GLASS - FIBRE REINFORCED
ACETAL CO-POLYMER

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SUMMARY

The glass fibre reinforced acetal copolymer system has been studied in detail. An attempt has been made to investigate some of the variables affecting the mechanical properties of the composite and evaluate their relative importance: these variables included processing methods, coupling agents, glass content and polymer viscosity.

These variables were first investigated using a compression moulded test system, but a rather poor level of properties was obtained and the results proved inconclusive. It was decided that compression moulding did not offer a useful evaluation of glass reinforced acetal and so an injection moulded system was investigated as well.

Injection moulded test pieces showed a considerably higher level of mechanical properties. An investigation of the effect of processing method revealed that a dry blended material showed generally superior mechanical properties to a material prepared on the two roll mill which in turn was superior to material prepared in the Buss Ko-kneader. It was shown that this resulted from increasing shear in the three processing methods, giving rise to a reduced fibre length in the composite.

Tensile properties and hardness have been shown to increase linearly with increasing glass content whereas impact strength goes through a definite minimum, which moves to a higher level of glass content with decreasing fibre length.

Polymer viscosity has been shown to have little effect on mechanical properties. Coupling agents exert a marked effect on tensile strength but no effect on tensile modulus - this is in exact accordance with theoretically predicted behaviour. Methacrylato - chromic chloride and γ-methacryloxypropyl trimethoxysilane appear to be the most effective coupling agents of those investigated.

One incidental result of this work has been to yield materials having, in the optimum direction, tensile strengths of up to 23,500 psi and moduli of nearly 2,700,000 psi - substantially higher than previously recorded for glass reinforced polyacetal.

An extensive literature survey has been carried out over the whole field of glass reinforced thermoplastics.

ACKNOWLEDGEMENTS

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CHAPTER I

GLASS-FIBRE REINFORCED THERMOPLASTICS - LITERATURE SURVEY.

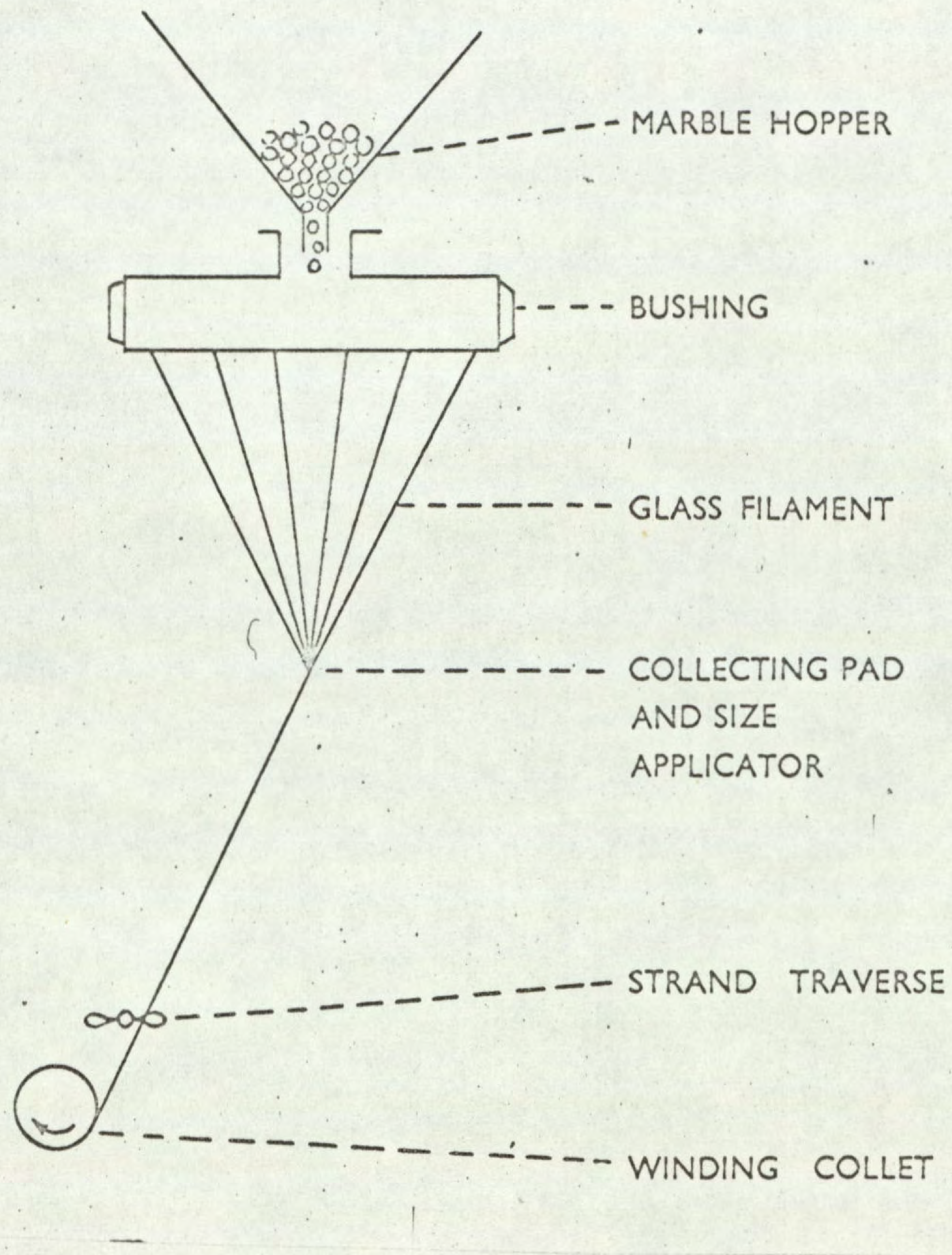
GLASS-FIBRE REINFORCED THERMOPLASTICS - LITERATURE SURVEY

A. Introduction.

Fibre reinforced thermosetting resins have been known and used for a considerable period of time but it is only in the last 5 - 10 years that reinforcement has been applied to thermoplastics with any degree of success. Materials which have been used as reinforcing agents for thermoplastics include glass fibres, asbestos fibres[1-7], various whiskers[7], carbon fibres[8-11] and even specially treated fillers such as kaolin[12,13] - the first two materials are by far the most important, however, at the moment.

There are two basic methods of preparing glass fibres; these involve extending a coarse filament, exuding from a platinum/rhodium bushing, either by a jet of air (or more commonly steam) or by pulling on to a drum. The latter process gives rise to the so called continuous filament glass fibre and it is this which is used for reinforcing plastics. Figure 1 [14] illustrates a typical continuous filament process. The glass is melted by resistance heating of the metal bushing; this heating must be accurately controlled in order to ensure adequate filament diameter regularity. Prior to winding of the filaments on to the drum they are collected together in order to form a consolidated strand. At or before this point the filaments are coated with a size: this contains a silane

FIGURE 1


MARBLE HOPPER
BUSHING
GLASS FILAMENT
COLLECTING PAD AND SIZE APPLICATOR
STRAND TRAVERSE
WINDING COLLET

or chrome coupling agent and a binder (usually of poly (vinyl acetate) emulsion), for applications in reinforced plastics. The purpose of the coupling agent is to promote adhesion to the polymer, and of the binder to prevent self-abrasion of the glass filaments during winding and subsequent chopping operations.

Glasses are supercooled liquids and, as such, contain short-term but no long-term order. The thermal history of the glass will thus affect the structure[15] and the surface structure of a glass fibre, which has been very rapidly quenched from 1200°C, will be appreciably different from that of bulk glass.

Yates and Trebilcock, in their study of the nature of glass fibre surfaces and coupling agent action[16], show that "E" glass may be considered to have weakly acidic SiOH groups and an equal number of more acidic sites caused by replacement of silicon by boron or aluminium atoms. They also show that the glass surfaces are very heavily hydrated, the degree of hydration being several times larger than that corresponding to a mono-molecular surface layer.

Sterman and Bradley[17] have carried out electron microscopy on a sized glass surface and have shown that the size tends to form agglomerates rather than spreading over the glass in a uniform film. The work has incidentally shown the extreme smoothness of the glass fibre surface, thus agreeing well with data from surface area measurements.

The picture that thus emerges is a smooth glass surface with both weakly acidic and strongly acidic sites: this structure is complicated by the presence of several layers of water and agglomerates of coupling agent.

The other part of the composites in which we are interested is the thermoplastic resins. Thermoplastics are of widely diverse chemical types but some generalisations are applicable[18]. Thermoplastics are high molecular weight polymeric materials which are solid at room temperature but which soften at elevated temperatures to give a viscous melt. It is this reversible softening which is relied upon in processing the materials, unlike the position with thermosets where an irreversible chemical reaction is involved during moulding.

Some thermoplastic materials, such as polyacetal or polyethylene, are partially crystalline, containing both ordered and disordered regions, whereas other materials, such as polystyrene, are totally amorphous.

In the formation of glass-reinforced thermoplastics we are thus involved with the interaction between a viscous, rather chemically inert, molten thermoplastic and a very smooth glass fibre whose surface is protected by several layers of water and contaminated by a certain amount of size. In certain cases, however, this generalisation need not be true: for instance, nylons are of rather lower viscosity than most thermoplastic polymers when molten and their chemical type, involving as it does a hydrogen bonded structure with several active groups, could scarcely be classed as inert. These differences result in glass reinforced nylons having an exceptionally high level of mechanical properties: another contributory factor towards this high performance is the capacity of nylon to absorb water from the surface of the glass into the bulk polymer.

Present interest in glass-fibre reinforced thermoplastics stems from patents granted to Fiberfil Corporation (in the U.S.A.) which described the production of an injection mouldable material from glass fibre and thermoplastics. Several other patents have since been filed describing glass-fibre reinforced thermoplastics production and there are now well over a dozen companies producing these materials.

The relevant literature has grown at a similar pace; about 500 articles have been published on glass-fibre reinforced thermoplastics. Baldanza[19] has reviewed certain aspects of glass-fibre reinforced thermoplastics in some depth and several short review articles have been written[20-30], but nowhere is there a complete and comprehensive account of this field.

The current boom in reinforced thermoplastics is due to two main reasons - their ease of processing and their high level of properties. Despite initial doubts about passing glass fibre through an injection moulding machine (it was felt that either the glass would be ground to a powder or the nozzle and gates would be blocked) it has been shown that with a little care glass-fibre reinforced thermoplastics can be processed with a higher degree of consistency than their unmodified counterparts.

Introduction of 20 - 40% of glass fibres into thermoplastics causes a dramatic improvement in mechanical properties, tensile and flexural properties being improved by 100 - 200% and even more in some cases. This makes glass-fibre reinforced thermoplastics directly competitive with such non-ferrous metals as aluminium, zinc or magnesium, especially when an assessment is made on a weight rather than on a volume basis. Impact properties are not improved in the same way as tensile and flexural properties since, with most thermoplastics, addition of glass fibres causes a transition from tough to brittle behaviour. Brittle materials exhibit a low resistance to crack propagation and a high sensitivity to notches in their surface; tough and brittle materials are usually distinguished by their stress-strain curves, brittle materials showing little or no yield. Figure 30 (page 161) shows the transition from tough to brittle behaviour which occurs on incorporating glass fibre into acetal copolymer.

The high creep (i.e. time dependent elongation under a constant load) of thermoplastics is one of their major deficiencies and the fact that this is substantially reduced in glass-fibre reinforced thermoplastics opens up a whole new range of potential applications for plastic materials.

Thermoplastics, in comparison with metals, possess two other major disadvantages - a high coefficient of thermal expansion ($8x10^{-5}$ for acetal compared with $2x10^{-5}$ for brass) and low maximum service temperature (about 100°C for acetal). Both of these properties show a useful improvement in glass-fibre reinforced thermoplastics. Electrical and chemical properties of glass-fibre reinforced thermoplastics are generally similar to those of the parent polymer.

A large number of factors go to determine the mechanical and thermal properties of glass-fibre reinforced thermoplastics, not least the actual polymer chosen for reinforcement. Nylons show a greater capacity for reinforcement than most other thermoplastics - this is probably due to their chemical composition giving rise to a strong interfacial bond between the polymer and the glass. The low melt viscosity of the nylons and their capacity to absorb water (normally present on the glass surface) may also be important in promoting a high composite strength.

Glass-fibre reinforced thermoplastics are heterogeneous materials and the properties, after injection moulding, will be anisotropic due to different degrees of fibre orientation in different directions. This means in practice that properties quoted in trade literature and elsewhere can only be taken as guiding values and, for critical applications, prototype mouldings must be made and tested.

Many other factors have also been shown to play a part in determining the properties of glass-fibre reinforced thermoplastics. These include glass fibre content, length and diameter, coupling agents and other additives and processing variables.

The object of the work described in this thesis was to examine some of these variables and evaluate their importance in determining certain mechanical properties of the glass-fibre reinforced acetal copolymer system. Before details of this investigation are given, the literature of glass-fibre reinforced thermoplastics generally will be discussed in some depth.

B. Production of Glass-Fibre Reinforced Thermoplastics.

(i) Long-fibre materials.

The first patent concerning the production of glass-fibre reinforced thermoplastics was one applied for by the Fiberfil Corporation in 1952 [31]. The process involved passing a suitably sized continuous strand of glass fibre through a bath containing polystyrene emulsion: the strand was then dried and chopped into granules. Further patents from Fiberfil described the extension of the process by passing the glass strand through a molten thermoplastic[32] and a modification to the apparatus allowing greater control over the tension of the strand and hence resin pick up[33].

Other patents in the 1950's from different companies[34-36] described very similar processes but were all pre-dated by the Fiberfil patent. A recent improvement to the normal strand coating process has been described[37] in which the glass strand runs helically inside the pellet instead of parallel. This is claimed to result in less fibre breakdown during injection moulding but no reason is given.

Materials made by the strand coating process have a fibre length which is determined solely by the chopping length (but some fibre breakdown will occur on injection moulding): such materials are known as long-fibre materials.

(ii) Short-fibre materials.

After the development of the Fiberfil process, several manufacturers investigated other, more severe, methods of compounding the glass fibre and the thermoplastic melt.

Various companies have taken out patents describing very similar processes[38-48]: these generally involve mixing together the polymer and chopped strand on a roll mill or in an extruder. Such materials generally contain very short glass fibres and are known as short-fibre materials.

Wilmes has given photographs showing the different structures of articles moulded from glass-fibre reinforced thermoplastic of the long-fibre and short fibre type[49]. Several authors have discussed the pros and cons of the two types of material: these are set out in most detail by Murphy[50]. Long-fibre materials generally have a higher level of properties (especially impact strength) but short-fibre materials are easier to process and are cheaper.

(iii) Concentrates.

A recent development in the field of glass-fibre reinforced thermoplastics has been the appearance of the so-called concentrates[51-56]. These are simply pellets containing thermoplastic polymer with a very high glass loading, which can be tumble blended with pellets of virgin polymer prior to the injection moulding. This development allows the moulder to select the exact level of glass loading that he requires.

(iv) Direct injection moulding of a dry-blend.

This technique involves direct blending of thermoplastic powder and chopped strand prior to injection moulding[52,57-64]. The process, although sounding simple, is in fact exceedingly complex as a very large number of variables are involved e.g. polymer particle size and geometry, moisture content and density of the polymer, mixing and blending variables, the number of filaments in each strand and the coupling agents on the glass. The dry-blending stage is said to require complex equipment[64] and hence most of the present interest in this method centres on high volume, low priced thermoplastics such as polystyrene, styrene-acrylonitrile copolymer and polypropylene[60]. Schlich et al[57,58] has compared the properties of test pieces moulded from dry blended materials, with those moulded from both long- and short-fibre materials; the former are almost universally superior due to less polymer and fibre degradation occurring. It is claimed that dry blend injection moulding can only be carried out on screw type injection machines.

(v) Polymerisation in the presence of glass-fibre.

All the preceding production methods involve total polymerisation of the thermoplastic prior to incorporation of the glass fibre. In one or two special cases however polymerisation has been carried out in the presence of glass fibre.

Several patents describe the compounding of caprolactam with glass fibres prior to polymerisation to nylon 6 [65-67]. The National Lead Company have described a process for encapsulating glass fibres with polyolefins[68-70]: this is done by treating the glass fibres with one part of a two-part catalyst system and then adding the other part of the catalyst with the olefin monomer.

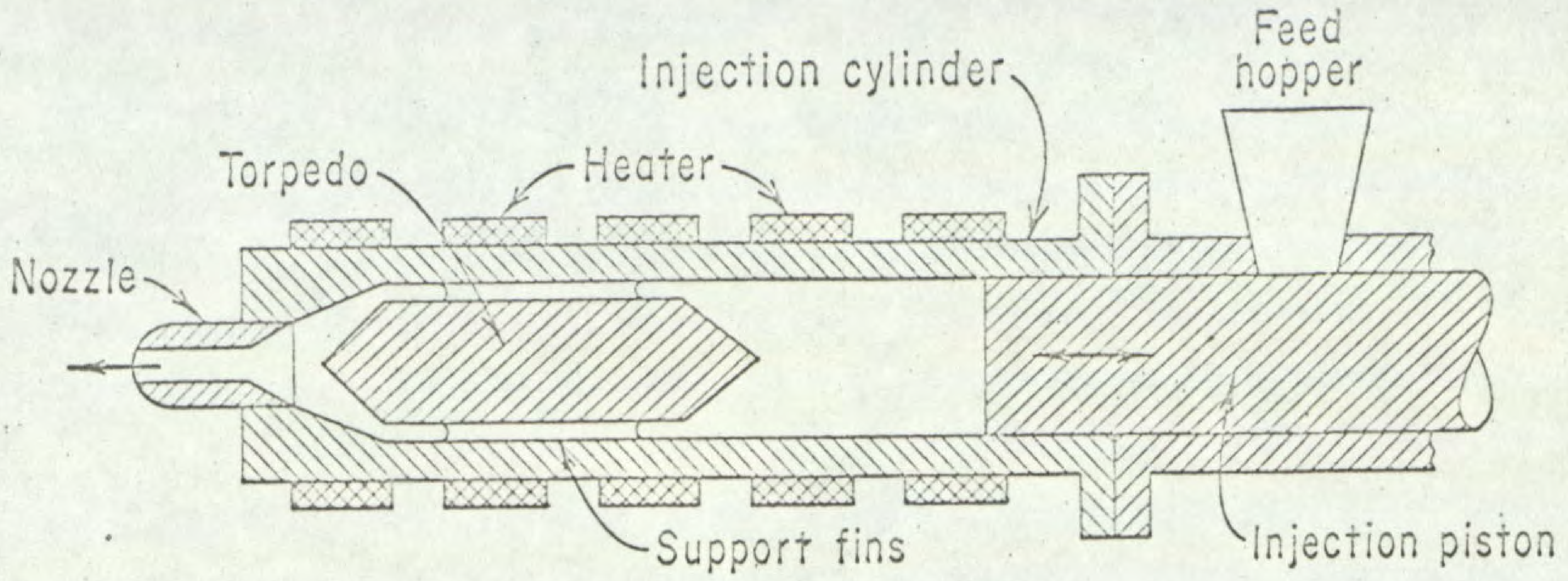
C. Processing of Glass-Fibre Reinforced Thermoplastics.

(i) Injection moulding.

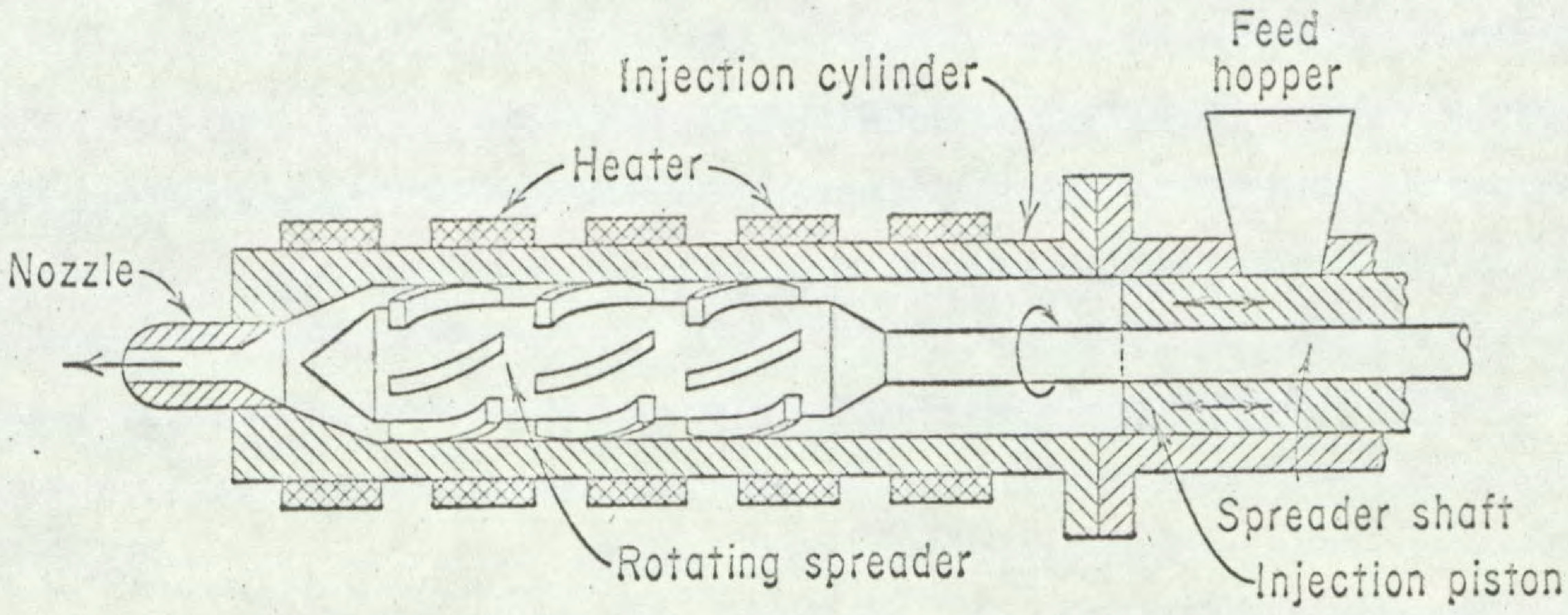
An injection moulding machine is simply a means of plasticising a material fairly rapidly and efficiently and injecting this into a mould where it solidifies. There are two basically different machines:- ram type and screw type. Figure 2 [71] shows three simple types of ram machine and also a single screw machine. The three ram machines all show different features designed to ensure more efficient heat transfer from the barrel to the material. The more recently designed screw type machines do not rely solely on heat transfer from the barrel, since the work done by the screw on the material produces heat internally and thus assists plasticising. This dual source of heating cuts down the risk of polymer degradation, especially where sensitive materials are concerned.

The injection moulding machine relies on forward movement of the ram or screw to provide injection pressure. Figure 3 [71] shows a typical injection mould with the various sections identified.

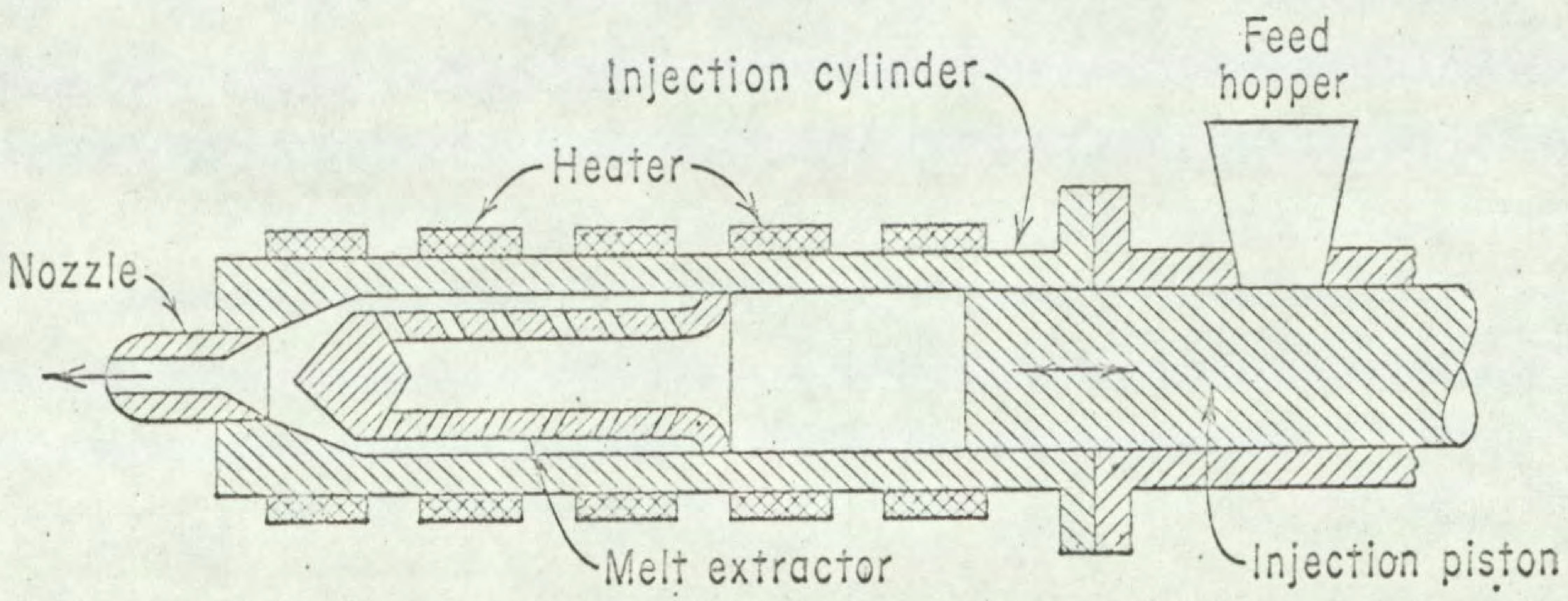
Injection moulding is by far the most important processing method for glass-fibre reinforced thermoplastics: the important requirements for successful injection moulding can be summarised



Conventional torpedo type cylinder. Torpedo spreads melted plastic into a thin layer between itself and cylinder's inner surface



Cylinder with rotating spreader. In this system, the finned spreader is driven by a shaft which runs through a hole in the injection plunger (piston); plunger moves forward for injection



Melt extractor cylinder. Plastic is forced through the core of the extractor and out of multiple radial holes into annular space between the body of the extractor and the inner wall of the cylinder

FIGURE 2

In the reciprocating screw cylinder, the material is plasticated by screw while the latter moves backward in the cylinder; for injection, the screw moves forward, as a ram

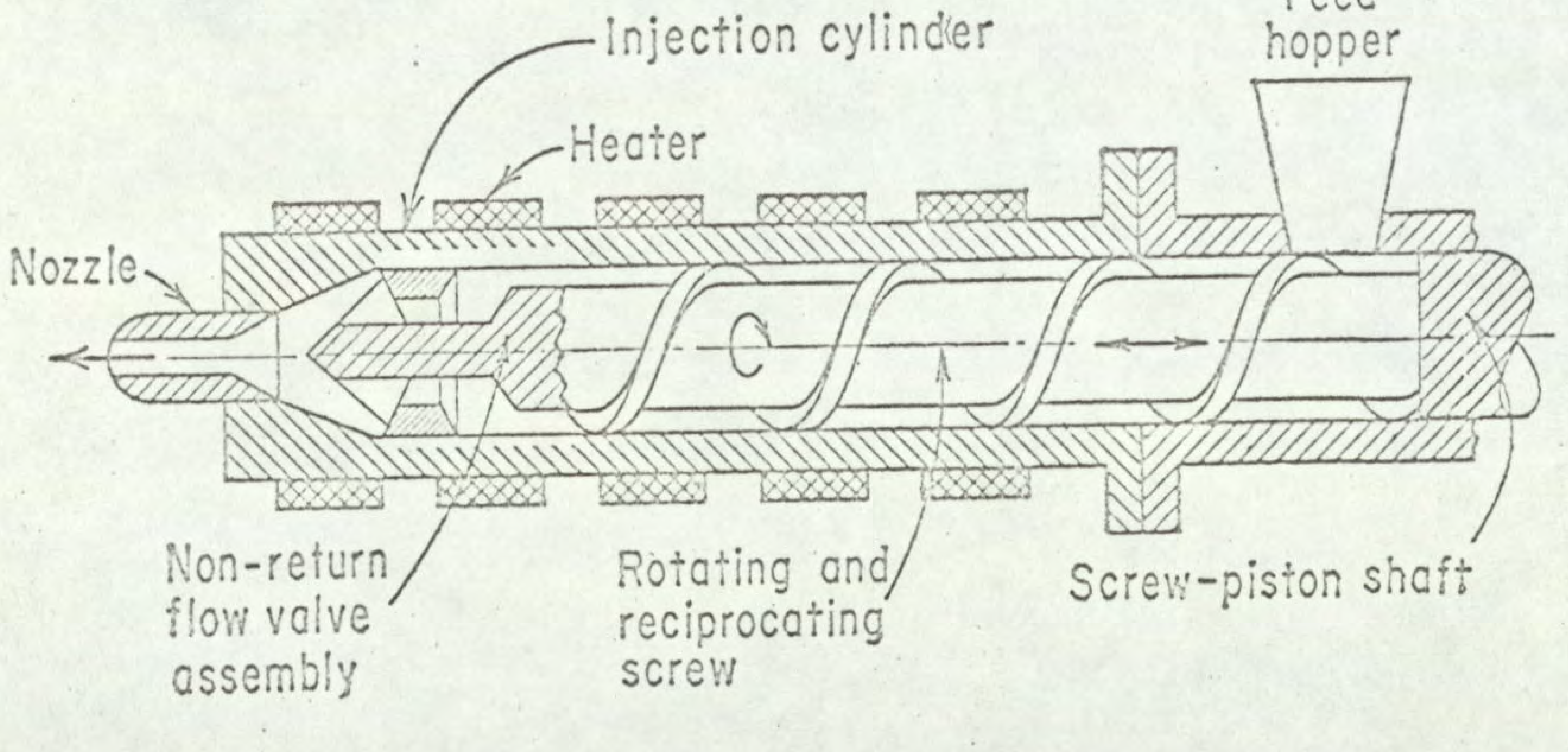
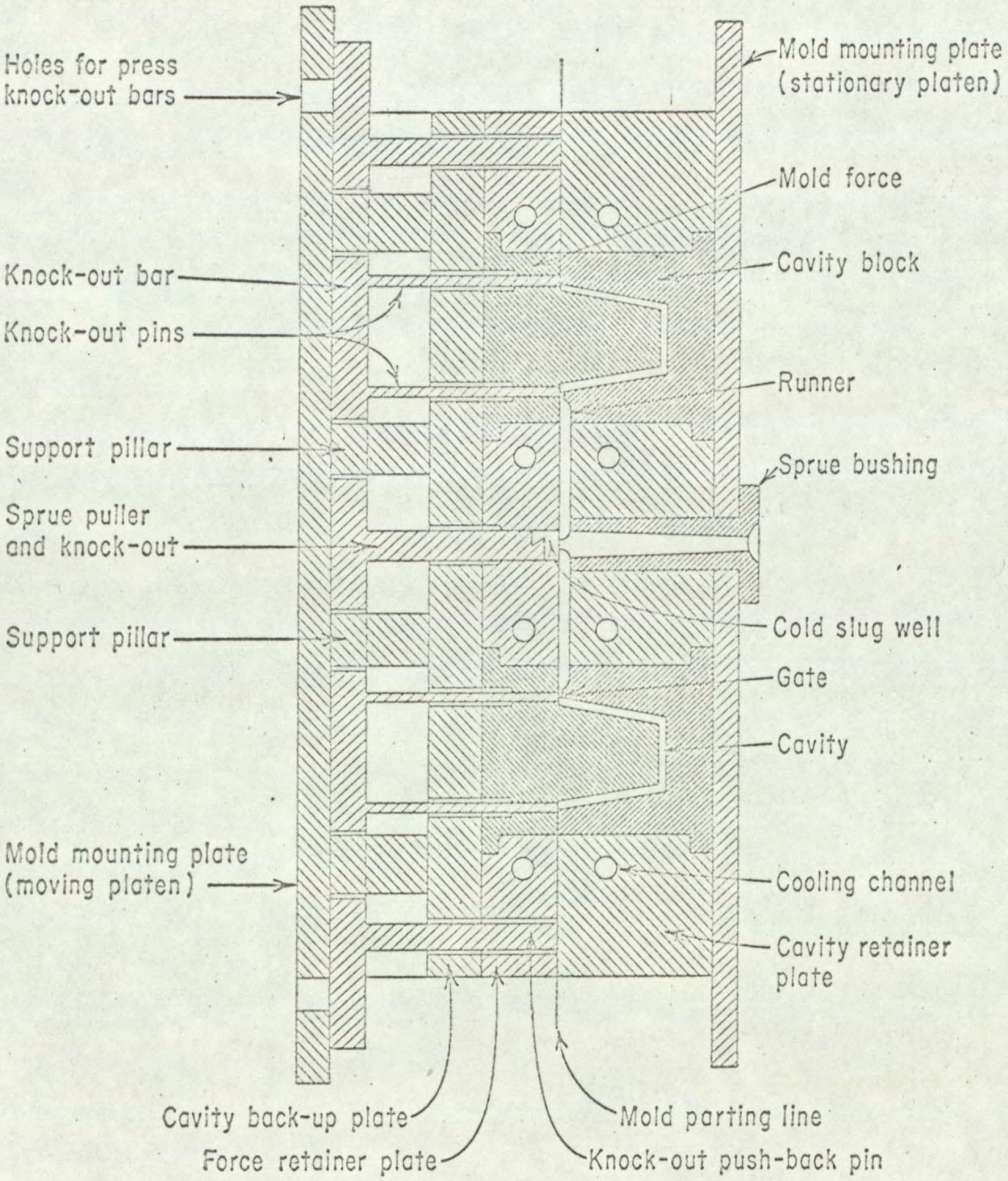


FIGURE 3



Cross-section of a two-cavity mold with runner system and provision for automatic ejection of parts as mold opens. In this case, cavities are edge gated in the form of a list.

(a) high injection speed[72,73]

(b) shot size $< 75\%$ total rated injection capacity[72,74,75]

(c) high injection pressure[73,75-77]

(d) high cylinder temperature[72,73,76,77]

(e) high mould temperature[72,75,78]

(f) sprue and runners as large and short as possible[72]

(g) either screw or ram type machines can normally be used, although use of the former may be obligatory in certain cases

The conditions are generally designed to ensure that the glass-fibre reinforced thermoplastic flows as rapidly as possible into the mould and premature freezing does not occur. It is claimed that this is critical because of the reduced heat content of the glass-fibre reinforced thermoplastic as compared with that of the unmodified thermoplastic (the glass does not melt during the injection moulding cycle and also has a lower specific heat than the polymer). This reduced heat content of glass-fibre reinforced thermoplastic melts does give rise to one advantage, however: cycle times can be 10 - 50% shorter than with unmodified thermoplastics[72,78].

Gate location is an especially important design feature where moulding of glass-fibre reinforced thermoplastics is concerned: it should be arranged so as to prevent sharp changes in the degree of fibre orientation. For instance in the simple case of a tensile bar end-gating is preferred: centre-gating will result in the material at the centre having different properties from the rest[79], due to the differing fibre orientation.

The mould shrinkage (i.e. the amount by which the moulded part is smaller than the mould) which occurs with glass-fibre reinforced thermoplastics is considerably less than with unreinforced thermoplastics[72, 78]. The mould shrinkage of acetal copolymer is reduced from about 2% to about 0.2% on addition of 20% glass fibre. The actual values realised will depend on the moulding conditions and will differ in different directions due to the anisotropy of moulded glass-fibre reinforced thermoplastics. This can render mould design difficult in some circumstances. Warping of the moulded part can occur in some cases, due to the heterogeneous nature of the glass-fibre reinforced thermoplastics, which results in different layers of material in the moulding having a slightly different composition[80-82]. The surface of glass-fibre reinforced thermoplastic articles is rougher than that of unmodified thermoplastics - the polymer, having a higher coefficient of expansion than the glass, displays the contours of the glass fibres underneath[83].

One final characteristic of injection moulded, glass-fibre reinforced thermoplastics is that weld lines tend to be prominent: this is claimed to be because the glass fibre tends to move faster than the melt and thus forms a weak, fibre enriched zone at the weld[73,76,77]. Weak weld lines can be strengthened by lowering the melt temperature (thus impeding the glass fibres from flowing ahead of the melt), lowering the concentration of glass, using shorter glass fibres or introducing over flow wells into the mould.

Some disagreement is apparent over the question of the wear on the barrel of injection moulding machines brought about by use of glass-fibre reinforced thermoplastics[84]. Wear is quite an important phenomenon as it leads to contamination of material, and more importantly, to loss of injection pressure. Certain cases of extreme wear with glass-fibre reinforced thermoplastics have been instanced but it appears that these are the exception and that, if processing is properly carried out, wear is not a great problem[85], especially where properly nitrided steels are used in the barrel of the injection moulding machine[79]. Mould wear can be avoided by using the technique of hot runner moulding[74] thus reducing the risk of more abrasive, semi-cooled material impinging on soft cavities in the mould.

Jäkel[86] has explained the rather surprising lack of wear with glass-fibre reinforced thermoplastics by pointing out that solid bodies in a flowing fluid (such as glass fibres in a thermoplastic melt) will tend to move in the positive direction of the velocity gradient (i.e. away from the walls of the injection moulding machine).

(ii) Other processing methods.

Very little information has been published on the extrusion of glass-fibre reinforced thermoplastics - it has been stated that extrusion is not a satisfactory processing method as the extruder screws cause fibre shortening and a deterioration in properties[87]. There are recent indications, however, that extrusion will soon be an acceptable method for processing glass-fibre reinforced thermoplastics.

Thermomechanical forming is not a widely used method of processing glass-fibre reinforced thermoplastic, as sheet material is not generally available and also, possibly, because of the high rigidity of glass-fibre reinforced thermoplastics. The development of glass-fibre reinforced, thermoplastic sheet materials suitable for processing on conventional metal stamping equipment has been described, however[88].

Major machining of glass-fibre reinforced, thermoplastic mouldings is undesirable since fibres may be severed in a critical position[87,89] and the exposed glass fibres might lead to excessive moisture absorption[87]. For minor finishing, carbide tipped tools should be used[89-91], to avoid excessive tool wear. Mechanical, adhesive and melt bonding of the glass-fibre reinforced thermoplastics is essentially similar to that for the unreinforced thermoplastic substrate[19].

D. Properties of Glass-Fibre Reinforced Thermoplastics.

(i) Physical Properties.

As is to be expected, the density of glass-fibre reinforced thermoplastics rises linearly with glass content[92,93]. The density is, however, usually very slightly less than that calculated theoretically, due to the presence of voids and vapour inclusions: a special process has been described for the production of glass-fibre reinforced polycarbonate and polyamide of theoretical density and, consequently, improved properties[43,44].

The moisture absorption behaviour of glass-fibre reinforced thermoplastics falls into two distinct groups. The nylons show a fall in moisture absorption on glass-fibre reinforcement[92,93], whereas other polymers usually show a slight rise(due to absorption via the resin glass interface). This fall with nylons is due to their high level of moisture absorption when compared with other polymers; replacement of some of the nylon by glass leads to a fall in moisture absorption, especially as the very strong polymer-glass bond in this case prevents ingress of water along the interface.

Cunliffe[94] states that glass reinforcement imparts a greyish tinge to nylon and Reichelt[30] points out that transparent thermoplastics become more opaque on reinforcement with glass fibre.

(ii) Mechanical Properties.

The glass-fibre reinforced thermoplastic system is a complex one and there are a multitude of variables involved, all of which can influence the ultimate mechanical properties of the composite.

Hall[29] has considered these variables and points out that one of the most important is the polymer chosen for reinforcement. If one considers three polymers of fairly similar mechanical properties - nylon, polycarbonate and polyacetal - then nylon shows by far the most dramatic improvement on reinforcement, the tensile strength being raised from 10,000 psi to 30,000 psi with 40% glass. With polycarbonate less improvement is obtained, and with polyacetal less still. Hall attributes this differing behaviour to the differing resin fluidities and compatibilities of the resin with the coupling agent used on the glass. The idea that the poor performance of glass reinforced polyacetal is due to poor resin-glass bond strength is borne out by Wagner et al[95] and Fraser[96]. They showed that the properties of glass reinforced polyacetal could be improved considerably by choice of an "active" coupling agent: for instance, a tensile strength of 9,700 psi with an inactive coupling agent was raised to 18,900 psi with an active one.

Hall has listed and classified some of the other variables which may affect composite properties[29] :-

- (1) Polymer Characteristics
    - (i) Viscosity
    - (ii) Reactivity
    - (iii) Solubility
    - (iv) Surface Tension
- (2) Glass Fibre Characteristics
    - (i) Chemical Composition
    - (ii) Fibre Diameter
    - (iii) Fibre Mean Length and Length Distribution
- (3) Additives
    - (i) Coupling Agent
    - (ii) Film Former
    - (iii) Lubricant
    - (iv) Anti Static Agent
- (4) Mixing Variables
    - (i) Temperature
    - (ii) Pressure
    - (iii) Shear Rate

Hall points out that the complex inter-relationships between these variables makes the isolation and investigation of any one exceedingly difficult.

No work has been reported, as far as is known, on the effect of polymer molecular weight (and hence viscosity) on the composite properties. Any investigation of the effect of polymer characteristics on composite properties will be severely restricted by the fact that a given polymer is only usually available at one or perhaps two levels of molecular weight.

A little work has been carried out on the effect of glass composition on the mechanical properties of glass-fibre reinforced thermoplastics. Fiberfil have reported the development of a modified E-glass composition especially suitable for glass-fibre reinforced thermoplastics[97]. Barthel et al[98,99] have investigated the use of A-glass fibres for reinforcement of nylon and report that, by use of optimum coupling agents, properties are obtained which are equivalent to those obtained by use of the more expensive E-glass fibres. With the exception of the above two , all of the data published on glass-fibre reinforced thermoplastics refers to, as far as is known, reinforcement by E-glass.

The percentage of glass in the composite will, of course, have a very considerable effect on mechanical properties and the number of references giving such data is too great to list exhaustively here. It can be said, generally, that tensile and flexural strength and modulus increase approximately linearly with glass content. Some workers with certain systems have reported, however, that at least 15% glass is needed before appreciable increase in tensile strength is obtained e.g. Streib and Oberbach[100] working with glass-fibre reinforced polycarbonate.

The variation of impact strength with glass content is not very clearly defined, several workers reporting widely different results[92,93,101-104]. Wagner et al[95] have studied the effect of glass content on the impact strength of glass-fibre reinforced polyacetal and appear to have established, from dart drop tests, that the energy required for crack initiation falls with increasing glass content whereas the energy required for crack propagation rises. The unnotched impact strength will thus depend on a balance between these two factors; the notched Izod impact strength, however, should rise with glass content (the notch serving as an initiated crack in brittle materials) - this was borne out by the observed results.

Effect of glass content on Drop Impact Resistance of 0.125" injection moulded sheet specimens.

Glass %	First Crack in.-lb	Addl. to Crack Through in.-lb	Notched Izod ft-lb/in
20	10	11	0.8
25	9	13	0.85
30	7	15	0.9
40	4	20	1.0

(reference 95)

The only systematic study of the effect of glass fibre diameter on properties appears to be that by Englehardt et al[105].

They studied a range of fibre diameters from "B" (0.000125") to "T" (0.000925) in a glass-fibre reinforced styrene-acrylonitrile copolymer system. The effect of fibre diameter on properties was not very great; for most properties G-fibres (0.000375") gave the best results although K-fibres (0.000525") were as good in certain cases.

One of the most difficult variables to investigate is the effect of fibre length on properties. Studies have been carried out[105] using chopped glass strand of various lengths and compounding these with polymer in an extruder etc. Little useful information is obtained from such studies as the fibre length will be reduced considerably during the compounding stage. The only way of determining the real effect of fibre length on properties is to produce the glass-fibre reinforced thermoplastic under conditions of increasing severity and then to determine the properties and the fibre length distribution. Fibre lengths have been determined by burning off or dissolving the polymer and then either measuring the glass fibres by means of a microscope[95,96] or using sieving techniques[104,106].

Williams et al[104] have shown a linear variation of tensile strength with glass fibre length over the range 0.01 - 0.02" for a glass-fibre reinforced nylon: a more efficient coupling system accentuated the effect of fibre length on properties, Filbert[106] has investigated the effect of fibre length on several mechanical properties; all showed a linear increase with fibre length but the increase was much more pronounced with impact and shear strengths than with tensile strength or flexural modulus.

Wagner et al.[95] used two different processing methods to prepare samples of glass-fibre reinforced polyacetal. Processing on a two roll mill gave material with an average fibre length of 0.3 mm (0.012") whereas processing in a Banbury mixer gave material with an average fibre length of 0.05 mm (0.002"). An investigation of the flexural modulus of the materials showed the two roll mill material to be superior, the Banbury material showing only a slight advantage over a material containing glass powder. Wagner et al. also carried out a rough calculation of the minimum fibre length required to fully stress the glass i.e. to break under high loads instead of slipping. Assuming that for excellent adhesion the shear strength at the resin-fibre interface equals the shear strength of thr resin, the critical length was shown to be 0.25 mm (0.01") i.e. less than the average fibre length of the two roll mill material but considerably more than that of the Banbury material.

Popper and Reichold[103] have studied the properties of several different glass-fibre reinforced nylons, containing various lengths of glass fibre. They found that a minimum fibre length of around 0.15 - 0.20 mm (0.006 - 0.008") [at a fibre loading of 20 - 40 %] was necessary in order to obtain any substantial degree of reinforcement. They attribute the necessity for fibre length and fibre concentration to be above a certain minimum value, to the concept of formation of a glass fibre structure of mutually matted fibres. Reichelt[30] has reached similar conclusions and has shown how the polymer can be burnt away from a glass-fibre reinforced nylon article to leave a structure of matted glass fibres in the shape of the original. Wilmes[49] has shown how creep properties also are improved with increasing fibre length in the range 0.05 - 0.35 mm (0.002 - 0.014").

All of the above remarks concerning fibre length refer to short-fibre type materials. Materials of the long-fibre type show marked differences in properties to the above, but this is not only due to increased fibre length but also to much poorer fibre distribution. The fibre bundles present in long-fibre material mouldings are especially effective in promoting higher impact strength[71].

Finally Hani and Hiraga[107] have also studied the effect of glass fibre length on flexural and impact properties but this was using a compression moulded poly(vinyl chloride) sheet material. Properties were appreciably lower with the shortest length of glass fibre used (0.38") but levelled out with higher lengths of glass fibre (1.18", 1.97" and 2.75").

The bond strength between the polymer and the glass fibre will obviously play an important part in determining the mechanical properties of a given glass-fibre reinforced, thermoplastic system. Harford and White[108] have pointed out, however, that very little is known about the strength of this bond, and that, to use the available theoretical relationships it is necessary to know the surface free energies of both glass and polymer. An attempt to get information about these parameters by surface tension measurements has revealed that equilibrium, as far as wetting of glass by molten polystyrene is concerned, was only reached extremely slowly.

Even though the actual nature of the bond between thermoplastics and glass is but poorly understood its importance has been well established empirically by the pronounced effect of coupling agents on the properties of glass-fibre reinforced thermoplastics, especially under wet conditions.[109-120] Murphy[24] has pointed out that the results obtained by different workers on optimum coupling agents for certain glass-fibre reinforced thermoplastic systems are sometimes inconsistent.

Wilmes[49] and Viventi et al[121] have suggested that this inconsistency may arise because the majority of results have been obtained using the compression moulded laminate model system (widely used for evaluating coupling agents with thermosetting resins); it is difficult to see how results so obtained can be transferred reliably to the actual production and processing methods used with glass-fibre reinforced thermoplastics.

Plueddemann[116] has pointed out that thermoplastics are processed at higher temperatures than thermosets: the reactivities of coupling agents to thermoplastics are temperature dependent and the temperatures used in injection moulding may cause thermal decomposition of the more unstable coupling agents.

Viventi et al[121] have shown that the presence of binders (e.g. polyvinyl acetate) on the glass tend to mask the efficiency of coupling agents at least as far as glass-fibre reinforced polystyrene is concerned. Englehardt et al[105] had attempted previously to evaluate "coupling agent only"systems but claimed that binders were necessary in many cases in order to handle and process the glass.

Little work has been reported on the effect of processing variables on the properties of glass-fibre reinforced thermoplastics, although, no doubt, much has been carried out. Englehardt et al[105] have studied the glass-fibre reinforced styrene-acrylonitrile copolymer system by removing material at certain stages in the processing cycle and investigating the properties using compression moulded test pieces. Samples were taken after initial dry blending, after passage through a compounding extruder and finally after injection moulding on both screw and ram type machines. The property most significantly affected by processing was notched Izod impact strength which fell steadily from 3.7 ft lbs/in (after the initial dry blending) through the processing sequence. Screw injection moulded material showed a higher level of properties than ram moulded material.

(iii) Thermal Properties.

One of the more important thermal tests is the determination of heat distortion temperature; this is carried out by supporting a standard specimen at each end and applying a specified load to the middle. The temperature is then raised at a certain fixed rate - the heat distortion temperature is that temperature at which the specimen reaches a specified deflection. The nature of the heat distortion temperature is such that one would not expect the dramatic improvements on reinforcement that one gets with tensile or flexural properties. Nevertheless useful increases are obtained. The heat distortion temperature seems to rise fairly rapidly with the first 15 -20% of glass and then levels out thereafter[51,83,92,93,101,103,122]; this behaviour is in sharp contrast to that of tensile and flexural properties.

Murphy[23,24] has pointed out that the lowered coefficient of expansion of glass-fibre reinforced thermoplastics enables easier mating with metals in multicomponent articles. The coefficient of expansion does vary with fibre orientation, however, and this can lead to warping in certain circumstances.

The specific heats of thermoplastics are lowered and thermal conductivities raised on glass-fibre reinforcement, as would be expected from the relative values of these properties for glass and thermoplastics.

(iv) Electrical Properties.

The effect of glass-fibre reinforcement on electrical properties is not nearly so marked as on mechanical and thermal properties. In general it can be said that the electrical properties of the nylons (and possibly polycarbonate) are improved on reinforcement, whereas most other polymers show no change or even a slight deterioration[23, 24, 30]. Utilisation of optimum coupling agents will facilitate the formation of a strong bond between resin and glass and thus help to maintain satisfactory electrical properties under wet conditions.

(v) Chemical Properties.

As far as the flammability testing of glass-fibre reinforced thermoplastics is concerned the effect of the presence of glass fibre is to prevent the molten polymer dripping away from the flame. This means that, on glass reinforcement, nylon ceases to be self-extinguishing - the flame is no longer deprived of its fuel by molten nylon dripping away. The prevention of dripping can enable some glass-fibre reinforced thermoplastics to pass flammability tests, where non-dripping is an important requirement (e.g. U.L. Subjects 94 and 484)[123].

Some confusion surrounds the effect of glass-fibre reinforcement on environmental stress cracking - this phenomenon occurs when a particular environment brings about chemical changes in the polymer, which result in the formation of microcracks at points of stress. Reichelt[30] states that polystyrene, styrene-acrylonitrile copolymer and polyolefins exhibit no change in their resistance to environmental stress cracking on glass-fibre reinforcement. Murphy[23], however, states that the presence of glass fibres markedly reduces stress cracking especially in polystyrene, styrene-acrylonitrile copolymer and polycarbonate and de Venuto et al[51,124] found that the stress crack resistance of a glass-fibre reinforced polyethylene was nearly double that for the unmodified polymer.

Naetsch[83] maintains that the maximum service temperature of nylon is not raised by the presence of glass fibre but most other workers[94,104,125-128] take the opposite point of view. Maxwell[125] states that the presence of glass fibres reduces the notch sensitivity of the embrittled surface layer, which is formed by surface oxidation.

Wagner et al[95] have studied the effect of boiling water on glass-fibre reinforced acetal copolymer and showed that the deterioration in flexural strength which occurred was non-reversible on drying before testing. They found that more efficient coupling agents cause a longer retention of flexural strength in boiling water. Indeed Viventi et al[121] used a similar boiling water test to evaluate the efficiency of coupling agents in a glass-fibre reinforced polystyrene system.

The behaviour of glass-fibre reinforced thermoplastics towards solvents, acids and alkalis is usually similar to that of the parent polymer.

E. Applications of Glass-Fibre Reinforced Thermoplastics.

Best and Wood[129] have carried out a study of the market potential for glass-fibre reinforced thermoplastics. Of the applications studied 34% were in the automobile industry. Half the applications could be divided into four categories:-

electrical insulators (21%)

gears, bearings and other high lubricity parts(16%)

housings (8%)

automobile large interior parts(6%)

Of the individual glass-fibre reinforced thermoplastics, nylon accounted for about half the applications, polystyrene about 18% and polycarbonate 14%. Glass-fibre reinforced thermoplastics appeared to compete almost equally with other plastics and metals.

PURPOSE OF EXPERIMENTS

PURPOSE OF EXPERIMENTS.

The original aim of the work described in this thesis was to investigate the glass-fibre reinforced acetal copolymer system in as much detail as time allowed, and determine which of the many variables involved were important from the point of view of mechanical properties. A literature survey of the whole field of glass-fibre reinforced thermoplastics indicated that the most important variables would probably be processing method, glass content and coupling agents and it was on these variables that work was concentrated.

It was originally hoped to use a compression moulded test system to avoid fibre orientation effects but the unexpectedly poor level of properties obtained with this system necessitated that further work be carried out with an injection moulded system. This meant that some attempt had to made to look at the fibre orientation in the moulded test pieces.

It was hoped that an incidental result of the work would be to lead to the obtaining of a glass reinforced acetal copolymer with mechanical properties improved over those previously reported.

CHAPTER II

EXPERIMENTAL.

EXPERIMENTAL

A. Materials

The polyacetal used for the main part of the experimental work was Kematal M90-04, manufactured by the Celanese Corporation in the United States and supplied in this country by Imperial Chemical Industries Ltd. A small amount of work was also carried out with other polymers; the polymers used and their characteristics are given in the following table.

	Polymer Type	Characteristics
Kematal M25-04	Acetal copolymer	Lubricated high molecular weight material with high melt viscosity (melt flow index 2.5).
Kematal M90-04	Acetal copolymer	Lubricated standard injection moulding grade of medium molecular weight and melt viscosity (melt flow index 9.0).
Kematal M140-04	Acetal copolymer	Lubricated low molecular weight

	Polymer Type	Characteristics
Kematal M140-04 (continued)		grade with low melt viscosity (melt flow index 140).
Delrin 500	Acetal homopolymer (end group blocked)	-

The E-glass fibre used in the experimental work was supplied by Turner Brothers Asbestos Company Ltd. - Glass Fibre Division of Rochdale. The bulk of the work was carried out with ECO-115; the fibres used with their characteristics are given in Table 1.

TABLE 1

Reference	Dressing	Coupling agent	No. of filaments per strand	Filament diameter	Size content
ECO 115	Polyvinyl acetate	Vinylsilane + chrome	204	0.00035-0.00039"	1.2%
XG 390	Polyvinyl acetate	Vinylsilane + chrome	50 - 204	0.00050-0.00054"	2.3%
XG 496	Polyvinyl acetate	Chrome complex	204	0.00045-0.00049"	0.9%
XG 438	Polyvinyl acetate	Methacrylato-silane+chrome	mainly102 some 204	0.00050-0.00054"	1.2%
XG 184	Alkyd	Aminosilane	204	0.00035-0.00039"	0.8%
Control glass	Polyvinyl acetate	None	204	-	-

The coupling agents identified by general type in the above table are more specifically:-

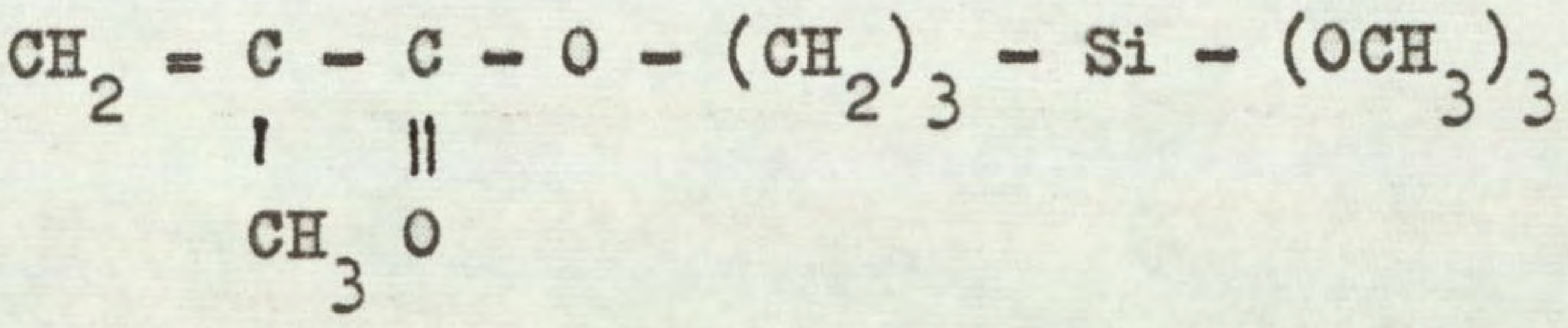
(a) Vinyl-tris(β-methoxyethoxy)silane: (vinyl silane)

$$CH_2 = CH - Si - (O.CH_2.CH_2.O.CH_3)_3$$

(b) γ-Aminopropyl-triethoxysilane: (aminosilane)

$$NH_2.CH_2.CH_2.CH_2 - Si - (OC_2H_5)_3$$

(c) γ-Methacryloxypropyl-trimethoxysilane (methacrylatosilane)



$$CH_2 = \underset{\substack{| \\ CH_3}}{C} - \underset{\substack{\| \\ O}}{C} - O - (CH_2)_3 - Si - (OCH_3)_3$$

(d) Methacrylato chromic chloride (chrome)

Complex coordinated structure involving chromium and water, hydroxyl, chlorine and methacrylic acid ligands (see reference 16)

The glasses were used almost exclusively in the form of 1/4" chopped strand: some work was also carried out using XG 496 with staple lengths of ½" and 1".

B. Processing.

Two fundamentally different types of machine were used for incorporating the chopped strand into the molten polymer: the first was a two roll mill and the second a Buss Ko-kneader. (see Appendix)

The two roll mill exerts a fairly low shear force on the melt (see chapter VII ,page 128).The mill was used at a surface temperature of 175°C (corresponding to a steam pressure of 180 - 185 psi above atmospheric). The procedure used was to introduce a weighed amount of polymer granules slowly on to the mill in order to build up a hide of molten polymer. The nip was opened wide and the glass fibre was introduced as quickly as possible on to the hide. The nip was then closed to 0.022" and the milling timed from this point. This setting was chosen as it provided a reasonable amount of "roll-over" at the nip for the kilogram of material used - this "roll-over" was relied on to distribute the glass fibre evenly through the polymer melt and thus form a homogeneous material. After milling was complete the composite material was removed as a hide, allowed to cool, broken up by hand and then chopped on a rotary cutter (see Appendix).

The Buss Ko-kneader relies on the action of a reciprocating interrupted Archimedean screw for its mixing efficiency, the shear being increased by the presence of steel pegs protruding from the wall of the barrel. Since this machine, as distinct from the two roll mill, is a continuous mixing machine, then it would be necessary to ensure a reasonably consistent feed if a homogeneous product were to be obtained by one passage through the kneader. Because of the difficulty of mixing polymer granules and chopped strand efficiently it was deemed necessary to chop the material after one passage through the kneader, and then subject it to a further passage. The Buss Ko-kneader was used at a screw speed of 30 r.p.m. (determined by timing a marker spot on the screw); the two barrel zones and the screw were adjusted to a nominal temperature of 160°C (the maximum attainable by the available heating arrangement) and the die to 150°C. The temperature of the material would have been appreciably higher due to the heat produced by the shear forces.

The Buss Ko-kneader and two roll mill both break the glass fibre down to a fraction of its original 1/4" length. It was desired therefore to devise some procedure for mixing together the polymer and the glass fibre which would result in considerably less fibre breakdown. With compression moulded samples it was possible to mix the molten polymer and the chopped strand simply by stirring the material by hand in the mould. This seemingly crude procedure gave rise to reasonably reproducible results.

Attempts were made then to apply such a procedure to injection moulded specimens. Polymer and glass fibre were mixed by hand stirring in a large tray heated in an oven at 210°C. The product was then broken up and chopped on the rotary cutter.

This resulted in a considerable degree of separation of the glass fibre, giving rise to a fluffed up product of very low bulk density. Quite surprisingly, this material could with efficiency be moulded on the plunger type injection moulding machine to give mouldings of quite acceptable properties. In view of the success of this procedure attempts were made to see if a dry blend of Kematal powder and chopped strand could be successfully moulded on a plunger type machine; workers in the United States have claimed that dry blends can only be successfully moulded on screw type machines.

The Kematal granules were first powdered on a hammer mill with a screen with 1/16" diameter holes (see Appendix). The Kematal was blended with the chopped strand in three different types of machine - a high speed mixer (the Papenmeier mixer), a Z-blade mixer (the Winkworth mixer) and a comb blender (the Rotocube mixer). These machines are described more fully in the Appendix . Care was taken not to shake or disturb the dry blend unduly, in order to prevent the separation of the dry blend into its constituents. The dry blends were moulded quite successfully on the plunger type machine.

In some cases dry blends were prepared using unsieved polymer; in other cases the polymer was sieved through a 30 mesh sieve (see Appendix) to remove particles above 400 micron. The sieving only exerted a very slight improvement on properties but was still adopted as standard practice after the initial experiments.

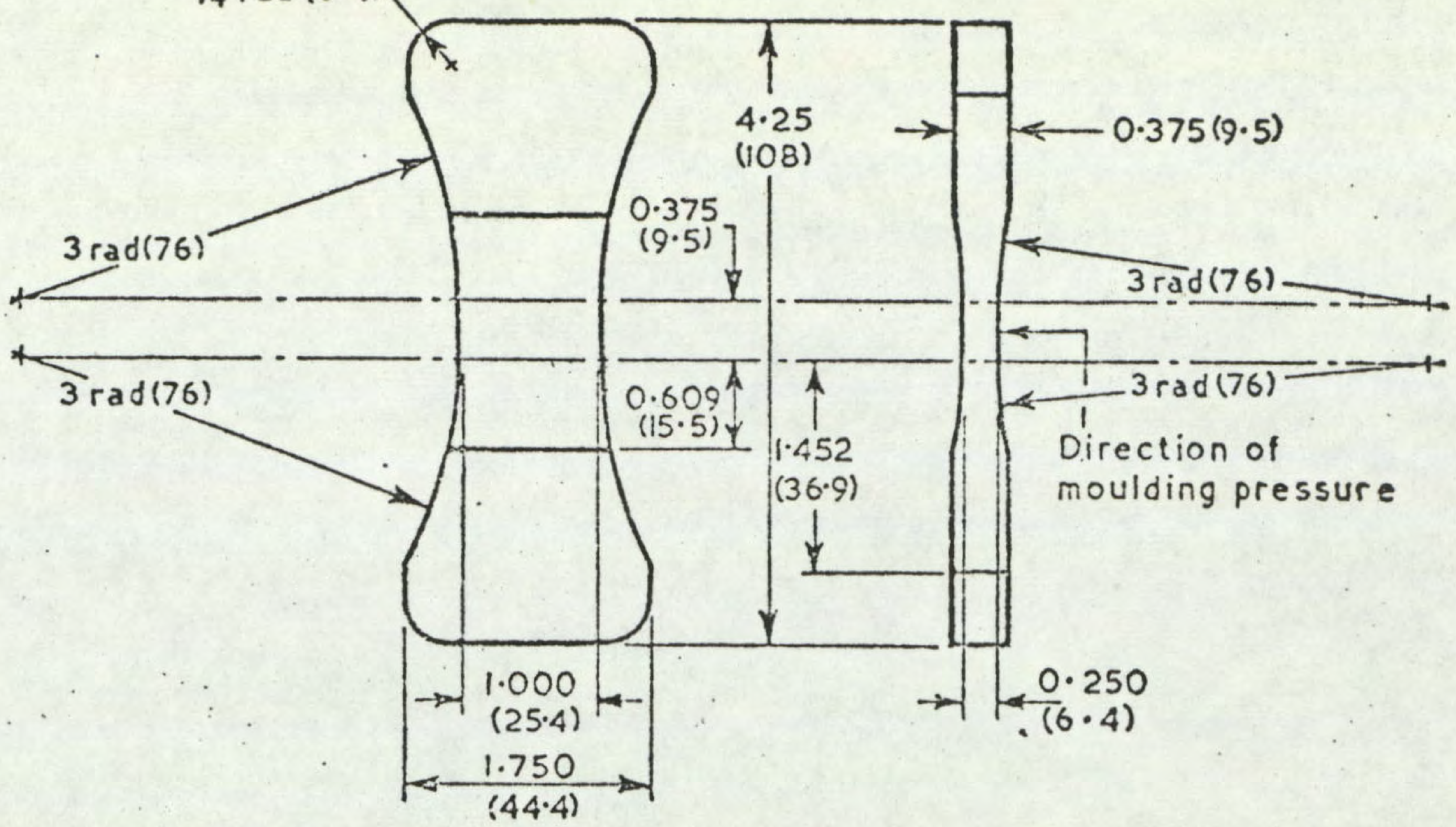
C. Moulding.

Initially it was decided that compression moulding would be the preferred procedure for preparation of test specimens in order to avoid the fibre orientation effects produced by injection moulding.

Preliminary work was carried out using the dumb-bell shaped specimen described in B.S.2782: Part 3: 1965 - method 301 A (see Figure 4). This test piece required quite a large amount of material, however, and also could not be used for tensile modulus determinations using the 2" span clip-on type extensometer. Use of this test piece was discontinued quite soon in favour of a 4" diameter disc. These mouldings were approximately 0.140" thick and were sawn into strips 0.400" wide. Each strip was measured with a micrometer before testing.

The compression moulding of thermoplastics is a fairly difficult technique and a considerable amount of trial and error was involved in devising a suitable process, The general procedure used was to melt the material in the bottom half of the mould at a temperature of 185°C (corresponding to a steam pressure of 180 -190 psi above atmospheric). The press was then opened and the two halves of the mould placed together; the press was then gently closed but no pressure was exerted on the mould. The cooling water was then turned on and, after a certain specified time, a pressure of 40 $\mathrm{kg/cm^2}$ was applied. After cooling, the

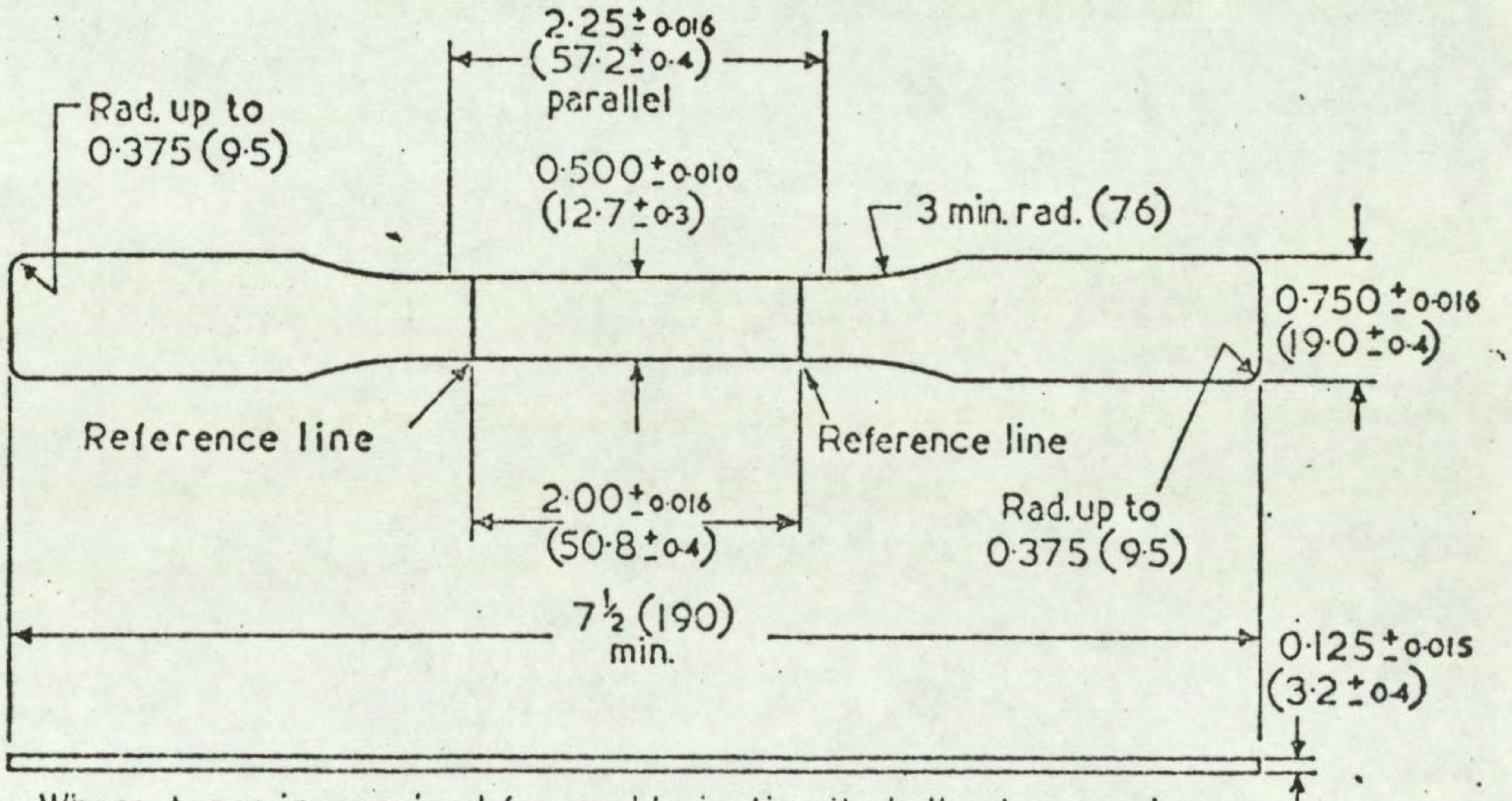
FIGURE 4



Dimensions in inches with millimetre equivalents in parentheses.
Tolerance on all dimensions ± 4 per cent.

Compression moulded
test piece

FIGURE 5



Where taper is required for mould ejection it shall not exceed
1° on each side

Dimensions in inches with millimetre equivalents in parentheses.

Injection moulded
test piece

mould and test piece were removed. The cooling time before application of pressure was generally about 240 secs and had to be chosen so that the material froze as it came to the land face of the mould. Too short a time resulted in too much material leaving the mould and no after-pressure being exerted on the moulding - too long a time resulted in the material freezing before application of pressure.

Although the above procedure was suitable for materials with glass contents above 15%, it was not satisfactory for unreinforced polyacetal or polyacetals with low glass fibre content. The lower viscosities of these resulted in their seeping away under just the weight of the top half of the mould, before pressure was applied. The procedure here adopted was to separate the two halves of the mould with spacers between the land faces and to remove these just before the end of the cooling cycle and application of pressure.

The compression moulding of glass reinforced polyacetal was not entirely satisfactory and a series of injection mouldings were carried out. The machine used for this work was a Manumold small plunger-type injection moulding machine (see Appendix). The barrel temperature was normally kept as close to 200°C as possible; the temperature was allowed to rise from this in order to successfully mould materials with high glass contents, up to a maximum of 230 - 240°C at a glass content of

50%. No cooling was applied to the mould, the temperature of this equilibriating at about 60°C. The Manumold was used at a hydraulic pressure of 1000 psi (its maximum) corresponding to a ram face pressure of 15,000 psi. All of the above conditions were designed to facilitate the filling of the mould with the rather stiff glass reinforced polyacetal melt.

Because of the nature of the chopped glass reinforced polyacetal and the polyacetal/glass fibre dry blends, hopper feeding was not possible. The materials were packed by hand using a brass rod; the materials of low bulk density (e.g. the dry blends with higher glass contents) had to be packed fairly hard to give a shot size sufficient to fill the mould.

The mould used was that for the waisted test piece described in B.S.2782: Part 3: 1965 - method 301 J (see Figure 5, page 48). Test pieces from any one batch of material only tended to vary by 0.001 - 0.002" in each direction and so calculations were made using average dimensions.

D. Testing.

The major properties determined were those of maximum tensile stress and initial tangent tensile modulus. These properties were determined on an E-type Tensometer using a crosshead speed of 0.25"/min: the temperature was kept as close as possible to 25°C.

Initial tangent tensile moduli were determined using a transducer type extensometer of 2" span clipped on to the centre section of the test piece. The transducer extensometer was coupled in directly to the chart drive at a setting giving an extension:chart movement magnification of 1:2000. The stress-strain diagram was automatically plotted up to the range of 100 lb full scale deflection: the plot was very nearly linear over this range and the tensile modulus was obtained from the gradient.

Maximum tensile stress was measured using a crosshead:chart movement magnification of 1:8 or 1:16 depending on the material and a full scale deflection of 1000 lb or 2500 lb, also dependent on the material.

For each compression moulded batch of material eight duplicate tests were carried out (two specimens from each of four discs); mean values of tensile strength and tensile modulus were calculated together with standard deviations. For each injection moulded batch of material twelve duplicate tests were carried out - once again mean values and standard deviations were evaluated.

An attempt was made to obtain some idea of the elongation at break from the tensile stress versus crosshead movement plot for the injection moulded test pieces. To do this the initial slippage of the specimen in the jaws had to be eliminated - this was done by drawing the tangent to the curve and extending this back to the axis. The elongation was measured from this point to the point of breakage (see Figure 6): this will not be an absolute value but should enable valid comparisons to be drawn between different materials.

Izod Impact tests were also carried out on injection moulded test pieces on an Avery machine (see Appendix). The test pieces were obtained by removing the centre section from tensile test pieces: these were fractured by striking the broad face of the bar. Packing pieces were used to hold the specimen in position as the machine was originally designed to take $\frac{1}{2}$"x$\frac{1}{2}$" bars. Two results were obtained from each of four specimens giving eight results in all: mean values and standard deviations were calculated.

Notched Izod impact strengths were also determined using the same type of test piece; the specimens were notched using a metal block (see Figure 7) and drawing a three cornered file along the

FIGURE 6

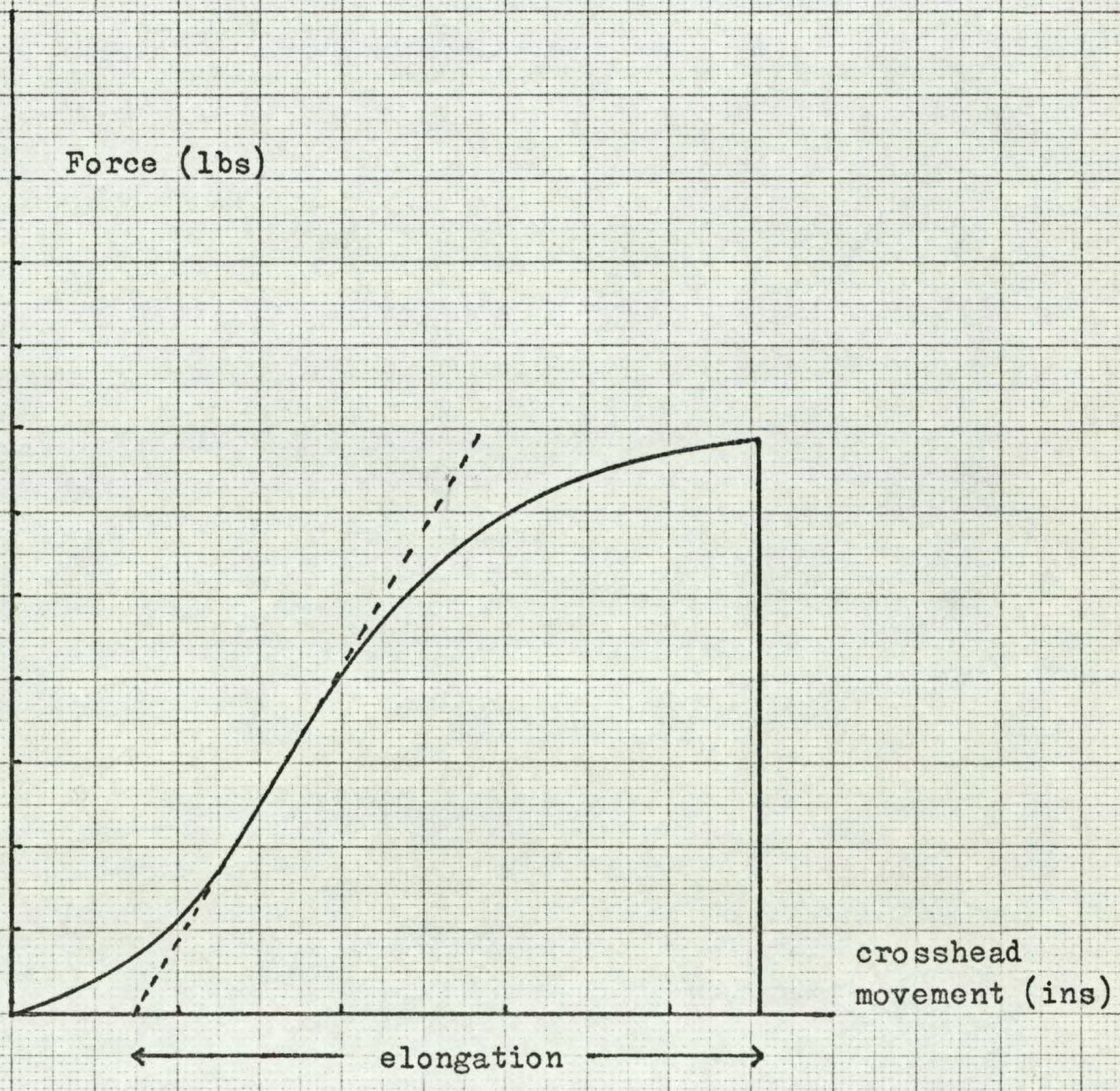
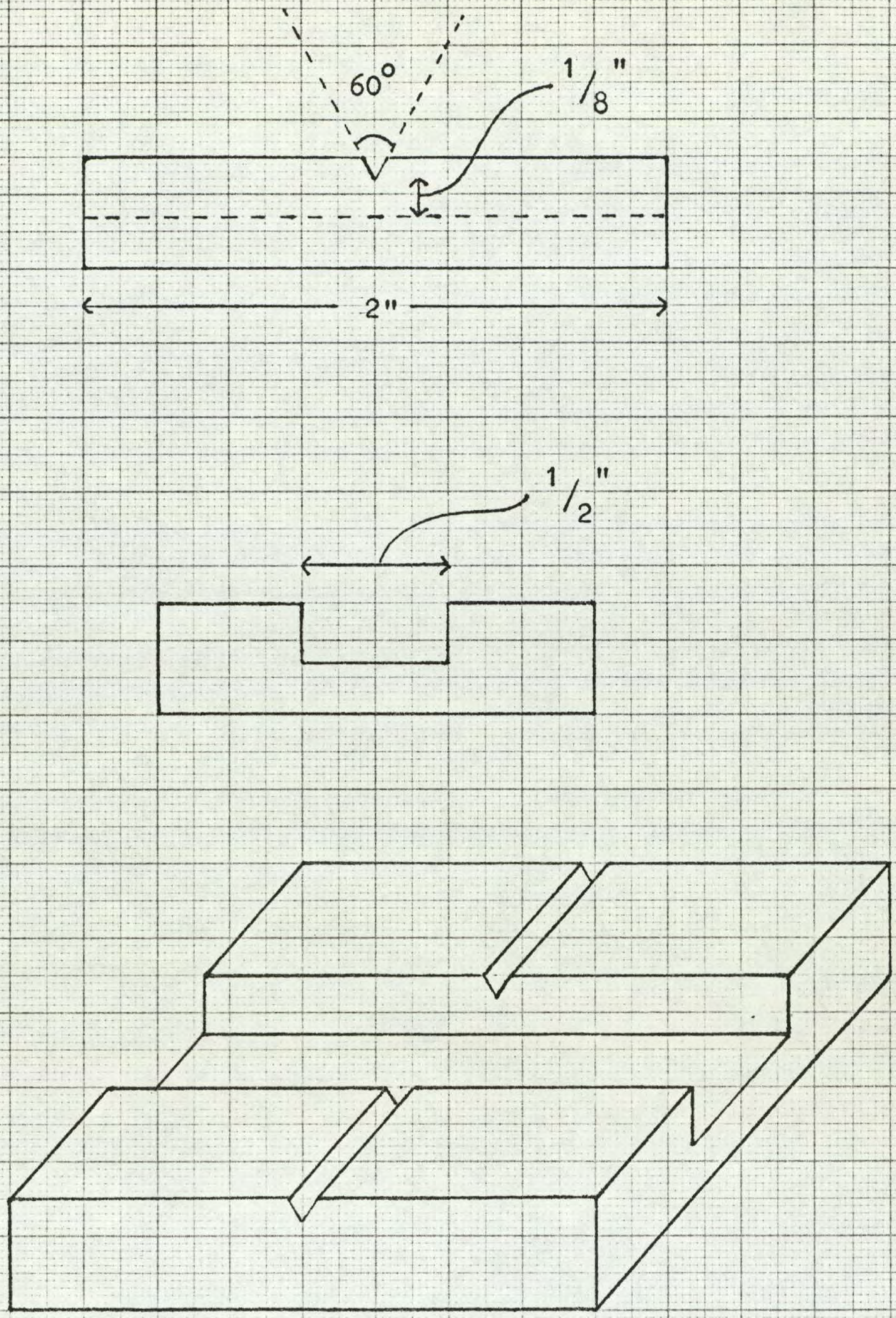


FIGURE 7



Notch Guide

V-shaped grooves. Once again eight duplicate results were obtained and mean values and standard deviations were calculated.

Finally Barcol hardness values were determined for the injection moulded specimens using the very simple Barcol Impressor (see Appendix). Here sixteen duplicate results were obtained - once again mean values and standard deviations were calculated.

E. Fibre Length and Orientation Studies.

Fibre length determinations were carried out using photographic microscopy for materials made by the Buss Ko-kneader and two roll mill. A section was removed from the centre of a test bar moulded from these materials and the polymer was removed by burning. The glass fibres were carefully dispersed in Teepol solution on a microscope slide and photographed through a microscope using a magnification of 25x (on to the negative). Three photographs were taken in different positions on each slide. The 35 mm negatives were printed at full plate size; the actual overall magnification (which was about 150x) was checked by photographing and enlarging a graticule under the same conditions. The fibres were measured from the print using a ruler and the results were plotted in the form of normalised histograms.

Fibre orientation studies were carried out using a visual microscopic method: the test pieces were first etched with concentrated nitric acid to remove the surface layer of polymer and expose the glass fibres. The test pieces were then placed on the turntable of a microscope (set at 0°) with the axis of the specimen lined up along one of the cross wires. The specimen was illuminated by oblique reflected light and slowly turned from -90° to $+90^{\circ}$, counting the fibres and noting the angle as they became parallel with the cross wire. The results were once again plotted in the form of a normalised histogram.

Only surface orientations were studied as the procedure was felt to be too tedious and too crude to be used extensively and insufficient time was available to devise a photographic procedure.

CHAPTER III

RESULTS FROM COMPRESSION MOULDED TEST PIECES.

RESULTS FROM COMPRESSION MOULDED TEST PIECES.

The results will be quoted in tabular form for convenience. The values given are the mean of eight duplicate results (see Chapter II, page 51); the other values quoted are the standard deviation both as an absolute value and as a percentage of the mean. The values have been quoted throughout in psi and not SI units; this has been done deliberately as nearly all the original work published on glass reinforced thermoplastics has been carried out in the United States.

For convenience of comparison some of the results are quoted in more than one table.

Table 2: showing the results of preliminary determinations of the tensile strength of glass reinforced polyacetal, using the compression moulded dumb-bell type test piece (Kematal M90-04 + 1/4" ECO 115 chopped strand)

TABLE 2

Material	Tensile Strength
Unreinforced Kematal	9,460
Buss Ko-kneader - 30 r.p.m. - 27% glass	7,730
Buss Ko-kneader - 30 r.p.m. - 27% glass	8,000
Buss Ko-kneader - 40 r.p.m. - 27% glass	7,370
Buss Ko-kneader - 40 r.p.m. - 27% glass	7,310
Two roll mill - even - 30 mins - 27% glass	8,950
Two roll mill - even - 5 mins - 27% glass	7,920
Two roll mill - 1.35:1 - 30 mins - 27% glass	8,840
Two roll mill - 1.35:1 - 5 mins - 27% glass	7,530

Table 3: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed by stirring in the mould (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 3

% Glass	Tensile Strength	Tensile Modulus
0	9,240 ± 40 (0.43%)	457,000 ± 15,000(3.28%)
5	8,890 ± 370(4.16%)	576,000 ± 64,000(11.11%)
10	9,280 ± 850(9.16%)	607,000 ± 80,000(13.18%)
15	9,530 ± 800(8.39%)	663,000 ± 67,000(10.11%)
20	9,930 ± 1,140(11.48%)	767,000 ± 99,000(12.91%)
25	9,870 ± 840(8.51%)	826,000 ± 76,000(9.20%)
30	11,490 ± 1,240(10.79%)	973,000 ± 102,000(10.48%)
35	11,490 ± 1,430(12.45%)	1,068,000± 159,000(14.89%)
40	9,970 ± 1,530(15.35%)	1,124,000± 120,000(10.68%)

Table 4: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed on the two roll mill for 15 minutes at 175°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 4

% Glass	Tensile Strength	Tensile Modulus
0	8,050 ± 480 (5.96%)	405,000 ± 25,000 (6.17%)
5	-	442,000 ± 47,000 (10.63%)
10	7,020 ± 410 (5.84%)	511,000 ± 25,000 (4.89%)
15	5,310 ± 370 (6.97%)	476,000 ± 47,000 (9.88%)
20	6,620 ± 660 (9.97%)	595,000 ± 94,000 (15.80%)
25	6,620 ± 350 (5.29%)	668,000 ± 46,000 (6.89%)
30	6,410 ± 630 (9.83%)	730,000 ± 97,000 (13.29%)
35	6,280 ± 150 (2.39%)	847,000 ± 71,000 (8.38%)
40	6,360 ± 360 (5.66%)	907,000 ± 50,000 (5.51%)
45	6,390 ± 470 (7.36%)	1,021,000 ± 55,000 (5.39%)
50	6,060 ± 370 (6.11%)	1,042,000 ± 87,000 (8.35%)

Table 5: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed in the Buss Ko-kneader - two passes at 30 r.p.m. and nominal 160°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 5

% Glass	Tensile Strength	Tensile Modulus
0	8,030 ± 1,100 (13.70%)	457,000 ± 32,000 (7.00%)
5	7,920 ± 150 (1.89%)	515,000 ± 37,000 (7.19%)
10	7,390 ± 100 (1.35%)	501,000 ± 43,000 (8.58%)
15	6,780 ± 210 (3.10%)	590,000 ± 56,000 (9.49%)
20	6,440 ± 330 (5.12%)	599,000 ± 58,000 (9.68%)
25	6,170 ± 150 (2.43%)	582,000 ± 60,000 (10.31%)
30	6,640 ± 200 (3.01%)	652,000 ± 22,000 (3.37%)
35	6,270 ± 420 (6.70%)	829,000 ± 53,000 (6.39%)
40	6,280 ± 260 (4.14%)	935,000 ± 114,000 (12.19%)
45	5,950 ± 830 (13.95%)	978,000 ± 53,000 (5.42%)
50	5,730 ± 350 (6.11%)	1,062,000 ± 81,000 (7.63%)

Table6: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed by stirring in the mould (Delrin 500 + 1/4" ECO 115 chopped strand).

TABLE 6

% Glass	Tensile Strength	Tensile Modulus
0	7,100 ± 480 (6.76%)	452,000 ± 30,000 (6.64%)
5	6,770 ± 1,270 (18.76%)	475,000 ± 60,000 (12.63%)
10	7,740 ± 1,310 (16.93%)	557,000 ± 127,000 (22.80%)
15	8,480 ± 1,510 (17.81%)	610,000 ± 65,000 (10.66%)
20	8330 ± 740 (8.88%)	746,000 ± 102,000 (13.67%)
25	11,480 ± 1,480 (12.89%)	961,000 ± 79,000 (8.22%)
30	9,120 ± 2,380 (26.10%)	899,000 ± 101,000 (11.24%)
35	9,370 ± 1,300 (13.87%)	1,040,000 ± 108,000 (10.38%)
40	7,260 ± 790 (10.88%)	1,006,000 ± 121,000 (12.03%)

Table 7: showing the effect of coupling agent on tensile strength and initial tensile modulus at various glass contents - material processed by stirring in the mould (Kematal M90-04 + various 1/4" chopped strands).

TABLE 7

	% Glass	Tensile Strength	Tensile Modulus
control (no coupling agent/P.V.A.)	10	8,120 ± 730 (8.99%)	533,000 ± 57,000(10.69%)
	20	9,990 ± 990 (9.91%)	731,000 ±140,000(19.15%)
	25	11,120 ± 1,060(9.35%)	861,000 ± 86,000 (9.99%)
	30	10,730 ±1,810(16.87%)	923,000 ±101,000(10.94%)
	40	9,870 ±1,890(19.15%)	1,130,000 ±163,000(14.42%)
XG 184 (aminosilane /alkyd)	10	9,110 ±1,070(11.75%)	524,000 ± 53,000(10.11%)
	20	9,580 ± 990 (10.33%)	651,000 ± 76,000(11.67%)
	25	10,480 ±1,410(13.45%)	818,000 ± 82,000(10.02%)
	30	11,130 ± 520 (4.67%)	944,000 ± 95,000(10.06%)
	40	8,970 ±1,810(20.18%)	1,042,000 ±153,000(14.68%)
XG 438 (methacrylato silane/P.V.A.)	10	8,850 ±1,190(13.45%)	544,000 ± 41,000 (7.54%)
	20	10,560 ±1,030 (9.75%)	813,000 ±119,000(14.64%)
	25	10,530 ±1,210(11.49%)	869,000 ± 65,000 (7.48%)
	30	11,560 ±1,170(10.12%)	1,004,000 ± 86,000 (8.57%)
	40	9,580 ±1,880(19.62%)	1,328,000 ±211,000(15.89%)
XG 496 (chrome/ P.V.A.)	10	9,010 ± 730 (8.10%)	542,000 ± 40,000 (7.38%)
	20	10,280 ±1,380(13.42%)	792,000 ±137,000(17.30%)
	25	10,780 ±1,020(9.46%)	899,000 ±119,000(13.24%)
	30	10,010 ±1,190(11.89%)	867,000 ±109,000(12.57%)
	40	8,190 ±1,580(19.29%)	1,155,000 ±167,000(14.46%)
ECO 115 (vinylsilane /P.V.A.)	10	9,280 ± 850 (9.16%)	607,000 ± 80,000(13.18%)
	20	9,930 ±1,140(11.48%)	767,000 ± 99,000(12.91%)
	25	9,870 ± 840 (8.51%)	826,000 ± 76,000 (9.20%)
	30	11,490 ±1,240(10.79%)	973,000 ±102,000(10.48%)
	40	9,970 ±1,530(15.35%)	1,124,000 ±120,000(10.68%)

In view of the rather inconclusive data presented in the preceding table attempts were made to elucidate the significance of coupling agents in so far as their effect on mechanical properties was concerned - this was done statistically by carrying out a variance analysis on the individual test results (from which the means in the preceding table were derived) for each glass as compared with the control glass. An example of such a variance analysis is shown in Table 8 (tensile modulus data).

From the variance analysis table the following quantities are derived:

(1) Correction factor (C.F.) = 772,450,849/80 = 9,655,636

(2) Total sum of squares = 13,409,665 - C.F. = 3,754,029

(3) Sum of squares between G.F. = 199,266,327/16 - C.F.=2,798,510

(4) Sum of squares between C.A. = 386,679,529/40 - C.F.= 11,352

(5) Error sum of squares = 13,409,665, - 99,969,057/8 = 913,533

Source of variance	Sum of squares	Degrees of freedom	Mean square error	F (variance ratio)
Between G.F.	2,798,510	4	699,628	53.6
Between C.A.	11,352	1	11,352	0.87
G.F. x C.A.	30,634	4	7,658	0.59
Residual	913,533	70	13,050	
Total	3,754,029	79		

TABLE 8

Glass fibre (G.F.) content	10%		20%		25%		30%		40%		
control glass	47*		230		329		534		529		
	111	+ 264	306	1,850	294	2,888	383	3,381	415	5,037	a 13,420
	42		94		521		535		475		
	121	69,696	77	3,422,500	335	8,340,544	462	11,431,161	529	25,371,369	b 48,635,270
	-9		26		234		295		756		
	12	35,138	302	585,378	315	1,102,174	291	1,510,313	691	3,385,383	c 6,618,386
	-63		414		425		538		697		
	3		401		435		343		945		d 180,096,400
vinyl-silane	55		138		443		394		636		
	47	853	214	2,135	199	2,608	530	3,785	748	4,992	a 14,373
	-16		404		284		522		450		
	139	727,609	309	4,558,225	294	6,801,664	442	14,326,225	659	24,920,064	b 51,333,787
	135		261		364		560		613		
	101	141,621	218	648,407	410	896,086	663	1,874,709	424	3,230,456	c 6,791,279
	120		427		352		390		783		
	272		164		262		484		679		d 206,583,129
	a d	1,117 1,247,689	a d	3,985 15,880,225	a d	5,496 30,206,016	a d	7,166 51,351,556	a d	10,029 100,580,841	27,793 772,450,849

* values given in the table are (E - 500,000)/1,000

\+ $\sum x$
$(\sum x)^2$
$\sum x^2$

a $\sum\sum x$
b $\sum(\Sigma x)^2$
c $\sum(\Sigma x^2)$
d$[\sum(\Sigma x)]^2$

The variance ratios are given in the following tables:-

TABLE 9

Tensile modulus data

Source of variance	Vinylsilane vs control	Aminosilane vs control	Methacrylato-silane vs control	Chrome vs control
Between G.F.	53.6	56.3	64.6	47.7
Between C.A.	0.87	2.39*	7.29*	0.30
G.F. x C.A.	0.59	0.66	1.50	0.45

TABLE 10

Tensile strength data

Source of variance	Vinylsilane vs control	Aminosilane vs control	Methacrylato-silane vs control	Chrome vs control
Between G.F.	6.84	7.55	8.65	7.87
Between C.A.	0.27	0.99	0.65	0.92
G.F. x C.A.	1.75	1.22	0.04	1.99

* significant effect of coupling agent on property.

Table 11: showing the effect of polymer viscosity on tensile strength and initial tensile modulus at various glass contents - material processed by stirring in the mould (various grades of Kematal + 1/4" ECO 115 chopped strand)

TABLE 11

% Glass	M.F.index Kematal	Tensile Strength	Tensile Modulus
0	2.5	7,790 ± 870 (11.17%)	396,000 ± 20,000 (5.05%)
	9.0	9,240 ± 40 (0.43%)	457,000 ± 15,000 (3.28%)
	14.0	8,860 ± 270 (3.05%)	418,000 ± 18,000 (4.31%)
10	2.5	9,650 ± 560 (5.80%)	559,000 ± 30,000 (5.37%)
	9.0	9,280 ± 850 (9.16%)	607,000 ± 80,000 (13.18%)
	14.0	8,020 ±1,560 (19.45%)	574,000 ± 37,000 (6.45%)
20	2.5	10,410 ±1,500 (14.41%)	732,000 ± 58,000 (7.92%)
	9.0	9,930 ±1,140 (11.48%)	767,000 ± 99,000 (12.91%)
	14.0	10,820 ± 640 (5.92%)	754,000 ± 47,000 (6.23%)
25	2.5	11,020 ±1,020 (9.26%)	845,000 ±136,000 (16.10%)
	9.0	9,870 ± 840 (8.51%)	826,000 ± 76,000 (9.20%)
	14.0	11,090 ±1,090 (9.83%)	832,000 ± 53,000 (6.37%)
30	2.5	10,150 ±2,540 (25.02%)	953,000 ±141,000 (14.80%)
	9.0	11,490 ±1,240 (10.79%)	973,000 ±102,000 (10.48%)
	14.0	11,240 ±1,500 (13.35%)	931,000 ±127,000 (13.64%)
40	-	-	-
	9.0	9,970 ±1,530 (15.35%)	1,124,000 ±120,000 (10.68%)
	14.0	11,850 ±1,220 (10.30%)	1,244,000 ± 62,000 (4.98%)

Table 12: showing the effect of alteration of milling variables on the tensile strength and initial tensile modulus of the composite (Kematal M90-04 + 30% 1/4" ECO 115 chopped strand).

TABLE 12

	Milling Time, mins.	Tensile Strength	Tensile Modulus
Even Roll Speed	0	7,400± 420 (5.68%)	804,000 ± 67,000 (8.33%)
	1	7,330 ± 280 (3.82%)	853,000 ± 41,000 (4.81%)
	5	7,050 ± 260 (3.69%)	869,000 ±108,000(12.43%)
	15	7,260 ± 570 (7.85%)	790,000 ± 70,000 (8.86%)
	30	7,370 ± 550 (7.46%)	888,000 ± 48,000 (5.41%)
	60	8,480 ± 880(10.38%)	943,000 ± 75,000 (7.95%)
1.35:1 Roll Speed	0	7,390 ± 230 (3.11%)	833,000 ± 61,000 (7.32%)
	1	7,400 ± 370 (5.00%)	831,000 ±53,000 (6.38%)
	5	7,200 ± 430 (5.97%)	853,000 ± 62,000 (7.27%)
	15	7,560 ± 420 (5.56%)	937,000 ± 74,000 (7.90%)
	30	7,490 ± 490 (6.54%)	881,000 ± 70,000 (7.95%)
	60	8,360 ± 420 (5.02%)	940,000 ± 86,000 (9.15%)

Table 13: showing the effect of milling time on properties of unreinforced Kematal.

TABLE 13

	Milling Time, mins	Tensile Strength	Tensile Modulus
1.35:1 Roll Speed	15	8,610 ± 40 (0.46%)	407,000 ± 7,000 (1.76%)
	30	8,480 ± 60 (0.71%)	400,000 ± 29,000 (7.25%)
	60	8,580 ± 30 (0.35%)	413,000 ± 10,000 (2.42%)

CHAPTER IV

RESULTS FROM INJECTION MOULDED TEST PIECES CONTAINING SHORT GLASS FIBRES.

RESULTS FROM INJECTION MOULDED TEST PIECES CONTAINING SHORT GLASS FIBRES.

The values given in the following tables are the mean of either twelve (tensile strength and modulus and elongation at break), eight (impact strength, both notched and unnotched) or sixteen (Barcol hardness) results. Tensile strength and modulus are quoted in psi and impact strength in ft-lbs for reasons given at the beginning of the previous chapter. Elongation at break is quoted in percentage and the values are comparative, not absolute values (see Chapter II).

Table 14: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed on the two roll mill for 15 minutes at 175°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 14

% Glass	Tensile Strength	Tensile Modulus
0	7,980 ± 110 (1.37%)	348,000 ± 22,000 (6.23%)
5	-	-
10	9,660 ± 250 (2.59%)	619,000 ± 11,000 (1.75%
15	9,790 ± 400 (4.09%)	752,000 ± 19,000 (2.49%)
20	10,540 ± 360 (3.39%)	904,000 ± 12,000 (1.29%)
25	12,050 ± 660 (5.52%)	1,123,000 ± 27,000 (2.36%)
30	12,570 ± 350 (2.79%)	1,323,000 ± 26,000 (1.94%)
35	12,970 ± 620 (4.78%)	1,519,000 ± 23,000 (1.51%)
40	16,040 ± 670 (4.15%)	1,822,000 ± 39,000 (2.12%)
45	18,080 ± 1,040 (5.73%)	2,110,000 ± 102,000 (4.85%)
50	19,070 ± 1,480 (7.77%)	2,409,000 ± 101,000 (4.20%)

Table 15: showing the effect of glass fibre content on elongation at break and hardness for material processed on the two roll mill for 15 minutes at 175°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 15

% Glass	Elongation at break	Barcol hardness
0	27.91 ± 3.86 (13.83%)	0
10	7.34 ± 0.51 (6.94%)	6.81 ± 0.73 (10.66%)
15	5.59 ± 0.34 (6.03%)	11.81 ± 0.95 (8.04%)
20	5.37 ± 0.18 (3.26%)	15.50 ± 1.12 (7.21%)
25	5.00 ± 0.25 (5.06%)	19.19 ± 1.07 (5.59%)
30	4.72 ± 0.11 (2.38%)	23.44 ± 1.00 (4.26%)
35	4.59 ± 0.16 (3.54%)	26.06 ± 0.83 (3.17%)
40	5.03 ± 0.18 (3.60%)	29.56 ± 1.54 (5.21%)
45	5.59 ± 0.69 (12.40%)	33.12 ± 1.41 (4.25%)

Table 16: showing the effect of glass fibre content on impact strength (both unnotched and notched) for material processed on the two roll mill for 15 minutes at 175°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 16

% Glass	Notched Impact Strength	Unnotched Impact Strength
0	0.265 ± 0.028 (10.51%)	>1.000
10	0.106 ± 0.007 (6.47%)	0.630 ± 0.054 (8.57%)
15	0.145 ± 0.025 (17.52%)	0.444 ± 0.064 (14.44%)
20	0.134 ± 0.006 (4.84%)	0.348 ± 0.030 (8.62%)
25	0.134 ± 0.006 (4.84%)	0.322 ± 0.030 (9.29%)
30	0.134 ± 0.010 (7.76%)	0.252 ± 0.020 (7.86%)
35	0.146 ± 0.014 (9.66%)	0.267 ± 0.029 (10.79%)
40	0.152 ± 0.007 (4.92%)	0.286 ± 0.019 (6.61%)
45	0.178 ± 0.013 (7.14%)	0.294 ± 0.026 (8.98%)
50	0.157 ± 0.016 (10.32%)	0.346 ± 0.096 (27.83%)

Table 17: showing the effect of glass fibre content on tensile strength and initial tensile modulus for material processed in the Buss Ko-kneader - two passes at 30 r.p.m. and nominal 160°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 17

% Glass	Tensile Strength	Tensile Modulus
5	8,090 ± 120 (1.54%)	416,000 ± 7,000 (1.76%)
10	7,720 ± 70 (0.95%)	459,000 ± 10,000 (2.09%)
15	7,520 ± 110 (1.50%)	553,000 ± 14,000 (2.58%)
20	7,430 ± 160 (2.12%)	645,000 ± 14,000 (2.15%)
25	8,180 ± 200 (2.44%)	789,000 ± 12,000 (1.51%)
30	8,020 ± 420 (5.18%)	845,000 ± 24,000 (2.87%)
35	10,260 ± 430 (4.23%)	1,243,000 ± 27,000 (2.20%)
40	10,250 ± 600 (5.88%)	1,395,000 ± 28,000 (2.03%)
45	10,490 ± 520 (4.97%)	1,546,000 ± 35,000 (2.28%)
50	11,140 ± 620 (5.53%)	1,752,000 ± 43,000 (2.48%)

Table 18: showing the effect of glass fibre content on elongation at break and hardness for material processed in the Buss Ko-kneader - two passes at 30 r.p.m. and nominal 160°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 18

% Glass	Elongation at Break	Barcol Hardness
5	19.81 ± 1.39 (7.02%)	2.44 ± 1.00 (40.90%)
10	17.93 ± 1.95 (10.87%)	6.00 ± 1.06 (17.68%)
15	13.81 ± 1.63 (11.81%)	9.31 ± 0.98 (10.55%)
20	10.41 ± 0.90 (8.62%)	13.25 ± 0.75 (5.66%)
25	5.84 ± 0.43 (7.43%)	14.81 ± 0.73 (4.90%)
30	5.44 ± 0.33 (6.09%)	16.75 ± 0.56 (3.34%)
35	4.22 ± 0.24 (5.70%)	19.69 ± 0.46 (2.35%)
40	3.94 ± 0.17 (4.21%)	21.12 ± 0.99 (4.70%)
45	3.78 ± 0.31 (8.26%)	24.94 ± 1.68 (6.72%)
50	3.91 ± 0.12 (3.12%)	27.75 ± 1.56 (5.63%)

Table 19: showing the effect of glass fibre content on impact strength (both unnotched and notched) for material processed in the Buss Ko-kneader - two passes at 30 r.p.m. and nominal 160°C (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 19

% Glass	Notched Impact Strength	Unnotched Impact Strength
5	0.184 ± 0.024 (13.26%)	> 1.000
10	0.187 ± 0.017 (9.25%)	> 1.000
15	0.136 ± 0.014 (10.66%)	> 0.926
20	0.144 ± 0.014 (9.79%)	0.664 ± 0.079 (11.88%)
25	0.129 ± 0.008 (6.05%)	0.399 ± 0.052 (13.06%)
30	0.116 ± 0.013 (11.55%)	0.314 ± 0.019 (5.92%)
35	0.096 ± 0.003 (3.44%)	0.193 ± 0.013 (6.74%)
40	0.094 ± 0.007 (7.34%)	0.187 ± 0.011 (5.83%)
45	0.092 ± 0.003 (3.80%)	0.157 ± 0.006 (3.57%)
50	0.089 ± 0.003 (3.71%)	0.150 ± 0.018 (11.80%)

Table 20: showing the effect of coupling agent on tensile strength and initial tensile modulus for material processed on the two roll mill for 5 minutes at 175°C (Kematal M90-04 + 35% various 1/4" chopped strands).

TABLE 20

	Tensile Strength	Tensile Modulus
control	13,950 ± 500 (3.56%)	1,542,000 ± 32,000 (2.05%)
XG 184	12,880 ± 670 (5.20%)	1,530,000 ± 38,000 (2.47%)
XG 438	15,450 ± 450 (2.94%)	1,520,000 ± 29,000 (1.91%)
XG 496	16,570 ± 750 (4.50%)	1,502,000 ± 33,000 (2.17%)
ECO 115	13,560 ± 530 (3.93%)	1,504,000 ± 25,000 (1.65%)
XG 390	10,120 ± 440 (4.38%)	1,478,000 ± 37,000 (2.49%)

Table 21: showing the effect of coupling agent on elongation at break and Barcol hardness for material processed on the two roll mill for 5 minutes at 175°C (Kematal M90-04 + 35% various 1/4" chopped strands).

TABLE 21

	Elongation at Break	Barcol Hardness
control	4.91 ± 0.21 (4.20%)	25.19 ± 0.95 (3.77%)
XG 184	4.66 ± 0.32 (6.85%)	24.19 ± 0.88 (3.65%)
XG 438	5.59 ± 0.37 (6.65%)	28.19 ± 1.24 (4.38%)
XG 496	6.03 ± 0.39 (6.53%)	28.12 ± 1.17 (4.15%)
ECO 115	4.69 ± 0.24 (5.13%)	24.56 ± 1.17 (4.77%)
XG 390	3.84 ± 0.17 (4.55%)	-

Table 22: showing the effect of coupling agent on impact strength (both unnotched and notched) for material processed on the two roll mill for 5 minutes at 175°C (Kematal M90-04 + 35% various 1/4" chopped strands).

TABLE 22

	Notched Impact Strength	Unnotched Impact Strength
control	0.157 ± 0.015 (9.81%)	0.264 ± 0.038 (14.28%)
XG 184	0.143 ± 0.006 (3.92%)	0.256 ± 0.018 (7.07%)
XG 438	0.184 ± 0.006 (3.26%)	0.360 ± 0.039 (10.94%)
XG 496	0.198 ± 0.014 (6.92%)	0.433 ± 0.048 (10.99%)
ECO 115	0.140 ± 0.007 (5.07%)	0.244 ± 0.025 (10.37%)

Table 23. showing the effect of alteration of milling variables on the tensile strength and initial tensile modulus of the composite (Kematal M90-04 + 30% 1/4" ECO 115 chopped strand).

TABLE 23

	Milling Time(mins)	Tensile Strength	Tensile Modulus
Even Roll Speed	0	11,430 ± 690 (6.08%)	1,235,000 ± 29,000(2.38%)
	1	11,020 ± 512 (4.65%)	1,228,000 ± 27,000(2.16%)
	5	11,160 ± 360 (3.23%)	1,300,000 ± 23,000(1.74%)
	15	11,330 ± 470 (4.18%)	1,298,000 ± 13,000(1.01%)
	30	11,190 ± 290 (2.63%)	1,283,000 ± 18,000(1.44%)
	60	11,250 ± 490 (4.36%)	1,247,000 ± 16,000(1.29%)
1.35:1 Roll Speed	0	11,870 ± 240 (2.00%)	1,247,000 ± 22,000(1.74%)
	1	11,280 ± 390 (3.50%)	1,199,000 ± 28,000(2.31%)
	5	10,960 ± 500 (4.59%)	1,279,000 ± 24,000(1.85%)
	15	11,200 ± 490 (4.35%)	1,274,000 ± 20,000(1.59%)
	30	11,420 ± 400 (3.54%)	1,275,000 ± 25,000(1.99%)
	60	12,890 ± 380 (2.93%)	1,295,000 ± 25,000(1.95%)

Table 24: showing the effect of alteration of milling variables on the elongation at break of the composite (Kematal M90-04 + 30% 1/4" ECO 115 chopped strand).

TABLE 24

	Milling Time (mins)	Elongation at Break
Even Roll Speed	0	4.91 ± 0.67 (13.69%)
	1	4.69 ± 0.23 (5.00%)
	5	4.38 ± 0.13 (2.93%)
	15	4.41 ± 0.16 (3.62%)
	30	4.41 ± 0.11 (2.55%)
	60	4.72 ± 0.19 (4.04%)
1.35:1 Roll Speed	0	4.59 ± 0.17 (3.81%)
	1	4.62 ± 0.18 (3.99%)
	5	4.22 ± 0.18 (4.15%)
	15	4.28 ± 0.18 (4.09%)
	30	4.44 ± 0.17 (3.94%)
	60	4.75 ± 0.10 (2.11%)

CHAPTER V

RESULTS FROM INJECTION MOULDED TEST PIECES CONTAINING LONG GLASS FIBRES.

RESULTS FROM INJECTION MOULDED TEST PIECES CONTAINING LONG GLASS FIBRES.

Table 25: showing the effect of glass fibre content on the tensile strength and initial tensile modulus for material processed by stirring by hand at 210°C and chopping on a rotary cutter (Kematal M90-04 + ECO 115 1/4" chopped strand).

TABLE 25

% Glass	Tensile Strength	Tensile Modulus
5	8,240 ± 130 (1.62%)	447,000 ± 7,000 (1.62%)
10	8,910 ± 170 (1.90%)	593,000 ± 10,000 (1.78%)
15	9,400 ± 230 (2.41%)	727,000 ± 19,000 (2.58%)
20	9,410 ± 290 (3.07%)	865,000 ± 27,000 (3.13%)
25	9,640 ± 280 (2.88%)	990,000 ± 40,000 (4.07%)
30	10,760 ± 370 (3.47%)	1,263,000 ± 45,000 (3.56%)

Table 26: showing the effect of glass fibre content on elongation at break for material processed by stirring by hand at 210°C and chopping on a rotary cutter (Kematal M90-04 + 1/4" ECO 115 chopped strand).

TABLE 26

% Glass	Elongation at Break
5	14.67 ± 2.17 (14.77%)
10	8.66 ± 0.95 (10.94%)
15	6.50 ± 0.15 (2.36%)
20	5.39 ± 0.27 (4.93%)
25	4.72 ± 0.16 (3.41%)
30	4.42 ± 0.20 (4.63%)

Table 27: showing the effect of different dry blending methods on the tensile strength and initial tensile modulus (Kematal M90-04 [powder] + 30% 1/4" ECO 115 chopped strand).

TABLE 27

Method	Tensile Strength	Tensile Modulus
Rotocube/5min	10,810 ± 420 (3.90%)	1,331,000 ± 65,000(4.90%)
Rotocube/60min	11,010 ± 620 (5.76%)	1,296,000 ± 89,000(6.86%)
Winkworth/5min	9,110 ± 460 (5.10%)	1,056,000 ±124,000(11.70%)
Winkworth/15min	8,220 ± 450 (5.40%)	983,000 ± 75,000(7.68%)
Papenmeier/5min	9,170 ± 580 (6.28%)	1,041,000 ± 90,000(8.64%)
Papenmeier/15min	9,780 ± 435 (4.45%)	1,173,000 ±112,000(9.56%)

Table 28: showing the effect of different dry blending methods on the elongation at break (Kematal M90-04 [powder] + 30% 1/4" ECO 115 chopped strand).

TABLE 28

Method	Elongation at Break
Rotocube/5min	4.27 ± 0.24 (5.68%)
Rotocube/60min	4.12 ± 0.19 (4.66%)
Winkworth/5min	4.12 ± 0.20 (4.89%)
Winkworth/15min	4.12 ± 0.19 (4.51%)
Papenmeier/5min	4.31 ± 0.59 (13.59%)
Papenmeier/15min	4.09 ± 0.14 (3.44%)

Table 29: showing the effect of sieving the powdered polymer through a 30 mesh sieve, before dry blending on the Rotocube, on the tensile strength and initial tensile modulus of the moulded composite (Kematal M90-04 + various 1/4" chopped strands).

TABLE 29

		Tensile Strength	Tensile Modulus
30% ECO 115	unsieved Kematal	11,000 ± 620 (5.67%)	1,296,000 ± 89,000(6.86%)
	sieved Kematal	11,800 ± 520 (4.45%)	1,360,000 ± 77,000(5.66%)
35% XG 496	unsieved Kematal	19,140 ±1,050(5.49%)	1,644,000 ± 85,000(5.18%)
	sieved Kematal	20,000 ±1,330(6.65%)	1,613,000 ± 60,000(3.69%)
35% XG 438	unsieved Kematal	18,460 ±1,360(7.38%)	1,703,000 ±121,000(7.10%)
	sieved Kematal	19,040 ± 740 (3.91%)	1,528,000 ±114,000(7.47%)

Table 30: showing the effect of sieving the powdered polymer through a 30 mesh sieve, before dry blending on the Rotocube, on the elongation at break of the moulded composite (Kematal M90-04 + various 1/4" chopped strands).

TABLE 30

		<u>Elongation at Break</u>
30% ECO 115	unsieved Kematal	4.12 ± 0.19 (4.66%)
	sieved Kematal	4.48 ± 0.29 (6.45%)
35% XG 496	unsieved Kematal	5.91 ± 0.24 (3.99%)
	sieved Kematal	6.41 ± 0.36 (5.63%)
35% XG 438	unsieved Kematal	5.84 ± 0.35 (5.94%)
	sieved Kematal	5.91 ± 0.44 (7.41%)

Table 31: showing the effect of glass fibre content on the tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [<30 mesh] + ECO 115 1/4" chopped strand).

TABLE 31

% Glass	Tensile Strength	Tensile Modulus
0	7,690 ± 215 (2.80%)	336,000 ± 12,000 (3.49%)
5	7,940 ± 210 (2.63%)	422,000 ± 16,000 (3.80%)
10	8,400 ± 260 (3.11%)	528,000 ± 23,000 (4.40%)
15	9,230 ± 280 (3.06%)	731,000 ± 37,000 (5.01%)
20	9,890 ± 400 (4.02%)	951,000 ± 58,000 (6.09%)
25	11,350 ± 600 (5.30%)	1,120,000 ± 70,000 (6.21%)
30	11,800 ± 520 (4.45%)	1,360,000 ± 77,000 (5.66%)
35	13,520 ± 830 (6.17%)	1,647,000 ± 149,000 (9.07%)
40	15,130 ± 1,300(8.61%)	1,990,000 ± 134,000 (6.72%)
45	16,690 ± 940 (5.65%)	2,222,000 ± 124,000 (5.57%)
50	17,770 ± 1,010(5.69%)	2,506,000 ± 124,000 (4.93%)

Table 32: showing the effect of glass fibre content on the elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [<30 mesh] + ECO 115 1/4" chopped strand).

TABLE 32

% Glass	Elongation at Break	Barcol Hardness
0	31.78 ± 3.42 (10.77%)	-
5	11.77 ± 2.02 (17.20%)	3.25 ± 0.90 (27.72%)
10	8.31 ± 1.05 (12.59%)	6.37 ± 0.86 (13.45%)
15	5.41 ± 0.38 (6.99%)	11.62 ± 0.86 (7.38%)
20	4.66 ± 0.22 (4.73%)	17.06 ± 0.66 (3.86%)
25	4.97 ± 0.31 (6.26%)	18.94 ± 0.83 (4.37%)
30	4.48 ± 0.29 (6.45%)	20.56 ± 0.70 (3.42%)
35	4.64 ± 0.30 (6.53%)	23.50 ± 1.12 (4.76%)
40	4.66 ± 0.38 (8.05%)	27.94 ± 0.90 (3.22%)
45	4.97 ± 0.32 (6.38%)	31.56 ± 1.06 (3.36%)
50	-	32.81 ± 1.13 (3.44%)

Table 33: showing the effect of glass fibre content on impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [< 30 mesh] + ECO 115 1/4" chopped strand).

TABLE 33

% Glass	Notched Impact Strength	Unnotched Impact Strength
5	0.246 ± 0.028 (11.46%)	>1.000
10	0.191 ± 0.018 (9.48%)	>0.911
15	0.174 ± 0.014 (7.99%)	0.469 ± 0.049 (10.45%)
20	0.199 ± 0.012 (6.13%)	0.416 ± 0.052 (12.50%)
25	0.240 ± 0.020 (8.25%)	0.404 ± 0.044 (10.92%)
30	0.325 ± 0.038 (11.69%)	0.423 ± 0.038 (8.94%)
35	0.334 ± 0.055 (16.44%)	0.459 ± 0.061 (13.27%)
40	0.389 ± 0.028 (7.28%)	0.598 ± 0.044 (7.39%)
45	0.520 ± 0.023 (4.50%)	0.754 ± 0.073 (9.68%)
50	0.751 ± 0.080 (10.63%)	0.906 ± 0.021 (2.37%)

Table 34: showing the effect of glass fibre content on the tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [<30 mesh] + XG 496 1/4" chopped strand).

TABLE 34

% Glass	Tensile Strength	Tensile Modulus
0	7,690 ± 215 (2.80%)	336,000 ± 12,000 (3.49%)
5	8,080 ± 270 (3.32%)	434,000 ± 30,000 (6.92%)
10	8,460 ± 240 (2.83%)	538,000 ± 35,000 (6.45%)
15	9,050 ± 320 (3.58%)	747,000 ± 101,000(13.53%)
20	10,950 ± 500 (4.57%)	848,000 ± 28,000 (3.28%)
25	12,760 ± 370 (2.92%)	1,073,000 ± 45,000 (4.18%)
30	14,790 ± 570 (3.84%)	1,266,000 ± 47,000 (3.69%)
35	20,000 ± 1,330(6.65%)	1,613,000 ± 60,000 (3.69%)
40	21,100 ± 1,120(5.29%)	1,919,000 ± 104,000(5.40%)
45	23,010 ± 1,030(4.50%)	2,331,000 ± 76,000 (3.27%)
50	23,500 ± 1,780(7.58%)	2,676,000 ± 235,000(8.80%)

Table 35: showing the effect of glass fibre content on the elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [<30 mesh] + XG 496 1/4" chopped strand).

TABLE 35

% Glass	Elongation at Break	Barcol Hardness
0	31.78 ± 3.42 (10.77%)	-
5	15.36 ± 2.28 (14.84%)	2.12 ± 0.40 (19.09%)
10	8.77 ± 0.70 (7.95%)	6.94 ± 1.20 (17.26%)
15	5.52 ± 0.20 (3.67%)	12.50 ± 0.94 (7.48%)
20	5.62 ± 0.24 (4.30%)	16.94 ± 1.03 (6.08%)
25	5.50 ± 0.19 (3.44%)	20.81 ± 1.07 (5.16%)
30	5.69 ± 0.17 (2.96%)	24.81 ± 0.88 (3.56%)
35	6.41 ± 0.36 (5.63%)	29.50 ± 1.70 (5.75%)
40	6.52 ± 0.46 (7.07%)	34.94 ± 1.98 (5.68%)
45	6.80 ± 0.46 (6.83%)	37.19 ± 1.24 (3.32%)
50	-	40.37 ± 1.96 (4.87%)

Table 36: showing the effect of glass fibre content on impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [<30 mesh] + XG 496 1/4" chopped strand).

TABLE 36

% Glass	Notched Impact Strength	Unnotched Impact Strength
5	0.217 ± 0.032 (14.88%)	>1.000
10	0.168 ± 0.011 (6.85%)	0.746 ± 0.068 (9.11%)
15	0.138 ± 0.006 (4.42%)	0.578 ± 0.106 (18.32%)
20	0.192 ± 0.010 (5.21%)	0.345 ± 0.038 (11.13%)
25	0.232 ± 0.013 (5.60%)	0.442 ± 0.023 (5.27%)
30	0.287 ± 0.019 (6.62%)	0.501 ± 0.038 (7.56%)
35	0.418 ± 0.024 (5.79%)	0.688 ± 0.050 (7.27%)
40	0.429 ± 0.043 (9.95%)	0.676 ± 0.056 (8.34%)
45	0.497 ± 0.033 (6.72%)	0.774 ± 0.097 (12.57%)
50	0.594 ± 0.066 (11.14%)	>0.942

Tables 37, 38: showing the effect of increased fibre length on the tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes (Kematal M90-04 [< 30 mesh] + XG 496 ½" chopped strand).

TABLE 37

% Glass	Tensile Strength	Tensile Modulus
5	8,040 ± 210 (2.63%)	413,000 ± 31,000 (7.60%)
10	8,750 ± 430 (4.87%)	523,000 ± 42,000 (8.09%)
15	9,590 ± 490 (5.10%)	699,000 ± 51,000 (7.30%)
20	10,880 ± 510 (4.67%)	856,000 ± 52,000 (6.12%)
25	13,220 ± 780 (5.93%)	1,123,000 ± 61,000 (5.41%)
30	14,940 ± 1,360(9.09%)	1,326,000 ± 149,000(11.21%)

(Kematal M90-04 [< 30 mesh] + XG 496 1" chopped strand).

TABLE 38

% Glass	Tensile Strength	Tensile Modulus
5	7,690 ± 220 (2.89%)	398,000 ± 19,000 (4.80%)
10	8,390 ± 290 (3.47%)	551,000 ± 59,000 (10.66%)
15	10,260 ± 780 (7.62%)	741,000 ± 95,000 (12.76%)
20	11,720 ± 1,120(9.52%)	964,000 ± 148,000(15.35%)
25	13,950 ± 960 (6.91%)	1,282,000 ± 151,000(11.76%)

Tables 39,40: showing the effect of increased fibre length on the elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes.

(Kematal M90-04 [<30 mesh] + XG 496 ½" chopped strand).

TABLE 39

% Glass	Elongation at Break	Barcol Hardness
5	13.75 ± 2.08 (15.10%)	1.50 ± 1.06 (70.67%)
10	6.73 ± 0.48 (7.11%)	8.19 ± 2.30 (28.06%)
15	5.66 ± 0.37 (6.49%)	11.87 ± 2.18 (18.33%)
20	5.56 ± 0.38 (6.89%)	18.06 ± 2.16 (11.98%)
25	5.34 ± 0.21 (3.93%)	21.00 ± 1.84 (8.75%)
30	5.44 ± 0.22 (4.08%)	23.60 ± 1.17 (4.94%)

(Kematal M90-04 [<30 mesh] + XG 496 1" chopped strand).

TABLE 40

% Glass	Elongation at Break	Barcol Hardness
5	13.61 ± 3.80 (27.92%)	1.75 ± 1.30 (74.23%)
10	6.37 ± 0.95 (14.88%)	7.12 ± 2.78 (39.06%)
15	5.78 ± 0.38 (6.53%)	9.31 ± 1.96 (21.05%)
20	5.33 ± 0.16 (3.05%)	17.80 ± 2.67 (15.02%)
25	5.62 ± 0.36 (6.33%)	22.06 ± 3.34 (15.16%)

Tables 41,42: showing the effect of increased fibre length on the impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes. (Kematal M90-04 [<30 mesh] + XG 496 $\frac{1}{2}$" chopped strand).

TABLE 41

% Glass	Notched Impact Strength	Unnotched Impact Strength
5	0.189 ± 0.030 (15.71%)	>1.000
10	0.141 ± 0.018 (13.05%)	0.513 ± 0.066 (12.94%)
15	0.174 ± 0.005 (2.76%)	0.429 ± 0.058 (13.47%)
20	0.237 ± 0.035 (14.77%)	0.486 ± 0.069 (14.22%)
25	0.247 ± 0.029 (11.94%)	0.431 ± 0.032 (7.38%)
30	0.244 ± 0.013 (5.29%)	0.452 ± 0.026 (5.80%)

TABLE 42

(Kematal M90-04 [<30 mesh] + XG 496 1" chopped strand).

% Glass	Notched Impact Strength	Unnotched Impact Strength
5	0.192 ± 0.044 (23.07%)	>1.000
10	0.141 ± 0.027 (19.08%)	0.621 ± 0.054 (8.70%)
15	0.148 ± 0.026 (17.37%)	0.374 ± 0.027 (7.30%)
20	0.166 ± 0.018 (10.90%)	0.298 ± 0.034 (11.38%)
25	0.193 ± 0.022 (11.66%)	0.368 ± 0.044 (11.93%)

Table 43: showing the effect of coupling agents on the tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes. (Kematal M90-04 [<30 mesh] + various 1/4" chopped strands [35%]).

TABLE 43

Glass	Tensile Strength	Tensile Modulus
control	13,930 ± 1,050 (7.56%)	1,506,000 ± 80,000 (5.31%)
ECO 115	13,520 ± 830 (6.17%)	1,647,000 ± 149,000(9.07%)
XG 496	20,000 ± 1,330 (6.65%)	1,613,000 ± 60,000 (3.69%)
XG 438	19,040 ± 740 (3.91%)	1,528,000 ± 114,000(7.47%)
XG 184	16,150 ± 1,040 (6.42%)	1,487,000 ± 132,000(8.85%)

Table 44: showing the effect of coupling agents on the elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes. (Kematal M90-04 [<30 mesh] + 35% various 1/4" chopped strands).

TABLE 44

Glass	Elongation at Break	Barcol Hardness
control	4.92 ± 0.30 (6.10%)	25.19 ± 1.55 (6.15%)
ECO 115	4.64 ± 0.30 (6.53%)	23.50 ± 1.12 (4.76%)
XG 496	6.41 ± 0.36 (5.63%)	29.50 ± 1.70 (5.75%)
XG 438	5.91 ± 0.44 (7.41%)	28.87 ± 0.99 (3.44%)
XG 184	5.70 ± 0.34 (5.88%)	29.81 ± 1.47 (4.92%)

Table 45: showing the effect of coupling agents on the impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes. (Kematal M90-04 [<30 mesh] + various 1/4" chopped strands [35%]).

TABLE 45

Glass	Notched Impact Strength	Unnotched Impact Strength
control	0.357 ± 0.023 (6.44%)	0.420 ± 0.042 (9.95%)
ECO 115	0.334 ± 0.055 (16.44%)	0.459 ± 0.061 (13.27%)
XG 496	0.418 ± 0.024 (5.79%)	0.688 ± 0.050 (7.27%)
XG 438	0.498 ± 0.032 (6.35%)	0.692 ± 0.090 (12.99%)
XG 184	0.533 ± 0.057 (10.64%)	0.726 ± 0.067 (9.19%)

Table 46: showing the effect of polymer viscosity on tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes. (Various grades of Kematal + 30% ECO 115 1/4" chopped strand).

TABLE 46

	Tensile Strength	Tensile Modulus
M25-04	8,130 ± 350(4.37%)	356,000 ± 13,000(3.73%)
M25-04+glass	13,420 ± 660(4.93%)	1,321,000 ± 54,000(4.07%)
M90-04	7,570 ± 110 (1.48%)	325,000 ± 7,000 (2.17%)
M90-04+glass	11,800 ± 520(4.45%)	1,360,000 ± 77,000(5.66%)
M140-04	7,620 ± 210(2.74%)	332,000 ± 10,000(3.06%)
M140-04+glass	12,870 ± 900(7.03%)	1,310,000 ± 42,000(3.22%)

Table 47: showing the effect of polymer viscosity on elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes. (Various grades of Kematal + 30% ECO 115 1/4" chopped strand).

TABLE 47

	Elongation at Break	Barcol Hardness
M25-04	34.56 ± 9.06 (26.21%)	0
M25-04+glass	4.81 ± 0.30 (6.30%)	23.06 ± 1.14 (4.96%)
M90-04	34.06 ± 4.96 (14.57%)	0
M90-04+glass	4.48 ± 0.29 (6.45%)	20.56 ± 0.70 (3.42%)
M140-04	38.75 ± 7.41 (19.11%)	0
M140-04	4.95 ± 0.33 (6.71%)	22.87 ± 1.05 (4.60%)

Table 48: showing the effect of polymer viscosity on impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes.
(Various grades of Kematal + 30% ECO 115 1/4" chopped strand).

TABLE 48

	Notched Impact Strength	Unnotched Impact Strength
M25-04	0.485 ± 0.084 (17.40%)	>1.000
M25-04+glass	0.307 ± 0.033 (10.85%)	0.515 ± 0.064 (12.37%)
M90-04	0.351 ± 0.072 (20.51%)	>1.000
M90-04+glass	0.325 ± 0.038 (11.69%)	0.423 ± 0.038 (8.94%)
M140-04	0.483 ± 0.057 (11.84%)	>1.000
M140-04+glass	0.305 ± 0.028 (9.34%)	0.472 ± 0.038 (8.05%)

Table 49: showing the effect of polymer viscosity on tensile strength and initial tensile modulus for material processed by dry blending in a Rotocube mixer for 10 minutes. (Various grades of Kematal + 30% XG 496 1/4" chopped strand).

TABLE 49

	Tensile Strength	Tensile Modulus
M25-04	8,130 ± 350 (4.37%)	356,000 ± 13,000 (3.73%)
M25-04+glass	15,160 ± 610 (4.04%)	1,279,000 ± 56,000 (4.41%)
M90-04	7,570 ± 110 (1.48%)	325,000 ± 7,000 (2.17%)
M90-04+glass	14,790 ± 570 (3.84%)	1,266,000 ± 47,000 (3.69%)
M140-04	7,620 ± 210 (2.74%)	332,000 ± 10,000 (3.06%)
M140-04+glass	14,490 ± 1,260(8.72%)	1,279,000 ± 63,000 (4.93%)

Table 50: showing the effect of polymer viscosity on elongation at break and hardness for material processed by dry blending in a Rotocube mixer for 10 minutes. (Various grades of Kematal + 30% XG 496 1/4" chopped strand).

TABLE 50

	Elongation at Break	Barcol Hardness
M25-04	34.56 ± 9.06 (26.21%)	0
M25-04+glass	5.58 ± 0.34 (6.15%)	25.87 ± 1.65 (6.39%)
M90-04	34.06 ± 4.96 (14.57%)	0
M90-04+glass	5.69 ± 0.17 (2.96%)	24.81 ± 0.88 (3.56%)
M140-04	38.75 ± 7.41 (19.11%)	0
M140-04+glass	5.48 ± 0.30 (5.45%)	24.40 ± 1.49 (6.13%)

Table 51: showing the effect of polymer viscosity on impact strength (both unnotched and notched) for material processed by dry blending in a Rotocube mixer for 10 minutes.
(Various grades of Kematal + 30% XG 496 1/4" chopped strand).

TABLE 51

	Notched Impact Strength	Unnotched Impact Strength
M25-04	0.485 ± 0.084 (17.40%)	>1.000
M25-04+glass	0.286 ± 0.025 (8.67%)	0.496 ± 0.046 (9.21%)
M90-04	0.351 ± 0.072 (20.51%)	>1.000
M90-04+glass	0.287 ± 0.019 (6.62%)	0.501 ± 0.038 (7.56%)
M140-04	0.483 ± 0.057 (11.84%)	>1.000
M140-04+glass	0.292 ± 0.018 (6.23%)	0.582 ± 0.044 (7.54%)

CHAPTER VI

FIBRE LENGTH AND ORIENTATION RESULTS

FIBRE LENGTH AND ORIENTATION RESULTS.

A. Fibre Length.

The fibre length determinations were carried out as described in the experimental chapter. The three photographs for each sample of material (for typical photographs see Plates 1 - 7) generally contained a total of 300 - 600 glass fibres. This was probably not sufficiently large to obtain a completely accurate fibre distribution but large enough to show up important differences between different batches of materials.

The results are given in the form of normalized histograms i.e. the number of fibres in each length batch is converted to a percentage of the total number of fibres before plotting.

Figure 8 shows the normalized histograms for the glass fibres from the following materials:

(a) Kematal M90-04 + 20% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C and compression moulded.

(b) Kematal M90-04 + 50% ECO 115 1/4" chopped glass strand processed on the two roll mill for 15 minutes at 175°C and compression moulded.

(c) Kematal M90-04 + 20% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C and injection moulded.

PLATE 1 - Glass fibres from material prepared by processing on the two roll mill for 15 minutes at 175°C and injection moulded. (Kematal M90-04 + 20% 1/4" ECO 115 chopped glass strand).

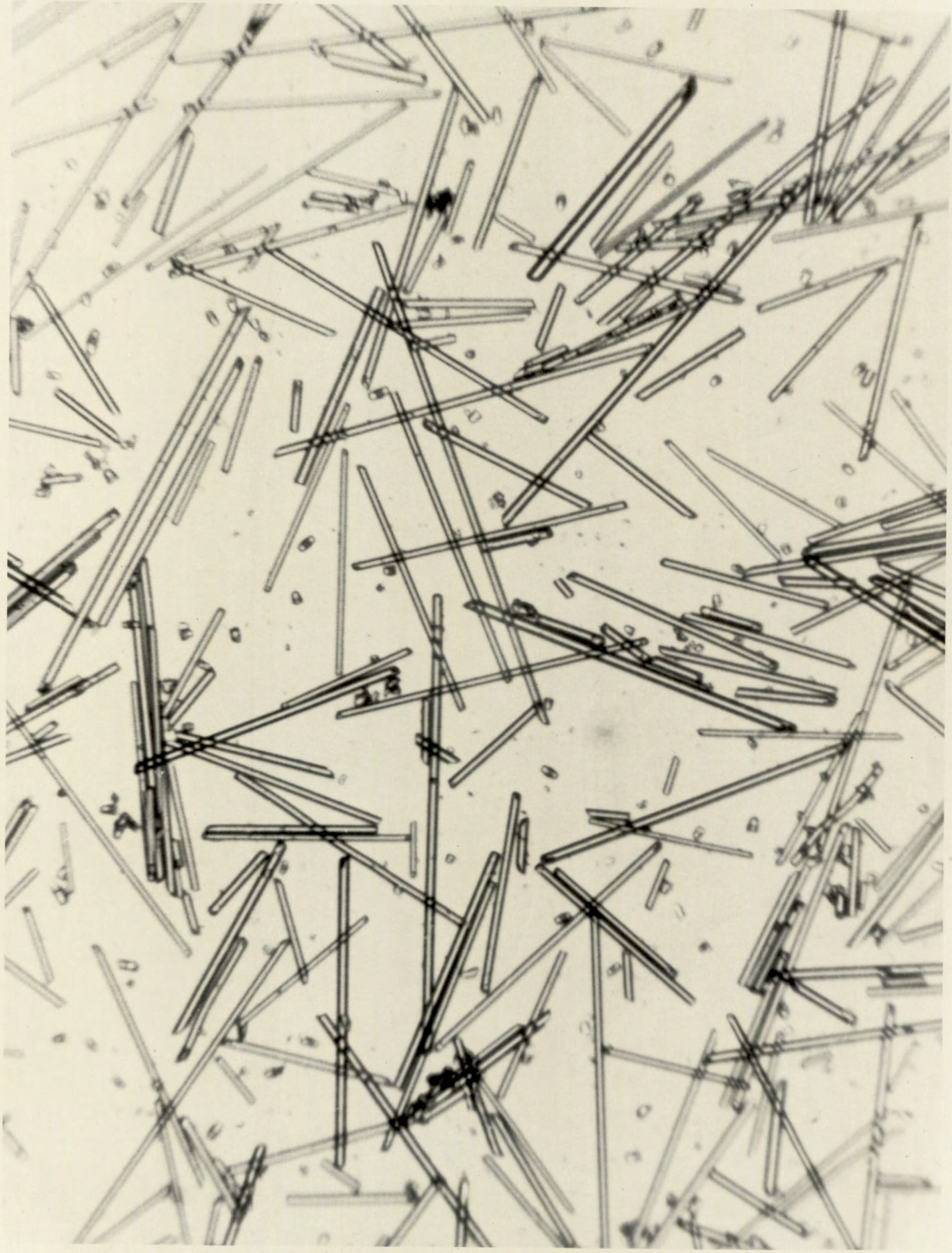


PLATE 2 - Glass fibres from material prepared by processing on the two roll mill for 15 minutes at 175°C and injection moulded. (Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand).

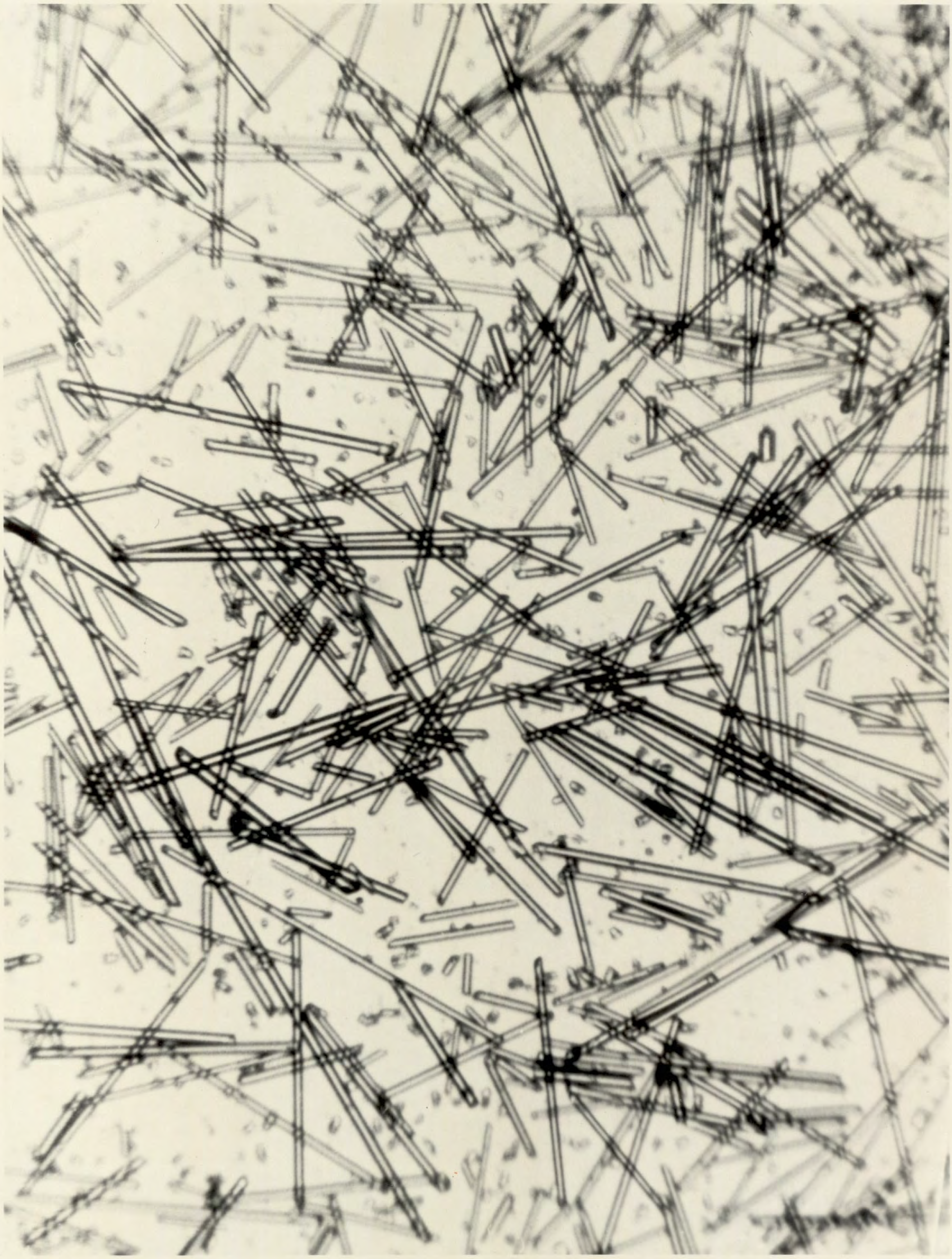


PLATE 3 - Glass fibres from material prepared by processing in the Buss Ko-kneader (two passes at 30 r.p.m. and a nominal 160°C) and injection moulded. (Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand).

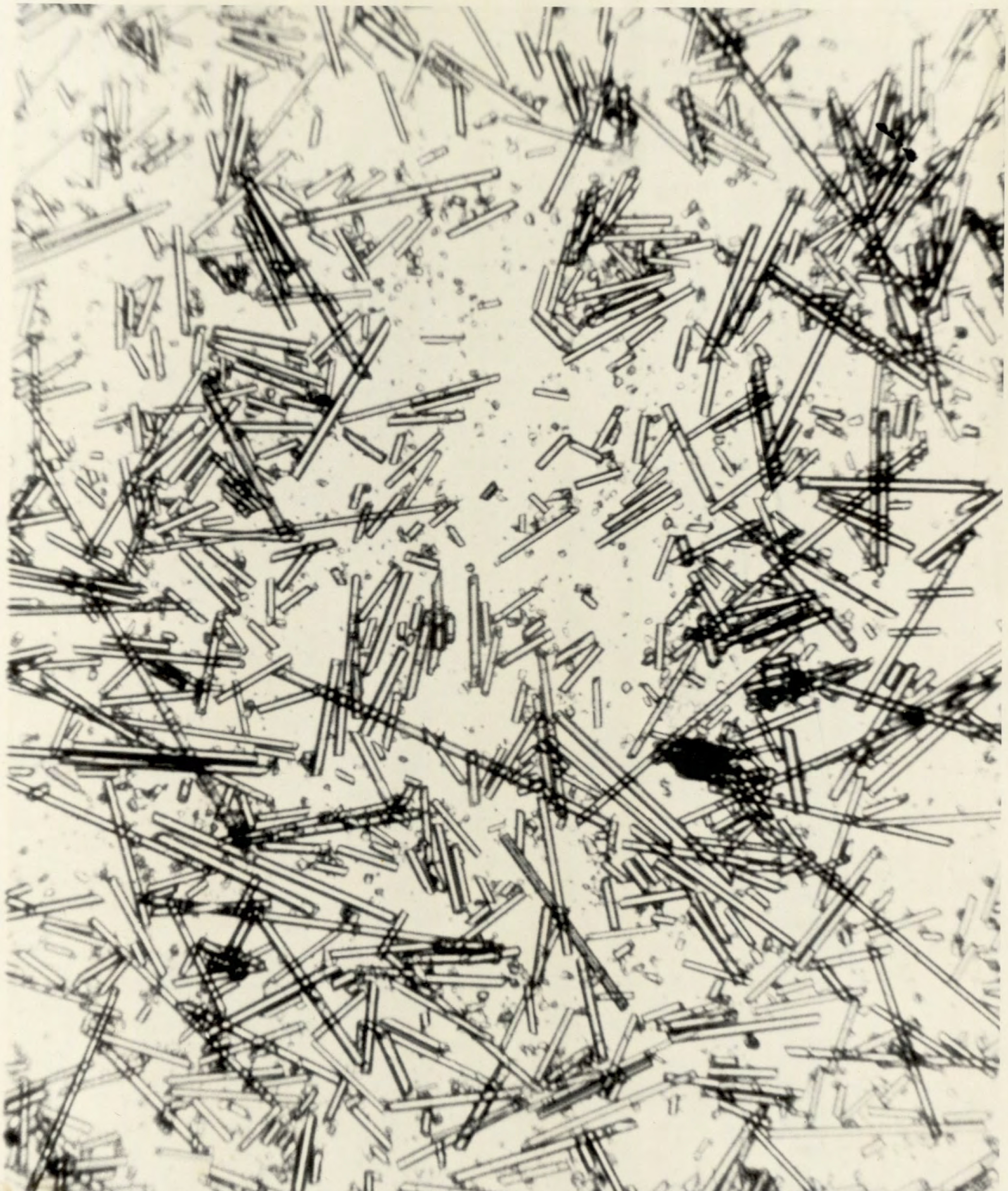


PLATE 4 - Glass fibres from material prepared by processing on the two roll mill for 0 minutes at 175°C and injection moulded. (Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand).

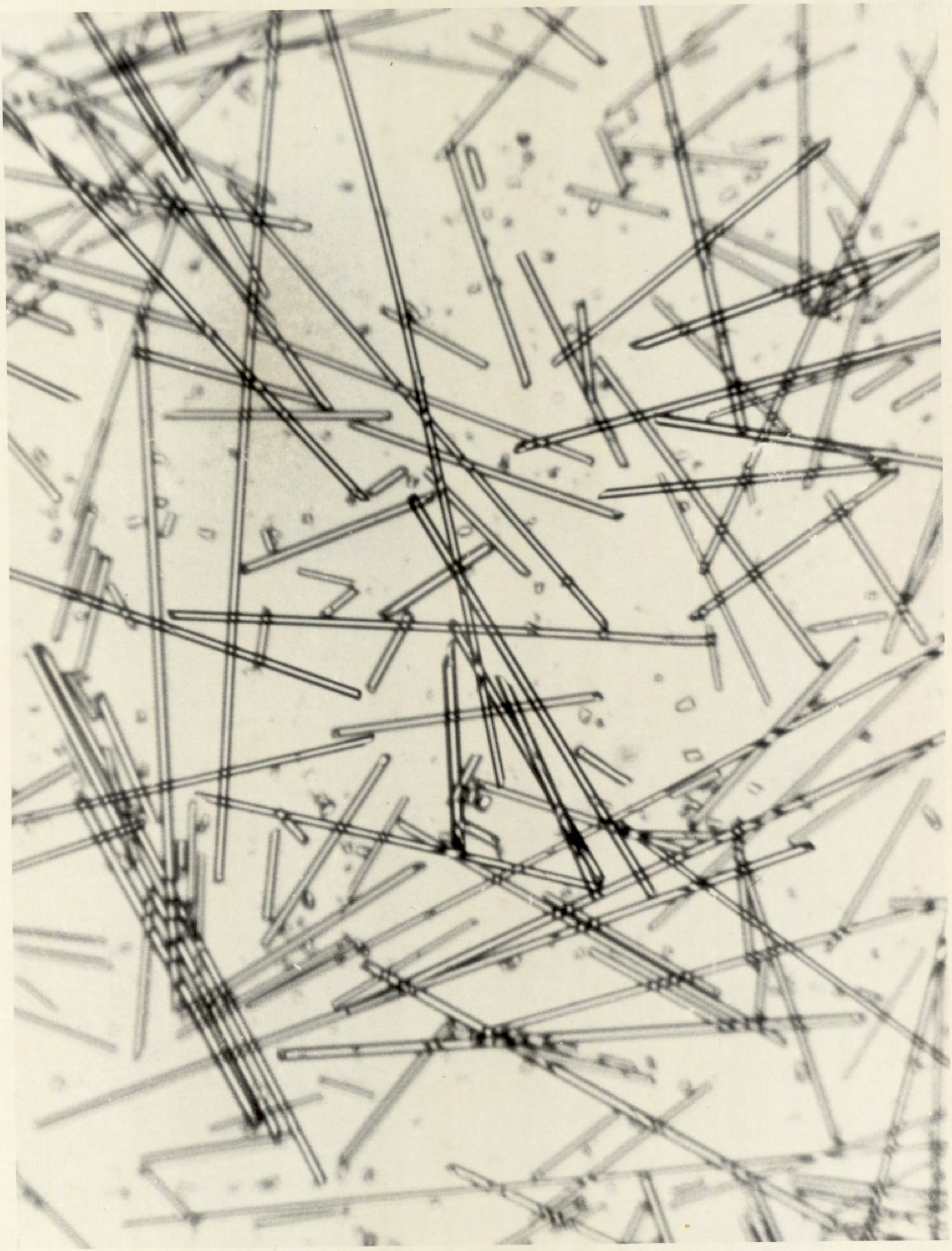


PLATE 5 - Glass fibres from material prepared by processing on the two roll mill for 1 minute at 175°C and injection moulded. (Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand).

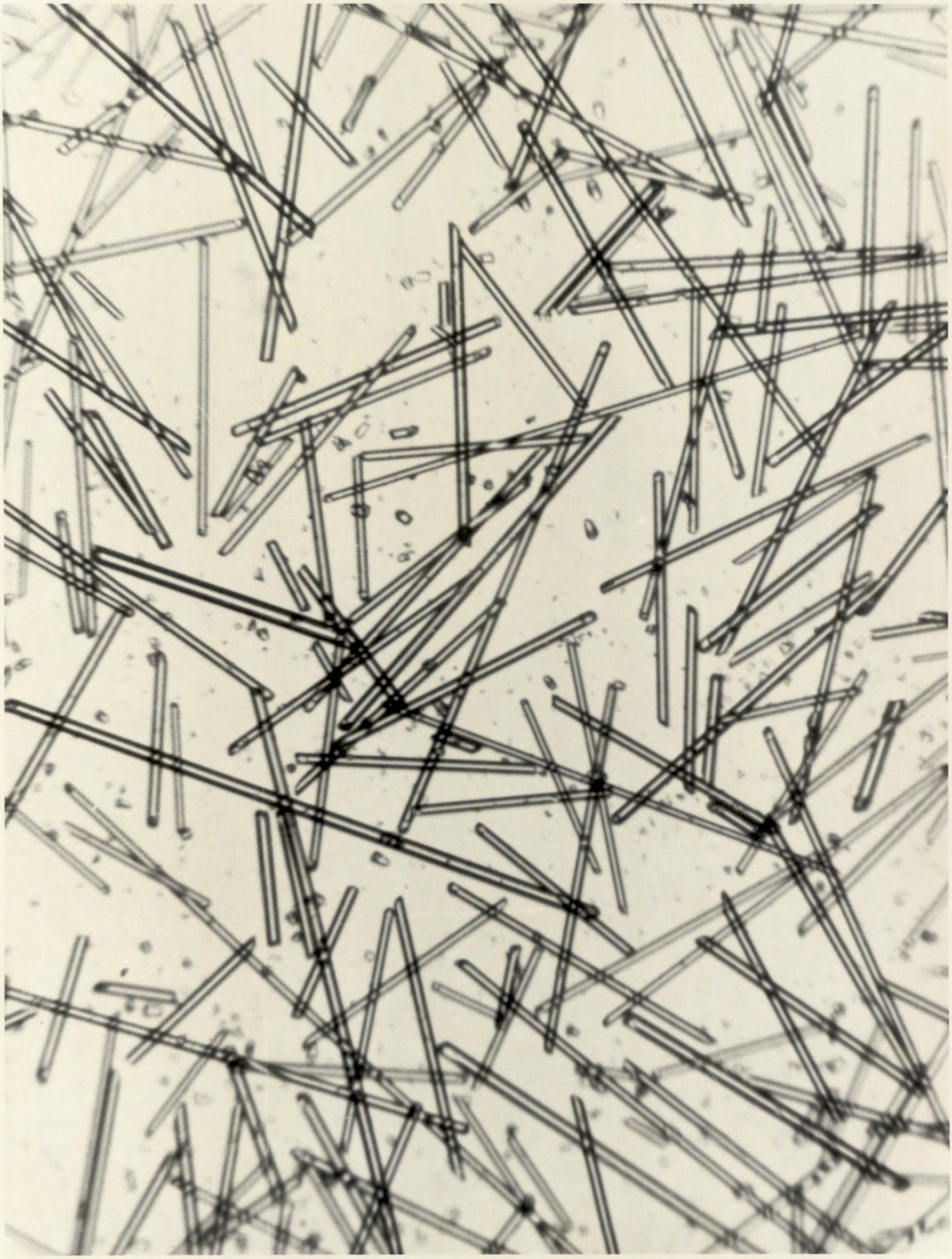


PLATE 6 - Glass fibres from material prepared by processing on the two roll mill for 5 minutes at 175°C and injection moulded. (Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand).

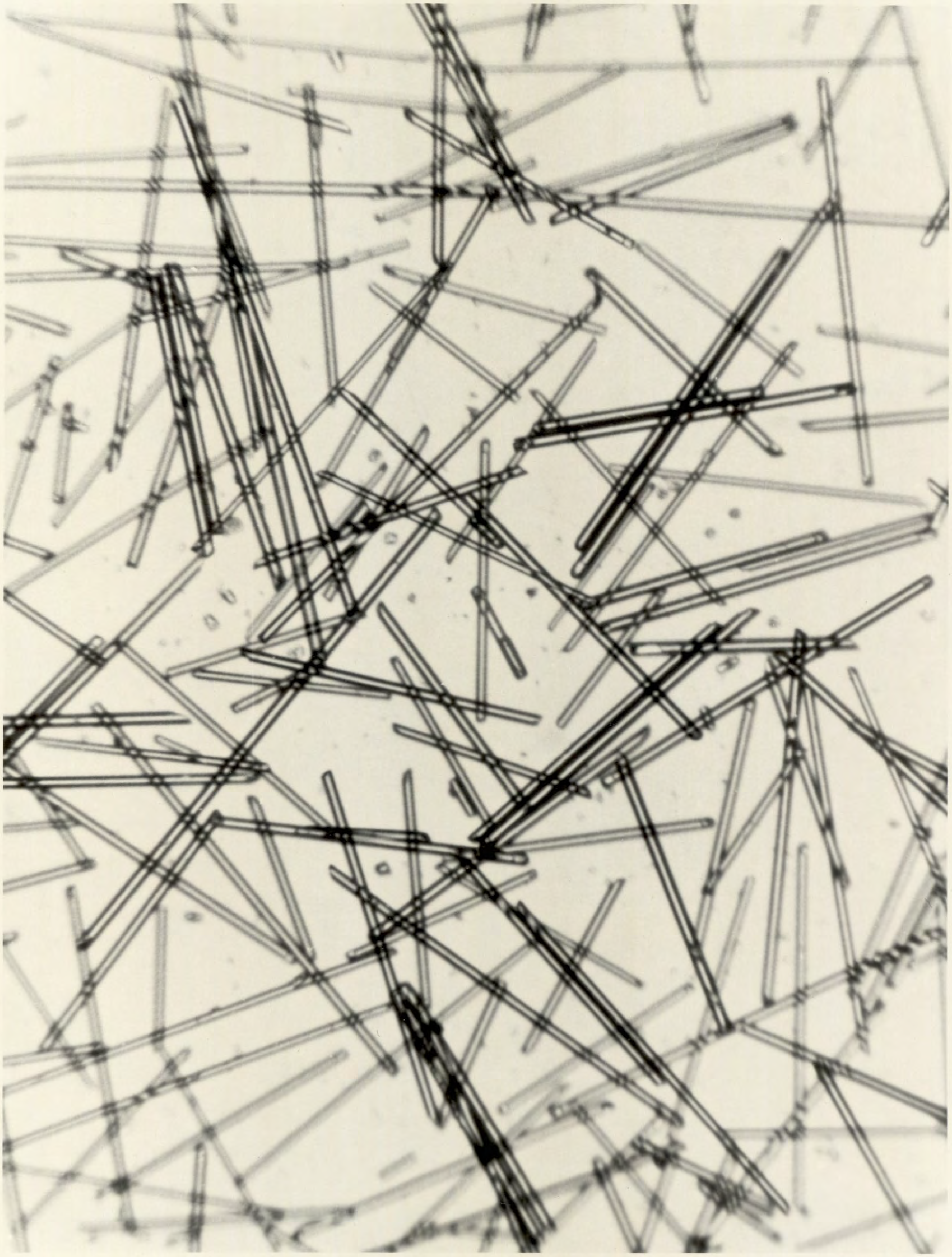


PLATE 7 - Glass fibres from material prepared by processing on the two roll mill for 60 minutes at 175 °C and injection moulded. (Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand).

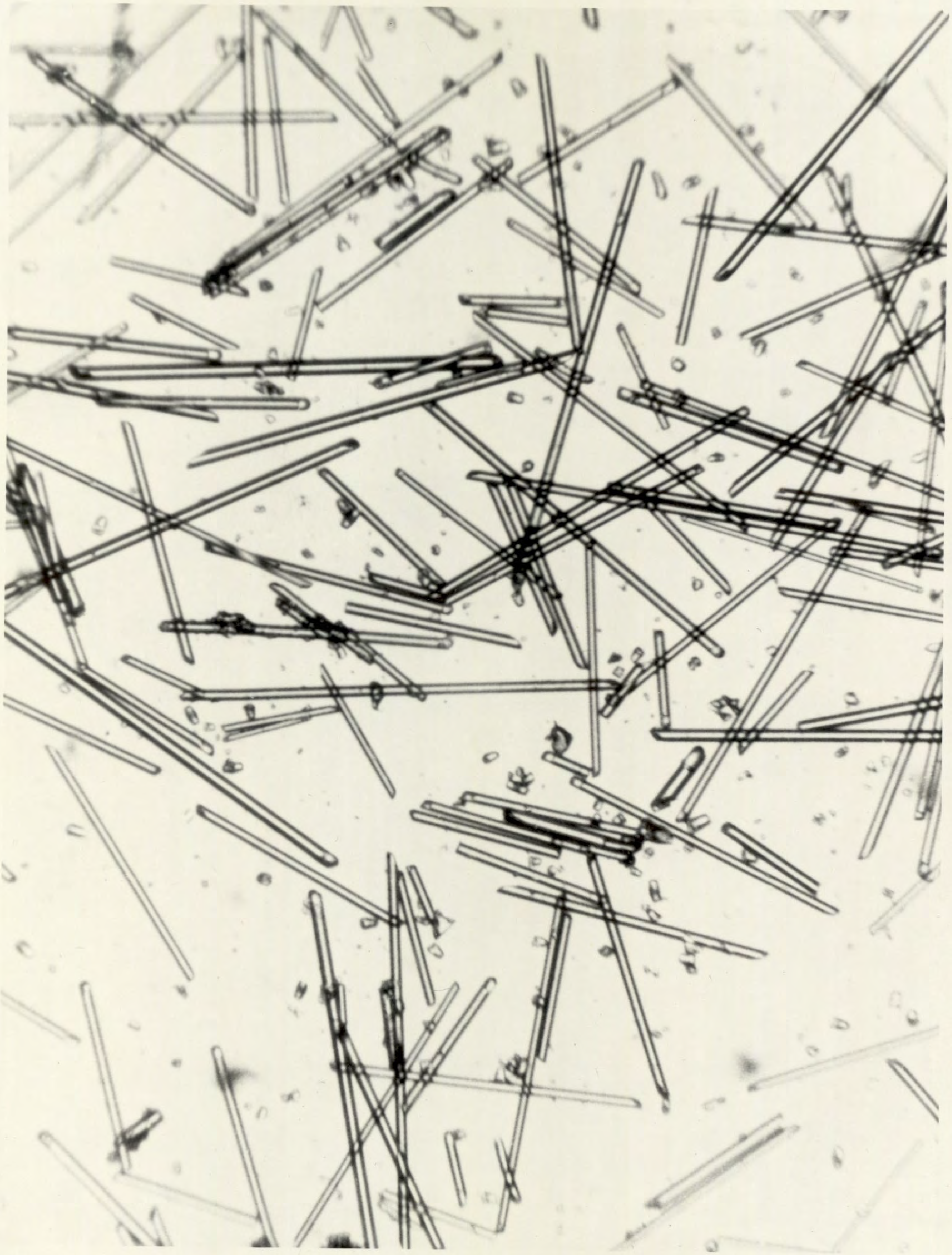


FIGURE 8


Glass fibre%
(population)
20
15
10
5
0
two roll mill
20% glass fibre
compression moulded
20
15
10
5
0
two roll mill
50% glass fibre
compression moulded
20
15
10
5
0
two roll mill
20% glass fibre
injection moulded
20
15
10
5
0
two roll mill
50% glass fibre
injection moulded
fibre length(mm)
0
.05
.10
.15
.20
.25
.30
.35
.40
.45
.50
.55
.60
.65

(d) Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C and injection moulded.

Figure 9 shows the normalized histograms for the glass fibres from material prepared by processing on the two roll mill at 175°C and injection moulded. The Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand was processed on the mill for

(a) 0 minutes (see Chapter II, page 43)

(b) 1 minute

(c) 5 minutes

(d) 15 minutes

(e) 30 minutes

(f) 60 minutes

Figure 10 shows the normalized histograms for the glass fibres from the following materials

(a) Kematal M90-04 + 20% 1/4" ECO 115 chopped glass strand processed in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C) and compression moulded.

(b) Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand processed in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C) and compression moulded.

Figure 11 shows the normalized histograms for the glass fibres from the following materials

FIGURE 9

Kenatal M90-04 + 30% EC0115/two roll mill

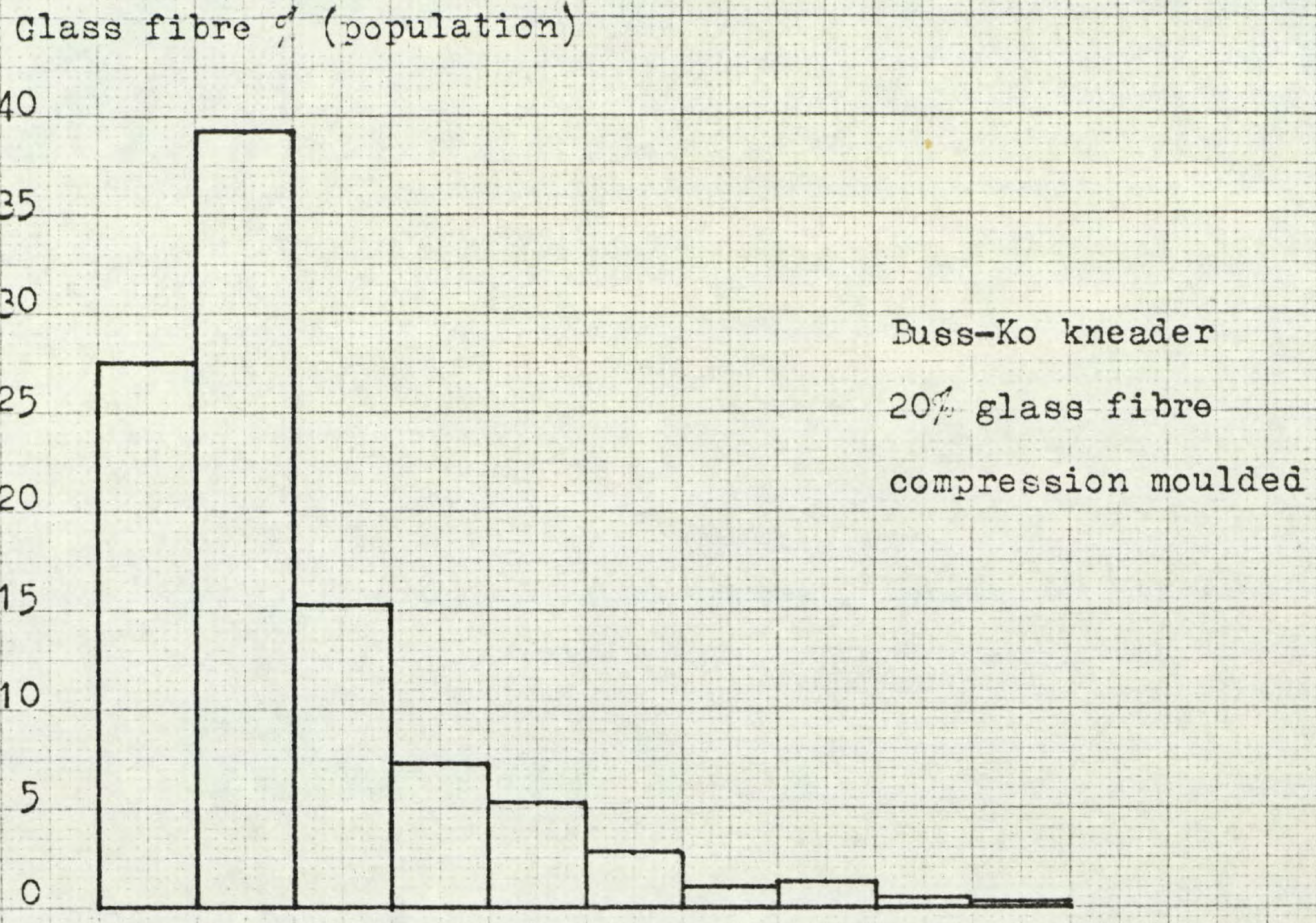
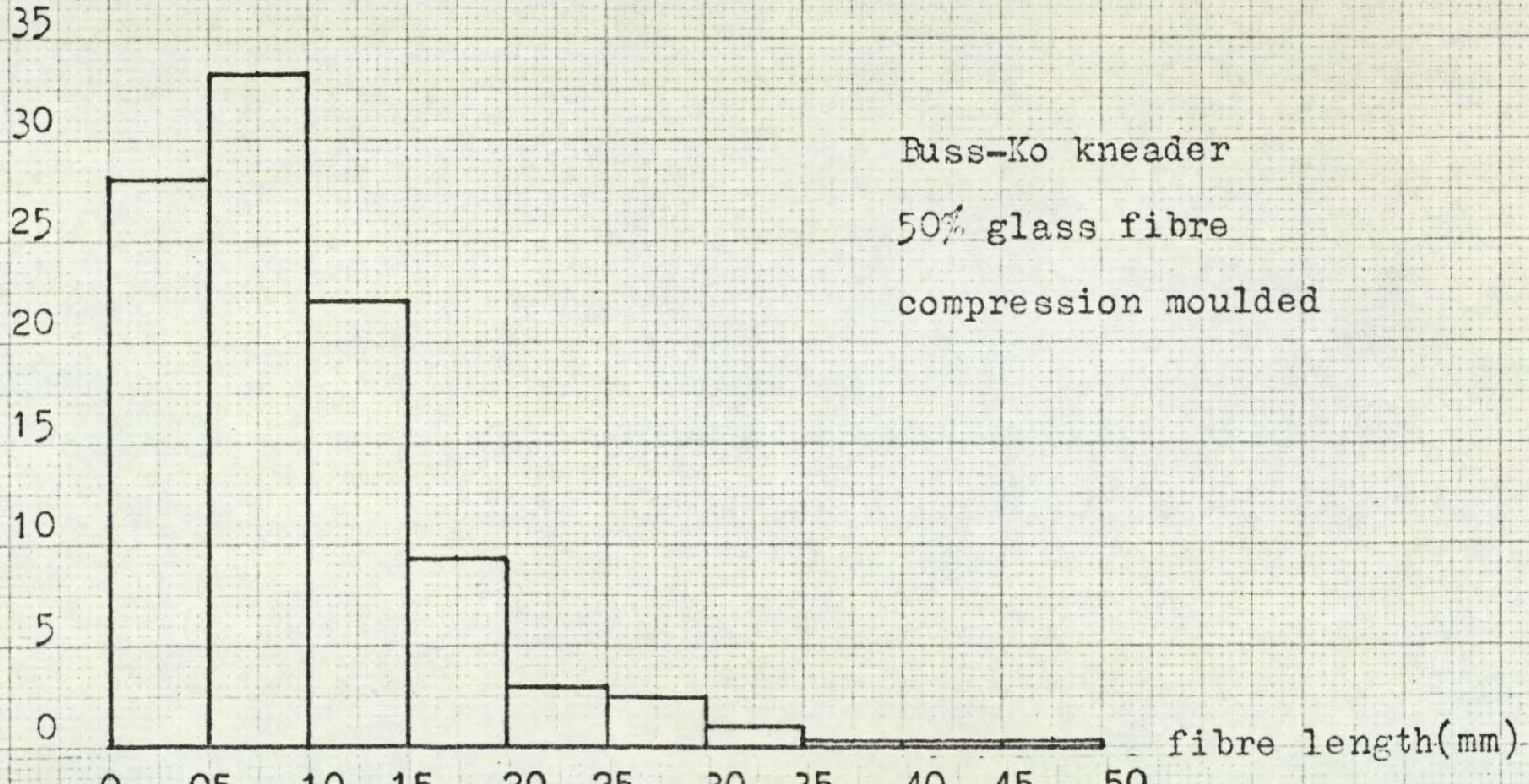

Glass fibre % (population)
40
35
30
25
20
15
10
5
0
Buss-Ko kneader
20% glass fibre
compression moulded

FIGURE 10


35
30
25
20
15
10
5
0
Buss-Ko kneader
50% glass fibre
compression moulded
fibre length(mm)
0
.05
.10
.15
.20
.25
.30
.35
.40
.45
.50

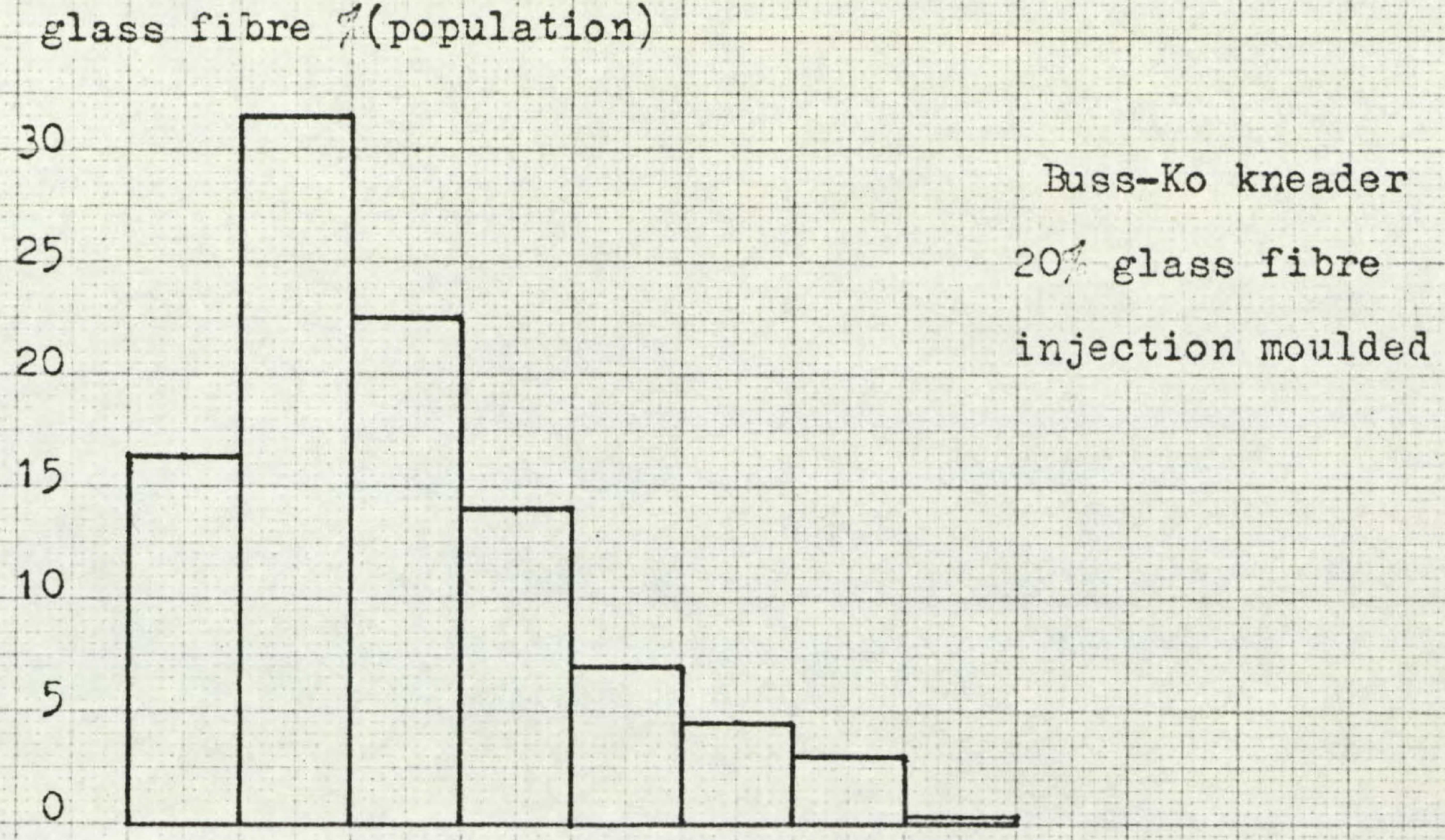
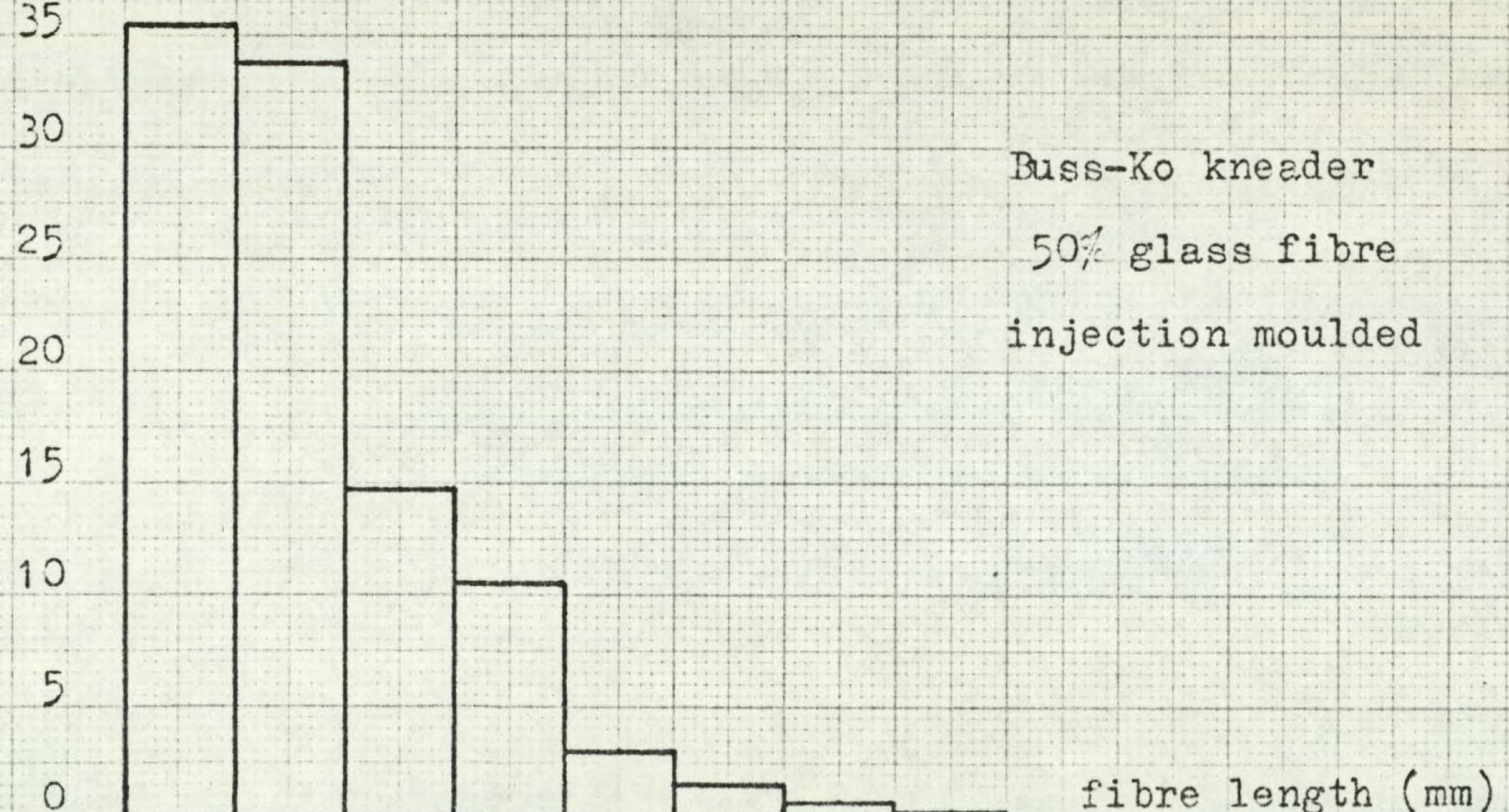

glass fibre %(population)
30
25
20
15
10
5
0
Buss-Ko kneader
20% glass fibre
injection moulded

FIGURE 11


35
30
25
20
15
10
5
0
Buss-Ko kneader
50% glass fibre
injection moulded
fibre length (mm)
0
.05
.10
.15
.20
.25
.30
.35
.40

(a) Kematal M90-04 + 20% 1/4" ECO 115 chopped glass strand processed in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C) and injection moulded.

(b) Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand processed in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C) and injection moulded.

B. Fibre Orientation.

The fibre orientation determinations were carried out as described in the experimental chapter. Only surface orientations were studied and generally orientations of 400 - 600 fibres were measured.

As with the fibre lengths, the results are given, for convenience, in the form of normalized histograms.

Figure 12 shows the orientation histograms for the broad face of injection moulded tensile bars prepared from the following materials

(a) Kematal M90-04 + 10% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C.

(b) Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C.

Figure 13 shows the orientation histograms for

(a) the broad face of a tensile bar, injection moulded from Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C.

(b) the narrow face (ca. 1/8" across) of a tensile bar, injection moulded from Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C.

Figure 14 shows the orientation histogram for the broad face of a tensile bar, injection moulded from Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand processed on the two roll mill for

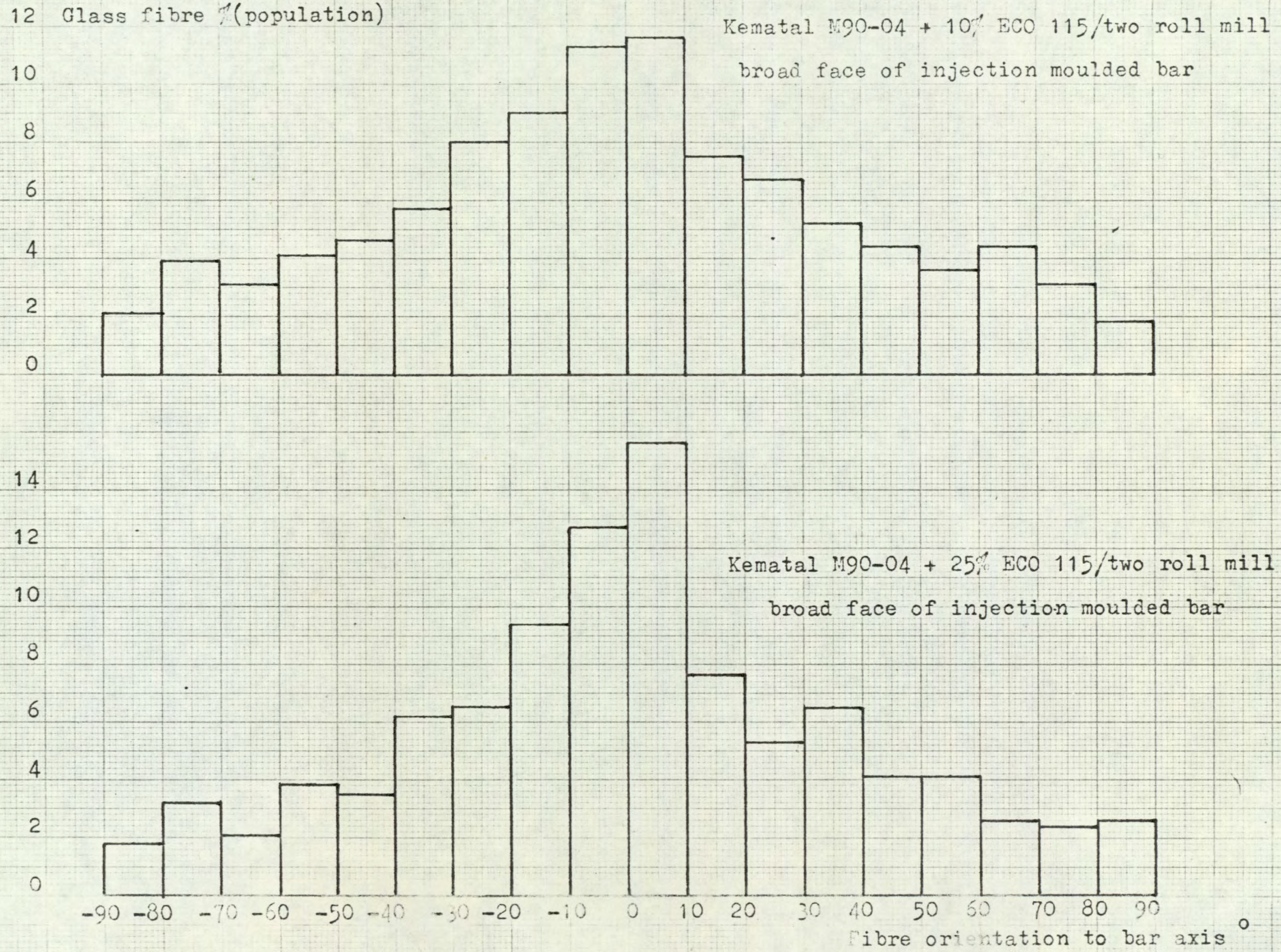

Glass fibre %(population)
12
10
8
6
4
2
0
Kematal M90-04 + 10% ECO 115/two roll mill
broad face of injection moulded bar
14
12
10
8
6
4
2
0
Kematal M90-04 + 25% ECO 115/two roll mill
broad face of injection moulded bar
-90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90
Fibre orientation to bar axis °

FIGURE 12

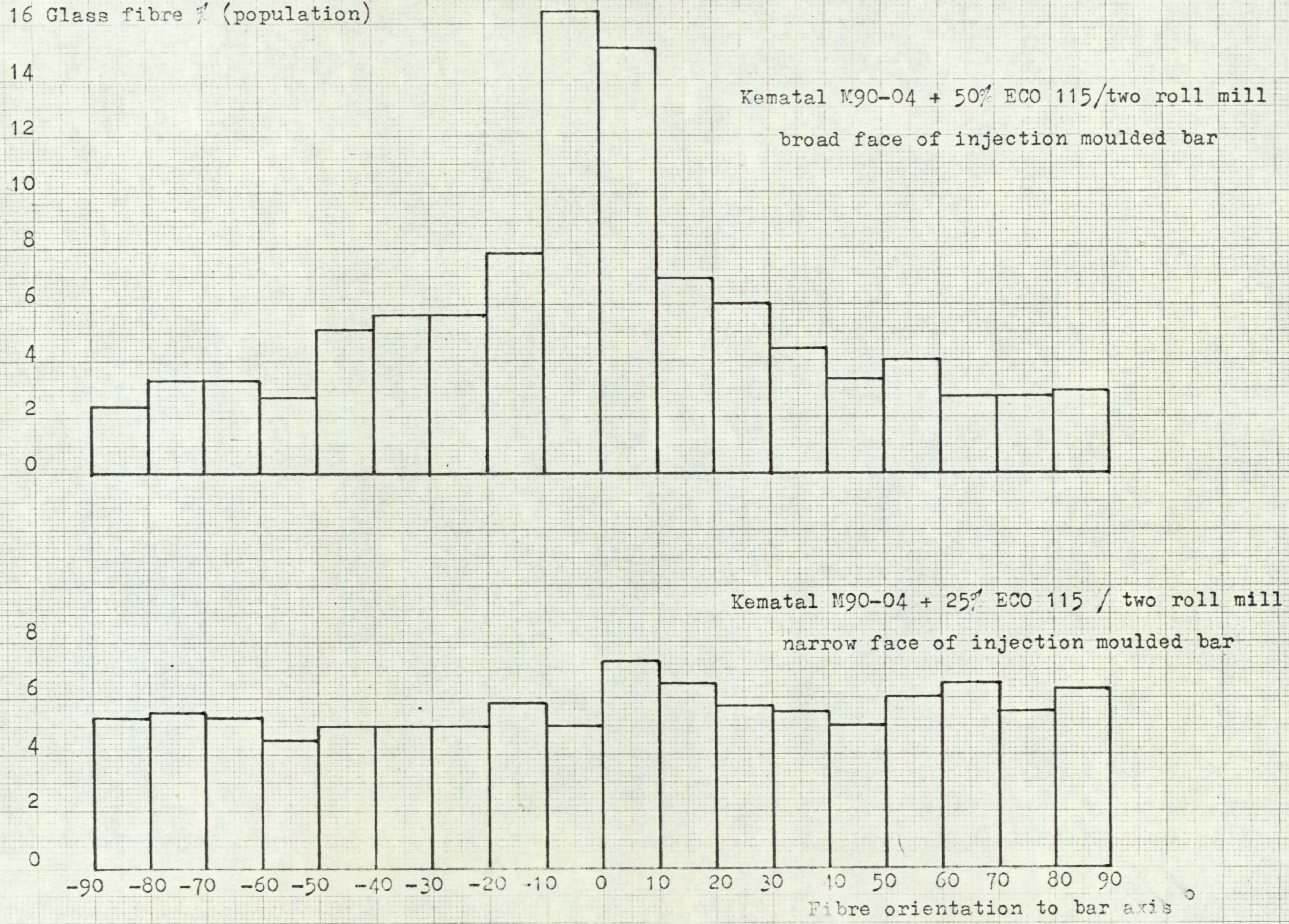

16 Glass fibre % (population)
14
12
10
8
6
4
2
0
Kematal M90-04 + 50% ECO 115/two roll mill
broad face of injection moulded bar
Kematal M90-04 + 25% ECO 115 / two roll mill
narrow face of injection moulded bar
8
6
4
2
0
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
Fibre orientation to bar axis °

FIGURE 13

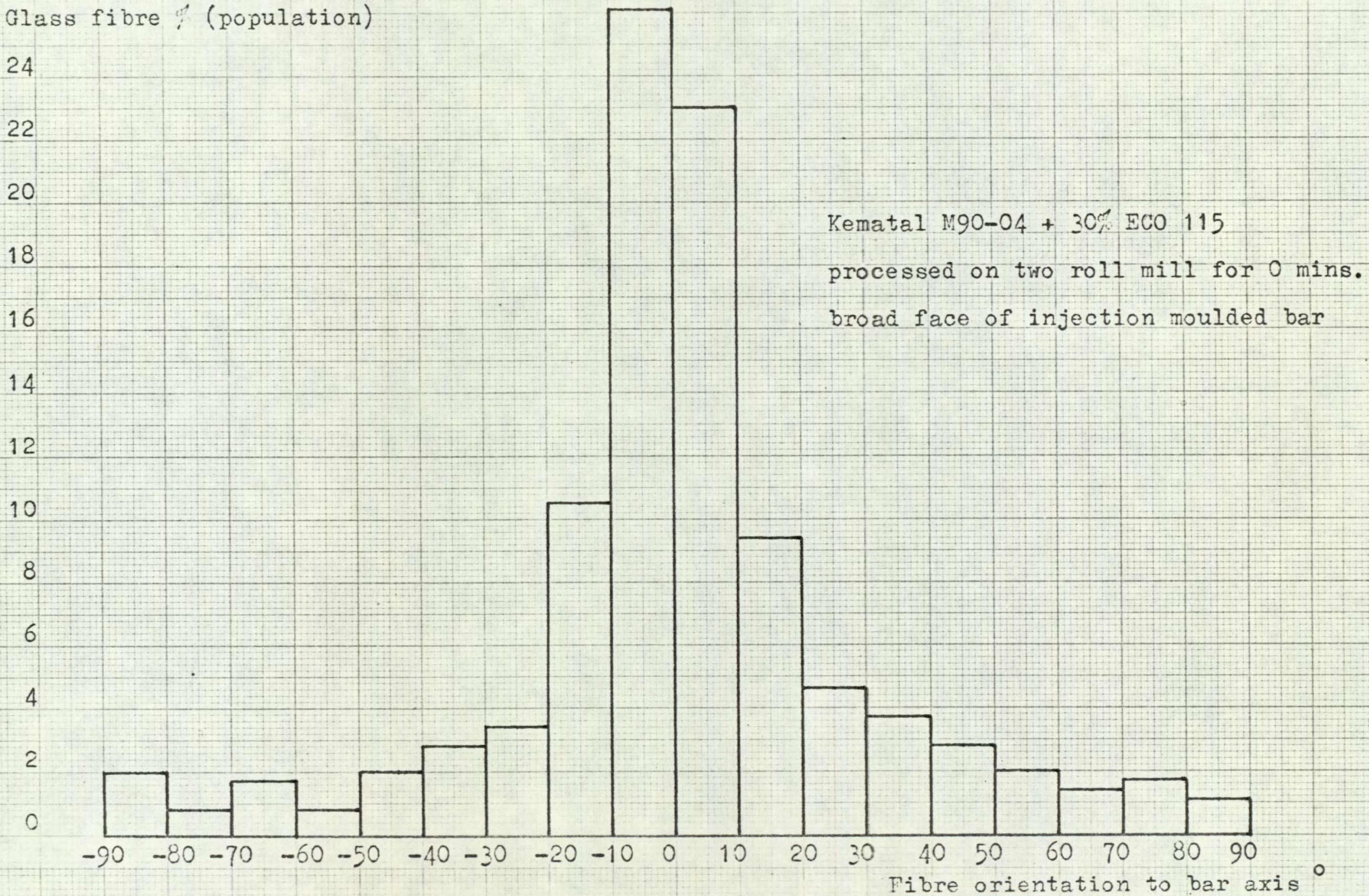

Glass fibre % (population)
24
22
20
18
16
14
12
10
8
6
4
2
0
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
Fibre orientation to bar axis °
Kematal M90-04 + 30% ECO 115
processed on two roll mill for 0 mins.
broad face of injection moulded bar

FIGURE 14

0 minutes (see Chapter II, page 43) at 175°C.

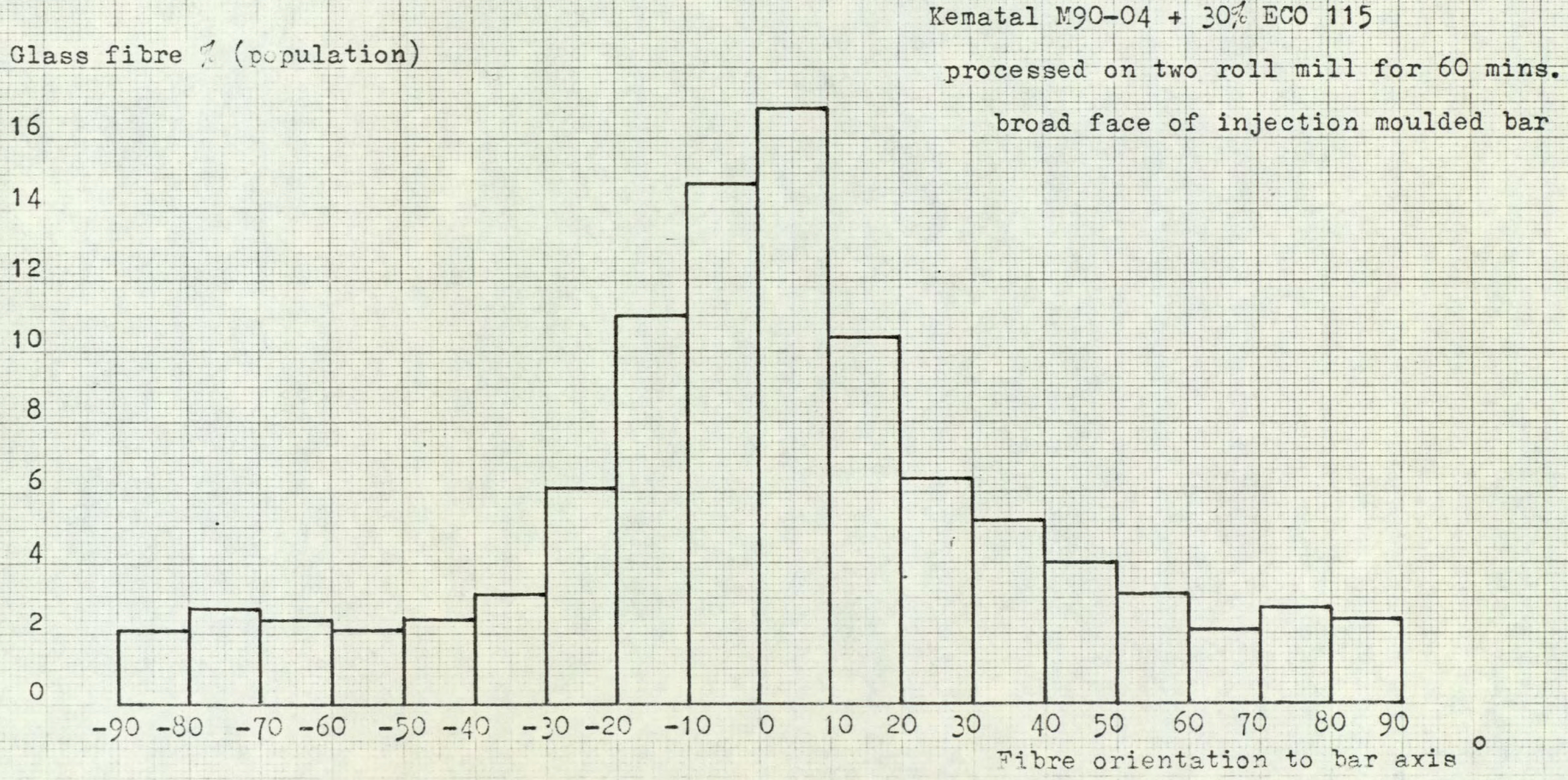
Figure 15 shows the orientation histogram for the broad face of a tensile bar, injection moulded from Kematal M90-04 + 30% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 60 minutes at 175°C.

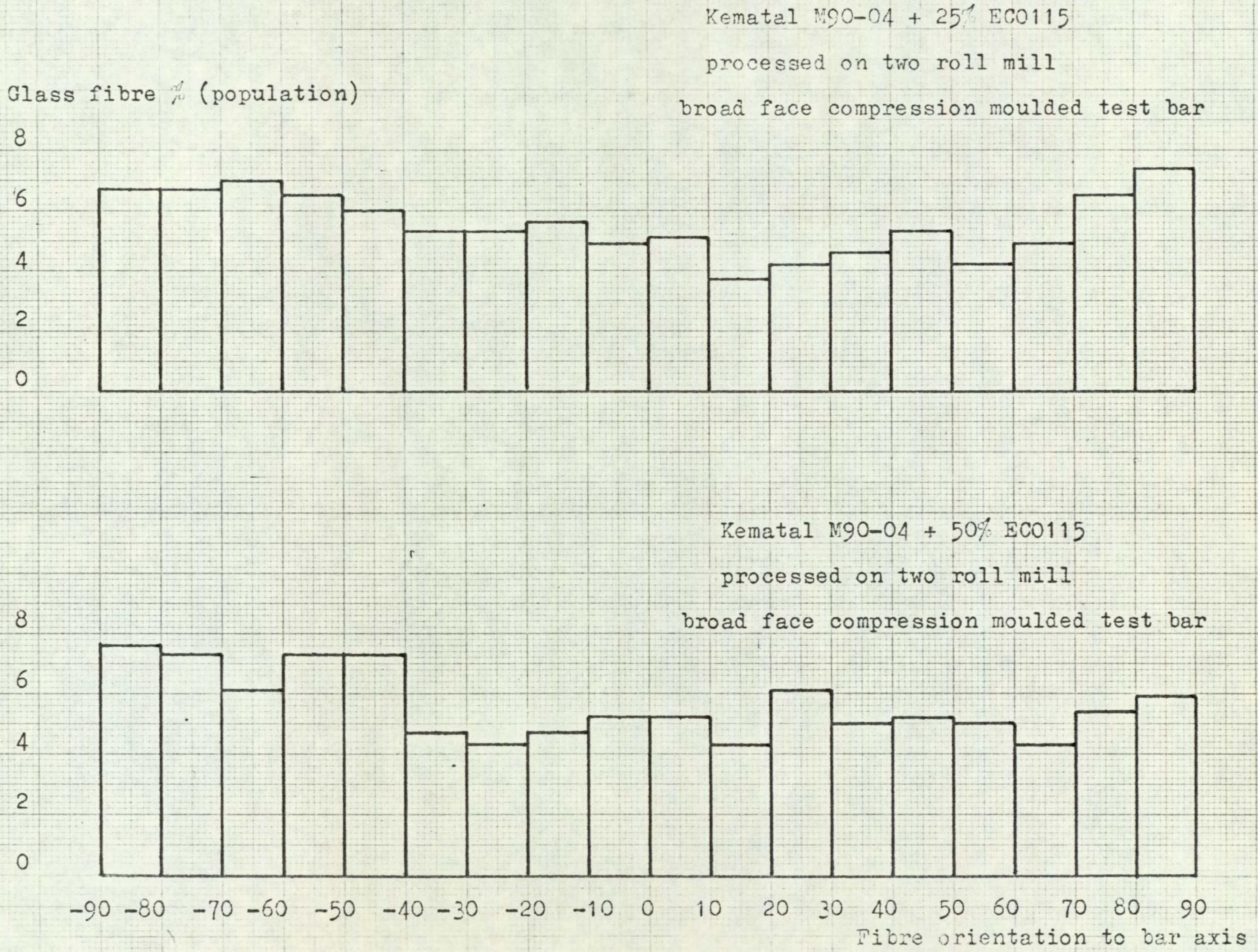
Figure 16 shows the orientation histograms for the broad faces of bars <u>compression</u> moulded from

(a) Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand processed on the two roll mill for 15 minutes at 175°C.

(b) Kematal M90-04 + 50% 1/4" ECO 115 chopped glass strand processed on thr two roll mill for 15 minutes at 175°C.

FIGURE 15


Kematal M90-04 + 30% ECO 115
processed on two roll mill for 60 mins.
broad face of injection moulded bar
Glass fibre % (population)
16
14
12
10
8
6
4
2
0
-90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90
Fibre orientation to bar axis °


Kematal M90-04 + 25% EC0115
processed on two roll mill
broad face compression moulded test bar

Kematal M90-04 + 50% EC0115
processed on two roll mill
broad face compression moulded test bar

FIGURE 16

CHAPTER VII

DISCUSSION

DISCUSSION

Initially, compression moulding was preferred to injection moulding in spite of the much longer cycle times with the former - forty to fifty minutes compared with one or two minutes. Compression moulding was chosen because it introduces less fibre orientation into the moulding than does injection moulding. With injection moulding, the flow of material through the gate and along the mould induces a fibre alignment along the bar axis. With compression moulding however much less fibre aligning melt flow occurs and what does occur will be of much less well defined direction.

Reference to the results quoted in Chapter III shows that glass fibre exhibits little or no reinforcing ability in acetal copolymer as far as evaluation in a compression moulded test system was concerned. This was in conflict with results reported by other workers using injection moulded systems. It was therefore thought possible that compression moulded test pieces might not provide a definitive evaluation of glass reinforced acetal copolymer. With this in mind it was decided to carry out further work using an injection moulded system. The complete transformation in properties which occurred on changing from compression to injection moulding confirmed the above idea. The possible reasons for this transformation will be discussed later. It should, possibly, be pointed out that nearly all of the actual applications of glass reinforced thermoplastics involve injection moulding - none, as far as is known, involves compression moulding.

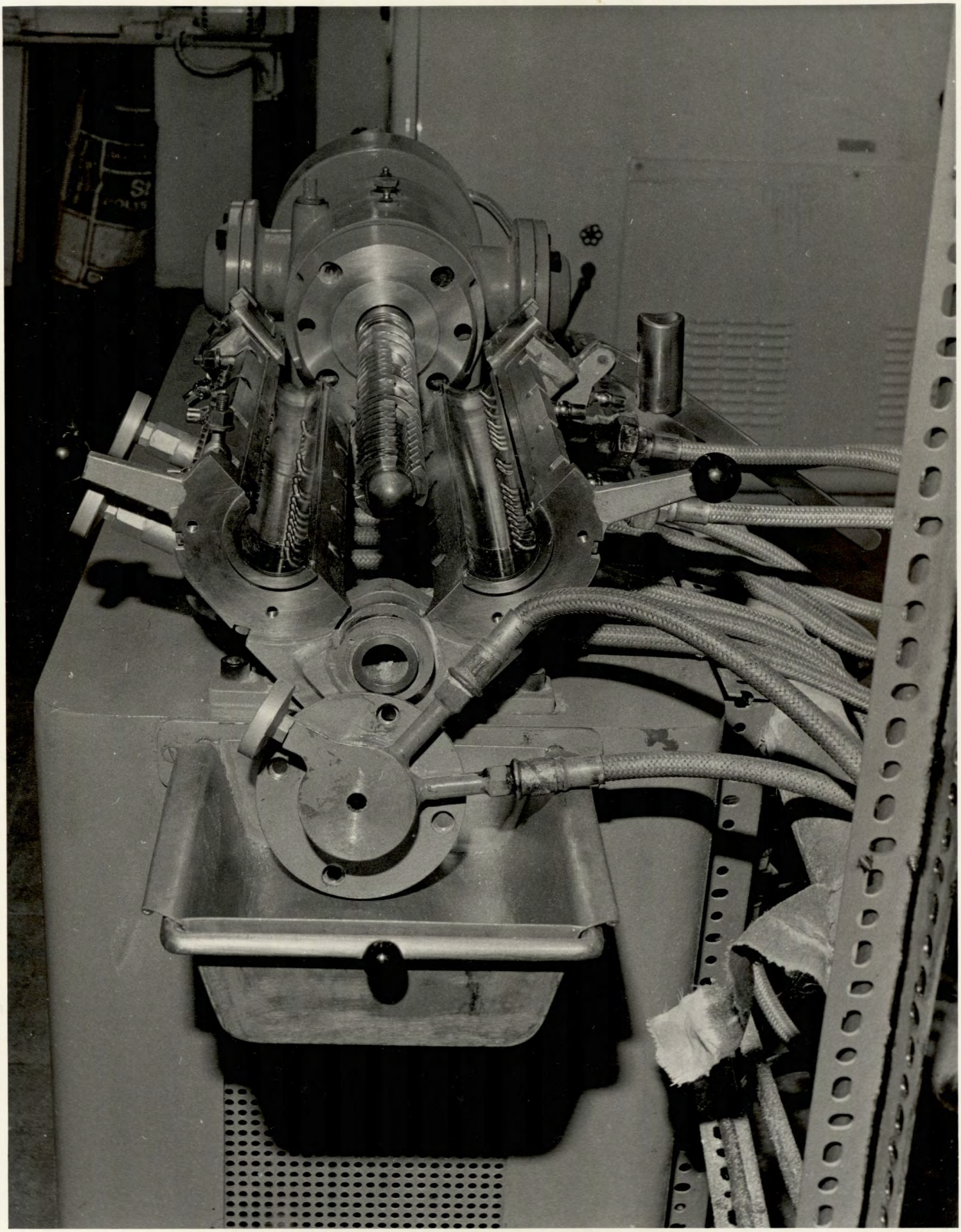
A. The Effect of Processing on Properties.

The machines used for mixing the polymer and glass fibre are best summarised in tabular form.

Buss Ko-kneader		Compression and Injection moulded
Two Roll Mill		Compression and Injection moulded
Hand stirred material		Compression and Injection moulded
Dry Blended on	Rotocube mixer Winkworth mixer Papenmeier mixer	followed by injection moulding

It is difficult to calculate the shear forces involved in the different processing methods without making unwarranted assumptions. Consideration of what happens to the material in the various processes will, however, give an idea of the relative magnitude of the shear forces and consequently the amount of fibre degradation which may be anticipated. In the Buss Ko-kneader the material is driven through under some pressure by the interrupted screw (see Plate 8). The pegs along the length of the barrel ensure that the material is subject to quite a high level of shear for nearly the whole of its passage through the machine. Indeed the temperature of the material, because of this shear, was some 30 – 40°C higher

PLATE 8 - View of the Buss Ko-kneader with the die removed and the barrel split.



than the nominal barrel temperature of the machine (160°).

The two roll mill offers a less severe method of processing: very little pressure is exerted on the material and this only when it passes through the nip i.e. a fraction of the time that it actually spends on the machine.

Analysis of the fibre length histograms shown in Chapter VI confirms the above ideas. The glass fibres present in the material processed in the Buss Ko-kneader are quite appreciably shorter than those present in material processed on the two roll mill. One interesting fact which emerges from the fibre length histograms is that processing on the two roll mill for increasing periods of time does not alter the fibre length distribution to any great extent. This is contrary to what was expected to happen, and must presumably be due to the velocity gradient at the nip lining up the fibres in such a way as to prevent their being damaged. One effect increased milling time did have, however, was to increase the bulk density of the chopped product (see Figure 17) presumably due to increased wetting of the glass by the polymer.

A visual examination of fibres in the materials processed by hand stirring and dry blending revealed a much lower level of fibre degradation (the polymer was carefully burned off from the composite prior to fibre examination). The hand stirred and compression moulded material showed virtually no fibre degradation and the fibres were still generally present as intact fibre bundles. In the hand stirred/injection moulded and dry blended/injection

FIGURE 17


Bulk Density
(gm/cc)
.7
.6
.5
.4
.3
.2
.1
(a)
(b)
(b)
(a)
(a) milling at 1.35 to 1 roll speed : ×
(b) milling at even roll speed : ⊙
Time of milling (mins.)
0
10
20
30
40
50
6

moulded materials the fibres were mainly dispersed from their original strands and a certain amount of fibre degradation had occurred; this was due to the injection moulding process being rather more severe than the compression moulding.

Having discussed the general characteristics of the processing methods, we will now discuss in some detail the effect of processing on certain mechanical properties.

The effect of processing on tensile properties is shown in Figures 18 and 19 for compression moulded material and in Figures 20 and 21 for injection moulded material.

For compression moulded material it can be seen that the hand stirred material is appreciably superior to materials prepared in the Buss Ko-kneader and on the two roll mill, which are fairly similar to one another. The poor properties (especially tensile strength) of the materials prepared on the two mixing machines might be presumed at first glance to be due to the short lengths of the fibres contained therein (see Figures 8 and 10, pages 111 and 114). Reference to the results obtained by injection moulding identical materials shows that this explanation cannot be valid. The improvement in tensile modulus which occurs on changing from compression moulding to injection moulding could just be attributed to the change in fibre orientation (see page 171). With the tensile strength, however, a change of kind, not of degree, occurs on going from compression to injection moulding with the two roll mill and Buss

FIGURE 18

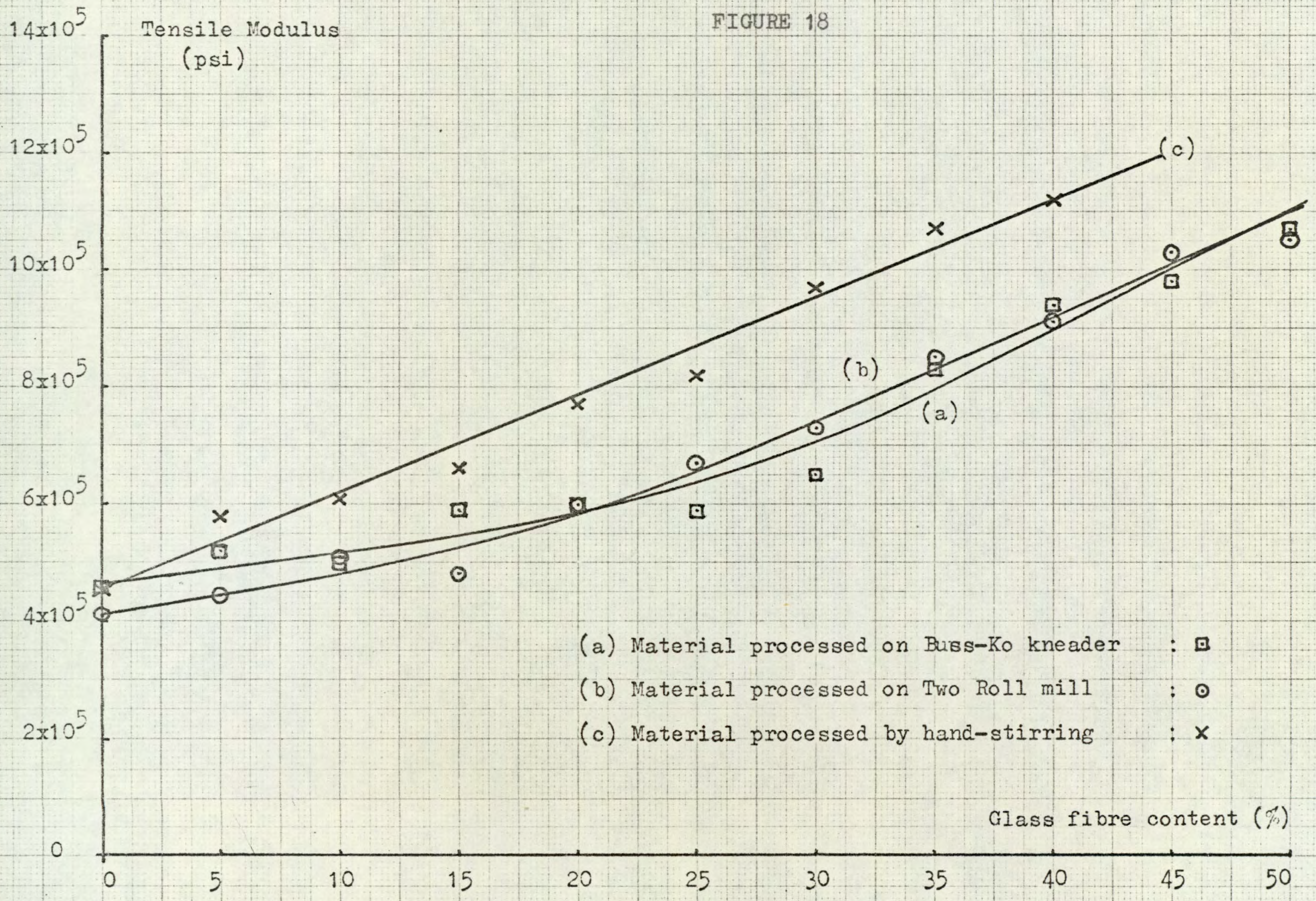

Tensile Modulus (psi)
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
(c)
(b)
(a)
(a) Material processed on Buss-Ko kneader : ⊡
(b) Material processed on Two Roll mill : ⊙
(c) Material processed by hand-stirring : ×
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50

FIGURE 19

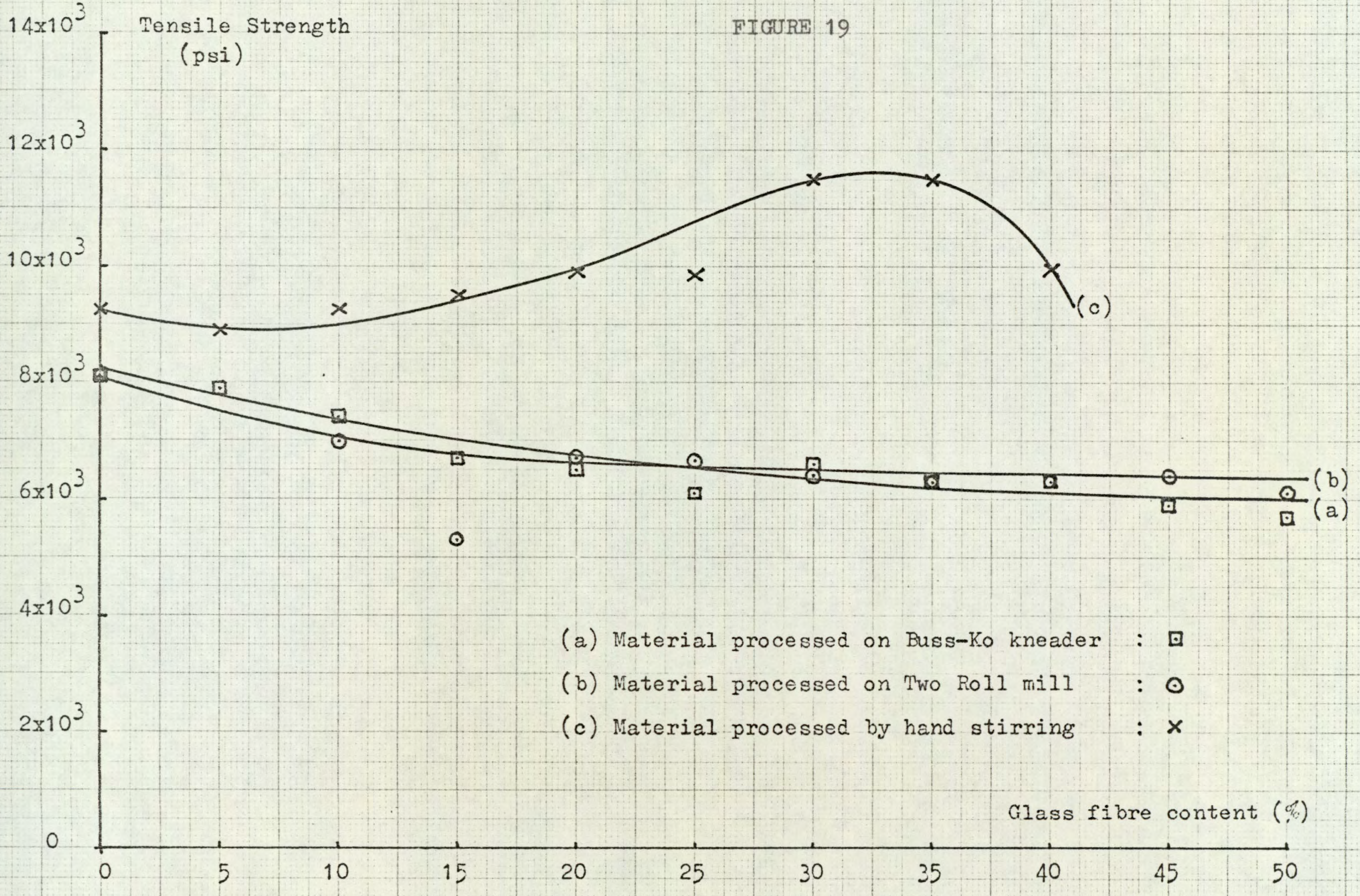

Tensile Strength (psi)
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50
(a)
(b)
(c)
(a) Material processed on Buss-Ko kneader : ⊡
(b) Material processed on Two Roll mill : ⊙
(c) Material processed by hand stirring : ×

FIGURE 20


Tensile Modulus
(psi)
28x10^5
26x10^5
24x10^5
22x10^5
20x10^5
18x10^5
16x10^5
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
0
5
10
15
20
25
30
35
40
45
50
Glass fibre content (%)
(a) M90-04 + ECO 115 / Buss-Ko kneader : ⊡
(b) M90-04 + ECO 115 / Two Roll mill : ⊙
(c) M90-04 + ECO 115 / dry blend : ×
(d) M90-04 + XG 496 / dry blend : +
(a)
(b)
(c)
(d)

FIGURE 21


Tensile Strength (psi)
24x10^3
22x10^3
20x10^3
18x10^3
16x10^3
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
(a) M90-04 + ECO 115 / Buss-Ko kneader : ⊡
(b) M90-04 + ECO 115 / Two Roll mill : ⊙
(c) M90-04 + ECO 115 / dry blend : ×
(d) M90-04 + XG 496 / dry blend : +
(d)
(b)
(c
(a)
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50

Ko-kneader prepared materials: with compression moulded material the tensile strength falls with increasing glass content while, with injection moulded material, the tensile strength rises sharply.

The poor tensile strength of compression moulded two roll mill and Buss Ko-kneader prepared materials cannot therefore be explained solely in terms of fibre length or orientation. Another possible reason for this low tensile strength is the formation of microcracks during the sawing of the compression moulded test pieces; these might seriously reduce the tensile strength while having little or no effect on the initial tensile modulus. If this was the true cause then it is difficult to see why the same should not apply to the hand stirred compression moulded material. In addition, preliminary results with the dumb-bell compression moulded test pieces (which were not sawn) were not significantly improved over those from the sawn strips (see Table 2, page 60).

One is forced, therefore, to the conclusion that the deficiency in tensile strength of compression moulded material prepared on the two roll mill or in the Buss Ko-kneader is due in some way to the compression moulding process itself. One possible defect in the test pieces is the presence of voids in the compression moulding: glass reinforced acetal is a brittle material and so would be very sensitive to the presence of such flaws, as far as high deformation properties (such as tensile strength) were concerned. If this is a true explanation then it is difficult to see, once again, why it does not apply also to hand stirred materials.

The most likely explanation for the weakness of compression moulded two roll mill and Buss Ko-kneader prepared materials lies with the fact that these materials are chopped into granules before use. During compression moulding there is not a great deal of material flow and points of weakness may occur along the lines of the original granule boundaries - there will be a very poor distribution of glass fibre across these boundaries. Reference to Plates 9 and 10 shows these boundaries in the compression moulded two roll mill and Buss Ko-kneader prepared materials.

Such granule boundaries will only occupy a tiny fraction of the length of the bar and thus would only exert a very small effect on tensile modulus. Fracture, however, would be expected to occur at these boundaries and so there would be a serious effect on tensile strength. No such granule boundaries will be present in the hand stirred compression moulded material. Also, injection moulding would be expected to remove these granule boundaries involving, as it does, a considerably greater degree of material flow and mixing than does compression moulding. The improvement in properties which is brought about by injection moulding can be seen by comparing Figure 21 with Figure 19.

Confirmation for the above ideas comes from microscopic examination of the fractured surfaces of materials prepared on the two roll mill and Buss Ko-kneader and prepared by either compression or injection moulding. The compression moulded material shows virtually no fibres protruding from the fractured surface, thus

PLATE 9 - fractured test pieces of
(a) compression moulded material from two roll mill (25% glass)
(b) compression moulded material from two roll mill (40%glass)
(c) injection moulded material from two roll mill (25% glass)
(d) injection moulded material from two roll mill (40% glass).

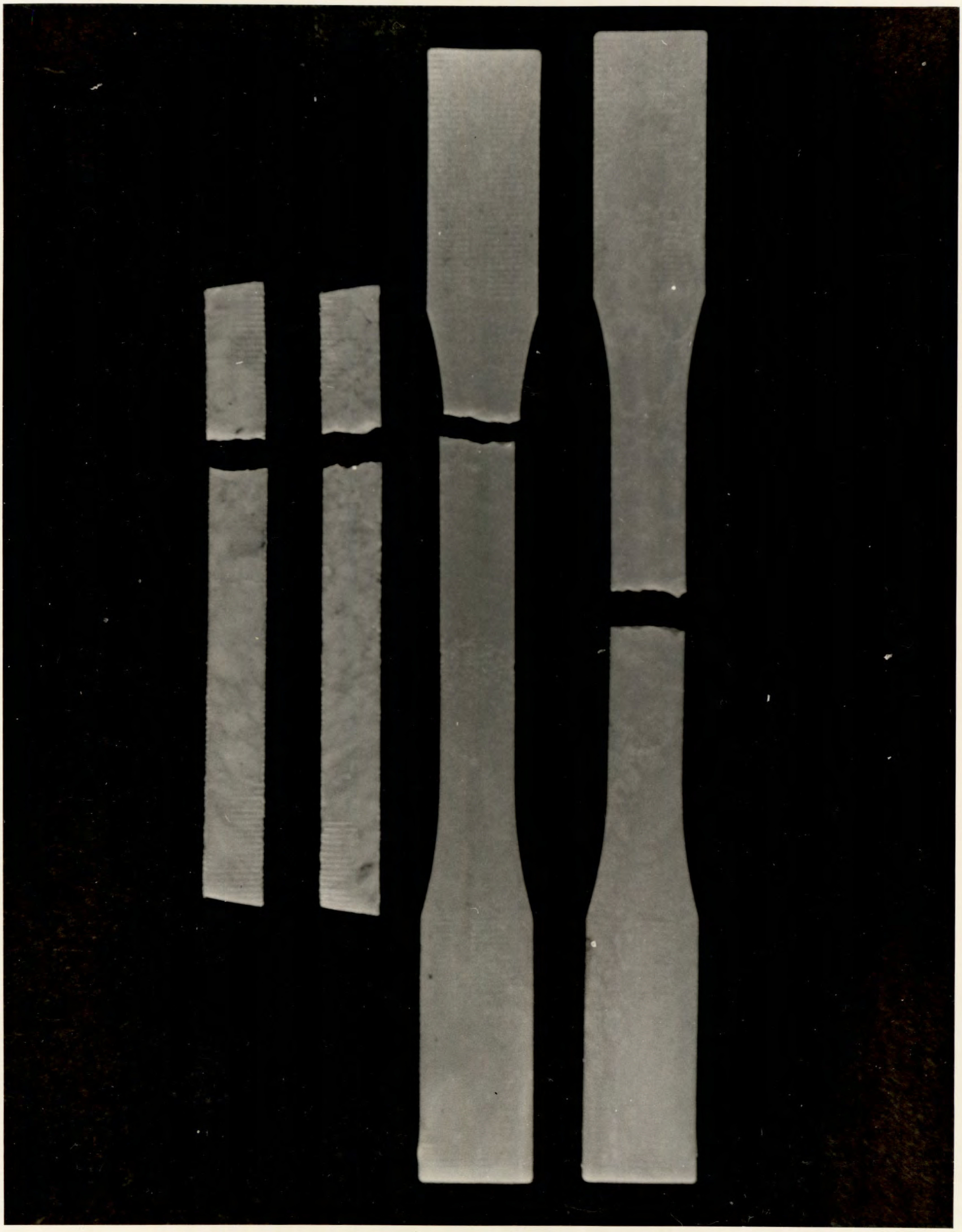
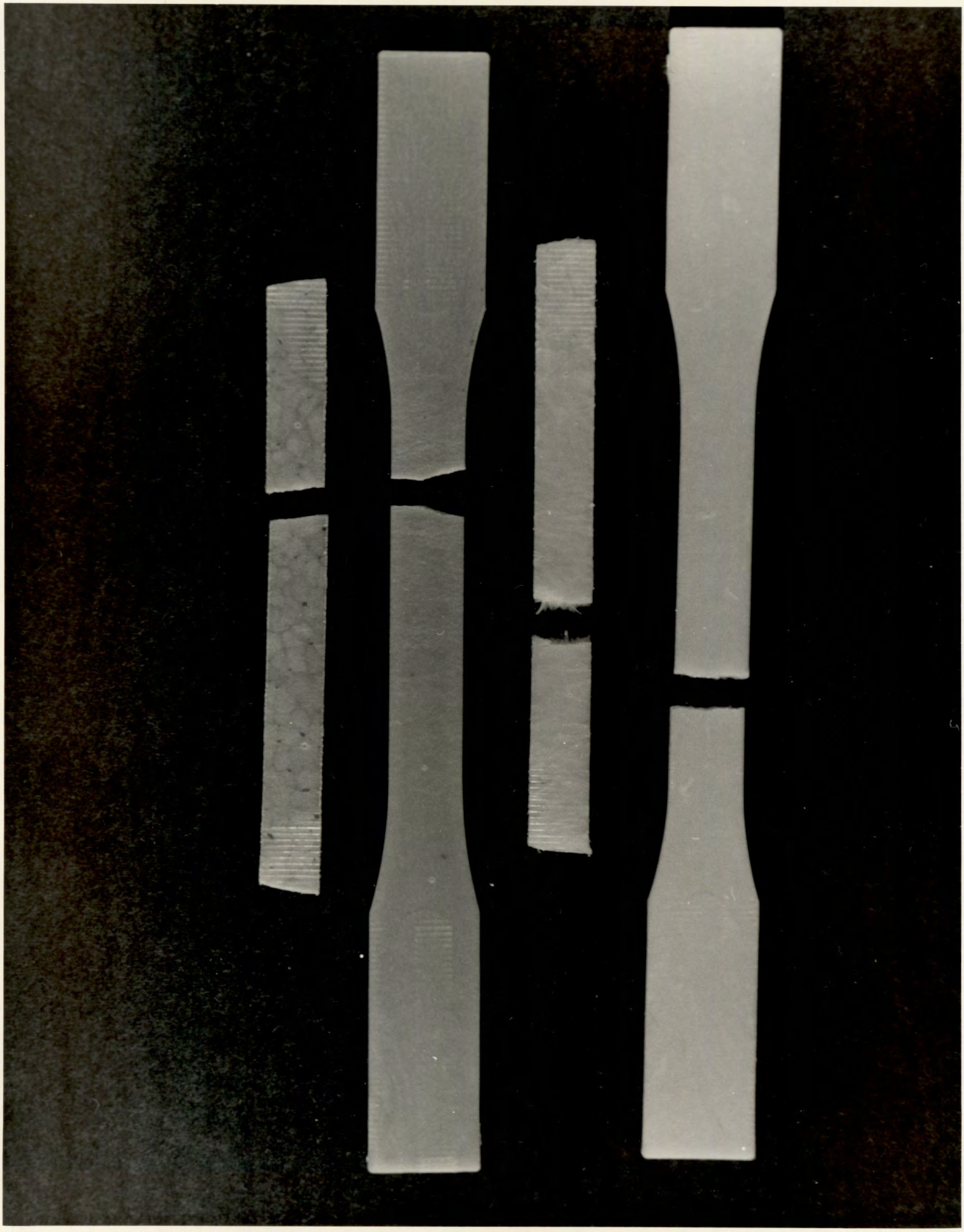


PLATE 10 - fractured test pieces of

(a) compression moulded material from Buss Ko-kneader (25% glass)
(b) injection moulded material from Buss Ko-kneader (25% glass)
(c) compression moulded hand-stirred material (25% glass)
(d) injection moulded dry blended material (25% glass).



fitting in with the idea of poor fibre distribution across the granule boundary (see plates 11 and 12)*. On the other hand, exactly similar materials, when injection moulded, show a profusion of glass fibres protruding from the surface of the fracture (see Plates 13 and 14). Plate 15 shows the very long (and poorly distributed) fibres protruding from the fractured surface of a hand stirred compression moulded material.

For the compression moulded specimens hand stirring was carried out in the mould: for injection moulding the hand stirring was carried out in a tray at 210°C. In view of the successful injection moulding of this chopped material (see Table 25, page 84) it was decided to attempt to mould dry blends on the small plunger type machine used - all the available literature indicated that this attempt would be unsatisfactory.

Dry blending was carried out on three fundamentally different types of machine:- a high speed mixer (the Papenmeier), a Z blade mixer (the Winkworth) and a blender (the Rotocube). The property levels obtained with each type of dry blending are given in Tables 27 and 28 (pages 85 and 86). Surprisingly it was the lowest shear machine - the Rotocube - which gave the best results, in spite of the fact that it did not even separate the filaments in each strand, even if the dry blending was carried out for an hour. Evidently sufficient dispersion and wetting occurred on passage through the injection moulding machine, to give satisfactory properties. These satisfactory results are quite interesting as previous workers with

* Magnification 150x.

PLATE 11 - fractured surface of a bar compression moulded from material prepared on the two roll mill for 15 minutes at 175°C (Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

PLATE 12 - fractured surface of a bar compression moulded from material prepared in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C).(Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

PLATE 13 - fractured surface of a bar injection moulded from material prepared on the two roll mill for 15 minutes at 175°C. (Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

PLATE 14 - fractured surface of a bar injection moulded from material prepared in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C).(Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

PLATE 15 - fractured surface of a bar compression moulded from hand stirred material (Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

dry blends suggest that complex blending equipment and use of screw type machines are necessary in order to obtain satisfactory properties. Comparison of Plate 16 with Plate 15 shows that the injection moulded dry blend contains much better dispersed fibres than the compression moulded hand stirred material; the injection moulded dry blend does still contain a few undispersed fibre bundles, however, - see Plate 17.

Tables 37 - 42 (pages 94-96) show the effect on properties of using a different staple length of glass fibre in the dry blend viz XG 496 glass (chrome coupling agent) of 1/4", 1/2" and 1" chopped lengths. In fact there was no great difference in properties. A rough visual examination of the glass fibres (after burning away the polymer from the moulded specimens) suggested that the 1/4", 1/2" and 1" chopped strands were all being broken down to a roughly similar length during injection moulding.

The effect of processing method on the tensile properties of injection moulded material can be seen from figures 20 and 21 (pages 133 and 134). The material prepared on the two roll mill and the dry blended material are very similar while the material prepared in the Buss Ko-kneader is inferior. This inferiority is almost certainly due to the very short fibre length present (see Figure 11, page 115). Wagner et al[95], in their paper on glass reinforced acetal copolymer, have used the expression

$$L_c/D = T_f/2S$$

PLATE 16 - fractured surface of a tensile bar injection moulded from a dry blend (Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand).

PLATE 17 - fractured surface of a tensile bar injection moulded from a dry blend (Kematal M90-04 + 25% 1/4" ECO 115 chopped glass strand) showing an undispersed fibre bundle.

where L_c = critical length of fibre

D = diameter of fibre

T_f = tensile strength of fibre

S = shear strength of the interface bond

to calculate a critical fibre length of 0.25 mm. The critical length of the fibre is the least sufficient length to cause it to break rather than slip in the matrix – fibres must therefore be above this length if their high strength is to be fully utilised. If one refers to the fibre length histograms (pages 111 – 115) then it can be seen that with the Buss Ko-kneader material virtually all the fibres are less than this critical length, over 50% being less than half this length. This is certain to cause a severe deterioration in composite properties thus fitting in with the observed results.

Tables 12,23 and 24 (pages 70, 81 and 82) show that for both injection and compression moulded test pieces, the tensile properties remain virtually unchanged with increasing time of processing on the two roll mill. This rather surprising observation is explained by reference to the fibre length histograms (pages 111 – 115), which show that a very rapid fibre breakdown occurs initially on the mill and then very little further breakdown occurs. One possible reason for this has already been postulated (see page 128).

Figure 22 shows the effect of processing method on elongation at break for injection moulded material. A somewhat inexplicable

FIGURE 22


Elongation at Break (%)
(a) M90-04 + ECO 115 (Buss-Ko kneader) : ⊡
(b) M90-04 + ECO 115 (Two Roll mill) : ⊙
(c) M90-04 + ECO 115 (dry blended) : +
(d) M90-04 + XG 496 (dry blended) : ×
(a)
(b)
(c)
(d)
Glass fibre content(%)
0
5
10
15
20
25
30
35
40
45
50
0
0
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1

minimum occurs in the plot of elongation against glass content - the position of this minimum is affected by the processing method used.

Comparison of Figures 23 - 26 shows the effect of processing method on Izod impact strength for injection moulded specimens. Once again the material prepared in the Buss Ko-kneader, with its short fibre length, is inferior but now materials prepared on the two roll mill and by dry blending are very different. It was stated in Chapter I that fibre length is especially important where impact strength is concerned and it is the differing fibre lengths of the various materials which explain their differing impact properties.

It can be seen that, on going from material prepared on the two roll mill to dry blended material, the notched impact strength (I_n) is improved considerably while the difference between unnotched and notched impact strengths ($I_u - I_n$) remains fairly similar. I_n can be crudely taken as representing a crack propagation energy (the notch representing an initiated crack), whilst $I_u - I_n$ represents a crack initiation energy. Thus the increased fibre length in the dry blended material brings about an increase in the crack propagation energy while the crack initiation energy remains substantially unaltered.

Finally Figure 27 shows the effect of processing method on hardness. Here it can be seen that the two roll mill gives rise to a material superior to that from dry blending - this may be due to the inferior fibre dispersion in the latter which could give

FIGURE 23

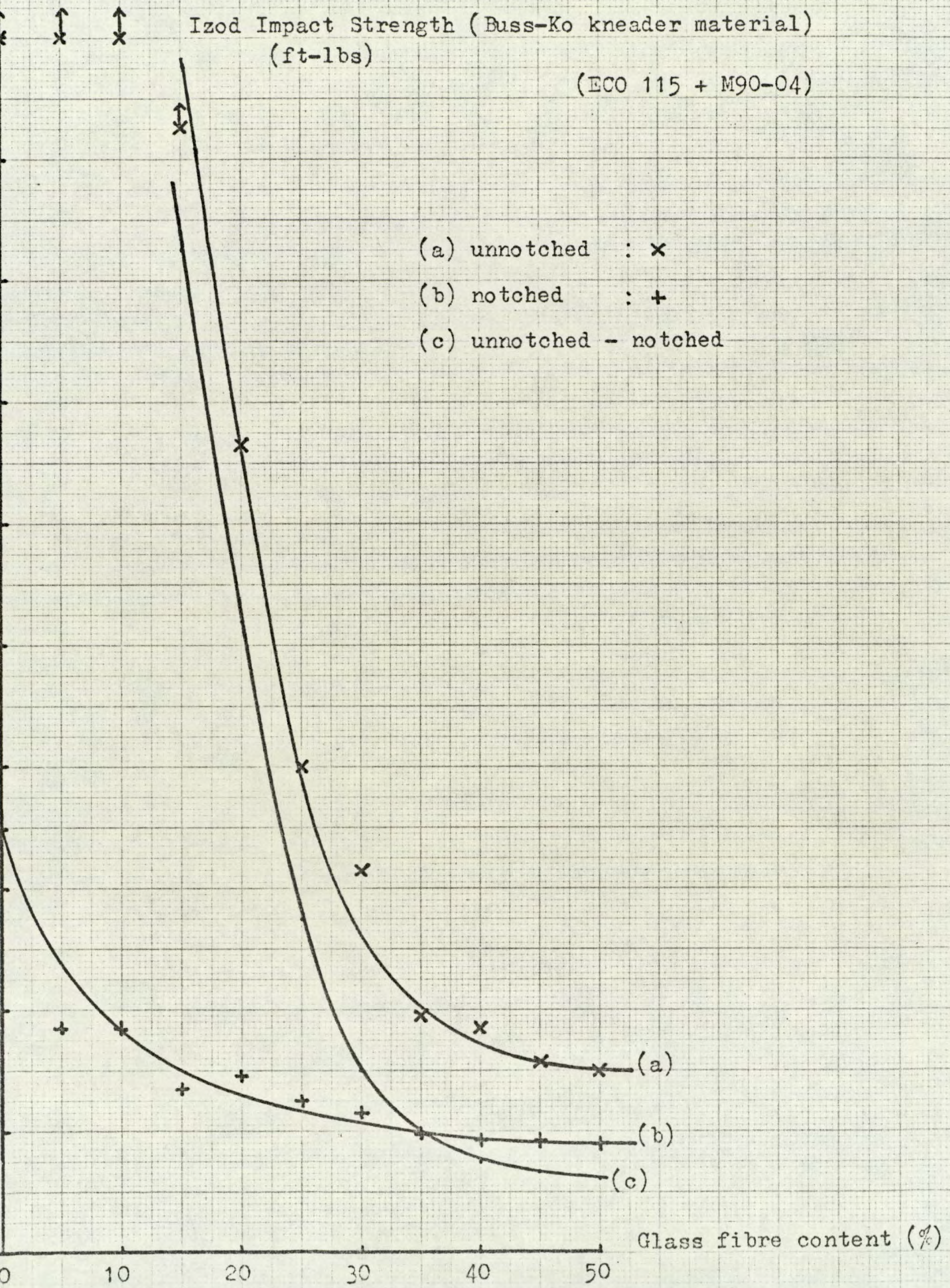

Izod Impact Strength (Buss-Ko kneader material)
(ft-lbs)
(ECO 115 + M90-04)
(a) unnotched : ×
(b) notched : +
(c) unnotched - notched
(a)
(b)
(c)
Glass fibre content (%)
0
10
20
30
40
50

FIGURE 24

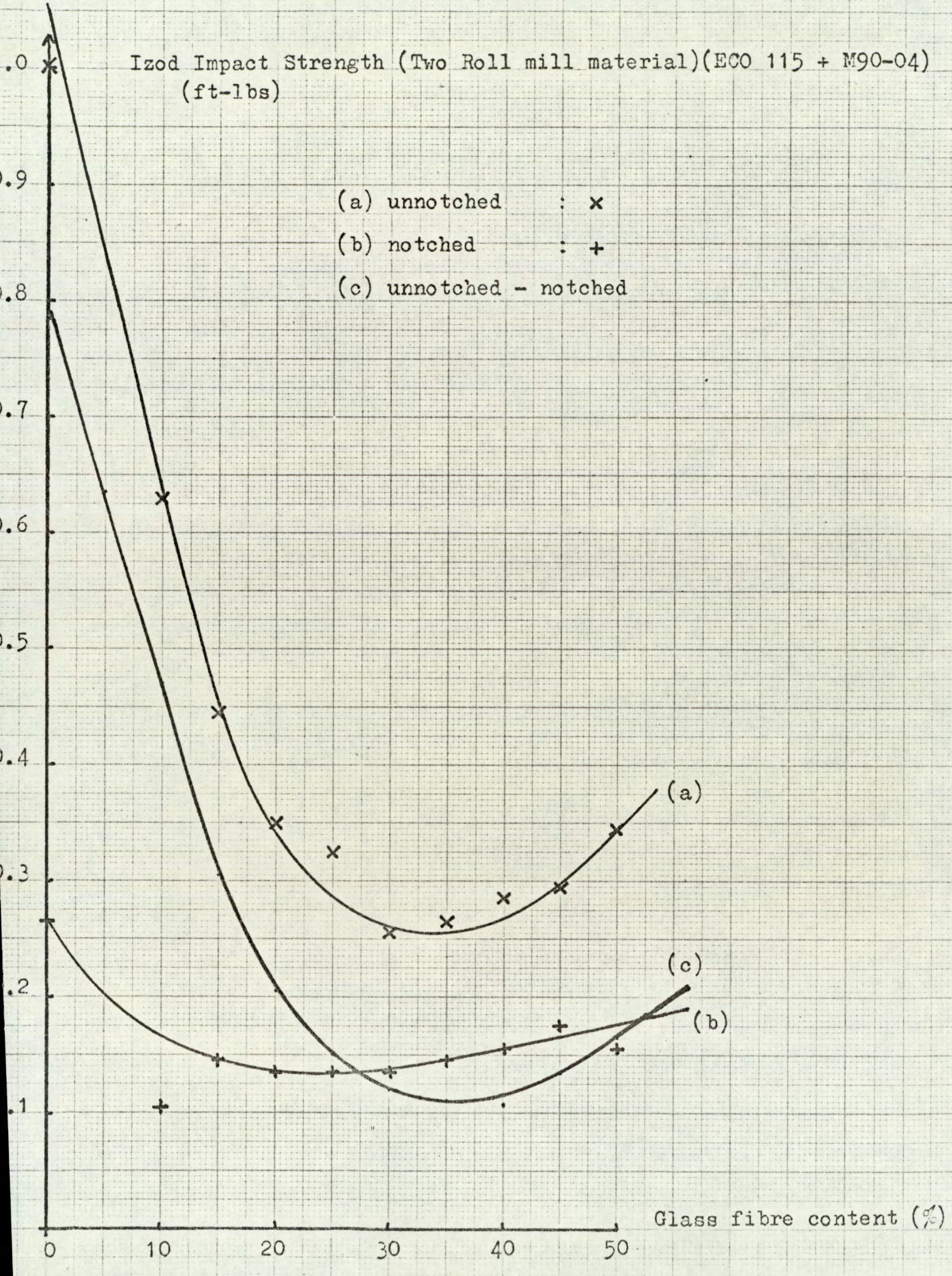

Izod Impact Strength (Two Roll mill material)(ECO 115 + M90-04)
(ft-lbs)
(a) unnotched : ×
(b) notched : +
(c) unnotched - notched
.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
(a)
(c)
(b)
Glass fibre content (%)
0
10
20
30
40
50

FIGURE 25

Izod Impact Strength (dry blended material)
(ft-lbs) (ECO 115 + M90-04)

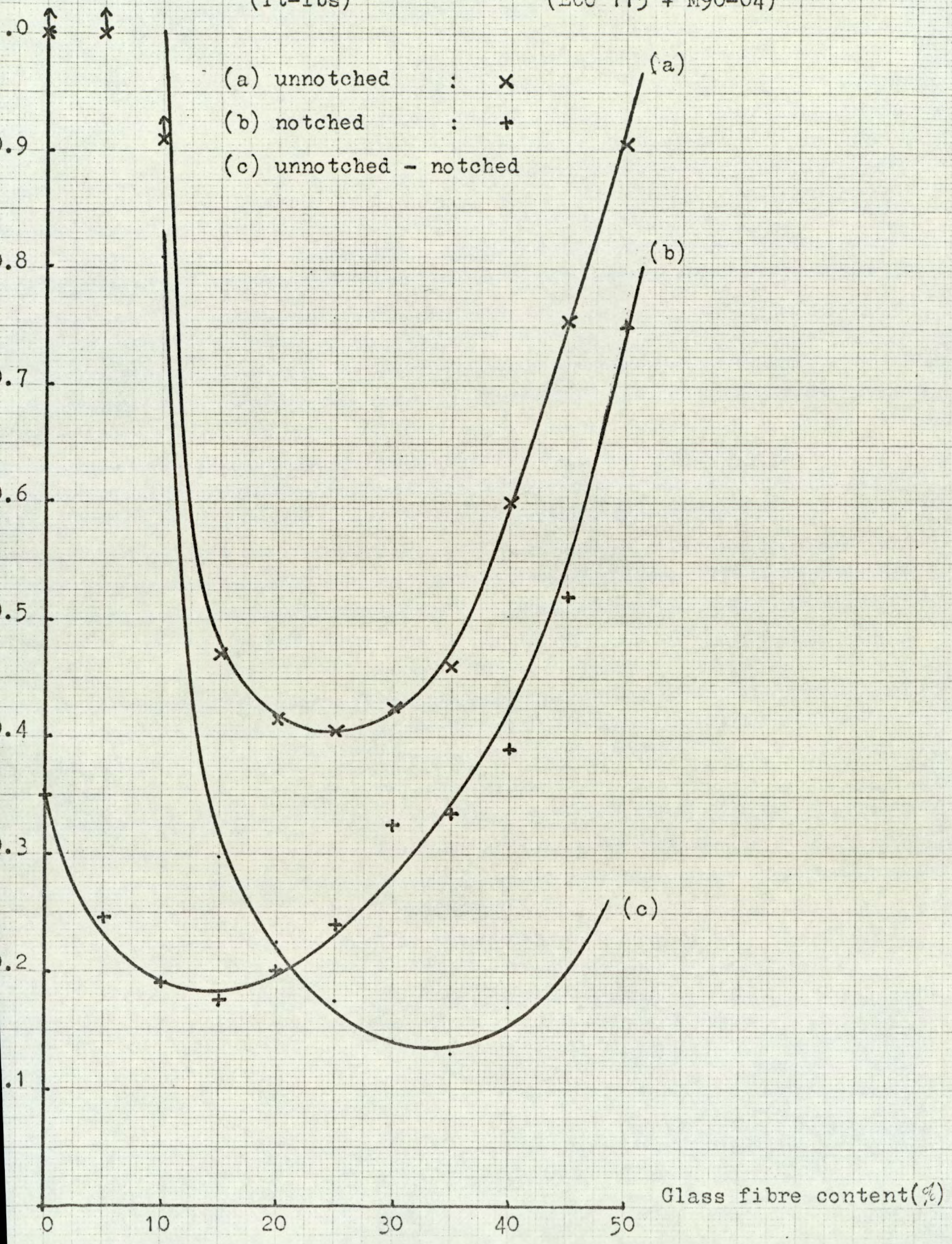


FIGURE 26

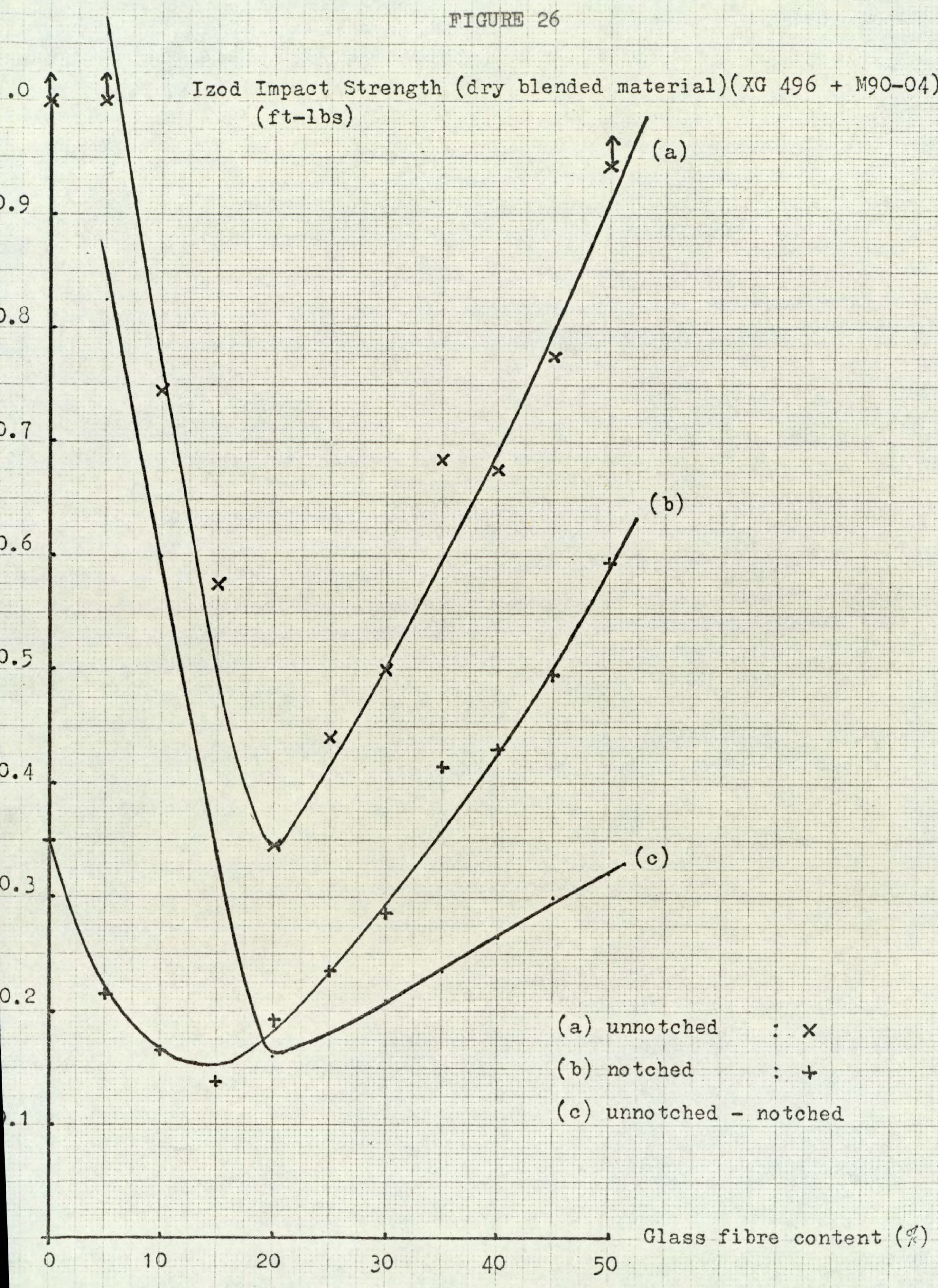

Izod Impact Strength (dry blended material)(XG 496 + M90-04)
(ft-lbs)
.0
.9
.8
.7
.6
.5
.4
0.3
0.2
.1
0
10
20
30
40
50
Glass fibre content (%)
(a)
(b)
(c)
(a) unnotched : ×
(b) notched : +
(c) unnotched - notched

FIGURE 27


Barcol Hardness
35
30
25
20
15
10
5
0
(a) M90-04 + ECO 115 / Buss-Ko kneader : ⊡
(b) M90-04 + ECO 115 / Two Roll mill : ⊙
(c) M90-04 + ECO 115 / dry blend : ×
(d) M90-04 + XG 496 / dry blend : +
(a)
(b)
(c)
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50

rise to "soft spots" at the surface. Once again, material prepared in the Buss Ko-kneader is poorest, presumably due once again to the very low restraining power of its short fibres.

It should perhaps be mentioned that the previous remarks concerning the effect of processing method on properties refer to systems based on Kematal M90-04 copolymer and 1/4" ECO 115 chopped glass strand (vinyl silane coupling agent and polyvinyl acetate binder). It is not necessarily correct to transfer conclusions reached above in unmodified form to other systems. For instance reference to Tables 43 and 20 will show that, as far as tensile strength was concerned, dry blended material was appreciably superior to material prepared on the two roll mill with glasses XG 496 (chrome coupling agent) and XG 438 (methacrylato silane coupling agent) whereas this was definitely not so with ECO 115 glass.

B. Effect of glass fibre content on properties.

One of the immediately obvious effects of increasing glass content, with injection moulded specimens, is the increasing deterioration of the surface (see Plate 18). The difference in coefficients of expansion of the polymer and the glass ensure that the contours of underlying glass fibres will be visible externally.

The restraining influence of the glass fibre on the coefficient of thermal expansion of acetal copolymer is illustrated very clearly in Plate 18 which shows the decreasing mould shrinkage of the composite with increasing glass fibre content.

As far as the effect of glass content on tensile properties is concerned it is interesting to look first at the general shape of various tensile break curves (see Figures 28 - 31). It should be stressed that these are not stress-strain curves, merely curves of force against crosshead movement as plotted directly by the tensile testing machine. The first observation is that the injection moulded unmodified acetal copolymer exhibits considerably tougher behaviour than compression moulded acetal. It was thought that this could have been due to micro-cracks induced on sawing the compression moulded discs, but the greater level of residual stress present in compression moulded specimens may also play a part. The area under the tensile break curves gives some idea of the energy required to fracture and it can be seen how badly the two roll milled/compression moulded material compares with the other materials. The reason for this has been discussed on page 136. It can be seen from

PLATE 18 - Tensile bars injection moulded from material prepared in the Buss Ko-kneader (2 passes at 30 r.p.m. and nominal 160°C). Kematal M90-04 with 0, 5, 10, 15, 20, 30, 40, 50% ECO 115 respectively.

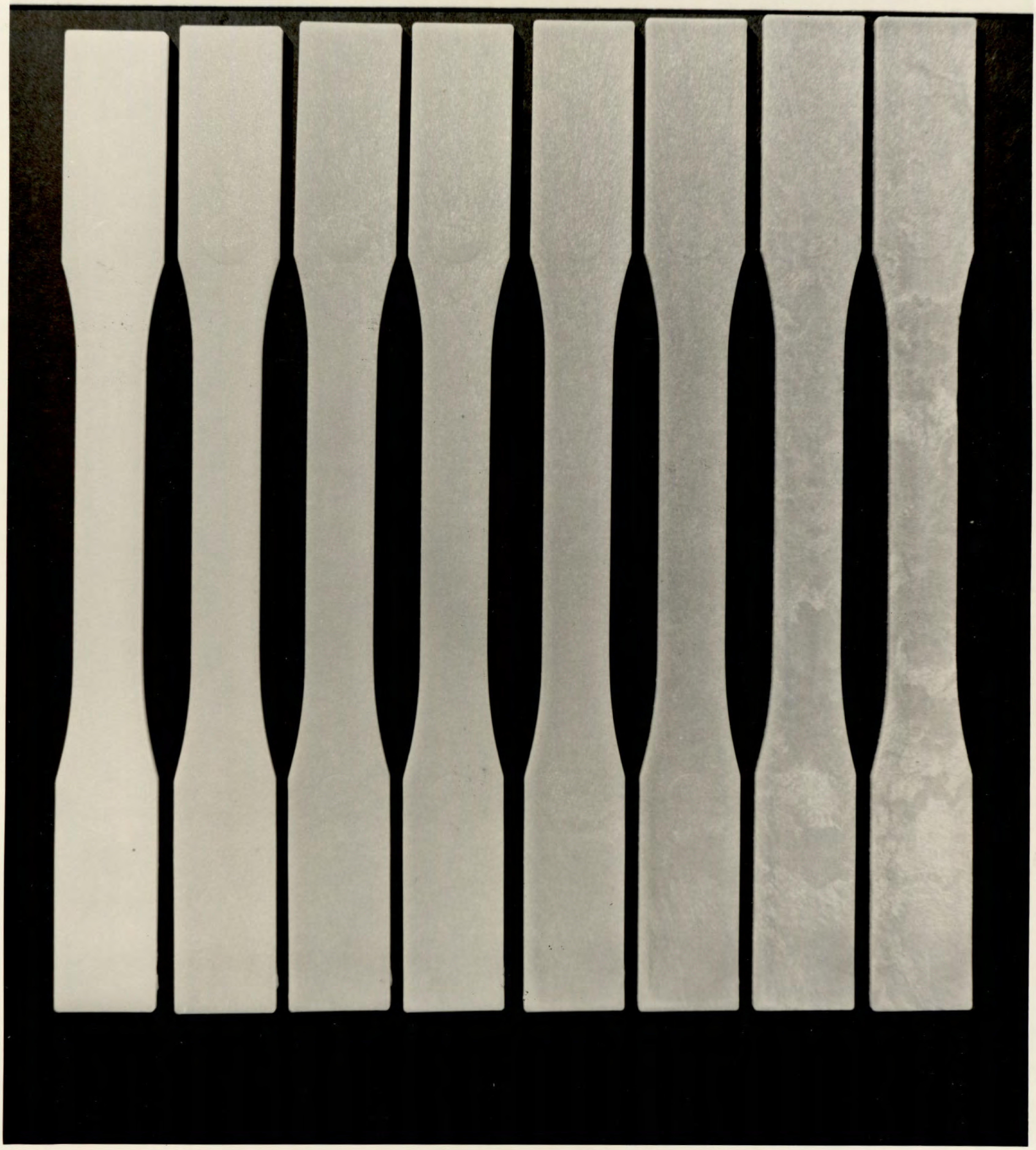
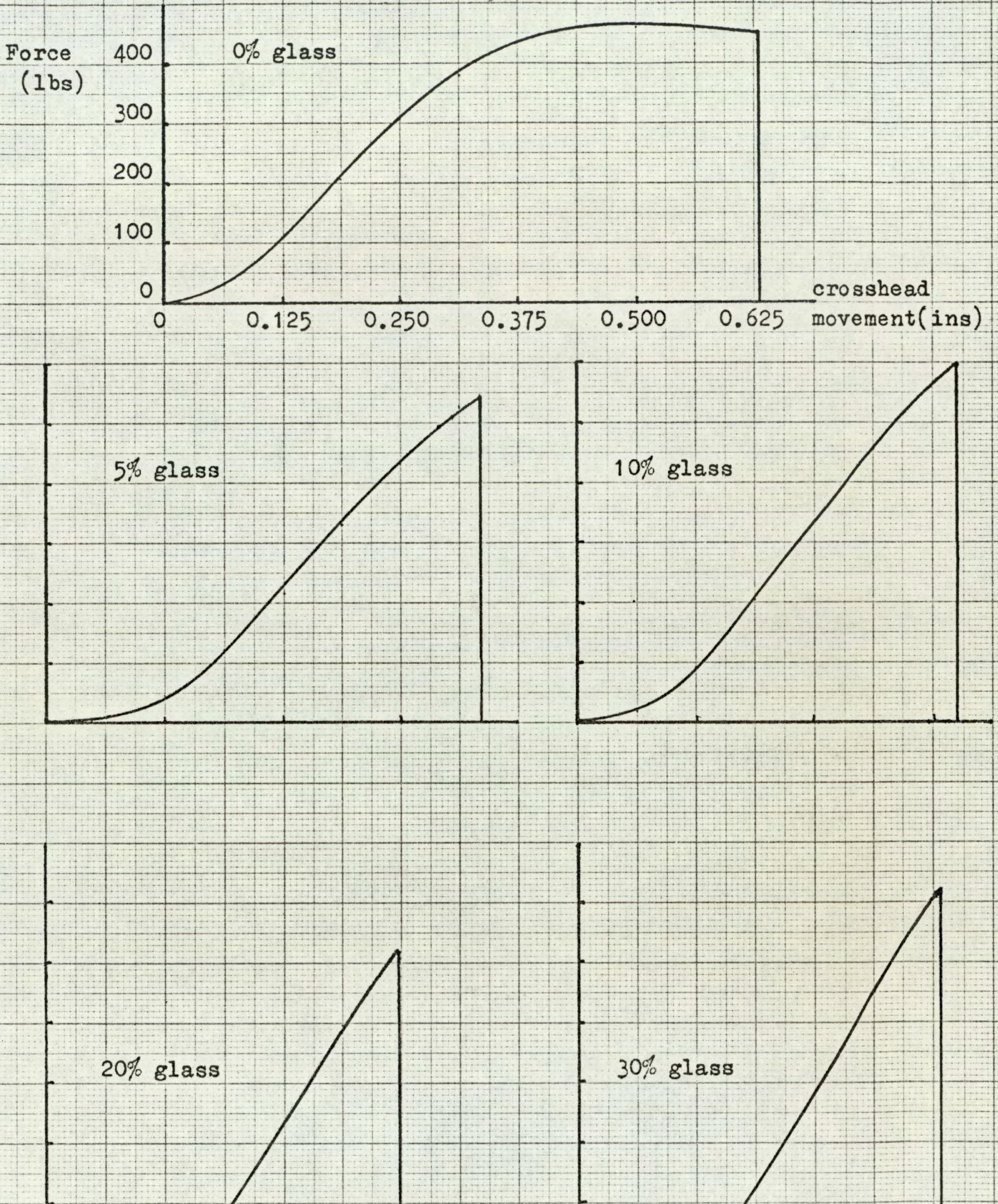


FIGURE 28

Two Roll Mill/compression moulded material.

FIGURE 29.



Hand stirred/compression moulded material.

FIGURE 30

Two Roll Mill/injection moulded material

FIGURE 31

Injection moulded dry blend

the tensile break curves that a fairly rapid transition from tough to brittle behaviour occurs with the introduction of quite low percentages of glass into the acetal copolymer (see also Plate 19).

Figures 18 -21 (pages 131 - 134), as well as showing the effect of processing method on tensile properties, also show the effect of fibre content on tensile properties.

Considering first the tensile modulus of compression moulded specimens, the hand stirred material shows a linear increase with increasing glass fibre percentage. This behaviour agrees very well with that recorded for a compression moulded glass reinforced polystyrene system by Lieng-Huang Lee[130]. The system was very similar to the one used here for acetal copolymer; it involved dry blending polystyrene powder with 1/4" glass chopped strand and compression moulding this into 1/8" thick sheets, test bars being cut from the moulded sheet. Lieng-Huang Lee quotes the equations

$$E_c = E_f V_f + E_m (1 - V_f)$$

applicable to a composite containing uni-directional continuous fibres and

$$E_c = K E_f V_f + E_m (1 - V_f)$$

for a composite containing random fibres, where

E = tensile modulus

V = volume fraction

K = fibre efficiency

and subscripts c, f and m refer to composite, fibre and matrix respectively.

PLATE 19 - fractured tensile bars from material prepared in the Buss Ko-kneader (two passages at 30 r.p.m. and a nominal 160°C): Kematal M90-04 + 0, 5, 10, 15, 20, 30, 40, 50% ECO 115 respectively.

The variation of tensile modulus is thus predicted theoretically to be linear with volume fraction of glass. Lees has attempted a more sophisticated treatment of the variation of tensile modulus with glass content in a paper entitled "A Study of the Tensile Modulus of Short Fiber Reinforced Plastics"[131]. He accepts that the"law of mixtures" equation (quoted above) agrees well with the observed behaviour of continuous and long fibre reinforced systems but claims that it does not agree with the observed behaviour of short-fibre reinforced systems. Lees suggests first that fibre-matrix adhesion may influence the tensile modulus but goes on to state that recent experimental work by others rules this out. This is supplemented by work which shows that for an inclusion whose modulus is greater than that of the matrix the radial stresses at the interface are directed towards the fibre. These radial stresses could thus provide the needed stress transfer force and render composite modulus independent of adhesion.

Lees points out that the other possible reason for non-agreement with the"law of mixtures" is that the assumption that the elongations of the fibre and matrix are equal (this assumption is implicit in the law of mixtures equation) is incorrect and that flow of the matrix with respect to the fibre occurs. Lees then derives a complex equation on the basis of this hypothesis and shows quite good agreement with his experimental results. This equation however still suggests that a linear variation of the modulus with the volume fraction of glass will be observed, as the theoretical non-linearity will be outside the range of experimental detection.

If the tensile modulus results for injection moulded specimens presented in this thesis are plotted against the volume fraction of glass then a very nearly linear plot is in fact obtained (see Figures 32 - 34). There is, however, some upward deviation from this line occurring at higher glass contents and it is interesting to speculate on the possible reasons for this. The theoretical and experimental observations by Lees, described above, apply strictly to fully orientated systems but the injection moulded acetal copolymer specimens do not have fully orientated fibres. This would only affect the linear variation of modulus with glass content if the degree of orientation varied with increasing glass content. Surface fibre orientation studies show that this indeed may be so (see Figures 12 and 13, pages 118 and 119), the degree of fibre orientation apparently increasing with increasing glass content. This must presumably be due, if true, to the glass fibres exerting some mutual effect, which causes fibres lined up along the bar axis to help in the aligning of others during the flow of the melt into the mould.

It is interesting at this stage to compare the tensile modulus variation with glass content, for both compression and injection moulded material prepared on the two roll mill (see Figure 35). Any weak spots in the compression moulding should not affect the tensile modulus significantly and so the difference between the two curves is probably mainly a reflection of the differing degrees of fibre

FIGURE 32

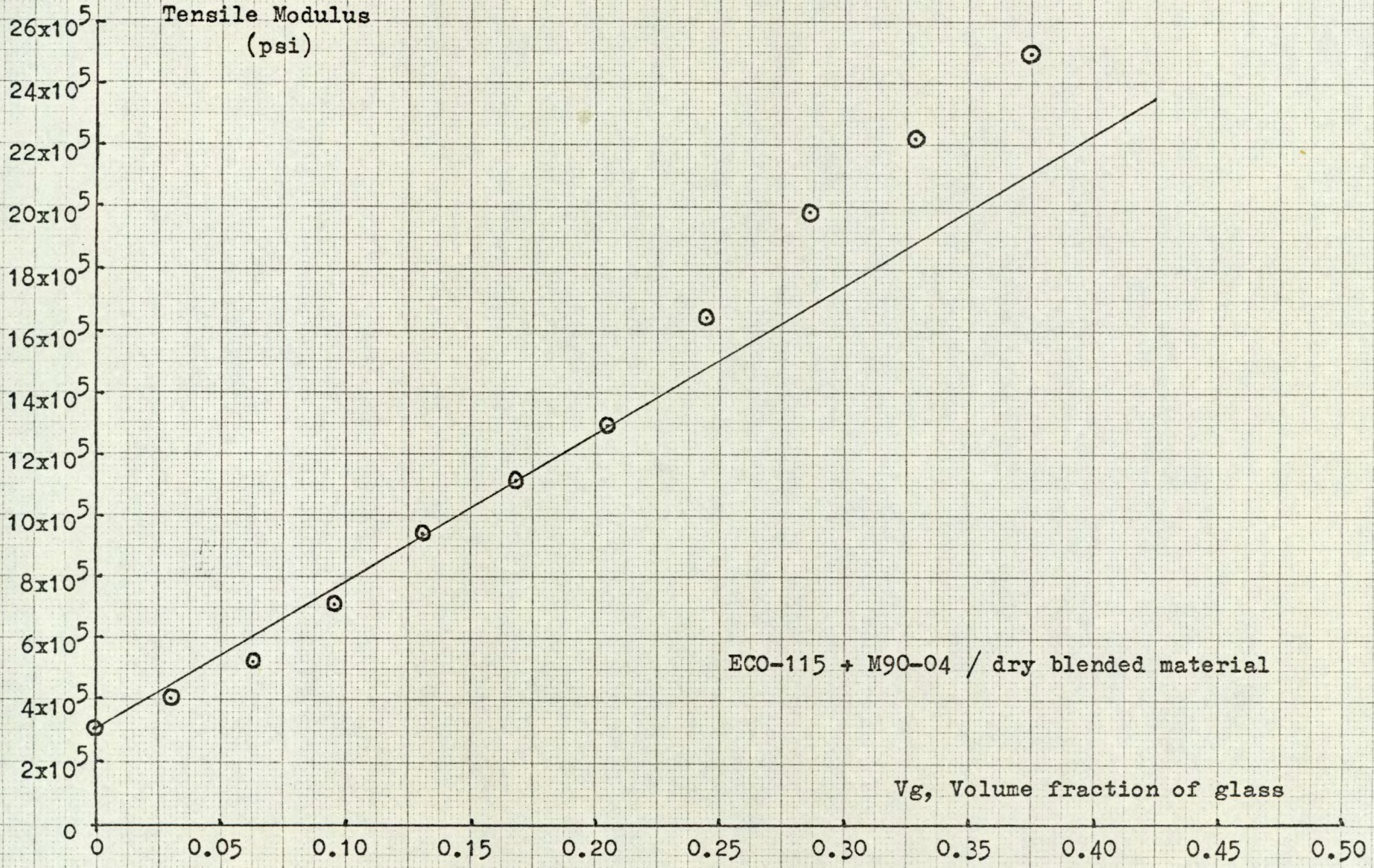
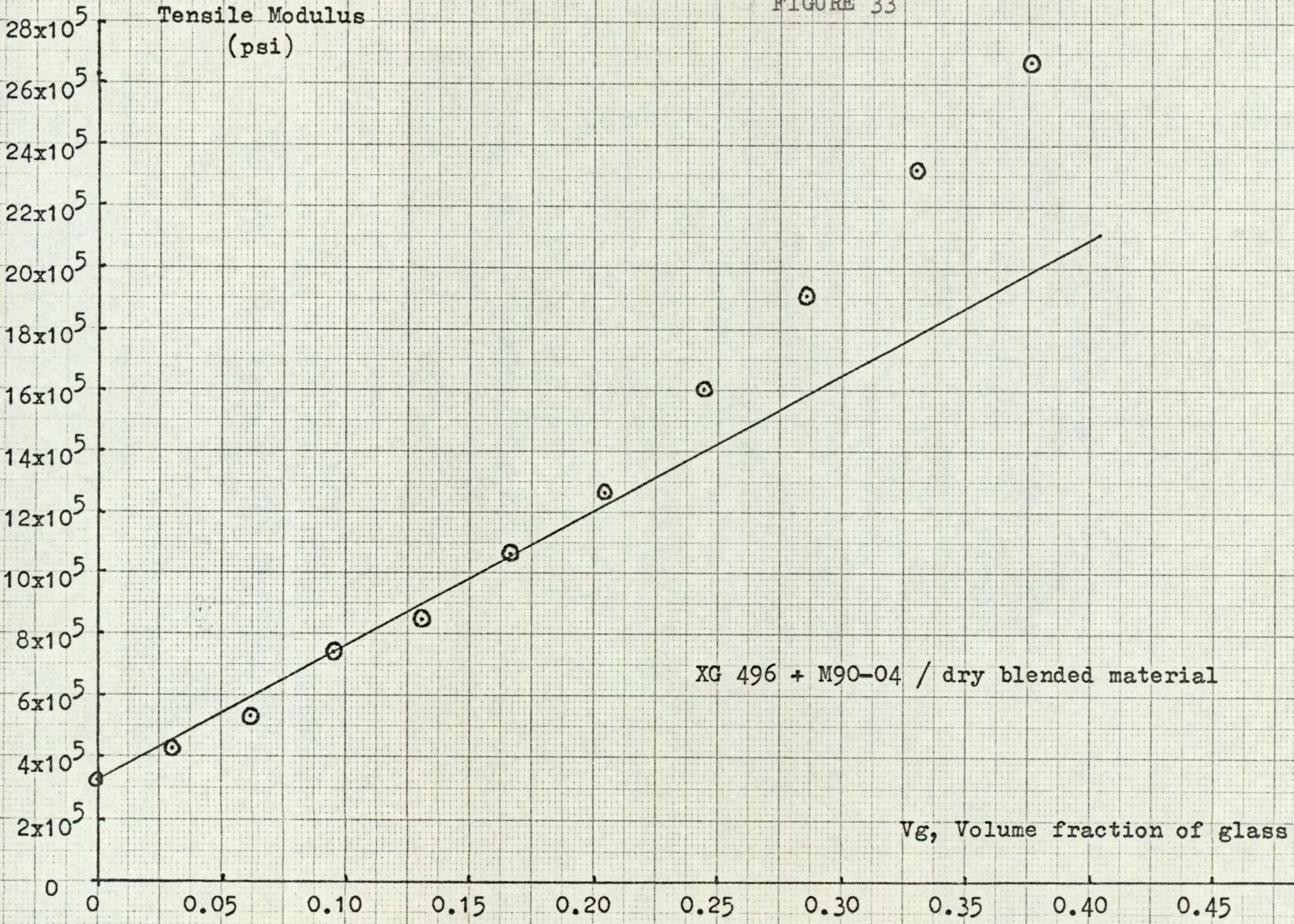

Tensile Modulus
(psi)
26x10^5
24x10^5
22x10^5
20x10^5
18x10^5
16x10^5
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
ECO-115 + M90-04 / dry blended material
Vg, Volume fraction of glass
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

FIGURE 33



Tensile Modulus (psi)
28x10^5
26x10^5
24x10^5
22x10^5
20x10^5
18x10^5
16x10^5
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
XG 496 + M90-04 / dry blended material
Vg, Volume fraction of glass

FIGURE 34

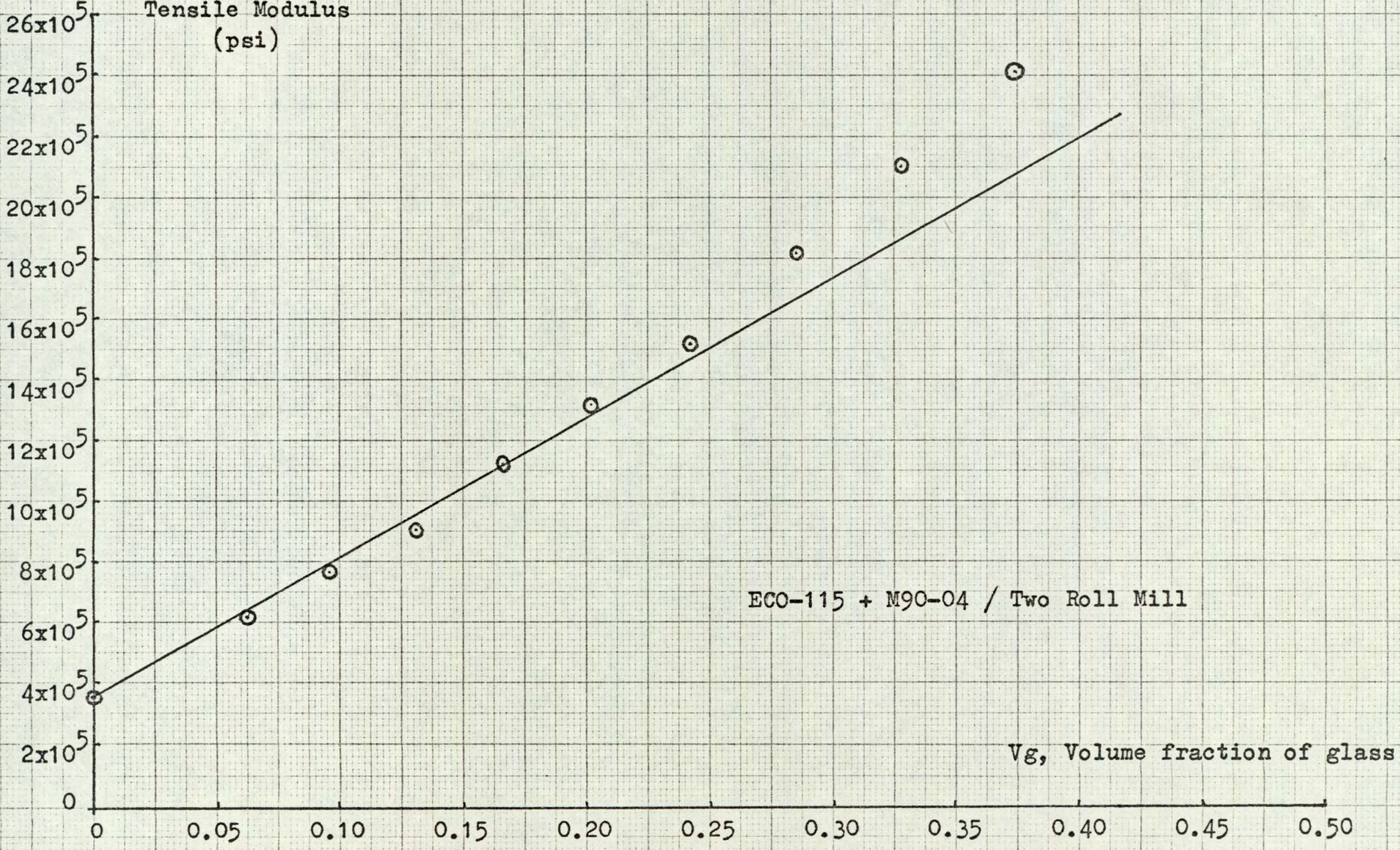

Tensile Modulus
(psi)
26x10^5
24x10^5
22x10^5
20x10^5
18x10^5
16x10^5
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
ECO-115 + M90-04 / Two Roll Mill
Vg, Volume fraction of glass
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

FIGURE 35


Tensile Modulus
(psi)
M90-04 + ECO 115 / Two Roll mill
(a) compression moulded and (b) injection moulded
(a)
(b)
Glass fibre content (%)
28x10^5
26x10^5
24x10^5
22x10^5
20x10^5
18x10^5
16x10^5
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
0
5
10
15
20
25
30
35
40
45
50

orientation. It is interesting to note that the "fibre utilisation" in the compression moulded specimens is almost exactly half that in the injection moulded ones. This suggests complete orientation in the injection moulded bars and randomisation in one plane in the compression moulded bars: in fact, however, this picture almost certainly represents an over-simplification, at least if surface orientations are any guide to internal orientations (see Figures 12 - 16, pages 118 - 123).

When the tensile strength behaviour of hand stirred compression moulded material is considered then a rather peculiar variation with glass content emerges (Figure 19, page 132). This consists of a fall, followed by a rise and then a further fall. This pattern is repeated consistently with glasses other than ECO 115 (see Figure 43, page 185). A possible explanation for this behaviour is as follows. Introduction of small percentages of glass into the matrix causes sites of easy crack initiation to be set up without there being sufficient glass present to form a reinforcing network. The subsequent rise in tensile strength is due to the forming of this reinforcing network. The final fall in tensile strength is due simply to the difficulty of wetting out high percentages of glass, which results in voids and faults in the moulded test piece. The pattern of tensile strength behaviour is very much like that observed by Lieng-Huang Lee[130] for his similar glass reinforced polystyrene system.

Lees has published a theoretical treatment of the variation of tensile strength with glass content in a paper entitled "A Study of the Tensile Strength of Short Fiber Reinforced Plastics"[132]. Lees commences by giving the Kelly and Tyson equations

$$\sigma_{uc} = V_f(1 - l_c/2l)\sigma_{uf} + V_m\bar{\sigma}_m \qquad \text{when } l \geqslant l_c$$

and $$\sigma_{uc} = (\tau l/d)V_f + V_m\sigma_{um} \qquad \text{when } l < l_c$$

where $l_c/d = \sigma_{uf}/2\tau$

σ = tensile stress

V = volume fraction

l = fibre length

l_c = critical fibre length

τ = shear strength

d = fibre diameter

$\bar{\sigma}_m$ = matrix tensile stress at composite failure

and subscripts c, m and f refer to composite, matrix and fibre respectively, u indicating the ultimate value of any quantity. He quotes a modified version of these equations due to Piggott and then goes on to modify both sets of equations to take account of a fibre length distribution rather than a fixed fibre length. Quite good agreement is obtained with experimental values, when account is taken of the difference in thermal expansions of the glass and the matrix, and the effect this will have in reducing τ, the shear strength of the interfacial bond.

Examining the results obtained with glass reinforced acetal copolymer in terms of the simple Kelly and Tyson equation, then one would expect a linear variation of tensile strength with the volume fraction of glass. In addition one would expect to observe a critical volume fraction V_{fc}; at fibre volume fractions below this no reinforcement would be obtained. It can be seen from Figures 36 - 38 that, for injection moulded test pieces, the tensile strength of the composite does indeed rise linearly with the volume fraction of glass. The critical volume fractions in the cases of Kematal M90-04 and ECO 115 glass processed on the two roll mill and by dry blending appear to be almost identical. On changing to a glass with improved coupling agent the critical volume rather surprisingly rises - it is felt that this effect is spurious, due probably to the greater uncertainty in fitting a straight line to the results in Figure 38.

None of the compression moulded materials show similar behaviour. The peculiar "switchback" pattern observed with the hand stirred material has already been discussed. The compression moulded materials from the Buss Ko-kneader and the two roll mill show a steady <u>fall</u> in tensile strength with increasing glass content - the reasons for this behaviour have already been discussed (see page 136).

Considering next the variation of elongation at break with glass content, all the curves display a minimum (Figure 22, page 149). This minmum moves to a decreasing level of fibre content as other

FIGURE 36

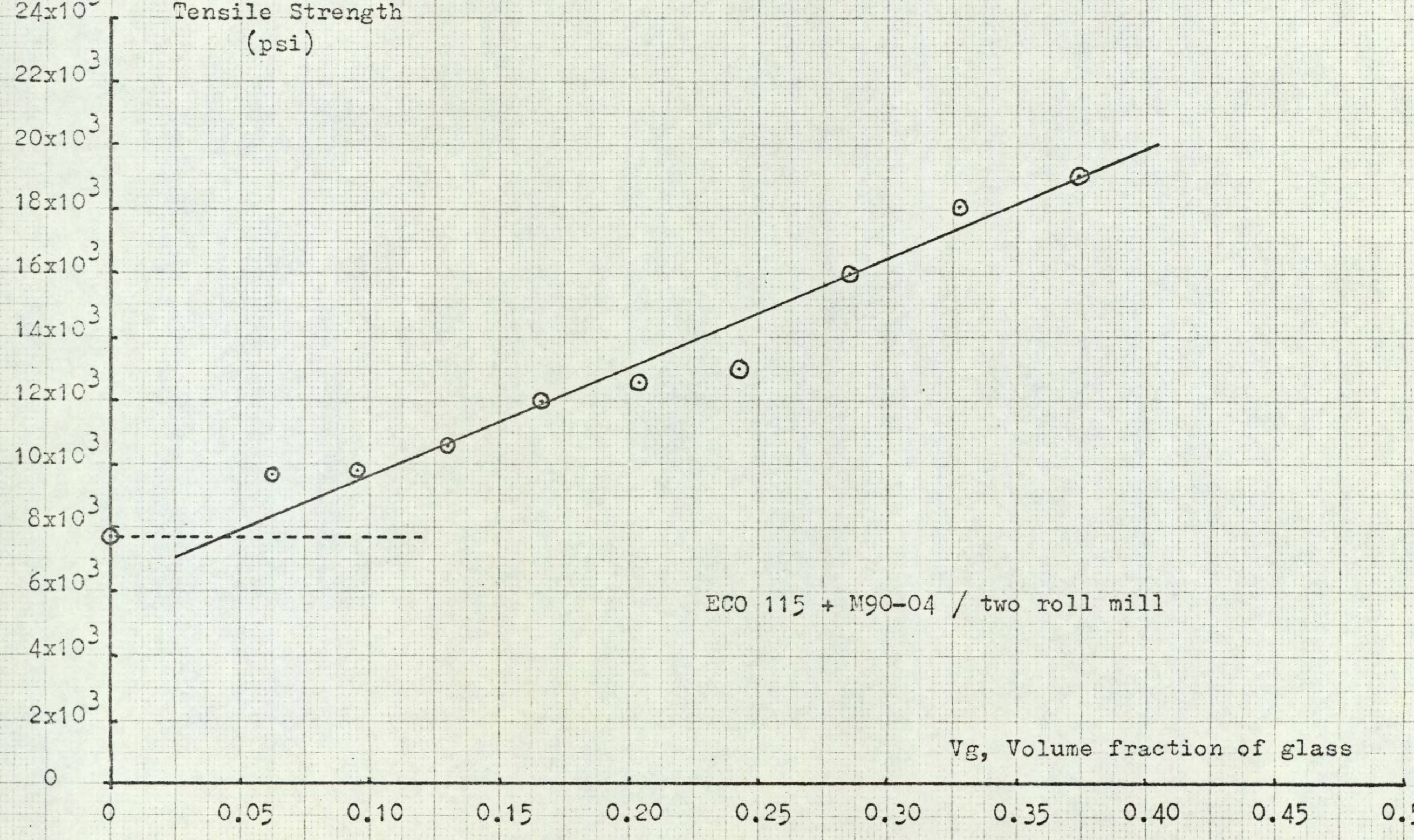

Tensile Strength
(psi)
24x10^3
22x10^3
20x10^3
18x10^3
16x10^3
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
ECO 115 + M90-04 / two roll mill
Vg, Volume fraction of glass
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

FIGURE 37

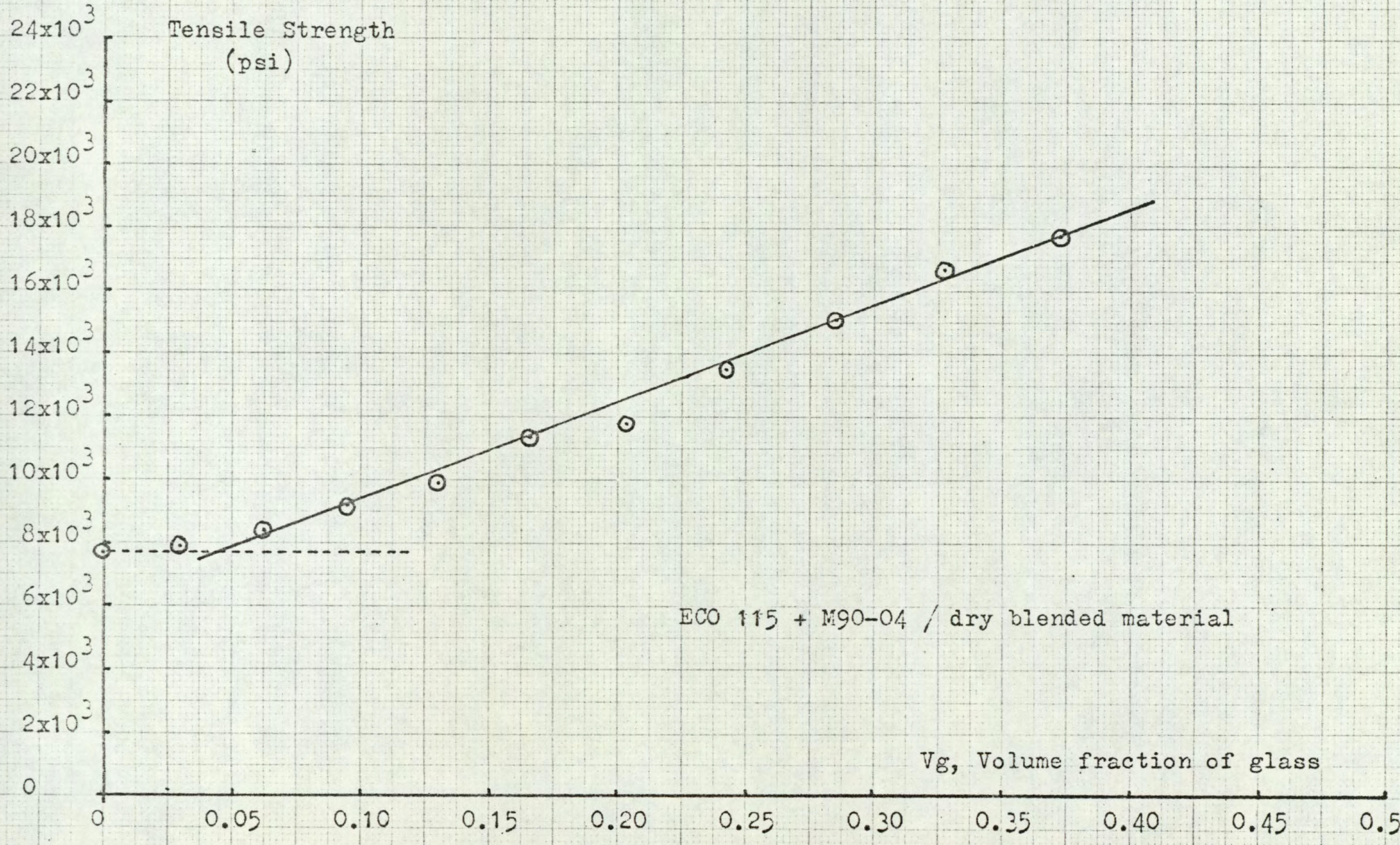
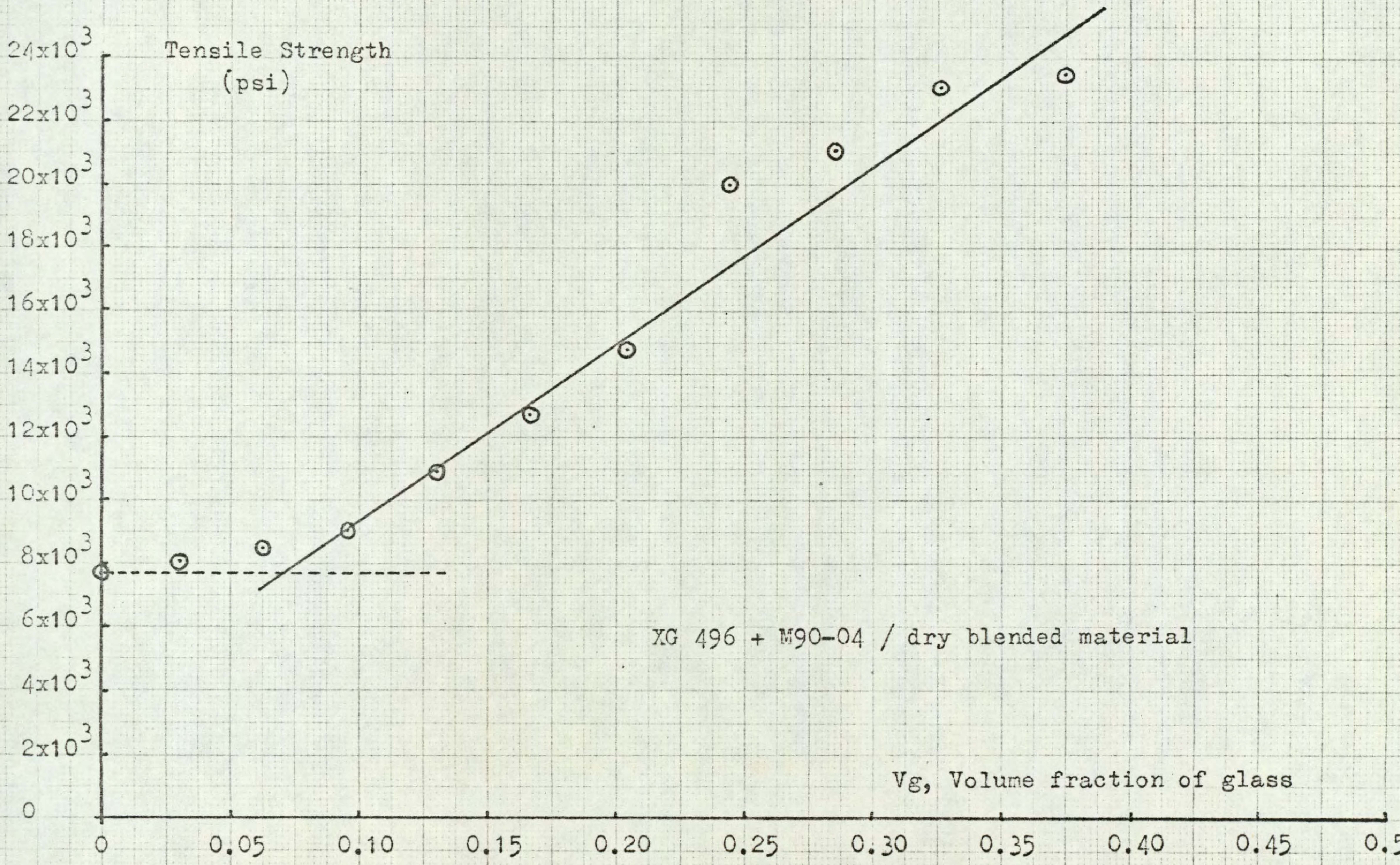

Tensile Strength
(psi)
24x10^3
22x10^3
20x10^3
18x10^3
16x10^3
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
ECO 115 + M90-04 / dry blended material
Vg, Volume fraction of glass
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

FIGURE 38


Tensile Strength
(psi)
24x10^3
22x10^3
20x10^3
18x10^3
16x10^3
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
XG 496 + M90-04 / dry blended material
Vg, Volume fraction of glass
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50

properties improve. The significance of this minimum is not understood.

An almost exactly similar pattern is observed when one considers the variation of impact strength with glass fibre content (see Figures 23 - 26, pages 151 - 154). The very short fibres present in the material prepared in the Buss Ko-kneader mean that impact strength falls off continuously with increasing glass content. With the other materials, however, a minimum is observed; increasing fibre lengths or improved coupling agents move this minimum to a position of lower fibre content. Unmodified acetal is a tough material but glass reinforced composites derived from it are brittle, and so unnotched impact strengths of the glass reinforced materials are never as good as that of the unmodified copolymer. It is the reduction in crack initiation energy which is brought about by the glass that is responsible for this phenomenon. The presence of glass fibre can hinder crack propagation, however, as is witnessed by the fact that, for the dry blended materials with more than 30 - 35% glass, the notched impact strength is actually higher than for the unmodified polymer.

Figure 27,(page 155) shows the linear increase in hardness with increasing glass content for several different materials. Finally, the reduction in the creep of Kematal brought about by the introduction of 25% and 50% glass fibre can be seen in Figure 39.

FIGURE 39


Strain(%)
Stress :- 5,000 psi
(a) Kematal M90-04 + 50% ECO 115 processed on two Roll Mill
(b) Kematal M90-04 + 35% ECO 115 processed on Two Roll Mill
(c) Kematal M90-04 + 35% XG 496 processed on Two Roll Mill
Kematal M90-04
(c)
(b)
(a)
10
9
8
7
6
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9
1 2 3 4 5 6 7 8 9
x10
1 2 3 4 5 6 7 8 9
x10^2
1 2 3 4 5
x10^3
Time(hrs)

C. The Effect of Polymer Viscosity and Type on Properties.

The effect of polymer viscosity on the tensile properties of compression moulded hand stirred material is summarised in Figures 40 and 41. The tensile strength behaviour is interesting; the "switchback" pattern observed with Kematal M90-04 (melt flow index 9) has already been discussed and a possible explanation given (see page 171). Support for this explanation comes from the behaviour observed with Kematals M25-04 (melt flow index 2.5) and M140-04 (melt flow index 14). The latter shows no fall in tensile strength on going from 30% to 40% glass, presumably indicating the easier wetting by the lower viscosity polymer. On the other hand the tensile strength with Kematal M25-04 starts to fall off above 20% glass content, indicating the much lower wetting ability of the higher viscosity material.

When one considers the tensile modulus of the compression moulded composites then it can be seen that the modulus is independent of polymer viscosity. This is presumably because the modulus is not significantly dependent on the shear strength of the bond between matrix and glass.

Reference to Tables 46 - 51 (pages 98 - 101) shows that, in injection moulded systems, use of polymers of different melt flow indices has very little discernable effect on properties; this applies to dry blends prepared with both ECO 115 (vinyl silane coupling agent) and XG 496 (chrome coupling agent) 1/4" chopped strands. This observation is interesting and use will be made of it

FIGURE 40

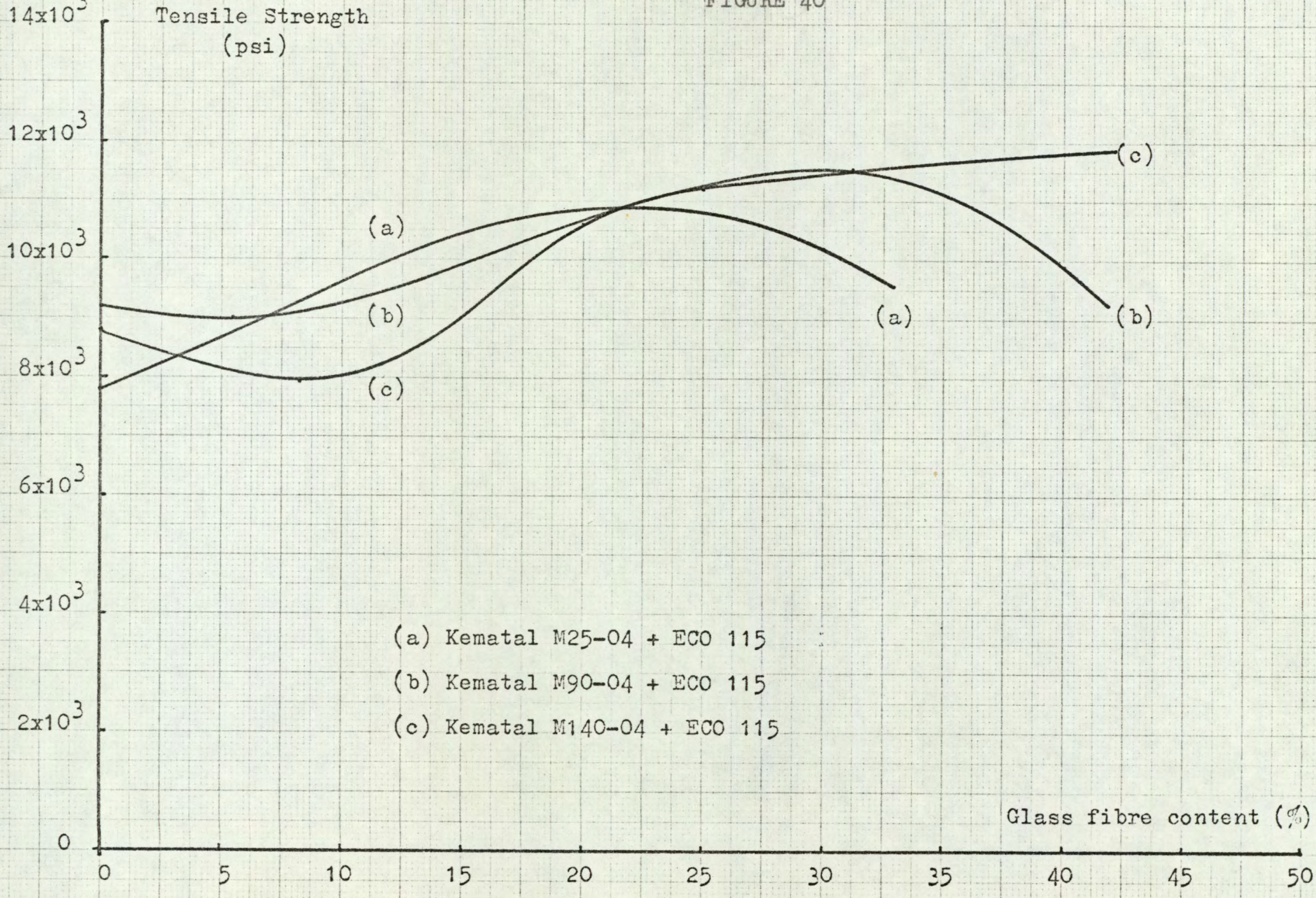
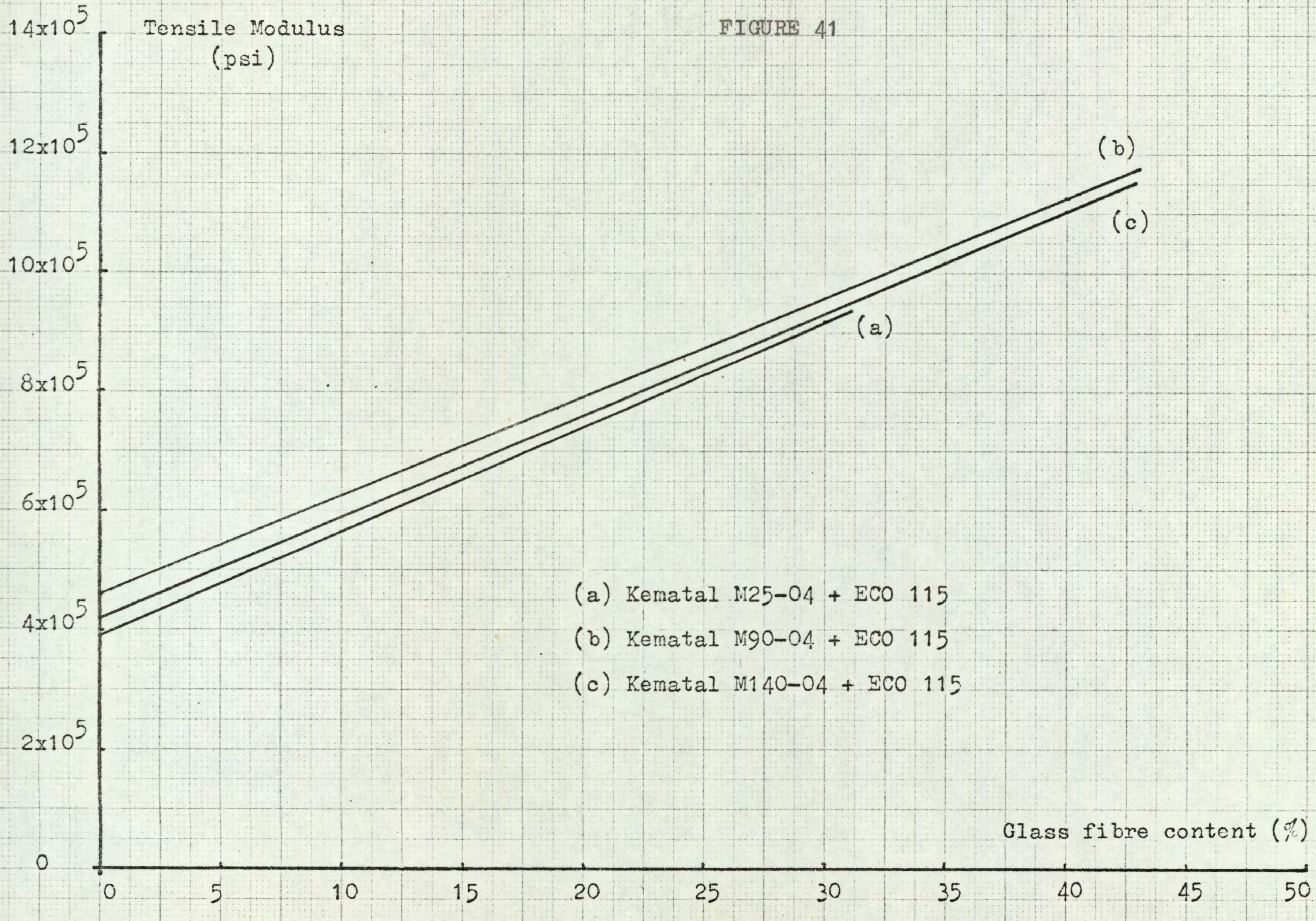

Tensile Strength
(psi)
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
0
5
10
15
20
25
30
35
40
45
50
Glass fibre content (%)
(a)
(b)
(c)
(a)
(b)
(c)
(a) Kematal M25-04 + ECO 115
(b) Kematal M90-04 + ECO 115
(c) Kematal M140-04 + ECO 115

FIGURE 41


Tensile Modulus
(psi)
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50
(a)
(b)
(c)
(a) Kematal M25-04 + ECO 115
(b) Kematal M90-04 + ECO 115
(c) Kematal M140-04 + ECO 115

when the nature of the glass-resin bond is discussed.

Very little work indeed has been done on the effect on properties of substituting an acetal homopolymer for the acetal copolymer used throughout this work. Table 6 (page 64) when compared with Table 3 (page 61) shows that the compression moulded Delrin (homopolymer) composite was possibly slightly inferior to the Kematal (copolymer) one. Little significance should be attached to this fact, however, as Delrin has a higher melting point than Kematal - the difference between the composites may merely reflect the different ease of mixing the polymers and glass by hand stirring at 185°C.

Delrin is appreciably less stable than Kematal and cases have been reported of explosion during injection moulding. It was therefore decided that it would be wise to avoid carrying out an injection moulded evaluation of Delrin, reinforced by glass fibres whose coupling agents might have an uncertain effect on the polymer stability.

D. The Effect of Coupling Agents on Properties.

The effect of coupling agents on both tensile modulus and tensile strength for hand stirred compression moulded materials is shown in Figures 42 and 43. The differences can be seen to be very small and in view of this it was decided to carry out a variance analysis to see whether the differences were statistically significant (see pages 66 - 68).

It was found that there was no significant difference as far as tensile strength was concerned. With respect to tensile moduli, XG 438 (methacrylato silane/P.V.A.) was significantly, but slightly better than the control, whereas XG 184 (aminosilane /alkyd) was significantly, but slightly, worse. Glasses XG 496 (chrome/P.V.A.) and ECO 115 (vinyl silane/P.V.A.) were not significantly different from the control. All of the above results were based on materials prepared by hand stirring.

This dependence of tensile modulus on coupling agent (and independence of tensile strength) is very surprising. Wagner et al[95], in their paper on glass reinforced acetal copolymer, pointed out that the strength of the glass resin bond (and hence the type of coupling agent used) should have little effect on low deformation properties, such as tensile modulus, whilst having a greater effect on high deformation properties, such as tensile strength. This idea was borne out by their results but is, unfortunately, contradicted by the results given here.

When one examines the results from the injection moulded test

FIGURE 42

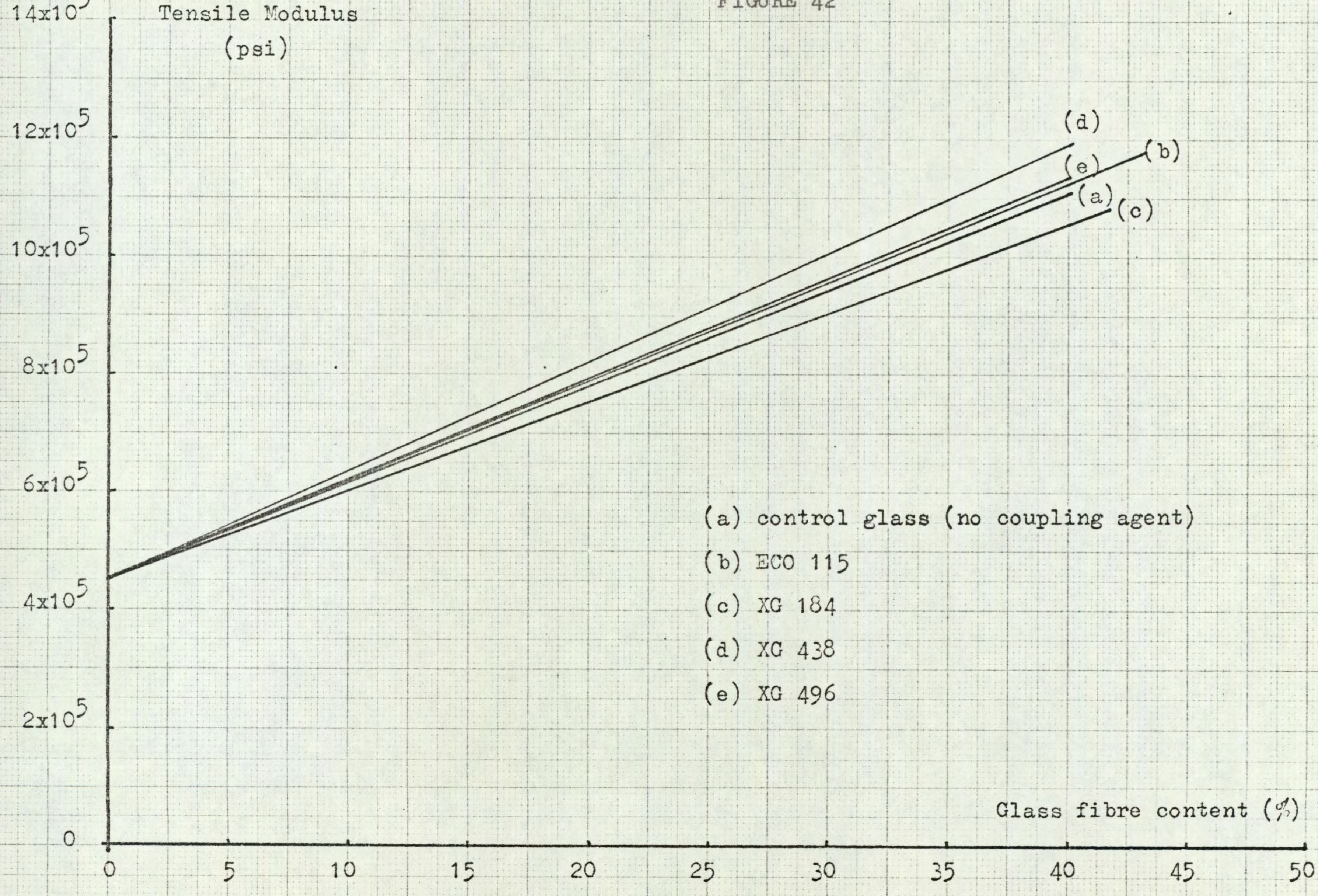
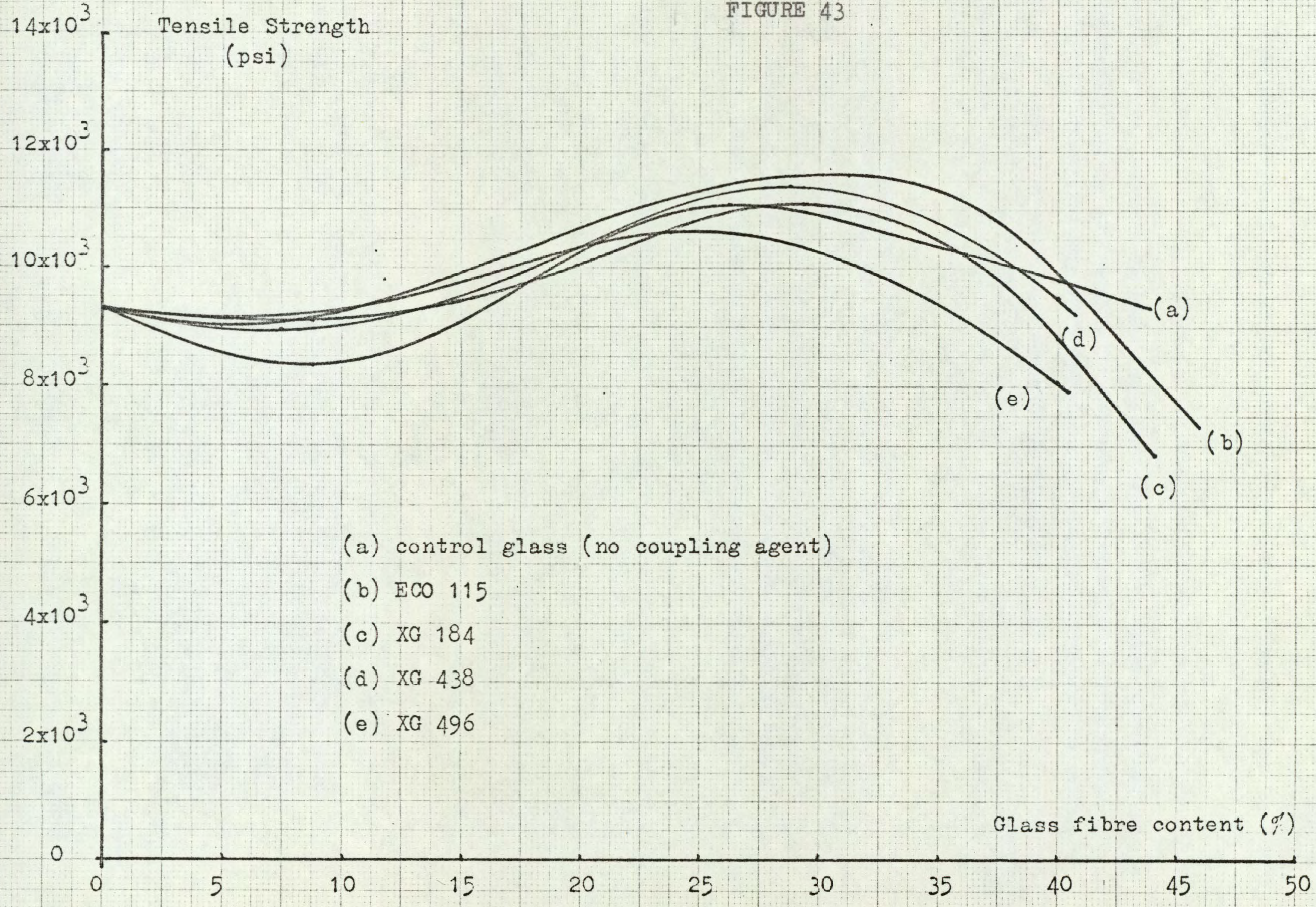

Tensile Modulus
(psi)
14x10^5
12x10^5
10x10^5
8x10^5
6x10^5
4x10^5
2x10^5
0
(d)
(b)
(e)
(a)
(c)
(a) control glass (no coupling agent)
(b) ECO 115
(c) XG 184
(d) XG 438
(e) XG 496
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50

FIGURE 43



Tensile Strength
(psi)
14x10^3
12x10^3
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
0
Glass fibre content (%)
0
5
10
15
20
25
30
35
40
45
50
(a)
(b)
(c)
(d)
(e)
(a) control glass (no coupling agent)
(b) ECO 115
(c) XG 184
(d) XG 438
(e) XG 496

system the picture is completely transformed, however: Tables 20 - 22 (pages 79 and 80) give the results for material prepared on the two roll mill and Tables 43 - 45 (pages 97 and 98) for material prepared by dry blending. As far as the material from the two roll mill was concerned γ-methacryloxypropyl-trimethoxysilane and methacrylato chromic chloride gave rise to tensile strengths which were significantly higher than for the control glass. On the other hand γ-aminopropyl triethoxysilane and vinyl tris(β-methoxyethoxy) silane gave rise to similar tensile strengths to the control: doubling the level of addition of the size containing the latter coupling agent considerably worsened the tensile strength. A very similar pattern of behaviour was observed with material processed by dry blending except that here the aminosilane occupied a position intermediate between the control and chrome as far as efficiency was concerned. It may be that the aminosilane/alkyd system is rather more susceptible to oxidation than the other systems, and so is seriously degraded during two roll milling.

Wagner et al[95], as stated previously, have also studied the effect of coupling agents on the tensile strength of a glass reinforced acetal copolymer system. They found that two coupling agents were active in improving tensile strength, one being of chrome type and the other of vinyl silane type. Other coupling agents, including another of vinyl silane type, were relatively inactive. Unfortunately it is difficult to compare the results obtained by Wagner with the results given in this thesis, as Wagner identified his coupling agents only by general type and did not disclose their exact structure.

As far as tensile modulus is concerned, it can be seen from Tables 20 and 43 (pages 79 and 97) that use of different coupling agents leaves this property virtually unchanged. This fits in exactly with the theory discussed by Lees (references 131 and 132; see pages 165 and 172), which shows that the equation for tensile strength includes τ , the shear strength of the glass resin bond, whereas this term is omitted from the equation for tensile modulus. The function of coupling agents is,of course,to increase the value of τ.

Reference to Tables 22 and 45 (pages 80 and 98), shows that as far as impact properties are concerned, glass with chrome or methacrylato silane coupling agents is appreciably superior to the control glass especially as far as material processed by dry blending is concerned. Once again glass with an aminosilane coupling agent shows up well with the dry blended system (being in fact superior to the other glasses used), whereas it is no better than the control glass with material processed on the two roll mill.

An exactly similar behaviour is observed with hardness. With the two roll mill materials the chrome and methacrylato silane coupling agents show themselves to be "active"; with the dry blended materials the aminosilane also becomes "active".

It would perhaps be in order at this stage to speculate to some extent on the nature of the bond between resin and glass and the manner of coupling agent action. Brookfield[133] in a review of glass-resin adhesion outlines the two theories of coupling agent action. The first theory involves the chemical bonding of glass to the coupling agent with the possibility of further bonding of the coupling agent to the resin. The second theory suggeststhat the function of the coupling agent is simply to assist in wetting and increase the coefficient of friction between the resin and the glass i.e. a purely physical action.

If we examine the results presented in this thesis from the point of view of the physical theory of coupling agent action, then it becomes apparent that wetting must be incomplete with the vinyl silane coupling agent (since a chrome coupling agent gives rise to a considerably higher level of mechanical properties). One would therefore expect that, with a vinyl silane coupling agent, the polymer viscosity should alter the degree of wetting of the glass and thus affect the mechanical properties. This in fact has been shown experimentally not to be so and so one must incline to the chemical theory of coupling agent action. The chemical behaviour of the three different grades of acetal copolymer would be expected to be fairly similar.

Support for the idea of chemical bonding in the glass-acetal copolymer composite comes from an observation by Wagner et al[95]. They observed that a correlation existed between the "activity" of a coupling agent and the decrease in the thermal stability of the polymer which it brought about i.e. "active" coupling agents caused increasing (but slight) thermal instability in the polymer. Wagner et al. showed that an increase in mechanical properties could be brought about by the presence of additives which caused a slight reduction in thermal stability of the acetal copolymer, by bringing about a controlled depolymerisation at the glass - polymer interface. It would seem reasonable to assume that the active chain ends formed during this depolymerisation react chemically with the coupling agent or glass and so give rise to a stronger interfacial bond. A correlation of coupling agent activity with thermal instability of the polymer was not attempted in the work described in this thesis, but it was noticed that materials containing glass with active coupling agents gave rise to a much stronger smell of formaldehyde during injection moulding than did materials with inactive coupling agents.

E. Conclusion.

The first important conclusion is that compression moulded specimens of glass reinforced acetal exhibit a much lower level of properties than specimens injection moulded from similar material. This is a difference of kind rather than degree - for instance the tensile strength of specimens compression moulded from materials prepared on the two roll mill falls with increasing glass content, while the tensile strength of similar injection moulded specimens rises sharply with increasing glass content. It would seem difficult to attribute this differing behaviour merely to differing degrees of fibre orientation: it would appear that some inherent defect is present in the compression moulding system, most probably the presence of flaws in the test pieces.

Considering next the usefulness of the various processing methods used, one can rule out hand stirring and the two roll mill as being of very limited commercial applicability. This would suggest therefore that direct injection moulding of a dry blend is the most promising of the processing methods investigated. It must be remembered however that the Buss Ko-kneader has only been used under one set of conditions: it may be that removal of some or all of the pins from the barrel wall might lower the shear forces to such an extent as to produce an acceptable level of mechanical properties. This idea is supported by the fact that simple extruders have been successfully used to produce glass reinforced thermoplastics. In spite of this, direct injection moulding of a dry blend would presumably still be preferred as it effectively eliminates a stage in the processing.

As far as glass content is concerned, processing by injection moulding becomes difficult at a 45 or 50% glass content. The use of larger injection moulding machines may help (the work in this thesis was carried out with a small Manumold), but 40% glass content may be the practical limit for mouldings of more complex shape than the simple tensile test bar.

The optimum coupling agents of those investigated appear to be methacrylato chromic chloride and γ-methacryloxypropyl - trimethoxysilane. It is interesting that both these coupling agents contain methacryl groups but no convincing reason can be found why such a group should be especially compatible with acetal copolymer.

APPENDIX

APPENDIX

Details of machinery used for the practical work in this thesis:-

A. Processing Machinery.

(1) Two Roll Mill

Joseph Robinson and Co. Ltd.
Gearing: even speed and 1.35:1
Rolls: 12" length x 6" diameter.

(2) Buss Ko-Kneader

Buss Ltd., Basle, Switzerland
Type: PR 46
Working pressure: 20 atm.
Apparatus no.: 50084-3
Heaters: barrel(2), nozzle(1) and screw(1).

(3) Rotocube Mixer

Foster, Yates and Thom Ltd., Blackburn, England.
Number 0, Size 9
Machine no. : M2186
Motor H. P. : 0.25

(4) Winkworth Mixer

Winkworth Machinery Ltd., Staines, England.
Type: 8Z Vac. Jkt.
Number: 2260

(5) Papenmeier Universal Schnell-Mischer

Günther Papenmeier, Pivitsheide b. Detmold

Masch. Nr. 800

Type: TLHK 8

Motor I: 1.1/1.6 Kw.

Agitator: 1500/3000 r.p.m.

(6) Junior Rotary Cutter

Blackfriars Rotary Cutters Ltd., London.

No : 63 762

Grid: 1/4" diameter holes

(7) "Walters Cutter"

Designed and made at B.I.P. Chemicals Ltd.

Eight inclined blades on a vertical spindle

Grid: 1/16" diameter holes

(8) Laboratory Mill

Christy and Norris Ltd., Chelmsford, England.

Size: 8"

Grid: 1/16" diameter holes

(9) Circular Saw

Funditor Ltd., London.

No. : 632/23

(10) Sieve Shaker

Endecotts (Filters) Ltd., London, England.

No. : E 20244 K

B. Moulding Machinery.

(1) Vertical Down-Stroke Press

T.H. and J. Daniels Ltd., Stroud, Glos.

No. : 653734

Ram diameter: 12"

W. P. : 2,000

Total tons: 100

Maximum stroke on ram: 30"

(2) Injection moulding machine (Manumold)

Florin Ltd., London, England.

Serial No. : 493

Hydraulic pressure: 1,000 psi

Hydraulic unit Serial no. : 493 H478

C. Testing Machinery.

(1) Type "E" Tensometer

Tensometer Ltd., Croydon.

Serial No. : A 150/33

Extensometer servo control serial no. : K 80/24

Transducer type extensometer, type: Y 1/113, serial no:K80-24

(2) Avery Izod Test Machine

Capacity: 1 ft-lb

Type: 6702

Number: 63748/1

Striking velocity: 8 ft/sec.

(3) Hardness test - Barber Coleman Impressor
Barber Coleman Ltd., Rockford, Illinois, U.S.A.
Model: GYZJ 934-1

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