D 1:1						
800	74.0	850 850	580 580	6.1 6.1	5.2 5.2	91.1 92.0	90.2 91.0	89.8 90.0	86.1 86.1	78.18 78.29	5300 5300	2635 2670
		850	580	6.1	5.1	90.5	89.5	89.5	85.5	77.63	5200	2600
1000	75.0	1030 1030	630 630	6.1 6.1	4.18 4.3	91.7 92.0	90.7 91.0	89.3 90.0	85.6 86.0	79.22 79.56	5850 5900	2650 2650
		1030	630	6.1	4.1	91.5	90.5	87.0	84.5	78.61	5750	2650
1200	76.0	1140 1140	680 680	6.1 6.1	3.11 3.2	91.3 92.0	90.7 91.0	88.3 89.0	85.1 88.0	80.37 80.60	6755 6800	2715 2720
		1140	680	6.1	3.1	91.0	90.5	87.5	81.5	80.10	6750	2700
1400	76.5	1350 1350	680 680	6.1 6.1	2.52 2.7	90.6 91.0	90.0 90.0	88.5 88.5	85.3 85.5	81.15 81.64	7250 7300	2780 2800
		1350	680	6.1	2.5	90.5	90.0	88.5	85.0	80.97	7200	2720
1600	77.0	1510 1510	680 680	6.1 6.1	2.2 2.2	90.4 90.5	90.0 90.0	87.8 88.0	84.8 85.5	81.26 81.58	7800 7900	2800 2850
		1510	680	6.1	2.2	90.0	90.0	87.5	84.0	80.97	7650	2800
1800	76.5	1710 1710	680 680	6.1 6.1	1.9 1.9	90.5 90.5	90.0 90.0	87.2 87.5	84.4 84.5	81.49 81.5	8425 8600	2825 2900
		1710	680		1.9	90.5	90.0	87.0	84.0	81.1	8300	2800
						Turner 2oz Machine Nozzle L:D 10:1						
1000	71.2	1060 1060	800 840	6.05 6.05	5.96 6.5	89.9 91.5	89.1 90.5	Results not available		75.06 76.06	8370 8600	4410 4430
		1060	840	6.05	5.7	88.0	87.5			74.04	8250	4250
1200	72.0	1220 1220	840 840	6.05 6.05	4.25 4.4	93.1 93.5	92.0 92.5			76.61 77.54	8900 8950	4440 4500
		1220	840	6.05	4.1	92.5	91.0			74.68	8850	4400
1400	72.5	1320 1320	840 840	6.1 6.10	3.38 3.5	93.5 93.5	93.0 93.0			76.33 77.11	9940 10000	4440 4500
		1320	840	6.10	3.3	93.5	93.0			75.91	9800	4400
1600	73.2	1480 1480	740 740	6.1 6.10	2.78 2.8	93.4 93.5	93.0 93.0			77.05 77.9	10870	4410 4450
											11000	
		1480	740	6.10	2.7	93.0				76.53	10700	4350
1800	73.5	1700 1700	740 740	6.1 6.10	2.41 2.5	93.0 93.0	92.6 93.0			77.72 79.19	12030	4390 4450
											12100	
		1700	740	6.10	2.4	93.0	92.5			77.02	11900	4350

Extended Injection Nozzle with pressure sensors in capillary

Turner 60g machine

Pressure psi			Flow Rate g/sec
Nozzle	Capillary 1	Capillary 2	
	Phenolic PF 11F		
8200	7500	3800	14.1
8200	7400	3950	17.2
9400	8000	4400	27.4
10600	8800	4700	32.0
12100	10000	5200	44
12800	11800	5760	53
13000	12100	6300	60
13000	12500	6600	66
	Urea UF 22I		
3600	1800	-	3.8
4000	2050	270	10.0
4600	2300	290	14.0
5900	2800	340	30.8
7000	3500	400	49.8
7400	6000	550	61.0
7600	7600	600	95.2

Viscosity Measurements, Instrumented Nozzle, Turner Machine

Material Phenolic PF5

Hydraulic Pressure psi	Shot Weight grams		Total Stroke		Inject. Time secs		Melt Pressure max psi		Melt Pressure min psi		Melt Temp. °C		Tip Temp. at start of stroke °C		Tip Temp. at end of stroke °C	
400	70.80	70.2 71.2	7.6	7.45 7.8	11.9	10.8 12.45	3090	3000 3200	2550	2500 2600	90.0	90.0 90.0	88.4	87.0 89.0	93.0	92.5 94.0
500	73.00	71.63 74.70	7.4	7.3 7.5	6.8	5.4 7.8	3950	4000 3800	2670	2600 2600	90.8	89.0 90.0	84.0	81.5 89.0	88.4	87.0 89.0
600	74.00	73.02 74.48	7.3	7.2 7.4	3.36	3.2 3.6	4220	4100 4300	2750	2700 2800	90.3	90.0 91.0	84.8	83.5 85.5	90.2	90.0 91.0
700	75.00	74.18 75.47	7.21	7.2 7.25	2.42	2.2 2.65	4550	4500 4600	2800	2800 2800	89.0	89.0 89.0	87.0	87.0 87.0	92.3	91.0 92.5
800	75.30	75.1 75.4	7.19	7.15 7.2	1.96	1.9 2.0	5220	5200 5250	2920	2800 3000	89.6	89.0 90.0	87.0	87.0 87.0	90.0	90.0 90.0
900	77.2	76.62 77.75	7.18	7.1 7.2	1.58	1.53 1.65	5640	5600 5650	2800	2800 2800	90.0	90.0 90.0	87.0	87.0 87.0	90.0	90.0 90.0
			Nozzle dia. 0.25"				L:D		1:1							
400	57.1	50.71 61.19	7.15	6.4 7.45	26.0	19.8 30.2	3760	3800 3700	3180	3200 3100	93	-	90.5		92	-
500	65.5	63.45 67.75	7.05	6.5 7.2	7.65	6.8 9.4	4210	4350 4050	3220	3250 3100	92.4	92.0 92.5	90.5	-	94.9	94.5 95.0
600	69.2	69.7	6.98	6.9 7.0	5.42	4.8 6.6	4650	4800 4500	3250	3200 3350	92.6	92.5 93.0	90.0	-	94.4	94.0 95.0
700	73.5	71.43 75.38	6.84	6.8 7.0	3.05	2.8 4.0	5380	5400 5300	3340	3550 3250	92.8	92.5 93.0	91	-	94.8	94.5 95.0
800	75.00	73.00 78.05	6.8	6.75 6.85	2.45	2.2 2.64	5630	5600 5700	3270	3300 3200	95.0	92.5 95.5	91	-	93	92.5 94.0
900	77.58	76.34 79.42	6.7	6.6 6.9	1.71	1.6 1.8	6180	6000 6300	3400	3400 3400	92.8	92.5 93.0	91	-	95	-
			Nozzle dia. 0.25"				L:D		5:1							
400	No satisfactory results															
500	56.8	50.46 58.86	7.3	7.1 7.6	16.3	14.0 20.0	4600	4650 4450	4000	4050 3950	93.0	93 93	89	-	91.1	90 92
600	59.1	56.74 62.28	7.05	7.0 7.1	7.7	6.4 8.0	5240	5400 5060	4050	4200 4100	95.0	95 95	90	-	92.0	91 92.5
700	67.4	64.90 70.42	7.03	6.8 7.1	4.34	3.6 5.8	6250	6130 6300	4360	4550 4200	95.4	95.0 95.5	95.5	-	92.0	91.5 92.5
800	71.3	70.53 71.94	6.9	6.8 7.0	3.38	3.1 4.03	6610	6400 6800	4320	4300 4400	95.5	95.5 95.5	95.0	-	91.0	90.0 92.5
900	73.0	71.11 74.62	6.9	6.8 7.0	2.43	1.9 2.8	7400	7600 7030	4060	4000 4100	95.7	95.5 96.0	87.1	-	89.5	89.0 90.5
			Nozzle dia. 0.25"				L:D'		10:1							

Hydraulic Pressure psi	Shot Weight grams		Total Stroke		Inject. Time secs		Melt Pressure max psi		Melt Pressure min psi		Melt Temp. °C		Tip Temp. at start of stroke °C		Tip Temp. at end of stroke °C	
400	69.0	67.9 72.6	7.1	7.0 7.2	10.6	8.6 14.5	2890	2950 2600	2240	2300 2100	94.7	94 95	86	-	90.8	90 91
500	71.8	70.7 72.62	7.05	7.0 7.35	4.52	4.0 4.8	3250	3400 3200	2260	2000 2450	95.0	92.5 97	86	-	90	90 90
600	76.0	75.05 77.3	7.0	6.9 7.0	3.24	2.9 3.8	3720	3800 3600	2400	2400 2400	94.1	94.0 94.5	86.5	-	90.5	90 91
700	79.8	79.58 76.52	6.9	6.6 7.15	2.7	2.15 2.9	4240	4350 4000	2750	3000 2500	92.8	92.5 93.0	86.5	-	91.0	90.0 91.1
800	79.2	79.15 80.47	6.91	6.9 7.0	1.65	1.2 1.83	4810	5000 4650	2750	2800 2700	94.7	94.5 95.0	86.5	-	90	89.5 90.0
900	80.0	79.03 81.77	6.82	6.7 7.05	1.48	1.4 1.6	5420	5700 5400	2350	2200 2750	94.8	94.5 95.0	85.75	-	89.9	89.5 90.0
			Nozzle dia. 0.188"				L:D		1:1							

NB. 1st figure shows mean of 5 - 10 determinations.
2nd figure shows max. and min. results.

Set Hydraulic Pressure	Stroke Efficiency	Stroke Length	Stroke Time	Melt Temp.	Shot Weight	Injection Pressure		
Kg/cm^2	%	psi	secs.	°C	grams	Initial Peak	Min.	Final Pe
					Bipel 3oz Machine Nozzle L:D $^1/_5$:1			
20	76.5	3.25	9.44 9.1 9.9	9.26 92.0 93.5	92.67 92.26 92.740	4300 4300 4300	2800 2800 2800	3700 3700 3700
30	79.5	3.25	3.07 2.7 3.5	94.0 93.5 95.0	95.58 94.8 98.08	5730 5500 6100	3350 3200 3600	5210 5100 5300
50	82.0	3.25	1.01 1.1 1.0	95.35 95.0 96.0	98.43 97.720 99.140	6520 6400 7400	4060 4000 4400	7880 7700 8200
70	82.5	3.25	0.67 0.60 0.70	96.4 96.0 97.0	99.79 96.64 100.620	6190 5100 6400	4580 4500 4600	9100 9000 9200
90	84.0	3.25	0.60 0.60 0.60	97.3 97.0 97.5	101.44 91.400 104.700	5800 5700 5900	4600 4500 4700	9350 9200 9700
					Bipel 3oz Machine Nozzle L:D 1:1			
20	74.0	3.25	12.12 11.9 12.6	91.8 91.0 92.5	89.11 88.44 89.500	4000 4000 4000	2780 2700 2800	3670 3700 3900
30	75.2	3.25	4.3 4.41 5.0	93.9 93.0 95.0	90.67 89.400 91.440	5500 5400 5700	3350 3300 3400	5220 5200 5300
50	77.5	3.25	1.12 1.1 1.2	95.8 95.0 97.0	93.35 92.89 95.26	6830 6600 7600	4200 4100 4500	8320 8200 8400
70	80.5	3.25	0.70 0.70 0.70	97.8 97.0 98.0	96.68 95.161 97.960	6420 6100 6900	4650 4600 5000	9940 9700 10200
90	82.5	3.25	0.60 0.60 0.60	98.4 98.0 98.5	99.27 98.380 99.890	6020 5800 6400	4820 4700 5000	9830 9600 10100
					Bipel 3oz Machine Nozzle L:D 5:1			
30	71.0	3.25	9.8 8.6 10.4	94.15 93. 95	86.48 84.42 87.72	6800 6800 6800	4330 4200 4600	5620 5500 5700
50	75.8	3.25	1.63 1.5 2.0	97.01 95.5 98.0	91.61 91.100 91.948	10490 10700 10400	5460 5400 5600	8670 8600 8700
70	77.5	3.25	0.79 0.70 0.80	99.3 98.500 100.5	93.43 91.82 93.826	12860 12400 13300	4670 4000 5100	10470 10200 10700
90	77.8	3.25	0.8 0.80 0.80	100.7 100.9 100.5	93.66 93.320 94.188	12650 12600 12800	5460 4900 5600	10920 10300 11200
					Bipel 3oz Machine Nozzle L:D 10:1			
50	73.5	3.25	2.46 2.3 2.7	98.55 98.0 99.5	88.24 87.942 88.602	10650 10600 10700	6060 6000 6100	8820 9000 8800
70	75.1	3.25	0.91 0.90 1.0	100.8 100 101	90.34 91.82 98.5	14010 14000 13800	6150 6400 5800	1280 11500 11100
90	76	3.25	0.70 0.70 0.70	101.45 101.0 101.5	91.48 91.26 92.144	15400 15300 15500	6180 6200 6400	1860 11700 11900

Results of air shot flow experiments,
Phenolic material with Bipel machine above,
Melamine MF24E with Turner machine below left,
Various materials with Turner machine below right.

Nozzle Pressure/flow rate results
for Melamine MF 24E Turner 60g machine

Screw Speed RPM	Back Pressure psi	Set Hydraulic Pressure psi	Nozzle Pressure psi	Flow Rate g/sec
80	set zero	300	5480	10.8
		500	9700	73.0
		750	10700	125.0
		1000	10600	125.0
		1500	10850	128.0
100	50	300	7500	26.5
		750	9900	110.0
		1500	9900	118.0
120	100	300	7000	46.7
		500	8800	105
		750	8550	124
		1000	8550	119
		1500	9100	127
		1900	8100	103

Barrel Temp. 95°C
Cycle Time 35 secs

Relationship between pressure and flow rate
Turner 60g machine

Nozzle Pressure MN/m^2	Flow Rate g/sec.	Nozzle Pressure MN/m^2	Flow Rate g/sec.
Phenolic PF 11F		Urea UF 22I	
1.9	1.0	46.0	26.5
2.0	2.0	70.1	70.1
7.8	4.3	76.3	94.8
17.0	12.5		
21.0	27.0	Urea UF 22J	
29.5	88.3		
30.0	90.7	51.9	12.8
29.0	98.2	52.0	26.2
		63.8	74.3
Phenolic PF 17A		73.1	94.8
25.2	15.0	Melamine MF 24E	
31.5	69.5	37.6	18.2
43.0	145.0	56.1	51.8
51.0	219.0	74.2	124.9
Phenolic PF 17B			
32.4	19.2		
46.1	65.0		
56.0	130.1		

mparison of Phenolics using Instrumented Nozzle Technique

t Hydraulic Pressure	Pressure (psi) 1	2	Nozzle Temp°C	Total Dist cm	Total Time secs	Shot Weight (grams)	Average Output Rate Grams/Sec
terial PF13A							
30	8,155	8,425	90.0	7.62 7.62	4.55	97.457	21.4
50	10,230	13,025	92.4	7.60	1.487	99.571	71.0
70	9,355	14,656	94.0	7.60	6.752	100.974	145.5
90	9,790	15,605	95.5	7.60	0.632	101.086	175.0
terial PF13B							
30	8,130	7,960	88.5	7.60	5.120	96.786	18.8
50	9,320	12,830	90.0	7.60	1:59	99.079	62.7
70	9,450	10,625	92.30	7.60	0.200	100.728	135.0
90	9,250	16,030	93.5	7.60	0.652	101.298	173.8
terial PF13B							
30	8,535	8,415	88.75	7.60	4.715	96.165	21.9
50	10,020	13,110	93.80	7.60	1.425	98.709	68.7
70	9,680	15,550	96.72	7.60	0.746	100.225	137.5
90	9,550	10,010	98.75	7.60	0.62	100.636	172.5

terial PF13D

t Hydraulic Pressure	Pressure (psi) 1	2	Nozzle Temp °C	Total Dist cm	Total Time sec	Shot Weight (grams)	Average Output Rate Grams/Sec
30	7,410	8,026	90.75	7.6	3.65	98.530	29.4
50	9,245	12,350	90.0	7.6	1.25	99.884	78.0
70	8,805	14,965	91.5	7.6	0.749	101.503	137.2
90	9,870	15,410	92.0	7.6	0.605	101.656	163.5
terial PF13E							
30	7,010	7,435	96.0	7.6	3·46	98.743	28.5
50	8,080	12,505	92.72	7.6	1·28	100.570	22.5
70	8,795	15,415	9.35	7.6	0.734	101.605	157.0
90	9,560	15,895	93.5	7.6	0.695	101.639	168.0
terial PF13F							
30	7,725	7,735	94.9	7.6	4.94	96.631	19.6
50	9,375	13,120	95.0	7.6	1.45	99.416	68.5
70	8,965	15,735	96.5	7.6	0.779	101.122	143.5
90	9,325	15,935	97.5	7.6	0.637	101.584	179.0

Set Hydraulic Press Kg/cm²	Shot Weight grams	Inject Time secs.	Melt Pressure psi	Melt Temp °C	Flow Rate g/sec.
50	87.0	4.78	9350	92.0	18.2
70	86.0	1.92	11550	92.1	44.8
90	86.02	1.1	12650	92.8	78.2
	Nozzle dia.	0.25"	L:D	5:1	
50	85.82	9.13	10650	92.0	9.4
70	86.0	4.0	14010	92.3	21.5
90	86.04	1.8	15400	92.5	47.8
Nozzle 3/16" dia.	Nozzle dia.	0.25"	L:D	10:1	
90 Kg/cm² 10:1	85.84	7.4	14575	93.0	11.6
5:1	85.88	4.52	12375	92.2	19.0
1:1	86.04	3.6	11000	91.8	23.9

Viscosity Measurements,
Instrumented Nozzle,

Bipel Machine,
Urea Formaldehyde UF6

3 Variable Torque Rheometer

The results given in this section were obtained using the following standard experimental conditions unless other conditions are specified.

Rotor speed (fast rotor)	30 r.p.m.
Temperature	85-88°C
Ram Pressure	40 p.s.i.
Charge weight (S.G. 1.3)	50 grams

Where the powder density of a material varied significantly from 1.3 g/ml, the charge weight was adjusted to give a constant melt volume.

The results given refer to the minimum torque value. The flow life referred to is the final peak torque value for all materials except for phenolics where the gel time or trace change point is recorded (see text). Where the peak torque value is available it is quoted as "peak torque". The temperature increase refers to the difference between the set temperature of the chamber and the final temperature at the flow life readings.

Except where the information has been used for graphical purposes, all results are the mean of 2 or 3 determinations, typical standard deviations are quoted in the text and also below.

Variabke torque rheometer, reproducibilty of results.

Minimum Torque Point									Final Peak Torque Point								
Time			Torque			Temperature			Time			Torque			Temperature		
	s.d	V	n	s.d	V	n	s.d	V	n	s.d	V	n	s.d	V	n	s.d	V
0	7.8	3.2	20	.41	.008	20	2.0	0.2	20	4.3	97.0	20	.51	.014	20	3.0	.47
3	11.6	11.2	13	.41	.014	13	2.8	0.65	13	15.4	19.8	13	.32	.004	13	3.1	.8
5	19	25.8	15	.25	.06	15	1.9	0.26	15	31	69	15	.20	.003	15	2.2	.35
3	16	20	13	.41	.014	13	2.3	0.44	13	28	65	13	.29	.007	13	1.9	.3
3	5.1	20	13	.16	.002	13	1.9	0.3	7	17.4	50	7	.24	.01	7	1.2	.21
3	12	12	13	.21	.004	13	2.0	0.33	7	10.2	17.4	7	.15	.004	7	1.5	.38
9	10	5.6	19	.25	.003	19	1.9	0.2	19	17.9	17.3	19	.28	.004	19	1.5	.13

n = number of test results used to calculate standard deviation

s.d = standard deviation

V = variance defined $\frac{sd^2}{n}$

Feasibility Test Materials

Melamine Phenolics

Material	PMF	1 →				2 →			
Temperature	°C	80	125	140	160	80	125	140	160
Min. Torque	NM	65	47	51	48	53	51	35	26
Flow Time	secs	308	125	70	80	273	110	40	65
Temp. Increase	°C	9	6	1	1	11.5	6.0	1	1
Material	PMF	3 →				4 →			
Temperature	°C	80	125	140	160	80	125	140	160
Min. Torque	NM	42	60	50	48	38	38	30	27
Flow Time	secs	467	193	100	85	1085	160	175	135
Temp. Increase	°C	9	6	1	1	9.5	2	1	1

Primary Evaluation Materials

Effect of Rotor Speed on Variable Torque Rheometer Results.

Rotor Speed RPM	Torque NM	Flow Time secs. Change Pt	Peak	Temp. Increase °C
Phenolic PF5				
20	29	630	980	6
30	30	350	480	5
40	25	220	350	6½
50	24.5	185	250	9
80	24	110	160	9½
90	23	90	-	11
100	24	70	-	11
120	22	50	-	11½
Urea Formaldehyde UF6				
20	25	-	365	7½
30	27.5	-	302	8½
45	28	-	190	9
60	27	-	160	11
80	26	-	120	10
100	26	-	100	13
115	25	-	73	10
120	24	-	65	13
130	23		60	14½

Effect of temperature on Variable Torque Rheometer results.

Temperature	Torque NM	Flow Time secs.	Temp. Increase °C
Phenolic PF 5			
80	30	252	5
100	23	182	4
130	17	127	3
150	12	66	3
170	8	41	0
Urea Formaldehyde UF6			
80	28	486	8½
100	29	245	4
130	18	166	4
150	13	71	2
170	20	21	1

Secondary Evaluation Materials

Material PF7	A	B	C	D	E	F	G	H	I
Temperature °C	88 →								→
Min. Torque NM	19	25	32	45	52	23	24	23	24
Flow Time secs	290	232	174	110	75	274	275	270	268
Temp. Increase °C	6	6	10	10	12	7	8½	9	6
Peak Time secs	-	-	-	-	-	478	483	473	480
Material UF8	A →			B →			C →		
Temperature °C	88	125	150	88	125	150	88	125	150
Min. Torque NM	35	21	12	38	34	15	39	26	25
Flow Time secs	986	403	251	350	213	122	260	160	160
Temp. Increase °C	7	4½	5½	8	5½	2½	7	6	2

Material PF9 Temperature °C		76	88	96	118	150
		A →				
Min. Torque	NM	30	26	21	19	8
Flow Time	secs	15000	287	220	155	60
Temp. Increase	°C	4	3	4	3	1
Material	PF9	B →				
Min. Torque	NM	30	22	18	14	8
Flow Time	secs	12800	313	254	167	58
Temp. Increase	°C	4	3	4	3	0
Material	PF9	C →				
Min. Torque	NM	28	22	17	12	8
Flow Time	secs	14000	374	293	187	60
Temp. Increase	°C	3	3	4	3	0
Temperature	°C	30	100	120	145	

	76	88	96	118
PF10	A →			
	36	24	19	7
	340	175	125	58
	6	2	1	-
PF10	B →			
	33	22	15	8
	197	128	100	50
	6	1	2	0
PF10	C →			
	41	27	22	8
	138	102	80	43
	7	1	2	-

Material	PF11	A	B	C	D	E	F
Temperature	°C	80 →					
Min. Torque	NM	22	24	28	21	19	17
Flow Time	secs	337	386	299	281	276	318
Temp. Increase	°C	4	4	5	4	3	4
Material	PF12	A →					
Temperature	°C	88	125	150			
Min. Torque	NM	58	50	28			
Flow Time	secs	210	280	>15000			
Temp. Increase	°C	11	11	13			
Init. Cure Rate	NM/sec	227	83	19			
Material	PF12	B →					
Min. Torque	NM	29	23	7			
Flow Time	secs	90	240	370			
Temp. Increase	°C	11	10	14			
Init. Cure Rate	NM/sec	430	220	106			
Material	PF12	C →					
Min. Torque	NM	20	13	4			
Flow Time	secs	45	80	210			
Temp. Increase	°C	12	12	16			
Init. Cure Rate	NM/sec	970	330	330			

Tertiary or Back-up Materials

	Comparison of Materials				Variable Torque Rheometer					Phenolic PF14					
Phenolic PF13	A	B	C	D	E	F	G	H	I	A	B	C	D	E	F
Temperature °C	88 →									88 →					
Min. Torque NM	27	23	24	21	22	21	20	19	18	21	22	23	20	20	22
Flow Time secs	238	271	263	287	360	350	368	340	370	360	345	315	345	345	330
Temp. Increase °C	8	7½	7	7	8	7	7	6	6½	4	4	3.5	3.8	4	3.8
Peak Time secs	422	478	400	490											

Material	15	A	B	C	D	E	F	G
Temperature	°C	88						
Min. Torque	NM	32	44	38	24	18	28	68
Flow Time	secs	240	160	260	215	350	280	298
Peak Time	secs	420	340	560	450	580	405	-
Temp. Increase	°C	10.5	11	14	9	10	12	11
Temperature	°C	125 →						
Min. Torque	NM	24	28	27	24	45	26	54
Flow Time	secs	200	113	225	140	95	95	65
Temp. Increase	°C	-	-	-	-	-	-	-
Temperature	°C	150 →						
Min. Torque	NM	17	20	16	14	19	20	53
Flow Time	secs	100	93	125	75	55	54	33
Temp. Increase	°C	-	-	-	-	-	-	-

aterial		PF 11F	PF 17A	PF 17B	UF 221	UF 22J	MF 24E
emperature	°C	88 →					
in. Torque	NM	17	25	16	23	33	22
low Time	secs	318	240	290	340	260	240
emp. Increase	°C	4	14	8	20	16	10

Material	PF18	A	B	C	D	E
Temperature	°C	88 →				
Min. Torque	NM	66	61	59	62	60
Flow Time	secs	185*	248*	250*	210*	246*
Peak Time	secs	286	310	343	315	330
Temp. Increase	°C	11	15	9	11	10

* Time to min. + 5 NM

Material	PF19	A	B	C	D	E	F	G	H	I	J	K
Temperature	°C	80 →										
Min. Torque	NM	38	17	15	12	30	56	36	35	23	27	22
Flow Time	secs	1140	990	690	600	495	780	840	210	470	510	90
Temp.	°C	20	12	14	14	14	11	16	20	16	22	21
Rate		11.6	10.4	14.8	27.6	33	8.3	9.7	11.8	13.8	7.7	3.0
Temperature	°C	150 →										
Min. Torque	NM	15.7	17.9	7.8	10.0	13.4	14.6	14.6	14.6	16.8	29.1	32.5
Flow Time	secs	105	120	120	120	105	45	135	30	150	270	165
Temp.	°C	13	14	-	-	6	-	11	22	26	24	8
Rate		100	45	35	66	38	130	87	30	33	11	11

Material	MPF	20A →			20B →			20C →		
Temperature	°C	88	125	150	88	125	150	88	125	150
Min. Torque	NM	43	14	14	39	12	11	18	15	13
Flow Time	secs	265	180	90	900	225	75	495	105	90
Temp. Increase	°C	15	16	16	14	16	19	11	11	12
Cure Rate	NM/sec	222	400	330	178	166	330	222	430	330

Material	UF21	A	B	C	D	E	F	G	H	I	J →			K →		
Temperature	°C	82 →										126	150	82	126	150
Min. Torque	NM	63	71	56	59	46	50	54	57	42	46	36	21	46	40	40
Flow Time	secs	70	158	170	118	347	164	241	197	331	286	140	90	215	90	80
Temp. Increase	°C	6	7	8.6	5	6.6	4.8	7.0	8.6	7	6.6	3	3	7	4	2

Material	UF22	A	B	C	D	E	F	G	H →		
Temperature	°C	88 →								125	150
Min. Torque	NM	40	34	39	34	35	32	35	44	22	16
Flow Time	secs	220	305	274	457	479	526	486	420	90	64
Temp. Increase	°C	9	7.5	8	6.5	7.5	7	7	8	4	2

Material	D1D1	23A →			23B →		
Temperature	°C	88	125	150	88	125	150
Min. Torque	NM	21	17	34	37	27	34
Flow Time	secs	336	210	16	395	231	15
Temp. Increase	°C	6	5	4	8	6.5	8

Material	MF	24A	24B	24C →			24D →				
Temperature	°C	88 →			125	150	80	90	125	140	160
Min. Torque	NM	28	32	36	236	28	44	28	16	8	6
Flow Time	secs	798	703	40	28	15	331	295	240	125	100
Temp. Increase	°C	11	10	11	9	7	6	5	5	5	2

4 Oscillating Disc Rheometer

The results given in this section were obtained using the Monsanto Rheometer Model MPV fitted with the standard 2-sided micro die. A one degree arc of oscillation was used. Unless otherwise stated the complex modulus results were obtained at 750 cycles/minute and 120, 140 and 150°C and the elastic modulus at 120°C and at 750, 100 and 25 cycles/minute.

The results are quoted for the minimum torque value. The gel time is the time for the torque to increase 2lb. in. above the minimum value, and the cure rate is the gradient of the initial half of the torque/time curve. The cure time is the time for the torque to increase to 90% of its maximum value.

Feasibility Test Materials.

Material	PMF 1	PMF 2	PMF 3	PMF 4
Temperature °C (120)				
Torque (lb/in)	140	125	105	28.3
Gel Time (secs)	120	124	113	232
Cure Time (secs)	105	262	300	1070
Cure Rate (lb/sec)	.66	.26	.33	.28
Max. Torque (lb/in)	152	157	169	145
Temperature °C (140)				
Torque (lb/in)	102	83	54	15
Gel Time (secs)	60	57	54	132
Cure Time (secs)	150	162	168	281
Cure Rate (lb/sec)	.63	.85	.79	1.1
Max. Torque (lb/in)	162	164	161	164
Temperature °C (150)				
Torque (lb/ins)	78	58	46	13.5
Gel Time (secs)	30	25.4	30	60
Cure Time (secs)	110	105	114	189
Cure Rate (lb/sec)	1.3	2.1	1.9	2.4
Max. Torque (lb/in)	168	168	160	162
Elastic Modulus				
Temperature °C (120)				
Rate of Oscillation (cs/min)				
750 (lb/in)	126	116	84	21.5
100 (lb/in)	86	53	33	11
25 (lb/in)	57	34	25	14.5

Primary Evaluation Materials

		Complex Modulus						Elastic Modulus		
Material Temperature °C	PF5 at 12.5c/s	100	120	130	140	150	160	120	140	160
Min Torque	lb in	48	19	14	11	7.5	5.0	11.0	7.0	5.5
Flow Time	secs	300	120	78	45	27	22	105	45	34
Cure Time	secs	1540	390	250	142	54	36	210	158	60
Cure Rate	lb in/sec	.09	.76	1.7	2.9	4.9	6.6	.79	4.5	5.5
Max Torque	lb in	145	164	160	165	165	174	160	160	172
Material	UF6									
Min Torque	lb in	119	61	49	46	39	49	48	34	27
Gel Time	secs	150	52	60	34	21	15	52	26	15
Cure Time	secs	360	252	120	78	48	41	340	38	40
Cure Rate	lb in/sec	.18	.69	0.9	3.2	4.0	5.9	.69	3.2	8.3
Max Torque	lb in	160	170	157	165	164	164	165	150	162
Material Rate of Osc.	PF5 sec^{-1} at 120°C	12.5	0.16		12.5	2.5	1.6	0.83	0.25	0.16
Min Torque	lb in	19.3	10		11.0	7.6	8.4	6.4	4.8	5.0
Gel Time	secs	105	232		120	210	225	234	255	274
Cure Time	secs	375	730		408	600	630	705	810	826
Cure Rate	lb in/sec	.75	.15		.76	.5	.42	.37	.27	.15
Max Torque	lb in	166	148		166	164	158	154	146	144
Material	UF6									
Min Torque	lb in	61	40		47	35	30	26.5	22	21
Gel Time	secs	52	80		75	75	75	75	75	75
Cure Time	secs	210	270		270	300	285	270	285	330
Cure Rate	lb in/sec	.69	.53		.69	.56	.54	.53	.53	.53
Max Torque	lb in	178	168		170	157	152	151	.146	166

Secondary Evaluation Materials

Material	PF7A	7B	7C	7D	7E	UF8A	8B	8C	PF9A	9B
Temperature °C (120)										
Torque (lb in)	11	16.3	28	52	90	42	134	140	12	12
Gel Time (secs)	105	105	90	97.5	112	63	90	42	105	107
Cure Time (secs)	395	340	292	282	256	216	138	40	203	225
Cure Rate (lbin/sec)	0.73	0.76	0.7	0.7	0.6	.81	.40	.04	.68	.54
Max. Torque (lb in)	165	165	165	170	170	158	168	165	172	162
Temperature °C (140)										
Torque (lb in)	9	11.5	17.5	28	49.5	30	124	134		
Gel Time (secs)	48	35	30	30	38	36	48	21		
Cure Time (secs)	205	162	142	137	141	78	77	160		
Cure Rate (lbin/sec)	3.3	2.02	202	1.9	1.3	3.3	.83	.35		
Max. Torque (lb in)	160	148	157	165	157	142	168	162		
Temperature °C (150)										
Torque (lb in)	18	10	15	26	50	25	105	133	9	8
Gel Time (secs)	.35	23.8	21.3	20	17.5	18	29	29	13.5	15
Cure Time (secs)	90	80	82.5	75	66.3	54	41	42	18	13.5
Cure Rate (lbin/sec)	5.3	40	3.3	2.5	4.8	5.8	2.4	1.1	10.7	10.7
Max. Torque (lb in)	138	165	160	162	159	162	166	166	163	162
Elastic Modulus Temperature °C (120) Rate of Oscillation (cs/min)										
750 (lb in)						42	134	156	8	7.2
100 (lb in)						20	86	122	6.3	5.5
25 (lb in)						13.5	70	106	6	4

Material	PF9C	PF10A	PF10B	PF10C	PF15A	15E
Temperature ^{o}C (120)						
Torque (lb in)	9.5	17	15.5	19	18.5	13.5
Gel Time (secs)	120	90	82.5	75	120	112
Cure Time (secs)	295	555	207	178	307	307
Cure Rate (lb in/sec)	.70	.54	1.02	1.52	1.2	0.4
Max. Torque (lb in)	165	166	162	160	174	161
Temperature ^{o}C (150)						
Torque (lb in)	7.5	10.5	12	16	9	12
Gel Time (secs)	15	16.5	9.8	3	30	22.5
Cure Time (secs)	13.0	41	33	24	270	85
Cure Rate (lb in/sec)	10.7	7.8	9.9	12.1	8.3	6.1
Max. Torque (lb in)	164	168	163	163	159	166
Elastic Modulus Temperature ^{o}C (120) Rate of Oscillation (cs/min)						
750 (lb in)	5	21	13	10		
100 (lb in)	4	19.3	12	8		
25 (lb in)	4	16	11	7		

Material	11A	11B	11C	11D	11E	11F	12A	12B	12C
Temperature ^{o}C (120)									
Torque (lb/in)	14.5	15.5	21	16	16.5	13.5	25	17	12.5
Gel Time (secs)	132	127	105	102	100	126	60	120	380
Cure Time (secs)	390	396	395	362	390	365	790	1460	-
Cure Rate (lb.in/sec)	.83	.81	.74	.74	.83	.88	.28	.1	.07
Max. Torque (lb.in)	182	180	176	161	182	172	164	150	-
Temperature ^{o}C (140)									
Torque (lb/in)	10	11.5	14	11.5	11	10	19	13	12.5
Gel Time (secs)	50	50	45	51	50	48	15	67	180
Cure Time (secs)	132	138	128	150	138	132	210	492	1350
Cure Rate (lb.in/sec)	3.92	3.7	3.18	3.18	3.7	3.7	1.1	.66	.33
Max. Torque (lb.in)	177	175	176	170	170	174	164	150	138
Temperature ^{o}C (150)									
Torque (lb/in)	13	13.5	15	14	12.5	11.5	22	10.5	4.5
Gel Time (secs)	34	36	33	33	31	34	6	24	74
Cure Time (secs)	97	96	84	90	84	97	96	141	190
Cure Rate (lb.in/sec)	4.8	5.5	5.2	5.5	5.2	5.5	3.02	1.82	1.27
Max. Torque (lb.in)	168	164	172	163	169	164	155	144	110
Elastic Modulus Temperature ^{o}C (120) Rate of OSC (cs/min									
750 (lb.in)	-	-	-	-	-	-	22	10.5	4.5
100 (lb.in)	-	-	-	-	-	-	22	10	5
25 (lb.in)	-	-	-	-	-	-	19	10.5	8

Material	PF13B	13E	13F	13G	13H	13I
Temperature ^{o}C (120)						
Torque (lb. in)	12.5	10	13	9.75	10.5	12
Gel Time (secs)	120	120	120	109	120	116
Cure Time (secs)	382	402	420	390	380	388
Cure Rate (lb in/sec)	.83	.7	.78	.74	.76	.83
Max. Torque (lb. in)	163	164	163	163	165	162
Material	**PF14A**	**14B**	**14C**	**14D**	**14E**	**14F**
Temperature ^{o}C (120)						
Torque (lb. in)	13.5	14.5	14.5	12.5	13	15
Gel Time (secs)	101.5	93.5	101	105	105	97.5
Cure Time (secs)	370	360	356	375	390	375
Cure Rate (lb in/sec)	0.8	.78	.78	.78	.86	.74
Max. Torque (lb. in)	159	161	153	157	163	159

Material	PF17A	17B	17C	17D	17E	17F
Temperature °C (120)						
Torque (lb in)	48	38	36	22	43	10
Gel Time (secs)	100	200	105	68	114	108
Cure Time (secs)	350	375	155	305	360	384
Cure Rate (lb in/sec)	.59	.58	.55	.71	.61	.72
Max. Torque (lb in)	184	163	142	150	182	168
Temperature °C (140)						
Torque (lb in)	21	28.5	20	9	23	8
Gel Time (secs)	425	49	48	18	50	30
Cure Time (secs)	138	150	168	108	158	111
Cure Rate (lb in/sec)	2.1	186	1.5	3.3	2.22	1.0
Max. Torque (lb in)	173	172	158	157	170	160
Temperature °C (150)						
Torque (lb in)	11	22	17	10	125	10
Gel Time (secs)	25.5	24	30	9	26	17
Cure Time (secs)	90	93	99	57	87	54
Cure Rate (lb in/sec)	3.9	25	4.0	5.6	3.7	1.8
Max Torque (lb in)	172	166	158	155	168	154
Elastic Modulus Temperature °C 120 Rate of Oscillation (cs/min)						
750 (lb in)	-	38	36	22	-	-
100 (lb in)	-	11.5	14	7.5	-	-
25 (lb in)	-	10.5	10.5	5	-	-

Material	PF19A	19B	19C	19D	19E	19F	19G	19H	19I	19J
Temperature °C (120)										
Torque (lb in)	30	26.5	13	12	14.5	21	19	60	49	118
Gel Time (secs)	142	142	203	225	204	132	188	120	120	186
Cure Time (secs)	492	470	542	552	552	434	485	314	530	560
Cure Rate (lb in/sec)	0.63	0.71	0.78	0.89	0.86	0.94	0.92	0.6	0.51	0.07
Max. Torque (lb in)	184	184	180	182	182	180	180	174	184	184
Temperature °C (150)										
Torque (lb in)	-	-	11.5	-	12.5	19.5	10	-	92	-
Gel Time (secs)	-	-	4.5	-	37.4	32	54	-	54	-
Cure Time (secs)	-	-	105	-	94	84	120	-	265	-
Cure Rate (lb in/sec)	-	-	61	-	70	84	56	-	29.2	-
Max. Torque (lb in)	-	-	178	-	178	168	171	-	154	-
Material	PF19K	20A	20B	20C	20D					
Temperature °C (120)										
Torque (lb in)	114	53	35	38	20					
Gel Time (secs)	186	94	110	165	101					
Cure Time (secs)	660	352	450	750	840					
Cure Rate (lb in/sec)	0.08	.59	.58	.26	.21					
Max. Torque (lb in)	180	190	188	173	150					
Temperature °C (140)										
Torque (lb in)	-	11	16	15	13.5					
Gel Time (secs)	-	76	70	81	42					
Cure Time (secs)	-	142	128	240	180					
Cure Rate (lb in/sec)	-	3.3	2.48	11-9.6	12.9					
Max. Torque (lb in)	-	164	173	161	160					
Temperature °C (150)										
Torque (lb in)	-	10	15	14.5	15.5					
Gel Time (secs)	-	39	46.5	25	24					
Cure Time (secs)	-	105	107	180	174					
Cure Rate (lb in/sec)	-	5.6	2.9	17.7	14.5					
Max. Torque (lb in)	-	178	172	156	156					

Material	UF22A	22B	22C	22D	22E	22F	22G	22H
Temperature °C (120)								
Torque (lb in)	150	116	79	89	148	68.5	64	149
Gel Time (secs)	12	60	71	64	67	60	60	147
Cure Time (secs)	40	113	188	160	105	170	210	147
Cure Rate (lb in/sec)	0.55	0.55	0.66	0.77	0.01	0.83	0.65	.98
Max. Torque (lb in)	158	162	160	170	159	160	160	180
Temperature °C (140)								
Torque (lb in)	138	90	54	49	128	48	34	133
Gel Time (secs)	20	33	36	50	45	29	36	72
Cure Time (secs)	160	60	81	90	66	66	64	95
Cure Rate (lb in/sec)	.26	2.8	3.3	3.3	0.63	3.3	3.3	9.5
Max. Torque (lb in)	160	160	156	165	155	156	152	174
Temperature °C (150								
Torque (lb in)	144	92	55	43	114	49	51	123
Gel Time (secs)	14	16.2	16.8	18	29	15.6	21	52
Cure Rate (secs)	25	49	42	49	49	45	50	82
Cure Rate (lb in/sec)	.44	3.7	4.8	8.3	1.8	5.5	5.5	2.38
Max. Torque (lb in)	168	168	164	160	161	168	160	176
Elastic Modulus Temperature °C (120) Rate of Oscillation (cs/min)								
750 (lb in)	148	116	79	69	148	68	NA	146
100 (lb in)	139	79	52	64	117	30	NA	124
25 (lb in)	122	73	33	42	90	46	NA	110

Material	DIDI23A	23B	MF 24A	24B	24C
Temperature °C (120)					
Torque (lb in)	102	128	125	33	42
Gel Time (secs)	120	135	165	94	120
Cure Time (secs)	218	375	225	285	420
Cure Rate (lb in/sec)	.21	..5	.11	.40	.53
Max. Torque (lb in)	136	157	148	170	172
Temperature °C (140)					
Torque (lb in)	61	98	104	24	24
Gel Time (secs)	30	78	66	41	90.5
Cure Time (secs)	132	156	126	120	174
Cure Rate (lb in/sec)	.86	.76	.97	.61	.91
Max. Torque (lb in)	154	162	164	160	164
Temperature °C (150)					
Torque (lb in)	69	56	100	26	10.5
Gel Time (secs)	33	47	42	21	43
Cure Time (secs)	90	120	78	60	114
Cure Rate (lb in/sec)	2.4	1.4	1.9	4.8	3.2
Max. Torque (lb in)	160	161	166	170	168
Elastic Modulus Temperature °C (120) Rate of Oscillation (cs/min)					
750 (lb in)	86	123	119	27.5	35
100 (lb in)	—	73	86	7	16
25 (lb in)	49	40	79	14	15

Results of Stress/Strain Measurement with Oscillating Disc Rheometer 120°C

Time		Factor	X	Y	Area
mins	secs	δ			
Phenolic PF 11C					
0	50	2	20.5	13.3	180.5
1	50	2	20.8	6.9	80.0
2	52	2	20.6	6.5	81.0
3	50	2	20.4	11.5	126.1
4	50	4	20.4	16.5	107.4
5	50	4	20.2	22.2	116.9
7	50	8	19.8	17.5	57.8
9	50	8	18.5	21.3	56.0
12	50	8	18.8	24.5	46.9
15	50	8	18.8	25.8	30.5
Phenolic PF 11D					
1	50	2	20.8	5.4	56.5
2	50	2	20.7	4.9	51.0
3	50	2	20.7	5.3	63.0
4	50	2	21.0	10.0	118
6	50	4	20.3	22	114.7
7	50	8	18.8	14.4	53.0
9	50	8	20.1	19.4	57.9
12	50	8	19.7	23.7	50.4
15	50	8	18.4	25.7	30.5
Phenolic PF 11E					
1	40	2	20.6	6.8	62.1
2	40	2	20.6	6.1	57.8
3	40	2	20.4	6.3	63.0
4	40	4	20.0	4.0	49.0
5	40	4	20.5	10.2	91.0
6	40	4	20.3	10.5	56.6
7	40	8	20.1	14.5	56.2
9	40	8	19.7	19.2	53.3
12	40	8	19.1	23.2	47.3
15	40	8	18.2	25.7	32.3
Phenolic PF 11F					
1	40	2	20.7	5.8	58.4
2	40	2	20.4	5.2	51.6
3	40	2	20.3	5.4	57.0
4	40	4	20.7	3.5	42.3
5	40	4	19.5	9.8	82.5
6	40	8	20.3	10.3	54.5
8	40	8	20.0	17.3	55.0
9	40	8	18.2	19.2	52.3
12	40	8	18.2	23.7	45.4
15	40	8	19.2	25.9	28.0

X, Y = horizontal and vertical axes of elipse.
δ = relative scale of X and Y.
area = area of elipse.
all scales in arbitrary units.

Time		Factor	X	Y	Area
mins	secs	δ			
Phenolic PF 17A					
0	55	2	20.4	14.2	175.8
1	34	4	19.4	5.4	59.5
2	34	4	20.5	5.0	55.3
3	34	4	20.5	4.8	55.7
4	34	4	20.4	5.4	62.3
6	34	4	20.2	18.1	112.1
8	34	8	19.8	17.2	44.5
9	34	8	19.5	19.3	35.9
12	34	8	18.2	22.2	28.4
15	34	8	19.3	23.3	23.3
Phenolic PF 17B					
1	00	2	20.8	4.6	55.4
1	30	2	20.2	4.2	45.4
2	30	2	21.0	5.9	52.5
3	30	2	20.5	14.8	105.5
4	30	4	19.5	14.4	69.2
5	30	4	20.3	21.1	94.2
6	30	8	20	13.2	54.3
7	30	8	19.8	15.9	60.8
8	30	8	18.5	18.8	64.5
9	30	8	20.0	20.4	73.0
12	30	8	18.3	18.3	48.0
15	30	8	18.2	22.9	39.2
Urea UF 221					
0	40	4	20	14.2	159.7
1	30	8	20.5	6.1	70.5
2	30	8	20.3	8.9	94.5
3	30	8	20.0	16.4	104.7
4	30	8	19.7	22.6	38.3
5	30	8	19.4	24.2	24.2
6	30	8	19.3	25.1	17.5
7	30	8	18.7	25.4	14.9
Urea UF 8B					
1	30	8	19.6	22.3	29.8
2	06	8	19.1	22.6	26.3
2	40	8	18.3	22.8	23.1
3	40	8	19.7	23.5	17.5
4	40	8	19.6	24.0	14.5
5	40	8	19.7	24.5	11.0
Melamine MF 24E					
0	55	4	20.2	18.7	178.2
1	33	8	19.1	8.1	67.4
2	33	8	20.2	8.4	73.0
3	33	8	20.2	8.4	76.4
4	33	8	20.5	8.4	85.2
5	33	8	20.3	12.7	117.4
6	33	8	20.1	17.4	93.0
7	33	8	18.6	20.8	57.0
8	33	8	19.8	22.7	41.8
10	33	8	19.3	24.4	24.2
12	33	8	18.3	25.3	18.8
15	33	8	18.2	26.0	15.0

5 Injection Moulding

Four injection moulding machines were used.

Turner	60g shot	CTA-2-ATS
Turner	120g shot	CTA-2-ATS
Bipel	90g shot	60/26
Ankerwerke	120g shot	V17-65

The latter machine belonged to ERDE and the comparison of phenolic materials carried out using that machine was undertaken by Dr. D. Simms of the ERDE.

Standard machine settings were used for most of this work although for many experiments, the injection pressure was varied. The standard machine settings are shown below for phendic materials. Urea formaldehyde materials required barrel temperatures of 86°C, mould temperatures of 150°C and cycle times of 35 seconds. Melamine formaldehyde materials were moulded as for phenolic materials but with barrel temperatures of 92-95°C.

Standard Machine Conditions and Details of Moulds used

Machine Settings Mould Characteristics		Turner CTA/2/ATS 60g	Turner CTA/2/ATS 120g	Bipel 60/26 90g	Ankerwerke U17-65 120g
Barrel Temp.	°C	88 & 92	92	90	95
Injection Pressure	MN/m^2	10	10	7	2 (hold)
Injection Speed		3.5	3.5	3.5	-
Screw Speed	RPM	60	60	60	71
Back Pressure	MN/m^2	Set Zero	Set Zero	0.4	Set Zero
Cycle Time	secs	45	45	45	41
Mould Temp.	°C	165	165	165	165
Mould gate		Tab.	None	Tab/Sub[+]	Tab.
Mould length mm		70	-	100/115	100 (dia)
width mm		115	-	100/115	-
thickness mm		3	-	3/1½	3

[+] Submarine gate, urea material

MATERIAL. Phenolic PF 5

ACHINE
CONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Capilary
ARREL TEMP 88 °C
OULD TEMP -- °C
YCLE TIME 45 secs

OMPUTOR
ELIABILITY
ACTOR
tenard error 372
Squared 0.93
td error x 100
quation const 4.65

PARAMETER Nozzle peak pressure psi x 1000		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(6.14) 6.15	6.83	7.55	6.75	6.86	(6.77) 7.05	7. 0	(6.65) 6.65	6.25
	3.5	5.90	(6.85) 6.60	6. 0	(6.66) 7.00	6.90	6.90	7.80	7.18	(6.60) 6.68
	4.3	5.94	6.40	(6.75) 6.85	7.18	(6.83) 7.05	6.98	(6.55) 8.15	7.45	6.83
1000 psi	2.5	7.95	8.50	(8.15) 9.10	8.05	(8.42) 8.05	8.10	(7.89) 7.90	7.40	6.83
	3.5	(7.58) 7.73	8.13	8.55	8.40	8.3	(8.50) 8.05	8.73	(7.£0) 7.95	7.25
	4.3	7.85	(8.16) 8.15	8.55	(8.35) 8.60	8.35	8.15	9.08	8.25	(7.55) 7.50
1300 psi	2.4	8.78	(9.13) 9.20	9.68	(8.25) 8.40	8.28	8.20	7.75	7.05	(6.43) 6.43
	3.5	8.70	8.93	(8.86) 9.20	8.83	(8.65) 8.50	8.83	(8.89) 8.58	7.90	6.95
	4.3	(9.06) 8.80	9.00	9.22	9.05	8.70	(8.55) 8.35	9.05	(7.84) 6.10	7.25

ACHINE
CONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Capillary
BARREL TEMP 88 °C
OULD TEMP 90 °C
CYCLE TIME 45 secs

or
ility Fector
ror 1.8
red 0.63
ror x 100 1.92
on Const.

PARAMETER Nozzle Melt Temp. °C		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(88.3) 88.6	88.8	88,4	90.6	91.1	(91.0) 90.7	89.1	(88.5) 89.5	89.2
	3.5	87.8	(87.2) 88.6	88.7	(90.2) 89.9	90.8	90.9	88.2	89.1	(89.6) 89.4
	4.3	87.4	88.4	(89.1) 88.6	89.5	(90.8) 90.5	90.8	(87.0) 87.7	88.8	89.2
1000 psi	2.5	90.7	91.0	(91.8) 90.6	92.3	(91.1) 92.7	92.4	(91.0) 90.1	90.6	90.3
	3.5	(90.5) 90.5	91.4	91.6	92.1	93.0	(93.0) 93.2	89.8	(92.8) 90.8	91.1
	4.3	90.3	(91.3) 91.3	91.6	(90.5) 91.8	92.9	93.3	89.5	90.7	(89.8) 91.1
1300 psi	2.5	91.0	(90.3) 91.4	91.0	(93.0) 92.0	92.5	92.5	89.3	89.8	(89.8) 89.6
	3.5	91.5	92.4	(93.0) 92.7	92.4	(93.0). 93.4	93.7	(86.9) 89.6	90.6	91.6
	4 .3	(92.5) 91.4	92.6	92.9	92.3	93.5	(93.0) 94.0	89.5	(93.5) 90.7	91.2

MACHINE
CONDITIONS
MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Capillary
BARREL TEMP 88 °C
MOULD TEMP 90 °C
CYCLE TIME 45secs

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ability Factors
Error 0.50
uared 0,98
error x 100 3.5
tion const.

PARAMETER Inj. time secs.		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(8.4) 8.27	7.33	6.75	6.09	5.23	(4.6) 4.74	4.13	(3.6) 3.36	2.95
	3.5	7.14	(7.0) 6.8	6.83	(4.6) 4.94	4.69	4.81	2.93	2.82	(2.7). 3.01
	4.3	7.11	6.93	(7.4) 7.11	4.94	(4.7) 4.84	5.1	(2.8) 2.95	2.95	3.30
1000 psi	2.5	2.85	2.93	(2.0) 2.35	2.73	(2.2) 1.89	1.42	(1.7) 1.84	1.09	0.70
	3.5	(2.6) 2.73	2.41	2.45	1.6	1.37	(1.5) 1.5	0.7	(0.9) 0.56	0.77
	4.3	2.71	(1.6) 2.55	2.75	(2.3) 1.58	1.5	1.79	0.68	0.69	(1.4) 1.07
1300 psi	2.5	2.12	(1.5) 1.21	0.67	(1.3) 2.07	1.25	0.79	2.25	1.51	(1.2) 1.14
	3.5	1.0	0.71	(1.0) 0.77	0.96	(0.8) 0.73	0.88	(1.1) 1.12	0.99	1.22
	4.3	(1.1) 0.91	0.36	1.07	0.93	(0.9) 0.87	1.19	1.09	(0.8) 1.13	1.52

MATERIAL. Phenolic PF 5

ACHINE
ONDITIONS
ACHINE Bipel 3oz
OZZLE Std. Inst.
OULD Plaque
ARREL TEMP 8 8 °C
OULD TEMP o165°C
YCLE TIME 45secs

OMPUTOR
ELIABILITY
ACTOR
Standard error 0.22
R Squared 0.90
Std error x 100
Equation const. 4.9

PARAMETER Weight grams		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(43.22) 43.64	(43.88) 44.03	(44.7) 44.34	(44.5) 44.22	(44.28) 44.61	(44.52) 44.93	(44.30) 44.48	(44.56) 44.87	(44.83) 45.18
	3.5	(43.88) 43.36	(44.00) 43.76	(44.34) 44.07	(44.48) 43.96	(44.48) 44.36	(44.86) 44.67	(44.84) 44.24	(44.50) 44.63	(45.11) 44.95
	4.3	(43.85) 43.21	(44.15) 43.63	(44.30) 43.95	(44.26) 43.94	(44.46) 44.24	(44.75) 44.55	(44.42) 44.12	(44.59) 44.52	(45.33) 44.83
1000 psi	2.5	(43.30 43.92	44.00) 44.27	(44.45) 44.54	((44.50) 44.41	(44.40) 44,76	(44.48) 45.02	(44.52) 44.57	(44.64) 44.92	(45.04) 45.19
	3.5	(43.65) 43.81	(44.65) 44.16	(44.44) 44.43	(44.50) 44.32	(44.73) 44.67	(45.13) 44.94	(44.67) 44.50	(44.70) 44.85	(45.35) 45.12
	4.3	(43.90) 43.73	(44.50) 44.08	(44.44) 44.35	(44.38) 44.24	(44.64) 44.59	(44.95) 44.86	(44.54) 44.43	(44.79) 44.78	(45.44) 44.05
1300 psi	2.5	(43.3) 44.10	(44.50) 44.41	(44.50) 44.63	(44.50) 44.50	(44.43) 44.80	(44.95) 45.03	(44.62) 44.57	(44.78) 44.87	(44.16) 45.10
	3.5	(43.90) 44.36	(44.60) 44.47	(44.55) 44.70	(44.25) 44.58	(44.90) 44.88	(45.13) 45.11	(44.64) 44.67	(44.68) 44.97	(44.67) 45.19
	4.3	(44.15) 44.12	(44.40) 44.43	(44.49) 44.69	((44.54) 44.55	(44.46) 44.85	(44.84) 45.08	(44.56) 44.64	(44.94) 44.94	(45.35) 45.17

ACHINE
ONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Plaque
ARREL TEMP 88 °C
OULD TEMP 165 °C
YCLE TIME 45secs

OMPUTOR
ELIABILITY
ACTOR
tandard error 3.21
Squared 0.97
td error x 100
uation const. 26.4

PARAMETER Flow pattern		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	A 3.0	A 3.1	A 2.3	A	A	Sl. B	A 2.0	Sl B	C
	3.5	A 3.4	A 3.1	A 2.2	A 1.0	A 1.4	Sl B	B	A/B	C
	4.3	A 3.2	A 3.1	A 1.7	A 2.9	A 1.5	Sl B	B	B	C
1000 psi	2.5	A 3.4	A 2.6	A 2.0	A 2.6	A 3.0	Sl B	-	B	C
	3.5	A 3.0	A 2.1	A 1.4	A 1.7	A 1.8	B	B	B	C
	4.3	A 2.7	A 2.2	A 1.5	A 1.6	A 1.3	B	B	B	C
1300 psi	2.5	A 3.4	A 3.3	A 1.5	A 2.6	A 1.7	C	A/B	A/B	C
	3.5	A 3.1	A 2.3	A 1.6	A 2,7	A 1.3	B	B	B	C
	4.3	A 2.8	A 1.3	A 1.3	A 1.4	A 1.3	C	B	B	C

ACHINE
CONDITIONS
ACHINE Bipel 3oz
OZZLE Std, Inst.
OULD Plaque
ARREL TEMP 88 °C
OULD TEMP 165 °C
YCLE TIME 45secs

COMPUTOR
RELIABILITY
FACTOR
Standard error 0.74
R Squared 0.58
Std error x 100
Equation const 88.5

PARAMETER Gloss		BACK PRESSURE								
INJECTION PRESSURE	INJECTION SPEED	60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	P	R	R	R	P	R	R	G	VG
	3.5	P	R	R	G	R	P	G	G	VG
	4.3	P	R	R	R	R	P	G	G	G
1000 psi	2.5	P	R	R	R	R	P	R	R	VG
	3.5	R	R	R/G	R		P	VG	VG	G
	4.3	R	R	R/G	R	R	P	VG	VG	G
1300 psi	2.5	P	R	R	R	R	P	G	G	VG
	3.5	R	R	R	P	VG	P	G	VG	G
	4.3	G	R	G	G	G	P	G	G	G

MATERIAL. Phenolic PF 5

ACHINE
ONDITIONS
ACHINE Bipel 3oz
OZZLE Std. Inst.
OULD Plaque
ARREL TEMP 88 °C
OULD TEMP 165°C
YCLE TIME 45secs

OMPUTOR
ELIABILITY
ACTORS
tandard error 0.079
Squared 0.99
td. error x 100
quation const. 11.6

PARAMETER Injection time secs		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(2.38) 2.38	(2.00) 2.34	(2.18) 2.31	(2.05) 2.17	(2.14) 2.16	(2.08) 2.16	(1.93) 2.05	(2.15) 2.07	(2.40) 2.09
	3.5	(1.10) 1.48	(1.05) 1.54	(1.16) 1.60	(1.25) 1.24	(1.45) 1.32	(1.09) 1.41	(0.97) 1.09	(1.10) 1.20	(1.30) 1.32
	4.3	(1.08) 1.40	(1.05) 1.48	(1.66) 1.56	(1.24) 1.15	(1.18) 1.26	(1.09) 1.37	(0.98) 1.00	(1.15) 1.13	(1.33) 1.27
1000 psi	2.5	(1.43) 1.41	(1.31) 1.34	(1.30) 1.28	(1.30) 1.28	(1.20) 1.25	(1.30) 1.21	(1.18) 1.26	(1.33) 1.24	(1.40) 1.24
	3.5	(0.60) 0.62	(0.50) 0.64	(0.53) 0.67	(0.50) 0.46	(0.57) 0.51	(0.52) 0.57	(0.46) 0.40	(0.53) 0.48	(0.55) 0.56
	4.3	(0.50) 0.56	(0.50) 0.61	(0.50) 0.66	(0.50) 0.40	(0.5) 0.47	(0.47) 0.55	(0.45) 0.33	(0.51) 0.43	(0.56) 0.54
1300 psi	2.5	(1.00) 1.11	(1.00) 1.01	(1.08) 0.92	(1.09) 1.08	(1.04) 1.00	(1.03) 0.94	(0.95) 1.13	(1.04) 1.09	(1.05) 1.05
	3.5	(0.45) 0.42	(0.39) 0.41	(0.42) 0.41	(0.40) 0.35	(0.42) 0.37	(0.40) 0.39	(0.35) 0.38	(0.42) 0.42	(0.43) 0.47
	4.3	(0.40) 0.39	(0.40) 0.40	(0.38) 0.42	(0.38) 0.31	(0.40) 0.35	(0.39) 0.40	(0.35) 0.33	(0.38) 0.40	(0.41) 0.42

MACHINE
CONDITIONS
MACHINE Bip 1 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 95 °C
MOULD TEMP 165 °C
CYCLE TIME 45secs

COMPUTOR
RELIABILITY
FACTOR
Standard error 0.096
R Squared 0.97
Std error x 100
Equation Const. 0.2

PARAMETER Shot weight. Grams		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(44.68) 43.71	43.88	43.88	44.11	44.43	(44.64) 44.57	44.26	(44.74) 44.72	45.01
	3.5	43.82	(43.88) 43.93	43.85	(44.26) 44.20	44.45	44.53	44.33	44.73	(44.84) 44.95
	4.3	43.91	44.00	(43.94) 43.91	44.29	(44.53) 44.52	44.58	(44.40) 44.41	44.79	44.99
1000 psi	2.5	44.04	44.17	(44.10) 44.12	44.39	(44.55) 44.66	44.76	(44.50) 44.48	44.89	45.14
	3.5	(44.20) 44.14	44.20	44.08	44.47	44.67	(44.70) 44.70	44.54	(45.00) 44.89	45.06
	4.3	44.23	(44.28) 44.27	44.13	(44.44) 44.55	44.73	44.74	44.62	44.95	(45.00) 45.10
1300 psi	2.5	44.12	(44.30) 44.20	44.10	(44.38) 44.41	44.64	44.68	44.45	44.82	(45.00) 45.01
	3.5	44.21	44.32	(43.94) 44.05	44.48	(44.64) 44.64	44.51	(44.54) 44.50	44.80	44.92
	4.3	(44.30) 44.30	44.28	44.10	44.56	44.70	(44.76) 44.65	44.57	(44.76) 44.85	44.96

MACHINE
CONDITIONS
MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 95 °C
MOULD TEMP 165 °C
CYCLE TIME 45secs

COMPUTOR
RELIABILITY
FACTOR
Standard error 4.42
R Squared 0.88
Std error x 100
Equation const 71

PARAMETER Flow pattern		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	A2.3					C		B1.2	
	3.5		A2.8		B2.1					C
	4.3			A 2.7		B 0.8		B 2.0		
1000 psi	2.5			A 1.0		B 1.1		B 1.5		
	3.5	A 1.5					C		B 1.0	
	4.3		A 1.5		B 1.4					C
1300 psi	2.5		A 1.6		B					C
	3.5			A 2.0		A/B		B 1.4		
	4.3	A 1.3					C		B	

MATERIAL. Phenolic PF 5

MACHINE CONDITIONS

MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 95 °C
MOULD TEMP 165°C
CYCLE TIME 45 secs

COMPUTOR RELIABILITY FACTOR
Standard error 0.93
R Squared 0.78
Std error x 100
Equation const 24.3

PARAMETER Gloss		BACK PRESSURE 60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
INJECTION PRESSURE	INJECTION SPEED	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	R					P		P	
	3.5		G		VG					P
	4.3			R		VG		VG		
1000 psi	2.5			VG		VG		VG		
	3.5	G					P		VG	
	4.3		VG		VG					P
1300 psi	2.5		G		G					P
	3.5			VG		VG		VG		
	4.3	R					P		VG	

MACHINE CONDITIONS

MACHINE Bipel 3 oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 95 °C
MOULD TEMP 165 °C
CYCLE TIME 45 secs

COMPUTOR RELIABILITY FACTOR
Standard error 0.095
R Squared 0.92
Std error x 100
Equation Const 14.8

PARAMETER Injection time secs		BACK PRESSURE 60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
INJECTION PRESSURE	INJECTION SPEED	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(2.18) 2 10	1.97	1.93	2.00	1.97	(2.02) 2.01	1.98	(2.00) 2.04	2.17
	3.5	1.00	(0.82) 0.90	0.88	(0.82) 0.96	0.95	1.01	0.99	1.07	(1.35) 1.23
	4.3	0.84	0.74	(0.70) 0.73	0.81	(0.85) 0.81	6.88	(0.90) 0.86	0.94	1.11
1000 psi	2.5	1.39	1.25	(1.16) 1.20	1.25	(1.21) 1.21	1.24	(1.19) 1.20	1.24	.37
	3.5	(0.55) 0.53	0.42	0.39	0.45	0.43	(0.50) 0.49	0.45	(0.50) 0.52	0.67
	4.3	0.44	(0.45) 0.33	0.30	(0.43) 0.37	0.35	0.42	0.38	0.45	(0.46) 0.31
1300 psi	2.5	1.10	(0.93) 0.96	0.89	(0.92) 0.93	0.83	0.90	0.84	0.97	(1.03) 0.93
	3.5	0.49	0.37	(0.35) 0.32	0.37	(0.37) 0.34	0.39	(0.37) 0.33	0.39	0.53
	4.3	(0.38) 0.46	0.34	0.30	0.35	0.33	(0.38) 0.38	0.32	(0.37) 0.39	0.53

MACHINE CONDITIONS

MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 88 °C
MOULD TEMP 190°C
CYCLE TIME 45 secs

Computor Reliability Factor
Standard error 0.24
R Squared 0.69
Std error x 100
Equation const. 0.7

PARAMETER Shot weight. Grams.		BACK PRESSURE 60 psi			120 psi			180 psi		
		SCREW SPEED			SCREW SPEED			SCREW SPEED		
INJECTION PRESSURE	INJECTION SPEED	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(44.05) 43.91	43.64	43.82	43.98	43.79	(43,90) 44.07	43.93	(43,86) 43.86	44.22
	3.5	43.99	(43.44) 43.68	43.82	(43.58) 43.88	43.66	43.89	43.68	43.54	(43.86) 43.86
	4.3	44:01	43.69	(43.96) 43.82	43.85	(43.90) 43.62	43.84	(43.76) 43.61	43.46	43.77
1000 psi	2.5	43.66	43.50	(43.95) 43.80	43.85	(43.91) 43.77	4 .15	(43.86) 43.92	43.95	44.42
	3.5	(43.06) 43.86	43.66	43.91	43.86	43.75	(43,06) 44.09	43.78	(43.86) 43.75	44.15
	4.3	43.92	(43.50) 43.70	3.95	(43.74) 43.87	43.75	44.08	43.74	43.70	(44.00) 44.12
1300 psi	2.5	43.38	(43.05 43.33	43.73	(43.68) 43.67	43.70	44.19	43.87	43.99	(44.66) 44.57
	3.5	43.70	43.60	(43.98) 43.96	43.81	(44.10) 43.81	44.26n	(43.80) 43.83	43.92	44.46
	4.3	(43.86) 43.78	43.63	44.03	43.85	44.00	(44.22) 44.27	43.83	(43.80) 43.90	44.44

MATERIAL. Phenolic PF 5

MACHINE CONDITIONS

MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 88 °C
MOULD TEMP 190 °C
CYCLE TIME 45secs

COMPUTOR RELIABILITY FACTOR
Standard error 0.49
R Squared 0.67
Std error x 100
Equation const 17.7

PARAMETER Gloss		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	R					R		P	
	3.5		R		R					P
	4.3			R		R		R		
1000 psi	2.5			R		R		R		
	3.5	R					G		G	
	4.3		R		R					P
1300 psi	2.5		R		R					P
	3.5			R		G		R		
	4.3	R					G		G	

MACHINE CONDITIONS

MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 88 °C
MOULD TEMP 190°C
CYCLE TIME 45 secs

COMPUTOR RELIABILITY FACTOR
Standard error 5.4
R Squared 0.92
Std error x 100
Equation const 45

PARAMETER Flow pattern		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	A 3.5					A/B		B/C	
	3.5		A 3.0		A 2.9					C
	4.3			A 3.1		A 2.8		A 2.4		
1000 psi	2.5			A 2.8		A 2.0		A 2.5		
	3.5	A 2.2					A/B		B	
	4.3		A 1.7		A 2.6					C
1300 psi	2.5		A 2.6		A 3.3					B/C
	3.5			A/B		A		A 1.7		
	4.3	A 1.0					A 1.3		B	

MACHINE CONDITIONS

MACHINE Bipel 3oz
NOZZLE Std Inst
MOULD Plaque
BARREL TEMP 88 °C
MOULD TEMP 190 °C
CYCLE TIME 45 secs

COMPUTOR RELIABILITY FACTOR
Standard error 0.032
R Squared 0.99
Std error x 100
Equation const 6.1

PARAMETER Injection time secs		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE	INJECTION SPEED	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
700 psi	2.5	(1.53) 1.51	1.43	1.44	1.52	1.49	(1.54) 1.54	1.55	(1.56) 1.56	1.66
	3.5	0.80	(0.63) 0.68	0.65	(0.81) 0.78	0.71	0.72	0.79	0.75	(0.80) 0.80
	4.3	0.75	0.62	(0.58) 0.58	0.73	(0.66) 0.64	0.64	(0.72) 0.73	0.68	0.72
1000 psi	2.5	1.05	0.99	(1.02) 1.01	1.05	(1.03) 1.03	1.10	(1.04) 1.07	1.09	1.20
	3.5	(0.45) 0.47	0.34	0.31	0.42	0.35	(0.40) 0.36	0.40	(0.44) 0.37	0.43
	4.3	0.46	(0.39) 0.34	0.31	(0.39) 0.42	0.35	0.36	0.40	0.37	(0.42) 0.43
1300 psi	2.5	0.84	(0.77) 0.80	0.84	(0.8) 0.83	0.82	0.35	0.83	0.87	(1.00) 0.99
	3.5	0.39	0.30	(0.32) 0.30	0.35	(0.29) 0.30	0.34	(0.33) 0.33	0.32	0.40
	4.3	(0.42) 0.41	0.31	0.30	0.36	0.30	(0.33) 0.33	0.33	(0.33) 0.31	0.38

MATERIAL. Urea formaldehyde UF 6

ACHINE
CONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Plaque
ACK PRESS 70psi
CREW SPEED 60rpm
NJ. PRESS 1400 psi

OMPUTOR
ELIABILITY
ACTORS
tandard error 183.6
Squared 0.52
td.error x 100
quation Const. 1.9

PARAMETER Peek nozzle press. psi x 1000		BARREL TEMPERATURE								
INJECTION SPEED	INJECTION TIME secs	80 °C			90 °C			98 °C		
		MOULD TEMP.			MOULD TEMP.			MOULD TEMP.		
		140°C	150°C	160°C	140°C	150°C	160°C	140°C	150°C	160°C
2.5	15	(14.93) 14775	14.76	14.86	14.80	14.76	(14.79) 14.80	14.93	(14.44) 14.84	14.84
	25	14.88	(14.94) 14.89	14.98	(15.04) 14.92	14.87	14.91	15.04	14.95	(15.15) 14.94
	35	5.38	15.39	(15.30) 15.48	15.41	(15.52) 15.36	15.39	(15.43) 15.52	15.42	15.41
3.5	15	(15.48) 15.90	14.88	(14.99) 14.95	14.91	(14.79) 14.83	14.85	(15.25) 15.00	14.88	14.85
	25	(14.30) 14.85	14.83	14.90	14.85	14.77	(14.91) 14.78	14.93	(14.23) 14.81	14.77
	35	15.18	(15.10) 15.15	15.21	(15.15) 15.16	(15.55) 15.08	15.08	15.24	15.11	(15.02) 15.06
4.3	15	15.14	(15.10) 15.10	15.15	(15.12) 15.11	15.01	15.00	15.18	15.03	(15.00) 14.97
	25	14.95	14.91	(15.00) 14.95	14.91	(14.69) 14.81	14.79	(15.00) 14.97	14.83	14.76
	35	(15.32) 15.14	15.09	15.13	15.09	14.98	(14.83) 14.98	15.13	(14.99) 14.98	14.91

ACHINE
CONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Plaque
ACK PRESS 70psi
CREW SPEED 60rpm
NJ. PRESS 1400 psi

OMPUTOR
ELIABILITY
ACTORS
tandard error 3.7
Squared 0.73
td.error x 100
quation Const. 2.6

PARAMETER Melt temp °C		BARREL TEMPERATURE								
INJECTION SPEED	INJECTION TIME secs	80 °C			90 °C			98 °C		
		MOULD TEMP.			MOULD TEMP.			MOULD TEMP.		
		140°C	150°C	160°C	140°C	150°C	160°C	140°C	150°C	160°C
2.5	15	(97.0) 96.2	94.7	95.1	102.0	101.0	(101.5) 101.9	102.9	(104.5) 102.2	1 3.5
	25	94.9	(94.0) 93.3	93.6	(96.5) 100.7	99.5	100.3	101.5	100.7	(97.5 101.8
	35	(91.5) 92.3	90.7	(97.5) 90.9	98.0	(103.2) 96.8	96.5	(104.0) 99.8	97.9	98.9
3.5	15	(97.5) 96.5	96.0	97.5	102.6	(103.0) 102.0	104.5	(104.0) 103.6	104.0	106.3
	25	(97.5) 96.0	94.5	96.8	102.0	(100.5) 100.59	(105.0) 103.8	103.0	(104.5) 103.3	105.5
	35	94.2	(87.5) 93.5	94.9	(99.5) 100.2	100.0	101.7	101.1	101.3	(105.5 103.4
4.3	15	96.3	(95.5) 96.7	99.0	(100.5 102.6	103.4	106.2	103.2	105.0	(103) 96.4
	25	96.4	96.8	(101.0) 99.0	102.6	(103.0) 103.4	106.1	(106.0) 105.0	104.8	107.9
	35	(98.0) 95.3	95.5	97.6	101.4	102.0	(104.5) 104.7	102.5	(100.5 103.5	07.5) 06.5

ACHINE
ONDITIONS
ACHINE Bipel 3oz
OZZLE Std Inst
OULD Plaque
ACK PRESS 70psi
CREW SPEED 60rpm
NJ. PRESS 1400 psi

OMPUTOR
ELIABILITY
ACTORS
tandard error 0.27
Squared 0.91
td.error x 100
quation Const. 1.4

PARAMETER Injection time secs		BARREL TEMPERATURE								
INJECTION SPEED	INJECTION TIME secs	80 °C			90 °C			98 °C		
		MOULD TEMP.			MOULD TEMP.			MOULD TEMP.		
		140°C	150°C	160°C	140°C	150°C	160°C	140°C	150°C	160°C
2.5	15	(2.0) 1.9	2.1	2.0	1.7	1.7	(1.6) 1.5	1.7	(1.5) 1.7	1.4
	25	2.3	(2.4) 2.4	2.3	(2.2) 2.1	2.1	1.8	2.2	2.1	(2.0) 1.7
	35	2.7	2.8	(2.7) 2.6	2.6	(2.0) 2.5	2.2	(2. 2.6	2.6	2.2
3.5	15	(2.4) 1.9	2.0	(1.7) 1.8	1.7	(1.6) 1.7	1.3	(1.8) 1.8	1.7	1.3
	25	(2.0) 2.2	2.3	2.0	2.0	(2.0) 2.0	(1.6) 1.6	(1.8) 2.1	2.0	1.6
	35	2.6	(3.1) 2.5	2.3	(2.5) 2.4	2.3	1.9	2.6	2.4	(1.8) 1.9
4.3	15	1.9	(2.1) 2.0	1.7	(1.9) 1.7	1.7	1.3	1.9	1.7	(1.3) 1.2
	25	2.2	2.2	(1.8) 1.9	2.0	(2.0) 1.9	1.5	(2.0) 2.2	2.0	1.5
	35	(2.4) 2.5	2.5	2.1	2.4	2.3	(1.7) 1.8	2.6	(2.5) 2.3	1.8

MATERIAL. Urea Formaldehyde

CHINE
NDITIONS
CHINE BIPEL 3 onz
ZZLE Std. Inst.
ULD Plaque
RREL TEMP 90 °C
ULD TEMP 150°C
CLE TIME 35 secs

IPUTOR
LIABILITY FACTORS
andard error 388
Squared 0:99
andard Error x 100
uation Constant 2.8

PARAMETER Peak Nozzle Pressure psi		BACK PRESSURE								
		30 psi			70 psi			120 psi		
INJECTION PRESSURE	INJECTION PRESSURE No. of turns	SCREW SPEED RPM			SCREW SPEED RPM			SCREW SPEED RPM		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
800 psi	2.5	(10,280) 10,260	9,940	9,490	9,820	9,610	(9,500) 9,250	9,680	(9,630) 9,490	9,260
	3.5	10,230	(10,350) 10,280	10,200	(9,430) 9,750	9,910	9,930	9,440	9,730	(9,700) 9,880
	4.3	9,950	10,310	(10,600) 10,520	9,430	(9,630) 9,890	10,210	(9,500) 9,090	9,670	10,120
1100 psi	2.5	14,610	14,280	(13,890 13,820	13,950	(13,200) 13,730	13,360	(13,330) 13,420	13,320	13,090
	3.5	(14,800) 14,550	14,600	14,510	13,850	14,000	(14,150) 14,010	13,260	(13,650) 13,540	13,680
	4.3	14,260	(15,100) 14,610	14,820	(13,250) 13,520	13,970	14,830	12,840	13,960	(13,850) 13,900
1400 psi	2.5	16,310	(15,730) 15,980	15,510	(15,900) 15,430	15,200	14,830	14,620	14,510	(14,300) 14,270
	3.5	16,230	16,280	(15,900) 16,180	15,300	(15,800) 15,450	15,450	(14,300) 14,440	14,710	14,840
	4.3	(15,680) 15,920	16,260	16,460	14,950	15,390	(15,860) 15,690	14,040	(14,500) 14,610	15,040

ACHINE
ONDITIONS
ACHINE Bipel 3
OZZLE Std. Inst.
OULD RAPRA Plaque
ARREL TEMP 90 °C
OULD TEMP 150°C
CLE TIME 25 secs

OMPUTOR
ELIABILITY FACTORS
d. Error 2.9
squared 0.60
d. Error x 100
quation constant 2.98

PARAMETER Melt. Temp. °C.		BACK PRESSURE								
		30 psi			70 psi			120 psi		
INJECTION PRESSURE	INJECTION PRESSURE	SCREW SPEED			SCREW SPEED			SCREW SPEED		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
800 psi	2.5	(96.3) 98.5	99.7	97.9	97.6	100.1	(99.5) 99.5	98.7	(101.5) 102.8	103.5
	3.5	96.2	(99.9) 97.3	95.4	(96.5) 95.1	97.5	96.9	96.0	100.0	(102.0) 101.0
	4.3	100.7	101.8	(101.0) 99.8	99.4	(99.3) 101.8	101.1	(101.0) 100.2	104.1	105.0
1100 psi	2.5	100.1	101.6	(101.8) 98.9	99.9	(101.5) 101.6	100.2	(102.0) 100.6	103.8	104.1
	3.5	(99.9) 98.2	98.5	95.8	96.7	98.3	(92.8) 96.9	97.1	(101.8) 100.4	100.5
	4.3	102.1	(101.6) 102.4	99.6	(99.5) 100.5	102.1	100.6	100.8	103.9	(103.5) 104.0
1800 psi	2.5	101.8	(101.8) 101.4	98.0	(99.5) 100.1	101.0	98.9	100.4	102.9	(102.2) 102.3
	3.5	98.1	97.6	(90.0) 94.2	96.3	(100.0) 97.1	94.9	(99.5) 96.3	98.7	98.1
	4.3	(101.8) 101.5	101.0	97.5	99.6	100.3	(102.3) 98.1	99.4	(100.8) 101.7	102.2

ACHINE
ONDITIONS
ACHINE Bipel 3 onz
OZZLE Std. Inst.
OULD Plaque
ARREL TEMP 90°C
OULD TEMP 150°C
CLE TIME 25 secs

IPUTOR
LIABILITY FACTOR
ANDARD ERROR 0.14
SQUARED 0.99
ANDARD ERROR x 100
UATION CONSTANT 4.95

PARAMETER INJECTION TIME Secs		BACK PRESSURE								
		30 psi			70 psi			120 psi		
INJECTION PRESSURE	INJECTION PRESSURE No. of turns	SCREW SPEED RPM			SCREW SPEED RPM			SCREW SPEED RPM		
		60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM	60 RPM	100 RPM	140 RPM
800 psi	2.5	(6.8) 6.7	6.1	5.9	6.6	5.9	(5.6) 5.6	6.6	(5.8) 5.7	5.3
	3.5	6.6	(6.0) 6.0	5.9	(6.5) 5.6	5.9	5.6	6.5	5.8	(5.4) 5.4
	4.3	6.2	5.7	(5.6) 5.6	6.2	(5.8) 5.6	5.4	6.3	(5.2) 5.5	5.2
1100 psi	2.5	3.2	2.9	(3.0) 3.0	3.2	(2.8) 2.8	2.7	(3.2) 3.2	2.6	2.4
	3.5	(3.1) 3.2	2.9	3.0	3.2	2.8	(3.7) 2.8	3.2	(2.6) 2.7	2.6
	4.3	2.9	(2.8) 2.7	2.9	(3.0) 3.0	2.6	2.7	3.0	2.5	(2.5) 2.4
1400 psi	2.5	2.0	(1.8) 1.9	2.2	(2.1) 2.0	1.8	2.0	2.0	1.7	(1.8) 1.7
	3.5	2.0	2.0	(2.6) 2.4	2.1	(2.0) 1.9	2.2	(2.1) 2.1	1.8	2.0
	4.3	(1.8) 1.8	1.8	2.3	1.9	1.8	(1.9) 2.1	1.9	(1.8) 1.7	1.9

FIGURES IN PARENTHESES ARE EXPERIMENTAL RESULTS. OTHER FIGURES ARE COMPUTOR PREDICTIONS

Use of instrumented nozzle to monitor injection moulding process.

Shot No	Initial Peak Press psi	Min Pressure psi	Final Peak Press psi	inj time secs	Stroke	Screw Back Press psi	Screw Back Time secs	Screw Back Distance	Shot Weight grams
1	10,600	9,900	10,600	0.85	1.9	-	-	-	
9									31.376
10									31.407
11	10,450	9,550	10,550	0.75	1.9	-	-	-	31.499
19									31.719
20	10,200	9,450	10,450	0.7	1.9	-	-	-	31.811
21									31.615
29									31.637
30	10.200	9,600	10,550	0.7	1.9	900	2.6	2.55	31.820
31									31.640
39									31.819
40	10,550	9,500	10,600	0.7	1.9	950	2.55	2.55	31.719
41									31.856
49									31.736
50	10,300	9,500	10,650	0.7	1.9	950	2.55	2.55	31.999
51									31.867
59									31.360
60									31.964
61	10,600	9,700	10,750	0.7	1.9	1000	2.7	2.55	31.868
69									31.905
70									31.929
71	10,300	9,500	10,650	0.62	1.9	1050	2.6	2.55	31.849
79									31.950
80	10,200	9,600	10,600	0.65	1.95	1000	2.72	2.55	31.938
81									31.773
89									31.7557
90	10.200	9,600	10,500	0.65	1.9	1000	2.6	2.55	31.759
91									31.713
99									31.999
100	10,100	9,550	10,550	0.68	1.95	1000	2.7	2.55	31.935
101									31.875
109									32.039
110	10,150	9,550	10,500	0.6	1.9	975	2.75	2.55	31.019
111									31.900
119									32.055
120	10,150	9,550	10,550	0.6	1.95	950	2.65	2.5	31.960
121									31.949
129									31.968
130	10,200	9,450	10,350	0.06	1.95	975	2.62	2.5	31.967
131									32.010
139									31.792
140	9,850	9,500	10,500	0.65	2.00	950	2.7	2.5	31.933
141									32.143
149									31.440
150	10,300	9,150	10,350	0.70	1.9	975	2.65	2.5	31.660
151									31.905
159									31.927
160	9,650	8,900	10,400	0.65	1.95	950	2.6	2.5	31.922
161									31.826
169									31.825
170	10,250	9,450	10,550	0.62	1.95	900	2.65	2.5	31.880
171									31.851
179									31.880
180	10,200	9.400	10,550	0.65	1.9	950	2.55	2.5	31.954
181									31.907
189									31.736
190	10,400	9,350	10,550	0.68	1.95	900	2.6	2.5	31.836
191									31.777
199									31.898
200	10,250	9,400	10,600	0.60	1.9	900	2.7	2.5	31.859
201									31.709
209									31.902
210	10,100	9,250	10,600	0.6	1.9	900	2.6	25	31.912
211									31.854
219									31.906
220	10,150	9,300	10,650	0.65	1.9	900	2.7	2.5	31.725
221									31.516
229									31.875
230	10.050	9,250	10,500	0.6	1.9	875	2.55	2.5	31.665
231									31.660
239									31.45
240	10,100	9,300	10,600	0.6	1.9	875	2.6	2.5	31.52
241									31.56
239									31.46
240	10,160	9,300	10,600	0.60	1.9	875	2.6	2.5	31.52
241									31.56
249									31.32
250	10,450	9,350	10,750	0.65	1.9	850	2.65	2.5	31.45
251									31.76
257									17.59
258									16.64
259	10,300	9,250	10,750	0.72	1.95	275	2.45	2.55	32.78
260									31.64
261									31.52
269									31.48
270	9,700	8,050	10,800	0.65	1.95	300	2.7	2.5	31.46

Use of instrumented nozzle to monitor injection moulding process (cont).

Shot No	Initial Peak Press psi	Min Pressure psi	Final Peak Press psi	inj time secs	Stroke	Screw Back Press psi	Screw Back Time secs	Screw Back Distance	Shot Weight grams
271									31.52
274	>12,000	10,800	11,500	3.35	-	550	2.35	2.55	32.5
275	>12,000								5.58
276	11,000	9,900	11,200	1.00	1.9	650	2.65	2.50	30.77
277									31.22
S 279									31.32
S 280	10,750	9,850	11,200	0.7	1.9	700	2.6	2.5	31.28
S 281									31.54
283									22.96
284	>12,000	10,050	»12,000	6.2	1.9?	650	2.4	2.55	25.28
285	10,600	9,800	11,200	0.8	1.95	650	2.6	2.50	32.04
289				0.6	1.9				31.60
290	10,250	9,650	10,800	0.6	1.9	650		2.5	31.442
291	10,150	9,650	10,800	0.6	1.9	650		2.5	31.660
292	10,150	9,700	10,800	0.6	1.9	675	2.5	2.5	-
293	10,100	9,600	10,700	0.6	1.9	650	2.5	2.5	-
294	10,100	9,900	10,900	0.6	1.9	650	2.5	2.5	-
295	10,350	9,950	11,000	0.6	1.9	650	2.5	2.5	-
296	9.900	9,600	10,900	0.6	1.9	650	2.5	2.5	-
297	10,150	9,650	10,850	0.6	1.9	650	2.5	2.5	-
298	10,200	9,650	10,750	0.6	1.9	650	2.5	2.5	-
299	10,100	9,650	10,700	0.6	1.9	650	2.5	2.5	31.544
300	10,150	9,700	10,800	0.6	1.9	650	2.5	2.5	31.498
301	10,150	9.750	10,850	0.6	1.9	650	2.5	2.5	31.620
302	10,150	9,750	10,900	0.6	1.9	650	2.5	2.5	-
303	10,150	9,700	10,900	0.6	1.9	650	2.5	2.5	-
304	10,150	9,700	10,800	0.6	1.9	650	2.5	2.50	-
305	10,100	9,650	10,850	0.6	1.9	650	2.5	2.5	-
306	10,200	9,250	10,900	0.6	1.9	650	2.5	2.5	-
307	10,050	9,100	10,800	0.6	1.9	650	2.5	2.5	-
308	10,250	9,450	10,900	0.6	1.9	650	2.5	2.5	-
309	10,200	9,350	10,900	0.6	1.9	650	2.5	2.5	31.493
310	10,100	9,250	10,850	0.70	1.9	-	-	-	31.404
311									31.684
319									31.454
320	10,250	9,300	11,050	0.68	1.9	-	-	-	31.359
321									31.439
S 329									30.358
330	10,400	10,150	11,400	1.00	1.9	650	2.5	2.55	32.259
331	712,000			>3.0					≃20

S = sprue sticking occurred

Effect of Cure Time on Moulding Properties

Material PF5

Cure Time secs	Barrel Temp °C	Mould Temp °C	Nozzle Peak Press psi	Melt Temp °C	Inj. Time secs	Screw Back Press psi	Screw Back Time secs	Gloss	Heat Dist Temp °C	Weight gram
30	88	165	10,460	90	0.53	700	2.68	VG	111	27.15
45	88	165	10,600	92.0	0.72	700	2.63	VG	116	26.88
60	88	165	11,030	92.5	0.93	720	2.57	P	112	26.26
30	95	165	11,000	92.0	0.52	770	2.48	VG	102	26.78
45	95	165	11,260	95.0	0.9	800	2.55	P	115	25.34
60	95	165	11,840	96.5	3.23	650	2.65	P	112	21.77
30	88	190	10,530	90.0	0.42	950	2.48	G	96	26.9
45	88	190	10,060	93.0	0.55	600	2.5	G	133	27.26
60	88	190	10,300	94.5	0.62	600	2.4	G	128	27.0

Injection Moulding Ankerwerke Machine
Phenolic Materials

Material	Pressure psi					Injection Time secs.	Temp. Increase °C
	Nozzle		Runner	Cavity			
	Peak	Hold-on		far	near		
Slow Injection							
PF11A	3960	4200	4250	3300	2800	3.8	4.0
B	3900	4200	4200	3230	2650	3.6	3.4
C	4150	4100	4150	3280	2650	3.7	4.3
D	3850	4200	4000	3200	2730	3.5	3.2
E	3800	4000	4000	3200	2600	3.4	3.3
F	4000	3950	3900	3200	2580	3.5	4.0
15A	4000	3800	2400	2550	1800	3.9	3.4
9A	3450	4400	-	2500	2500	3.4	3.5
Fast Injection							
PF11A	7600	4250	4100	3150	2700	.73	10
B	7300	4200	4300	3075	2580	.61	8.3
C	7400	4400	4400	3200	2750	.7	8.8
D	6900	3840	3700	2950	2480	.57	8.8
E	6680	4510	4300	3500	2900	.6	9.2
F	6960	4500	4400	3280	2750	.62	9.1
15A	7000	4400	4000	2950	2700	.7	9.0

Injection Moulding Turner 60g machine with
Runner-Capillary Mould

Pressure MN/m^2			Flow Rate g/sec
Nozzle	Capillary		
Phenolic PF 11F			
69.2	7.1	3.1	47.5
67.0	6.5	2.9	52.6
57.3	6.4	2.4	40.0
54.1	6.6	2.8	34.0
43.7	4.3	2.5	14.7
43.0	4.8	1.7	20.1
33.0	3.2	1.0	13.8
Phenolic PF 15A			
87	9.3	4.8	52.6
74	7.7	2.5	40.0
59	5.2	1.9	16.7
Phenolic PF 17B			
51	5.6	2.8	15.8
43	4.3	1.7	10.5
33	3.9	1.5	8.4
20	2.6	0.9	3.4
Urea UF 22I			
108	11.2	5.2	30.6
103	10.4	4.8	19.4
85	8.2	4.1	9.2
Urea UF 22J			
112	12.0	5.2	19.1
85	8.1	3.9	9.2

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A REVIEW OF THE METHODS OF CHARACTERISING THE FLOW/CURE PROPERTIES OF THERMOSETTING PLASTICS MATERIALS

by

K. T. Paul

Shawbury Shrewsbury SY4 4NR England

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A Review of the Methods of Characterizing the Flow/cure Properties of Thermosetting Plastics Materials

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1. Introduction

The ability of some chemicals to react to form resinous materials was known to the chemists of the late 19th century. Early materials were modified natural products e.g. celluloid, but in 1872 Bayer reported the formation of phenol-aldehyde materials. These were initially studied for academic reasons but in the early 1900's, Baekeland discovered techniques for controlling and modifying the phenol-aldehyde reaction to produce commercially useful products. Thus the world's first synthetic materials were obtained which were initially exploited by the General Bakelite Company of America.

The success of these materials prompted further research and in 1918 John prepared urea formaldehyde resins which were subsequently exploited by the British Cyanamid Company. Melamine formaldehyde resins were known by 1940 and were closely followed by "contact resins", the forerunners of today's polyester resins. Epoxy materials followed shortly afterwards and more recently diallyl phthalate, and other more sophisticated materials have been developed.

Phenol-aldehyde materials were intially cast or moulded in fully positive moulds. This type of mould was gradually developed into the vertical and horizontal semi-positive type of mould which together with the flash mould offered advantages over the earlier positive mould.

The development of the transfer moulding process was relatively slow. Transfer moulding offers considerable advantages over the earlier compression technique in that it enables the use of lower pressures, shorter moulding cycles and the production of more complex shapes containing delicate inserts.

Early attempts to injection mould thermosets were made in the late 1940's using ram machines but the process did not achieve any significance until the advent of the screw injection machine in 1957. A period of intensive development occurred in both machinery and materials and today in-line screw injection moulding of thermosets is an accepted commercial process. This process offers advantages over compression and transfer moulding techniques because it allows even shorter cycle times with the accompanying advantages of increased productivity and reduced cost. Other advantages are also obtained although it is doubtful if it will completely replace other moulding techniques because each process has advantages which make it more suitable for certain applications.

Just as the development of moulding technology has lagged behind the development of materials, so the development of methods of characterising materials has apparently lagged still further behind.

Before discussing the historical development of testing techniques it is perhaps wise to remind ourselves of the thermoset moulding process. The application of heat and pressure to a thermoset will initially cause the material to fuse and to form a viscous liquid which will flow throughout the mould. At the same time, a chemical reaction takes place which causes the viscosity of the material to increase until flow is prevented by the onset of crosslinking i.e. the material gels. The reaction continues and the material becomes rigid when it has cured. The moulding of thermosets is therefore composed of three effects, fusion, flow and cure, all of which are intimately connected and are influenced by temperature, pressure and the process of deformation.

Early methods of characterising thermosets were based on production moulding techniques and often a small mould was used to produce data which would be correlated with a larger production mould. Many types of mould were used ranging from a closed cup mould to an open mould where no restriction was placed on the flow of the material. Different types of mould produced results related to various parts of the flow-cure process and frequently could not be correlated with each other and were difficult to apply in moulding production. The results were frequently expressed in different ways, e.g. pressure, time, distance, number of cavities filled etc., and different manufacturers often used different test methods. This lead in the 1930's to several pleas for a standardised test procedure.

The development of the Rossi-Peakes tester of 1934 produced a method which indicated the flow of the material over the complete flow-cure period instead of the combined flow/cure effects which were measured by the earlier tests. While this represented a considerable improvement and enabled materials to be more closely characterised it had certain limitations which were recognised by its inventors.

Flow-time curves were obtained in 1939 using a form of instrumented mixer but this work was limited to the determination of viscosity before curing takes place.

Although newer moulding techniques have been and are being developed, little work has been carried out to improve the original methods of material-characterisation or to relate these to the conditions encountered in the newer processes.

The last decade has seen considerable increase in the amount of literature concerning the characterisation of thermosets over a wide range of shear rates and temperatures. New instruments e.g. an oscillating disc rheometer, a rotational viscometer have been developed and more traditional equipment e.g. the capillary viscometer have been used under more realistic conditions. Much of this work has aimed at the determination of fundamental viscosity parameters.

2. Survey of Methods of Determining the Flow/Cure Characteristics of Thermosetting Materials

For convenience, test procedures have been split into several categories according to the way in which the test is carried out. Many of these categories have been sub-divided.

2.1 This section contains various tests which were developed quite early and relate directly to compression moulding techniques, e.g. Cup Flow Test.

2.2 The capillary techniques were intended to overcome certain disadvantages of the test described above and usually approximate to transfer moulding procedures. They include the capillary viscometer which is more usually used for rheological studies.

The following sub groups may be made.

2.2.1 Capillaries of very short land length which minimise time dependent effects, e.g. Monohole test mould.

2.2.2 Capillaries of longer land length which are used for rheological studies and which allow time dependent effects to be studied e.g. Capillary Viscometer.

2.2.3 Capillaries of long land lengths in which the material is retained throughout its whole flow and cure life. This section may be further subdivided into straight and curved capillaries, e.g. Rossi Peakes Flow Test and Spiral Flow.

2.3 The rotational test system in which the material is sheared in a closed mould may be further sub-divided into various types, e.g. rotational viscometers, variable torque rheometer and extruder.

2.4 Oscillating techniques have been described for use with thermosets and include an oscillating capillary system as well as the more usual oscillating disc rheometer.

Several of these techniques, e.g. Farol Weissenburg Rheogoniometer may also be used as rotational devices.

2.1 Test Procedures Based on Compression Moulds

2.1.1 Cup Mould

A procedure in which material is placed in a beaker mould is described by Forrer. The punch is lowered on to the material and the hydraulic pressure rises until the material starts to flow. The pressure then remains constant until the excess material has flowed out of the mould when the mould closes and the pressure once again rises. The duration of the softening and flow period is used to specify the plasticity of the material. Early test moulds were of different geometry and of both positive and semipositive types.

This technique is described as an excellent method which is speedy, if somewhat imprecise, and has the advantage of indicating cure time (blister free), the surface finish of the final article, the presence of flow lines and any resin filler separation (1).

This technique was developed into the BPF Cup Flow test for testing PF's at specified temperatures, pressures and mould design (2). This test is suitable for UF's and reference (3) shows how this test may be used to measure cure time as well as flow time.

The effect of variations of mould temperature, charge weight and form, loading and press closing times, and rate of ram travel are discussed by Wainwright (4).

The basic cup flow test has appeared in several forms and various ways of expressing the results have been suggested. Schwittman suggested in 1942 that the pressure should be measured as a function of time while keeping the mould separation constant but two years later suggested keeping the pressure constant and measuring the mould separation as a function of time.

Schwittman developed the cup flow technique to measure pressure/time curves. He concludes that viscosity/time data is really required but that mechanical difficulties prevent this (1942) and that pressure time curves give considerably more useful information than the more usual flow time (5).

This technique is further explored in conjunction with a mechanical cure test which was similar to the Izod impact test and measured the flexural impact strength of cups prepared with different cure times. Pressure/time and distance/time curves are given for materials containing different types of fillers (5), (see Figures 1a and 1b).

A limitation of the cup flow is that it measures the fusion and flow characteristics of a free flowing powder rather than the fusion, flow and cure interaction, i.e. it measures the time for a material to become fluid rather than the duration of fluidity (6).

The cup flow mould has been modified to evaluate the complete flow process and, in this form, it resembles the orifice or capillary flow technique.

Approximately twice the normal charge weight of material is used and the cup mould is altered so that the excess material escapes by flowing up two semi circular slots 1 mm deep which are cut into the upper part of the cup.

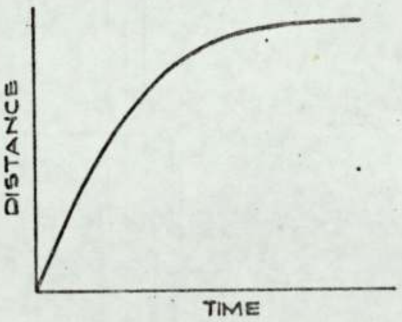


FIG. 1a

Fig. 1a Typical distance/time curve for cup mould

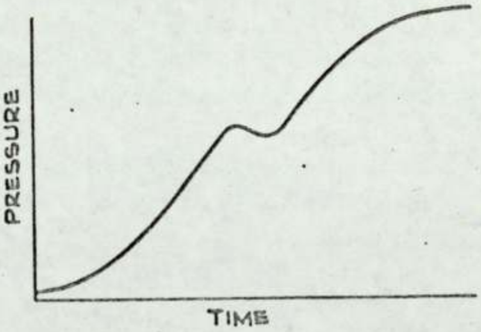


FIG. 1b

Fig. 1b Typical pressure/time curve for cup mould

The stroke of the press and occasionally moulding pressure are recorded with reference to time. The effects of charge weight, temperature and pressure for materials having good and poor flow characteristics are studied.

The flow capacity of the material is indicated by the rate at which material flows through the orifice while the speed of hardening governs the duration of flow.

An alternative method is to undercharge the mould and to measure the height of the resultant moulding (8).

In 1948 the basic cup flow test was adapted by the ASTM which specified a constant mould separation and determined a pressure at a specified time (9).

Woebcken suggested the measurement of pressure at constant time and specified mould separation in 1953 (10).

The measurement of time at constant pressure and specified mould separation was adapted as a standard test by Britain in 1956 (11) and by Germany in 1955 (12).

The disadvantages of this procedure are that it is limited to stiff flow materials and while it enables the determination of batch to batch variations it cannot be used with certainty to determine if different types of thermosets have the same moulding index. The cup test does not correlate well with any other conventional flow tests and while useful for compression moulding techniques it is of little use with transfer moulding materials (13).

Karas has criticised the cup flow mould since it gives inadequate indication of material flow characteristics for compression moulding using a complex mould and still less for transfer and injection moulding (14), while Sundstrom, Walters and Goff conclude that the cup flow test is the least useful of the six types of test they evaluated (15).

2.1.2 Multi-Cavity Mould

An unusual test is described by Norton, which requires the use of a mould containing a large number of cavities. The plasticity of a material is denoted by the number of complete mouldings which are produced under specified conditions of temperature and pressure when material is placed in the centre of the mould and yet results in a specified flash thickness.

The main draw-back of this system is the number of experiments required to obtain the required flash thickness and the method is described as "a series of tests on a single cavity mould varying the pressure each time" (16).

2.1.3 Parallel Plate

A relatively simple technique is to squash a specified amount of material between two parallel steel sheets under specified conditions of temperature and pressure. The flow of the material is described by the thickness of the resultant disc at its centre or at a specified diameter. The diameter of the disc may also be used as a measure of flow (1).

This method is an adaption of the Williams Test developed for use with rubber materials, in which the disc thickness was expressed as a function of time (17).

The test is simple but requires the same volume (not weight) of material to be used, the perfect parallelism of the plates and a constant state of cleanliness and polish of the plates.

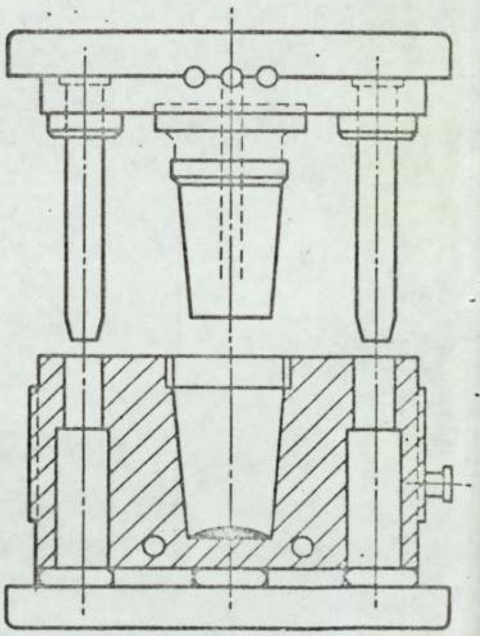


Fig. 2 Typical cup flow mould

FIG.2

This technique was reported in use with both urea and phenolic materials by Wainwright who describes its use and the effect of process variables on the results and also indicates the reproducibility of the test. Difficulties are encountered with finely ground materials and the effect of using pelleted materials is described (4). Other authors indicate that the test is inadequate with UF materials (18).

The chief disadvantage of this type of test is that no two materials can be tested under identical conditions since the pressure is applied over an area which increases as the flow of the material is increased i.e. high flow materials are effectively tested under conditions of lower pressure than stiff flow materials (7).

Another criticism of this test is that separation of fillers and fibre reinforcement can occur with low viscosity resins e.g. epoxy materials (19).

The rheology of the disc flow test was discussed by Pinfold (20).

2.1.4 Compaction Test

The compaction of powders is studied by Kunin and Yarchenko who concluded that three stages of compaction occur. Initially the particles are forced closer together, secondly brittle and plastic deformation takes place and finally a volumetric compression. Equations are developed which enable characteristic constants to be obtained for materials (21).

This technique, in which a positive cylindrical mould is used at low temperature to investigate the pelleting characteristics of thermosets is further described in reference (22). This measures plastic flow at temperatures of 50 - 100°C and is used to study the compaction of powder materials. Typical results are shown in Figure 3. Equations are developed from the test results.

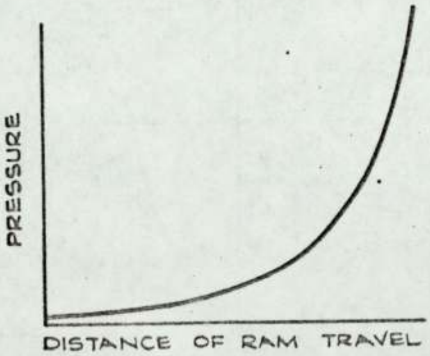


FIG. 3

Fig. 3 Typical pressure/distance curve for compaction test

2. 2 Capillary Techniques

2.2.1 Short Capillary (Orifice Type)

Early versions of an orifice flow test are described in detail by several authors (23, 24, 25). These are reviewed by Forrer (1) who concludes that although the method is used in the rubber industry it does not lend itself to advantageously determining the plasticity of polymerisable materials since the time required for the test is excessive. The results, which are usually expressed as the amount of material extruded, are criticised in that they are the resultant of plasticity and cure time and do not determine the plasticity alone.

The basic test is described as a heated ejection pot with a small opening at the bottom. Pressure is exerted onto the material via a ram. Alternative ways of expressing the results are as the time required to extrude a specified weight of material or to extrude a specified length.

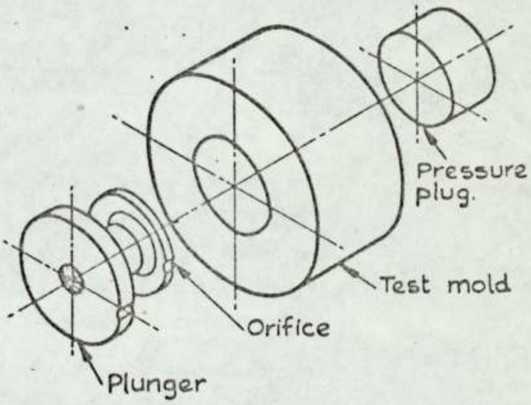


FIG. 4

Fig. 4 Orifice test mould showing two orifices in punch

A form of orifice test in which two small half round dies are used is described by Kerr and Dontje (26) who use the instrument to evaluate DAP materials, see Figure 4. Material is placed in a heated mould, and pressure is applied to the upper ram. The material is extruded through two small orifices in the punch lip. The results were expressed as flow time and percentage flow with varying pressures. The results approximate to a straight line graph using semilog paper.

These results were compared to those obtained using a Brabender Plastograph and a series of three dimensional models constructed to explain differences. It is noted that the orifice technique does not separate the flow and curve effects.

The author also studies the flow path of material in the pot.

A similar technique is described (27) as a telescoping positive mould of 2-5 inches diameter with one or more slots cut into the punch. The flow is related to the amount of material remaining in the mould. Alternatively extrusion takes place from the centre and the extrudate measured.

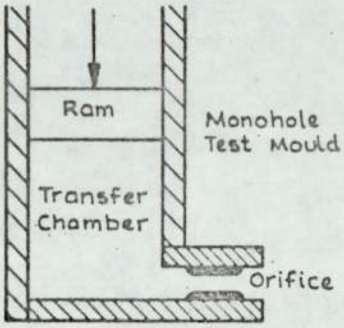


FIG.5

Fig. 5 Monohole test mould

The Monohole mould has been used to investigate the flow of injection moulding phenolics (28) Figure 5. The test is a modified version of the Japanese Standard test JISK 6911 and is used to show the effect of residence time on material flow.

Material is placed in the heated chamber and preheated for 3-5 minutes. Pressure is applied for 2 seconds only and then reapplied for 2 seconds every 60 seconds. The results (see Figure 6) show an optimum residence time for the material to reach its optimum flow characteristics. This time varies between compounds, but may be correlated with the injection moulded spiral flow test.

The method below has been described for use with amino materials and consists of a transfer pot

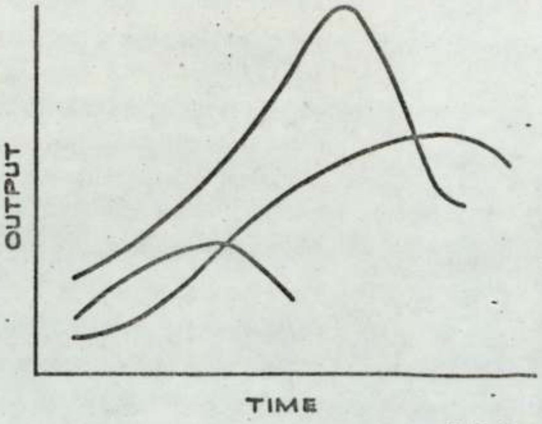


FIG.6

Fig. 6 Flow rate/preheat time curves for various thermosets monohole test

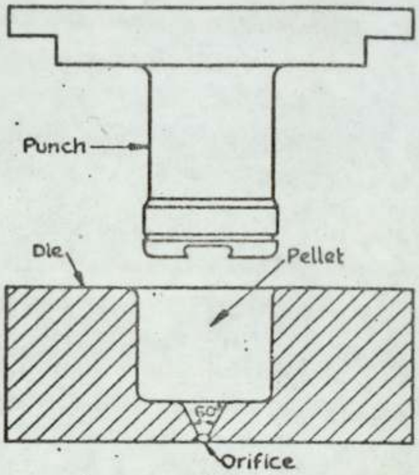


FIG.7

Fig. 7 Orifice test mould

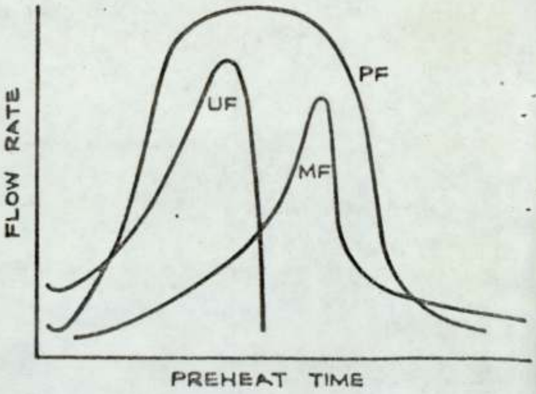


FIG.8

Fig. 8 Output/time curves for orifice test fitted with a small orifice of diameter 0.08" and length 0.03" Figure 7. The equipment is used to determine the effects of temperature, pressure and chamber residence time on the flow characteristics of the material. Typically, the material is placed in the pot and held at 140°C. After 5 minutes, the material is extruded and the results expressed as the percentage of material extruded Figure 8.

This technique is used to measure the flow of a material at typical barrel temperatures (100°C) as well as at mould temperatures (150°C) and is claimed to correlate with the performance of the materials in an injection barrel. Graphs are shown which highlight the differences in flow duration between various materials.

The validity of this technique has been shown by a number of tests using an injection moulding machine (29, 30).

The use of the injection moulding machine nozzle as a viscometer has also been described (31, 32). Melt from the screw is ejected from the nozzle and the ejection time is used in conjunction with the ejection pressure and melt temperature as a measure of the material viscosity.

2.2.2 Medium Length Capillary (Rheological Type)

The capillary viscometer is a well known type of instrument used widely to determine the rheological properties of a wide range of materials (33). It is not proposed to discuss this instrument in detail nor to examine the interpretation of its results but merely to describe its use with thermosetting materials.

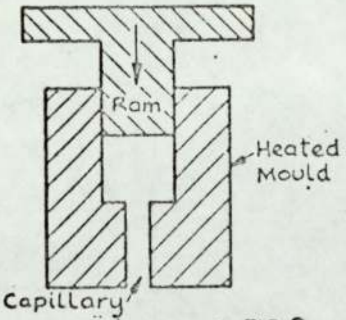


FIG.9

Fig. 9 Typical capillary flow equipment

A capillary test which is intermediate between the orifice and a true capillary is used to measure the flow properties of nylon and glass filled polyester materials (34) Figure 9. Dies of different diameters (1/8", 1/4" and 1/2") but of constant land length (1/2") were used and the results were quoted as the pressure required to extrude material at constant speed at 73°C. These results in conjunction with a gel time and a peak exotherm (150°F) were used to characterise the material. The regularity or lack of regularity of the pressure is used to indicate the uniformity and the apparatus is used to control, reformulate, develop materials and to predict moulding performance.

The flow of glass fibre filled polyester dough materials has been investigated in a capillary viscometer at 20°C (35). The authors point out that these materials have a non-ordered distribution of assymetric shaped particles and that the flow process is affected by a change in the dimensions of the filler which is brittle and can break up during flow. The effects of fibre break up with varying runner size have been studied elsewhere (36, 37) and the authors choose conditions such as to minimise fibre break down.

Capillaries of 9-12 mm dia, 5-100 mm length and of 30-180° entry angle were used to determine rate and force of extrusion. The analysis of results is given.

The extrusion pressure initially shows a peak followed by fluctuations which are caused by the inhomogeneity of the material and may be used to show differences between various production batches. Shear due to flow only occurs at the capillary wall (max. thickness of 2 mm).

The results were used in conjunction with a comparison of mechanical properties before and after extrusion to determine the optimum geometry of a nozzle system for use with the injection moulding of these materials as well as to characterise the material.

DAP and PF materials are characterised by determining the time, pressure, temperature relationships using a modified small bore capillary extrusion rheometer at a constant extrusion rate (38).

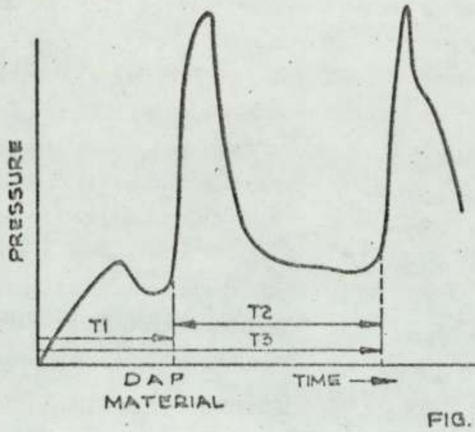


FIG. 10a.

Fig. 10a Pressure/time curve for DAP material

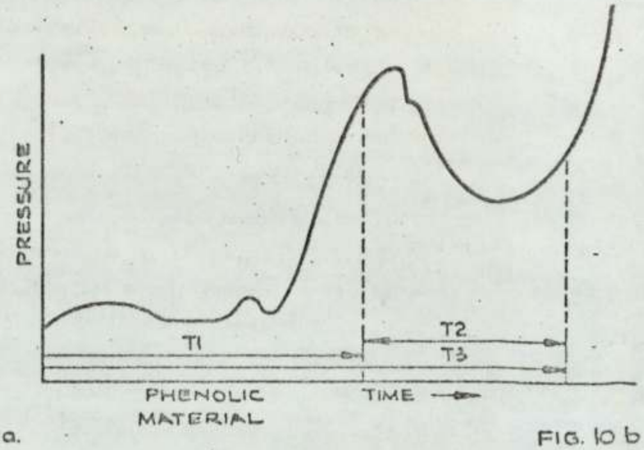


FIG. 10 b

Fig. 10b Pressure/time curve for PF material

The interpretation of the trace is determined by measuring the sol/gel ratio, the swelling index, the molecular weight and the infra red absorption with varying residence time.

Multi-coloured materials are used to show that the flow of DAP's is laminar but the material is inhomogeneous while tunnelling occurs with phenolics especially at the higher temperatures. (Thermoplastics and rubbers are also evaluated).

Typical traces are shown in Figures 10a and 10b.

T_1 is the time preceeding plastic flow, T_2 the time of plastic flow and T_3 the total flow time. These results correlate with transfer moulding techniques and the writers suggest that the ratios T_2/T_3 should be as large as possible.

High temperatures (175°C) cannot be used because the material sets up too rapidly. Typical flow times are quoted as

125°C	15 mins.
150°C	1 min.
175°C	10 secs.

The authors state that flow rate is independent of die size and that the results may be used to calculate apparent viscosities, but these results will be of doubtful accuracy in view of the rapidly changing character of the melt during the test period.

The authors conclude that flow/pressure results correlate with transfer moulding, a record is obtained of crosslinking and that semi-qualitative data is obtained (with respect to the Mooney) which may be related to processing conditions and also provides apparent viscosity data. The extrusion of thermosets at a constant rate of flow through a capillary has been studied to determine the rheological characteristics of the material, i.e. the duration of the plastiviscous state and the resistance of the material to flow.

Shear rates of 1 - 100 $\sec^{-1}$ were studied using circular and slit dies.

The curves show the initial compression and break up of the physical structure followed by the plastiviscous flow region and then the hardening reaction Figure 11. Results may be used to calculate shear stress/shear rate data.

The article includes a comparison of capillary flow data, the Kanavec Plastimeter and the Raschig flow test. The authors concluded that capillary data may be correlated with the Kanavec results but that the Raschig test is inadequate since it does not show viscosity time effects (39).

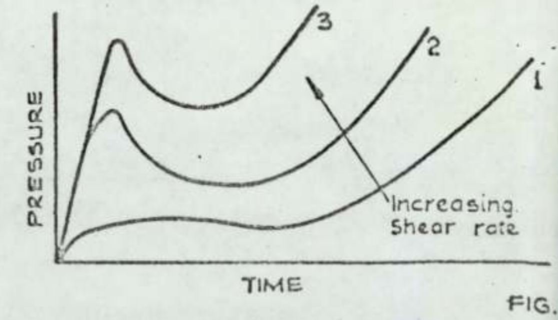


FIG.11

Fig. 11 Pressure/time curve for PF material showing effect of increasing shear rate

The use of an injection moulding machine to characterise thermosetting materials is described (40). The effect of pressure drop on the flow of material through a sprue, sprue entry resistance and the effect of mould pressure on the strength properties are established. The results are used to establish the rheological laws for the thermosets and to serve as a basis for calculating flow and for the determination of optimum processing conditions.

A range of materials are studied, each material having been characterised in the Kanavec Plastimeter.

This approach to the problem of material characterisation involves long and complex experiments and this work has been followed by a series of experiments based on a capillary viscometer.

A paper by Sokolov and Kanavets discusses the rheology of thermosets in a capillary (41). This analysis uses the chemical-physical mechanism of "disperse" systems (42, 43) as a theoretical basis for calculation. The effects of low shear rates were determined using a rotational viscometer.

The measurement of viscosity was carried out during the period of plastiviscous flow, the duration of this period having been determined previously.

There was no slip between the wall of the capillary and the material. This was shown by the direct relationship between the pressure and the land length at constant shear rates and also by the lack of difference between capillaries of rough and smooth finishes.

The technique used was to measure the extrusion pressure at constant extrusion rate.

The authors concluded that an increase in the shear rate causes the viscosity to decrease while die entry effects increase.

Equations are derived to enable the injection moulding parameters to be calculated and procedures are quoted to determine rheological properties, sprue entry effects, resistance to flow in channels, moulding pressure, mould filling time and the necessary dimensions of sprue channels.

Meyer (44) studies the flow properties of phenolic materials in a capillary viscometer, concludes that the method is suitable for use with phenolics, and that capillaries of greater than 10 :1 L :D are required.

The apparent viscosity at 120°C decreases rapidly with increasing shear gradient i.e. phenolic materials show pseudoplastic behaviour, and conform to the Power Law.

The author comments that capillary devices are cheaper and offer a more simple means of obtaining high shear rates than the rotational type of viscometer.

The use of a capillary in conjunction with an injection moulding machine is described (45). Viscosity data is calculated using the Ostwald-de-Waele equation and assumes that the material does not slip at the capillary wall, that time dependent effects such as rheopexy and thixotropy do not occur and that there is a uniform development of the flow profile over the whole capillary length.

2.2.3.1 Long Capillary (straight type)

A general review article by Thater outlines the various types of test in which the material is forced from a transfer chamber into a long thin chamber which is used to measure flow (46).

The Raschig test involves placing a standard weight of material into a heated transfer pot. Pressure is applied and the material is forced into the end of a rectangular mould. The flow is assessed by measuring the cull thickness.

This method was developed by Krahl Figure 12 who substituted a tapering capillary for the mould and used the length of the moulding at a specified temperature and pressure as a measure of flow. This technique is fully described (8, 47).

The Hessen system in which an open top cylindrical mould 50 mm dia, with varying wall thickness is used is described by Thater. The flow is measured as the height of the wall of the moulding.

The Rossi Peakes, von Meysenbug/Zwick (discussed in more detail overleaf) and Ericksen/Raschig systems which use circular or rectangular dies and which express results as a flow length as a function of time at constant pressure are also out-

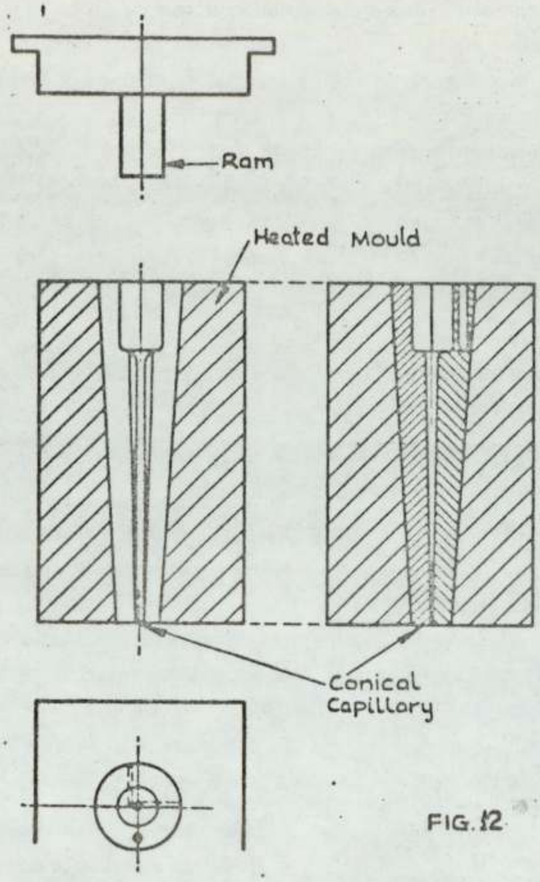


FIG. 12

Fig. 12 Test mould Krahl Type

lined. Although the results are occasionally quoted as the pressure required to give a specified flow length the Ericksen/Raschig may be used to indicate pressure as a function of time using a constant speed of extrusion i.e. at constant shear rate. This system is mentioned and (48) its use with phenolic materials is discussed in comparison with the disc and cup flow tests. The authors claim that the conical runner is more discriminating than other systems but that the section of the runner has little effect. The stiffness of the final extrudate is used to indicate the cure of the material, the time to give a standard deflection being preferred.

The use of a transfer system having seven capillaries of varying diameter is described by Burns (44) (see Figure 13). The flow time (press closure time) is measured and the plasticity of a material is given by the sum of the products of the length of flow in a capillary and the capillary number. The capillaries are numbered 1 to 7 in order of decreasing size which results in the flow of a material in the smallest capillary receiving greater stress. (A diagram of a circular slide rule is included as an aid to calculation).

Advantages claimed for this technique are that it gives more useful information than the use of a single orifice, that it permits visual assessment of the moulded parts, that flow in small cavities is emphasised, that it may be used for thermoplastics as well as thermosets and that it is simple and cheap.

A disadvantage is that resin can separate from the filler and will flow into the narrow capillaries (50).

The development of the Rossi Peakes tester was described in detail in 1934 (27, 51, 52) in an article which considers the theoretical aspects, design details, the effect of pressure and temperature on test results, the accuracy and sensitivity of the instrument, as well as the use of this equipment for determining effects such as mould poisoning, mould finish and lubrication, material control and moisture content for phenolic materials. A limited study of urea materials is included.

The Rossi Peakes tester (see Figure 14) is basically a capillary viscometer in which the material flow is measured as a function of time by means of a weight loaded sensor which is in contact with the extrudate. The sensor is weighted to prevent the formation of porosity in the extrudate. A typical

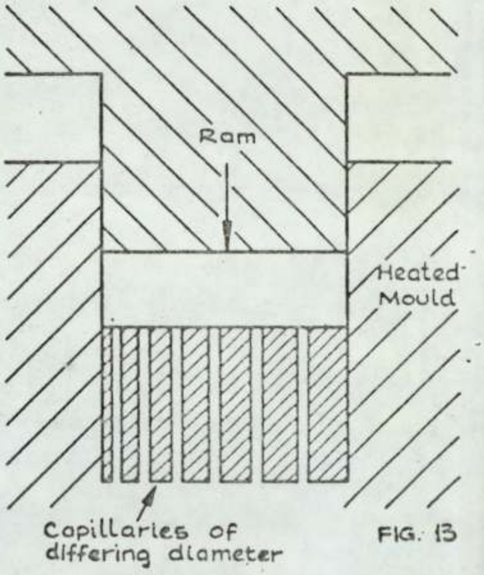


FIG. 13

Fig. 13 Test mould Burns Type

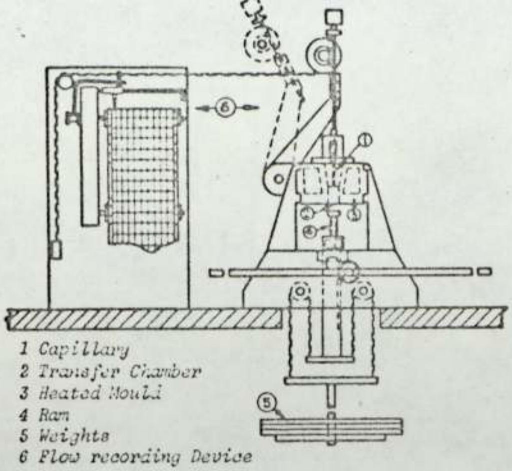


FIG. 14

Fig. 14 Rossi Peakes Flow Tester

trace is shown in Figure 15a. Typically the total distance of flow is measured although the preferred technique is to measure the flow length over a range of pressures to produce a pressure/flow curve, Figure 15b.

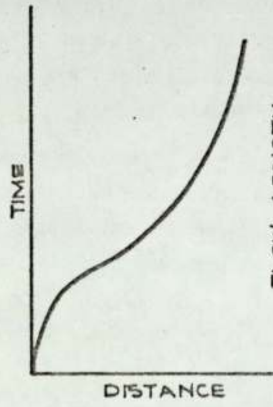


FIG. 15a

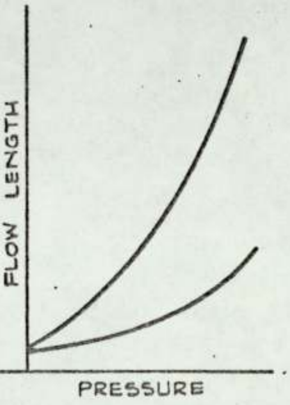


FIG. 15b

Fig. 15a Distance/time curve for Rossi Peakes Flow Tester. PF

Fig. 15b Flow length/pressure curve for Rossi Peakes Flow Tester. PF

It is noted that these curves show a similiarity to rate of flow/pressure curves and that with certain materials, a definite yield pressure exists, other materials show a linear log plot of pressure against length while some materials show no rational behaviour (N.B. these materials are all based on phenolformaldehyde resins).

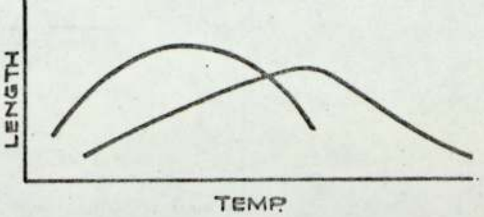


FIG. 16

Fig. 16 Flow length/temperature curves for 3 grades of UF material, Rossi Peakes Flow Tester

Although the flow tester measures plastic properties as distinct from minimum cure times or production rates, cure times may be measured by using a conical mould instead of the open ended capillary. In this case blister free times are determined.

A discussion of test procedures indicates that the distance time curve may be used to show the effects of fusion, flow and the gradual reduction of flow due to curing reactions and also to show the different flow/cure behaviour of different materials. It is also noted that laminar flow occurs and that cured material may adhere to the capillary while more fluid materials flow in the centre, i.e. the flow life of the material is measured not its cure time.

The effects of charge size were discussed and the writer concludes that equal volumes of material based on the final moulded density provide the best comparisons. Pelleted materials are used throughout the work.

The use of the instrument to determine the effects of mould poisoning and the time of its duration (a negative lubricant effect of one material on subsequent material), and the evaluation of different mould lubricants is discussed in detail. The effects of material control e.g. variations in resin control and moisture content are shown and compared to the physical properties of the final moulding.

Flow length/temperature curves are included for three urea compounds Figure 17.

The author concludes the the Flow Tester is very useful in solving problems associated with the manufacture and use of thermosets although it was found that the flow tester will not predict commercial performance in every case. Various improve-

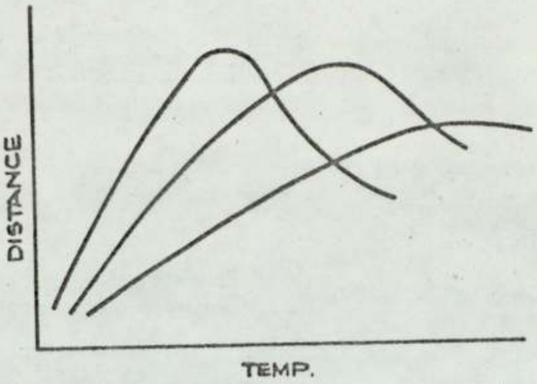


FIG. 17

Fig. 17 Distance/temperature curves Rossi Peakes Flow Tester

ments were also required following an extended period of trial and development.

The Rossi Peakes Flow Tester is described in USP 2, 066, 016 and its use to evaluate preheated materials is discussed discussed (53).

The use of the Rossi Peakes Flow Test (also referred to as the Olsen Test) is discussed (50) and compared to the Cup Flow Test and the Plasticity Set Index (49). Both one and two stage phenolics are investigated.

The author concludes that no single test will give sufficient information from which moulding behaviour in a variety of commercial moulds can be predicted. The determination of plasticity is insufficient and it is of practical interest to relate plasticity to cure.

The Rossi Peakes flow tester was adopted as a standard test method by the ASTM in 1948, revised in 1959 and reapproved without change in 1961 (54).

A recent paper (55) given at the British Society of Rheologists Conference discusses the replacement of the original string, weight and pencil recording equipment with a linear transducer fitted to the ram and an electronic recorder. By determining the difference in extrudate length at $\frac{1}{4}$ second intervals, the viscosity of the material is calculated using the Poiseuilles Equation Figure 18. The effects of temperature and pressure were described and also preheating of the material.

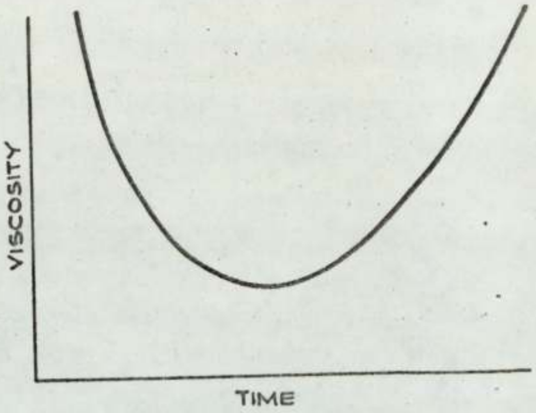


FIG. 18

Fig. 18 Viscosity/time curve derived from distance/time curves

Pressure versus minimum viscosity curves were shown for glass filled DAP and alkyd materials and show a dilatant effect. Practical examples of the use of this technique included the calculation of gate size required for a material, and the determination of batch to batch variations of materials, these differences were shown by the distance/time curve but could not be shown by other test methods e.g. disc flow.

Reasonable correlation with injection moulding is claimed and materials which show a minor peak in the viscosity/time curve are known to cause a pause in the injection stroke Figure 19.

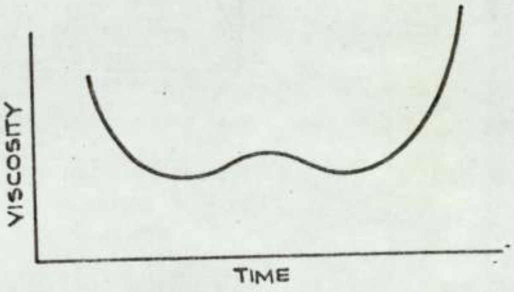


FIG. 19

Fig. 19 Viscosity/time curve showing small centre peak

Amino and phenolic materials have been evaluated although the results are described as "peculiar to the type of material under evaluation".

Many comments have been made concerning the usefulness of the Rossi Peakes Flow Tester. These comments are often contradictory and are listed below:

a) A useful technique which offers advantages over the more usual test procedures (52).

b) It has the advantage of using a small sample weight and is highly reproducible (52).

c) It uses too small a sample to give reproducible results (46).

d) It is too complicated for practical usage (58).

e) The results may be correlated reasonably well with injection moulding (55).

A limiting factor would seem to be that the shear rate will vary considerably during a test run.

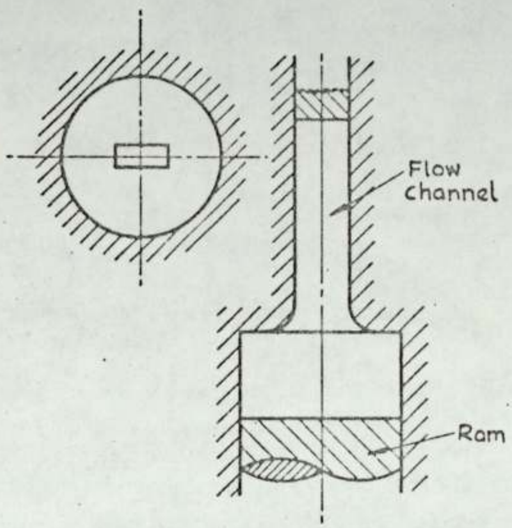


FIG.20

Fig. 20 Zwick Flow Tester

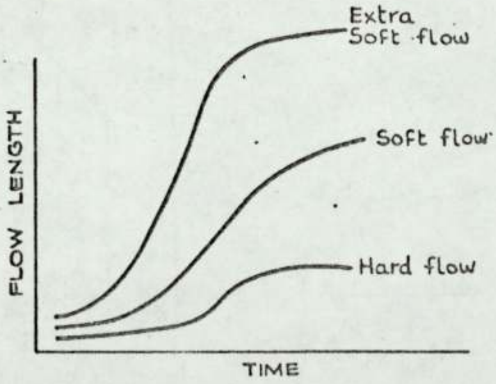


FIG.21a

Fig. 21a Distance/time curves for materials of different flow characteristics

The Rossi Peakes flow test is criticised by Thater and Ulbricht who state that it is of little use with UF's. This is because the low pressures and the low charge weights used are not compatible with the high loads required to make UF's wet metal surfaces. This deficiency, which does not occur with phenolics, has lead to the development of the Zwick tester (18).

The Zwick system Figure 20 is similar to the Rossi Peakes tester but has a larger cavity and die which is of rectangular section, uses higher pressures and will handle coarse materials. It is a more modern piece of equipment in that it replaces the string and weights of the Rossi Peakes with more sophisticated systems. It is described in detail in (57) and its use to evaluate a range of thermosets is described in reference (58). Figure 21 shows typical flow length/time results.

The author also discusses the use of the instrument with thermoplastics.

A comparison of the Rossi Peakes/Zwick and Krahl tests with PF's is given together with a limited evaluation of amino materials (59).

Thater (46) examines the flow pattern in the Zwick tester and investigates the density distribution, impact strength and flexural strength of the extruded rod. He concludes that this type of instrument is less satisfactory than the Kanavec Plastimeter, since it has poorer reproducibility, is less true to processing conditions and does not indicate cure times.

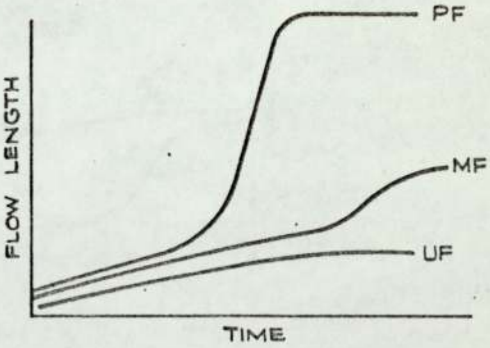


FIG.21b

Fig. 21b Distance/time curves for different materials

In a more detailed evaluation of the Zwick system the instrument is evaluated for amino materials. This is because the standard disc flow test is inadequate for UF materials while the Rossi Peakes system uses too small a charge weight and too low pressures to give reproducible results with UF's although satisfactory results are obtained with PF's.

The results of an evaluation of the effects of pigmentation, moisture content, pressure and charge weight for melamine materials are given. It is interesting to note that an optimum charge weight exists for maximum flow length for a free flowing material. Test results indicating the level of reproducibility are also shown.

The writers conclude that the Zwick system gives good reproducibility with amino materials and that it is suitable for control testing (60).

Ulbricht and Rudiger describe the use of the Zwick, Kanavec and Cup test (with distance/time recording equipment) but do not compare their usefulness (61).

The Zwick instrument is used to determine the flow characteristics of a range of MF materials containing a cellulosic filler (62).

Flow/time relationships are quoted for a range of materials including MF modified with urea, acetoguanamine and benzoguanamine. The effects of resin condensation and water content are shown and the authors indicate that optimum levels exist (63).

Smoll and Pungs determine the flow length as a function of preheat time using the Zwick equipment for fast curing phenolics (64) Figure 22.

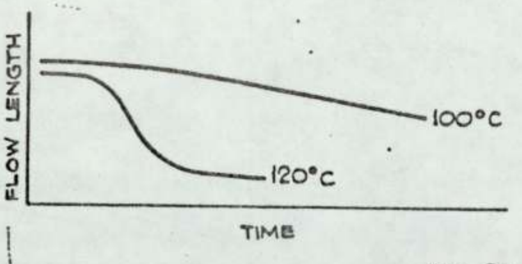


FIG. 22

Fig. 22 Distance/time curves showing effect of temperature on flow length

The authors claim good comparison with the results obtained from a plunger/screw injection moulding machine and state that the Zwick results agree with differences shown by the Brabender Plastograph.

The use of the Zwick apparatus was used to determine the flow and flow stability during the development of a phenolic material for injection moulding, and has also been used to investigate the use of plasticisers (polyester type) with phenolics (65) Figure 23.

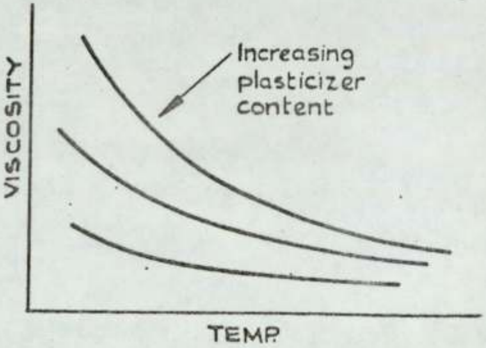


FIG. 23

Fig. 23 Viscosity/temperature curves showing effect of plasticiser addition

The Rossi Peakes/Zwick/Rashig technique is examined by Menges, Ehrentraut and Dalhoff who show the effects of pressure, temperature and flow rate using a three dimensional diagram for a phenolic material (66) Figure 24.

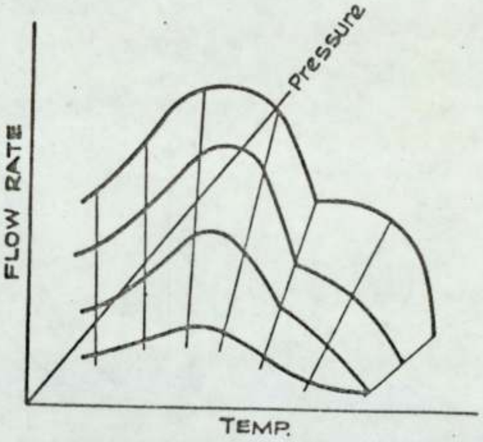


FIG. 24

Fig. 24 Relationship of flow rate, temperature and pressure

Materials of different colours are used to illustrate the flow pattern within the chamber and die. The effects of moisture content of the material, the influence of preheating, charge weight, material form and ram close time as the flow curves are investigated. Curves are shown for a material containing extra lubricant. A typical flow curve is shown below together with its interpretation Figure 25.

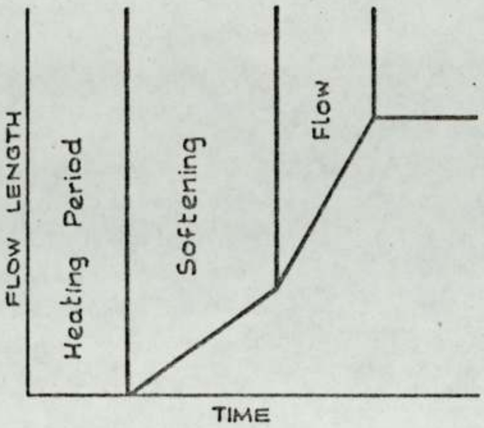


FIG.25

Fig. 25 Interpretation of Zwick Flow Test results

The authors conclude that this test system is useful to compare materials and also as a quality control instrument.

The Zwick system is unsuitable for use with long glass fibre filled materials since the fibres tend to felt in the chamber (67).

2.2.3.2 Long Capillary, (Spiral Type)

The Spiral mould (MIOM test procedure) is reviewed by Forrer (1). The mould consists of a transfer pot, the exit of which ejects material into the start of a spiral groove. The ejection process takes place in 2-3 seconds while the material is allowed to cure for 2-3 minutes before removal from the mould. The flow is quoted as an arbitary number related to the length of the spiral moulding.

An article by Spiwak (13) discussed the use of a spiral flow mould to overcome the disadvantages of the cup flow test when used with DAP materials. Different types of spiral mould are described for various applications. Thus the IBM spiral (1/8" dia 1/2" round 102" long) spiral is suggested for soft flow materials, the Mesa spiral trapezoidal section 0.25" wide, 0.032" deep and 48" long is recommended for stiffer materials, both tests are intended to be used for transfer moulding materials for electronic encapsulation work.

The effects of long and short fibre reinforcement are briefly mentioned as are the effects of temperature.

Mention is made of the fact that closely controlled conditions (temperature 300 ± 3°F) are required and the plasticity of a material is indicated by the length of the spiral moulding.

The spiral mould technique has been further refined (58) by the addition of a linear transducer to determine the rate of filling of the mould as well as the flow length Figure 26. Its use with transfer materials is described.

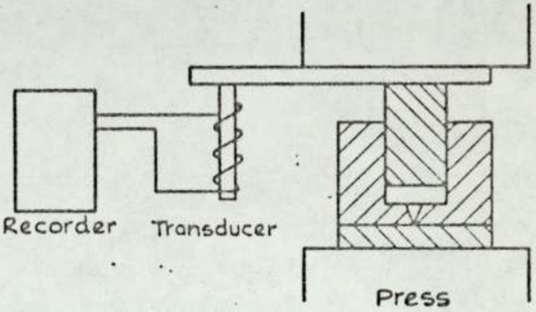


FIG. 26

Fig. 26 Diagramatic representation of instrumented spiral flow test (TR 58)

A position time curve is produced which may be used to determine rate of fusion with respect to time (i.e. early or late) flow time and enables differences to be determined in materials having the same flow length.

This technique has the advantage of being simple and may be fitted into a normal press. It is best used for medium and high flow materials and is suitable for use with PF, MF, UF epoxy, alkyd and polyester based materials.

The Epoxy Moulding Materials Institute standardised on the 1/8" half round spiral mould to test long flow encapsulation materials (69). The technique is described (70) and graph of spiral flow length versus transfer pressure, cull thickness, delay, temperature and ram speed are shown. Recommendations for pot dimensions, temperature and pressures are given. The article claims that the spiral flow test in conjunction with a gel time will enable a material to be characterised although it will not predict the material behaviour in complex moulds.

The instrumented spiral flow (EMMI type) was further developed by Heinle and Rodgers (71) who added a velocity transducer to the linear transducer described above to obtain a better interpretation of the position/time trace. In addition to the spiral length, the flow time (AB) is also obtained Figure 27.

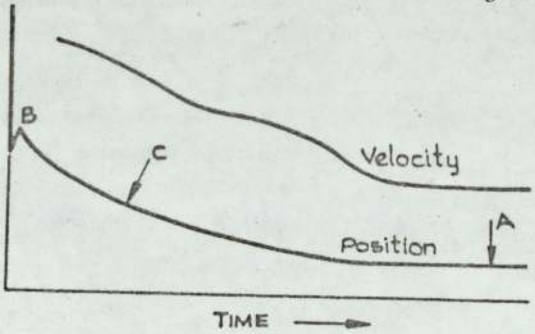


FIG. 27

Fig. 27 Distance/time and velocity/time curves

A later paper describes how this information which is in the form of pressure drop, flow rate data may be used to calculate material viscosities. This enables minimum viscosity to be used as the parameter for flow measurement.

The use of this instrument to study melting and curing rates is also claimed. When combined with temperature and pressure data the authors show that the materials have a non-Newtonian flow behaviour.

The materials evaluated were a two step phenolic for injection moulding and an epoxy material.

The spiral mould has been used in conjunction with an injection moulding machine to study the effect of process variables on a phenolic material (29). The effects of barrel residence time, temperature, screw speed and mould temperature on the spiral length are shown Figures 28a, 28b and 28c.

The author studies the fusion process by means of pressure transducers placed at intervals along the injection barrel. The effect of process variables is also studied and also the correlation of the Monohole test with injection moulding. An advantage of this technique is that it is simpler than the injection process but it does not take screw barrel geometry into account.

The author concludes that pressure development in the screw is different from that of thermoplastics and that low temperature flow in the barrel is not always similar to high temperature flow in the mould. This technique is also mentioned by Brooks (133).

Karas (13) describes the use of a spiral technique to overcome the difficiencies of the cup flow test. The spiral test measures the material viscosity,

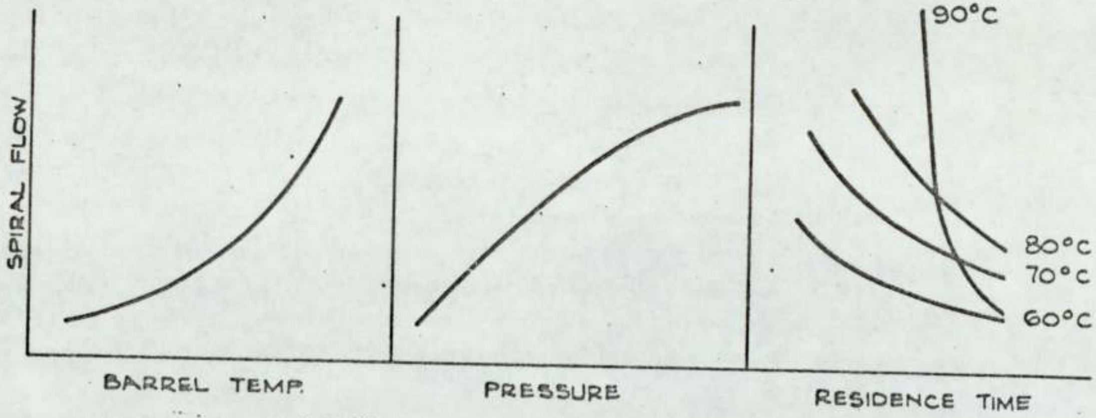


FIG 28a FIG. 28b FIG. 28c

Fig. 28 Relationship between spiral flow length and a) Barrel Temperature; b) Injection Pressure; c) Barrel Residence Time.

cure time in the transfer pot (i.e. residence time) transfer pressure and ram speed but must be correlated with moulding practice. Improvements to the basic system are suggested e.g. the use of a ram position indicator, the use of side chambers along the flow path linked to the spiral by restricted gates and the use of core pins in the spiral to study weld line effects.

The use of gates in the spiral has been suggested to study runner/gate/mould systems and, together with thermocouples to study frictional heating effects.

The spiral flow length (72) does not increase proportionally with pressure because the resistance to flow increases with increasing flow length and because of cure effects. The flow path (i.e. the flow distance/time curve) is more important than the spiral length since it shows how rapidly a mould will fill (30).

2.2.4 Comparison of Capillary Types

A general comparison of several types of capillary test is described in reference (14) for a range of glass filled DAP and PF materials. A flow bar test and the cup flow test are also included.

The distance time curve was obtained for each procedure using a linear transducer fitted to the press table. Typical results are shown in Figure 29.

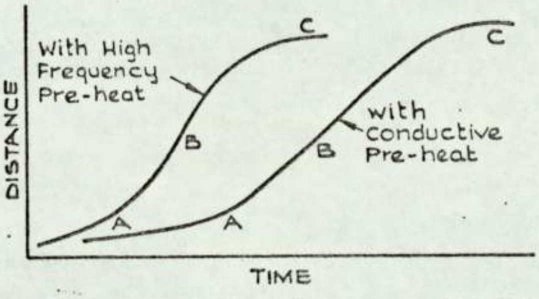


FIG. 29

Fig. 29 Distance/time curves showing effect of conductive and high frequency preheating

The authors conclude that the different capillaries give different distance/time curves. Thus the orifice and Zwick systems give longer linear sections to the curve than the spiral type.

The results of pressure against flow rate gave straight lines or smooth curves when plotted on log log axes. The relative positions of the curves for each class of material remain constant when the results of each test method are compared for each class of material but are not constant when DAP's and PF's are considered together.

The flow curves indicate that the materials obey the Power Law but the authors point out that the experiments were not carried out under isothermal conditions and that the experiments do not conform to the conditions specified by the theory used to develop the Power Law. The writers point out that the agreement between test and theory could be purely fortuitous and that frictional heating effects will lower the viscosity of the material and will compensate for the increase in condensation.

2.3 Rotational Systems

2.3.1 Rotational Viscometers

An early rotational test device has been described by Schwittmann (72).

The lower punch rotates causing the material to be deflected in a manner shown in Figure 30. The rotor is driven at a constant torque and the fusion/cure process is assessed by measuring the speed of rotation. A stiff or partially cured material will thus reduce the speed of rotation more than a low viscosity material. The instrument will thus indicate the viscosity time curve for a material and the chief advantage claimed for this technique is that it indicates the separate effects of flow and cure rather than the combined effects of flow and cure (Figure 31). When calibrated the system is claimed

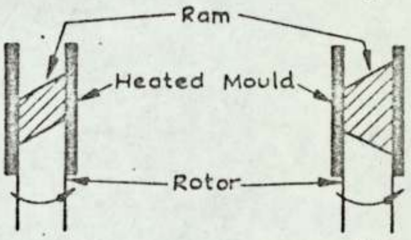


FIG. 30

Fig. 30 Rotational test device (Schwittman)

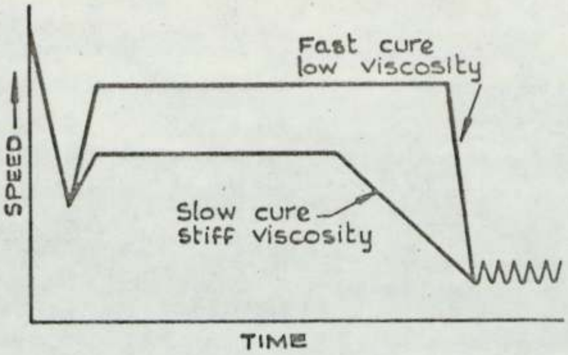


FIG. 31

Fig. 31 Typical rotor speed/time curve (Schwittman)

to be suitable for technological, practical and research work. This technique was not developed for technical reasons (1942) and does not seem to have been developed subsequently (5).

Rotational viscometers of the type first described by Kanavets in 1956 have appeared in several forms and have been used to measure different aspects of flow cure process. The analysis of the results is, however, similar for each instrument.

Although Kanavets work was initially published in 1956 (73), it is convenient to refer to the work of Ehrentraut published in 1966 since this has the considerable advantage of being translated into English (74, 75).

A diagram of the Kanavec Plastimeter is shown in Figure 32. The apparatus consists of a heated cylinder with a hemispherical top which forms the compression ram. The outer rotates and load transmitted to the mandrel is determined by the deflection of a balance arm.

The speed of rotation is 1 revolution in 1,235 seconds which corresponds to a shear rate of 0.014 $secs^{-1}$ and was chosen to eleminate excessive velocity gradients. The outer mould and centre mandrel are splined to prevent the material slipping at the wall.

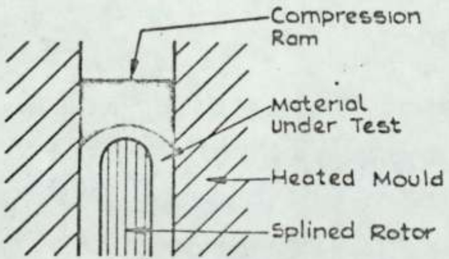


FIG.32

Fig. 32 Kanavec Plastimeter.

Materials in pellet form are placed into the upper chamber, fused and forced into the measuring chamber when rotation of the mandrel commences. The material is therefore fused and undergoes a compression moulding operation before viscosity measurement starts. The compound is subjected to a time constant shear deformation and the resistance of the compound to deformation is registered as a function of time.

Calculation of viscosity is based on the principle that equilibrium exists between the balance and the moment acting on the specimen, that the moment is caused by the internal friction of the material and that the magnitude of the internal friction varies with viscosity (73).

A typical trace is shown in Figure 33.

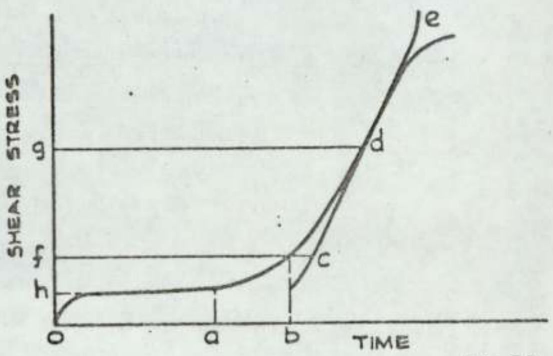


FIG. 33

Fig. 33 Typical shear stress/time curve for Kanavec Plastimeter

The time interval 0-a is the time the material is in a viscous state at viscosity h. The rate of cure is obtained from the gradient ce. Values of 4×10^7 poise (shear stress 5 kgf/cm^2) are interpreted as the end of the viscouse state f and of 2×10^9 poise as the minimum state of cure at which a moulding may be removed from the mould d. This is claimed to be equivalent to an acetone extraction of 6% which is specified by the relevant Czech standard. The cure curve continues until a peak value is reached when the specimen breaks up. This is claimed to be full cure (73) although this is disputed by other writers. The rate of cure is the gradient at a viscosity of 2×10^9 poise (equivalent to a shear stress of 25 Kgf/cm^2).

The use of the instrument to evaluate the effects of temperature on the material properties and calculations of the approximate initial polycondensation activation energy are shown.

The results are also used to predict the most favourable compression moulding conditions and to relate these results to various moulding thickness.

The use of the instrument as a standard test and a material specification is also suggested.

$$\text{Material Number} = \frac{\text{Dwell time in viscous state at } 170^{\circ}\text{C}}{\text{Effective Viscosity at } 120^{\circ}\text{C}}$$

Material Numbers >30 very good flow
<30 poor flow

Minimum cure time at 170°C
<55 secs. very rapid cure
>90 secs. slow cure

This reference concerns phenolic materials only.

The Durograph (76, 77) is basically a Kanavec Plastimeter in which electronics have been used to record torques, temperatures etc. The use of this instrument is described in a manner similar to that given above.

The relationship of the Kanavec Plastimeter to injection moulding is considered by Ehrentraut and Dalhoff (78). Similar points (shear stress of 5 and 25 kgf/cm^2) to those chosen by Kanavets are selected to specify the material. It is concluded that a few isolated crosslinks occur during the viscous state and that the complete moulding operation must take place before a limiting shear stress of 25 kgf/cm^2 is reached since the material cannot be compacted at higher viscosities. This also represents the safety limit for material in the barrel. The material must not be disturbed within the shear stress limits of 5 - 25 kgf/cm^2 since this will cause internal stressing of the moulding. Above the upper limit cure proceeds but little change in physical properties occur. At high cure times, properties can decrease due to a splitting off of low molecular weight products.

The information obtained from this instrument is useful in setting up an injection moulding machine but the final adjustments need to be made by observing the machine performance. A knowledge of the time during which the viscous state exists is particularly important since this may be used to predict the barrel life of the material.

An alternative approach is to use the Kanavec trace to calculate the work done on the material, but this is not discussed in detail.

The basic Kanavec Plastimeter has been modified to investigate injection moulding.

Kanavets and Sokolov describe (79) the use of the instrument in conjunction with a capillary to determine the effects of forcing a material through a small orifice at high rates (Figure 34).

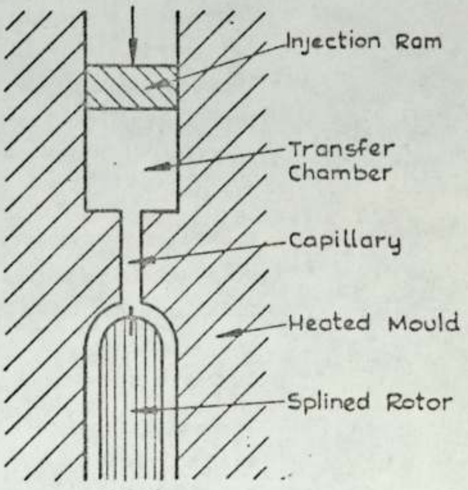


FIG.34

Fig. 34 Kanavec Plastimeter modified with capillary feed

Pelleted materials are placed in a small transfer chamber and preheated before being forced at high speed through a capillary into the measuring chamber of the Plastimeter. A thermocouple is positioned at the top of the rotor and the viscosity/time curve is measured in the usual way.

This technique is claimed to provide a method of assessing the technological properties of thermosets under the conditions of injection moulding, to establish the effects of basic parameters, and their effects on the process and properties and to provide a method of calculating dwell times for all moulding sections.

The significance of this technique is detailed in reference (80).

It has been shown that shear rates in sprue channels can reach 10^4 sec^{-1} and that shear rates of this order can affect the physico/chemical properties of the moulding material. The author refers to various writers (81-85) who have proved that mechanical action can degrade molecules to form macroradicals and cites the mastication of rubber as an example of this process (86). Three dimensional networks can be broken down to produce a phenomenon known as chemical flow (87). Linear systems are also effected since side branches may be removed (73, 88, 89). As a result, reactive sites are produced which lead to denser products, faster reaction times and as a result a predominance of crosslinked polymer units in chains rather than in separate aggregates (89). The articles formed from thermosets by this treatment are therefore more rigid than articles formed by directed moulding.

It has been shown that a four fold decrease in viscosity occurs by increasing the shear rate from 0.015 to 10^3 sec^{-1} and that the minimum plastic (Bingham) viscosity is due to the complete dispersion of structure forming systems.

These effects have been studied by forcing material at high shear rates through a capillary into the measuring chamber of the Kanavec Plastimeter. The results are compared to those obtained from the more usual compression technique described above.

Conditions are such as to simulate injection moulding in that the material is preheated to 90-100°C before injecting into the Plastimeter which is maintained at 170°C.

Typical results are shown in Figure 35 indicating that the material emerging from the capillary has a lower viscosity but has a faster rate of cure than the compression moulded material. The temperature of the material emerging from the capillary is stated to be the same as that of the compression moulded material. The authors concluded that the differences are due to the mechanico-chemical degradation which takes place in the capillary.

Final conclusions are that mechanico-chemical phenomena play an important part in injection moulding, that the technique described above reflects the conditions of injection moulding which are not shown by other test methods (the Raschig and Zwick system are specifically mentioned in the text), that flow of thermosets in a narrow channel at high shear rate gradients causes a reduction in effective viscosity and an increase in hardening rate, and that the mechanico-chemical processes increase the rigidity of the final moulded product.

It should be noted that a comparison of physical and electrical properties of specimens prepared by compression moulding, transfer moulding with RF heating and inline screw transfer concludes that little or no difference is observed in the properties of screw and RF heat transfer materials. In particular, the flexural strength of RF heater transfer moulded specimens is marginally but consistently greater than inline screw samples which is in turn greater than compression moulded samples (90).

The Kanavec Plastimeter is available commercially (? USSR) and is known as the PPR-1 Plastimeter (91). The use of the Plastimeter for Urea and Melamine formaldehyde materials is described (92). This work was carried using material of cup flow 7-10 seconds to investigate the rheological properties of amino resins.

The Plastiviscous state of urea resins is characterised by a shear stress of 2.5 - 5.0 kgf/cm^2 although this limit is reduced by preheating of the material.

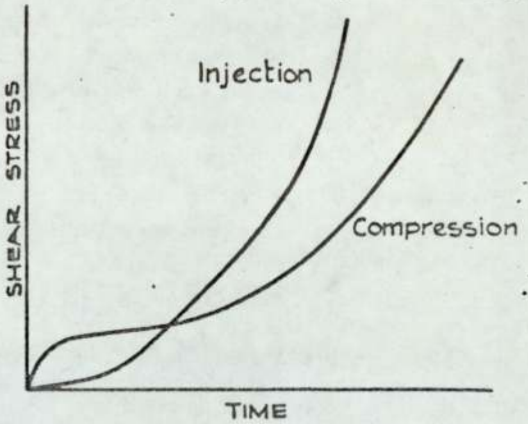


FIG. 35

Fig. 35 Comparison of effects of injection and compression moulding on shear stress/time curve (Kanavec Plastimer)

Hardening times were determined by the time required to reach a shear stress of 25 kgf/cm^2 for ureas and 50 kgf/cm^2 for melamine based materials.

It was possible to obtain exponential equations relating the plastic time to the temperature and the cure time to the temperature for melamine materials. Test results with urea materials showed too great a scatter to permit this treatment.

The results were used to determine the conditions for moulding and articles from a melamine material. In each case shorter cure times at higher temperatures were recommended.

The article concludes that different batches of ureas of similar cup flow show considerable differences in technological properties as determined by the Kanavec Plastimer.

The problems of heating a pellet in a hot chamber are discussed with reference to the Kanavec Plastimeter (93).

Examples of the use of the Kanavec Plastimeter in industry include utilisation of Plastimeter data to calculate optimum processing schedules for thermosets (MF, UF and PF), to calculate the cure time of phenolics and to evaluate materials for injection moulding (74, 75, 76).

The Kanavec Plastimeter is preferred to the Zwick system since it is nearer to process conditions and indicates cure times. A disadvantage is that it does not measure viscosities during flow (46).

Most work concerning the Kanavec Plastimeter has been carried out at very low shear rates because the plastimeter has been used to determine viscosity/time characteristics after the material has completed any moulding operation i. e. when it would normally be a stagnant melt.

The Plastimeter has been used to obtain viscosity data over a shear rate range of 14 x 10^3 to 10^2 sec^{-1}. Frictional heating effects are compensated for by the use of a viscosity/temperature curve determined with the Plastimeter at low shear rates (0. 014 sec^{-1}) where frictional heating does not occur.

The authors show that the main reduction in viscosity occurs between 1 - 100 sec^{-1} and that the duration of the plastiviscous state at 170°C is reduced by 4 - 5 times by an increase in shear rate from 0. 014 to 10^2 sec^{-1}. Of this reduction 1.5 - 2 times is the result of shear rate while the remainder is due to frictional heating effects.

The results are used to calculate mould dwell times for mouldings of varying thicknesses.

This work is expanded in reference (98), which discusses the rheology of the Kanavec Plastimeter and the use of this instrument to study thermosets at shear rates of 10^{-2} to 10^2. secs^{-1}. The rotational viscometer is claimed to overcome the disadvantages of a capillary

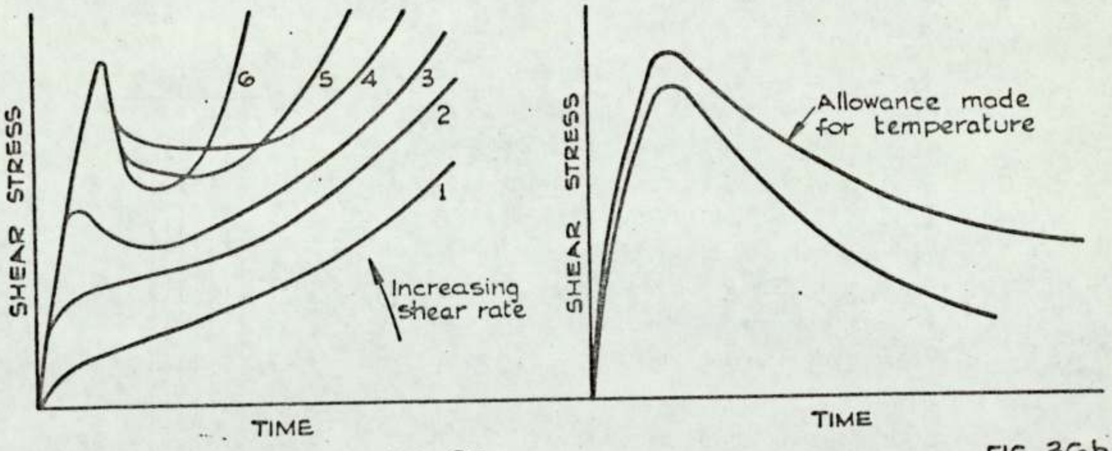


FIG. 36a

FIG. 36b

Fig. 36 Shear stress/time curves showing effects of a) increasing shear rate; b) frictional heating type which are given as, entry effects which break up the structure of the material, the impossibility of obtaining steady state conditions with thermosets and the impossibility of obtaining shear due to slipping of the material on the walls of the capillary. The rotational device generates frictional heat at higher shear rates but this is allowed for by using a previously determined viscosity temperature curve.

Typical results are shown in Figures 36a and 36b.

At low rates of shear (0. 014 - 0. 16 sec^{-1}), there is a monotonic increase in shear stress up to a constant value. The rate of increase in shear stress is commensurate with the rate of relaxation. In the initial stages of deformation, there is a sharp rise in the curves since the rate of relaxation lags behind the rate of rise of the stress. The limit is reached when the rate of relaxation increases so much that further increase in shear stress becomes impossible. Increase in the rate of deformation leads to an increase in elastic deformation in the material, the resistance to viscous flow increases and the relaxation processes are not able to develop. With increase in shear stress flow becomes superimposed on the elastic deformation. After reaching the maximum, the descending part of the curve changes to the portion corresponding to steady state conditions of flow, although in practice a small increase in shear stress occurs indicating the presence of polycondensation reactions. Steady state shear is therefore not an absolute characteristic of a thermoset but is on average value obtained from the plastiviscous state.

On reacting a critical rate of deformation (figures of 10 sec^{-1} and 30 sec^{-1} are quoted for two grades of phenolic material) the magnitude of steady state stress decreases with increase in shear rate. An increase in shear rate of 14 x 10^{-3} to 10^{2} sec^{-1} produces a viscosity decrease of approximately 3 orders which is said to compensate for the reduction in mould filling time due to increased temperature caused by frictional heating.

The authors claim that capillary or capillary-rotational system do not show a drop in shear stress with increasing shear rate because steady state flow is not obtained with thermosets and that the mechanical effects have no significant effect because of the duration of the process of deformation in these instruments.

The work of Ehrentraut is described in greater detail in reference (75), shows that the Kanavec Plastimeter may only be used to give a guide to cure time. This is because the various physical properties show a maximum value at an optimum cure time but that the optimum cure time is not necessarily the same for all properties (31, 99).

The Kanavec Plastimeter can however be used to indicate the processing conditions to be used for a material (100). The results must be modified to allow for variations in the section of the moulding.

The article describes the processes of injection and compression moulding and in particular study that the duration of the plastiviscous states indicates the time available for the moulding process without the material starting to cure.

The advantage claimed for the Kanavec type of instrument is that it enables cure rates to be studied unlike instruments having a high speed of rotation (e.g. the Plastograph) which result in a high degree of chain scission. It can therefore be used to measure viscosity time effects without disturbing or heating the melt.

The rotational viscometer has been modified for use with the injection moulding machine (101). The apparatus is fitted in place of the mould and receives melt from the injection nozzle. The viscosity/time relationship is measured in a similar

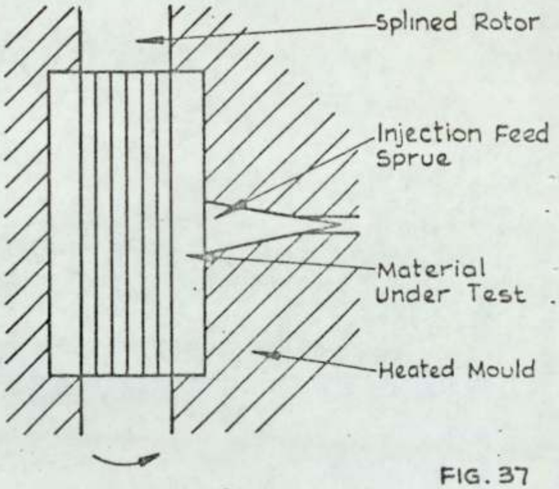


FIG. 37

Fig. 37 Mould Chamber Brabender Durocorder

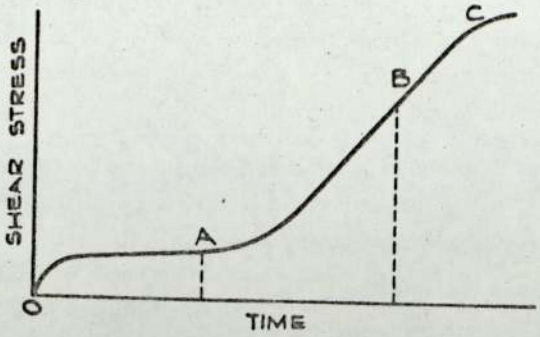


FIG. 38

Fig. 38 Shear stress/time curve, Brabender Durocorder

manner to the Kanavec Plastimeter and the same interpretation is used to relate the results to moulding practice. This apparatus is known as the Brabender Durocorder and is shown in Figure 37, and typical results in Figure 38.

The author states that in the lower part of the curve (OA) a direct relationship between shear stresss and apparent viscosity exists. For the centre portion of the curve (AB) a relationship exists between the quantity of un-crosslinked material (i.e. the acetone soluble fraction) and the resistance of the material to the shear forces (102). This zone describes the behaviour of the material as it changes from an intrinsically viscous material to an elastic one (103). Hooke's Law may be applied to the material at the upper part of the curve (BC which may be used to measure the shear modulus of the material).

This equipment is claimed to be more useful than more conventional test procedures since it relates closely to the injection moulding process. It enables materials to be evaluated under practical production conditions and provides the data necessary for determining machine parameters. It also enables the effects of processing conditions e.g. the effect of screw and cylinder design, nozzle design and type of gate on the flow/cure relationship of the material to be determined. A realistic method of assessing newly developed materials is also claimed.

It has been shown that the flow/cure curve can be used to estimate the pressures necessary for moulding, the time available for processing and the time required for full cure (104).

Comparative moulding tests using a mould of variable mould/runner thickness have shown that of the results given by the Durocorder the shear stress of the material in the plastic phase represents a measure of the required injection pressure.

Relationships between the material temperature and the mould residence time and between the degree of cure (acetone solubility) and the minimum hardening time at various mould temperatures are shown in reference (105). The latter were obtained by freezing the moulding in solid carbon dioxide to stop the chemical reaction. Acetone solubility figures for the feed material and for the material leaving the nozzle are also quoted.

Although published work has dealt with the use of the Durocorder exclusively with phenolic materials, the manufacturers state it is suitable for all thermosets including urea, epoxy and DAP materials (106).

Relationships between the viscosity time curve as determined with a Kanavec Plastimeter, percentage solubility, surface resistivity, volume resistivity, dielectric characteristics and curing time at 150°C and 190°C for three grades of phenolic materials, all properties being measured on the Kanavec specimen (107, 108).

These results were used to calculate the rate of development of electrical properties and were compared to the properties of moulded discs.

The article points out that although a Kanavec shear stress of 60 kgf/cm^2 was chosen, it may be obtained with a variety of temperatures and times. The electrical properties vary with temperature and time and it is necessary to evaluate these effects in conjunction with the cure curve obtained from a Kanavec Plastimeter (the latter indicates the mechanical properties of the material) in order to obtain the optimum cure conditions. The reasons for differences between the types of phenolic and aniline formaldehyde materials is discussed and the results used for determining a shear stress level for each type of material relating to its electrical properties. High degrees of cure may be obtained by post storing the moulding. This process aids the removal of volatiles and results in improved dielectric properties.

The Mooney Viscometer is intended for rubber materials but is included since it gives similar results to the Kanavec type of instrument and the interpretation of the results is of interest since rubbers are basically thermosetting polymeric materials.

The work of Frank and Kleine Albers may be referred to (109).

The Mooney Viscometer is a rotational instrument using a disc-shaped rotor and a rotor speed of 2 rpm (shear rate 1.6 sec^{-1}) Figure 39. Typical results are shown in Figure 40, oa representing the zone during which materials must be compounded and moulded, ab the cure or vulcanising zone, bc the plateau area where little change in physical properties occurs and cd a reversion zone where molecular degradation takes place. Although the Mooney Viscometer is more sensitive for viscosity measurement than the Monsanto Rheometer (110), it operates at relatively low shear rates and is less useful for cure measurements.

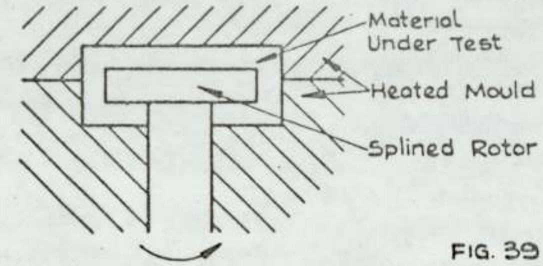


FIG. 39

Fig. 39 Mooney Viscometer

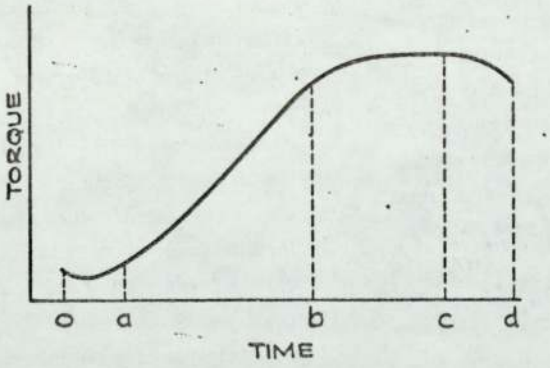


FIG. 40

Fig. 40 Torque/time trace, Mooney Viscometer

The Weissenburg Rheogoniometer and various cone and plate viscometers have been described in the section dealing with oscillating systems but may also be used as rotational instruments.

2.3.2 Variable Torque Rheometer

An instrument which is frequently referred to in the literature is the Plastograph, a variable torque rheometer by Brabender Figure 41. This is essentially a small internal mixer in which the torque transmitted to the mixing head may be recorded as a function of time. The melt temperature is also recorded. The mixer has two, triangular shaped rotors which rotate in opposite directions at a differential speed of 3:2.

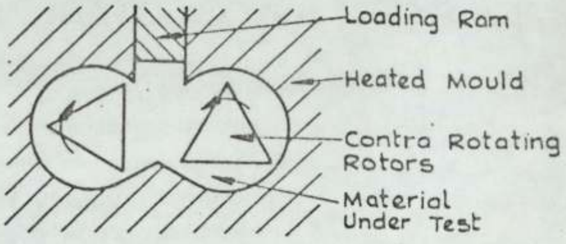


FIG. 41

Fig. 41 Brabender Plastograph

The Plastograph was used by Speitmann in 1939 to study the Plasticity of phenolic, amino and glyptal resins (111). U-shaped curves were obtained for unfilled materials and were used to determine the resin viscosity, viscosity/time effects, hardening speeds, the effect of acceleration, quality control of materials (including resins and fillers) and as a means of determining material storage characteristics, the latter being carried out in conjunction with a standard moulding test.

Messing (19) concludes that the Plastograph enables a limited statement to be made concerning the viscosity and initial hardening rate of a material but that the material is not completely characterised because each hardening rate needs to be measured separately. The buckling of compression moulded pieces of varying cure times is suggested as a true measure of cure.

The interpretation of the trace is described in Figure 42 (26). The advantage claimed for the Plastograph is that it separates the two effects of flow and cure and does not measure a combination of these two.

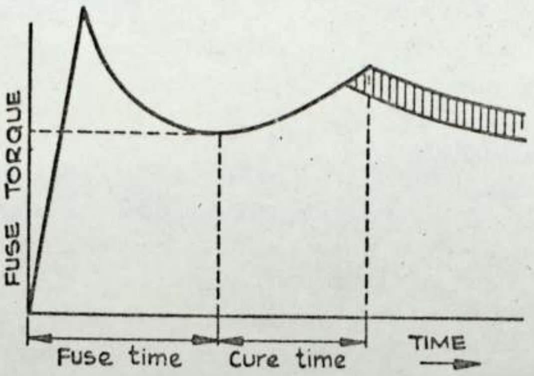


FIG. 42

Fig. 42 Torque/time trace, Brabender Plastograph (Kerr & Donje)

The authors use the plastograph to evaluate a range of glass-filled DAP and PF materials over a range of temperatures, rotor speeds and sample weights. Difficulties were experienced with the latter since low sample weights gave poor reproducibility while high sample weights merely broke shear pins. Figures indicating reproducibility are quoted. The author comments that cure torque is dependent on the degree of pre-cure of the resin.

The author concludes that the torque rheometer results do not simulate the conditions of compression or transfer moulding, discusses the reasons for this and constructs three dimensional models to explain these differences.

A general article discussing the use of the plastograph for thermosets including DAP materials shows an initial decrease in troque as the sample is subjected to heat softening (112). Both torque and trace width decrease to a minimum. An increase in torque is observed at the onset of scorch and the torque will increase to a peak value at the point where the rotors of the mixer begin to break up the crosslinked sample to produce a crumb. Throughout this region the band width will show a large rate of change suggesting the increase in modulus which results from crosslinking. The peak represents a reproducible end point for quality control tests for this type of material.

A more detailed interpretation of the torque/time trace is suggested by Ehrentraut and Dalhoff (78), who use the instrument to evaluate a range of phenolic materials intended for the injection moulding and transfer moulding process.

Referring to Fig. 43

1-2 Softening state with slight initial condensation.

3 The start of crosslinking and the practical limit of the material for moulding purposes, which may be used as a specification for an injection moulding material. The sudden decrease in torque is possibly explained as the decomposition of an inhibitor which previously had retarded the decomposition of the hexamine.

4 The maximum torque value at which almost the entire compound is cured and crosslinking has been completed.

4-5 The material is pulverised by the action of the rotors. This action prevents the use of the instrument to determine the degree of cure of a material.

The temperature is increased by the shearing action of the rotors, the amount of heat generated depending on the viscosity of the materials.

A subsequent paper states that the Plastograph is well suited for comparative tests and provides information concerning the suitability of a material for a particular process, e.g. transfer or injection moulding but not for determination of fundamental properties (104).

The construction and operating principle of the Plastograph is explained by Varodhochary (113). The use of the plastograph with thermosets is explained and results are quoted for the fusion time, the minimum viscosity, the time till flow is restricted by the onset of cure, the rate of cure and cure time. The effects of sample weight and rotor speed are described for DAP materials.

Examples of the use of the Plastograph in solving industrial problems encountered with the inconsistent processing of PF's, the effect of lubricants in phenolics and the prediction of high temperature cure times and shelf life of epoxies are given.

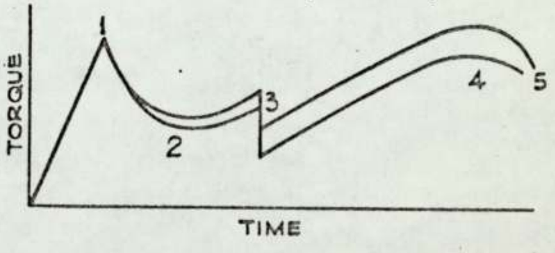


FIG. 43

Fig. 43 Torque/time trace, Brabender Plastograph (Ehrentraut & Dalhoff)

The author states that the plastograph is more suitable for evaluating the flow/cure characteristics than the older compression or transfer moulding systems since these may be unsatisfactory with thin walled mouldings, the large number of tests required to ensure reproducibility and for variable tool temperatures.

The plastograph is also used by Choi (114) to evaluate the flow/cure characteristics of DAP's in terms of the material and process variables namely fillers, resin precure, shear rate and temperature.

Mention is also made of the use of the two short screws instead of the more usual rotors. The screws were developed specifically to handle high viscosity materials such as UF and PF materials and are claimed to simulate the screw action of an injection moulding machine.

The author states that asbestos and cellulose filled materials show non-Newtonian flow behaviour and that apparent viscosity decreases with shear rate.

The plastograph (115) has been used to investigate the effects of peroxide and inhibitor concentration on type and storage life on the flow/cure properties of glass filled polyester moulding materials in dough and prepreg form. The effects of temperatures and rotor speed are shown. The authors claim a high level of reproducibility and state that the instrument may be used for production quality control.

The Plastograph is not really suitable for use with long glass fibre reinforced materials since the fibres form rings around the rotors at low speeds while higher rotor speeds cause severe fibre degradation. The use of short fibres eases these problems (67).

The comprehensive study of the use of the Plastograph for a wide range of materials has been carried out by Schreiber (116). The object of this work was to establish the suitability of the test method for observing the curing process of thermosets under defined conditions and to establish the optimum test conditions and the reproducibility of the equipment.

The results are compared to Kanavec Plastimeter and to test results obtained using the extruder attachment (15 mm screw dia L/D 12 :1) to the Plastograph.

Materials studied are:-

Wood filled	two step phenolic
Cellulose filled	melamine phenolic
Cellulose filled	melamine formaldehyde
Wood filled	dicyandiamide-formaldehyde
Asbestos filled	dicyandiamide-formaldehyde
Inorganic filled	epoxy
Glass filled	polyester
Glass filled	diallyl phthalate
Glass filled	diallyl isophthalate

Photographs and diagrams depict the effect of sample weight, temperature, and rotor speed on the torque/temperature/time results. Figures are also quoted for the reproducibility.

The author concludes that although the frictional heat developed in the chamber makes comparison of dissimilar materials difficult, it is an extremely important aspect since frictional heating is encountered in material processing. A limitation because of this is that stiff materials will develop more heat and therefore appear to cure faster than a lower viscosity material which may in fact cure faster but which will develop less heat.

The Plastograph produces characteristic data for materials but the minimum and maximum torques may be obtained at different temperatures and it is therefore impossible to apply the test results to other processes with different parameters.

An article discussing the rheology of elastomers is of interest in that it stresses the need to evaluate materials under the conditions of shear that they will encounter in processing (117). A series of elastomers are evaluated using a Mooney viscometer, a Brabender Plastograph and a capillary viscometer and the authors conclude that either of the latter two instruments are more suitable than low shear rate tests and that materials do not necessarilly have the same viscosities at low and high shear rates.

Lee and Purdon (112) developed a rheological analysis for the Plastograph and showed that the results may be used to calculate fundamental viscosity data for various materials of Newtonian and non-Newtonian flow behaviour.

The analysis is based on the assumptions namely that the plastograph is two adjacent co-axial cylinder viscometers, that the rotor geometry is equivalent to a cylinder and that the measured torque is the resultant of the shear forces which occur in each cylindrical viscometer.

The further references are quoted (119) and (120) good correlation is claimed between plastograph results and the results from a capillary viscometer for polystyrene based materials.

An interpretation of the torque time curve is given by Choi (121) in which torque readings are expressed as a ratio of the peak torque. The ratio is termed relative viscosity and being dimensionless is claimed to be of value. Relative cure is also expressed as the ratio of the area under the exotherm curve determined by calorimetric methods and the writer plots a curve of relative viscosity against relative cure to characterise the material (DAP).

A similar type of instrument has been developed by Davo of Troisdorf (122, 123) but no reference occurs concerning its use with thermosets.

RAPRA work concerning the use of the variable torque rheometer with thermosets will be reported in a future Research Report.

2.3.3 Extruder Systems

The use of a small laboratory extruder to evaluate a wide range of thermosets has been described by Schreiber (93). A screw diameter of 15 mm, L/D ratio 12 :1 and a nozzle diameter 3 mm; a screw speed of 30 rpm and a barrel temperature of 90°C were used.

Screw torque curves were obtained which showed a constant value indicating a material viscosity although being an equilibrium system, the results did not indicate the hardening time.

The author concluded that this was a very useful technique since it could be related to injection moulding (116).

2.4 Oscillating Systems

2.4.1 Capillary Type

An early oscillating viscometer was based on a capillary system, see Figure 44. The results are obtained by measuring the time of oscillation which will depend on the damping effect i.e. viscosity of the sample under test (72) Figures 44 and 45.

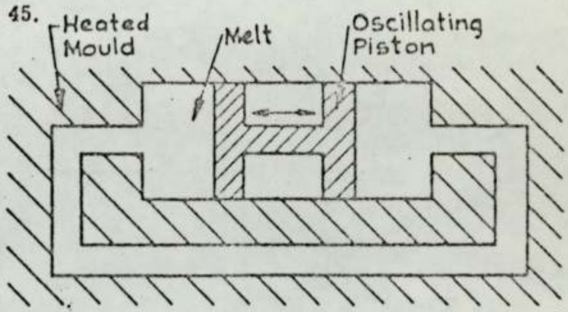


FIG. 44

Fig. 44 Oscillating capillary device (Schwittman)

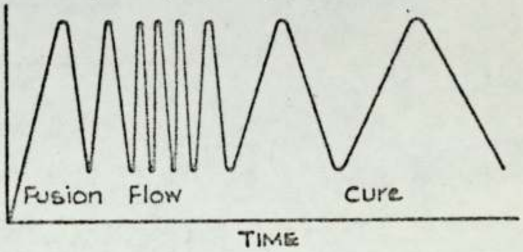


FIG. 45

Fig. 45 Flow/time curves for oscillating capillary device.

Although this technique has been suggested for use with thermosetting systems, it does not seem to have been developed for what would appear to be obvious problems.

2.4.2 Probe Type.

The Wallis-Shawbury Cureometer has been suggested for use with thermosets, although it was originally designed for use with rubber compounds (124).

Material is heated in a closed chamber and exerts a damping action on an oscillating probe. This damping action is measured and recorded on a time basis. A typical trace is shown in Figure 46. The band width indicates the material viscosity, a wide band represents a low viscosity i.e. it exerts a small damping action and the time to the parallel section represents the curve time.

Materials tested were phenolic and urea moulding materials. Unfortunately difficulties were

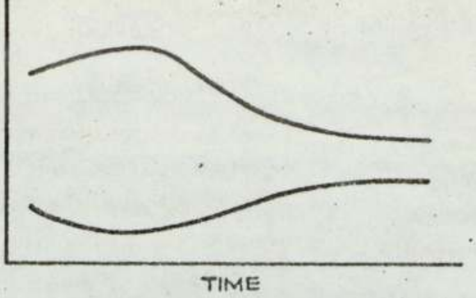


FIG.46

Fig. 46 Flow/time trace for UF moulding material Curometer

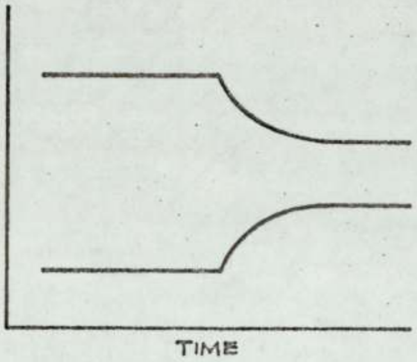


FIG.47

Fig. 47 Flow/time trace for epoxy resin Curometer

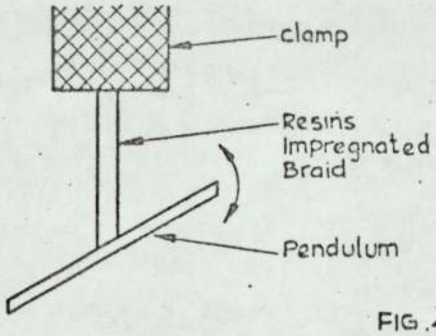


FIG.48

Fig. 48 Torsional pendulum

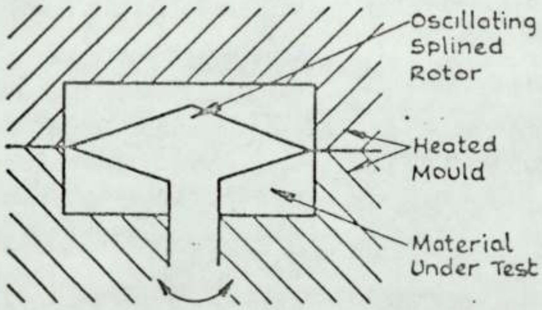


FIG.49

Fig. 49 Oscillating disc rheometer (Monsanto)

experienced concerning the lack of pressure on the material (i.e. it was possible merely to shear a sintered powder rather than a melt) and the relatively low strength of the instrument (it was designed for rubber). The instrument operates at low rates of shear.

More satisfactory results were obtained with liquid resins e.g. phenolic and epoxy materials Figure 47.

2.4.3 Torsional Pendulum

The torsional pendulum (125) is a relatively simple approach. A braid, impregnated with resin, is used as the suspension arm of a torsional pendulum Figure 48. The period of oscillation of the pendulum is recorded and variations in the period of oscillation indicate the increasing stiffness of the braid due to the increasing cure of the resin. This technique has been successfully used to study the crosslinking reactions of phenolic and polyester resins although it is unsuitable for granular materials. The possibility exists of using an extruded worm as the pendulum.

2.4.4 Disc Rheometer

The torsional system may be used with granular materials if the sensor is placed in a cavity which contains the material under test. This type of instrument, available as the Monsanto Rheometer, is illustrated in diagrammatic form in Figure 49 and was developed primarily for the evaluation of rubber materials. The temperature and speed of oscillation may be varied and the results obtained as the torque exerted on the rotor due to the damping action of the material under test, i.e. the dynamic shear modulus. The maximum shear rate obtainable is approximately 100 sec^{-1} at 750 cycles/sec, the limit being imposed by mechanical difficulities encountered with drive and measuring the forces imposed on the rotor. A full discussion of this instrument and its use for rubber is given (126, 127) which also includes a comparison of the Monsanto Rheometer with the Mooney Viscometer, a rotation viscometer having a fixed speed of 2 rpm. Advantages which are claimed for an oscillating disc are that it can be used at higher shear rates and that it will measure cure rates with greater accuracy.

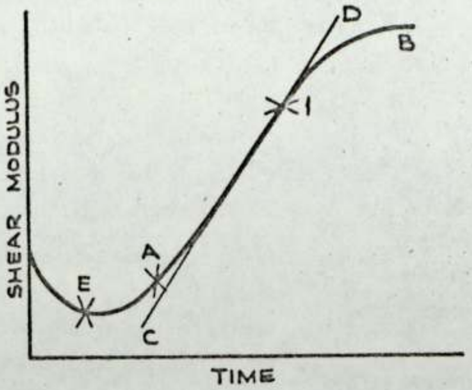


FIG. 50

Fig. 50 Flexural modulus/time trace, Monsanto Rheometer

This is because the small amplitude of the oscillation does not cause the sample to break up until full cure is approached. This happens during the early states of cure with a rotational viscometer.

The use of the Monsanto Rheometer with thermosets has been suggested (128). The report deals with DAP (glass and asbestos filled) materials, epoxy, phenolic and silicone compounds. A typical rheometer trace is shown in Figure 50. This curve shows a dynamic viscosity/time curve. The point of gelation is marked A, cure at B and the cure rate is indicated by the tangent CD. The minimum viscosity is shown E.

This technique is claimed to be more useful than the ASTM cup flow test since it correlates better with moulding practice. It is claimed to permit the determination of the optimum temperature and time for moulding and has been used to determine the effects of catalysts, inhibitors and particle size distribution.

An investigation of glass filled diallyl isophthalate materials using a Monsanto Rheometer concludes that within experimental limits, the best combination of moulding conditions for screw injection moulding could be selected from rheometer results. Empirical models were developed to describe moulding conditions which were subsequently used to increase production rate and quality (129).

Some doubts exist concerning the use of the Monsanto Rheometer with thermosets and in particular with phenolic and amino resins. Reservations were expressed by Monsanto at Ruabon because rigidity of the material which may cause damage to the instrument, the large cure shrinkage of the material compared to rubber and the good metal wetting properties of phenolics which may have an adverse effect on the microscopic surface finish of the rotor. The latter is particularly important because it directly effects the reproducibility of the instrument. Problems of reproducibility are also expected with amino materials (110). The recommendations of Monsanto Instruments both in Europe and America are that the Rheometer should not be used with thermosets although the authors of reference (128) state that they had not encountered any trouble during several hundred runs with thermosets (106).

The Weissenberg Rheogoniometer, a cone-and-plate viscometer has been used to measure viscosity time curves of unfilled catalysed polyester resins at room temperature (130). The results are obtained as relative strain vs. time and enable viscosity and normal forces to be measured.

The use of the Rheogoniometer is limited by the sticking of the cured resin to the platens and the consequent risk of damage during separation. The instrument gives good reproducibility but is limited to studying the middle range of the viscosity time curve. It is unsuitable for use with highly filled materials and cannot be used with materials which are not in melt or frozen melt form.

A cone and plate viscometer has also been used to examine the flow behaviour of resol resin. The authors conclude that these materials show non-Newtonian flow behaviour consistent with the intermolecular hydrogen bonding which is said to be a significant factor in the curing process (131).

3. Characterisation of Materials for Injection Moulding — A General Discussion

Before discussing the methods of characterising thermosets, it is wise to study the changes which occur during processing.

When a thermoset material is heated it starts to soften to form a stiff putty-like material (curve AB Figure 51). At the same time a chemical reaction takes place which causes the degree of condensation of the material to increase (curve CD). The resultant viscosity time curve is therefore U-shaped, the material passing from a solid, through a liquid phase and finally to a solid (curve EF). Both the rate of softening and the rate of condensation are dependent on the temperature and the condensation reaction is normally exothermic.

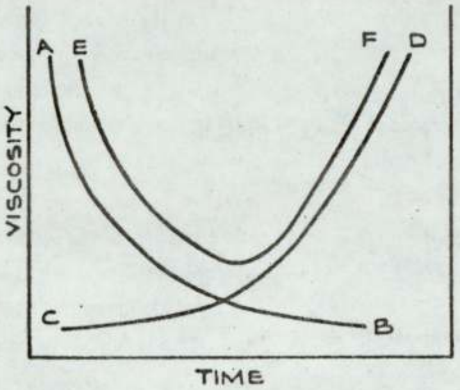


FIG. 51

Fig. 51 Viscosity/time curves for thermosetting material

In addition to this, many thermosets contain water or liberate water of condensation or a gas which can act as a plasticiser and increase the flow of the material (27).

The molten material flows under the action of pressure. The flow may be divided into two components, the resistance of the material to flow i.e. the viscosity of the material and the resistance of the material to flow over metal surfaces, i.e. friction or lubrication effects. The contribution of these two effects can vary with increasing condensation (104). The position is further complicated during the fusion process since solid powder may be present and the friction of powder to powder and of powder to metal is therefore important. The basic resin is itself changing throughout the fusion/flow/cure process (132) due to the condensation process which is further complicated by the possibility of mechanical effects, leading to lower effective viscosities and faster crosslinking reactions.

In the compression moulding process, the material fuses, flows at low shear rates and cures within the confines of the mould. With transfer moulding, the material is fused in a heated chamber by either conduction or R.F. heating and is forced through a runner at relatively low shear rates into the mould where it cures. In the injection moulding process the material is heated and fused partly by conduction but mainly by frictional heat developed by the screw in the barrel. The latter is partly due to internal friction i.e. viscosity effects and partly due to external friction i.e. lubrication effects. The molten material is held at a relatively low temperature (e.g. 80-100°C) until it is forced at very high shear rates (10^3 - 10^4 sec^{-1}) through a series of runners and gates into the mould. The material is heated during this process by frictional effects to a relatively high temperature (e.g. 130-150°C). Once in the mould the material is heated by conduction under static conditions until cure is complete when the moulding is ejected. There are thus several parts to the injection process each of which must be related to the properties of the material.

Since the material is fused in the barrel by the frictional heat of the screw, an excessively low viscosity or a high level of lubrication will result in a low plasticisation rate while a low level of lubrication or a high viscosity can result in an excessively high frictional heat build-up and in premature gelation of the material. The material must also be relatively stable at barrel temperature (132). The particle size and shape (grind) can also effect the fusion process (7).

Short cure times require the use of high moulding temperatures and thus the material must be heated rapidly during its passage from the barrel to the mould. This is accomplished by frictional heating caused by the use of high shear rates. The material is also required to cure rapidly at high temperatures (31).

It is thus apparent that the properties of materials which must be controlled if materials are to run continuously and satisfactorily on injection machines must include the friction properties, plasticity and reaction rate i.e. viscosity/time characteristics at relatively low temperatures and shear rates as well as at high temperatures at both low and high shear rates. Results show that low viscosity at high temperatures and low shear rates do not necessarily result in low viscosity under other conditions.
Most of the test procedures described in this report are used to characterise and control injection moulding materials and must be discussed in the context of injection moulding requirements.

Early test methods were based on compression or transfer moulding techniques and invariably measured a single point e.g. a time, pressure or flow length under specified conditions of temperature and pressure. Since the tests were carried out in moulds of different shapes and sizes the shear rates and the relative significance of flow and cure varied between different tests. It is therefore not surprising that different test methods give different relative results and often cannot be correlated with each other or with a production mould. Examples of this are quoted by Wainwright (4), Brooks (133) and Fina (134).

Fig. 52 Comparison of material flow properties determined by various test procedures:

52a Cup Flow, Disc Flow, Rossi Peakes

Test Method	Materials				
Cup Flow (secs)	12	12	12	12	12
Extrusion test (length in.)	1.5	1.25	1.24	0.7	0.15
Extrusion test (press. for 1 in.)	0.28	0.26	0.29	0.40	0.53
Disc thickness (in.)	0.022	0.024	0.032	0.037	0-0.35
Minimum Moulding Pressure (tons) (Similar to cup flow)	3.5	3	5.5	4	5

Temp. 325°F

These figures all relate to phenolic materials of varying composition (4).

52b Rossi Peakes, Plasticity Index, Cup Flow Type

Test Method	Material (Phenolic Type)					
Rossi Peakes Flow Length	50	75	75	85	70	70
Plasticity Index	22.3	26.4	26.4	21.1	23.3	-
Tube Base (Cup Flow Type)	22	14	10*	15*	16*	15*

* Pressure reduced for these results

52c Rossi Peakes flow length vs. Cup Flow, Disc Flow vs. Cup Flow

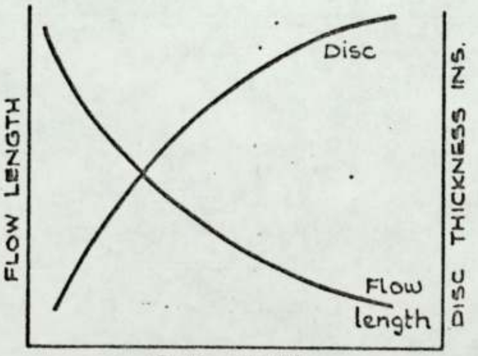


FIG. 52c

52d Disc Flow vs. Cup Flow

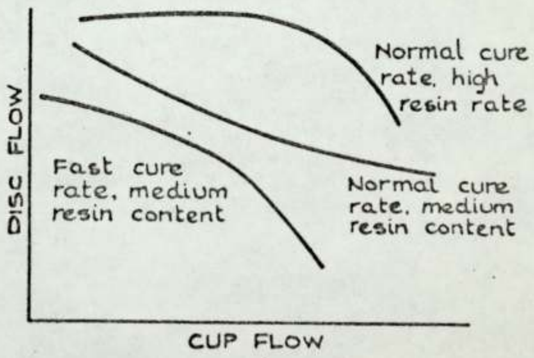


FIG.52 d

Test Methods	ASTM-D-731 and variants			Old D-731	Plunger Tests		
Flow Grade	D-731, Min Force, lb X 10^{-3}	US Polymeric, Min Pressure, psi	Durez Plasticity Grade	Cup Time to Close, sec	Transfer, 10^{-3} psi	Williamson Throughput, %	Archimedes Spiral Flow, in.
Extra Hard	25	3730	NA[b]	30	15	13.6	NA
Very Hard	20	2800	4	25	11.4	17.7	NA
Hard	15	2240	5	20	8.96	22.3	NA
Medium	10	1490	8	15	5.95	33.6	0.1
Medium Soft	8	1190	10	12	4.75	42.1	1.3
Very Soft	5	1000	16	8	2.98	67	2.6
Extremely Soft	2.5	364	32	3	1.45	NM[c]	2.5.9
Low Pressure	2	300	NA	NM	1.20	NM	3.15
Very Low Pressure	1.5	224	NA	NM	0.90	NM	NA

Results representative of round robin testing. [b] Not available. [c] Not measurable.

Lack of correlation undoubtedly resulted in dissatisfaction of these procedures and led to many companies modifying the basic test procedure to obtain a more satisfactory result and also to an increase in the number of test procedures (134). Another reason is that the moulding performance of thermosets is influenced by many physical and chemical factors, each involving the effects of temperature, velocity and composition. Detailed rheological and reaction kinetics data would be needed to analyse the moulding process theoretically and even if available the resultant equations could only be solved for simple mould geometries. The result has been the growth of many empirical flow tests (15).

The inadequacies of these test methods were recognised many years ago (4, 25) and claims have been made that they do not even indicate the performance of a material for use in an intricate compression mould, still less for transfer moulding and even less for injection moulding. Although these tests can be used to give indications of mouldability, reservations must be made when they are used for the injection moulding process (135, 136).

Methods which measured a flow path were developed e.g. Rossi Peaks Flow test giving results which could be related to the viscosity/time curve.

The advantages claimed for this procedure were that it would distinguish between materials having different flow/cure characteristics but having the same overall flow length. Although this represents a considerable improvement over the earlier techniques it still had its limitations which were recognised even in 1934 (25).

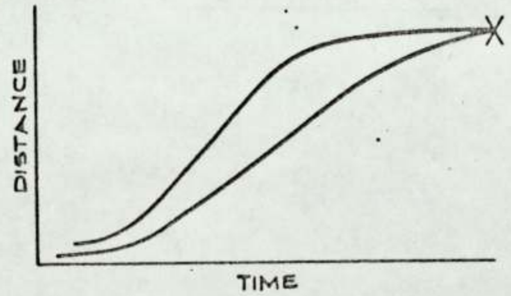


FIG. 53

Fig. 53 Distance time curve showing different flow paths for the same flow length

The need to test a material using the same rate of deformation as encountered in the moulding process was recognised by Forrer in 1933 (1), while Schwittman in 1939 recognised the need to obtain viscosity time curves but could not develop his ideas concerning a rotational viscometer because of technical difficulties (72).

The most important types of test proceedure are outlined below. It is important to inspect each system with reference to the conditions of injection moulding i.e. temperatures of 80 - 170°C and shear rates of up to 10^4 sec^{-1}.

Several of the older types of test e.g. spiral flow, and capillary flow have been developed by the addition of flow path indicating systems, by the replacement of pencil, string and weight systems with high speed electronic measuring and recording equipment and by the use of a constant shear rate rather than constant pressure systems. However, many of the main deficiencies of this equipment still remain and are even more objectionable if materials are to be injection moulded. The objections are basically that the time of deformation (i.e. shear rate) and the temperature of the test do not relate to the process concerned. This comment need not necessarily apply to all examples of these tests.

Capillary viscometers have been used to obtain rheological data over a wide range of temperatures and shear rates. Considerable success is claimed for this technique in that it enables a material to be characterised over shear rates and temperatures found in injection moulding, but it is claimed to be less suitable for measuring time dependent effects. The variable torque rheometer is often used to investigate thermosets and may be used to simulate the barrel conditions. The instrument indicates the viscosity time relationship of a material up to its gelation point and has the added advantage of allowing the determination of frictional heating effects. It is the only test method which permits the study of the fusion process - all other capillary or rotational systems receive melt from a compression, transfer or injection process.

The rotational viscometer has been used to evaluate materials over a wide range of temperatures and shear rates (up to 10^2 sec^{-1}). (10^2 sec^{-1} seems to be the upper limit for both rotational or oscillating systems). It is frequently used to determine the effects of various aspects of the moulding process i.e. it is used to receive a melt from a capillary, or from an injection barrel. In this form it acts as a mould to measure the viscosity time characteristics at a low shear rate. These results are then related to the viscosity time characteristics of the original material and hence show the results of various aspects of the injection moulding process.

Although the particle size and shape can have an important effect on the friction and hence fusion properties of a material (7) there is little information on this topic except for references (31, 137, 138) which indicate the effects of particle size on the flow of thermosetting powders in hoppers. Although no information is available concerning the use of an annular shear cell, RAPRA experience has shown it is a feasible technique for measuring powder to powder and powder to metal frictional forces.

It is perhaps a sad reflection on the thermoset industry that the test methods at present used to characterise thermosets for injection moulding are, with few exceptions those of 40 years ago (134). The inadequacies of these tests were recognised in the 1930's but at least the testing techniques used were representative of the then current moulding techniques, a justification which cannot be applied to the present day injection moulding process. It is ironic that several tests are now used to measure a single flow parameter indicating a degree of sophistication less than that of 1930-40 at which time it was considered barely adequate.

As recently as 1969 it was reported (139) that many present day methods of characterising thermosets are less sensitive than the injection moulding process itself and that the injection moulding machine is often regarded as the only satisfactory test system. One author states that much of the trouble experienced in thermoset injection moulding is due to a lack of relevant viscosity/time data (132).

The recent increase in published work dealing with the determination of thermoset characteristics and their correlation with thermoset injection moulding indicates that industry has recognised its shortcomings and has adopted a more promising approach to material characterisation (139). The final comment may be made by M. Forrer and while these words were written in 1933, they may still be applied to the moulding of thermosets (1).

"What is still lacking at the present time is a standard test method, the adoption of which would allow for a common language being spoken between manufacturers of material and moulders. The test in question must be simple, and speedy to answer the requirements of industry... The conditions of moulding must be approached as nearly as possible, especially as regards the time used for deformation, if this time is longer and it is to do with polymerisable material, the result will be distorted by the premature curing of the material. It is necessary to agree on the temperature at which the plasticity is measured and also on the pressure and on the speed of application of this pressure.... Lastly, it is necessary to express plasticity in figures. The figures may be arbitrary, but it is necessary that everyone adopts the same scale".

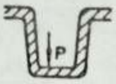
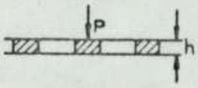
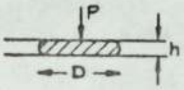
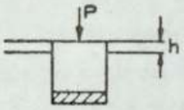
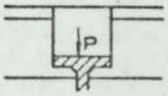
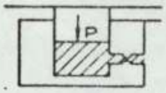
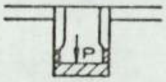
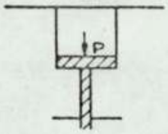
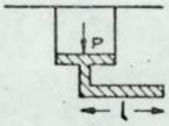
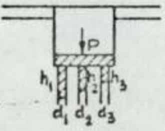
4. References

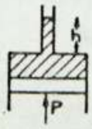
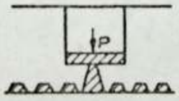
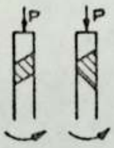
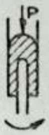
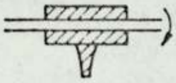
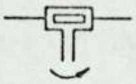
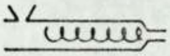
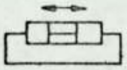
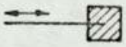
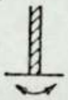
1. M. Forrer, Brit. Plast. Year Book, 1933, p. 68-92.
2. Anon., Brit. Plast., July 1934, p. 54-56.
3. H.W. Powell, Brit. Plast., 8, 1934, p. 106.
4. C. Wainwright, IPI Trans., 6, 1937, p. 9-28.
5. A. Schwittmann, Kunstst., 12, 1942, p. 365-7.
6. A. Schwittmann, Kunstst., 3, 1946, p. 49-52.
7. Anon., Plastics, 9, 1944, p. 426-432.
8. M. Krahl, Brit. Plast., 11, 1934, p. 235-240.
9. ASTM D-731
10. W. Woebcken, 1953
11. BS 2782/1
12. DIN 534 65
13. L. Spiwak, Plastic Technol., 5, 1965, p. 41-2.
14. F.C. Karas, Mod. Plast., 1, 1963, p. 140-2.
15. D.W. Sundstrom, L.A. Walters, C.S. Goff, SPE 26th Antec 1968, p. 561-8.
16. A.I. Norton, Plastics, 7, 1931, p. 193.
17. I. Williams, India Rubber World, 69, 1924, p. 516.
18. R. Thater, K. Ulbricht, Plaste und Kaut., 4, 1965, p. 224-8.
19. M. Messing, Kunstst., 12, 1965, p. 948-51.
20. R.N.F. Pinfold, Brit. Soc. Rheol. Conf., 1970.
21. N.F. Kurin, B.D. Yurehenko, Soviet Plastics, 6, 1965, p. 28-32.
22. A.S. Perevertov, V.I.L. Manyashin, I.F. Kanavets, A.D. Sokolov, Soviet Plastics, 9, 1968, p. 39-41.
23. Giornale, Chim. Ind. et Appl., 5, 1923, p. 342.
24. R.W. Griffith, IRI Trans., 1, 1926, p. 303.
25. J. Behre, Kautschuk, 8, 1932, p. 2.
26. D.L. Kerr, A.J. Donje, SPE 22nd Antec March 1966; Mod. Plast., 10, 1966, p. 147/215.
27. G.L. Peakes, Brit. Plast., 2, 1934, p. 214-6.
28. Y. Morita, SPE 22nd Antec March 1966, SPE J., 3, 1966, p. 57-60.
29. J.E. Ferriday, Plastics, 9, 1968, p. 1010-11.
30. R.L. Hughes, SPE J., 3, 1970, p. 26-32.
31. R. Wallhausser, Kunstst., 6, 1969, p. 326-332.
32. S. Matsuda, T. Tsujitu, Japan Plastics, 4, 1968, p. 45-54.
33. Van Wozer, Lyons, Kim, Colwell, 1963.
34. A.F. Tornes, S.S. Feuer, Mod. Plast., 4, 1959, p. 124-134.
35. G.G. Stankoi, E.B. Trostyanskaya, Yu.N. Kazanskii, V.V. Okovskor, O.Ya. Mikhassuak, Soviet Plastics, 9, 1968, p. 47-49.
36. A.S. Sindarorskaya et al, TEI Series Production and Processing of Plastics, No. 3, 1965, p. 5.
37. L. Spiwak, SPE J., No. 6, 1963, p. 557.
38. J.W. Heyd, R.M. Brodbeck, L.W. Hartzel, L.E. Brown, J. Poly. Sci., Vol. 3, 1965, p. 1911-39.
39. A.S. Perevertov, A.D. Sokolov, I.F. Kanavets, V.K. Maryashin, Soviet Plastics, 1, 1969, p. 68-72.
40. A.D. Sokolov, I.F. Kanavets, Soviet Plastics, 12, 1964, p. 23-28.
41. A.D. Sokolov, I.F. Kanavets, Soviet Plastics, 3, 1966, p. 22-25.
42. N.V. Mikhailov, P.A. Rebinder, 33, Koll Zh., 17.2.1955.
43. P.A. Rebinder, L.V. Ivanora - Chumakova, "Uspektu Khim Tekhn. Polumerov, Sb2, 1957, p. 146.
44. G. Meyer, Plaste und Kaut., 11, 1966, p. 660-3.
45. B. Pulvermacher, Dipl. Work at IKV, Aachen Tech. College, 1968.

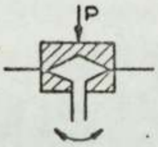
46. R. Thater, Plaste und Kaut., 10, 1963, p.35-9.
47. M. Krahl, Kunstst und Gummi, 10, 1940, p.168-9.
48. W. Woebcken, T. Basbous, K. Rashig, H. Mandler, Kunstst., 12, 1967, p.974-983.
49. R. Burns, Brit. Plast., 1, 1940, p.214-216.
50. L.M. Debing, S.H. Silberkraus, Ind. Eng. Chem., 8, 1941, p.973-5.
51. G.L. Peakes, Brit. Plast., 3, 1934, p.475-81.
52. G.L. Peakes, Brit. Plast., 4, 1934, p.516-19.
53. G.L. Peakes, Mod. Plast., 6, 1937, p.39-41.
54. ASTM D569-59.
55. G.H. Goulbourne, Brit. Soc. Rheol. Conf. 1970.
56. C.P. Vale, Amino Plastics
57. C.M. von Meysenbug, Kunstst, 2, 1955, p.48.
58. C.M. von Meysenbug, Kunstst., 1, 1957, p.14-17.
59. D. Northmann, G. Meyer, Plaste und Kaut., 3, 1961, p.115-120.
60. R. Thater, K. Ulbricht, Plaste und Kaut., 10, 1963, p.35-39.
61. K. Ulbricht, B. Rudiger, Plaste und Kaut., 5, 1966, p.290-292.
62. T. Bertz, R. Hohn, M. Gehrmann, Plaste und Kaut., 4, 1966, p.209-11.
63. T. Bertz, R. Hohn, A. Herrmann, Plaste und Kaut., 11, 1966, p.664-5.
64. K. Smoll, W. Pungs, Kunstst., 7, 1967, p.533-5.
65. R.S. Barshtein, A.L. Peshekhonova, I.I. Krothora, Soviet Plastics, 4, 1969, p.42-43.
66. G. Menges, P. Ehrentraut, W. Dalhoff, Gummi Kunstst. Asbest., 8, 1966, p.943-53.
67. Anon., Kunstst Berater, 1, 1968, p.46.
68. K.R. Hoffmann, Mod. Plast., 4, 1967, p.131-2.
69. EMMI - 66 - 1
70. Anon., Mod. Plast., 2, 1968, p.104-8.
71. P.J. Heinle, M.A. Rodgers, SPE RETEC Dec. 1968.
72. A. Schwittmann, Kunstst., 1939, p.7.
73. I.F. Kanavets. Determination of the technological characteristics of thermosetting plastics ITEIN ANSSR, No-1-56-66, 1956 (in Russian).
74. P. Ehrentraut, Kunstst., 10, 1966, p.695-707.
75. P. Ehrentraut, Rheol. Acta., 1, 1968, p.64-74.
76. O. Gottfert, Plast. Verarbeiter, 8, 1968, p.609-615.
77. Gottfert, Feinwerk, Technik, GmbH.
78. P. Ehrentraut, W. Dalhoff, Kunstst., 6, 1967, p.439-446.
79. I.F. Kanavets, A.D. Sokolov, Soviet Plastics, 5, 1965, p.30-35.
80. I.F. Kanavets, A.D. Sokolov, Soviet Plastics, 6, 1965, p.24-28.
81. M. Pike, W.F. Watson, J. Polym. Sci., 1952, 9, No.3, p.229.
82. I. Furukawa et al., J. Soc. Rubb. Ind., 1957, 30, No.8, p.653.
83. P. Yu. Butyagin et al., Vys. Soed., 1, No.6, 1959, p.865.
84. S.E. Bresler et al., Vys. Soed., 1959, 1, No.9
85. M.M. Mirakhmedov, Dissertation NIIPM 1962.
86. B. Karmin, B. Betts, Sb. Investigation in the field of high molecular compounds, Izd. AN SSSR 1949.
87. V.A. Kargin, T.I. Sogolova, DAN SSR 1956, 108, 4.
88. G.L. Slonimskii et al., DAN SSR 1953, 93, 311.
89. I.F. Kanavets, L.G. Batalova, DAN SSR 1957, 114, 5.
90. R.W. Bainbridge, SPE 22nd Antec 1966.
91. N.N. Danilkin, I.F. Kanavets, Soviet Plastics, 5, 1969, p.58.
92. S.A. Kolesvikova, A.I. Polovinchenko, A.D. Sokolov, I.F. Kanavets, Soviet Plastics, 3, 1969, p.36-39.

93. A.D. Sokolov, Soviet Plastics, 7, 1963, p.31-36.
94. A.D. Sokolov, Soviet Plastics, 5, 1969, p.23-26.
95. A.D. Sokolov, Soviet Plastics, 6, 1969, p.28-32.
96. A.D. Sokolov, Soviet Plastics, 5, 1969, p.26-29.
97. N.N. Danilkin, I.F. Kanavets, Soviet Plastics, 11, 1969.
98. N.N. Danilkin, I.F. Kanavets, Soviet Plastics, 1, 1970, p.27-30.
99. A. Lundberg, Kunstst., 4, 1960, p.214-218.
100. P. Ehrentraut, W. Dalhoff, Kunstst., 6, 1967, p.434-446.
101. G. Menges, P. Ehrentraut, W. Dalhoff, Kunstst., 12, 1967, p.957-64.
102. W. Gabel, G. Meyer, Plaste und Kaut., 1967, 1, p.16-22.
103. W. Gabel, Gummi Asbest Kunstst., 1968, 7, p.751-57.
104. G. Menges, W. Dalhoff, Kunstst., 9, 1969, p.584-92.
105. W. Dalhoff, Kunstst. Technik, 10, 1970, p.365-369.
106. Communications with RAPRA.
107. V.A. Kiseleva, A.D. Sokolov, I.F. Kanavets, Soviet Plastics, 2, 1970, p.32-38.
108. V.A. Kiselera, Soviet Plastics, 4, 1969, p.34-38.
109. A. Frank, A. Klein-Albens, Communication from Dev. Labs of Ankewerke and Krauss Maffei.
110. Visit Report to Monsanto, Ruabon.
111. M. Speitmann, Brit. Plast., 1, 1939, p.447-453.
112. W.T. Blake, R.J. Onufer, C.W. Brabender Instruments.
113. S.N. Varadhochary, SPE J., 6, 1967, p.99-103.
114. S.Y. Choi,. SPE RETEC, 1968.
115. K. Scholts, H. Bergs, O. Otromke, Kunstst., 1, 1967, p.635-7.
116. B. Schreiber, Kunstst., 6, 1969, p.362-67.
117. E.A. Collins, J.T. Oetzel, Rubber Age, 5, 1969, p.62-5.
118. G.C.N. Lee, J.R. Pardon, Polym. Eng. Sci., 10, 1969.
119. J.E. Goodrich, R.S. Porter, Polym. Eng. Sci., 1, 1967.
120. L.L. Blyler, J.H. Daane, Polym. Eng. Sci., 3, 1967.
121. S.Y. Choi, SPE J., 6, 1970, p.51-4.
122. Z. Doboczky, Plastverarbeiter, No.10, 1970, p.863-8.
123. H. Bisping, Plastverarbeiter, No.10, 1970, p.869-72.
124. A.L. Soden, RAPRA Report, 1960.
125. M.F. Dramm, C.W. Dodge, L.E. Nielson, Ind. Eng. Chem., 1, Vol.48, p.76-81.
126. R.W. Wise, G.E. Decker, Rubb. World, 3, 1962, p.68-71.
127. R.W. Wise, G.E. Decker, Rubber Age, 5, 1964, p.51-75.
128. R.M. Brodbeck, L.W. Hartzel, Rubber and Plastics Age, 9, 1969, p.651-5.
129. B.L. Talwar, L.T. Ashlock, SPE J., 10, 1970, p.42-46.
130. J.L. Henson, A.J. Lovatt, G.S. Learmonth, J. Appl. Polym. Sci., Vol.11, 1967, p.2543-2552.
131. D.P. Stricos, Diss. Abs. 25. 3. Sept. 1964, p.1526.
132. L.D. Fishbert, D.C. Longstreet, Mod. Plast., 6, 1969, p.92-103.
133. P.H. Brooks, Rubber and Plastics Age, 12, 1966, p.1285-8.
134. P. Fina, Plastics Technol., 2, 1966, p.27-29.
135. A. Rothenpieler, Kunst und Gummi, 3, 1966, p.79-86.
136. W. Bauer, K. Eichler, Industrie Anzeiger, 11, 1968, p.15-17.
137. H. Mandler, Plastverarbeiter, 11, 1965, p.675.
138. M. Bussian, Plaste und Kaut., 12, 1968, p.898-903.
139. J. Kestler, Mod. Plast., 8, 1969, p.58-59.

5. Summary of Thermoset Flow and Cure Tests

Test Method	Diagram	Type of Measurement	Parameters Measured	Conditions of Test Specified Parameters
Compression Techniques				
Flow Cup		Flow Path Flow/Cure Combination	$P = f(t)$ $h = f(t)$ P Ti Ti	h, Te P, Te h, Te, h P Te h P Te h
Multi Cavity Mould		Flow/Cure Combination	No. of cavities filled	P Te h
Disc Flow		Flow/Cure Combination	D and/or h	P, Te
Compaction Test		Compaction Flow Path	$P = f(h)$	Te
Capillary Type				
Orifice Flow		Flow/Cure Combination " Flow Path	q t p	P Te Ti (residence) q Ti e P h Te
			$q = f(t)$	P Te
			t, q	P Te
Capillary Viscometer		Flow Rate Flow Path	q $P = f(t)$	P Te q
Long Capillary (Straight Type)				
Flow Mould		Flow/Cure Combination	t	P Te
Multi Capillary		Flow/Cure Combination	$h_1h_2h_3$ etc.	P Te $d_1d_2d_3$ etc.

Rossi Peakes/Zwick		Flow/Cure Combination Flow Path " "	h h = f(t) h = f(t) P	P Te P Te P Te h Ti Te capillary can be conical
Long Capillary Spiral Type				
Spiral Flow		Flow/Cure Combination Flow Path	1 h = f(Ti)	P Te P Te Ti (residence)
Rotational Type				
Rotational Plunger		Flow Path	Rotor Speed = f(t)	P Te Torque
Kananvec Plastimeter Durograph		Flow Path	Torque = f(t)	P Te Rotor Speed
Modified Kanavec Plastimeter		Flow Path	Torque = f(t)	P Te Rotor Speed
Durocorder		Flow Path	Torque = f(t)	Fed by injection m/c
Variable Torque Rheometer		Flow Path	Torque = f(t)	P Te
Mooney Viscometer		Flow Path	Torque = f(t)	Te Rotor Speed
Extruder		Flow/Cure Combination	Torque	Te Screw Speed
Oscillating Types				
Oscillating Capillary		Flow Path	Osc Ti	Te P
Oscillating Probe		Flow Path	Osc Ti	Te Rate of Osc
Torsional Pendulum		Flow Path	Osc = f(t)	Te

Oscillating Disc		Flow Path	Torque = f(t)	P Te Osc
Rheometer Monsanto Farol Weissenburg Rheogoniometer			Torque = f(t) P	Te Osc

Key:-

P	Pressure
H	Thickness
l	Length
D	Diameter
Te	Temperature
Ti, t	Time
q	quantity (e.g. output of die)
Osc Ti	Period of Oscillation
f	function (e.g. P = f(t). Pressure as a function of time)

Thermosets Injection Moulding. 2.

Flow Data and Process Reproducibility by Monitoring

R.R. Whisson and K.T. Paul

Part 1 of this series of articles was published in the December 1973 issue of this journal.

Considerable use of and experience with sensors for measuring and monitoring thermoplastic melt conditions during processing already existed at RAPRA. It was a logical extension of the knowledge gained to employ similar techniques in thermoset injection moulding, particularly in view of some of the reported claims made (1,2) for the utilisation of the data obtained. The basis of these claims was to regard the injection moulding machine as a viscometric device and to equip it with suitable instrumentation to obtain information on material output and displacement rates over the practical range of conditions necessary for the production of mouldings, i.e. to quantitatively determine the material flow properties at the nozzle by ejecting to air. Work at RAPRA on thermoplastics injection moulding has shown that monitored information was also valuable in assessing the reproducibility of the process and for re-establishing process conditions when moulding parts.

DETERMINATION OF VISCOSITY DATA

As for previous process monitoring work at RAPRA the most convenient location for the measurement of melt conditions was the nozzle of the injection moulding machine. A nozzle adaptor was constructed to take a piezoelectric transducer and a melt thermocouple, both instruments being located flush with the internal bore of the adaptor. The adaptor had a threaded end onto which the nozzle tip was screwed. Nozzle tips of varying L/D ratios were made and a melt thermocouple was inserted into a blind hole ending ⅛" away from the orifice of the nozzle. The general arrangement of the instrumented nozzle/adaptor assembly is shown in Figure 1. A rectilinear potentiometer, was coupled to the screw to measure its displacement. All instruments transmitted their signals to a u/v recording oscillograph which gave a readout on photographic paper. Both the Turner machine and the Bipel machine were fitted with similar instrumentation. Process conditions used on each machine were arranged to be as near as practicable to typical production settings. Hydraulic pressure was varied to five different levels for each of the nozzles examined which differed in L/D ratio and orifice diameter. Machines were arranged to eject the full swept volume of the barrel into air on automatic cycle, the ejected material being collected and weighed.

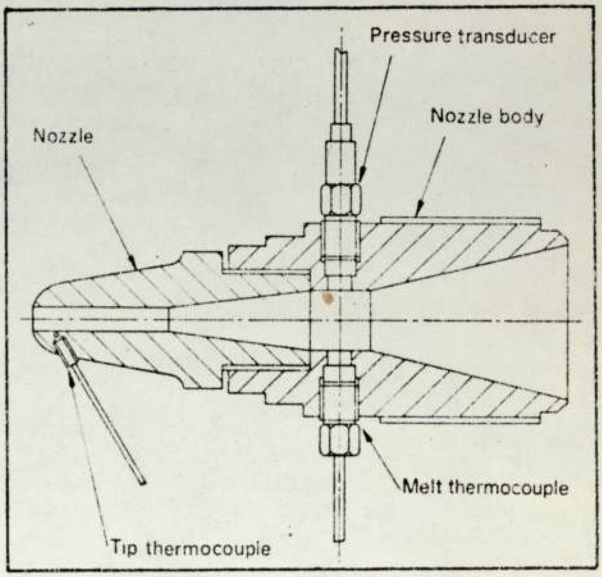


Figure 1. Instrumented nozzle

Approximately 40-50 shots were taken at each pressure setting and the initial 5-10 shots were discarded to allow the machine to reach equilibrium after resetting. Monitored information typical of the Turner machine with either the 2 oz or 4 oz barrel is illustrated in Figure 2. After an initial rapid increase the pressure remained fairly constant at lower set

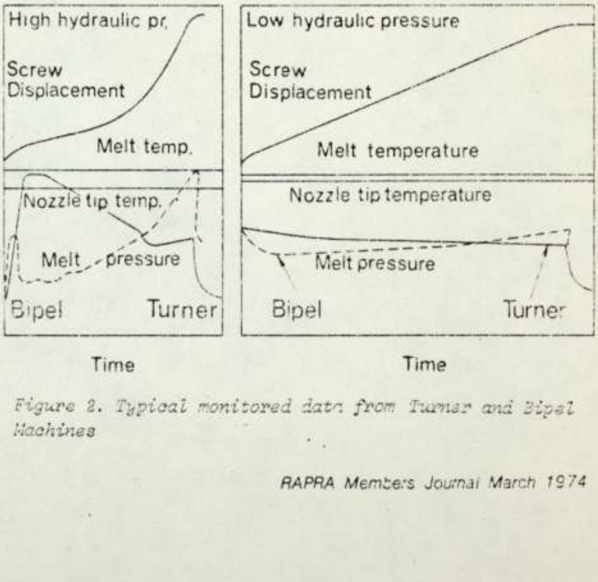


Figure 2. Typical monitored data from Turner and Bipel Machines

hydraulic pressures on the machine but as the set pressure was increased the initial pressure rapidly deteriorated to a level some 30 to 60% lower. As the screw stroke ended, pressure again began to rise. Nozzle melt temperatures remained fairly constant but nozzle tip temperatures increased by 4 to 5 C towards the end of the screw stroke. At lower set hydraulic pressures a fairly constant screw displacement rate was obtained but at the higher pressures it increased towards the end of the screw stroke. The results showed that in general high hydraulic pressures gave shorter extrusion times and screw strokes and higher shot weights. Longer nozzle tips resulted in longer extrusion times and lower shot weights but had no measurable effect on screw stroke. Above a hydraulic pressure of 1000 to 1200 psi these relationships remained unaltered. It was inferred that this was due to increased resistance to flow of melt through a given nozzle as the set pressure was increased. Sometimes a central pressure peak was obtained and in general changes in nozzle pressure reflected similar changes in the hydraulic pressure. Distinct differences can be seen between the monitored information from the Turner machine and that obtained from the Bipel machine as illustrated in Figure 2. An initially high peak pressure was obtained with the Bipel which corresponded to a period of slower screw movement. A sudden drop in pressure occurred as the screw displacement rate increased. Pressure then increased quickly, terminating in another peak on completion of the screw stroke. This second pressure peak exceeded the initial pressure when using shorter nozzles and higher set pressures. Both melt temperature and screw displacement rate were almost constant at the higher pressure settings and with the use of shorter nozzles. Nozzle melt temperatures increased by several degrees as the level of set pressure was increased. As with the Turner machine, shorter extrusion times and higher shot weights were recorded at the higher pressure settings and longer extrusion times and lower shot weights were obtained with longer nozzles. It is probable that differences in the monitored data are due to dissimilarities in the two hydraulic systems. It was inferred, from screw stroke vs. shot weight plots, that back flow of material along the screw depended on the resistance to flow of material at the nozzle and was exaggerated by longer extrusion times. Because the output/pressure data obtained from either the Turner or Bipel monitored results was not consistent enough it was not possible to calculate accurate viscosity data. Furthermore it was apparent that screw displacement rate could not be used as a measure of output rate since the pressure time curve could not be related to the screw displacement-time curve. Beck (3) concluded from similar work that the rate $\Delta P/Q$ may be used as an indication of viscosity and reported that pressures, temperatures and output rates were effectively constant during each shot. These findings are, however, contrary to RAPRA work.

Beck used a series of instrumented nozzles of different L/D ratio fitted to an injection moulding machine to determine the viscosity characteristics of phenolic moulding materials.

He concluded that the pressure/flow rate relationship was similar to that of a Bingham Plastic and that the material flowed as a central plug surrounded by a thin layer of liquid at the wall of the flow channel.

The equation used to describe this flow condition was

$$Q = \frac{R^4 \ \Delta P/L}{8\eta} \ 1 - \frac{4x}{3} + \frac{x^4}{3}$$

where Q = extrusion rate
η = viscosity of liquid layer
ΔP = pressure drop over nozzle length
R = nozzle radius
L = length of nozzle
x = ratio of central plug to radius R

The value of x was found to be independant of machine settings and was a basic property of the material. The ratio $Q/\Delta P$ is therefore directly proportional to the viscosity of material providing R and L are constant i.e. for a standard injection machine nozzle.

The values of $Q/\Delta P$ have been calculated using RAPRA data and are given below. These results do not agree with the published data although it should be noted that Beck used long injection times (up to 12 seconds) and did not encounter the wide variations in pressure and displacement rate observed by RAPRA.

Table 1. Pressure/flow rate data for various nozzle L:D ratios.

Set Hydraulic Pressure psi	Nozzle L:D $\Delta P/Q$ P_1	1:1 $\Delta P/Q$ P_2	Nozzle L:D $\Delta P/Q$ P_1	10:1 $\Delta P/Q$ P_2
	Turner 4oz barrel			
800	250	222	-	-
1000	176	132	1420	1110
1200	111	79	390	315
1400	81.5	57	244	193
1600	77.5	51.5	200	144
1800	77.2	46.8	196	138
	Turner 2oz barrel			
800	272	202	-	-
1000	237	173	520	390
1200	198	144	380	288
1400	170	122	338	244
1600	161	110	304	210
1800	151	101	287	196
	Bipel 3oz			
30	1010	830	-	-
50	133	132	386	290
70	141	95	182	131
90	141	99	148	108

P_1 = Maximum recorded pressure at nozzle
P_2 = Mean " " " "

COMPARISON OF MATERIAL FLOW PROPERTIES

Monitored data was found to be useful for comparison of the flow characteristics of different batches of the same material. The results in Table 2 show that material B had a marginally higher peak pressure and nozzle temperature than Material A resulting in a lower melt viscosity and a consequent higher ram pressure transmission to the nozzle. Comparison with results obtained from the variable torque rheometer showed that minor differences in their flow/cure behaviour existed.

Table 2. Comparison of two batches of Bakelite X19465/45

Material		Batch A			Batch B*		
Set hydraulic pressure	psi	1200	1400	1600	1200	1400	1600
Shot weight	gms	83.45	82.0	81.19	82.6	83.12	82.59
Melt pressure peak	psi	5790	6150	6250	7160	7530	7680
min	psi	2250	2200	2120	2350	2450	2360
Hydraulic pressure peak	psi	1080	1200	1230	1080	1220	1240
min	psi	590	590	590	625	625	625
Stroke length Initial	cms	1.1	1.15	1.1	1.1	1.1	1.1
Final	cms	6.0	6.05	6.0	6.0	6.0	6.0
Stroke duration	secs	1.01	0.95	0.95	1.1	1.0	1.0
Melt Temp. Initial	°C	93.2	92.7	93.4	94.5	94.0	94.5
Final	°C	93.2	92.7	93.4	94.5	94.0	94.5
Nozzle tip temp. Initial	°C	80.35	79.5	79.0	82.5	82.0	82.5
Final	°C	80.35	79.7	79.7	83.0	82.0	82.5

In a further series of tests monitored information was obtained from six batches of Bakelite X19471/45. An output rate/pressure data graph was produced and is shown in Figure 3. Differences in the test melt temperature prevented a true comparison from being made but nonetheless distinct changes in flow characteristics were measurable — particularly at high extrusion rates.

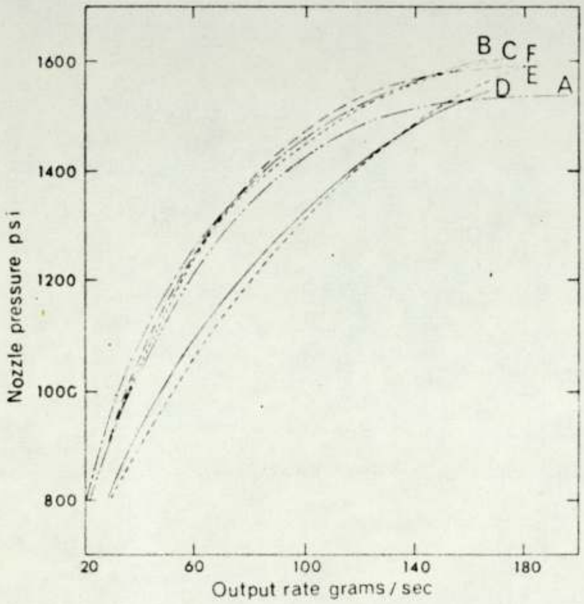


Figure 3. Pressure/flow rate curves for six batches of phenolic

Table 3. Resetting of machine conditions from monitored data.

Experiment Number	1	2	3	4
Shot weight, grams	38.3	38.6	40.40	39.2
Melt pressure, psi Peak	5850	5860	5850	5850
min	3430	3460	3440	3290
Hydraulic pressure, psi Peak	590	590	590	590
min	590	590	590	590
Stroke length, cms Total	3.7	3.7	3.9	3.7
Stroke duration, secs	29.7	30.2	30.3	30.2
Melt temp. °C Initial	102	102.4	101.3	101.5
°C Final	102	102.3	101.3	101.5
Nozzle top temp. °C Initial	102	102.3	102.5	102
Final	108	108.5	109	109

1. Initial run to set conditions for moulding
2. Pressure decreased, reset by master trace
3. Pressure increased, reset by master trace
4. Temperature altered, reset by master trace

Each set of figures represents the average of 5 mouldings.

RESETTING OF PROCESS CONDITIONS

Work on thermoplastics injection moulding has established that monitored data could be employed to re-establish process conditions on a later occasion with the same combination of material, mould and machine. This was of practical industrial importance because of the wastage of time and losses occurring from rejects which are caused by attempting to reset conditions on the machine controls and dials or attempting to make adjustments for batch to batch variations.

The machines examined were set up to produce plaque mouldings using the process conditions given in Part 1 and a plaque mould 4½" x4½" x0.06" thick fed by a 0.030" film gate. As was expected the monitored data obtained with a machine producing mouldings was completely different to that obtained by injecting the material to air. A preliminary run was performed to establish suitable moulding conditions and a master trace was recorded for these conditions. The values taken from this trace are shown in column 1 of Table 3. Lower and higher injection pressures were set on the machine and re-established by reference to the master trace. Adjustments were first made to the feed setting and injection speed until the master trace of screw displacement had been matched and then the injection pressure was re-adjusted to approach the recorded nozzle pressure level. Similar experiments showed that this technique could also be used with air shots (Table 4).

Table 4. Resetting process conditions of a U/F compound by monitoring.

Bipel Jcs	Injection Pressure psi		Stroke Length ins		Stroke secs		Nozzle Temp °C		Shot Weight grams	
	Mean	Max. Min.	Mean	Max. Min.	Mean	Max. Min.	Mean	Max. Min.	Mean	Max. Min.
Original	9.071	9.250 8.900	1.75	1.75 1.75	[illegible]	0.60 0.50	94.6	95.6 92.5	51.77	52.18 51.14
Reset 1	9.326	9.000 9.000	1.75	1.75 1.75	0.51	0.55 0.50	93.2	94.0 92.5	51.56	52.12 51.27
Reset 2	9.113	9.350 8.900	1.76	1.80 1.75	0.40	0.40 0.40	92.9	94.5 90.6	50.91	51.33 50.04

Temperatures (columns 2 and 3 Table 3) were also altered and re-set similarly (column 4). Each figure represented the average of 5 consecutive mouldings.

INTERACTION OF PROCESSING CONDITIONS

The effect of altering the back pressure, screw speed, injection speed and injection pressure on the nozzle pressure, temperature and screw displacement rate was determined together with the effect of different mould and barrel temperatures on screw displacement rate.

Optimum machine settings existed which gave higher melt temperatures and faster injection times coincided with a high melt pressure. More severe machine settings produced erratic results which were probably due to precure of the material. The reported results were for short-term runs only and were not directly comparable since they were obtained at different stages of the programme and consequently different moulds, had been employed. However, it is the trends which are important rather than individual differences.

Table 5. Effect of mould temperature on melt viscosity.

Barrel Temp	Mould Type	Mould Temp	Injection Times (mild/harsh conditions)
88°C	Capillary Viscometer	90°C	8.4 - 0.8
88°C	Plaque tool tab gate	165°C	2.38 - 0.41
95°C	" " " "	165°C	2.18 - 0.37
88°C	" " " "	190°C	1.53 - 0.31

The results in Table 5 indicated that high mould temperatures resulted in a lower viscosity melt which produced a lower back pressure on the melt at the nozzle. High barrel temperatures tended to give less reproducible results because of a tendency to precure, particularly when using harsher machine settings.

REPEATABILITY OF PROCESS CONDITIONS AND MOULDING

Past work on thermoplastics injection moulding has shown that process irreproducibility does occur in production. Such variations are of a random nature, are not normally detected and result in changes in moulding properties. There was no reason to expect that the situation would be different for thermoset injection moulding.

The Bipel machine was fitted with sensing instruments connected to an oscillograph recorder monitoring a moulding period of approximately 8 hours to determine the process and moulding variations occurring.

The recordings showed that the first 250 shots were fairly consistent in monitored properties although a slight downward trend in both injection time and back pressure was detected. From shot 251 to 285 an erratic pattern developed which was caused by deliberate variation of the mould open time. Short mouldings were obtained and higher nozzle pressures and longer injection times were recorded, probably as a consequence of reduced melt flow through the nozzle because of the longer dwell time in the barrel. Steady conditions prevailed from shots 321 to 329. The injection time for shot 330 increased from 0.6 to 1.0 seconds with increases in the pressure levels to 11,400. The next moulding was incomplete and exhibited a screw displacement time of 3 seconds and pressures above 12,000 psi. Other random short mouldings exhibited similar process variations.

The results obtained indicated that, as with thermoplastics injection moulding, variations in the process conditions do arise although repeated runs need to be conducted to confirm this. One factor of some importance was that comparatively small increases in the mould open time could start a chain reaction of events leading to reject mouldings. Similar work by ERDE has supported these findings.

Another factor influencing mould filling but not directly concerned with these repeatability experiments is that of longer mould cure times which effectively increase melt viscosity at the nozzle as a result of the longer dwell time. This aspect will be examined in more detail in the concluding part of this article.

REFERENCES

1. K.T. Paul, RAPRA B Report 441, March 1971
2. S.H. Nazar and R.R. Whisson, RAPRA Tech. Review No. 50, Nov. 1969
3. R.H. Beck Jr., SPE J., May 1971, Vol. 27, p. 43-8.

Thermoset Injection Moulding

Part 3. Effects of Processing Conditions on Mouldings

R.R. Whisson and K.T. Paul

The preceding parts of this report have been concerned with the development of techniques for melt characterisation and an understanding of the changes occurring in the barrel and nozzle of the injection moulding machine during processing. This concluding part is concerned with the progressive changes occuring in flow/cure behaviour during mould filling, culminating in the production of mouldings. Of particular relevance to industrial practice is the relationship between the important properties of the moulding which govern their quality and the change made or variations arising in process conditions. If such correlations could be discovered by suitable means a valuable tool would be provided for optimising process conditions in production. The characterisation of flow/cure behaviour of the material at the nozzle by the techniques previously described and its relationship to moulding quality would link up the various parts of the investigation.

In order to confine the experimental work to realistic limits within the time allocated to the project it was necessary to define the criteria of quality by which mouldings would be assessed. These were, (a) visual appearance in terms of flow lines and surface finish, (b) moulding thickness and distortion, (c) heat distortion temperature and degree of cure, (d) flexural modulus and flexural strength and (e) weight of mouldings. Also it was necessary to confine variations of processing parameters to those which were regarded as being of greatest importance. These were screw speed, back pressure, injection speed and injection pressure. All other conditions were kept as constant as possible although slight adjustment was sometimes necessary to attain a satisfactory standard of moulding. Additional experiments were also performed at different levels of injection temperature, mould temperature and cure time. Thus for each moulding criterion to be examined a total of 81 experiments was necessary as shown in Table 1. In order to reduce the amount of experimental work, a computer technique was used to predict results from only 27 experimentally determined results as indicated by the diagonal line. These experiments were statistically selected from the complete set and a computer programme was developed based on a multiple regression analysis. The feasibility of this technique was checked from one complete set of experiments based on a programme of 4 variables each at 3 levels. The results of a selection of these experiments were analysed by the computer and the predicted results of other experiments were compared to the observed experimental value to test the validity of the programme.

The results were quite good and most equations could be used with a reasonable degree of certainty. In general, the machine measurements, e.g. pressure, temperature, etc. were quite satisfactory. Injection times were less good, while the remote testing experiments ranged from poor to fair. An attempt to correlate the flow marks, i.e. visual appearance factors, was unsuccessful. The equation for the thickness of the moulding, both at the gate and at the base of the moulding and the moulding weight, was good and that for the width of the moulding was fairly good. This latter property gave some measure of the distortion of the moulding.

Equations developed for the heat distortion point, flexural strength and flexural modulus were fairly good.

Table 1. Moulding Criteria for Bakelite X19465/45

PARAMETER Moulding Weight Grams		BACK PRESSURE								
		60 psi			120 psi			180 psi		
INJECTION PRESSURE psi	INJECTION SPEED (No. turns)	SCREW SPEED RPM			SCREW SPEED RPM			SCREW SPEED RPM		
		60	100	140	60	100	140	60	100	140
700	2.5	43.22	43.88	44.7	44.5	44.28	44.52	44.3	44.56	44.88
	3.5	43.88	44.0	44.34	44.48	44.48	44.86	44.84	44.5	45.11
	4.3	43.85	44.15	44.3	44.26	44.46	44.75	44.42	44.59	44.33
1000	2.5	43.3	44.0	44.45	44.45	44.4	44.48	44.52	44.64	45.04
	3.5	43.65	44.65	44.44	44.5	44.72	45.13	44.67	44.68	45.35
	4.3	43.9	44.5	44.44	44.38	44.64	44.95	44.54	44.79	45.44
1300	2.5	43.3	44.5	44.5	44.5	44.48	44.34	44.62	44.78	45.16
	3.5	43.9	44.6	44.55	44.25	44.9	45.13	44.64	44.68	45.32
	4.3	44.15	44.4	44.5	44.54	44.46	44.34	44.56	44.84	43.35

MACHINE CONDITIONS

MACHINE Bipel

NOZZLE STD

MOULD Plaque

BARREL TEMP 88°C

MOULD TEMP 165°C

CYCLE TIME 45 secs.

MOULDINGS FROM REPROCESSED MATERIAL

In Part 2 (1) it was shown that flow/cure advancement of compound in its passage through the barrel of the screw injection moulding machine was a function of the screw, barrel/nozzle geometry as well as of machine settings. Thus with the Turner machine, little change in flow/cure behaviour occurred, even after the compound has been reprocessed four times. In sharp contrast the flow/cure properties of the same compound, passed once through the barrel of a Bipel machine or an Ankerwerke machine showed appreciable changes, the Ankerwerke machine showing even greater changes than the Bipel. It was therefore important to know how the properties of mouldings were affected by reprocessing of material on the various machines examined.

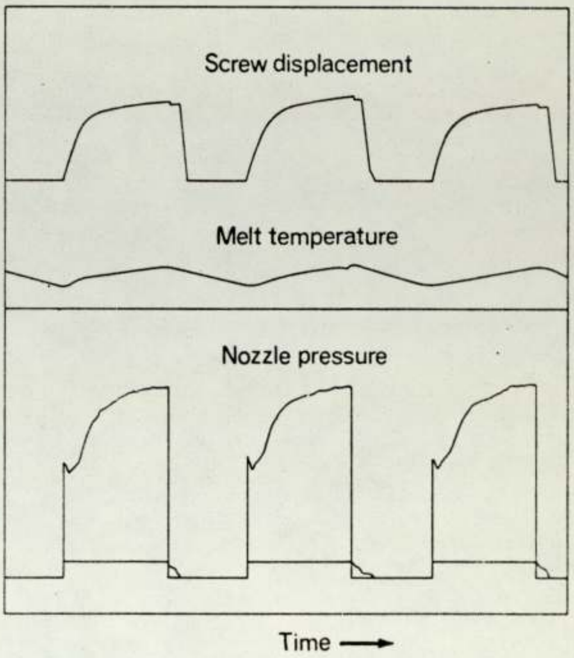


Figure 1 Monitored data from reprocessed material

The phenolic compound reprocessed once on the Turner machine and twice as shown in Part 2 was used to make mouldings with the plaque mould using the process conditions shown in Table 1 of Part 1. (2). The appearance of the mouldings was assessed along with data on melt pressure and temperature obtained at the nozzle of the machine and measurement of screw displacement. (Table 2). The type of monitored information exhibited on moulding reprocessed material is depicted in Figure 1. This preliminary trial indicated that reprocessing had only a small effect on the appearance of mouldings this being the result of a marginal stiffening in flow characteristics previously observed or because of an increased proportion of fines in the reprocessed material through successive regranulation, or a combination of both effects. Mouldings prepared from material reprocessed on the Bipel machine were of poorer quality and showed different nozzle pressure and temperatures. Material which had been reprocessed twice was difficult to mould and gradually cured in the nozzle. In contrast, material that had been reprocessed once on a 4 oz Ankerwerke machine was difficult to mould. The quality of mouldings varied considerably and only 2 out of 10 mouldings were satisfactory. Material which had been reprocessed twice could not be ejected properly from

Table 2. Comparison of Mouldings from Reprocessed Material. Turner 2 oz Machine

			Virgin Material Mean		Reprocessed Once		Reprocessed Twice	
Shot Weight grams	Max	Max	42.81	43.89	42.89	43.35	43.09	44.67
	Min	Min		41.96		41.18		40.23
Melt Pressure psi	Peak	Max	6630	6700	6753	7000	7262	7600
		Min		6450		6600		6700
	Min	Max	3710	3800	3736	3900	3872	4000
		Min		3650		3650		3650
Stroke Length cms	Initial	Max	0.5	0.65	0.55	0.63	0.53	0.65
		Min		0.45		0.45		0.45
	Total	Max	3.05	3.25	3.25	3.06	3.1	3.4
		Min		2.95		2.6		2.9
Stroke Duration secs		Max	15.4	15.8	15.4	15.5	15.4	15.7
		Min		15.0		15.2		15.3
Nozzle Tip Temp °C	Initial	Max	100.1	101	100.1	101	100.1	101
		Min		100		100		100
	Final	Max	100.1	101	100.1	101	100	100
		Min		100		100		99.5
Quality of mouldings			Sl. twisted		Sl. twisted		Sl. twisted	
Satisfactory			50%		40%		-	
Slight flash			40%		20%		56%	
Slight porosity			10%		40%		44%	

the nozzle because of decreased melt mobility. Appreciably reduced flow properties were recorded from flow tests on the material reprocessed on this machine.

VARIATION OF MOULDED QUALITY

The effect of varying the more important process conditions on the properties of mouldings was examined at 3 levels of the process setting employed. Air shot material was taken for the subsequent determination of flow/cure properties using the variable torque rheometer and the Monsanto rheometer.

The process conditions selected for phenolics were injection pressure, back pressure, screw speed and injection speed, each of which was varied individually at a minimum, maximum and intermediate setting. Three experimental runs were conducted in which the following procedure was adopted at each condition.

The process settings are shown in Table 3. The melt temperature was increased with Run 2 and the mould temperature was increased in Run 3. All other conditions were unchanged. For the urea-formaldehyde compound, Tables 4 and 5, two sets of conditions were selected so as to obtain a more general evaluation of processing effects. On Run 11, back pressure, screw speed, injection speed and pressure were varied keeping the barrel temperature, mould temperature and cycle time constant. On Run 12, temperature conditions were varied at set pressure conditions i.e. barrel temperature, mould temperature, cycle time and injection speed were varied whilst maintaining back pressure, injection pressure and screw speed. In evaluating either phenolic or urea mouldings, the first five mouldings produced at each setting varied were discarded, the next ten successive mouldings were retained for examination and lastly three air shots were collected for the flow test. A plaque mould was employed in the experiments but all phenolic mouldings were prepared with a tab gated tool and the urea mouldings with a submarine gated tool.

Table 3. Experimental Plan for Phenolics

	Process Conditions					
Varied	Back Pressure	psi	60	120	180	
	Screw Speed	rpm	60	100	140	
	Inj Speed		2.5	3.5	4.3	
	Inj Pressure	psi	700	1000	1300	
Fixed			Run 1	Run 2	Run 3	Run 4
	Barrel Temp	°C	88	95	88	88
	Mould Temp	°C	165	165	190	165
	Cycle Time	secs	30	30	30	*

* Variable Cycle Time 30, 45, 60 secs

Table 4. Experimental Plan for Urea Run II Materials

	Process Conditions				
Varied	Back Pressure	psi	30	70	120
	Screw Speed	rpm	60	100	140
	Inj Speed		2.5	3.5	4.3
	Inj Pressure	psi	800	1100	1400
Fixed	Barrel Temp	°C	90		
	Mould Temp	°C	150		
	Cycle Time	secs	30		

Table 5. Experimental Plan for Urea Run 12

Varied	Barrel Temp	°C	80	90.	98
	Mould Temp	°C	140	150	160
	Cycle Time	secs	15	25	35
	Inj Speed		2.5	3.5	4.3
Fixed	Screw Speed	rpm	70		
	Back Pressure	psi	70		
	Inj Pressure	psi	1400		

NB Injection Speed. High number means fast speed
Low number means low speed

VISUAL APPEARANCE

Surface gloss was graded arbitrarily by grouping mouldings as either poor, fair, good or very good. Flow marks were produced on the mouldings in three basic patterns as shown in Figure 2. Where possible a quantitative indication of the extent of flow has been attempted by measuring the distance of the visible flow lines exhibited from the far end of the moulding for Type A. Both gloss and flow marks were examined on all the 10 mouldings produced at each process setting.

None of the phenolic mouldings produced from the varied machine settings gave mouldings of good gloss free from flow marks. The greatest gloss was obtained on mouldings produced under medium screw speed conditions. Surface gloss was also improved to a lesser extent whenever any of the other process conditions was increased separately, apart from higher mould temperatures which had the opposite effect. When either screw speed, injection speed or back pressure was reduced, a patchy moulding surface was obtained. The use of a high screw speed in conjunction with a high back pressure produced mouldings with a matt or 'Frosted' Surface, probably as the result of rapid surface cure.

The process settings altered had apparently no effect on gloss of the urea mouldings.

Similarly, as the levels of the processing condition altered were reduced, a worsening of appearance from flow marks resulted. The layered or wave type filling pattern of Type A disappeared as the levels of the processing condition were increased and was

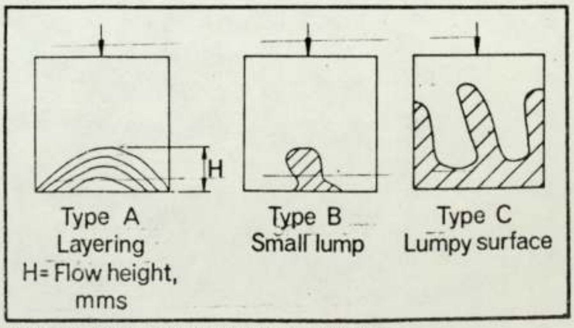


Figure 2. Flow patterns on phenolic mouldings

replaced by a rough area opposite to the gate. (Figure 2B). At the maximum levels of the process setting used, the type B flow pattern changed to the Type C pattern. The variation in the flow marks reflected a change in the cavity filling pattern, largely caused by increased melt velocity through the tab gate resulting in jetting and more turbulent flow. Higher melt and mould temperatures tended to reduce the flow marks.

A limited number of phenolic mouldings and all urea mouldings were prepared using a submarine gate. The material flowed outwards from the gate producing good quality mouldings without flow marks.

DIMENSIONAL CHANGES

The diagram in Figure 3 shows the dimensions of the plaque moulding which were measured, the broken lines exaggerating the type of distortion which occurred and the solid lines indicating the mould cavity shape. The difference between L_2 and L_1 was recorded as the shrinkage in width of the moulding. Thickness of the moulding was measured at a central point along these sides.

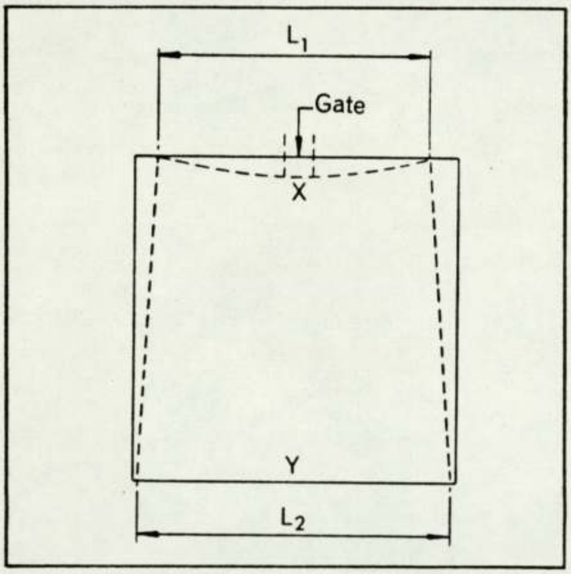


Figure 3. Dimensional measurement of mouldings
——— theoretical moulding ; - - - - - - - actual moulding

Some warping of the phenolic mouldings was noticeable but no attempt was made to measure this since it might reflect their lack of rigidity on ejection from the mould. Higher back pressures and screw speeds minimised the dimensional change and, in general, increasing the levels of any of the process conditions tended to reduce dimensional variations.

With the urea mouldings, all of which were produced in the submarine gated mould, a slight change of the order of ± 0.1% in width was recorded. Similar insignificant changes in thickness were recorded near the gate for both runs. Part thickness opposite the gate was greater for Run 11 under more severe process settings but showed no appreciable change for Run 12. Urea mouldings were observed to be less flat near to the gate and the degree of flatness was more pronounced on one side of the moulding than on the other. The distortion was more pronounced for Run 11 than Run 12. The least amount of distortion was produced when high back pressures were used with intermediate injection pressures or high injection pressure in conjunction with intermediate back pressures. None of the mouldings was free from distortion.

WEIGHT

At barrel temperature of 165 C and mould temperatures of 88 C the weight of phenolic mouldings was increased by about 4% when using more severe process settings. Increasing the level of the varied parameters at higher temperature levels caused little change in shot weight.

The urea mouldings, however, increased in weight by about 6%, largely as barrel temperatures were raised. Higher back pressures and injection pressures were a secondary cause. Increased screw speed, injection speed and mould temperature produced the least increase in weight.

HEAT DISTORTION TEMPERATURE

Samples for the heat distortion test were cut from the first third of the moulded plaque nearest to the gate and transverse to the direction of melt flow. The method of test employed was to B.S.102G.

There was no distinct correlation between the results of HDT and the process variable due to the wide scatter of figures obtained. This was not surprising since the mouldings were apparently undercured when ejected from the mould i.e. they were still soft and pliable (low 'green strength'). It was found that, by post curing, the HDT could be increased from about 130 C to 168 C in the case of the phenolic mouldings. General undercure of mouldings was supported by the increase of HDT with increase in cure time (and thereby increasing the cycle time) shown in Table 6.

Table 6. Effect of Longer Cure Time on HDT of Phenolic Mouldings

Barrel Temp °C	88	95	88
Mould Temp °C	165	165	190
Cycle Time secs	Heat Distortion Temperature °C		
30	111	102	96
45	116	115	133
60	112	112	128

There was a noticeable trend towards higher HDT as mould temperature was increased for both phenolics and ureas.

FLEXURAL PROPERTIES

Samples were taken from the same location in the plaque as for HDT. Flexural strength and flexural modulus were measured to B.S. 304A and B.S. 304D respectively.

Similarly to the HDT results a wide scatter was again obtained for flexural strength with an indication of some increase with higher mould temperatures.

Individual flexural modulus results were again widely scattered but the pattern remained relatively constant irrespective of change in process variables.

GENERAL CONCLUSIONS

A number of conclusions and experimental techniques have been derived from this study. Methods for characterisation of the polymer for processing, setting up, optimising and monitoring processing conditions have been investigated (see Parts 1 & 2). A computerised multivariable regression analysis programme has been applied to predict the effect of machine variables on polymer flow and properties of mouldings.

REMOTE TESTING OF PROCESSED COMPOUNDS

(Part 1)

In the injection moulding process a number of variables may influence the properties of mouldings — these may arise from variations in the input polymer or in the operation of the moulding process.

A number of methods have been employed to characterise the processing properties of the input polymer. These methods have included the RAPRA Torque Rheometer, the Monsanto Rheometer, cup and disc flow methods and a series of test procedures used by polymer manufacturers. The efficacy of these methods in showing differences in the polymer varied considerably. However, significant differences in the flow character of batches of thermosets and between phenolics and ureas was shown by all the flow measuring techniques employed. The RAPRA Torque Rheometer and Monsanto Rheometer showed differences in polymers which were overlooked by other methods.

FLOW DATA AND PROCESS REPRODUCIBILITY BY MONITORING

(Part 2)

It was found that simply resetting barrel temperature and hydraulic pressure was inadequate and that re-establishment of screw displacement and nozzle melt conditions was essential. The monitoring system recorded random variations in a sequence of mouldings. These variations could lead to faulty mouldings. It was felt that this system of monitoring could be effectively developed to afford control of the mouldings, establishment of optimum conditions and provision of flow data.

THE EFFECT OF PROCESSING CONDITIONS ON MOULDINGS

(Part 3)

Optimum machine settings exist to produce mouldings of high gloss, minimum flow marks, minimum warpage, heat distortion point and maximum mechanical properties although these are not necessarily identical for each property. However, most properties are approaching their optimum for machine settings which result in the minimum melt viscosity.

One of the major requirements of the programme was that the moulding conditions employed should reflect normal industrial practice. Employing typical conditions it was found that all the mouldings made were undercured in that distortion readily occurred on removal from the mould and their heat distortion temperatures could be considerably increased by post stoving. Clearly longer dwell times, or cure times or mould temperatures would overcome this problem if necessary.

A computerised system was used to analyse the results of the moulding study to correlate properties of mouldings with machine conditions. This met with a mixed success in that reasonable correlations were observed for mechanical and physical properties such as heat distortion temperature, flexural strength, flexural modulus, dimensions and weight whereas no correlation existed for the visual properties of flow marks and gloss. Variations can be expected in some of these areas because of the observed undercure of the mouldings. Similarly, no correlations were derived in the computer assessment of flow marks and gloss. This is not surprising because of difficulties in quantifying the observed result.

A visual examination of mouldings for gloss and flow marks indicated that the machine conditions for good gloss were those which produced a maximum flow rate. The limit of this flow rate was determined by cure conditions in the mould. The process monitoring procedure was shown to be most effective in establishing these optimised conditions within the limits of the reproducibility of the machine employed.

Trends in the mechanical and physical properties of urea mouldings with processing conditions were similar to those observed in phenolics. The main difference noted was in the parameters influencing gloss and warpage and this may well arise from the use of a mould having a submarine gate and therefore different filling characteristics.

Many of the techniques used in this project are clearly worth further development. For example, the use of the RAPRA Torque Rheometer and the Monsanto Rheometer will show significant differences in the flow behaviour of polymers. To relate these differences to behaviour on a production moulding machine can be a long process in which the computer analysis method could be usefully employed. This investigation has provided a possible approach which would need confirmation by applying it to a large range of batches of material, other materials, machines and moulds. Clearly the moulder would be considerably assisted if moulding conditions could be quickly and reliably established and monitored and methods for doing this have also been shown to be feasible.

REFERENCES

1. R.R. Whisson and K.T. Paul, RAPRA Members Journal, March 1974, p. 64

2. R.R. Whisson and K.T. Paul, RAPRA Members Journal, Dec. 1973, p. 308