THE SYNTHESIS AND EVALUATION OF FRIEDEL-CRAFTS POLYMERS.

by

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SUMMARY.

The application of the Friedel-Crafts reaction to the production of polymers having novel and useful properties has been studied. Particular attention has been paid to the potential use of such materials in high temperature electrical insulation applications. Several resin systems have been examined and an attempt has been made to correlate the initial structure of the reactants and their reactivity with the properties of the resins produced.

p-Xylylene glycol dimethyl ether (p-XGDME) was used as the reactive monomer in the bulk of the work. Terphenyl and diphenyl oxide (DPO) were chosen as substrate monomers because of their comparatively large size in the hope that they would yield polymers with well spaced cross-links which would be flexible enough for insulation applications. In the case of terphenyl this was not achieved but with DPO a resin was produced which had attractive handling characteristics and could be used as an impregnating resin for the windings of high temperature electrical machines. Mouldings and laminates of good electrical properties were also produced but the interlaminar bonding in glass cloth laminates was rather poor.

Different solvents were shown to have very marked effects on the rate of the DPO/p-XGDME reaction and also on the properties of the resins produced. One resin was found to give much improved glass/resin bonding than was achieved with the bulk prepared DPO/p-XGDME resins.

The curing mechanisms of a terphenyl and a DPO resin were examined by infra red spectroscopy and by weight loss, and in both cases loss of unreacted monomer occurred during cure. Further condensation took place yielding additional cross-links; and simultaneously oxidation of methylene bridges to carbonyls, and methoxymethyl groups to carboxylic acid groups occurred.

The deactivated molecule, 4, 4'di(chloromethyl) benzophenone, was substituted for p-XGDME in an attempt to limit branching in the polymer but its reactions were very slow and the products no more linear. The literature discrepancy about the melting point of 4,4' di(chloromethyl) benzophenone was resolved in favour of 103°C.

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PATENT POSITION.

In connection with the work to be described in this thesis Associated Electrical Industries Ltd has been granted,

British Patent 1,163,435 "Catalytic Condensation of Ethers" and has outstanding,

British Patent Application 43004/68 Improvements in, or relating to resin bonded laminates and their manufacture.

The Ministry of Technology holds patents relating to the use of p-dichloroxylylene and p-xylylene glycol dimethyl ether in the preparation and cross-linking of polymers. These are British Patents 1,024,222 and 1,094,181 respectively.

Chapter 1.

INTRODUCTION.

1.1. Aim.

The work to be described was undertaken in part fulfilment of Ministry of Technology Contract No. KS/1/390/CB43(a)2, placed with Associated Electrical Industries Ltd, for the study of Friedel-Crafts polymers, particularly in relation to their suitability for use as electrical insulating materials.

Interest in these polymers arose directly from the work of Phillips and his co-workers (1,2) who showed that p-dichloroxylylene (p-DCX), and later p-xylylene glycol dimethyl ether (p-XGDME), could be used very generally in preparing polymers with other aromatic compounds. Polymers containing aromatic nuclei, prepared by this or other methods, could be cross-linked using these compounds. Using $SnCl_4$ as catalyst, these workers showed that the reactions could be readily controlled and stopped to give soluble, fusible polymers of low molecular weight. These could be processed easily and cured - i.e. converted to solid, infusible, insoluble, cross-linked resins - simply by further heating. The polymers showed good thermal stability.

The aim of the work was, therefore, to prepare polymers by using the Friedel-Crafts alkylation reaction, and to investigate their thermal, mechanical and dielectric properties with a view to their eventual application as electrical insulants. Implicit in this aim was the modification of the properties of any polymer to meet the requirements of some specific application. This could involve, for example, attempts to increase the hot bond strength of a resin to be used in impregnation; or attempts to improve the flexibility of resins in the hope of producing a new wire enamel.

1.2. Friedel-Crafts Reactions.

Alkylation reactions under the influence of $AlCl_3$ were first described by Friedel and Crafts (3) in 1877 and these are still regarded as the most typical examples of Friedel-Crafts reactions. However, since then, $AlCl_3$ has been found to catalyse many more types of reactions, such as acylation, isomerisation, polymerisation, sulphonylation, etc.; and many more catalysts, such as Lewis acids, proton acids, and chalcides have been found to be effective in promoting these reactions. In an attempt to define the present day scope of Friedel-Crafts reactions Olah (4) gave the following statement. "In a general sense we may say that today we consider Friedel-Crafts type rections to be any substitution, isomerisation, elimination, cracking, polymerisation or addition reactions taking place under the catalytic effect of Lewis acid type acidic halides (with or without co-catalyst) or proton acids. One of the original characteristics of the reaction, namely that hydrogen halide should be evolved in the course of the reaction, is by no means a limiting condition any more."

Nevertheless, for the purposes of the work to be described, only those reactions leading to alkylation of aromatic compounds will be considered. Even more specifically, only the alkylation reactions involving haloalkyl or alkoxyalkyl compounds are appropriate to the work and other alkylations will be neglected.

In their first paper in 1877 Friedel and Crafts (3) described the $AlCl_3$ catalysed alkylation of benzene with amyl chloride, ethyl iodide, and methyl chloride to give amyl benzene, ethyl benzene, and toluene respectively. They made no attempt to explain the mechanism beyond saying that the hydrohalide was formed by combination of a halogen atom from the alkyl halide, and a hydrogen atom from benzene; and that the two residues combined to give the final hydrocarbon.

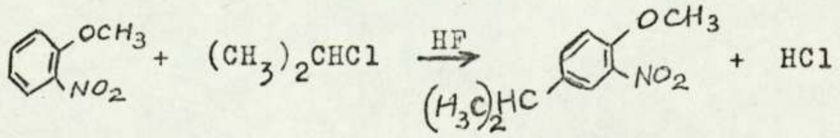
Alkyl halides are the commonest alkylating agents although many other types of compounds can also be used, e.g. alkanes, alkenes, alcohols, esters, aldehydes, ketones, and, as mentioned before, ethers. For alkyl halides and ethers the overall reactions are:-

$$ArH + RX \longrightarrow ArR + HX$$

$$ArH + ROR' \longrightarrow ArR + R'OH$$

There is no single order of catalyst activity which applies in all circumstances. It depends on many factors, such as the substrate, the alkylating agent, and the solvent. An example of the effects of solvent is the powerful catalytic effect of $AlCl_3$ in nitrobenzene (5) while $AlCl_3$ solutions in ethers, ketones, and alcohols are catalytically inactive in the alkylation of hydrocarbons (6).

The facility with which alkylation of substituted aromatics can be effected is governed by the well-known rules of activation and de-activation. Electron donating substituents, such as alkyl, hydroxyl, or alkoxyl groups activate the nucleus towards alkylation; whereas electron withdrawing groups, such as nitro, carbonyl, or sulphone de-activate the nucleus. When both types of groups are present the final effect is the resultant of their individual effects. Thus, although nitrobenzene cannot normally be alkylated, o-nitro anisole can be iso-propylated readily in 85% yield (7).



Polyalkylation occurs readily and was noted by Friedel and

Crafts in their first paper (3). This can readily be explained by activation of the aromatic nucleus by the first alkyl substituent making it more reactive towards further alkylation (8). This explanation has been countered by Francis (9) who claimed that alkyl groups on a benzene nucleus had little effect on the rate of further alkylation. His explanation was that alkylation took place in a heterogeneous system, specifically in a catalyst layer, which preferentially extracted early reaction products into itself, thus making polyalkylation easy.

De-alkylation can also be effected by Friedel-Crafts catalysts. As a result of this, isomerisation leading to a different arrangement of substituents around the ring occurs frequently in Friedel-Crafts reactions. Consequently, it is difficult to predict which of the possible isomers is likely to be formed. Iso-propyl and t-butyl groups are particularly readily transferred from one position to another on the same nucleus, or even from one nucleus to another. It has been demonstrated that, on stirring with $AlCl_3$, ethyl benzene gives substantial quantities of polyethyl benzenes and benzene (10).

1.2.1. <u>Mechanism of Friedel-Crafts Reactions.</u> Lewis acids contain unfilled electronic orbitals which enable them to accept electron pairs from donor molecules, and to form complexes with them. Alkyl halides as a group are strong donors because of the lone pair electrons on the halogen. These compounds readily form complexes with Lewis acids.

$$RX + SnCl_4 \longrightarrow R^{\delta+}XSnCl_4^{\delta-}$$

Complex formation causes stretching of the C-X bond in RX and, if R^+ is a stable carbonium ion, complete ionisation of the complex occurs allowing the carbonium ion to act as an electrophilic alkylating agent.

$$R^{\delta+}XSnCl_4^{\delta-} \longrightarrow R^+ + [XSnCl_4]^-$$

$$R^+ + [XSnCl_4]^- + ArH \longrightarrow \left[Ar{<}^{H}_{R}\right]^+ + [XSnCl_4]^-$$

$$\left[Ar{<}^{H}_{R}\right]^+ + [XSnCl_4]^- \longrightarrow ArR + H^+ + [XSnCl_4]^-$$

$$H^+ + [XSnCl_4]^- \longrightarrow HX + SnCl_4$$

Similarly with ethers the oxygen atom has a lone pair and readily donates these to the Lewis acid to form a complex. These lead, as above, to a weakening of the O-C bonds, one of which breaks to give a carbonium ion which acts as an alkylating agent in exactly the same way as shown above.

$$ROR' + SnCl_4 \longrightarrow R^+ + [R'OSnCl_4]^- \xrightarrow{ArH} ArR + R'OH + SnCl_4$$

Some of these complexes are sufficiently stable to be isolated. Parker (11) and his co-workers, for example, have isolated a crystalline 1:1 complex of benzyl chloride and stannic chloride in the course of their work on the polymerisation kinetics of benzyl chloride.

The ease with which the ether cleavage reaction occurs depends on the basicity of the ether (i.e. the nature of the groups attached to the oxygen atom) and on the acidity of the catalyst (12). Primary alkyl ethers are very stable while benzyl ethers are readily split. The ease of splitting can be represented as aralkyl > tertiary > secondary > primary and in instances of mixed ethers this order determines which bond breaks preferentially. According to this scheme, therefore p-xylylene glycol dimethyl ether (CH_3OCH_2-⌬-CH_2OCH_3) would be expected to form the carbonium ion CH_3OCH_2-⌬-CH_2^+ very readily and this should then react with other aromatic nuclei Following this, or even concurrently, another carbonium ion could be formed involving the second $-CH_2OCH_3$ group. This would lead to further reaction.

1.3. Friedel-Crafts Reaction in the Preparation of Polymers.

As stated earlier the Friedel-Crafts reaction can be used to prepare and cross-link polymers (1).

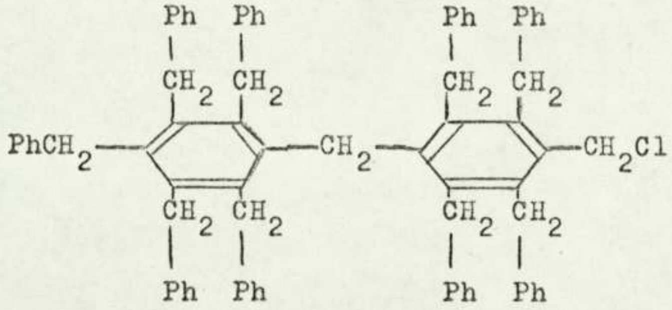
1.3.1. Polybenzyl. It has been known for many years that benzyl chloride condenses readily in the presence of Friedel-Crafts catalysts. When heated with $AlCl_3$, benzyl chloride reacts in an uncontrollable manner yielding an off-white, porous, insoluble, infusible mass (13). However, if a milder catalyst, like $SnCl_4$ or BF_3-etherate, is used the reaction proceeds smoothly to give a soluble, glassy, yellow, solid resin (14). It has been shown by Phillips (1) that the soluble polybenzyl can be converted to an insoluble, infusible, mechanically strong resin by cross-linking with p-DCX in the presence of $SnCl_4$.

The structure of polybenzyl has been the subject of controversy for a number of years. Any acceptable structure must take account of the very high concentration of mono-substituted benzene rings in the product as shown by infra red spectroscopy (15, 16); and also the alternating aromatic and methylene groups (16). These requirements rule out a linear molecule in which all benzene rings, except terminal ones, are disubstituted; and also a polystilbene structure, $\left[-\underset{\text{Ph}}{\underset{|}{\text{CH}}}-\right]_n$ which has the correct elemental composition but contains no methylene groups.

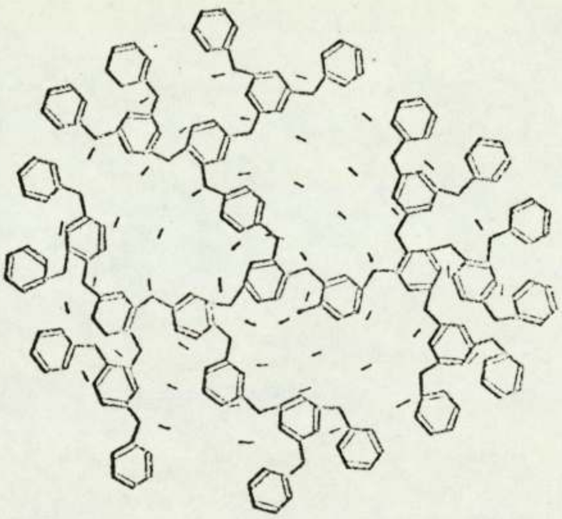
Proposals which meet the stated requirements are:

1. Random branching (17) which assumes that each nuclear hydrogen atom has an equal chance of being substituted by a benzyl group.

2. "Sow and Piglet" branching (15).



3. Globular molecule (16) which is similar to "Sow and piglet" but has much less extensive branching.



In this the outside layer consists of monosubstituted rings while the rings in the inner layers are mostly tri-substituted. Parker arrived at this structure after studying the ratio of different carboxylic acids formed on oxidation of polyphenylethyl which he believed to have the same structure. He found large quantities of benzene mono-, and tri-carboxylic acids; and only very small traces tetra-, penta- and hexa-carboxylic acids.

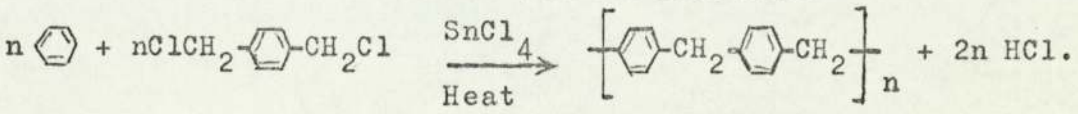
Parker's proposed structure is certainly consistent with all the evidence which he and earlier workers presented. This is particularly true with regard to the evidence from oxidative degradation which was not available to the earlier workers and cannot be explained on the basis of their proposed structures.

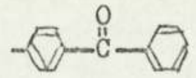
Polybenzyls of similarly branched structures have been prepared from benzyl alcohol (18) and benzyl ethers (19).

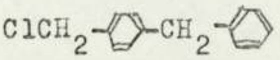
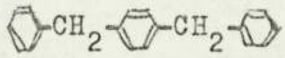
Ellis and his co-workers (20) have studied the fluorescence in polybenzyl, which has been noted by several workers, and concluded that it was due to benzyl substituted 9-phenyl-, or 9,10-diphenyl anthracene. They propoaed a mechanism by which such a structure could be formed. Montaudo and co-workers (21) also attributed the fluorescence to substituted anthracenes. Ellis and his colleagues (20) presented spectroscopic evidence for the formation of benzyl, and diphenyl methyl, carbonium ions when $SnCl_4$ was added to benzyl chloride.

Kennedy and Isaacson (22) reported the preparation of a partially crystalline polybenzyl by condensation of benzyl chloride in solution at -135°C.

1.3.2. <u>Polymers based on p-Dichloroxylylene</u>. As mentioned in 1.3.1. Phillips (1) demonstrated that the soluble polybenzyl could be cross-linked using p-DCX. He also showed that the Lewis acid catalysed reaction of p-DCX with other aromatic compounds containing at least two nuclear hydrogen atoms led to polymers according to the idealised formula for the benzene reaction.



Among the compounds shown by Phillips to react with p-DCX were benzene, naphthalene, terphenyl, diphenyl oxide, triphenyl borazole, and octaphenylcyclotetrasiloxane. Non-reactive compounds included chlorobenzene, o-dichlorobenzene, nitrobenzene and benzophenone all of which contain deactivating atoms or groups. p-Phenyl benzophenone did, however, react, presumably in the p-phenyl ring which would be much less affected by the deactivating carbonyl group. The first aralkyl substituent in this ring would activate it so that further reaction would occur readily to give a polymer with pendant  groups.

Grassie and Meldrum (23) have studied the structure of the early products of the benzene/p-DCX reaction and shown that the first two products are  and . Branching occurs later in the polymerisation. They have also examined (24) the polymers prepared from p-DCX and several heterocyclic compounds, and have concluded that the thiophene/p-DCX polymer is more thermally stable than their benzene/p-DCX polymer. Other heterocyclics gave no advantage in thermal stability.

1.3.3. Polymers based on p-xylylene glycol dimethyl ether. The evolution of HCl in practical applications is at best undesirable and, in many instances, intolerable, because of its corrosive effects. To overcome this a second series of Friedel-Crafts polymers was introduced by Phillips and his co-workers (2). These were based on p-xylylene glycol dimethyl ether (p-XGDME) in place of p-DCX so that the harmless methanol was liberated in place of HCl during the reaction. This again has been shown to be a reaction of widespread applicability although higher temperatures were required than for p-DCX.

Polymers which produce HCl on curing are unacceptable in electrical machines and consequently only those based on p-XGDME were considered worthy of study in this programme.

1.3.4. Other polymers prepared by the Friedel-Crafts Reaction. Vanschiedt and his co-workers (25, 26) prepared polyarylene methylenes by the acid catalysed reaction of aromatic hydrocarbons (durene, p-xylene) with difunctional compounds such as formaldehyde; the bischloromethyl derivatives of durene, p-xylene and benzene; and bisacetoxymethyl derivatives of durene and p-xylene. The polymers produced had melting points in the region 240-325°C; were highly crystalline; and were soluble only at high temperatures. No application has been reported.

According to Nowak (27) one commercially available impregnating varnish is prepared by the self-condensation of p-chloromethyl diphenyl oxide.

The patent literature also includes references to similar reactions. These include the self-condensation of haloalkyl (28, 29) and alkoxy alkyl diphenyl oxides (30, 31); and the preparation of resins from aromatic compounds and dihalomethyl aromatic compounds (32,33), or dialkoxymethyl aromatic compounds (34,35).

1.4. Thermal Stability.

1.4.1. General Considerations. The thermal stability of a polymer implies two completely different concepts and only in strictly limited circumstances can it be defined by quoting a temperature.

When a polymer is heated two types of changes occur. Firstly there are reversible physical processes; and secondly, there are irreversible chemical reactions. Physical changes, such as softening, limit the temperature at which most thermoplastic materials can be used. For thermosets (and for some thermoplastics) the assignment of a maximum service temperature is much more complex involving consideration of physical, and chemical changes. A time limit appropriate to the temperature must be set since the chemical changes are time dependent.

The physical changes which occur involve the motion of atoms, groups, chain segments, and whole molecules. The changes are manifested as the glass transition temperature, Tg, at which segments of polymer chains acquire sufficient energy to rotate freely; and, at higher temperature, as the crystalline melting point, Tm, at which the crystallinity of the polymer disappears completely and movement of polymer molecules, relative to one another, becomes possible. These changes are reversible since, when the temperature is again lowered, the energy of the molecules and segments is reduced and their freedom to move is again restricted.

The irreversible chemical changes involve the competing processes of cross-linking and decomposition which occur concurrently at rates dependent on the temperature. The cross-linking process, up to a certain cross-link density, (about one per ten chain units) leads to an improvement in the mechanical strength of a polymer. Further cross-linking leads to embrittlement. Thermal and oxidative effects lead to scission of bonds and consequently to deterioration in mechanical properties. Frequently, however, during degradation free radicals are formed which can lead to further cross-links. These may or may not be beneficial depending on the degree of cross-linking already present. From the foregoing it is obvious that during an ageing process a point is reached beyond which all the effects cause loss of mechanical (and electrical) properties.

Only for a thermoplastic material which does not degrade below its Tg is it possible to specify the thermal stability by quoting a single temperature. In this case the limit is set by the totally reversible drop in physical properties which occurs at the Tg, and not by chemical decomposition. Even in this case, however, consideration must be given to the effects of the environment in which the material is to be used.

For thermoplastics which degrade below their Tg's and for thermosetting polymers temperature, time, and environment are all factors which must be included in defining the material's thermal stability. In the context of electrical insulation the environmental factor includes the effect of different components of the insulation system on each other as well as the influence of atmosphere, humidity and contamination on the insulants.

The resistance of organic compounds to thermal degradation depends on the strength of its bonds. These include the primary valence bonds which are the most important; and also secondary bonding forces such as dipolar attraction, van der Waals forces and hydrogen bonding. In addition to these effects resonance stabilisation of cyclic or conjugated systems also contributes to overall stability.

1.4.2. Thermally Stable Poymers. In attempts to prepare thermally stable polymers, by far the greatest attention has been given to the incorporation of resonance stabilised aromatic and heterocyclic rings in the main chain. The resistance to degradation of such polymers depends largely on the linkages between the cyclic units. Examples of such materials abound and only a few will be mentioned. Several comprehensive reviews of the subject have been given by Idris Jones (36).

The fully aromatic polyphenylenes have been prepared using different methods by Goldfinger (37); Marvel and co-workers(38,39); Kovacic and Kyriakis(40); and Long (41). Only the polyphenylenes prepared by Long have found any application but their use is likely to be severely limited by the objectionable nature of the processing which is required. This involves the condensation of disulphonyl chlorides with low molecular weight polyphenylenes with the elimination of HCl and SO_2.

Polyphenylene methylenes have been discussed in 1.3 and represent a special case of the polyphenylene alkylenes. Parker (16) prepared a polymer analogous to polybenzyl by the self-condensation of phenyl ethyl chloride. Szwarc (42) has described the low pressure pyrolysis of p-xylene to give a linear, film-forming poly-p-xylylene.

In addition to these purely hydrocarbon polymers there are many examples of polymers consisting essentially of aromatic rings linked by functional groups. These include:-

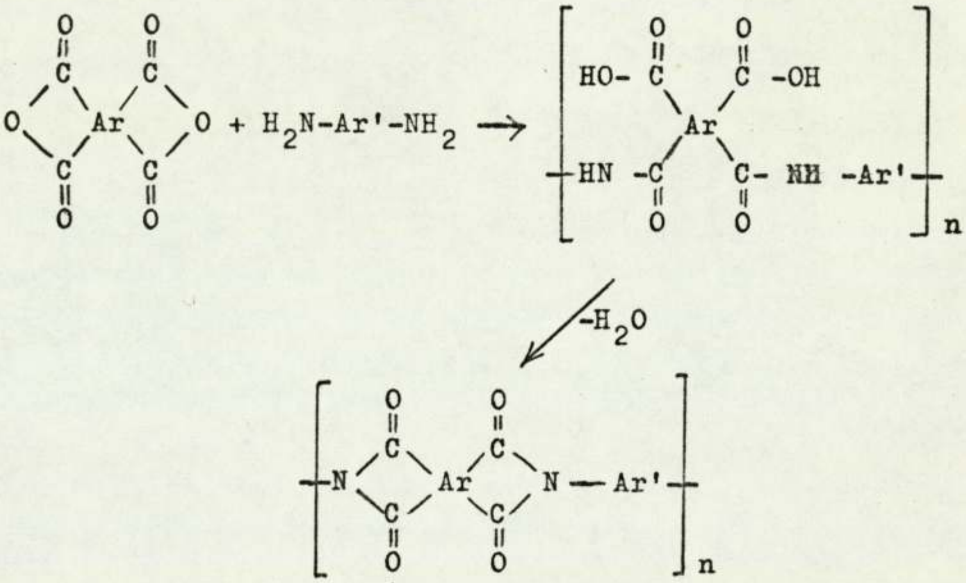
The aromatic polyamides, an example of which is commercially available as sheet and yarn. It is believed to be the condensation product of m-phenylene diamine and isophthaloyl dichloride(36).

The aromatic polyethers, such as the commercially available thermoplastic material, PPO (poly 2,6 -dimethyl phenylene oxide). This polymer is prepared by the oxidative coupling of 2,6 -dimethyl phenol in the presence of CuCl/pyridine (43).

The polysulphides which have been prepared by Tsunawaki and Price (44) by the self-condensation of alkali metal salts of halothiophenols.

The polysulphones which have been prepared by Cudby et al (45) by the $FeCl_3$ catalysed reaction of disulphonyl chlorides on reactive dinuclear aromatic compounds or self-condensation of a dinuclear aryl sulphonyl chloride. In these the deactivating effect of the $>SO_2$ group prevents branching.

Heterocyclic ring containing polymers, of which there are many, depend for their sucessful application on the two stage process by which they are prepared. The first stage is the preparation of a high molecular weight, soluble prepolymer which can be further reacted to give the required polymer. This is illustrated by the polyimides which were developed independently in Britain by Idris Jones (46) and in America by Edwards (47). The method involved the reaction of an aromatic dianhydride with an aromatic diamine in solution to yield the intermediate polyamic acid which on subsequent dehydration gave the polyimide.

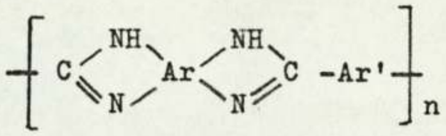


One of the commercially available polyimides is made from pyromellitic dianhydride and 4,4' -diamino diphenyl oxide, but polyimides have been prepared using a wide selection of dianhydrides and diamines.

Other heterocyclic polymers which have been prepared include:-

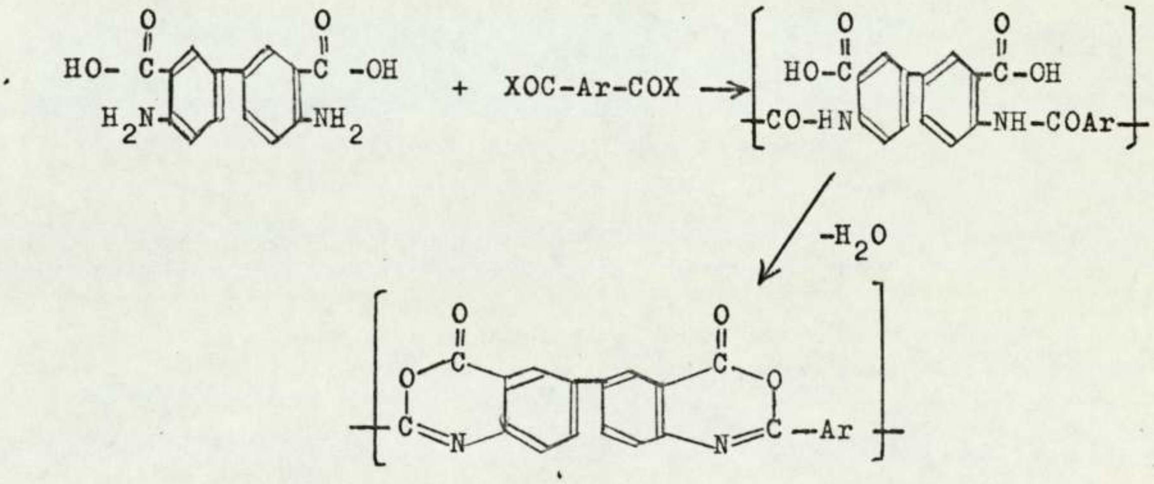
Polybenzimidazoles which were synthesised and studied by a number of workers including Vogel and Marvel (48). The method used was the condensation of an aromatic tetramine with the diphenyl ester of an aromatic dicarboxilic acid.

The general structure of the polymer was



A commercial form of the polymer is available as a high temperature adhesive.

Polybenzoxazinones which were synthesised by Yoda (49, 50) and his co-workers in Japan. The preparation was carried out by condensing 4,4'-diamino diphenyl 3,3'-dicarboxylic acid with an aromatic dicarboxylic acid halide. This yielded a soluble polyamic acid as the precursor to the final polybenzoxazinone formed by dehydration.



1.4.3. <u>Comparative Thermal Stability</u>. Wright and his co-workers (51) using isothermal thermogravimetric analysis have compared the thermal stabilities of aromatic polyamides based on phenylene diamines and the three benzene dicarboxylic acids. They showed that the polyamides fell into two distinct groups. The first group, with poorer thermal atability, consisted of polymers with at least one ortho linkage. The stability of the second group was better than the first and improved as the linkage changed from meta-meta to meta-para to para-para. Preston (52) showed similarly that the thermal stability of polyamides improved as the proportion of para-para linkages increased.

Wright and co-workers also reported on polymers prepared from terephthaloyl chloride and dinuclear diamines with different linkages between the rings. From this work they showed the following order of decreasing thermal stability in air for the linkages between the aromatic rings:- Direct link $>$ $-SO_2-$ $>$ $-N{=}N-$ $>$ $-SO-$ $>$ $-CH_2-$ $>$ $-CH{=}CH-$.

Bower and Frost (53) studied the isothermal weight loss in helium of polypyromellitimides based on different dinuclear diamines. They found the following order of decreasing thermal stability:- Direct link $>$ $-O-$ $>$ $-S-$ $>$ $-CH_2-$ $>$ $-\overset{CH_3}{\underset{CH_3}{C}}-$. Results from differential thermal analysis in nitrogen (54) were substantially the same but included several other linkages. Their order of stability was:-

Direct link $>$ $-O-$ $>$ $-CH_2-$ $>$ $-CH_2-CH_2-$ $>$ $-SO_2-$ $>$ $-\overset{CH_3}{\underset{CH_3}{C}}-$.

The carbonyl group has been shown to have superior thermal stability to the ether bridge and the sulphone group (55).

Thus both in air and in inert conditions the order of stability of the internuclear linking groups is substantially the same. The order in air is given in Table 1.1.

Direct link between nuclei

$-CO-$

$-O-$

$-SO_2-$

$-CH_2-$

$-CH{=}CH-$

$-CH_2-CH_2-$

$-\overset{CH_3}{\underset{CH_3}{C}}-$

Decreasing Thermal Stability. $\downarrow$

Table 1.1. Relative Thermal stability in Air of some linking Groups between aromatic nuclei in polymers.

From the results reported there is some doubt about the position of the $-SO_2-$ group. In inert atmospheres, Nishizaki and Fukami (54) found the $-CH_2-$ and $-CH_2-CH_2-$ groups more stable than $-SO_2-$.

It can be deduced from all the considerations discussed in this section that for the most stable aromatic polymers it is desirable to have the aromatic nuclei linked para-para with one of the stable linkages near the top of the Table 1.1. It is also desirable to avoid oxidisable or activating substituents such as alkyl or alkoxyl groups on the aromatic nuclei. In the event of substitution it is desirable to have a symmetrical pattern.

Phillips (1) showed that his Friedel-Crafts polymers had greatly improved thermal stability compared with phenolic resins. In the light of the foregoing discussion this is to be expected because of the absence of the hydroxyl group, whose activating influence is the main cause of the mediocre thermal stability of the phenolics. The Friedel-Crafts polymers were considered suitable for long term use in air at temperatures around 200°C. They were thus approaching the thermal stabilities of the heterocyclic aromatic polymers and since their preparation was so simple they could be regarded as potentially cheap. They were, therefore, considered to be of sufficient interest to warrant an investigation into their potential application as high temperature electrical insulating materials. Some of the basic requirements of insulants are described in 1.5. which follows.

1.5 Insulation.

1.5.1. General Considerations. The function of insulation is to prevent the flow of electricity except as dictated by the engineering requirements. To achieve this, insulating materials are used to effect physical separation of conductors. Consequently insulating materials must possess mechanical properties which enable them to perform this duty for the design life of the equipment at temperatures up to its maximum operating temperature. Obviously thermal stability is an important factor in meeting this requirement. Secondly the insulating material must prevent the flow of electricity through itself. It must have high electric strength and insulation resistance and low dielectric loss tangent and permittivity values. Thirdly, insulation must allow the transfer of heat to the atmosphere to avoid excessive heat build up due to normal operation and heating of the insulation as a result of dielectric loss.

As indicated above the mechanical properties of solid insulating materials play a very important part in their sucessful application. During assembly insulating materials must withstand automatic or manual handling techniques which will inevitably include tension, compression, flexing, abrasion and even hammering. In general, final assemblies are subjected to similar effects to an extent dependent on the environment and application in which the equipment is used. Deterioration of mechanical properties usually resulting from thermal or oxidative degradation, precedes dielectric failure and is usually the direct cause of it. Cracks occur, which may, in the worst circumstances, allow adjacent conductors to touch. Alternatively pockets of ionisable gases may be formed which can lead to corona discharge; or moisture may penetrate leading to deterioration in dielectric properties of the materials and the insulation system as a whole.

It was hoped that from the present work materials might be developed which would be suitable as an impregnating resin; a bonding resin in laminates; a bonding resin in mouldings filled with mineral fillers; and possibly as a wire enamel.

1.5.2. Impregnation. The windings of electrical machines are impregnated with resin primarily to bond the turns to each other and to other parts of the system to avoid damage due to vibration and abrasion. Subsidiary advantages gained from impregnation are increased electric strength by replacing air by a solid dielectric; improved heat dissipation; improved moisture resistance; and prevention of ingress of dirt, metal particles and corrosive fluids.

Therefore, a good impregnating resin must firstly penetrate and wet the windings, without adversely affecting the primary insulation on the conductor, and be able to cure to give a smooth impervious surface with good chemical and moisture resistance. Adhesion to the windings and to other parts of the structure, including the frame assembly, and other insulation is important. A high bond strength must be maintained at the maximum operating temperature of the equipment. The best electrical properties are not essential although high electric strength and insulation resistance and low dielectric loss are desirable.

1.5.3. Laminates. Resin bonded laminates are widely used in the electrical industry as insulated boards, as coil winding formers, as rods and tubes. For most applications good mechanical strength at the operating temperature is important. This depends on a good bond between the resin and the glass, paper, asbestos or mica substrate. Much work has been carried out on coating glass fibres with coupling agents which will form strong bonds both to the glass and to the resin. Many glass finishes are now available some developed for particular varnishes. Other substrates have not had similar treatment. Another factor influencing the mechanical properties of laminates is the presence of voids in the laminate. These can arise either from trapping volatile matter during cure or from rupture of resin/substrate bonds to relieve stresses which can build up due to unequal expansion of resin and substrate.

The electrical properties, similarly are affected by poor bonding and by the presence of voids in the laminate. This is particularly so if exposure to high relative humidity or contact with liquid water is involved, when water absorption causes serious deterioration in properties. Surface resistance and resistance to tracking are frequently important on control equipment; and in applications such as radomes, low dielectric loss and moisture resistance are essential.

From the foregoing paragraphs it will be obvious that good wetting of the substrate by the resin and a strong bond between the resin and substrate are essential if a successful laminate is to be made. The resin used should preferably be sufficiently flexible to accommodate stresses due to unequal expansion of resin and substrate. Preferably, also, when using a condensation polymer the reaction should be taken as far as possible before pressing the laminate to avoid trapping volatiles; but, at the same time, sufficient flow must be retained to bond the laminations together, and to fill small interstices with resin. The thermal stability of the resin must clearly match the requirements of the application, a special case being printed circuit boards where the laminate must withstand immersion in solder baths.

1.5.4. Mouldings. Filled mouldings find application in the electrical industry as terminal blocks of many kinds including the familiar power plugs and sockets, car distributor bodies and caps and special terminal blocks for electrical machines of all sizes. They are also used as coil spools, switches and insulators for power lines.

The resins for moulding require similar properties to those of laminating resins. Again wetting of the filler and a good resin/filler bond are essential to ensure flow of the moulding compound as an entity and prevent its separation into resin and filler phases. The thermal stability requirement is dictated by the application as are the electrical requirements. In most of the examples quoted resistance to tracking is important and good electric strength is also frequently essential.

1.5.6. Wire Enamels. The primary insulation on wire conductors is normally a resin film which is deposited on the wire by drawing the wire through a resin solution and then through an oven to cure the resin. Usually to achieve the necessary build of resin several passes through the solution are required. The resin used in this application must have good adhesion to the substrate, and to itself; must be flexible and abrasion resistant to allow for winding; and must have good film forming properties giving coatings free from pinholes. Usually good electric strength and low dielectric loss are necessary. The thermal requirements are dictated by the engineering design.

CHAPTER 2.

EXPERIMENTAL METHODS, INSTRUMENTS AND MATERIALS.

The general outline of the experimental methods used in the course of the present work are described in this chapter. In some instances specific details are not given here but are included in appropriate places in the main text.

Brief descriptions are given of the analytical and test instruments which were employed.

A final section lists the principal materials which have been used.

2.1. Preparative Methods.

2.1.1. The Preparation of Resin using p-XGDME. Typically these resins are prepared by the reaction of p-XGDME with another aromatic compound containing at least two hydrogen atoms which are attached to a single aromatic nucleus or to separate nuclei which are not sterically hindered or deactivated by, for example, $\rangle CO$ or $\rangle SO_2$ groups to such an extent that the reaction is prevented.

The reactants are heated together to 125° - $220^\circ C$ with a catalyst either in bulk or in solution and the progress of the reaction is monitored by measuring the volume of methanol which distils off. The reaction can thus be stopped at any predetermined stage and, for example, a resin syrup of a given viscosity can be obtained with DPO or a solid, but fusible, polymer with a fixed melting range can be obtained using mixed terphenyls (Santowax R).

By way of example, the bulk preparation of a DPO/p-XGDME resin is described in detail.

Reactants.

1360g DPO

1594g p-XGDME

10ml 20% by volume $SnCl_4$ in 1,2-dichloroethane.

The DPO and p-XGDME were heated together with stirring to 175°C in a 5 litre reaction vessel fitted with a stirrer, a distillation head, a thermometer and a spare inlet for catalyst addition. One third of the catalyst was added and the reaction temperature was maintained at 175°C. The remaining catalyst was added in two further aliquots to maintain an approximately steady reaction rate. The reaction was continued until 500ml distillate had been collected. This represents 64% of the theoretically available methanol (492ml), plus 8ml 1,2-dichloroethane which was added with the catalyst. The reaction was stopped by cooling and an amber coloured resin with purple fluorescence was obtained with a viscosity of approximately 35 Stokes at 23°C.

2.1.2. The Study of Effects of Solvent and Catalyst on DPO/ p-XGDME Resin.

Reaction mixture.

68g DPO	(0.4M)
66.4g p-XGDME	(0.4M)
400ml solvent	
Catalyst	(0.002M).

The mixture, omitting the catalyst, was heated to 130°C to remove any water before putting the top of the reaction vessel in place. The temperature was raised to 175°C and the catalyst was added either in solution in the solvent, or in DPO, or in the case of $TiCl_4$, neat, using a syringe. Heating was continued until 19.2ml methanol (60% theoretical) had been collected or, in the case of apparent lack of reaction, for several hours to establish that no methanol could be obtained.

Before use, the solvents were stored over barium oxide and the manipulation of the catalysts was carried out using "dry box" techniques to ensure, as far as possible, anhydrous conditions in the reaction vessel.

2.1.3. Moulding of Terphenyl Resin based Moulding Compounds.

The constituents of the moulding powder, typically

40 p.b.w. resin
30 p.b.w. asbestos
30 p.b.w. clay

were roughly ground and mixed together on differential mixing rollers with the two rollers heated to 90°C and 150°C respectively. A "blanket" formed readily on the cooler roller. After 10 minutes this was removed, cooled and ground so that it would pass through a No. 8 sieve. It was then used in moulding either in granular form or after being compacted cold into pellets. In some cases a further pre-cure was used.

The moulding powder was placed in the heated mould and pressed. "Breathing" of the mould was used on some occasions.

The details of the moulding procedures are specified in Chapter 4.

2.1.4. Moulding of DPO Resin based Moulding Compounds.

The constituents of the moulding compound, typically

40 p.b.w. resin
30 p.b.w. asbestos
30 p.b.w. clay

were mixed together in a "Z-blade" mixer till a uniform consistency was obtained. In some cases the compound was moulded as a dough without further pre-cure.

For most applications, however, the dough was pressed into a sheet about $\frac{1}{8}$" thick and pre-cured to a B-stage before being ground so that it would pass through a No. 8 sieve. It was then placed in a heated mould and pressed. "Breathing" of the mould was used on some occasions.

The details of the moulding pocedures are specified in Chapter 7.

2.2. Analytical Methods.

2.2.1. The Determination of Melting point. About 0.2g granulated resin was placed in a 75 x 10mm test tube which was immersed in an oil bath. The oil bath was heated at approximately 3°C/ minute and the temperature at which the resin was seen to flow was noted and regarded as the melting point.

2.2.2. The Determination of Gel Time. About 2g resin was placed in a 150 x 10mm test tube and, if necessary, melted. It was then placed in an oil bath at 200°C and the resin was stirred with a copper wire. The viscosity of the resin increased and a point was reached when the resin became rubbery, bubbles could no longer rise to the surface and the stirring wire could not readily be withdrawn. The time to reach this stage was taken as the gel time.

2.2.3. The Determination of Molecular Weight using Mechrolab Vapour Pressure Osmometer, Model 301A. Vapour Pressure Osmometry depends on the variation in vapour pressure of solutions of different concentrations. The theoretical background of the subject has been discussed by Mueller and Stolton. (56).

Drops of solvent and solution are placed on matched thermistors in a controlled temperature chamber and as a result of the difference in their vapour pressures a difference in temperature is recorded. To counteract this a measured resistance is inserted, the value of which is related to the concentration of the solution.

Standardisation is normally carried out using solutions of benzil in the solvent to be used. The temperature of the instrument is allowed to stabilise at the desired level and the benzil solutions are used to obtain a calibration curve, $\frac{\Delta R}{M}$ against M (the molarity of the solution) and to obtain the value $K = \frac{\Delta R}{M}$ at $M = 0$ for carbon tetrachloride. K can be obtained graphically or by calculating the equation of the best fitting straight line by the method of least squares.

Solutions of the unknown are similarly prepared and $\frac{\Delta R}{C}$ is plotted against C (the concentration of the solution in g/l). This gives a value of $\frac{\Delta R}{C}$ at $C = 0$ which is divided into the K value for the solvent to give the molecular weight of the unknown.

2.2.4. Use of the Epprecht Rheomat. The Epprecht Rheomat is an instrument used to make rheological measurements on liquids by rotating a cylindrical bob inside a cup filled with the liquid to be tested. The principles involved in such rotating cylinder viscometers and the variations, which are used in their design, have been described by Dinsdale and Moore (57) while the interpretation of the experimental results has been discussed by Hediger (58).

The bob can be rotated at different rates and the torque required to maintain the speed is measured giving effectively a viscosity/shear rate relationship for the liquid. A Newtonian liquid gives a straight line relationship between torque and shear rate when plotted on the special graph paper provided, and deviations from Newtonian behaviour show up as graphs of different forms. For a series of solutions all behaving as Newtonian liquids, viscosities can be compared by making measurements on each at a single shear rate.

2.2.5. Elemental Analysis. The carbon and hydrogen analyses on 4,4'-dichloromethyl benzophenone were carried out on an F&M C,H and N analyser, Model 185. The chlorine was determined by standard analytical techniques.

2.2.6. **Infra Red Spectroscopy.** The infra red spectrometer used was a Grubb Parsons GS 2a double beam grating instrument. This gave spectra linear in wavelength with scale changes at 2.5, 3.5 and 5μ.

2.2.7. **Thermogravimetric Analysis.** Thermogravimetric analyses were carried out on a Stanton TR - 1 thermobalance fitted with a furnace which could operate up to 1,000°C. A second more precise calibration could also be obtained over the range 20 - 500°C. Only two of the six possible rates of temperature rise were used- viz, 4°C /minute and 7°C /hour.

2.2.8. **Vapour Phase Chromatography.** Most of the chromatographic work was carried out on a Pye chromatograph fitted with a 4 ft. separating column and an argon detector.

A Perkin Elmer F11 programmed temperature capillary column chromatograph fitted with a flame ionisation detector was also used.

Both instruments were coupled to recorders fitted with peak area integraters.

2.2.9. **Void Content of laminate.** The density of the laminate was measured by preparing a solution of bromoform in carbon tetrachloride in which a small piece of laminate neither sank nor rose to the surface when inserted below the surface of the solution. Under such conditions the density of the laminate and the solution were, therefore, equal. The density of the solution was measured using a specific gravity bottle.

Similarly the density of a small piece of cured resin, moulded under pressure, was determined in a solution of bromoform in methyl ethyl ketone.

The density of 'E' glass was obtained from the manufacturer's

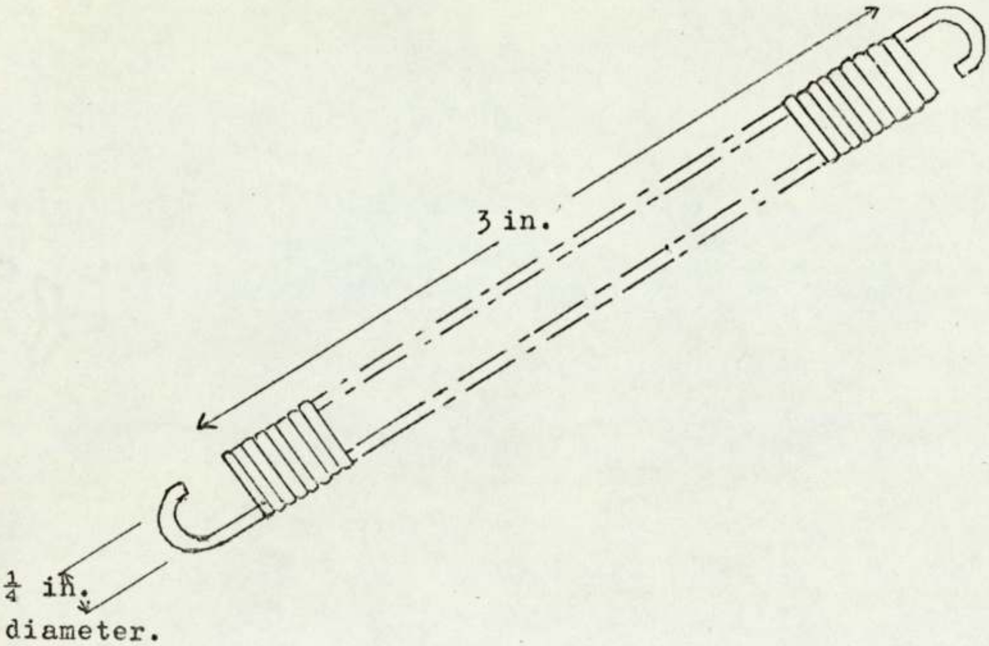


Figure 2.1. DEXTER COIL USED FOR BOND STRENGTH MEASUREMENTS.

literature.

The resin content of the laminate was obtained by burning off the resin.

From these figures the volume fractions of glass and resin in the laminate were calculated; and, by subtraction, the void content was obtained.

2.3. Mechanical and Electrical Testing.

2.3.1. Shear Strength. Shear strength measurements were carried out by punching a $\frac{1}{4}$ inch diameter hole in moulded discs using the Hounsfield Tensometer with a speed of cross head drive of 0.059 inch/minute.

This test was based on BS 2782, Part 3/305.

2.3.2. Flexural Strength. Flexural strength measurements on laminates were made by breaking $\frac{1}{2}$ inch wide strips of laminate in the Hounsfield Tensometer with a 2 inch effective length of sample. Again a cross head drive speed of 0.059 inch/minute was used.

This test was based on BS 2782, Part 3/304

2.3.3. Impact Strength. Impact strengths were measured on Izod notched specimens with $\frac{1}{2}$ inch x $\frac{1}{2}$ inch cross sections, using an Avery instrument.

This test was based on BS 2782, Part 3/306A.

2.3.4. Bond Strength of Resin using Dexter Coils (59). Helical coils of contiguous turns of wire were wound on a $\frac{1}{4}$ inch mandrel. After removing the mandrel the coils were cut into 3 inch lengths and finished as shown in Figure 2.1. In all the tests described, the wire used was polyimide enamelled copper wire 0.040 inch in diameter.

The coils were coated with resin by immersing them vertically for sufficient time to allow air bubbles to rise to the surface of the resin. They were withdrawn, drained and heated to cure the

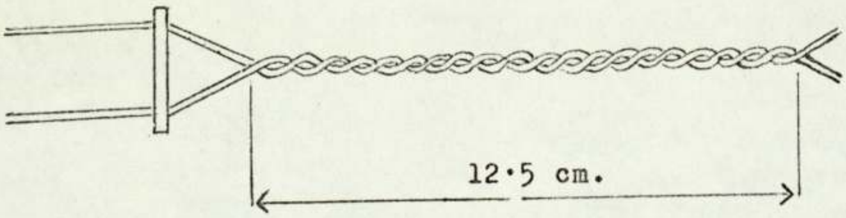


Figure 2.2. TWISTED PAIR (IEC 172).

resin. Bond strength results were then obtained by breaking the coils in flexure at the mid point of a 1 inch effective length using a Hounsfield Tensometer. A cross head drive speed of 0.059 inch/minute was used and the force required to break the coil was taken as the bond strength of the resin. Bond strengths at elevated temperature were obtained by fitting a small oven over the specimen.

2.3.5. The "Twisted Pair" Test. The test specimens were prepared by twisting together the two ends of a single length of 0.040 inch polyimide enamelled copper wire in a controlled manner. The loop formed where the wire was initially bent over was cut to give, in effect, specimens consisting of two wires twisted together as shown in Figure 2.2.

The specimens were divided into four batches of 30. Each batch was coated with a different resin which was then cured. The test pieces were aged cyclically at three temperatures, ten specimens from each batch at each temperature.

After each cycle all the specimens were tested by applying a 1 KV proof voltage between the two wires. The time to failure for each specimen was thus determined and the geometric mean life for each resin/enamel system at each temperature was calculated. These values were plotted on Arrhenius plots (log life v $\frac{1}{T^{o}A}$) to obtain, by extrapolation, the temperature for a 20,000 hour life.

Detailed instructions for carrying out the test are given in IEC publication No. 172.

2.3.6. Measurement of Permittivity and Dielectric Loss Factor. The permittivity (or dielectric constant) of an insulating material is the ratio of the capacitance of a capacitor completely and exclusively filled with the material to the capacity of the same electrode assembly in air.

The dielectric loss factor ($\tan\delta$) of an insulating material is the tangent of the loss angle, by which the phase shift between current and voltage deviates from $\pi/_2$, in a capacitor, the dielectric of which consists exclusively of the insulating material.

Measurements of permittivity and $\tan\delta$ were carried out using a Schering bridge into one arm of which was inserted a capacitor made from the material under test. After balancing the bridge the necessary calculations were made.

These tests were based on BS 2782 Part 2/205.

2.3.7. Volume Resistivity. The resistance was measured at 500 V D.C. between opposite faces of the sample and from this measurement the volume resistivity was calculated.

$$\text{Volume Resistivity} = \frac{\text{Resistance} \times \text{Electrode area}}{\text{Thickness of Specimen.}}$$

This test was based on BS 2782 Part 2/202.

2.3.8. Electric Strength. The "rapidly applied voltage" method which was used, involved applying a steadily increasing voltage across the sample so that breakdown occurred in from 10 to 20 sec. The breakdown voltage divided by the thickness of the sample is its electric strength.

This test was based on BS. 2918.

2.4. Materials.

Below are listed the principal materials which have been used together with their suppliers.

Material	Supplier.
Aluminium bromide (Anhydrous)	Fisons Scientific Apparatus
Aluminium chloride (Anhydrous)	E. Merck
Asbestos FR 72	Turner Bros. Asbestos Co.
Asbestos FR 342	Turner Bros. Asbestos Co.

Material	Supplier.
Amide-Imide varnish	Sterling Varnish Co.
Ball Clay 975	English China Clay Co.
Benzoyl peroxide	Novadel Ltd.
Carbon tetrachloride	Fisons Scientific Apparatus.
Clays RLO 968-970	English China Clay Co.
1.2-dichloroethane	Fisons Scientific Apparatus.
Diphenyl oxide	ICI
4,4'-dimethyl benzophenone	Pilot Chemical Co.
Durene	British Drug Houses.
EEL 3.	Esso Petroleum Co.
Fiberfrax	Carborundum Co.
Ferric chloride (Anhydrous)	British Drug Houses.
Glass cloth Y 360 Y 094	Fothergill and Harvey
Methylal	Fisons Scientific Apparatus.
Monomethoxymethyl durene	Bush Boake Allen Ltd.
Orthophosphoric acid	Fisons Scientific Apparatus.
Polyimide film	Du Pont.
Polyimide enamelled wire	London Electric Wire Co.
Potassium carbonate (Anhydrous)	Fisons Scientific Apparatus.
Santowax R. (mixed terphenyls)	Monsanto Chemical Co.
Sodium hydrogen carbonate	Fisons Scientific Apparatus.
Skydrol 500	Monsanto Chemical Co.
Stannic chloride(Anhydrous)	Fisons Scientific Apparatus.
Sulphuric acid	British Drug Houses.
Sulphuryl chloride	British Drug Houses.
Toluene	British Drug Houses.
p-Xylylene glycol dimethyl ether	Albright and Wilson.

CHAPTER 3.

RESINS BASED ON TERPHENYLS.

The first resins were prepared using mixed terphenyls (Santowax R) and p-XGDME with $SnCl_4$ as catalyst. The Santowax R was chosen because of the comparatively large terphenyl molecule which, it was hoped, would lead more readily to high molecular weight and keep the cross-links farther apart than in the analagous benzene resin. Since Santowax R contains o-, m-, and p-terphenyls the resin produced from it would be expected to have a less regular structure than that from p-terphenyl alone. Such considerations suggested that a degree of flexibility in the final resin might be obtainable with these starting materials.

3.1. Preparation of Terphenyl/p-XGDME Resins with $SnCl_4$ Catalyst.

Initially polymers were made using Santowax R/p-XGDME in the ratios 1/1.2, and 1/1.5; and p-terphenyl/p-XGDME in the ratio 1/1.2. The general method was as described in Section 2.1.1 and the actual conditions were as given in Table 3.1.

Resin No.	Reactants Santowax M	p-XGDME M	$SnCl_4$	Reaction Temp. °C	Conversion %	Gel Time at 200°C. Minutes.	M.Pt. °C
3.1	0.5 (1)	0.6 (1.2)	2ml 10% soln. in $(CH_2Cl)_2$	175-200.	69	10	60
3.2	1.5 (1)	2.25 (1.5)	0.6ml $SnCl_4$	175-200.	64	9	58
3.3	0.2 p-terphenyl (1)	0.24 (1.2)	1ml 10% soln.in $(CH_2Cl)_2$	180-190.	64	11	62

Table 3.1. Details of Terphenyl/p-XGDME Resins.

The figures in brackets indicate molar ratio of reactants.

The conversion of these resins to moulding powders and their subsequent use in producing mouldings showed them to cure only very slowly. An investigation into catalyst activity was, therefore, undertaken to try to find a faster curing resin which could be used to produce mouldings in an acceptable time.

3.2. Study of Catalyst Activity.

The self-condensation of p-XGDME was used to assess catalyst activity. Two groups of catalysts were examined - the typical Lewis acids, and a group of clays with and without added acids. The method was as described in 3.2.1.

3.2.1. Experimental Method. 90g p-XGDME was weighed into a 3-necked, 250ml flask fitted with a distillation head, a stirrer, and a thermometer. The distillation head carried a thermometer, and a water condenser leading to a measuring cylinder. The flask was heated in a fluidised sand bath to 150°C when 10^{-3}moles of catalyst, dissolved or suspended in 10g p-XGDME, was added. The temperature of the reaction mixture was maintained at 150°C ±2°C for 1 hour and the volume of methanol which distilled off was measured.

To test the clays, the procedure was modified so that 20g clay and 100g p-XGDME were both loaded cold and rapidly heated together to 150°C. Again the volume of methanol which distilled off in 1 hour at 150°C was measured. It was found that virtually no distillation occurred below 150°C.

The compounds tested, with the volume of distillate collected, are listed in Table 3.2.

Catalyst	Volume of Distillate in 1 hour
$SnCl_4$	7.2ml
$SnBr_4$	5.3ml
$SnCl_4$ + p-dichloroxylylene	7.8ml
$SnCl_2$ + p-dichloroxylylene	3.2ml
$FeCl_3$ + p-dichloroxylylene	12.8ml
$SnBr_4$ + p-dichloroxylylene	6.5ml
Ball clay 975 (20g)	3.4ml
RLO 968 (20g)	2.9ml
RLO 969 (20g)	10ml in less than 10 min.
RLO 970 (20g)	10ml in less than 10 min.
HCl washed Ball clay 975 (20g)	10ml in less than 10 min.
HCl washed Ball clay 975 (20g)	10ml in 12 min.
Ball clay 975 (10g) + 1ml conc HCl	2.3ml
Ball clay 975 (10g) + 0.1ml conc H_2SO_4	10ml in 5 min.
Ball clay 975 (10g) + 0.1ml 88% H_3PO_4	10ml in 5 min.

The following catalysts gave no reaction under the conditions of test:- $SnCl_2$, $Fe\ Cl_3$, $AlCl_3$, $SnBu_4$, BF_3 etherate, $CoCl_2.6H_2O$, $ZnCl_2$, $HgCl_2$, $TiCl_4$, $SbCl_5$, $ZrCl_4$, H_2SO_4, H_3PO_4, stannous octoate zinc octoate, zinc 8 hydroxy quinoline salt. Each of these was also tested in conjunction with 1g p-dichloroxylylene which had no effect except in the cases of $SnCl_2$ and $FeCl_3$ (see above).

Table 3.2. Comparison of Catalyst Activity.

As can be seen the two clays RLO 969 and RLO 970 were found to be very active compared with RLO 968 and Ball clay 975. RLO 968 was a clay with a high iron content; RLO 969 was an acid washed version of RLO 968; and RLO 970 was bleached kaolin, a pure form of kaolinite.

3.2.2. Further Examination of Clays. 5g samples of RLO 968, 969, 970, and Ball clay 975 were each extracted with 100ml distilled water and the pH of each extract was measured with the following results.

RLO 968	6.12
RLO 969	3.36
RLO 970	4.80
Ball clay 975	6.12

Ball clay 975 was washed with hydrochloric acid and dried. Its catalytic activity was found to have been increased to the level of the active clays. This increase in activity could not be achieved simply by adding hydrochloric acid to the clay/p-XGDME mixture. On the other hand the addition of 0.1ml 88% orthophosphoric acid or sulphuric acid, inactive by themselves, to the clay/p-XGDME mixture increased the catalytic activity to, at least, that of the active clays.

A further series of experiments was carried out to assess the effect of clay/H_3PO_4 ratio, and the catalyst to p-XGDME ratio, on the rate of reaction. On this occasion a temperature of 135°C was used to reduce the reaction rate and the time to collect 10ml methanol was recorded as follows.

Catalyst Mixture.	Time for 10ml methanol.
20g Ball clay 975/0.1ml H_3PO_4	Stopped before 10ml.
20g Ball clay 975/0.2ml H_3PO_4	22 min.
20g Ball clay 975/0.5ml H_3PO_4	20.5 min.
50g Ball clay 975/0.5ml H_3PO_4	8 min.

It can be seen therefore, that a phosphoric acid/clay ratio of 0.1ml /10g is needed to give the best reaction rate and that increasing this ratio to 0.5ml /10g has only a marginal effect. However, if the acid and clay are both increased, while maintaining the same ratio to each other, the reaction rate increases in direct proportion to the amount added.

3.3. Clay catalysed Terphenyl /p-XGDME Resins.

Following the work on catalysts described above Santowax R resins were prepared using an acidified clay catalyst as detailed in Table 3.3.

Resin No.	Reactants Santowax R. M	p-XGDME M	Catalyst	Reaction Temp°C	Conversion %	Gel time at 200°C minutes.	M.Pt °C
3.4	1.5 (1)	2.25 (1.5)	5g ballclay 0.05ml 88%H_3PO_4	140- 170.	71	10	68
3.5	1.5 (1)	2.625 (1.75)	"	150- 180°.	68	11	70

Table 3.3. Details of Clay catalysed Terphenyl /p-XGDME Resins.

The figures in brackets indicate molar ratio of reactants.

3.4 Distillate.

During the preparation of the resins the distillation temperature was observed to rise considerably above 64°C, the boiling point of methanol. Direct application of VPC showed the presence of a small amount of methylal (dimethoxy methane) but no high temperature boiling component.

The distillate was fractionally distilled and yielded, in addition to the major fraction containing the methylal and methanol, a small residue which was identified as p-XGDME(2%).

The formation of methylal in the reaction provides a further possible cross-linking compound since it is a difunctional ether. However, since it has such a low boiling point (38°C) it seems unlikely that it could significantly affect the course of the reaction.

A vapour phase reaction has, however, been carried out in which methylal and DPO were heated together at 260°C with $SnCl_4$ in a sealed vessel for 16 hours. After this time a small amount of a resinous material was formed in the vessel and this was shown by infra red spectroscopy to contain DPO and methylene units. Thus under favourable conditions methylal can be made to react with DPO to give a resin.

A similar reaction was found to take place when methylal and DPO were refluxed together for 4 hours. After allowing to stand for several weeks unreacted DPO crystallised out leaving a light brown liquid containing some resin identical to that mentioned above.

3.5. Resin Cure.

Three aspects of the cure of Resin 3.1 were examined. These were weight loss, examination of volatiles, and an infra red spectroscopic examination of the changes which took place.

3.5.1. Weight loss. An isothermal weight loss at 220°C in air was determined giving a value of 10.2% which was constant after 2½ hours.

A further sample was heated rapidly in air to 200°C and this temperature was maintained until constant weight was achieved.

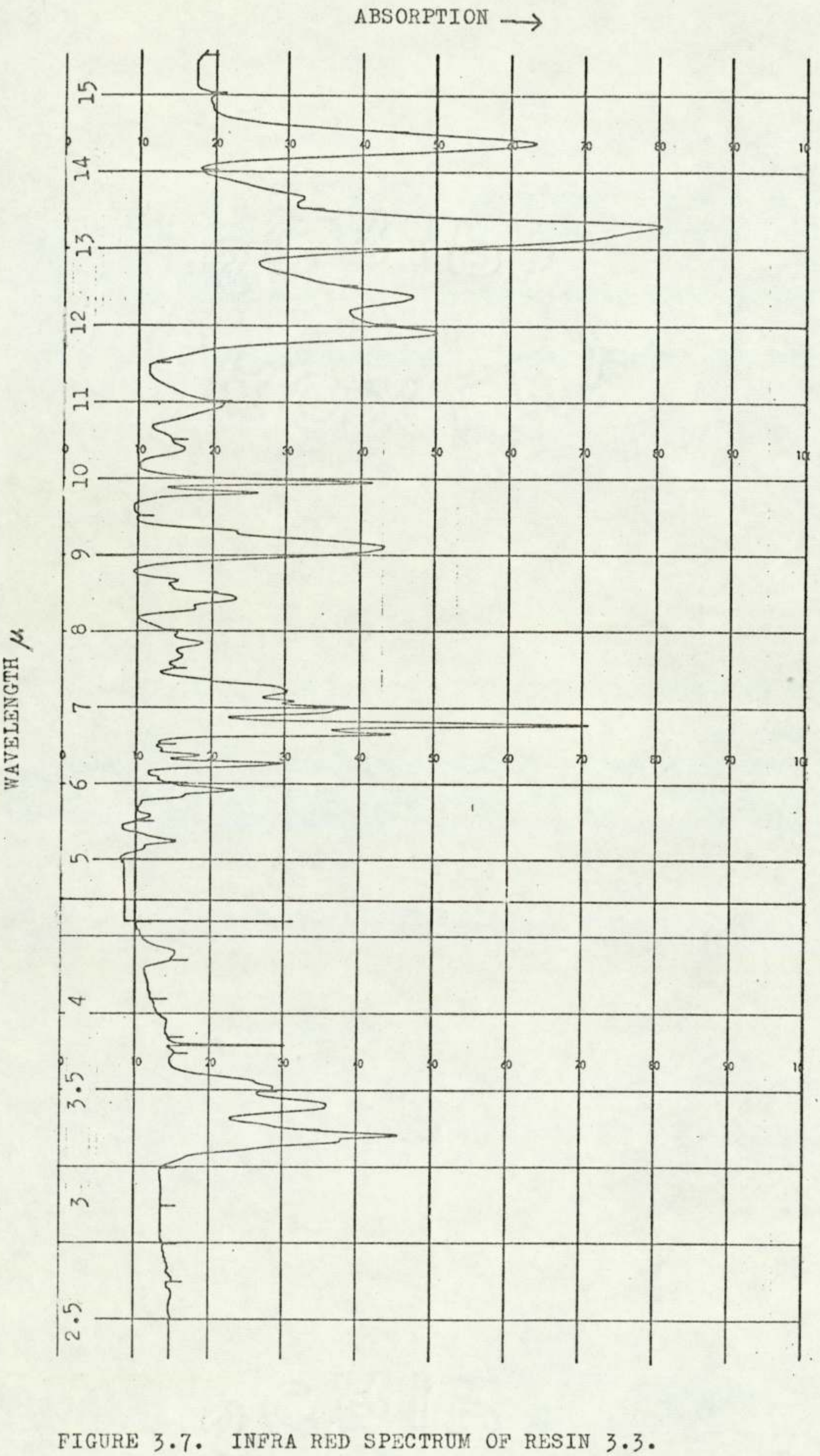


FIGURE 3.7. INFRA RED SPECTRUM OF RESIN 3.3.

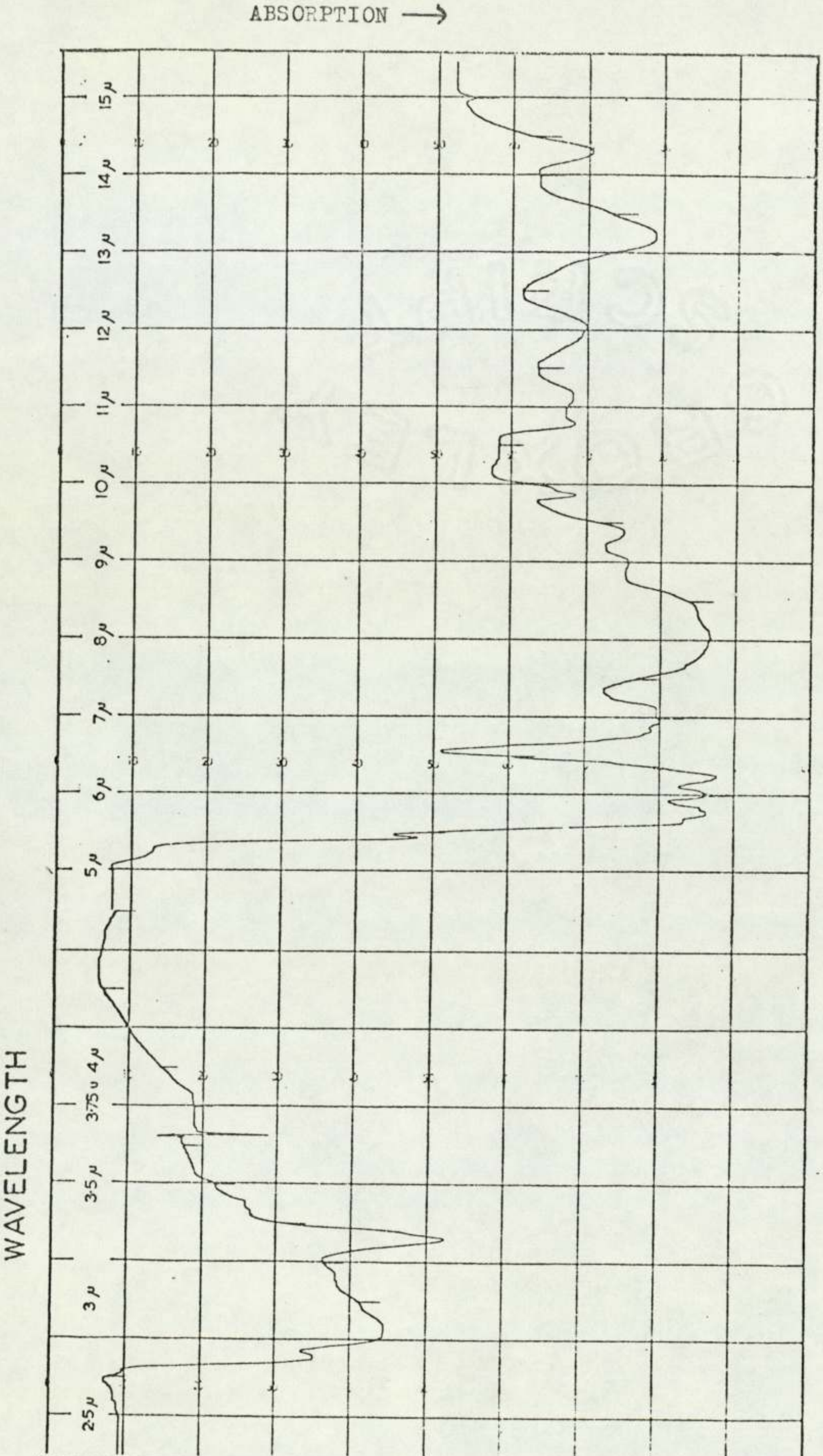


FIGURE 3.6. INFRA RED SPECTRUM OF RESIN 3.1 AFTER HEATING 24 HOURS AT 200°C, 24 HOURS AT 250°C AND 16 HOURS AT 300°C.

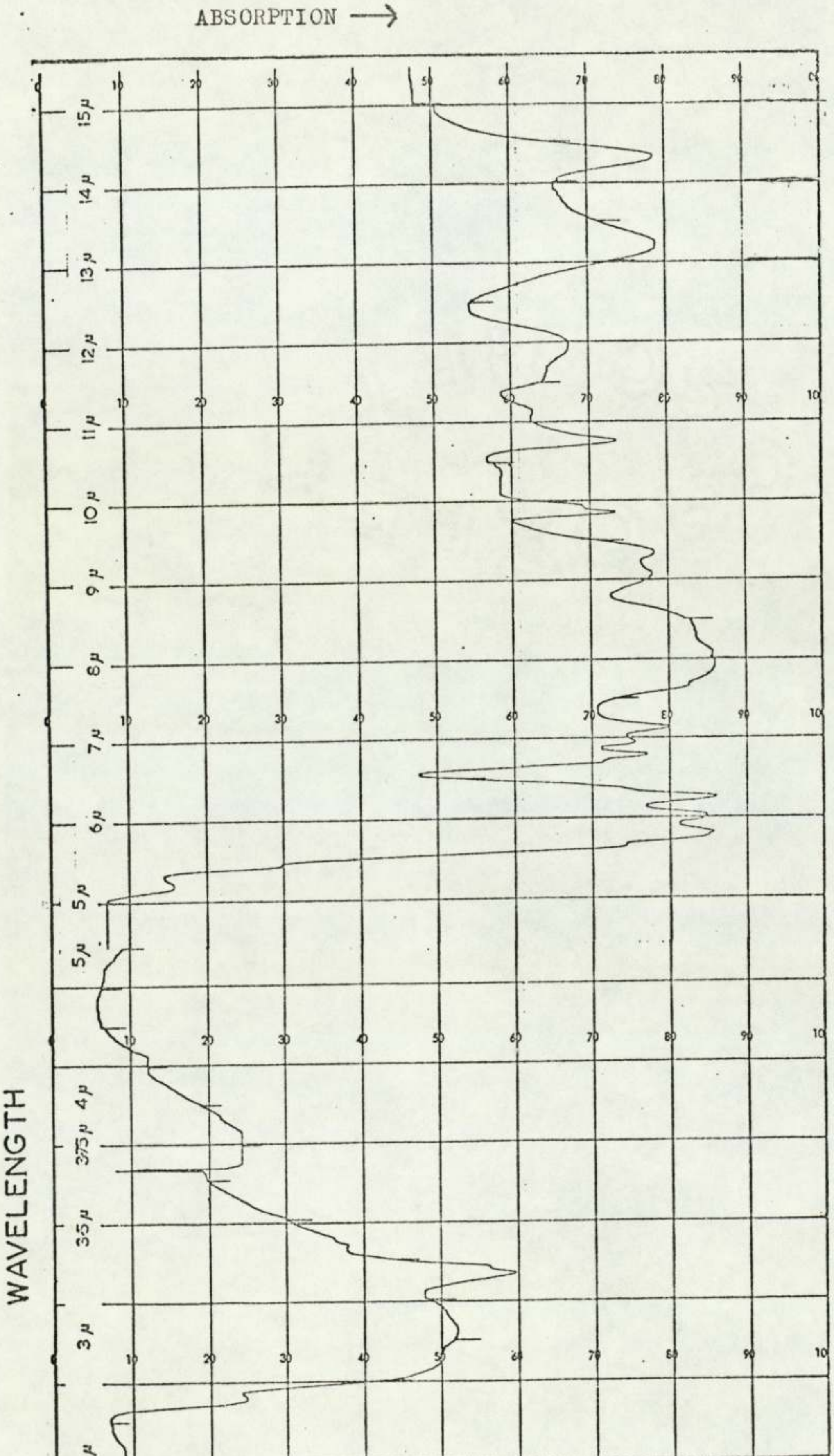


FIGURE 3.5. INFRA RED SPECTRUM OF RESIN 3.1 AFTER HEATING 24 HOURS AT 200°C PLUS 24 HOURS AT 250°C.

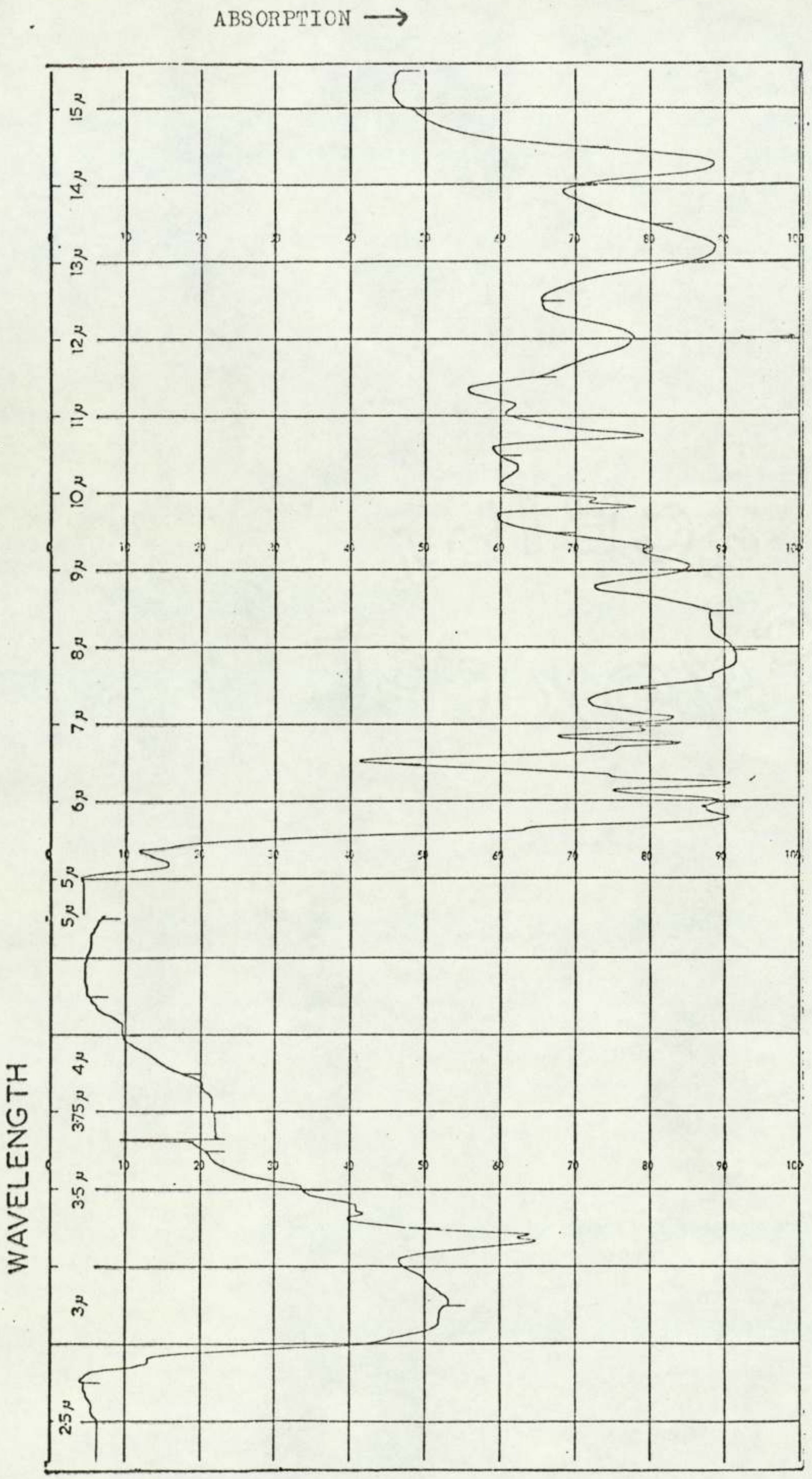


FIGURE 3.4. INFRA RED SPECTRUM OF RESIN 3.1 AFTER HEATING 24 HOURS AT 200°C

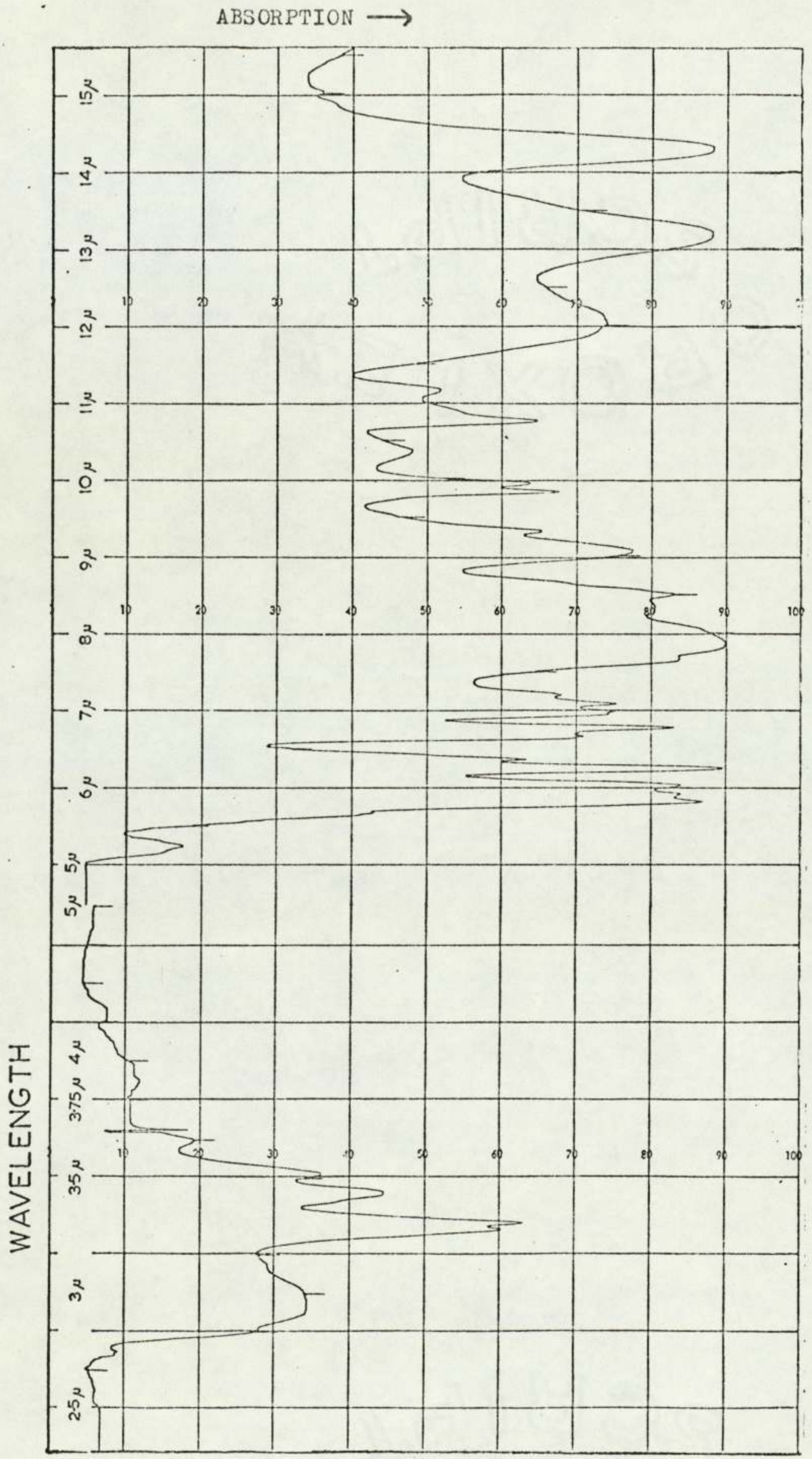


FIGURE 3.3. INFRA RED SPECTRUM OF RESIN 3.1 AFTER HEATING 4 HOURS AT 200°C.

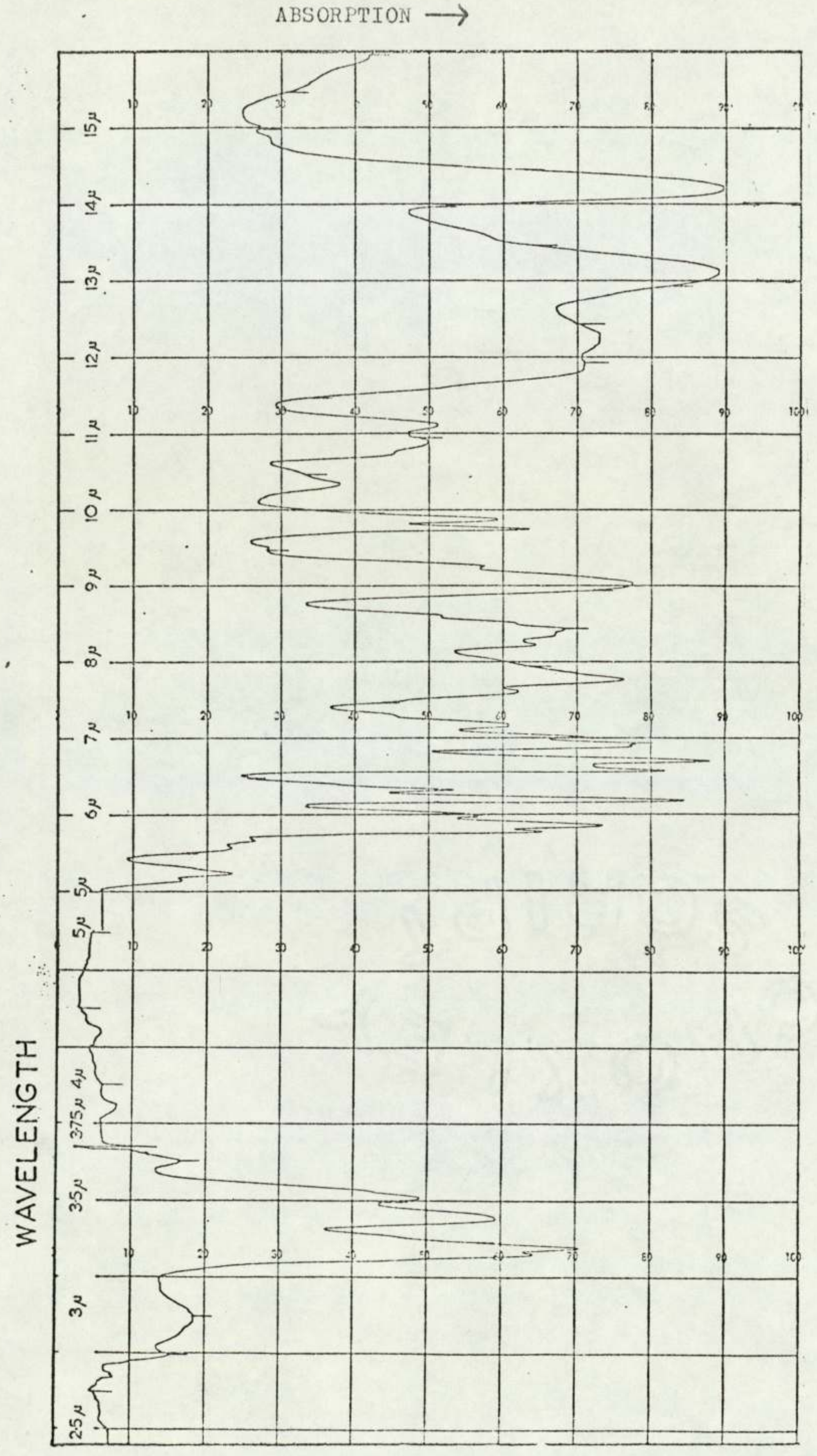


FIGURE 3.2. INFRA RED SPECTRUM OF RESIN 3.1 AFTER HEATING 1 HOUR AT 200°C.

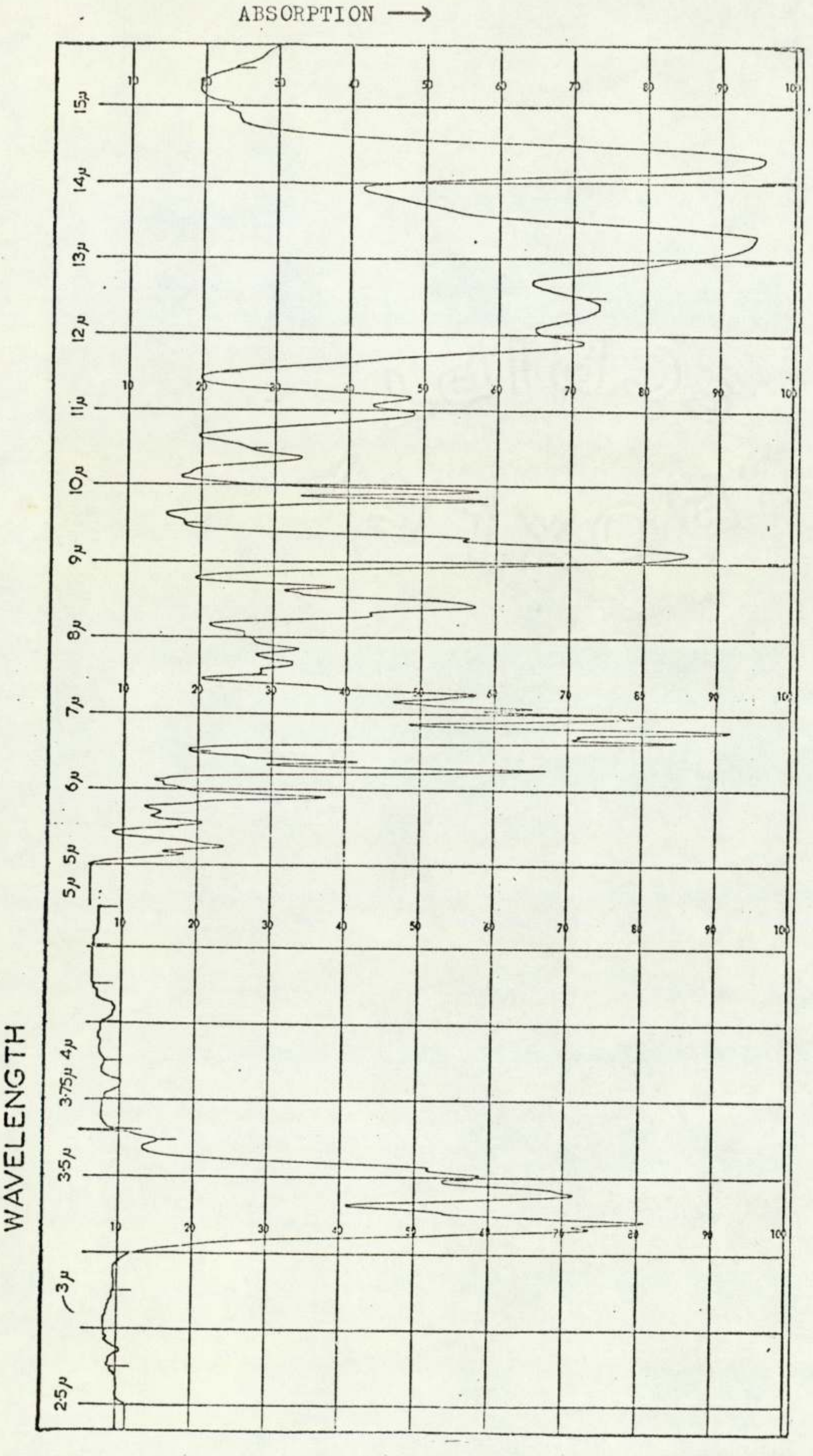


FIGURE 3.1. INFRA RED SPECTRUM OF RESIN 3.1 AS PREPARED.

The temperature was then successively raised to 240°, 270° and 300°C and heating was continued to constant weight at each temperature. An overall weight loss of 11% was obtained compared with a loss of 6.7% calculated for the loss of remaining methanol.

The same procedure with Resin 3.4 gave a weight loss of 8.4% compared with a theoretical methanol loss of 6.8%.

3.5.2. Examination of Volatiles during Cure. The volatile matter produced when Resin 3.1 was cured was condensed and examined by infra red spectroscopy. It was shown to contain both starting materials and a small amount of an unidentified aromatic aldehyde.

3.5.3. Infra Red Spectroscopy. A sample of Resin 3.1 was heated on a sodium chloride disc in an oven at 200°C for 24 hours, at 250°C for 24 hours and finally at 300°C for 16 hours. Infra red spectra were recorded after various intervals and some of these are recorded in Figures 3.1 - 3.6 . The changes which occured are discussed in 3.7.3. The spectrum of Resin 3.3 is also shown in Figure 3.7 and differences between this and the initial spectrum of Resin 3.1 are also discussed in 3.7.3.

3.6 Thermogravimetric Analysis.

A cured sample of Resin 3.1 was heated (4°C/minute) in air on the thermobalance. The thermogram in Figure 3.8 shows a "triggering temperature" of 475 - 500°C.

The cured Resin 3.4 was compared with a cured silicone resin MS 997 and 'Kapton' polyimide film by heating (7°C/ hour) in air on the thermobalance. The thermograms are shown in Figure 3.9.

3.7 Discussion.

3.7.1. Catalyst Examination. No systematic examination of catalyst activity in the condensation of ethers with aromatic compounds has been undertaken although a considerable number of papers have been published on the reactions of various ethers with BF_3 as catalyst. These have been reviewed by Schriesheim (60).

The work described in this chapter indicates the surprising conclusion that in the self-condensation of p-XGDME at 150°C some of the traditionally active Friedel-Crafts catalysts, such as $AlCl_3$, $FeCl_3$ and H_2SO_4 were totally inactive while $SnCl_4$ which is usually regarded as a mild catalyst showed up as the most active of the Lewis acids examined.

Since it was not possible to use a strictly comparable quantity of the clays in this experiment a fixed weight of clay was chosen which was thought to be tolerable in a resin prepared with 100g of p-XGDME.

A Westinghouse Electric Corporation patent (61) describes the use of a clay with added HCl as catalyst for the condensation of ethers and suggests that the activity is a result of the conversion of iron impurities in the clay to $FeCl_3$. The present work has shown that this explanation is incorrect, or only partially correct, since an acidic but substantially iron-free clay (RLO 969) was much more active than a slightly acid clay containing a fairly high iron content. The significant feature has been shown to be the acidity of the clay.

It should be noted that the self-condensation of p -XGDME contrasts with the behaviour of p-DCX which has been shown both by Phillips (1) and Grassie (23) not to react with itself to any measurable extent, under the conditions which they employed in preparing their polymers. The difference can probably be explained by the stronger activating influence of the $-CH_2OCH_3$ group compared with $-CH_2Cl$.

3.7.2. Distillate. The presence of methylal has been noted in the distillate formed during the resin preparation. This could arise from the combination of a $-OCH_3$ and a $-CH_2OCH_3$ group. The $-OCH_3$ group is formed when the p-XGDME ether linkage is cleaved and the $-CH_2OCH_3$ group could be formed by splitting off from the p-XGDME such as occurs in the isomerisation of hydrocarbons under the influence of Friedel-Crafts catalysts.

Methylal has been shown to be capable of reacting with DPO and could have some influence on the final resin although this is likely to be very small because of the small quantity of methylal involved and its low boiling point.

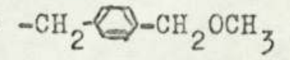
3.7.3. Cure of Resin and Resin Structure. Thermogravimetric analysis showed a weight loss greater than could be explained simply by removal of residual methanol from the resin. Examination of the volatile matter produced during cure showed, not surprisingly, that, in addition to methanol, unreacted terphenyl and p-XGDME could be detected.

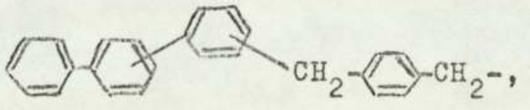
When the cure of the resin was examined by infra red spectroscopy the first changes in the spectrum involved the disappearance of bands at 11.9 and 12.4μ which were present in the spectra of Santowax R and p-XGDME, respectively, showing loss of unreacted starting materials.

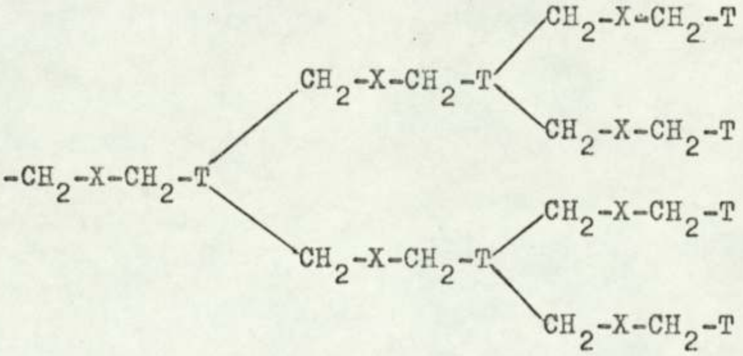
Diaryl ketonic and aromatic carboxylic acid bands appeared at 6.05 and 5.9μ respectively even within the first hour's heating at 200°C. On further heating these carbonyl absorptions increased in intensity and other bands characteristic of carboxylic acids developed at 3μ (very broad), 7μ and 8μ (both broad) and a fairly sharp absorption at 10.8μ. At the same time the $-CH_2-$ and $-CH_3$ absorptions ($3.4 - 3.5\mu$) and the alkyl ether absorption at 9.12μ diminished steadily. In the later stages conversion of the carboxylic acid groups to anhydride occurred. Carbonyl bands appeared at 5.41 and 5.64μ and a reduction was noted in the intensity of the 3μ and 10.8μ bands, both of which are associated with vibrations of the -OH group in the carboxylic acid.

Other changes occurred in the $11-12.5\mu$ region which gave rise to a new absorption at 12μ after four hours at 200°C and the disappearance of the 12.4 and 11.8μ bands already mentioned. This was followed by the development of further absorptions at 11.5μ as a shoulder on the 12μ band and eventually a band at 11.5μ while at the same time the absorption at 5.25μ, which could be associated with a p-disubstitution pattern, gradually decreased and almost disappeared.

These changes can be explained by a gradual change towards a more complex substitution pattern since they involve a shift in the positions of the absorption bands towards higher frequencies, although it is difficult to say precisely what these patterns are. This difficulty arises from the overlapping of the regions in which different absorptions occur and, more particularly, from the fact that electron withdrawing substituents, such as $>C=O$, are known to modify the frequencies at which the ring -H vibrations occur. In the spectrum of benzoic acid, for example, absorptions occur at 14.01 and 12.41μ (62) whereas the normal positions for the out of plane vibrations of ring -H atoms in monosubstituted aromatics are 14.08 - 14.49 and 12.99 - 13.70μ (63)

Despite all these changes there remains a very high concentration of monosubstituted benzene rings which shows conclusively that an end-to-end reaction does not occur. This may be because, when one position on a terminal benzene ring is substituted the remaining positions are activated by the electron donating property of the  group and the activation so caused is strong enough to override the difficulties arising from the steric effect of bulky substituents around the ring. The second substituent would then enter the same ring as the first and a polymer with pendant diphenyl groups would result.

Alternatively, and much more probably, a shell like structure such as proposed by Parker for polybenzyl(16) could explain the high concentration of monosubstituted rings which persist even after cure. If the polymer is regarded as being built up of units of the structure , represented by T-CH_2-X-CH_2- in the diagram below, there will always be a high concentration of monosubstituted rings around the outside of the molecule irrespective of the arrangement in the interior of the molecule. On this basis one possible structure for the polymer would be:-



etc.

In view of the low concentration of p- disubstitution it seems likely that the extra p-XGDME molecules react with X units in the foregoing structure giving $-CH_2OCH_3$ end groups which can take part in further reaction.

The fact that when subjected to thermogravimetric analysis the polymer eventually degrades completely leaving no carbonaceous char suggests that its structure is highly branched with many sites for degradation. This would be in agreement with the shell like structure and would discount a highly cross linked structure.

The infra red spectrum of the resin prepared from p-terphenyl shows a stronger p-disubstitution band than that from the mixed terphenyl but otherwise is very similar.

The strengthening of the resin during cure can be attributed partly to the formation of fresh links by condensation of the $-CH_2OCH_3$ group with a benzene ring but also to the chain stiffening caused by the conversion of $-CH_2-$ to -CO- between aromatic nuclei. Hydrogen bonding following conversion of $-CH_2OCH_3-$ to -COOH can also be expected to make a contribution to strength as can the anhydride bonds formed in the later stages of cure.

Chapter 4.

COMPOSITE MATERIALS BASED ON TERPHENYL/p-XGDME RESINS.

4.1. Moulding.

In moulding practice it is economically desirable that the moulding cycle should be as short as possible and it was decided early that a maximum moulding time of 30 minutes should be imposed. The criterion used was that the moulding should be removable from the mould without distortion and should not distort on post-cure.

First attempts at moulding were made using Resin 3.1. (Chapter 3) mixed with fillers as follows:-

40g Resin 3.1.
30g Asbestos FR 72
30g Ball clay 975

However, the cure in the mould was so slow that some method of accelerating this stage had to be found.

4.1.1. Incorporation of Extra Stannic Chloride. Moulding powders containing additional $SnCl_4$ were prepared as described in 2.1.3. and mouldings were made from them as detailed in Table 4.1. Shear Strength values obtained for the discs described are shown in the final column.

Moulding Powder.	Moulding Technique.	Shear Strength tons/in^2.
MP 4.1 40g Resin 3.1 30g Asbestos FR 72 30g Ball clay 975 0.3ml $SnCl_4$.	Powder was preheated 10 minutes at 200°C. Pressed into pellets cold. Pellet preheated for 5 minutes at 200°C. Placed in the mould at 200°C.	1.08 - 2.28.

Moulding Powder	Moulding Technique.	Shear Strength tons/in^2.
MP 4.1 (continued)	Mould closed with "Breathing" 4 times as it closed and after 5 and 10 minutes. Pressed at 3tons/in.^{2} for 30 minutes at 200°C. Post-cured for 24 hours at 240°C.	
MP 4.2 40g Resin 3.1 30g Asbestos FR342 30g Ball clay 975 0.3ml $SnCl_4$.	Identical procedure.	1.73- 3.67.
MP 4.3 40g Resin 3.2 30g Asbestos FR342 30g Ball clay 975 0.3ml $SnCl_4$.	Identical procedure	2.5- 3.5.

Table 4.1 <u>Preparation of Mouldings using $SnCl_4$ catalysed Terphenyl/p-XGDME Resins.</u>

The shear strength results obtained from MP 4.2 were higher than those from MP 4.1 showing that the longer fibre asbestos FR342 gave some benefit thus explaining why it was adopted in the later work. Results from MP 4.3 were slightly better than those from MP 4.2 showing a slight advantage from the higher p-XGDME/ Santowax R ratio

4.1.2. Moulding using Clay catalysed Terphenyl/p-XGDME Resins.

As a consequence of the above results, when the clay catalysed resins were examined in moulding compositions, only resins with Santowax R/p-XGDME ratios of 1/1.5 and 1/1.75 were used. Moulding powders, using Resins 3.4 and 3.5 were prepared as described in 2.1.3. and these were moulded into discs as detailed in Table 4.2. Shear strength values are given in the final column.

Moulding Powder	Moulding Technique.	Shear Strength tons/in.^{2}
MP 4.4 400g Resin 3.4 300g Asbestos FR342 300g Ball clay 975	Powder pre-cured 120minutes at 200°C. Pelleted cold. Pellet pre-heated 10 minutes at 200°C. Moulded at 200°C. as MP 4.1.—4.3.	2.45-3.07.
MP 4.5 400g Resin 3.5 300g Asbestos FR342 300g Ball clay 975	Powder pre-cured 180 minutes at 200°C then as MP 4.4	2.50-2.78.

Table 4.2 Mouldings using Clay catalysed Terphenyl/p-XGDME Resins.

These results showed that the higher p-XGDME content in the Resin 3.5 used in MP 4.5 gave no advantage over MP 4.4. Future experiments were, therefore, carried out using the moulding powder MP 4.4 which gave mouldings with a slightly lower mean shear strength than MP 4.3 but with a very much narrower spread of results.

4.1.3. Effect of Additional Cure. All the results so far quoted were obtained after post-curing the discs for 24 hours at 200°C. Several discs were further post-cured and the shear strengths obtained are listed in Table 4.3

Moulding Powder	Post Cure		Shear Strength tons/in^2.
MP 4.2	48 hours 200°C		1.97
	"	+ 24 hours 240°C	2.46
	"	+ 24 hours 270°C	2.51
	"	+ 24 hours 300°C	2.54
MP 4.3	24 hours 200°C		2.49,2.49
	"	+ 24 hours 240°C	2.85, 2.69
	"	+110 hours 240°C	2.91, 3.37
MP 4.4	24 hours 200°C		2.45 -3.07
	"	+ 24 hours 240°C	2.95 -3.55

Table 4.3 Effect of Post-Cure on Shear Strength of Mouldings.

In all cases post-cure has given greater shear strength but the actual increase has not been very great (ca 25%) and not very temperature dependent within the range examined. All the values obtained were well short of that of a wood flour filled phenolic moulding which was tested and found to be 6.7 tons/in^2.

4.1.4. Quality of Mouldings. None of the mouldings prepared as described above was of good quality. The main defect was that all mouldings showed distinct grain boundaries indicating lack of flow of the moulding powder. When the pre-cure of the powder

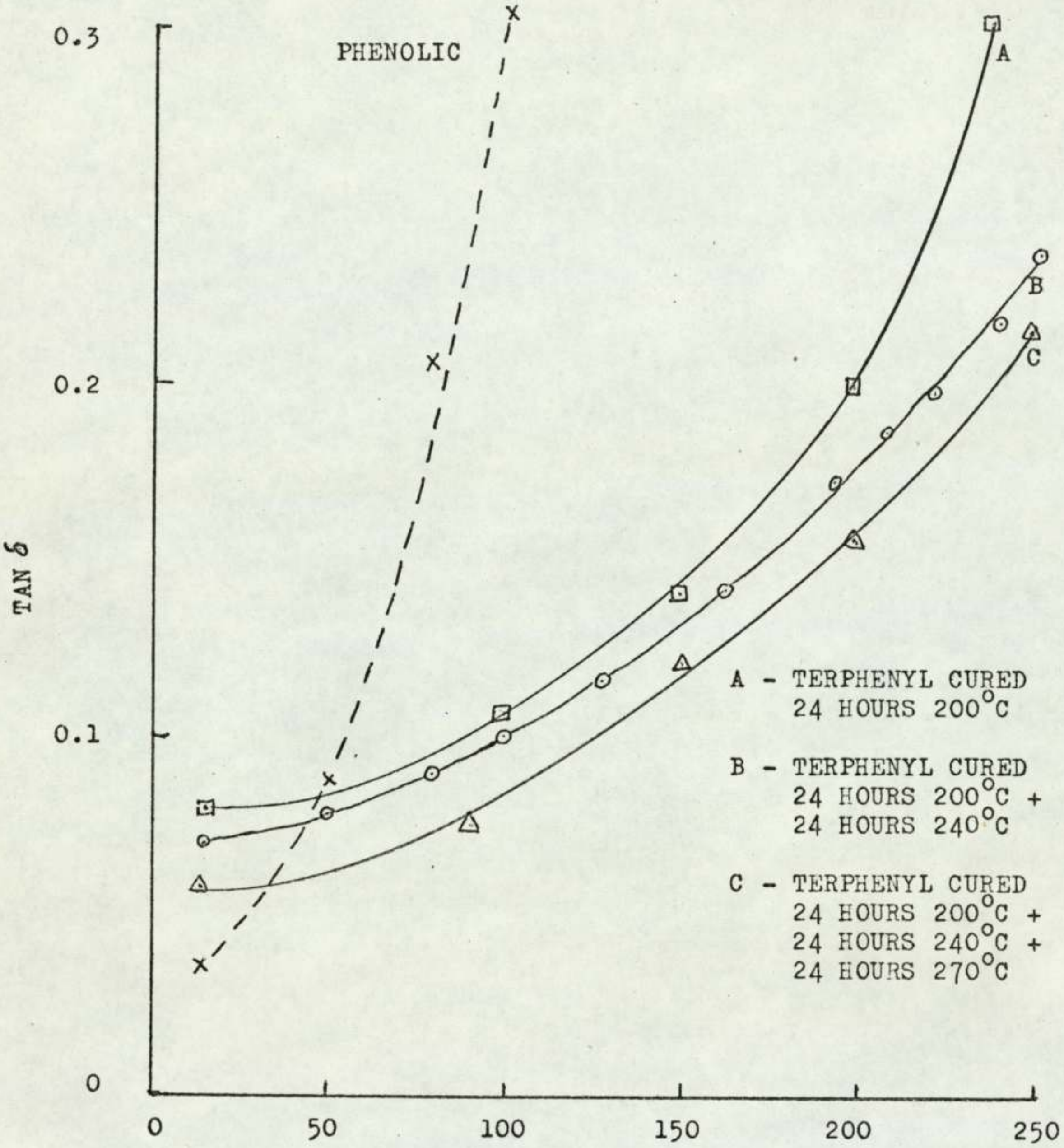


FIGURE 4.1. TAN δ v TEMPERATURE FOR TERPHENYL RESIN BASED MOULDING AFTER DIFFERENT CURE SCHEDULES COMPARED WITH AN ELECTRICAL GRADE PHENOLIC MOULDING.

was reduced to allow for greater flow the resin oozed out of the press during moulding and even under this condition grain boundaries remained visible.

The effects of several established flow promoters and other materials which might conceivably act in this capacity were investigated but none was found which significantly improved the appearance of the mouldings. The following materials were examined:- stearic acid, calcium stearate, naphthalene, furfural and Santowax R.

An experiment was carried out in which the moulding powder was pre-cured in an atmosphere of carbon dioxide to prevent surface oxidation of the granules. Although the surface colour of the moulding powder was much lighter than when pre-cured in air, moulded discs still showed distinct grain boundaries.

4.1.5. Electrical Properties of Mouldings. The dielectric loss factor for a 4½ inch diameter by ⅛ inch thick moulded disc made from MP 4.4. has been measured as a function of temperature after different stages of cure and the results are shown in Figure 4.1 along with the results for an electrical grade phenolic moulded disc.

Electric strength values and comparative tracking index have also been obtained on the same disc with the results given below.

Electric Strength (rapidly applied voltage) 37 V/mil.

C.T.I. (50 drops IEC 112) 200 - 250.

4.2. Possible Applications other than Mouldings.

4.2.1. Film supported on Woven Glass Cloth. Pieces of glass cloth were double dipped in a 40% solution of Resin 3.4. in 1,2 dichloroethane with a drying period of 5 minutes at 100°C between dips and a cure of 24 hours at 200°C after the second dip. No application could be envisaged for the impregnated glass cloth which became brittle and distorted after cure.

4.2.2. Film on Copper. Pieces of degreased copper foil were dipped in chromic acid for 30 seconds, washed and dried. They were immersed in a 20% solution of Resin 3.4 in 1,2-dichloroethane, slowly withdrawn and cured at 200°C for 24 hours. The film of resin was extremely brittle and could obviously not be used as an enamel.

4.2.3. Impregnated Coils. Helical coils of polyimide enamelled wire were impregnated with a 40% solution of Resin 3.4 in 1,2-dichloroethane and cured for 24 hours at 200°C plus 24 hours at 240°C. The bond strength of these coils was measured and a mean value of 9 lb was obtained compared with 54 lb. for specimens impregnated with an amide-imide impregnating varnish.

4.3. Discussion.

No application was found for which the terphenyl based resins were satisfactory. All the specimens prepared had poor mechanical properties due to the brittle nature of the resin. This caused distortion of impregnated glass cloth, poor bond strength in the impregnated coils and lack of adhesion of films on copper.

In moulding the lack of flow of the moulding powder as an entity was a serious shortcoming. When pre-cure of the moulding powder was reduced to encourage flow it was only the resin which flowed out and it seems probable that the grain boundaries which were so obvious on the mouldings represented areas of high resin content which were substantially unreinforced. These regions would be formed by squeezing resin out from individual granules. The presence of such areas could account for the low values obtained for the shear strengths of all the discs prepared.

The much faster resin preparation achieved by using the clay /H_3PO_4 catalyst did not give a correspondingly faster cure of the moulding either in the mould or subsequently in the oven. This may be due to the effect of the clay filler which, although only slightly acid, could, when present in large quantities, mask any effect of catalyst in the resin.

Chapter 5.

RESINS BASED ON DIPHENYL OXIDE.

In assessing the inter-relationship of technologically useful properties with resin structure the programme was extended to include resins based on diphenyl oxide (DPO). It was hoped that because of its flexibilising ether link, DPO, when reacted with p-XGDME, would yield polymers less brittle than the analogous terphenyl resins.

Phillips (2) has reported the preparation of both DPO/p-DCX and DPO/p-XGDME resins and concluded that they could possibly be used as impregnating resins but that their slow cure made them unsuitable for laminating or moulding.

5.1. Preparation of DPO/p-XGDME Resins. The resins described in Table 5.1. were prepared.

Resin No.	Reactants DPO moles	p-XGDME moles	Catalyst	Reaction Temp. °C	Conversion. %	Gel time at 200°C mins.
5.1	10(1)	10(1)	6ml 10% by volume $SnCl_4$ in $ClCH_2CH_2Cl$.	190-210	60	60
5.2	8(1)	9.6(1.2)	10ml 20% by volume $SnCl_4$ in $ClCH_2CH_2Cl$.	175	64	7
5.3	1.6(1)	2.4(1.5)	2.5ml 20% by volume $SnCl_4$ in $ClCH_2CH_2Cl$.	175	62	6
5.4	1.5(1)	2.52(1.68)	"	175	61	6
5.5	1.5(1)	2.625(1.75)	"	175	64	5

Resin No.	Reactants DPO moles	p-XGDME moles	Catalyst	Reaction Temp.°C	Conversion. %	Gel time at 200°C mins.
5.6	1.25(1)	2.5(2)	2.5ml 20% by volume $SnCl_4$ in $ClCH_2CH_2Cl$.	175	59 gelled	-
5.7	8(1)	9.6(1.2)	30g Ball clay 975 0.3ml 88% H_3PO_4.	130-140	64	12
5.8	8(1)	9.6(1.2)	10ml 10% by volume $SnCl_4$ in $ClCH_2CH_2Cl$.	190-210	62	10

Table 5.1. Preparation of DPO / p-XGDME Resins. The figures in brackets indicate the molar ratio of DPO/p-XGDME.

As the proportion of p-XGDME in the resin increased the viscosity of the resin also increased until, with the ratio 1/2 in Resin 5.6, gelation occurred at only 59% conversion.

5.2. Cure of Resin.

The cure of Resin 5.2 has been examined by weight loss, by study of the acetone soluble matter in the gelled resin and by infra red spectroscopy.

5.2.1. Weight loss during cure. The resin was heated at 200°C for one hour and then at 260°C to constant weight using the thermobalance. The following values were obtained for weight loss.

Weight loss on heating for 1 hour at 200°C	to constant weight at 260°C	Theoretical loss due to loss of methanol.
20.1 %	21.3 %	8.0 %

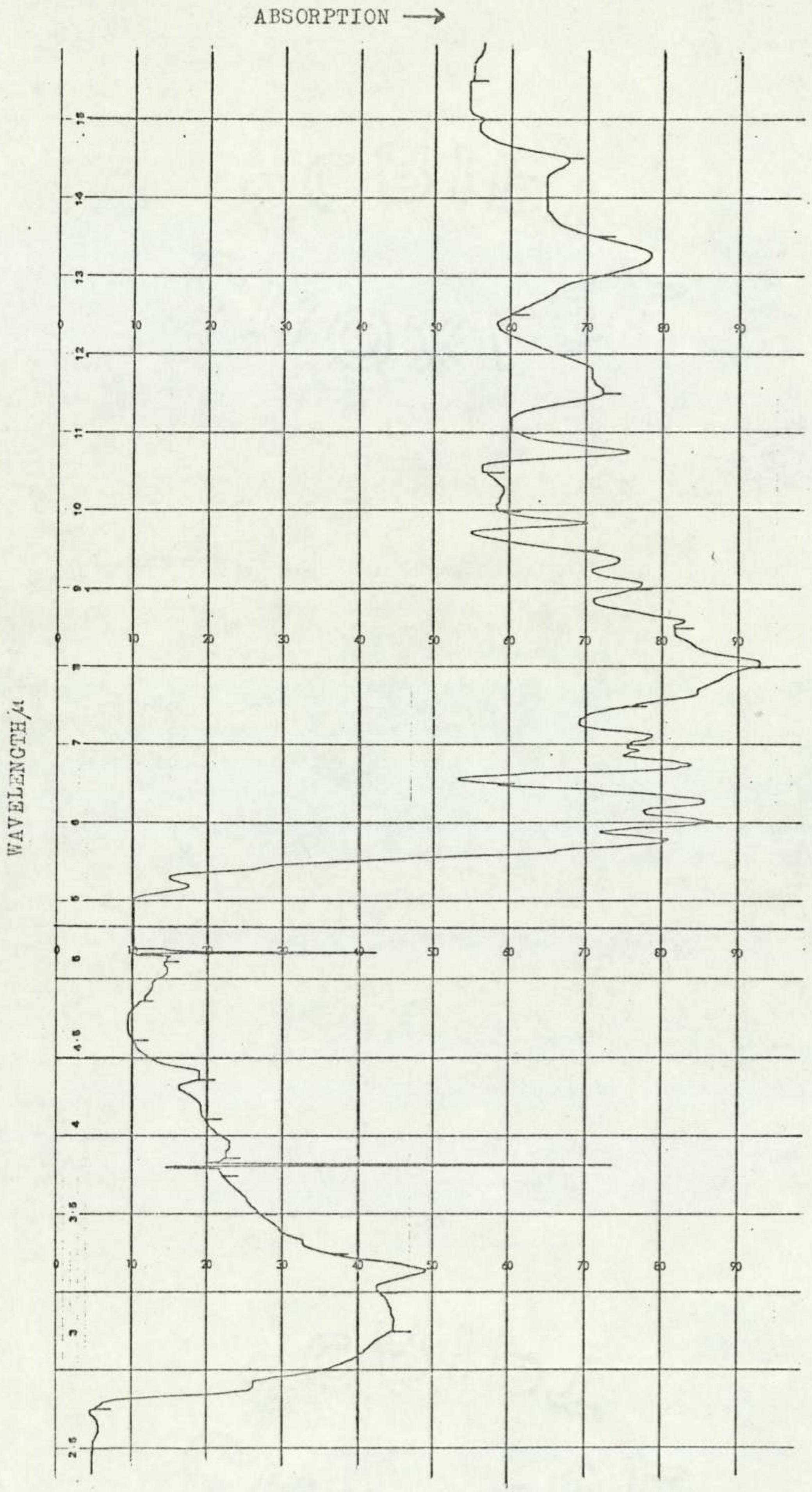


FIGURE 5.5. INFRA RED SPECTRUM OF RESIN 5.2 AFTER HEATING 24 HOURS AT 200°C PLUS 35 HOURS AT 260°C.

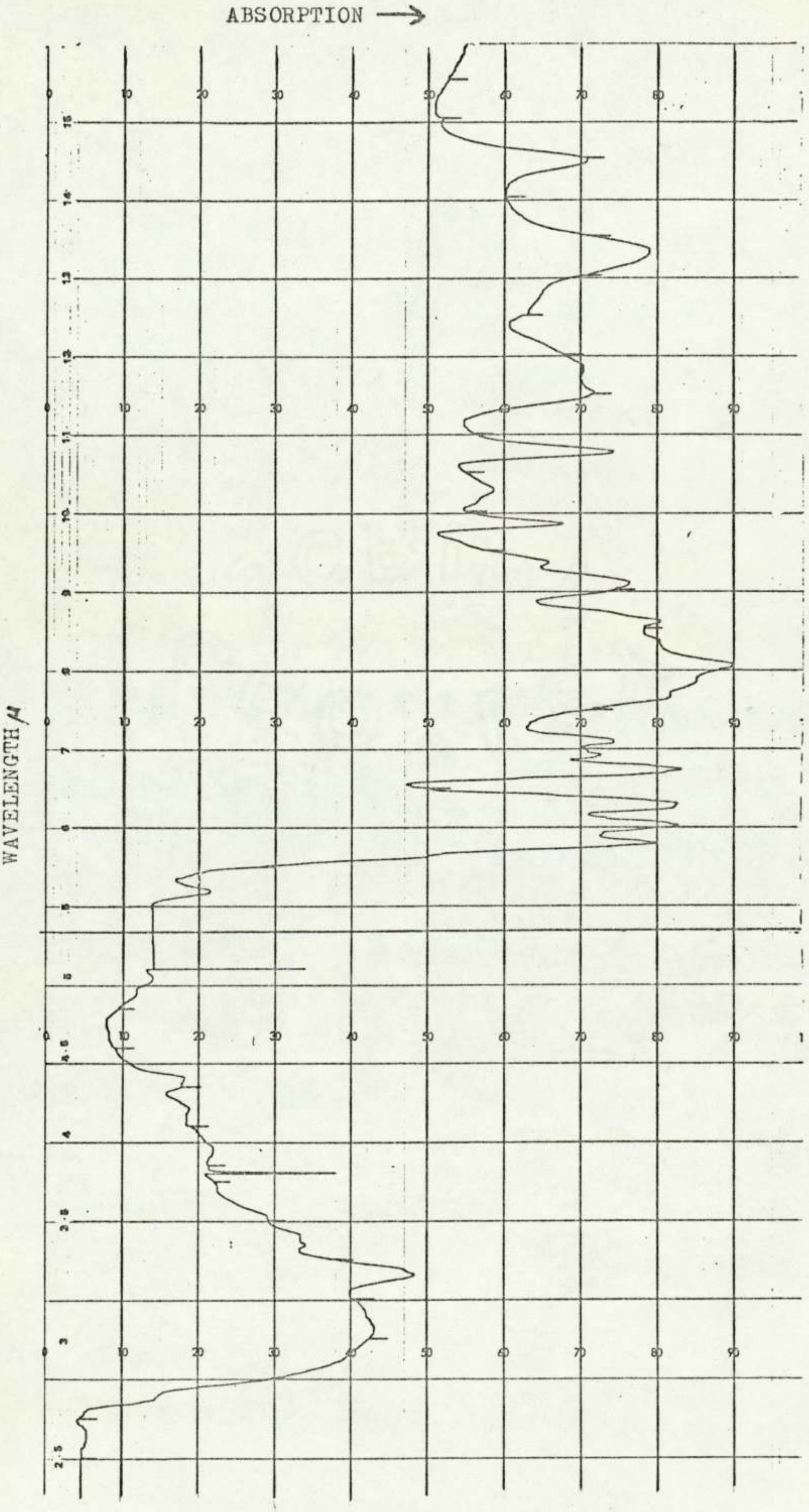


FIGURE 5.4. INFRA RED SPECTRUM OF RESIN 5.2 AFTER HEATING 24 HOURS AT 200°C.

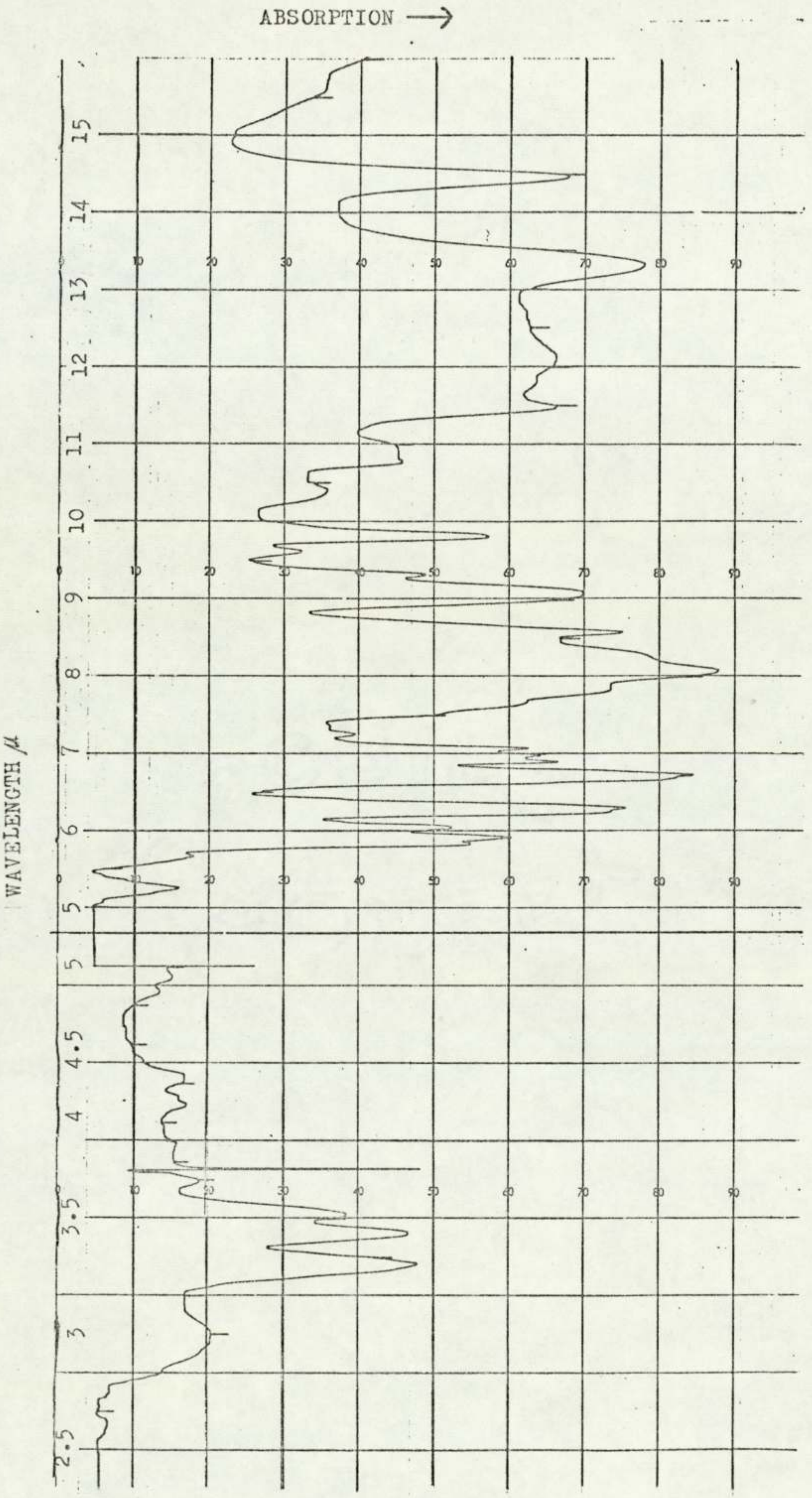


FIGURE 5.3. INFRA RED SPECTRUM OF RESIN 5.2 AFTER HEATING 1 HOUR AT 200°C.

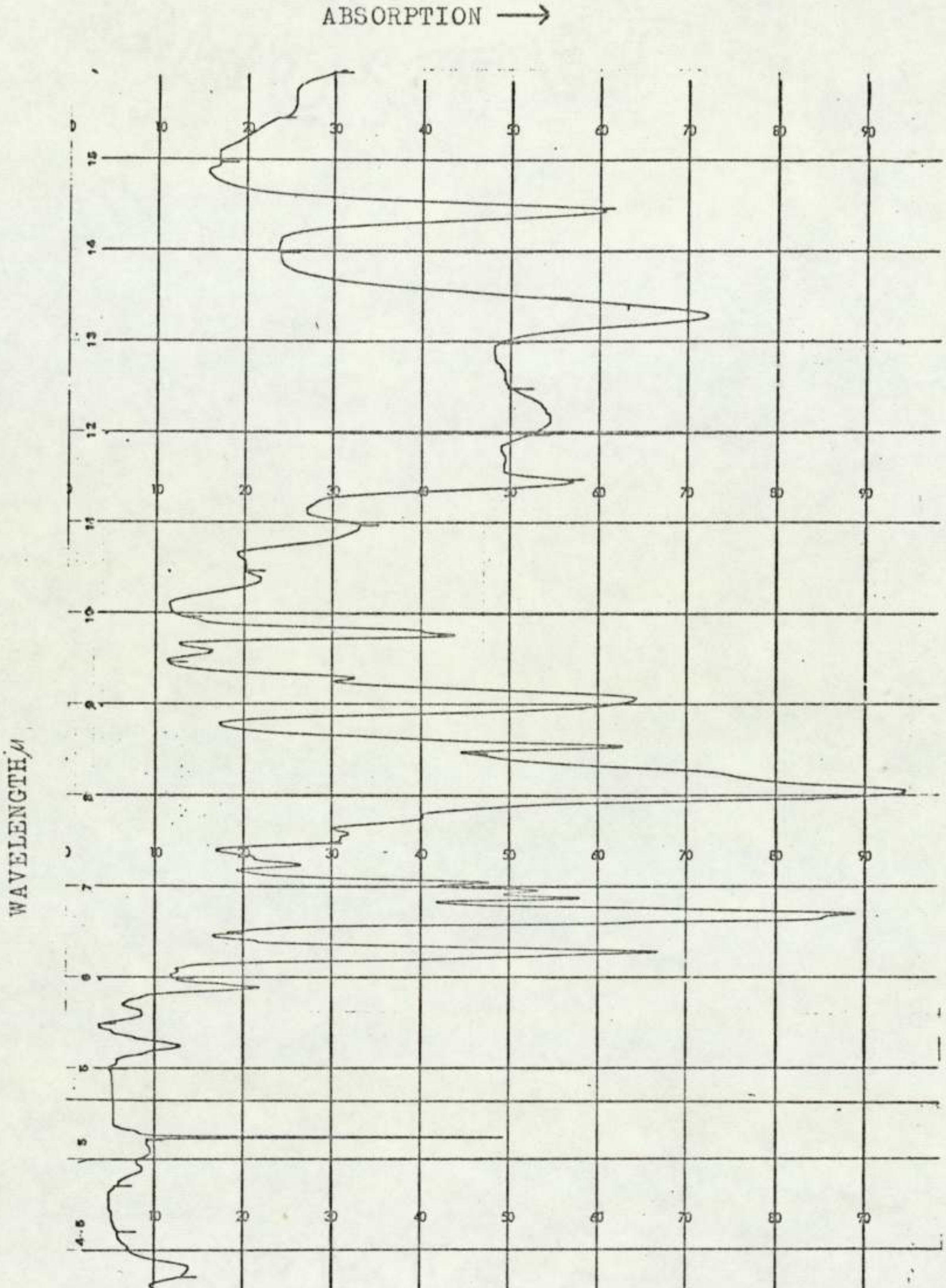


FIGURE 5.2. INFRA RED SPECTRUM OF RESIN 5.2 AFTER HEATING 15 MINUTES AT 200°C.

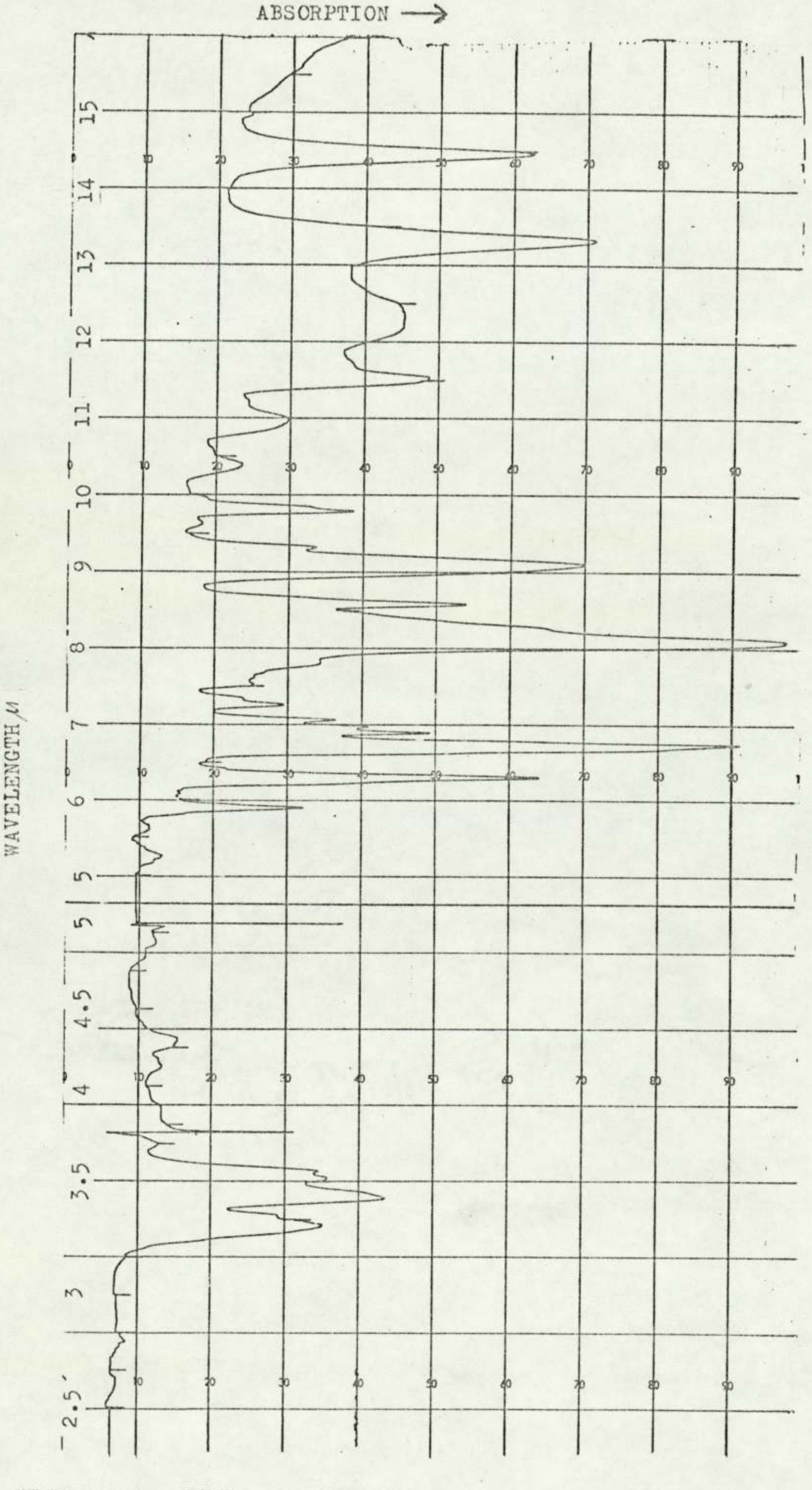


FIGURE 5.1. INFRA RED SPECTRUM OF RESIN 5.2 AS PREPARED.

5.2.2. Examination of Acetone Extract from Gelled Resin. The resin was gelled by heating at 200°C in an oven and approximately 5g of the gel was extracted (Soxhlet) for 2 hours with acetone. The acetone extract was examined by VPC and found to contain both DPO and p-XGDME in the ratio 1/0.38; as well as low molecular weight reaction products, which were shown to be present by infra red spectroscopy.

5.2.3. Infra Red Study of Cure. A film of the resin was heated on a sodium chloride plate for 24 hours at 200°C and then for 35 hours at 260°C and the infra red spectrum of the resin was recorded at intervals. Selected spectra are shown in Figures 5.1-5.5. The features which were noted were similar to those seen in the cure of the terphenyl based resin and are discussed in 5.7.1.

5.3 Study of Acetone Extracts of Gelled Resins.

The procedure described in 5.2.2. wos applied to Resins 5.1 to 5.6 and the results are given below in Table 5.2.

Resin	Reactant Ratio of DPO/p-XGDME	Ratio of DPO/p-XGDME in Solvent
5.1.	1/1	1/0.13
5.2.	1/1.2	1/0.38
5.3.	1/1.5	1/0.56
5.4	1/1.68	1/1.9
5.5	1/1.75	1/2.3
5.6	1/2	1/4

Table 5.2. DPO / p-XGDME Ratio in Acetone Extract compared with Reactant Ratio.

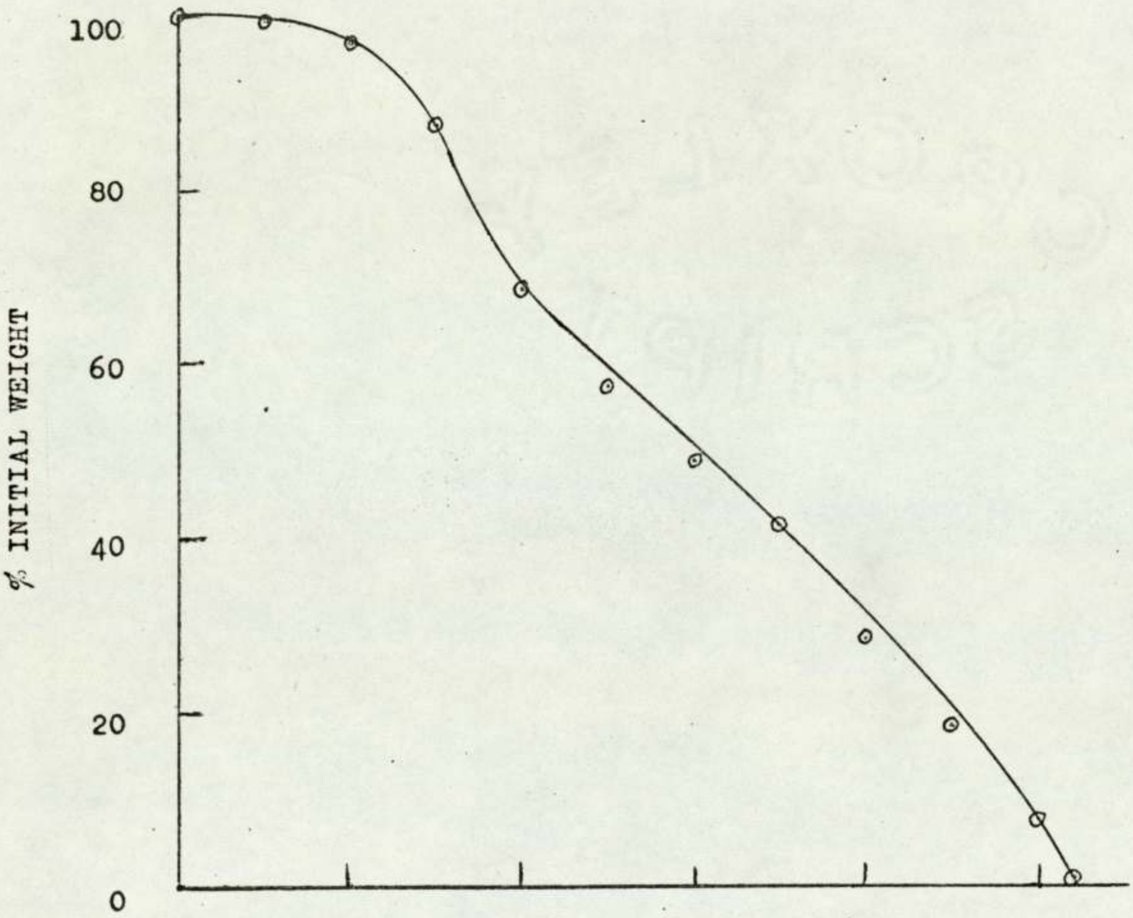


FIGURE 5.8. THERMOGRAM FOR RESIN 5.2.

HEATING RATE: 4°C / minute.

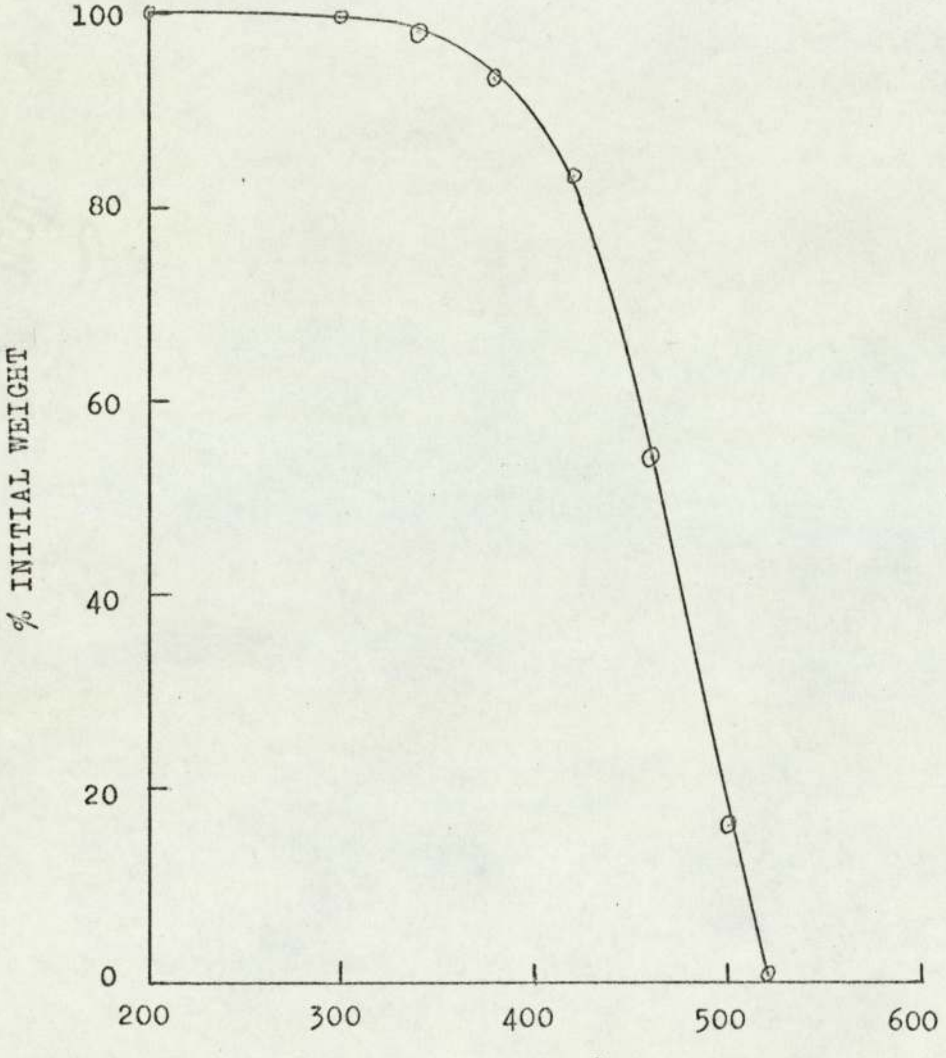


FIGURE 5.7. THERMOGRAM FOR RESIN 5.3.

HEATING RATE: 7°C/ hour.

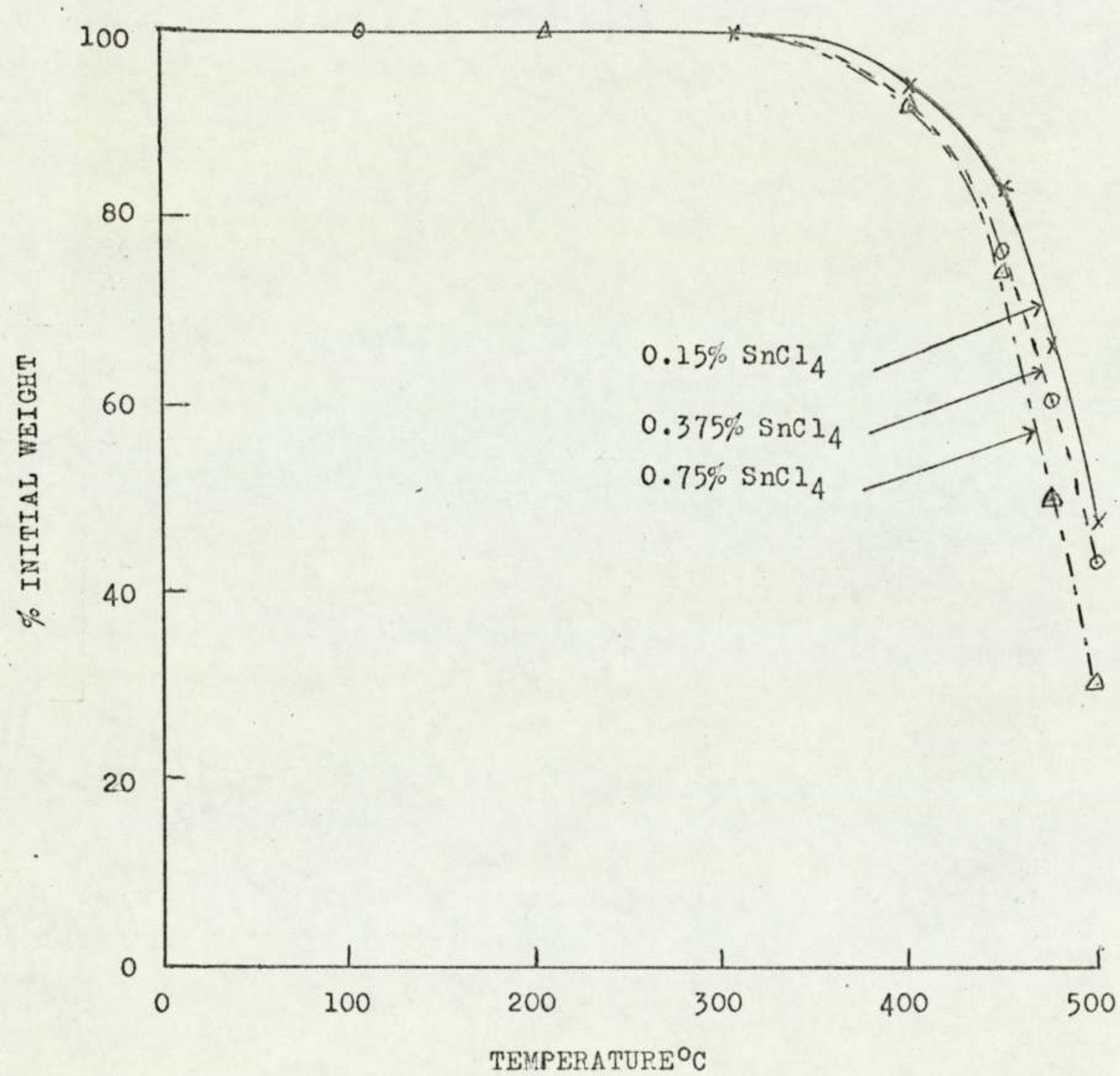


FIGURE 5.6 THERMOGRAMS FOR RESIN 5.2 WITH DIFFERENT CATALYST CONCENTRATIONS.

HEATING RATE : 7°C / hour.

5.4. Volatile Loss during Cure.

The loss in weight during cure has been determined on Resins 5.1. - 5.6. as described in 5.2.3. with the results given in Table 5.3.

Resin No.	Reactant Ratio DPO/p-XGDME	Weight loss % After 1hour 200°C	Weight loss % Constant weight at 260°C.	Theoretical loss of methanol %.	Extra loss %
5.1.	1/1	31.9	45.8	8.6	37.2
5.2	1/1.2	20.1	21.3	8.0	13.3
5.3	1/1.5	20.8	23.1	9.9	13.2
5.4	1/1.68	16.2	17.2	10.9	6.3
5.5	1/1.75	17.9	19.2	10.8	8.4
5.6.	1/2	15.8	17.3	12.2	5.1

Table 5.3. Volatile loss during Cure for Resins with different DPO /p-XGDME Ratios.

5.5. Thermogravimetric Analysis.

Samples of Resin 5.2., with its original catalyst concentration and with added catalyst, were cured for one hour at 200°C followed by 16 hours at 260°C. Thermograms (7°C/hour) for these samples were recorded to establish whether adding catalyst to assist processing had adversely affected thermal stability. The thermograms are shown in Figure 5.6.

A thermogram (7°C/hour) for Resin 5.3 is shown in Figure 5.7 while a thermogram (4°C/minute) for Resin 5.2. is shown in Figure 5.8.

5.6 Preparation of Resin by Stepwise Addition of p-XGDME.

Reactants:- 340g DPO

398.8g p-XGDME

2.5ml 20% by volume $SnCl_4$ in 1,2-dichloroethane.

Method 1. The DPO and 50g p-XGDME were heated to 175°C and 0.8ml of catalyst solution was added. The remainder of the p-XGDME was added in 50ml aliquots at 15 minute intervals and the remaining catalyst was added in two portions to sustain the reaction. The temperature was kept as near to 175°C as possible but this was difficult because of the numerous additions. When 64% of the theoretically available methanol had been collected the reaction was stopped and a resin, much more viscous than normal for 64% conversion, was obtained.

Method 2. 10ml additions were used and the reaction was taken as far as possible before the next addition was made. When about 200ml p-XGDME had been added the viscosity began to rise sharply and at 250ml the resin gelled.

5.7. Discussion.

5.7.1. Cure of Resin 5.2 and Resin Structure. The cure of Resin 5.2. involved the loss of 20% by weight of volatile matter during heating for one hour at 200°C and at 260°C until the weight was constant. This is double the loss experienced in the cure of the terphenyl resin and may represent a difference in volatility of DPO (b.p. 255°C.) compared with terphenyl (b.p. o- 332°C, m- 365°C, p- 427°C) or a lower viscosity of the DPO resin when hot compared with the terphenyl resin at the equivalent extent of reaction.

The examination of the acetone extract of the gelled resin showed that after gelation both DPO and p-XGDME were present and could readily be extracted, but not in the same ratio as was

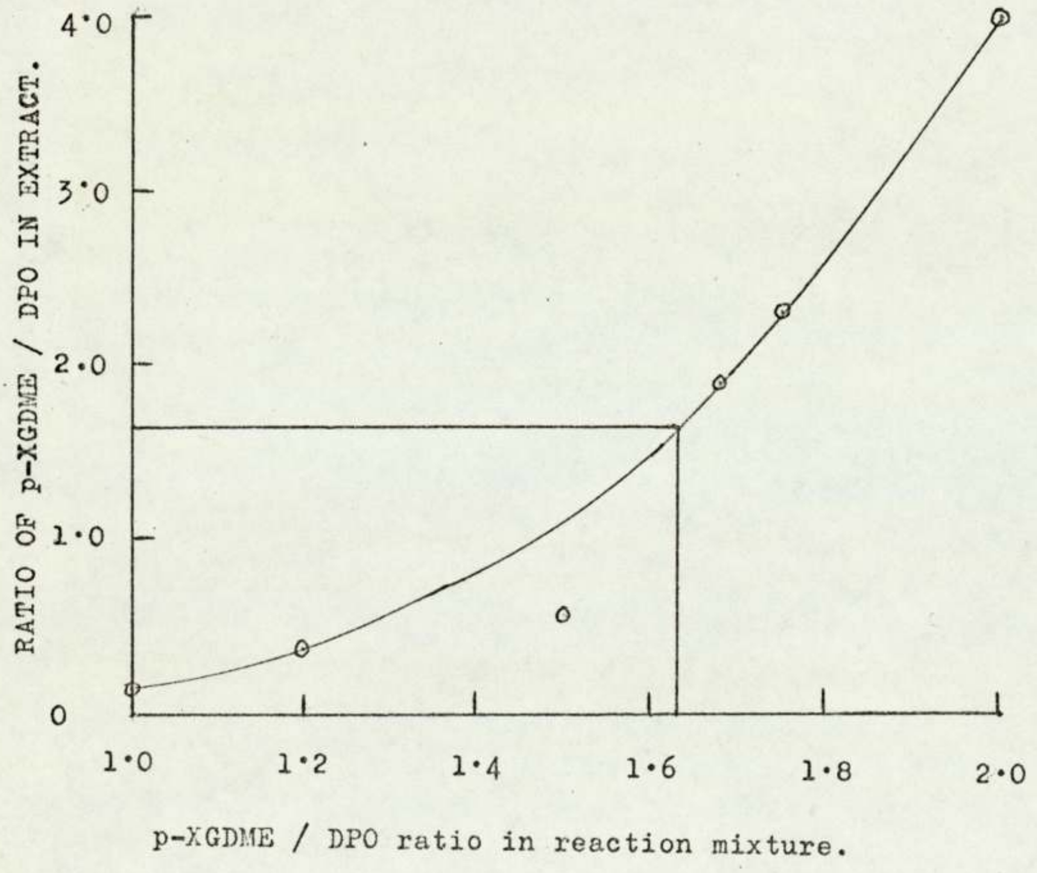


Figure 5.9. p-XGDME / DPO RATIO IN EXTRACT COMPARED WITH RATIO IN REACTION MIXTURE.

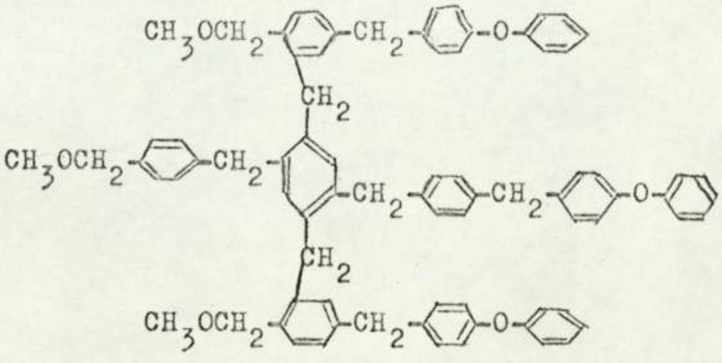
originally present.

The infra red spectra show changes very similar to those noted in the cure of the terphenyl resin. Diaryl ketonic carbonyl (6.05μ) and carboxylic acid (3.0, 5.9, 8.0 and 10.8μ) absorptions developed steadily while, at the same time, $-CH_2-$ and $-CH_3$ absorption bands at 3.4 and 3.5μ and at 7.25μ disappeared. Simultaneously, changes took place in the 10-13μ region. These changes involved a movement to shorter wavelength in the absorption maxima showing a greater complexity of substitution but, as mentioned in 3.7.3, the presence of so many carbonyl groups prevented any clear identification of these substitution patterns. Again, as with the terphenyl resin, the monosubstitution pattern was still very marked at the end of the cure cycle suggesting that the DPO resin, also, has a very highly branched structure with terminal phenoxy groups.

The thermograms for the DPO resins show them to degrade completely on heating to 700°C at 4°C/minute, leaving no carbonaceous char. This again supports the idea of a very highly branched structure with many potential sites for breakdown.

The work on the acetone extracts of the separate resins showed DPO/p-XGDME ratios in the extracts which varied with the ratios used in preparing the resins, but in all cases examined, the ratio in the extract differed from the reactant ratio. In Figure 5.9 the extracted ratio is plotted against the initial reactant ratio and the graph suggests that at a ratio of 1/1.63, the initial and extracted ratios should be equal. If this is the case the ratio of DPO/p-XGDME in the resin must also be 1/1.63 which would appear to be a preferred composition. Reduced to more meaningful terms, this suggests a ratio of 3 molecules of

DPO to 5 molecules of p-XGDME. There are several ways in which such a ratio could be accommodated including the following:-



This could readily be built up into a complex highly branched structure with terminal phenyl groups still only monosubstituted.

The strengthening of the resin during cure comes about partly by the formation of further cross links but also due to the chain stiffening caused by the conversion of $-CH_2-$ to $>C=O$ and by the introduction of hydrogen bonding with the formation of carboxylic acid groups by oxidation of terminal $-CH_2OCH_3$ groups. As was shown when the terphenyl resin was heated to 300°C dehydration also occurs yielding further chemical bonds via anhydride groups.

5.7.2. Stepwise Addition of p-XGDME. This was carried out to allow the maximum opportunity for the formation of unbranched chains by carrying out the preparation in a DPO rich medium in the hope of limiting the self-condensation of p-XGDME. In both methods however, increased branching appeared to take place yielding a very viscous resin by Method 1. and a gel by Method 2. before the reaction had been taken as far as intended. Unreacted DPO floated to the surface of each on cooling.

These observations suggest that the reactivity of p-XGDME to DPO/p-XGDME reaction product is much greater than its reactivity to DPO itself thus causing a gel to form in an environment of DPO.

5.7.3. Thermogravimetric Analysis. The thermograms in Figure 5.6 show that the triggering temperature for the three resins are not affected by the catalyst concentration but that when breakdown has started it continues more rapidly with a higher catalyst concentration. Therefore, at operating temperatures which would necessarily be well below the triggering temperature, no loss in thermal stability would be experienced by raising the $SnCl_4$ concentration to assist processing.

Chapter 6.

OPTIMISATION OF DPO/p-XGDME RESIN.

The resin prepared by the bulk polymerisation of DPO and p-XGDME showed encouraging properties when used to impregnate coils of polyimide enamelled wire, and as the bond in glass cloth laminates (Chapter 7). Consequently, to obtain the best possible resin based on DPO and p-XGDME a systematic optimisation programme, involving consideration of the variables in the resin preparation, was carried out.

A preliminary series, in which bond strength of impregnated Dexter coils (See 2.3.4) was used as the criterion for assessing the resins, showed bond strength to be too much affected by the resin viscosity. To overcome this difficulty the retention of bond strength on ageing was adopted as the property to be optimised.

6.1. Optimisation Programme.

Seven variables, entering into the preparation of the resin, were considered at the levels indicated in Table 6.1.

Variable	Levels	
	-	+
A. Ratio of p-XGDME to DPO	1.2	1.3
B. Volume of $SnCl_4$	0.3	0.4ml
C. Concentration by volume of $SnCl_4$ soln.	10	15%
D. Maximum reaction temperature	200	210°C
E. Temperature of catalyst additions	170-190	180-200°C
F. Number of catalyst additions	3	5
G. Extent of reaction	60	64%

Table 6.1. Levels of Variables in first stage of Optimisation.

Eight resins were prepared with the parameters shown in Table 6.2.

Resin	Level of each variable						
	A	B	C	D	E	F	G
6.1.	-	-	-	+	+	+	-
6.2	+	-	-	-	-	+	+
6.3	-	+	-	-	+	-	+
6.4.	-	-	+	+	-	-	+
6.5	+	+	-	+	-	-	-
6.6	+	-	+	-	+	-	-
6.7	-	+	+	-	-	+	-
6.8	+	+	+	+	+	+	+

Table 6.2 Details of Resins in first stage of Optimisation.

In each case 340g diphenyl oxide was used and the reaction was carried out with stirring in a 1 litre reaction vessel in a heating mantle.

Each of the Resins 6.1 to 6.8. was used to impregnate eight 3 inch x $\frac{1}{4}$ inch Dexter coils of 0.040 inch polyimide enamelled wire. These were drained for 30 minutes at $50^{\circ}C$ and cured for 1 hour at $200^{\circ}C$, 16 hours at $260^{\circ}C$ and 5 days at $300^{\circ}C$. The bond strength of each resin was determined at room temperature by breaking every coil near one end, in the Hounsfield Tensometer. The coils were aged for a further 5 days at $300^{\circ}C$ after which they were all broken again at the opposite end to the first break.

The percentage retention of bond strength for each resin was calculated and is shown in Table 6.3. These are related to the variables in Table 6.4.

Resin	Bond Strength (Mean of 8 Determinations) lb. After 5 days at 300°C	After 10 days at 300°C	% Retention.
6.1	51.6	31.1	60.3
6.2	61	39.5	64.7
6.3	55.9	40.1	71.7
6.4	49.6	31.4	63.3
6.5	44.9	26.2	58.3
6.6	53	35.6	67.2
6.7	46.9	30.4	64.8
6.8	54.8	36.7	67

Table 6.3 Bond Strength Retention on ageing Resins 6.1 -6.8.

Variable	Mean +	Mean −	Difference
Ratio of reactants	64.3	65.0	-0.7
Volume of $SnCl_4$	65.4	63.9	+1.5
Concentration of $SnCl_4$ solution	65.6	63.7	+1.9
Maximum reaction temperature	62.2	67.1	-4.9
Catalyst addition temperature	66.5	62.8	+3.7
Number of catalyst additions	64.2	65.1	-0.9
Extent of reaction	66.7	62.6	+4.1

Table 6.4 Percentage Bond Strength Retention related to Variables for Resins 6.1 - 6.8.

From Table 6.4 it can be seen that the variables which appear to have an important effect are:-

Maximum reaction temperature.

Extent of reaction.

Temperature of catalyst addition.

Concentration of catalyst solution.

Further investigation of these variables was undertaken. However, it will be seen from the data in Table 6.4 that the catalyst was preferably added at as high a temperature as possible while the reaction temperature was preferably as low as possible. The number of variables could thus be reduced to three by always adding the catalyst at the maximum reaction temperature. The levels of the three fixed quantities, and the levels of the three variables, used in the second stage are given in Table 6.5. Details of the resins prepared are given in Table 6.6.

Variable	Levels		
	–	+	
A. Ratio of p-XGDME/DPO	1.2		Fixed
B. Volume of $SnCl_4$	0.5ml		Fixed
F. Number of catalyst additions	3		Fixed
C. Concentration of $SnCl_4$ solution	15	20%	
D. Maximum reaction temperature	195	200°C	
G. Extent of reaction	64	66%	

Table 6.5 Levels of Variables in second stage of Optimisation.

Resin	Level of each variable C	 D	 G
6.9	+	+	+
6.10	+	-	-
6.11	-	-	+
6.12	-	+	-

Table 6.6 Details of Resins prepared in second stage of Optimisation.

The Resins 6.9 to 6.12 along with 6.3 as a control, were used to impregnate Dexter coils which were cured and aged as before. Bond strength retention values are given in Table 6.7 and these are related to the variables in Table 6.8

Resin	Bond Strength (Mean of 8 Determinations) lb After 5 days at 300°C	 After 10 days at 300°C	% Retention
6.3	52.5	38.6	73.6
6.9	49	30.4	62.1
6.10	44.2	31	70.1
6.11	52.9	37.1	70.1
6.12	40.3	20.8	51.6

Table 6.7 Bond Strength Retention on ageing for Resins 6.3 and 6.9 to 6.12.

Variable	Mean +	Mean -	Difference
Concentration of $SnCl_4$ solution	66.1	60.9	+5.2
Reaction temperature	56.9	70.1	-13.2
Extent of reaction	66.1	60.9	+ 5.2

Table 6.8 Percentage Bond Strength Retention related to Variables for Resins 6.3 and 6.9 - 6.12.

From Table 6.8 it is seen that again the maximum reaction temperature is the most important factor.

For the third stage the concentration of the catalyat solution was fixed at 20% by volume, and the extent of reaction at 64% (the 66% resins were too viscous).

A further three resins 6.13 - 6.15 were prepared at progressively lower reaction temperatures, i.e. 185, 175 and 170°C. These were used along with Resin 6.10 as a control to obtain values of bond strength retention as before. Resin 6.10 differed from 6.13 - 6.15 only in having been prepared at 195°C. Results shown in Table 6.9 indicate that Resin 6.14, prepared at 175°C, was the best. (See overleaf).

Resin	Bond Strength (Mean of 8 Determinations)lb		% Retention
	After 5 days at 300°C	After 10 days at 300°C	
6.10	42.5	29.3	69
6.13	48.1	36.1	75
6.14	47.7	36.9	77.4
6.15	48.7	36.4	74.7

Table 6.9 Bond Strength Retention on ageing for Resins 6.10 and 6.13 - 6.15.

Details of the preparation of 6.14 were as follows:-

340g DPO

398.8 p-XGDME

2.5ml 20% by volume $SnCl_4$ in 1,2-dichloroethane added in 3 portions at 175°C, the maximum reaction temperature.

The reaction was taken to 64% completion as judged by the volume of methanol evolved.

The statistical significance of the results obtained was not determined but they were regarded simply as indications of what factors were more important than others. When relatively small experiments are involved it is justifiable to do this since, if assumptions made are wrong, this will be shown up quickly without the expenditure of much effort. These indications were used to plan the subsequent work, the results from which were wholly consistent, thus justifying the early assumptions.

6.2. Discussion.

After the first experiment it was found that the reactant ratio had very little effect on the results obtained. At first sight this is surprising since a higher proportion of p-XGDME would be expected to give a more highly cross-linked and, therefore, more stable system. However, as shown in Chapter 5 there is evidence of a preferred resin structure irrespective of the original reactant ratio. The non-dependence of thermal endurance on reactant ratio found in the optimisation programme lends further support to the idea of a resin structure unrelated to the ratio of the reactants.

The effect of the number of catalyst additions was also very small but since the reaction rate had a tendency to fall off it was decided to continue the practice of adding the catalyst in several aliquots to maintain an acceptable reaction rate. The volume of catalyst used and the concentration of the catalyst solution added also had only minor effects suggesting that the resin structure obtained is independent of these variables and that the resin stability is not seriously affected by an increase or decrease in catalyst concentration. Since the ageing temperature, 300°C, was substantially lower than the triggering temperature for the resin these results are in agreement with those discussed in Chapter 5 from thermogravimetric analysis.

The overriding importance of reaction temperature appears to indicate that at lower temperature a structure is formed which is less susceptible to degradation. This could be a less highly branched structure and it is probable that at lower temperatures the reaction is more selective, yielding a more linear molecule and that as the temperature is raised a loss of selectivity in the reaction is experienced.

It was also found that the catalyst should be added at as high a temperature as possible and presumably it was this factor which affected Resin 6.15 at 170°C giving a less stable resin than that at 175°C. Overall the best balance of advantage from low reaction temperature and disadvantage from low catalyst addition temperature was obtained at 175°C.

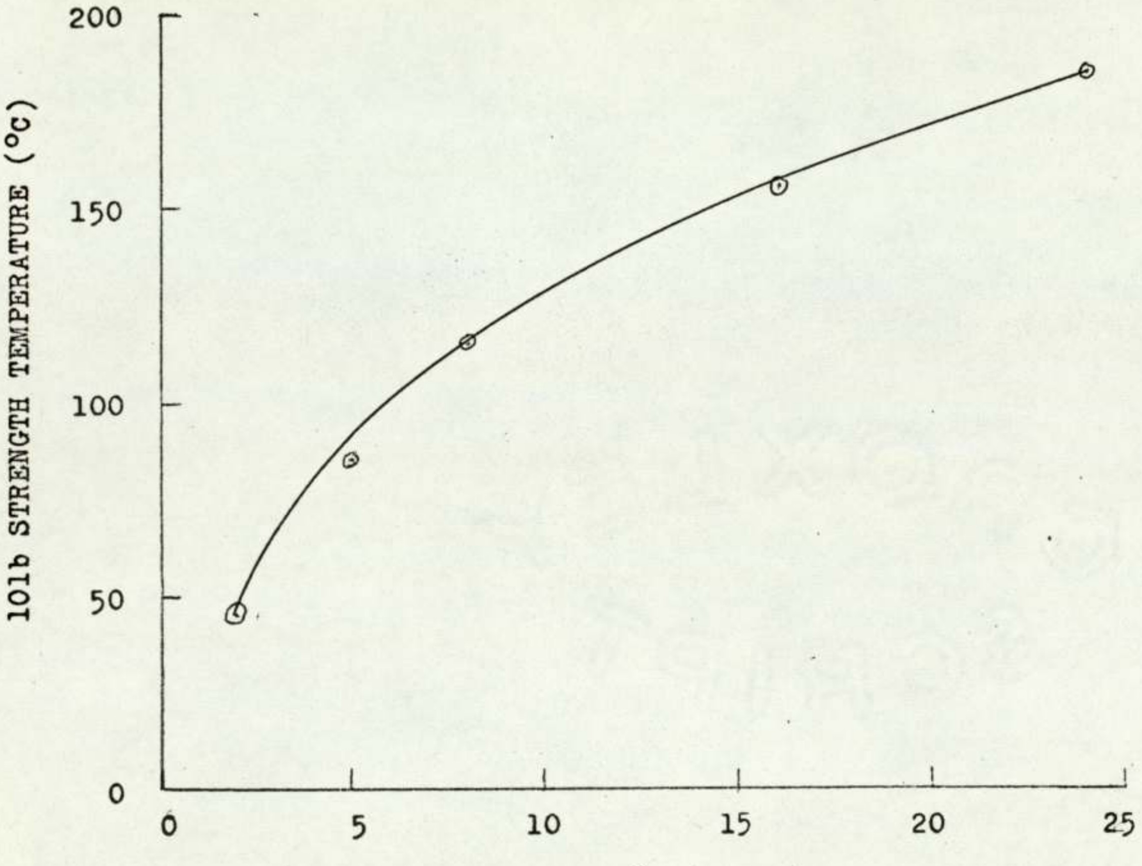


FIGURE 7.3. MAXIMUM TEMPERATURE FOR 10lb BOND STRENGTH v CURE FOR DEXTER COILS COATED WITH RESIN 5.2.

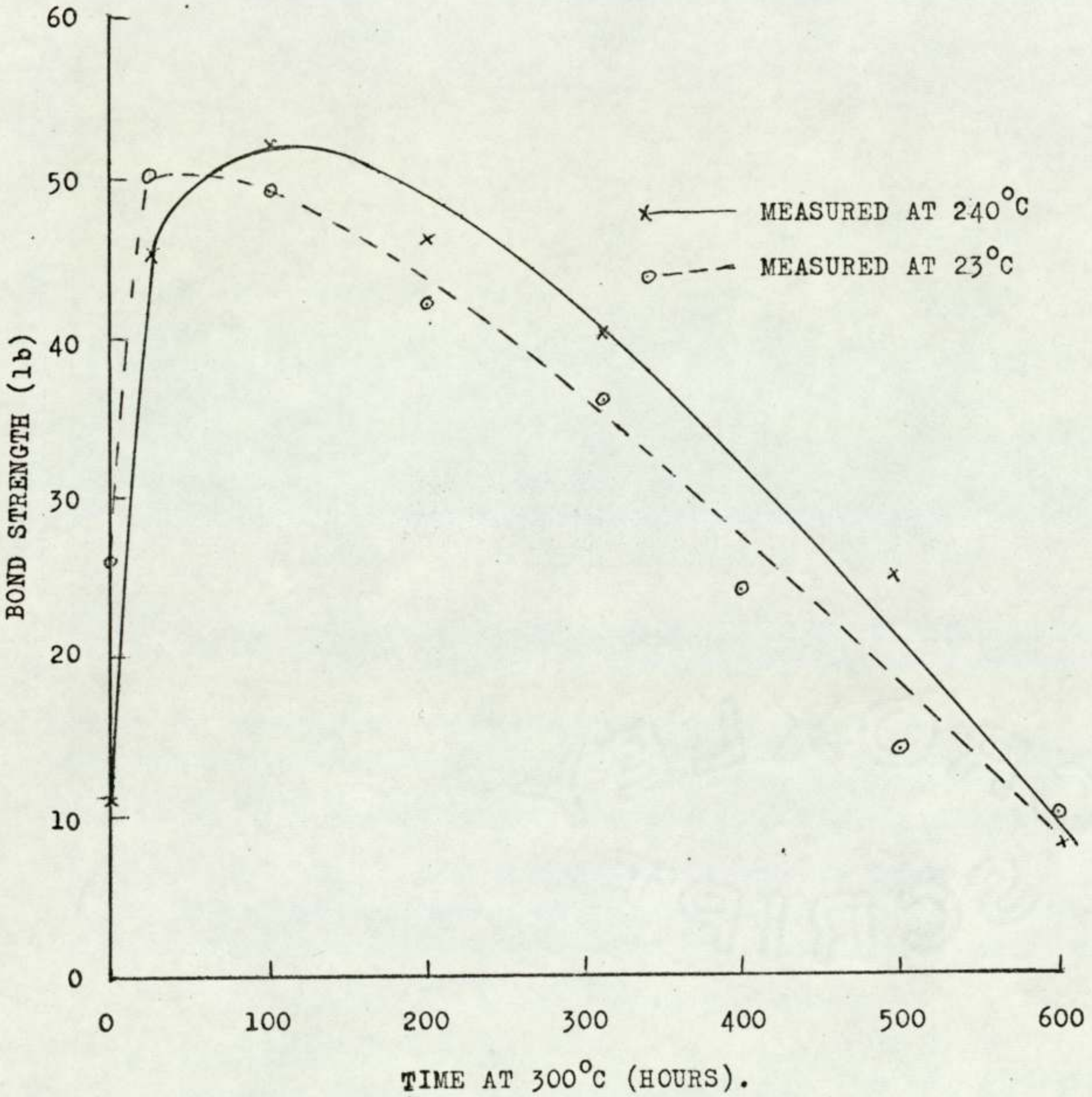


FIGURE 7.2. BOND STRENGTH v AGEING FOR DEXTER COILS COATED WITH RESIN 5.2.

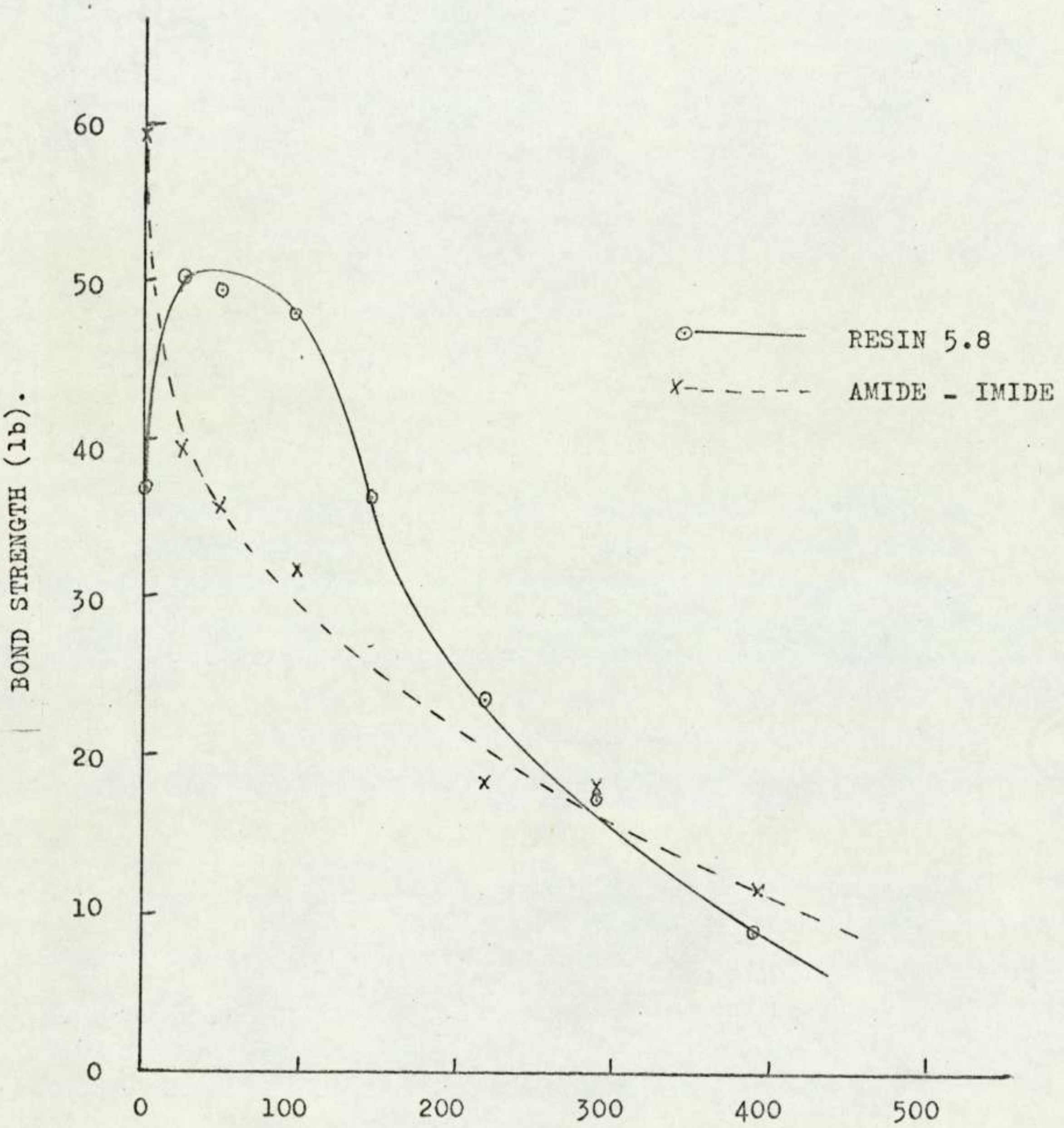


FIGURE 7.1. BOND STRENGTH v AGEING FOR RESIN 5.8 AND AN AMIDE-IMIDE VARNISH

Chapter 7.

COMPOSITE MATERIALS BASED ON DPO/p-XGDME RESINS.

The resins based on DPO/p-XGDME have been found to have much more attractive handling and processing characteristics than the terphenyl resins. The composites prepared from the DPO resins described in this chapter have shown encouraging properties in certain applications.

7.1. Bond Strength.

Resin 5.8 was used to impregnate Dexter coils of 0.040 inch polyimide enamelled wire. These were cured for 1 hour at 200°C and 16 hours at 260°C. A similar series of coils was impregnated with an amide-imide varnish, and cured for 2 hours at 120°C, 2 hours at 150°C, 4 hours at 200°C and 6 hours 250°C according to the maker's instructions.

Bond strengths were measured as described in 2.3.4., at 23°C after periods af ageing at 300°C. The results are given in Figure 7.1. and show that the two systems are roughly equivalent.

Following the optimisation programme described in 6.1. bond strength results were obtained at 23°C and at 240°C for Resin 5.2 after ageing at 300°C. These results are given in Figure 7.2 and indicate the significant improvement in bond strength retention achieved as a result of the optimisation programme.

Hot bond strength of Resin 5.2 has been examined as a function of cure time at 200°C. In this experiment the temperature was determined at which the bond strength fell to 10 lb which is regarded as the minimum practically useful value. The results are shown graphically in Figure 7.3.

7.2. Twisted Pairs.

The "twisted pair" technique, as described in Chapter 2, has

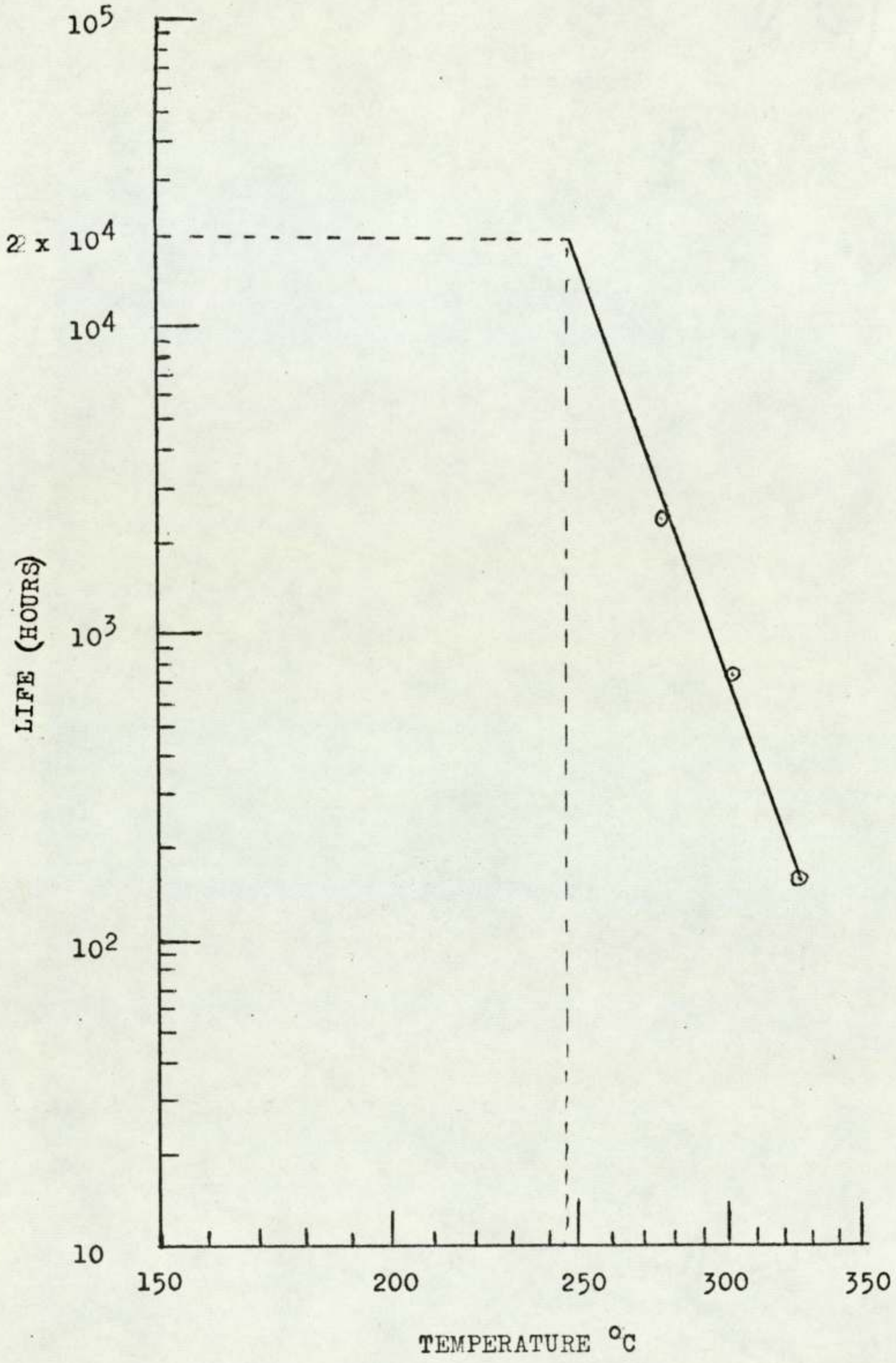


FIGURE 7.4. LIFE-TIME v TEMPERATURE FOR POLYIMIDE / RESIN 5.2 SYSTEM.

been used to compare the thermal endurance of Resin 5.2., a silicone and an amide-imide varnish used to coat 0.040 inch polyimide enamelled wire. Results for the three systems, plus unvarnished polyimide enamelled wire, are given in Table 7.1 together with the extrapolated temperature corresponding to a life of 20,000 hours.

Enamel/Resin System	Life in hours at temperature			20,000 hour
	275°C	300°C	325°C	Temp. °C
Polyimide enamel alone	2,467	685	142	245
Polyimide/Amide-imide	1,836	690	143	235
Polyimide/Silicone	2,886	776	176	248
Polyimide/Resin 5.2	2,424	757	163	245

Table 7.1. Life versus Temperature for Polyimide/Resin Systems.

In Figure 7.4. the results for the Polyimide/Resin 5.2 system are shown in the form of an Arrhenius plot extrapolated to give a 20,000 hour life at 245°C. The equivalent temperatures for the other systems were obtained similarly.

7.3. Moulding.

7.3.1. Preparation of Mouldings. Moulding compositions were prepared as in 2.1.4. One inch diameter discs were moulded, and shear strength measurements were made, as described in Table 7.2.

Moulding Composition	Technique	Shear Strength tons/in^2.
MP 7.1 40g Resin 5.8 with $SnCl_4$ concentration increased by eightfold. 30g Fibrefrax 30g Ball clay 975	Precured 5 minutes at 200°C Moulded 30 minutes at 200°C and 3 tons/in^2. with breathing 4 times in first minute and after 5 and 10 minutes. Postcured 16 hours at 260°C.	3.02-4.15.
MP 7.2 40g Resin 5.7 30g Asbestos FR342 30g Ball clay 975	No precure. In mould as a dough at 250°C. 2 minutes contact pressure with breathing after 1 minute. Pressure of 3 tons/in^2. applied and held for 30 minutes. Removed hot and postcured 16 hours at 260°C.	3.44
	As above but pressed 25 minutes.	3.82
	" " " 20 "	4.15
	" " " 15 "	3.49
	" " " 10 "	4.35
	" " " 5 "	4.07

Table 7.2. Details of Moulded Discs using DPO/p-XGDME Resins.

However, when attempts were made to mould more complex specimens with thicker sections the production of volatiles became troublesome and a pre-cure had to be used. Impact strength specimens and pin bowls were moulded as described in Table 7.3.

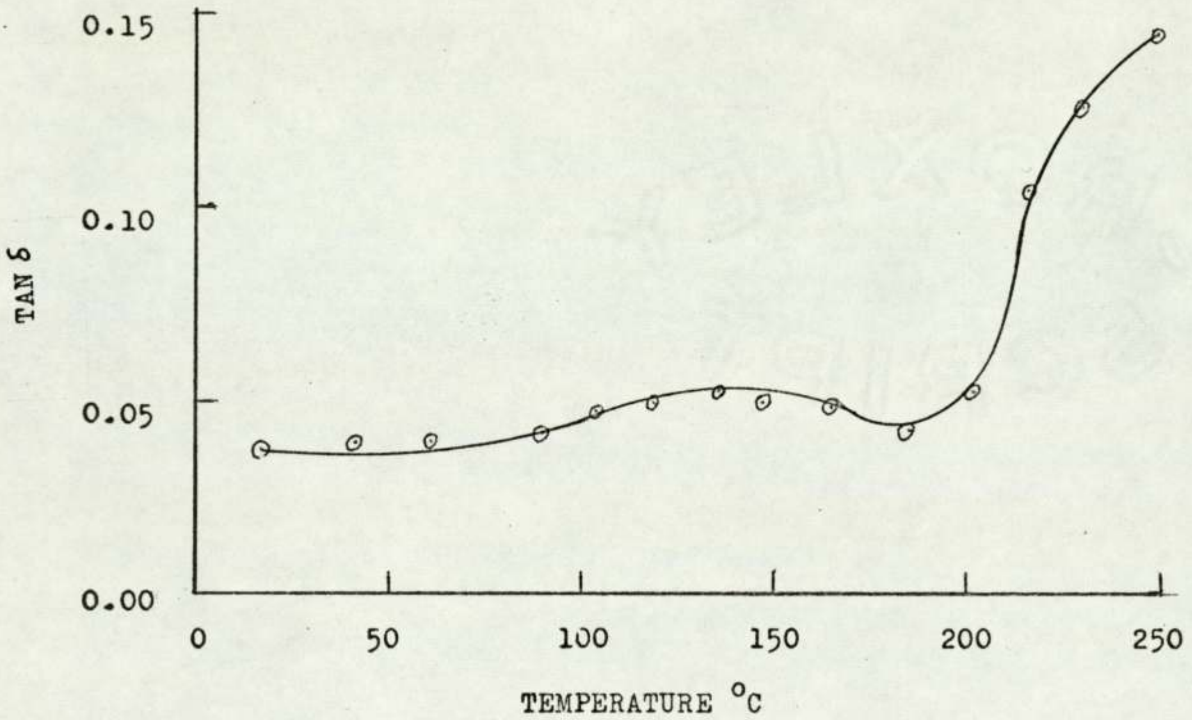


FIGURE 7.5. TAN δ v TEMPERATURE FOR MOULDED DISC

Moulding Composition	Moulding Technique	Impact Strength. ft.lb.
MP 7.2	Precured 30 minutes at 200°C. Ground up and passed through a No.8 sieve. Placed in impact strength mould at 250°C. Applied 3 tons/in^2 at 250°C for 30 minutes. Removed hot and postcured 16 hours at 260°C.	0.28- 0.40.
MP 7.2	Same technique was used for pin bowls except that the moulding temperature was 200°C. To obtain satisfactory hot release a PTFE film was sprayed on the mould surfaces from an aerosol and baked for 2 hours at 250°C.	

Table 7.3. Methods of Moulding Impact Strength Specimens and Pinbowls.

No mechanical strength tests were applied to the pinbowl mouldings. They were merely assessed subjectively and, using the above procedure, results were condidered satisfactory. Hot release was achieved but the moulding was not hard and firm, and care was necessary to avoid distortion.

7.3.2. Electrical Tests on Mouldings. Dielectric loss tangent versus temperature has been determined on one of the MP 7.1 discs and the results are shown in Figure 7.5. Electric strength was determined on an MP 7.1 disc by the "rapidly applied voltage" method and found to be 163V/mil for an 82mil thick sample.

The tracking index, determined according to IEC 112, was found to be 200-250.

7.4. Laminating.

7.4.1. Laminate Preparation. With the $SnCl_4$ catalysed resin it was found impossible to use the conventional pre-impregnation of glass cloth, followed by "B-staging" and dry lay-up in the preparation of laminates because they would not cure in the press. This could be due to the loss of catalyst during pre-cure, either by volatilisation, or by hydrolysis. However, a wet lay-up technique was found to be possible using a resin activated with additional $SnCl_4$. If the resin was activated with $FeCl_3$ a dry lay-up method could be used. Using the acid clay catalysed Resin 5.8 either wet or dry lay-up techniques were applicable. The laminates described in Table 7.4. were prepared.

Laminate	Technique
L 7.1 0.006 inch thick glass cloth with methacrylate chromic chloride finish (T5). Resin 5.8 with $SnCl_4$ increased eightfold.	17 layers of glass cloth were laid up with the resin spread between them. The wet stack was pre-cured 45 minutes at 150°C, and pressed at 400lb/in^2 and 250°C for 1 hour. Post-cured 16 hours at 260°C.
L 7.2 Glass cloth as L 7.1. Resin 5.8 with 1g $FeCl_3$ added per 100g resin.	18 layers of glass cloth were impregnated with a 65% solution of the resin in 1,2-dichloroethane and pre-cured individ-

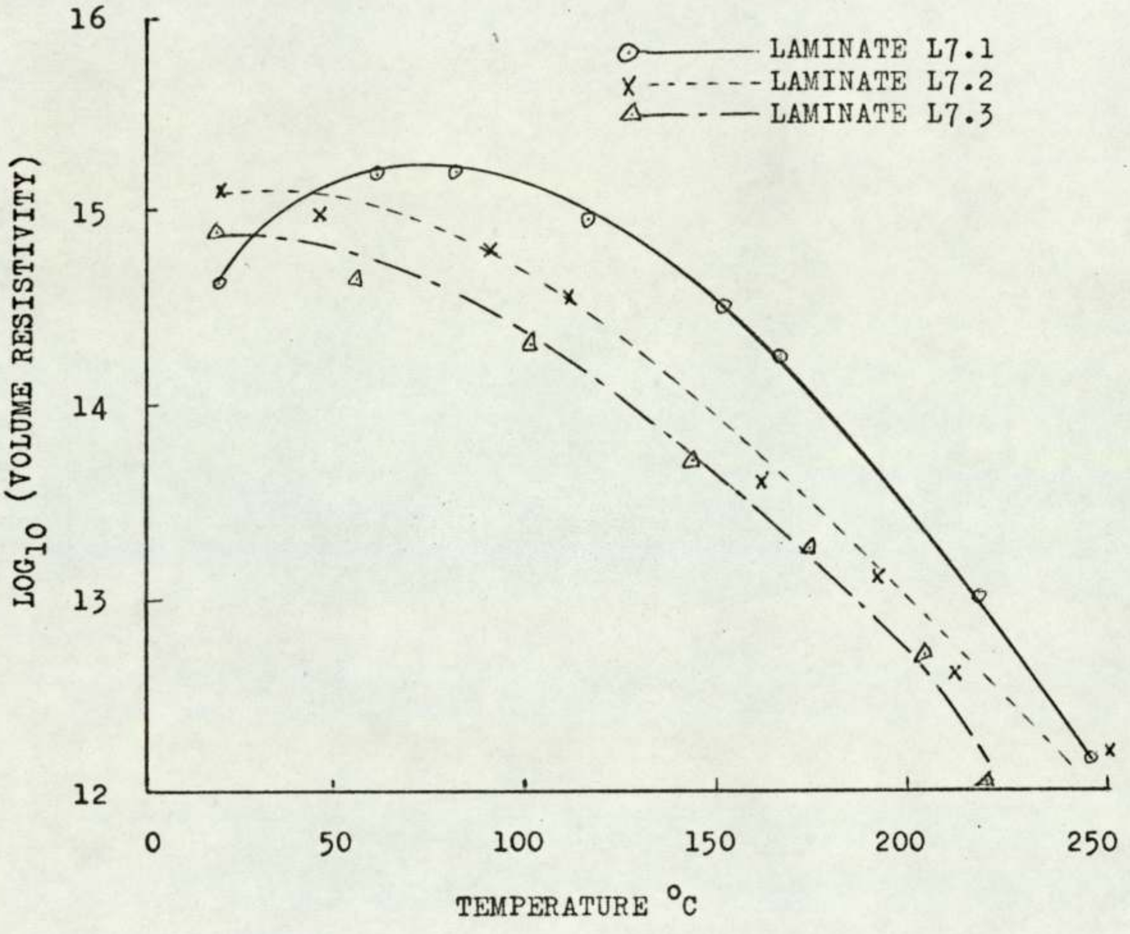


FIGURE 7.8. VOLUME RESISTIVITY v TEMPERATURE FOR GLASS CLOTH LAMINATES.

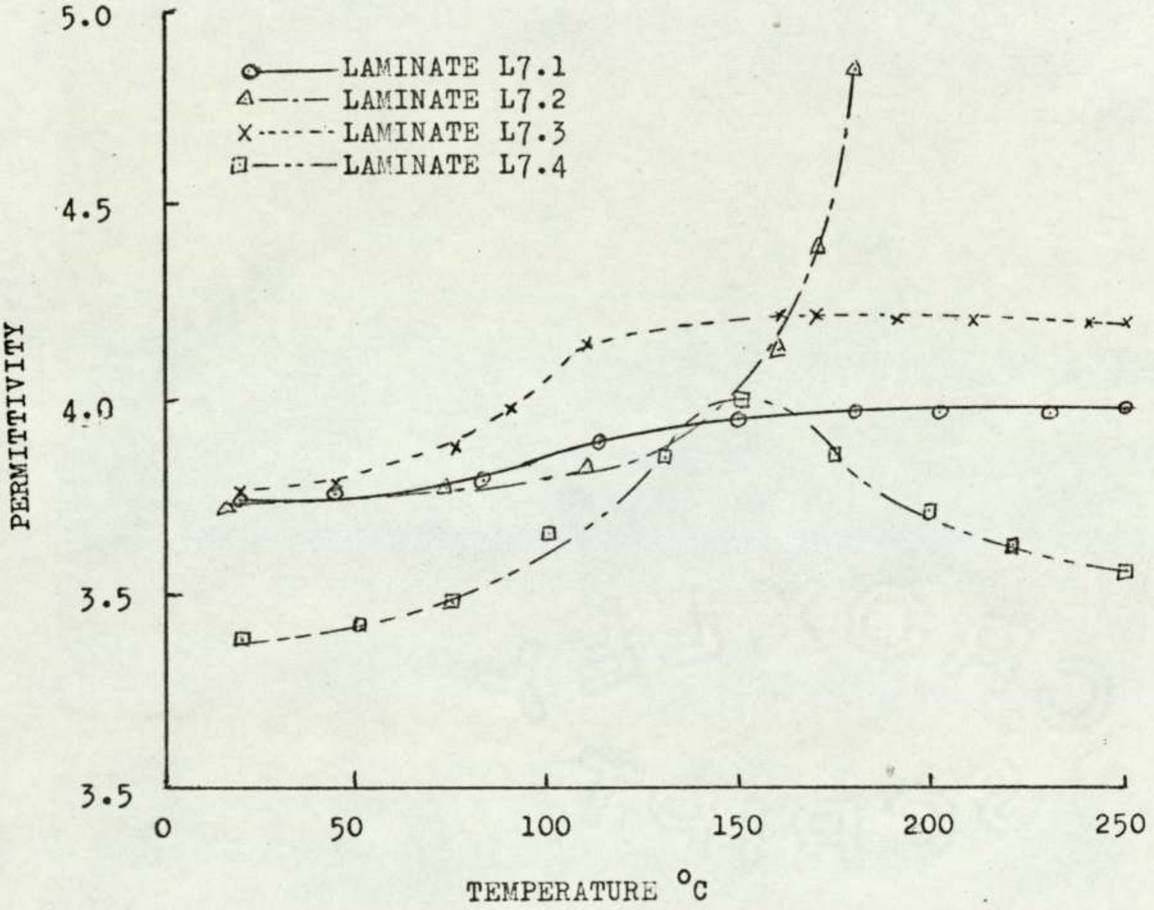


FIGURE 7.7. PERMITTIVITY v TEMPERATURE FOR GLASS CLOTH LAMINATES.

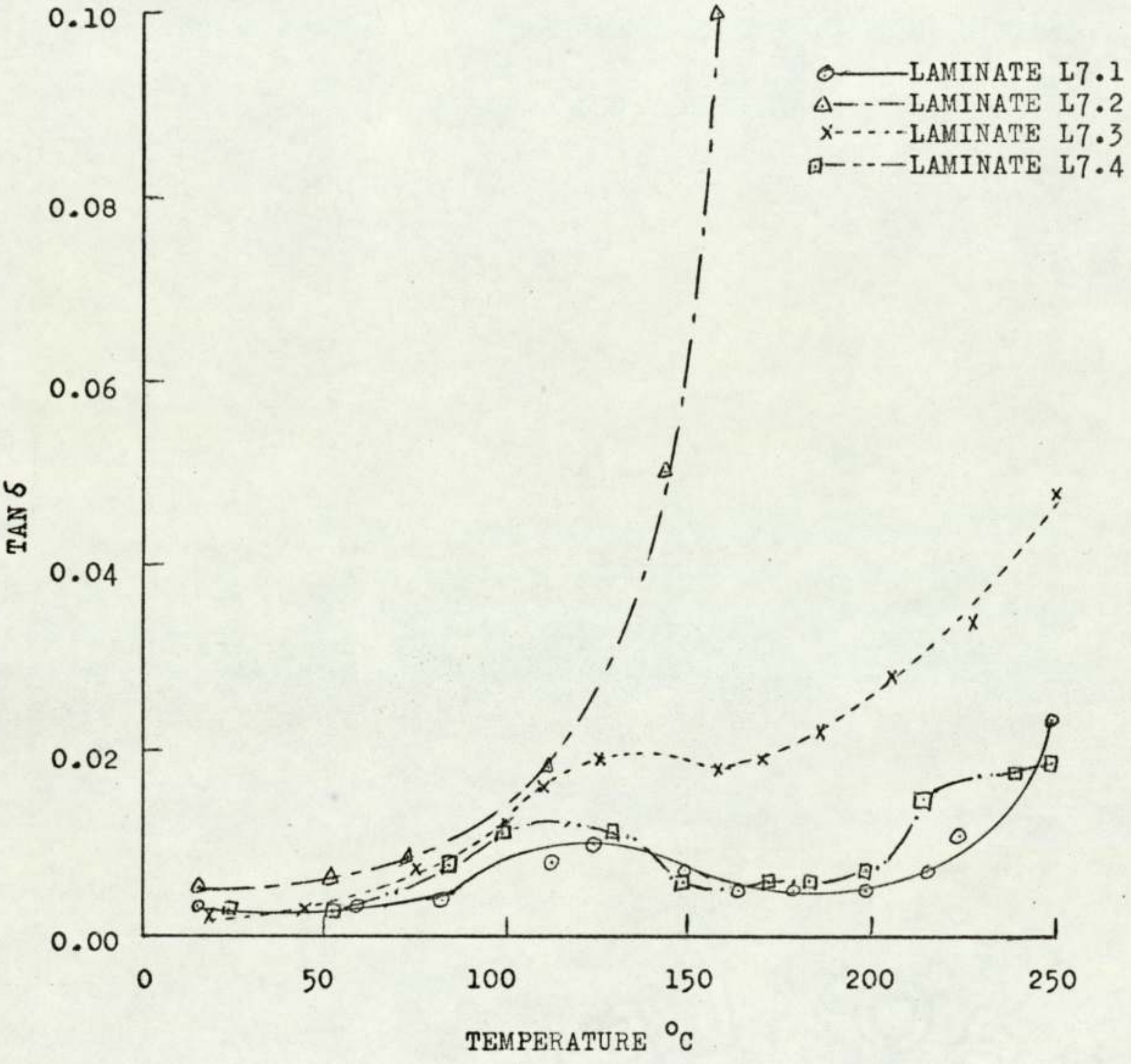


FIGURE 7.6. TAN δ v TEMPERATURE FOR GLASS CLOTH LAMINATES

Laminate	Technique
L 7.2 (continued).	ually for $2\frac{1}{4}$ minutes at 130°C. Stacked and pressed at 250°C to $\frac{1}{8}$inch stops for 1 hour. Post-cured 16 hours at 260°C.
L 7.3 Glass cloth same as L7.1. Resin 5.7 as prepared.	18 layers of glass cloth were laid up wet and pre-cured for 15 minutes at 150°C before being pressed to 0.125 inch stops at 250°C for 1 hour. Post-cured 16 hours at 260°C.
L 7.4 Glass cloth as L 7.1. Resin 5.7.	Glass cloth was impregnated by passing a continuous length through a 65% by weight solution of the resin in 1,2-dichloroethane It was pre-cured by passing at 1 ft/minute through a 6ft drying tower whose temperature increased to 190°C near the top. 12 layers of cloth were stacked and put in the press at 250°C with contact pressure for 5 minutes. 350 lb/in^2 was applied and held for 1 hour. Post-cured 16 hours at 260°C.

Table 7.4. Details of DPO/p-XGDME Resin bonded Glass Cloth Laminates.

7.4.2. Electrical tests on laminates. Dielectric loss tangent, permittivity and volume resistivity versus temperature at 50Hz were measured on these laminates and are shown in Figures 7.6 - 7.8. Dielectric loss tangent and permittivity were measured for the laminates between 200 and 100,000 Hz and found to be

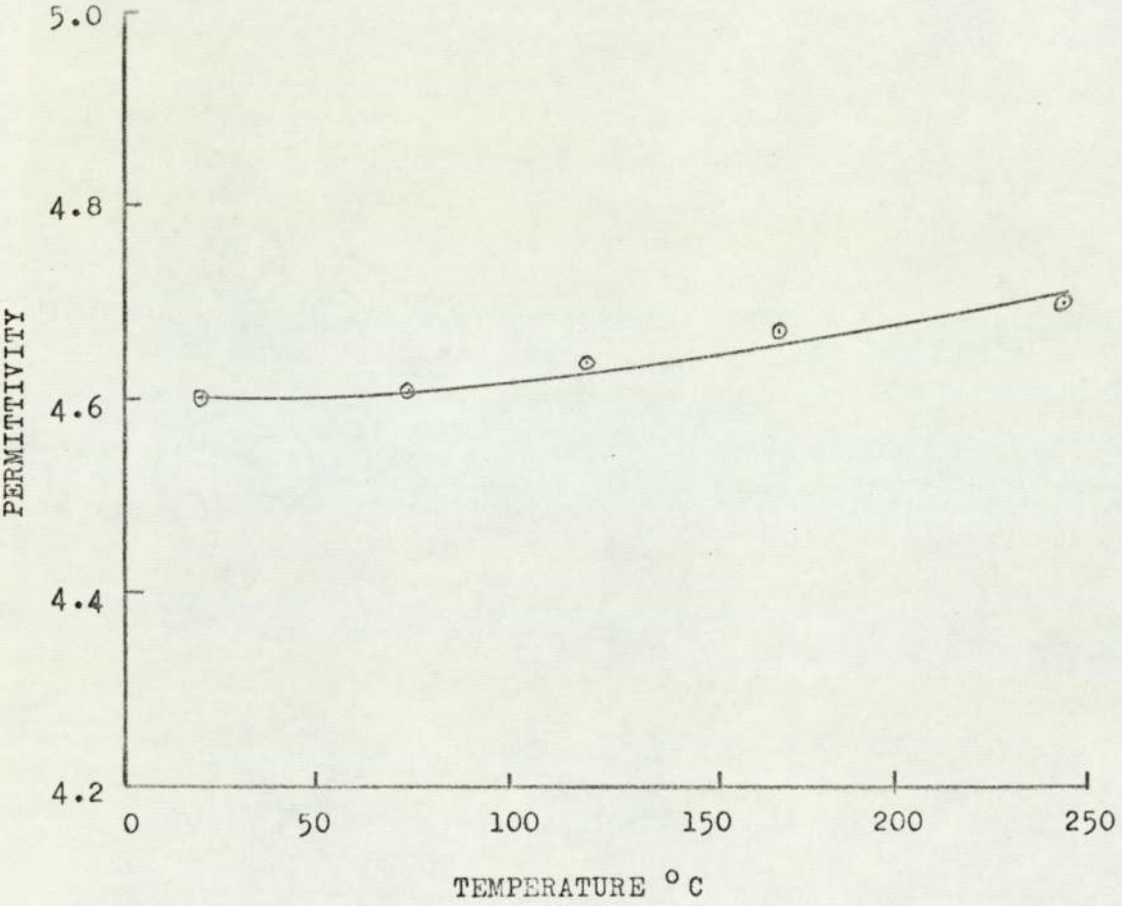


FIGURE 7.10. PERMITTIVITY v TEMPERATURE AT 9.368 GHz FOR LAMINATE L7.1.

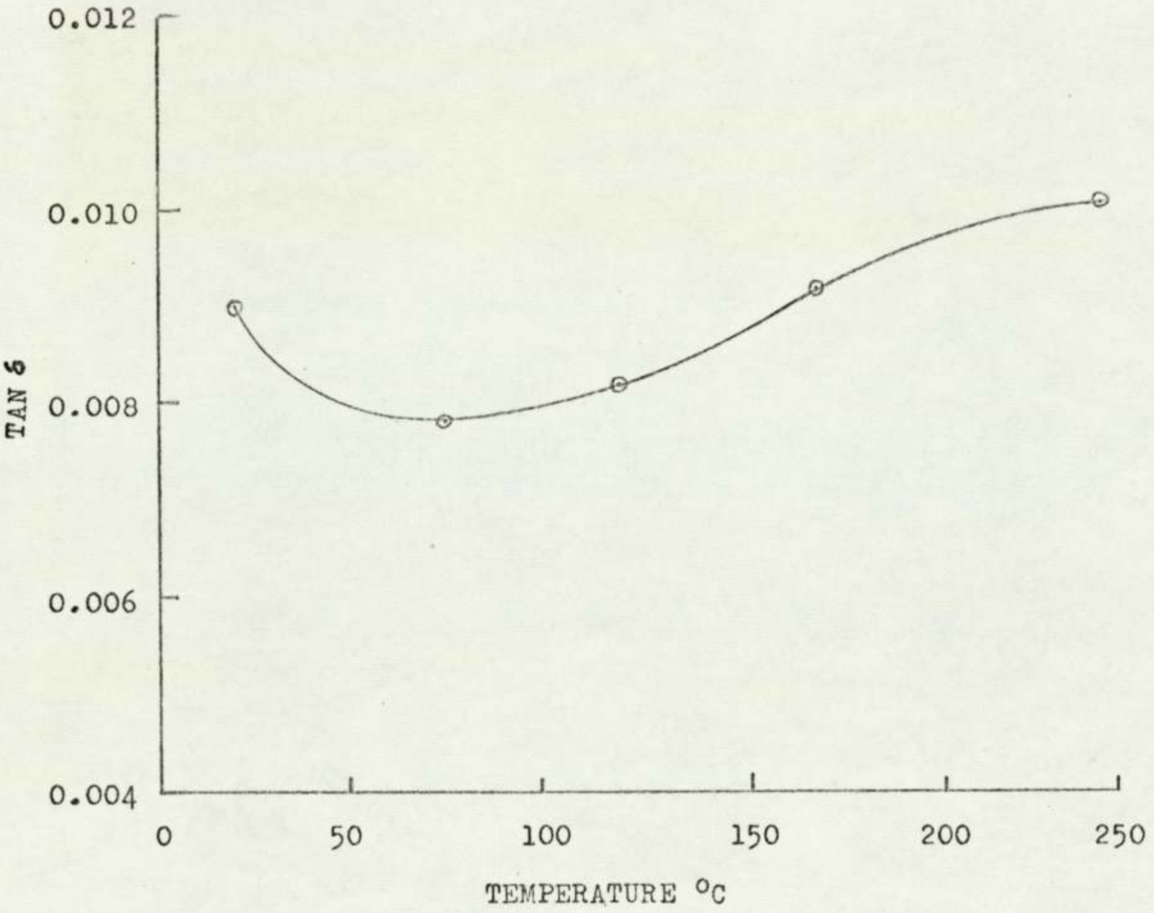


FIGURE 7.9. TAN δ v TEMPERATURE AT 9.368 GHz FOR LAMINATE L7.1.

substantially independent of frequency. All laminates gave values of tanδ below 0.001 and permittivity values of 3.6 to 3.9 throughout the entire frequency range.

Laminate L7.1 has been examined at X-band frequency (9.368GHz) and has been found to have very good tanδ and permittivity versus temperature characteristics, as shown in Figures 7.9 and 7.10.

The breakdown voltage of a 0.047 inch thick L7.4 laminate has been measured at 23°C and at 250°C by the "rapidly applied voltage" method.

Electric strength at 23°C = 420V/mil

Electric strength at 250°C = 320V/mil

The tracking index (IEC 112) has been measured on an L7.4 laminate and found to be 150-175.

7.4.3. Water Absorption of Resins and Laminates. Water vapour absorption of cured samples of Resins 5.2 and 5.7, and glass cloth laminates L7.1 and L7.4 bonded with these resins has been measured after exposure to 96% R.H. at 40°C for up to 29 days. The results are summarised in Table 7.5.

Days at 96%	Water Vapour Absorption in mg/cc.			
R.H., 40°C	Resin 5.2	Resin 5.7	Laminate L7.1	Laminate L7.4
1	1.6	2.5	4.9	5.2
3	2.1	2.6	6.4	5.2
29	2.3	3.2	6.6	5.2

Table 7.5. Water Absorption of Resins and Laminates.

All samples returned to their original weights after being in the laboratory atmosphere for 24 hours.

The tanδ values for laminates L 7.1 and L 7.4 were measured at 23°C after exposure to 96% RH at 40°C for seven days giving the values shown in Table 7.6. The original values obtained before exposure are shown for comparison.

Laminate	Tanδ before humidity cycle.	Tanδ after humidity cycle.	Tanδ after storing dry after humidity cycle.
L 7.1	0.003	0.072	0.008
L 7.4	0.003	0.021	0.006

Table 7.6 Effect of Moisture on Tanδ of Laminates.

The values were determined only at 23°C since it had already been shown that the water absorption was reversible and heating would merely have resulted in loss of absorbed water.

7.4.4. Void Content. The void content has been determined on two pieces of Laminate L 7.4 by the method described in 2.2.9. The results are given in Table 7.7.

	Sample 1.	Sample 2.
Density of Laminate	1.70g/cc	1.68g/cc
Density of glass	2.54g/cc	2.54g/cc
Density of resin	1.18g/cc	1.18g/cc
Resin content by weight	39.7%	40%
∴ Void content by volume.	2.44%	3.53%

Table 7.7. Void Content of Laminate.

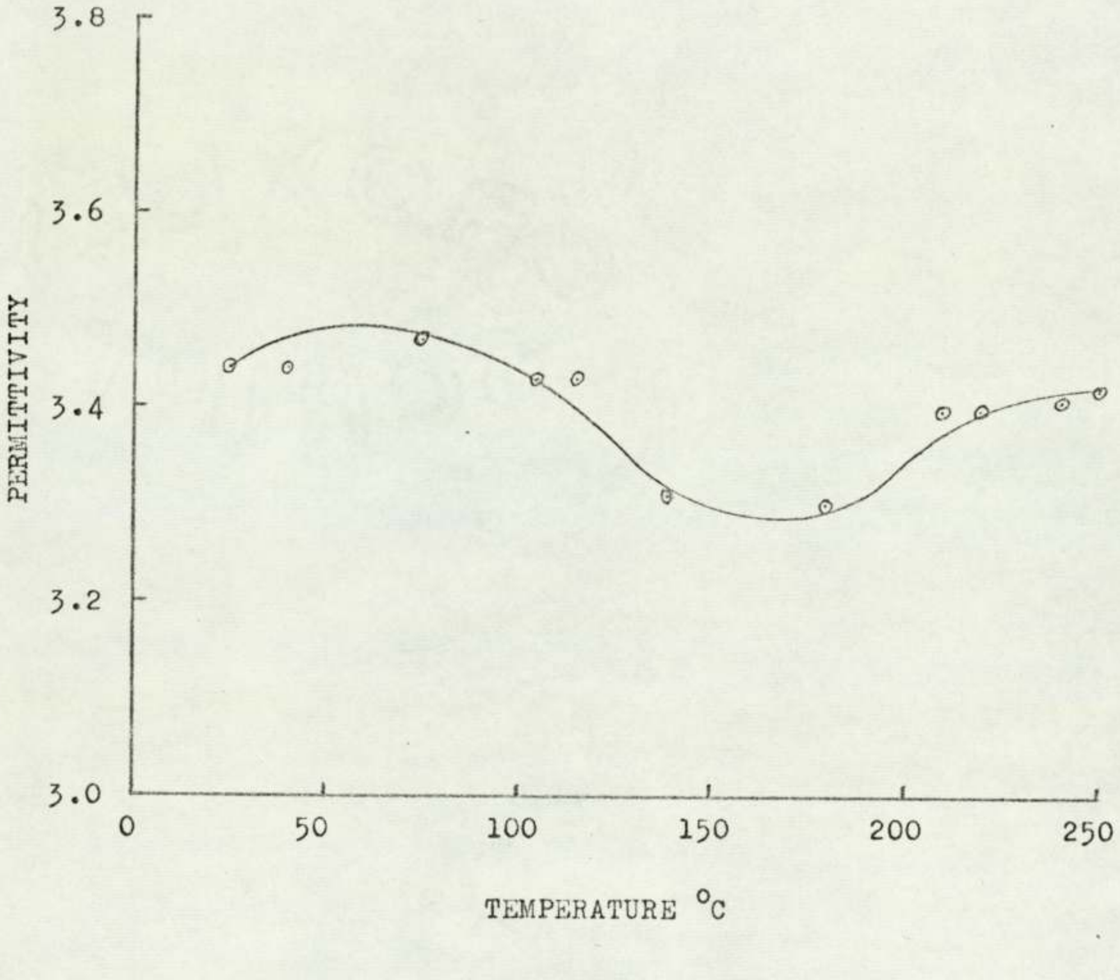


FIGURE 7.12. PERMITTIVITY v TEMPERATURE FOR MICA PAPER LAMINATE.

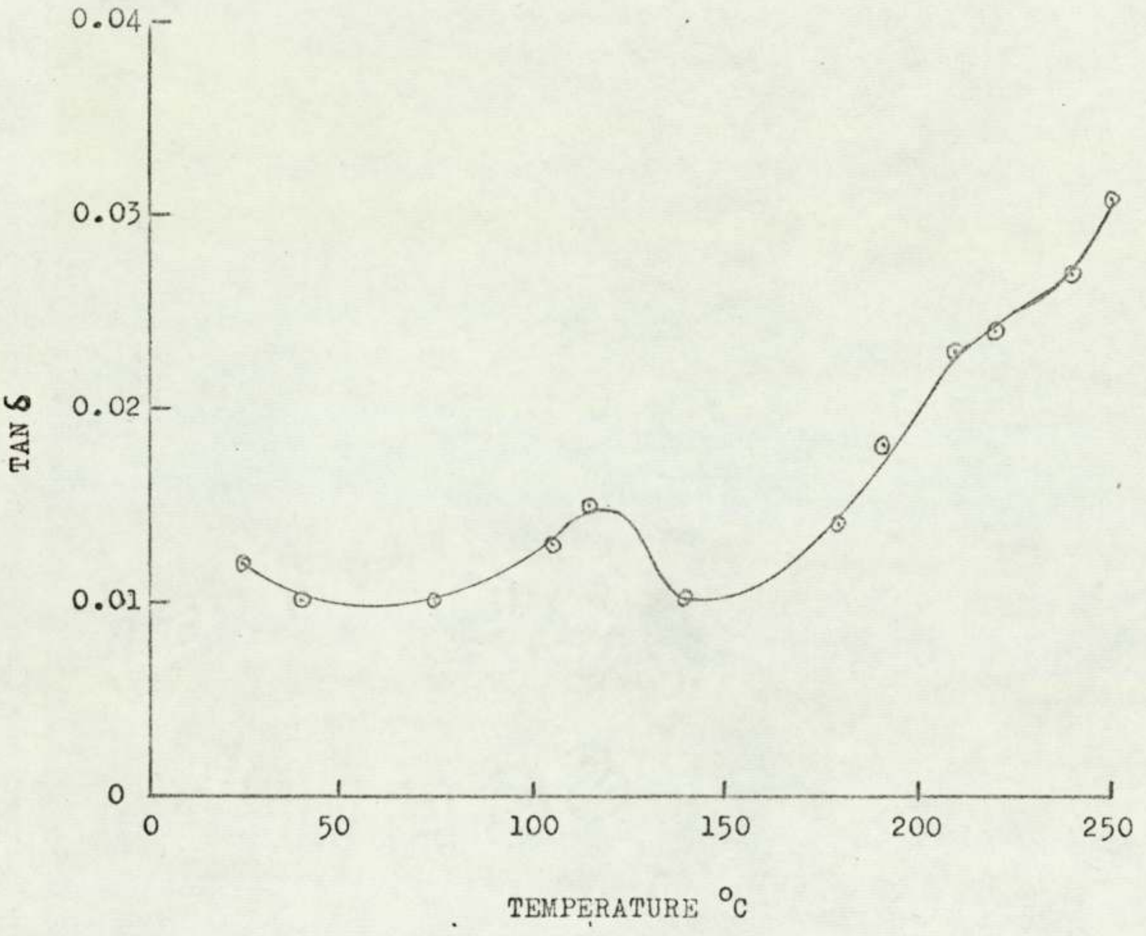


FIGURE 7.11. TAN δ v TEMPERATURE FOR MICA PAPER LAMINATE

7.4.5. Ageing Laminates. Two L 7.4 laminates were cut into ½ inch wide strips and aged at 250°C after the normal post-cure of 16 hours at 260°C. Flexural strength was measured at 23°C and at 200°C with the results in Table 7.8.

Ageing Period in weeks at 250°C.	Mean Flexural Strength lb/in^2. 23°C	200°C.
0	17,700	2,100
1	14,500	12,350
2	11,350	10,950
6	9,350	8,550

Table 7.8. Variation of Flexural Strength with Ageing.

7.4.6. Mica Papar Laminate. A laminate was prepared using untreated, unbacked mica paper, 0.003 inch thick. This was impregnated with a 33% by weight solution of Resin 5.7 in 1,2-dichloroethane by soaking for 5 minutes, and pre-cured for 2 minutes at 200°C. 9 layers of the pre-impregnated mica paper were stacked and pressed at 100lb/in^{2}at250°C for 1 hour after which the laminate was removed from the press and post-cured for 16 hours at 260°C.

Dielectric loss tangent and permittivity results versus temperature are given in Figures 7.11 and 7.12 and represent values which are better than most currently available epoxy resin bonded mica paper laminates.

7.5. Electric Strength of Resin film.

Pieces of aluminium sheet 9 inches x 2½ inches x 0.0135 inches were coated with Resin 5.2 by double dipping in the resin with a

45 minute cure at 200°C between dips and after the second dip. The resin was finally cured for 16 hours at 260°C. A coating 0.0018 inch thick was obtained. Electric strength was measured by the "rapidly applied voltage" method at 23°C and 240°C and again at 23°C after immersion in water at 23°C for 24 hours.

Electric strength, before immersion, at 23°C = 2.72KV/mil
Electric strength, after 24 hour water immersion, at 23°C = 2.38KV/mil
Electric strength at 240°C = 2.88KV/mil.

7.6 Resistance to BP Enerjet 53.

BP Enerjet 53 is a currently used ester based hydraulic fluid and lubricant in high speed aircraft. Electrical equipment is being designed for spray cooling using this fluid.

Dexter coils of 0.040 inch polyimide enamelled wire were coated with Resin 5.2 and divided into two batches which were cured according to the schedules given below. Control samples were removed from each batch and the remaining samples were immersed in BP Enerjet 53 for 7 days at 200°C. Bond strength was measured on each coil with the results given in Table 7.9.

Cure schedule	Mean Bond Strength lb.	
	Control coils	Immersed coils
1 hour 200°C + 16 hours 260°C	24	37.7
1 hour 200°C + 16 hours 260°C + 24 hours 300°C.	38.5	41.3

Table 7.9 Effect of BP Enerjet 53 on the Bond Strength of coils impregnated with Resin 5.2.

7.7. Discussion.

7.7.1. Resin 5.2. as an Impregnating Resin. As explained in Chapter 1. an impregnating resin for use in electrical machines must develop and maintain sufficient bond strength at the operating temperature to prevent movement of the windings relative to each other and to the frame assembly under the influence of electromagnetic and mechanical forces.

Resin 5.2, the optimised version of the DPO/p-XGDME/$SnCl_4$ resin, shows very good 240°C bond strength which even surpasses its room temperature value after a few days ageing at 300°C. This unusual behaviour may indicate the release of internal stresses at higher temperature; and that, when cold, these stresses make the resin brittle. The hot bond strength represents a considerable advance over the silicones and, even after only a 2 hour cure at 200°C, Resin 5.2 gives a better hot bond strength than a silicone varnish, when fully cured according to the maker's recommendations.

The retention of a useful level of bond strength for 500 to 600 hours at 300°C is an improvement over the performance of a commercially available amide-imide varnish which lasts for 400 hours at this ageing temperature and is currently used in aircraft equipment operating at temperatures in excess of 200°C.

In breaking the Dexter coils impregnated with Resin 5.2 the break occurred in the resin while with the amide-imide towards the end of its life, the site of fracture was the interface between the copper conductor and the polyimide enamel following the formation of an oxide layer on the copper. This indicates that Resin 5.2 acts as a more efficient barrier to oxygen than the amide-imide which could prove valuable in high temperature applications where copper oxidation and subsequent loss of adhesion of enamel is a problem.

The "twisted pair" tests indicate equivalent lives for polyimide enamel wire alone and impregnated with Resin 5.2 showing that the system is entirely compatible. The silicone gives a marginal improvement but, of course, does not have comparable hot bond strength and the amide-imide causes some de-rating of the polyimide enamelled wire.

The good bond strength of the resin; its compatibility with polyimide enamelled wire; and the fact that it is solventless making it unlikely that it would affect any other insulant make Resin 5.2 an attractive resin for impregnating the windings of high temperature machines. In aircraft equipment its resistance to aircraft hydraulic fluids and lubricants is also a very important asset.

7.7.2. Laminating. Glass cloth laminates bonded with the acid clay catalysed Resin 5.7 have advantages in good electrical properties and disadvantages in rather poor mechanical properties.

Dielectric loss tangent and permittivity values are outstanding and are extremely well maintained over a wide range of temperature and frequency. The tan δ value reaches only 0.03 at 250°C while an epoxy novolak bonded glass cloth laminate gives a value of 0.1 at 150°C and a cycloaliphatic epoxy glass laminate, although better, still has a tan δ of 0.1 below 200°C.

The electric strength of the laminate is not outstanding and taken in conjunction with the good electric strength of the resin, this merely confirms the presence of faults in the laminate. The electric strength of the laminate is not seriously affected by temperature, in line with the findings on other electrical properties. The tracking resistance is at least as good as phenolic laminates.

Mechanical properties are, however, not good. The laminations can be peeled apart without great difficulty and flexural strength is only 18,000lb/in^2 compared with values of around 70,000 lb/in^2 for the best resin bonded glass cloth laminates. However, after ageing for a few days at 250°C the flexural strength at 200°C is at least 80% of its room temperature value.

The void content of the laminates, 2-3.5 % by volume, is high for a top quality, electrical grade laminate and the electrical properties of these laminates are adversely affected by water absorption although not as seriously as might be expected. The water absorption of the laminate, containing 40 % resin is several times that of the resin itself indicating faults in the laminate which may arise from volatiles produced during cure, or from stresses due to unequal contractions of glass and resin. The water absorption is reversible as shown by the return of the laminate to its original dry weight and the recovery of its electrical properties after dry storage. This shows that the water was not chemically combined in the laminate and did not cause any permanent deterioration of the laminate. Some improvement in mechanical properties and in moisture resistance could possibly be achieved by improved processing techniques leading to a reduction in the void content.

The mica paper laminate is surprisingly successful, despite the brittle nature of the resin, and could indicate a fairly close match between the thermal expansion of mica and the resin. The values for mica are $6 \times 10^{-6}/^{o}C$ normal to the plane and $10 \times 10^{-6}/^{o}C$ in the plane of the crystal. The electrical properties are at least as good as the best currently available cycloaliphatic epoxy bonded mica paper laminate.

7.7.3. Mouldings. The quality of the mouldings, which was eventually achieved, was adjudged to be reasonably satisfactory. For thin discs a dough moulding was satisfactory but when more complex mouldings, such as impact strength specimens and pinbowls containing thick sections (ca 0.5 inch) were attempted a substantial pre-cure was found to be necessary to prevent "blowing" of the mouldings. This is caused by trapped volatile compounds which expand causing bubbles and cracks in the mouldings when pressure is released, or during subsequent post-cure.

Values of shear strength recorded - up to 4 tons/in^2 are considerably lower than the 6.7 tons/in^2 recorded for a wood flour filled phenolic moulding. The impact strength of 0.4 ft lb on a $\frac{1}{2}$inch x $\frac{1}{2}$ inch notched bar specimen compares reasonably well with those of phenolic mouldings which cover the range 0.15 to 1.75ft lb. The values achieved are considered useful and it is envisaged that the moulding powder could be applicable to the production of high temperature electrical grade mouldings.

Chapter 8.

DPO/p-XGDME RESINS PREPARED IN SOLUTION.

8.1 General Considerations.

From the results so far presented it has become clear that the DPO/p-XGDME polymers prepared in bulk were highly branched and that during cure substantial cross-linking occurred. The polymer molecule has been shown to contain many diphenyl oxide end groups which have presented sites for the initiation of thermal and oxidative degradation. Consequently the ultimate thermal, mechanical and electrical properties have not been realised.

Post-curing and ageing of the resins were shown to improve mechanical and electrical properties. This indicated that considerable cross-linking was taking place during these periods whereas, in general, it is desirable to have a system in which post-cure is not necessary to achieve optimum properties.

Elastomers have cross-link densities of the order of one cross-link per 100 chain units while a polyester resin with 1 cross-link to less than 8 or 9 chain units is brittle. It would seem, therefore, that for the DPO/p-XGDME resin 1 cross-link to 5 or 10 aromatic backbone units would be desirable for optimum mechanical properties.

A fundamental change in the structure of the Friedel-Crafts resin was obviously required to give the improved properties which were sought. Chemical alterations could be envisaged such as using p-DCX which has been shown by Grassie and Meldrum to give linear products in the early stages of co-polymerisation with benzene (23), Durene could be used to limit the number of available sites for branching. One chemical approach is described in 9.4.

The possibilities for altering conditions in bulk reactions are rather limited and have been explored in respect of the DPO/p-XGDME reaction as described in 6.1.

Using preparation in solution there is much more scope for modifying the reaction conditions. The solvents used must have certain properties. They must not react as substrates in Friedel Crafts reactions. For aromatic compounds this normally means that they contain deactivating substituents. Neither must they be capable of acting as substituting agents for aromatic compounds under the conditions employed. They must have high boiling points; and the ability to dissolve the reactants, the catalyst and the products.

With these considerations in mind a selection of solvents was made covering a wide range of permittivities. Catalysts were chosen to cover a range of expected activities as judged by behaviour in other Friedel-Crafts reactions. The molar ratio of DPO/p-XGDME was fixed at 1/1 to assist in obtaining reduced branching.

8.2. Preparation of DPO/p-XGDME Resins in Solution.

The solvents examined were nitrobenzene, o-chloronitrobenzene, o-dichlorobenzene, and decahydronaphthalene (decalin) with permittivities of 34.8, 20.0, 9.9 and 2.3 respectively. The catalysts were $AlBr_3$, $SnCl_4$, $TiCl_4$, and p-toluene sulphonic acid.

The general method was as described in 2.1.2.; details and observations are given in Table 8.1.

Resin No.	Solvent	Catalyst	Time to 60%	Comments
8.1	o-dichloro benzene	$SnCl_4$	1 hour 35 minutes	Distillation started 15 minutes after initial catalyst addition and then continued steadily.
8.2	Nitro benzene	$SnCl_4$	30 minutes	Very vigorous immediately following catalyst addition Some solvent boiled over with methanol and was returned to reaction vessel when reaction moderated.
8.3	o-chloro nitro benzene	$SnCl_4$	5 minutes	Even more vigorous. Treated similarly.
8.4	Decalin	$SnCl_4$	No reaction in 4 hours.	$SnCl_4$ was not soluble in decalin. It was added in diphenyl oxide. The reaction mixture changed from pale golden yellow to muddy green-brown. Eventually a brown muddy precipitate was formed.
8.5	Decalin	$AlBr_3$	No reaction in 4 hours.	$AlBr_3$ added in DPO. Pale green solution. Muddy precipitate.
8.6	Nitro benzene	$AlBr_3$	No reaction in 4 hours.	Yellow solution.

continued:-

Resin No.	Solvent	Catalyst	Time to 60%	Comments.
8.7	o-dichloro benzene.	$AlBr_3$	No reaction in 2 hours.	$AlBr_3$ added in DPO. Yellow-green solution.
8.8	o-chloro nitro benzene.	$AlBr_3$	No reaction in 4 hours.	$AlBr_3$ added in DPO. Yellow solution.
8.9	o-chloro nitro benzene.	$TiCl_4$	No reaction in 3 hours.	Catalyst added in DPO, Yellow solution.
8.10	nitro benzene.	$TiCl_4$	No reaction in 4 hours.	Catalyst added in DPO. When no reaction after 2 hours additional 1g (approx) $TiCl_4$ was added neat. Still no reaction. Brown solution.
8.11	o-dichloro benzene.	$TiCl_4$	No reaction in 3 hours.	$TiCl_4$ added neat. Amber solution with precipitate.
8.12	decalin	$TiCl_4$	No reaction in 3 hours	$TiCl_4$ added neat. Yellow-brown solution. Dark brown precipitate.
8.13	nitro benzene	p-toluene sulphonic acid.	No reaction in 6 hours.	Catalyst added in solution in nitrobenzene in 3 portions at 0,15 and 30 minutes. Yellow solution. Yellow-brown precipitate.

Table 8.1. <u>Details of DPO/p-XGDME Resins prepared in solution.</u>

8.2.1. Non-Volatile Matter in Resins prepared in Solution. The fact that no reaction was observed when $AlBr_3$, in particular, and $TiCl_4$ were used as catalysts was so surprising that it was felt that some secondary reaction involving evolved methanol might have masked the original reaction producing the methanol. To examine this possibility the non-volatile matter was determined on 1g samples of all the solutions shown in Table 8.1 with the results shown in Table 8.2. These indicate that some slight reaction has taken place, particularly with nitrobenzene and o-chloronitrobenzene as solvents, but do not alter the surprising conclusion that $SnCl_4$ is much more active in this reaction than $AlBr_3$.

Resin No.	Solvent	Catalyst	Non-Volatile matter. %	Non-Volatile matter. Total g	Nature of residue.
8.1	o-dichloro benzene.	$SnCl_4$	14.2	90.9	Solid
8.2	nitrobenzene.	"	17.1	102.6	Solid
8.3	o-chloronitro benzene.	"	15.4	102.6	Solid
8.4	decalin	"	0.7	3.5	Viscous liquid
8.5	"	$AlBr_3$	-	-	-
8.6	nitrobenzene	"	3.2	19.6	Viscous liquid
8.7	o-dichloro benzene.	"	-	-	-
8.8	o-chloronitro benzene.	"	1.5	10.2	Viscous liquid

continued:-

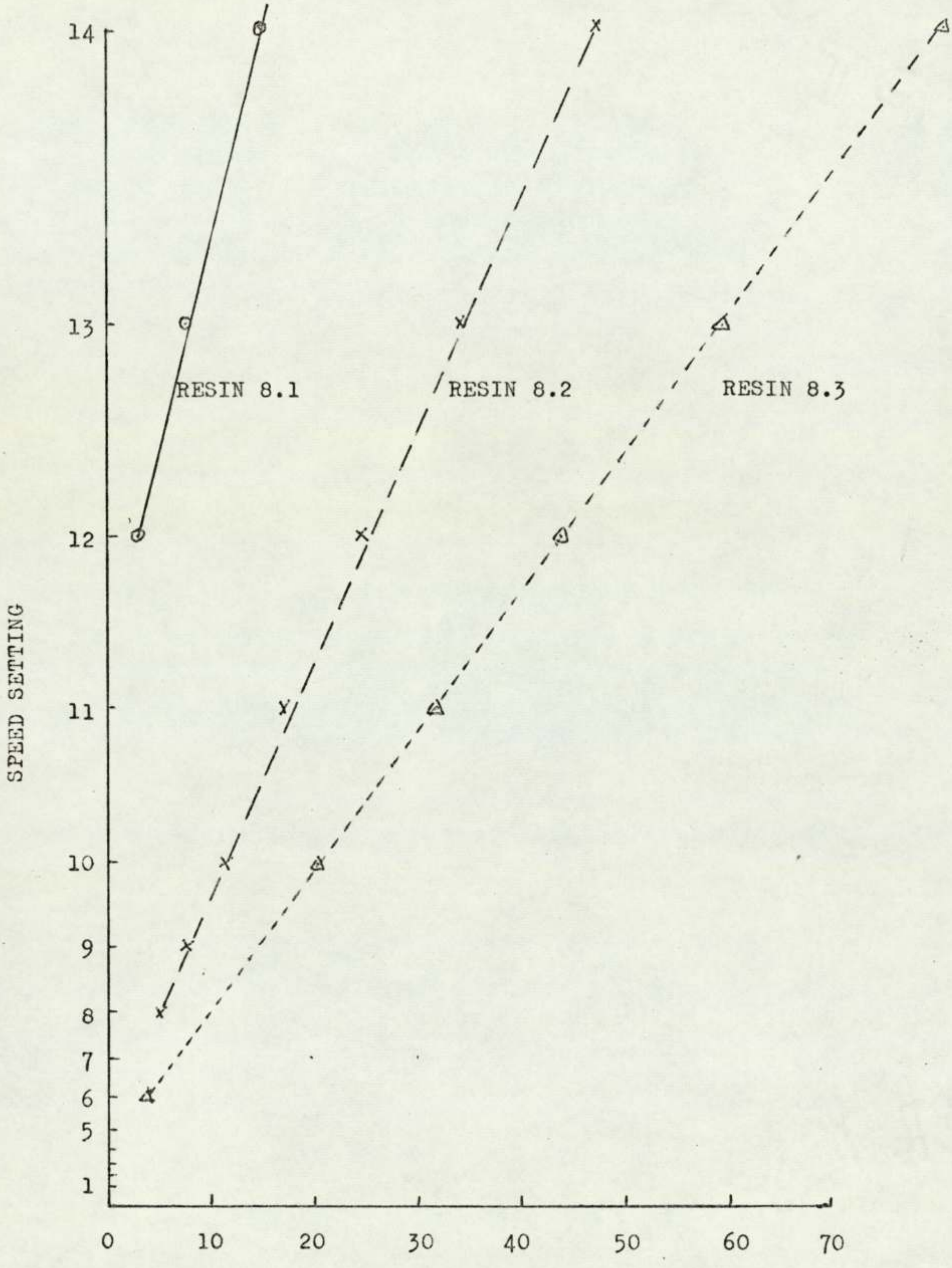


FIGURE 8.1. RHEOGRAMS FOR RESINS 8.1, 8.2, AND 8.3.

Resin No.	Solvent	Catalyst	Non-Volatile Matter. %	Total g.	Nature of residue.
8.9	o-chloronitro benzene.	$TiCl_4$	5.1	34.8	Viscous liquid
8.10	nitrobenzene	"	6.6	40.5	Viscous liquid
8.11	o-dichloro benzene.	"	-	-	-
8.12	decalin	"	-	-	-
8.13	nitrobenzene	p-toluene sulphonic acid.	-	-	-

Table 8.2. Non-Volatile matter in resin solutions listed in Table 8.1.

8.2.2. Viscosity of Resin Solutions. The use of the Epprecht Rheomat is described in Chapter 2. It was used to compare the viscosities of Resins 8.1 - 8.3. The results for each of the resin solutions are shown, on the special graph paper supplied with the instrument, in Figure 8.1. This shows straight line relationships for each solution indicating Newtonian behaviour. However, the large differences in actual viscosities suggested that the viscosities of the solvents might be directly affecting the results. Consequently to 8.1 in o-dichlorobenzene was added an equal volume of nitrobenzene and to 8.2 was added an equal volume of o-dichlorobenzene. To take account of the small difference in solids content additional mixed solvent was added to 8.2.

The two new solutions were re-examined at a single shear rate (setting 15) giving the following results.

Resin Solution	Scale reading
8.1 + nitrobenzene	19.2
8.2 + o-dichlorobenzene	28

Thus a distinct difference in viscosity remains after equalising solvent system, solids content and extent of reaction.

8.3 The $SnCl_4$ catalysed reaction in o-chloronitrobenzene.

This reaction was found to take place very rapidly (Table 8.1) and it was decided to look at it rather more closely by reducing the reaction temperature to 130°C. At this temperature the preparations detailed in Table 8.3 were carried out with the observations recorded there.

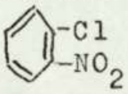
Resin	Reaction Mixture.		Catalyst.	Solvent	Observations.
No.	DPO	p-XGDME	$SnCl_4$		
8.14	102g 0.6M	99.6g 0.6M	0.78g	225ml	Gelled at 70% conversion.
8.15	68g 0.4M	66.4g 0.4M	0.52+ 0.26g	400ml	Reaction produced only 66% of theoretically available CH_3OH despite raising temperature to 175°C and adding extra 0.26g $SnCl_4$. Solid resin on evaporating solvent.
8.16	68g 0.4M	66.4g 0.4M	0.52g	225ml	Gelled at 66% conversion.

Table 8.3 Resins prepared in o-chloronitrobenzene solution.

8.4 Resins prepared in o-dichlorobenzene.

The resins described in Table 8.4. were each prepared in 400ml o-dichlorobenzene.

Resin	Reaction Mixture.		Catalyst.	Observations.
No.	DPO	p-XGDME		
8.17	68g (0.4M)	66.4g (0.4M)	0.52g $SnCl_4$	Reacted to 80% conversion. Solid resin when solvent removed. A similar preparation gelled at 85% conversion.
8.18	"	"	0.52g $SnCl_4$ 5g Ball clay 975 0.05 ml H_3PO_4.	Reacted at 175°C to 40% conversion with $SnCl_4$ as catalyst. Cooled to 160°C and added clay/acid. Reaction continued at 160°C to 78% conversion. Only slight settling of clay which could be overcome by occasional stirring.
8.19	"	"	5g Ball clay 975 0.05ml H_3PO_4.	Reacted at 155°C to 75% conversion when gelation occurred.

Table 8.4 Resins prepared in o-dichlorobenzene solution.

8.5 Comparison of Resins 8.15 and 8.17.

8.5.1. Thermal Stability of Solution prepared Resins. Thermogravimetric analysis in air at 4°C/minute and 7°C/hour were carried out on Resins 8.15 and 8.17 after each had been cured for 1 hour at 200°C and 16 hours at 260°C. The thermograms are shown in

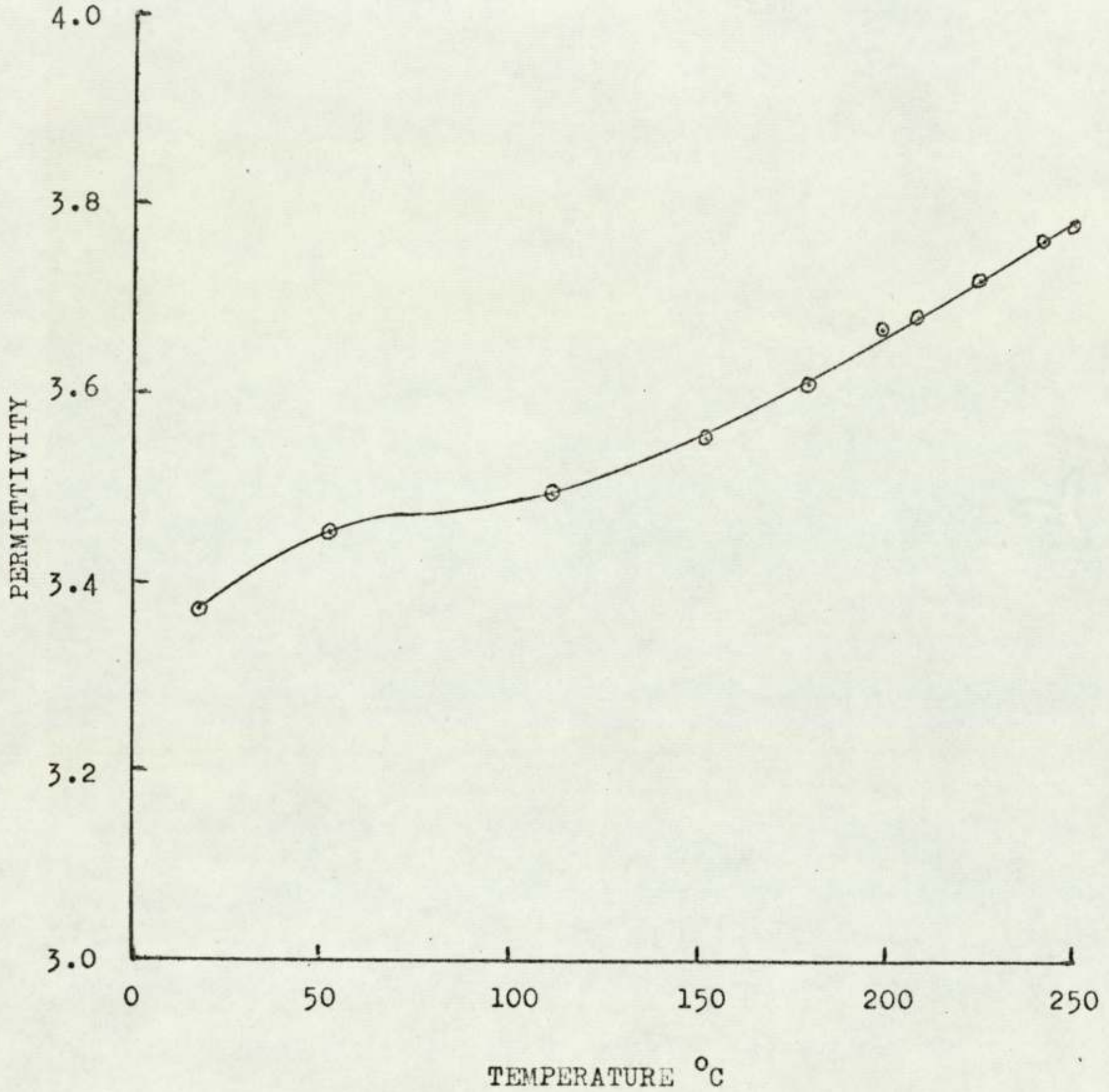


FIGURE 8.7. PERMITTIVITY v TEMPERATURE FOR GLASS CLOTH LAMINATE L8.1.

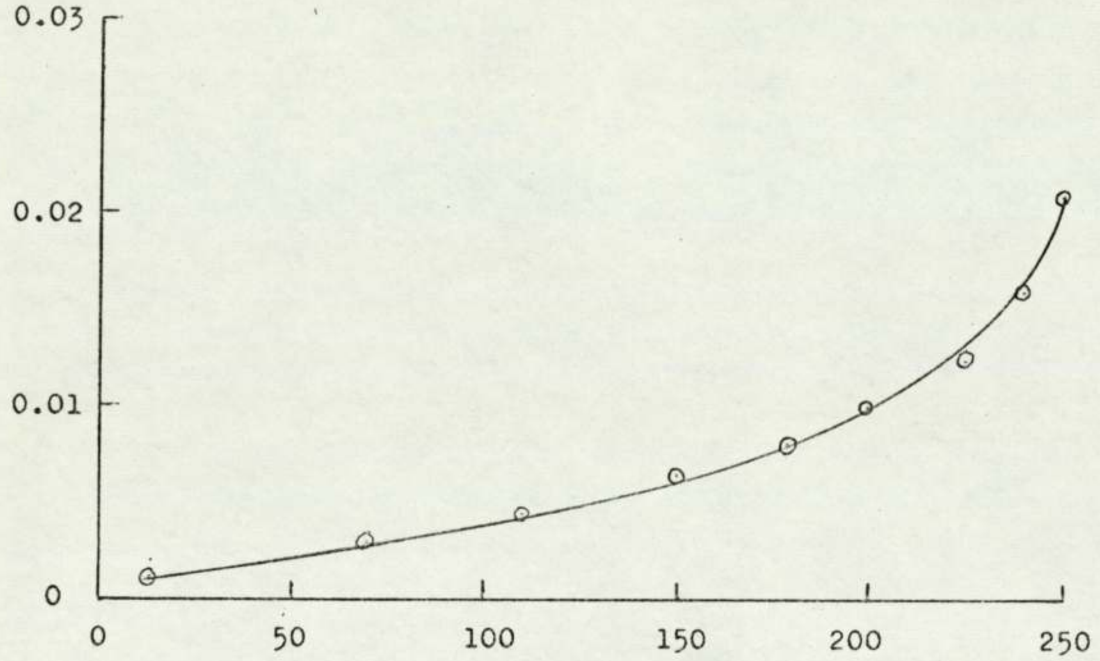


FIGURE 8.6. TAN δ v TEMPERATURE FOR GLASS CLOTH LAMINATE L8.1.

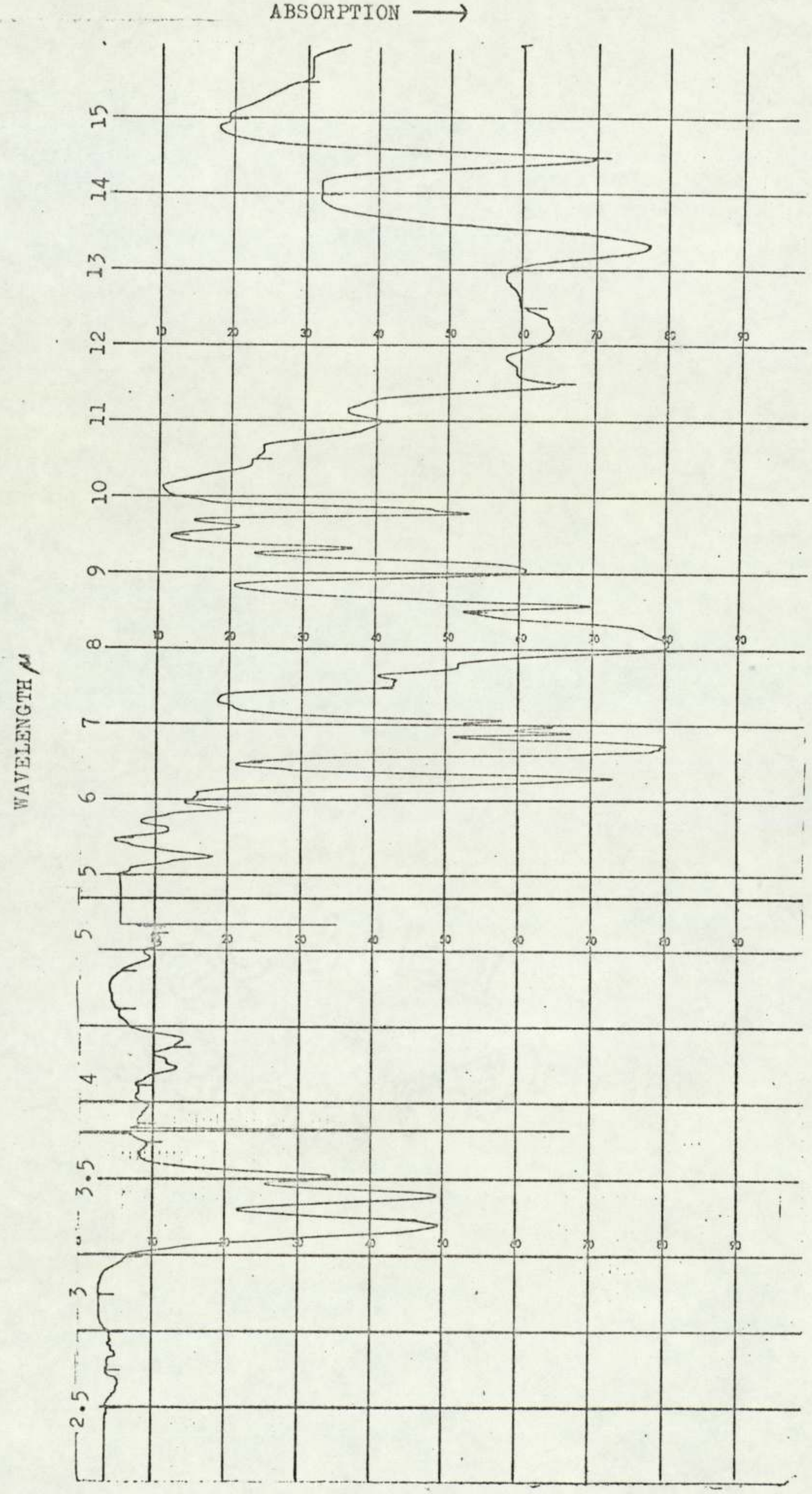


FIGURE 8.5. INFRA RED SPECTRUM OF RESIN 8.17.

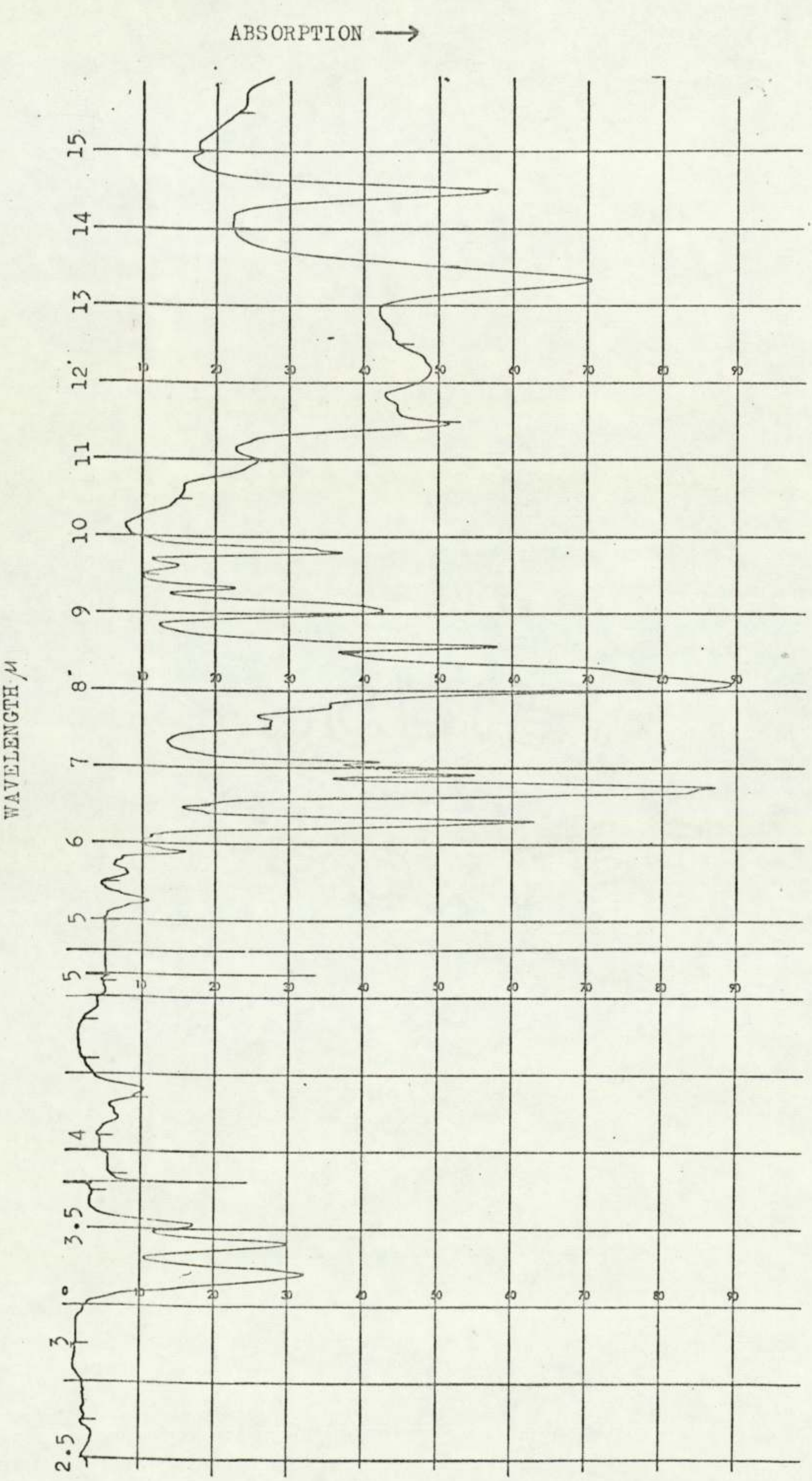


FIGURE 8.4. INFRA RED SPECTRUM OF RESIN 8.15.

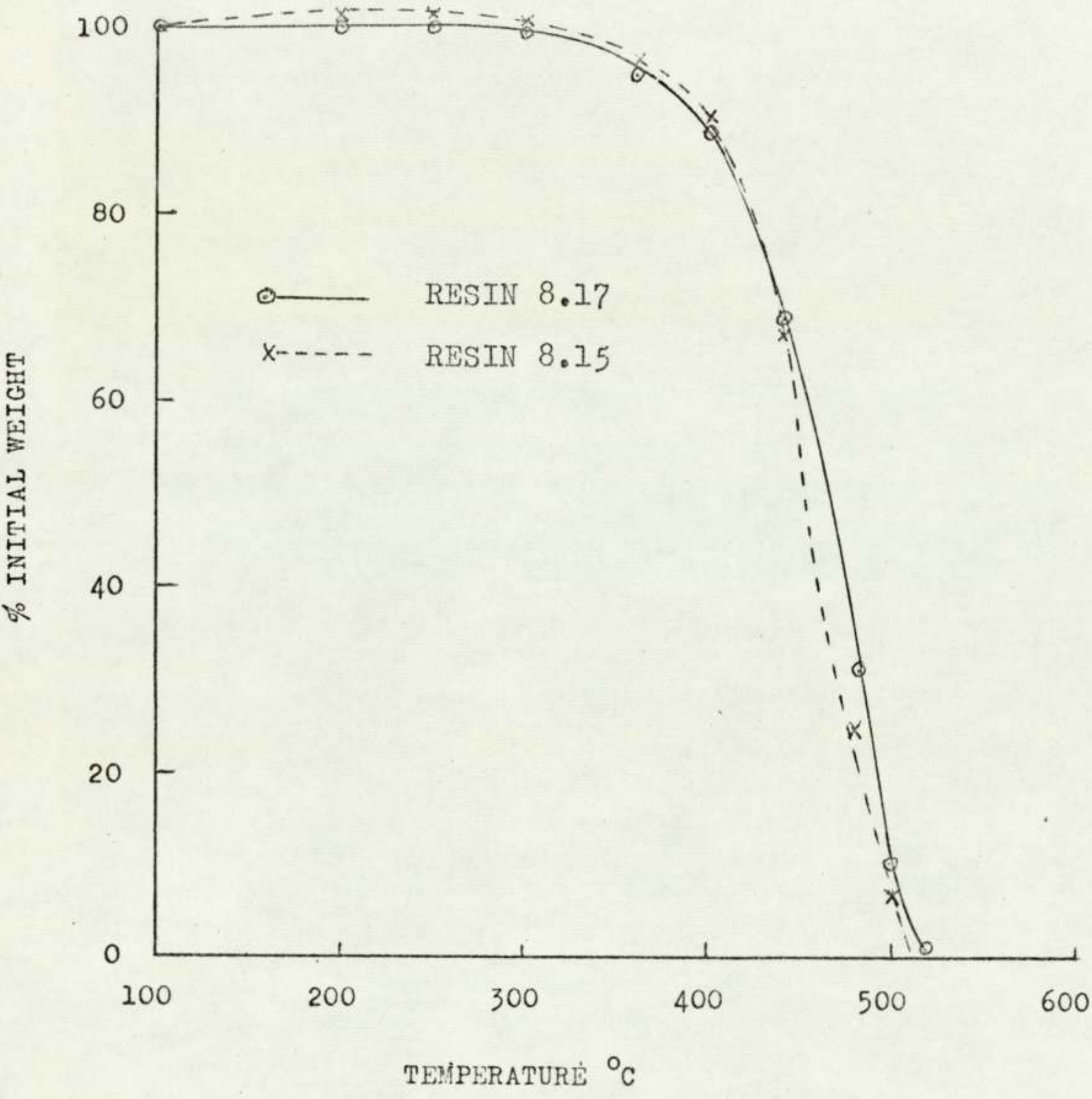


FIGURE 8.3. THERMOGRAMS FOR RESINS 8.15 AND 8.17.
HEATING RATE: 7°C/hour.

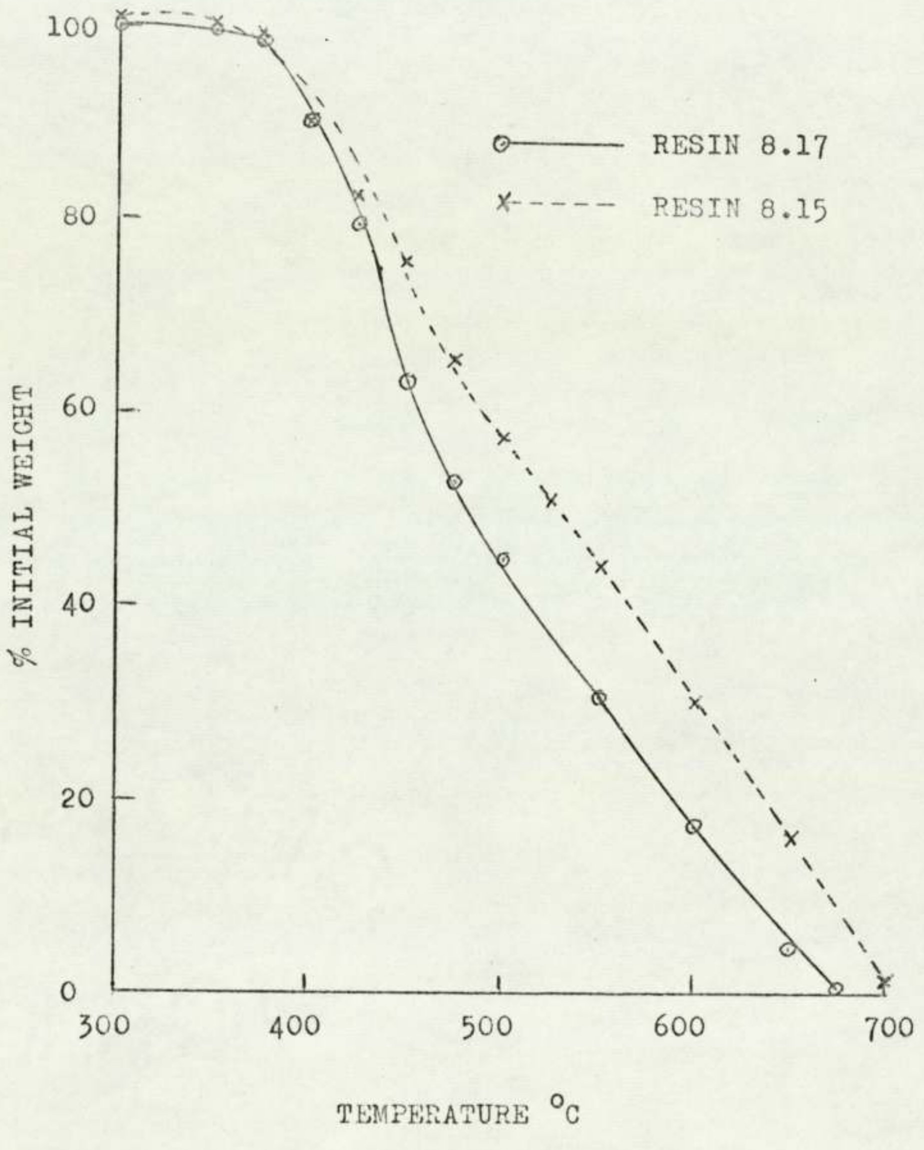


FIGURE 8.2. THERMOGRAMS FOR RESINS 8.15 AND 8.17.

HEATING RATE: 4°C/ minute.

Figures 8.2 and 8.3.

8.5.2. Infra Red Spectroscopy. The infra red spectra of Resins 8.15 and 8.17 were recorded and are shown in Figures 8.4 and 8.5.

8.6. Composite Materials based on Solution prepared Resins.

8.6.1. Laminating using Resin 8.18. A glass cloth laminate was prepared using the above resin as described in Table 8.5.

Laminate.	Glass cloth.	Technique.
L 8.1	Y094 with T12 finish 0.006inch thick.	Cloth was passed through the resin solution four times with a cure of 2 minutes at 250°C between dips and 5 minutes at 250°C after the final dip. A 12 layer 6 inch x 6 inch laminate was laid up and pressed at 500lb/in.^{2} for 1 hour before being post-cured for 16 hours at 260°C.

Table 8.5. Preparation of laminate with Resin 8.18.

Tan δ and permittivity values were measured as functions of temperature and later repeated after a further cure of 16 hours at 260°C. The results of both sets of measurements are shown in Figures 8.6 and 8.7.

The flexural strength of Laminate L8.1 was measured at 23°C and at 200°C after ageing at 250°C with the results given in Table 8.6.

Weeks at 250°C.	Flexural strength in lb/in.^{2} 23 °C	200°C
0	29,500	
1	25,550	26,900
2	22,500	24,800
4	18,700	23,900
6	17,100	19,900
10	13,800	15,200

Table 8.6 Flexural strength versus ageing for Laminate L 8.1.

8.6.2. Film Forming Properties of Resin 8.15. A preliminary experiment was carried out to assess the film forming properties of Resin 8.15. A piece of aluminium foil was cleaned by immersion in chromic acid, washed and dried. It was then dipped in the solution of Resin 8.15 at 50°C. A smooth coating was formed which remained flexible after ageing for 1 week at 250°C. Adhesion to the aluminium substrate was good but no mechanical testing was carried out.

8.7. Discussion.

8.7.1. Resins. From the viscosity measurements it was concluded that Resin 8.1., prepared in o-dichlorobenzene, was the least branched of the resins prepared in solution. This was to some extent supported by the fact that in o-dichlorobenzene gelation occurred at 85% conversion, whereas, in o-chloronitrobenzene, gelation occurred as early as 66% conversion as judged by the volume of distillate.

However, the strange behaviour of Resins 8.15 and 8.16 cast doubts on the above conclusion. Resin 8.16 was prepared at 130°C and, after reacting smoothly, gelled at 66% conversion as judged by the volume of distillate. In the preparation of Resin 8.15 distillation took place steadily for a time, but gradually slowed down, and eventually stopped at 66% conversion. Even increasing the temperature to 175°C and adding additional catalyst failed to produce any more distillate. The resin remained in solution.

On evaporation of the solvent from Resin 8.15 a solid resin was obtained, whereas, at 66% conversion a liquid would have been expected. Furthermore, the solid was not a gel as shown by the fact that it could be melted and solidified repeatedly. This suggested that, in some way, reaction beyond 66% had taken place without liberating an equivalent amount of methanol.

This problem has not been resolved but it appears that evolution of methanol is not an entirely satisfactory guide to the extent of reaction. In this connection it is interesting to note that Overhultz and Ketley (64) were unable to correlate HCl evolution with the molecular weights of polymers prepared using various di(chloromethyl) aromatic compounds with other methyl substituted aromatic compounds. Also Montaudo and co-workers (65) showed that the molecular weight of polybenzyl prepared with $SnCl_4$ as catalyst was almost independent of extent of reaction. They concluded that the reaction was not a normal polycondensation and proposed that it took place by a stepwise reaction of monomer on polymer. They further suggested that this reaction took place much faster than the monomer-monomer chain initiation process.

The non-volatile matter recorded for resins which had supposedly reacted to the same extent, namely 60%, showed considerable differences in the total weights of resin produced in each solvent. This would appear to indicate differences in the extents of reaction but could possibly be explained by a difference in the comparative rates of the monomer-monomer, and monomer-polymer reactions. This would result in different proportions of volatile, low molecular weight; and non-volatile, higher molecular weight, polymer. The non-volatile matter results also indicated that the $SnCl_4$ catalysed reactions were much more rapid than those with any of the other catalysts examined.

Infra red spectra and thermograms for Resins 8.15 and 8.17 were very similar, although the resins were reacted, nominally to 66% and 80% conversion respectively.

It can be seen, therefore, that much of the behaviour of the resins in solution remains to be explained. The large differences in reactivity using the different solvent/catalyst systems holds out considerable hope that the resins produced could be modified, possibly to give a linear polymer which could then be cross-linked as desired.

8.7.2. Composites. The laminate based on Resin 8.17 had dielectric loss tangent and permittivity which were equivalent to the best previously obtained using bulk prepared resins. Its resistance to tracking was superior to phenolics. Its flexural strength and ageing characteristics were much better than the best of the previous laminates. Taken in conjunction with the indications of greater linearity, the improved mechanical properties could be construed as indicating that the resin had less brittle characteristics and was better able to accommodate the built in stresses without causing the glass-resin bonds to fail.

The film forming properties of Resin 8.15 shown in the one simple experiment showed promise.

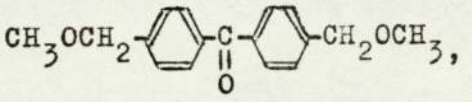
Chapter 9.

THE CHEMICAL APPROACH TO LIMITING CROSS-LINKING.

9.1. General Considerations.

The self-condensation of p-XGDME has been shown in 3.2.1 to occur readily. This means that co-polymers which include p-XGDME are bound to be highly branched. Consequently, in attempting to prepare more linear polymers it would be advantageous to use a reacting difunctional compound, incapable of self-condensation, in the place of p-XGDME.

Highly substituted and deactivated compounds were both considered. However, from the point of view of thermal stability, substitution was not desirable. Consequently, the choice fell on the deactivated compounds, particularly since Phillips (1) had reported that p-DCX did not react with benzophenone.

4,4'di-(methoxymethyl) benzophenone (DMMBP),  , was chosen for study but was not commercially available. It was decided to synthesise it via 4,4'-dimethyl benzophenone which could be chlorinated and subsequently methylolated.

4,4'-dimethyl benzophenone was prepared by the Friedel-Crafts condensation of toluene with carbon tetrachloride in the presence of $AlCl_3$ according to the procedure described by Vogel for benzophenone (66). A product was obtained which melted at 92-93°C in fair agreement with the published figure of 95°C.

9.2. Attempted reaction of 4,4'dimethyl benzophenone and p-XGDME.

5.25g 4,4'dimethyl benzophenone, 5g p-XGDME and 0.5ml 10% by volume $SnCl_4$ in 1,2-dichloroethane were heated together in a boiling tube to 160°C when reaction started. The temperature was maintained for 15 minutes when gelation occurred after which the resin was further heated for one hour at 160°C.

After cooling the solid which was obtained was powdered and extracted (Soxhlet) for 3 hours with 1,2-dichloroethane. During this time 3.2g 4,4' dimethyl benzophenone was extracted. It was not established whether more ketone could be extracted by more prolonged treatment. The ketone was identified by its melting point and its infra red spectrum.

9.3. Chlorination of 4,4' dimethyl benzophenone.

Reaction mixture:

105g 4,4' dimethyl benzophenone.
150g sulphuryl chloride
5g benzoyl peroxide
500ml carbon tetrachloride.

The dimethyl benzophenone, sulphuryl chloride and carbon tetrachloride were heated together at reflux and the benzoyl peroxide was added in 1g portions over 8 hours while refluxing was continued. After cooling, the reaction mixture was washed with aqueous sodium hydrogen carbonate and water, dried over anhydrous calcium chloride and concentrated by evaporation. The waxy solid was recrystalised several times from dichloroethane and petroleum ether (60 - 80°C) and a fraction (18g: yield 13%) melting at 103°C was obtained.

The remainder of the solid material was recovered by evaporation and re-chlorinated as follows:-

100g partially chlorinated dimethyl benzophenone
135g sulphuryl chloride
500ml carbon tetrachloride
3g benzoyl peroxide.

The partially chlorinated dimethyl benzophenone and 1g benzoyl peroxide were dissolved in 200ml carbon tetrachloride and heated to reflux. The sulphuryl chloride and the remaining benzoyl peroxide dissolved in the 300ml of carbon tetrachloride were added slowly over 2 hours. Refluxing was continued for a further 5 hours after which the product was processed as before to give a further 10g of the di(chloromethyl) benzophenone (DCMBP) melting at 103°C.

Elemental analysis gave C 65.2,H 4.6 , Cl 25.4 ,O 4.8 % (Difference).
(Theoretical C 64.5 ,H 4.3 , Cl 25.5, O 5.7 %)
The M.W. was measured by Vapour Pressure Osmometry and found to be 281± 5 (Theoretical 279).

9.4. Preparation of Polymers using 4,4'-di-(chloromethyl) benzophenone.

Before proceding to the preparation of DMMBP, polymers were prepared using DCMBP to establish whether the ketone gave any advantage over p-XGDME. Details of resin preparations are given in Table 9.1.

Resin No.	Reactants	Technique	Observation.
9.1	2.79g DCMBP(0.01M) 1.7g DPO (0.01M) 0.1g Ball clay 975 0.01ml 88% H_3PO_4.	Mixture was heated for 3 hours at 140°C, 5 hours at 160°C and 2 hours at 190°C. The HCl evolved was passed into NaOH solution.	Gelled at 55.5% conversion. Hard brittle resin on cooling.

Resin no.	Reactants	Technique	Observation.
9.2	13.95g DCMBP(0.05M) 8.5g DPO (0.05M) 1 ml 10% by volume $SnCl_4$ in 1,2-dichloroethane.	Mixture was heated at 160°C for 1 hour, then 200°C for 1 hour. The HCl evolved was passed into a NaOH solution.	Gelled at 60.6% conversion.
9.3	2.79g DCMBP(0.01M) 1.35g Durene(0.01M) 1 ml 1% by volume $SnCl_4$ in 1,2-dichloroethane.	Mixture was heated at 190°C for 1½ hours. Temperature raised to 260°C. Heated in a bunsen flame and further HCl was evolved. HCl passed in to NaOH solution.	Pale green solid at 23.5% conversion. Did not melt at 260°C. Continued to 40.4% conversion. Only partly soluble in 1,2-dichloroethane.
9.4	2.79g DCMBP(0.01M) 1.35g Durene(0.01M) 50 ml o-dichlorobenzene 1 ml 1% by volume $SnCl_4$ in dichloroethane.	Heated for 17 hours at 170°C. HCl evolved passed into NaOH solution.	Only 19% conversion. Very slow reaction.

Table 9.1. <u>Polymers prepared using DCMBP.</u>

9.5. Discussion.

The work described in this chapter was an attempt to use one of the many possible deactivated compounds in place of p-XGDME in order to eliminate self-condensation which was such a prominent feature of the behaviour of p-XGDME.

4,4'-dimethyl benzophenone was prepared without difficulty The attempted reaction of this compound with p-XGDME showed that little or no reaction occurred. This demonstrated that, even in the presence of the two methyl groups, the aromatic rings in 4,4'-dimethyl benzophenone were sufficiently de-activated to prevent reaction. The preparation of DCMBP was, therefore, carried out.

DCMBP had been prepared previously by Connerade (67) by chlorination of 4,4'-dimethyl benzophenone with chlorine under ultra violet irradiation. He found a melting point of 110.5°C. Later Golden (68) prepared DCMBP using sulphuryl chloride, in the presence of benzoyl peroxide, as the chlorinating agent; and reported a melting point of 103°C.

The method used in the present work was similar to that of Golden and the melting point of the DCMBP was found to be 102-103°C. The authenticity of this DCMBP was established by vapour pressure osmometry and elemental analysis. The melting point reported by Golden has thus been confirmed.

The polymer preparations using DCMBP produced very disappointing results. In the DPO/DCMBP resins gelation occurred at around 60% conversions as judged by evolution of HCl showing that no advantage in reduced branching, compared with the analogous DPO/p-XGDME resin, had been achieved. The reaction was sluggish even at high temperature. This was particularly noticeable when the acidic clay catalyst was used. With durene the reaction was so slow, both in bulk and in o-dichlorobenzene solution, as to be of no practical value.

As a result of these findings work on DCMBP was discontinued. It was expected, by analogy with the behaviour of p-DCX and p-XGDME, that DMMBP would react even more slowly than DCMBP and consequently plans to prepare DMMBP were abandoned.

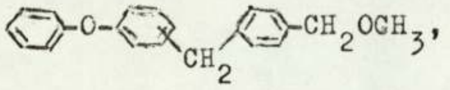
Chapter 10

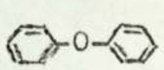
CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK.

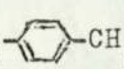
10.1. General.

From the theoretical viewpoint a greater understanding has been obtained of Friedel-Crafts polymerisation reactions. Contrary to initial expectations, the use of terphenyl does not lead to a more linear product than simpler aromatic molecules, e.g. benzene. Analogy with benzyl chloride suggests that the polymer has a highly branched structure. The number of potential reaction sites in the monomer appears to be an important, possibly the most important, criterion in determining the nonlinearity of the product. Thus, terphenyl has 14 unsubstituted sites, diphenyl oxide has 10 and benzene has 6. The need to introduce non-aromatic linkages, e.g. methylene or ether, to improve flexibility, coupled with the above principle, provides at least an empirical understanding of the molecular requirements of the substrate monomer for optimum physical properties.

The reactant molecule(p-xylylene glycol dimethyl ether, p-dichloroxylylene, etc.)also possesses potential substrate reactive sites, as evidenced in the self-condensation of p-xylylene glycol dimethyl ether described in 3.2.

An added complication arises from the fact that a dimer is apparently more reactive than the substrate monomer, e.g. 

, the dimer formed from 

 and CH_3OCH_2--CH_2OCH_3, is more readily substituted than diphenyl oxide itself by p-xylylene glycol dimethyl ether (See 5.6 and 5.7.2.). It is for this reason that the distribution of products at, say, 64% conversion is not typical of that found in normal polycondensation reaction systems. The evidence presented here suggests that a considerable amount of unreacted monomer exists at this stage and that, by the same token, the polymeric product is of higher molecular weight than would be expected in such a condensation polymerisation system.

The preliminary results obtained in solvents of different polarity and dielectric constant suggest that the influence of the reaction medium may be sufficient to alter the balance of the effects mentioned above, and to lead to a more linear product than was obtained from the reaction under simple melt conditions.

From a technological point of view a more exhaustive assessment of several of the resins has been carried out. Technological properties appropriate to electrical insulation applications, such as mouldings, laminates, and impregnation of machine windings, have been investigated. In some instances practically useful levels of important properties have been achieved, such as the impregnating resin based on diphenyl oxide and p-xylylene glycol dimethyl ether.

A brief summary of the results obtained from the various classes of polymers is presented in the sections which follow.

10.2. Terphenyl/p-XGDME Resins.

Although the resins based on terphenyls and p-XGDME show good thermal stability they are unsuitable for any electrical insulation application because of their brittleness. They possess highly branched structures which are probably similar to that of polybenzyl. During cure the resin-forming condensation reaction continues leading to crosslinking and increased molecular weight. At the same time extensive oxidation of methylene bridges and methoxymethyl end groups occurs leading to the formation of ketonic and carboxylic acid groups.

The acidic clay catalyst enables the resin preparation to be carried out at considerably lower temperatures than are practicable when $SnCl_4$ is used as catalyst. In the cure of the resins, however, the increased reaction rate is much less evident.

10.3. Bulk Prepared DPO/p-XGDME Resins.

The thermal stability of these resins is equivalent to that of the terphenyl/p-XGDME resins. Their handling and processing characteristics are much more attractive. Again they are highly branched but the greater flexibility of the ether link gives a less brittle resin which is suitable for impregnating the windings of high temperature electrical machines.

The thermal ageing characteristics of these resins are largely independent of the ratio of the reactants used in their preparations. Taken in conjunction with the other evidence presented in Chapters 5 and 6, this suggests a preferred composition for the resin of DPO/p-XGDME in the ratio 3/5.

The electrical properties of laminates and mouldings based on these resins are attractive but the laminates exhibit poor inter-laminar bonding which is reflected in poor all round mechanical properties.

10.4. DPO/p-XGDME Resins Prepared in Solution.

Solvent effects are very marked. The reaction rate differs by at least an order of magnitude between o-dichlorobenzene and o-chloronitrobenzene when $SnCl_4$ is used as a catalyst.

One resin, prepared in o-dichlorobenzene solution, shows much improved glass to resin bonding when used to make glass cloth laminates. A second resin, prepared in solution in o-chloronitrobenzene shows very good wetting of aluminium foil and gives rise to a resin film with good adhesion.

10.5. Work on 4, 4'-di(chloromethyl) benzophenone.

The melting point of 4, 4'-di(chloromethyl) benzophenone is now definitely established as 103° C.

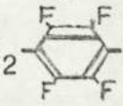
The resins which were prepared using DCMBP have no practical application. They show no advantage in linearity compared with the analogous p-XGDME resins and their preparation is much slower. Again it is probable that the dimer is activated to such an extent that the deactivation caused by the carbonyl group is overcome. The same type of reaction as has been postulated for the p-XGDME resin preparations is then likely to take place leading to a substantially similar, highly branched structure.

10.6. Recommendations for further work.

It would be valuable to carry out some confirmatory experiments relating to the origin of branching, to determine the relative importance of i) substrate

and ii) self-condensation of reactant monomer.

Additionally, the presence of methylal in the reaction products has been demonstrated. The influence of this on the pattern of further reaction should be determined.

A convenient way of determining the relative importance of these factors is to eliminate each in turn. This may conveniently be done by the use of, e.g. durene; p-tetrafluoroxylylene glycol dimethyl ether (CH_3OCH_2--CH_2OCH_3)(the fluoroaromatic analogue of p-XGDME)(69). The role of methylal can most conveniently be determined by normal kinetic techniques using known added amounts at the beginning of, and at known intervals during, the reaction.

The effect of reaction medium on the polymerisation reaction is obviously an important factor. Apart from general studies in this respect, the apparently unique effect of o-chloronitrobenzene should be investigated. The specific importance of nitro and chloro substituents on the same molecule, and the importance of dielectric constant in conjunction with this, could be investigated by e.g. the use of mixtures of chloro and nitro substituted aromatic solvents.

The kinetic course of the reaction in solution would make a convenient and rewarding study.

From the technological viewpoint, possibly the most important potential area for the use of these polymers, apart from their use as impregnating resins, is in glass cloth laminates. The mechanical properties of existing laminates in this context are markedly dependent on the glass/resin bond. Investigations in this rather complex area would probably be rewarding in terms of improved mechanical properties.

The most marked technological improvements in this class of materials will, however, undoubtedly follow from the production of more closely controlled (i.e. less branched) molecular structures in the initial stages of the polymerisation reaction.

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