THE CROSSLINKING OF POLYESTERS

A study of network formation
by physical methods.

by

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SUMMARY

Unsaturated polyester resins copolymerize with styrene giving crosslinked products. The useful properties of the crosslinked material depend greatly on the extent of completion of the reaction, which is difficult to determine chemically. It is important to know how to assess the degree of crosslinking, and how physical, electrical and mechanical properties change during the curing reaction.

A commercial polyester, of known constitution, was cured isothermally under standardized conditions. Dielectric constant, electrical dissipation factor, d.c. volume resistivity, refractive index, tensile strength, dynamic shear modulus, logarithmic decrement, Young's modulus at audio frequencies, volatile content, % extractable matter, and resistance to various aqueous solutions were all measured at intervals throughout the curing process. Because the conditions were standardized, the relationship between the various properties could be considered.

In addition, an infrared spectroscopic method was devised by which the extent of chemical reaction could be assessed in an approximately quantitative way. This method possesses the advantage that no prior removal of unreacted material is necessary.

The extent of reaction of styrene monomer, as determined spectroscopically, was in agreement with the determination by volatile content.

Changes in resistivity were found to be related to the weight fraction of reacted unsaturation. The maximum slope of the semilogarithmic resistivity-time curve was proportional to the reaction rate. Apparent activation energies by resistivity, refractometry and gel time measurement were similar.

Tensile strength did not become appreciable until over half the reaction had occurred. It was then proportional to the percentage of reacted unsaturation.

A small fraction of the polyester did not undergo reaction, but remained unattached, acting as a plasticizer.

Electrical and mechanical damping terms were the quantities which changed most in the latter stages of cure, and seem useful for assessing the degree of crosslinking in this region.

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THE PROBLEM

Unsaturated polyesters are copolymerized with vinyl monomers, such as styrene, to give insoluble products made up of three-dimensional network polymers. The crosslinking reaction is a free radical addition process which, while rapid at first, dies away almost imperceptibly. It may continue after the material has been in service for some time.

Undercure

The crosslinking reaction may be incomplete, either because it is still continuing, or because it has stopped prematurely without complete utilization of the functional groups. These conditions are known as temporary and permanent undercure. Analogous phenomena are found in the case of other thermosetting resins. Undercure is undesirable commercially, both because it imparts very inferior properties, and because the change in properties with time can itself create design problems. The extent and type of undercure is often difficult to determine in practice.

Physical properties of network polymers

Until recently, little was known of how physical properties changed during the cure of thermosetting resins. In the last fifteen years, many studies have been made using a wide variety of resins and techniques. Unfortunately, these studies suffer from the lack of any standardized polymerizing conditions. The diversity of resins, initiators, accelerators, fillers and cure temperatures make interrelation of one property with another impossible. It was therefore thought desirable to measure several important properties under standardized conditions. Properties depending on relaxation phenomena would be particularly interesting.

Chemical measurements

Since network structure is most easily described in terms of crosslink density, extent of reaction of functional groups, and other chemical parameters, it would be necessary to determine some of these quantities and to correlate the physical properties with them. Most chemical methods applicable to network polymers of this kind are tedious, and in some cases of doubtful accuracy, so there is a need for new methods of chemical analysis.

Technological significance

Techniques selected to give fundamental academic information on the changes taking place during reaction would probably be far too sophisticated for direct use in production and quality control. They would, however, be useful in evaluating catalyst systems, the effect of additives on gel and cure times, the relationship between network structure and certain physical properties, optimum cure temperatures, and the extent of homogeneity in large cured structures.

Some of these studies might indicate techniques which could be adapted to real technological conditions, either in polyesters or in similar materials such as epoxy and phenol-formaldehyde resins.

PART ONE : INTRODUCTION

1. Unsaturated polyester resins and their mode of crosslinking.

1a Historical development

Unlike some polymers, which achieve prominence in a short time, polyester resins have reached their strong position in the plastics industry fairly slowly.

In the nineteenth century, Berzelius produced a resinous substance by reacting a polyfunctional acid (tartaric acid) with glycerol. Similar materials were made commercially in the early years of the present century, using phthalic anhydride and glycerol. These were modified with vegetable oils, and marketed as lacquers for wood and metal articles.

Carothers (1929) developed preparative methods for various polyesters. Ellis (1940) patented a process for copolymerizing maleic polyesters with monomeric styrene, in the presence of a peroxide. (The earlier resins did not include a vinyl crosslinking monomer.) Ellis suggested that, in addition to being used as lacquers, the products might be moulded.

The Second World War brought rapid growth in the production of polyesters. Glass-reinforced resins were found suitable for aircraft radomes, boat hulls, water tanks and car bodies. Polyesters also found some application in the electrical industry.

Since then, new curing systems have been introduced, enabling large structures to be made in single units at low temperatures, and allowing thick sections to be cured. Marine applications(in trawlers, submarines and hovercraft) are becoming common. At the present time, about 85% of polyester resin output is used in glass laminates rather than castings; the surfacing of roads and floors accounts for some of the unreinforced usage. Small items such as buttons involve a surprising proportion of the remainder.

New applications have led to new problems. There is a continued need for more knowledge about the curing process, and its effect on the products.

1b The constitution of polyester resins

Many excellent text-books describe the manufacture of polyester resins in some detail, and explain why certain ingredients are preferred. (Bjorksten, 1956; Boenig, 1964: Parkyn, 1967.) The essential constituents of a modern polyester resin are: (1) a glycol such as propylene or ethylene glycol (2) an unsaturated acid, usually maleic or fumaric (3) a saturated acid, often phthalic anhydride; (4) a small proportion of inhibitor, e.g. hydroquinone (5) a crosslinking vinyl co-monomer, usually styrene. This is present to the extent of about 30 to 40 % by weight.

The function of the co-monomer is to convert an otherwise intractable, pitchlike material into a convenient solution, and to crosslink the fumarate unsaturation. It also imparts particular properties; methyl methacrylate gives improved weathering ability and transparency, while triallyl cyanurate improves heat resistance. The factors affecting the choice of monomer are discussed by Smith (1966). Styrene is extremely suitable from many viewpoints, and is also cheap.

The properties of the resin depend on both the ingredients used and the exact polyesterifying conditions. The acid number is of particular importance in deciding when a resin has reached the desired stage. Since the shelf life of a resin is not often more than about a year, a long research programme must inevitably use different batches which will vary to some extent in properties. Usually these variations are not great. In any case, a given batch tends to "drift" during storage.

1c Side effects in polyesterification

It is possible to consider the cure of polyester resins without being unduly concerned about the polyesterification reaction by which they are produced. Most of the departures from straightforward polyesterification, such as those discussed by Parker (1966), are only marginally relevant. Glycol loss, oxidative destruction of double bonds, and the debatable possibility of loss of fumarate unsaturation by glycol addition (Felici, 1963) are mentioned. The other point, discussed more fully in Parker's review is maleate-fumarate isomerization.

It has now been established conclusively that such isomerization occurs, usually to a high degree. For many years, polarographic evidence supported this view, but there were doubts whether this might have occurred to some extent during preliminary hydrolysis. Hayes, Read and Vaughan (1957) showed that the infrared spectrum of a resin made from maleic anhydride was identical with that obtained from a resin made from fumaric acid. Both contained the absorption peak at 12.95 microns, characteristic of the trans-configuration, but no evidence of the cis- form. Later, Park and co-workers (1961) devised a method for estimating the extent of isomerization by an infrared absorbance ratio method.

Recently, N.M.R. has been used. Curtis (1964) showed that, when 1,2 propylene glycol was used, at least 95% isomerization took place, mainly in the early stages of reaction. This percentage was decreased by the use of less sterically hindered glycols, such as ethylene glycol, but increased by the presence of aromatic acids or by high reaction temperatures.

The importance of this is that maleate and fumarate isomers copolymerize differently with styrene, giving different products. In the maleic - styrene reaction, the reactivity ratios are $r_M = 0.005$ and $r_S = 6.52$, but for the fumarate polymerization they are $r_F = 0.07$ and $r_S = 0.30$. The resulting differences in the products have been discussed both by Park and co-workers (1961) and by Funke and Janssen (1961).

1d The crosslinked polyester network

The thermosetting polymer network is made up of two kinds of connected chains. These will be referred to as the primary or polyester chains, and the polyaddition or copolymer chains.

The original polyester chains become the primary chains of the network, (changed only in that the unsaturated groups are reacted), and serve to connect the chains with the styrene.

The polyaddition chains consist of fumarate and styrene links. The number of styrene links between the fumarate crosslink points is a matter of debate, but widely thought to be about two or three on average.

This network is shown schematically in Fig. 1, the continuous lines depicting the polyester chains, and the broken lines representing styrene polyaddition chains. It will be seen that unreacted sites remain. The presence of some intramolecular crosslinks, where a styrene bridge connects two parts of the same chain, is also shown in this figure. Such a network can be described in terms of :

its crosslink density
the proportion of fumarate sites reacted
the amount of residual comonomer
the length of the styrene bridges
the average molecular weight of each chain type

the concentration of totally unattached chains
the proportion of the material which is part
  of a "loose end" (attached to the network
  by only one crosslink) and
the extent of formation of homopolymer.

The molecular weight of the copolymer chains alone is of the order of 10,000 or about six times that for the condensation chains, for styrenated polyesters of the commonest kind. Variations in the properties of resulting resins can be made by altering the ratio of saturated to unsaturated acid, by inserting long-chain acids or glycols or ring compounds, or by altering the proportion of styrene present. These matters have been reviewed by Hayes (1964).

Recently, Funke (1967) reasserted that a principal factor in the nature of the final product is the condition under which the "primary" network is formed, i.e., the network formed at or around the gel point. Once this network is formed, there are limits to the modifications which can be introduced.

2. Technological Significance of the Degree of Cure.

2a The changes in resin properties during cure

Thermosetting resins undergo a chemical crosslinking process, which converts them from powders or liquids into hard, massive solids. In the early stages of this conversion process, the materials are virtually useless, and the majority of studies have therefore concentrated on the latter part of the cure. In that part the properties usually approach terminal values asymptotically, but sometimes a maximum or a minimum is seen. Wohnsiedler et al (1956) cured filled and unfilled M/F resins, and found that the unfilled resins gave sigmoid curves, but the filled ones showed maxima, and the heat distortion temperature, flexural strength, water absorption values and Young's modulus in flexure all reached their optimum values at different times.

If the cure time is particularly short, M/F and P/F resins may be cured on the outside (because of contact with the hot mould surface) but undercured inside. Polyester resins, on the other hand, sometimes show an undercured tacky surface where oxygen inhibition is allowed. In both classes, the exothermic polymerizations will normally ensure that the centre is thoroughly cured, given enough time.

Polyester and epoxide resins undergo gelation. This is the most important change in their properties during cure. At a certain point, the viscosity increases steeply, and eventually reaches infinity as the liquid becomes an elastic gel. This gel still contains a great deal of soluble material, but some of the molecules produced by crosslinking extend throughout the material.

In the post-gelation stage a polyester resin goes through a rubbery stage, which eventually changes to a glassy, viscoelastic solid retaining a little flexibility. The last stage of cure causes a degree of embrittlement to occur, unless the resin structure is deliberately designed to give a flexible product.

2b The causes of undercure

Different resins have different requirements for complete cure. In the case of phenolics, Drumm, Dodge and Nielsen (1956) came to the conclusion that the factors of most importance were first catalyst concentration, second cure temperature, and thirdly cure time. If polyester resins were to be studied in the same way, it would not be likely that the same conclusions would appear. Extra catalyst would be more likely to cause undercure than to ensure rapid cure.

In polyester-glass laminates, the main causes of undercure may be said to be as follows:-

(1) insufficient styrene or other co-monomer.
(2) styrene loss by evaporation, particularly before gelation, but also afterwards.
(3) air trapped in loosely woven glass mat
(4) moisture adsorbed on the glass
(5) moisture in mineral fillers
(6) the wrong quantities of initiator and accelerator
(7) too low a cure temperature
(8) trace inhibition. (Phenolic-type compounds, sulphur, vulcanised rubber containing sulphur, carbon black, anatase and copper compounds are known to inhibit cure.)

The effect of moisture on the cure of polyester resins has been examined by Judd (1968). He found that it had very little effect up to a concentration of about 0.25%; it then retarded considerably, and increasingly so up to about 5% by weight. So the temperature and humidity at which glass mat is stored before use may have an important effect on the extent of cure obtained.

Tamaka (1961) discussed the effect of oxygen on the gelation of polyesters, and the tendency of oxygen to interfere with such reactions was examined by Berger and co-workers (1952).

In many situations, complete cure may be closely approached simply by post-baking at a high temperature. This is preferred to high temperature cure, as the latter process causes considerable exothermic heat to be evolved, cracking thick sections of the moulding.

Frequently raising the temperature is not practicable at any stage; if the moulding is particularly large, it may not be possible, and in the case of encapsulated components, it would damage the electronic units inside. Yet such units are particularly sensitive to penetration by moisture, which will be more in evidence if the resin is undercured.

As a result, there is a need for polymerizing systems which can be relied on to give complete cure at moderate temperatures, and for a technology whereby such systems may be evaluated as they are devised.

2c The effects of undercure

If undercure does occur, there will be some inferiority in the products, but this may not be easily seen. The effects on the useful properties of the moulding may only become apparent when serious and perhaps catastrophic failure occurs in service. Gross undercure has been blamed for the leaching out of resin by river-water from the fibres of a glass-reinforced polyester boat. (Ministry of Aviation, 1961.) It has already been mentioned that moisture penetration shortens the life of electronic apparatus encapsulated by resin. Mechanical strength, weather resistance and heat resistance are also impaired. Chemical resistance is inferior.

Parkyn (1955) distinguishes between temporary undercure, where the crosslinking continues imperceptibly during the early stages of the service life of a moulding, and permanent undercure, in which the reaction stops before the unsaturated sites have reacted. He points out elsewhere (1967) that serious design problems are caused if it is necessary to design for a material which is continually changing its properties. In this period of change the resin may shrink slightly, and Young's modulus sometimes falls because of poorer adhesion to the fibre reinforcement.

The problems which may arise in cure technology from a lack of knowledge of the curing schedules are not confined to the latter stage of reaction. Cywiński (1960) has described how the curing samples pass through a " machinable" stage, after which they may become so brittle that fracture and splintering occur during machining, drilling and punching. It is therefore necessary to know the mechanical properties of the product from an early stage. The remarks of Haran, Gringras and Katz (1965) on the need for a method of process control, whereby metal inserts may be taken out of a moulding just prior to gelation, emphasize this. The prediction of the entire cure path is desirable.

2d Definition of complete cure

The stage at which cure is strictly complete may be defined in different ways. It is not always possible to obtain complete reaction of all the unsaturated groups of the polyester chains, since steric factors prevent the reaction of some of the fumarate groups. The extent of their reaction depends on the cure temperature. For the purposes of this work, the definition given by the Joint Services Research and Development Committee on Plastics will be adopted. (Ministry of Aviation, 1961.)

A fully cured resin is one in which cure has ended, either because all the ethylenic unsaturation has finally disappeared, or because the reactive sites which remain are prevented from reacting by steric factors. Thus a resin may be "fully cured" at a low temperature, but on raising the temperature further cure may take place. The lower temperature is sometimes called a "pseudo equilibrium" temperature, as opposed to the true equilibrium temperature, (usually over 100°C.) where further increase in temperature does not cause further cure.

In physical terms, the Committee defines full cure as the achievement of satisfactory properties which do not change with time.

The quantity of fumarate sites left unreacted at the end depends on such considerations as the type of vinyl monomer, the proportion of monomer and the structure of the polyester chain. Methyl methacrylate monomer tends to react with itself readily rather than with the fumarate groups. In resins crosslinked by MMA, as little as 40% of the fumarate groups may be reacted. Using styrene, complete reaction can be closely approached.

In this work, it will be convenient to measure the extent of reaction by the proportion of each type of unsaturation reacted, and collectively by the proportion of all unsaturation (styrene and fumarate) reacted. Alt (1962[1]) concluded that, provided sufficient styrene was used and none lost by evaporation, the proportions of the two types of unsaturation left in the latter stages of reaction were of the same order.

3. Aspects of the chemistry of the crosslinking reaction.

3a The three stages of the crosslinking process

It is convenient to divide the crosslinking of polyesters into three parts. According to Demmler and Schlag (1967), the first stage may be regarded as the pre-gelation period, the second as the post-gelation part (up to the point where diffusion control of the propagation steps occurs) and the third as continuation of the reaction by diffusion of vinyl monomer through the network, or by postcure at an elevated temperature.

In the first stage, radicals are formed by reactions involving the initiator and accelerator, but many are lost by reaction with the inhibitor or by simple recombination reactions. Other radicals react with the double bonds of the polyester and the styrene. Some growth occurs, and a few very large molecules appear. After an increase in viscosity, gelation occurs at a low conversion. The molecular weight distribution is very heterogeneous in the region where gelation begins. This is because, once a few polyester molecules have undergone reaction, the resultant large molecule is statistically more likely to undergo further reaction, having more sites than any primary polyester chain. As a result, infinite structures appear even though a great deal of monomer survives.

In the second stage, the destruction of free radicals by inhibitor does not occur. The high viscosity of the medium slows down the termination reactions (but not, at this stage, the propagation steps) and so an acceleration in the overall reaction rate is observed. This is accentuated by exotherms, but it also takes place under isothermal conditions. This is known as the Trommsdorf effect. The point at which this occurs will be discussed later.

Diffusion control eventually hinders the propagation reactions as well, and the T_g reaches the cure temperature. Provided some styrene remains, the reaction will continue (in the sense that this styrene will add on to the existing chains). Further post-cure at an elevated temperature frees the polyester segments for further reaction.

3b Initiating systems

Benzoyl peroxide may be used as an initiator, either alone or in combination with a tertiary amine. The amine allows the polymerization to be carried out at ambient temperatures instead of about 80°C. The mechanism of the accelerator given by Berndtson and Turunen (1954) is

$$2\ (C_6H_5COO)_2 + (CH_3)_2N.C_6H_5$$

$$\rightarrow 2C_6H_5COO + (C_6H_5CO)_2O + (CH_3)_2.NO.C_6H_5$$

Methyl ethyl ketone peroxide (MEKP) and cyclohexanone peroxide (HCH) are also used, in conjunction with cobalt naphthenate or cobalt octoate. The mode of operation of this system given by Demmler and Schlag (1967) is

$$R\,O\,OH + Co^{++} \xrightarrow{\text{fast}} RO. + OH^{-} + Co^{+++}$$

$$R\,OO\,H + Co^{+++} \xrightarrow{\text{slow}} ROO. + H^{+} + Co^{++}$$

$$ROO. \longrightarrow R. + O_2$$

Hydroperoxides obtained commercially are usually mixtures of several compounds, perhaps as many as twelve. The cure behaviour of a system therefore depends on the source of the initiator.

Many other systems have been devised, and recently vanadium systems have become common. The choice of system is discussed by Cywinski (1960), by Noller and co-workers (1961) and by Chesner and Preston (1964). Special systems for special applications have been given by Brinkman and Dines (1964), and multi-component systems are described by Harrison, Mageli and Stengel (1960). Systems for cold curing have been given by Mikhailova and co-workers (1967).

The first-mentioned benzoyl peroxide system and the cobalt-based hydroperoxide systems are still the most used initiators. There are some alleged differences between the paths of cures by these two types of initiator. Alt (1962^1) draws attention to this when he says that the amine-catalysed systems give a very rapid cure which dies away somewhat abruptly. The cobalt systems give a more even rate of reaction. Parkyn (1967) suggested that, when used for thin sections, the tertiary amine-catalysed reaction does not go to completion at the low temperatures normally used.

3c Gelation in unsaturated polyester resins

This phenomenon has been examined both theoretically and experimentally by a large number of investigators. Flory (1941) outlined the classical theory of gelation in polyfunctional systems, according to which a homogeneous (monodisperse) polymer of long chain length, undergoing random crosslinking, need have only one crosslinked unit per primary chain present. For polymers with the Flory "most probable" distribution of molecular weights, given by

$w_x = x\ (1-p)^2\ p^{x-1}$ (symbols are given in the Appendix)

the weight average degree of polymerization (DPw) is twice the number average (DPn), and we have one crosslinked unit for two primary chains.

Polyester resin chains are not long in this sense; the number-average molecular weight is usually between 1000 and 2500. Nor is the crosslinking random. Nevertheless the conclusion that there need be very little reaction at gelation is applicable. Stockmayer (1944) calculated the number of molecules (N) present at gelation compared with the original number, N_o. He found that for a heterodisperse polymer,

$$N_o / N = 4/3$$

Gordon, Grieveson and McMillan (1956) applied the theories of Flory and Stockmayer to the crosslinking of a polyester resin by MMA. They decided that, neglecting a small amount of cyclization, their results were consistent with these theories. They used the equation

$$\phi_c = 1/f_F \ (DP_{wp} - 1) \ (DP_{wc} - 1) \ \ldots\ldots\ldots\ldots \ (3.1)$$

to give ϕ_c, the fractional conversion of fumarate unsaturation at the gel point, in terms of the weight-average degree of polymerization of the condensation and polyaddition chains. f_F is the fraction of polymerized unsaturation which is of the fumarate type. DP_{wc} was found from the number-average expression DP_{nc}, which could be determined by end-group titration. DP_{wp} was approximated to that for MMA homopolymer found by using viscometry. ϕ_c was found from shrinkage measurements.

Equation 3.1 was modified and used in a later publication (Gordon and McMillan 1957) in the form :

$$B = R/(R+1)f_F^{\ 2} \ (DP_{wp}-1) \ (DP_{wc}-1) \ \ldots\ldots\ldots \quad (3.2)$$

where the new symbols, B and R, refer respectively to the critical conversion at gelation of all unsaturation, and to the initial molar feed ratio of fumarate compared with total unsaturation, i.e.

$$R = [F_o]/([F_o]+[M_0]) \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.3)$$

Results for both MMA and styrenated polyesters were given, and for a styrenated example the conversion at gelation was only about 2.5% of the total, assuming $f_F = 0.50$.

An interesting point emerging from the first of these two papers was that, for the MMA system under study at least, the time of gelation (t_g) was independent of the initiator concentration for isothermal cures. This was adduced as evidence for the chain reaction nature of the process. Sedov (1966) assumed that the gel time t_g was closely similar to the induction period, (t_i) when he considered the relationship between gel time and initiator concentration. He derived, and found experimentally, that for benzoyl peroxide - tertiary amine systems

$$t_g = K' / [I]\ [A] \quad \text{..........................} \qquad (3.4)$$

Smith and Bennett (1959) obtained a relationship

$$a' \, (t_g)^{n'} = [A] \, / \, [I] \quad \text{.....................} \qquad (3.5)$$

In some writings it is not clear what gel time is being considered. In particular it is not certain that all gel tests are carried out under strictly isothermal conditions.

Gelation can be delayed to quite high conversions by copolymerizing in solution. Burnett, Hay and Smith (1964) reacted polyethylene fumarate (PEF) with styrene in dilute dioxan solution, delaying gelation until the reaction was more than half complete. They were then able to measure the partial conversion molecular weight, M_n^*, which is given by

$$M_n^* = dW / dN = \frac{\overline{M_n}^{\,2}}{\overline{M_n} - W \left(\frac{d\overline{M_n}}{dW} \right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.6)$$

It is important to note that solution polymerization does not follow the same course as bulk polymerization. The extent of cyclization increases markedly with dilution (Burnett, Pearson and Smith, 1966). As a result, the reaction is fundamentally changed by this technique.

3d The post-gelation stages

Attention has already been drawn to the Trommsdorf effect. Gordon and McMillan (1957) found that the acceleration in overall rate set in more or less immediately at gelation when MMA was used as a co-monomer, but much later for systems of short DP_{wp}, such as those involving styrene or triallyl cyanurate. More recently, Judd (1965) found a change in rate at the gel point for styrene-based polyesters where the overall rate was low, but where the rate was not low no change was observed.

Funke, Knodler and Feinauer (1961) showed that the copolymer composition equation is applicable to polyesters in the post-gelation stage. They calculated the theoretical gross composition of the copolymer, and found reasonable agreement with the experimental results. Some additional aspects of the post-gelation stage will be considered in chapter 7.

3e Degradative hydrolysis of Polyester Networks

The three-dimensional network polymer composed of condensation and polyaddition chains can be degraded quantitatively by splitting the condensation chains with alkali in a high - boiling solvent. The reaction is shown in Fig.3. (Hamann, Funke and Gilch, 1959; Funke and Hamann, 1962.)

The copolymer of styrene and fumaric acid obtained can be separated, but it is not satisfactory to titrate the polymeric acid groups because of their marked tendency to undergo association. The ratio of styrene to fumaric acid can be determined from the oxygen content by elemental micro analysis, and the total yield gives the extent of reaction.

Gnauck and Fijolka (1967) varied this technique by hydrolysing a maleic anhydride/hexane diol polyester and liberating quantitatively the non-crosslinked polyester acid for direct titration in the solution.

Alekseyeva and Spasskii (1960) hydrolysed some polyesters with sulphuric acid, determined the free fumaric acid with Ioffe's reagent, and the styrene by microanalysis, as in Funke's case. A later paper (Alekseyeva, Semerneva and Spasskii, 1963) reported that hydrolysis of polyesters by concentrated sulphuric acid, alcoholic potassium hydroxide and cold aqueous potassium hydroxide all gave incomplete hydrolysis. On the other hand, hydrolysis with <u>hot</u> aqueous alkali gave the product with the expected composition and yield, corresponding to complete hydrolysis.

3f The formation of homopolymer

The last authors mentioned found difficulty in obtaining the desired degradation product. It had already been stated, in their previous paper, that the ratio of styrene to fumaric acid units in the polyaddition chains was in one case 1 to 1.7, which meant that fumaric units reacted together with no styrene bridge at all, even though styrene was available. This was in contradiction to the conclusion of Hamann and Funke, who found that the ratio was always much less than 1 to 1, using data on completely polymerized systems. Spasskii claimed that the ratio of styrene to fumarate increased steadily as the reaction proceeded, and that because his samples were taken from an earlier stage of reaction the product was rich in fumarate.

The reactivity ratios suggest a strong alternating tendency in the copolymerization, but Hayes, Read and Vaughan (1957) claimed to have isolated polystyrene from a cured polyester resin. On the other hand, Goto and Suzuki (1955) and Hamann, Funke and Gilch (1959) found none, even at very high styrene ratios. The opacity observed in some resins was attributed by Katz and Tobolsky (1964) to actual polystyrene homopolymer, and not simply to long sequences of styrene units in a genuine copolymer, as suggested by Funke and Hamann (1962). It is interesting to note that, when they examined the products from the solution copolymerization of PEF with styrene in dioxan, Burnett, Hay and Smith (1964) did not find either any homopolymer or even any particularly enriched copolymer.

Inevitably, some aspects of polyester chemistry will be met again in chapter 7, when chemical techniques for assessing cure are considered. The reader is referred to the text-books by Boenig (1964) and by Parkyn (1967) and to the literature cited in this present chapter for further details.

4. Simple tests and semi-empirical process Control Devices.

4a <u>The requirements of a test method</u>

Whereas in laboratory trials, simplicity of operation can be sacrificed, in real technological practice it may be paramount. The methods for deciding when a moulding has reached the required stage of crosslinking must be applicable in a wide variety of circumstances, and should be capable of giving reliable results in the hands of unskilled personnel.

In this chapter, methods are discussed which have either already been applied to thermosetting resins, or have been suggested. Their suitability for polyester resins in particular is considered. Brief reviews of this subject are relatively frequent in the literature, as would be expected for a matter of considerable commercial interest. (Parkyn, 1955; Barr, 1956; Tomkins, 1958.) It is not therefore suggested that this account is comprehensive, but an attempt has been made to select for discussion techniques which are representative.

4b Hardness

This is probably the simplest technique used, in practice (but not in its underlying theory). Different kinds of instrument exist, which measure different properties. Some hardness tests, particularly in the surface coating industry, rely on measuring the resistance of a resin to scratching, while the majority employ indentors of various shapes. Indentors measure the modulus of the material. Several commercial instruments have been devised for indentation tests. In all cases, the main criticisms made of such tests are the same; that there is not sufficient change in the hardness of resins during cure (Tomkins, 1958), and that there is very great variation in the readings obtained on a given sample, particularly when glass or other reinforcement is present. Robinson (1962) showed that, using a Barcol GY ZJ - 934-1 meter, cured castings registered between 30 and 50 arbitrary units, but that the presence of glass increased the scatter. For a single typical casting specimen, 100 readings ranged between 35 and 45.

An aircraft air duct was moulded from glass-reinforced resin. Pressure was applied to the mounting flange, but not to the walls. As a result, there was about 60 to 70% glass in the flange, but only about 35%

in the walls. The flange portions had a mean hardness of 56, and the walls about 30.

Tomkins (1958) described the early development of hot needle indentors. McSheehy (1966) used the hot needle type of indentor as an inspection tool to check the completeness of cure of encapsulating resins. He points out that no one level of hardness can be said to indicate completion, since some resins have much lower terminal hardness values than others. Learmonth, Tomlinson and Czerski (1968) compared the utility of Barcol and hot needle indentors and concluded that, while having the advantage of being portable, the Barcol instrument was less sensitive, and two or three models were needed to cover the whole range of values met in the curing reaction studied.

It has been found that the precision of Barcol readings depends on human factors, varying from laboratory to laboratory quite considerably (Scott Bader Report, 1959). This report concluded that the change in hardness over a period of about sixteen months was about the same as that obtained from three hours' postcure at 80°C. Styrene evaporation can contribute to this increase by decreasing the plasticization of the polymer. Cywinski (1960) also thinks that the Barcol and Rockwell indentors are insufficiently sensitive, and describes a number of other hardness tests. These include a pencil test. In this test the resistance of the casting or laminate to pencils of a range of hardness is observed. Using a modification of this, which concerns solvent resistance rather than hardness, the immersion time needed for a sample to be scratched by a particular pencil is measured.

4c Other simple tests

In their first report on the assessment of cure of resins, the Ministry of Aviation (1961) described several tests which had been tried. The majority did not detect which specimens were slightly undercured. Examples of these were :

(i) the extent of staining by boiling in a dye; a 1% solution in methanol of 1:4 diamino anthraquinone was most promising for spot tests.

(ii) the rate of leaching of a dye from the resin onto filter paper (the dye was phenolphthalein; the filter paper was soaked in alkali)

(iii) the extent of fluorescence under U.V. light

(iv) cross-breaking strength and Young's Modulus in flexure

(v) ball rebound : the measurement of the height of rebound of a steel ball from a laminate surface.
Other investigations were more promising. Specimens boiled in water for two hours showed a loss of weight after drying to constant weight, due to the leaching out of resin by water. This loss of weight could be very approximately related to the extent of cure, but the time required for heating to constant weight was quite considerable.

4d Solvent extraction

Another of the more promising investigations concerned the extraction of soluble material from the crosslinked network by a suitable solvent. Acetone extraction was therefore examined in a second Ministry of Aviation Report (1965) more fully. The first problem in such a procedure is to obtain finely powdered samples for extraction, without mechanically heating the resin. Further cure can also take place during heating in a solvent. Cellulose extraction thimbles were found to be unsatisfactory. Eventually a technique was evolved which gave improved results compared with hardness tests. Even then, solvent extraction did not differentiate between small differences in cure.

Judd (1966) found that acetone extraction gave better results than any others he had tried, but did not find any ready agreement between acetone extraction, hardness and resistivity measurements.

4e Water absorption

Tests to determine the weight change of resin samples immersed in water are affected by the soaking time. The filler or reinforcement also has a big effect; Wohnsiedler and co-workers (1956) found that unfilled M/F resins had water absorption values which behaved asymptotically with cure time, but filled ones went through an optimum value.

Romanenkov and Machavariani (1965) state that the water absorption values of GRPs does not level out for several years in some cases. Considerable scatter results if only 24 hours is allowed. Penetration occurs through microscopic pores, cracks, capilliaries and cavities. Glass fibres are surrounded with air cavities and occlusions, so water passes more quickly along the fibre direction than perpendicular to it.

The absorption process has been studied by optical microscopy, scanning electron microscopy and electron probe X-ray microanalysis. (Ashbee, Frank and co-workers, 1967). These authors say that immersion is followed by water uptake, hydrolysis, swelling, increased molecular mobility, further polymerization and consequent shrinkage. It is difficult to see how further polymerization could occur in such circumstances. Many cracks, totally enclosed within the resin, were observed and attributed to osmotic pressure at included inorganic impurity sites.

Leitheiser and Dalluge (1962) observed the changes in flexural strength at elevated temperatures after soaking specimens in water. Marked dependence on the curing conditions was found, but this was not elaborated.

Steel (1967) suspended cast and laminated film in water at various temperatures, and measured the time taken for cracks to appear in the films. This was found to be related to the cure time.

4f Mechanical tests

Since both mechanical properties and heat resistance are of vital importance in the service life of thermosetting resins, considerable work has been done to measure the heat distortion temperatures and cross-breaking strength of resins at various stages of cure. Morgan and Vale (1959) measured the impact strength, cross-breaking strength and tensile strength of melamine resins during cure. The behaviour of different resins appears to vary considerably. Cross-breaking strength has been found to be very unreliable as an indication of the extent of crosslinking of polyester resins. Wohnsiedler and co-workers (1956) found that Young's modulus in flexure did not change at all in the range of cure studied.

The extent of crosslinking of a polyester resin can be changed by curing for different times or by altering the ratio of unsaturated to saturated acid. This was done by Bockstahler and co-workers (1954) who measured the increase in the heat distortion temperature of polyester resins as the available number of crosslinking sites was increased by incorporating more fumaric acid.

The same criticism may be made of the methods outlined above as was made of the use of hardness as a test for degree of cure. That is, such methods are not sufficiently sensitive to small changes in cure. They are also dependent on adherence to somewhat arbitrary test conditions, since in most cases absolute physical properties are not measured. On the other hand, they are simple and often rapid. The techniques described below measure physical properties of resins during cure, and in some cases are non-destructive. Those examples which can be, or have been, adapted to direct use in production inspection tests will be indicated.

5. The measurement of Physical Properties.

5a Specific gravity and refractive index

A typical polyester casting resin may increase its specific gravity from about 1.13 to 1.21 during cure. Turanov and Sokolov (1965) followed the hardening of both filled and unfilled unsaturated polyesters by calorimetry and by dilatometry. It was found that the two methods did not agree in their indication of the extent of reaction. The calorimetric method implied that reaction had ceased, while dilatometric changes were still observable. Spasskii, Tarasov and Tokarev (1959) used the law of additivity of specific volumes to calculate the percentage of reacted double bonds. They also carried out the same calculation by the law of additivity of specific refractions. These methods agreed. It should be noted that, like the majority of such studies on polyester resins, this work was confined to an examination of cured samples, though the extent of reaction varied. No attempt was made to monitor the whole curing process.

This was, however, achieved by Dannenberg (1959). This worker provided a method of following the entire polymerization of epoxy resins, using only an Abbe refractometer. An almost perfectly isothermal reaction could be carried out between the prisms of the refractometer.

Protection of the prisms was achieved by using suitable plastic films. The total increase in refractive index was much the same for a given group of catalysts, but the increase observed up to the gel point varied considerably. This method appears to have the advantages of simplicity and accuracy, where it is desired to compare rates of reaction with new catalyst systems or to study the effect of additives. Procedures for process control testing were given.

An ordinary viscometer is a more limited tool, since it is not applicable beyond gelation, but Gordon and Grieveson (1955) developed a viscodilatometer which could measure simultaneously both free flow and flow through a plug. These measurements gave the viscosity and shrinkage before gelation. More recently, the post-gelation part of polymerization reactions has been investigated by observing electromagnetically induced vibrations of a minute nickel sphere embedded in the polymer (Gordon and Ward, 1968).

5b Electrical properties

One of the largest groups of measurements on curing resins is that made on dielectric properties. Recently, there has been increased interest in such methods. The nature of the electrical properties concerned is outlined by Parkman (1965), Sharbaugh (1965), Mikhailov and Sazhin (1960) and McCrum et al (1967). It is widely believed that conduction in high polymers is ionic and that the ions originate from catalyst residues, unpolymerized monomer, moisture and other impurities. Some experiments have shown that conductivity is a function of purity (e.g., Warner reported in 1948 that the conductivity of a polymer could be decreased by a decade by one purification). Electronic conduction is sometimes a contributing factor of importance (Parkman, 1965; Seanor, 1968), while protonic conduction has been postulated for polyamides (McCall and Anderson, 1960).

It may easily be seen that increased crosslinking results in less mobility for current carriers, and so the resistivity increases. The mobility of polar groups in an alternating field becomes similarly restricted. Decreased mobility brought about by increasing crystallization has the same effect on the resistivity (Amborski, 1962).

Kienle and Race observed the increase in resistance of a sample of an alkyd resin, during its polyesterification and subsequent cure, as long ago as 1934. During the first stage, the acid value, ester and saponification values were recorded, providing a correlation between electrical and chemical data. It was found that a plot of resistance against % polyesterification was linear up to quite high conversions, when there was some departure from this simple relationship.

After the war, Fineman and Puddington (1947) took this approach further, and made resistivity measurements on curing phenol-formaldehyde, resorcinol-formaldehyde and unsaturated polyester resins. In the latter case they used concentric copper tubes for electrodes; slight retardation would be observed in comparison with some other electrode materials. These observations were made alongside measurements of the changes in density, but the results were not discussed in any detail.

In the late nineteen-fifties and early sixties, a series of experiments on the monitoring of the cure of resins by resistivity techniques has been reported in successive papers by Warfield and a number of collaborators. This work arose out of the need for fully cured epoxide resins for encapsulation. In 1958 he described a continuous current monitoring device (CCMD), working on the principle of Ohm's law. Resins were polymerized in disposable cans, using either strip or concentric cylinder electrodes.

Warfield and Petree (1959) regarded the slope of a plot of log resistivity (ρ) against time as proportional to the rate of reaction. Using such plots, they found values for the energy of activation of the overall reaction (E_a). In apparent disagreement, Purdon and Morton (1962) observed that, for the bulk polymerization of styrene, log resistivity was not linear with respect to time, but that the resistivity itself was. Using ρ_o = the resistivity of the monomer, (i.e. at time zero), they found that the percentage conversion C was given by

$$C = 5.48 \, (\rho - \rho_o) / \rho_o \qquad \text{..........} \qquad (5.1)$$

This relationship held until a certain critical conversion C_c was reached. Then a sharp kink was observed. The authors interpreted C_c as the point of maximum packing in the molecules. After passing this point, ions would have to drain through, rather than pass between, molecules.

Using a "hopping" model, in which ions are considered to jump from one site to another through the material, Fava and Horsfield (1968) supplied a theoretical justification for the empirical conclusion of Warfield and

Petree that the rate of reaction is proportional to the log of the resistivity. They used an equation attributed to Stevels (1948)

$$\rho = \frac{6kT \quad e^{Eh/kT}}{ne^2 d^2 bf'} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.2)$$

where d is the distance between hopping sites, f' is a constant proportional to the vibration frequency of an ion, b is a constant proportional to the number of sites around an ion, e is the charge on an ion, E_h is the potential barrier against the hopping process, and k is Boltzmann's constant (n is the density of the ions in the medium).

From (5.2) they derived

$$\ln \left(\frac{d \ln \rho}{dt} \right) = \text{constant} - E_a/RT \quad \ldots\ldots\ldots\ldots \quad (5.3)$$

which is the Warfield - Petree expression for determining E_a.

A CCMD apparatus has been used by Judd (1964) to study the early stages of cure of polyester resins. In comparison with the quite small changes he found in Barcol and water absorption values, the changes in resistivity were very great. The cell used in this work, and elsewhere, was of the parallel plate type. Polytetrafluoroethylene plates were used, and metal foil electrodes attached to them by pressure-sensitive adhesive. The advantages claimed for this design of cell are considerable. Delmonte (1959) used a similar shape, but with glass plates.

More recently, Judd (1966) found slightly different results using continuous and intermittent voltages. The general trend was the same, but the magnitude of the values differed a little. A.C. resistivity was employed by McGowan and Mathes (1962) to produce a simple production control test, using removable pinhead electrodes, which could detect undercure, improper mixing, temperature variation or the presence of extraneous material.

Olyphant commented (1966) that a.c. conductivity (σ) could not be expected to behave in the same way as d.c. values since the d.c. conductivity would decline more or less monotonously, but a.c. would not. The reason lies in the relationship between the a.c. conductivity and the electrical loss tangent tan δ : For a frequency f and dielectric constant ϵ',

$$\sigma = \epsilon' f \alpha \tan \delta \ldots\ldots\ldots\ldots\ldots\ldots \qquad (5.4)$$

In most cases, tan δ goes through a maximum at some stage. As a result, σ will be affected by this and will not necessarily decline as expected.

Olyphant goes on to discuss resistivity, dielectric constant and loss tangent as cure parameters. The changes in these properties during cure may be understood, to some extent, as the "mirror-image" of the changes caused by temperature changes in fully cured resins. The increase in molecular freedom due to a rise in temperature in a cured resin is analogous to the increase in freedom which would be observed if the crosslinking process could be gradually reversed, under isothermal conditions.

Some investigations on the electrical properties of cured resins are relevant here, because such investigations can determine whether cure is complete. Warfield (1959) found that when a resin was completely cured, a plot of log ρ against temperature was reproducible. If cure were incomplete, repetition of the plot gave a line of increased slope, shifted slightly upwards. If the first run had caused some degradation, the reverse occurred. From the slope of these lines, values of the energy of activation for the electrical conduction process (E_c) were obtained. Warfield and Petree (1961^1) classified polymers according to their E_c values. E_c was assumed to increase with the degree of crosslinking. Exceptions to the classification were recognized. It has been found that the value of E_c can be altered drastically by slight structural modifications; Amborski (1962) lowered E_c for polyethylene terephthalate from 79 to 11 kcals/mole by replacing a quarter of the terephthalic acid by sebacic acid, thus reducing crystallization. In another paper, Warfield and Petree (1961^2)discuss the possibility that rapidly polymerized specimens might contain "micelles", or aggregates, of highly crosslinked material in a matrix of more lightly crosslinked resin. Such micelle formation might raise E_c. Erath and Spurr furnished evidence (1959) from electron microscopy that such micelles exist, and Funke (1967) suggests that crosslinking in polyesters is by no means uniform. Steele has reported on the effects of rate and bulk of polymerization on E_c (1963). This term cannot be used as a reliable indication of the average state of crosslinking, even if it were desirable to heat specimens to the temperatures necessary (150°C).

The great majority of these experiments have been carried out on epoxide polymers. Warfield measured the T_g of these and other polymers by the observation of changes in slope of the plots of log ρ against T. Pava and Horsfield (1968) repeated these experiments, however, and obtained curves rather than lines, with no clear evidence of a sharp T_g. They suggested that, instead of using log ρ as an indication of cure, E_h might be better employed, obtained from

$$E_h = kT \ln \rho / \rho_o \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.5)$$

They also discuss the possible effects of polarization currents, which decay slowly as a space charge gradually forms at the electrodes. If such a phenomenon were present, the true conductivity would be given by the instantaneous reading at $t=0$. On the other hand, if displacement currents due to dipole orientation occurred, the true reading would be obtained by extrapolation to $t=\infty$. The latter was thought to be likely. Rather less has been reported recently on permittivity and loss tangent determination. Delmonte (1959) considered that these properties were much more informative than was resistivity. He found that ϵ' fell suddenly after a slight initial inflexion, and then reached a level value, which was the same for all resins. Tan δ reached a minimum at the onset of gelation, and then rose to a peak which coincided with the maximum value of $- d\epsilon' / dt$. This interesting report contained an inconsistency, which has been noted by later writers. Delmonte associated the peak in tan δ with gelation, while at the same time noting that it shifted according to the frequency. Clearly a frequency-dependent peak cannot be identified with the viscosimetric gel point.

This was also realised by Haran, Gringras and Katz (1965). They were concerned with detecting the onset of gelation in epoxy resins, in order to extract inserts and leave cavities. Using a cell similar to that of

Delmonte, they found that the time taken to the minimum value of tan δ (t_M) and to the peak value (t_P) were both linear with respect to the logarithm of the frequency. (The minimum here is the pre-gelation minimum, not the terminal value, which is asymptotic and cannot be defined.) No particular connection between gel time and the peak in tan δ was found.

A patent was taken out by Holdsworth (1966) which described a device utilising dipole orientation in cure estimation. It was particularly intended for thermosetting coatings; by inducing an alternating current voltage and recording the decay of this voltage, both the degree of cure and the thickness of the coating could be found simultaneously. Such a device seems more immediately practicable than any based on resistivity measurement, but this too has been applied, if rather more tentatively, to realistic situations. Kinna and Warfield (1966) monitored the cure of large reinforced structures, by embedding three cells at various depths in filament-wound tubes, and recording resistivity during cure and the subsequent post-cure.

Phenolic resins, (novolaks cured with cyclic formals) were found to go on curing for several weeks when van Beek (1964) studied the reaction by measuring the a.c. properties of these materials. He suggested that part of the electrical losses must be due to the catalyst used. The same suggestion had been made, in the context of a different polymerization, many years earlier by Ehrlich and de Lollis (1953). They studied the dielectric properties of a copolymerizing mixture of styrene and acrylonitrile.

While some workers use null methods, others have employed field strengths of various sizes for resistivity measurements. It has been shown that very high field strengths can cause accelerations in the rate of the polymerization and can lower E_c (Warfield and Petree 1963). The relationship between E_s, the field strength, and ρ is discussed by Sazhin and Shurikhina (1966) on the basis of the equation, applicable to the glassy state :

$$\rho = a\, e^{-b E_s} \qquad \text{...............} \qquad (5.6$$

where a, b are constants.

It can be seen that, despite the complications in electrical measurements, several workers have thought this kind of approach a profitable one. It is likely that the application to technological practice will be developed in the future.

6. Dynamic Mechanical Measurements.

6a. Introduction to Dynamic Mechanical Testing

In the past thirty years, as plastics have become more widely used, the deficiencies of those test methods originally designed for metals have become more and more obvious. The unsatisfactory nature of impact testing is illustrated by Karas and Warburton (1961), who give a concise account of the theory and practice of dynamic mechanical tests. The mechanical properties of polymeric materials depend on the temperature and the rate of testing, and more information can be obtained from measurements of the response to a periodically varying force, over a temperature or frequency range, than from traditional flexural, tensile or impact data. This is also emphasized by Riddell and O'Toole (1968) in their article on the dynamic testing of glass-reinforced thermoplastics.

Text books by McCrum et al (1967), Nielsen (1962), Ferry (1961) and Kolsky (1963) provide useful information on dynamic testing, including its application to crosslinking.

We can classify the techniques commonly used in polymer studies according to their frequency range, and according to their mode of vibration. Examples of such techniques are given in the table below, together with examples of references.

TABLE 1

Frequency range	Vibrational Mode	Machine	Reference	
Low	Free, torsion	torsion pendulum	McCrum (1959) May and Weir (1962) Pierce and Holdsworth (1966)	PTFE epoxies paint films
Low	forced, non-resonance	Lazan-Maxwell rotating beam	Maxwell (1956)) Dekking (1961))	various polymers
Low	forced, non-resonant	Weissenberg rheogoniometer	Henson (1967) Learmonth and Lovett.	polyester resins
Audio	forced, resonant	vibrating reed	Doyle (1956)	glass reinforced polyesters
Ultra sonic	bulk-wave longitudinal	Apparatus for measuring velocity and attenuation of waves	Dietz and co-workers (1956)	M/F resins

Certain other machines will also be mentioned. Reference should be made to the papers cited for detailed descriptions of the instruments.

When a thermosetting resin is partially cured, it is still comparatively flexible. It shows a lower modulus and a higher damping capacity than is found in fully cured resins. Studies of the cure of these resins may be carried out, either by obtaining single isothermal readings at various cure times, or by "thermoprofiles". These are curves made by plotting modulus and damping against temperature. It is usual to cover a wide temperature range, frequently below 0°C. A schematic diagram illustrating thermoprofiles is given in Fig.4.

6b. Use of the torsional pendulum

It is not usually practicable, even if desirable, to obtain dynamic measurements over a wide and continuous range of frequencies. Several expensive machines are required, since each one has limited applicability.

If only one frequency is available, it is usually better that it should be a low one. The torsional pendulum operates in the range 0.2 to 10 c/s. A specimen (cylindrical, rectangular or tubular) is clamped vertically with one end held fixed and the other attached to an inertial bar or disc. By imparting a small twist to the bar or disc, the specimen is subjected to shear oscillations. These are gradually damped out by the internal friction in the sample. Precautions are taken to ensure that pure shear is involved, without tension or compression by the inertial system. Various methods are available to obtain a permanent record of the oscillations. (See Fig.5 for a typical decay trace from a direct trace-recorder.)

It may be shown (Nielsen, 1962) that the shear modulus G' is given by

$$G' = K\,I\,(4\pi^2 + \Delta^2_g) / P^2 \;\ldots\ldots \qquad (6.1)$$

where I is the moment of inertia of the entire oscillating system, and Δ_g is the logarithmic decrement, defined by

$$\Delta_g = \ln A_n / A_{n+1} = K \ln A_n / A_{n+k} \quad \ldots\ldots \qquad (6.2)$$

P is the period of an oscillation, A_n is the amplitude of oscillation of the nth vibration, and A_{n+k} is the amplitude of the (n+k)th swing, etc. So k is an integer, and K is an experimental constant depending on the specimen geometry. The shear modulus G' is strictly the dynamic storage modulus, as opposed to the loss modulus, which is related to the quantity of energy dissipated as heat rather than stored.

The complex modulus $G^* = G' + i\,G''$ ..... (6.3)

and the loss modulus G" is given by

$$G'' = G' \left(4\pi \; \Delta_g / 4\pi^2 + \Delta_g^2 \right) \quad \ldots\ldots \qquad (6.4)$$

This instrument has been used to study crosslinking, but the majority of torsional pendulum studies have been on thermoplastic materials. Reference has already been made to Drumm, Dodge and Nielsen (1956), who obtained modulus-temperature and damping-temperature thermoprofiles on cured novolaks. The transition temperature was indicated by a fall in G' and a peak in the value of the logarithmic decrement. The transition point rose with increase of catalyst level, cure temperature and cure time, and specimens cured with 10% hexamethylene tetramine did not show a transition temperature at all in the range of temperature available. This did not establish that maximum crosslinking had occurred.

In measurements with the torsion pendulum and similar dynamic instruments, specimen fabrication is crucial. McCrum (1967) prefers rectangular geometry, because it is convenient, but also because there is a larger surface for heat exchange with the surroundings for a given cross-sectional area, and a lower torsional rigidity. So long as resins are not to be cured isothermally before testing, such rectangular specimens can be readily cast in polytetrafluoroethylene moulds (Lowell, 1968). Reinhardt found that, when cast in heat-dissipating steel moulds, rectangular specimens underwent uneven shrinkage, giving concave sides and stress concentrations, (1965). He recommended circular cross-sections, for which equation 6.1 reduces to

$$G' = K' I L / P^2 r^4 \quad \ldots\ldots\ldots\ldots \quad (6.5)$$

for rods of length L and radius r, and small values of Δ_g. Hence the radius must be known accurately.

6c Coated and impregnated braids

Only the stages of cure during which the resins possess a modulus of the order of 10^8 dynes/sq.cm. upwards may be investigated by torsional pendulums. To overcome this, and enable the whole polymerization to be studied, some workers have employed braids. The specimen is replaced by an inert substrate (glass fibre, nylon, etc.) on which the curing resin is impregnated.

Lewis and Gillham (1962) suspended a 34cm. nylon braid from a torsion head assembly in a glass tube, and surrounded it with a thermostatted bath. An inertial mass was hung on the lower end of the braid and, after coating with resin, the vibrations were timed with a stop-watch. Evaporation of monomer was countered by keeping the braid in contact with catalysed monomer, and recoating just prior to gelation. The results were quoted as curves of relative rigidity modulus G against cure time. The polymer was an epoxy resin.

This principle was developed further (Lewis and Gillham, 1963). The volume fraction of nylon material in the braid (as opposed to voids), ϕ_B, and the volume fraction of void ϕ_V were determined. Then the true modulus of the resin, G', was calculated using the equation

$$G/G' = 1 + k_s\phi_B + k_v\phi_v \,/\, 1 - (s'_s\,\phi_B + s'_v\,\phi_v)^2 \quad \ldots (6.6)$$

the remaining terms being constants.

Braid techniques have the great advantage that they can be used continuously throughout cure. Unfortunately, evaporation remains a problem, and the calculation of real dynamic quantities from relative rigidity terms must be regarded as tentative. The idea has been extended to the machines operating in the audio-frequency range.

6d Other low and audio-frequency techniques

The Weissenberg rheogoniometer is a sophisticated viscometer employing a truncated cone and plate. It is capable of measuring both tangential and normal forces during oscillatory shear, using very low amplitudes indeed and low frequencies. Attempts have been made to study the early stages of cure of polyester resins by this means. Henson, Lovett and Learmonth (1967) followed the early stages, and Dominic (1967) and Yip (1968) extended the range covered. The shear modulus obtained at completion of cure was exceptionally low (10^6 dynes/sq. cm.) instead of 10^{10} dynes/sq. cm. as obtained by other means. Such discrepancies suggest that contact between the specimen and the platens is impaired when the glassy state is reached. This technique is still being evaluated.

The rotating beam apparatus uses a cylindrical rod specimen, held in a chuck and rotated while under load at its free end. The deflection as a result of the rotating motion and the deflecting weight combined give the values of the dynamic quantities (modulus and damping capacity). This device is capable of use in the range 5×10^{-4} to 160 c/s. and is useful for unusually high rates of shear.

Dekking (1961) found several practical difficulties and these in his opinion were sufficient to require the abandonment of the method. In particular, for samples with high tan δ values, the heat generation could be so great that a rise in temperature of 50°C. per second was caused. Other problems arose, connected with the alignment of the sample. It does not appear to be adaptable for the study of the cure of resins.

Probably the most widely used dynamic mechanical testing instrument is the vibrating reed. A short specimen in the form of a rectangular strip is vibrated electromagnetically, one end being fixed. The amplitude of oscillation is displayed on an oscilloscope, and the frequency tuned to give maximum amplitude. When it has been ascertained that the resonant frequency or a known harmonic has been obtained, Young's modulus is calculated from the expression:

$$E' = k' \, d \, L^4 \, w^{-2} \, f_r \ldots\ldots\ldots\ldots\ldots\ldots \qquad (6.7)$$

for a specimen of length L, thickness w, density d and fundamental resonance frequency f_r. k' is a constant. In order to determine the damping, the bandwidth technique illustrated in Fig.6 is used. After finding the frequencies f_1, f_2 at which the amplitude is $1 / \sqrt{2}$ of its maximum value, the logarithmic decrement is given by

$$\Delta_E = \pi E'' / E' = \pi \tan \delta = \pi (f_2 - f_1) / f_r \qquad (6.8)$$

Resonance methods suffer from the disadvantage that they are not usually strictly isochronous, as the frequency alters according to the nature of the specimen, and for fixed modulus and dimensions it cannot be controlled. Since the results obtained at varying frequencies are only approximately comparable, allowance has to be made for this in assessing their value. Fortunately, for many materials the variation in modulus with frequency is very small indeed over a wide frequency range.

During the latter stages of crosslinking, the damping factor falls progressively. The progress of the damping after full cure (in the region of thermal ageing) was studied by Doyle (1956) using triallyl cyanurate-based glass reinforced polyester laminates. He found that the damping rose again as ageing set in; the process was observed up to the start of delamination.

As in the case of the torsional pendulum, there is a disadvantage in that reed specimens cannot be made of liquid resins, and recourse must be made to using coated braids. The conversion equations have been worked out by several workers for this arrangement. Jenkins and Karre (1966) cured the epoxy resin Epon 828 in this way. The rate of crosslinking was also found by measuring the rate of disappearance of the epoxy infrared band at 915 cm^{-1}. Apparent energies of activation by these two methods agreed.

Lewis (1963) carried out a similar study using a glass fibre braid. He found that, in the course of the curing reaction, the damping displayed three peaks; a small one at gelation, a large one later, and finally a small one. There were also three peaks in the damping thermoprofile. The third one disappeared after the heating process necessary to obtain the thermoprofile, and it was found that this disappearance was associated with the total disappearance of residual epoxy groups. The catalyst system used affects the damping curves obtained from epoxy resins.

Imai (1967[1]) used a coated metal substrate to observe the cure of unsaturated polyester resins by the vibrating reed technique. He deliberately took no precautions to minimise the free evaporation of styrene monomer. Very marked delays in polymerization were found at low concentrations of initiator and accelerator.

A linear relationship was found between the logarithm of the dynamic storage modulus and the acetone-insoluble gel portion. The loss modulus also showed the same relationship. In order to obtain the true moduli from apparent values, the following equations were employed:

$$E' = \frac{2E'_s\left[\left(\frac{W_{s+f}}{W_s}\right)\left(\frac{f_{s+f}}{f_s}\right)^2 - 1\right]}{\left(1 + \frac{2h_{s+f}}{h_s}\right)^3 - 1} \quad \ldots\ldots\ldots \quad (6.9)$$

$$E'' = \frac{2E_s'\left[\left(\frac{W_{s+f}}{W_s}\right)\left(\frac{f_{s+f}}{f_s}\right)^2\left(\frac{f_2 - f_1}{f_{s+f}}\right) - \tan\delta_s\right]}{\left(1 + \frac{2h_{s+f}}{h_s}\right)^3 - 1} \qquad (6.10)$$

The dynamic storage modulus E' and the loss modulus E" of the polyester resin specimen are given here in terms of the weights w, thicknesses h, resonant frequencies f and loss angles δ of the materials. The subscript f applies to the film of resin, s to the steel substrate, and s+f to the coated specimen.

Imai found a single peak in the loss modulus, occurring when the storage modulus had reached less than half its maximum value. The loss modulus continued to decline after changes in the storage modulus had become imperceptible.

Several other applications of the vibrating reed to cure studies have been made. Almost without exception these have been on epoxide polymers. The number of dynamic studies of any kind on polyester resins is much smaller.

6e Ultrasonic vibrations

Several years ago, experiments were conducted to see whether the velocity and attenuation of ultrasonic waves changed greatly during the cure of thermosetting resins. It was concluded by McDonald, Robinson and Rahon (1948) that the change was not great enough. They used longitudinal waves at 150 kc/s and the greatest change observed was 20% increase in velocity, for a phenolic resin filled with wood-flour.

Shortly afterwards, Sofer and Hauser (1952) concluded from measurements of the bulk modulus at 2.3 Mc/s that this method was of interest. A rapid change in velocity occurred, as the attenuation went through a maximum. Filled melamine resins showed a dip in the attenuation after its maximum, and before asymptotic levelling out (Dietz and co-workers 1956). The possibility of continuous monitoring of the velocity of ultrasonic waves during the moulding process, without removing the resin from its mould, was stressed by Sofer, Dietz and Hauser (1953).

6f Ball Rebound Methods

Experimentally, this technique is quite different from the others, although the same properties are eventually obtained. A thin slab of plastic is placed on a massive anvil, which contains a heating element, and the assembly placed in a glass chamber which can be evacuated or filled with inert gas. Steel balls are dropped onto the specimen, and the rebound height measured against a scale. The time of contact between ball and plastic can be measured electronically. As the ball strikes the plastic, the latter vibrates with a frequency f given approximately by

$$f = 1/\ 2t_c \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.11)$$

where t_c is the contact time in seconds. For cured polyesters, the frequency is about 10^4 c/s. The % energy absorbed by the specimen, E_e, is given by

$$E_e = 100\ (1 - h/h_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.12)$$

where h is the rebound height from a drop height h_o. The logarithmic decrement is given by

$$\Delta = \tfrac{1}{2}\,(1 - e^{*2}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.13)$$

e^* being the coefficient of restitution between ball and sample.

Several papers have described such instruments. Barrett and Gordon (1959) studied the cure of both styrenated and MMA polyester resins using density and ball rebound measurements. Gordon and Grieveson (1958) obtained E_e - T thermoprofiles for various resins, including styrene-based polyester glass laminates, during cure. The peaks of these curves moved along the temperature axis and broadened during cure. It was found that, unlike polyesters and epoxides, P/F resins do not have an equilibrium temperature, but continue to cure ever faster as the temperature is raised, until pyrolysis begins. Gordon and McMillan (1957) describe the final stage of cure of a polyester resin in terms of the rebound properties. Plots of E_e against T were given for the final states of cure corresponding to different monomer feed ratios. It was found that the temperature at which E_e reached 50% varied over a range of 50°C, but that the average value did approximate to the cure temperature, as expected. (Since $E_e = 50$ corresponds to relaxation times of the same order of magnitude as the contact time, this condition would be achieved near the glass transition temperature.)

The rise in T_g with the change in the molar feed ratio R was then expressed by a semi-empirical equation

$$T_{50}\,(R) = T_{50}\,(0) + aV - bW_f - c\,W_m \;\ldots\ldots\ldots \qquad (6.14)$$

where W_f, W_m are plasticization parameters associated with the presence of free unattached fumarate chains and the unreacted methacrylate monomer. $T_{(50)}$ (0) corresponds to R = 0, i.e., the value for polymethylmethacrylate. V is a measure of the concentration of crosslinks. Statistical expressions were derived for V and W_f.

Despite the abundance of publications on the dynamic properties of thermosetting resins, there are still very few describing the cure of polyester resins, and in particular no correlations between dynamic and chemical states of cure.

7: Chemical determinations of the degree of cure of polyester resins.

7a. Scope of the discussion

Whereas in the case of physical, electrical and dynamic mechanical measurements, work carried out on other materials is often relevant to polyester resins, this is less true of chemical studies. For the most part, the relevant literature is confined to that on polyesters themselves, except for some mention of techniques developed for epoxide polymers.

The extent of reaction of functional groups is recognized as a fundamental indication of the degree of cure. Other factors affect the properties, but these are usually considered under different headings. An example is the change in properties which may take place after the completion of reaction, as a result of further heat treatment. Residual co-monomer and residual unreacted fumarate sites are usually measured either by titrimetric techniques or by hydrolysis followed by elemental microanalysis. It has been found that the styrene continues to decrease by adding on to existing chains, after the propagation reactions of the macroradicals have been limited by diffusion control. Fumarate bonds are freed for reaction by heating into the softening region.

In this section titration, hydrolysis and instrumental methods for assessing styrene and fumarate groups in cured polyester resins will be considered.

7b Determination of residual styrene by titration

Alt (1962^2) describes a determination of residual styrene unsaturation, by extracting the powdered resin with solvent, and titrating the extract with Wij's solution. He also determined the residual peroxide initiator iodometrically. By weight loss experiments, it was found that appreciable unreacted styrene remained after storing for 56 days at room temperature.

A method for determining styrene in uncrosslinked polyesters, but applicable to the extract from cured ones, was given by Schumann and Kleeberg (1965), who reacted the solution in 2-ethoxy-ethanol with mercuric acetate, and then titrated it with methanolic hydrochloric acid.

7c Hydrolysis giving the polyaddition copolymer

This method of determining the extent of reaction has already been mentioned, in chapter 3, section c. While a few experiments may not present much labour, the use of such a technique for the study of several different states of cure and several systems is time consuming. The same may be said of the titrimetric techniques mentioned earlier.

7d Gas Chromatography

The use of gas chromatography to determine the styrene in an uncrosslinked polyester resin was outlined by Esposito and Swann (1965), and the principle later used in detecting unreacted styrene in crosslinked resins by Partridge and Partridge (1966).

Sections of laminates were extracted with three solvents (methylene chloride, acetone and water), and at various times the solutions were chromatographed. Styrene was estimated, and traces of cobalt and copper also determined separately. The water solution showed progressively less and less cobalt extracted as cure continued. The time necessary for equilibrium to be established between the swollen resin and methylene chloride solvent was seven days at room temperature.

7e Electron Spin Resonance (ESR)

The main radical reactions in the crosslinking of polyester resins are: those between initiator and activator, recombination of radicals, disproportionation, hydrogen transfer and propagation.

Demmler and Schlag (1967) found that, using ESR, they could detect a rapid rise in radical concentration at an early stage in the curing process. The level quickly became approximately constant, and it remained so until the radical concentration fell sharply in the later stages of post-cure. The end of reaction could thus be identified with the time when the concentration of radicals declined to a very low value. It is not possible to determine the extent of cure by this method, since the radical concentration does not change appreciably for the majority of the reaction, and many radicals remain "frozen" in the network without being in a position to react.

Two kinds of radicals were identified: the styryl, and one in which the radical electron was conjugated between several double bonds. The fumarate radical was not detected because of superimposition by other species.

No increase in radical concentration was observed, when the initiator alone was increased in concentration, but when the accelerator concentration [A] was increased, the radical concentration $[R]$ was found to be proportional to $[A]^{\frac{1}{2}}$. It was not possible to detect any radicals in a solution of a mixture of cobalt naphthenate and a hydroperoxide.

7f. Infrared Spectroscopy

The infrared spectrum of a polyester resin contains certain peaks due to the unsaturated groups. These gradually decline in intensity during cure, and other peaks remain unchanged. The main features of the spectrum have been described by Grisenthwaite (1959). The measurement of the unsaturated peaks may be made, using one of the unchanged peaks as an internal standard, by an absorbance ratio technique. The usual peak chosen as a standard is the carbonyl stretching band, at 1737 cm^{-1}. (See Fig.7)

Hamann, Funke and Gilch (1959) used the infrared spectrum to confirm the composition of a styrene-fumaric acid copolymer. Hayes, Read and Vaughan (1957) showed the difference in qualitative terms between the spectra of cured and uncured resins.

Alekseyeva, Semerneva and Spasskii (1963) reported that no change occurred in the spectrum except at 1654cm^{-1}. In particular, no change was observed at 975 cm^{-1}, despite the fact that the fumarate group was thought to absorb in this region. This evidence is directly contradicted by Burnett, Hay and Smith (1964), who measured conversion of their solution-polymerized polyesters by the optical density of the peaks at 977 cm^{-1} and 1640 cm^{-1}. This agreed with the conversion as measured by the increase in weight of the copolymer.

In an earlier paper, Alekseyeva and Spasskii (1960) examined the spectrum of a copolymer separated from the unreacted material. They measured the styrene reacted by the increase observed at 705 cm^{-1}, using the carbonyl band as an internal standard.

Imai (1967[2]) applied infrared spectroscopy to the examination of polyester coatings. He first determined the weight loss, due to styrene evaporation (which was considerable) then separated off unreacted material and made the crosslinked polymer into a potassium bromide disc. The reacted styrene was then determined using the combined styrene-polyester peak at 695 cm^{-1} and employing the 740 cm^{-1} peak as a standard. A base line was drawn parallel with the abscissa, at the point of the peak at 715 cm^{-1}.

Such a method does not accurately describe the normal curing reaction, because considerable styrene evaporated (up to 10% of the total weight of resin and styrene combined). A <u>decrease</u> in density during cure was observed. The main conclusion drawn was that styrene took a greater part in the later than the earlier stages of reaction.

It is noteworthy that the crosslinking of epoxide resins has been studied frequently by I.R., and often without any prior separations. This involves casting the resin between sodium chloride plates. Feltzin, Longenecker and Petzer (1965) used this method to study the effect of temperature and catalyst content on cure rates. No difference was observed between the temperatures recorded by a thermocouple actually in the resin and by one on the external surface of the plates. This is contrary to the conclusion of Jenkins and Karre (1966) that it is essential to have the thermocouple in the resin itself. Feazel and Verchot (1957) used potassium bromide plates made by the pressed disc technique, and cured the resin between them, in a clamp made from the receptacle shell of a coaxial cable connector.

Comparably simple experiments have not been reported for polyester resins, though Dannenberg, Forbes and Jones (1960) drew attention to the convenience of attenuated total reflectance spectroscopy (ATR) for assessing the cure of coatings.

7g Other Chemical Methods

Since considerable heat is evolved in the crosslinking of unsaturated polyester resins, differential thermal analysis (DTA) has been considered for measuring the extent of reaction. It has been used for the investigation of the cure of phenolic resins by White and Rust (1965); as the degree of cure increases, the area under the exotherm peak diminishes. The applicability to polyester resins had already been tested by Johnson, Hess and Miron (1962) using isophthalic acid as a reference standard. The DTA runs were virtually post-cures, in which the area of the differential temperature versus time curve corresponds to the amount of cure taking place. It involves heating the sample at a known rate. They found that the data obtained gave a smoother curve than did that from flexural strength and flexural modulus readings.

Little has been recorded about the use of nuclear magnetic resonance spectroscopy (NMR) to detect under-cure in polyester resins. Losche (1959) applied this technique to epoxide polymers. It was reported by Grad and Al'Shits (1967) that the second moments of the NMR lines for some polyester resins were unchanged after curing for ten days. Some differences between theoretical and experimental values were found.

Comparatively simple techniques continue to be used in preference to more sophisticated methods. Filson (1962) described a procedure for exposing a laminate surface to bromine and then determining the unreacted bromine by titration. He found that no unsaturation was left after 24 hours. This suggests that the method lacks sensitivity. The problem of the bromine not always penetrating the laminate to the same extent was realised. Most methods detect unsaturation after considerably longer than a day, unless the cure temperature is very high.

8: The present state of the technology of the cure of polyester resins.

8a Castings and laminates

Glass reinforced laminates are much more difficult than castings when an assessment of the state of cure is required. They are hetrogeneous, and their physical properties are less well understood. Voids and other defects are common. They are also more likely to be locally undercured than castings. Nevertheless, the problem with castings is also quite considerable. In thick sections the temperature reached is variable throughout the structure, and the extent of cure varies similarly. Doubts have been expressed about the ability of amine systems to cure completely a thin section at moderate temperatures (Parkyn, 1967). Reliable methods are required for the rapid evaluation of new catalyst systems, and for studying the effect of additives on cure. It is likely that techniques developed for castings may in some cases be adaptable to laminates, and to resins other than polyesters.

8b Correlations between chemical and other techniques

Attention has already been drawn to the fact that when a resin is cured and various properties are measured throughout cure, the changes in the properties do not always correspond with each other. One property may cease to change, while another capable of more sensitive measurement continues to indicate the continuation of reaction.

Most measurements on polyester resins have consisted of measurements of one or perhaps two properties. It is quite uncommon to find a series of properties monitored during cure, using the same resin and the same polymerizing conditions. The desirability of carrying out infrared or chemical observations alongside physical studies on the same resin has been stressed often (Slowinski and Claver, 1955; Warfield and Petree, 1958) but rarely carried out.

It is already known in rough qualitative terms what most of the changes in common physical properties are. Some uncertainty remains in the less accessible cases - particularly the nature of the changes in loss angle in the early and middle stages of cure. On the whole, however, it is in the correlation of one property with another that the value of the measurement programme envisaged would lie.

It is considered that a study of casting resins, where such correlations are practicable, might be very worthwhile, and might provide information useful in developing tests for assessing the cure of reinforced polyesters. It is also likely that such information would have some relevance to other thermosetting resins.

The essential features of a programme of correlative studies of this kind are:

(1) A resin should be used which is of known preparation and composition.

(2) Tests should, in most cases, give values of physical properties rather than test data dependent on arbitrary conditions.

(3) Conditions of polymerization should be the same in all tests. The initiator and accelerator should be at a constant level. The temperature should be fixed. The cure must be isothermal.

(4) The polymerizing system should be slow, to enable many tests to be carried out in a thorough and careful way without appreciable change in the cure state.

(5) The system should give a long "asymptotic" period, when properties approach (but do not actually reach) their terminal values.

8c Choice of methods for the present study

Instrumental methods of determining residual unsaturation would be more convenient than traditional hydrolytic procedures. While neither of these methods is likely to be very accurate, the progress and cessation of cure could be observed with less labour by infrared spectroscopy than either by the titration of styrene or by alkaline degradation of the network.

Dynamic mechanical tests are non-destructive, yet measure properties of immediate practical significance. They are particularly suited to the study of crosslinking. It would not be easy to adapt such methods to use on real mouldings, but this can be said of the majority of methods.

Electrical properties can be measured on a wide variety of sample shapes, and, as indicated earlier, can be used for process control purposes both before and after gelation. The change in magnitude of volume resistivity in particular is very great. Unfortunately, such methods are sensitive to the presence of the slightest traces of extraneous material, and also to temperature variation. Like dynamic mechanical methods, they are also affected by imperfections such as voids and microscopic cracks.

The work of Dannenberg on refractive index could readily be applied to unsaturated polyester resins. It is to be expected that such a property would be very sensitive to changes in unsaturation. As a simple method of studying cure rates accurately, it is hard to imagine a more suitable property.

It may be noted that, with one exception, all the above kinds of property are concerned with the response of materials to vibrations of various frequencies.

Certain other properties and tests suggest themselves, because they have a bearing on the service life of the product rather than because they indicate the level of cure reached. It is possible, by this approach, to discover what level of undercure is in fact a matter of practical concern, and (for instance) what eventual change in ultimate tensile strength might be expected from a casting containing a given percentage of residual styrene.

In addition, carrying out one of the usual cure tests such as an acetone extraction procedure, would show how far such a method distinguishes between resins of slightly differing mechanical properties.

The chief limitations in the choice of techniques from such a list are usually time and the availability of expensive apparatus. In the case of this work, a wide range of apparatus has been available, and the choice has therefore only been restricted by the available time. Even so, certain instruments which were available and were considered for use (such as DTA), were not eventually chosen because, at present, insufficient is known about the application of such techniques to this kind of problem.

It was decided to carry out a large number of tests under one set of conditions, rather than explore a few in great depth. The proposed investigations are summarised in the plan at the start of the following section.

SCHEMATIC ILLUSTRATION OF CROSSLINKED POLYESTER NETWORK. CONTINUOUS LINES REPRESENT POLYESTER BACKBONE CHAINS. DOTTED LINES REPRESENT STYRENE/FUMARATE POLYADDITION CHAINS.

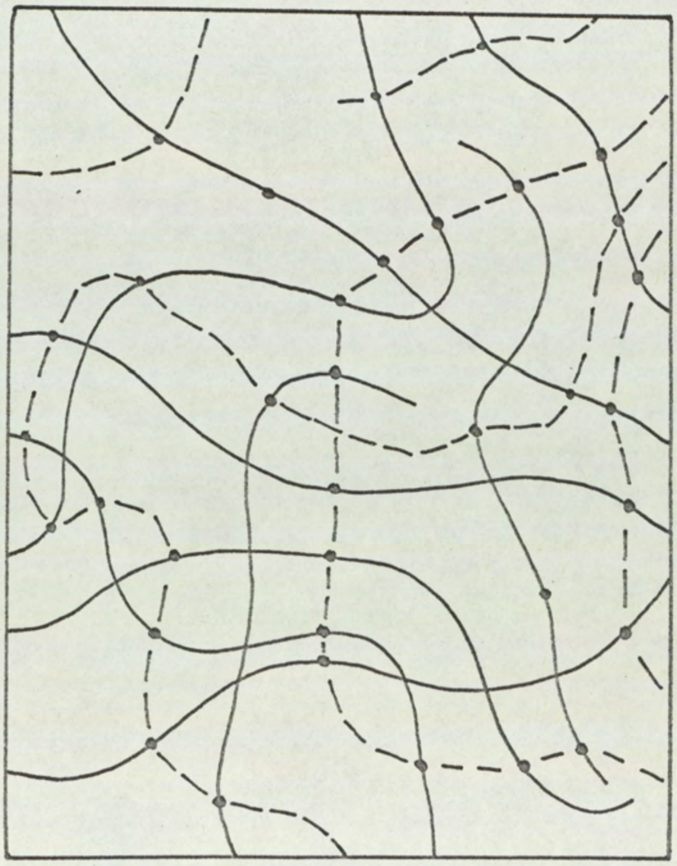


FIG. 1

FIG. 2 THE CROSSLINKING REACTION

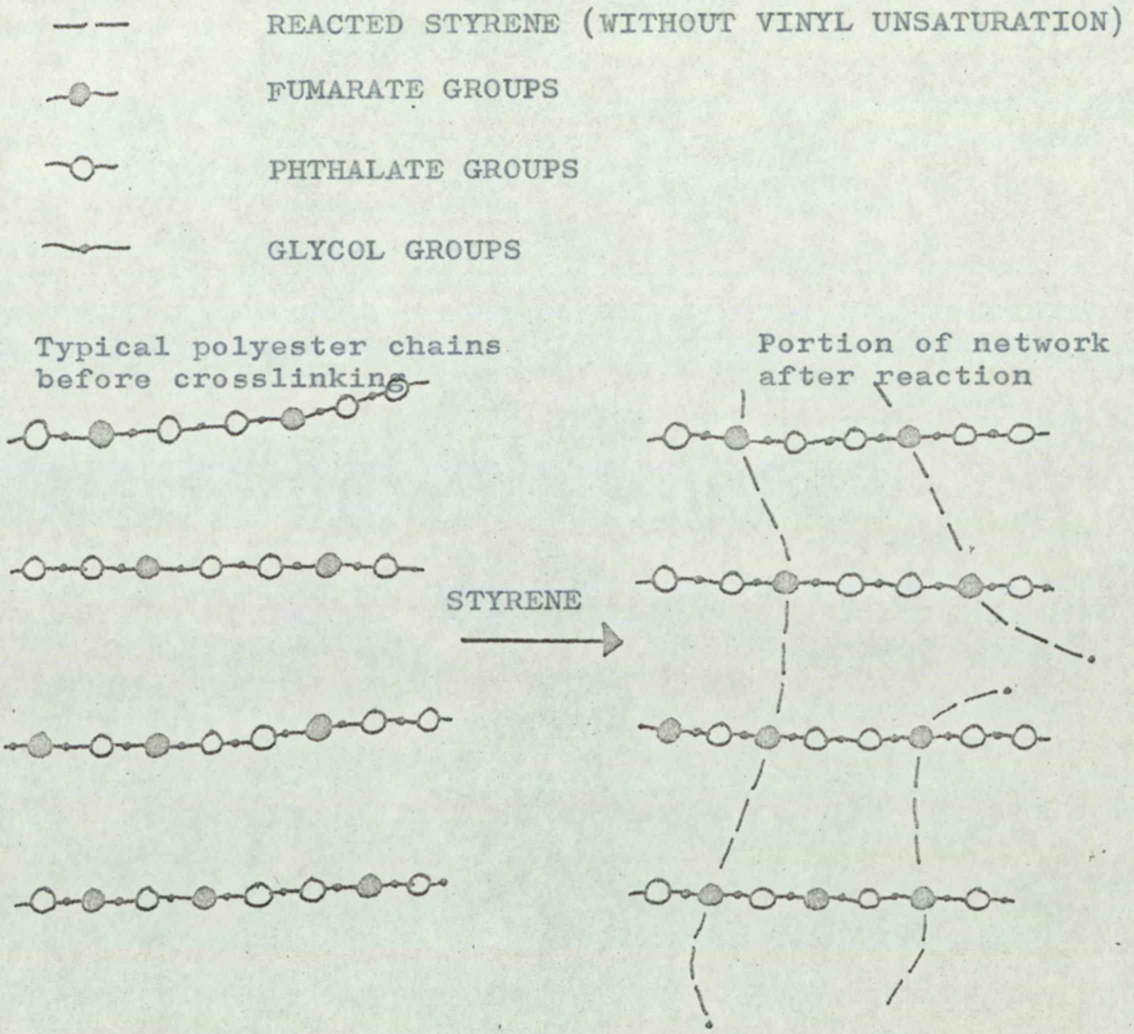
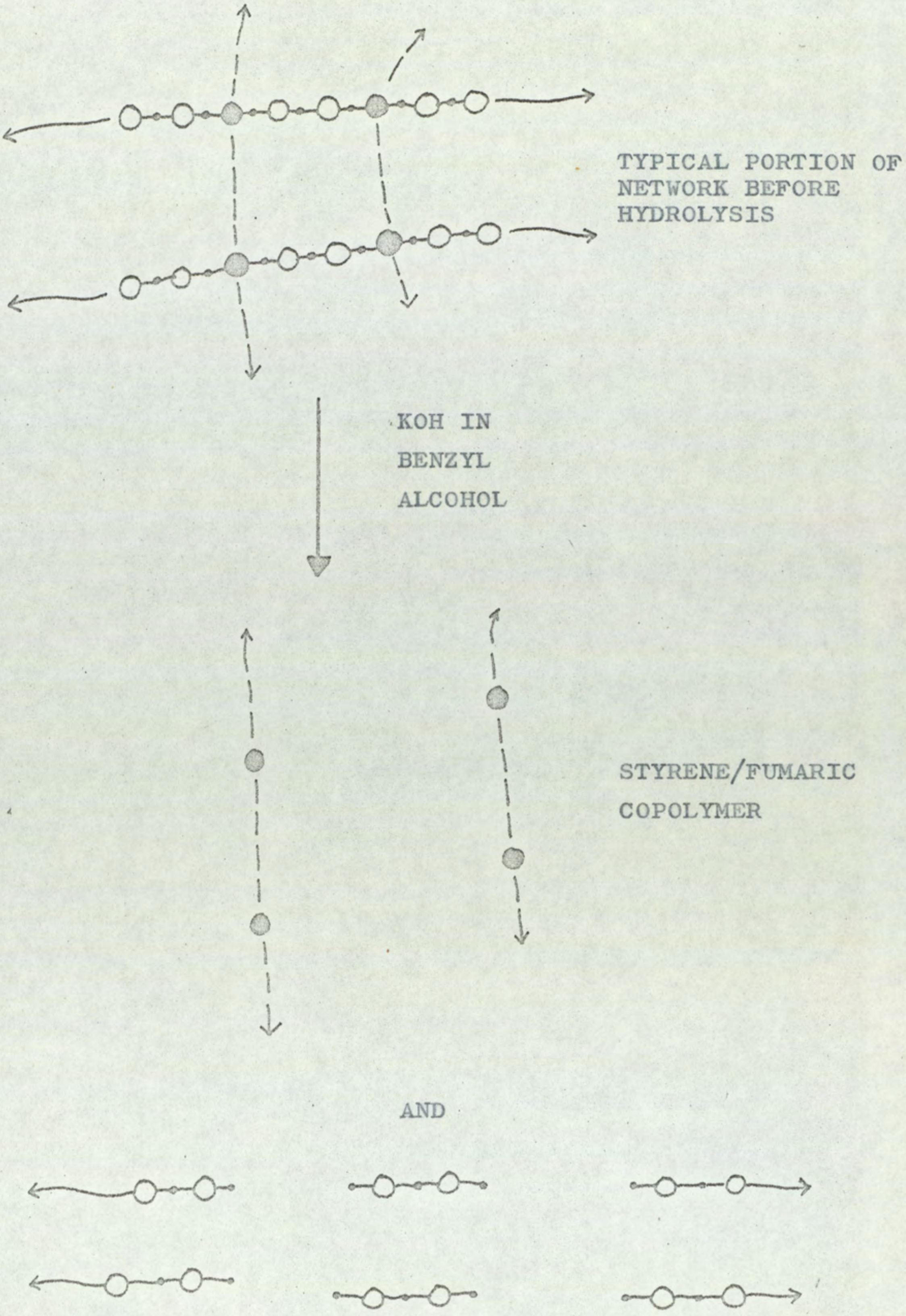


FIG. 3 DEGRADATIVE HYDROLYSIS OF POLYESTER NETWORK BY ALKALI

Letters have the same meaning as in Fig.2.



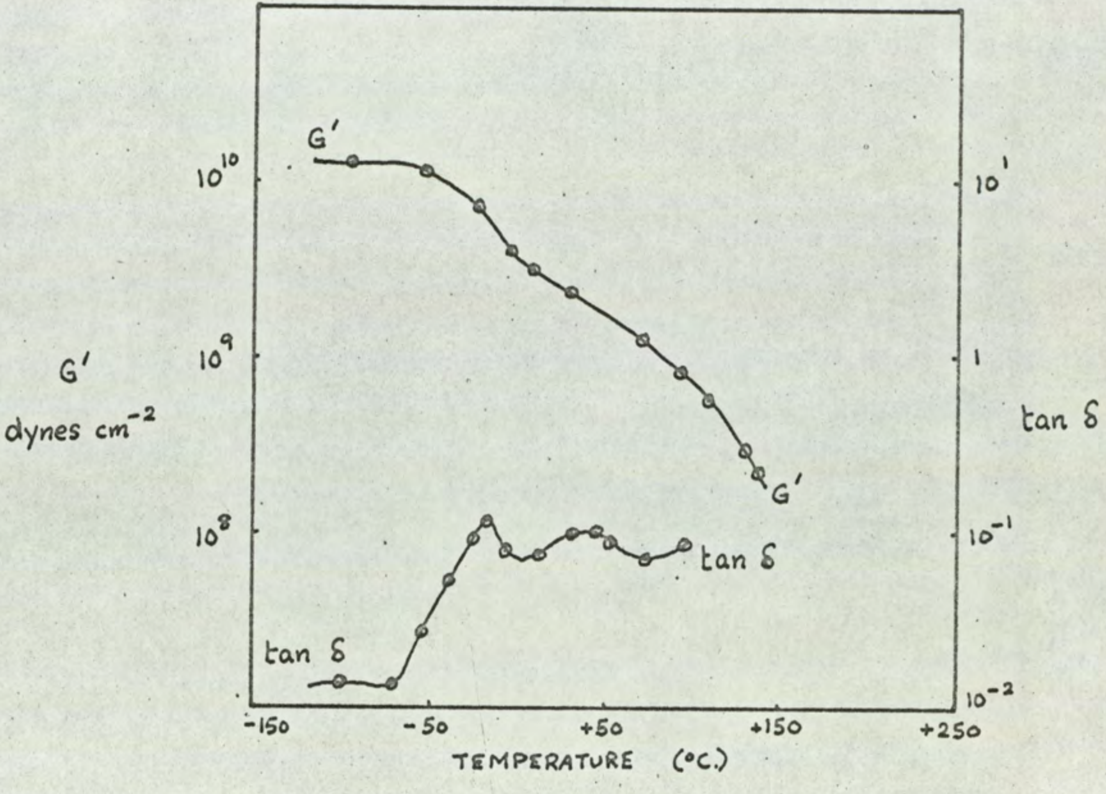
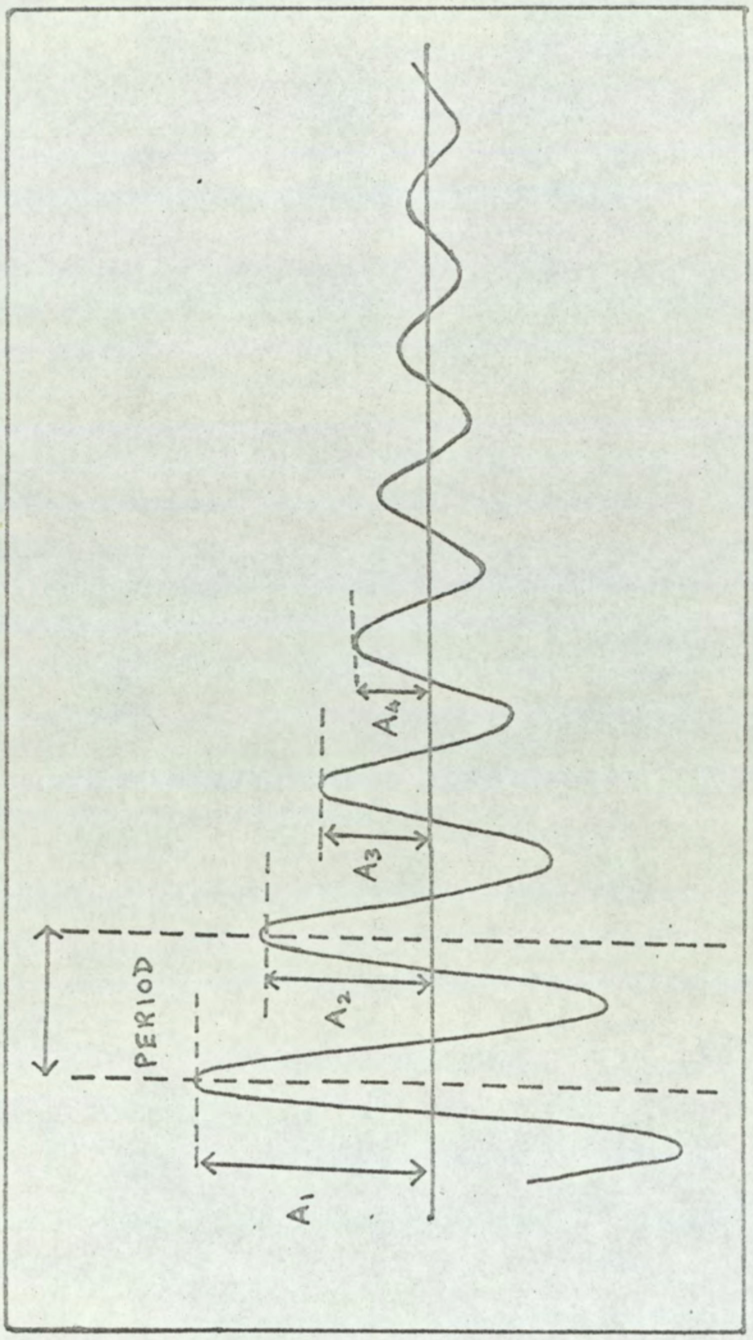


FIG. 4

TYPICAL THERMOPROFILE SHOWING CHANGES IN G' AND IN DAMPING AT THE TRANSITION REGION.

FIG. 5

TORSIONAL PENDULUM DECAY TRACE, SHOWING PERIOD P
(RECIPROCAL OF NATURAL FREQUENCY)
DAMPING $\Delta_g = \ln \frac{A_n}{A_{n+1}}$



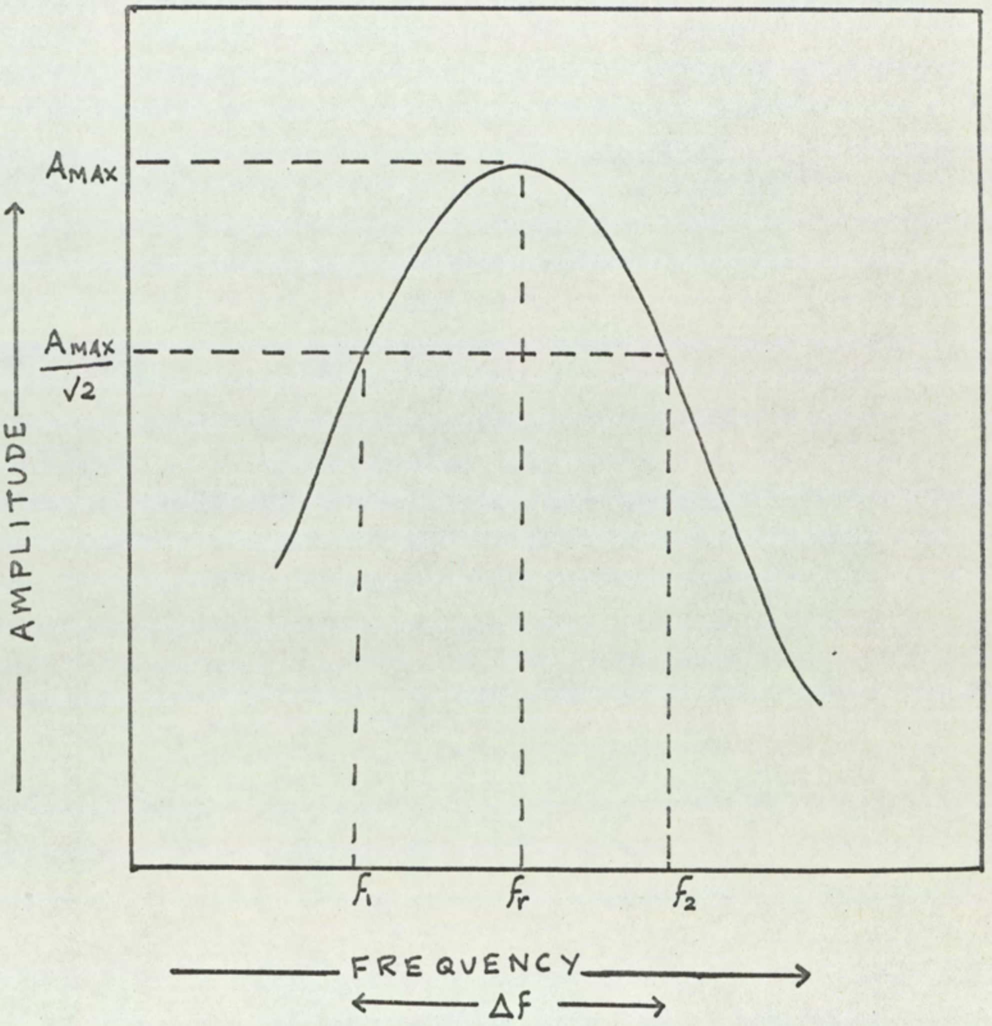


FIG. 6 THE BANDWIDTH METHOD FOR DETERMINING DAMPING CAPACITY. (NOT TO SCALE)

$$\Delta_E = \left(\frac{f_2 - f_1}{f_r} \right) . \pi$$

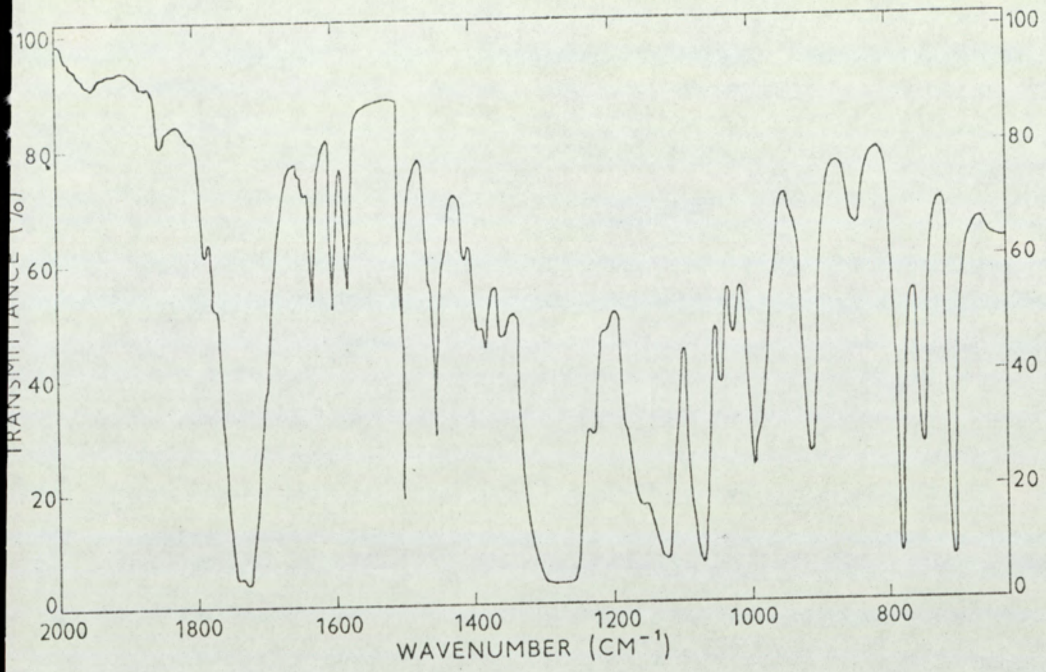


FIG. 7

INFRARED SPECTRUM OF BEETLE 4116
(BEFORE CURE)
RESIN CAST BETWEEN ROCK SALT PLATES.
0.025 mm. POLYTETRAFLUOROETHYLENE SPACER.

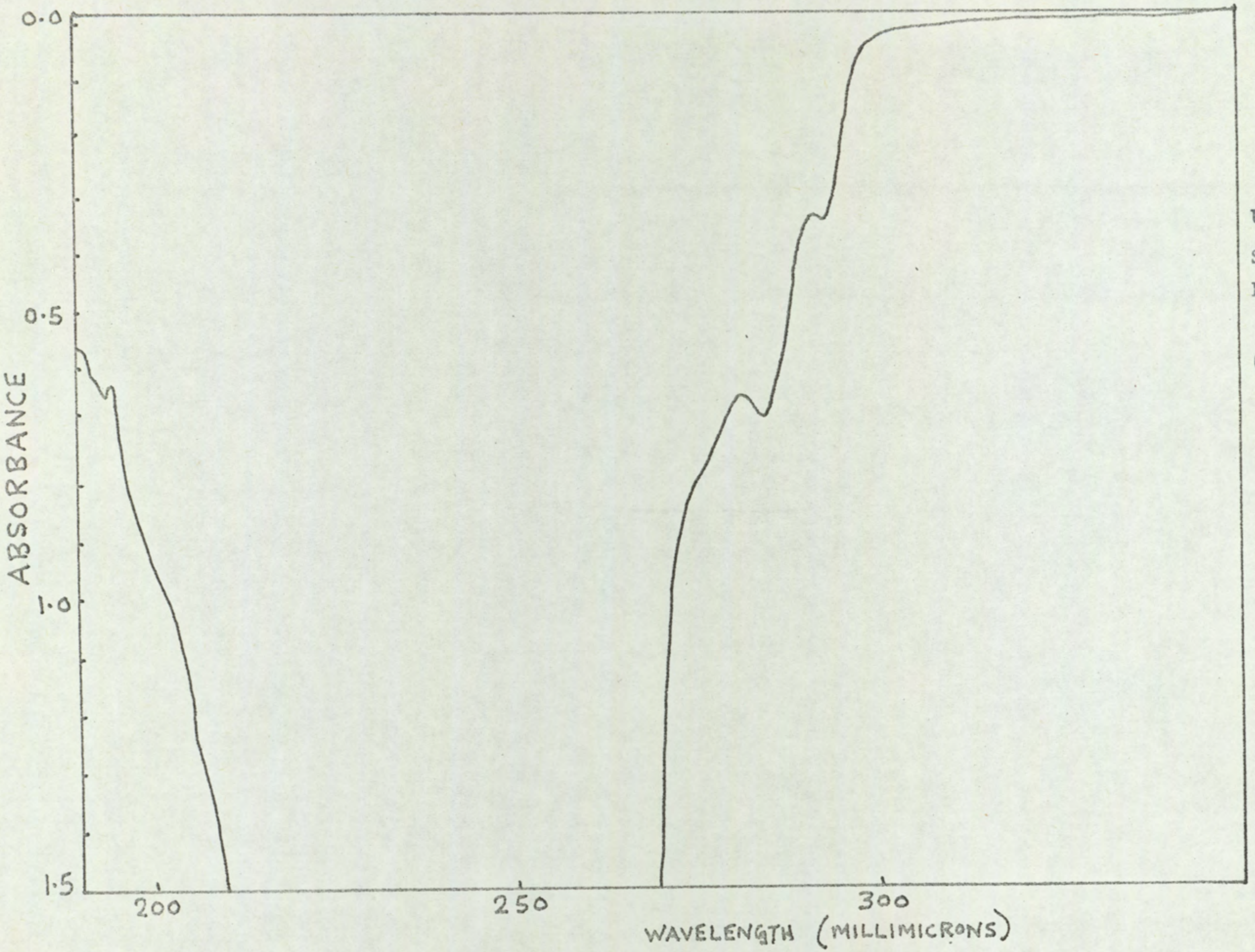


FIG. 8

ULTRAVIOLET
SPECTRUM OF
BEETLE 4116

(SOLUTION IN
CHLOROFORM)

PART TWO:

EXPERIMENTAL PROCEDURE AND RESULTS

9. Plan of experiments

The experimental work may be divided into two parts: (1) work carried out under constant standardised conditions, in order to obtain correlations between properties (2) experiments involving some departure from these conditions, e.g., a change of cure temperature. Unless otherwise stated, the experiments reported and discussed here belong to the first category.

Experiments carried out under standardised conditions

A commercial unsaturated polyester resin was cured, at 45°C., and various measurements were taken throughout the curing process. The properties measured were:

* d.c. volume resistivity
* a.c. dielectric constant and loss at 1 kc/s and 10 kc/s
* shear modulus and damping factor at 1 c/s
* Young's modulus, and the corresponding damping term, at audio frequencies.
* residual unsaturation, by infrared spectroscopy
* refractive index
* water absorption and chemical resistance by 7-day immersion

* tensile strength

* cross-breaking strength

* % volatile content

* % extractable matter

Additional experiments

* In one case, a different resin was used.

* In order to obtain activation energies, the cure temperature was varied.

* A second initiating system was used for comparison with the first. The accelerator concentration was occasionally trebled.

* The concentration of styrene was varied.

* The effect of cure temperature on the degree of cure was examined.

* The electrical properties of the fully cured resin were examined as a function of temperature.

All departures from "standard conditions" will be indicated wherever they occur.

9b Materials used

The resin used was Beetle 4116, supplied by B.I.P. Chemicals Limited, Oldbury, near Birmingham. The materials used to make this resin were maleic anhydride, phthalic anhydride and 1,2 propylene glycol in a molar ratio 1:2:3. As received, it contained styrene monomer and hydroquinone inhibitor.

Beetle 4116 is a low reactivity, general purpose resin. It is suitable for use where thick sections have to be moulded, since exotherms are not great. It is recommended for hand lay-up, and in particular for car and boat fabrication.

Some of the properties given as a guide for users by the manufacturers are those listed in Table 2.

The properties of polyester resins are subject to some slight variation from batch to batch. Any given batch also changes its properties after being stored at room temperature for more than a few months.

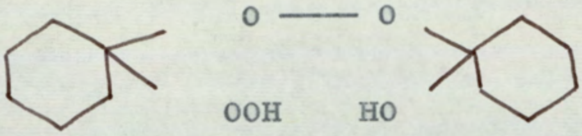
Gel times, solid contents, acid numbers, number-average molecular weights and viscosities were checked for the batches used.

A second resin was used for a few electrical experiments. This was designated RT4. It was obtained from Scott Bader Co. Ltd., and contained fumaric acid, propylene glycol and isophthalic acid in the mole ratio 3:4:1, together with 37% $^{w}/_{w}$ styrene.

TABLE 2

Uncured resin	
viscosity at 25°C.	4.3 poises
specific gravity, 25°C.	1.11
acid value (mg.KOH/g.)	16
gel time (1% benzoyl peroxide, 82°C.)	8 minutes
Cured 1/8 inch castings	
specific gravity, 25°C.	1.20
Barcol hardness, type 934/1	42
Tensile strength, psi. 25°C.	6,800
Water absorption, 7 days, 25°C.	0.49%
Power factor, 10^6 c/s	0.010

Benzoyl peroxide from Laporte Co. Ltd., was used as the usual initiator, in the form of a 60% paste in dimethyl phthalate. In addition, some cyclohexanone peroxide (HCH) was employed. This was Cyclonox B-50, from Novadel Ltd. Cyclonox B-50 is a mixture of several peroxy and hydroperoxy compounds, the dominant constituent being 1 hydroxy, 1' hydroperoxy dicyclohexyl peroxide:-



Benzoyl peroxide was used in conjunction with N,N' p-dimethyl toluidine (DMT) (from BDH Chemicals). As supplied, this had a refractive index of $n_D^{20} = 1.545$. It was used as a dilute solution in dibutyl phthalate. Cyclohexanone peroxide was used in combination with cobalt naphthenate, obtained as a 6% solution in white spirit from the Yorkshire Dyeware and Chemical Co. Ltd.

9c. Preliminary examination of the resin

The oldest batch available had begun to "drift" considerably, having a viscosity of 12 poises and an acid number of 20. Its solid content was 35.5% whereas the usual solid content was about 38% by weight. The other batches had properties which corresponded with those outlined by the suppliers.

The chemical constitution of the resin was already fairly well known, from the known starting materials and their proportions. It was expected that negligible cis isomer (maleate) would be present; the infrared spectrum (Fig.7) confirms this. The styrene content was evaluated from the solid content (38.0%) and from the ultraviolet method of Hirt, Schmitt and Stafford (1955). This method gave a value of 39.4%, and the value was taken to be the mean of these two figures, i.e., 38.7%.

The ultraviolet spectrum obtained (Fig.8) varied slightly from sample to sample, and while the styrene value was reasonable, this method did not give a reliable determination of the phthalate and fumarate present. The results obtained were inconsistent with the formulation used to make the resin, and so the fumarate and phthalate contents were calculated from the initial molar feed ratios.

Thus, the constitution of the resin was calculated to be:-

styrene	38.7	parts per hundred by weight
phthalate	35.5	" " " " "
fumarate	12.3	" " " " "
glycol	13.5	" " " " "
	100	

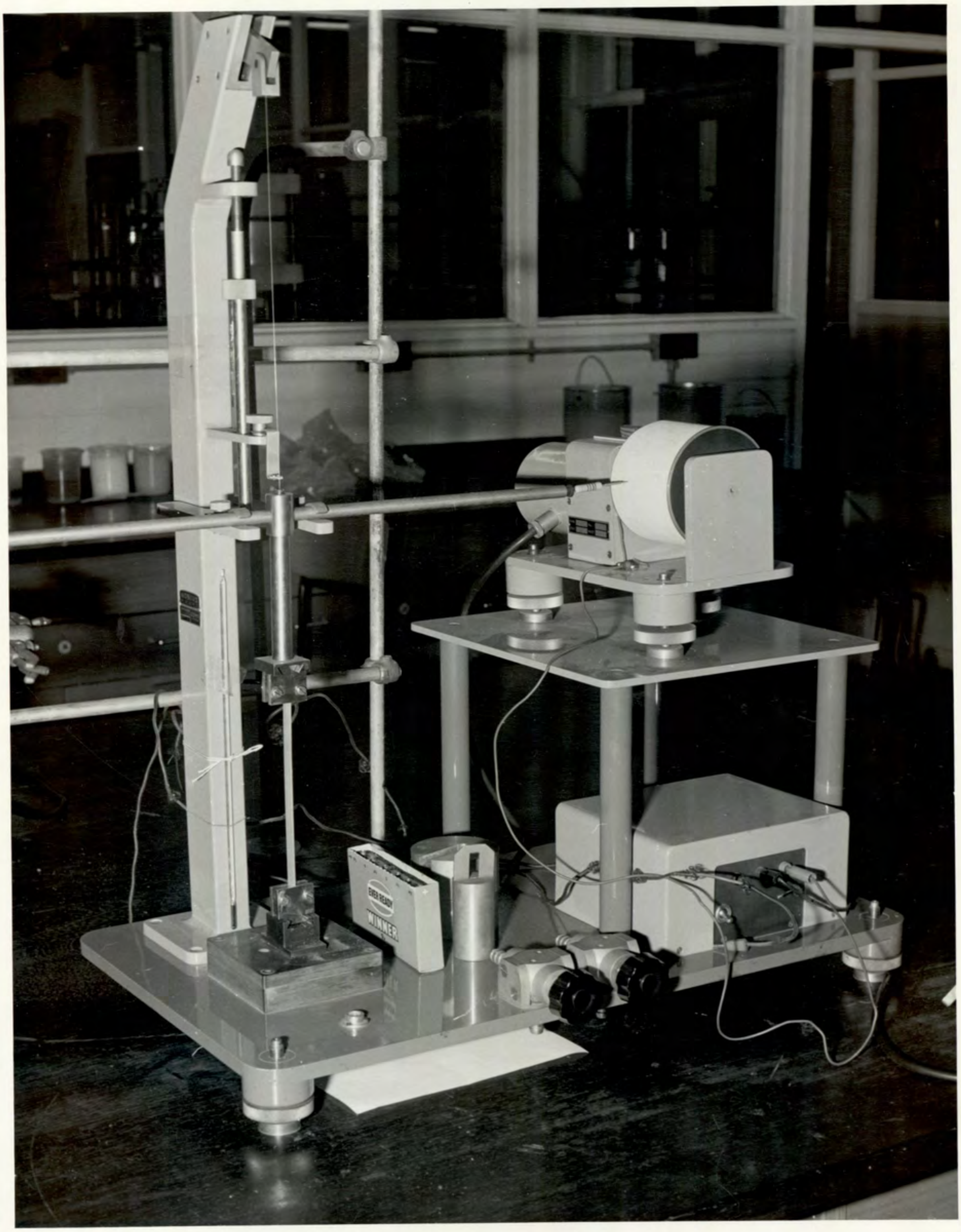
In this context, the phthalate and fumarate units are to be regarded as the respective acids without their two acidic hydrogen atoms, and the glycol is regarded as having lost its two hydroxyl groups.

The number-average molecular weights were found by end-group titrations and confirmed by vapour-pressure osmometry. They varied between 1820 and 2000, and were usually about 1920.

Using the standard S.P.I. gel test (except that a test tube 25mm wide was used), a gel time of 3 minutes was obtained using 1.25% benzoyl peroxide.

FIG. 9 MARCONI TF1313A 0.1% UNIVERSAL BRIDGE, USED FOR MEASURING A.C. DIELECTRIC CONSTANT AND LOSS, AND D.C. VOLUME RESISTIVITY. THE POLYMERIZATION CELL IS ALSO SHOWN, IN A BEAKER ON TOP OF THE BRIDGE.

FIG.10. NONIUS TORSIONAL PENDULUM. INERTIA WEIGHTS AND COUNTERPOISE (NOT IN USE) REST ON THE BASEPLATE ADJACENT TO THE BATTERY.



9d. Mixing procedure

The standard conditions for correlative experiments were as follows:-

100 grams of resin was divided into two parts, and to one part was added 1.00 part by weight of benzoyl peroxide, while to the other was added 0.007 parts by weight of DMT accelerator. Each portion was thoroughly mixed, and de-aerated for five minutes under vacuum at room temperature. The two parts were then united and, after ensuring that no more peroxide remained undispersed, poured into the polymerization cell or mould. (The cell was pre-heated to the polymerization temperature of 45°C.)

In experiments involving the cobalt - HCH system, the same procedure was adopted, but the proportions were:-

Resin in styrene	100	parts	by	weight
HCH	0.75	"	"	"
cobalt naphthenate	0.17	"	"	"

The decrease in weight during five minutes de-aeration was of the order of 0.5%.

9e. Electrical measurements

A Marconi 0.1% universal bridge, type TF1313A, was used to measure the d.c. volume resistivity, dielectric constant and loss tangent during cure. The bridge has an upper limit in resistance measurements of 1.1×10^{8} ohms, giving resistivities up to about 3×10^{10} ohm-cm. (The specimen usually has an area : thickness ratio of less than 300.) The range of measurements available was therefore expanded by using a 90 megohm shunt in parallel with the specimen. This gave a range of resistivities up to about 5×10^{13} ohm-cm.

Capacitance and loss ranges were more than sufficient for the monitoring of the crosslinking of this resin. Two frequencies (1 kc/s and 10 kc/s) were available for a.c. measurements using an internal oscillator, and frequencies up to 30 kc/s using an external oscillator. The bridge and sample cell are shown in Fig.9.

The cell was of the parallel-plate type, similar to those used by Delmonte (1959) and Judd (1965). Glass plates (5 inches square and 3/16 inch thick) were preferred to PTFE because they facilitated inspection at various stages, and any air bubbles or cracks could be seen. Circular electrodes of aluminium foil were attached to the glass by pressure-sensitive adhesive, and rolled with steel rollers until a smooth

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wrinkle-free surface was obtained. The electrodes had projecting, non-overlapping tabs by which they were connected to the bridge terminals. The glass plates were separated by nitrile rubber gaskets about 0.1 inch thick.

The resistance of the connecting leads was 0.6 ohm. Corrections were made for fringe and stray capacitances, as illustrated in Appendix 1.

The cell was pre-heated in an air oven with a forced draught, able to control to 0.5°C. After the cell was filled, the top was sealed with PVC tape, to prevent styrene evaporation. It was found that the addition of the tape did not affect the readings. Decrease in volume during cure was very small and probably corresponded with normal shrinkage. Readings were taken every few minutes in the early stages of cure, until the resistivity values began to level off. The following runs were carried out:-

E. 1 cure at 45°C
E. 2 cure at 55°C
E. 3 cure at 60°C
E. 4 cure at 65°C
E. 5 cure at 70°C
E. 6 cure at 45°C using the cobalt-HCH initiating system.
E. 7 cure at 19°C using three times as much DMT as in E.1.
E. 8 cure at 45°C Styrene content 44.8% by weight.
E. 9 cure at 60°C Styrene content 30.0% by weight.
E.10 the second resin, designated RT4, was cured at 65°C using the benzoyl peroxide amine system.

The effect of time on the resistivities of samples (in the absence of any crosslinking) was examined and found to be quite small.

After the resistivity ceased to show any changes, some samples were examined to find the temperature dependence of the electrical properties. Full cure was ensured by heating for 24 hours at 100°C., then checking that the plots of log ρ against T were reproducible. In some cases, it was necessary to cure for two or three days at 160°C., but the increase in ρ due to the heating at this temperature was quite small. Long periods were required to reach thermal equilibrium at each successive temperature. Equilibrium was indicated by a constant resistivity value. In most cases, only about twenty degrees Centigrade per working day could be covered. Cooling, prior to repeating the measurements, also had to be slow, otherwise cracks could be observed and the specimen had to be abandoned.

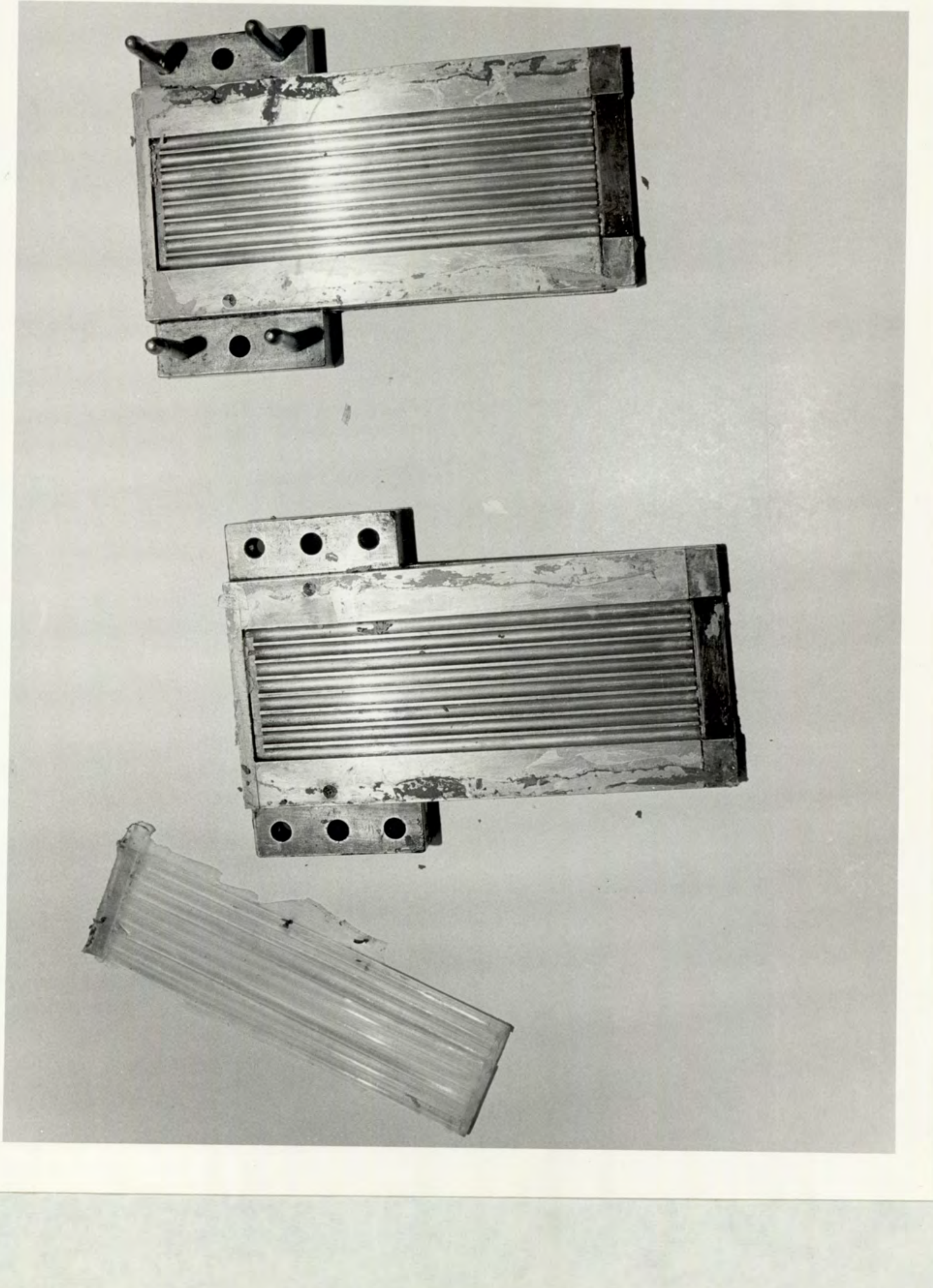
9f. The torsional pendulum

A commercial instrument supplied by Nonius (Delft, Holland,) was used. This model has been described elsewhere (Learmonth, Pritchard and Reinhardt 1968) and it has recently been improved (Nederveen and van der Wal, 1967). The inertia bar is arranged above the specimen, and the weight of the bar and any attached weights are counterbalanced so that the specimen is subjected only to shear, not to tension or compression. Traces, giving permanent records of the oscillations, were obtained by utilising a spark across a gap between the oscillating inertia bar and a revolving drum. The drum carried waxed recording paper, and was connected to an induction coil and a 6-volts grid-bias battery. The pendulum is shown in Fig.10.

There are four possible positions of the attached inertia weights, giving five possible moments of inertia and five possible frequencies for a given specimen. Specimens of about 3 inches or 6 inches could be used, giving further variation in frequency if desired. The determination of the moments of inertia is given in Appendix 2.

A specially constructed steel mould (Fig.11) enabled eight specimens to be cast at a time. These could be either of circular or rectangular cross-section.

<u>FIG.11</u> STEEL MOULD USED FOR CASTING RODS OF CIRCULAR CROSS-SECTION.
THE PHOTOGRAPH SHOWS THE MOULD JUST AFTER OPENING, WITH THE EIGHT RODS NOT YET SEPARATED.



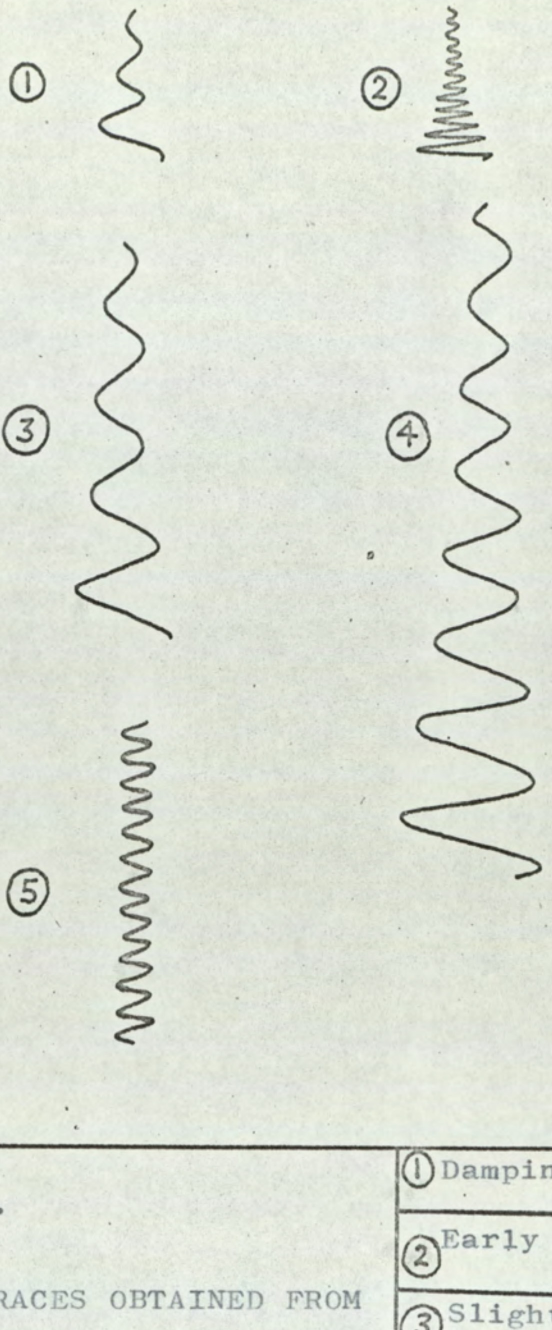


FIG. 12.

DECAY TRACES OBTAINED FROM THE TORSIONAL PENDULUM

① Damping too high to measure	(I_3)
② Early stage of cure	(I_5)
③ Slightly later stage	(I_1)
④ Cure further advanced	(I_1)
⑤ Steel specimen	(I_5)

For I Values see Table 32.

Only the cylindrical geometry was used. The specimen length was usually 6 inches, and the diameter (measured either with a micrometer, in 25 places, or by immersion in a liquid) about 0.230 inches.

Thermocouples immersed in the resin during polymerization showed that, because of the relatively massive nature of the steel mould, and its good heat dissipation, only small temperature elevation occurred. At a nominal temperature of 45°C the maximum temperature reached was 46½°C. This rise was regarded as almost unavoidable for the making of specimens of the size required. Much larger exotherms were observed when the resin was cast in a thin-walled metal tube 1.25 cm. in diameter; 60°C was frequently reached. When a glass tube of the same dimensions was used, the temperature exceeded 175°C.

An advantage of low temperature cure was that cracks were less likely. The specimens were examined under polarised light to see whether stress concentrations could be seen, and any specimens containing such defects were rejected. Other specimens were rejected because, having once been taken out of the mould, they began to warp during further heating.

Measurements were made at ambient temperatures (20°C to 24°C) according to the procedure described in the relevant Nonius manual (Nonius, 1960). Typical traces are shown in Fig.12. It was not possible to obtain satisfactory traces until cure had been taking place for about six hours.

A small frequency range was employed, and modulus results were interpolated to 1 c/s. Interpolation was difficult in the case of logarithmic decrement measurements at low cure times, as the values varied greatly from one position of the moment of inertia to another.

As a result, decrement values plotted in Fig.27 were obtained not by interpolation but by approximation using the nearest frequency to one cycle per second. Considerably more decrement values than modulus values were recorded. It is probable that a better recording system would largely eliminate the more serious fluctuations in decrement values.

FIG.13 DAWE DYNAMIC TESTING MACHINE. THE SPECIMEN SHOWN IN THE TEST-BENCH IS LARGER THAN WAS USUALLY USED. THE DYNATRON SCALING UNIT IS PLACED ON TOP FOR THE PURPOSES OF THE PHOTOGRAPH.

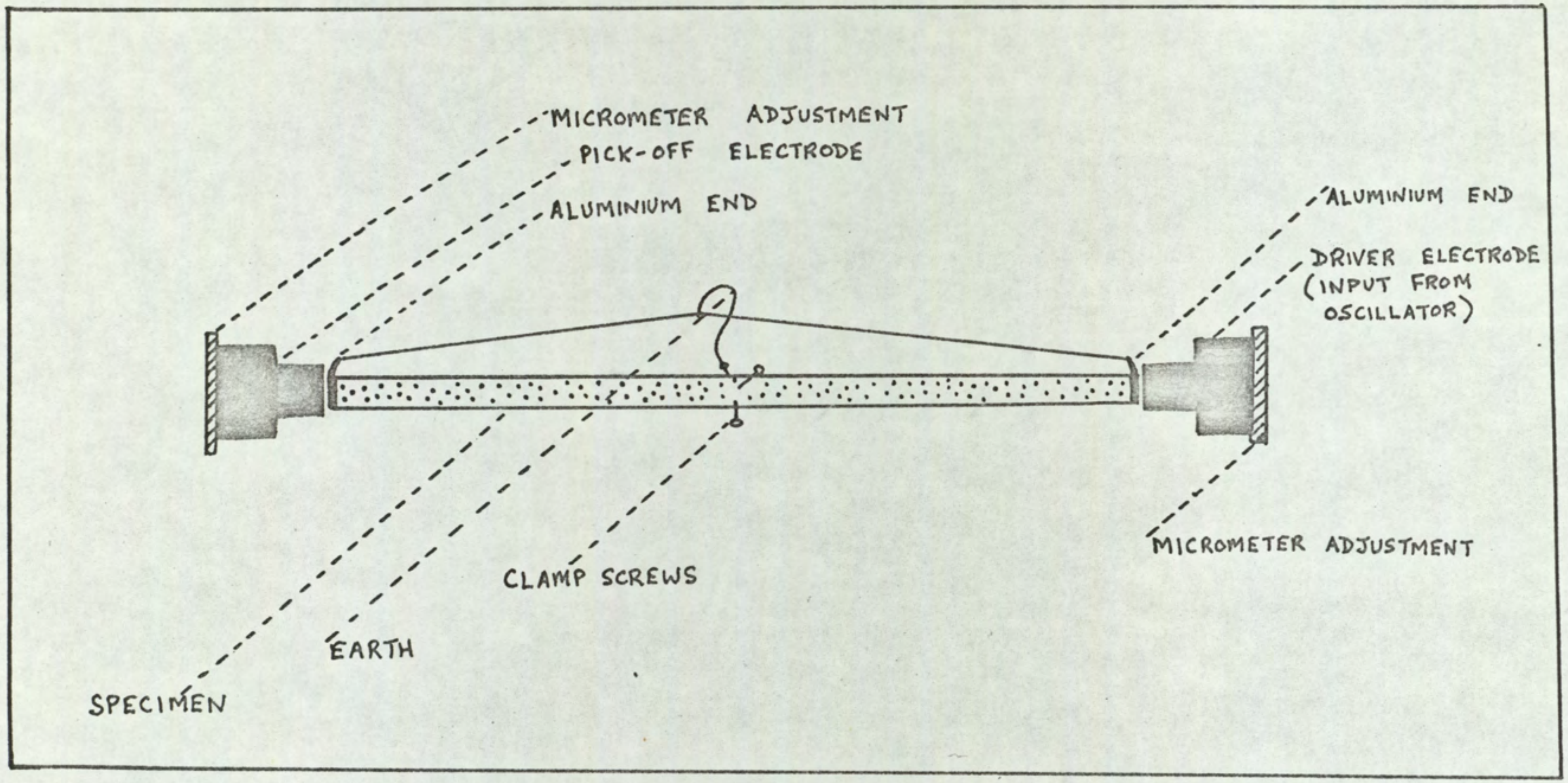


FIG. 14.

FUNCTIONAL DIAGRAM OF TEST BENCH AND SPECIMEN USED IN DAWE DYNAMIC TESTER

9g. The resonant rod technique

The dynamic testing machine made by Dawe Instruments Co. Ltd., Type 1825B, was used. This is shown in Fig.13. It consists in essence of a 6 watt audio oscillator (Frequency range 20 c/s to 20 kc/s), a means of transmitting a signal from the oscillator to a specimen rod clamped horizontally at its mid-point, and a means of detecting the resultant oscillations of the rod and displaying the signal induced by these oscillations on a double beam oscilloscope. The test-bench holding the specimen is portrayed in Fig.14. Electrostatic transducers transmit the signal from the oscillator, and pick up the vibrations at the other end of the rod. To make the transducers, small aluminium discs were cemented to each end of the rod, and brought up by micrometer screws to within about thirty microns distance of the electrodes. The gap was the smallest that could be obtained without a spark passing across. A bias voltage of 500 volts d.c., applied to both electrodes, prevents polarity changes from giving rise to a double cycle of vibration, and provides a polarising voltage for the pick-off electrode.

The ends of the rod needed to be very carefully machined, so as to be flat and perpendicular to the long axis of the specimen. Otherwise, good resonant peaks were impossible to obtain. Careful alignment of the specimen in the test-bench was also crucial.

As the frequency is altered, the amplitude of vibration of the rod alters and passes through a maximum value. When a maximum has been obtained, it is necessary to ensure that the fundamental mode has been found, rather than an overtone.

From the resonant peak, Young's modulus and logarithmic decrement were obtained. (See Appendix 3.)

Several practical difficulties were met in finding good resonant peaks. It proved necessary to mount the specimen on a concrete block to prevent vibrations due to slight movements in the room from interfering with the oscilloscope traces. Some specimens, although carefully prepared, did not give satisfactory resonance peaks, although no obvious explanation for this presented itself. Microscopic flaws, not detectable by other means, may have been responsible.

It was necessary to use an independent frequency monitor capable of measuring the small differences in frequency on which the bandwidth technique depends. A Dynatron scaling unit (type 1009D) proved adequate for this purpose. The frequency recorded by the external counter was always about ½% greater than that recorded on the oscilloscope scale.

It was not possible to control the frequency, except by altering the length of the rods used. Tests showed that, in the particular range of crosslink density under study, the frequency did not affect the modulus and damping appreciably anyway. The measurements were carried out therefore under only approximately isochronal conditions. Nor was it considered that slight variations in temperature were critical at the high crosslink densities under investigation, but nevertheless, temperature control to ± 1°C was achieved using a large (hemicylindrical) expanded polystyrene jacket through which warm air was periodically passed. The measurement temperature was 23°C.

9h. Infrared spectroscopy

Three techniques were tried: (i) polymerization between rock salt plates, (ii) use of potassium bromide discs, and (iii) attenuated total reflectance spectroscopy. The last two techniques were not fully developed, although there seemed no reason why they should not ultimately prove quite satisfactory. Typical spectra from all three techniques are shown (Fig.15.)

All spectra were recorded on a Perkin-Elmer 237 infrared grating spectrophotometer. In the work described elsewhere (Learmonth and Pritchard, 1967), the rock salt plates, with the resin between them, were heated in an air oven, but it was later found preferable to use a specially constructed cell heater. The heater was a 60-watt element in a steel jacket which was machined to fit the plates closely. The heater was controlled by a Cressall voltage regulator and a constant voltage transformer. A direct-reading thermocouple was embedded in plasticine against the edge of the metal jacket adjoining the rock-salt. After the temperature had been held constant for an hour, it was assumed that the temperature of the small heating jacket was uniform throughout, and that the plates in contact with it were very close to this temperature.

Samples for the preparation of potassium bromide discs, and for all other techniques involving finely divided resin, were obtained by allowing the rods used for the dynamic mechanical measurements to touch against a circular saw blade for about half a second. Small fragments were obtained. Any heating taking place did not seem sufficient to make a difference to the state of cure. The grinding time was also kept short.

ATR spectra were recorded using a KRS-5 thallous bromide-iodide crystal at an angle of 40°.

(KBr disc and ATR techniques will not be described in detail, since they do not form a significant part of the experimental spectroscopic work.)

For comparison purposes, spectra were recorded of the following:-

(i) The original polyester resin in styrene solution
(ii) The original polyester resin in xylene
(iii) Xylene
(iv) The original polyester resin without any solvent (KBr disc)
(v) Styrene
(vi) Di-n-octyl phthalate
(vii) The original resin, containing a known excess of styrene
(viii) The resin after cure and post-cure at 90°C.

The analytical procedure was based on an empirical approach. The absorbance ratios for certain peaks were measured at intervals throughout cure. These peaks were:-

the 1737 cm^{-1} carbonyl band
the 915 cm^{-1} styrene band
the 985 cm^{-1} fumarate and styrene band

Let A_{985} = the absorbance of the sample at 985 cm^{-1},

and $\left[\frac{A_{915}}{A_{1737}}\right]_t$ = the ratio of the absorbances at 915 and 1737 cm^{-1}, at time t.

Then s = % of styrene remaining at time t

$$= \frac{\left[{}^{A_{915}}/_{A_{1737}}\right]_t - 0.023}{\left[{}^{A_{915}}/_{A_{1737}}\right]_o - 0.023} \quad 100$$

and f = % fumarate remaining at time t

$$= \frac{\left[{}^{A_{985}}/_{A_{1737}}\right]_t - k_1 s - 0.031}{k_2}$$

where k_1 = constant of proportionality = 7.36×10^{-4}

k_2 = " " " = 9.05×10^{-4}

0.031 is the contribution assigned to phthalate absorption at 985 cm^{-1}

0.023 is the value of $\left[\frac{A_{915}}{A_{1737}}\right]$ when s = o.

Thus, the styrene concentration could be determined directly, and the fumarate concentration could be ascertained by the use of the second peak ratio, provided that the contribution due to the phthalate groups could be ascertained. This was deduced from the spectrum of the pure compound di-n-octyl phthalate.

Typical values of the absorbance ratios are shown in Table 16.

Although the thickness of the films used was known, this information was not necessary, because of the use of an internal standard. The thickness (.007 to .025 mm) was not employed in any calculations, and no absolute spectroscopic terms were calculated.

The following runs were carried out:-

S.1 Cure at 45°C using the standard system
S.2 Cure at 60°C " " " "
S.3 Cure at 70°C " " " "
S.4 Cure at 45°C using the cobalt/HCH system

9i. Refractometry

A precision Abbe refractometer, illuminated by a sodium lamp, was employed to follow the refractive index changes during cure. Thermostatting to ± ½°C was achieved by a Churchill closed-circuit type circulatory system. The refractometer prisms were protected from the polyester resin with silicone mould release fluid, and the surroundswere treated with Simoniz wax polish. After addition of the resin to the lower prism, the upper prism was closed onto it, and the gap between their surfaces sealed with plasticine. Provided that the mould release was thoroughly applied, protection of the prisms was easier than Dannenberg appears to have found (1959) using epoxide resins. Moreover, a sharp boundary was obtained, until the later stages of reaction, when (perhaps because of shrinkage) definition was rather suddenly lost. At this point, internal reflection of the light at the interface of the prism and sample was employed, giving an inverted field with a faint but definite boundary.

The following runs were carried out:-

R.1 cure at 45°C.

R.2 cure at 55°C.

R.3 cure at 60°C.

R.4 cure at 65°C.

R.5 cure at 70°C.

R.6 cure at 19°C. using three times the normal amine accelerator.

R.7 cure at 70°C. 44.8% styrene

R.8 cure at 70°C. 50.1% styrene

R.9 cure at 45°C. cobalt/HCH system.

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9j. % volatile matter

The volatile matter in the resin at various stages of cure was determined. The partly cured resin was powdered, and soaked for several hours in a 2% chloroform solution of diphenyl picryl hydrazyl, to prevent any further reaction. The samples were then heated at 140°C until constant weight was reached. This took periods of time varying from 24 hours to 5 days.

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9k. Water absorption and chemical resistance values

An arbitrary test was devised, in which portions of the cylindrical rods previously mentioned were immersed in various solutions for seven days and then re-weighed. Four liquids were used:

(1) distilled water
(2) 3% sodium chloride
(3) 10% sodium hydroxide
(4) 4 N sulphuric acid

The immersion temperature was 21°C ± 2°C.

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91. Solvent extraction

Powdered samples were taken after various stages of cure from near the end of the rubbery period onwards. These samples were extracted with cold chloroform in conical flasks fitted with ground glass stoppers, and stored in dark cupboards except for periodic shaking. The extraction time was one week. The residues were filtered through sintered glass crucibles, and dried at 70°C to constant weight. Ninety minutes was sufficient drying time. The weight of residue was found, and in a few cases, this residue was submitted for carbon and hydrogen analysis.

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9m. Tensile strength and cross-breaking strength

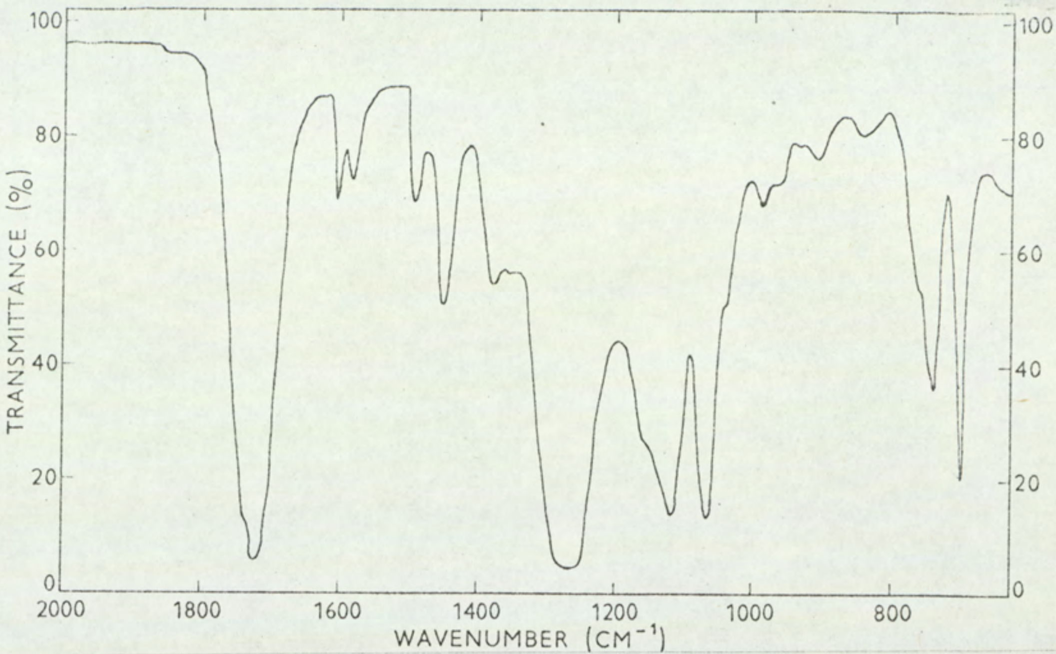
Instead of making a special tensile mould small enough for isothermal cure to be possible, the tensile tests were carried out using the same cylindrical rods which were made for use on the torsional pendulum. Special grips were available which proved satisfactory for these specimens. An E-type tensometer (Tensometer Limited) was used (Fig.16). Conditions of test were:-

Specimen length	3 to 6 inches.
Motor speed	1320 r.p.m.
Cross-head speed	0.75 inches per minute
Load cells	25 to 500 lbs.
Cure time	5 hours to 120 hours.

The same kind of rods were also used in cross-breaking tests, carried out on a Howden cross-breaking machine. These tests were subsequently abandoned, because no approach to any kind of reproducibility could be made. The only repeatable element in these tests was that the rods were too flexible to break at all in this machine, up to a cure time of about 42 to 45 hours. Thereafter, a wide scatter of results was obtained, probably due to flaws in the specimens. No results are presented for this test.

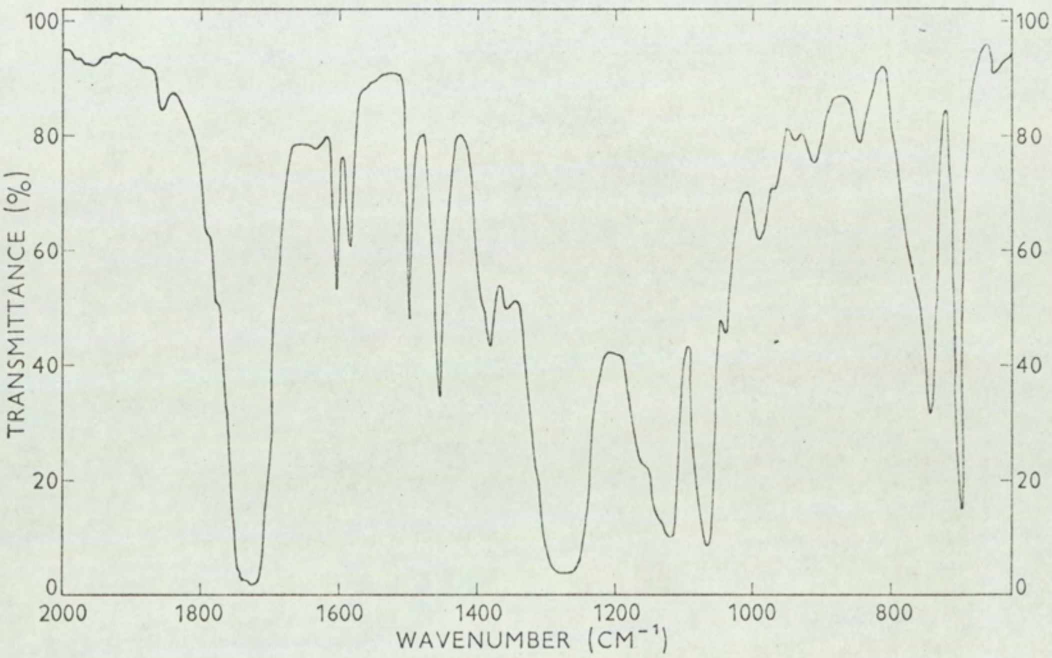
. 15 (a)

TLE 4116
ED FOR 5 HOURS
70°C
CK SALT PLATES)



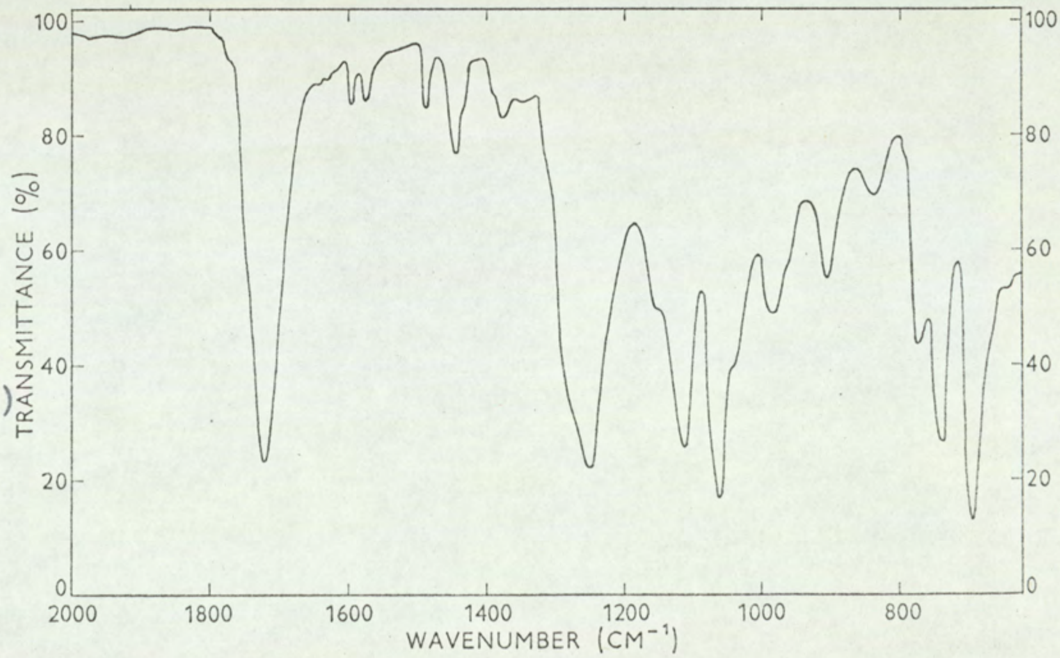
. 15 (b)

TLE 4116
ER CURE (UNDER
-ISOTHERMAL
DITIONS)
TASSIUM BROMIDE
C)



. 15 (c)

TLE 4116
ER CURE FOR
OURS AT 60°C
TENUATED TOTAL
LECTANCE: KRS-5
STAL: ANGLE 40°)



9n. The Weissenberg rheogoniometer

This instrument was not used by the present author, but certain other workers have investigated the cure of polyester resins in the same laboratory, and their findings have been compared with the author's from time to time. For the details of the experimental work, reference should be made to Henson, Lovett and Learmonth (1967) or to Dominic (1967). The relevance of this work to the present thesis lies in the fact that Dominic's system closely resembles the one used here; it differs only in having three times as much accelerator. As a result, the present writer carried out some refractometric and electrical runs using Dominic's system, [illegible]

9o. Gel times

Gelation times were observed at 45°C., 55°C., 60°C., 65°C., and 70°C. using the standard system. Test-tubes of diameter 5 mm were immersed in constant-temperature water-baths, and the gel times observed by stirring. The times were found to depend on and be delayed by stirring, so this was kept to a minimum.

9p. The effect of temperature on the degree of cure

The effect of the cure temperature on the properties of the material obtained was studied. In order to make comparisons, certain rather arbitrary cure times had to be selected. The following procedure was adopted:-

The cure time at 45°C. was taken to be that time at which the refractive index had ceased to increase at more than 0.00010 per hour. If this time is called t_{45}, then the times t_T for other temperatures were chosen so as to be in inverse proportion to the refractometric rate constants.

i.e. $$t_T = t_{45} \cdot k_{45}/k_T$$

It must be noted that these times were not terminal values, and that cure at any of the temperatures concerned would eventually be capable of giving better values for most of the properties. It was not practicable to select level-off values, because at moderate temperatures at any rate, these would have been inordinately long.

Properties were then measured after cure at various temperatures for the times t_T. These times were:-

at 45°C.,	40 hours.
at 60°C.,	8 hours.
at 65°C.,	5½ hours.
at 70°C.,	3½ hours.

10. RESULTS

TABLE 3

Changes in the electrical properties of the resin during cure at 45°C.

Time hrs. mins.	Dielectric constants (10 kc/s)	(1 kc/s)	log ρ	tan δ (10 kc/s)	(1 kc/s)
0 - 08	6.02	-	8.69	0.095	0.895
0 - 17	6.01	5.90	8.62	0.121	1.162
0 - 25	6.00	6.02	8.60	0.138	1.330
0 - 33	5.99	6.00	8.60	0.143	1.405
0 - 40	5.99	6.03	8.61	0.145	1.370
0 - 50	5.98	6.00	8.62	0.147	1.385
0 - 57	5.98	6.03	8.63	0.145	1.350
1 - 04	5.97	6.01	8.64	0.145	1.364
1 - 12	5.97	6.00	8.65	0.143	1.375
1 - 31	5.97	6.01	8.67	0.140	1.320
1 - 58	5.91	6.00	8.80	0.137	1.287
2 - 07	5.90	6.00	8.83	0.136	1.250
2 - 18	5.90	5.93	8.84	0.133	1.235
2 - 33	5.88	5.93	-	0.129	1.168
3 - 00	5.91	5.94	8.84	0.107	0.975
3 - 08	5.91	6.01	8.87	0.100	0.900
3 - 23	5.92	6.02	8.91	0.087	0.754
3 - 53	5.98	6.11	8.93	0.060	0.445
4 - 10	5.98	6.12	9.20	0.049	0.327
4 - 22	5.92	6.10	9.26	0.045	0.263
4 - 37	5.93	6.10	9.36	0.039	0.205
5 - 03	5.93	6.10	9.53	0.035	0.200
5 - 23	5.91	6.10	9.68	0.034	0.097
5 - 33	5.90	6.04	9.75	0.033	0.084
5 - 43	5.90	6.03	9.82	0.033	0.074
6 - 00	5.82	6.02	9.96	0.035	0.058
6 - 20	5.79	6.02	10.13	0.037	0.047
6 - 43	5.78	6.00	10.31	0.041	0.041
6 - 54	5.71	6.00	10.29	0.043	0.039
7 - 07	5.68	5.94	10.55	0.048	0.038
7 - 27	5.62	5.91	10.72	0.050	0.037
7 - 52	5.41	5.89	10.93	0.056	0.040
8 - 08	5.41	5.80	11.07	0.057	0.040
8 - 23	5.34	5.73	11.20	0.060	0.041
8 - 38	5.30	5.70	11.33	0.062	0.044
9 - 50	5.00	5.51	11.84	0.062	0.056
10 - 10	4.96	5.49	11.95	0.064	0.058
10 - 30	4.85	5.35	12.07	0.068	0.060
11 - 00	4.73	5.20	12.24	0.066	0.062
11 - 20	4.62	5.10	12.44	0.064	0.062
11 - 45	4.54	5.00	12.46	0.062	0.062
12 - 15	4.41	4.85	12.79	0.057	0.062
12 - 40	4.25	4.63	12.88	0.050	0.059
13 - 05	4.19	4.52	12.91	0.047	0.058

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Table 3 continued

Time	Dielectric constants		log ρ	tan δ	
hrs. mins.	(10 kc/s)	(1 kc/s)		(10 kc/s)	(1 kc/s)
13 - 45	4.15	4.46	13.01	0.042	0.054
14 - 55	4.04	4.31	13.08	0.037	0.050
16 - 25	3.99	4.24	13.16	0.032	0.046
17 - 25	3.96	4.20	13.18	0.030	0.042
17 - 55	3.96	4.20	13.18	0.029	0.041
25 - 00	3.91	4.12	13.25	0.022	0.034
32 - 30	3.89	4.02	13.31	0.018	0.029
34 - 30	3.86	4.06	13.31	0.017	0.029
38 - 00	3.81	3.95	13.34	0.018	0.028
40 - 30	3.79	3.95	13.35	0.018	0.027
56 - 30	3.79	3.94	13.54	0.016	0.026

N.B. In this table and all other parts of this thesis, the d.c. volume resistivity is in ohm-cm.

TABLE 4

Changes in the electrical properties of the resin during cure at 55°C.

Only representative readings are shown here.

Cure Time (hrs. mins.)	Dielectric constant (10 kc/s)	Tan δ (10 kc/s)	log ρ
0 - 05	6.88	0.173	8.40
0 - 11	6.82	0.205	8.45
0 - 15	6.78	0.222	8.42
0 - 21	6.78	0.235	8.46
0 - 25	6.77	0.245	8.47
0 - 29	6.73	0.245	8.49
0 - 36	6.72	0.245	8.52
0 - 47	6.70	0.222	8.58
0 - 53	6.71	0.200	8.62
1 - 06	6.77	0.142	8.72
1 - 15	6.82	0.099	8.83
1 - 38	6.88	0.043	9.25
1 - 48	6.86	0.036	9.50
1 - 58	6.82	0.035	9.71
2 - 15	6.70	0.039	10.10
2 - 38	6.40	0.052	10.81
3 - 13	5.81	0.061	11.69
3 - 40	5.34	0.063	12.27
4 - 05	5.10	0.052	12.69
4 - 37	4.92	0.045	12.90
5 - 45	4.77	0.037	13.02
6 - 55	4.73	0.031	12.98
8 - 45	4.66	0.027	13.09
23 - 00	4.57	0.018	13.32

TABLE 5

Changes in the electrical properties of the resin during cure at 60°C.
Only typical representative readings are given here.

Time	Dielectric constant		log ρ	Tan δ	
(Mins.)	(10 kc/s)	(1 kc/s)		(10 kc/s)	(1 kc/s)
7	6.10	6.06	8.52	0.195	1.926
13	6.05	5.95	8.49	0.199	2.395
19	6.02	5.91	8.48	0.245	2.440
24	6.00	5.88	8.49	0.252	2.555
32	5.96	5.80	8.50	0.249	2.540
35	5.95	5.77	8.51	0.246	2.508
41	5.95	5.68	8.52	0.240	2.462
47	5.94	5.67	8.56	0.215	2.137
54	5.98	5.56	8.63	0.165	1.630
60	6.00	5.91	8.71	0.125	1.165
77	6.08	6.19	9.20	0.043	0.240
88	6.02	6.20	9.66	0.031	0.080
110	-	-	10.73	-	-
113	5.69	6.01	-	0.049	0.040
128	5.36	5.81	11.37	0.062	0.050
172	4.49	4.90	12.29	0.047	0.058
216	4.28	4.59	12.58	0.036	0.052
330	4.03	4.28	12.86	0.027	0.041
470	4.02	4.19	13.01	0.022	0.035
585	3.96	4.10	13.08	0.019	0.031

TABLE 6

Changes in the electrical properties of resin RT4 during cure at 65°C.

Cure Time (minutes)	Dielectric constant 10 kc/s	tan δ 10 kc/s	log ρ
5	5.30	0.119	9.65
12	5.26	0.145	9.57
17	5.19	0.161	9.54
25	5.16	0.161	9.55
31	5.13	0.157	9.57
35	5.12	0.151	9.60
45	5.10	0.138	9.65
52	5.09	0.127	9.70
60	5.09	0.113	9.75
67	5.09	0.089	9.86
73	5.05	0.054	10.08
87	4.38	0.024	11.44
91	4.25	0.025	11.81
100	4.21	0.027	12.13
103	4.26	0.025	12.19
117	4.19	0.024	12.36
125	4.15	0.023	12.38
132	4.10	0.023	12.43
142	4.13	0.023	12.48
165	4.10	0.023	12.54
185	4.11	0.022	12.59
210	4.08	0.022	12.64
245	4.04	0.022	12.65
1200	3.73	0.015	12.91

TABLE 7

Changes in the electrical properties of the resin during cure at 70°C.

Only representative readings are shown here.

Cure time (minutes)	Dielectric constant (10 kc/s)	Tan δ (10 kc/s)	log ρ
0 - 04	6.96	0.222	8.27
0 - 08	6.92	0.249	8.25
0 - 14	6.83	0.285	8.21
0 - 20	6.78	0.280	8.25
0 - 23	6.67	0.251	8.29
0 - 29	6.83	0.173	8.62
0 - 38	6.93	0.075	8.85
0 - 47	6.97	0.032	9.47
0 - 50	6.90	0.032	9.73
0 - 59	6.49	0.047	10.68
1 - 08	6.08	0.060	11.41
1 - 15	5.70	0.058	11.75
1 - 28	5.15	0.051	11.92
1 - 39	5.02	0.041	12.05
2 - 12	4.88	0.034	12.19
3 - 05	4.79	0.029	12.30
4 - 25	4.72	0.024	12.38
5 - 48	4.65	0.021	12.47
8 - 08	4.62	0.019	12.49

TABLE 8

Electrical properties of the resin during cure at 45°C.

The cobalt naphthenate-cyclohexanone peroxide system was used.

Only typical representative readings are shown here.

Time (mins.)	Dielectric constants		Electrical Dissipation factors Tan δ	
	(10 kc/s)	(1 kc/s)	(10 kc/s)	(1 kc/s)
1	6.91	6.94	0.009	0.063
3	6.88	6.91	0.009	0.066
5	6.86	6.84	0.010	0.070
9	6.82	6.83	0.010	0.075
16	6.79	6.82	0.011	0.078
23	6.78	6.82	0.011	0.079
30	6.78	6.86	0.012	0.073
36	6.78	6.86	0.012	0.066
45	6.78	6.91	0.013	0.048
52	6.72	6.88	0.014	0.035
56	6.48	6.69	0.018	0.026
60	6.36	6.59	0.021	0.024
65	6.36	6.61	0.024	0.036
72	6.00	6.42	0.028	0.024
81	5.76	6.12	0.034	0.025
92	5.45	5.98	0.039	0.028
99	5.29	5.74	0.049	0.033
108	5.06	5.53	0.061	0.044
117	4.90	5.38	0.062	0.054
142	4.64	4.82	0.062	0.057
200	4.41	4.65	0.057	0.060
295	4.19	4.38	0.052	0.058
1170	4.15	4.22	0.042	0.051

Resistivity

Time (minutes)	log ρ	Time (minutes)	log ρ
4	9.57	61	11.49
7	9.55	67	11.85
13	9.54	74	12.20
17	9.57	81	12.52
20	9.64	97	12.96
24	9.75	109	13.06
33	10.06	168	13.18
43	10.52	250	13.23
54	11.11	503	13.36

TABLE 9

Changes in volume resistivity during polymerization at 19°C.

The accelerator concentration was .021% by weight, i.e., three times that in the standard system.

Only the early stages of polymerization were recorded.

Time (minutes)	log ρ
5	9.20
8	9.13
12	9.09
17	9.05
20	9.04
23	9.03
26	9.03
30	9.03
33	9.04
37	9.05
41	9.07
43 (gelation)	9.09
48	9.13
53	9.17
57	9.21
61	9.24
66	9.28
84	9.43
89	9.45
105	9.54
120	9.57
133	9.65
143	9.67

TABLE 10

Changes in the electrical properties of the resin during the early stages of cure at 45°C.

The styrene content was 44.8% in this case.

Only representative readings are given here.

Time (hrs. mins.)	Dielectric constant 10 kc/s	log ρ	tan δ 10 kc/s
0 - 05	6.01	8.73	0.113
0 - 20	5.91	8.64	0.151
0 - 35	5.84	8.62	0.162
0 - 45	5.83	8.63	0.165
0 - 55	5.83	8.64	0.162
1 - 25	5.72	8.79	0.154
1 - 55	5.78	8.85	0.131
2 - 25	5.80	8.93	0.099
3 - 15	5.89	9.13	0.066
4 - 10	6.08	9.42	0.040
5 - 05	6.11	9.69	0.033
5 - 30	6.09	9.83	0.032
6 - 15	6.01	10.11	0.035
7 - 15	5.61	10.53	0.047
47 - 30	3.90	13.67	0.014

TABLE 11

Changes in the electrical properties of the resin during cure at 60°C.

The styrene content was 30% by weight instead of the normal 38.7%.

Only representative results are given here.

Cure Time (hrs.mins.)	Dielectric constants (10 kc/s)	(1 kc/s)	log ρ	Tan δ (10 kc/s)	(1 kc/s)
0 - 07	6.55	-	8.72	0.123	-
0 - 10	-	6.22	8.64	-	1.415
0 - 13	6.48	6.36	8.68	0.159	1.592
0 - 17	6.45	6.36	8.67	0.173	1.740
0 - 22	6.42	6.50	8.67	0.185	1.821
0 - 28	6.39	6.42	8.68	0.195	1.855
0 - 34	6.38	6.33	8.69	0.185	1.760
0 - 40	6.40	6.51	8.73	0.161	1.423
0 - 51	6.42	6.57	8.90	0.090	0.735
1 - 00	6.43	6.63	9.11	0.057	0.372
1 - 10	6.39	6.63	9.45	0.040	0.142
1 - 20	6.29	6.56	9.89	0.042	0.061
1 - 35	6.03	6.44	10.47	0.057	0.045
1 - 58	5.51	6.10	11.31	0.080	0.059
2 - 24	5.01	5.62	12.04	0.080	0.077
3 - 03	4.60	5.13	12.57	0.064	0.075
4 - 05	4.41	4.83	12.76	0.047	0.062
5 - 40	4.32	4.56	12.88	0.038	0.050
7 - 45	4.34	4.60	12.92	0.033	0.044

TABLE 12

Effect of temperature on the electrical properties of the fully cured resin.

Temp. (°C.)	Dielectric constant (10 kc/s)	(1 kc/s)	Log ρ	Tan δ (10 kc/s)	(1 kc/s)
86	3.30	3.43	13.44	0.020	0.034
88	3.36	3.56	13.46	0.026	0.044
94	3.52	3.75	13.29	0.031	0.049
102	3.63	3.95	13.08	0.040	0.057
106	3.59	3.89	13.04	0.040	0.052
109	3.74	4.06	12.83	0.046	0.062
114	3.94	4.28	12.68	0.047	0.056
121	4.15	4.51	12.41	0.052	0.053
128	4.29	4.57	12.15	0.045	0.044
133	4.50	4.80	11.99	0.044	0.046
139	4.49	4.71	11.79	0.035	0.040
147	4.52	4.74	11.52	0.031	0.046
151	4.51	4.70	11.49	0.029	0.050
158	4.69	4.89	11.23	0.027	0.056
162½	4.59	4.80	11.18	0.028	0.062

TABLE 13

Effect of temperature on the electrical properties of the fully cured resin. In this run, the styrene content was lowered to 30% by weight.

Temp.	Dielectric constants			Tan δ	
(°C.)	(10 kc/s)	(1 kc/s)	Log ρ	(10 kc/s)	(1 kc/s)
71	3.68	3.76	-	0.015	0.023
84½	3.87	4.08	13.72	0.031	0.048
92½	3.98	4.29	13.44	0.038	0.059
97½	4.09	4.50	13.13	0.048	0.064
104	4.39	4.81	12.85	0.058	0.063
108	4.49	4.92	12.67	0.058	0.062
113	4.54	5.01	12.45	0.060	0.057
118	4.74	5.16	12.15	0.058	0.053
128	5.11	5.41	11.74	0.046	0.044
135	5.16	5.44	11.41	0.041	0.047
144	5.21	5.48	10.90	0.034	0.047
151	5.23	5.49	10.63	0.030	0.056
157	5.20	5.45	10.39	0.030	0.071
160½	5.19	5.42	10.43	0.029	0.074
167½	5.34	5.60	10.05	0.031	0.106

TABLE 14

The effect of time on the resistivity of uncatalysed resin at 45°C.

Time from bridge switch-on (minutes)	Log ρ
1	9.483
3	9.496
4	9.504
6	9.508
8	9.509
19	9.512
23	9.513
27	9.513
30	9.513
36	9.514
49	9.516
60	9.517
67	9.518
95	9.522
130	9.527
190	9.530
225	9.535
270	9.540
340	9.548

Fully cured samples showed virtually no change in resistivity with time when measured at 80°C.

TABLE 15

Changes in shear modulus (G') and logarithmic decrement (Δ_g) with cure time.

Cure Time (hours)	Frequency (c/s)	G' (x 10^{-10}) (dynes/sq.cm.)	Δ_g
6	2.09	0.58	0.606
	0.33	0.53	0.748
	0.84	0.57	0.562
	0.67	0.53	0.650
	0.47	0.55	0.602
7	2.15	0.63	0.437
	0.32	0.52	0.455
	0.86	0.61	0.596
	0.71	0.60	0.578
	0.48	0.59	0.522
8	2.23	0.70	0.447
	0.34	0.62	0.589
	0.91	0.65	0.469
	0.75	0.65	0.532
	0.49	0.64	0.560
11	2.78	1.03	0.210
	0.44	0.98	0.219
	1.10	1.01	0.178
	1.04	1.28	0.179
	0.64	1.00	0.185
16	2.64	1.06	0.162
	0.43	1.06	0.206
	1.06	1.08	0.191
	0.91	1.06	0.174
	0.66	1.05	0.182
21	2.74	1.08	0.228
	0.44	1.06	0.252
	1.12	1.10	0.232
	0.94	1.08	0.251
	0.67	1.09	0.252
44	1.15	1.12	0.146
	0.46	1.11	0.192
	2.98	1.22	0.144
	0.65	1.09	0.172
	0.96	1.10	0.161
73	2.99	1.26	0.138
	0.48	1.20	0.176
	1.18	1.20	0.144
	0.98	1.20	0.152
	0.72	1.17	0.164
187	3.03	1.28	0.104
	0.49	1.27	0.110
	1.21	1.28	0.104
	1.04	1.22	0.093
	0.71	1.27	0.107
Postcured for 3 hours at 80°C.	3.14	1.37	0.045
	0.51	1.41	0.057
	1.26	1.37	0.054
	1.10	1.37	0.055
	0.72	1.37	0.055

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TABLE 16

Results obtained by the resonant rod technique.

Cure time (hrs)	V (cm/sec)	Δ_E	f_1 c/s	f_r c/s	f_2 c/s	d gm/c.c.	L cm.	E' x10^{-10} (dynes/ sq.cm.)
4¼	1.24	-	-	3608	-	1.15	17.25	1.78
5¼	1.44	-	-	4147	-	1.16	17.35	1.44
6¼	1.45	0.510	3874	4205	4555	1.16	17.25	2.44
7½	1.63	0.452	4325	4704	5004	1.16	17.35	3.05
9¼	1.63	0.381	4274	4584	4830	1.16	17.50	2.99
10¼	1.67	0.291	4570	4782	5014	1.16	17.50	3.25
12½	1.64	0.281	4500	4733	4924	1.16	17.48	3.17
13¾	1.75	0.244	4804	4991	5191	1.16	17.61	3.59
14½	1.77	0.284	4892	5096	5350	1.16	17.39	3.62
16½	1.74	0.240	4870	4987	5250	1.16	17.44	3.50
18	1.84	0.150	5110	5262	5361	1.16	17.50	3.94
19	1.77	0.150	4948	5085	5190	1.16	17.50	3.66
20½	1.83	0.172	5144	5257	5432	1.17	17.44	3.95
21¼	1.88	0.196	5200	5362	5535	1.17	17.61	4.17
22	1.84	0.156	5196	5307	5460	1.17	17.39	4.04
23¾	1.88	0.172	5244	5396	5538	1.17	17.51	4.14
24½	1.94	0.157	5482	5595	5760	1.17	17.40	4.39
26	1.94	0.117	5492	5581	5700	1.18	17.39	4.42
28	1.88	0.123	5289	5400	5501	1.18	17.48	4.21
29	1.93	0.155	5332	5506	5604	1.18	17.52	4.40
31	1.97	0.104	5604	5692	5801	1.18	17.31	4.55
36	1.93	0.140	5570	5705	5826	1.18	16.82	4.36
40	1.93	0.117	5519	5631	5729	1.18	17.14	4.41
60	2.03	0.092	5730	5804	5900	1.18	17.50	4.86
70	2.03	0.082	6606	6701	6780	1.19	15.28	4.96
130	2.04	0.076	5951	5993	6094	1.19	17.11	4.99

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TABLE 17

Typical absorbance ratios obtained from the infrared spectra of resin samples and comparison substances.

Peak A = the peak at 915 cm^{-1}
Peak B = the peak at 985 cm^{-1}
Peak C = the peak at 1737 cm^{-1}

Resin in styrene	Sample No.	Ratio A/C	Ratio B/C
	1	0.256	0.213
	2	0.235	0.188
	3	0.230	0.191
	4	0.233	0.195
	5	0.224	0.188
	6	0.245	0.213
	7	0.240	0.191
	8	0.205	0.198
	9	0.224	0.195
	average	0.232	and 0.192
Polyester in xylene		0.023	0.115

(The xylene used in making the solution had negligible absorption in the range under consideration.)

di-n-octyl phthalate		-	0.087

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TABLE 18

Values of the residual unsaturation, determined by measurements of the absorbance ratios of the infrared peaks at 915 cm^{-1} (Peak A), and 985 cm^{-1} (Peak B) to the absorbance at 1737 cm^{-1} (Peak C).

Cure temperature 45°C.

Time (hours)	Ratio A/C	Ratio B/C	% Residual Styrene	% Residual Fumarate
0.00	0.256	0.195	100.0	100.0
1.25	0.246	0.190	95.8	97.8
2.25	0.229	0.184	88.4	97.8
2.75	0.238	0.180	92.2	90.0
4.75	0.232	0.177	89.6	89.0
5.50	0.211	0.176	81.0	94.5
5.75	0.221	0.164	85.0	78.0
6.75	0.202	0.150	76.8	69.3
8.00	0.160	0.132	58.9	63.9
9.50	0.139	0.104	49.8	40.7
9.75	0.145	0.121	48.0	60.6
10.50	0.104	0.109	34.7	58.2
11.75	0.102	0.100	33.9	48.5
12.75	0.116	0.104	39.8	48.5
13.75	0.095	0.102	30.9	53.9
15.50	0.102	0.104	33.9	52.9
16.50	0.083	0.088	25.7	41.9
20.00	0.084	0.079	26.1	31.8
24.50	0.070	0.082	20.1	39.4
48.00	0.059	0.077	15.4	38.5
68.00	0.051	0.067	12.0	29.6
120.00	0.048	0.078	10.8	42.9

TABLE 19

Values of the residual unsaturation, determined by measurements of the absorbance ratios of the infrared peaks at 915 cm^{-1} (Peak A), and 985 cm^{-1} (Peak B) to the absorbance at 1737 cm^{-1} (Peak C).

Cure temperatures 60°C and 70°C.

Only representative results are quoted here.

60°C.

Time (hrs)	Ratio A/C	Ratio B/C	% Residual Styrene	% Residual Fumarate
0.00	0.235	0.188	100.0	100.0
0.75	0.224	0.185	94.8	93.5
2.00	0.202	0.162	84.8	75.6
3.50	0.151	0.115	60.4	44.0
4.50	0.106	0.106	39.3	51.1
7.00	0.067	0.074	20.6	30.9
9.00	0.063	0.089	19.9	47.9
31.00	0.058	0.061	11.9	19.5

70°C.

Time (mins)	Ratio A/C	Ratio B/C	% Residual Styrene	% Residual Fumarate
7	0.214	0.166	90.9	77.2
13	0.196	0.150	82.2	66.8
18	0.178	0.143	73.9	64.2
23	0.148	0.131	59.6	63.4
29	0.140	0.120	55.7	54.5
38	0.122	0.093	47.2	30.0
46	0.106	0.085	39.9	27.6
56	0.084	0.069	29.3	18.7
66	0.076	0.069	25.4	22.0
77	0.062	0.060	18.6	17.1
89	0.056	0.056	15.8	15.4
100	0.063	0.058	19.2	14.6
115	0.051	0.046	13.2	6.5
130	0.051	0.051	13.2	11.4
145	0.049	0.050	10.9	12.2
160	0.048	0.045	10.6	6.5
190	0.048	0.044	10.6	6.5
220	0.046	0.045	10.1	7.3
310	0.048	0.043	10.6	4.1

TABLE 20

Changes in the refractive index during cure at 45°C.

Cure time (minutes)	R. I.	Increase in R.I. (units of the 5th place of decimals)
60	1.53516	0
120	1.53534	18
280	1.53810	294
300	1.53966	450
315	1.54067	551
335	1.54227	711
390	1.54605	1089
405	1.54724	1208
420	1.54817	1301
430	1.54862	1346
455	1.55000	1484
475	1.55095	1579
490	1.55152	1636
525	1.55317	1801
550	1.55363	1847
560	1.55433	1917
570	1.55468	1953
590	1.55522	2007
605	1.55568	2053
615	1.55593	2078
725	1.55996	2481
1110	1.56100	2585
1190	1.56157	2643
1240	1.56138	2623
1290	1.56169	2654
1330	1.56191	2675
1590	1.56162	2646

The temperature was then raised quickly to 60°C.
Further changes occurred:-

Time (minutes)	R. I.	Increase over initial 60°C value
0	1.55692	0
45	1.55746	54
95	1.55800	108
200	1.55847	155
230	1.55858	166
295	1.55876	184

A similar treatment at 70°C raised the refractive index from 1.55635 to 1.55703 (69 units) over a period of 270 minutes. The terminal value of the refractive index after normal 70°C polymerization was 1.55753, and at 60°C, 1.55859. Thus the post-cures gave similar terminal values to those obtained by direct cure at these temperatures.

TABLE 21

Changes in the refractive index during cure at various temperatures.

Time (mins)	Increase in R.I. (Units of the 5th place of decimals)			
	55°C.	60°C.	65°C.	70°C.
4	-	-	5	-
5	0	41	-	247
8	-	-	-	495
11	-	-	-	730
13	-	-	21	-
15	-	-	-	1025
20	19	443	-	1333
25	-	-	-	1612
29	-	-	397	-
30	-	797	-	-
34	-	-	679	-
35	19	-	-	-
38	-	-	-	2265
39	-	-	928	-
40	-	1142	-	-
44	-	-	1221	-
45	-	-	-	2455
50	-	1482	-	-
54	-	-	1643	-
55	-	-	-	2714
60	34	-	-	-
64	-	-	1968	-
65	-	-	-	2917
70	-	1671	-	-
74	-	-	2208	-
75	57	-	-	3065
84	-	-	2411	-
85	-	1950	-	-
89	-	-	-	3144
90	341	-	-	-
94	-	-	2590	-
95	448	-	-	-
100	539	2196	-	-
105	-	-	-	3207
110	778	-	-	-
120	989	2409	-	-
130	1193	-	-	-
134	-	-	2932	-
140	1372	-	-	-

TABLE 21 continued

Time (mins)	Increase in R.I. (Units of the 5th place of decimals)			
	55°C.	60°C.	65°C.	70°C.
145	1465	-	-	-
150	-	-	-	3294
165	-	2610	-	-
170	1805	-	-	-
185	2027	-	-	-
189	-	-	3051	-
195	2118	2731	-	-
220	-	-	-	3322
225	2368	-	-	-
235	2439	-	-	-
240	-	2877	-	-
265	2570	-	-	-
285	2693	2913	-	-
289	-	-	3130	-
300	2726	-	-	-
330	-	2940	-	-
350	2845	-	-	-
384	-	-	3145	-
390	2889	-	-	-
405	-	2940	-	-
415	2892	-	-	-
1350	-	-	3234	-
1375	3063	-	-	-
1810	3066	-	-	-

TABLE 22

Changes in the refractive index during cure at 45°C. The accelerator concentration was 0.021% by weight, i.e., three times that in the standard system.

Cure time (minutes)	Increase in R.I. (units of the 5th place of decimals)
4	29
6	50
9	170
14	220
17	250
20	329
23	334
27	380
30	405
33	446
37	488
42	535
46	572
51	615
58	711
65	755
73	834
86	963
100	1123
113	1162
129	1313
154	1518
202	1835
261	1989
271	2214

(This run was not taken to completion)

TABLE 23

Effect of styrene content on change in refractive index during cure at 70°C.

Time Mins.	Increase in R.I. (units of the 5th place of decimals)		
	Styrene content 38.7%	Styrene content 44.8%	Styrene content 50.1%
1	-	52	0
5	247	-	-
6	-	348	202
8	495	-	-
11	730	712	-
12	-	-	465
15	1025	-	601
16	-	1084	-
19	-	-	800
20	1333	-	-
21	-	1430	-
23	-	-	1033
25	1612	-	-
26	-	1713	-
31	-	1980	-
32	-	-	1587
38	2265	-	-
41	-	2413	-
43	-	-	2153
45	2455	-	-
46	-	2626	-
49	-	-	-
55	2714	-	2595
56	-	2904	-
63	-	-	2869
65	2917	-	-
71	-	3222	-
75	3065	-	-
76	-	3277	-
80	-	-	3364
89	3144	-	-
91	-	3372	3493
105	3207	-	-
107	-	-	3664
121	-	3392	-
125	-	-	3782
141	-	3420	-
150	3294	-	-
158	-	-	3878
161	-	3439	-
201	-	3461	-
220	3322	-	-
241	-	3485	-
293	-	-	3947
307	-	3522	-

TABLE 24

Increase in the refractive index of the resin during cure at 45°C.

The cobalt - cyclohexanone peroxide system was used.

Time (mins)	Increase in R.I. (units of the 5th place)
3	16
5	61
7	145
10	263
14	362
17	521
23	730
25	759
28	877
32	1009
37	1135
42	1281
49	1451
57	1630
63	1725
68	1812
77	1936
86	2066
92	2162
100	2232
122	2404
139	2524
155	2551
180	2616
209	2664
238	2699
261	2695
321	2736
412	2774
500	2786

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TABLE 25

% volatile matter as a function of cure time.

Cure time (hours)	% volatile matter
0.75	40.2
3.50	33.9
4.50	32.5
6.00	25.7
8.00	24.1
11.25	15.2
18.00	13.5
24.00	11.2
25.50	11.6
28.00	12.3
30.00	10.0
32.00	10.2
51.00	8.2
160.00	8.2

p. 124

TABLE 26

% gain in weight of cured resin specimens after seven days immersion in various liquids at 21°C.

Cure time at 45°C. (hours)	Distilled Water	3% Sodium Chloride	10% Sodium Hydroxide	4N Sulphuric Acid
4¼	- 0.077	- 0.113	- 0.444	- 0.041
7	- 0.012	-	-	-
7¾	- 0.108	- 0.036	- 1.460	- 0.141
10¼	+ 0.272	-	-	-
21	+ 0.334	+ 0.288	- 0.536	+ 0.260
30½	+ 0.400	-	-	-
35	+ 0.560	-	-	-
42	+ 0.305	+ 0.292	- 0.901	+ 0.258
67	+ 0.300	+ 0.267	- 0.467	+ 0.261
87	+ 0.284	+ 0.252	- 0.086	+ 0.213
92	+ 0.352	-	-	-
125	+ 0.389	-	-	-
149	+ 0.335	-	-	-
164	+ 0.298	+ 0.296	- 0.178	+ 0.250
230	+ 0.287	+ 0.264	+ 0.025	+ 0.232

p. 125

TABLE 27

Changes in the ultimate tensile strength during cure at 45°C.

Cure time (hours)	Ultimate tensile strength (p.s.i.)
5	80
7	88
9	164
10	226
11	289
12	704
13	3400
15	3840
16	3175
18	3985
19	3705
21	3875
23	5295
31	6600
40	6760
45	6390
73	6800
88	6420
160	6780

The % elongation at break declined from about 23% in the 5 - 10 hours stage to about 4% in the 100 - 170 hours stage.

Tensile modulus reached a maximum of about 1.4×10^5 p.s.i.

TABLE 28

% extractable matter as a function of cure time.

Cure time (hours)	% extractable matter
3.50	38.0
3.50	34.0
7.00	35.2
9.75	31.9
18.00	21.9
23.00	13.0
25.50	24.0
28.00	16.9
30.00	10.0
52.00	11.9
90.00	10.0
167.00	11.1
182.00	12.8
230.00	10.8

p. 126

TABLE 29

Data used in the drawing of Arrhenius plots (see Fig.33).

Temperature of cure °C	$(d\log\rho/dt)_{max.}$	$k_r \times 10^5$ (from refractometric data) $sec.^{-1}$	$k \times 10^5$ (resid. styrene) $sec.^{-1}$	recip. gel time (hrs.)
45	1.39×10^{-4}	4.28	4.10	1.16
55	4.16×10^{-4}	13.55	...	2.72
60	7.10×10^{-4}	21.40	...	3.75
65	1.04×10^{-3}	33.40	...	5.21
70	1.61×10^{-3}	41.02	41.04	9.25

k_r and k refer to pseudo first order rate constants.

TABLE 30

Effect of cure temperature on the degree of cure.

Cure temp. (^{o}C.)	45	60	65	70
Cure time (hrs.)	40	8	5½	3½
Increase in R.I.	2660	3060	3170	3470
Shear modulus (G', x 10^{-10}) dynes/sq. cm.	1.13	1.33	1.32	1.37
Log. dec. (shear)	0.153	0.081	0.079	0.069
Young's modulus (E', x 10^{-10}) dynes/sq. cm.	4.85	4.80	4.44	4.84
Log. dec. (extension)	0.120	0.082	0.082	0.079
Increase in log. ρ over initial value	4.90	4.50	4.60	4.10
% residual styrene	22.0	19.4	11.1	9.3
% residual fumarate	38.2	36.5	17.1	4.1

FIG.16 E-TYPE TENSOMETER.

DISCUSSION

PART THREE: DISCUSSION

11.1 General introduction

The main aims of the experimental work described were:

(1) to study the effect of curing time on a large number of physical properties, and to interpret these in terms of the development of a three-dimensional network structure.

(2) to obtain correlations between the chemical and physical changes taking place during crosslinking

(3) to assess potential techniques for determining the degree of cure of casting resins, and to decide whether any might be suitable for application to reinforced polyesters.

In order that (2) should be achieved, a method of estimating the extent of the chemical reaction had to be developed.

The measurement of a large number of properties was thought preferable to the close study of a few. Because of this, limited time was available for the development of any one technique. This gave rise to two limitations affecting the usefulness of the data obtained.

First, only one resin could be studied in any detail. Second, reproducibility was inevitably poorer than would have been the case if only three or four techniques had been used. The worst reproducibility was in the measurement of crossbreaking strength, water absorption and chemical resistance. Solvent extraction results were liable to quite considerable scatter, but this is commonly found. Other measurements were much more satisfactory.

Accepting these factors, a wide-ranging programme was fulfilled. The experimental results obtained are presented either as graphs or in tabular form, but in a few cases both are used. Where there appears to be a discrepancy between the actual readings in graphs and in tables, this is because the two represent different (but almost superimposing) runs.

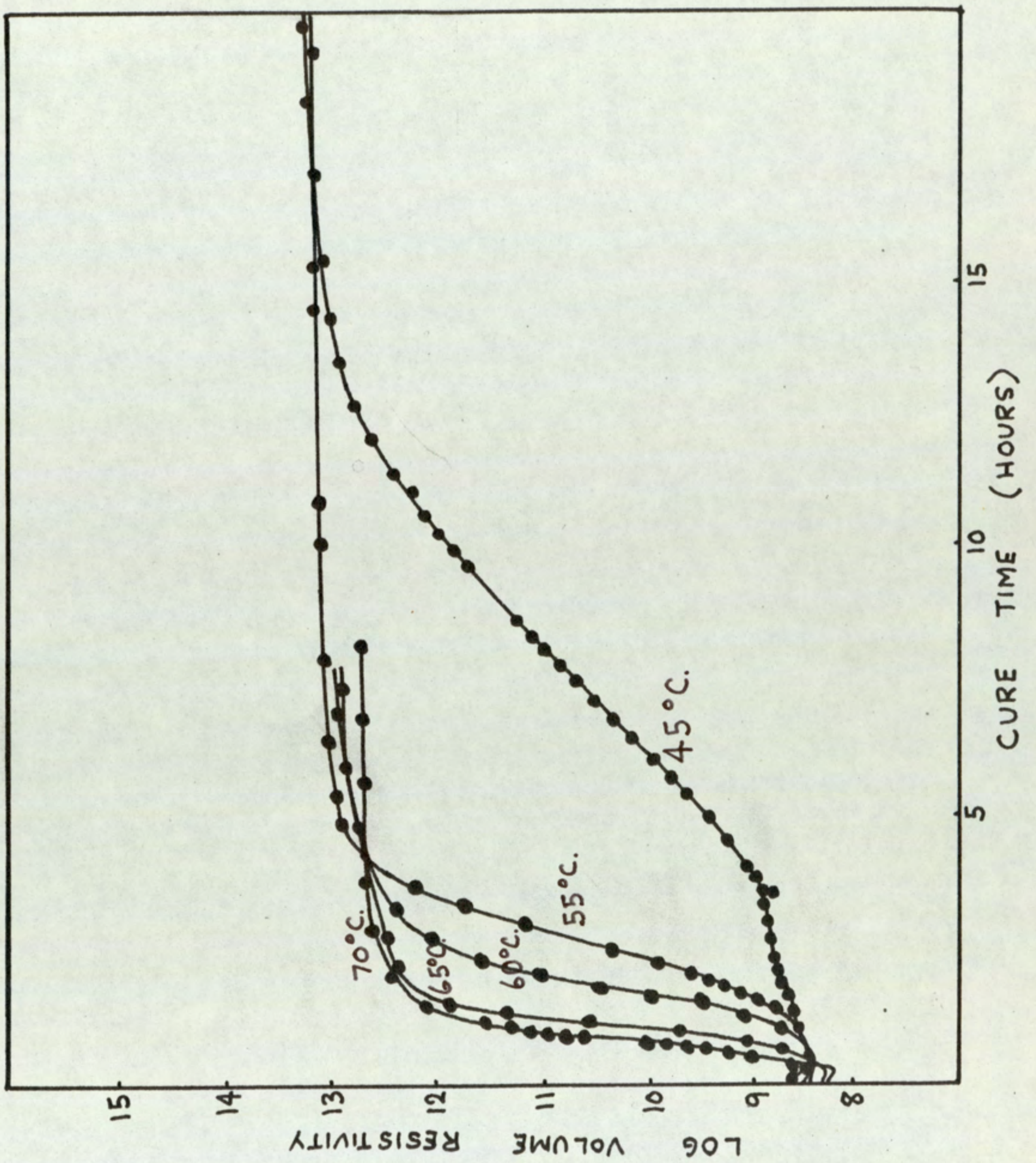
The lists of figures and tables (to be found at the beginning of the thesis) indicate where any specific results may be located.

The discussion considers first the electrical measurements, then mechanical measurements; thirdly the chemical, infrared and refractive index studies; and finally the correlations between various properties.

The "standard" formulation given in the experimental section should be assumed unless an alternative one is specifically mentioned.

If no cure temperature is indicated, this may be assumed to be 45°C.

FIG. 17



EFFECT OF CURE TIME ON D.C. VOLUME RESISTIVITY AT VARIOUS CURE TEMPERATURES

11.2 Electrical measurements

Some workers have urged that caution should be used in applying d.c. volume resistivity data on polymers in general (Reddish, 1962) and in kinetic studies in particular (Fava and Horsfield, 1968) on account of the time-dependent nature of the conduction process. The technique used here employs a bridge, instead of the more common method based on a simple application of Ohm's law. If the resistivity is particularly time-dependent, it would become impossible to maintain the bridge in balance. This difficulty was not met during the study of the cure of these resins. A fully cured sample was maintained at 80°C. for several hours, and no change in resistivity was noted during this time. A sample of uncured, uncatalysed resin at 45°C. did undergo a slight increase in resistivity with time (see table 14) but this was very small. After a time the change in ρ became almost linear instead of lessening, suggesting that it was partly due to slight evaporation of styrene. The problem of styrene evaporation hardly arises in studies of the actual cure of the resins, because after gelation very little occurs.

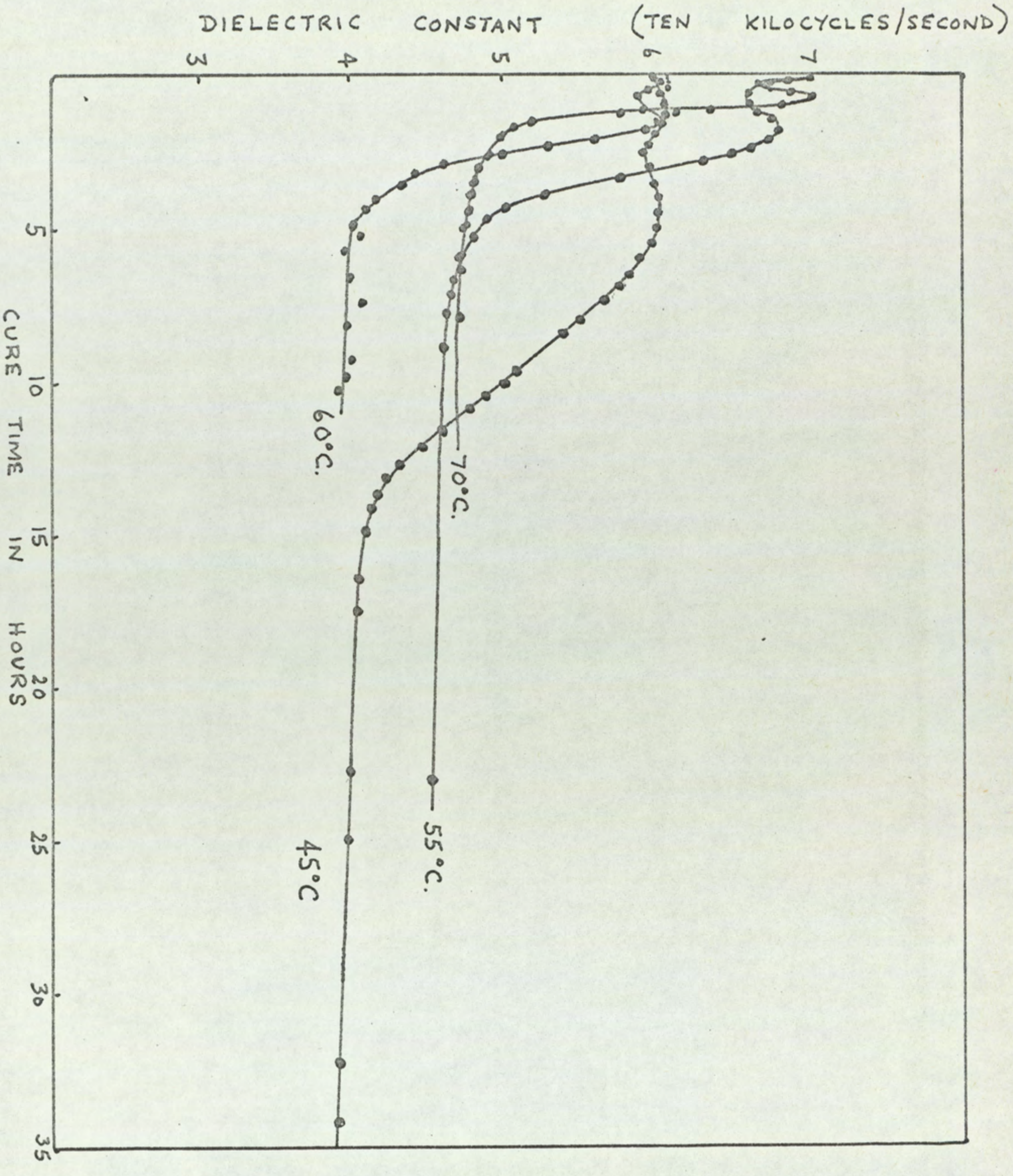
The volume resistivity of the curing resin declined in the first few minutes in the oven, then gradually rose, and the maximum rate of increase was reached. (See fig. 17). The initial decline was not due entirely to the resin being heated to the oven temperature, since when polymerization was carried out at room temperature the same fall occurred. It is more probable that the conductivity increases as a result of the formation of additional current carriers after mixing. There was no appreciable difference between the initial resistivity of the uncatalysed resin and that containing cobalt naphthenate and cyclohexanone peroxide, (see tables 14 and 8 respectively) but the resistivity of samples containing benzoyl peroxide and a tertiary amine was lower by a decade (table 3). All four initiator and accelerator additives were mixed with diluents.

It is noticeable that below 60°C., the temperature of appreciable thermal decomposition of benzoyl peroxide, a fairly long induction period occurred and the reaction was quite slow because of the low accelerator concentration. Above 60°C., the resistivity rose so rapidly that readings had to be taken almost continuously. The logarithm of the resistivity was linear with respect to time, (and not the resistivity itself, as Purdon and Morton (1962) found for styrene polymerizations).

Only in the slow-cured 45°C. samples was the Trommsdorf effect evident as a definite kink in the rate curve. This kink is quite clearly shown at about three and a half hours, which is approximately four times the gel time. Such a position for the Trommsdorf effect agrees with the findings of Gordon and McMillan (1957) that diffusion control of the termination reactions takes place

FIG. 18

EFFECT OF CURE TIME ON DIELECTRIC CONSTANT, AT VARIOUS CURE TEMPERATURES.



well after gelation for styrene-based polyesters. Methyl methacrylate-crosslinked polyesters show a Trommsdorf effect at the gel point itself.

The fact that no sudden increase in the magnitude of the resistivity is found on passing from the soluble to the gel condition shows that there is no sudden increase in the microviscosity at this point. The primary network formed at gelation is open, with relatively few crosslinks, and does not impede the current carriers much more than the branched but soluble structure does just before gelation. Only a small section of a polymer chain needs to be displaced to allow current carriers to pass, whether the resin is gelled or not.

The slope of the log resistivity - time curve is believed to be proportional to the rate of reaction. Values of $(d \log \rho/dt)_{max}$ were measured and tabulated in table 29. The Arrhenius plot from this data is shown in Fig.33 p213. The overall energy of activation for the reaction, as measured by $(d\log \rho/dt)_{max}$ is very similar to that obtained by refractometric, spectroscopic and gel time measurements.

One of the features of resistivity - time plots is the rather sudden level-off, as if diffusion control of the propagation reactions sets in quite sharply at a particular stage. This point is the time when the T_g of the crosslinked polymer reaches the cure temperature.

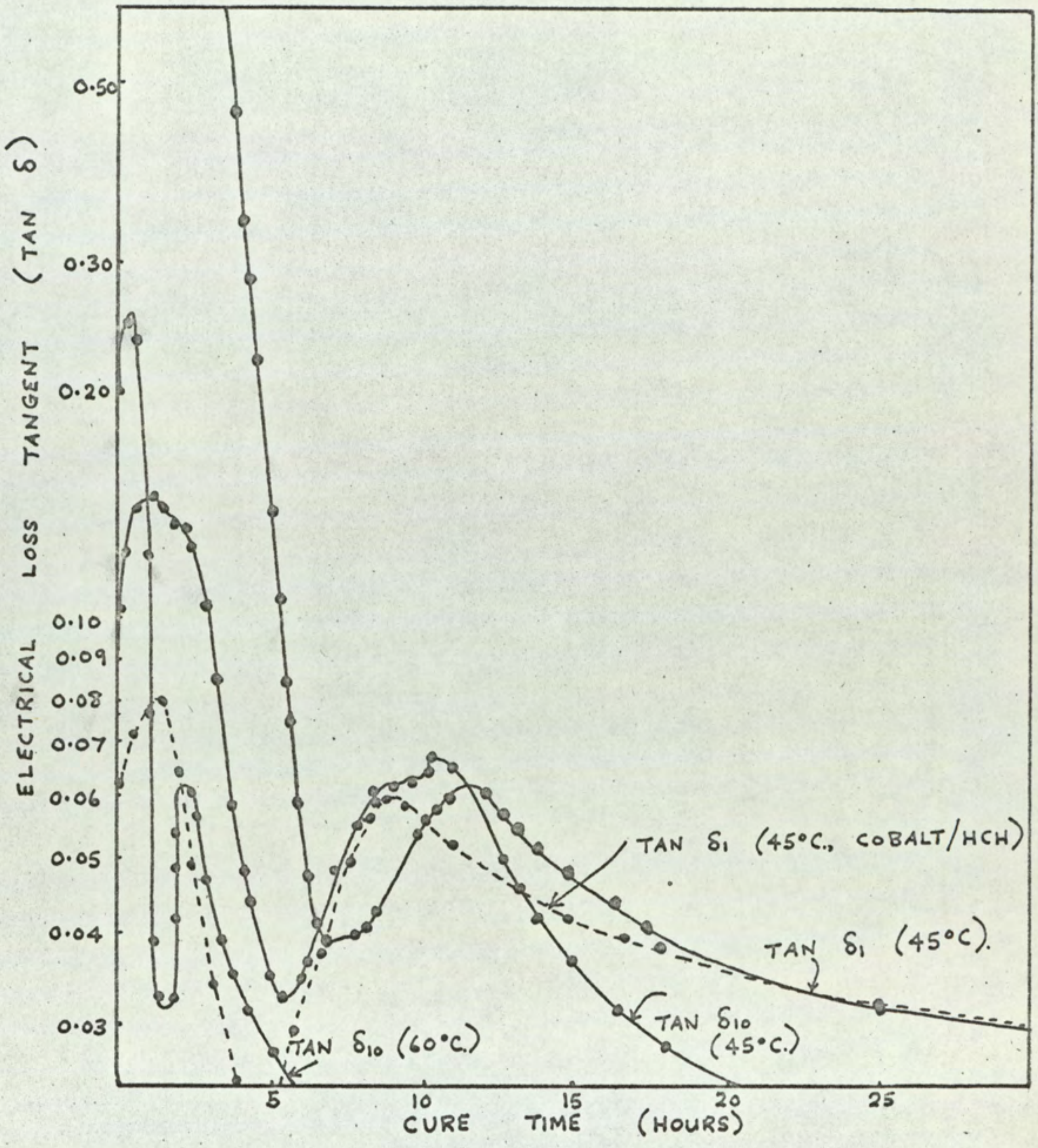


FIG. 19

EFFECT OF CURE TIME ON TAN δ

Thereafter there is still an increase in resistivity, but at a very much slower rate. This increase soon became imperceptible, at least with the apparatus available.

Ultimate values of ρ were higher for cures at low temperature than for cures at higher temperature, because the temperature dependence of the resistivity is negative. For this reason, Fava and Horsfield (1968) suggested that the quantity $kT\log\rho/\rho_0$ should be regarded as the cure parameter rather than $\log\rho$.

It is striking that the ultimate values of the resistivity were not nearly as great as those recorded by Warfield and Petree (1961) for Laminac 4116, which is identical to Beetle 4116 except for any differences which may exist between the manufacturing practices of B.I.P. Chemicals Limited and the American Cyanamid Company (both resins have identical formulations). They obtained values of the order of 10^{16} ohm-cm . at 60°C. These differences can be explained by any one of several variables affecting the resistivity of high polymers. These include the choice of initiating system, purity, freedom from moisture, number-average molecular weight, molecular weight distribution, and the proportion of unesterified phthalic anhydride and other starting materials.

One other factor is the rate of polymerization. This does not appear to have been fully investigated, but

Warfield and Petree (1961^2) believe that low rates of polymerization give low values of both resistivity and activation energy for the conduction process. On this basis, the 45°C. cure would be expected to give a low ultimate resistivity, but this would not apply to cures above 60°C.

It is rather more surprising that the second resin used, RT4, should have a volume resistivity in the same range as Beetle 4116, despite the possession of many more crosslinking sites (see table 6). This resin was never fully cured, because it had an extremely high T_g and in order to complete the cure, heating would be necessary up to temperatures which would have damaged the polymerization cell. This damage would interfere with readings. So this resin was not examined further.

The dielectric dissipation factor, or loss tangent, ($\tan \delta$), was measured at two frequencies; 1 kc/s and 10 kc/s, along with the dielectric constants. These terms will be distinguished by the symbols $\tan \delta_1$, $\tan \delta_{10}$, ϵ'_1, ϵ'_{10}. (See Figs. 19 and 18.)

The early stages of cure are marked by considerable frequency dependence of the loss tangent, the 1 kc/s reading being about a decade higher than the 10 kc/s one. Both then fall sharply to a minimum value, the lower frequency tangent reaching its minimum first. At this minimum, the ratio of the two was less than 2:1.

Both tangents then rose to a maximum, (approximately 0.060). It is probable that this maximum is associated with the transition from the rubbery to the glassy state. Such a transition would be frequency-dependent. It is significant that the volume resistivity shows a sudden fall-off in rate of reaction, corresponding with diffusion control of the propagation steps because of immobilization of the reacting chains, at about the time of the peak in tan δ_1, and just after the peak in tan δ_{10}. This is after about 12 or 13 hours at 45°C. The peaks in the loss tangent may be regarded as analogous to those found at the glass transition temperature when the loss tangent is measured as a function of temperature, and are of about the same magnitude.

The final values of tan δ were not determined, because excessive time would be used in waiting for the changes to become imperceptibly small. Tan δ_{10} approached 0.010 after 100 hours at 45°C. When most properties were no longer showing detectable changes, the dissipation factor (and, incidentally, its mechanical analogue) continued to decline.

One area could not be fully investigated; this was the behaviour of the electrical loss tangent in the very early stages of reaction. A peak appeared here also, just before the sudden decline to a minimum value (see Fig.19). Whether this peak was frequency-dependent, and what relationship it bore to the gel point, could not

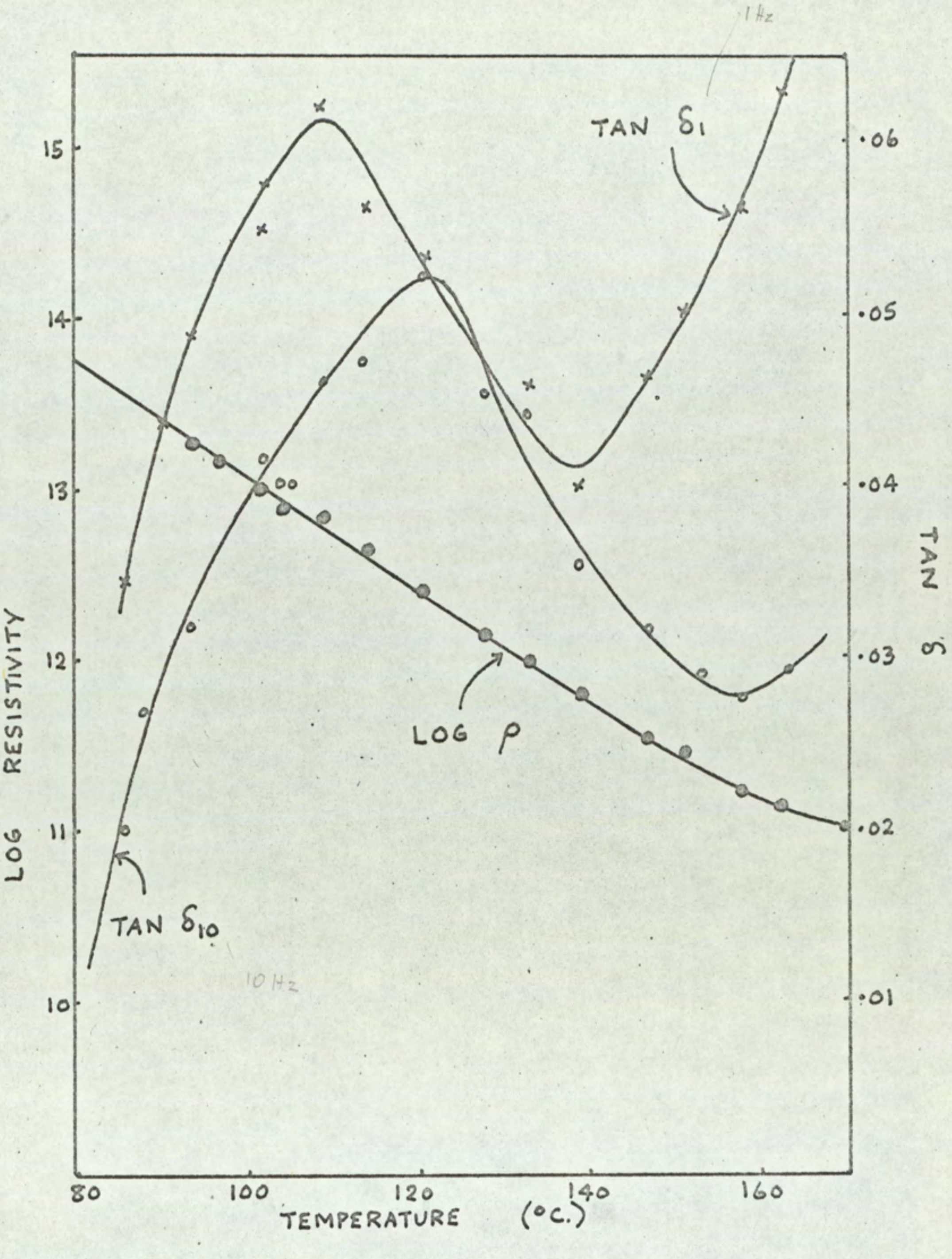


FIG. 20

LOG RESISTIVITY AND TAN δ AS A FUNCTION OF TEMPERATURE (BEETLE 4116, FULLY CURED) be ascertained because the effects of polymerization and rising temperature overlapped. In retrospect, a better measuring technique would have been developed if the polymerization cell had been suspended in a constant temperature silicone oil bath instead of an air oven. Whatever the heat conducting capability of the surrounding medium, however, liquid polyester resins have themselves very poor heat conducting qualities. Scarcely any reports on the electrical properties of curing resins claim to give real values of these properties in the first few minutes of cure at elevated temperatures, though this could be done for cure at room temperature under isothermal conditions.

The dielectric constants did not show such great changes in magnitude as most of the other properties measured. ϵ'_1 and ϵ'_{10} were closely similar to each other throughout cure, the latter being slightly lower. Curing at 45°C., the entire change in ϵ'_{10} was only from about 6.0 to 3.7.

Moreover, the changes which did occur were largely confined to the period before and around the transition to the glassy state. Fig.18 shows the dielectric constant falling a little at first, then going through a maximum, and falling precipitously towards its levelling-off value.

The terminal value for the dielectric constant in these circumstances is dependent on the degree of

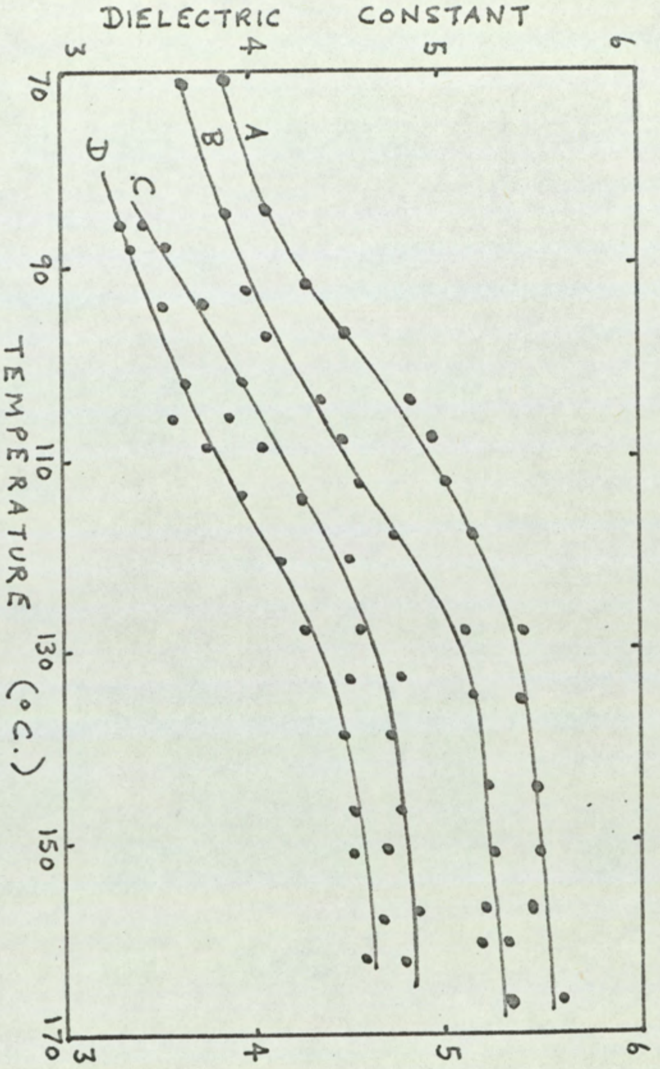


FIG. 21

DIELECTRIC CONSTANTS AS A FUNCTION OF TEMPERATURE (BEETLE 4116, FULLY CURED)

A, 30 % STYRENE, 1 kc/s
B, 30 % STYRENE, 10 kc/s
C, 38.7 % STYRENE, 1 kc/s
D, 38.7 % STYRENE, 10 kc/s

crosslinking attained at the end of the cure, and also on the temperature at which it is measured, i.e. the cure temperature. High degrees of crosslinking give low dielectric constants, but are achieved more readily at higher temperatures which themselves favour lower dielectric constants. Thus these two factors compete, and this may explain why the terminal values of ϵ' are not found to be in the same order as the cure temperatures. It is probable that a much higher degree of crosslinking is reached at 60° and 70°C. than at 45° and 55°C., even though the temperature difference is quite small, because of the more ready decomposition of the benzoyl peroxide.

Some cures involving departures from the standard system were carried out. The cobalt/HCH initiated polymerization underwent a greater total change in dielectric constant (Table 8) than did the benzoyl peroxide/amine system at the same temperature (Table 3). No difference was observed between the two systems in the ultimate values of the resistivity but the total change in ρ was actually less for the cobalt system.

RT4 has different polar groups (more fumarate, and isophthalate instead of orthophthalate). This resin had a lower dielectric constant than 4116 throughout cure (Table 6). The effect of decreasing the styrene content from 38.7 to 30% is to increase the dielectric constant, but the total fall in ϵ' remains the same. The relationship between the styrene content and ϵ' is

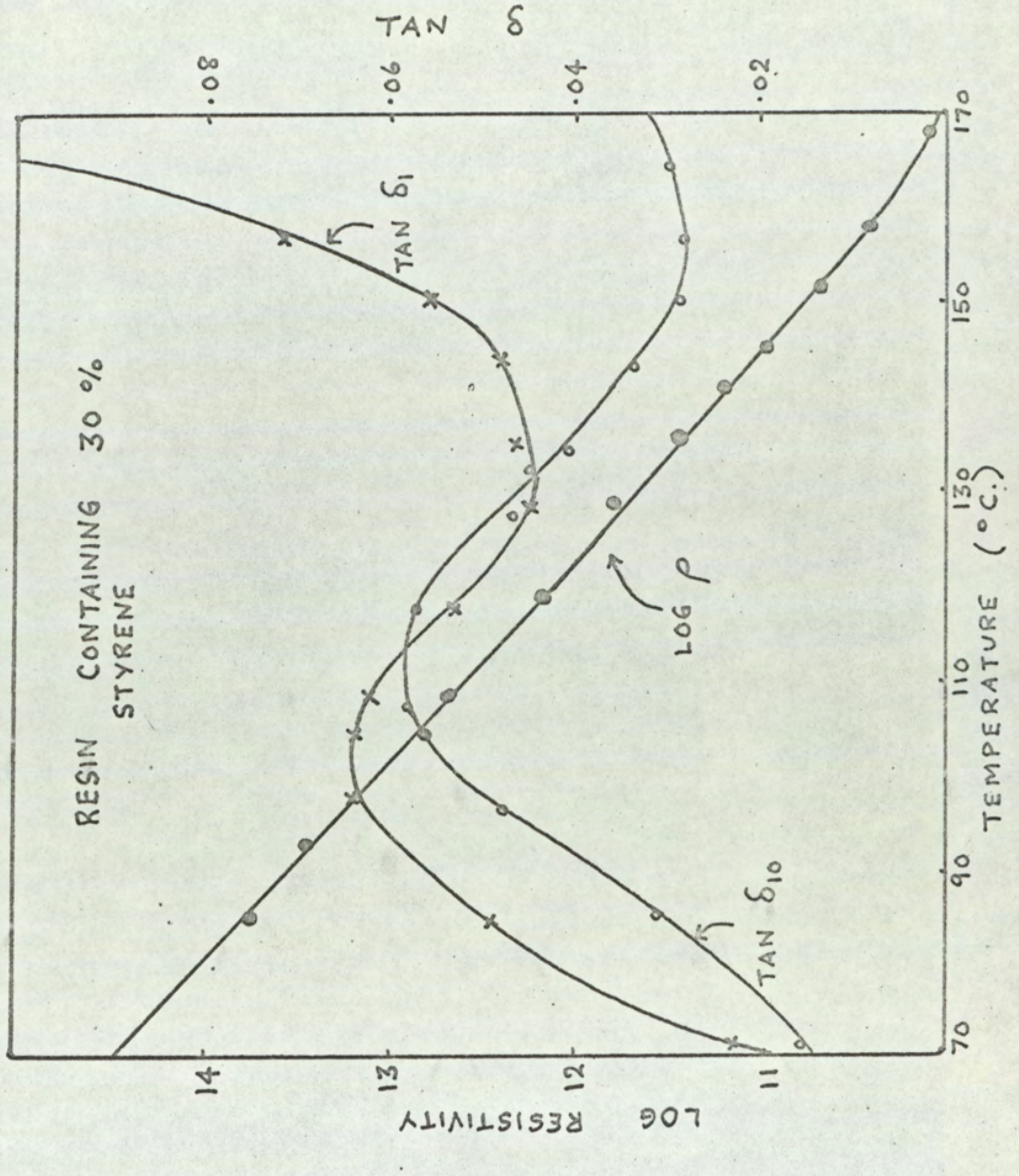


FIG. 22

LOG RESISTIVITY AND TAN δ AS A FUNCTION OF TEMPERATURE (BEETLE 4116, FULLY CURED: STYRENE LEVEL LOWERED TO 30%)

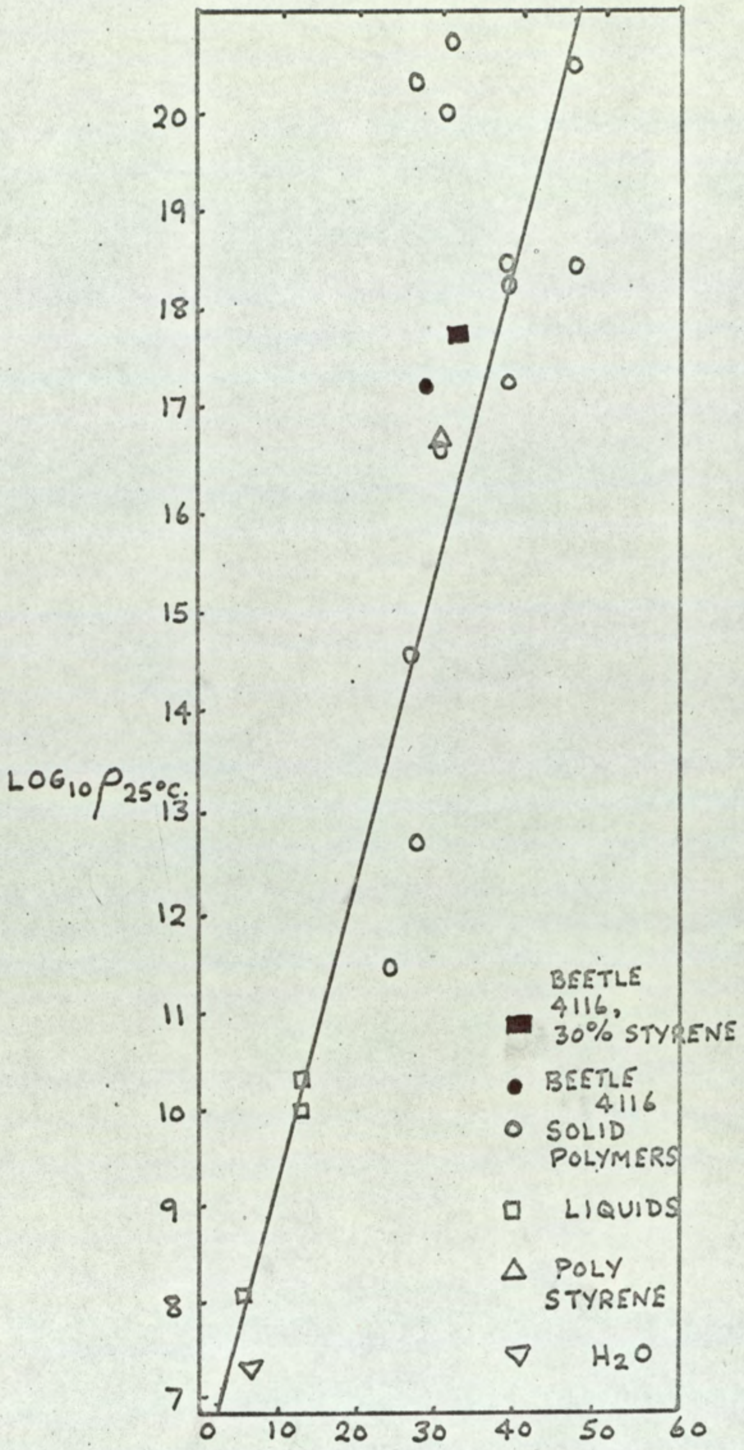
not straightforward and is believed to change as the styrene proportion increases (Tucker and Hastings, 1962).

The measurement of electrical properties as cure parameters seems worthy of further consideration, but is clearly not without serious difficulties. Unlike many tests, these are rapid and can be applied continuously throughout cure. They detect not only undercure but many other anomalous situations such as variations in temperature, mixing conditions and purity. Volume resistivity changes over many decades in the cure of a typical polyester resin. It also levels off rather suddenly and earlier than the loss tangent, but there is some uncertainty whether this would still be so if a more sensitive means of measuring high resistivities were to be used. The agreement between runs was found here to be very much better than expected, perhaps because the hydrophobic styrene monomer prevented much moisture variation.

The electrical dissipation factor could not be measured so accurately as the other properties, but its behaviour during cure was quite regular and smooth curves were obtained.

Any process control test based on electrical property measurement would require excellent temperature control and thorough cleansing and drying procedures. The effect of the presence of glass reinforcement, fillers, other additives and consequent inhomogeneities and voids is such that any use of electrical resistivity measurements

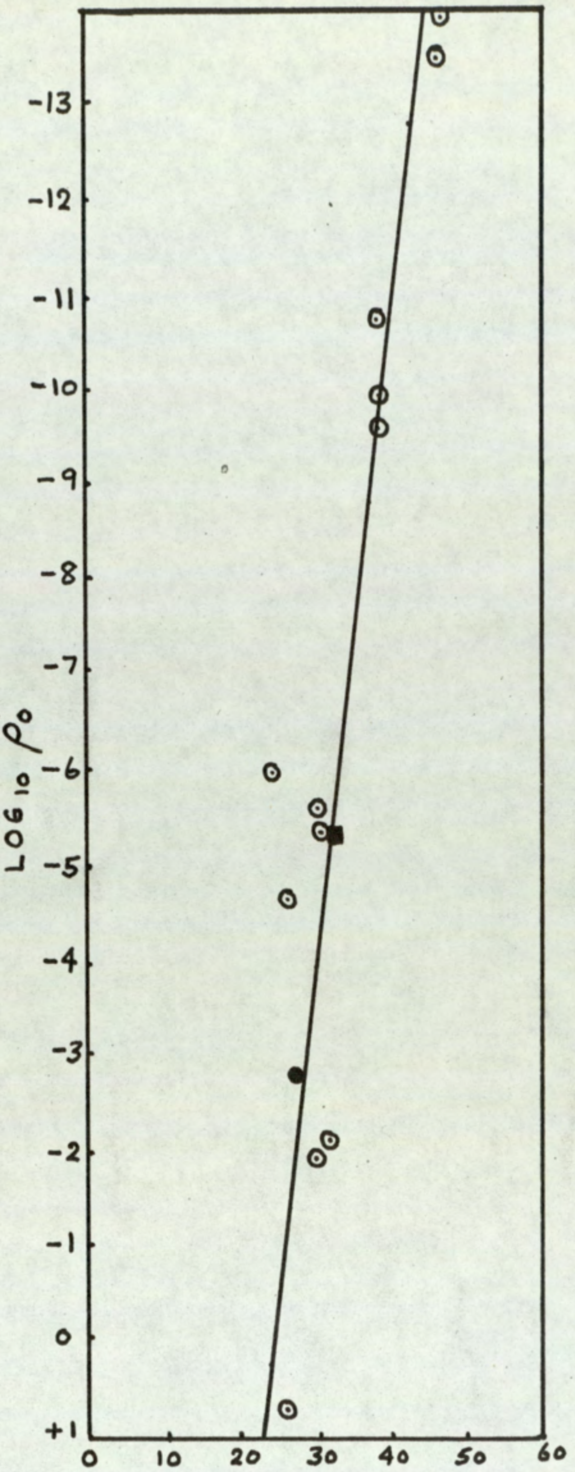
FIG. 23



RELATIONSHIP BETWEEN LOG$_{10}$ $\rho_{25°C}$ AND Ec FOR VARIOUS MATERIALS, INCLUDING FULLY CURED SAMPLES OF BEETLE 4116. (WARFIELD AND PETREE, 1962.)

FIG. 24

RELATIONSHIP BETWEEN $\mathrm{LOG}_{10}\ \rho_o'$ AND Ec FOR VARIOUS MATERIALS, INCLUDING FULLY CURED SAMPLES OF BEETLE 4116. (WARFIELD AND PETREE, 1962.)



on curing composites would be necessarily difficult.

The electrical properties of the cured resin are shown in Figs. 20 and 21. The corresponding results for a resin sample containing 30% styrene are shown in Figs. 21 and 22. The data is recorded in Tables 12 and 13.

Resin samples cured at 60°C. for 8 hours, 100°C. for 24 hours and 130°C. for six hours did not give reproducible plots of log resistivity against temperature. The resistivity continued to rise slowly until the temperature was held at 165°C. for 4 days. After this a very slight increase was halted, and the resistivity became constant. Whether this period would have been followed eventually by a decline (as some properties such as flexural modulus frequently are after heat-ageing) was not determined. Sturman (1968) reports that dough moulding compounds containing about 25% of polyester resin continue to increase their insulation resistance during degradation until most or all of the resin has been destroyed or volatilized. This increase is, however, caused by the presence of other materials besides resin. It is very probable that degrading polyester resins, in the absence of glass and other filling materials, show a decline in resistivity until eventually the electrical properties resemble those of carbon. It is somewhat surprising that Beetle 4116, not being a resin of particular heat stability, should withstand 165°C. for several days. The reason is probably that the tests were carried out in almost complete absence of oxygen; the cells had no outlet to the atmosphere except a narrow slit sealed with adhesive PVC tape. (The tape very slowly degraded.) It is interesting that Ebers and co-workers (1950) subjected some polyester laminates to 260°C. for 5 hours and found 29% decrease in weight in air, but no decrease in weight at all in sealed tubes. Wright and Blythe (1957) found that the flexural strength of some polyester laminates was still increasing even after 100 hours at 150°C. Part of the increase in strength (and in resistivity) is probably due to removal of volatiles and it is difficult to separate effects due to this from those due to postcure and from heat ageing.

After the resistivity became constant and plots of log ρ against T became fairly reproducible, the curves in Figs. 20 - 22 were obtained. The position of the glass transition kink in the resistivity-temperature line was not easy to detect, and the choice of 130°C. as a likely figure is somewhat tentative. It compares with 126°C. reported by Warfield and Petree (1963) for a similar polyester. The resin containing 30% styrene seemed to have a T_g in the region of 125°C.

E_c was found to be 27.5 kcals/mole for the standard resin system, and 31.2 kcals/mole for the one containing 30% styrene. Even the latter figure is only two thirds of that reported by Warfield and Petree (1961^1) for Laminac 4116, and seems low in view of the theoretical conclusion of Taylor (1961) that E_c must normally be higher than 25 kcals/mole for any dry amorphous substance. In other respects, however, the results obtained here agree well with some of the conclusions of Warfield and Petree (1962). They discuss the existence of a compensation law, analogous to that relating the frequency factor A and the energy of activation in chemical reaction kinetics. They postulate a similar, universal law such that E_c is linearly related to the constant ρ'_o in the equation:

$$\rho = \rho'_o \, e^{E_c/RT}$$

$$\text{i.e. } \log_e \rho = \log_e \rho'_o + E_c/RT \ \ldots\ldots\ldots\ldots \quad (11.1)$$

Also, E_c is linearly related to the logarithm of the resistivity at a reference temperature, e.g., 25°C.

It has been found here that for Beetle 4116, $\log_{10} \rho'_o = -2.8$ and $\log_{10} \rho_{25^\circ C} = +17.2$. The same resin containing 30% styrene had $\log_{10} \rho'_o = -5.3$ and $\log_{10} \rho_{25^\circ C.} = +17.7$. Fig.23 shows that the figures for $\log_{10} \rho_{25^\circ C.}$ lie as near to the straight line drawn by Warfield and Petree as do many of the points they insert themselves representing polymers, copolymers, organic liquids and water. Moreover, in Fig.24 the two values of $\log_{10} \rho'_o$ lie on the line itself. The original authors of these diagrams regard the position of a polymer on these lines as an indication of its microviscosity, which increases with high E_c and low $\log_{10} \rho'_o$ values.

The slow polymerization rate may have contributed to the low values of E_c by giving comparatively uniform crosslinking without the formation of micelles.

Dielectric constants increase gradually over a temperature range in the region of the glass transition temperature (Fig.21). At the higher temperature end of the measuring range, a fall is to be expected because of the effect of increased thermal agitation on the orientation of polar groups.

The electrical dissipation factor shows a peak in the region of the T_g, and a second rise at higher temperatures (160 - 170°C). The second rise is commonly attributed to ionic conductance (Sutherland and Funt, 1953). The tan δ_{10} peak is both later and lower than that for tan δ_1, and the rise due to conductance also sets in later at higher frequencies.

Similar measurements were made on resin RT4, but no peak in tan δ was found until 150°C. This resin had a structure calculated to give a very high softening point. It was not fully cured, and this information is not therefore included here. The temperature range covered for the resin (in a slightly undercured state) was 70°C. to 170°C. Such data as was obtained suggested that the ultimate values of the resistivity and of E_c would probably be appreciably higher than for 4116, but not to the extent expected.

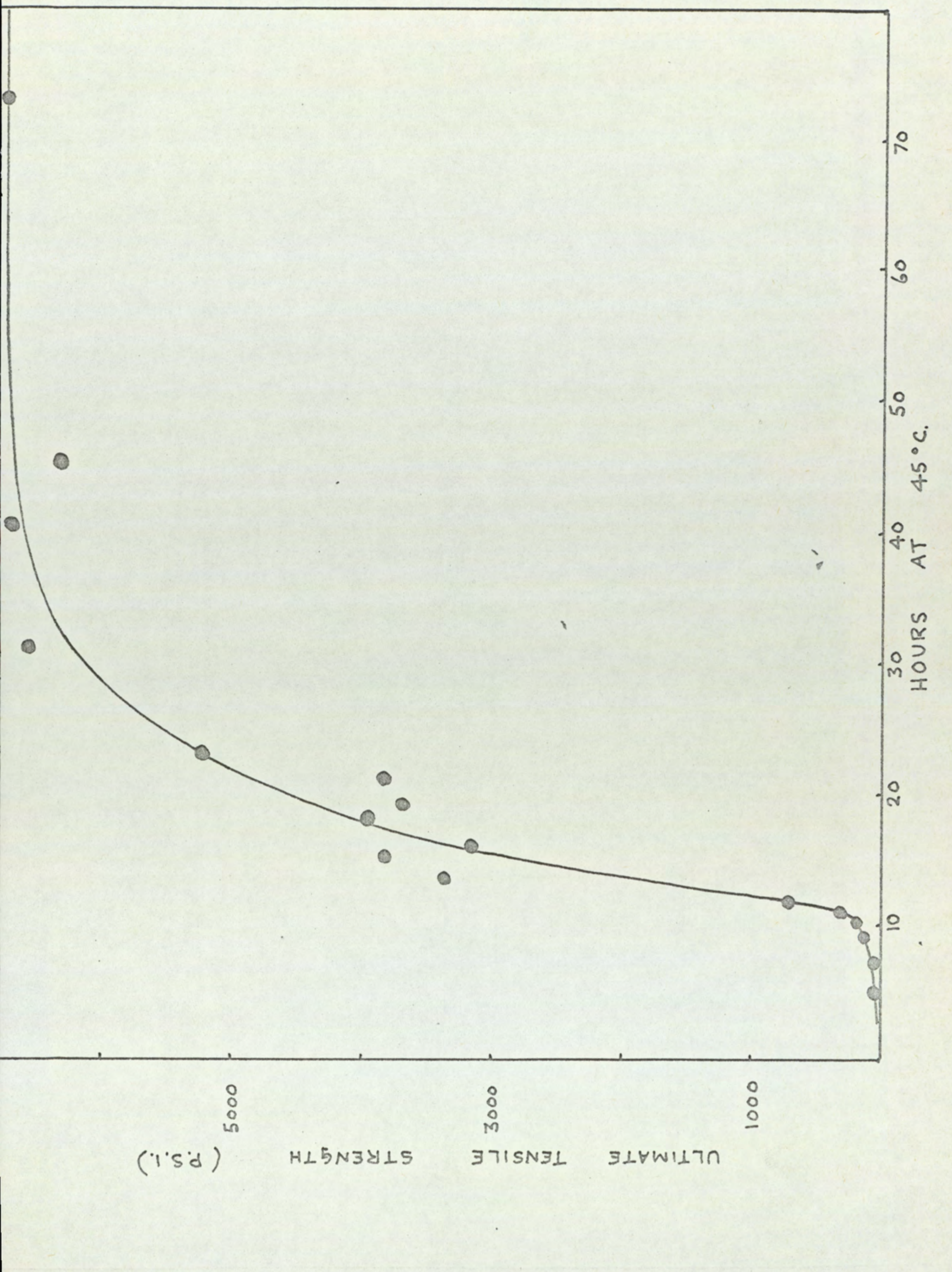
The "ultimate" values of log resistivity at various temperatures, calculated from equation 11.1, are compared below with those actually obtained by curing at these temperatures until levelling off occurred. The "levelling-off" values are those which are found by continuing measurements until the changes become very small, but undoubtedly these values would be further increased slightly by prolonged curing for several days or weeks at the temperature concerned.

TABLE 31

Cure temperature °C.	log ρ (from equation 11.1)	log ρ actually reached
45	16.1	13.5
55	15.6	13.0
60	15.3	12.9
70	14.8	12.8

Thus the degree of cure reached even at 70°C. is much lower than that likely to be reached after postcuring above 100°C. Other properties which were measured (and are discussed later) also suggest that the degree of cure obtained without postcure is very much lower than that actually possible.

FIG. 25 EFFECT OF CURE TIME ON TENSILE STRENGTH



11.3 Mechanical experiments

These consisted of: torsional pendulum studies over most of the post-gelation period; resonant rod experiments over the same range; tensile tests over a similar range of crosslinking, and crossbreaking strength tests, which were abandoned.

Dynamic mechanical testing, like a.c. dielectric testing, is usually carried out over a temperature or a frequency range. For various reasons, it is often found inconvenient to do this in mechanical testing on curing resins. A single test at a single frequency and test temperature is therefore carried out at various cure times (Imai, 1967[1]); (Lewis and Gillham, 1963); (Jenkins and Karre, 1966). This method was adopted here.

The two dynamic tests used do not duplicate one another. One involves free vibrations at low frequency, in shear; the other is a forced-vibration, resonant, audiofrequency technique involving submission of the specimen alternately to tension and compression. The two storage moduli found by these machines are G' (shear) and E' (tension) and the respective logarithmic decrements are termed here Δ_g and Δ_E.

Specimen preparation was identical in the two techniques. In a few cases, identical specimens were used for both techniques. Certain differences in the conditions of test should be noted. The Dawe instrument generated vibrations of very small amplitude; the torsional pendulum oscillations were comparatively large. The latter measurements extended over the decade from 0.4 to 4 c/s approximately; but the resonant rod measurements were over a range from about 3.6 to 7 kc/s.

All mechanical properties show a very great change in the region where measurement first becomes practicable, and this is particularly marked in the tensile strength graph (Fig.25) which begins at 5 hours cure time. Fig. 26 shows a very considerable increase in G' between 8 and 11 hours; below 8 hours, the moduli have to be regarded with caution, because the damping is so high that measurement of both properties is difficult, and in any case equation (6.5) is no longer valid at such high values of Δ_g.

The later stages of cure are indicated by the levelling out of the sigmoid curves for G' and E' and also for tensile strength (Figs. 27, 29 and 25). The last-named becomes more uncertain in the latter stages because embrittlement causes many unusually low readings and apparently premature failures. This is most noticeable after more than 60 hours. Tensile results were, however, very much more consistent than crossbreaking strength tests, which were eventually abandoned. The only definite conclusion from these was that the specimens first became stiff enough to break in this flexural test at about 45 hours cure time.

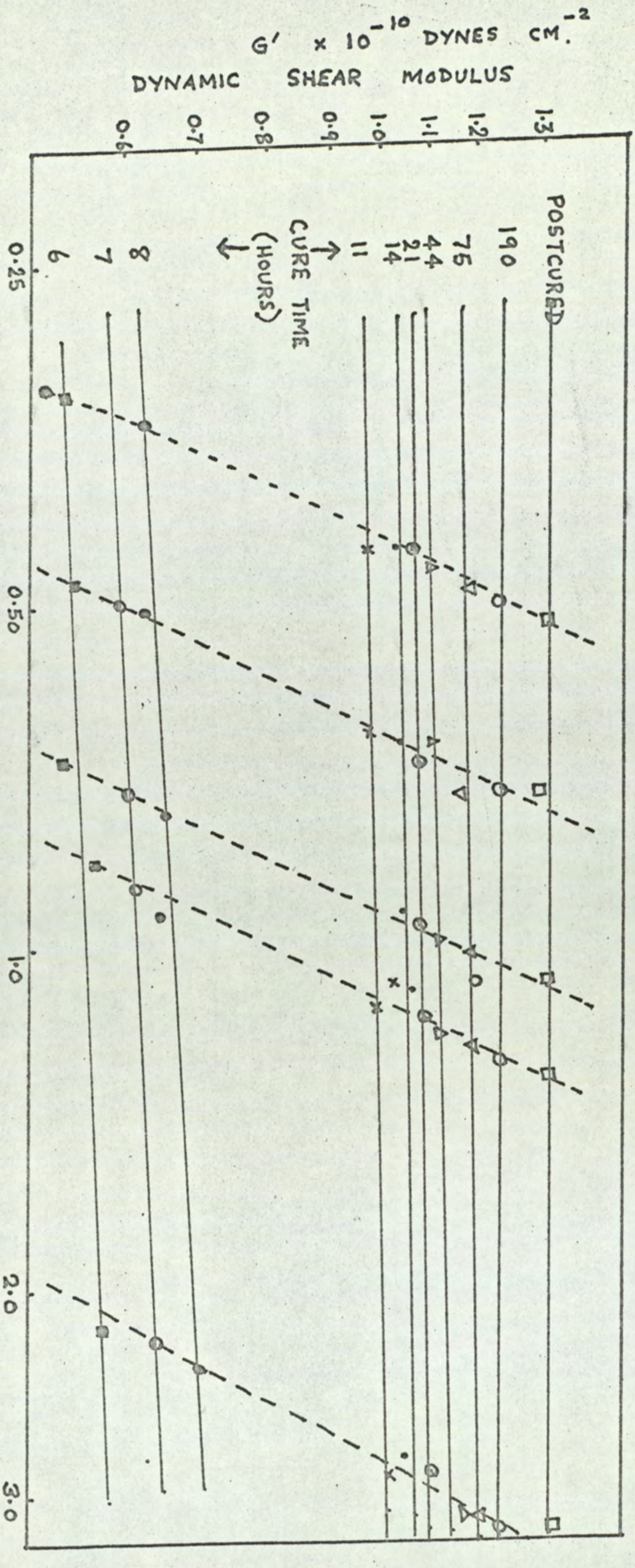


FIG. 26

DYNAMIC SHEAR MODULUS AS A FUNCTION OF FREQUENCY AT VARIOUS CURE TIMES. POSTCURED SPECIMEN HEATED FOR 3 HOURS AT 80°C AFTER 100 HOURS AT 45°C.

Both Fig. 26 and Fig. 28 imply frequency dependent properties for undercured resins, but frequency-independent properties for cured ones. There is some difficulty in drawing firm conclusions about this dependence without a larger frequency range being used. It does appear, however, in all the present work and in that of Reinhardt (1965), that the modulus G' increases slightly with frequency and the logarithmic decrement goes down. Fig. 26 is a logarithmic plot, and because

$$G' = \text{constant x } \frac{IL}{d^4 P^2} = \text{constant x } \frac{ILf^2}{d^4} \quad .... \quad (11.2)$$

then

$$\log G' = \text{intercept} + 2 \log f \quad .... \quad (11.2a)$$

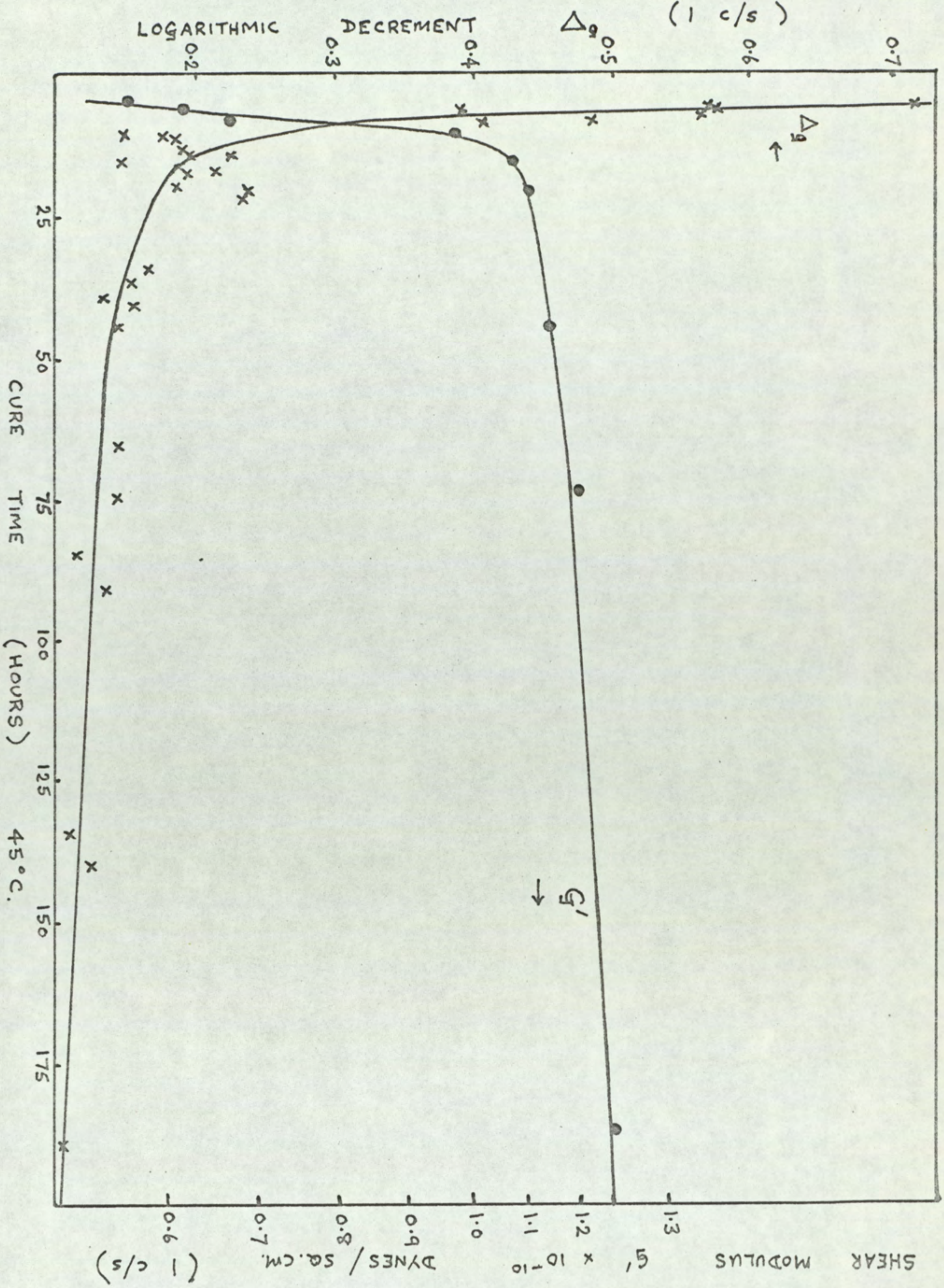
for specimens of fixed dimensions and at constant I. Table 32 gives the slopes of the dotted lines in the figure; the average is 2.05.

TABLE 32

Moment of Inertia (gm. cm.^{2})	Slope
$I_1 = 1.65 \times 10^6$	2.09
$I_2 = 5.31 \times 10^5$	2.12
$I_3 = 2.54 \times 10^5$	2.11
$I_4 = 1.78 \times 10^5$	2.06
$I_5 = 2.88 \times 10^4$	1.89

Imai (1967^1) found that the storage modulus E' began to level off while the changes in the loss modulus G" were still quite considerable. The results here suggest that

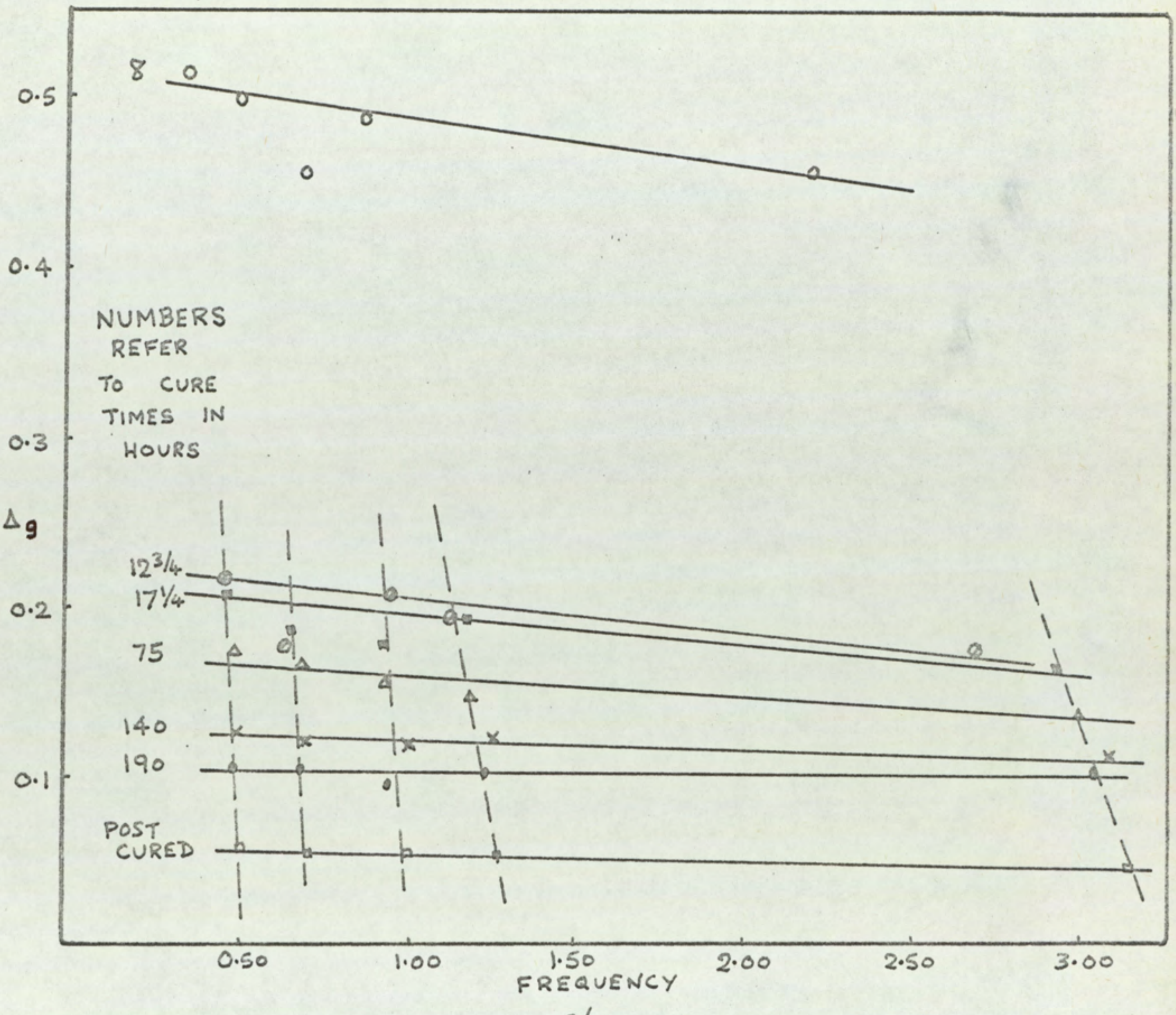
FIG. 27



EFFECT OF CURE TIME ON DYNAMIC SHEAR MODULUS AND LOGARITHMIC DECREMENT the changes in E' became almost undetectable while the decrease in Δ_E was still being observed (Fig.29) but this was not so in the shear experiments, both modulus and damping continuing to change throughout the measuring time. It was found, however, that raising the cure temperature had a greater effect on the logarithmic decrement than on the modulus (see Table 30).

For reasons stated in the experimental section, more values of Δ_g than of G' were recorded. The reason for a considerable scatter in decrement readings at a particular stage of cure is probably a combination of two factors. One is the special difficulty and inaccuracy involved in using the recording system with which the Nonius pendulum was fitted, particularly for measuring decrements at the high frequency side. This has now been recognized (Nederveen and van der Wal, 1967), and the reproducibility reported by this author elsewhere could probably be improved with a better recording system. (Learmonth, Pritchard and Reinhardt, 1968). (The average mean deviation found was 2% for measurements of the shear modulus after 24 hours cure time, and 5% for the decrement.) The second reason is that small differences in the very low activator concentration, and variability in the distribution of the benzoyl peroxide initiator, cause slight variations in reaction rate from run to run and also, within a given run, for different specimens. This would be likely to show its effect most clearly at the

FIG. 28



LOGARITHMIC DECREMENT, MEASURED USING A TORSIONAL PENDULUM, AS A FUNCTION OF FREQUENCY AT VARIOUS CURE TIMES. POSTCURED SPECIMEN HEATED FOR 3 HOURS AT 80°C AFTER 100 HOURS AT 45°C.

point where the decrement curve changes direction. Completely homogeneous dispersion of initiator and accelerator is difficult to achieve. The decrement Δ_E is similarly affected, and in both cases readings were not usually taken on the same specimen twice, but where techniques lend themselves to continuous monitoring on the same specimen throughout (e.g. refractive index, resistivity, infrared absorption) this problem is not met.

The possibility that this scatter is caused not by the factors mentioned, but by the existence of a small loss peak, such as that reported by Lewis (1963) in his work on epoxide-coated braids, has not been entirely discounted. The peaks he found were, however, associated with particular functional groups present in the epoxide curing reaction. Further work would establish whether this subsidiary peak exists, but in any case it must be small. (Reference to this peak as subsidiary presumes that the initial decline in the decrements is the second half of a large peak occurring in the 3 to 6 hours cure region.)

Δ_g and Δ_E follow closely similar paths despite the difference of between 3 and 4 decades in frequency. This frequency difference must, however, be the reason why the two moduli invariably differ by more than a factor of 3. (Assuming the maximum value for Poisson's ratio, $E' = 3G'$ for measurements at the same frequency and temperature.) In practice, in the latter stages of cure, $E' = 4G'$ approximately.

Fig.29 also shows the change in the velocity of sound through the resin at various cure times. For a material of attenuation α (nepers cm.) the velocity of sound v cm/sec. at a frequency $\omega = 2\pi f$ is given by the relationship

$$E' = d\,\omega^2 v^2 (\omega^2 - \alpha^2 v^2) / \omega^2 + \alpha^2 v^2)^2 \quad \ldots\ldots \quad (11.3)$$

(Nielsen, 1962.)

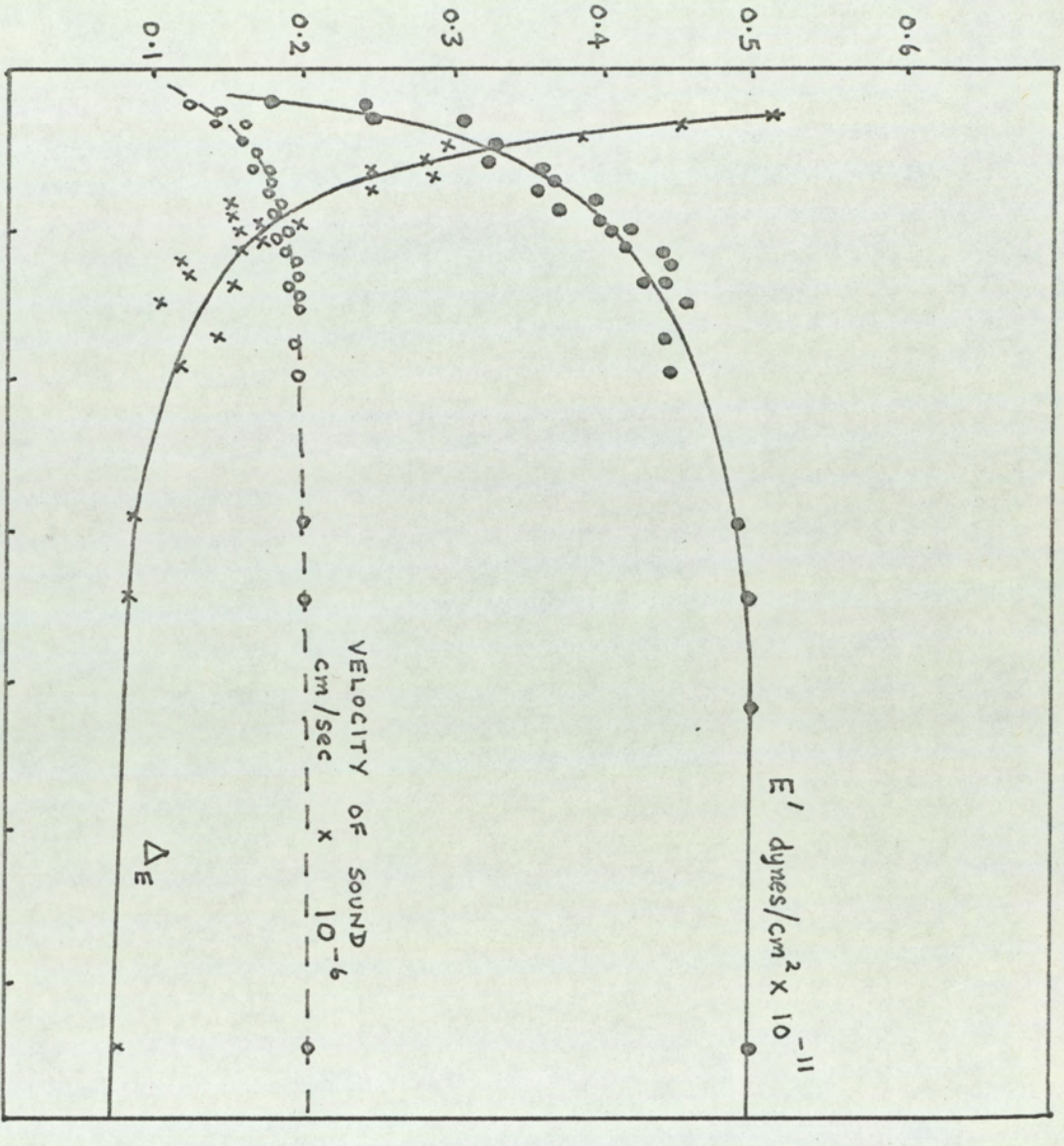
At low values of α, this reduces to

$$E' = d\,v^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11.4)$$

so the velocity of sound in the rod specimens undergoes the same kind of change as does the Young's modulus, but the increase is less apparent. It is probably better, for the determination of the cure of resins by measurement of the velocity of sound, to use the straightforward method of timing the passage of a bulk wave through the medium, using the method reported by Sofer, Dietz and Hauser (1953). This technique has the advantage over the audiofrequency resonance method, of being readily applicable throughout both the liquid and the post-gelation stages. It does have the disadvantage, however, of giving the modulus as the compound term $K' + 4/3\ G'$, K' being the bulk modulus, so that in order to determine either K' or G' separately a fresh

FIG. 29

EFFECT OF CURE TIME ON YOUNG'S MODULUS, LOGARITHMIC DECREMENT AND VELOCITY OF SOUND, AS MEASURED BY RESONANT ROD.

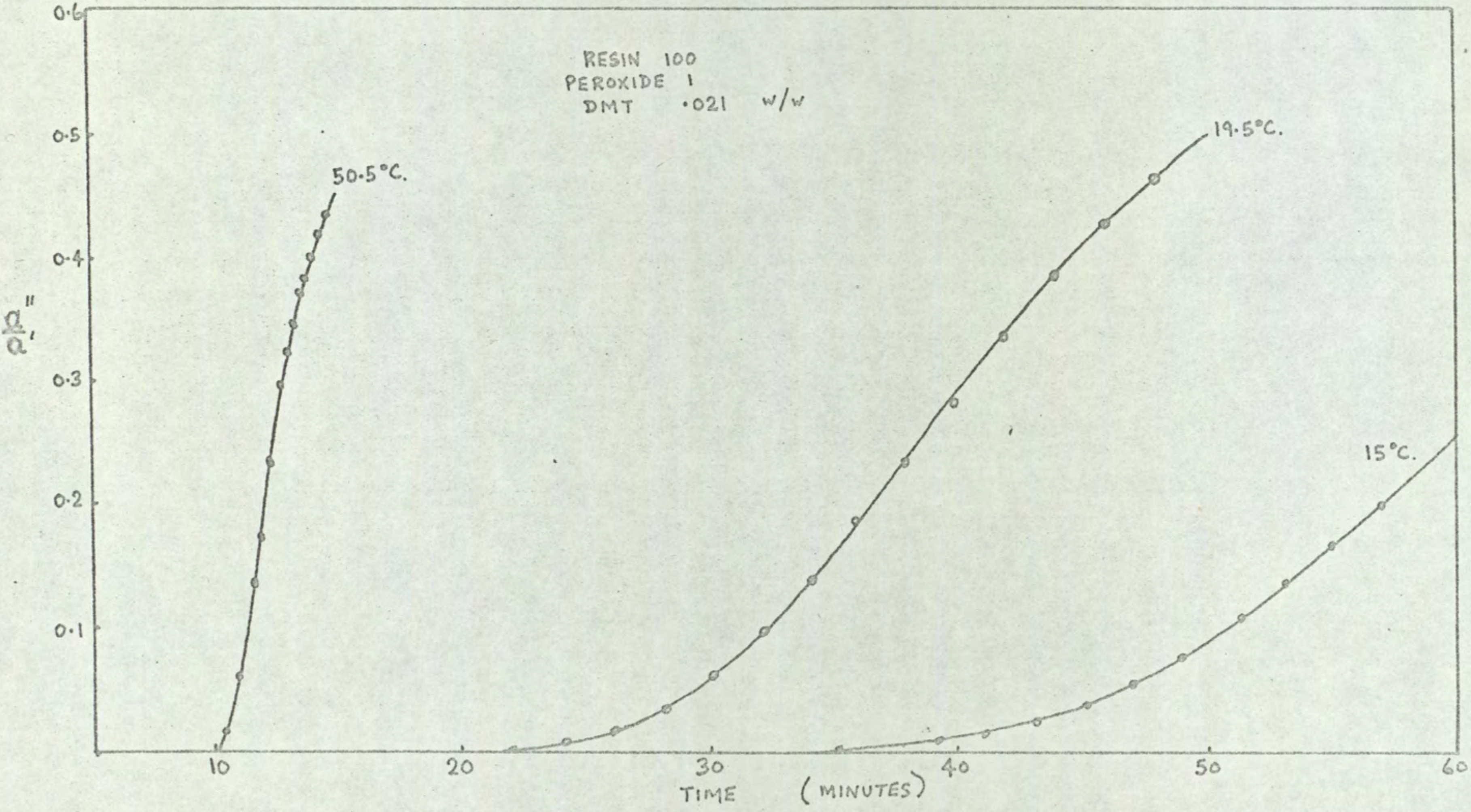


estimation of the other one must be made. The method described was applied by Sofer and Hauser (1952) to the cure of Laminac 4116 using a frequency of 2.3 Mc/s, and they obtained a value for the velocity of sound of 2.39 x 10^5 cm/second at the stage when the curing reaction appeared to have levelled off. This compares with about 2.05 x 10^5 cm/second for Beetle 4116 in the present experiments.

Both the torsional pendulum and the Dawe machine are clearly sensitive to changes in the crosslinking density of resins. Unfortunately the difficulty of using either of them, and particularly the latter, in studying glass reinforced polyesters is very great. Voids and inhomogeneities have a marked effect on the longitudinal waves generated in the specimen by the resonant method. It is probable that the torsional pendulum does not give such great problems, but this too would be better confined to the study of unreinforced resins. Neither machine, used here, gives information on the early stages of cure, but both could be adapted to do so; the torsional pendulum could be converted to a braid, and in the other case the resin could be cured in a metal tube and the whole tube and contents subjected to longitudinal vibrations.

The Weissenberg rheogoniometer is much better suited to a study of the early stages of cure, particularly before gelation and immediately after, but for reasons given by Dominic (1967) it is less reliable in the later

FIG. 30 CHANGE IN DYNAMIC PROPERTIES OF BEETLE 4116 DURING THE EARLY STAGES OF CURE, AS MEASURED BY DOMINIC (1967) USING A FAROL-WEISSENBERG RHEOGONIOMETER.



stages. Some typical results obtained by Dominic are given in Fig.30. He used the same resin, the same concentration of benzoyl peroxide, and three times as much amine as in the standard system described previously. The ordinate in Fig.30 is a"/a', and a", a' refer to the maximum amplitudes of displacement of the plate and cone of the viscometer, in radians. The term a"/a' is related to the dynamic shear modulus (Maxwell model) γ_M by

$$\gamma_M = \frac{a''}{a'} \cdot \frac{3dC_3\alpha(K - I\omega^2)\cos(\phi + C_4 - C_2)}{2\pi r^3 C_1} \quad \ldots\ldots (11.5)$$

(Weissenberg, 1964.)

C_1, C_2, C_3, C_4, are correction terms involving a"/a', and the other terms refer to the geometry and the inertia constants of the rheogoniometer (see list of symbols in the Appendix).

It was found that the modulus γ_M became measurable in the region of the gelation point. Recently Yip, in an extension of this work, found the dynamic shear modulus at gelation to be 2.5×10^4 dynes/sq.cm.

It is not possible to correlate the values of these moduli, determined by Dominic and Yip, with the extent of crosslinking, using the equations of rubberlike elasticity. The difference in the accelerator concentration means that reaction rates were quite different in the I.R. cell to those in the rheogoniometer. Equations applicable to rubberlike substances, such as

$$G' = \frac{dRT}{Mc}\left(1 - \frac{2Mc}{Mn}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11.6)$$

(Mc = molecular weight between two crosslinks)

have however been applied to fully crosslinked polyester resins above their T_g by Katz and Tobolsky (1964) who found that the agreement in practice was surprisingly good.

11.4 Chemical, spectroscopic and refractometric experiments

In view of the considerable work reported by Funke and co-workers on the estimation of the extent of reaction of styrene and fumarate groups in crosslinked polyesters by degradative hydrolysis (Hamann, Funke and Gilch, 1959; Funke, Knodler and Feinauer, 1961; Funke and Hamann, 1962) the use of alternative methods here should be justified.

The reasons why an I.R. spectroscopic method was preferred are, first that there is some doubt, already mentioned, whether the hydrolysis procedure always gives complete quantitative yield of the desired hydrolysis product (Alekseyeva, Semerneva and Spasskii, 1963); secondly, the hydrolysis method is comparatively time-consuming and is not so suitable for development as a test method for the continuous study of entire curing reactions as is an instrumental method.

Thin films cast between rock salt plates can be investigated at various reaction times, without lengthy hydrolysis reactions and subsequent separation procedures. This method of calculation of the % residual unsaturation is given on page 120.

An important advantage of this method is that there is no need to carry out a prior separation of unreacted material from the copolymer formed. Such a separation is not merely time-consuming, but in practice extremely difficult to carry out satisfactorily (Gordon, Grieveson and McMillan, 1955).

The accuracy with which f is determined is less than that for s, since while s depends only on r_1, f depends both on r_1 and r_2. The results obtained are given in tables 18 and 19, and in fig. 31.

It can be seen from this data that the residual styrene after curing at 45°C for 80 hours is still 11%, although the proportion continues to fall beyond the time for which measurements were made. About 30% of the fumarate remains unreacted, and this does not appear to be changed by the last few hours of cure. Carrying out the reaction at a higher temperature, e.g., 70°C., a much higher proportion of the fumarate sites is used up. The styrene is also more fully reacted. Most of the fumarate reaction occurs comparatively early in the crosslinking process, and the later stages of cure involve mainly styrene. This conclusion was also drawn by Imai (1967^2). The following table shows the increase in the ratio of reacted styrene to fumarate at various cure times:

TABLE 33

Cure time (hours)	Temp. (°C.)	Mole ratio Styrene : fumarate
5	45	2.95
$7\frac{1}{2}$	45	3.55
10	45	4.10
40	45	4.38
70	45	4.40
0.5	70	3.19
1	70	3.20
3	70	3.34
5	70	3.36

The initial molar feed ratio was 3.46: 1 (styrene in excess).

First-order type plots of the reacted styrene for these cures were drawn. These were approximately linear for a short period after gelation, and gave rate constants (k) which were proportional to the resistivity rate expressions. They were also approximately equal to the refractometric rate terms (k_r):

$$k_r = k = 0.28 \left(\frac{d\log\rho}{dt}\right)_{\max.} \quad \text{..........} \quad (11.7)$$

(see Table 29 and Fig.33.)

Styrene bridges of between two and three styrene units initially, and perhaps more than three later, seem to be indicated by the styrene : fumarate ratio, unless very long styrene "loose ends" form. The ratios obtained here from the 45°C. cure agree qualitatively with those reported by Hamann, Funke and Gilch (1959). They always found that the final ratio was decidedly higher than the initial one. In the case of a resin with an initial molar ratio of 3.08 : 1, these workers found a final ratio of 5.35: 1.

Clearly the ratio found depends on the conditions of cure. If the resins are heated above their T_g and the fumarate sites are freed to react instead of being frozen, then the ratio is lower than otherwise.

The determination of styrene by infrared spectroscopy was compared with the results of direct volatilization. It was not regarded as certain that the volatilization method would give a quantitative assessment of residual styrene, but it should if the following four conditions hold.

(1) That no further cure takes place during volatilization
(2) That no degradation occurs during volatilization
(3) That styrene is the only volatile material present in partially crosslinked resins, or if not, that the quantity of other volatile materials is known.
(4) That no styrene dimer, trimer, etc., is formed which is involatile.

Condition (1) is fulfilled if the polymerization reaction is stopped by the addition of a chloroform solution of 2,2' diphenyl 1-picryl hydrazyl. The powdered resin is soaked in this chain stopping reagent for several hours.

Condition (2) is justified because at 140°C., although long term degradation may take place over several weeks or months, the weight loss is extremely small over a period of days. If this were not so it would be impossible to obtain a condition of constant weight after volatilization. Weight loss up to 0.02% per day was sometimes found and this was neglected as quite insignificant.

Assumptions (3) and (4) are not strictly true, because some free phthalate (unesterified) and some dimeric styrene are generally believed to be present in polyester resins. The quantity of free phthalate or other unesterified acid may be assessed very approximately by consideration of the fraction p of esterified acid groups. This is found from the number-average molecular weight to be about 0.95. The remaining 5% unesterified acid groups do not all belong to unesterified molecules of phthalate and fumarate, since some are attached to the ends of polyester chains. The quantity of unreacted acid must therefore be quite small, and is still further reduced if any unreacted fumaric acid should enter into crosslinking. The quantity of dimer present is unknown.

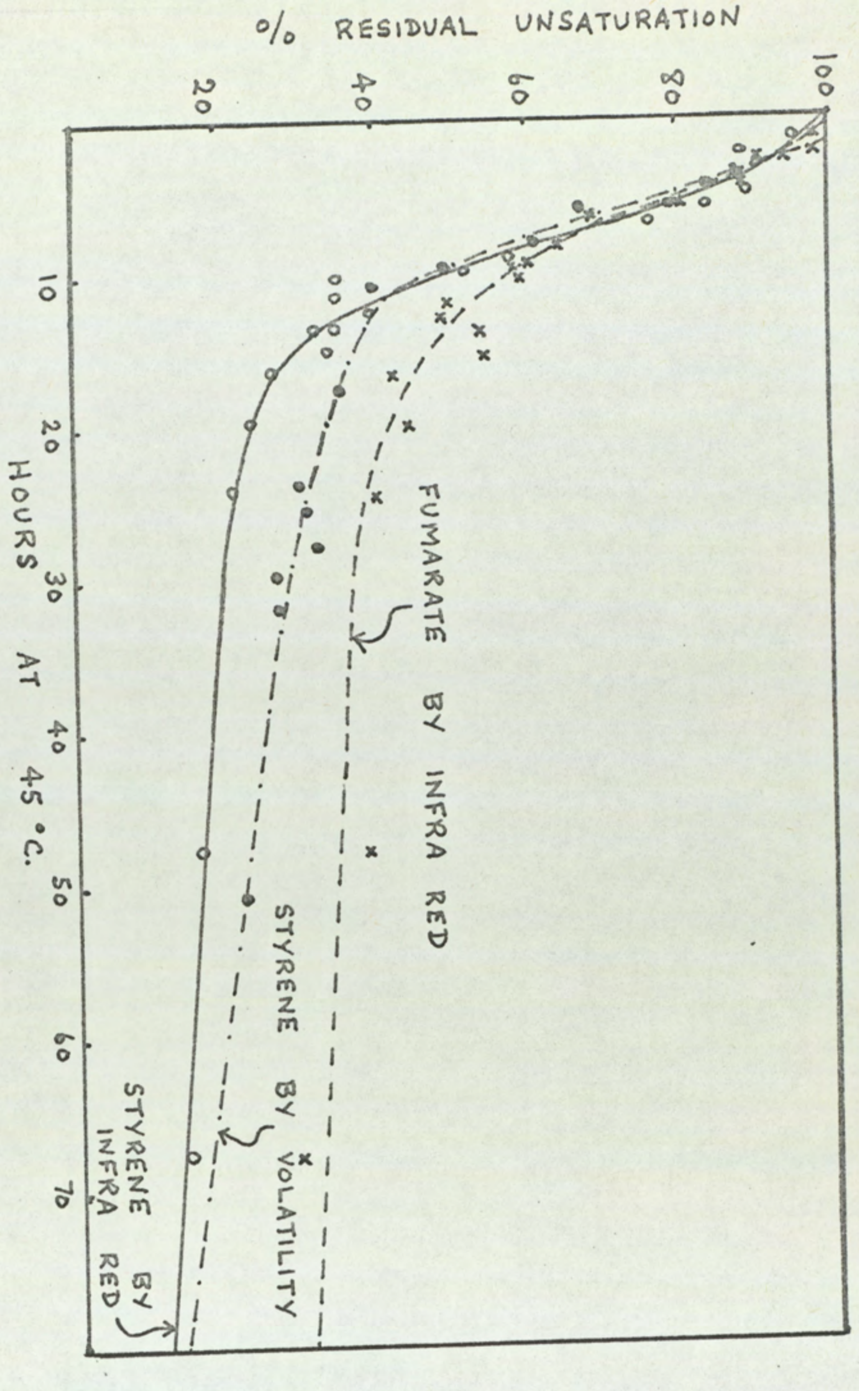


FIG. 31

EFFECT OF CURE TIME ON % RESIDUAL UNSATURATION

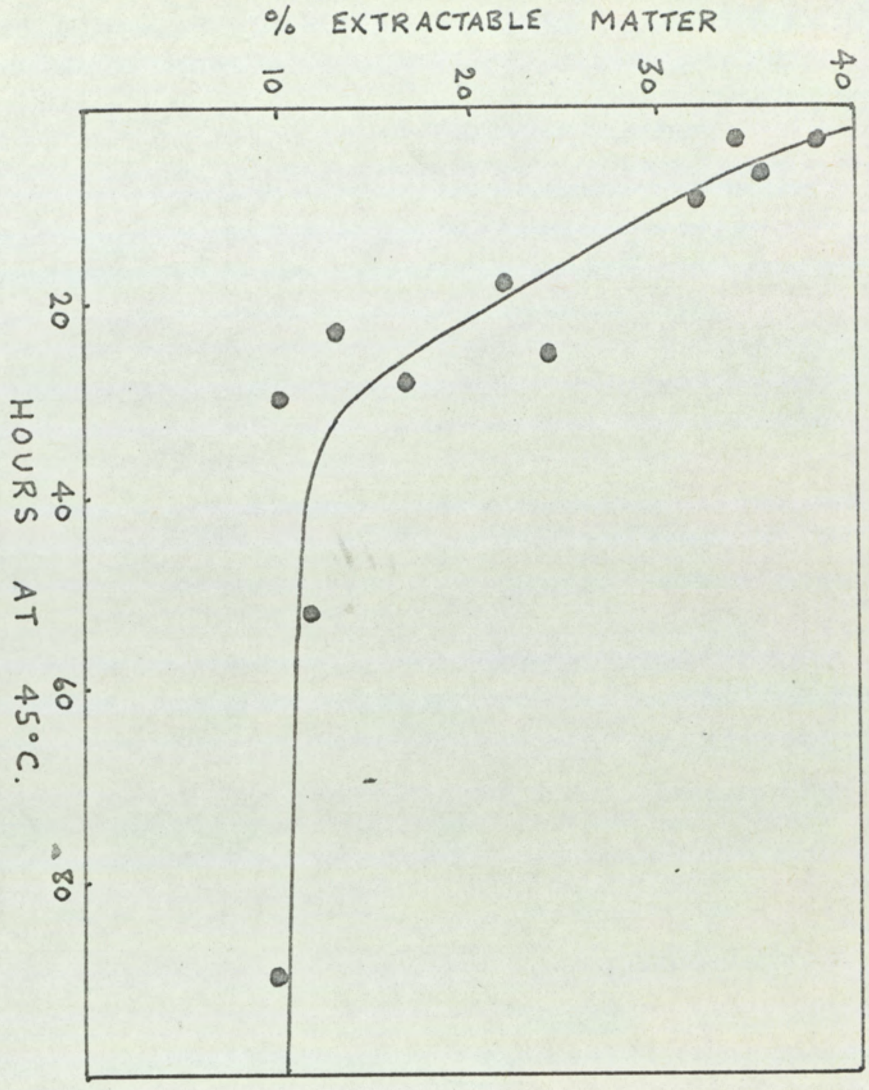


FIG. 32

EFFECT OF CURE TIME ON % EXTRACTABLE MATERIAL (CHLOROFORM EXTRACTION, 7 DAYS AT ROOM TEMPERATURE)

Styrene has a marked tendency to react with fumarate groups, and it is unlikely that dimer would cause appreciable errors in the determination of styrene by volatilization. Insofar as dimer interferes, it lowers the apparent % of unreacted styrene, while free phthalate raises it.

Fig.31 shows that the agreement between the determination of styrene by I.R. and by volatility is excellent in the region from gelation up to the point where diffusion control of the propagation reactions sets in. Before gelation, volatility results were slightly high in residual styrene. After the fall-off in reaction rate, volatility results were again high by up to 8% compared with spectroscopic data. This disagreement gradually lessened until the two techniques appeared to give virtually the same results at long cure times.

The fact that the data reported here on solvent extraction (Fig.32 and Table 28) suffers from some experimental variability is not surprising in view of the widespread difficulties with this procedure (Tomkins, 1955; Sofer and Hauser, 1952;) (Ministry of Aviation, 1965). No doubt some considerably improved results could be obtained given a long period of time for preliminary development of extraction procedures. The extractable matter found at the end of the cure at 45°C. was about 10% of all the original weight. This 10% probably consists of free styrene (perhaps 2 or 3%); totally unattached polyester chains, i.e., chains which have not taken part in any crosslinking; and some sol material which includes crosslinks. At high conversions, the proportion of the latter material is probably quite low, as the complexity of the sol portion declines steadily after gelation. It therefore appears that under these conditions, a significant proportion of polyester has avoided any crosslinking reaction. This unattached polyester resin undoubtedly affects the properties of the cured product, probably by acting as a plasticizer in the same way as does monomeric styrene (Gordon and McMillan, 1957). These authors derived an expression for the concentration of unattached network chains in terms of the original fumarate concentration. This expression was:

$$C_F = F_o \quad (1 - p)^2/(100 - pf) \quad \ldots\ldots\ldots\ldots \quad (11.8)$$

C_F being the concentration in moles of unattached chains, F_o the initial molar concentration of fumarate units (both referred to unit volume), and p, f have the meanings previously given.

The molecular weight $\overline{M}_n'$ of these unattached chains must be less than $\overline{M}_n$, that for the original chains, because longer chains containing more fumarate double bonds are always more likely to crosslink than short ones. Gordon and McMillan deduced that:

$$\overline{M}_n' = 100\,\overline{M}_n\,(1 - p)\,/(100 - pf) \quad \ldots\ldots\ldots\ldots \quad (11.9)$$

Among the unattached chains themselves there will be some

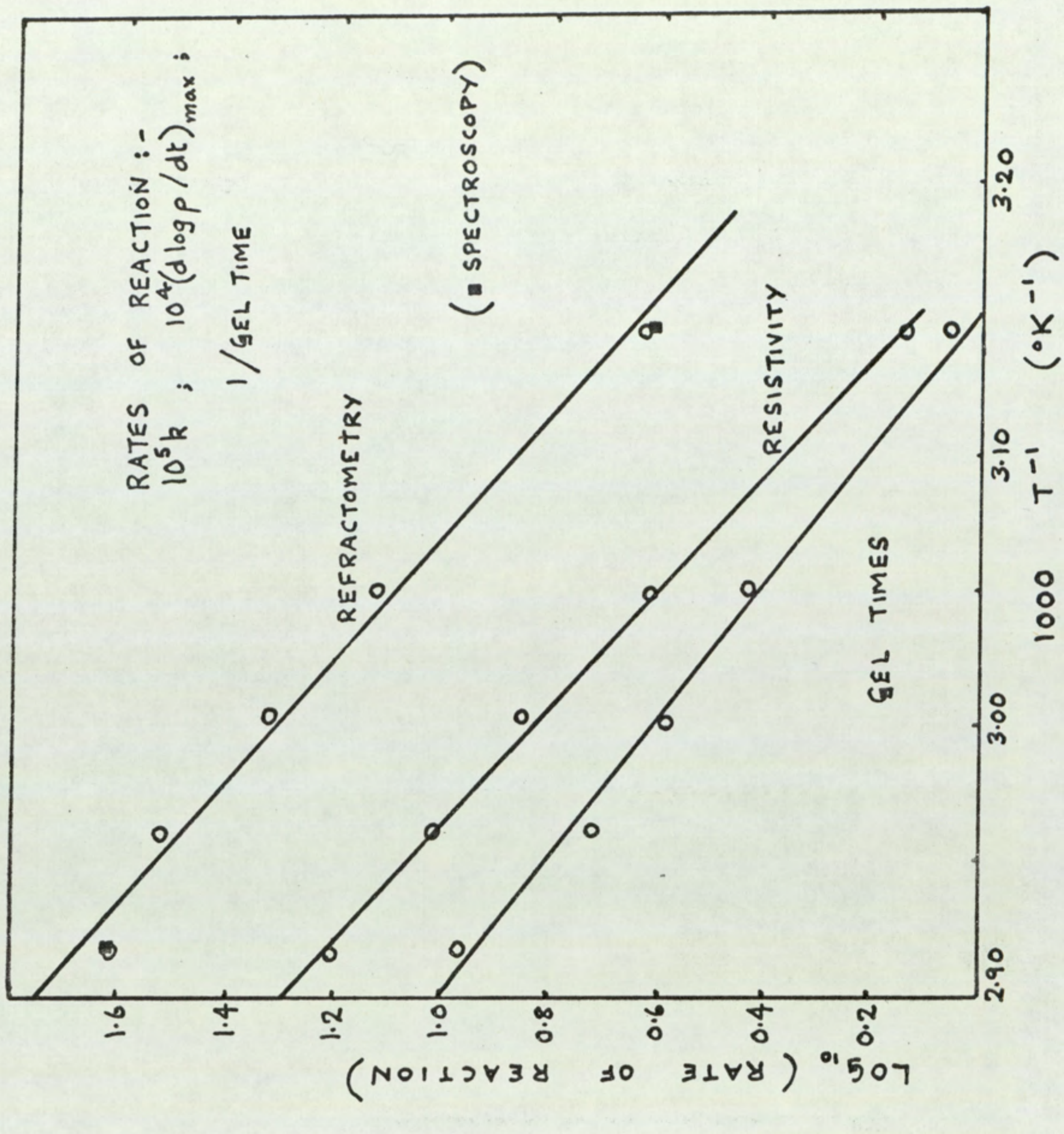


FIG. 33

ARRHENIUS PLOTS OF LOG (REACTION RATE) AGAINST TEMPERATURE.

OVERALL ACTIVATION ENERGIES FOUND ARE AS FOLLOWS:-

By refractometry, E_a = 20.6 kcals/mole

By resistivity, E_a = 21.1 kcals/mole

By gel times, E_a = 18.4 kcals/mole

which cannot combine chemically with the network (neglecting the possibility of continued polyesterification after the crosslinking process has started). This is because some very low molecular weight species probably possess no double bonds. This proportion is difficult to estimate, but assuming a Flory distribution of molecular weights for the resin, i.e., assuming:

$$w_x = x(1-p)^2 p^{x-1} \quad \dots\dots\dots\dots\dots\dots \quad (11.10)$$

then the weight fractions w'_x of species without double bonds such as PG (phthalate - glycol pairs) etc., may be calculated by considering all theoretically possible x-mers and assuming that all are equally possible.

TABLE 34

x (number of units in oligomer)	Species without double bond	w'_x (neglecting H & OH end groups)
1	P; G	0.00155
2	PG	0.00260
3	PGP;GPG	0.00286
4	PGPG	0.00285
5	PGPGP;GPGPG	0.00250
6	PGPGPG	0.00155
7	GPGPGPG;PGPGPGP	0.00176
8	PGPGPGPG	0.00087
9	PGPGPGPGP;GPGPGPGPG	0.00134
10	PGPGPGPGPG	0.00056

Thus the weight fraction of x-mer containing no double bonds declines steeply after the first few values of x, for both odd and even x. The total weight of "unattachable" material, as a percentage of the styrene solution, is about 1.1%. This is much smaller than the extracted portion. If the resin obeys (11.10), a considerable minority of it must be uncrosslinked even though it possesses crosslinking sites. (?)

Refractive index changes during cure are shown in Figs. 34 and 35 and Tables 20 - 24. At 45°C. very long induction periods usually preceded the reaction. This was not found at the higher temperatures. Changes were reminiscent of those in resistivity; an initial fall, probably due to temperature changes, was followed by a gradual acceleration and a linear portion, and finally a levelling off towards an asymptotic plateau.

The total increase in refractive index at a higher temperature T_1 was found to be about the same as that achieved by curing at a lower temperature T_2 and then postcuring at T_1.

The total increase in refractive index during cure increased as the cure temperature increased. Changes in the later stages were rather difficult to detect.

The effect of altering the initial molar ratio of styrene to fumarate is shown in Fig.35. Little difference in the rate of increase in refractive index was found, but the total increase became larger as the initial ratio of styrene to fumarate increased. Thus the increase I is not so important as the fraction of the total or ultimate increase I_{oo} which can occur. Resins which have less than usual styrene may be almost completely cured at quite low values of I.

The results of water resistance and chemical resistance tests were not sufficiently satisfactory to draw conclusions from them. Certainly no great improvement was found in resistance at long cure times. The test procedure needs further development.

The effect of cure temperature on properties is shown in Table 30. The effect of raising the cure temperature is to increase the change in properties during cure, but the total increase in resistivity lessens slightly because the temperature dependence of the resistivity of the unpolymerized resin is less than that for the cured material. Values of Young's modulus did not show any significant trend.

11.5 Correlations between properties

One of the aims of the present work is to show the changes in physical, mechanical and electrical properties as a function of the extent of chemical reaction.

The extent of reaction has been defined for most present purposes as the weight fraction of all unsaturated groups, regardless of whether they are styrene or fumarate, which has reacted. The distinction between the two types of unsaturation is important, however, and therefore in some cases both total unsaturation and fumarate separately have been considered.

Some of the properties measured would not be expected to be simply related to the extent of reaction. This is particularly true of mechanical and electrical damping terms, which do not decline monotonously but change direction several times during the curing process. Young's modulus is non-existent before gelation, and in any case was not measured until well after this point, so the range of cure which could be covered is limited. In addition, the reaction of all 100% unsaturated groups was not approached at the temperature most frequently used, so a further reduction in the scope of correlation curves must be tolerated.

Fig.36 shows the increase in the resistivity over its initial value, ρ_0, as a function of the extent of reaction, and the nearest straight line is drawn (dotted)

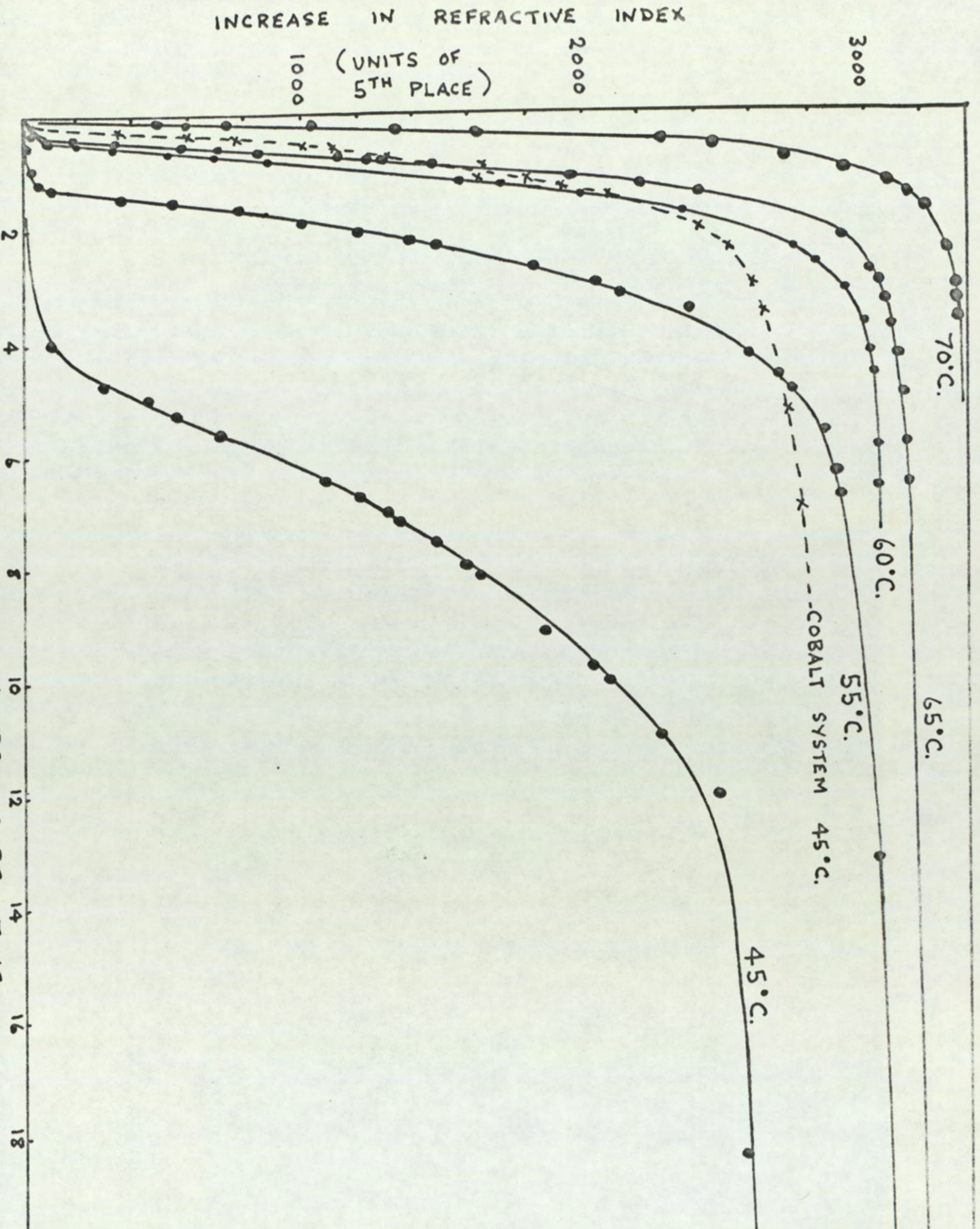


FIG. 34 EFFECT OF CURE TIME ON THE REFRACTIVE INDEX AT VARIOUS CURE TEMPERATURES

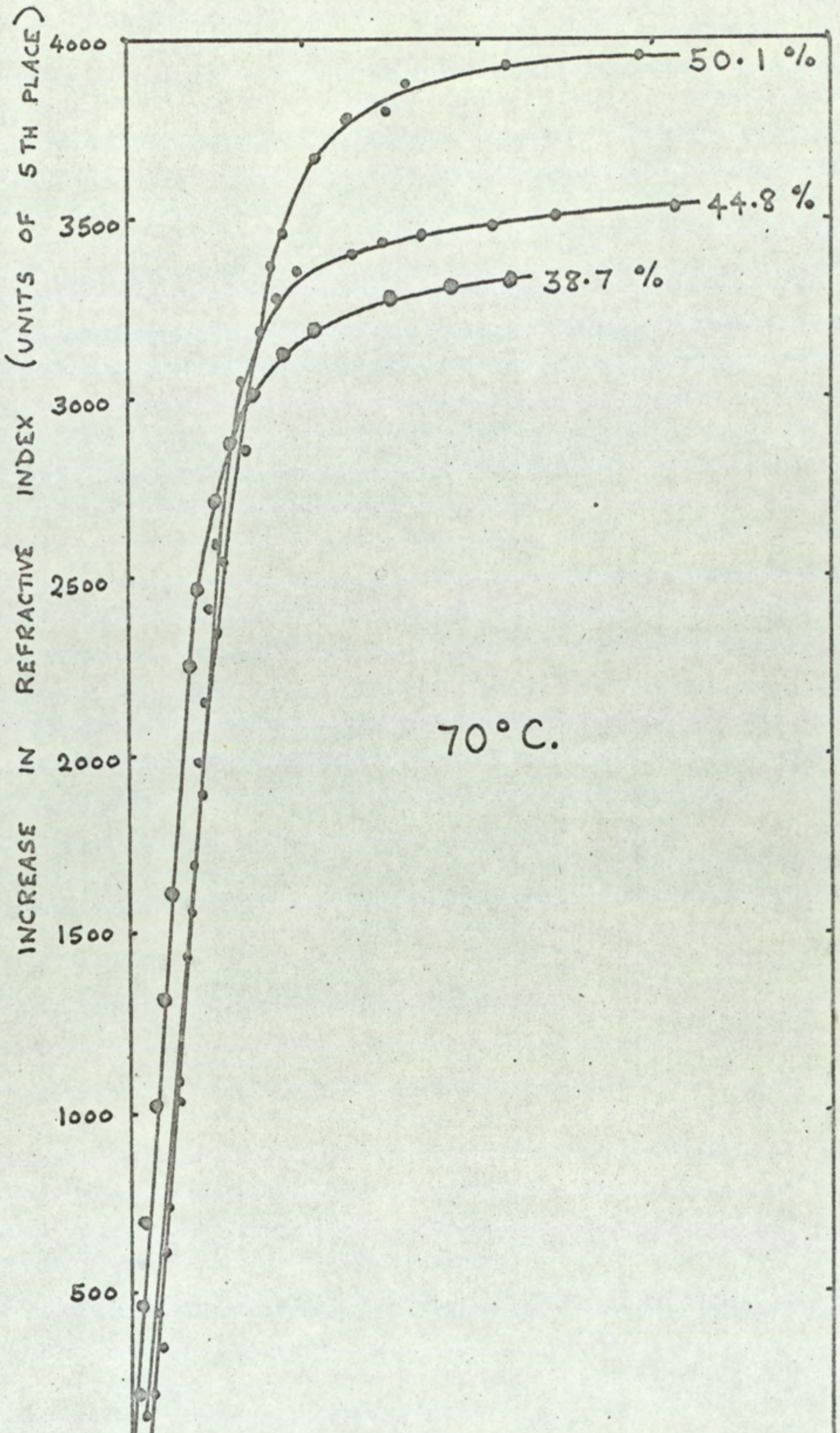
almost superimposed on it. The curve is almost linear for all the range considered, but it is probable that at higher conversions there is some departure from linearity, as reported for other polymerization reactions (Purdon and Morton, 1962; Kienle and Race, 1934). This is borne out by the fact that the total increase in the logarithm of the resistivity (from the initial value to that obtained after postcuring at temperatures up to 165°C.) is 7.6, which is more than the value predicted by extrapolating Fig.36 to 100% conversion (6.4). Within the range studied, however, the linear relationship holds. It was found to hold for the cure of epoxy resins by Magee and Rotariu (1960) who also used infrared spectroscopy.

It is not yet known how widely applicable the relationship is between resistivity and extent of reaction. Preliminary work suggests that the line has a similar slope when cure is carried out at 70°C., when the polyester is cured by a cobalt system, and when the styrene content is altered slightly (Learmonth and Pritchard, 1969).

The changes in refractive index are due to the decrease in the concentration of unsaturated groups. The specific refraction R_c of a copolymer formed by copolymerizing x mole fraction of A and (1-x) mole fraction of B is

$$R_c = xR_A + (1 - x) R_B \quad .... \quad (11.11)$$

FIG. 35



EFFECT OF STYRENE LEVEL ON REFRACTIVE INDEX CHANGES DURING CURE AT 70°C.

The specific refraction is defined by

$$R = \frac{n^2-1}{n^2+2} \cdot \frac{1}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11.12)$$

for a substance of refractive index n and density d.

As a result, in order to relate the increases in refractive index to the extent of reaction of the functional groups, it is necessary to measure the densities of both the styrene and the polypropyleneglycol phthalate fumarate, and of the copolymer (isolated from unreacted material), and to measure the refractive indices of these materials at each cure temperature. This has been done for certain polyesters by Spasskii and co-workers (1959).

This correlation was not possible because the necessary density and refractive index data, particularly for the isolated copolymer, was not available. It was noticed, however, that the increase in refractive index (measured, as Dannenberg (1959) suggested, in units of the fifth place of decimals) was quite closely proportional to the extent of reaction of styrene and of fumarate. This is not altogether unexpected, because the density changes taking place are not great, so that approximately

$$I = a\,M_s + b\,M_f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11.13)$$

I is the increase in refractive index after the reaction of M_s mole fraction of styrene and M_f mole fraction of fumarate. The theoretical case where complete reaction of all unsaturation takes place is where $M_s + M_f = 1$. The two constants a and b were found by inserting into (11.13) experimental values of I, M_s and M_f. It was then found that the same constants gave values for I which agreed quite well with the experimental ones, when other values of M_s and M_f were inserted at different cure temperatures (see Fig.37). a was found to be 28.0 units for each 1% reacted styrene, and b was 10.6 units for each 1% reacted fumarate. These values apply only to the resin under consideration. Complete reaction of all unsaturated species, if it could be achieved, would therefore be accompanied by an increase of approximately

$$28.0 \times 100 + 10.6 \times 100 = 3860 \text{ units.}$$

If the initial refractive index = 1.53516, then the final value = 1.57376. In practice, the increase achieved varied slightly, but was always less than 3860. At 45°C., the increase is about 2650; curing at 70°C., it is about 3350. This is consistent with the fact that resins cured by this system at 45°C. are seriously undercured and those cured at 70°C. are also undercured but less seriously. The agreement found between experimental and calculated values for the cure at 70°C. is particularly close, and is probably fortuitous. The differences appearing towards the end suggest that perhaps infrared determinations of residual unsaturation are inaccurate when the ratios of the absorbances measured become very small. Unfortunately, since the relationship between I and the extent of reaction is empirical and approximate, no conclusions can be drawn with certainty. The disagreement between the predicted and experimental values of I in the early stages of the 45°C. cure is probably exaggerated by the tendency of the refractometric runs at this temperature to be prefaced by long induction periods, sometimes with a rather gradual acceleration afterwards.

G' and E' are only very approximately proportional to the extent of reaction of fumarate double bonds and of all reactive unsaturation (Fig.38). The apparently greater steepness of the shear modulus curves is due to the scale of this figure. In fact the increases in the two moduli are comparable. Even at the lowest level of crosslinking studied, the values for these moduli far exceed the calculated values given by Yip (1968) on the basis of the theory of rubberlike elasticity (this is expected since this theory becomes inapplicable at an early stage). They also far exceed the experimental values determined by Yip using the Weissenberg rheogoniometer.

As expected, the reaction of fumarate double bonds has a greater effect on the moduli than the reaction of styrene, since the latter does not necessarily lead to the formation of crosslinks, though it may cause molecular entanglements which would contribute to the modulus.

It can be seen from Fig.39 that more than half the unsaturated groups have been reacted together before the tensile strength exceeds 200 p.s.i. This is just before the beginning of the rubber-to-glass transition indicated by the peaks in the dielectric dissipation factor and the fall-off in rate of change of volume resistivity. Shortly after this transition, the tensile strength rises steeply and is then found to be proportional to the extent of reaction. The linear range is from 800 p.s.i. to the maximum of 6800 p.s.i. This maximum coincides with the value quoted by the manufacturers of the resin. The last part of the curves in Fig.39 is uncertain because tensile strength values become more widely scattered at long cure times.

Fig.40 depicts the relationship between the moduli G' and E' and the gel content. Imai (1967^1) found that the semi-logarithmic plot was linear. This was not found to be the case in this work, though the E' curve approximates to a straight line. It might be expected that the modulus, being dependent on both crosslinks and entanglements, would not follow the same course as the gel content, since in measuring the latter the entanglements are allowed to relax out by solvent swelling and so may not contribute to the result.

Recently Imai and Okawa (1968) have thought it necessary to modify their technique, which allowed styrene evaporation to take place freely, and use a three-layer "sandwich". This is a coated metal braid in which the resin is covered by aluminium foil or, in some cases, cellophane. Reaction rates and paths were then found to be quite different.

The correlation curves shown here suggest that, provided the extent of chemical crosslinking is known approximately from infrared spectroscopy, many physical properties can be predicted. More work on a variety of resins and polymerizing conditions is necessary in order to establish definite relationships between properties.

11.6 Assessment of cure

Most of the methods studied give a fair indication of the extent of reaction, but most appear to depend on careful adherence to simple systems and test conditions. Even the most promising tests present many difficulties in application to glass reinforced plastics. Dynamic mechanical tests appear to be capable of providing useful data on curing systems for unreinforced cast resin. Electrical methods may be suitable for development for glass reinforced laminates. The properties which seem to be most sensitive to changes in crosslinking in the later stages of cure are the mechanical and electrical damping terms.

Whichever method is used for the assessment of cure, each resin and polymerizing system presents a new problem, since the range of values for any given property during cure depend on the formulation and curing conditions.

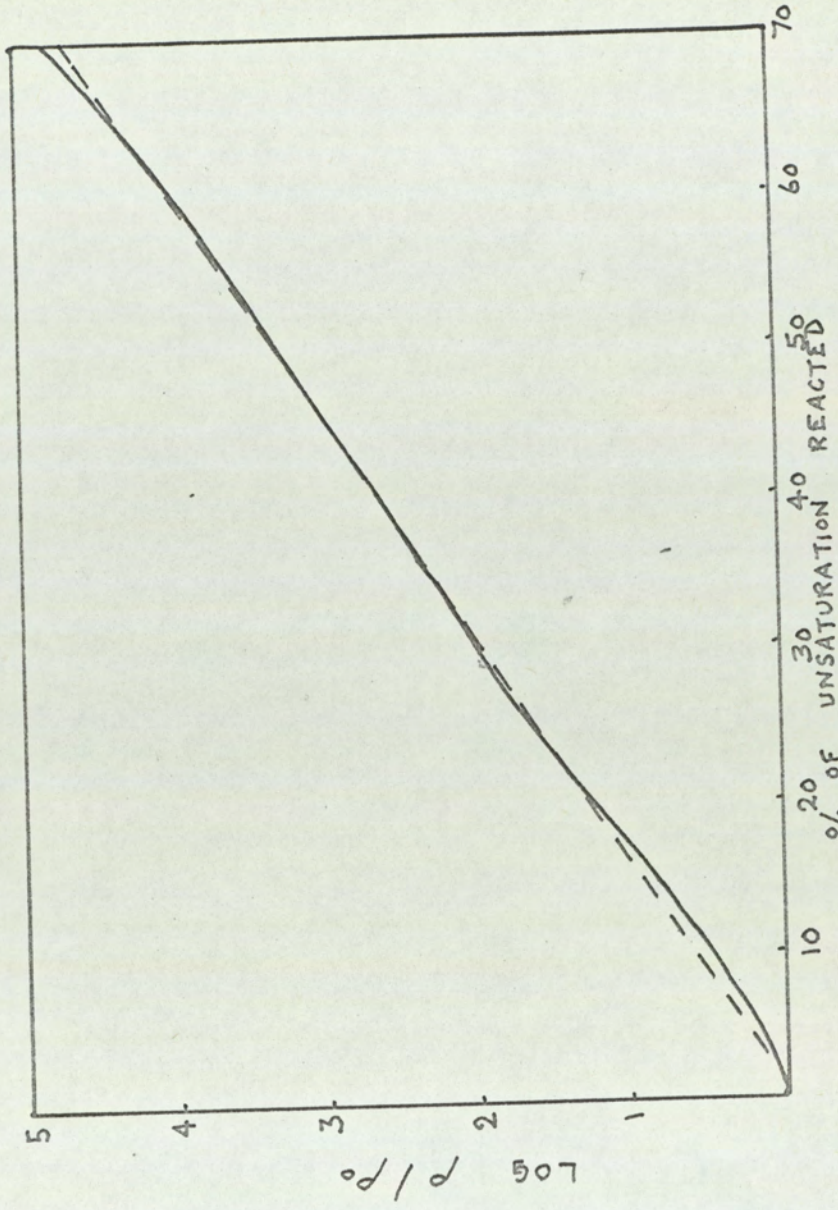
CONCLUSIONS

The effect of curing time on a large number of physical, mechanical, electrical and chemical properties of an unsaturated polyester resin has been investigated. By keeping cure conditions isothermal and constant from one property study to another, it has been possible to consider the changes in any one parameter in relation to the others.

In particular, the changes in the properties as a function of degree of reaction have been considered. The chemical measurements have been made by developing an infrared method which does not depend on preliminary separation of the unreacted material. This infrared method gives results for the extent of reaction of styrene, which are in general agreement with volatility studies. Rate of reaction, measured spectroscopically, agrees with rates measured by refractometry and the activation energies determined by the latter method are similar to those given by resistivity and gel time measurements. The slope of the semilogarithmic resistivity-time graph is constant for a considerable period in the post-gelation stage, and is proportional to the reaction rate.

The dielectric constant changes are less informative than those taking place in the dissipation factor. The

FIG. 36



INCREASE IN LOG ρ ABOVE ITS MINIMUM VALUE, LOG ρ_o, AS A FUNCTION OF THE WEIGHT % OF REACTED UNSATURATION.

DOTTED LINE REPRESENTS THE NEAREST STRAIGHT LINE.

latter exhibits two peaks, one of which could not be located precisely for experimental reasons. The other peak corresponds with the transition to a glassy material, and with the fall-off in reaction rate. The increase in the logarithm of the resistivity is closely proportional to the extent of reaction of the unsaturated groups.

Refractive index changes provide a simple and accurate method of studying reaction rates and extent of cure.

An appreciable minority of the polyester chains seem to avoid crosslinking, remaining in the resin and acting as a plasticizer.

More than half the unsaturated groups are reacted before the resulting product has any appreciable tensile strength.

All the resin samples cured in this work were considerably undercured, in comparison with those subjected to postcure at progressively higher temperatures up to 165°C. The resistivity continued to increase until the resin had been heated at this temperature for 4 days, in the absence of oxygen.

The techniques studied do not lend themselves easily to the assessment of cure of reinforced resins, but may be quite suitable for casting resins. It may be possible to adapt the electrical techniques to the study of glass reinforced polyester laminates. The properties which change most in the later stages of cure are the damping factors. These continue to change when many properties are not showing significant alteration.

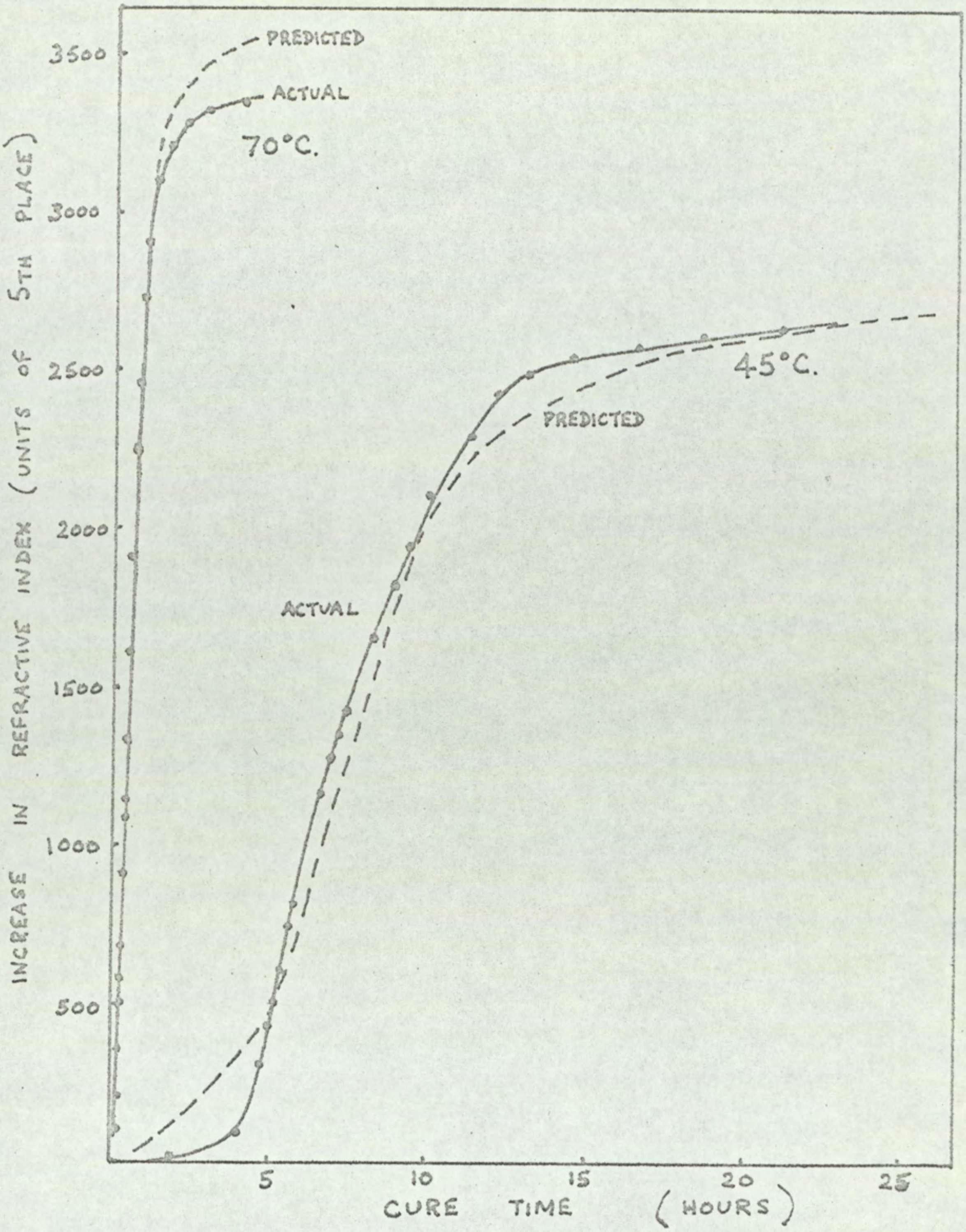


FIG. 37 COMPARISON BETWEEN EXPERIMENTALLY DETERMINED CHANGES IN REFRACTIVE INDEX AND THOSE PREDICTED BY THE SIMPLE PROPORTIONALITY RELATIONSHIP OF EQUATION (11.14)

RECOMMENDATIONS FOR FURTHER WORK

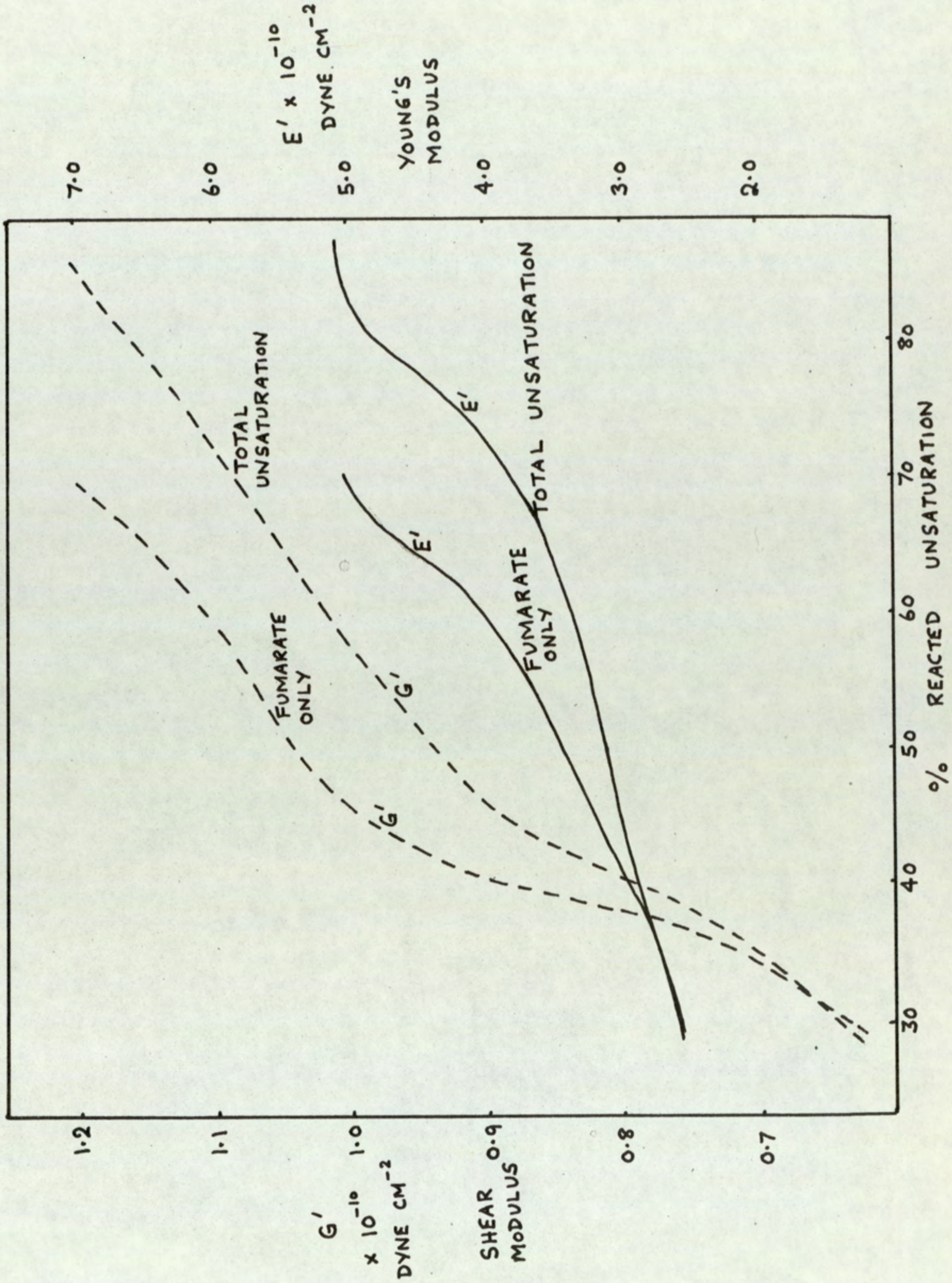
Many unresolved problems remain which could be investigated best using a fast-curing system at room temperature. This would enable a single specimen to be tested on the torsional pendulum at intervals and the possible existence of a subsidiary loss peak examined. The position of the first loss peak in the electrical experiments could also be examined further, and its dependence on frequency determined.

The infrared method should be extended so as to be usable as a potassium bromide disc technique or other infrared technique, enabling sections of thick mouldings to be examined for a quantitative assessment of the extent of reaction of the two types of unsaturation.

A preliminary examination of the effect of glass fibre, of various types, and in various concentrations, on the electrical properties of curing resins should be made.

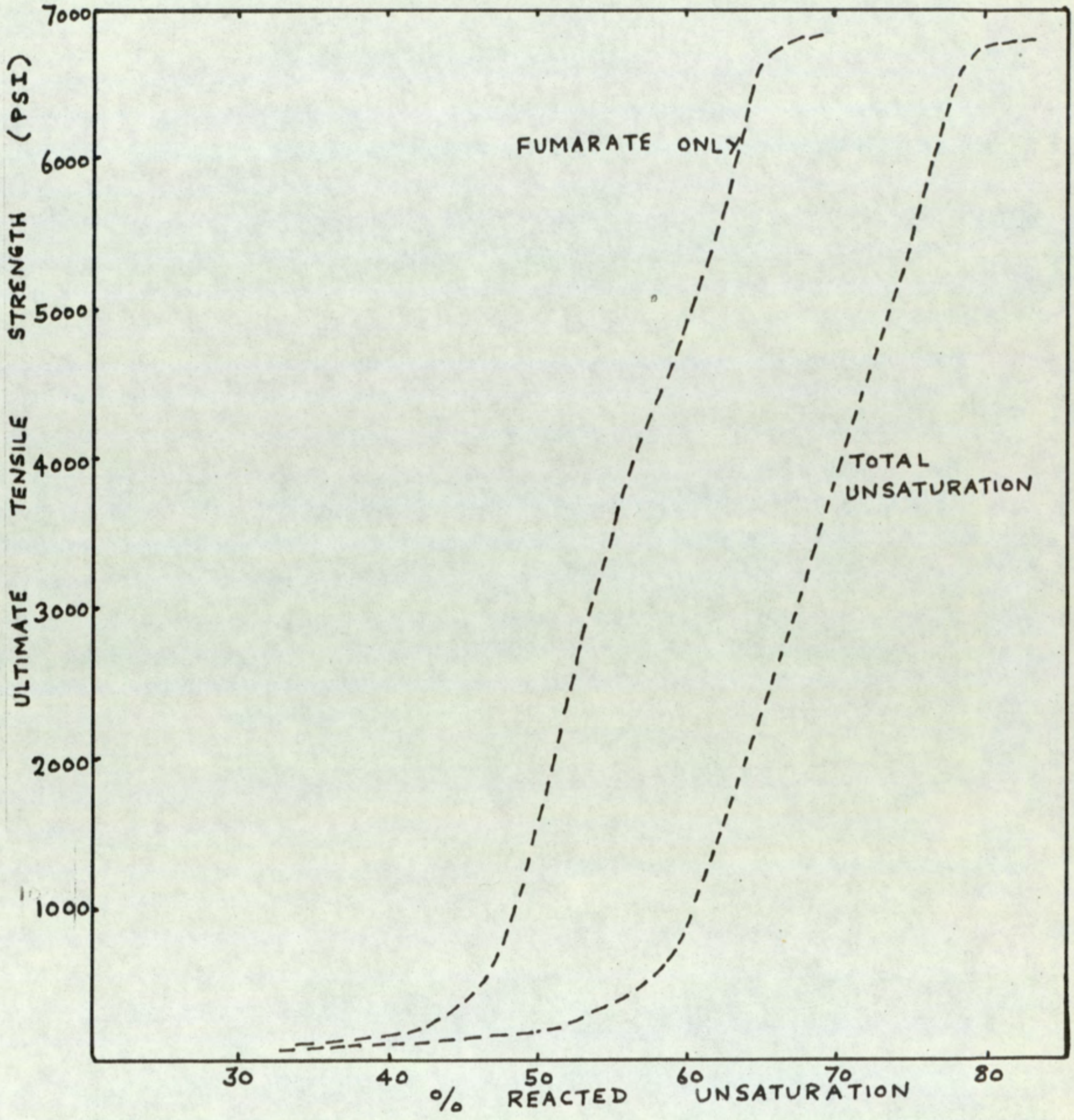
In almost all cases the experiments carried out in this present project suffer from the lack of comparable data on other different resins and polymerizing systems. Certain techniques for studying the crosslinking process, notably the torsional pendulum, might be used further for an investigation of the extent to which the conclusions drawn here are generally applicable.

FIG. 38



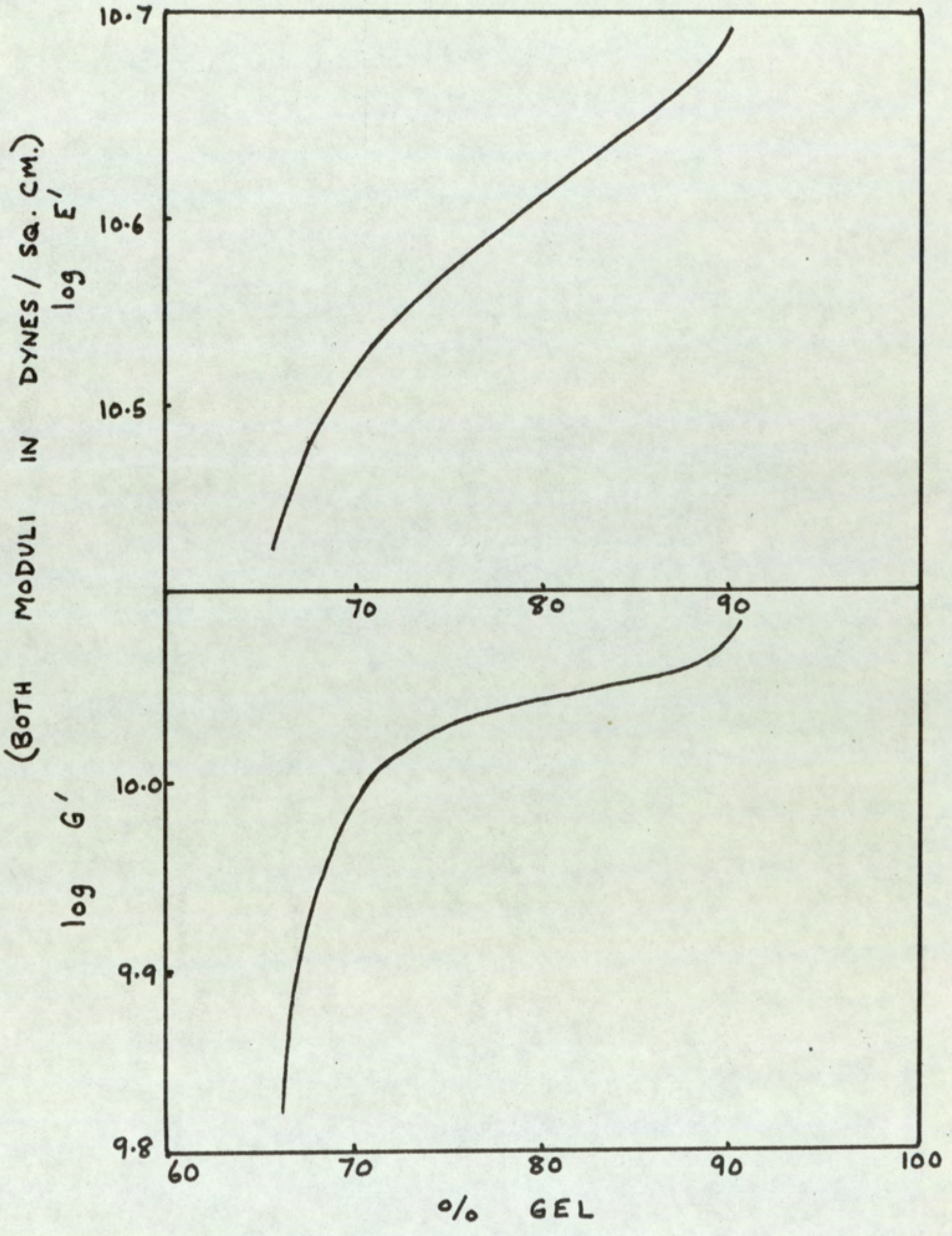
DYNAMIC STORAGE MODULI AS FUNCTIONS OF WEIGHT %
REACTED UNSATURATION

FIG. 39



TENSILE STRENGTH AS A FUNCTION OF WEIGHT %
REACTED UNSATURATION.

FIG. 40



DYNAMIC STORAGE MODULI AS FUNCTIONS OF % GEL

APPENDIX

APPENDIX 1

Corrections for use in two-electrode determinations of dielectric constant, according to

ASTM D150 - 65 T

and based on A. H. Scott and H. L. Curtis, "Edge Correction in the Determination of Dielectric Constant", J. Res. Nat. Bur. Stand., 22, 747 (June, 1939).

Assuming equal-sized disc electrodes (smaller than the specimen), the diameter being d cm. and the separation t cm., then

$$E' = \frac{C_s \text{ (corrected)}}{C_v} \quad \text{where}$$

C_s = capacitance found experimentally

C_v = capacitance of the same electrode configuration when taken up by free space

$C_v = 0.06954 \frac{d^2}{t}$ picofarads

The corrections made to convert C_s to C_s(corrected) are for edge or fringing capacitance only. Provided the lead capacitance is small, and the measuring electrode is grounded, this is the only correction required for routine measurements.

C_s corrected = $C_s - C_e$

$C_e = P\ (\ 0.019\ E'_s - 0.058 \log t + 0.010\ )$

P = the perimeter of the electrodes in centimetres

E'_s = the approximate dielectric constant, $\frac{C_s}{C_v}$.

So

$$E' = \frac{C_s}{C_v} - \frac{P}{C_v} \left(0.019\, E'_s - 0.058 \log t + 0.010\right) .$$

This assumes that the thickness of the electrodes is negligible in comparison with their separation.

APPENDIX 2

Calculation of the moments of inertia of the oscillating systems used for determining the shear modulus by means of the torsional pendulum

Let I_x ($x = 1, 2, 3, 4$) represent the moment of inertia of the oscillating system in cases where the attached weights (each of mass m grams) are placed l_x cm. from the vertical axis of symmetry of the system. ($l_1 > l_2 > l_3 > l_4$).

Let I_5 be the moment of inertia without any weights attached.

Then

$$I_x = 2m \left(l_x^2 + \frac{b^2}{12} + \frac{d^2}{16}\right) \text{ gm. cm.}^2$$

for weights of thickness b cm. and diameter d cm.

Hence I_x may be found directly. A steel specimen, whose frequency-independent dynamic shear modulus is G_s, is then used for two values of I, including I_5. If the length of the specimen is l and g is a shape factor dependent on the cross-section of the specimen, then the two frequencies of vibration f_x and f_s give I_5 as follows:-

$$\frac{gG_s}{l} = 4\pi^2 f_x^{\,2} \,(I_x + I_5) \qquad \text{(weights attached)}$$

$$\frac{g^G s}{l} = 4\pi^2 f_5^{\,2} \,(I_5) \qquad \text{(no weights attached)}$$

so equating the two right hand sides,

$$f_x^{\,2} \,(I_x + I_5) = f_5^{\,2} \, I_5$$

and $I_5 = \dfrac{f_x^{\,2} \, I_x}{f_5^{\,2} - f_x^{\,2}}$

Here,
$b = 3.32$ cm.
$d = 7.15$ cm.
$f_1 = 1.70$ c/s
$f_5 = 10.42$ c/s

Hence the results given in Table 32 were calculated.

APPENDIX 3

The calculation of dynamic quantities

a. The torsional pendulum.

To calculate the dynamic shear storage modulus G', the following equation was used:-

$$G' = \frac{1.525\ LI}{r^4\ P^2} \quad \text{dynes/sq. cm.}$$

To evaluate the logarithmic decrement, several values of $\ln \frac{An}{An + 1}$ were computed and the average taken.

b. The audiofrequency resonant rod machine

At fundamental resonance, for a wavelength λ,

$$\frac{\lambda}{2} = L, \text{ and } V = f\lambda = 2fL$$

Also $$V = \sqrt{E/_d}$$

(d = density of specimen)

So $E = V^2d = 4f^2L^2d$

The damping term Δ_E was calculated from the expression

$$\Delta_E = \pi \frac{(f_2 - f_1)}{f_r}$$

where f_2, f_1, f_r have the meanings given in Fig. 6.
Thus Δ_E is a measure of the "bluntness" of the resonance peak.

APPENDIX 4 : LIST OF SYMBOLS

Symbols not listed here, unless stated otherwise, are empirical constants.

a'	maximum amplitude of oscillation of cone of rheogoniometer
a''	maximum amplitude of oscillation of plate of rheogoniometer
$[A]$	accelerator concentration
A_n	amplitude of the n^{th} oscillation
b	constant, proportional to the number of available hopping sites around an ion
B	critical fractional conversion at gelation of all unsaturation
C	conversion
C_c	Critical conversion
C_e	edge capacitance
C_F	concentration of unattached polyester chains, in moles per unit volume
C_s	experimentally determined approximate capacitance
C_v	vacuum capacitance
d	diameter
d	density
d	distance between hopping sites
DP_{wp}	weight average degree of polymerization of polyaddition chains
DP_{np}	number average degree of polymerization of polyaddition chains
DP_{wc}	weight average degree of polymerization of condensation chains

DP_{nc}	number average degree of polymerization of condensation chains
e	charge on an ion
e^*	coefficient of restitution
E'	dynamic (Young's) storage modulus
E''	dynamic (Young's) loss modulus
Ea	apparent overall activation energy for crosslinking
E_c	activation energy for conduction
E_h	potential energy barrier for ionic hopping process
E_e	% energy absorbed by specimen in ball rebound experiment
E_s	field strength (volts/cm.)
E'_s	Young's storage modulus for a steel substrate
E'_{s+f}	Young's storage modulus for a braid specimen
f	frequency
f	% residual fumarate unsaturation
f'	constant, proportional to the vibrational frequency of an ion
f_F	fraction of all polymerized unsaturation which is of the fumarate type
f_s	resonant frequency (substrate)
f_{s+f}	resonant frequency (braid)
f_1, f_2	frequencies at which the amplitude of vibration of a specimen is $^1/_2$ of the maximum
f_r	fundamental resonant frequency
$[F_o]$	initial concentration of fumarate double bonds (moles per unit volume)
g	shape factor, dependent on cross-section of specimen
G	relative rigidity modulus
G'	dynamic shear storage modulus

G"	dynamic loss modulus
G*	complex shear modulus
G_s	dynamic shear modulus of steel specimen
h	rebound height
h_o	dropping height of steel ball
h_s	thickness (substrate)
h_{s+f}	thickness (braid specimen)
I	moment of inertia
I	increase in refractive index
$[I]$	initiator concentration
k	Boltzmann constant; also rate constant determined by measuring rate of reaction of styrene
k_r	rate constant determined refractometrically
k_T	rate constant at T^o absolute.
K	torsional elastic constant for torsion bar of rheogoniometer
K'	bulk modulus
l_1, l_2, etc.	distance of attached weights from vertical axis of symmetry of torsional pendulum
L	distance between clamps; effective specimen length
m	mass of inertia weights
$[M_o]$	initial concentration of crosslinking monomer (moles per unit volume)
M_s	mole fraction of reacted styrene
M_f	mole fraction of reacted fumarate
$\overline{M}_n$	number average molecular weight
$\overline{M}_n'$	number average molecular weight of uncrosslinked (unattached) polyester chains

$\overline{M}_n{}^*$	partial conversion molecular weight
n	refractive index
n	density of ions in the conducting medium
N	number of molecules per unit volume at any stage of crosslinking
N_o	number of molecules per unit volume initially
p	fraction of carboxyl groups which undergo esterification
P	period of natural oscillation
P	perimeter of electrode
r	radius of specimen
r_1, r_2	ratio of absorbances at 915 to 1737 cm^{-1} and 985 to 1737 cm^{-1} respectively
r_F, r_m, r_s	monomer reactivity ratios for fumarate, methyl methacrylate and styrene
R	gas constant
R	specific refraction
R	monomer feed ratio
$[R]$	free radical concentration
s	% residual styrene
t	electrode separation distance
t_c	contact time in rebound experiments
t_g	gel time
t_i	induction period
t_m	time to minimum in electrical loss tangent
t_p	time to final maximum in electrical loss tangent
t_T	arbitrary cure time at T^o absolute
T	absolute temperature

$T_{50}(R)$	temperature at which $E_e = 50\%$ at feed ratio R
T_g	glass transition temperature
v	velocity of sound
V	crosslinking parameter
w	thickness of specimen
W_s	weight of substrate
W_{s+f}	weight of braid specimen
w_x	weight fraction of condensation polymer consisting of x-mer
W'_x	weight fraction of condensation polymer consisting of x-mer, and containing no reactive fumarate unsaturation.
W	weight of copolymer per unit volume
W_f	plasticization parameter related to unattached polyester chains
W_m	plasticization parameter related to free crosslinking monomer
α	cone angle in radians
α	attenuation
γ_M	dynamic shear modulus (Maxwell model) determined by means of the rheogoniometer
Δ_E, Δ_g	logarithmic decrements (extension and shear)
δ	loss angle
δ_s	loss angle of substrate
$\tan\delta$	electrical loss tangent
ϵ'	dielectric constant
ϵ'_s	approximate dielectric constant ($\epsilon'_s = \frac{C_s}{C_v}$)

ϕ	Phase difference between stress and strain (rheogoniometer).
ϕ_B	Volume fraction of braid material in a braid
ϕ_c	fraction of fumarate material reacted, at the gel point
ϕ_v	volume fraction of void in a braid
λ	wavelength
ρ	d.c. volume resistivity
ρ_o	volume resistivity before polymerization
ρ_o'	constant relating ρ with E_c and T
σ	a.c. conductivity
ω	angular frequency (radians per second)

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The Cross-Linking of Polyester Resins under Thin-Film Conditions

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Infrared spectrophotometric and refractometric techniques for examining the polymerization cycle are discussed

In previous publications (1, 2) the authors outlined how unsaturated polyester resins are copolymerized with unsaturated monomers, such as styrene, to give three-dimensional cross-lined networks. In this project, the investigation of this reaction was continued by using techniques which are applicable in fairly strictly isothermal conditions. The results are compared with those of the previous papers, which discussed dynamic modulus, damping and indentation studies.

The same polymerizing system, mixing conditions and cure temperature were used; with the same commercial, low viscosity general purpose resin. This contained one mole of maleic anhydride, three of propylene glycol and two of phthalic anhydride. Analysis of the resin by solid content and by ultraviolet methods (3) indicated a styrene content of 38.7% by weight. The reaction was followed by refractometric and infrared spectrophotometric techniques.

Peak Exotherms

The cross-linking reaction is exothermic, and since polyester resins in solution in styrene are initially very poor heat conductors, a reaction in bulk tends to depart from true isothermal conditions very readily. By keeping the temperature, catalyst and activator low, this effect can be minimized. For instance, in a stainless steel tube of 1.30 cm diam, 25 cm long, this resin system was polymerized at 45°C and gave a peak temperature of approximately 50°C. Substitution of a glass tube of the same dimensions can cause a rise in temperature to as much as 170°C.

In the mold used for the dynamic experiments(2), the polyester was only a thin section in comparison with the steel surroundings, and the peak temperature was only 1½° above the oven temperature. In this work, only minute quantities of resin were used and the conditions could be said to be practically isothermal.

Infrared Analysis

The cross-linking reaction studied is an addition copolymerization between styrene and the unsaturated (maleate or fumarate) groups in the linear polyester chains. The resulting three-dimensional network is therefore made up of the original polyester chains combined with copolymerization chains which consist of styrene and fumarate groups. The number of styrene molecules between cross-link sites is quite small.

When the resin cures, the infrared spectrum shows the following main features: a constant unchanging portion related to the saturated part of the polyester backbone, and a gradually changing group of bands related to the reacting unsaturated groupings. More than one band is available to follow the disappearance of these groups, and any of them may be related to the fixed carbonyl band as an internal standard. In this particular resin, one of the possible bands (at 12.9 microns), eventually forms a shoulder and is rather difficult to measure. The change in the appearance of the spectrum during cure is shown in *Figure 1*.

Previous Work

Hayes, Read and Vaughan (4) cured a thin film of polyester resin between rock-salt plates and measured the decrease in absorption, at 12.9 microns, due to unsaturated polyester groups. It was necessary to correct for overlapping styrene absorption. They then calculated the final ratio of reacted styrene to reacted polyester double bonds in the product. No mention was made of any study of the course of the reaction apart from its final state.

Alekseyeva and Spasskii (5) compared the intensity of the double bond peak at 1654 cm^{-1} with that of the carbonyl at 1737 cm^{-1}. The styrene entering the copolymer could then be measured by

Nomenclature

A_i	Parameters for the regression function, Equation 12.
b	Pressure coefficient, psi.$^{-1}$
D	Capillary diameter, in.
L	Capillary length, in.
P	Pressure, psi.
P*	Pressure above atmospheric pressure, psig.
Q	Volumetric rate of flow, in.^{3}/sec.
R	The gas constant.
r	The radial coordinate.
T	Temperature, °F.
$\overline{V}$	Average velocity in capillary, in./sec.
v_h	Hole volume, in.^{3}
v_z	Axial velocity, in./sec.
z	Axial coordinate.
$\dot{\gamma}$	Shear rate, sec.$^{-1}$
$\dot{\gamma}_w$	Shear rate at the capillary wall, sec.$^{-1}$
$\dot{\gamma}_{tw}$	Corrected shear rate at the wall, sec.$^{-1}$
ΔP	Pressure drop along the die, psi.
μ	Viscosity, lb_f sec./in.^{2}
μ_a	Apparent viscosity, lb_f sec./in.^{2}
μ_{at}	Viscosity at atmospheric pressure, lb_f sec./in.^{2}
τ	Shear stress, lb_f/in.^{2}
τ_w	Shear stress at the capillary wall, lb_f/in.^{2}
τ_{exit}	Shear stress at capillary exit, lb_f/in.^{2}

Some of the assumptions used in the flow model were checked by comparison to results obtained by Gerrard, Steidler and Appeldoorn (14), who based their analysis on a more general model. They used a Newtonian oil for which the viscosity-pressure dependence was known, and solved the basic flow equations including the radial velocity component and viscous heating effects. The radial velocity was shown to be very small, in spite of the high shear rates used in their experiment. However, a considerable effect of viscous heating was demonstrated, which may cast some doubt on the isothermal flow assumption. In order to estimate the possibility of temperature rise in polymer melt viscometry, the heat generation functions for the oil and polyethylene were compared. This function, which may be estimated by the shear stress times the shear rate and is proportional to the rate of heat generation, was not greater than 10^5 lb/in.^{2} sec for polyethylene while in the experiments conducted by Steidler and co-workers it was in the order of 10^6-10^7 lb/in.^{2} sec.

The highest shear rates to which the polyethylene was exposed were 100 times lower than those of the oil, and the Reynolds number was around 10^{-5} for the polymer compared to 20 for the oil. These numbers demonstrate that the isothermal assumption in this analysis is justified. The heating effects in the case of the Newtonian oil gave rise to a radial viscosity gradient similar to the one in the non-Newtonian polymer melt. This similarity increases the confidence in comparing the radical velocities.

The experimental results show only a slight effect of shear rate on the pressure coefficients of polyethylene. This supports the assumption of a constant pressure coefficient used in the derivation.

Precaution should be taken in choosing experimental temperature levels. Low temperatures at which the melt may solidify at elevated pressures as well as high temperatures detrimental to the polymer stability should be avoided.

Finally, in order to test pressure-viscosity equilibrium conditions, experiments were conducted after keeping the polymer in the rheometer under hydrostatic pressure equal to the extrusion pressure, prior to the extrusion for 10-20 min. These experiments reproduced the results which were obtained by using the procedure described in the experimental section.

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Ilan J. Duvdevani received an MS degree in Chemical Engineering (Plastics Option) from Stevens Institute of Technology in 1965. His basic training as a chemical engineer was at Technion-Israel Institute of Technology where he received a BS in 1962. He was affiliated with Western Electric's Engineering Research Center in Princeton, N. J., as a Research Engineer in the plastics processing department. At present, he is at Stevens, pursuing full time studies towards a PhD degree.

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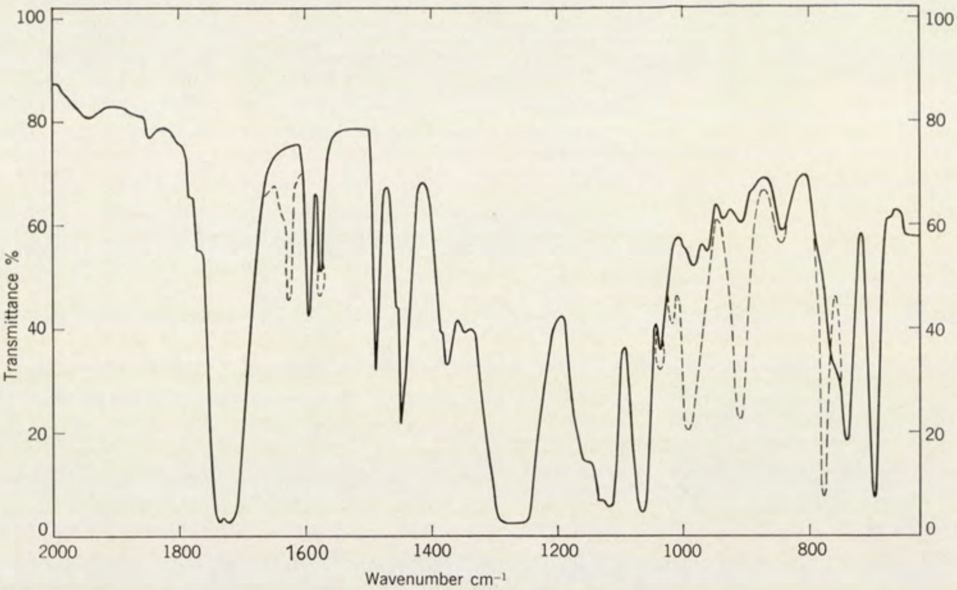

Figure 1. The infrared spectrum of the resin before and after cure.

the increase in the absorption at 705 cm^{-1} due to the benzene rings. This necessitated their hydrolysing the product and separating off all unreacted monomer. The results were compared with double bond estimations by other methods, notably the changes in specific gravity and refractive index (6).

As part of a study of this reaction, Hamann, Funke and Gilch (7) confirmed their determinations of the composition of the reacted product by resorting to an infrared examination, using the carbonyl band of the ester formed after reaction with diazomethane. The styrene component was found from the carbon-hydrogen stretching band of the aromatic nucleus.

Both infrared (8,9) and refractive index (10) techniques have been used to monitor the analogous curing reactions of epoxy resins, but little seems to have been reported on polyester resins except for studies on the final products. It was therefore thought useful to relate the decrease in styrene monomer at 45°C to the physical changes taking place as the network forms.

Experimental Spectroscopy

One hundred parts of resin in styrene were catalysed with one active part of benzoyl peroxide (as 60% paste), and 0.007% N,N′ dimethyl para toluidine, used as a 5% solution in dibutyl phthalate. After thorough mixing and de-aerating, a spot of the mixture was placed on a polished NaCl plate using a 0.025-mm polytetrafluoroethylene spacer. It was necessary to ensure that the plates were free of any alcohol used in the polishing process and that the resin added was sufficient to fill completely the small space provided by the spacer, so that no air was present.

The spectrum was obtained on a Perkin-Elmer 237 grating instrument, and the cell was then placed in a forced-draught oven at 45°C.

A spectrum was run at intervals until the change became very slight. It was possible to separate the NaCl plates without damage after use, as the adhesion of the polyester was not great. The wavelengths were calibrated with a polystyrene standard.

Reference spectra were obtained under identical conditions for monomeric styrene, the alkyd in styrene, the alkyd in xylene, the xylene solvent and di-n-octyl phthalate.

The styrene was estimated by measuring the decrease in the ratio of the absorbance of the vinyl peak at 915 cm^{-1} to that of the carbonyl at 1737 cm^{-1}.

The measurement of polyester unsaturation was also attempted, using the 985 cm^{-1} peak, and allowing for overlapping styrene. A small correction

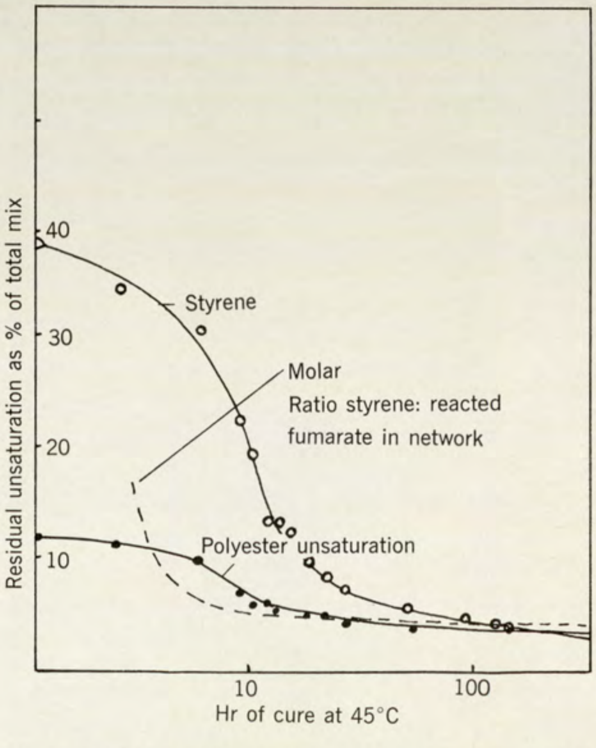

Figure 2. The infrared analysis of residual unsaturation as a function of cure time. Time is logarithmic.

was applied for the presence of a contribution from phthalate groups. Again, the peak area was related to the carbonyl standard. A study of the spectrum of the resin suggested strongly that, by the criteria of Park et al. (11), the polyester unsaturation is very largely in the form of fumarate rather than maleate, and the terms "fumarate unsaturation" and "polyester unsaturation" are here used interchangeably.

Experimental Refractometry

A precision Abbé refractometer was used with a sodium lamp. Methods for determining the refractive index of casting resins without damaging the prisms are described in reference (10). In this work, silicone mold release fluid was preferred to the use of protective plastics films. The edges of the prisms were sealed with plasticine to prevent the loss of styrene, and the prisms themselves were heated by water circulation from a thermostatted bath.

Discussion

Completeness of Cure: The system used to crosslink the polyester does not appear to give a complete cure, under the conditions used. This is not to say that a complete cure could not be achieved at any temperature. 70°C would be quite satisfactory to cure the resin in a few hours. At the temperature used (45°C), however, only a proportion of the available unsaturation is used. From *Figure 2*, it can be seen that the proportion of the total mix which was unreacted styrene fell from 38.7% to about 5% by the time 100 hr had elapsed. If a bulky molding had been made instead, the slight exotherm would have sufficed to cause a reasonable cure with this system at a nominal temperature of 45°C.

The "final" product after about 120 hr cure can be seen from *Figure 2* to have between one third and one half its polyester sites still unused. Presumably, these are sterically protected from the available free styrene unless the temperature is raised.

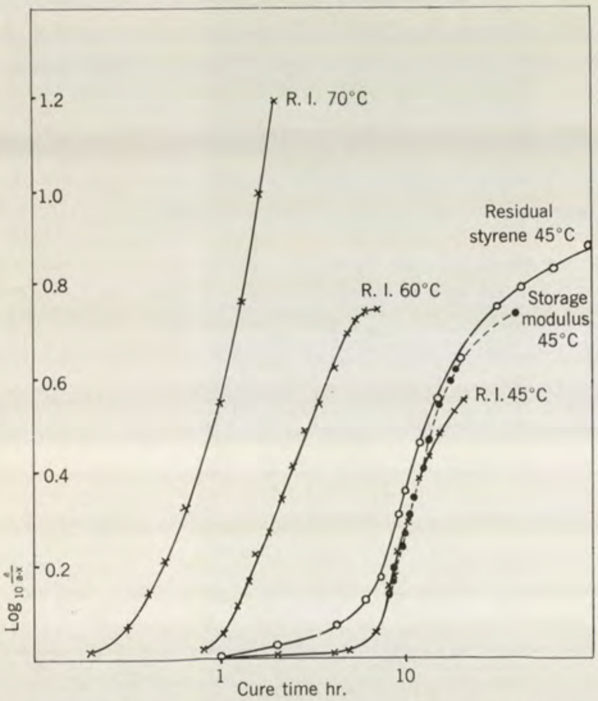

Figure 3. The rate curves obtained by three techniques: infrared, refractometry and measurement of modulus. Time is logarithmic.

The ratio of reacted styrene molecules to reacted fumarate molecules in the network was 4.77:1. This figure may be compared with one quoted by Hamann Funke and Gilch (7). These workers used a resin of closely similar initial molar feed ratio, and the degradative hydrolysis product they obtained showed a ratio of 5.35 moles of styrene to one of reacted fumarate.

Reaction Characteristics: A small fall was observed in the refractive index at the beginning of each polymerization. This was also noted by Dannenberg (10), and he attributed it to the hydrogen bonding of the amine used. The increase in refractive index at any given time was therefore said to be the increase over the minimum value reached after this small decrease, rather than the initial value.

It can be seen (*Figure 3*) that the reaction displayed the following characteristics:

- An induction period, short at the higher temperatures but appreciable at 45°C.
- An acceleratory period, a region of maximum rate.
- A fall-off to zero rate over a very long time.

The induction period is due to the clean-up of the hydro-quinone inhibitor by which polyester resins are protected against premature drift, and to the removal of very slight traces of oxygen or other impurities from the system. There has been mention (12) of the difficulty of getting reproducible rate curves with low catalyst concentration in the presence of oxygen.

The acceleratory period is marked by what in extreme cases appears as a kink, but in others is just a sharp upward turn at a certain point. This is the Trommsdorf effect, whereby at the gelation point, the termination step is controlled by diffusion before the propagation reaction is similarly affected. The result is an increase in the rate after gelation. Later on, the rate falls off as the propagation step is affected by diffusion control as well.

Overall Energy of Activation: It was in order to find this quantity, E, that the only departure from the fixed temperature of 45°C was made. Rate curves were plotted using the first order expression $\log_{10} a/a\text{-}x$ against time, where a refers to the initial concentration, and x to the quantity consumed at time t. The reaction is not thought to be strictly first order; however, it is first order with respect to styrene and to fumarate separately, and since the styrene is in considerable excess, it gives first order plots when physical data are used.

A value for a had to be assigned for the runs measuring refractive index. Since infrared data suggest that the reaction is substantially complete after 6 hr at 70°C, the value chosen for a was the value of the increase in refractive index at the end of the 70°C experiments; i.e. 3600 units of the fifth place of decimals. This value can also be arrived at by using one of the correlation curves (*Fig. 4*) and extrapolating to zero styrene. The first order equation is:

$$\frac{2.303}{k}\log_{10}\left(\frac{a}{a-x}\right) = t, \qquad (1)$$

so the slope gives k, the reaction rate constant at the temperature of reaction. For two different temperatures T_1 and T_2, the rate constant varies according to:

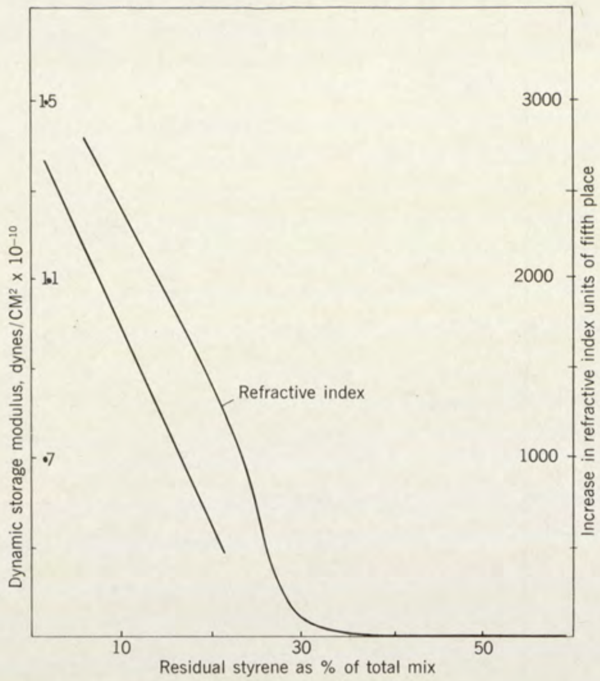

Figure 4. Correlation curves between (a) dynamic modulus and (b) refractive index and the styrene content of the curing resin.

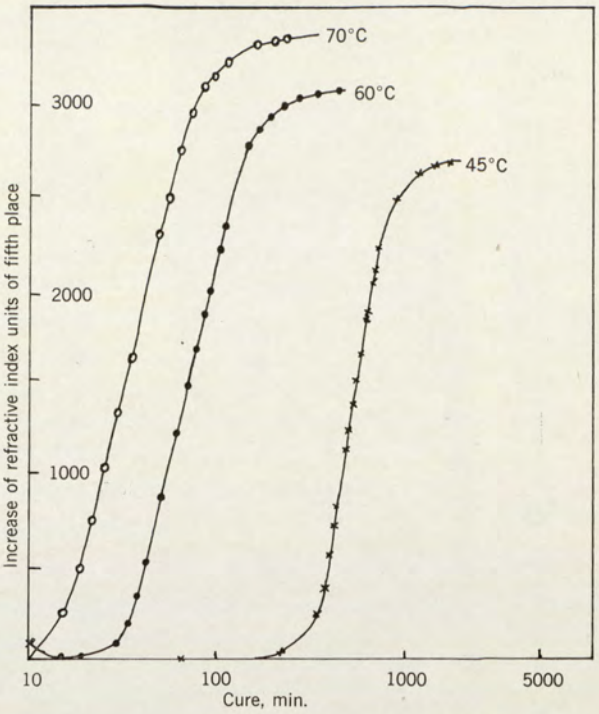

Figure 5. The refractive index of the resin as a function of cure time at various temperatures. Time is logarithmic.

$$\log k_1 - \log k_2 = \frac{E}{2.303\,R}\,\frac{(T_1 - T_2)}{T_1T_2}, \qquad (2)$$

and so the activation energy E was found.

The rate constant k is not analogous to the rate constant for simple chemical reactions. It is a compound of several rate constants for the separate reaction steps—initiation, propagation etc. The method for finding the individual rate constants is discussed in textbooks of polymerization kinetics (13). In a normal vinyl addition polymerization, for instance, the overall rate constant is

$$k = \frac{(fk_dk_p^2)^{1/2}}{k_t}, \qquad (3)$$

where f is the efficiency of utilization of primary free radicals, k_d the rate constant for the decomposition of the initiator and k_p and k_t are corresponding terms for propagation and termination. No attempt was made to determine the equivalent constants for this reaction.

Correlation Curves: Correlation curves were drawn (*Figure 4*) showing the relationship between the quantity of residual styrene and the refractive index, and between the residual styrene and the dynamic storage modulus. It was decided to relate the physical properties to the styrene rather than to the total unsaturation, because there exist several methods for determining residual styrene (e.g. gas chromatography, infrared and titration), and on the whole these seem to be easier and more reliable than the methods for polyester unsaturation. Also, the styrene component is in such excess that the correlations approach linearity for the greater part of their length even without the fumarate being taken into account. A larger deviation would be expected for such a property as refractive index, and this is seen here. Had the cure temperature been high enough to permit fumarates to continue reacting in quantity for a longer period, this particular curve would have given further departure from linear appearance. In this case, it is seen that the latter part of the reaction is largely the incorporation of styrene into the network (*Figure 2*).

Results

The values of the overall rate constants obtained are shown in *Table 1*.

Table 1. Overall rate constants

Method	Temp °C	k × 10^4 sec^{-1}
Refractometry	45	0.43
Refractometry	60	2.14
Refractometry	70	4.10
I.R. (styrene)	45	0.41
Dynamic storage modulus	45	0.39

Initial refractive index at 45 degrees: 1.53516

The overall activation energy calculated from the above refractometric runs was:

- 21.2 kcal/mole at 45° and 70°C.
- 18.4 kcal/mole at 60° and 70°C.

(*Continued on page 59*)

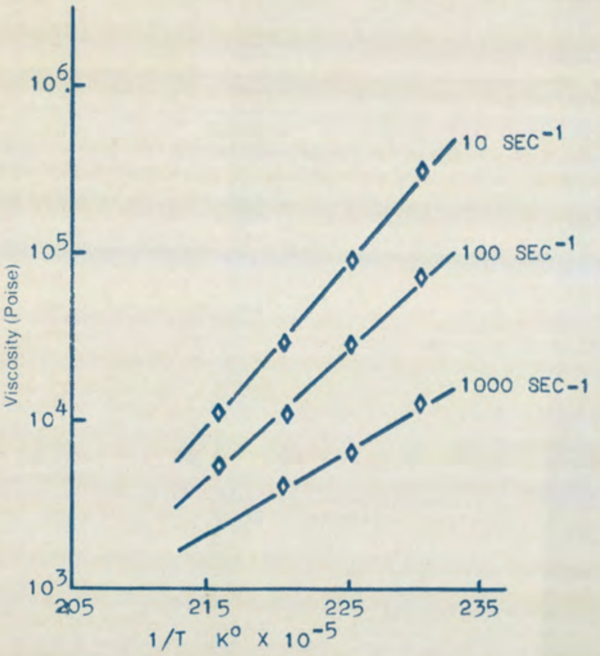

Figure 1. Log viscosity vs 1/T for Estane 58092 with shear rate as a parameter.

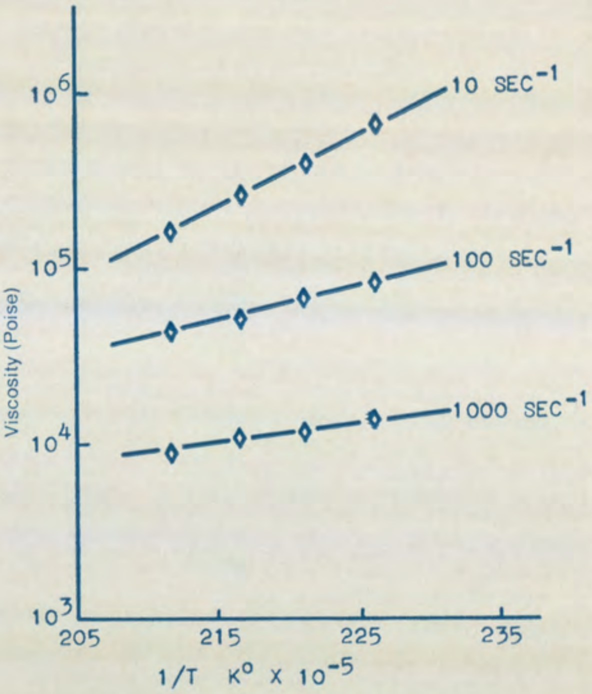

Figure 2. Log viscosity vs 1/T for Texin 355D with shear rate as a parameter.

Extrusion of Thermoplastic

Equipment design and operating conditions affect extrudate

During the past several years there has been an increasing demand for materials which have a combination of outstanding physical properties and the ability to be processed on conventional thermoplastic processing equipment. Of these, the thermoplastic polyurethanes occupy the unique position bridging the gap between the rubbery elastomers and the rigid plastics. These materials possess a wide range of properties, from a hardness of 75 Shore A to 60 Shore D and consequently exhibit a wide range of processing conditions. This treatise outlines general conditions for the extrusion of these materials and provides specific operational data for several commercially available materials. General equipment recommendations for the extrusion of polyurethanes can be applied to all forms.

Properties of Urethanes

The physical properties of the thermoplastic polyurethanes cover a broad range as shown in *Table 1*. The extreme toughness of these materials which make them so useful to industry also makes them somewhat more difficult to extrude, in terms of power requirements and developed pressures, than polyethylene and flexible vinyl.

The thermoplastic polyurethanes have no definite melting point but soften gradually on heating, in a manner similar to flexible vinyl. However, they do achieve a fluid state similar to low density polyethylene at temperatures below the point of degradation. The initial softening points range from 250-275°F, and the materials generally process at temperatures ranging from 320 to 410°F. Temperatures above 430°F generally result in polymer degradation as evidenced by bubble formation.

The change of viscosity resulting from temperature variations can be seen in *Figures 1* and *2* showing log viscosity vs 1/T with shear rate as a parameter for Estane 58092 and Texin 355D. In most extrusion processes, shear rates in the order of 100 sec^{-1} are realized. The variation of viscosity with temperature shown in these figures is typical for the thermoplastic polyurethanes. It is this large variation in melt viscosity that allows these materials to be extruded in processes as different as shape extrusion and melt lamination.

Although melt index is commonly used as a guide to processability of common polymers, the melt index of the polyurethanes varies considerably with minor changes in testing conditions. However, values of 10 to 30 mg/10 min at 365°F and 73 psi have been reported.

nylon material, filling the outer periphery.

There are many potential applications where this process can be used, and in some instances it can be reversed; whereby the pressure can be applied from the exterior periphery, forcing the material toward the center (such as might be used for ring gears, cams, etc.).

Vacuum Molding

Air and volatiles are greater detriments in transfer molding than in compression molding. They are responsible for unfilled parts, weld joints resulting in lower strength and slower molding cycles. Proper air venting reduces these difficulties, but there are certain limitations in air venting—particularly in deep portions, dead ends and sharp corners within the mold where it is not possible to incorporate an ejector or activated pin for rapid discharge of volatiles and air.

The Vacu-Mold process mitigates these problems. It provides instantaneous evacuation of volatiles while the cavity is being filled.

Mold temperatures depend on the type of thermosetting material being molded, but are generally in the range of 280° to 400°F. The higher temperatures can be used with this vacuum process without a burning condition at dead ends because of the continuous movement of the material and due to the absence of air within the cavity.

Recommended transfer pressures are the same as for conventional transfer molding, 4,000 to 12,000 psi, depending on the type of material. Plunger speed, however, can be very fast, 3 to 5 sec, and still fill out satisfactory parts. The range of vacuum under which this process is operated depends on the size of the cavity, the size of the vent and the time in which the air should be evacuated from the cavities. Best results in test runs were in the range of 15 to 25 inches of vacuum. Lower vacuum can be used if longer time is allowed for the evacuation period.

This process is also adaptable to certain types of compression molding. It is, however, much more difficult to use in compression than in transfer molding. It can only be applied where large preforms are used directly over an impression within the cavity. An example is in the wire connector towers in the automotive distributor cap. Vacuum channeling from several different points seems quite complicated. However, since only drilling of holes is involved, it should actually be quite economical.

About the Author

William R. Windover holds a BS degree in Business Administration from the University of Buffalo. He also has degrees in Tool Design and Machine Design from the Erie County Technical Institute. He joined Durez Division of Hooker Chemical Corp. in 1956. He is a past president of the Buffalo Section SPE and is presently on their Board of Directors. He is immediate past chairman of the Plastics in Automotive PAG and is presently chairman of the Thermosetting PAG.

The Cross-Linking of Polyester . . .

(Continued from page 49)

That these figures differ is expected since the initiation step is affected by temperature. Below 60°C the benzoyl peroxide is decomposed by reaction with the tertiary amine, but above 60°C it decomposes whether an activator is present or not.

Conclusions

The study of this polymerizing system has been carried an important stage further by relating some physical changes to chemical ones occurring in the system. A method was developed which rapidly assesses the efficiency of a new system in cross-linking polyester resins, under approximately isothermal conditions, and which detects comparatively slight undercure. Modifications to the infrared technique would be necessary to apply this to non-isothermal conditions.

Acknowledgment

Acknowledgment is made to Mrs. S. Whiting for assistance with the infrared laboratory work.

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About the Authors

G. S. Learmonth received his PhD in chemistry at Edinburgh in 1935. He is senior lecturer in plastics technology at the University of Aston in Birmingham, England. His present work is in the field of polymer degradation and cross linking. His experience includes work in the fields of paint, ammunition filling, and reinforced plastics.

G. Pritchard graduated from Saint Andrews in Scotland in 1961 with a BS in chemistry. His experience includes several years in the rubber industry, polymer synthesis and teaching. He is currently working for his PhD.

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Development of Plastics Automotive Fan Shrouds

Use of plastics offers promise of an improved cooling job

A number of different methods have been used during the history of the automotive industry for the rejection of waste engine heat. During most of this period, the most common method has been by circulation of a liquid cooling medium, usually water or a mixture of water and an ethylene glycol antifreeze. Through the use of a radiator and fan, the cooling medium is brought into contact with large quantities of air, thus removing the waste heat that has been rejected by the engine to the coolant. There are several ways to evaluate how well this task is performed.

Air to Boil is the ambient air temperature at which the cooling system would just begin to boil under a given set of test conditions, which simulate operation of a heavily loaded vehicle at normal speeds. The higher the value of *Air to Boil,* the more effective is the cooling system. This index then includes the effect of the radiator size, the fan size and drive ratio and the heat rejection of the engine.

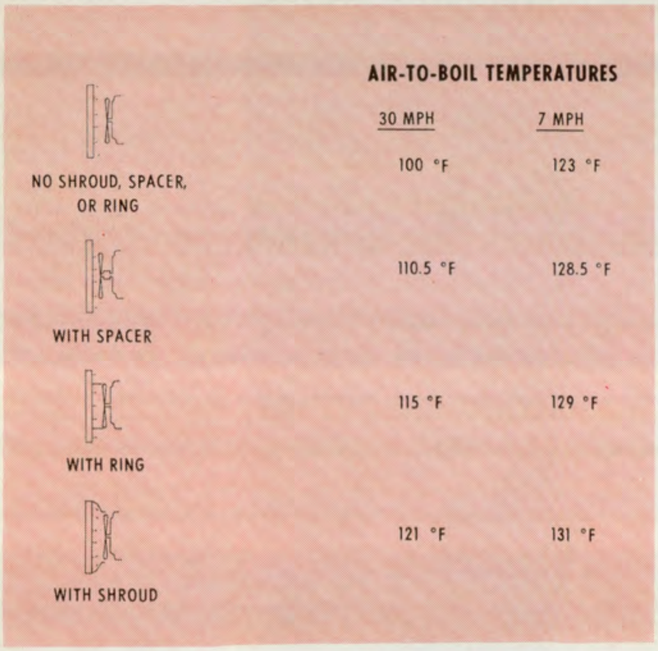
Idle Cooling is evaluated by idling the engine after operating it under a given set of idle entry conditions, which generally duplicate operating conditions of a heavily loaded vehicle traveling at turnpike speeds. Elapsed time between the start of the idle test and the onset of cooling system boiling gives a measure of the cooling system's effectiveness. A slightly more sensitive measure is a plot of radiator-top tank temperature against time during the idle test. The criterion of cooling efficiency in the *Idle Cooling* test is time: the longer it takes to reach boiling, the more effectively is the excess heat being thrown off.

Value of Fan Shrouds

The function of fan shrouds is to direct and conduct air from the radiator to the fan. This improves the fan efficiency and thereby the overall cooling efficiency. A shroud usually is used where the engine is mounted some distance away from the radiator.

Shown in *Figure 1* are various fan-radiator arrangements for routing the cooling air. The fan at the top is a considerable distance from the radiator. Its air moving capacity is misdirected, since its flow can circulate around the fan blade tip without flowing through the radiator. In the second example, the long spacer helps the fan draw air through the radiator, but there is still some recirculation, and the long spacer develops some undesirable loads on the water pump bearing. The fan ring is an approach to the shroud, but it does not allow the fan to draw air through the entire radiator core. The shroud not only allows shortening of the fan spacer but also enables the fan to draw air through the entire radiator core. Both the fan ring and the fan shroud help fan air delivery by making the fan blade tips more efficient.

Figure 1 illustrates how cooling performance may be improved by the use of a fan shroud. These are test results from a typical light duty truck. Even in such a vehicle, which relies to a great degree on ram air for cooling air flow, the improvement in cooling is significant when the shroud is used. The long spacer gives 5 to 10° higher *Air to Boil* (*ATB*), the fan ring gives 6 to 15° higher *ATB*, and the fan shroud 8 to 21° higher



	AIR-TO-BOIL TEMPERATURES	
	30 MPH	7 MPH
NO SHROUD, SPACER, OR RING	100 °F	123 °F
WITH SPACER	110.5 °F	128.5 °F
WITH RING	115 °F	129 °F
WITH SHROUD	121 °F	131 °F

Figure 1. Effect of radiator—fan arrangements.

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Cure of Polyester Resins. II

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Synopsis

The copolymerization reaction between unsaturated polyesters and styrene has been studied by a torsional pendulum. The accuracy of the dynamic-mechanical measurements obtained is discussed briefly, and the results are compared with those of previous work on the change of hardness during cure.

INTRODUCTION

The crosslinking of unsaturated polyesters by a copolymerization reaction between the double bonds from maleic or fumaric acids and styrene has previously been followed by various means. In a previous paper[1] methods were reviewed and hardness was measured during cure by Barcol and hot needle indentation methods. The study of this process of crosslinking has been continued by using dynamic-mechanical methods.

It is to be expected that dynamic-mechanical measurements of shear modulus and mechanical loss factor will show significant and characteristic changes during copolymerization. The modulus of elasticity has been shown to be directly proportional to the number of crosslinks at a given temperature and frequency.[2] Mechanical damping probably depends on the number of free reactive chain ends in the system[3] and should decrease during crosslinking.

Dynamic-mechanical tests involve the measurement of the deformation of a specimen in response to a sinusoidally varying stress. Such methods have been used extensively in studying polymeric materials[4,5] and indeed in studying fully crosslinked polyesters.[6,7] Special techniques of this type have been used to study the cure of resins other than polyesters.[8,9]

In order to cover the spectrum of applied frequencies and the range of viscoelastic behavior expected from a polyester resin, it is necessary to use a variety of instrumental techniques.

In this paper we describe the study of the crosslinking of a commercial, general-purpose, low-viscosity resin, B.I.P. Beetle 4116, by the use of a torsion pendulum. Some experiments were also carried out on a rather different resin from Scott Bader & Co. Ltd.

The torsion pendulum was used only from 0.5 to 5 cps.

Torsion Pendulum

The oscillations of a horizontal torsion bar suspended by a fine wire are damped by a test specimen which is clamped in a vertical position, fixed rigidly at its lower end to the base of the instrument. The natural oscillations of the pendulum are thus damped to an extent which depends on the modulus and mechanical damping of the polymer used. Many different recording systems have been used to record the oscillations; in this case the instrument, (Nonius, Delft, Holland) used an induction coil and a spark track through conducting recording paper.

The shear modulus G (in psi) is obtained from the period of oscillation p (in seconds) and the damping from the ratio of two successive amplitudes, as follows for samples of rectangular section:

$$G = 5.588 \times 10^{-4} LI/WD^3\mu p^2$$

where the logarithmic decrement is given by:

$$\Delta = \ln (A_1/A_2) = \ln (A_2/A_3) = \ln (A_n/A_{n+1})$$

and where L, W, and D are the length, width, and thickness, respectively, of the specimen (in inches), I is the polar moment of inertia of the system (in grams-square centimeter), μ is a shape factor depending on the ratio of the dimensions, and A_n is the amplitude of the nth peak.

Alternately, for cylindrical specimens of radius r'',

$$G = 2.22 \times 10^{-5}\, LI/r^4p^2$$

Since G depends on the frequency, which varies with the cure of the resin, it is necessary to make alterations to I by attaching weights to the torsion bar. This gives a plot of G against $1/p$, from which G at a single fixed frequency (say, 1 cps) may be interpolated.

Reproducibility

There are few errors inherent in the method of measurement. Apart from occasional slippage in the clamps or nonaxial alignment of the specimen, the main source of error is in the measurement of the dimensions of the specimen. Air damping can effect the results appreciably where internal friction is low. Care is required in reading the graphical records obtained, especially at high frequency. T.N.O., Delft,[10] who devised the instrument, claim an accuracy under favorable circumstances of ±2% for the modulus and ±5% for the damping factor.

The specimens of rectangular cross section used initially underwent shrinkage during cure, in such a way as to give faces with stress concentrations at the edges. Cylindrical ones were therefore adopted for preference in later work.

In addition to these general factors, the errors peculiar to the polymerizing system used are: (*a*) the error due to any nonuniformity of destruction of free radicals in the mass; (*b*) variation of the temperature of the sample with time during curing. The reaction is strongly exothermic and so the temperature rises to an extent dependent on the sample size and type of mold.

A major objective of the work described here was to test the reproducibility of the results in these respects. Hence several castings were made under identical conditions.

EXPERIMENTAL

Formulations Used

The formulations used are given in Table I.

TABLE I

	Parts (by weight)		
	A	B	C
Beetle resin 4116	100	100	—
Scott Bader resin (isophthalic acid–fumaric acid–propylene glycol)	—	—	100
Benzoyl peroxide	1	1.25	1
N,*N*-Dimethyl *p*-toluidine	0.05	0.035	0.035
Curing temperature, °C.	35	70	70

Casting Procedure

A steel mold was used to cast eight specimens simultaneously. This mold could be used to give specimens of rectangular cross-section having dimension 6.0 ± 0.4 in. × 2.75 ± 0.010 in. × 0.140 ± 0.010 in. or alternatively cylindrical specimens, 6.0 ± 0.4 in. × 0.230 ± 0.010 in. diameter.

The composition was mixed very thoroughly and deaerated briefly under a moderate vacuum. It was then poured carefully into the mold and heated in an air oven. After a certain time the mold was opened, and the specimens replaced loose in the oven to be removed at regular intervals.

All measurements were made on specimens conditioned to a temperature of 25 ± 1°C.

The pendulum was calibrated, in order to calculate the moments of inertia used, by using a steel specimen which was assumed to have a modulus independent of the frequency changes involved.

RESULTS

Figure 1 shows how the changes in the shear modulus with time of cure for formulation A compare with the changes in Barcol hardness and hot needle indentation.

Figure 2 shows the changes in modulus and damping (logarithmic decrement) of another resin (formulation C) cured at 70°C.

In addition to the data shown in these figures, castings were prepared at the same cure time, in order to assess the reproducibility both of the method

TABLE II
Reproducibility for Shear Modulus G' for Formulation B, 24 hr. Cure at 45°C.

Specimen no.	$G' \times 10^{-9}$, dyne/cm.^{2} Casting 1	Casting 2	Casting 3	Casting 4	Casting 5	Casting 6	Casting 7	Standard mean deviation between casting operations, %[a]
1	11.75	11.48	11.75	10.96	12.05	11.90	11.60	2.62
2	11.00	11.22	11.50	11.45	11.05	11.10	11.50	1.69
3	12.02	11.00	11.01	11.55	11.80	11.16	11.10	3.09
4	12.02	11.02	10.97	10.84	11.00	11.94	10.94	3.73
5	11.08	11.52	10.98	10.69	10.45	11.23	11.12	2.61
6	11.20	11.02	11.08	11.01	11.13	11.27	10.92	0.85
7	11.45	11.25	10.80	11.15	11.13	11.45	11.20	1.25
Standard mean deviation between specimens in the same casting, %[b]	3.34	1.52	2.43	2.26	3.56	2.45	1.79	

[a] Average mean deviation for different casting operations = 2.26%.

[b] Average mean deviation for different specimens in the same casting: 2.48%.

TABLE III

Logarithmic Decrements for Formulation B, 24 hr. Cure

	Logarithmic decrement Δ							
Specimen no.	Casting 1	Casting 2	Casting 3	Casting 4	Casting 5	Casting 6	Casting 7	Standard mean deviation between casting operations, %[a]
1	0.196	0.217	0.200	0.228	0.210	0.199	0.220	4.76
2	0.212	0.237	0.218	0.225	0.234	0.215	0.213	3.84
3	0.207	0.220	0.204	0.258	0.199	0.215	0.218	5.78
4	0.192	0.246	0.209	0.239	0.221	0.236	0.200	7.72
5	0.208	0.228	0.213	0.257	0.220	0.220	0.234	5.30
6	0.190	0.236	0.221	0.211	0.236	0.210	0.224	5.04
7	0.222	0.232	0.216	0.256	0.214	0.215	0.216	4.97
Standard mean deviation between specimens in the same casting, %[b]	4.56	3.46	3.01	6.28	4.56	3.24	3.21	

[a] Average mean deviation for different casting operations: 5.34%.

[b] Average mean deviation for specimens in the came casting: 4.05%.

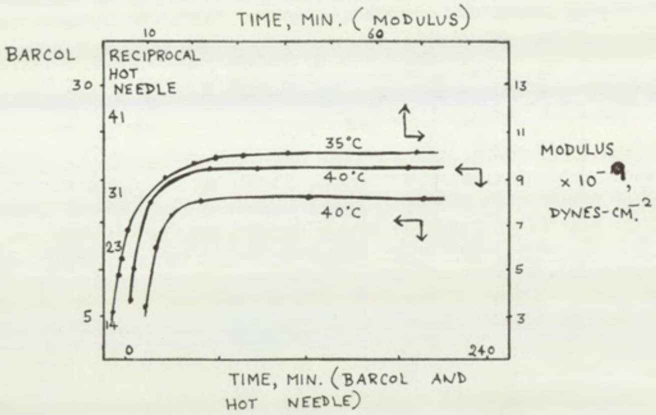

Fig. 1. Changes in shear modulus, Barcol hardness, and hot needle indentation (Formulation A).

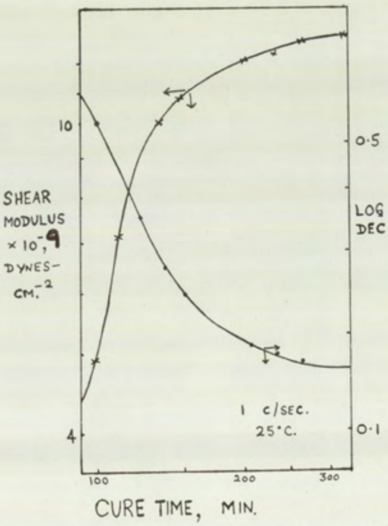

Fig. 2. Changes in modulus and damping during cure at 70°C. (Formulation C).

and of the reaction path. Seven specimens were prepared at a time, in one operation, and seven different casting operations were performed, making 49 specimens in all.

Moduli and logarithmic decrements are tabulated in such a way that the variation from specimen to specimen in the same casting, and also the variation between casting operations can be seen (Tables II and III).

It appears that there is little difference between the standard deviations obtained for the moduli in a given operation and the same deviation between several casting operations. In fact the latter appears slightly lower; although this would not be expected, the difference is too small to be significant. Damping terms are obtained which are predictably less consistent between castings than between specimens in the same casting, and the magnitude of the standard deviation in all cases agrees with the figures given by T.N.O. for torsional pendulum used.[10] The implication here seems to be that for a given mold shape and size, there is no great difference between the state of reaction at a given time in one run and that in another.

CONCLUSIONS

The progress of crosslinking, as defined by measurements with the torsional pendulum, is closely related to that given previously by hardness tests (Fig. 1).

None of these methods can be used until well after gelation, though Lewis has used torsional braid techniques, which are basically similar, to give some indication of the earlier stages of reaction.

Figures 1 and 2 show that rapid changes are occurring in both modulus and damping at the point where measurements start. Hence other methods are required to supplement this technique by covering the earlier stages of cure.

Clearly we have defined the second part of a sigmoid curve, which shows the decrease in rate of curing. This fall-off in rate is associated with a decrease in the number of double bonds sufficiently mobile to take part in crosslinking, with a decrease in the concentration of free radicals, and with a decrease in the mobility of the system due to increasing crosslink density.

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The Dynamic Behavior of Undercured Polyester Resins,

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A mechanical test using the resonance principle was applied to produce longitudinal vibrations in a cylindrical rod from which Young's modulus was determined

The commercial need for a clear understanding of the relationship between the various changes in a curing thermosetting resin is well known (1, 2, 3). Undercured resins are inferior (4), but long cure times are uneconomical. Also, theoretical knowledge of three-dimensional network formation is somewhat limited, owing to the difficulty of chemical reactions with cross-linked materials.

Several investigators have followed particular properties of polyester resins during cure—for instance, resistivity (5), Young's modulus (6), and the velocity and attenuation of ultrasonic waves (7). In each case a different resin and polymerizing system, and often different conditions of temperature, etc., have been used, whereas in the work described below the conditions have been standardized (except where stated), and so correlation between physical and chemical results is possible.

The present program began with an examination of resistivity and hardness (8), but the conditions were not quite identical with those following, namely torsional modulus and loss tangent (9), refractive index (10), and spectroscopic measurements of residual unsaturated groups (10). The present work is similar to that described earlier using a torsional pendulum (9), except that instead of a freely vibrating system at low frequency giving a shear modulus, we have a forced vibration apparatus, operating (in tension and compression) in the audio frequency range, giving Young's modulus.

Dynamic Mechanical Testing Techniques

In dynamic testing, the response of a material to a sinusoidally varying stress is observed. The energy stored in the specimen is expressed as a storage modulus, G′ (for shear) or E′ (for extension). The energy lost may be expressed by a corresponding loss modulus, G″ or E″ or by a related damping term. These terms are explained in detail elsewhere (11, 12).

Various machines operating in the audio frequency range utilize the resonance peak obtained when an amplitude-frequency curve is plotted. The value of the resonance frequency obtained gives a direct measure of the Young's modulus at that frequency. Among different resonance instruments, the vibrating reed is perhaps most common. In this work, however, longitudinal waves are set up in a rod clamped at its mid-point.

Instrumentation

A long, thin, cylindrical specimen rod was clamped at its mid-point by three symmetrically arranged screws. At each end of the rod, machined so as to be flat and perpendicular to the long axis, small aluminum plates were attached by a thin layer of adhesive. These plates were connected to each other and to earth (*Figure 1*).

A 6-watt audio oscillator transmits a signal to a driver electrode which is located by a micrometer arrangement to within about 30 microns of the aluminum plate on one end of the specimen, thus providing an electrostatic transducer. The output signal generated at the other end of the rod is amplified and displayed on an oscilloscope below the display of the input signal. A bias voltage of up to 500 volts dc, applied to both electrodes, prevents polarity changes giving rise to a double cycle of vibration, and provides a polarizing voltage for the pick-off electrode.

The specimen vibrates in the longitudinal mode. The frequency with this oscillator could be varied from 20 cps to 20 Kc and was measured by an external frequency counter. It is not necessary to measure the absolute value of the amplitude to obtain the frequency response curve (*Figure 2*).

Evaluation of Results

The dynamic storage modulus E′ of a rod of length L cm, density ρ gm/cc, and attenuation α nepers/cm is given by:

$$E' = \frac{\rho\omega^2 v^2(\omega^2 - \alpha^2 v^2)}{(\omega^2 + \alpha^2 v^2)^2} \quad \text{dynes/cm}^2, \tag{1}$$

where v is the velocity of sound at angular frequency, ω.

Where α is small, as it is for the polyester resins used here, this expression reduces to:

$$E' \simeq \rho v^2 \tag{2}$$

At fundamental resonance, the wavelength, λ, is twice the length of the rod, so:

$$E' = 4\rho L^2 f_r^2 \text{ at frequency } f_r. \tag{3}$$

Instead of using the term attenuation, the quantity evaluated here to indicate the damping is Δ_E, the logarithmic decrement, obtained from the expression:

$$\Delta_E = \frac{\pi \Delta f}{f_r}, \tag{4}$$

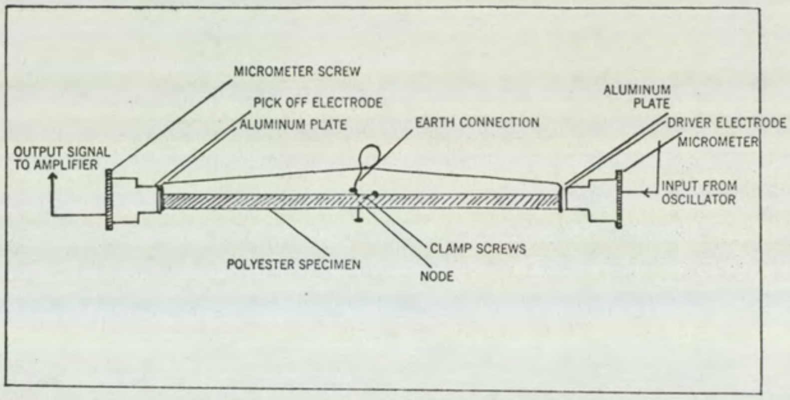

Figure 1. Test apparatus for the audio frequency tester (courtesy of Dawe Instruments Co., Ltd.)

where Δf is the frequency range for which the amplitude is at least $1/\sqrt{2}$ of its maximum value. Δ_E may be related to α by:

$$\alpha \simeq \frac{\Delta_E}{2L}, \tag{5}$$

and α is defined by the expression:

$$D = D_o e^{-\alpha x} e^{i}\left(\omega t - 2\pi \frac{x}{\lambda}\right), \tag{6}$$

where D is the deformation due to a wave of wavelength λ at a point x along the strip. Specimen calculations are given in *Table 1*.

In a resonance experiment it is impossible to fix the frequency, and the normal procedure is to use quasi-isochronous measurements over a limited range. The range of frequencies used was from 4 to 6.5 kc. However, determinations of E′ and Δ_E over a range of

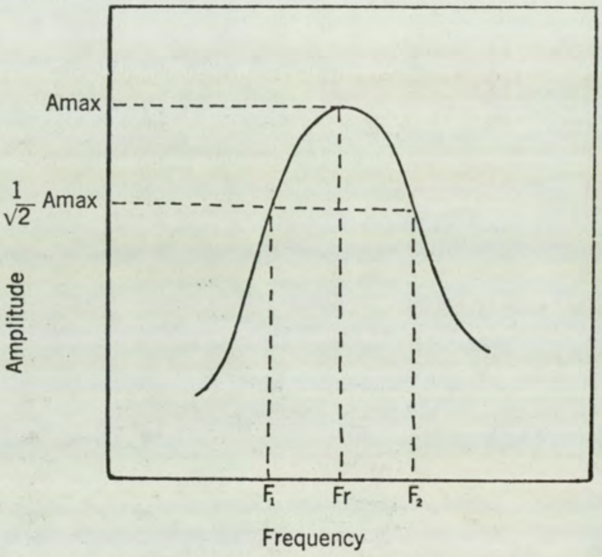

Figure 2. Frequency response curve.

Table 1. Specimen results

Cure time, hr at 45°C	f_1, cps	f_r, cps	f_2, cps	ρ, gm/cc	L, cm	E′, dynes/cm^2 $\times 10^{-10}$	Δ_E	v, cm/sec $\times 10^{-5}$	G′, dynes/cm^2 $\times 10^{-10}$	Δ_G
7¼	*	3670	*	1.16	17.38	1.88	*	1.28	—	—
8½	*	4110	*	1.16	17.38	2.36	*	1.43	0.350	0.630
9½	4067	4353	4704	1.16	17.52	2.69	0.459	1.53	0.475	0.535
10¾	4315	4674	4988	1.16	17.52	3.10	0.452	1.64	0.625	0.450
12	4295	4622	4858	1.16	17.52	3.03	0.382	1.62	0.750	0.370
13½	4483	4691	4922	1.16	17.52	3.12	0.294	1.64	0.880	0.320
15	4581	4805	4998	1.16	17.52	3.28	0.272	1.68	0.975	0.305
16½	4850	5036	5215	1.16	17.51	3.60	0.226	1.76	1.010	0.288
17¾	4901	5120	5370	1.16	17.51	3.72	0.288	1.79	1.030	0.277
19¼	4894	5009	5256	1.16	17.51	3.56	0.227	1.78	1.051	0.271
21¼	5077	5213	5349	1.16	17.51	3.86	0.164	1.82	1.053	0.264
24	5264	5383	5559	1.17	17.30	4.07	0.173	1.86	1.080	0.250
28¾	5334	5450	5558	1.18	17.25	4.19	0.129	1.88	1.100	0.233
38¾	5631	5765	5896	1.17	16.72	4.35	0.144	1.93	1.150	0.210
63½	5734	5830	5915	1.17	17.50	4.84	0.097	2.04	1.175	0.170
130	6005	6041	6163	1.18	16.39	5.18	0.082	1.98	1.230	0.130

* No value of Δ_E was assigned here, because the frequency response curve was too wide and shallow.
f_1 and f_2 refer to the limits where the amplitude was at least $1/\sqrt{2}$ of its maximum value.

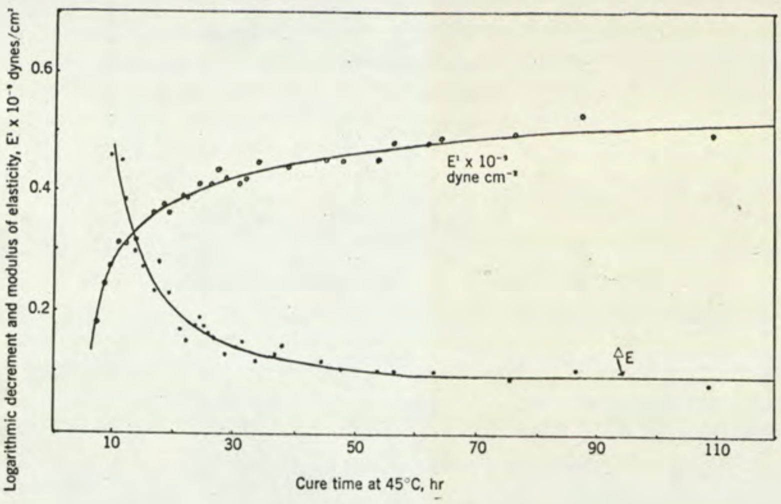

Figure 3. The effect of curing time on Young's modulus and damping of polyester resin castings.

frequencies from 2 to 12 kc, obtained by altering the dimensions of the sample, showed very little effect of frequency on modulus and damping in this particular range. No doubt the frequency dependence of both properties is more marked in the early stages of cure, but this region was not studied.

Experimental Procedure

One hundred parts by weight of B.I.P. Beetle 4116 polyester resin in styrene, one active part by weight of benzoyl peroxide in paste form, and 0.007 parts of N, N′ dimethyl para-toluidine were mixed, de-aerated and poured into a stainless steel mold. Styrene evaporation was prevented by a lid, and the mold was placed in a forced-draft oven at 45°C. Thermocouples immersed in trial samples showed no significant exotherm (the peak temperature obtained was 46°C) on account of the thin cross-section used. Each molding produced eight rods approximately 6 in. × 0.230 in.

Infrared measurements on this system (10) show that at the temperature used, a complete cure was not obtained after 120 hours. Some specimens were therefore prepared at 70°C, since infrared work suggested that the reaction was substantially complete after six hours at 70°C.

The rods were measured and weighed and their mid-points marked. After the aluminum plates had been attached, readings were taken. Fundamental resonance was assured by the use of the input display to compare the excited vibration frequency with that of the input signal. It was necessary to reweigh and measure the specimens after further curing, as the density increased by about 2½% during the range of curing investigated.

A temperature jacket made of expanded polystyrene was used to keep the specimen at approximately 24°C ± 1°, by means of a stream of warm air.

Accuracy Limitations

According to the manufacturer, the instrument is capable of giving modulus values to an accuracy of 0.01% for materials of this type, and damping values to 1%. This presupposes the use of a frequency monitor, since the oscillator scale could not be tuned to better than 1 in 10^4. Clearly, the dimensions of the specimen must be known with a high degree of accuracy, but the modulus is proportional only to the first power of the length and entirely independent of the radius for this rod.

In practice the limitations of the accuracy of the technique seemed more serious and stemmed from other considerations. Slight shifts in the position of the clamp screws affected the position of the resonance peak, and the width of the air gap at the electrostatic coupling electrodes affected the shape of the peak, as is usual with this kind of technique (13). If the end of the rod was not completely flat and perpendicular to the long axis, or if slight warping had occurred in the latter stages of cure (in the case of specimens removed previously from the mold) no satisfactory result could be obtained. Rods less than 5 in. long did not give good resonance peaks.

In spite of these disadvantages, the method gave a fair indication of the degree of cure of the samples, and the results obtained for the velocity of sound in the cured resin agree with those of others on the same material (7). (It is unlikely that the difference in frequency used by Sofer and Hauser in their non-resonance method would affect the velocity of sound very much in a fully cured resin.) The extent of scatter of readings obtained is indicated in *Figure 3*. As indicated earlier, the values of E′ and Δ_E are not to be read as completely isochronous.

Discussion of Results

Familiar sigmoid curves analogous to those reported elsewhere (5, 6, 7, 8, 9, 10) were obtained. At 45°C these curves did not reach their asymptotic values even after several days. They do not cover the whole range of polymerization, as unlike the bulk-wave method of Sofer and Hauser (7) the technique does not lend itself readily to study of the liquid stage. (A complex modulus could be found by curing the

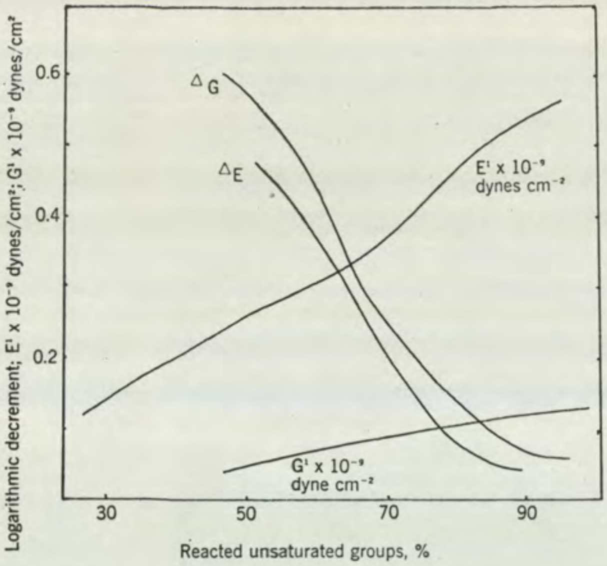

Figure 4. The relationship between the dynamic properties of the castings and the extent of cross-linking.

resin in a metal tube and vibrating the tube.) Since the gelation stage was not included, no peak was found in the damping term Δ_E. This property became easier to estimate in the intermediate and later stages of cross-linking, when the bandwidth was reduced considerably. Different specimens showed slightly different cure curves which could be superimposed by a small shift of the horizontal axis.

Correlation Curves

The method for estimating the extent of reaction of the unsaturated groups has already been described (10). The percentage of reacted unsaturation at a given time was plotted against the dynamic properties obtained by both the resonance method given here and the torsional pendulum (9).

Taking into account the degree of error inherent in quantitative infrared work on thermosetting resins, the curves shown (*Figure 4*) approximate to straight lines in their central portions, but not in the high degree-of-reaction portion. The similarity between the values of Δ_E and its analogous Δ_G (from shear experiments) is very marked, suggesting only a slight frequency dependence of this property over the range from 5 to 5,000 cps. These similarities are shown in *Table 1*.

Using the relationship

$$E = 2G(1 + \nu),$$

where ν = Poisson's ratio, the expected value for E at 50% conversion would be 1.6×10^{-10} dynes/cm² if $\nu = 0.35$, whereas E' is in fact shown to be 2.7×10^{-10} dynes/cm². This suggests a considerable increase in shear modulus between the two frequency ranges employed.

The last 10% of chemical unsaturation can be seen to be responsible for an appreciable increase in both moduli, which remain in almost a linear relationship to the extent of reaction, but the damping expressions level out slightly, approaching the same value of about 0.060, which corresponds to the state when all unsaturation has reacted. This state is not usually reached.

At the temperature of cure used (45°C) it seems from infrared measurements that the fumarate (polyester backbone unsaturation) groups do not react very much in the latter stages, and the reaction therefore must proceed by styrene adding on to the copolymerization chains, the fumarate cross-linking sites being sterically protected. On the other hand, the end portions of the curves (from 87 to 97% unsaturation reacted) are taken from data at 70°C, when the fumarate sites are nearly all able to react, and the maximum possible cross-linking is approached. In so far as damping can be related to the number of loose chain ends and free-moving segments in the network, the utilization of the extra fumarate cross-linking sites does not seem to reduce these loose chain ends.

Conclusions

The use of a resonance technique involving longitudinal vibrations in the audio frequency range can give parameters which have an almost linear relationship with the degree of cure of a polyester resin, as chemically defined. Although the possible sources of error in the technique make it less attractive than the torsional pendulum method earlier described, useful comparisons have been made with other results. Further work in a frequency range of 50 to 1000 cps is required before these results can be fully utilized.

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