

THE EFFECT OF THE STRUCTURAL PARAMETERS OF POLYESTER RESINS ON
THE MECHANICAL PROPERTIES OF POLYESTER MOULDING COMPOUNDS

- by -

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ABSTRACT

A detailed study of the effect of polyester resin structural parameters on the mechanical properties of sheet moulding compounds has been carried out. The investigation involved the synthesis and mechanical testing of a series of unsaturated polyester resins and the incorporation of these resins into sheet moulding compounds (SMC) with their subsequent testing.

Two main structural parameters were varied, firstly the degree of unsaturation of the resin (i.e. maleic:phthalic ratio), and secondly the amount of diol excess added to the reaction vessel during the resin synthesis thereby varying the hydroxyl value of the resin.

It was found that the properties of the resins, both structural and mechanical, were interdependent. Altering the maleic:phthalic ratio was found to effect the hydroxyl value, notch sensitivity, shrinkage, and modulus of the resin.

Low resin hydroxyl values were found to give SMC with low tensile strength and low fracture toughness. Unusually high hydroxyl values enhanced the toughness but the SMC did not show the expected increase in tensile strength.

Surprisingly the toughness of SMC appears insensitive to the notch sensitivity of the resins despite the relatively wide range of resins used and their range of notch sensitivities. It was concluded that debonding was the predominant mechanism by which failure occurred in these composites and that the bond strength was enhanced by the use of a matrix resin with a suitably high hydroxyl value. A high hydroxyl value being dependent on the diol excess and the maleic:phthalic ratio of the resin.

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**Dedicated to my
Mother and
Father**

Chapter I

INTRODUCTION

1.1 General introduction

Sheet moulding compound (SMC) is an unsaturated polyester resin impregnated composite containing chopped-strand mat or rovings. As the name suggests the composite is in a sheet form and is manufactured by metering a polyester resin slurry onto the surface of the polythene films between which the glass reinforcement is sandwiched. The product is allowed to mature for a time during which thickening occurs and the resulting material is a leather-like hide which can be moulded by conventional compression moulding techniques. It is attractive to the moulder in that it can be easily handled and allows the incorporation of relatively large amounts of glass reinforcement. Furthermore it has excellent mould flow characteristics and produces strong mouldings of good quality and surface finish.

The main reason for employing fibrous composites in many structural applications is that they permit the use of a large volume of a high strength, stiff, brittle fibrous material. The strength and stiffness of glass reinforced plastics (GRP) result mainly from the glass fibre itself and the polymer matrix acts as an adhesive to transfer load between fibres. The fibres also increase the toughness of the brittle matrix material and thus the composites show a greater resistance to crack growth than the matrix alone. For the optimum performance of a composite material, sufficient adhesive strength at every point along the polymer glass interface is needed to transfer the load through the matrix from fibre to fibre. If the interfacial bond is weak, failure may result even at very low stress.

The polyester resin matrix present in SMC is important for the above reasons but significantly the polyester resin effects the thickening reaction vital to SMC usage. This thickening reaction is dependent upon the chemical backbone of the polyester and thickening results from a reaction with an alkaline earth oxide thickener.

1.2 Research aims and methods

The aim of this research was to gauge the importance of fundamental polyester resin structural parameters. This was carried out by synthesising in the laboratory a series of polyester resins. There were two methods of resin synthesis and the series involved a range of maleic:phthalic ratios (unsaturated acid:saturated acid) being incorporated into the polyester backbone. For two ratios the amount of excess propane 1.2 diol added was varied in order to be able to gauge the effect of resin hydroxyl value on the eventual SMC. The hydroxyl value of a resin is known to affect its thickening reaction.

Each resin was chemically analysed to record their actual structure and then cast specimens mechanically tested. All testing was in the tensile mode and as the ultimate use of the resin would be as a matrix resin it was felt important that the notch sensitivity of each resin should be known. This was done by the tensile testing of single edge notched specimens and values for fracture toughness (K_{IC}) ascertained.

SMC was then manufactured from each resin and hot press moulded into flat sheets. From these sheets specimens were cut and the mechanical properties and fracture toughness of the SMC found.

1.3 Synopsis of results

Data collected showed that properties of a polyester resin are interdependent. Altering the maleic:phthalic ratio was found to effect the hydroxyl value, notch sensitivity, shrinkage and modulus of the resin.

Low resin hydroxyl values were found to give SMCs with low tensile strength and low toughness. Unusually high hydroxyl values enhanced the toughness of the SMC but did not show the expected increase in tensile strength.

Surprisingly the strength and fracture toughness of the SMC was found to be insensitive to the notch sensitivity of the matrix resin.

It was concluded that that debonding was the predominant mechanism by which failure occurred in these composites and that the bond strength was enhanced by a suitably high hydroxyl value.

Chapter 2

2.1 The fracture of polymers

2.1.1 Introduction

Fracture mechanics is concerned with quantifying the concept of 'toughness' or 'resistance to crack growth'. When a loaded body fractures it does so at selected points within the material, and not as a whole as one would expect in a homogenous material. This is due to the presence of flaws, and it is this fact, and the manner in which these flaws propagate under stress, that is the basis of fracture mechanics (1).

Early work was concerned with brittle failure, but the development of the important concept of a stress intensity factor K , as a single parameter description of the elastic stress field in the vicinity of a crack tip, has encouraged the application of fracture mechanics to virtually any type of crack growth. The study of fracture in inorganic glass (2) and metals (3) is well advanced. The investigation of fracture in organic polymers began slowly, but there have been numerous investigations into the fracture of uncrosslinked polymers such as polystyrene (4) and polymethylmethacrylate (5). This was due to their extensive utilisation industrially and to their availability in reasonably reproducible and characterisable forms.

Attention has now been given to the study of fracture in crosslinked polymers, especially polyesters (6), epoxides (7), and phenol formaldehyde resins (8), as well as vulcanised rubbers (9). Further attention has been paid to both the fracture of reinforced uncrosslinked polymers (10) and crosslinked polymers (11).

Any crack toughness test is simply a model fracture experiment on a specimen that has been provided in advance with a suitable crack. The specimen is so designed that the value K , can be calculated from the observed load and the dimensions of the specimen and its crack.

2.1.2 Measurement of fracture mechanics parameters

Griffith (12) postulated an energy balance criterion to explain the fracture stress of a brittle material containing a crack. He stated that for extension to occur, the strain energy released as the crack extends must exceed the energy required to create new surfaces.

For elastic fracture, in a specimen with a through-thickness crack of length 'a', the relationship between the applied fracture stress, is either

$$\sigma_f = \left(G_c \frac{E}{\pi a} \right)^{\frac{1}{2}} \quad \text{plane stress conditions,}$$

or

$$\sigma_f = \left(G_c \frac{E}{\pi a} (1 - \mu^2) \right)^{\frac{1}{2}} \quad \text{plane strain conditions,}$$

where E is Youngs Modulus, μ is Poissons Ratio, and G_c , the critical energy release rate per unit thickness with respect to crack length of fracture, is equal to 2γ the fracture surface energy per unit area.

Hence

$$\sigma_f = \left(2E\gamma / \pi a \right)^{\frac{1}{2}}$$

An alternative interpretation of fracture phenomena was developed by Irwin (13) and is generally known as the stress intensity approach. Considering the analyses due to Westergaard (14) and Irwin (15) the stresses in the vicinity of a crack tip could be expressed in the following form,

$$\sigma_{ij} = K / (2\pi r)^{\frac{1}{2}} \cdot f_{ij}(\theta) + \dots$$

where K is a function of the applied stress, test specimen geometry, and the initial dimensions of the crack. K increases with applied stress until a critical value K_C is reached, when crack extension occurs.

Crack extension can occur under tensile stress, known as Mode I extension, or under shear stresses, known as Mode II, and antiplane shear, Mode III.

Under Mode I extension K_I may be interpreted physically as a parameter which reflects the redistribution of tensile stress, in a body due to the introduction of a crack. Unstable fracture occurs when K_I reaches a

critical value K_{IC} , for edge notched plates,

$$K_{IC} = \sigma \sqrt{a} Y \left(\frac{a}{W} \right),$$

where K_{IC} is the value of K_I at which catastrophic failure occurs, a is the crack length, W is the width of the plate, and Y is a calibration function which defines K_{IC} for the specific body under consideration.

Therefore the fracture stress of a component is,

$$\sigma_{max} = \sqrt{\frac{K_{IC}^2}{\pi C_o}}$$

where C_o is the critical crack length or critical flaw size.

Andrews (1) compared the energy balance and stress intensity factor approaches. For plane strain they may be related by

$$(1 - \mu^2) K_{IC}^2 = 2E\gamma = EG_c$$

and so $G_{IC} = 2\gamma = \frac{K_{IC}^2 (1 - \mu^2)}{E}$ for true brittle fracture.

2.1.3 Factors affecting the fracture toughness of polymers

The calculation of the fracture surface energy, γ , can be carried out theoretically provided that an assumption is made about the mechanism of fracture, e.g., that it occurs by the breaking of primary covalent bonds, or the rupture of secondary bonds, or by interchain slippage. The value of γ for uncrosslinked glassy thermoplastics was calculated by Berry (4) to be about 0.45 Jm^{-2} . In practice it is found that the experimentally determined values are much higher. Berry (5) found that γ for polymethylmethacrylate was about 300 Jm^{-2} while the value for polystyrene was considerably higher still.

The discrepancy between theory and experiment was explained in terms of stress induced viscous flow in the vicinity of the crack tip. This was supported by the appearance of coloured fracture surfaces suggesting the formation of an oriented film producing interference colours (4, 5).

Work on crosslinked polymers has shown lower fracture surface energies, although these are still much higher than their theoretical values (16). For example, Berry crosslinked methyl methacrylate with

ethylene glycol dimethylacrylate co-monomer. The resulting co-polymer possessed a fracture surface energy of $46.5 \pm 5.3 \text{ Jm}^{-2}$. (5 or 6 times lower than PMMA). The inherent flaw size was reduced 3-fold and there appeared to be an increase in craze resistance.

Literature values of γ determined for crosslinked polymers (17) exceed those expected from theory, thereby suggesting viscous flow even in crosslinked polymers. Investigations have shown that the fracture surfaces of crosslinked polymers possess fewer distinctive features than those of the thermoplastic glasses such as PMMA (see figures 1 and 2).

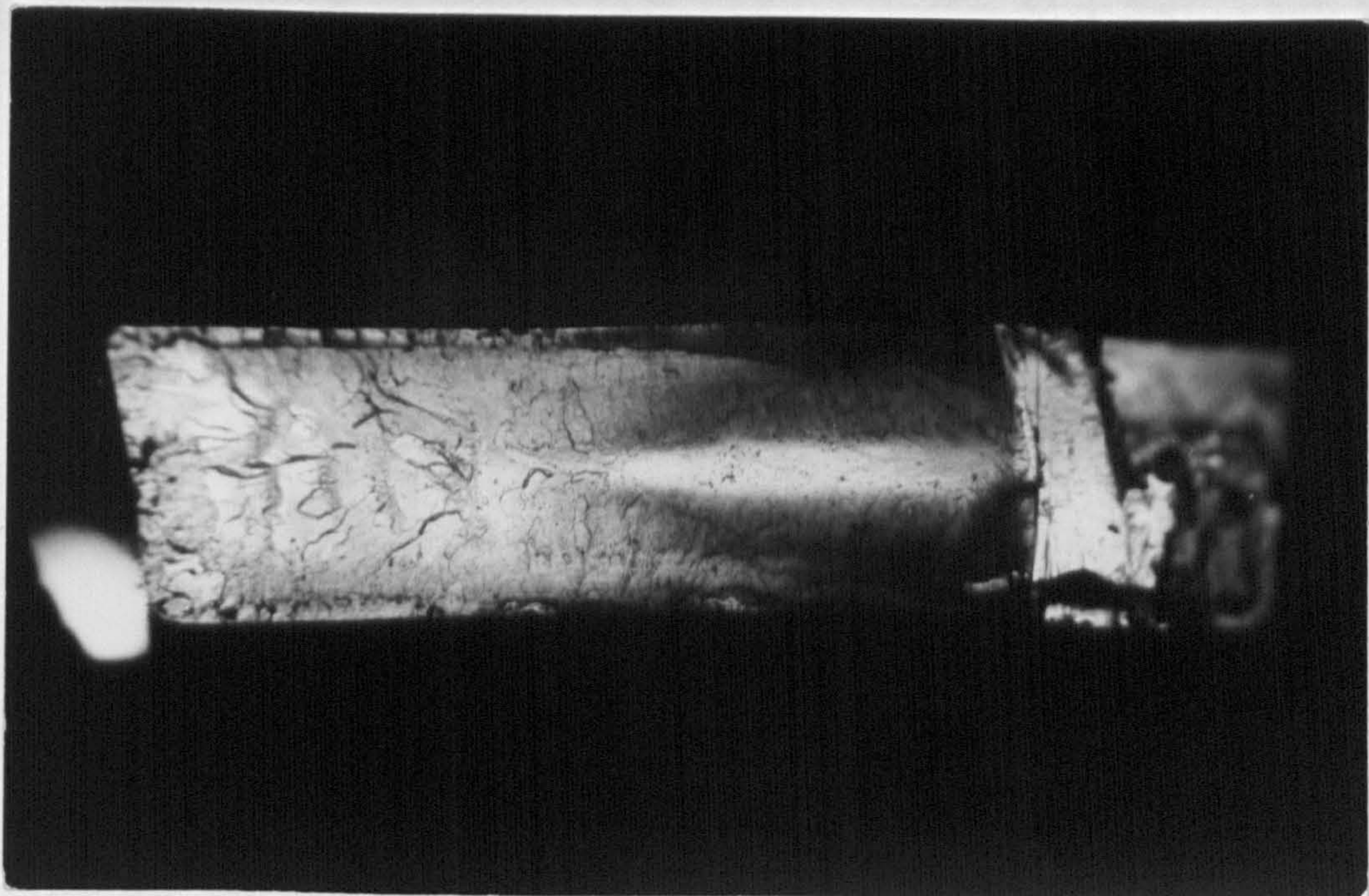


Fig. 1 Photomicrograph of polymethylmethacrylate

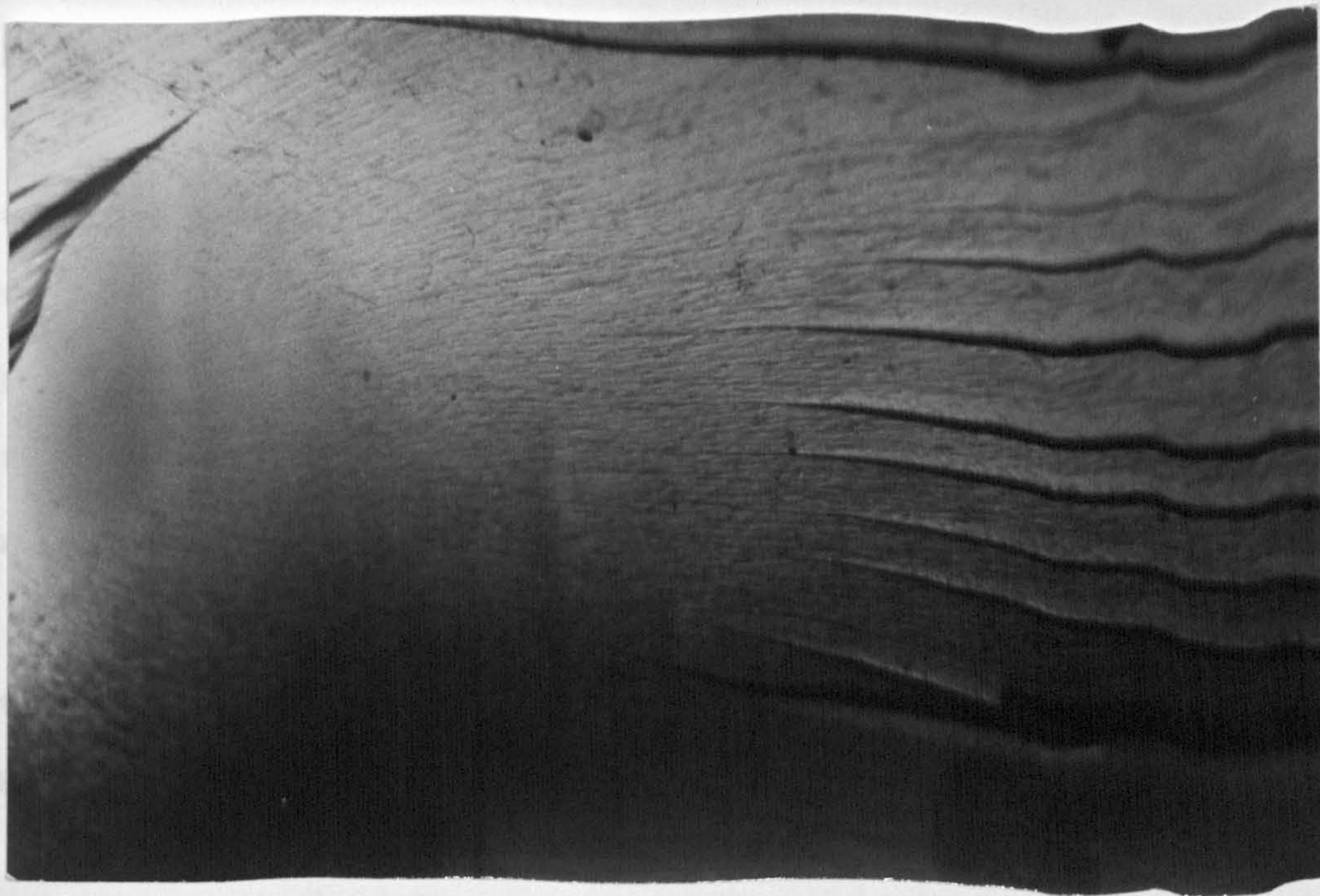


Fig. 2 Photomicrograph of a cured polyester resin

2.2 Unsaturated polyester resins

2.2.1 Production

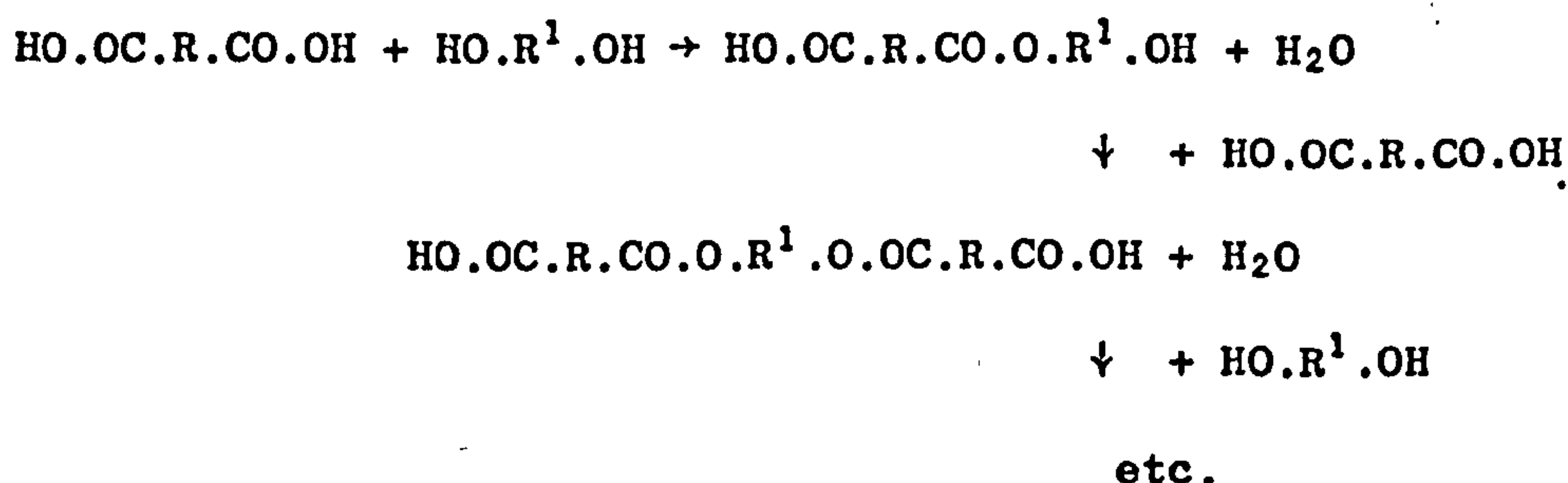
The term unsaturated polyester resin is used to describe the polycondensation product of a diol and diacid dissolved in a crosslinked vinyl monomer. In 1929 Carothers (18) prepared linear polyesters from ethane diol and phthalic and maleic anhydride, and Bradley (19) showed that the unsaturated forms of these polyesters could be cured to infusible and insoluble products. Ellis (20) reported that the addition of styrene increases the rate of cure thirty fold, and that the rate was further promoted by the addition of a benzoyl peroxide catalyst.

Hurdis (21) introduced tertiary aromatic amines in 1944 which accelerated the effect of the benzoyl peroxide catalyst thereby allowing room temperature cure. This was further improved by the development of cobalt naphthenate as an accelerator, and its use with other peroxide catalysts.

Most commercial resins are synthesised from three basic components;

a diol, an unsaturated diacid, and a crosslinking monomer, for example, propane 1.2 diol, maleic anhydride (MA) and styrene respectively. In addition it is common for there to be a saturated diacid component, usually phthalic anhydride (PA) or isophthalic acid. The polyesterification is a typical polycondensation reaction between roughly stoichiometric proportions of the diacids and the diols, with usually a slight excess of the diol components as these tend to be lost more easily during the reaction the diol usually being the more volatile component.

With the diols and diacids both being difunctional, the esterification reactions continue step by step building up a linear chain molecule.



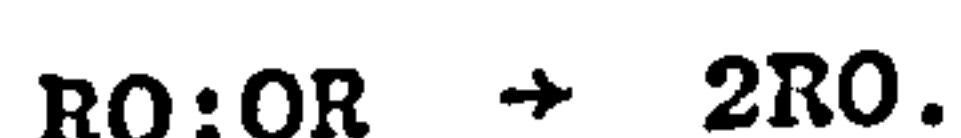
Theoretically, chains of indefinite length can be built up but in practice the reaction is only continued until some 10 to 30 links (ester linkages) have been formed, giving polyesters with molecular weights in the region 1000 - 2000.

The unsaturated polyester formed is stabilised by adding small quantities of phenols and is then dissolved in styrene, to give the viscous liquids known as unsaturated polyester resins.

2.2.2 Structure

Polyester resins are cured by a free-radical co-polymerisation reaction. Initiators may be used to enable the reaction to take place at room temperature.

The peroxide catalyst breaks down,



to give two free radicals. Each free radical is able to react with the vinyl monomer so forming a new free radical



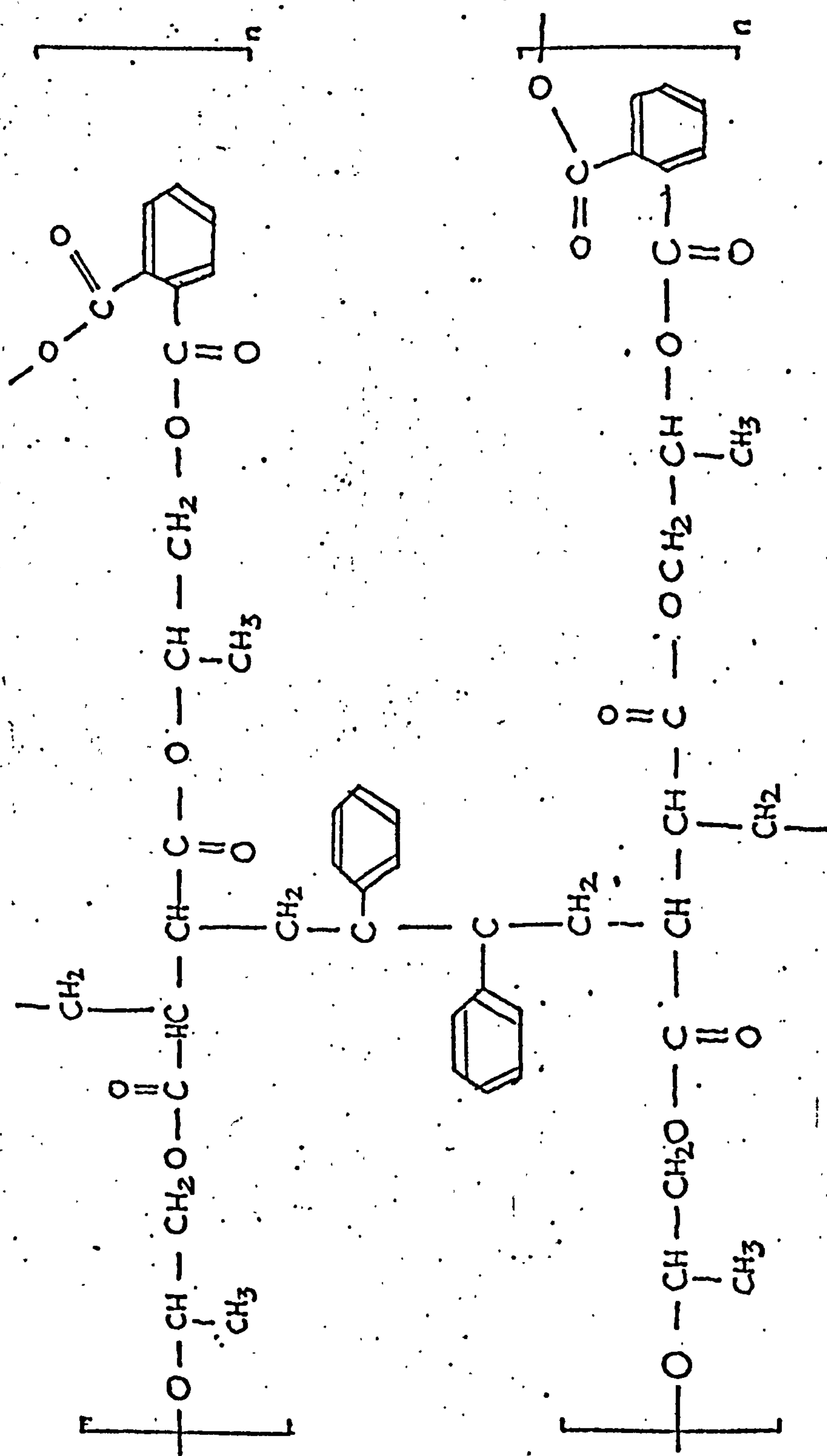
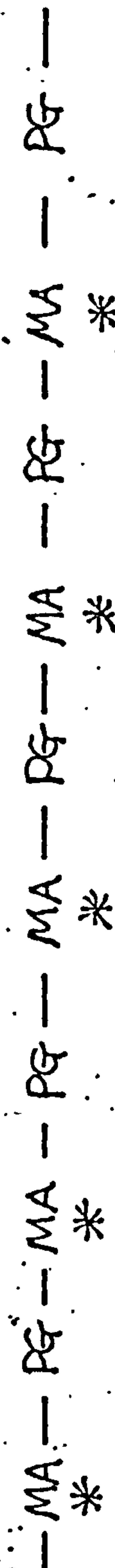
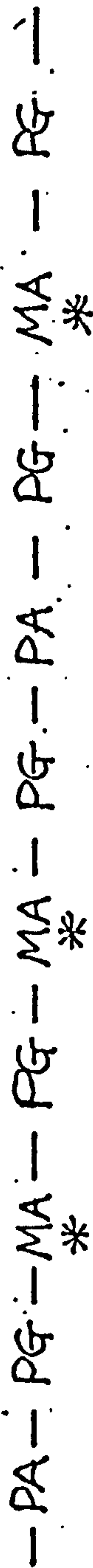


Fig. 3. Idealised polyester resin structure (phthalic anhydride, maleic anhydride, propane 1.2 diol, and styrene)



* = crosslinking site

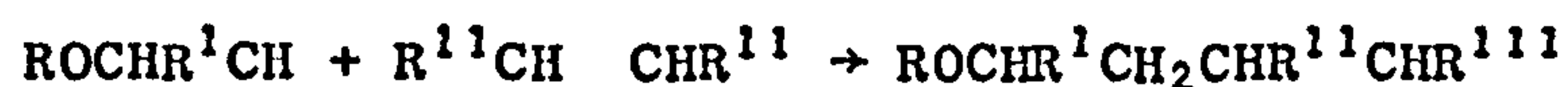
PA = phthalic anhydride

PG = propane 1.2 diol

MA = maleic anhydride

Fig 4. Polyester chain backbones

A rapid chain reaction is initiated and the crosslinked structure is built up.



etc.

On average there are two styrene residues between linked polyester chains (22) and the structure of typical resin manufactured from maleic anhydride, phthalic anhydride, propane 1.2 diol and styrene is shown in Figure 3. Hamaan, Funke and Gilch (23) established that homopolystyrene (as distinct from long styrene polyaddition bridges), is detectable in cured polyesters only when the mole fraction of styrene in the uncured resin reaches 0.9.

The acid components have important effects on the unsaturated polyester backbone. Firstly the unsaturated component provides sites for styrene to crosslink the polyester chains (See fig. 4). Secondly the saturated acid while spacing the unsaturation has two important effects; (a) prevents the polyester from crystallising and becoming less compatible with styrene and (b) produces rigidity in the polyester backbone and in most cases raises the heat distortion temperature (24).

Polyester castings exhibit an increase in tensile and flexural strengths with an increase in the degree of unsaturation, until a maximum is reached. Parker (25) showed that a maximum tensile strength occurs at about 50-60% mole unsaturation. Boenig (22) makes the important point that tensile maxima are generally found to shift to lower unsaturation levels in compositions containing a higher proportion of styrene. For a maleic anhydride, phthalic anhydride, propane 1.2 diol polyester, Parker (26) showed the tensile maximum to be at 59% unsaturation with 30% by weight of styrene. Tensile moduli however, in 40% by weight styrene polyesters, increase as the degree of unsaturation is decreased.

2.2.3 The fracture of unsaturated polyester resins

Cured polyester resins can vary from being very flexible to hard

brittle materials. The latter are generally stronger and more resistant to chemicals, and thus form the basis for most commercial resins for structural applications. The presence of a flaw in these brittle materials will considerably reduce their strength. In an elastic material the work required to fracture the specimen would equal the surface energy resultant from the two new surfaces. However even in a brittle cross-linked material there is a certain amount of plastic deformation which accompanies the fracture and adds to the fracture energy so as to exceed the expected surface energy (17).

Broutman and McGarry, having worked with polymethylmethacrylate (16) and then lightly crosslinked polymethylmethacrylate (17), turned their attention to thermosetting resins as these can be considered highly crosslinked. They found that the effect of crosslinking was to inhibit viscous flow or plastic deformation at the tip of the crack. The surface work or fracture energy of the polyester resin measured was found to be a factor of 10 smaller than that of the linear polymers, but still much higher than the theoretically estimated value. The fracture surface energy obtained for the unsaturated resin of Broutman and McGarry was 12 Jm^{-2} and in the same order as Diggwa's (6) result of 42 Jm^{-2} . These both compare with the estimated value of 0.45 Jm^{-2} for a glassy polymer where one would expect flow. This indicated that even for a highly crosslinked polymer a large amount of viscous deformation or plastic deformation may occur ahead of a growing crack.

Christiansen and Shortall (27) have studied the change in fracture toughness (K_{IC}) of a cured polyester resin with variation in resin flexibility, catalyst content and cure temperature. They found that the fracture energy increased from 22.8 Jm^{-2} to 28.5 Jm^{-2} with an increase of 20% in the flexibiliser's content. However changing the cure temperature and altering the catalyst content over a small range (0.5 to 2.0 volume per cent) was found to have very little effect on the fracture energy.

Broutman and McGarry (17) recorded the effect of adding increasing amounts of styrene monomer to an unsaturated polyester resin. They found that although adding styrene increased the measured fracture surface energy, the increase was insignificant until more than 50% by weight styrene was added. Above 50% there was a rapid increase of fracture surface energy against styrene content (Fig. 5). They suggested that above 50% styrene content no further crosslinking bridges form, and that the increase in fracture energy is due either to there being longer styrene linkages or to the formation of homopolystyrene. However Hamann, Funke and Gilch (23) established that homopolystyrene is detectable in cured polyesters only when the mole fraction of styrene reaches 0.9. Also Boenig (22) suggests that excess styrene does in fact increase the styrene bridge length as well as produce styrene rich areas which lead to problems such as crazing (28) and increased shrinkage on curing (22).

2.2.4 Fracture surfaces of crosslinked polymers

Broutman and McGarry (17) had found that surface features became less and less apparent as crosslinking increased. However although the polyester resin with 30% styrene had an almost featureless surface, the casting with 61% styrene had a large number of fine striations. Owen and Rose (29) had studied the fracture surfaces of unsaturated polyester resins containing different quantities of flexibilising additive. With no additive, the chief features were (i) a small area of river markings adjacent to the initial notch tip, followed by (ii) a smooth surface region (see fig. 6) and (iii) subsequent development of roughness further from the notch. This region contained conic markings. Addition of flexibilising additive caused an increase in the region of stable crack growth and the surface markings became geometrically defined.

Christiansen and Shortall (27) also observed "river lines" running from the initial notch through the mirror region into a mist region and then giving way to a region of 'hackle' and crossbranching. The river lines result from the crack propagating at slightly different levels and

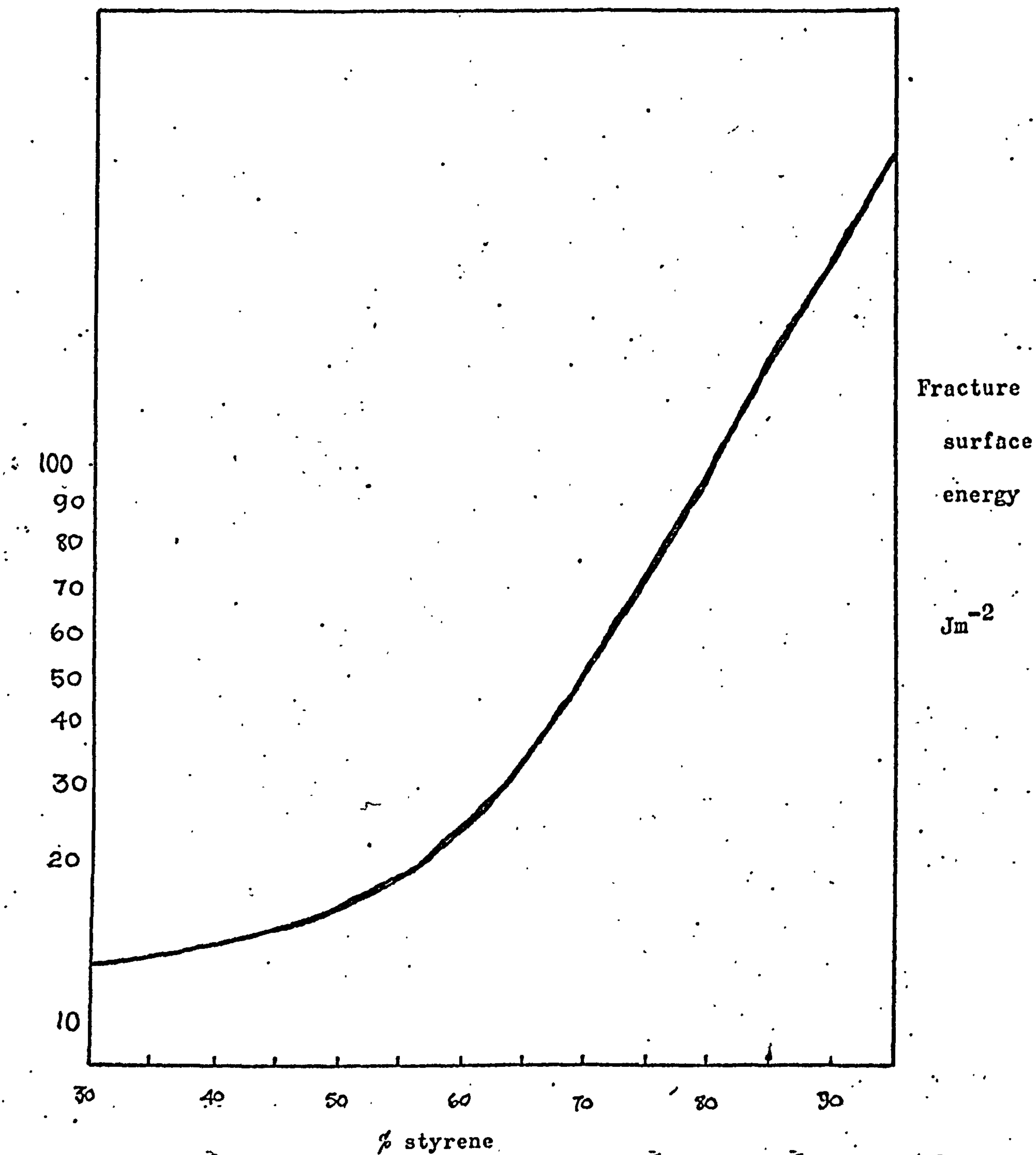


Fig.5 The effect of an increase in styrene content on
the fracture surface energy (γ) of Paraplex 43

(after Broutman & McGarry (17))

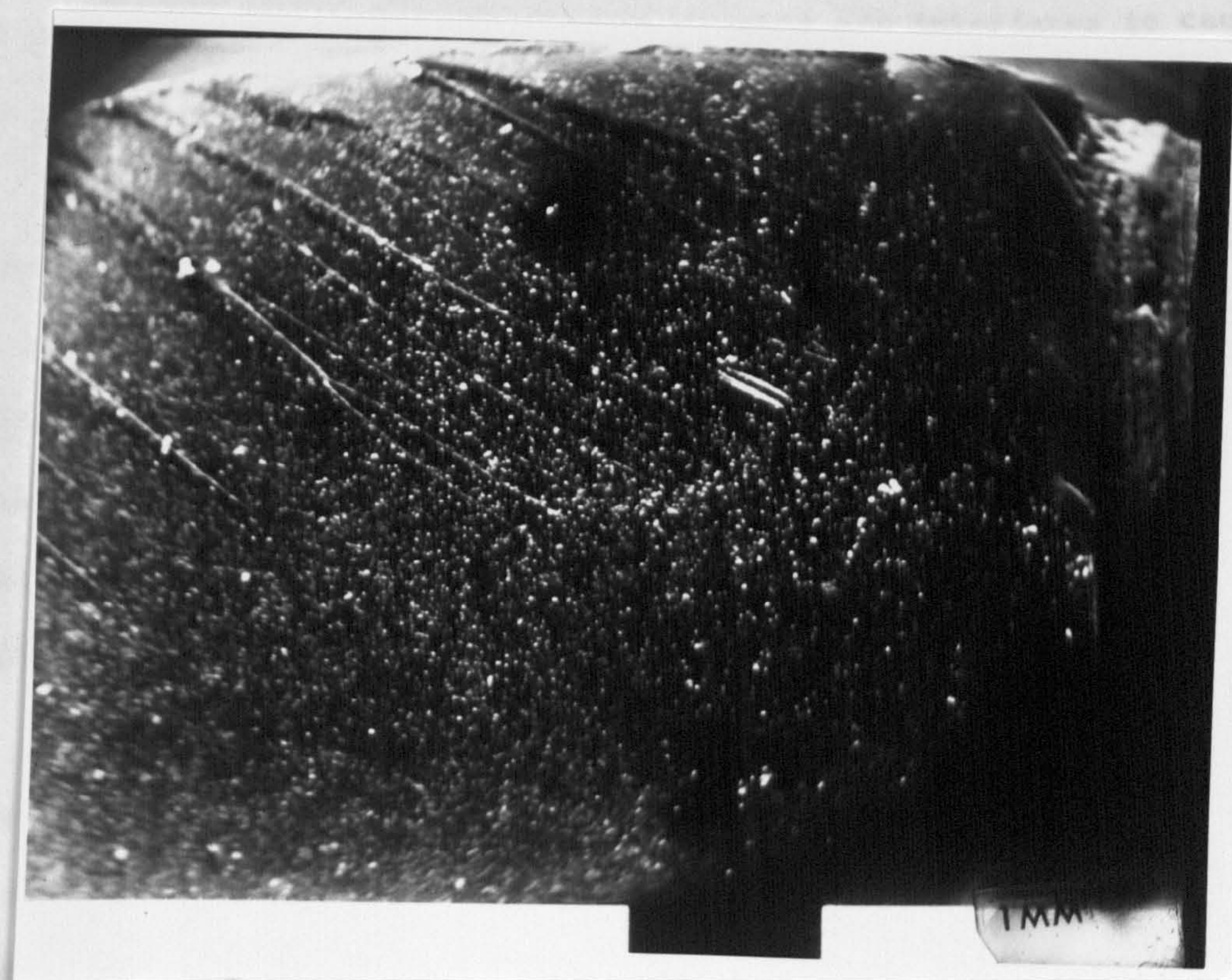


Fig. 6 **Smooth region of a cured polyester resins fracture surface**

long individual cracks can be seen in the mirror region; accompanying these cracks are filaments. Turner and Nelson (30), working on brittle phenolformaldehyde resins, made similar observations and distinguished five regions of the fracture surfaces (see Fig. 7). Their second region, which corresponds to the "river lines" was said to be due to a layer of crazed matter formed ahead of the crack, through which the crack travels, generating stress waves which are reflected off interfaces to cause buckling of the surface film.

Christiansen and Shortall observed with the aid of scanning electron microscopy "microhackle" in the mist region giving evidence of a small amount of plastic deformation. In the hackle region the fracture surfaces become very uneven, indicating that multiple crack formation and bifurcation has occurred. There are mounds and depressions left on the surface indicating that some parts of the material maintained structural integrity.

The study of fracture processes in crosslinked polyester resins reveals that the effect of crosslinking is to reduce fracture energy and usually to produce a smoother fracture surface than those found in uncrosslinked polymeric glasses. Although there may be rough areas on the surface there is a notable absence of areas of stable crack growth.

A cured polyester resin is a brittle glassy solid of very little practical use for load bearing applications. However, thermosetting unsaturated polyester resins are used extensively as matrix materials in fibre-reinforced composite systems. The polyester resins have sufficiently low viscosities at room temperature to enable them to penetrate between closely packed fibres without significantly damaging them. The matrix material in these systems must be able to transfer stress to a fibre and can have a significant effect on the overall mechanical properties and fracture resistance of the composite.

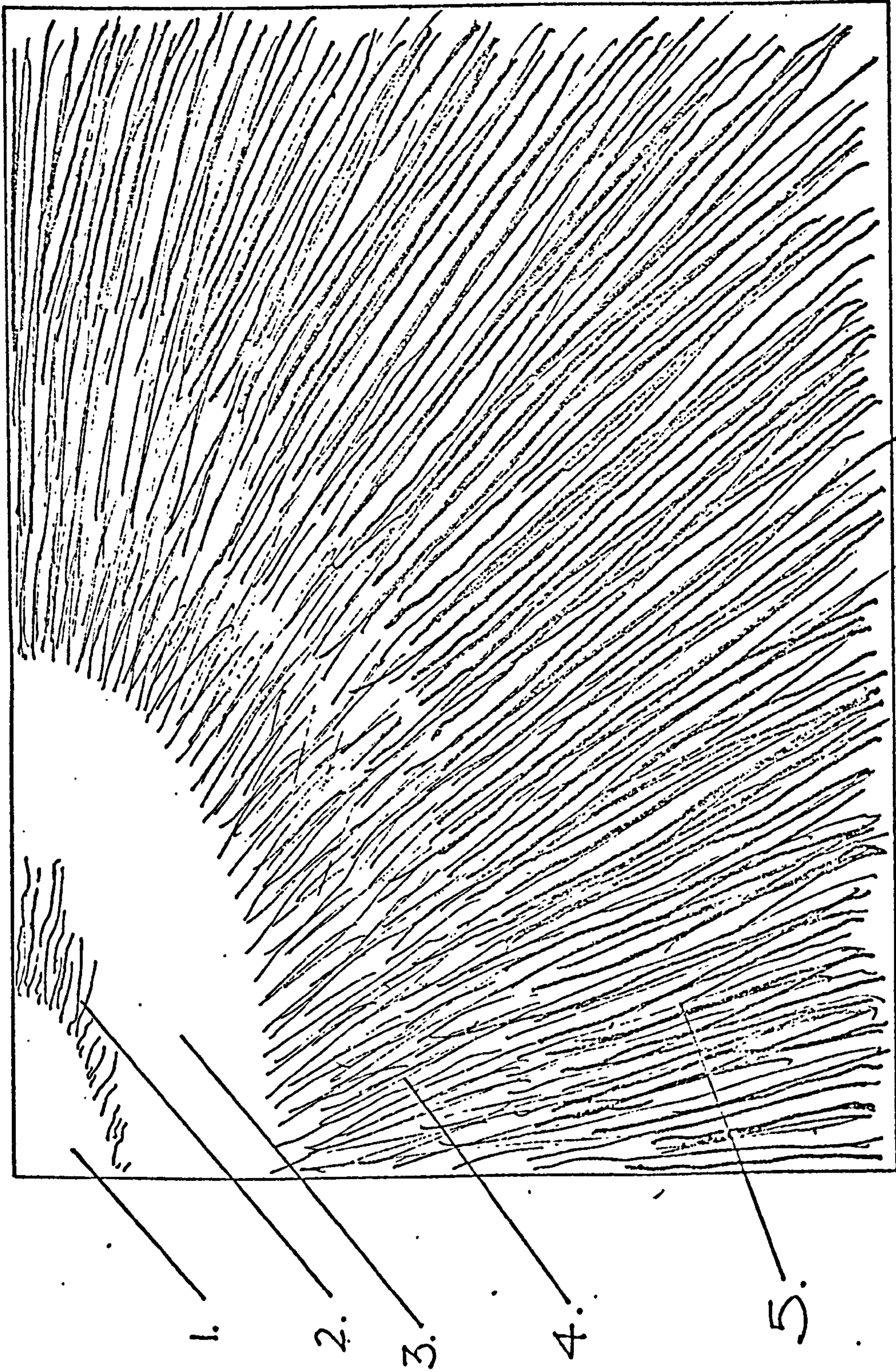


Fig. 7 . Schematic representation of the fracture surface markings
on phenol formaldehyde resins fractured in tension
(after Nelson and Turner) (30)

2.3 Filled and reinforced polyester resins

2.3.1 Glass fibre reinforcement

The main reason for employing fibrous composites in many structural applications is that they permit the use of a large volume fraction of a high strength, stiff, brittle fibrous material. The strength and stiffness of glass fibre reinforced plastics result mainly from the glass itself and the polymer matrix acts as an adhesive to transfer load between the glass fibres. The fibres also increase the toughness of the brittle matrix material and thus composites show a much greater resistance to crack propagation than the matrix alone.

During the 1930's the main use of glass fibre yarn and fabric was as a reinforcement for electrical insulation systems. A glass composition was developed to meet these requirements. This was a calcium-alumina-boro-silicate glass which was capable of being drawn into fine filaments, and became known as "E Glass"; it was soon realised that its high strength and Young's modulus and its resistance to weathering made it ideal as a reinforcement for thermosetting resins. The properties of E Glass fibres (31) are listed in Table 1.

Because single glass filaments are easily damaged mechanically, they are coated by a textile or plastic size which protects them. It also binds the filaments into a strand. The plastic size contains a coupling agent which is compatible with polyester resins. The incorporation of a coupling agent improves the bond between the glass and the resin, and so improves the mechanical properties of the reinforced laminate (see fig. 8).

Waring (31) discusses the type of coupling agent used and states that those used are believed to allow some degree of flexibility in the interface bond. This enhances the transfer of strain and improving the properties of the laminate.

There are two distinct categories of glass fibre reinforcement; those processed in textile machinery (namely yarns and fabric) and those which can be used in strand form. Chopped strands are available in 6 mm

TABLE 1Properties of E Glass

Specific Gravity	2.6
Fibre diameter	5 - 15 microns
Tensile strength	1.5 GN m^{-2}
Modulus of elasticity	70 GNm^{-2}
Heat resistance	1500°C
Coefficient of linear expansion	$2.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Elongation at break	4%

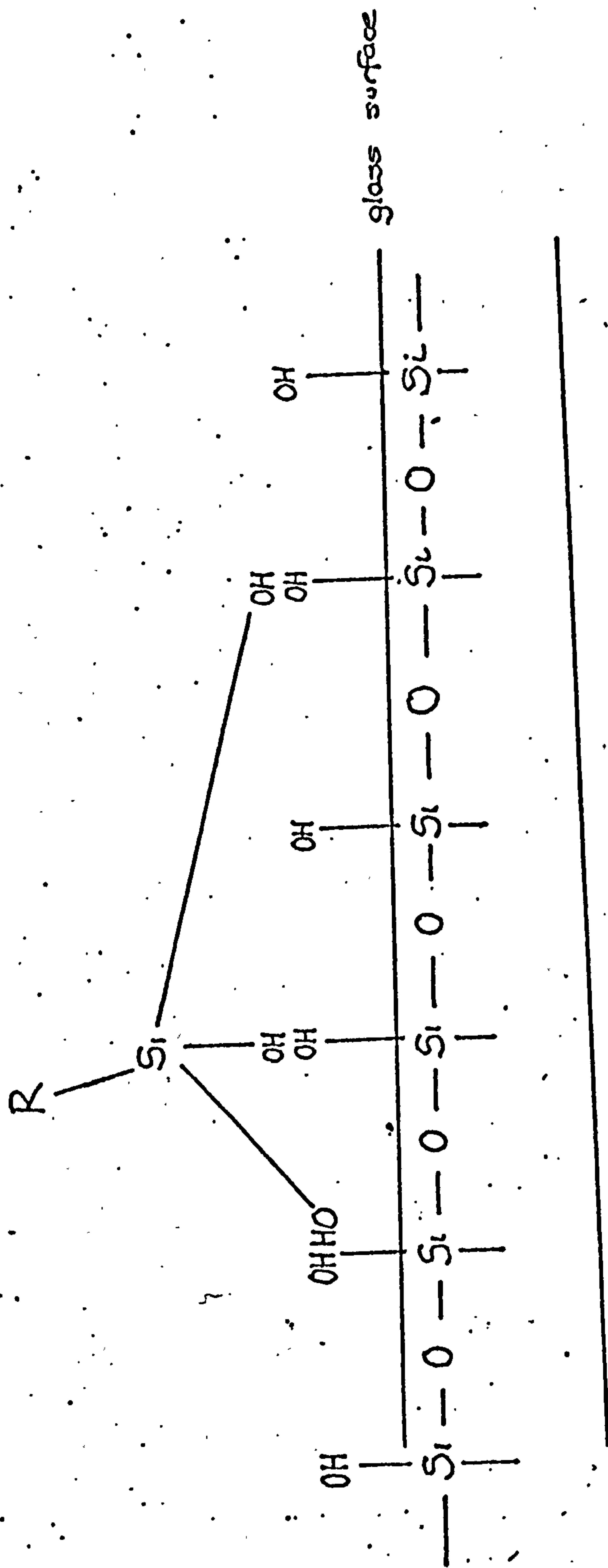


Fig. 8 An idealised representation of the role of a coupling agent

and up to 100 mm lengths. The strength of the glass reinforced moulding falls when the strand length falls below 16 mm. A development of chopped strands is chopped strand mat (CSM). This is a non-woven mat made from chopped strands randomly distributed to ensure uniformity of strength in all directions. The strands of the mat are generally bound together with either an emulsion (usually polyvinyl acetate based) or a polyester powder binder. The binder dissolves in the polyester resin and facilitates impregnation of the glass reinforcement.

2.3.2. Mechanical properties of glass reinforced plastics

The tensile strength of short, discontinuous fibre reinforced systems is a complex function of many variables. There exist several analytical expressions which predict tensile strengths, taking into account some of these variables. Kelly & Tyson (32) developed the following equation for the tensile strength of an aligned discontinuous fibre composite:-

$$\sigma_{uc} = V_f \left(1 - \frac{\ell_c}{2\ell}\right) \sigma_{uf} + V_m \sigma_m$$

where, σ_{uc} , σ_{uf} and σ_m are the composite, fibre and matrix ultimate strengths respectively, V_f and V_m are fibre and matrix volume fractions, ℓ is the actual fibre length, and ℓ_c is the critical fibre length. For fibres with $\ell < \ell_c$ complete stress transfer cannot occur. This means that unless the fibres are long enough slipping will occur and that fibres will pull out rather than accept the strain to break.

$$\sigma_{uc} = \frac{\tau}{d} \ell V_f + V_m \sigma_m \text{ for } \ell < \ell_c$$

ℓ_c has been defined as $\frac{\ell_c}{d} = \frac{\sigma_{uf}}{2\tau}$

where d is the diameter of the fibre and τ is the interfacial shear strength.

Lees (33) reported that experimental values were lower than those predicted by Kelly, and attributed this to the presence of residual stresses (resulting from the difference in thermal contraction of glass

and resin). He also suggested that the crack sensitivity of the matrix material may have an effect on the composite strength.

Lavengood (34), in evaluating Lees' modified equation for the tensile strength of a composite, concluded that the fibre strength is reflected in the strength of random fibre mat composites, and that failure occurs due to the tensile fracture of fibres. This is in contrast to composites reinforced with aligned short fibres where the fracture initiation is confined to the matrix and to the interface.

Carswell and Borwick (35) have investigated the tensile behaviour of chopped strand mat polyester composites. They observed very thin specimens in transmitted light during loading, and saw that cracks formed at right angles and 45° to the axis of loading. They concluded that the mechanism of failure was a gradual crazing of the resin leading to failure of the reinforcement, and hence ultimate failure of the composite. Owen and Dukes (36) reported that at 30% of the ultimate tensile strength of the composite, damage could be associated with fibres lying perpendicular to the direction of the load. With increasing load the damage spread to fibres aligned at progressively smaller angles to the load axis. The cracking of the matrix material began at 70% of the ultimate tensile strength.

From these observations it was concluded that the strength of the bond between the glass and the resin is of primary importance in the onset of damage. Carswell and Borwick (36) suggested that, as crazing of the matrix occurs, its load bearing capacity is reduced and it will no longer transfer the load to the fibres effectively. Eventually, the glass fibres break, or pull out of the matrix. This leads to failure of the composite.

It is known that high strain magnifications occur in the matrix and Kies (37) proposed a model whereby a strain magnification of 20 could occur in glass resin composites for very close packed fibres. His "analysis" suggests that resin matrices with high elongations to failure

could result in stronger composites. However resins having high elongation generally have low moduli and low strength (36).

Van der Beck and Hamm (38) concluded that a resin strain-to-failure of 2-3% was most likely to give the best tensile strength. Owen and Rose (39) reported that the stress at which the onset of debonding commenced in tension was insensitive to resin flexibility. At the same time they showed that resin cracking prior to failure was suppressed by the more flexibilised resin composites.

2.3.3 Fracture characteristics of glass reinforced polyester resins

The characterisation of a composite material with respect to crack initiation and propagation is important for any potential structural and engineering application. Following the work of Wu (40), several papers have been published dealing with the application of Linear Elastic Fracture Mechanics to composite materials with notches. Wu considered the case of a unidirectional glass reinforced epoxy resin with a crack parallel to the direction of the fibres. He reported the K_C did not vary significantly with crack length. Konish et al (41) concluded that the failure mechanisms of specimens tested were crack dominated and that the procedures of LEFM could be applied. Owen and Bishop (42) stated that the applicability of LEFM to glass reinforced polyester resin depended on the type of reinforcement and the orientation of the starter crack. For a unidirectional reinforcement, with the crack parallel to the reinforcement, K_C values were independent of crack length. Whereas for random mat or weave reinforcement, the K_C values showed some dependence on crack length. Ellis and Harris (43) studied the effect of test variables on the fracture properties of some fibre reinforced epoxy resins. They found that the work of fracture values depended on the dimensions of the test specimen, crack length and the type of test, as well as being quite sensitive to the orientation of the crack with respect to the fibre axis.

Beaumont and Harris (44) reported that γ_I the fracture surface

energy, (calculated from K_{IC}) was independent of strain rate but that the total energy of fracture γ_F (derived from the total area under the load deflection curve), increased with increasing strain rate. In all cases γ_F was greater than γ_I . It was suggested that as the crack propagates, fibres begin to pull out behind the crack tip as the fracture faces separate. If there is some interfacial shear stress between the fibres and matrix, another energy absorption term has to be added to. In general, the interfacial shear stress will be strain-rate-dependent because of the viscoelastic nature of the matrix. This strain rate dependence of pull out energy will make γ_F similarly dependent.

The fracture surface energy of a composite, γ_c , is greater than γ_f and γ_m (the respective fracture surface energies of the glass reinforcement and matrix). There must therefore be additional energy absorbed in the process. For example, relaxation of a fibre when it snaps (45), δr , debonding energy released during separation of fibre and resin (46); δd , fibre pull out energy, overcoming friction of the fibre/resin interface, δF , (47) therefore $\gamma_c = \gamma_f + \gamma_m + \gamma_r + \gamma_d + \gamma_p + \dots$

One or more of these fracture processes may control different stages in the complete fracture of the composite. Dibenedetto (48) concluded that a total absence of adhesion between fibre reinforcement and matrix would eliminate γ_r and γ_d resulting in the energy dissipated being principally γ_p . If the fracture was parallel to the fibre direction of a unidirectional composite the fracture surface energy would not be unlike γ_m . Dibenedetto went on to state that too much adhesion decreases the debonded length, thereby decreasing γ_d and lowering the toughness. An intermediate bond of adhesion however would give optimum properties since then one must debond and crack bridging fibres.

Fila, Bredin and Piggott (49) agreed that poor fibre-matrix adhesion favours fracture toughness but, that as Harris et al (50) had stated, leads to an ease of splitting parallel to fibres and a loss of shear strength. Piggott's (45) mechanism stated that a crack propagating

through a matrix does not break fibres but that the stress transfer between matrix and fibre does. The effectiveness of fibre reinforcement in toughening brittle materials depends on the fibre's strength and diameter (which should be large), and its modulus (which should be low).

Mandel et al (51) reported that K_Q , the candidate stress intensity factor, was insensitive to notch configuration and notch root radius, up to a radius of 0.24 mm. It was also concluded that the properties of the matrix may have very little effect on the toughness of composites. This again implies that the fibre properties and interface conditions determine the toughness of the composite.

It was suggested that the toughness of laminates results from the growth of subcracks which blunt major cracks, and reduce stress concentrations.

2.4 Sheet moulding compounds

2.4.1 The concept

By the middle of the 1960's the reinforced plastic industry had grown to a substantial size through the use of conventional resins and conventional processing and moulding techniques. These processing techniques included hand lay-up, spray-up, filament winding and compression moulding via wet lay-up procedures (52). The need for new materials, processing techniques, and product handling equipment, especially the need for a processable plastic material that could be produced almost continuously, which could be handled in an automated press, and the quality of which could approach that of metal components manufactured by the stamping process in the automotive and related industries (53) was evident. Sheet moulding compound, SMC, was first introduced in 1967-1968 and since then has achieved importance as a major class in the field of thermosetting moulding compounds (54-56). SMC could be compression moulded into finished products in relatively short periods of time in an automated process (57).

It consists of a resin-impregnated composite containing chopped-strand glass mat or rovings. It is manufactured by metering an unsaturated polyester resin slurry onto the surface of two facing polyurethane or polythene films between which the glass is sandwiched. The product is allowed to mature for a time during which thickening occurs (58-60).

During the time it matures, it changes from a sticky consolidated sheeting compound which is unusable to a material of leather-like feel which is readily handleable. This material can be moulded in matched-metal moulds (61).

Compounds are formulated to provide stiffness, toughness, electrical insulation, and fire resistance, etc., to the moulding. (Often combinations of two or more of these qualities.) Unfortunately, because of the shrinkage of the polyester resin problems occur. These are aggravated by the filler and glass which do not undergo thermal shrinkage. These two factors combine to give surface waviness, warping, surface cracks, and internal voids. Fortunately methods to counteract resin shrinkage have been devised (62).

The addition of 5% by weight of fine powdered low density polyethylene to either standard or chemically thickened systems reduces faults induced by shrinkage. To achieve even lower shrinkage (63) a two phase system with a participating component was introduced. As polymerisation of the polyester begins, the dispersed phase, usually a vinyl syrup (64) expands because of simultaneous homopolymerisation and offsets the shrinkage of the polyester phase. A polyester resin: acrylic syrup ratio of 60:40 is reported by Espenshade and Lowry (65) to give minimum shrinkage.

2.4.2 The production of SMC

2.4.2.1 The process

The production of SMC is summarised in Figs. 9 and 10. The process (66) demands that the polyester resin, filler, release agent and nil

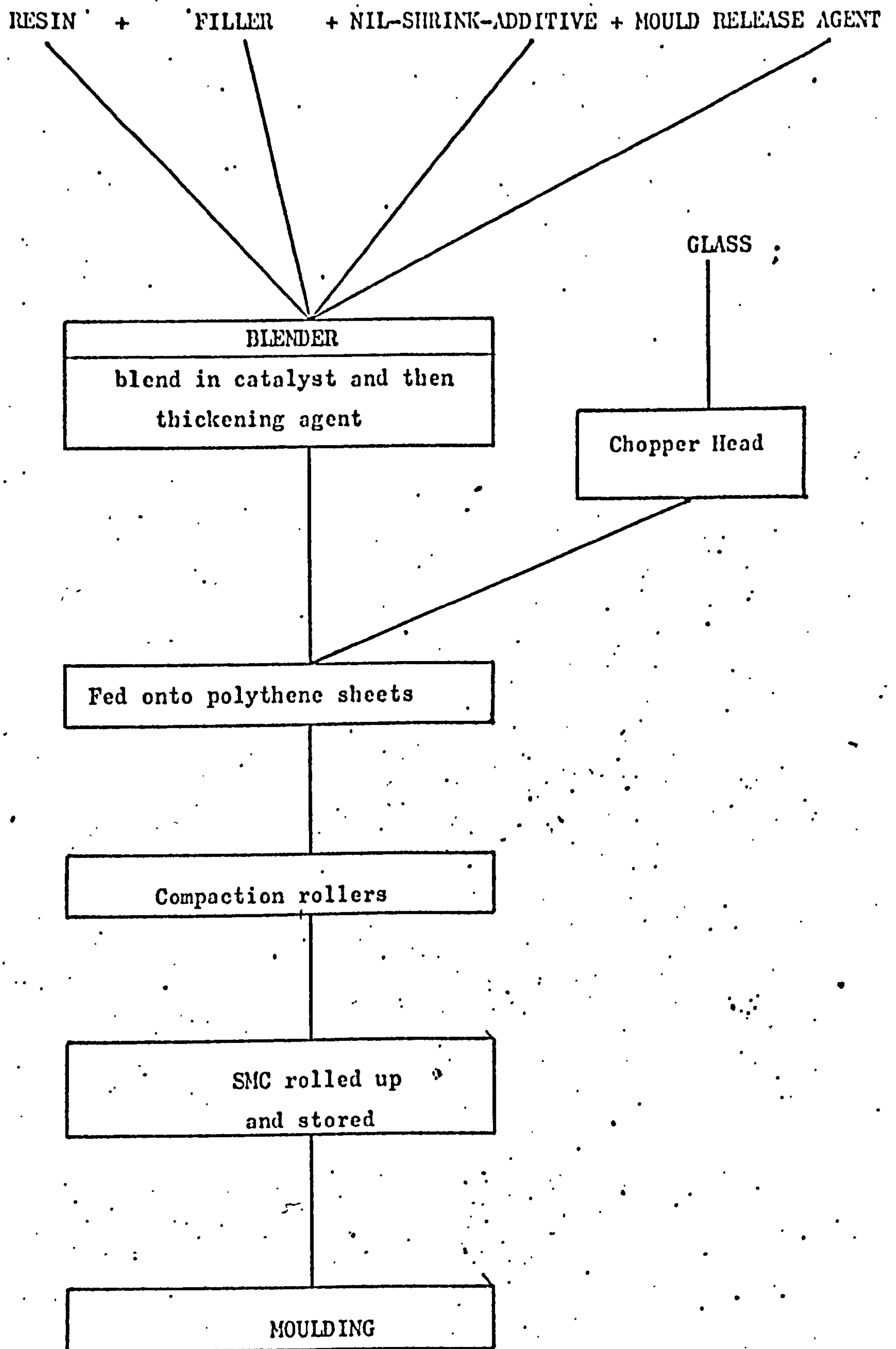


Fig. 9.

The production of SMC

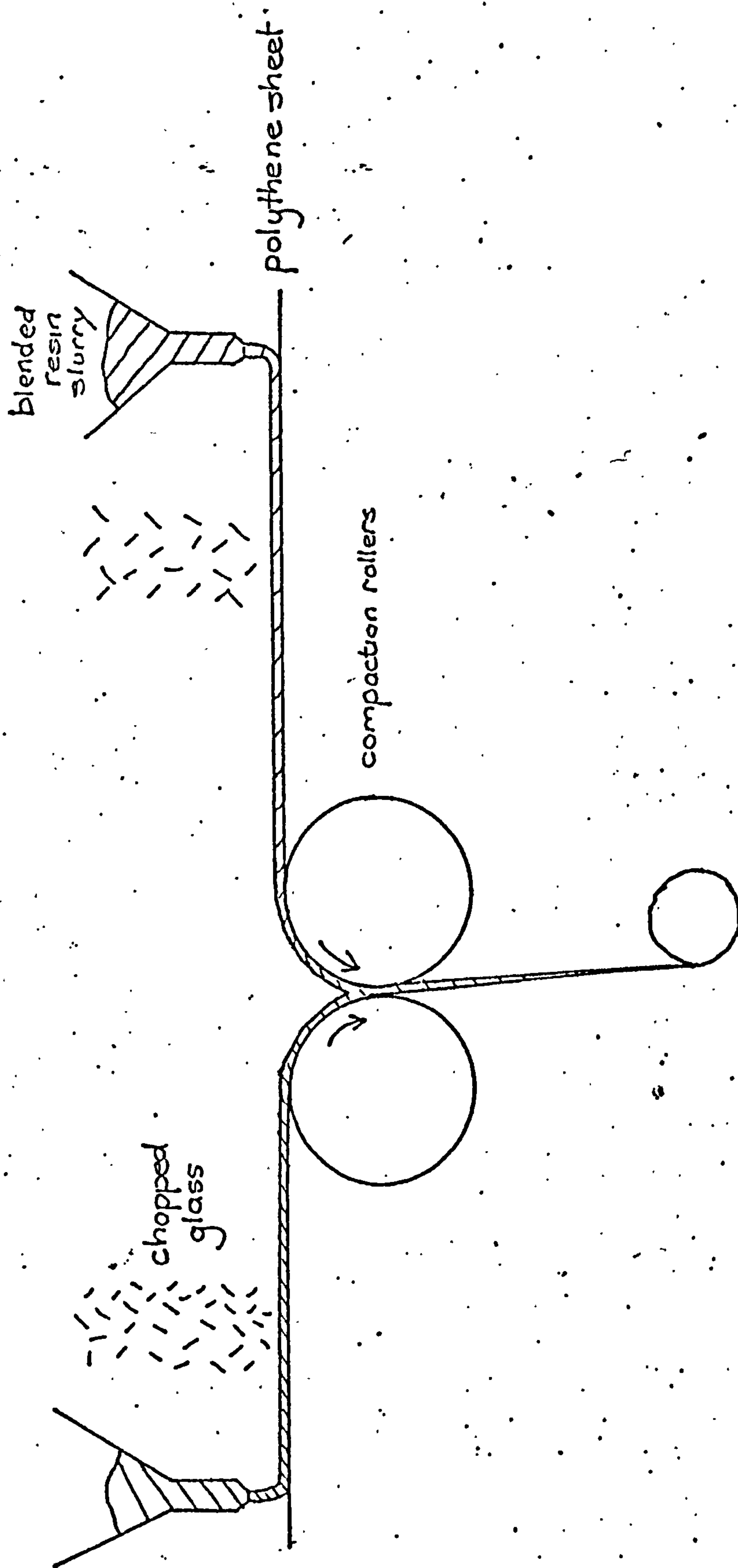


Fig 10. The basis of an SMC production unit

shrink additive are mixed together to ensure homogeneity of the slurry. It is at this point that the catalyst is mixed in, followed by the addition of the thickening agent. As the thickening reaction begins immediately it is important to deposit the resin slurry onto the polythene sheets of the SMC machine to complete the process.

As shown the glass and SMC slurry are then compressed between the polythene sheets. The compound formed is usually 1.8 to 3.2 mm thick, and any desired width (67). It is then deposited on rollers and allowed to thicken until the polythene is capable of being peeled from the moulding compound. Although it is important that this is possible, it is also important that the thickening reaction does not lead to an unacceptably high viscosity.

2.4.2.2 Materials in SMC compounding

The polyester resin used should ideally have a low viscosity to permit easy mixing but the viscosity should be high enough not to cause separation from the other ingredients. The resin should also cure rapidly to allow short moulding times. It is also important that it has high hot strength to permit removal of the part from the mould without damage. This can be built into the resin by using aromatic saturated diacids such as phthalic anhydrides.

There are four common groups of fillers; (52)

- (i) silicas and silicates
- (ii) carbonates
- (iii) sulphates
- (iv) oxides

The most commonly used filler is calcium carbonate (68) and usually these materials are classified by particle size.

The glass used in SMC formulations is usually 50 mm in length, and is either in the form of chopped rovings (gravity fed into the polythene sheeting) or as chopped strand mat. Glass contents of from 5% to 50% (W/W) have been used in SMC and as Young (52) points out 5% glass contents

Constituent	%
Unsaturated polyester resin	20 - 30
Nil-shrink additive	Up to 20
Glass reinforcement	20 - 30
Filter	28 - 35
Mould release agent	1
Thickener	1
Catalyst	1

Table 2. Typical formulation for SMC.

offer little or no mechanical advantage while 50% contents because of the nature of the viscous resin slurry results in moulding problems.

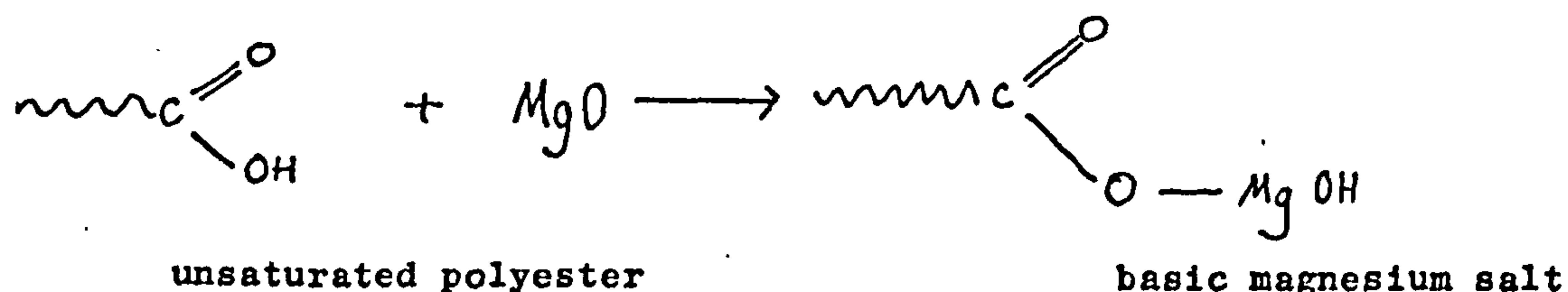
A release agent is also mixed into the resin slurry, and makes possible the easy removal of the SMC piece from the mould. Release agents are usually stearates and are commonly used at 1-3% levels. The catalyst used in SMC must be suitable for hot cure. Benzoyl peroxide is a suitable catalyst and permits moulding over a wide range of temperatures but is not stable over long periods. Tertiary butyl perbenzoate requires higher moulding temperatures but it is very stable and permits high temperature mixing.

2.4.2.3 The thickening reaction

Before the 'resin-slurry' impregnates the glass fibre, a thickening agent, usually magnesium oxide, is added. The SMC process is only feasible because the mixture of polyester resin, filler, and catalyst can be thickened sufficiently to yield a tack-free sheet stiff enough to permit easy handling (69).

The thickening reaction is also important because the rate of thickening decides the degree of wet out of the glass fibre reinforcement. The mechanical properties of such a composite as SMC will be dependent on how well bound the glass is to the matrix. A slurry that thickens rapidly (70) may not impregnate the glass fully and in the case of a chopped strand mat solubilise the mat binder.

In 1951 Frillette was issued a U.S. patent (71) which covered the use of various metallic oxides and hydroxides. He used large amounts of Group IIA oxides and hydroxides. Recently Szemericsanyi (72-74) gave details of the thickening reaction by the above oxides and hydroxides. She postulated that the reaction takes place in two stages. Initially a basic salt is formed through the reaction of a carboxyl group on the polyester with one mole of earth oxide.



The second stage proposed involves the formation of a complex in which two carboxyl groups co-ordinate with the basic salt formed in the final stages of reaction

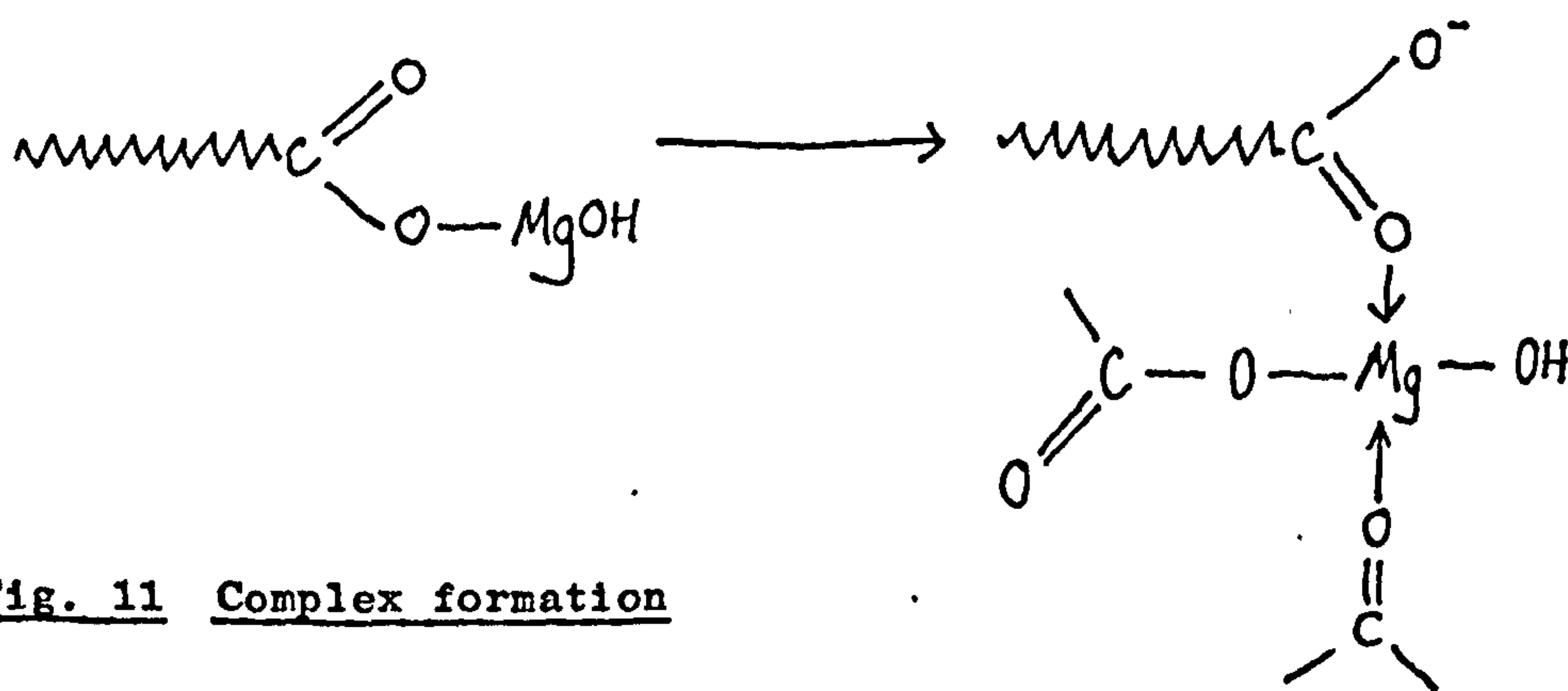


Fig. 11 Complex formation

Alvey (75) noticed that when magnesium oxide is added to a polyester resin the thickening reaction seems to be in two stages. Firstly a high rate of viscosity increase up to about 0.4 to 0.8×10^6 c.p., followed by a gradual increase up to the 10^7 c.poise range (see Fig. 12). The initial period lasts 10-20 hours, the second period lasting until 800 hours after the magnesium oxide is first added to the resin. Alvey found that at fifty hours the log of the viscosity was linearly related to the molar thickener; resin ratio up to a ratio of 2:1. Alvey established that when sodium hydroxide was added in excess to the resin it thickened. He postulated therefore that the initial thickening reaction was accounted for by the formation of an ionic salt and perhaps subsequent ionic interaction between neutralised polymer chains. Magnesium oxide is a superior thickening agent in that it is difunctional and can more easily effect a chain lengthening reaction.

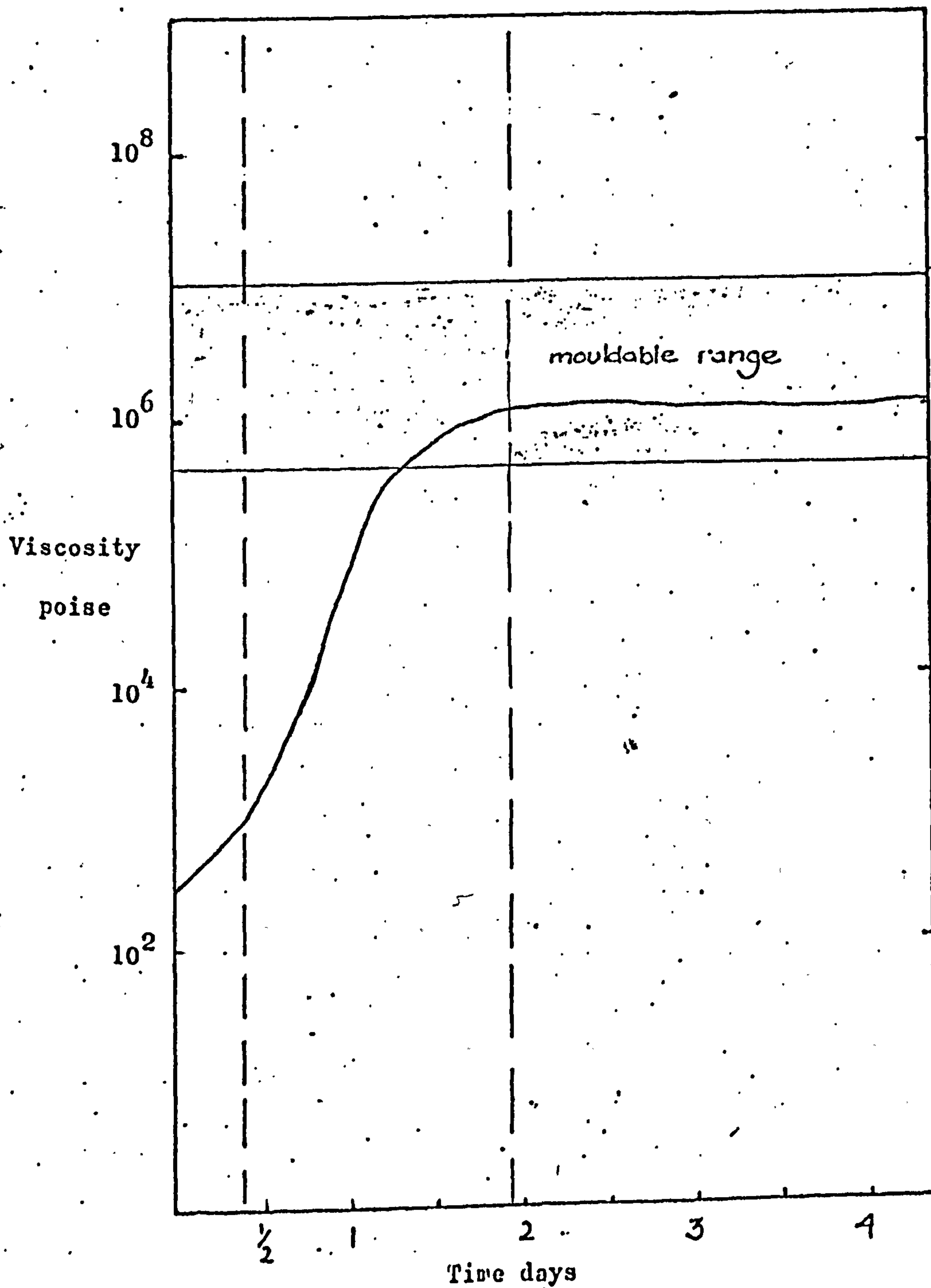


Fig 12 Typical thickening curve of SMC resin

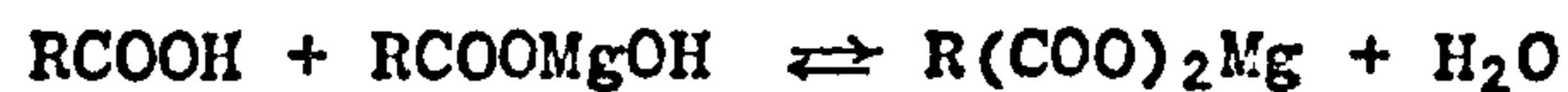
Warner (69) stated several rules for the thickening reaction. Firstly, the thickening rate is proportional to the acid number of the resin. He observed that for an acid value of zero there was no thickening observed after 60 hours. Secondly, the thickening rate is inhibited by the hydroxyl functionality of the resin, and if the hydroxyl value is more than three times the acid value, the resin will possibly not thicken at all. Thirdly, of equivalent molecular weights of resin, thickening increases with functionality of the thickening agent, and also at equivalent functionality thickening increases with the molecular weight of the resin.

As already stated, there are two stages to the thickening reaction, a first stage which determines how well impregnated the glass reinforcement is, and how soon the SMC is handleable, and a second stage which determines how long it is mouldable. From all evidence it seems that the first stage is an initial equilibrium reaction yielding a higher molecular weight salt.

Mechanisms have been put forward to explain second stage thickening. One mechanism (69) claims that the viscosity increase is due to a network being built up as a result of weak hydrogen bonding between adjacent polyester chains. Temperature affects the second stage, and refrigeration increases the shelf life, suggesting that the proper orientation of the polymer molecules is necessary. This supports the hydrogen bonding mechanism. It is also thought that there is a contemporaneous viscosity-reaction because of the formation of the magnesium complexes already mentioned. It is known that any water present in the resin (75) increases the initial rate of thickening, probably because of the improved solubility of the magnesium oxide. But water also reduces the ultimate viscosity reached, and this is thought to be because of the hydrolysis of the magnesium carboxylate salt.

Burns et al (76) while agreeing with the first stage thickening hypothesis, feel that the second stage arises from chain entanglement of

the then higher molecular weight polyester species. They explain the effects of water reducing the eventual viscosity by the combination of two factors.



The condensation reaction is reversible, and the equilibrium will be disturbed by the addition of water, resulting in fewer higher molecular weight species being formed. Also water will induce a higher dielectric constant of the reaction medium again causing dissociation of the dicarboxylate salt so limiting the effective value of the higher molecular weight species.

As Warner stated, for the SMC process to be practical the thickening reaction must satisfy certain criteria:

- (a) thickening must be slow enough to allow wet-out and impregnation of the glass reinforcement.
- (b) thickening must be fast enough to allow handling required by moulding operations as soon as possible after the SMC production.
- (c) thickening must give a viscosity low enough to permit sufficient flow to fill out the mould at reasonable pressures.
- (d) thickening must give a viscosity high enough to carry the glass reinforcement along as it flows in the mould.
- (e) thickening must stop in the mouldable range to give a long useful shelf life.

2.4.2.4 The moulding of SMC

One of the greatest problems in SMC technology is the wide variation in mechanical properties often encountered in the product. Furns et al (77) undertook a detailed study of property variability introduced in the moulding of SMC. They found that presentation of the charge to the mould was the most important single factor influencing the property

variability of the moulded SMC part.

They recorded the tensile strengths of standard batches of SMC over six months and data was found to range from 20 to 85 MNm^{-2} . Regular charge geometry brought about a reduction in the coefficient of variability from 40% to 15%.

They found that provided a minimum press dwell time was exceeded that this part of the moulding process was an insignificant factor with regard to the mechanical properties of the SMC. However it did affect the surface finish gloss. An acceptable finish was not achieved for a dwell time of less than 1.5 minutes. At the same time they did find that there was a proportional relationship between the tensile strength of the moulded part and the moulding pressure.

A moulding pressure of 3.5 MNm^{-2} gave an average tensile strength of 70 MNm^{-2} , while a moulding pressure of 15 MNm^{-2} gave an average tensile strength of 85 MNm^{-2} .

The effect of the press closure speed was found to be dependent on the size used on the glass fibre. For a soluble size a variation in press closure speed was found to be negligible. However, with an insoluble size a fast closure speed was found to decrease the tensile strength of the resulting SMC. Burns postulated that this was due to the rigid fibre bundles causing inefficient air removal during the moulding process.

Methven (78) has studied the flow behaviour of SMC and DMC in the mould by monitoring the press. He found that the flow time could be correlated with the resin gel time, the shorter the gel time the shorter the flow time. He pointed out the importance of careful catalyst selection to be compatible with the moulding procedure. He showed that with compression moulding it is important that the material should flow for a sufficient time to fill the mould completely before gelation. It should then cure rapidly to reduce the mould cycle time. Methven found that t-butyl peroctoate had a longer cure time than gel time, while

t-butyl perbenzoate had a longer gel time than cure time. He also showed that variations in catalyst concentration level has little effect on the flow lengths of the moulding compound.

Thompson (79) carried out a similar programme recording pressure variations of the platens thereby providing information on cure and shrinkage. He found that easier flow was experienced at higher press temperatures. However, at 170°C, although there was at first less resistance to flow, that after three seconds a steady pressure rise commences and the time required for mould filling was found to increase. He illustrated how moulding dynamics were dependent on charge size and SMC maturity as well as moulding temperature.

As the press closes layers of SMC directly in contact with the tool surfaces are heated, thus reducing their viscosity, and are squeezed out radially exposing fresh surfaces to heating. Movement of material increases the rate of heat transfer (80) into the SMC. The overall result is the greater ease of flow observed with a very small charge area.

2.4.2.5 Mechanical properties of SMC

The typical mechanical properties of moulded SMC have been well documented (81). Table 3 shows some relevant data and it is interesting to note that the fracture strain of the glass is in the order of 4% yet that of the moulding compound is much lower.

Table 3 Mechanical properties of typical SMC

	Tensile strength MNm ⁻²	Elongation at Break %	Young's Modulus GNm ⁻²
SMC (82)	100	1.4	11.2
SMC (83)	86.1	1.33	11.9
Glass Fibre	1300	3.8	70

The mechanical properties of polyester moulding compounds account for many of their technological applications. Ogorkiewicz (84, 85) indicated that much of the improvement in the stiffness of the compound was due to the filler. However the filler did not increase the strength

and that their tensile strengths (37 MNm^{-2}) were similar to those of the polyester resin (32 MNm^{-2}). They found that the tensile strengths of a similar SMC were in the order of 100 MNm^{-2} . They thought this implied that the short fibres (6.4 mm) utilised in DMC were shorter than the critical fibre length. They estimated a critical fibre length of 4 mm from study of the pull out lengths, however Hancock and Cuthbertson (88) suggest that l_c for glass fibre or fibre bundles in a polyester resin is 13 mm.

Burns and Pennington (89) have shown that the filament diameter and strand length of the glass fibre used has little or no effect on composite properties and pointed out that it should be possible to produce SMC with significantly shorter strand lengths than the usual 50 mm at present utilised. This would bring about a consequent enhancement of flow properties.

They did show that bundle tex (the linear density of the individual strands) and size type are significant variables in determining mechanical properties. They found that tensile strength decreases with increasing bundle tex.

2.4.2.6 The fracture of SMC

Harris and Cawthorne (82) made an attempt to explain the fracture behaviour of both sheet and dough moulding compounds. They found that for DMC fracture energy parameters were dependent on the notch depth to width of specimen ratio. All these parameters, including the apparent fracture toughness, did not include a contribution from pull out. The work of fracture term which did include a contribution from pull out was found to be most independent of relative notch depth.

Sheet moulding compounds were found to give far superior fracture resistance compared with DMC. However if one considers the total work to fracture SMC values are only marginally superior to those obtained for DMC. Outwater and Murphy (46, 90) who summarised the theoretical approach suggested that the energy absorbed in debonding fibres and not

frictional work associated with fibre pull out was the largest contributor to fracture energy. In the DMC and SMC investigated Harris found that pull out lengths were rarely larger than a few bundle diameters and that in these circumstances pull out cannot make any substantial contribution to the work to fracture.

Harris and Cawthorne concluded that the fracture toughness is a simple function of the fibre/weight fraction and that the major contribution to the work of fracture was from the work of fibre/resin debonding. They also noted that values ($3.5 \pm 0.6 \text{ MNm}^{-3/2}$) obtained for the fracture toughness from notched tensile specimens were only 80% of the value ($4.4 \pm 1.0 \text{ MNm}^{-3/2}$) obtained from bending tests. However scatter was far less.

In a paper concerned solely with DMC (91) the same authors found that above the T_g of the matrix resin the energy contribution from fibre pull out to the total work to fracture was significant. The amount of work to initiate was found to be unaffected by changes in matrix properties at the resins T_g . However, there is a reduction in the work to initiate fracture when the fibre bundles cease to act as single large diameter bundles. When baked on resin begins to flow there is a reduction in toughness.

In a further paper (92) the same authors prepared a series of binary glass/resin and chalk/resin as well as three component moulding compounds. They found the addition of up to 20 to 30% of short glass fibre (6.4 mm) to the resin increased the fracture energy by over a hundredfold. Also, doubling the fibre length increased the toughness by 50%. They also made the important point that the angularity of the filler affects the work to fracture. They found that moulding compounds containing crushed calcite had lower work-to-fracture values than those containing precipitated chalk. This was thought to be due to fibre damage occurring during blending and pressing as well as during fracture. The damage was caused by the angular fragments of calcite.

As is discussed by Harris and Cawthorne there are serious difficulties in the way of a proper interpretation of the strength and toughness of these materials not the least of which is the fact that exact details of structure and composition of these materials is rarely available.

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

The experimental programme was designed to establish whether any close relationship exists between the structure and properties of the matrix resin and the mechanical properties of the sheet moulding compound (SMC). It was decided to keep as constant as possible all material and process variables. Those quantities varied were:

- (a) the degree of unsaturation of the resin,

this was done by altering the

maleic:phthalic ratio of the resin's diacid component

- (b) the hydroxyl value of the resin,

this was carried out by two methods.

Firstly different diol excesses were added to the reaction vessel (5%, 7½% and 10%) and secondly the resins were synthesised by two different methods I & II.

The experimental programme was as follows:-

- (i) preparation of polyester resins with specified structures
- (ii) analysis of polyester resins
- (iii) measurement of the mechanical properties of the cast resins
- (iv) production of SMC
- (v) measurement of the mechanical properties and study of the fracture characteristics of SMC.

3.2 Preparation of unsaturated polyester resins

A number of polyester resins were synthesised in the laboratory (see Fig. 15) (93). The starting materials were maleic anhydride (ex Monsanto Chemicals), phthalic anhydride (ex Laporte chemicals) and propane 1.2 diol (ex Shell Chemicals). As far as was possible the same procedure was carried out for each synthesis and table 4 shows a typical synthesis. Two resins with a molar diol excess of 10% one for each method of synthesis, were synthesised for each level of unsaturation (maleic:phthalic ratio). The formulations chosen were 50%, 67%, 75%,

85% and 100% levels of unsaturation. A resin with a 50% level of unsaturation has a formulation of:

10 moles of phthalic anhydride

10 moles of maleic anhydride

20 moles (+ % excess) of propane 1.2 diol

a resin with a 100% level of

unsaturation has a formulation of;

20 moles of maleic anhydride

20 moles (+ % excess) of propane 1.2 diol

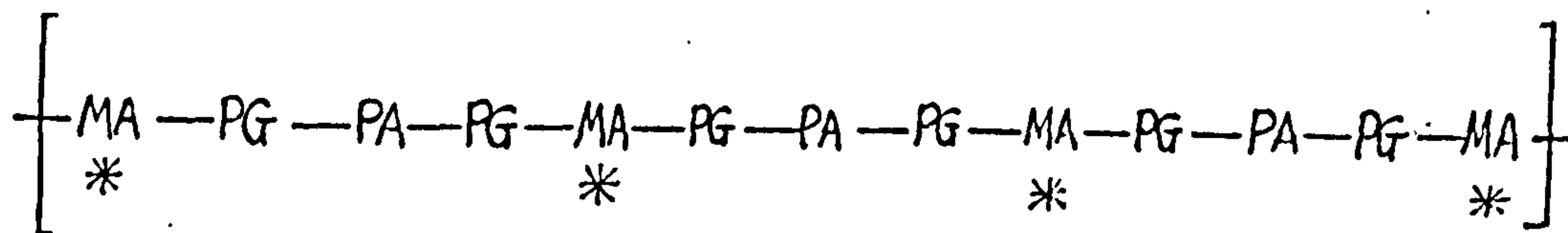
So as to attempt to gauge the effect of differing hydroxyl values the resin on the eventual mechanical and fracture behaviour of the SMC, as well as synthesising resins of 67% and 75% unsaturated with a 10% diol excess, resins were synthesised with 7½% and 5% diol excesses.

Table 4

Typical resin synthesis

Hours after commencement	Vessel °C temp.	Still head °C	Water collected ml (theoretical yield 20 mole)
½	185	100	1 mole
1	190	100	2 mole
3	190	100	12 mole
3½	200	92	14 mole
10	200	92	19 mole

Note:- In a 20 mole diol plus 20 mole diacid synthesis, Xylene is added to azeotrope off the remaining water, after 3 hours. Then after 10 hours, if synthesised by method I, the synthesis would be taken to an acid value of 35 then the xylene would be distilled off; if synthesised by method II, the synthesis would be taken to an acid value of 45 followed by vacuum distillation until an acid value of 35 was obtained. The acid value of a resin is defined as the number of milligrams of potassium hydroxide needed to neutralise 1 gram of resin. The resin is



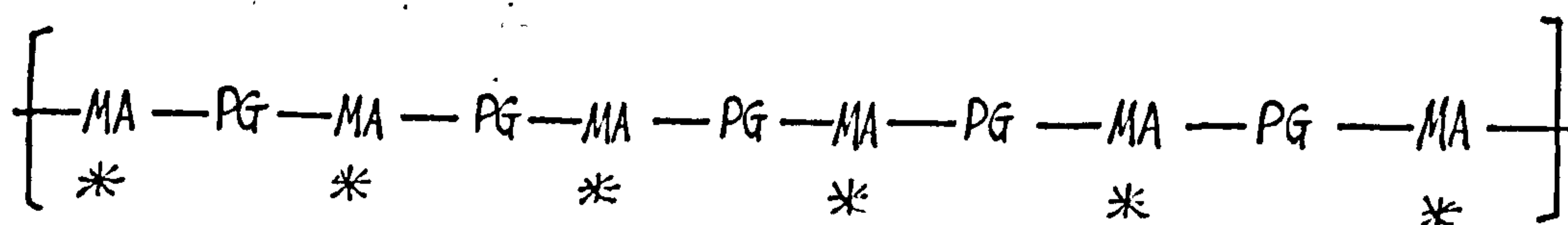
MA = MALEIC ANHYDRIDE

PA = PHTHALIC ANHYDRIDE

PG = PPROPANE 1.3 DIOL

* = CROSSLINKABLE SITE

Fig. 13. Idealised structure for a resin with 50% unsaturation



MA = MALEIC ANHYDRIDE

PG = PHTHALIC ANHYDRIDE

* = CROSSLINKABLE SITE

Fig. 14. Idealised structure for a resin with 100% unsaturation

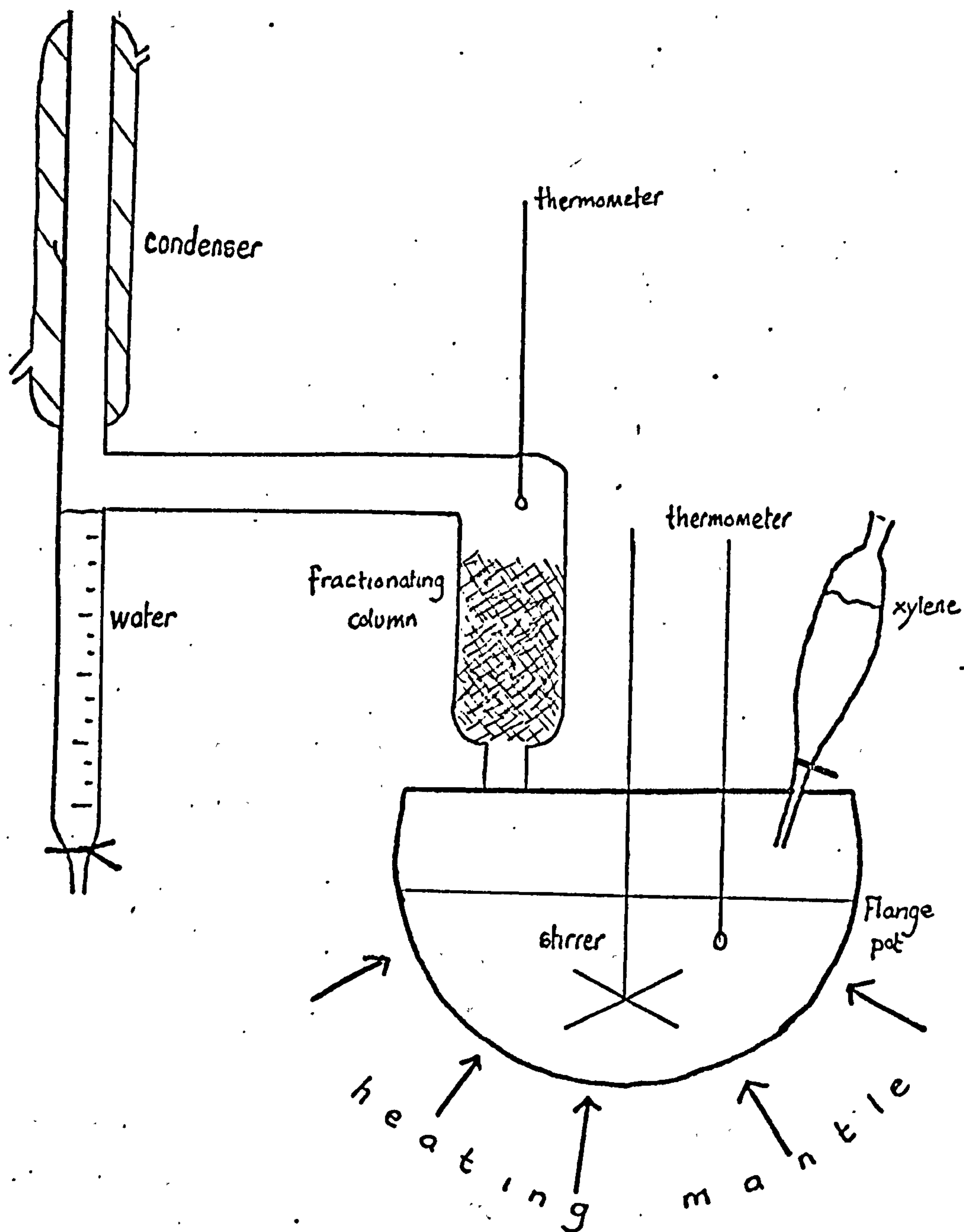


Fig. 15 Apparatus used in a polyester resin synthesis

then cooled to 120°C at which stage 10 ml of a solution of hydroquinone was added (1g to 10 ml of dibutyl phthalate). Styrene is then used to dissolve the resin to a viscosity of 8 poise at 20°C.

The polyester resins were dissolved in sufficient styrene monomer (ex Forth Chemicals) to produce a viscosity of 8 poise at 25°C.

3.3 Analysis of resins

Each polyester resin was analysed to determine three quantities:

- (a) solids content
- (b) acid value
- (c) hydroxyl value

The solids content or non-volatile content of the resin was determined by heating a two gram sample of the resin in an oven at 120°C for two hours. This causes all the volatile styrene to evaporate and leaves the base resin.

The acid value of a polyester resin is defined as the number of milligrams of potassium hydroxide needed to neutralise 1 gramme of polyester resin. The method used is that recommended by BS 2782 (94). A known weight of resin, dissolved in neutralised acetone, is titrated against a standardised solution of methanolic potassium hydroxide.

$$\text{Acid Value (solids)} = \frac{56100 \times A \times B}{C} \times \text{NVC}$$

where A = number of millilitres of potassium hydroxide

solution needed to neutralise the sample of polyester resin;

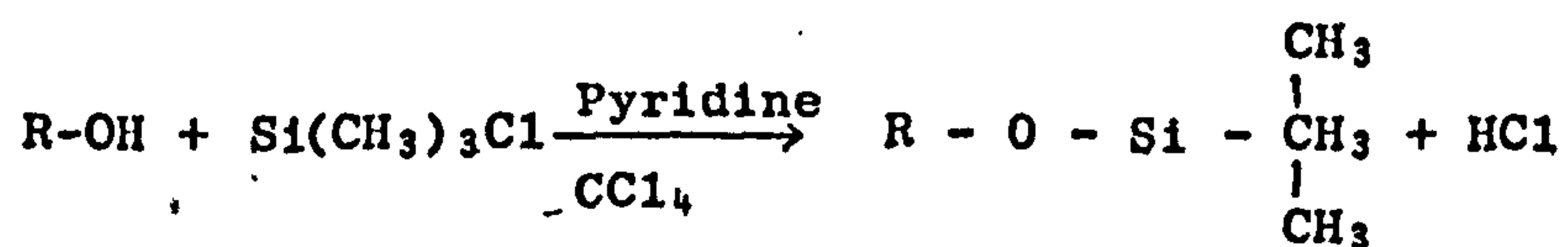
B = molarity of potassium hydroxide solution;

C = mass of polyester resin sample; and NVC = solids content of resin.

The solids content is needed because the acid value refers to the acid value of the non-volatile content of the resin. If a destyrenated sample was used the multiplication by the solids content is unnecessary.

The determination of hydroxyl value was based on an NMR method proposed by Hase and Hase (95). They decarboxylated their samples with diazomethane, and then treated them with chlorotrimethylsilane. Any

hydroxyl groups were thereby silylated as follows:



The NMR peak of the -OH proton has now undergone a ninefold enhancement and can easily be distinguished at 10 τ . If a known weight of internal standard is added, then the peak of the internal standard can be compared with that at 10 τ and thus the hydroxyl value of the original compound (R - OH) can be calculated.

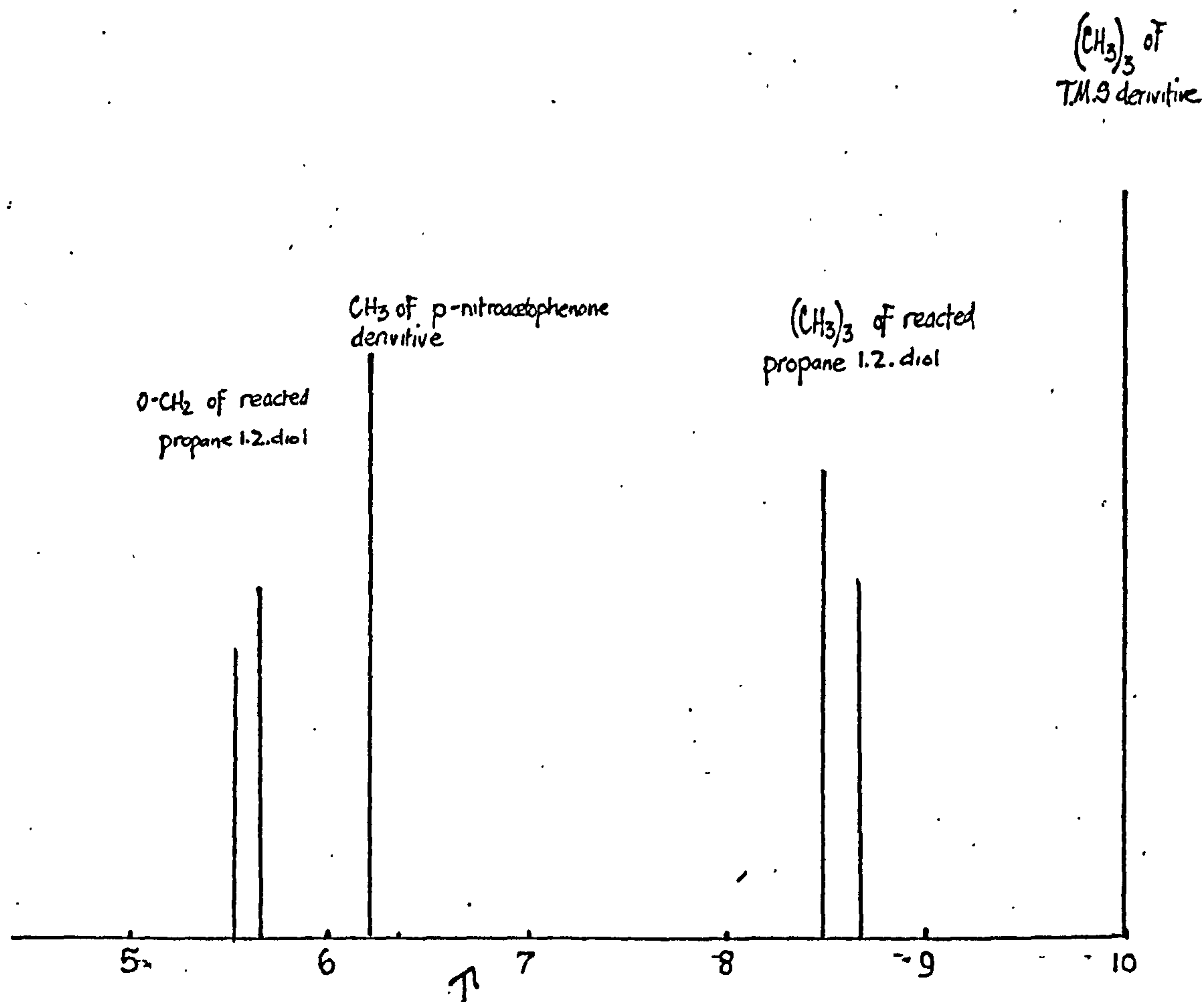


Fig. 16

T.M.S. derivative of a polyester resin

The method used in this work was adapted in that, the acid value being known, the decarboxylation was not carried out. One gramme of styrene free polyester resin was dissolved in 2 ml of dry carbon tetrachloride to which was added 2 ml of analar dry pyridine. Approximately 100 µg of p-nitroacetophenone was then added, and the mixture was sealed in a round bottomed flask with a serum cap.

2 ml of dry trimethylochlorosilane was then added using a clean dry syringe and the flask was left at ambient temperature for 30 minutes before the excess solvent was vacuum distilled off at 70°C. This removes (as well as the solvent) any traces of hexamethylsiloxane impurity, which can be formed when the chlorotrimethylsilane reacts with any moisture present.

The residue was then dissolved in analar chloroform. Usually deuteriochloroform would be used but the peak due to the hydrogen proton of chloroform in no way interferes with those at 6τ and 10τ of the internal standard and silylated derivative respectively. The NMR spectrum was then obtained for the dissolved compound and the integrals at 6τ and 10τ recorded.

The value obtained of course included the added value for the acid value of the resin. The combined acid and hydroxyl value was found by:

$$\text{OH} + \text{COOH value} = \frac{h_{10} \times 3 \times g_s \times 56100}{h_6 \times 9 \times g_p \times \text{M.W.s}}$$

Where OH + COOH = combined hydroxyl and carboxyl value in mg of potassium hydroxide per gram of resin

h_{10} = height of peak at 10τ

h_6 = height of peak at 6τ

g_s = weight of standard (p-nitroacetophenone)

g_p = weight of polyester resin

MW_s = molecular weight of standard (p-nitroacetophenone)

3.4 Measurement of the tensile properties of the cast resins

3.4.1 Sample preparation

The polyester resins were cast into dumbbell shapes as recommended by BS 2782/301J (94). A silicone rubber mould was manufactured by casting around injection moulded polyformaldehyde standard 301J specimens. On the silicone rubber curing, the specimens were removed and the excess rubber removed with a scalpel.

The mould was then placed on a flat glass surface covered with melinex sheeting. The melinex was used so that samples could easily be removed from the mould. For every one hundred grammes of resin, one gramme of methyl ethyl ketone peroxide and one gramme of 0.5% cobalt naphthenate solution accelerator was added. The polyester resin was then poured into the mould and left to cure. Gelation usually took 45 minutes at $20 \pm 2^{\circ}\text{C}$, although the all maleic resin gelled in 35 minutes. After standing for eighteen hours, the specimens were post-cured for three hours at 80°C .

3.4.2 Determination of tensile properties

For each set of resins, determinations were made of:

- (a) the ultimate tensile strength,
- (b) the tensile modulus,
- and (c) the elongation at break.

All specimens were tested on a Model 1114 Instron and broken with a crosshead speed of 10 mm/min. The specimen was gripped in the jaws in a sheaf of fine grade emery paper so as to avoid slippage of the test piece. So as to evaluate the moduli an Instron Strain Gauge Extensometer (2620-015) of gauge length 25 mm was attached to the specimens.

3.5 Determination of fracture toughness of cast resins

The fracture toughness of the cast polyester resins was determined by loading single edge notched specimens (See Fig. 17). The specimens were given a 30° notch using a milling tool and the nominal notch

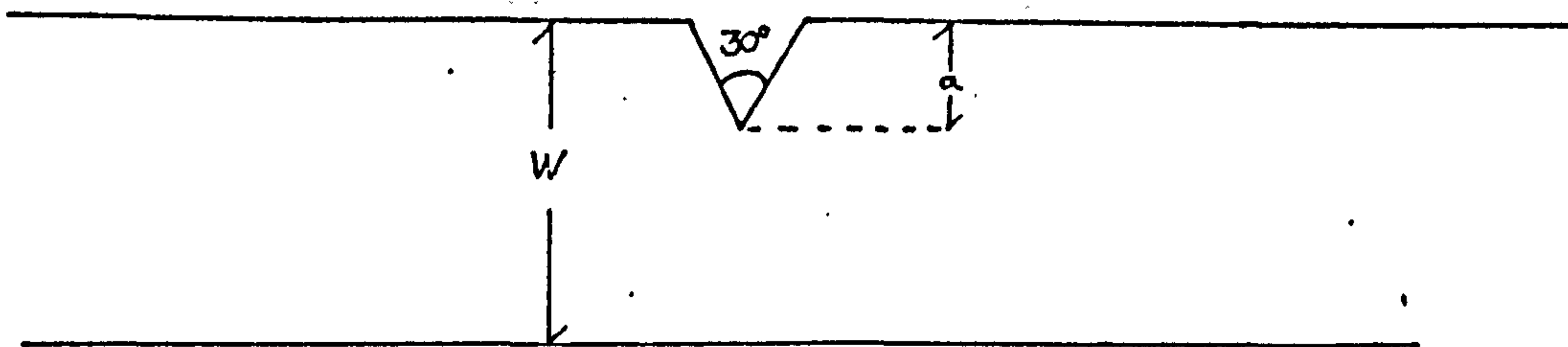


Fig. 17 Single edge notched (SEN) test piece

depth:width ratio was 0.3. The notch was then sharpened using a scalpel. All specimens were inspected under a X100 travelling microscope and a grid used to establish that the notch tip radius was smaller than 0.1 mm. The travelling microscope was also used to measure the notch depth.

All specimens were loaded on a Model 1114 Instron and broken with a crosshead speed of 1 mm/min. The stress intensity factor K_{IC} , is related to the fracture load, P , the initial crack length, a , the sample thickness, t , and the width of specimen, W , by (96).

$$K_{IC} = \frac{P}{tW^{3/2}} \left[1.99 \left(\frac{a}{W} \right)^{1/2} - 0.41 \left(\frac{a}{W} \right)^{3/2} + 18.7 \left(\frac{a}{W} \right)^{5/2} - 33.48 \left(\frac{a}{W} \right)^{7/2} + 53.85 \left(\frac{a}{W} \right)^{9/2} \right]$$

3.6 Manufacture of sheet moulding compound

Polyester resin from each resin synthesis was used to make a resin slurry. The components of the resin slurry are listed in Table 5. Calcium carbonate, finely ground polythene and zine stearate were dispersed in the polyester resin using a high shear mixer. As this generated considerable heat, the slurry was then left to cool for a day before the tertiary butyl perbenzoate catalyst was added. The last reagent added was the magnesium oxide thickener. After addition the slurry was mixed for two minutes and then transferred to the SMC machine (see Fig. 18).

TABLE 5

Compounding of SMC

COMPONENT	<u>CONTENT</u> expressed as parts per 100 of resin by weight
Polyester resin	100
Calcium carbonate filler	110
Magnesium oxide	1
Polythene (finely ground)	5
Zinc stearate mould release	4
Tertiary butyl perbenzoate catalyst	0.75

Calcium carbonate

ex Norwegian talc

Magnesium oxide

ex Sherman Chemicals

TBP Catalyst (Triganox C)

ex Akzo Ltd.

Polythene (Coathylene)

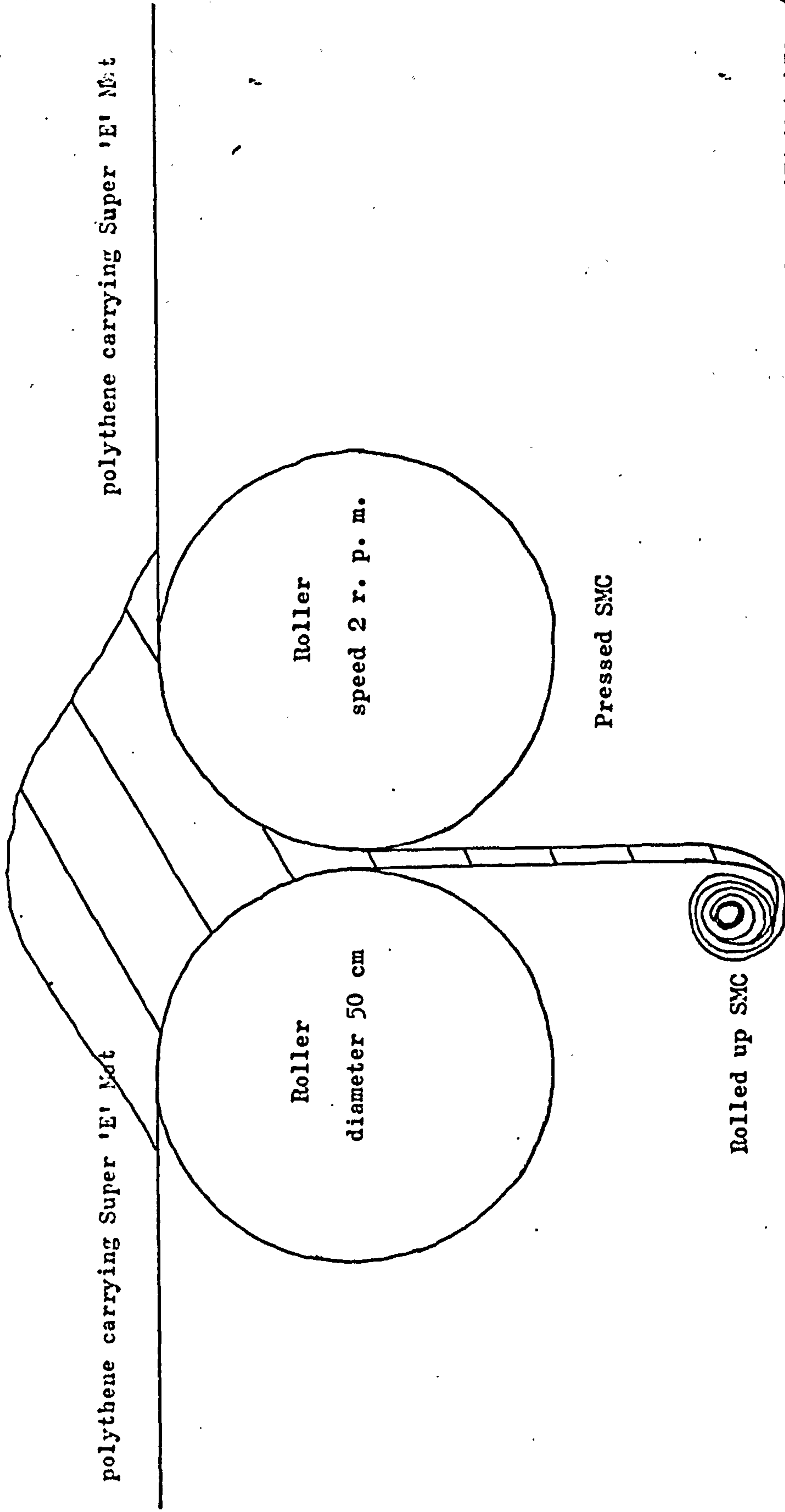
ex Cole Chemicals

Zinc stearate

ex Albright and Wilson

Note: usually, due to shrinkage on cure, a nil-shrink component is added. In this project 5 pphr of coathylene (finely ground polythene) was used. This quantity is insufficient to give nil-shrink SMC but does give a smooth surface finish.

polyester resin slurry



Super 'E' Mat 450 g/m²
(ex Fibreglass Ltd.)

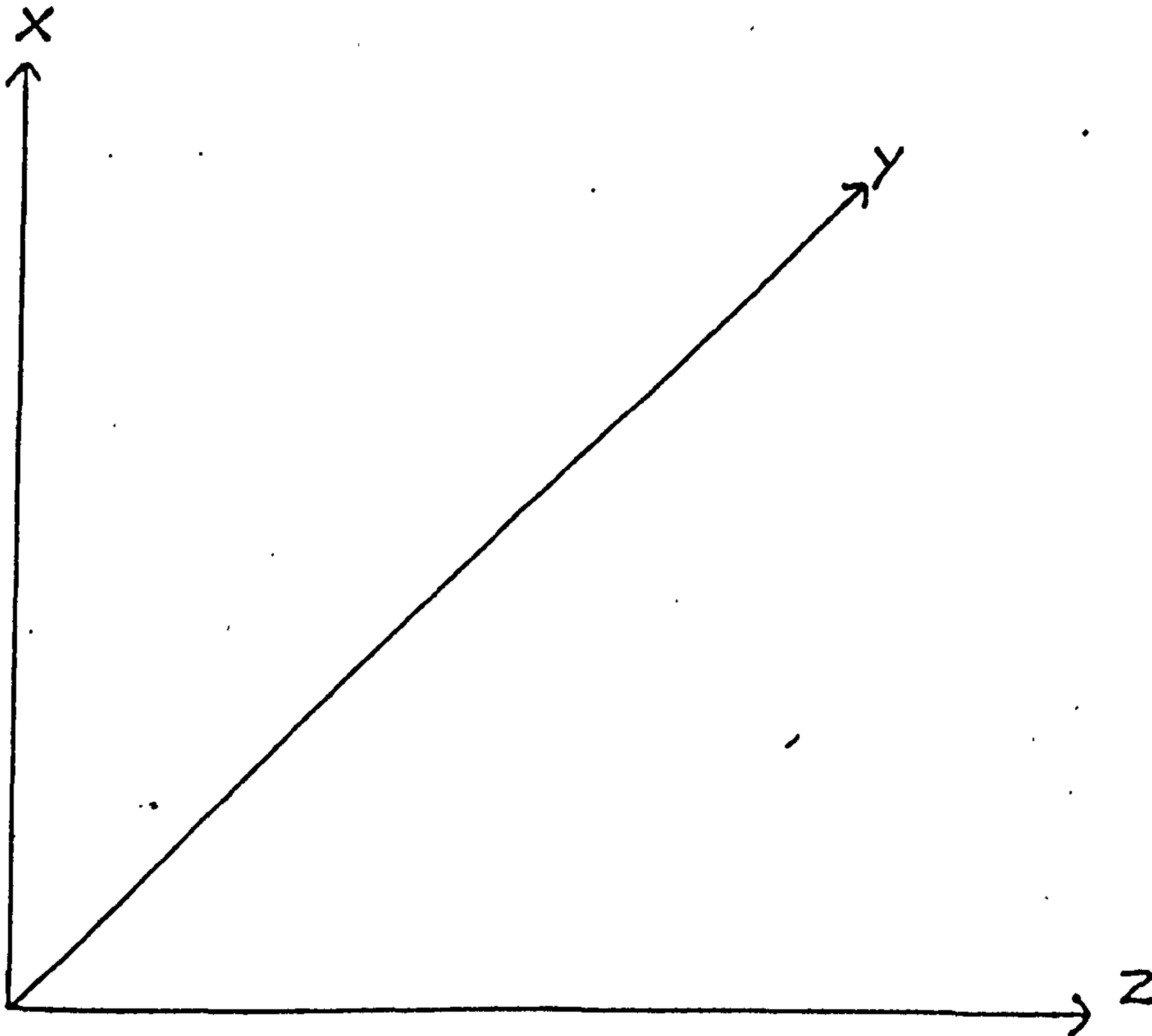
The sheet moulding compound was then prepared using random glass chopped strand mat (Super 'E' mat) which has an average glass strand length of 50 mm and weight of 450 g/m^2 . The SMC was rolled up and left to mature for two weeks at $20^\circ \pm 2^\circ \text{C}$.

After two weeks the SMC was cut into 250 mm square charges. Two charges weighing approximately 460 g were applied to the mould, and cured between 350 mm square platens on a Bipel press. The moulding pressure was 6000 kN/m^2 with a press close time of $2\frac{3}{4}$ mins. The temperature of the top platen was 145°C and of the lower was 150°C . The sheets of SMC were 304 mm square.

3.7 Measurement of the mechanical properties of SMC

3.7.1 Sample preparation

The SMC was cut into 250 mm by 25 mm strips using tungsten carbide tipped circular saw. All the SMC specimens were cut from the moulded sheets in the three specified directions so that any directional anisotropy could be detected.



3.7.2 Determination of tensile properties

For each batch of SMC the following mechanical properties were determined,

- (1) ultimate tensile strength
- (2) tensile modulus
- (3) elongation at break
- (4) energy of rupture

The specimens were broken in the tensile mode using a Model 1114 Instron at a crosshead speed of 100 mm/min. So as to evaluate the elongation at break, a strain gauge extensometer (2620-015 Instron) of gauge length 25 mm was attached to the specimen.

The energy dissipated during the tensile test, or energy of rupture, was obtained by integrating the area under the stress-strain curve using an integrator (Instron).

3.8 The fracture of SMC

3.8.1 Sample preparation

The strip geometry used for tensile mechanical properties was also used to determine the fracture toughness, except that a 30° notch was introduced (see Fig. 17) using a milling tool. The depth of the notch was such that the notch:width ratio (a/W) was approximately 0.3. The notch was then sharpened using a scalpel observed using a 100X microscope. The notch depth was measured and each specimen was checked to ensure that the notch root radius was less than .1 mm.

3.8.2 Single edge notch (SEN) tensile tests

The use of the single edge notch tensile specimen for measuring the fracture toughness of most metallic materials, and also for some polymeric materials (29), as well as for glass reinforced epoxy and polyester resins (98). The SEN specimen is found to be economical with regard to available test material and test machine capacity.

A calibrated strain sensor (Nene instruments) was placed on the specimen so as to measure the opening of the crack. The strain sensor

is quite sensitive and displacement values of up to 5×10^{-2} mm could easily be measured from the chart.

The specimen was broken at a crosshead speed of 10 mm/min. The load displacement records were analysed in accordance with the procedure recommended in ASTM E399-71T (99). Figure 19 shows a typical load displacement curve. It becomes increasingly non-linear at higher values of applied load. To determine the load corresponding to crack initiation, a tangent OA is drawn at the origin of the curve. The slope of line OA is measured, and another line OP₅ is drawn with a slope 5% less than that of line OA. Another line OP₁₀ is drawn through the origin with a slope 10% less than that of OA. P₅ and P₁₀ are the loads of the intersection of these lines with the load displacement curve.

The load of crack initiation, P_I, is then defined as follows:
if the load at every point which precedes P₅ is less than P₅, then P_I is P₅, if however, there is a maximum load preceding P₅, then this maximum load is P_I. The ratio P₁₀/P_I is calculated and if this ratio does not exceed 1.10, then the load P_I can be used to calculate the candidate stress intensity factor K_{IQ}, using the following relation,

$$K_{IQ} = \frac{P_I}{tW^{\frac{1}{2}}} \left[1.99 \left(\frac{a}{W} \right)^{\frac{1}{2}} - 0.41 \left(\frac{a}{W} \right)^{\frac{3}{2}} + 18.7 \left(\frac{a}{W} \right)^{\frac{5}{2}} - 38.48 \left(\frac{a}{W} \right)^{\frac{7}{2}} + 53.85 \left(\frac{a}{W} \right)^{\frac{9}{2}} \right]$$

where P_I = load established from load displacement records

a = initial crack length

t = thickness of specimen

W = width of specimen

The term "candidate stress intensity factor" is used because the method described has been primarily established for metallic materials and with these materials it corresponds to the critical stress intensity factor if the specimen geometry meets the recommendations of ASTM E399-71T (99). No such recommendations exist for composite materials.

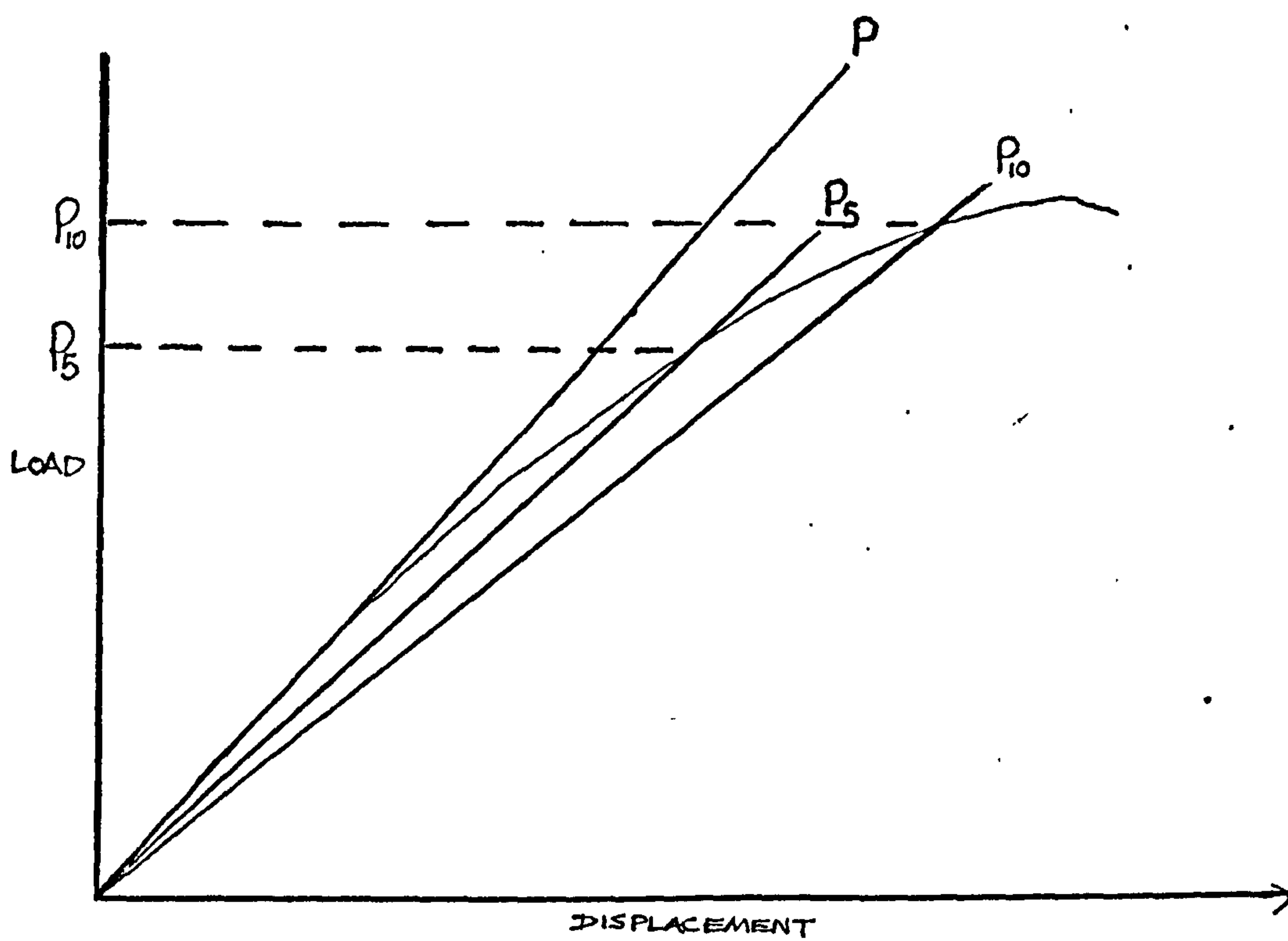


Fig. 19 Typical load displacement curve showing calculation of P_I

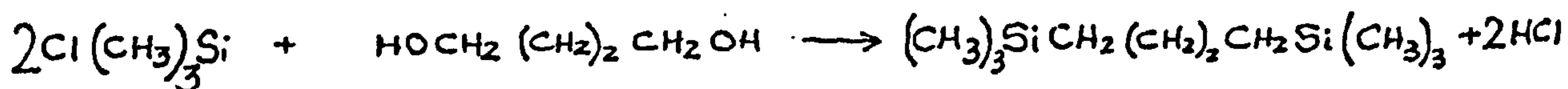
Chapter 4

RESULTS

4.1 Resin synthesis and analysis

Tables 6 and 7 show the resins synthesised and the results of their subsequent analysis. The solids content was the mean of three determinations and the figure for the acid value was similarly obtained. Both values are obtained from simple tests and both show very little variation (94). For example for a mean solids content of 62.3% for resin E_I, values of 62.25, 62.29 and 62.27 were obtained. Variation of the acid value is larger but values can be expressed with confidence as ± 1.5 . The errors are those inherent in any titration method using phenolphthalein as an indicator.

The hydroxyl value allocated to each resin has greater variation than the two previously discussed parameters. Preliminary experiments were carried out using the silylation method on two model compounds, butane 1.4 diol and hydroxy-phenylacetic acid. The reaction of butane 1.4 diol proceeds as follows:-



The NMR analysis of a sample of this product dissolved in deuteriochloroform gave the following spectrum (Fig. 20).

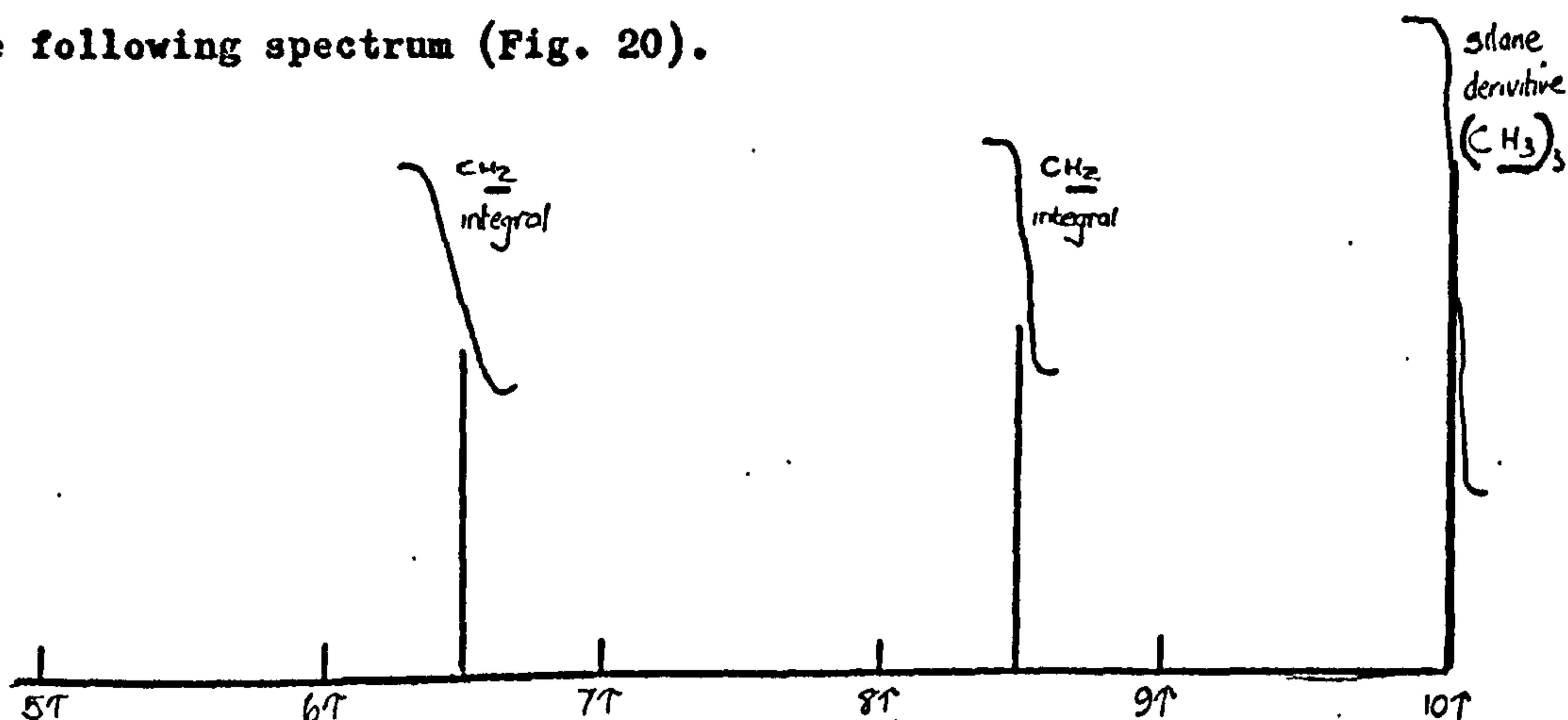


Fig. 20. The NMR spectrum of silylated butane 1.4 diol

The peak at 10τ is that belonging to the two trimethyl groups $-(CH_3)_3$, the other two peaks of 6.5τ and 8.5τ being due to the two sets of methylenic protons $-(CH_2)_2$. Therefore with full reaction of the butane diol the integral of the peaks at 10τ and 8.5τ should be in the ratio of 18:4. Ten such experiments were carried out with butane 1.4 diol and each ratio reduced to a x:40 reading. A mean figure of 182 with a standard deviation of 6 was obtained for x. This gives an error of less than 2% for the reading and even less when one considers that this is a ninefold enhancement of the true hydroxyl proton content.

The experiments carried out with hydroxyphenylacetic acid showed that, even when carboxyl groups and hydroxyl groups are silylated, errors were not increased.

However when carrying out the identical tests but using the integral of the internal standard p-nitroacetophenone to calculate the hydroxyl value of butane 1.4 diol error were increased and standard deviations of $\pm 5\%$ from the real value were obtained.

The hydroxyl values in tables 6 and 7 are the mean of five readings and the standard deviations obtained were never greater than $\pm 10\%$.

4.2 Mechanical properties of cast polyester resins

Tables 8, 9 and 10 show the values obtained for the basic tensile properties of the cast resins. Each figure is the mean of results obtained from testing ten dumbell specimens.

The spread of results obtained for the elongation at break and tensile strength was high and standard deviations of $\pm 30\%$ of the stated value were the least obtained. This must be born in mind when considering the significance of different values for different resins.

The tensile moduli values for each resin again showed wide variation but not as large as those experienced for the previously mentioned parameters. Standard deviations were in the region of 10-15%.

TABLE 6

Analysis of resins synthesised with different glycol excesses

Resin	% Glycol Excess	Solids Content %	Acid Value mg KOH	Hydroxyl Value mg KOH
C _I	10	66.6	39	60
D _{II}	10	66.8	40	60
C _I ⁷	7½	64.0	35	30
D _{II} ⁷	7½	65.0	37	30
C _I ⁵	5	54.2	44	47
D _{II} ⁵	5	65.0	44	25
E _I	10	62.3	39	82
F _{II}	10	63.2	32	30
E _I ⁷	7½	60.7	35	50
F _{II} ⁷	7½	56.6	34	25
E _I ⁵	5	54.6	32	15
F _{II} ⁵	5	53.3	38	20

TABLE 7

Analysis of resins of differing maleic:phthalic ratio

Resin	Unsaturated Acid as Mole % of total Acid %	Solid Content %	Acid Value mg KOH	Hydroxyl value mg KOH
A _I	50	68.4	32	50
B _{II}	50	69.3	39	75
C _I	67	66.6	39	60
D _{II}	67	66.8	40	60
E _I	75	62.3	39	82
F _{II}	75	63.2	32	30
G _I	85	58.0	44	25
H _{II}	85	61.5	37	35
J _I	100	56.6	36	30
K _{II}	100	60.3	39	20

TABLE 8 Mechanical properties of cast polyester resins with differing maleic:phthalic ratios (i.e., degree of unsaturation).

Matrix resin	Degree of Unsaturation %	Elongation at Break %	Ultimate Tensile strength MN/m ²	Tensile Modulus GN/m ²
A _I	50	0.83	23.9	3.52
B _{II}	50	0.81	24.5	3.41
C _I	67	1.05	26.7	3.54
D _{II}	67	1.23	38.3	3.73
E _I	75	1.20	37.1	3.54
F _{II}	75	1.29	44.0	3.53
G _I	85	1.83	43.6	2.74
H _{II}	85	1.66	43.6	2.73
J _I	100	1.40	34.8	2.75
K _{II}	100	1.76	48.2	3.12

TABLE 9 , Mechanical properties of cast polyester resins with different diol excesses (degree of unsaturation 67%)

Matrix Resin	Diol Excess %	Elongation at Break %	Ultimate Tensile Strength MN/m ²	Tensile Modulus GN/m ²
C _I	10	0.85	26.7	3.54
D _{II}	10	1.23	38.3	3.73
C _I 7	7.5	1.08	32.3	3.38
D _{II} 7	7.5	0.89	27.1	3.77
C _I 5	5	1.15	38.2	3.56
D _{II} 5	5	1.09	33.8	3.55

TABLE 10 Mechanical properties of cast polyester resins with different diol excesses (degree of unsaturation 75%)

Matrix Resin	Diol Excess %	Elongation at break %	Ultimate Tensile Strength MN/m ²	Tensile Modulus GN/m ²
E _I	10	1.20	37.1	3.14
F _{II}	10	1.29	44.0	3.53
E _I 7	7.5	0.89	28.5	3.27
F _{II} 7	7.5	1.28	39.1	3.34
E _I 5	5	0.95	30.8	3.23
F _{II} 5	5	1.29	35.1	2.75

4.3 Fracture properties of cast polyester resins

Tables 11 and 12 list the measured fracture properties of notched cast polyester resins. The values show the mean and standard deviation stress intensity factors (K_{IC}) calculated from the results of ten test specimens.

TABLE 11 Stress intensity factors and crack extension force of
polyester resins

	Degree of unsaturation %	K_{IC} MN/m ^{3/2}	G_{IC} N/m
A _I	50	.712 (\pm .095)	119.4
B _{II}	50	.716 (\pm .121)	120.8
C _I	67	.605 (\pm .063)	103.4
D _{II}	67	.558 (\pm .072)	75.1
E _I	75	.562 (\pm .067)	90.5
F _{II}	75	.562 (\pm .047)	80.5
G _I	85	.488 (\pm .106)	65.9
H _{II}	85	.410 (\pm .058)	55.4
J _I	100	.324 (\pm .039)	34.4
K _{II}	100	.448 (\pm .043)	57.9

TABLE 12

Stress intensity factors and crack extension forces
of polyester resins synthesised with different
glycol excesses

Resin	Diol Excess %	Degree of Unsaturation %	K_{IC} MN/m ^{3/2}	G_{IC} N/m
C _I	10	67	.605 (\pm .063)	103.4
D _{II}	10	67	.558 (\pm .072)	75.1
C _I ⁷	7.5	67	.606 (\pm .068)	87.7
D _{II} ⁷	7.5	67	.550 (\pm .086)	80.5
G _I ⁵	5	67	.576 (\pm .091)	83.9
D _{II} ⁵	5	67	.491 (\pm .084)	61.9
E _I	10	75	.562 (\pm .067)	90.5
F _{II}	10	75	.562 (\pm .047)	80.5
E _I ⁷	7.5	75	.483 (\pm .042)	64.2
F _{II} ⁷	7.5	75	.462 (\pm .088)	57.5
E _I ⁵	5	75	.437 (\pm .092)	53.2
F _{II} ⁵	5	75	.407 (\pm .124)	54.2

4.4 The mechanical properties of SMC

Tables 13 and 14 show the mechanical properties of the SMC produced with those matrix resins analysed and characterised in Tables 6 and 7. All the values for tensile strength and tensile modulus were normalised to a glass content of 20%. On testing each SMC the glass contents were found to vary between 19 and 21% and over this short range (82) the mechanical properties are found to be directly proportional to the glass content. The typical formulation of the SMC was

	<u>Resins & Volatiles</u>	<u>Glass</u>	<u>Filler</u>
<u>Parts by weight</u>	38	20	42

All the SMC was tested in three directions, 45° to each other. This was done to ensure that no anisotropy existed in the individual sheets of the SMC, introduced perhaps during the manufacture of the chopped strand mat or the subsequent production of the SMC. Table 15 shows the tensile strength mean of three specimens tested in each direction compared with the mean and standard deviation of all nine specimens.

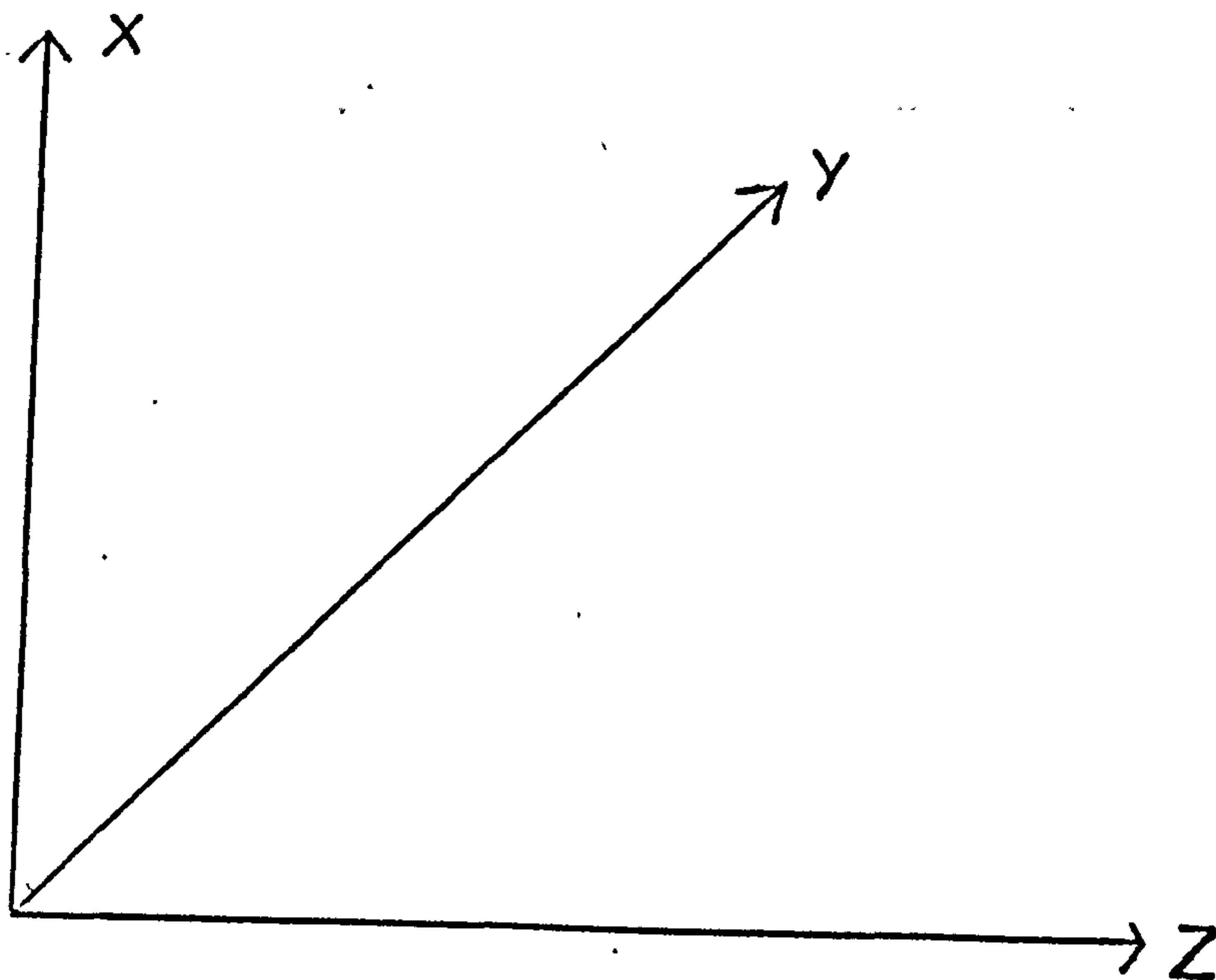


TABLE 13 Mechanical properties of SMC produced with resins of
different maleic:phthalic ratio

Matrix Resin Code	Degree of Unsaturation %	Elongation at Break %	Ultimate Tensile Strength MN/m ²	Tensile Modulus GN/m ²
A _I	50	1.29 (\pm .24)	86.3 (\pm 17.2)	10.1 (\pm 0.9)
B _{II}	50	1.23 (\pm .23)	89.0 (\pm 14.3)	10.5 (\pm 0.8)
C _I	67	1.45 (\pm .38)	84.0 (\pm 18.9)	11.5 (\pm 1.2)
D _{II}	67	1.76 (\pm .21)	89.3 (\pm 18.2)	11.7 (\pm 1.2)
E _I	75	1.75 (\pm .18)	86.5 (\pm 11.5)	11.9 (\pm 0.7)
F _{II}	75	1.87 (\pm .27)	99.8 (\pm 17.4)	11.4 (\pm 1.3)
G _I	85	1.48 (\pm .35)	74.9 (\pm 18.1)	10.1 (\pm 0.9)
H _{II}	85	1.63 (\pm .25)	76.6 (\pm 12.3)	9.4 (\pm 1.2)
J _I	100	1.42 (\pm .27)	70.1 (\pm 21.2)	10.5 (\pm 1.3)
K _{II}	100	1.45 (\pm .29)	75.0 (\pm 17.3)	9.0 (\pm 0.8)

TABLE 14 Mechanical properties of SMC produced using different
diol excesses

Resin	Diol Excess %	Elongation at break %	Ultimate tensile strength MN/m ²	Tensile Modulus GN/m ²
C _I	10	1.45 (± .38)	89.8 (± 18.9)	11.5 (± 1.2)
D _{II}	10	1.76 (± .21)	94.7 (± 18.2)	11.7 (± 1.2)
G _I 7	7.5	1.65 (± .33)	96.7 (± 14.7)	11.4 (± 0.6)
D _{II} 7	7.5	1.96 (± .24)	91.5 (± 18.4)	11.4 (± 0.8)
G _I 5	5	1.56 (± .17)	63.0 (± 17.6)	10.7 (± 0.9)
D _{II} 5	5	1.64 (± .25)	73.4 (± 16.9)	11.0 (± 1.1)
E _I	10	1.75 (± .18)	86.5 (± 11.5)	11.9 (± 0.7)
F _{II}	10	1.87 (± .27)	99.8 (± 17.4)	11.4 (± 1.3)
E _I 7	7.5	1.78 (± .31)	97.5 (± 9.3)	11.8 (± 0.8)
F _{II} 7	7.5	1.67 (± .26)	89.0 (± 10.7)	11.3 (± 0.7)
E _I 5	5	1.10 (± .14)	81.6 (± 16.2)	10.0 (± 0.9)
F _{II} 5	5	1.65 (± .27)	82.6 (± 15.4)	11.0 (± 0.4)

TABLE 15 Tensile strength (MN/m²) in three directions (X, Y and Z)
compared with the mean and standard deviation of each
resin's SMC

Resin	\bar{X}	\bar{Y}	\bar{Z}	Total Mean and Standard Deviation
A _I	82.7	86.7	89.5	86.3 (\pm 17.2)
B _{II}	84.7	90.9	91.4	89.0 (\pm 14.3)
C _I	89.9	86.2	81.7	89.8 (\pm 18.9)
D _{II}	91.7	94.8	85.4	94.7 (\pm 18.2)
G _I ⁷	95.6	90.0	104.5	96.7 (\pm 11.5)
D _{II} ⁷	95.7	94.2	84.6	91.5 (\pm 17.4)
C _I ⁵	56.9	59.2	72.8	63.0 (\pm 17.6)
D _{II} ⁵	69.8	73.2	77.2	73.4 (\pm 16.9)
E _I	89.2	91.5	78.8	86.5 (\pm 11.5)
F _{II}	91.8	100.5	107.1	99.8 (\pm 17.4)
E _I ⁷	93.5	108.4	90.6	97.5 (\pm 9.3)
F _{II} ⁷	88.7	84.2	94.1	89.0 (\pm 10.7)
E _I ⁵	75.2	83.1	86.5	81.6 (\pm 16.2)
F _{II} ⁵	78.9	90.3	88.6	82.6 (\pm 15.4)
G _I	78.5	76.7	69.5	74.9 (\pm 18.1)
H _{II}	87.7	71.3	70.8	76.6 (\pm 12.3)
J _I	67.0	82.5	60.8	70.1 (\pm 21.2)
K _{II}	78.7	67.0	79.3	75.0 (\pm 17.3)
Mean	83.5	85.0	84.1	

TABLE 16

Energy to failure (tensile work) of SMC

SMC Resin	Degree of Unsaturation %	Diol Excess %	Energy to failure MJ/m ³
A _I	50	10	49.0
B _{II}	50	10	69.3
C _I	67	10	61.0
D _{II}	67	10	52.3
C _I ⁷	67	7.5	72.1
D _{II} ⁷	67	7.5	68.0
C _I ⁵	67	5	34.3
D _{II} ⁵	67	5	54.8
E _I	75	10	61.9
F _{II}	75	10	77.1
E _I ⁷	75	7.5	70.7
F _{II} ⁷	75	7.5	57.4
E _I ⁵	75	5	61.9
F _{II} ⁵	75	5	53.5
G _I	85	10	34.9
H _{II}	85	10	55.6
J _I	100	10	47.1
K _{II}	100	10	49.4

There is no significant directional anisotropy observed for tensile strength or the tensile modulus.

Table 16 gives the energy required to break each tensile test piece. The energy to failure for each matrix resin's SMC was expressed in MJ/m³.

4.5 Fracture behaviour of sheet moulding compound

The candidate stress intensity factors were obtained for each SMC and are shown in Tables 17 and 18. Values are expressed as the mean of nine test results. The standard deviation is also shown. The nine test pieces were taken from the sheets by cutting in three directions, three test pieces for each direction, at 45° to each other, as in the previous section. The means of these three specimens are shown in Table 19 and are compared with mean and standard deviation. The candidate crack extension force (G_Q) is also shown in Tables 17 and 18. This is calculated from K_Q using the formula.

$$G_Q = \frac{K_Q^2 (1 - \mu^2)}{E}$$

where E = young's modulus of the particular SMC, and μ = Poissons ratio. In this particular case, μ was always given the value 0.3, estimated as the value for the Poisson's ratio of the matrix.

As the SEN specimens had different notch depth: specimen width ratios Fig. 21 shows the variation of candidate stress intensity factors with the notch depth ratio.

Tables 20 and 21 show values for K_p and K_{I_1} . K_p represents the stress intensity factor, based on the maximum load. This value of the stress intensity factor then defines the point of catastrophic failure of the material.

TABLE 17

Candidate stress intensity factors of SMC produced with
resins of different glycol excess

Matrix Resin	Diol Excess %	K_Q MN/m ^{3/2}	G_Q KN/M
C _I	10	7.03 (\pm 0.61)	3.86
D _{II}	10	7.25 (\pm 0.42)	4.05
G _I ⁷	7.5	6.92 (\pm 0.61)	3.78
D _{II} ⁷	7.5	7.39 (\pm 0.41)	4.64
C _I ⁵	5	6.69 (\pm 0.61)	3.78
D _{II} ⁵	5	7.36 (\pm 0.54)	4.43
E _I	10	7.94 (\pm 0.34)	4.76
F _{II}	10	7.03 (\pm 0.27)	3.88
E _I ⁷	7.5	7.26 (\pm 1.08)	4.00
F _{II} ⁷	7.5	7.32 (\pm 0.51)	4.27
E _I ⁵	5	6.44 (\pm 0.73)	3.73
F _{II} ⁵	5	6.94 (\pm 0.42)	3.99

TABLE 18

Candidate stress intensity factors of SMC produced with
resins of differing maleic:phthalic ratios

Matrix Resin	Degree of Unsaturation %	K_Q MN/m ^{3/2}	G_Q KN/M
A _I	50	5.64 (\pm 0.38)	2.83
B _{II}	50	6.01 (\pm 0.86)	3.09
C _I	67	7.03 (\pm 0.61)	3.86
D _{II}	67	7.25 (\pm 0.42)	4.05
E _I	75	7.94 (\pm 0.34)	4.76
F _{II}	75	7.03 (\pm 0.27)	3.88
G _I	85	7.30 (\pm 0.87)	4.88
H _{II}	85	7.44 (\pm 0.67)	5.33
J _I	100	6.75 (\pm 0.72)	3.91
K _{II}	100	7.64 (\pm 0.64)	5.24

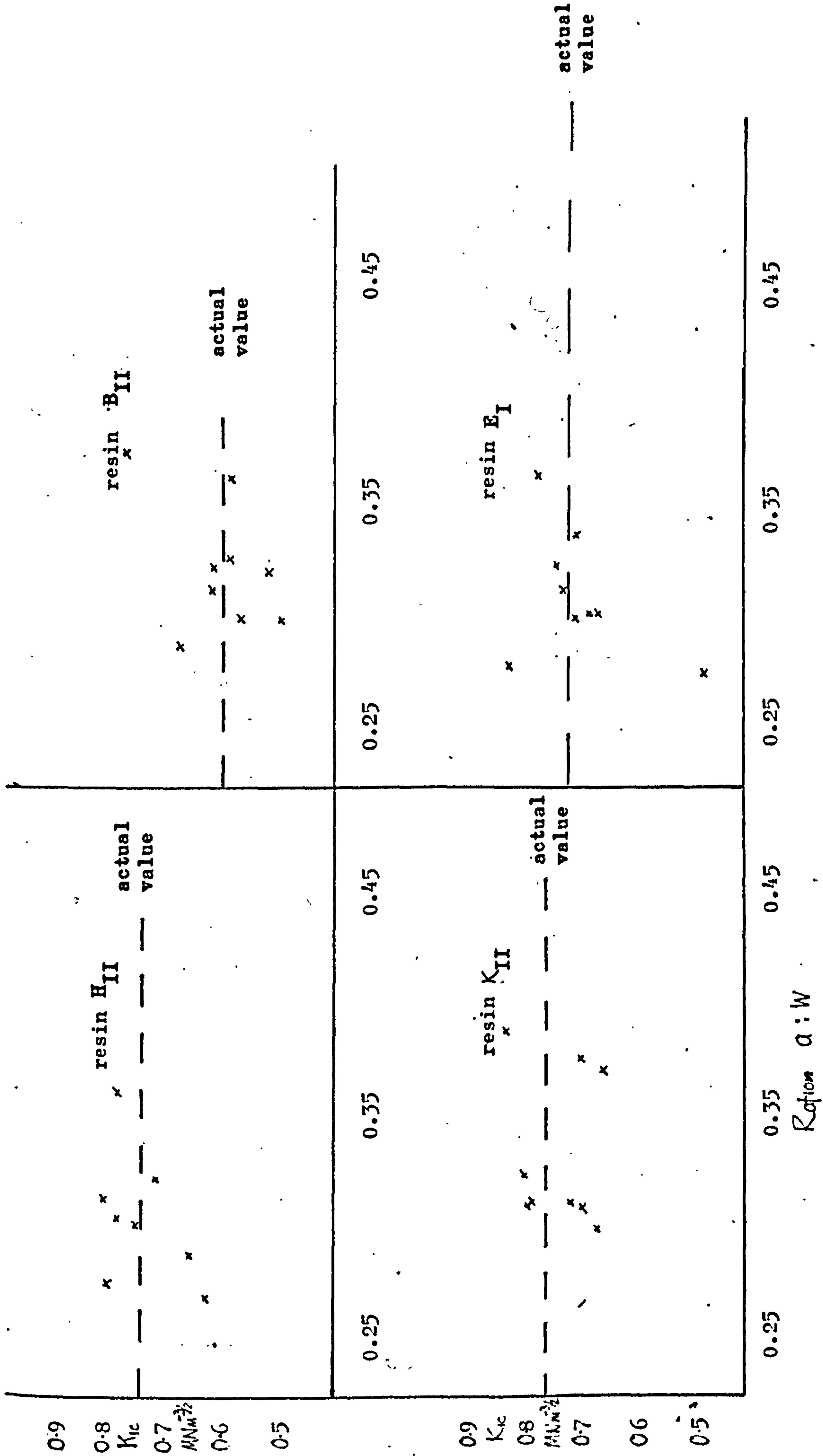


Fig. 21 Variation of K_Q of SNC with notch depth: specimen width ratio

TABLE 19 Stress intensity factors ($\text{MN}/\text{m}^{3/2}$) in three directions (X, Y & Z)
compared with the mean and standard deviation of each resin's SMC

Resin	\bar{X}	\bar{Y}	\bar{Z}	Mean & Standard Deviation
A _I	5.83	5.60	5.44	5.64 (\pm 0.38)
B _{II}	6.62	5.58	6.03	6.01 (\pm 0.86)
C _I	6.89	7.19	7.01	7.03 (\pm 0.61)
D _{II}	7.45	7.21	7.09	7.25 (\pm 0.42)
C _I ⁷	6.67	6.97	7.12	6.92 (\pm 0.61)
D _{II} ⁷	7.39	7.32	7.47	7.39 (\pm 0.41)
C _I ⁵	6.51	7.03	6.53	6.69 (\pm 0.61)
D _{II} ⁵	7.09	7.51	7.48	7.36 (\pm 0.54)
E _I	8.07	7.72	7.96	7.94 (\pm 0.34)
F _{II}	6.94	7.19	6.95	7.03 (\pm 0.27)
E _I ⁷	6.96	7.48	7.34	7.26 (\pm 1.08)
F _{II} ⁷	7.32	7.29	7.33	7.32 (\pm 0.51)
E _I ⁵	6.37	6.26	6.79	6.44 (\pm 0.73)
F _{II} ⁵	7.04	6.61	7.26	6.94 (\pm 0.42)
G _I	7.53	7.46	6.97	7.30 (\pm 0.87)
H _{II}	8.01	7.21	7.07	7.44 (\pm 0.67)
J _I	6.54	7.02	6.69	6.75 (\pm 0.72)
K _{II}	7.88	7.50	6.93	7.64 (\pm 0.64)
Mean	7.06	7.01	6.97	

TABLE 20 Peak load intensity factors (K_p) and non - linear intensity factors (K_I) of SMC produced with resins of different maleic: phthalic ratios.

SMC Resin	K_p MN/m ^{3/2}	K_I MN/m ^{3/2}
A _I	7.11	3.63
B _{II}	7.29	3.93
C _I	7.83	3.34
D _{II}	8.56	4.26
E _I	8.51	4.53
F _{II}	7.92	4.04
G _I	8.39	5.07
H _{II}	8.57	5.50
J _I	8.37	5.01
K _{II}	8.65	4.38

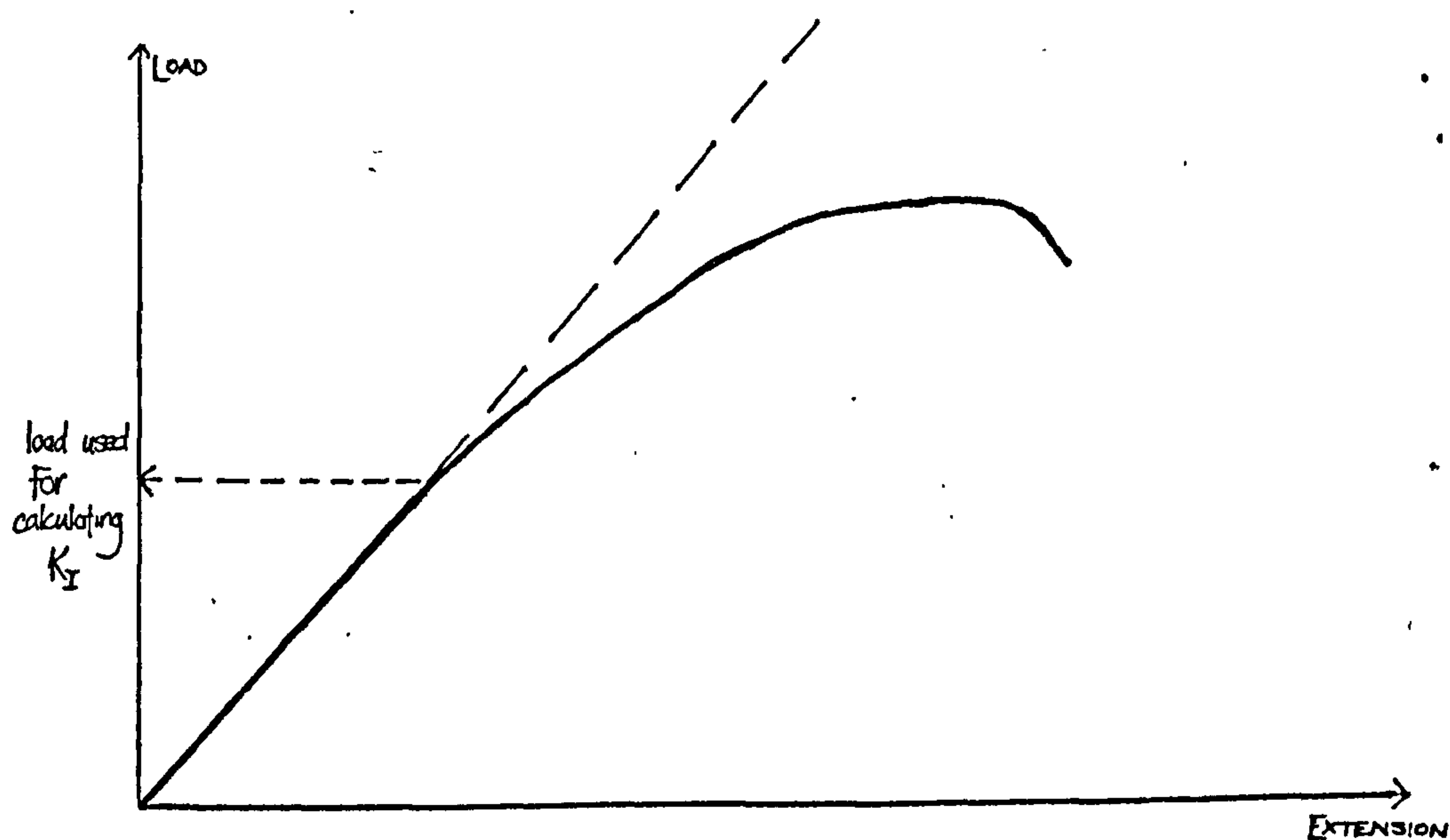
TABLE 21 Peak load intensity factors (K_p) and non - linear intensity factors (K_I) of SMC produced with resins of different glycol excess.

SMC Resin	K_p $MN/m^{3/2}$	K_I $MN/m^{3/2}$
C_I	7.83	3.34
D_{II}	8.56	5.06
C_I^7	7.24	3.42
D_{II}^7	8.58	4.95
C_I^5	7.19	3.68
D_{II}^5	7.71	5.53
E_I	8.51	4.53
F_{II}	7.92	3.54
E_I^7	8.47	4.36
F_{II}^7	8.17	4.61
E_I^5	7.71	4.06
F_{II}^5	7.64	4.16

K_I , the third value in the table, is calculated from the load at which the load displacement curve becomes non-linear.

Fig. 22

Calculation of K_I from load extension record



Chapter 5

DISCUSSION - PART ONE

5. The effect of altering the hydroxyl value of the resin on the strength and fracture toughness of polyester moulding compounds.

5.1 Polyester resins

The synthesis of unsaturated polyester resins to achieve predetermined chemical characteristics is rendered difficult by the fact that several properties are closely inter-related. It is not always practicable to achieve equally close control over all the variables as would be the case if they were independent.

An attempt was made to prepare all resins with acid values of 35 ± 3 , but as can be seen this was not always possible (Tables 6-7) and minor compromises were necessary. In synthesising resins with different diol excesses, the amount of styrene needed to be added to the alkyd to obtain a viscosity of 8 poise (at 25°C) increases as the diol excess decreases. (As one of the effects of the hydroxyl value is to hinder the thickening reaction of the SMC slurry, it was felt that all the resins should have the same initial viscosity). This was due to the loss of diol during the initial stages of the synthesis. An exotherm occurs when the flange pot temperature reaches $115-120^{\circ}\text{C}$, the exotherm being the result of the breakdown of the maleic anhydride component. Some of the more volatile diol is therefore lost (22) and then condensed with the water of reaction.

A polyester will have either carboxyl or hydroxyl end groups. The more carboxyl groups present the more viscous the polymer solution (22). Therefore a polyester resin with few hydroxyl groups will need more dilution with styrene to bring it to a predetermined viscosity. Those resins with a higher initial diol excess are liable to have higher hydroxyl

values as they have diol to compensate for the diol losses encountered during the earlier part of the synthesis. These resins will need less styrene added.

A ramification of this diol loss is that those resins of low diol excess become more viscous earlier in the synthesis than do those with a high diol excess. In this situation the synthesis must be terminated before the originally planned acid value.

The method of determining the hydroxyl value of the resins was found to be suitable for polyesters. There are methods described in the literature (100) which use acetylation with a pyridine (or ethyl acetate) catalyst. The excess acetic acid formed is then back titrated with methanolic potassium hydroxide and hence the hydroxyl value found. However, these methods are widely agreed to be inconsistent for polyesters. Unfortunately polyesters react under acidic conditions to give lactones. Also the acetylation reaction is further hindered by the difficulty of hydrolysing the polyester samples.

Hydroxyl values generally increase with increasing diol excess as can be seen from Table 7. There are some anomalies however, such as resin F_{II}. Although resin F_{II} has a diol excess of 10% it has a hydroxyl value of 30. This compares with the resin E_I which has a similar diol excess of 10%, yet has a hydroxyl value of 82. However F_{II} has been synthesised to a much lower acid value thereby making necessary the reaction of more diol. This once more illustrates the interdependence of a polyester's chemical properties.

By employing a polyester resin as a matrix material, the mechanical properties of the eventual composite could be expected to be different with each formulation of resin used. Each resin will provide a matrix material with different mechanical characteristics. All the polyester resins tested behaved in a brittle fashion. Fig. 23 shows a typical load displacement record for a polyester resin.

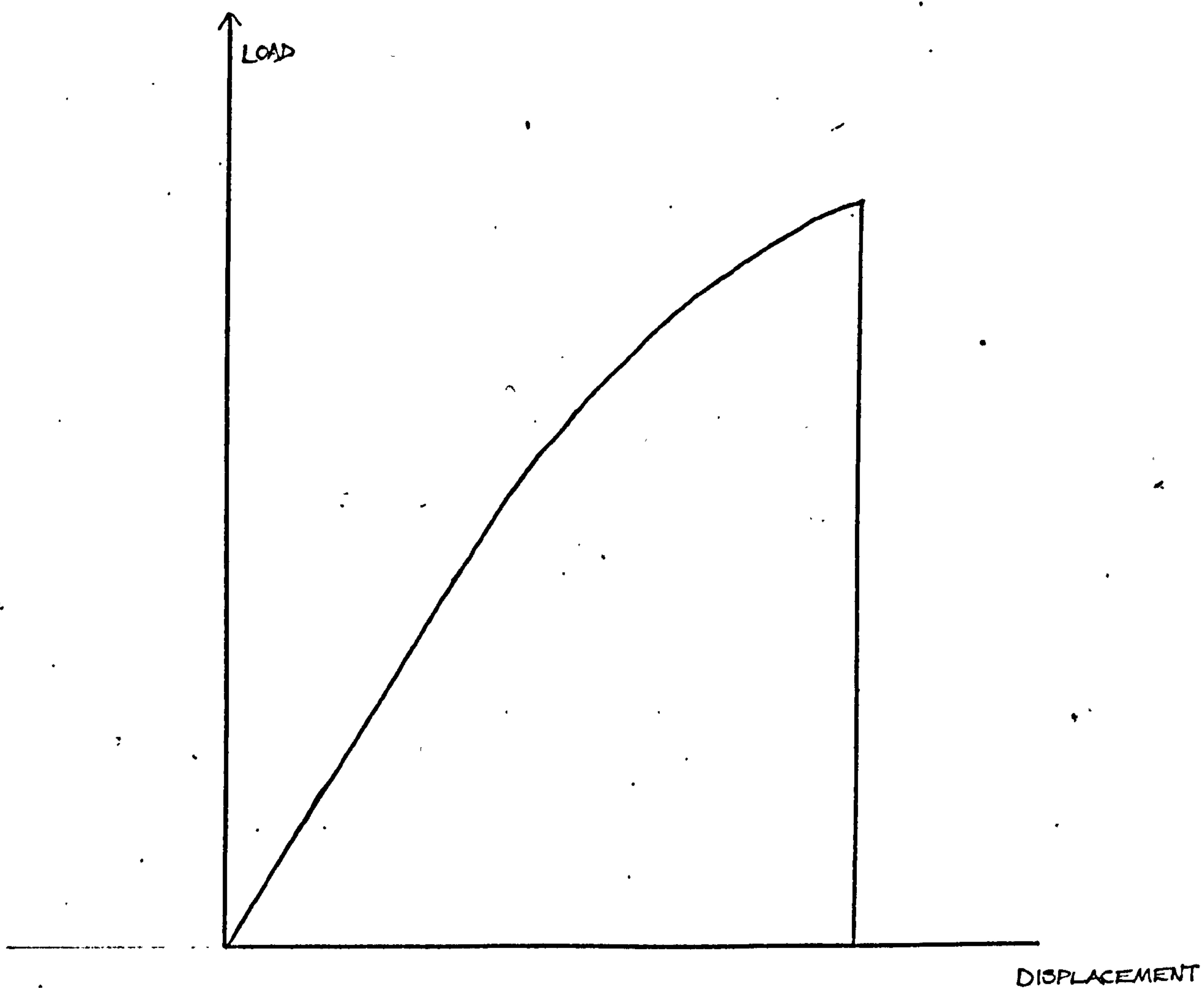


Fig 23 A typical load displacement record for a polyester resin

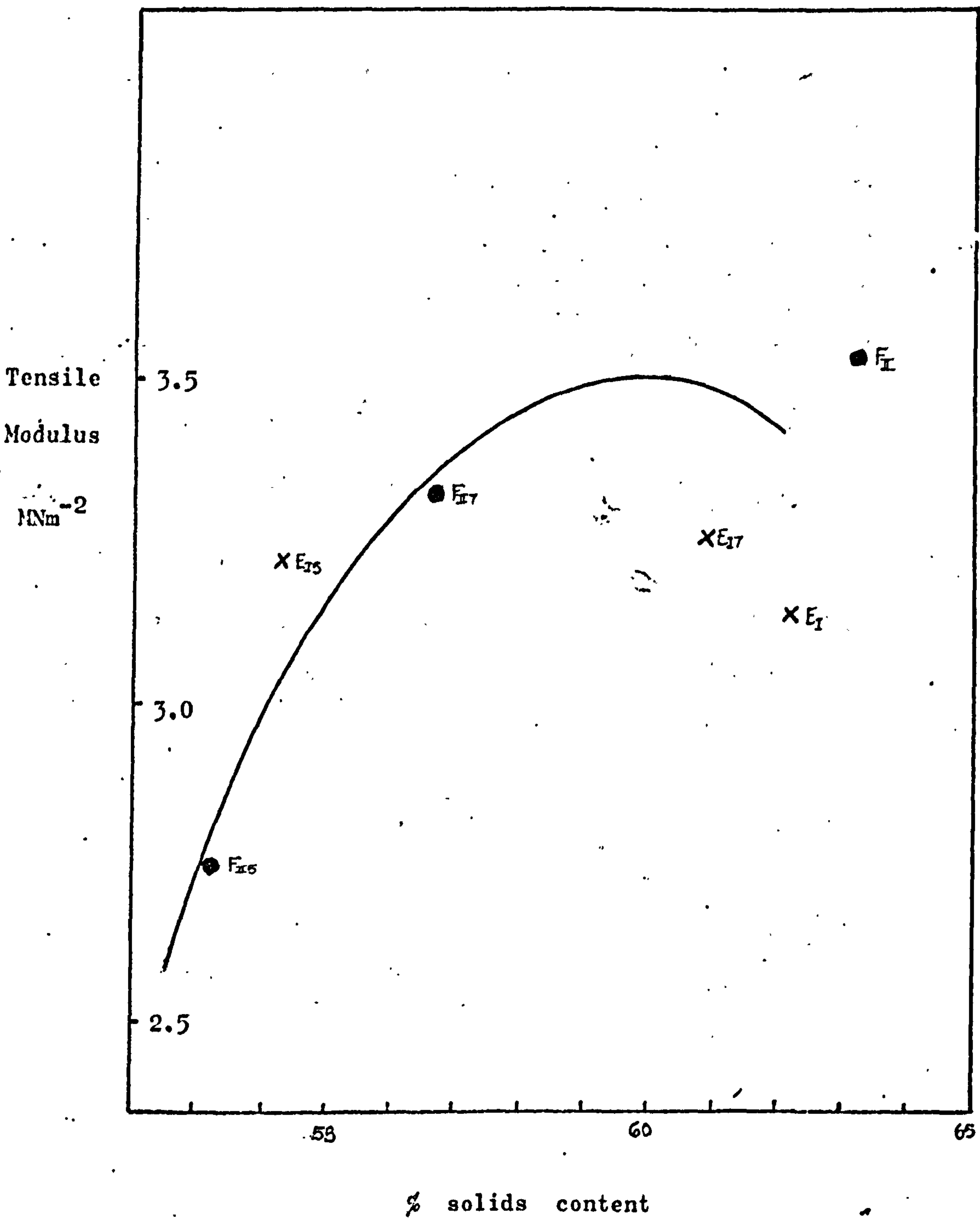


Fig. 24

Variation of tensile modulus with solids content

(75% unsaturated)

Different diol excesses have no significant effect on either the ultimate tensile strength, elongation of break, or tensile modulus. All of the resins have an elongation at break within the range $1.07 \pm 0.22\%$, which is little lower than that quoted for conventional SMC resins (82). A possible reason for this will be discussed later.

It is interesting to note that the tensile modulus of those resins with 75% maleic acid seem dependent on the solids content of the resin. As the solids content increases so does the tensile modulus (see Fig. 24) and this agrees with the work of Parker (25) who found that at these unsaturation levels a solids content of 70% for the resin would correspond with the maximum tensile modulus. No such dependence is observed for the resins with 67% unsaturation.

The notch sensitivity of the cast resins is shown in tables 11 and 12. The tests established that the material in all cases was notch sensitive and therefore suitable for the application of linear elastic fracture mechanics concepts.

Table 12 shows that the stress intensity factor K_{IC} (as well as G_{IC} , the crack extension force) are significantly affected by the amount of excess diol added in the synthesis. Extra diol increases the values obtained for K_{IC} and G_{IC} , as is obvious in Figures 25 to 28.

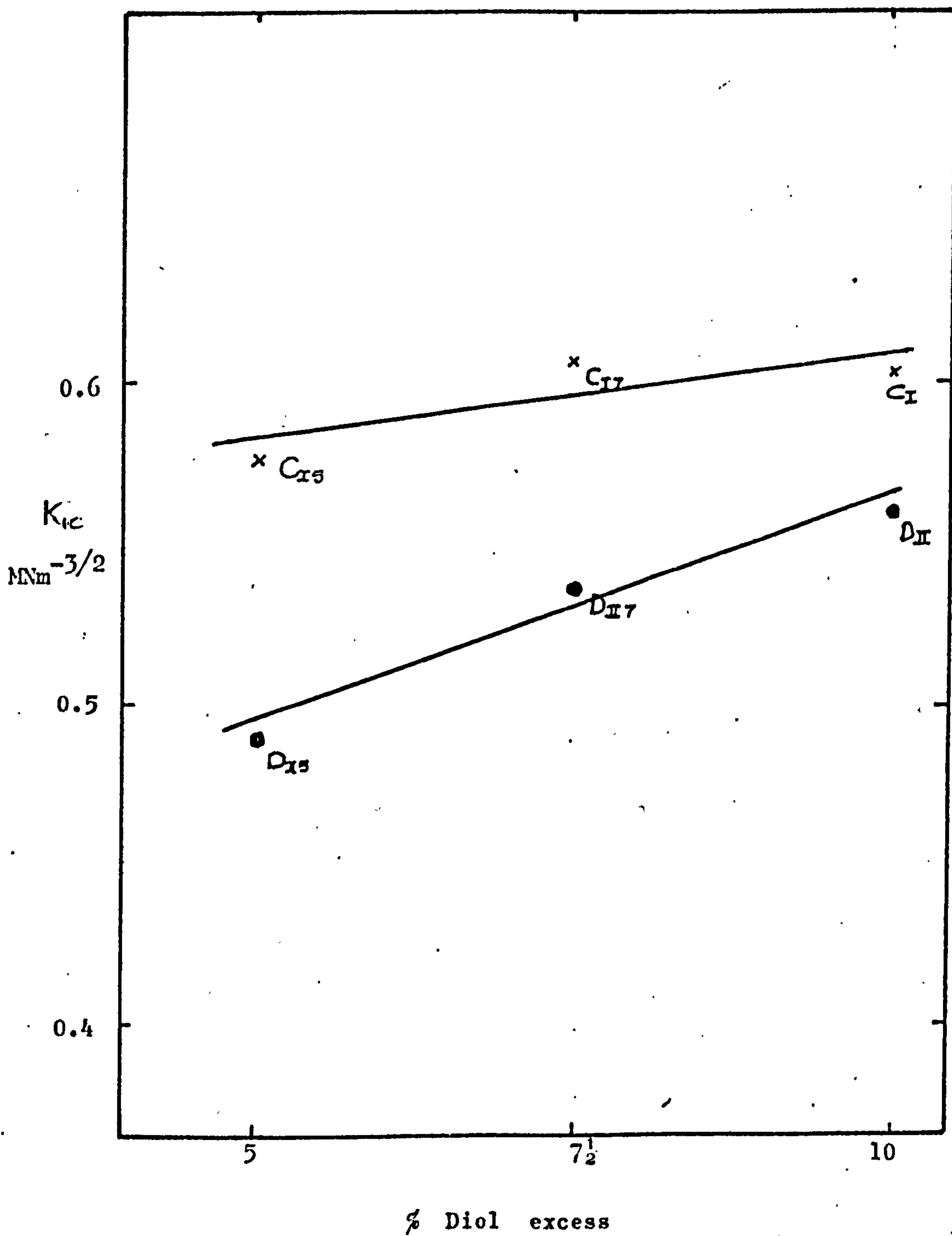


Fig. 25

Variation of K_{IC} with excess diol for matrix resins

(67% unsaturation)

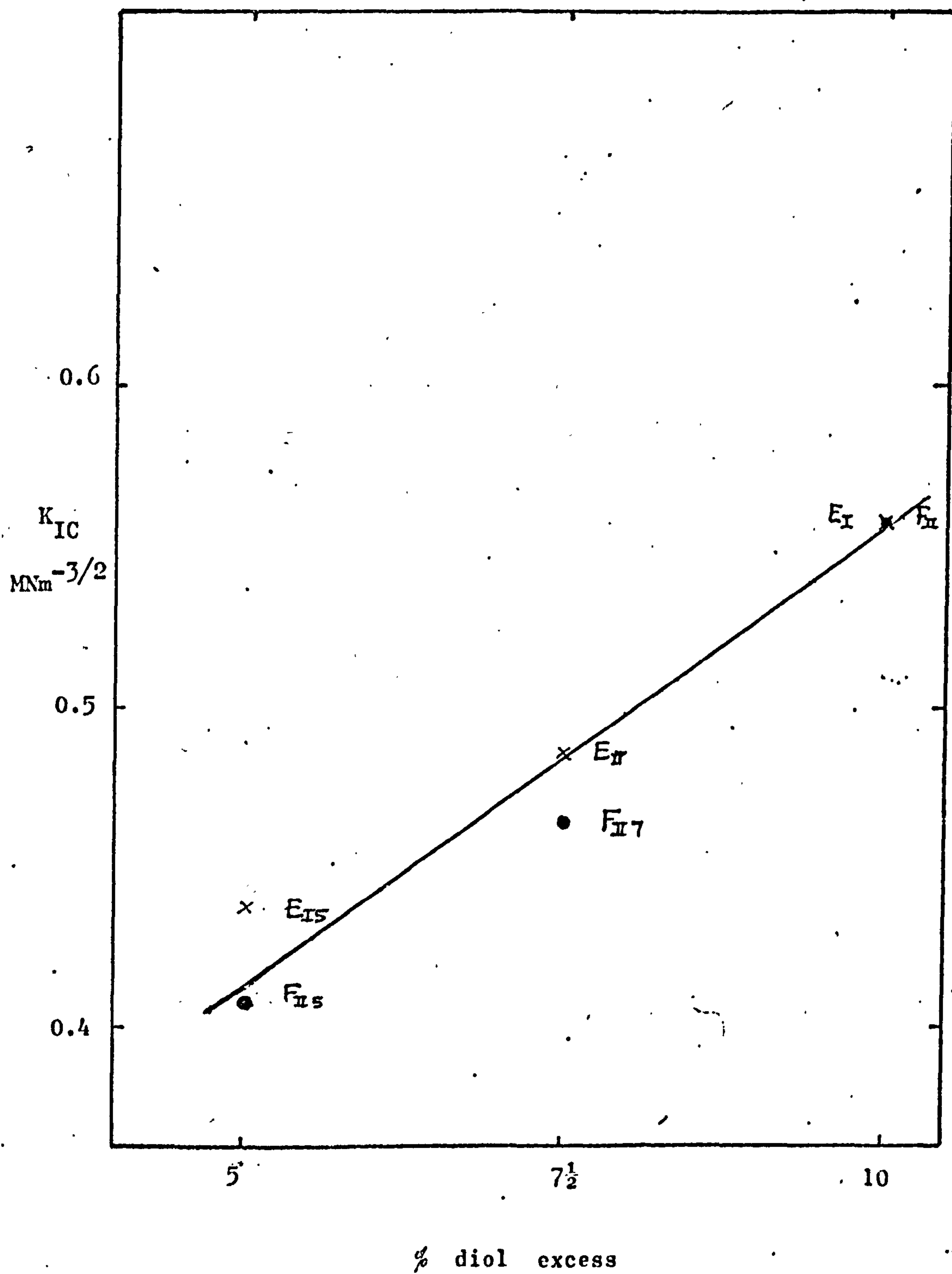


Fig. 26

Variation of K_{IC} with excess diol for matrix resins

(75% unsaturation)

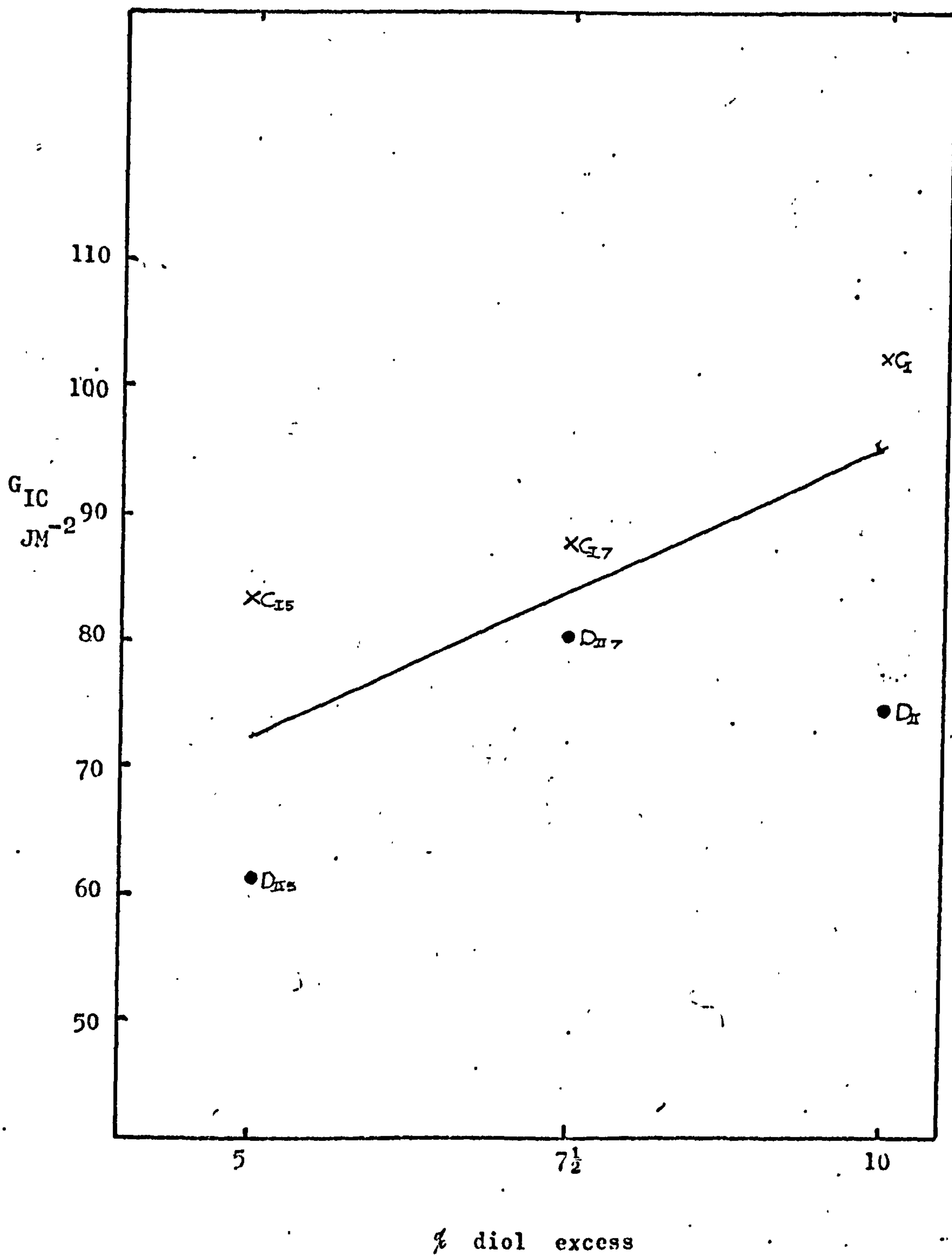


Fig. 27

Variation of G_{IC} with diol excess

(67% degree of unsaturation)

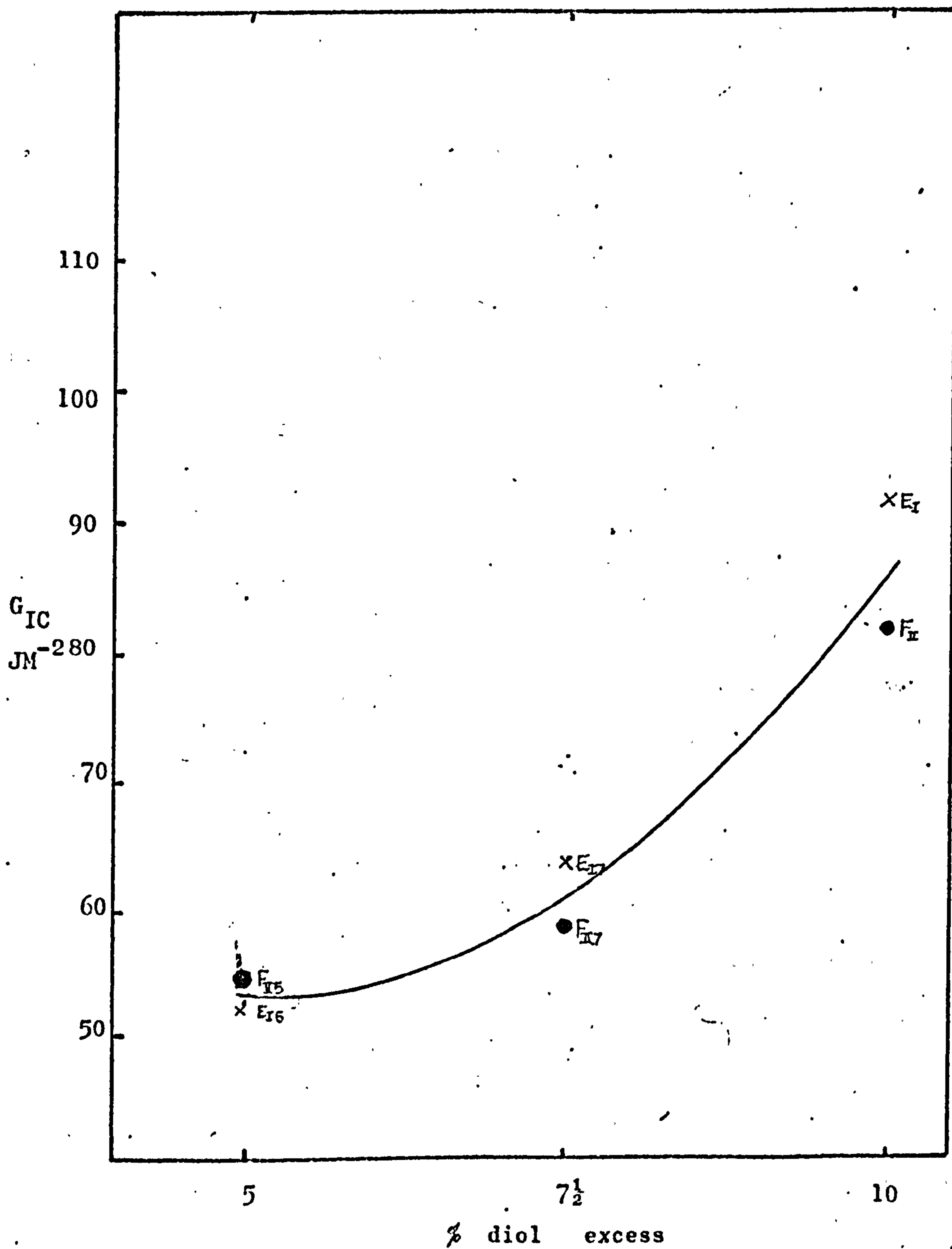


Fig. 28

Variation of G_{IC} with diol excess

(75% degree of unsaturation)

It is also noticeable that the resins synthesised by Method I have superior notch sensitivity.

This is explained by the fact that during the resin synthesis an attempt is made to reach an acid value in the region of 35. This involves the loss of carboxyl functionality by reaction with the hydroxyl tipped diol. This is facilitated by the addition of more diol, therefore a resin with an originally low excess diol will form a resin of higher molecular weight species than that synthesised with a higher diol excess. (see Fig 29). The presence of low molecular weight species in the cast polyester resin will mean that energy will be absorbed by the flow of this material in the vicinity of the propagating crack.

There is also the already mentioned fact that some of the more volatile diol is lost during the early stages of the reaction. This will enhance the previously mentioned effect where the resins of higher diol excess will have more diol left to react with the carboxyl end groups of the acids and growing polyester. It is also interesting to note that the series of resins (E and F) synthesised with 75% unsaturation show more markedly the increase in K_{IC} and G_{IC} with increasing diol excess, although always having lower values than their complementary resins (C and D) synthesised with 67% unsaturation. The higher the unsaturation content the higher the exotherm in the initial stages. It is this exotherm which causes the major loss of diol.

The resins synthesised by Method II generally have lower values for K_{IC} and G_{IC} than their Method I counterparts. During the latter stages of their manufacture these resins synthesised by Method II have a vacuum applied. This vacuum is applied while the reaction vessel temperature is at 200°C and in fact the acid value of the resin is in the region of 45. It removes the unwanted xylene, unreacted glycol and perhaps some low molecular weight constituents of the polyester. This vacuum was applied until the end of the synthesis. Those resins

synthesised by Method I had the vacuum applied only when the acid value had reached a suitable level and heating had stopped. The vacuum was then applied for only five minutes to remove all the volatile xylene. These resins therefore are more likely to retain these low molecular weight components.

The presence of low molecular weight species in the cast resin will enhance flow at the tip of the propagating crack. It is known that there is a certain amount of plastic deformation which accompanies the fracture (17) of polyester resins even though they are crosslinked. This plastic deformation increases the fracture energy so that it exceeds the expected surface energy. This plastic deformation will be enhanced by the presence of low molecular weight species.

Microscopy has been used to study the surfaces of fractured polymers. As a general rule the amount of detail present on the surface increases with increasing fracture toughness (30) or plastic deformation. However, there was found to be very little difference between the fracture surfaces of these cast resins. Figs. 30 and 31 show typical fracture surfaces. Fig. 30 shows the fracture surface adjacent to the notch. Fine lines are seen to radiate from this area suggesting a certain amount of flow in the early stages of crack extension; these fine lines are termed river markings and are well documented (29). Away from the notch a smooth surface is observed before the subsequent development of ribs is seen radiating away from the notch (Fig. 31).

Fig. 32 shows the fracture surfaces of three specimens of the resin C₁7. The uppermost is the fracture surface of a single edge notched specimen, the next is the fracture surface of an un-notched tensile specimen, and the bottom is that of a tensile specimen which fractured at a void present in the specimen. The three surfaces are interesting in that they show the controlled fracture of the single edge notch specimen in stark contrast with that of the tensile specimen which has deep and intense features. The third specimen shows an intermediate situation. There is to a

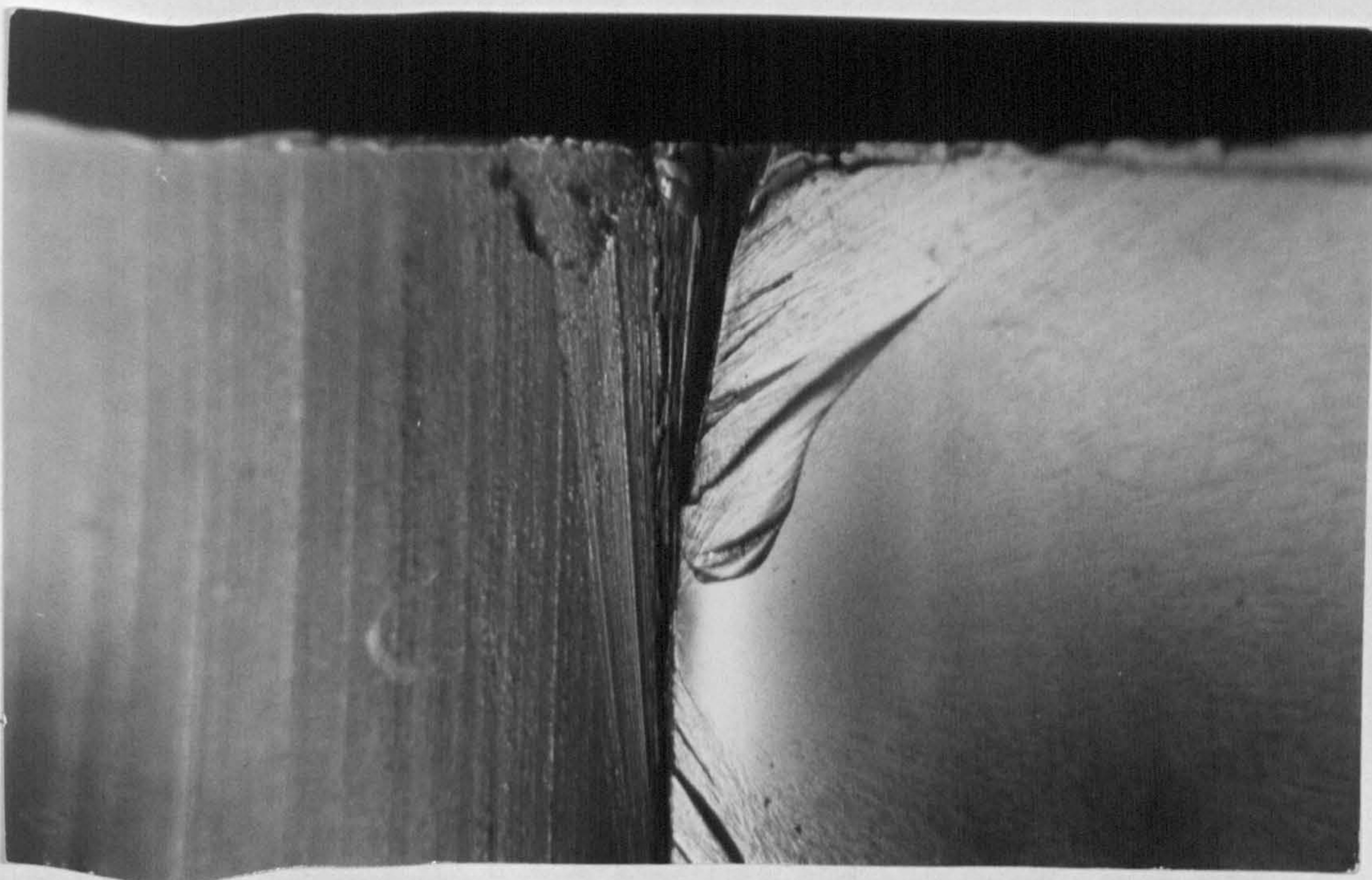


Fig. 30 Typical fracture surface adjacent to notch

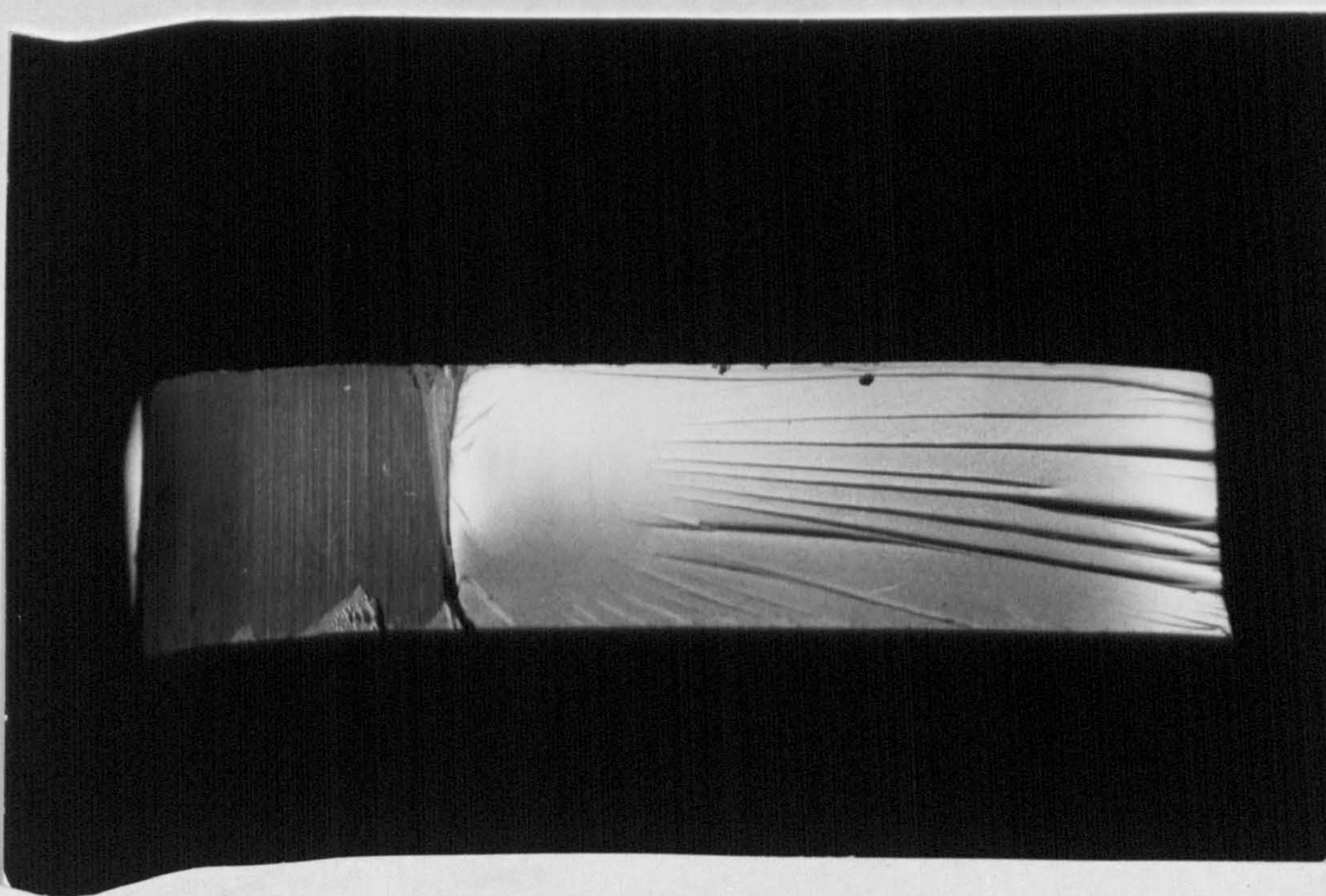


Fig. 31 Fracture surface showing smooth surface and subsequent
radiating ribs

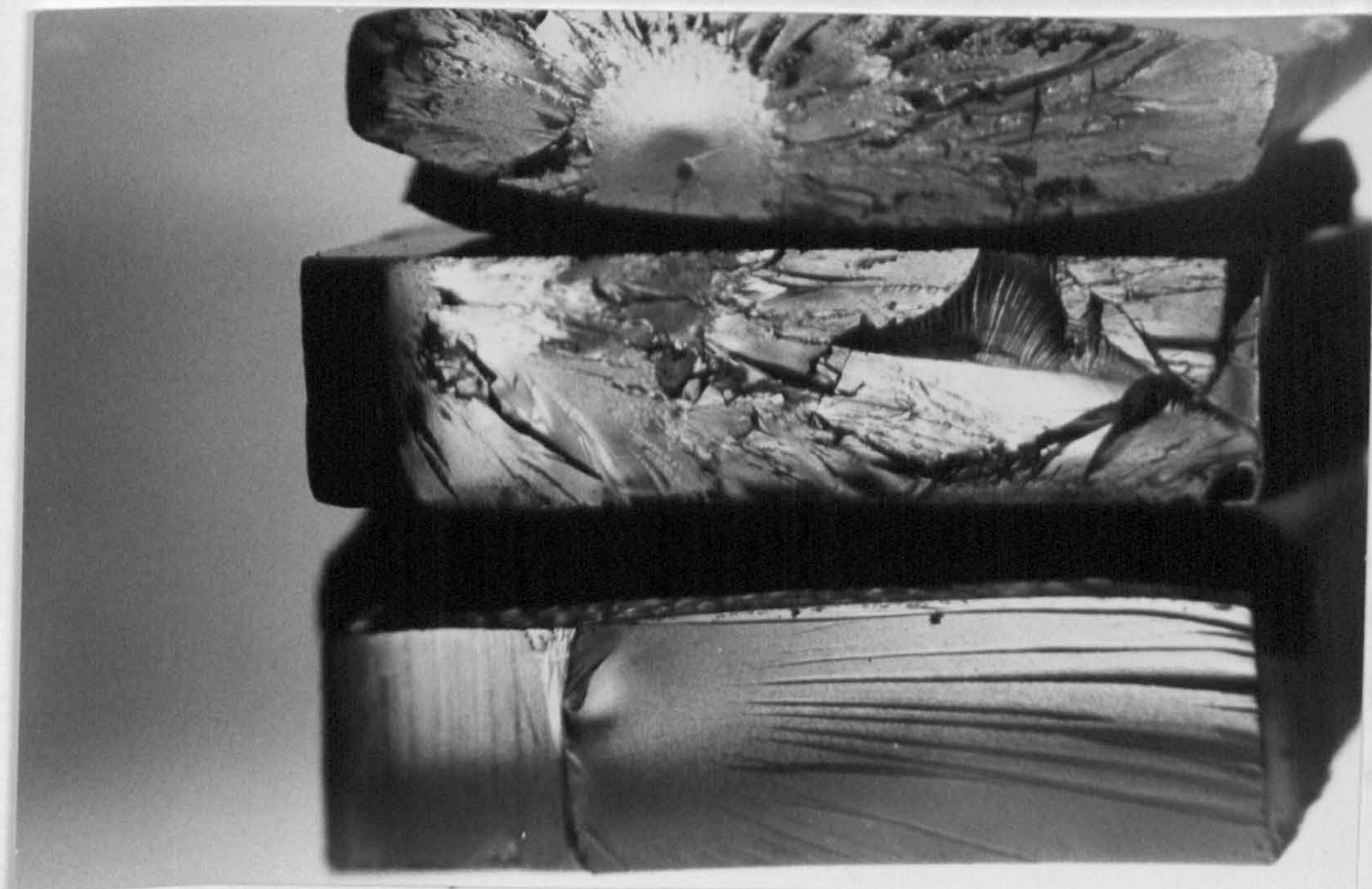


Fig. 32 Fracture surfaces of three C_I7 specimens

- (a) single edge notched specimen
- (b) tensile specimen
- (c) tensile specimen containing void

certain extent controlled fracture away from the site of the void eventually running into a region of rough features more characteristic of the un-notched specimen.

These features illustrate the point made by Christiansen and Shortall (27) that with materials as brittle as polyesters it is important to preclude specimens with obvious flaws and minimise surface flaws by polishing the specimens intended for tensile strength testing. They may be polished with fine grade emery paper and then jewellers polish.

Tensile modulus is a structure - sensitive property, but elongation at break and tensile strength of materials depend on specimen quality, i.e., flaw concentration, distribution and nature.

5.2. Sheet moulding compound (SMC)

5.2.1 Tensile mechanical properties

The mechanical properties of fibre composites are directional, i.e., they depend on the direction of applied stress and the fibre orientation. Many materials are anisotropic and this behaviour often limits the use of composites.

Anisotropy through fibre orientation can be introduced into the composite in two ways; firstly in the manufacturing of the glass mat then secondly by the flow of the reinforcement in the mould.

Table 15 shows the result of testing each SMC in three directions, two perpendicular and the other intermediate. The cumulative means of the three directions X, Y and Z, show no significant differences. There are obvious differences for each SMC but these are comparable with those found by Burns (77) under ideal conditions, and are to be expected. It is not altogether surprising that there is no apparent directional anisotropy. The mould design was very simple and would seem to preclude any anisotropy caused by uneven flow of the SMC components in the mould. The charge

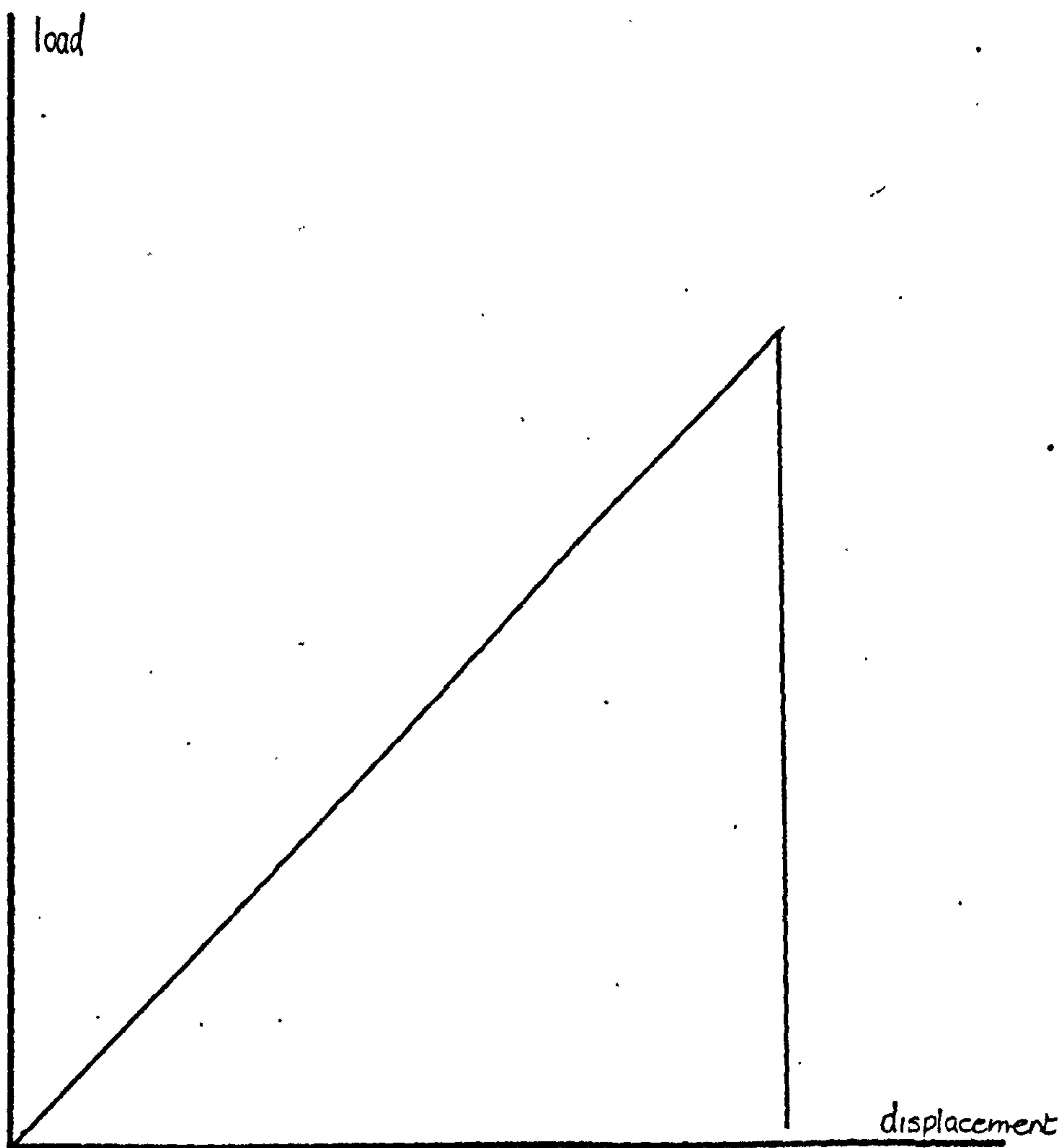


Fig. 33 Load displacement record of a notched polyester resin

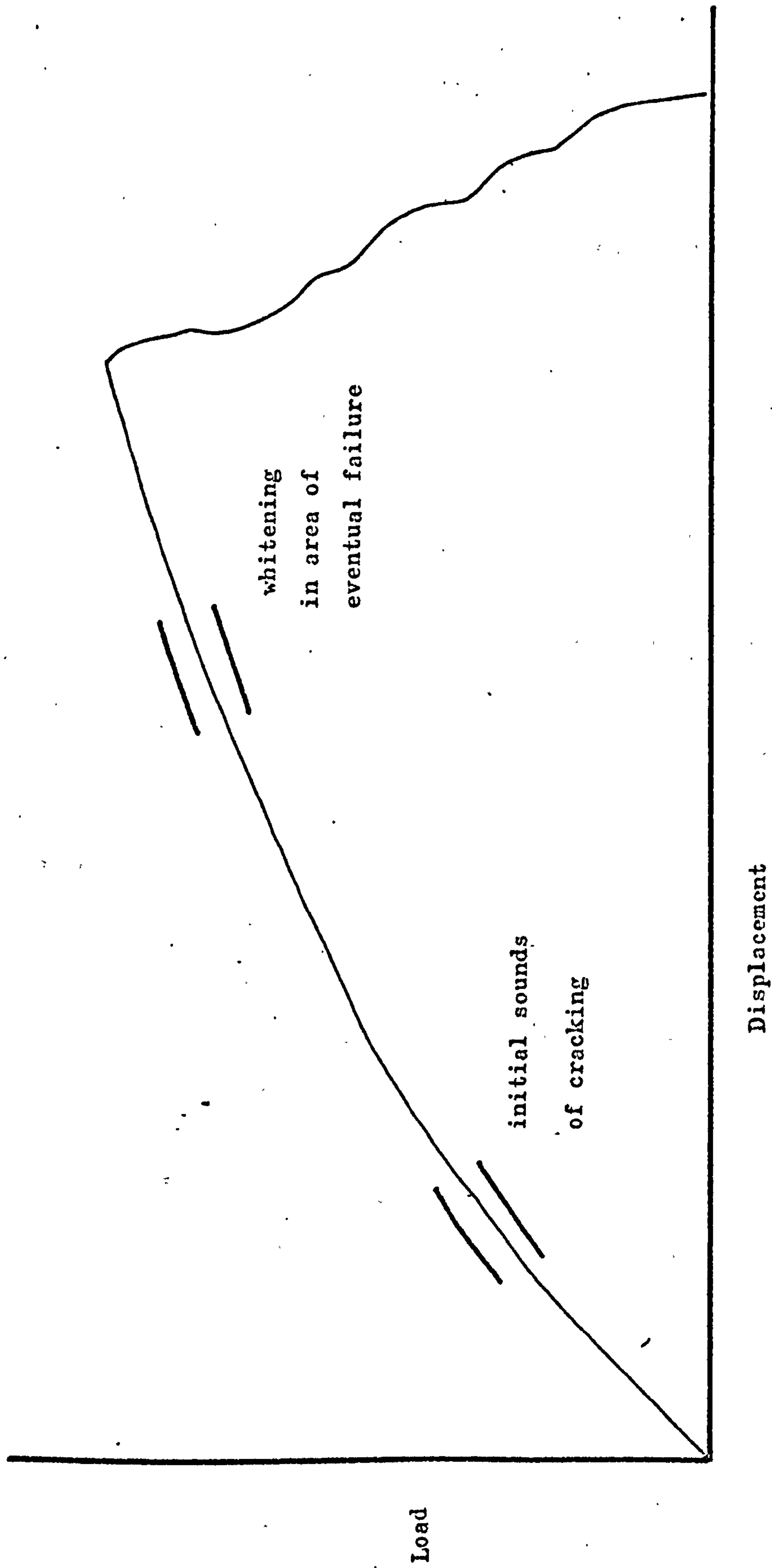


Figure 34 Typical load displacement record for a tensile SMC specimen

geometry was maintained throughout the entire experimental programme as this was found by Burns to be of the utmost importance when considering the variability of SMC mechanical properties. Other variables such as press dwell time, press closure speed and moulding pressure were also standardised. The results obtained for the tensile mechanical properties of the SMC would appear to be dependent only on the matrix resin employed.

Conventional test methods have been used to evaluate the elongation at break, ultimate tensile strength and tensile moduli of the manufactured sheet moulding compound. Figure 34 shows a typical load displacement curve for a SMC tensile specimen.

"Cracking" is heard in the range of 30-40% of the ultimate tensile load. There is also a 'whitening' of the specimen in the area where it eventually fails.

The cracking is thought to be due to fibres debonding on application of a tensile load, the debonding according to Owen and Dukes (36) occurring with fibres transverse to the load direction. They followed microscopically the debonding process encountered in a glass reinforced polyester resin and have shown that debonding starts occurring along these fibres. With increased loading, debonding occurs along fibres inclined at progressively smaller angles to the load direction (see Figure 35).

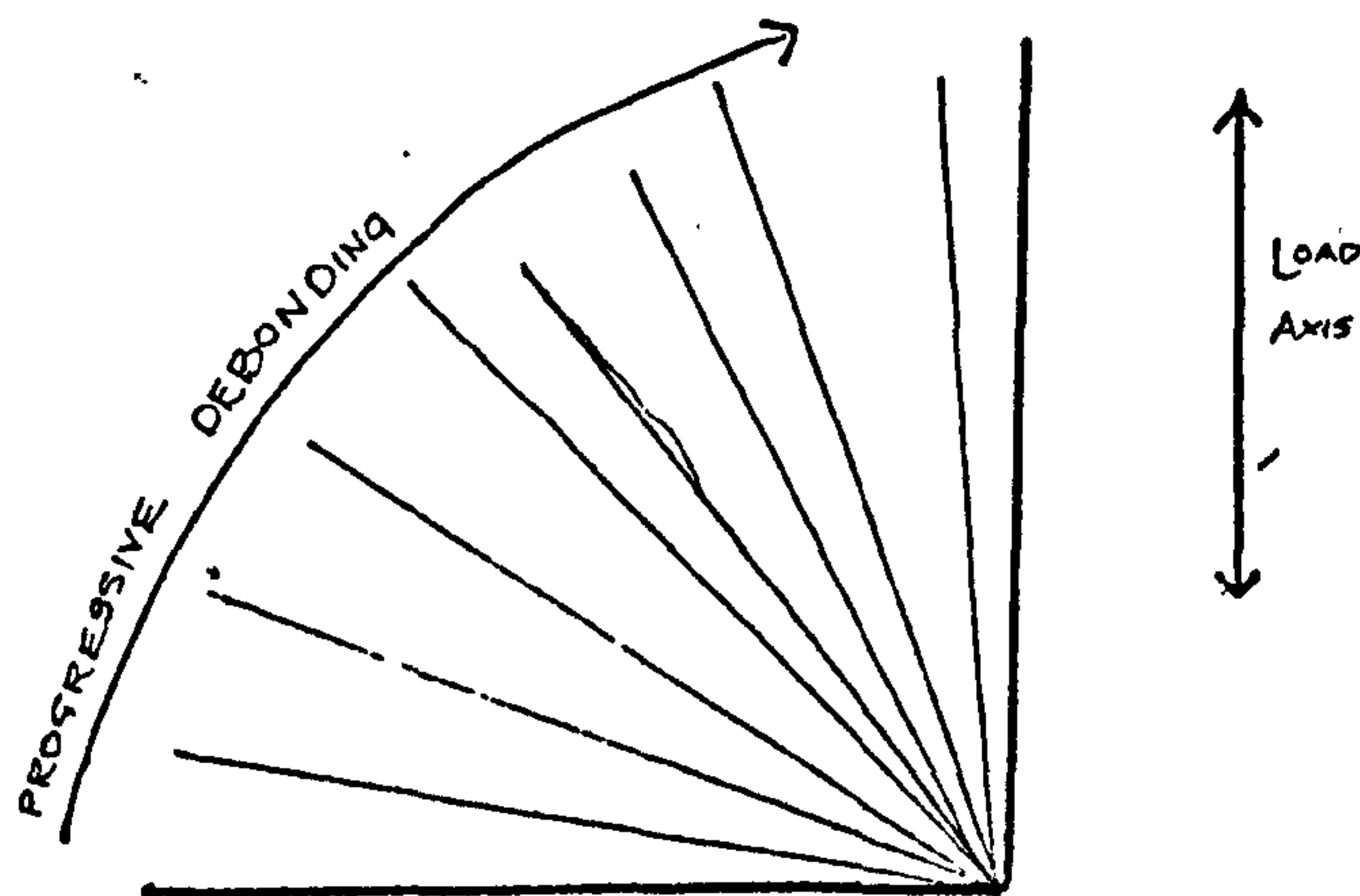


Figure 35 Progression of debonding from misaligned to aligned fibres

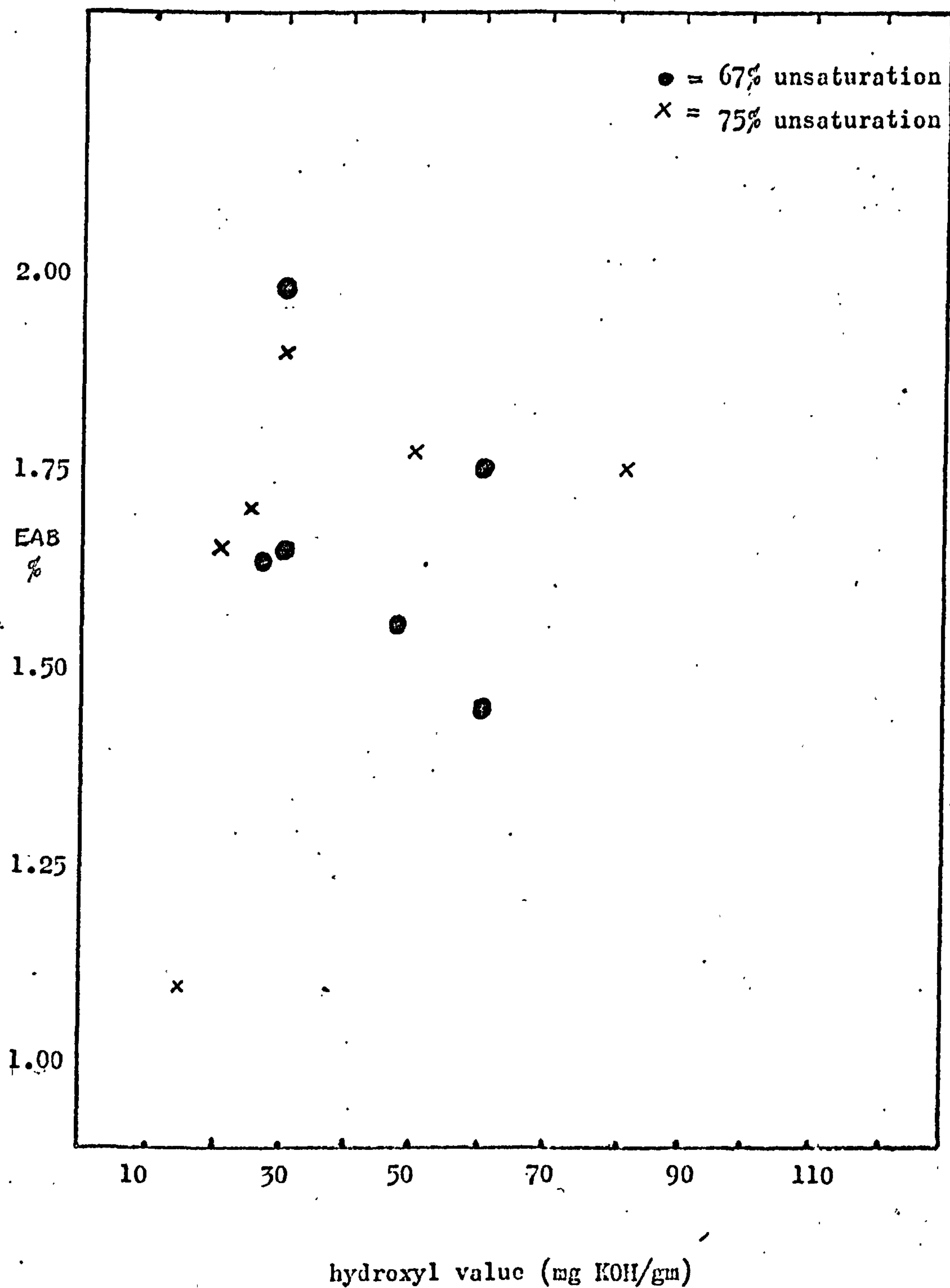


Figure 36 · Variation of elongation of break with hydroxyl value

When the debonding occurs along these fibres, there are associated cracks in the matrix adjacent to the fibres. The whitening of the specimen shows an area where locally debonded regions have joined up and the resin rich surface of the specimen crack. Eventually crack propagation through the matrix occurs as does local fracture of fibres aligned with the load. The tensile fracture of the specimen results after fibre pull out and fracture of fibres.

5.2.2. Relationships between hydroxyl number and SMC tensile mechanical properties

5.2.2.1 Elongation at break

Table 14 shows the results obtained for the compounds manufactured from matrix resins with different diol excesses. Elongation at break is generally low (82) for SMC (1-2%) as is the case with these specimens. Two results D_{II}7 (1.96%) and E_I5 (1.10%) seem inconsistent.

E_I5's result is very significant being in excess of two standard deviations from any other mean. Resin E_I5 has the lowest recorded hydroxyl value, 15 mg KOH. It would seem that over a broad range the elongation at break is possibly independent of the resin hydroxyl value but that at low values similarly low values for elongation at break are obtained.

Comparison of the SMC properties with those of the corresponding resin indicates that the elongation at break is independent of the resin's mechanical properties.

5.2.2.2 Tensile strength

Figures 37 and 38 indicate the effect of the resin's hydroxyl value on the ultimate tensile strength of the SMC. Both groups show that a low hydroxyl value tends to give the SMC a low tensile strength. Increased hydroxyl values show a higher figure for tensile strength, but this improvement is not maintained.

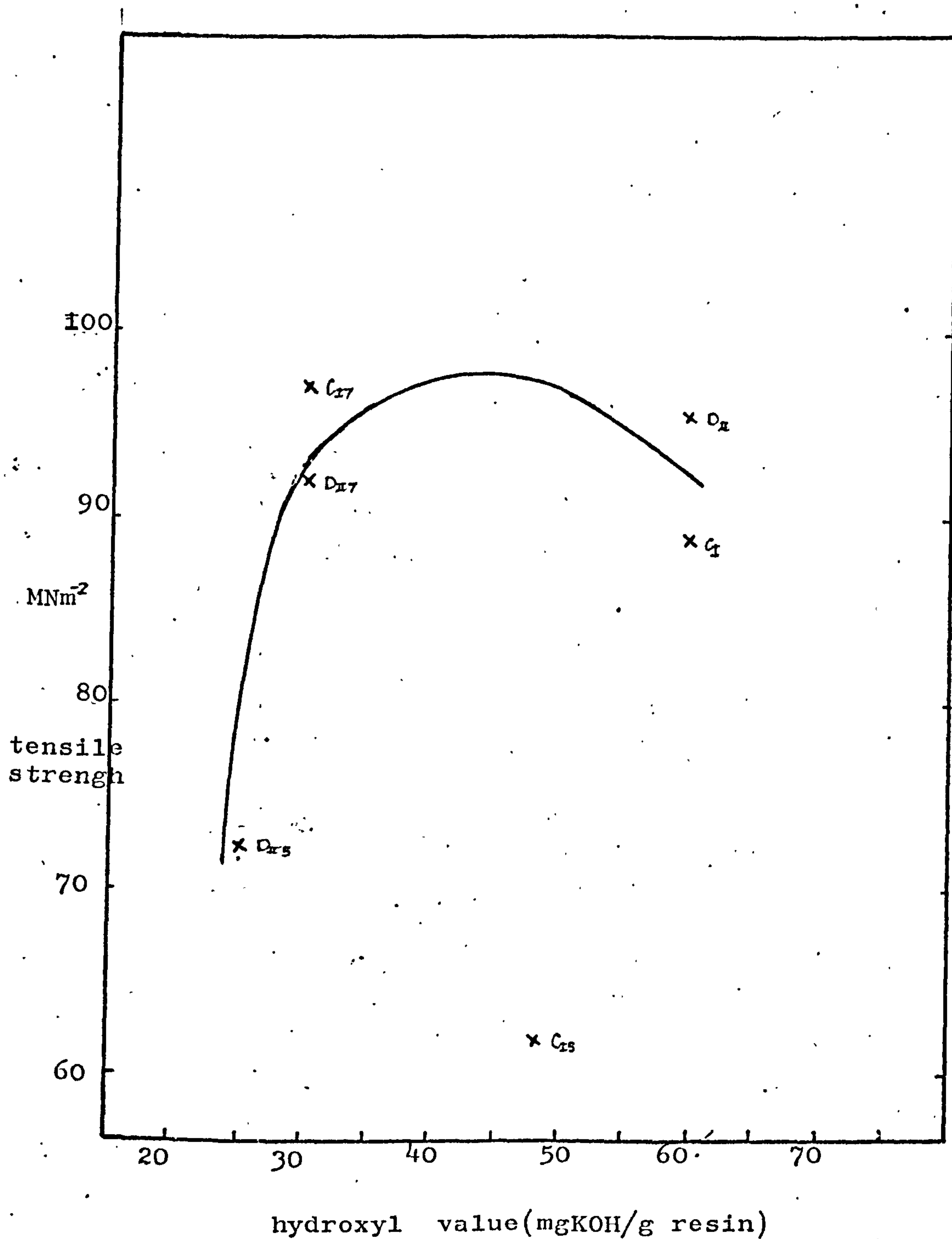


Figure 37 UTS of SMC compared with hydroxyl value
(67% unsaturation)

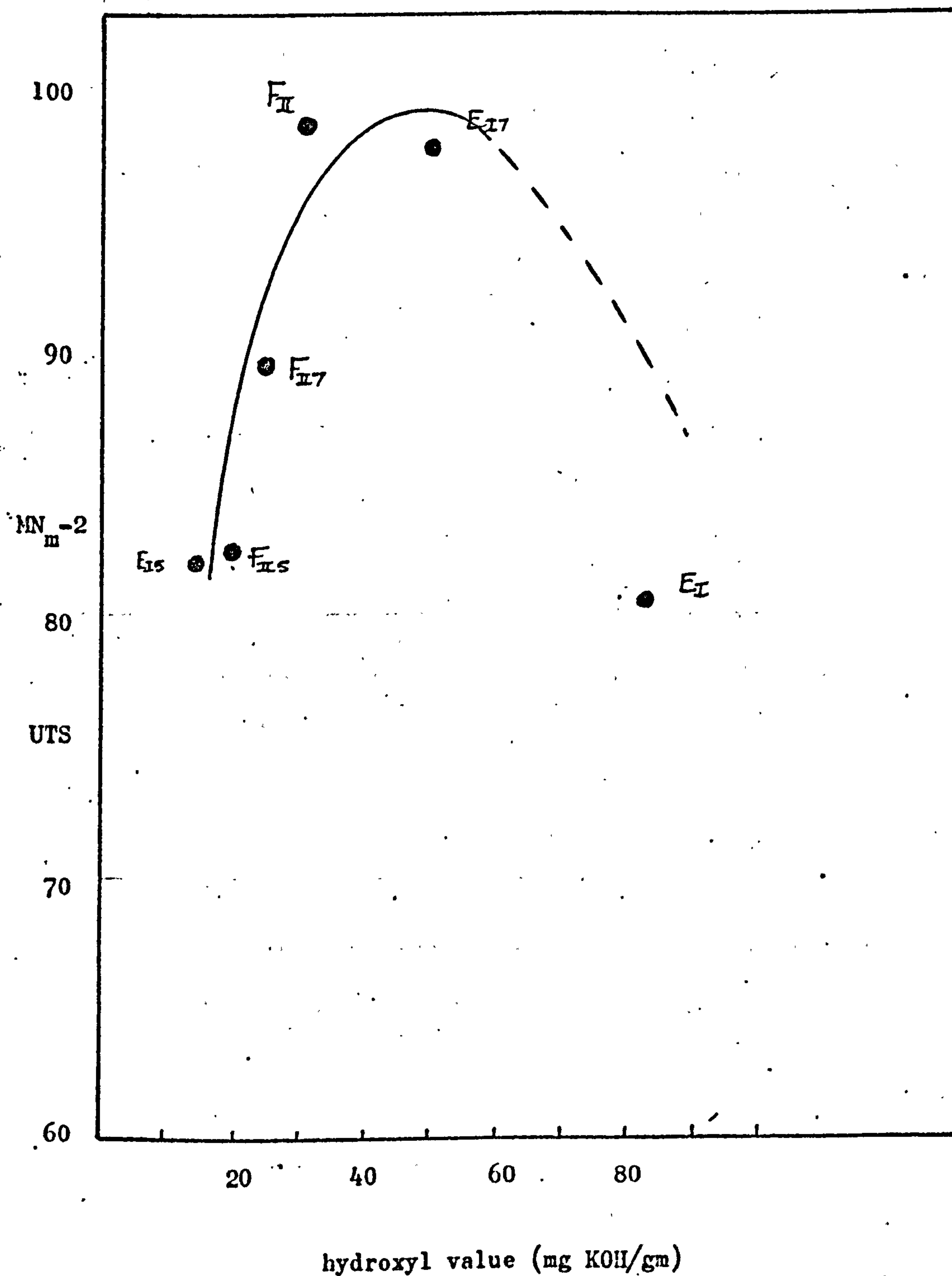


Figure 38 UTS of SMC compared with hydroxyl value (75% unsaturation)

SMC manufactured with a matrix resin of low hydroxyl value will fail prematurely because of the poor fibre matrix bond. The reason for a maximum is that at higher values, high bond strengths will be formed. Consequently, on fibre fracture taking place a large amount of elastic stored energy is dissipated which cannot be absorbed in the resin matrix and composite failure occurs.

It is interesting to note that SMC C_I5 seems to have an anomalous value for its ultimate tensile strength. Considering that resin C_I5 was synthesised with a diol excess of 5% it has a surprisingly high hydroxyl value of 47. The corresponding resin synthesised by Method II has a hydroxyl value of only 20. Although further tests were undertaken to check the hydroxyl value no difference was found.

5.2.2.3 Tensile modulus

Figures 39 and 40 show the variation of tensile moduli with hydroxyl value. There is general increase in modulus with hydroxyl value and this trend is compatible with the results obtained for the tensile strength. The modulus of a composite is a small strain property, dependent on the reinforcement and the nature of its bond to the matrix. A poorly bonded reinforcement will not enhance the stiffness of a material to the same extent as a well bonded reinforcement.

It is noticeable that on the hydroxyl value rising 15 to 30 a lot more improvement in stiffness is obtained than when the hydroxyl values increase up to 80. This would tend to suggest that with these particular systems the optimum bond is formed with a hydroxyl value of 30-40 mg KOH.

5.2.2.4 Energy to failure

The figures obtained for the energy - to - failure reflect very closely the values obtained for ultimate tensile strength. This is not surprising as the polyester matrix in all cases is brittle in character and will not be able to absorb energy. Therefore the energy to failure becomes a function of the ultimate tensile strength, the elongation at break and the tensile modulus, unlike the low-energy SMC studied by Lundberg (82) and Collister (87).

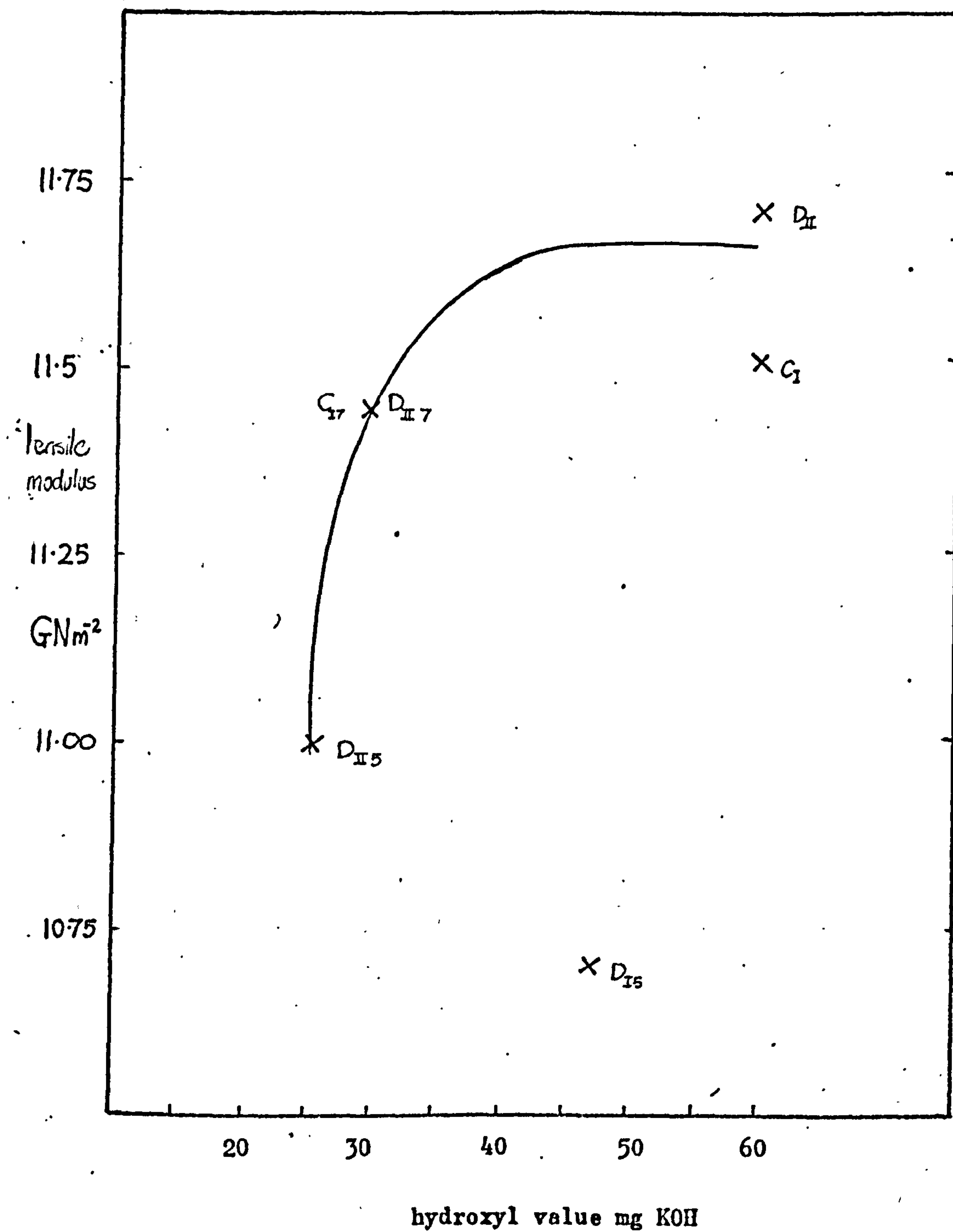


Fig. 39 **Variation of tensile modulus with hydroxyl value**
(67% degree of unsaturation)

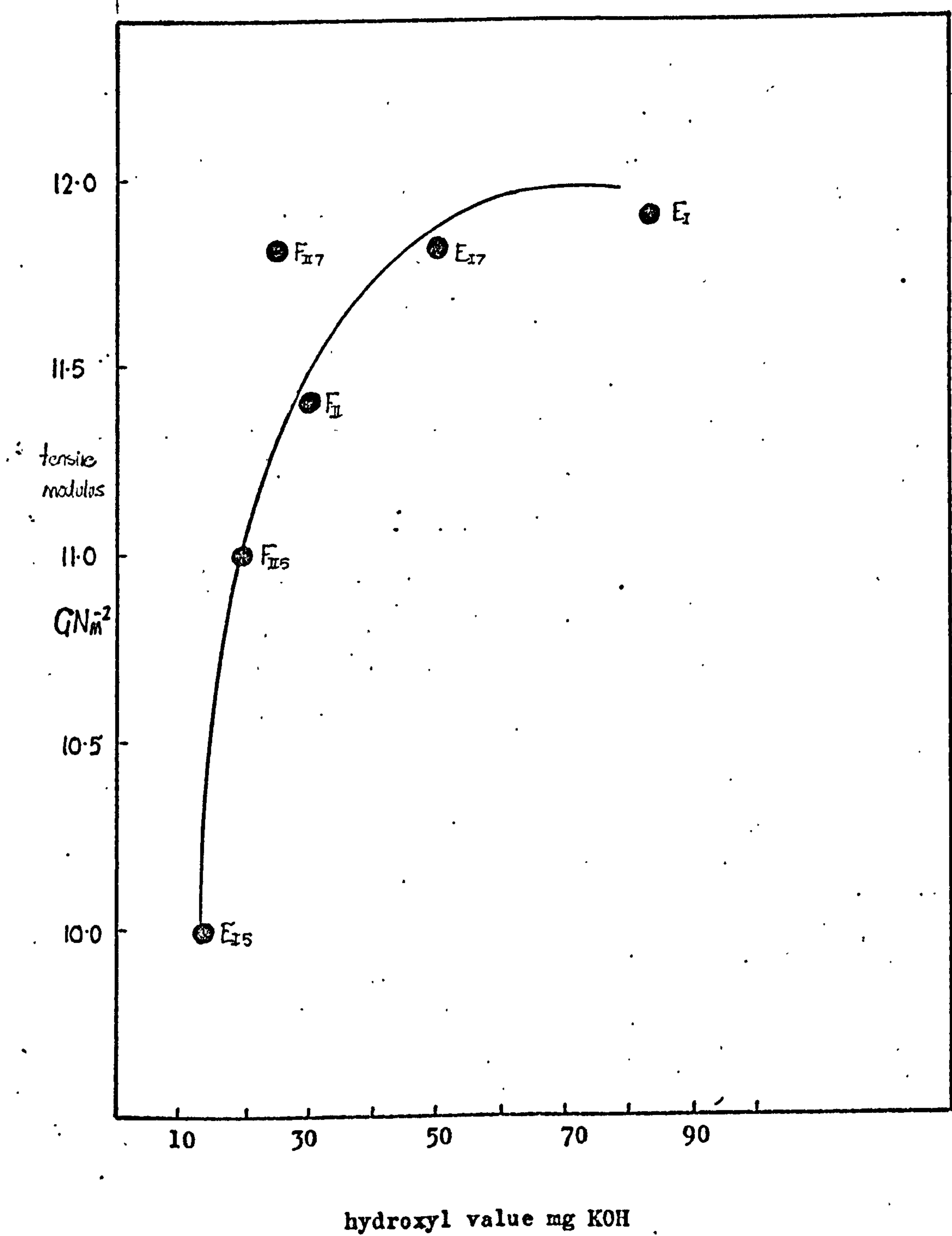


Fig. 40 Variation of tensile modulus with hydroxyl value

(75% degree of unsaturation)

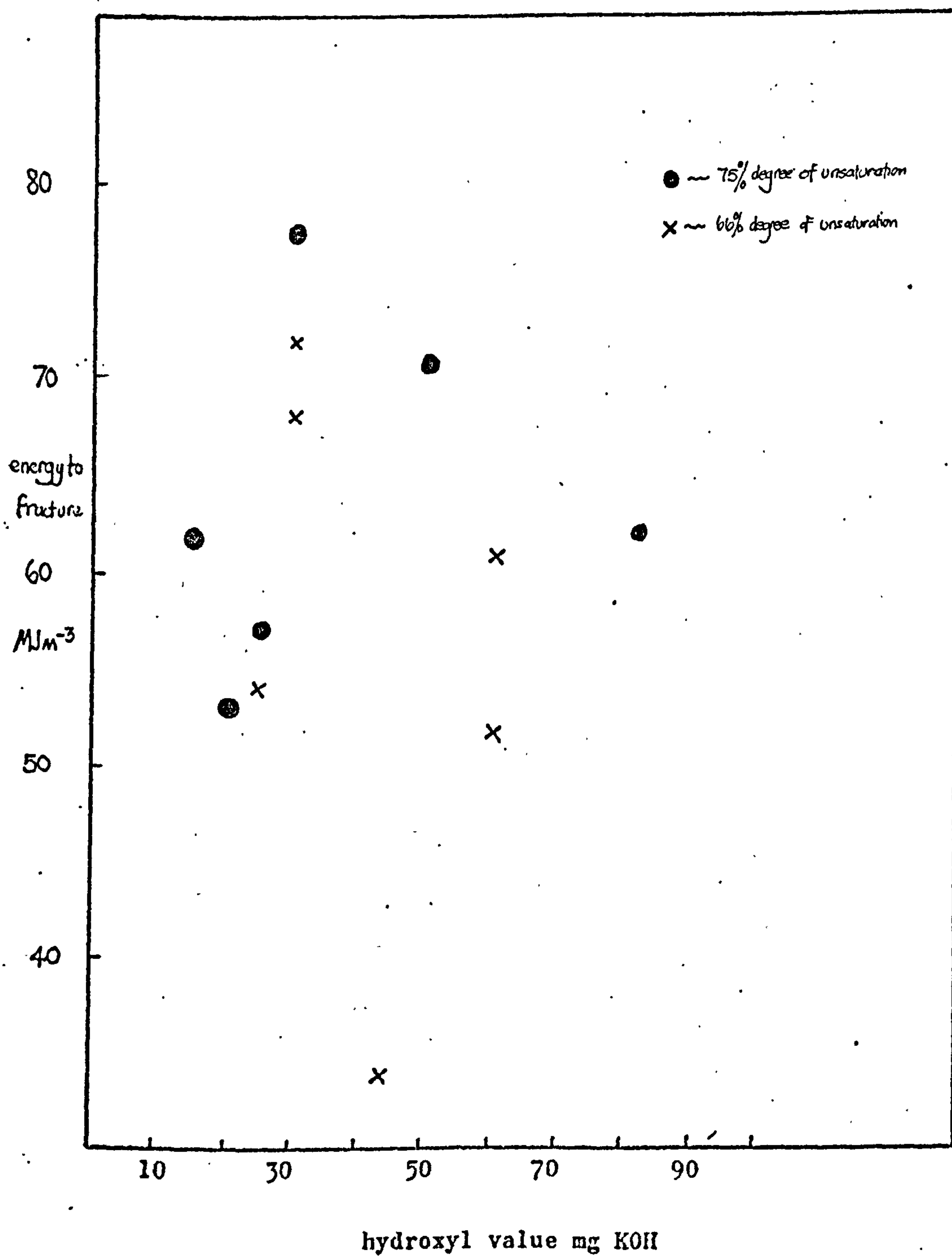


Fig 41 Variation of energy-to-fracture with hydroxyl value

Again those materials manufactured with a resin that has a hydroxyl value in the region of 30 mg KOH have the highest recorded values for energy to failure, 77.1 MJ/m³ (FII).

5.2.3 Fracture toughness of SMC

Single edge notched (SEN) specimens were broken to evaluate the candidate stress intensity factors for sheet moulding compounds. The specimens were found to fracture at far lower loads than would be expected from the reduction of their cross-sectional area and were thus notch sensitive. For an isotropic material, the thickness (t) of the test specimen should satisfy the following relationship (101).

$$t \geq 2.5 \left(\frac{K_Q}{\sigma_y} \right)^2$$

Substituting the values of K_Q and σ_y for the sheet moulding compound,

$$t \geq 2.5 \text{ mm.}$$

Therefore the specimens satisfy the thickness requirements for plane strain conditions.

Figure 21 shows K_Q values expressed as a function of the initial crack length (the ratio (a/W), where W is the width of the specimen and a the depth of the notch). Although the nominal initial crack length was 0.35 some variation was observed. No perceptible dependence of K_Q on the initial crack length was encountered over the ranges tested.

Figure 32 shows the load displacement record for a notched polyester resin casting. Figure 42 shows the load displacement record for a notched SMC specimen. It can be seen from this that the fracture process is more controlled. This is especially true of resins A1 and BII, for which the stable crack propagation stage is greater than that of any of the other SMC tested.

It is immediately noticeable from Table 17 that unlike the tensile strength and tensile moduli values obtained for the SMC, the figure obtained for the candidate stress intensity factor shows less variation.

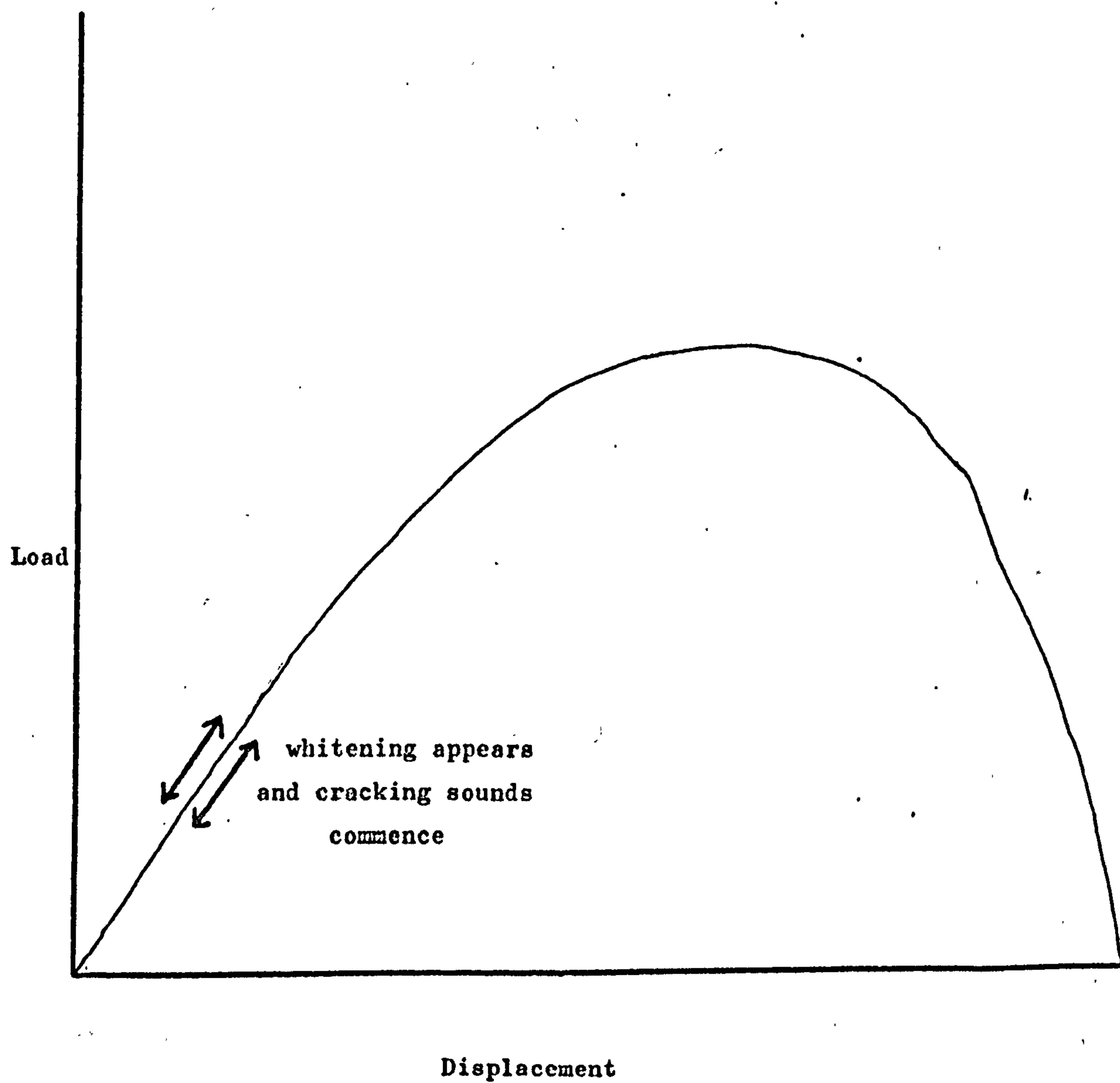


Figure 42 The fracture of SMC

It was observed during the SEN tests that damage near the crack tip started at very low values of applied load (approx 30% of P_{max}). A whitening of the SMC appeared on both sides of the crack and produced noticeable cracking sounds. This is probably due to debonding of the fibres and subsequent cracking of the matrix parallel to the notch. This whitening was observed up to 5 mm both sides of the crack plane.

2.5.3.1 Candidate stress intensity factor

Table 17 shows the effect of increasing diol excess on the candidate stress intensity Factor, K_Q . As the diol excess is reduced there is a general fall in K_Q , although in both groups SMC produced by method II with a diol excess of 10%, namely D_{II} and F_{II} , have lower values than would be expected. The crack extension force, G_Q , follows similar trends to those shown by K_Q values.

It is at once noticeable that there is no significant variation in toughness values obtained for the SMC. The values for nine of the SMC tested occur in the range $7.15 \pm 0.25 \text{ MNm}^{-3/2}$. The remaining three SMC are manufactured from resins C_{I5} , E_I , and E_{I5} . The value obtained for E_I is $7.94 \text{ MNm}^{-3/2}$, the highest recorded and E_I also has the highest recorded hydroxyl value of 82mg KOH.

E_{I5} has the lowest recorded value for K_Q of $6.44 \text{ MNm}^{-3/2}$ while at the same time having the lowest recorded hydroxyl value of 15mgKOH. It would appear that the toughness of the SMC tested was over a large range insensitive to the hydroxyl value of the matrix resin.

However at low hydroxyl values the debonding contribution to the composite toughness appears to be minimal as the glass is so poorly bonded. At higher hydroxyl values, the glass is more likely to be properly impregnated which would bring about an increase in the bond strength of the composite. This is indicated in the higher figure obtained for the SMC's toughness. These

results agree with the theories of Dibenedetto (48).

Resin C₁₅ has the low figure of $6.69 \text{ MN}_m^{-3/2}$ for its SMC K_Q value but has a high value of 47mgKOH for its hydroxyl value. It has already been noted that the matrix resin C₁₅ has a value for its hydroxyl number which seems higher than would be expected and this is further evidence of that fact.

Tables 20 and 21 show values for K_p , G_p and K_I . K_I is in all cases lower than K_Q as would be expected. K_I is derived from the load at which non-linearity is first noticed in the load displacement record. It is interesting to note that although cracking and debonding in these polyester composites begins at 30% of the maximum load, the load displacement record for the material does not become non-linear until approximately 55-65% of the maximum load is reached. This is because as stated before the transverse fibres which debond first do not carry any load in the direction of the applied load, and hence their debonding should not affect the load bearing capacity of the entire specimen.

It can be thought that the non-linearity in the load displacement record is associated with the onset of debonding of the fibres aligned with the load direction and the crack extension in the matrix. The quantity $K_Q - K_I$ or ΔK_I can be considered as a measure of the crack growth resistance of the material. Figures 44 and 45 show the variation of ΔK_I with the K_{IC} value obtained for the matrix resin.

It is obvious that as the notch sensitivity of the matrix resin increases (K_{IC} decreases) so that the initial resistance to crack growth is reduced. Owen and Rose (29) have already reported that debonding in tensile testing was insensitive to resin flexibility, but that resin cracking was suppressed by the more flexibilized resin. It would appear in this case that resin cracking was to an extent suppressed by the less notch sensitive resins over the range tested and that during this period of the load displacement curve the dominating mechanism was crack extension in the matrix

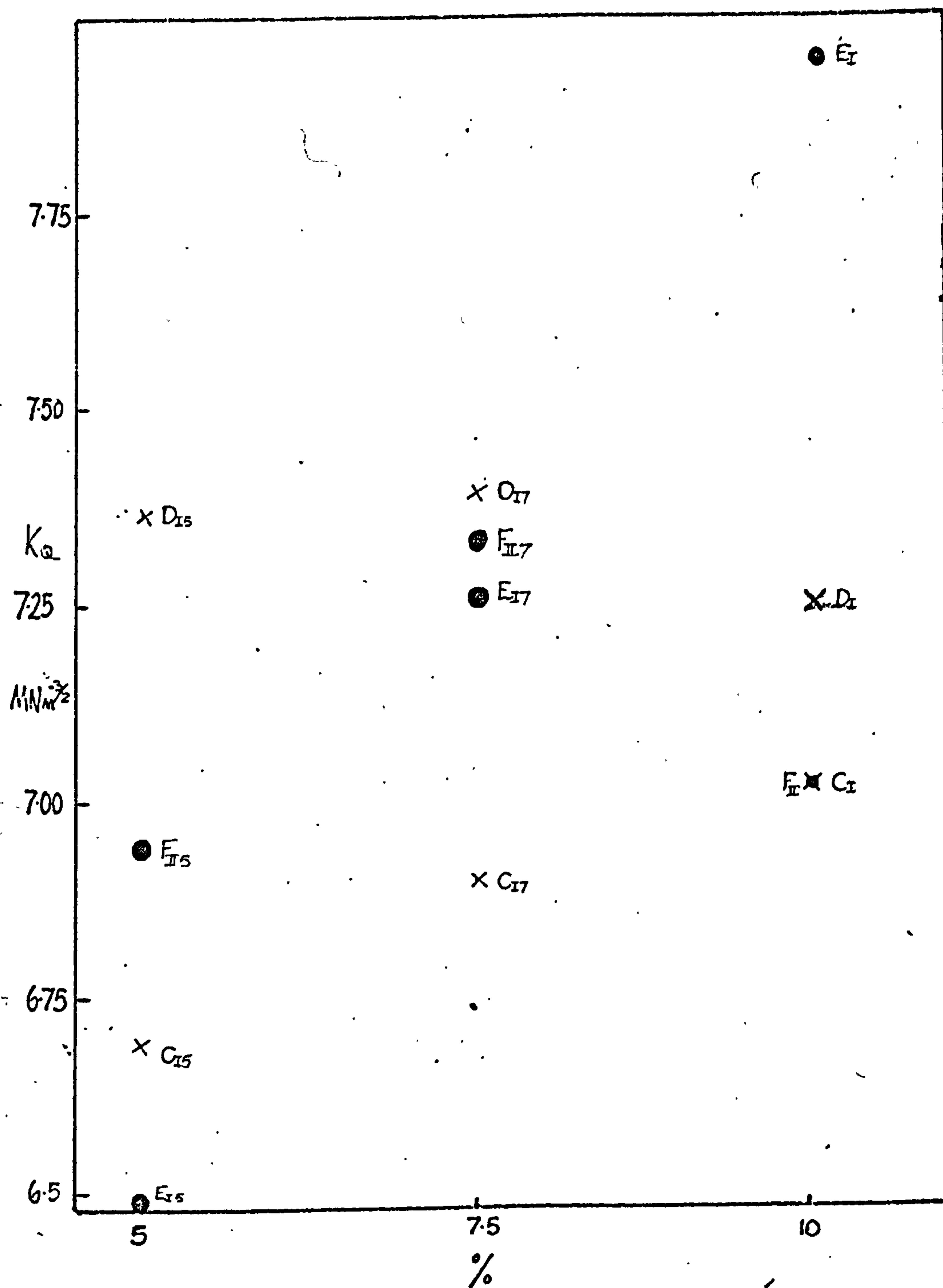


Fig. 43. Variation of candidate stress intensity factor (K_Q) with diol excess of matrix resin.

adjacent to the notch.

The value expressed for $K_p - K_Q$ (or ΔK_p) shows no such relationship probably indicating perhaps that after a certain amount of crack propagation energy is absorbed by a complex set of mechanisms: debonding, fibre pullout, and stress relaxation being examples.

The debonding of fibres is obviously taking place throughout the macro-failure of the notched specimen. However it would appear that over a wide range the amount of debonding is insensitive to the hydroxyl value and only at very high or very low values of hydroxyl value are significant effects seen.

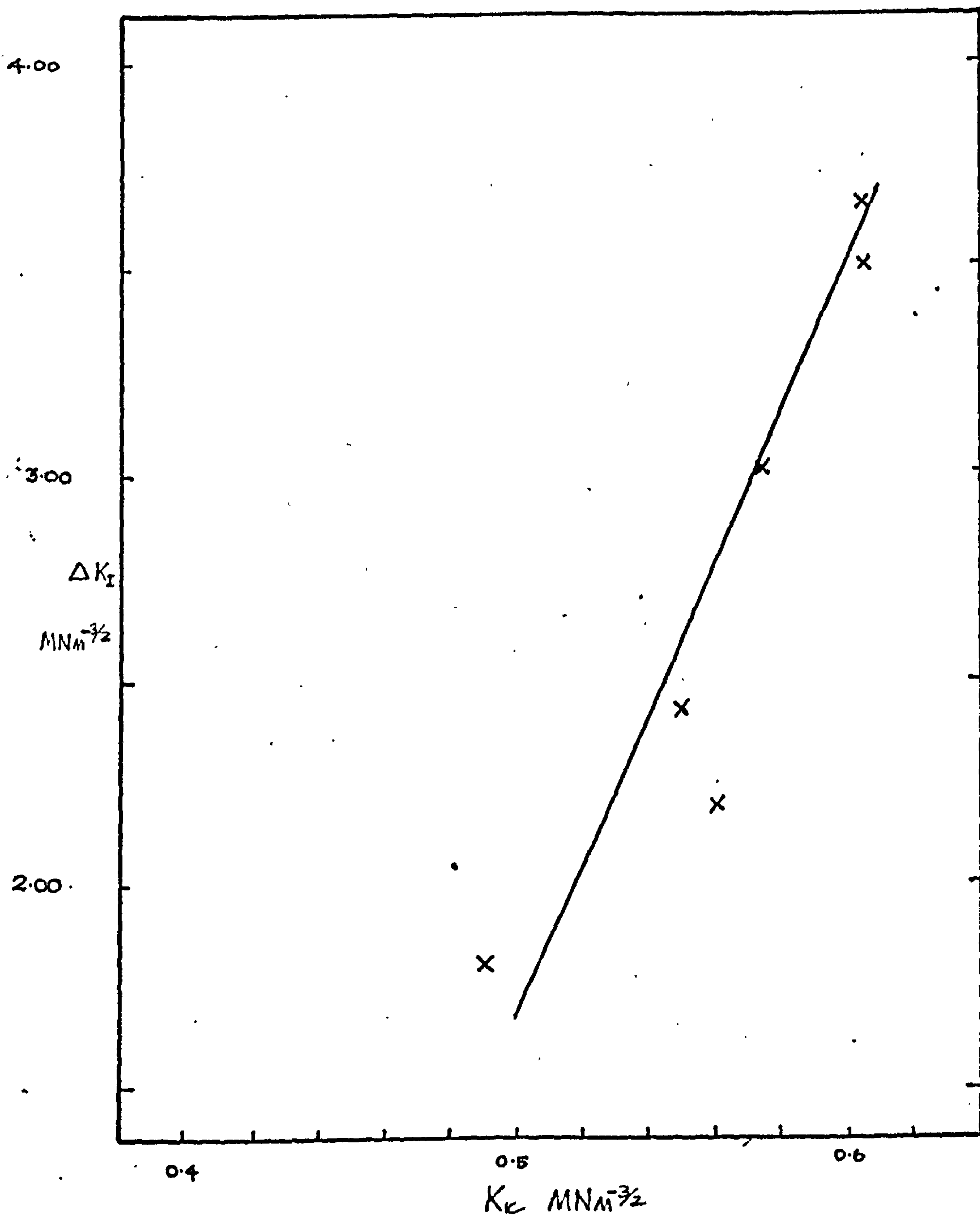


Fig. 44. Variation of ΔK_I with K_{IC} of the matrix resin (67% unsaturation).

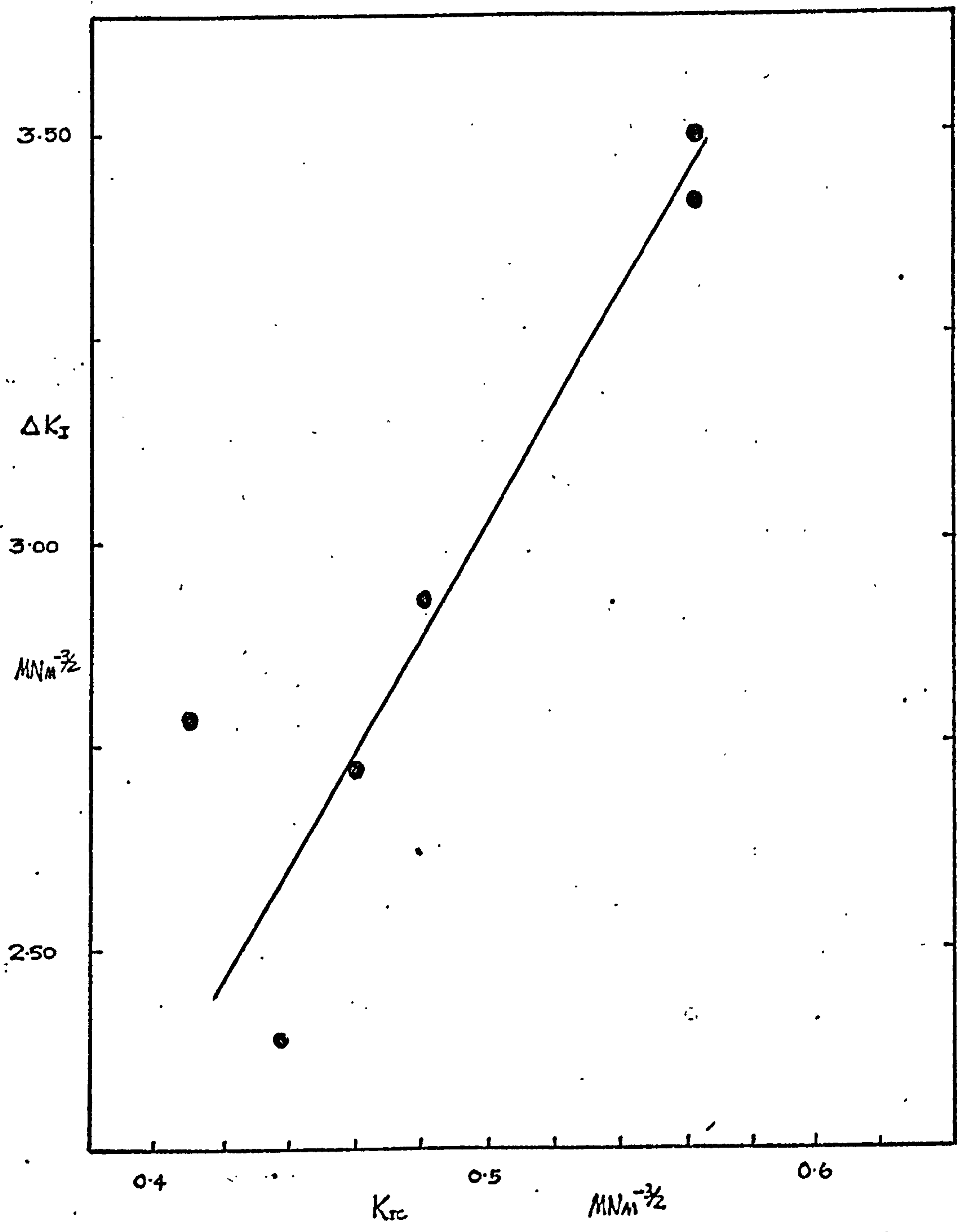


Fig. 45. Variation of ΔK_I with K_{IC} of matrix resin
(75% unsaturation).

Chapter 6

DISCUSSION - PART TWO

6. The effect of the maleic:phthalic ratio of the polyester resin on the strength and fracture toughness of the subsequent SMC

6.1 Polyester resins

As has already been stated in 5.1 there are several difficulties in attempting to synthesise polyester resins with predetermined chemical characteristics. From Table 7 it can be noticed that as the degree of unsaturation increases so the solids content required for a given viscosity falls. More significantly the hydroxyl value also falls.

→
degree of unsaturation (maleic:phthalic ratio) increases
←
solids content decreases
←
hydroxyl value decreases

In a 1:1 maleic:phthalic ratio synthesis (50%) the amount of volatile diol condensed with the water of reaction was found to be 0.8% by weight of the total condensation products. In a total maleic synthesis (100%) the figure rose to 1.4%. This is almost a half mole of diol lost from the reaction.

This increase in the loss of diol is due to the higher exotherm experienced during the initial stages of the reaction. This exotherm is due to the breakdown of the maleic anhydride.

The amount of lost diol obviously affects the speed of reaction and in fact the ease of reaction. Where a large amount of diol is lost, there will be less diol available to react with carboxyl tipped species in the reaction. As the number of carboxyl tips defines the acid value so the unavailability of this diol increases the difficulty of achieving the prescribed acid value. Therefore resins A_I and B_{II} have solids contents of 68.4 and 69.3 respectively while J_I and K_{II} have solids contents of 56.6 and 60.3 respectively.

An illustration of the interdependence of the properties of a polyester resin is the hydroxyl value of A_I which is lower than would be expected. However A_I also has the lowest acid value recorded.

All the resins behaved in a brittle fashion when loaded in the tensile mode. Again the variation in test results was wide and must be treated with due caution. However Table 8 shows that the ultimate tensile strength and elongation at break exhibit a general increase with increasing maleic content.

The tensile modulus generally drops with increasing maleic content. This is due to the decreasing presence of the rigid phthalate group in the polyester backbone. These figures generally agree with the findings of Parker (25, 26) who with a resin of the same structural components and solids contents of 70%, found that the tensile modulus achieved a maximum of 59% unsaturation. He also found that on increasing the styrene content that the modulus maximum shifted to a lower degree of unsaturation. The resins tested had styrene contents in the 30 to 45% range and the highest values for tensile moduli are obtained for those resins with the lowest degrees of unsaturation.

Results for the fracture toughness measurement (K_{IC}) are shown in Tables 11 and 12. K_{IC} decreases with increasing maleic content. Figure 46 shows the relationship between K_{IC} and the degree of unsaturation.

Table 22 also lists the resins of 67% unsaturation synthesised with different diol excesses alongside its corresponding 75% resin.

Table 22 Comparison of K_{IC} at two levels of unsaturation

67% Unsaturation		75% Unsaturation	
Resin	K_{IC}	K_{IC}	Resin
C_I	0.605	.562	E_I
D_{II}	0.558	.562	F_{II}
C_I 7	0.606	.483	E_I 7
D_{II} 7	0.550	.462	F_{II} 7
C_I 5	0.576	0.437	E_I 5
D_I 5	0.491	0.407	F_{II} 5

All evidence suggests that those cast resins with a lower maleic content (lower degree of unsaturation) have a higher stress intensity factor. Increasing the maleic content of the resins makes more crosslinkable sites available. One can consider the structures in a simplified form,

if A = maleate group

B = phthalate group

C = propylene group

<u>Degrees of unsaturation</u>	<u>Structure of linear polyester</u>	<u>Number of styrene molecules per maleate group</u>
50% ACBCACBCACB	2
67% ACBCACACBCAC	1.5
75% ACACBCACACACBCA	1.33
87% ACACACBCACACA'	1.15
100% ACACACACACA	1

Broutmann and McGarry (17) had found a similar relationship with polymethylmethacrylate. By increasing the number of crosslinkings they found that the fracture toughness decreased. This is because crosslinks

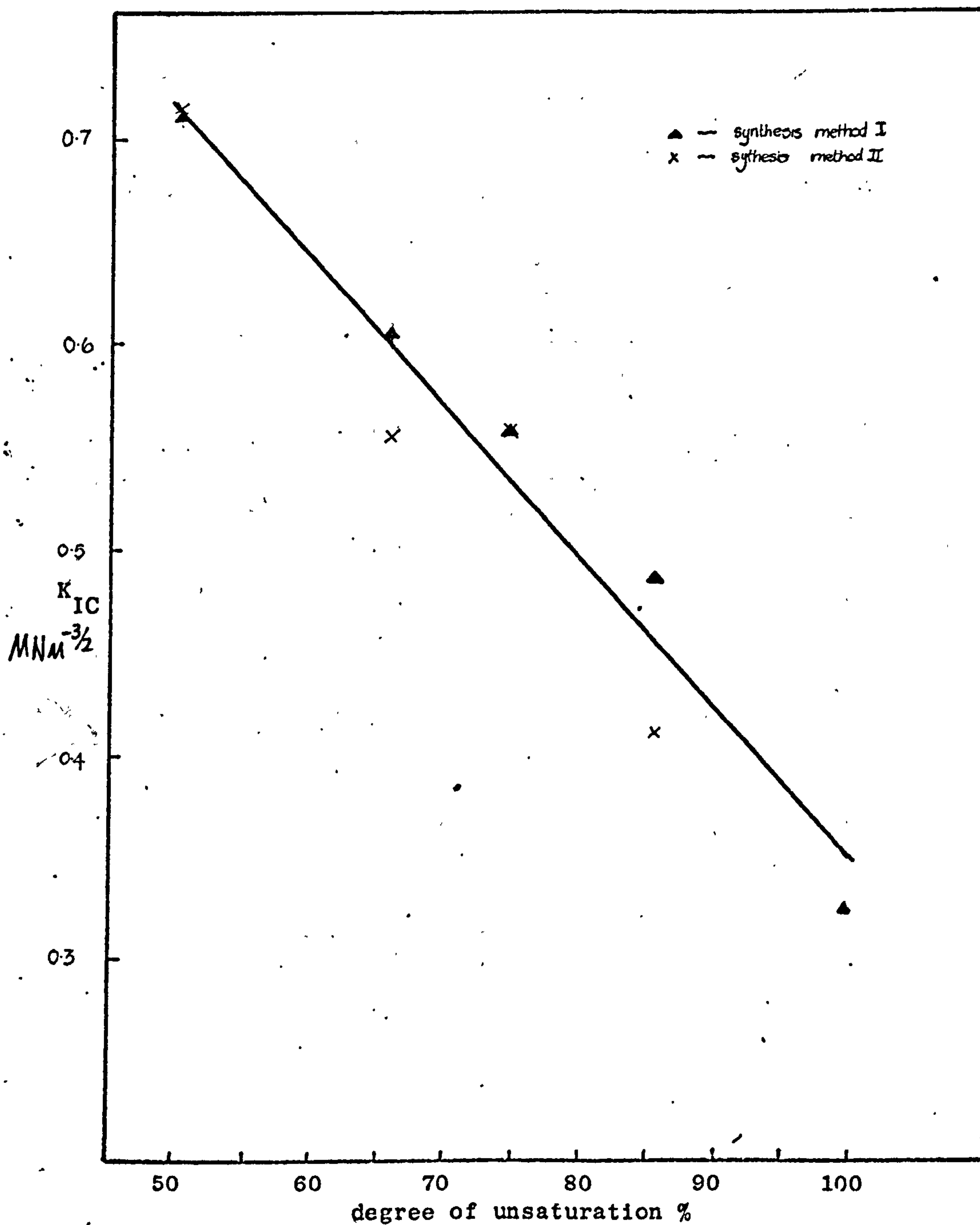


Fig. 46 Variation of K_{IC} with the degree of unsaturation of the matrix resin.

hinder the ability of the material to flow on the application of stress.

The amount of styrene present is in all cases sufficient to provide one styrene molecule per maleate crosslinking site. However the number of styrene molecules available for crosslinking increases as the degree of unsaturation decreases. Broutman and McGarry (17) had suggested that the increase in the toughness of similar polymers would be due to the styrene bridge length increasing. In this case it would appear that the increase in toughness with decreasing unsaturation is because either (i) substantially less crosslinkable sites are available or (ii) the styrene bridge length increases.

It should also be remembered that the phthalate molecules present in the backbone are very rigid and will inhibit any flow to an extent. The effect of the increasing degree of unsaturation is therefore quite marked.

6.2 Mechanical Properties of SMC

The results for the tensile mechanical properties are subject to the same qualifications made in Section 5.2. Again approximately the same trends are seen for the three parameters measured as can be seen in Figures 47-49.

The highest values are consistently obtained by those SMCs made with matrix resins of intermediate unsaturation levels. We are now considering two components of the resin.

—————→
increasing hydroxyl value
—————→
viscosity decreases
—————→
impregnation improves.

The hydroxyl value of the resins affects the viscosity of the polyester formulation and hence its ability to impregnate the glass mat. Secondly the degree of unsaturation controls two factors, the notch sensitivity of the resin and the degree of shrinkage.

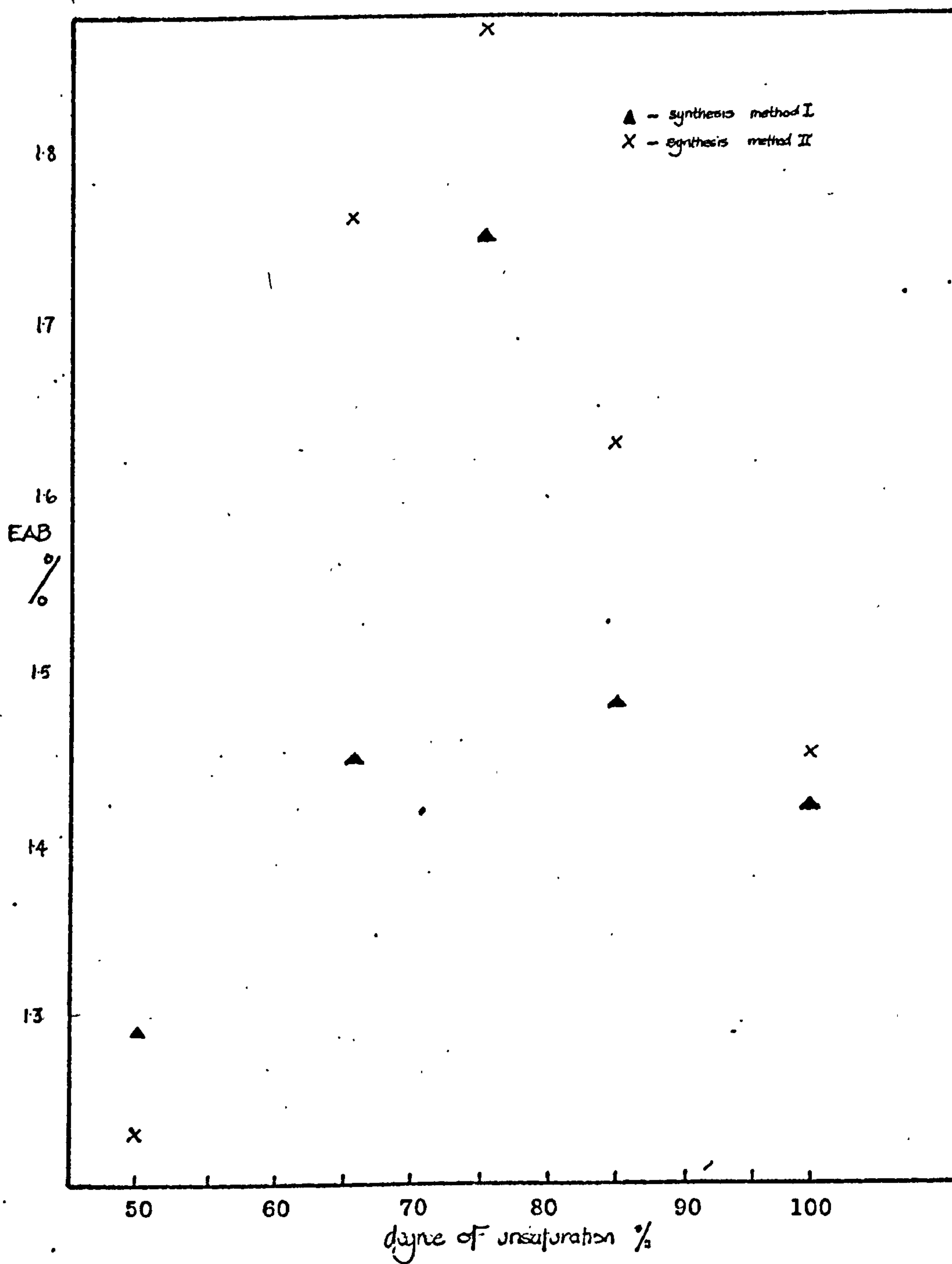


Fig. 47 Elongation at break of SMC compared with matrix resin degree of unsaturation.

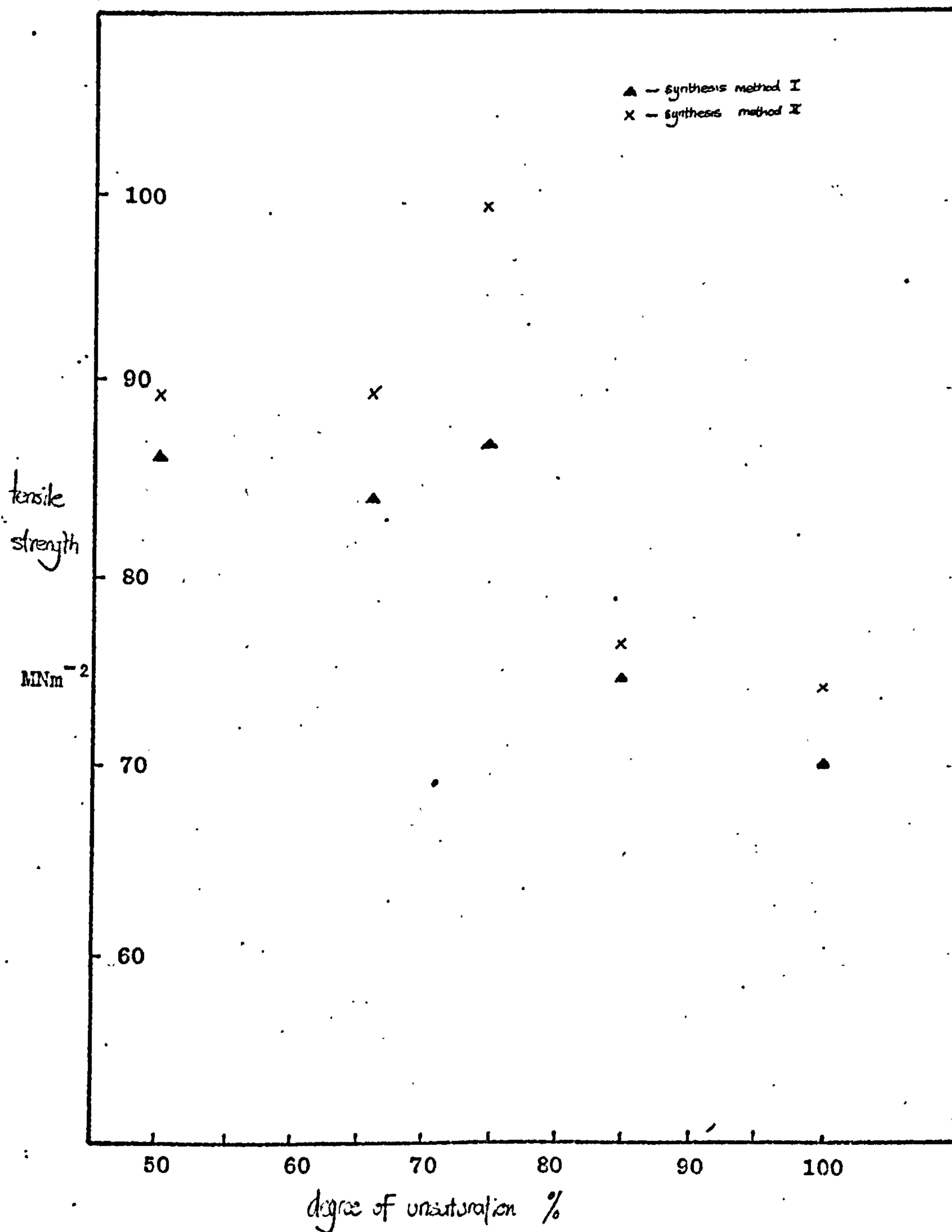


Fig. 48 Ultimate tensile strength of SMC compared with matrix resin degree of unsaturation.

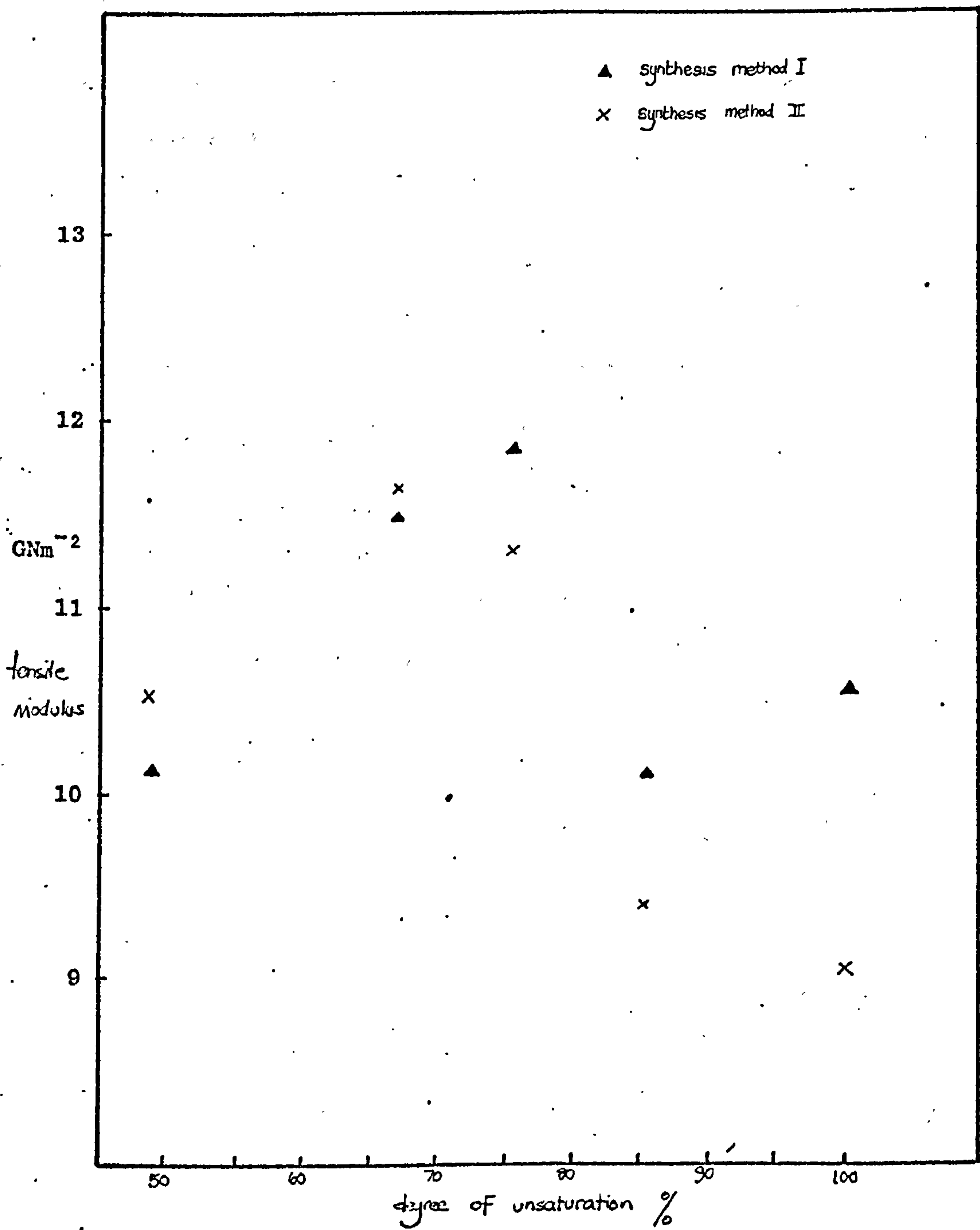


Fig. 49 Tensile modulus of SMC compared with matrix resin degree of unsaturation.

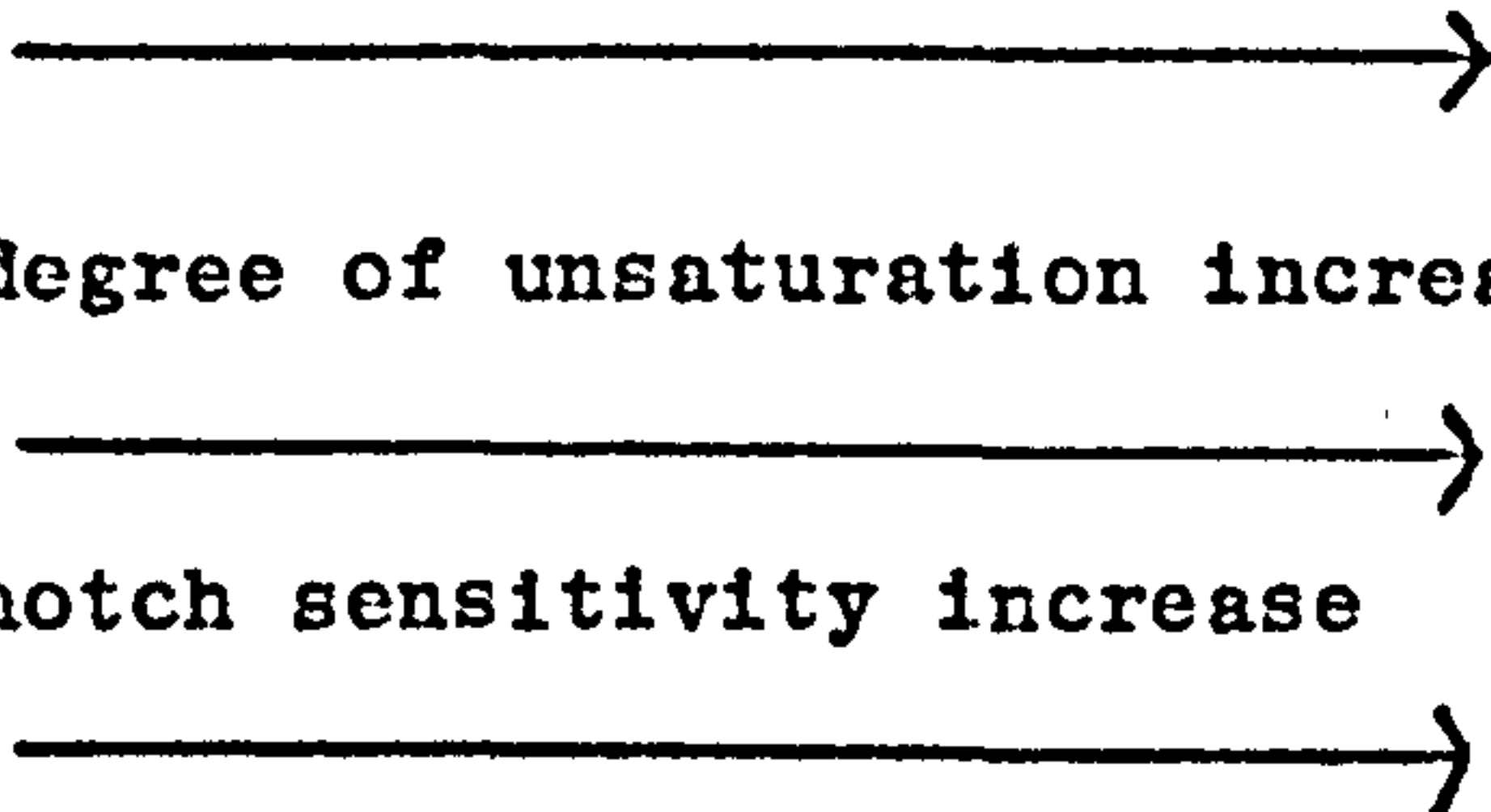

 degree of unsaturation increases
 notch sensitivity increase
 shrinkage increases.

Figure 48 shows that in four of the five cases there is no significant difference between the SMCs produced with the resin synthesised by methods I and II. However SMCs E_I and F_{II} have significantly different tensile strengths. F_{II} has a lower hydroxyl value of 30 compared with the value of 82 for E_I . The E_I resin formulation will be able to impregnate the glass more thoroughly and thereby provide a far superior glass matrix bond for the composite.

When a fibre fractures, especially an aligned fibre, the stored elastic energy in the fibre which is in excess of that needed to create fracture surfaces of the filament is instantaneously released and must be absorbed or transmitted by the matrix in the vicinity of the filament failure (51). Usually most of the fibres at this stage will be debonded with only frictional forces existing at the fibre interface. However in the case of E_I the bond between the fibre and matrix will be so much greater that less debonding will have taken place. Consequently on the fibre breaking the energy dissipated will be greater, resulting in the complete failure of the matrix.

In an ideal situation matrix cracks are formed to absorb the strain energy released from the broken fibres. If the matrix is notch sensitive the cracks propagate the entire width of the specimen and fibres bridging the matrix crack start breaking or pulling out of the matrix, resulting in the complete failure of the specimen. Increasing the maleic content of the resin increases the notch sensitivity of the resins and thus there is seen to be a reduction in the tensile strength of the composite for matrix resins G_I , H_{II} , J_I and K_{II} . These resins have the lowest K_{IC}

values, 0.488, 0.410, 0.324 and 0.448 respectively.

As has already been stated, the level of unsaturated acid also affects the shrinkage of the matrix material. The actual thickness of measured test specimens was

A _I	3.7 mm
B _{II}	4.2 mm
C _I	3.4 mm
D _{II}	3.4 mm
E _I	3.4 mm
F _{II}	3.4 mm
G _I	3.2 mm
H _{II}	3.3 mm
J _I	3.4 mm
K _I	3.2 mm

It would appear therefore that only SMC A_I and B_{II} differ in the amount that they shrink, the other resins seemingly all shrinking to 3.3 ± 0.1 mm. The higher the shrinkage of the matrix the higher the radial compressive stresses developed at the glass matrix interface in these composites. This increased radial compressive stress should aid the transfer of load from matrix to fibres. The role of friction forces becomes important as soon as fibres start debonding. These forces developed at the fibre matrix interface are capable of transferring the load from matrix to fibres efficiently.

The lack of these forces may explain why SMCs A_I and B_{II} have lower values for tensile strength than would be expected as these resins are the least notch sensitive.

The tensile moduli of the SMC show a gradual increase with increasing unsaturation until a maximum is reached at around 70% unsaturation. At higher unsaturation levels the values fall off to some extent.

As seen in the last chapter, matrix resins with the higher hydroxyl values generally give SMC with higher tensile moduli. There is some evidence that the SMC tensile moduli are dependent on the moduli of the matrix resin (see Fig. 50). In the previous chapter no such relationship was found. However with the latter case the moduli of the resins varies from 2.73 to 3.73. There with the matrix resins synthesised with different diol excesses no such range of modulus values was obtained.

It should always be remembered that those resins having the highest tensile moduli themselves also generally have the highest hydroxyl values and the two factors are both likely to be contributory.

6.3 Fracture behaviour of SMC manufactured with resins of different unsaturation levels

The variation of K_Q for the SMC with the level of unsaturation is shown in Figure 51. Except for four resins, all the SMC have their candidate stress intensity factors lying in the range $7.35 \pm 0.32 \text{ MNm}^{-3/2}$. This is surprising as the structure and hence the notch sensitivity of the resin varies widely. It is even more intriguing when one considers that the least notch sensitive matrix resins A_I and B_{II} have the lowest recorded values for the candidate stress intensity factors, K_Q , (5.64 and $6.01 \text{ MNm}^{-3/2}$ respectively) of their SMC.

When a load is applied to a notched specimen debonding takes, firstly at the interface of transverse fibres. However eventually load bearing fibres will debond and it is important at this point that frictional forces exist at the fibre interface to transfer the load from matrix to fibres. Resins A_I and B_{II} , both undergoing less shrinkage, will not have the radial compressive forces to provide these frictional forces.

SMC E_I has a higher K_Q value than would be expected but as has been stated this is probably because of resin E_I 's high hydroxyl value of 82. This will allow the glass reinforcement to be well impregnated by the resin slurry and give higher bond strengths.

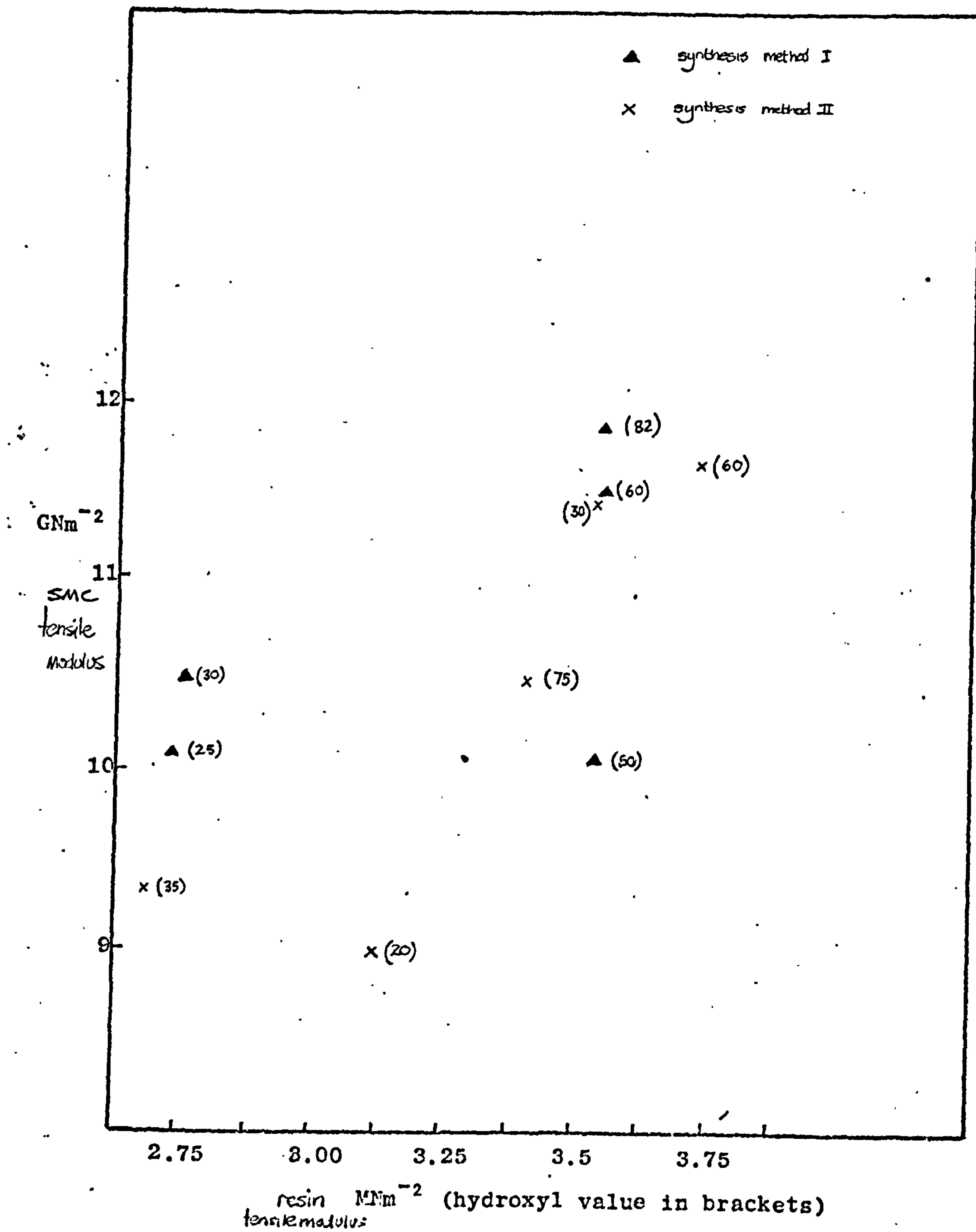


Fig. 50 Comparison of SMC tensile modulus with matrix resin tensile modulus.

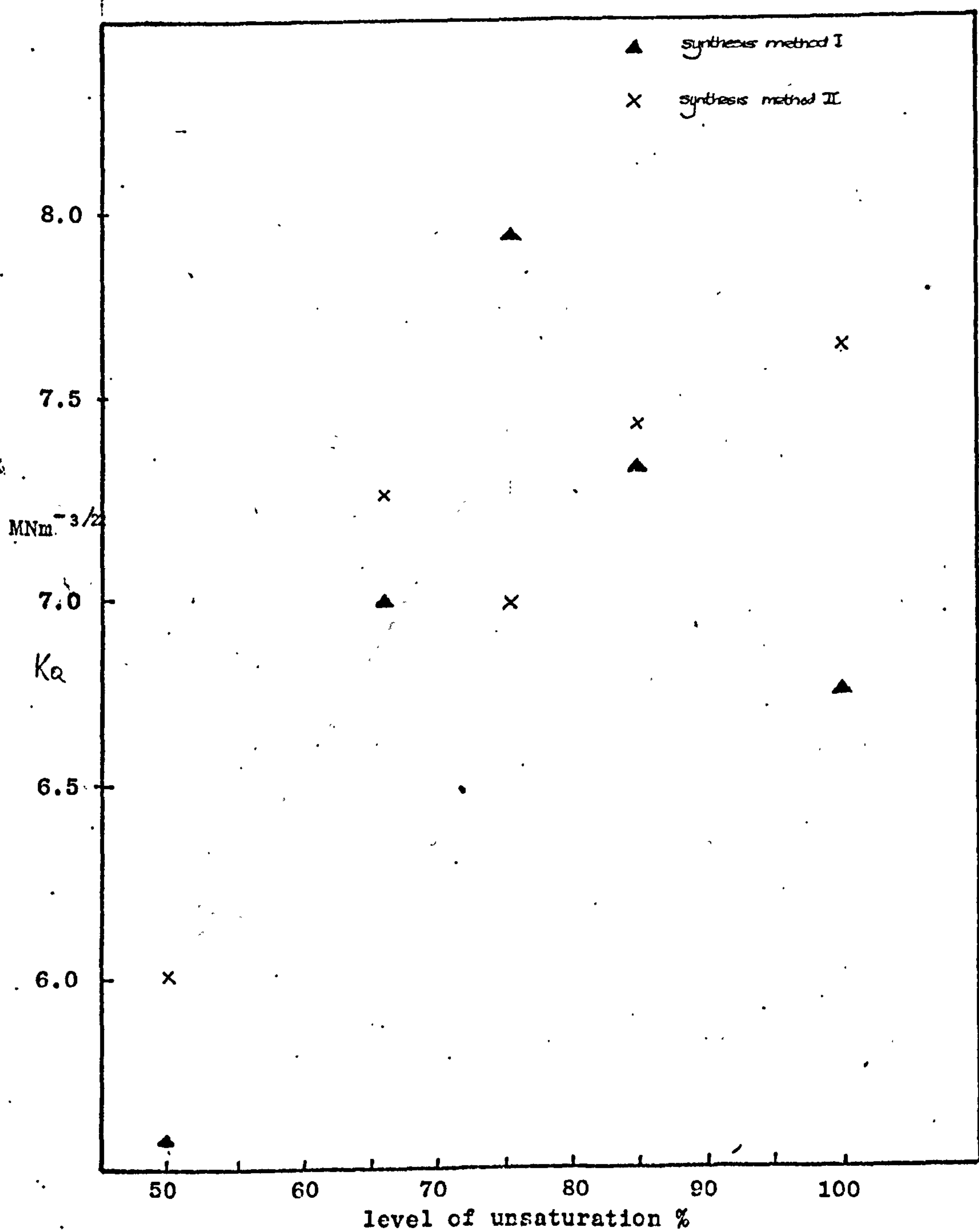


Fig. 51 Variation of candidate stress intensity factor (K_Q) with matrix resin degree of unsaturation.

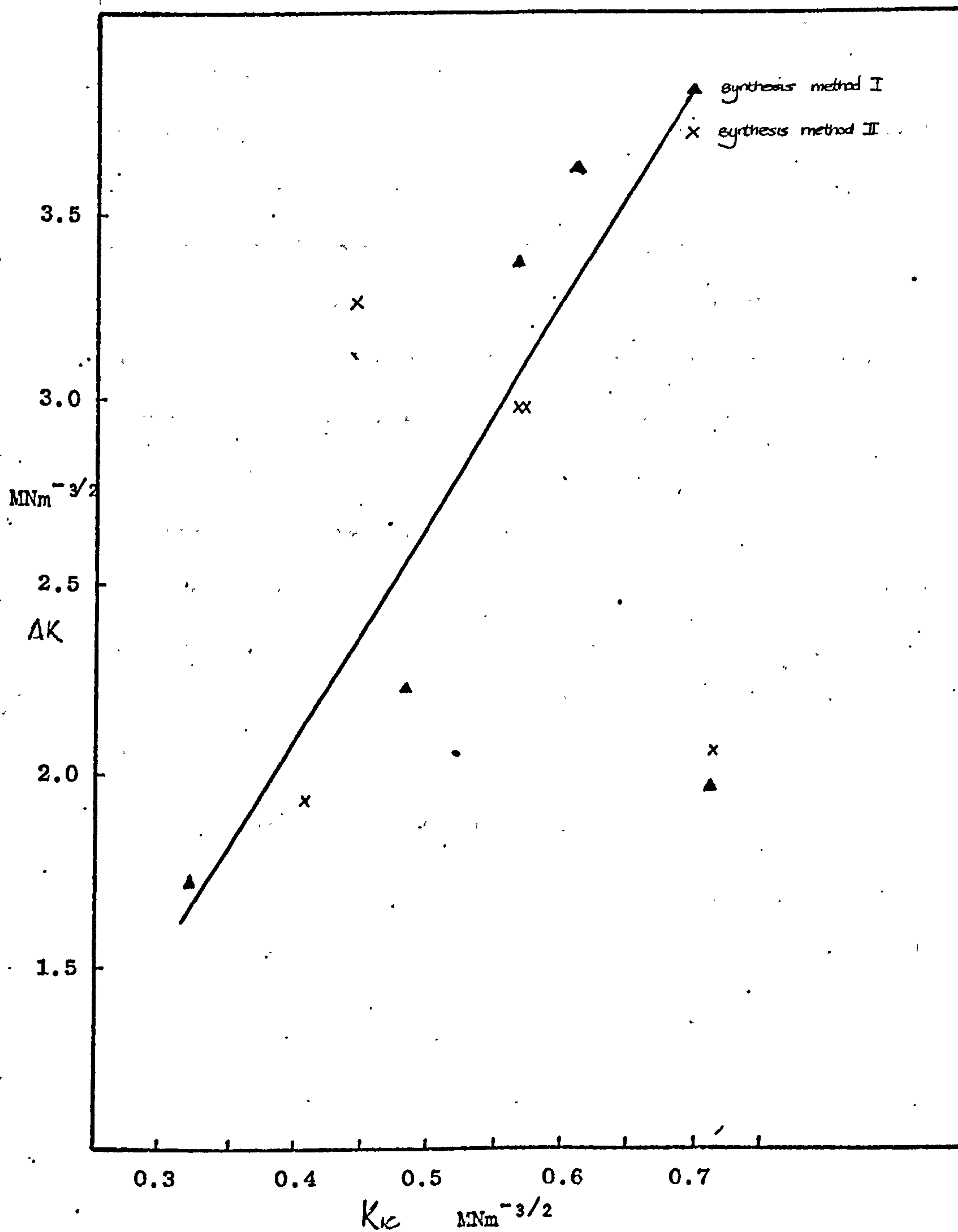


Fig. 52 Variation of SMC ΔK ($K_Q - K_I$) with matrix resin stress intensity factor (K_{IC}).

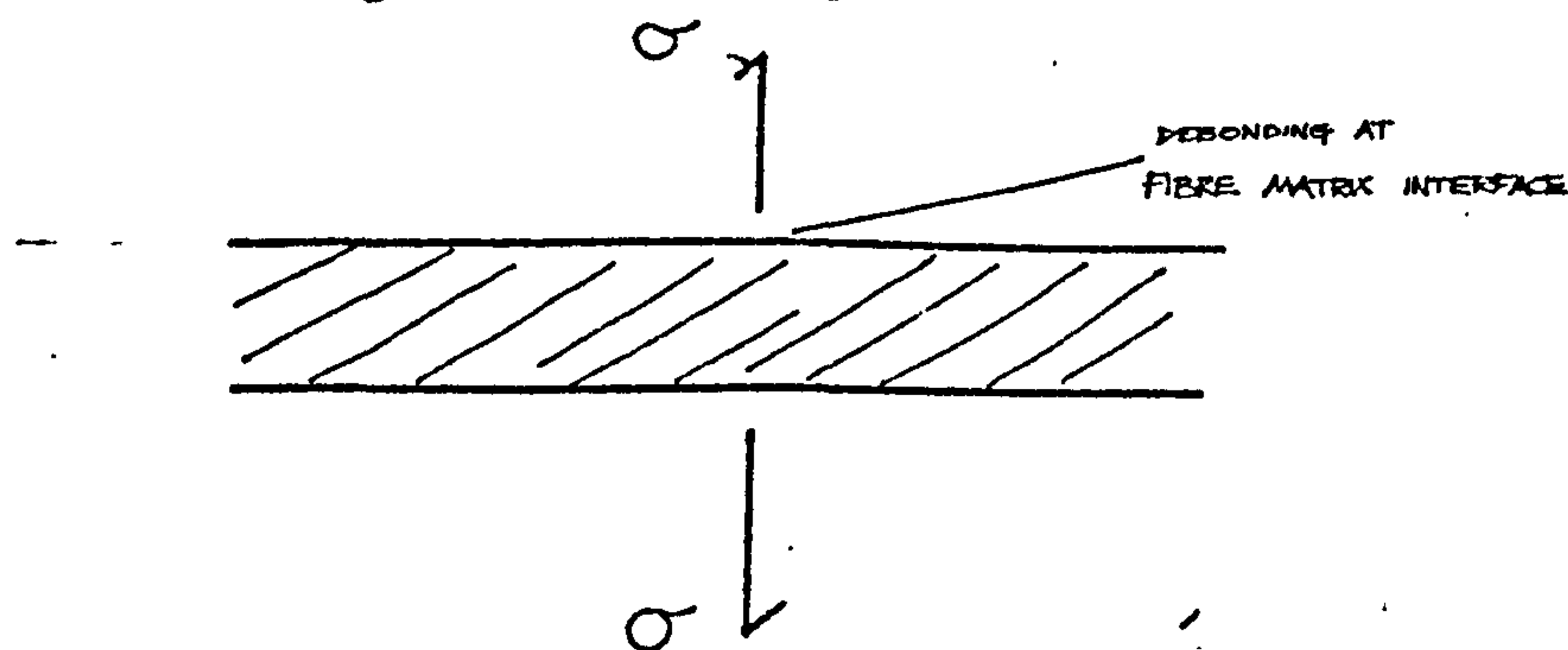
Similarly K_{II} has a lower value for K_Q and this is because of its low hydroxyl value of 20 mg KOH. The resin slurry will thicken rapidly and a poor matrix-glass bond will be formed.

The experimentally observed values of fracture toughness indicate that improving the bond strength of the fibre matrix interface results in a higher value of fracture toughness parameters. This is in contrast with the behaviour of aligned short fibre composites where a reduced bond strength increases the value of toughness. In random fibre composites such as SMC, the transverse fibres act as the source of crack initiation. Since the transverse fibres are very sensitive to the interface condition, the transverse fibres debond easily and increase the stress concentration in the matrix. The matrix fails due to its notch sensitivity before the debonding spreads to other fibres to any significant extent. The final fracture occurs by fibres breaking and some pull out.

It can be postulated that at low bond strengths the fracture properties are controlled by the matrix crack propagation resistance. Again there appears to be a marked relationship between the notch sensitivity of the resin and the quantity $\Delta K (K_Q - K_I)$. (Fig. 52).

One is therefore able to put forward the following regime of failure:

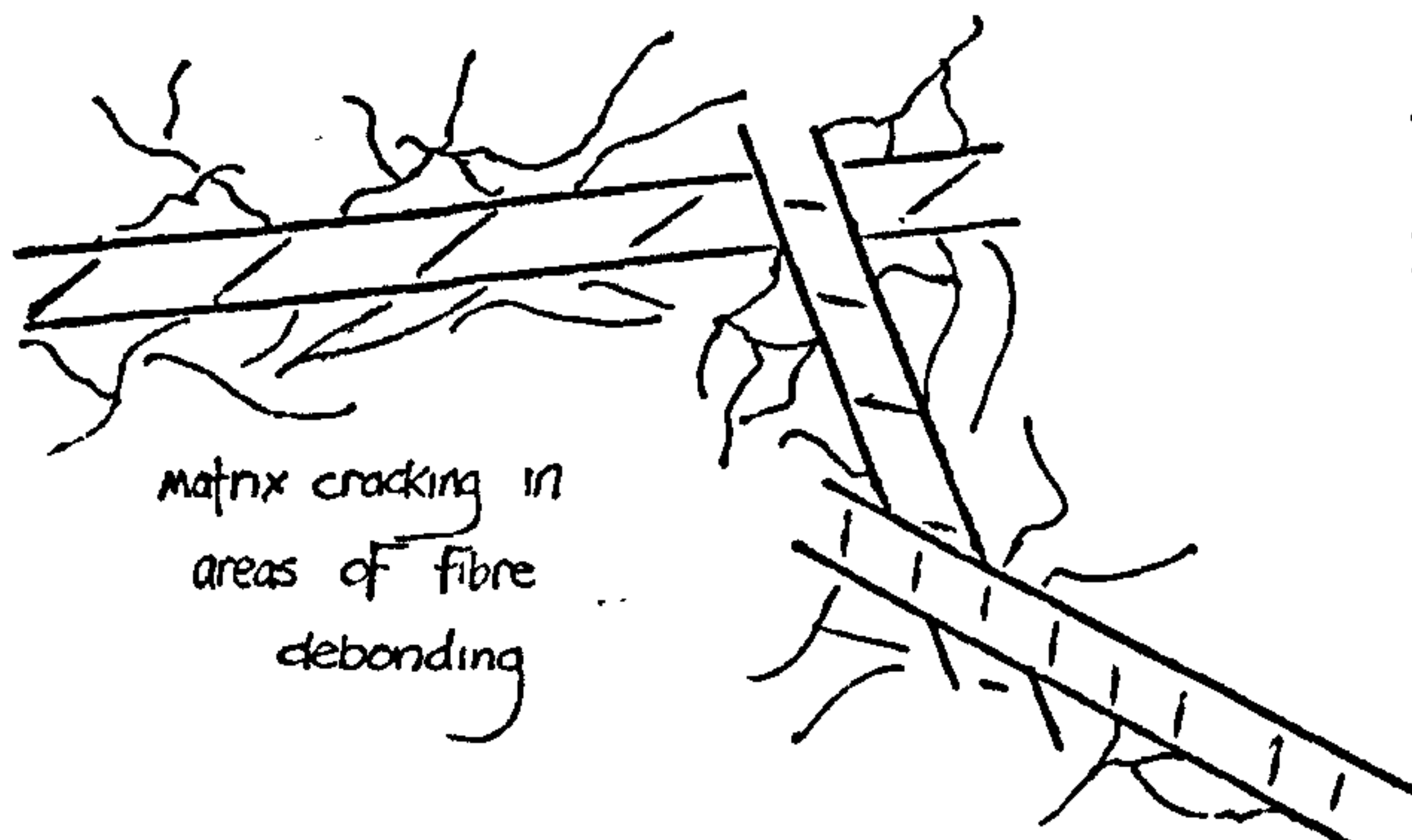
(1) debonding of transverse Fibres



Increased bond strength is brought about by resins with high hydroxyl values allowing good impregnation by a low viscosity resin slurry.

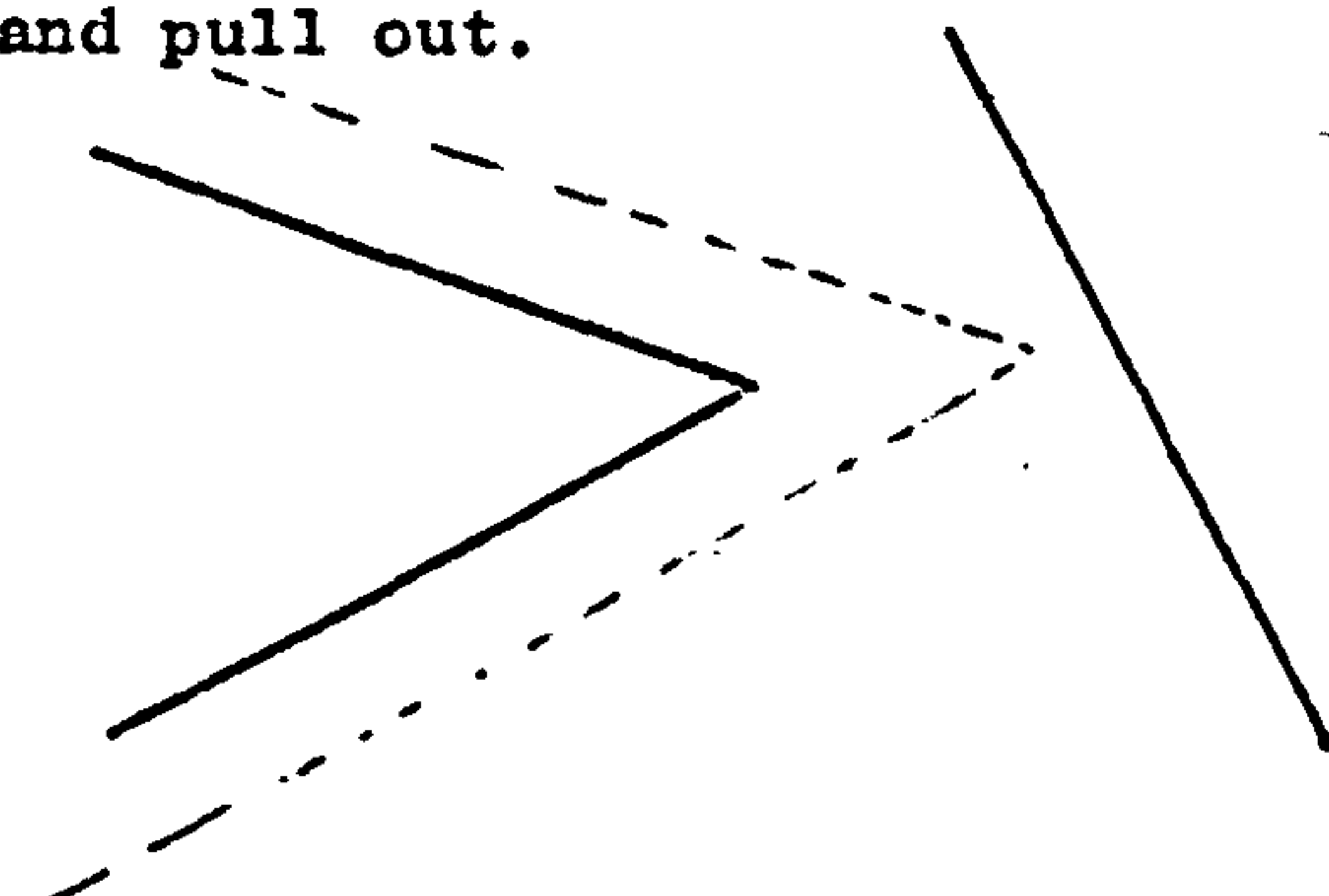
(ii) A period of debonding of fibres at progressively lower angles, to the applied load and matrix transfer of load.

(iii) Associated resin cracking.

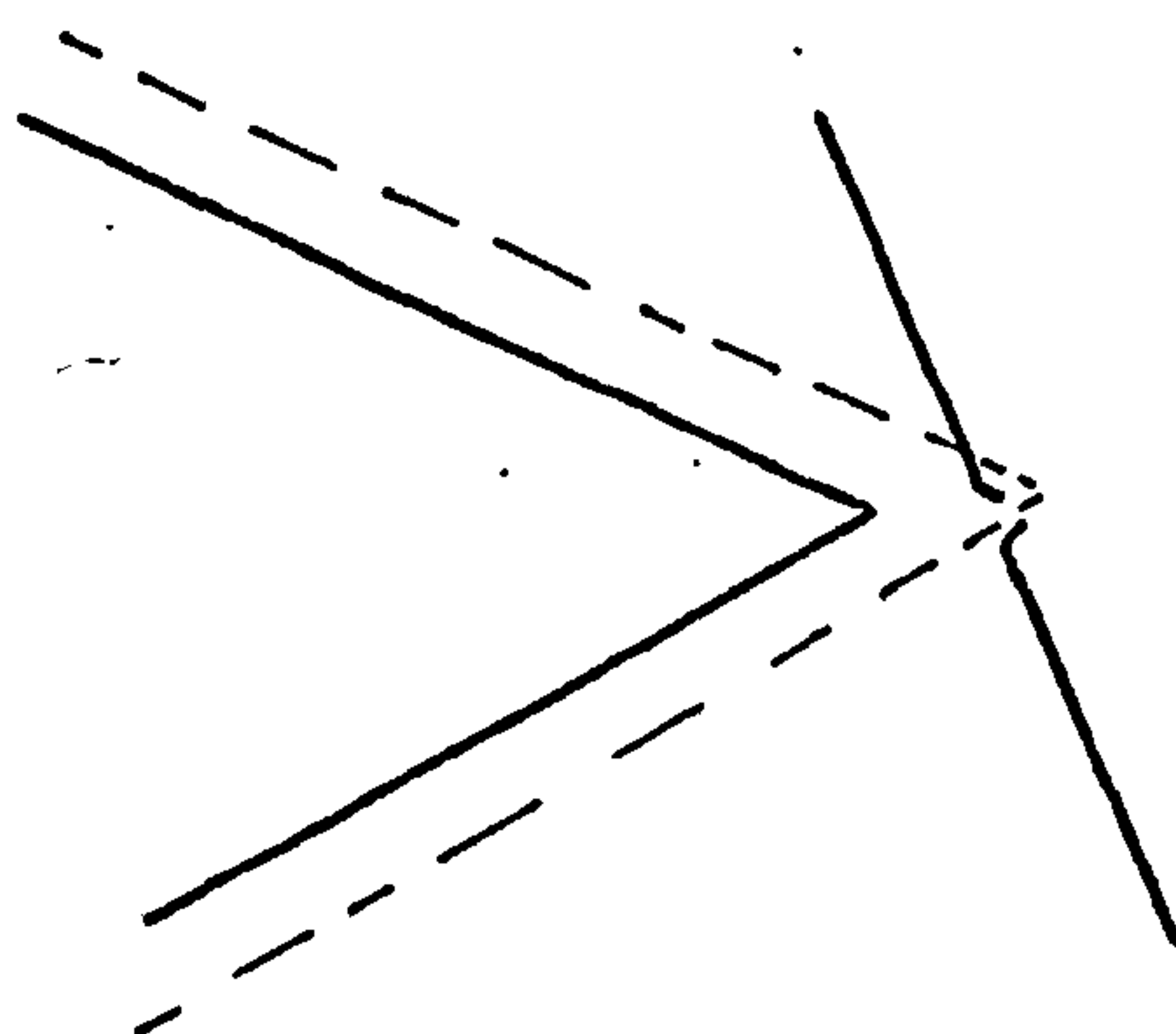


A matrix resin with a higher K_{IC} value will therefore increase the toughness of the composite.

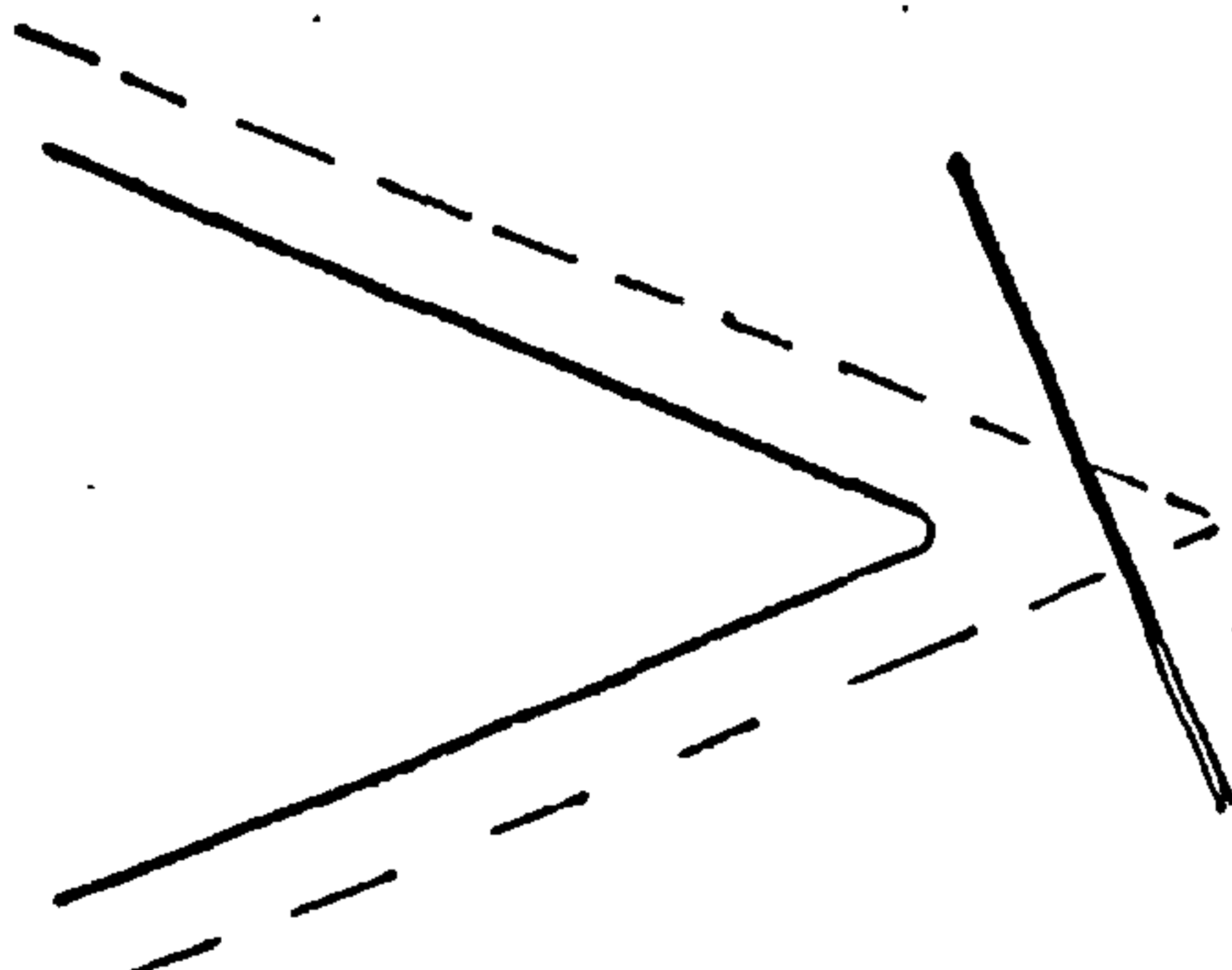
(iv) Crack propagation through the matrix added to fracture of fibres and pull out.



(a) advancing crack front



(b) Fibre Fracture



(c) Fibre pull out

Stage (ii) is attenuated in the case of resin A_I and B_{II}. Although these matrix resins have the highest K_{IC} values of $0.712 \text{ MNm}^{-3/2}$ they are hindered by the ability to transfer load from matrix to fibres through frictional forces. In these two examples energy is absorbed at a much earlier stage by the breakdown of the matrix.

Chapter 7

CONCLUSIONS

7.1 The strength of SMC

Incorporation of brittle glass fibres into a brittle resin matrix results in tougher and stronger composite materials. The composite strength and modulus values are affected by the matrix resin structure and properties. The nature of the fibre matrix bond affects the composite strength properties. Resins with an intermediate hydroxyl value 30-40 mg KOH appear to give the highest recorded values for tensile strength. Low hydroxyl values give the lowest recorded values for tensile strength. Higher hydroxyl values do not give the expected further increase.

The modulus of elasticity is a small strain property of a material. A direct relationship was found between the modulus of the matrix resin and the modulus of a composite. There is also a contributory effect from the viscosity of the resin at the time of impregnation of the glass. Resins with a high hydroxyl value enhance the stiffness of a composite.

The failure mechanism for these compounds is similar to that of related glass reinforced composites. Initial damage to these materials occurs as a result of debonding of those fibres transverse to the load direction. The debonding starts spreading to the neighbouring fibres as the load on the material is further increased. The catastrophic failure of the material occurs when the aligned fibres start breaking.

The overall conclusion is that the resin is important to the strength and modulus of the SMC in several ways. Firstly the modulus of the resin has some bearing on the modulus of the SMC. The unsaturation level of the resin dictates its notch sensitivity and shrinkage; these two parameters have been shown to affect the tensile strength. The hydroxyl value of the resin has also been shown to affect the mechanical properties of the resin.

All these parameters are interdependent. Such is the nature of a

polyester resin that altering the unsaturation level will have profound effects on hydroxyl value, notch sensitivity, shrinkage and modulus.

7.2 The Fracture of SMC

Fracture properties of sheet moulding compounds have been determined using single edge notched specimens. It was concluded that these materials were notch sensitive, and over the range of notch depths employed in the study the fracture properties of the SMC were not significantly affected.

Measurements of fracture properties on randomly reinforced materials naturally show high variability. Over a wide range of hydroxyl values the toughness of the SMC shows no significant variation. However at low hydroxyl values the toughness of the SMC is reduced significantly. Also at very low hydroxyl values the toughness is enhanced.

Debonding of the fibres near the crack tip starts occurring at small fractions of the maximum fracture load, usually less than 30 per cent. A strong bond strength, brought about by impregnating the glass with a low viscosity resin slurry (high hydroxyl value) will enhance the toughness.

Over a wide structural range the toughness of the SMC is insensitive. However at low unsaturation levels toughness values fall rapidly. The polyester resin matrix shrinks on curing, at low unsaturation levels this shrinkage is at its lowest. Because of this radial compressive forces are greater in SMC of higher unsaturation level. This increased compressive stress helps in the transfer of load from matrix to fibres just as the increased normal force provides greater friction force.

The role of friction forces becomes more important when fibres start debonding. Where debonding is greater friction forces developed at fibre matrix interface are capable of transferring the load from matrix to fibres efficiently and thus premature tensile failure of the matrix does not occur.

Surprisingly the toughness of SMC appears insensitive to the notch sensitivity of the resins, despite the relatively wide range of resins used and their range of notch sensitivities. However from data obtained from the load-deflection curves it appears that the notch sensitivity controls the crack growth resistance of the SMC. There is a marked relationship between the toughness of the resin and the energy absorbed on going from crack initiation (K_I) to catastrophic failure (K_Q).

It is concluded that the debonding mechanism is dominant in these materials when a good bond exists of the fibre matrix interface. However for both these composites with high and low resin matrix bond strengths the fracture energy is controlled to a certain extent by the fracture resistance of the matrix material.

Again the fracture properties are seen to be dependent on the chemical parameters of the matrix resin. Optimum properties are obtained with a resin that supplies the SMC with a high bond strength (high hydroxyl value). The toughness is also enhanced with a matrix which has high fracture resistance and is able to supply radial compressive forces of fibre matrix interface once debonding has taken place.

Chapter 3

FUTURE WORK

This work has indicated certain selective features necessary of a polyester resin to enable it to produce SMC with the appropriate mechanical properties. However the following qualifications are important.

The mould used in this study was of the simplest form. To enable the full characterisation of a matrix resin a more complex mould would be necessary. There is every possibility that with a more complex moulding, the flow of the SMC charge will become very important. Resins of different hydroxyl value may flow differently in a more complex situation.

Commercial SMC contains far more nil-shrink additive than that used in this study. Usually the additive is in the ratio 40:60 with the polyester resin. The additive may have a definite effect on the properties of the SMC and mute or enhance the effect of the different polyester resins.

A thorough analytical study of polyester resins used in SMC could prove instructive. Little work has been done on the exact structure of the resin such as its quantity of low molecular weight constituents. Also as the hydroxyl value is so important in its effect on the fibre-matrix bond it would be interesting to find the effect of synthesis process variables and constituents on the hydroxyl value.

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