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CHEMICAL MODIFICATION OF PERFLUOROPOLYETHER OLIGOMERS AND EFFECTS ON COMPATIBILITY AND PROPERTIES OF EPOXY RESINS

BY

FAIZA ZITOUNI

A DOCTORAL THESIS

Submitted in partial fulfillment of the requirements for the Award of Doctor of Philosophy of the Loughborough University of Technology

1992

Supervisor: Dr L. Mascia

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DEDICATION

To my beloved parents,

sisters and brother
ACKNOWLEDGEMENTS

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I am grateful to Dr David Gabe for his help and moral support.

I would like to thank Dr M Gilbert, staff and technicians within the IPTME Department for their assistance and cooperation.

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ABSTRACT

The incorporation of fluorine in epoxy resins has been the focus of research for many years, aiming to reduce water absorption and to improve the degradation resistance in hot-moist environments. To this end resins have been synthesised from fluorinated monomers while crosslinking was induced by conventional hardeners.

In the present work conventional diglycidyl ether of bisphenol A epoxy resins were modified by the addition of small amounts of perfluoropolyether oligomers containing functional groups at the chain ends. Compatibilisation of these oligomers in epoxy resins was achieved through end-capping and chain extension reactions.

Such modifications of the fluoroligomers only affect marginally the viscosity of the resin mixture. Using hexahydrophthalic anhydride as the main hardener and through selective curing procedures the morphology of the crosslinked resins was controlled to produce either transparent formulations, consisting essentially of an IPN monophase structure, or opaque systems containing precipitated spherical particles. Perfect adhesion is exhibited at the particle interface with the matrix, i.e. there was a complete absence of debonding during fracture.

With the incorporation of small amounts (ca. 3.6%) of the perfluoropolyether, both types of system exhibit very large improvements in fracture resistance, particularly flexural strength and fracture toughness, i.e. up to 75% and 600% respectively, with only a
small reduction in modulus and glass transition temperature. The changes in the mechanical properties are particularly important in that the two-phase systems exhibited improved toughness, while the IPN systems showed an increase in strain at break after ageing.

With the present curing agents, however, no real improvements in water absorption have been observed. This is probably the result of the formation of a network that is not sufficiently tight to create physical restrictions for the diffusion of water molecules which may reach the highly polar hydroxyl and, possibly, carboxylic acid groups to form strong associations.

This aspect needs to be investigated further as it is not clear why the expected reduction in water absorption has not been achieved.
1. INTRODUCTION

Epoxy resins are an important class of polymeric thermosetting materials which are widely used in both structural (e.g. fibre composites and adhesives in aircraft, guided weapons, ship and vehicle construction) and non-structural (e.g. coatings, encapsulation) engineering applications.

Commercial epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones. Optimum properties are obtained by crosslinking these epoxy resins into a three dimensional insoluble and infusible network. The crosslinking agents used are organic materials containing active hydrogen. The most commonly used ones are polyamines or polycarboxylic acids and their anhydride derivatives. Epoxy resins have low cure shrinkage compared with other types of resins (e.g. unsaturated polyester resin). In addition, there is no evolution of volatiles during cure which means that low curing pressures can be used during fabrication and there is reduced risk of void formation.

Epoxy resins have been used in structural adhesive formulations because of their good wetting ability and their formation of strong bonds with many substrates [1] due to the presence of epoxide, hydroxyl, amine and other polar groups within the epoxy system. For structural adhesives with good elevated temperature capability, a high glass transition temperature (Tg) is essential to retain the adhesive strength at high temperature. However unmodified cured systems with relatively high Tg are brittle and can produce catastrophic failure of the adhesive
In many applications, such as in the protective coating of metals, this brittleness can be a disadvantage.

For their satisfactory deployment in many applications neither brittleness nor any reduction in the glass transition temperature are desirable. In spite of these apparently conflicting requirements many researchers have attempted to improve the toughness of epoxy resin without detrimentally affecting their thermal and environmental qualities.

The idea of combining two or more different materials to obtain a new material with synergistic or additive properties has been a wide field of research in polymer composites and polymer alloys.

One method consists of the incorporation of brittle rigid particles such as alumina, silica or glass spheres. However, whilst this approach induces a small degree of toughening [2] it is mainly used for economical reasons.

Another method aimed to diminish the brittle nature of epoxy resin by using various internal plasticisers which reduce the steric hindrance of functional macromolecular chains [3,4]. The general types of plasticisers which have been used include the following:

- Long-chain aliphatic amines (as part of the curing agent)
- Carboxyl-terminated polyesters
- Long-chain organic compounds containing hydroxyl functional groups
- Long-chain aliphatic epoxide materials including epoxidised oils.
These modifiers are compatible with epoxy resins and cause a considerable reduction in the glass transition temperature of the cured system.

Plasticisation has been shown to improve the toughness but only at the expense of heat distortion temperature and therefore elevated temperature performance.

Realising this limitation it was decided to search for an alternative approach involving the incorporation of elastomers, which phase separate during the curing process, into the resin.

Various types of thermosetting resins including epoxies, phenolics, polyesters and polyimides have been modified to increase their toughness. Elastomer modified resins have been studied for over 30 years and most of the work has been focused on modified epoxy resins.

The elastomeric system which has received the most attention is the carboxyl-terminated butadiene acrylonitrile (CTBN) liquid polymer [5-10]. In general, this type of polymer bears free carboxyl groups at the chain ends, and in some cases distributed along the chain.

The CTBN-epoxy prepolymer mixture is homogeneous but the CTBN precipitates as a discrete phase when the resin is cured. Moderately active curing agents (such as piperidine) provide better phase separation than the more active agents (such as triethylenetetramine). Toughness is also enhanced by the addition of bisphenol A [12].
The incorporation of liquid CTBN into brittle epoxy resin gives a significant increase in fracture toughness with a simultaneous decrease in the glass transition temperature and modulus. It has been suggested that the enhanced toughness is derived from crazing and shear band formation. This is explained by the fact that the precipitated rubber phase improves the crack resistance and apparently introduces energy dissipation mechanisms [13].

The degree of toughening achieved depends on the epoxy-rubber compatibility, the volume fraction of the dispersed rubber particles, the particle size and particle size distribution. This in turn depends on the rubber composition (chemistry), concentration and cure conditions [14,15].

The optimum toughening effect is generally obtained within a range of acrylonitrile content from 12% to 18%. The preferred catalyst to promote carboxyl-epoxy reaction in CTBN modified systems is triphenylphosphine (TPP) [16].

A tentative study has also been reported on the use of amine functionalised silicones to toughen fluorinated resins [17]. Attempts to introduce fluorine atoms in the network of crosslinked epoxy formulations have also been made through the addition of specially functionalised fluoroelastomers with the aim of enhancing simultaneously the toughness and thermal stability characteristics [18]. In the latter case the elastomer and the resin/hardener components were mixed from solutions to obtain an initially monophase system which would subsequently allow the precipitation of the elastomer into fine particles through post-curing heat treatments. The practical
difficulties of removing the solvent from such systems impose severe limitations, making them usable only in thin layer systems, such as adhesives or fibre impregnations. Furthermore the large increase in viscosity resulting from the solubilisation of a high molecular weight polymer in the resin constitutes a major disadvantage in low pressure processes.

In general, composites based on epoxy resins are widely used in aerospace and advanced marine applications because of their high strength to weight ratio. However, the deterioration in their mechanical properties is related to environmental conditions. In high humidity environments, epoxy resins absorb moisture. Many attempts have been made to reduce this sensitivity to moisture. The most successful approach has been to include a halogen in the network structure [19].

OBJECTIVES

The main objectives of this study are to investigate the possibility of improving the properties of epoxy resins particularly toughness, water absorption and heat ageing resistance by the incorporation of small amounts of perfluoropolyether oligomers.

In order to achieve these objectives, it is required to carry out the following:

a) chemical modification of the perfluoropolyether in order to impart compatibility with epoxy resin;

b) control the final morphology of the cured modified formulations in order to develop either a monophase or a two-phase structure.
2. LITERATURE REVIEW

2.1 FLUORINATED EPOXY RESIN SYSTEMS

The increasing depletion of natural resources has led researchers to put more effort into the development of durable products and materials with better properties. The introduction of fluorine atoms into polymeric materials, mostly through polymerisation of fluorinated monomers gives rise to attractive properties [20], such as low surface energy and low coefficient of friction [21], reduced flammability and improved chemical resistance as well as excellent electrical properties and high temperature endurance [22].

Although fluorine is inherently expensive [23], fluorinated polymers have found use in many applications where performance is more critical than cost. An example, is the use of fluoro-epoxies as bonding agents and in high quality protective coatings in both aircraft [24] and undersea applications [25].

During the last two decades, the basic chemistry of high quality epoxy materials has been explored primarily by Griffith and Field [26,27]. The most interesting of the fluoroepoxy materials were found to be the diglycidyl ethers of 1,3,5 fluoroalkylbenzene (see Figure 1). These epoxies are cured with conventional epoxy curing agents, generally amines or acid anhydrides. The cured products have superior properties to conventional cured epoxies. One of the interesting properties is the low water absorption [28]. For example, 0.35% by weight water absorption of an anhydride cured fluoro resin is obtained
for an immersion period of six months, while conventional cured epoxy resins absorb ten times or more this amount [29]. Other desirable properties are the low surface tension, lower friction coefficient [21] and low refractive index [27].

Griffith also reported that the fluoroepoxides are substantially more dense than the conventional epoxy resins. However, in some applications such as aircraft, this is a negative quality, especially for composites in lightweight structures.

Where \( n = 3 \) to 7

**FIGURE 1: MOLECULAR STRUCTURE OF FLUORINATED EPOXY-RESIN**

Recently, Twardowskei and Geil [30] studied the behaviour of a 10% highly fluorinated epoxy resin blended with Epon 828 (DGEBA: diglycidyl ether bisphenol A). They were attempting to combine the valuable properties of the fluoroepoxy with the more generally useful properties of conventional epoxy-resin. However, the two resins were found to be incompatible, resulting in the precipitation of spherical domains 10-20 \( \mu \)m diameter, while the surface layers contained an appreciable amount of fluorinated resin. Furthermore, the mechanical
properties of the blend were similar to those of unmodified DGEBA cured resin.

Honn [31] indicated that various commercially available fluorinated resins are insoluble in liquid epoxy resins and do not react with them. However, solution varnishes result in cured coatings combining the adhesion of the epoxies with low water transmission as well as the chemical resistance and flexibility of the fluorinated materials. Also Griffith and Bultman [29] produced heavily fluorinated crosslinked epoxy coatings for naval applications. These coatings are claimed to be tough, durable and have the desirable properties normally associated with fluorine containing materials.

Schweiker and co-workers [32] suggested that the inclusion of long chain fluorinated diols, with the chemical structure HOCH$_2$CH$_2$(CF$_2$)$_m$CH$_2$CH$_2$OH (where $m = 3$ to $8$) into polymer chains, results in useful highly fluorinated materials having the desirable properties of PTFE. On the other hand, it has been reported that the use of fluoroaliphatic diols produces polymers that are hydrolytically unstable [33]. Griffith and coworkers [34] indicated that increasing the fluorine content in polymeric materials reduces their glass transition temperature (Tg). However this effect is not desirable in some applications and the authors showed that increasing the crosslink density of the fluorinated polymer increases its Tg.

2.2 INTERPENETRATING POLYMER NETWORKS (IPNs)

An interpenetrating polymer network is defined as a combination of two polymers both in network form, at least one of which is synthesised
and/or crosslinked in the immediate presence of the other [35]. They are held together by permanent entanglements formed by crosslinking of the component networks. In addition to blending and copolymerisation, IPNs represent a third mechanism by which polymer properties can be improved. IPNs can be divided into simultaneous and sequential types.

In a simultaneous IPN, the crosslinkable monomers are mixed together and then polymerised separately through different mechanisms. However, in a sequential IPN, first one type of monomer is crosslinked then a second type of monomer is added and polymerised within the network of the first. Another type of IPN is called the semi-IPN, where only one of the polymers forms crosslinks. In other words, it consists of a molecular mixture of a thermoset and a thermoplastic polymer. The thermoset polymer gives high-temperature and chemical resistance, while the thermoplastic provides toughness and resistance to impact [36].

In recent years, a great deal of work has been done on interpenetrating polymer networks [37]. These materials are generally produced by mixing two low molecular weight functionalised linear polymers in the liquid state (solution, dispersion, or in the form of bulk liquid prepolymer), shaping them into the desired form (i.e. coating, moulding, etc) and finally crosslinking them in situ. Klein reported [36] that not all polymers can be combined to form IPNs and that the two polymers must be compatible in order to avoid phase separation and to achieve a greater improvement in mechanical properties.
2.2.1 Interpenetrating Polymer Network Approach to Toughen Epoxy-Resin Systems

One approach to enhance the toughness of brittle thermosetting systems is to prepare a thermoplastic/thermoset blend consisting of one linear polymer and one highly crosslinked polymer. Such a system is called semi-IPN.

Selfton and co-workers [38] have incorporated high performance polyaromatic thermoplastics into epoxy resin systems. The idea is to carry over the very high toughness of the thermoplastics into the epoxy resin system. The results have shown that it is possible to control the semi-IPN morphology by modifying the thermoplastic backbone. The different morphologies so obtained give rise to different degrees of toughening by involving different energy absorbing mechanisms.

Several other workers [39,40] have reported that the modification of epoxy resin by a thermoplastic polymer shows an increase in toughness over the unmodified thermoset.

Another approach to the formation of IPN molecular structures has been reported by Sperling [41] and Touhsaent et al. [42]. These workers synthesised two polymer networks by simultaneous independent reactions in the same container. They indicated that inter-crosslinking reactions were eliminated in the simultaneous interpenetrating networks (SIN’s) by combining free radical (acrylate) and condensation (epoxy) polymerisation. By this method they modified epoxy resin with poly(n-butyl acrylate) polymer. They found that a two-phase morphology emerged with the dispersed rubber domains in the range of 0.1-0.5 μm diameter. The dimension of the dispersed rubber phase domains and
the extent of molecular mixing between the two components were found to depend on the relative polymerisation rates (or gel times) in relation to the rate of phase separation.

Better mechanical properties were obtained when the reaction conditions were slightly outside the simultaneous conditions. Also in some of the SINs the main glass transition temperature was higher than the cured epoxy resin due to the entrapment of low molecular weight epoxy in the n-butyl acrylate phase.

Other reports [43,45] showed that the combination of various chemical types of polymeric networks often results in different controlled morphologies. These produced IPNs with synergistic properties such as improved adhesion, higher shock absorption and enhanced stress-strain properties.

2.3 WATER ABSORPTION IN EPOXY RESINS

The use of epoxy resins in a large number of structural applications results in their exposure to a water environment, which can cause a degradation of properties. The rate of moisture absorption is a function of temperature and humidity conditions. The sorbed water plasticises the epoxy resin, thus lowering the glass transition temperature (Tg) [46,47] and deteriorating the mechanical properties (e.g. strength and modulus) [48,49]. Absorbed water can also hydrolyse ester groups and cause chemical decomposition.

In order to understand the nature of water absorption by epoxy resins, a number of workers have studied this phenomenon [56-58,65]. Moy
and Karasz [46] examined sorption and diffusion of water in a high Tg epoxy (i.e. > 200°C) using several techniques such as DSC (differential scanning calorimetry), IR (infrared), NMR (nuclear magnetic resonance) and electronic microscopy. The results indicated that the plasticisation effect is due to a strong interaction between the dispersed water and some specific segments or groups in the polymer. However, the exact sorption sites are not clearly identified.

Antoon and Koenig [50] used FTIR (Fourier-transform infrared spectroscopy) in order to characterise the interaction of a crosslinked epoxy resin with sorbed water vapours and evaluate the vibrations of sorbed water as well as the polymer chain vibrations. The results have shown that water primarily affects the vibrations of the polar species in the polymer by a weak hydrogen bonding with these species.

Mears [51] proposed that the diffusion of penetrant molecules into polymers depends on two factors: the forces of attraction between the polymer and the penetrant molecules, and the availability of appropriate molecular size holes in the polymer network. The first factor involves the chemical nature of the penetrant and the polymer. The relatively high water absorption of epoxy resins derives from the presence of hydroxyl (OH) groups in the epoxy chains which attract the polar water molecules. The second factor, on the other hand, concerns the presence of holes determined by the polymer morphology, which in turn depends on the crosslink density and molecular chain stiffness.

Diamant and co-workers [52] proposed that the moisture diffusion into epoxy resin is influenced by four important factors, i.e. the polymer network structure, the resin polarity which determines polymer-
moisture affinity, the formation of a two-phase structure, and the development of microdamage under severe humidity conditions.

The general consensus is that in the curing of epoxy resins, groups such as hydroxyl, secondary and tertiary amines are produced [53]. Residual epoxide and primary amine groups are also present. Such functional groups are considered to be mostly responsible for the high water absorption of the epoxy resin due to the possibility of hydrogen bond formation. Furthermore, water can also react with epoxide groups leading to the formation of additional hydroxyl groups. Water also catalyses the reaction of the epoxide group with amine or hydroxyl groups.

Studies have been made to identify the sites in the cured resin structure with which the absorbed moisture interacts. These studies used IR [54] and NMR [55] and revealed that the interaction occurs at a primary or secondary amine site or at a hydroxyl site. The reports on NMR results have shown that the interaction between the resin network and the absorbed moisture is weak.

Fisher et al. [57] studied the Tg and moisture absorption of a tetraglycidyl epoxy cured with an aromatic diamine agent as a function of cure conditions. The results show that the amount of moisture absorption increased with extent of cure due to the increase in number of hydroxyl groups formed. The data confirmed that the absorbed moisture interacts primarily with the hydroxyl sites created by curing, i.e. in the vicinity or the amine groups which have reacted with the epoxy groups.
Attempts have been made to improve the hydrophobicity of epoxy resins. Barie and Sagoo [56] studied the effect of halogen containing substituents on the sorption and transport of water in cured epoxy resins, such as tetraglycidyl 4,4'-diaminodiphenyl methane/diaminodiphenylsulfoxide (TGDDM/DDS) systems. The results indicate that the introduction of halogen containing groups reduced the sorption over the whole activity range. However, the effect is greatest for the fluorine containing system. The mechanism by which the presence of halogen reduces moisture absorption is still unclear.

Fisher et al. [57] and Hu et al. [58] demonstrated that the water absorption of epoxy TGDDM/DDS can decrease significantly by reacting the residual functional groups (i.e., hydroxyl -OH, amine -NH₂, and epoxide -CH - CH₂) with appropriate blocking reagents. About 75% reduction in moisture absorption was obtained when the residual functional groups were blocked by silylation, cyanoethylation, or carboxylation. The optimum results were obtained when the blocking reagents contained fluorine.

Fluorinated epoxy resins were found to possess very low water absorption properties compared to pure unmodified epoxy resins [28]. A typical equilibrium water absorption for an immersed conventional epoxy is about 4.0% by weight. However, the fluoroepoxides were found to absorb 0.3% after one year immersion [59]. Another example shows that an anhydride cured fluoroepoxy absorbs only 0.35% by weight, whereas a conventional epoxy absorbs 3.5% or more by weight for an immersion period of six months [29].
2.4 TOUGHNESS ENHANCEMENT OF EPOXY RESINS

Epoxies and other thermosetting polymers are inherently brittle due to their highly crosslinked structure. On the other hand, thermoplastics (e.g. polycarbonate and polysulfone) are much tougher due to the large free volume available in these amorphous materials.

Nevertheless, it is surprising to note that there is a unique class of thermosetting materials having fracture energies comparable to those of thermoplastic polysulfones, namely the elastomer modified epoxy resins.

This new generation of rubber toughened epoxies are two-phase systems consisting of relatively small rubber inclusions dispersed in and bonded to the brittle epoxy matrix.

The research work on elastomer-modified resins was pioneered at the B.F. Goodrich Company over 30 years ago [60]. Research groups in companies such as Hexcel, Narmco, and Hysol-Dexter (previously Shell) have devoted considerable effort to the development and processing techniques of toughened resin products. Only some of this work has, however, been published in the patent literature. The pivotal work of McGarry and others [61-65] and the continuing effort of B.F. Goodrich [66-70] enhanced the interest for further investigation of elastomer modified epoxy resins. They produced specific additives such as CTBN and ATBN corresponding respectively to carboxyl-terminated butadiene-acrylonitrile and amino-terminated butadiene acrylonitrile, for toughening epoxy resins.
Epoxies are the only class of thermosets for which rubber toughening has been proven to be efficient. The technique has been applied to unsaturated polyesters, polyimides and even phenolics with much less satisfactory results [70].

Epoxy resins have been toughened with a variety of elastomeric substances, including reactive liquid acrylonitrile copolymers (the classic CTBN and ATBN solid rubbers), fluoroelastomers, polysiloxane, acrylonitrile rubbers, and ether-ester thermoplastic elastomers. Even with acrylonitrile butadiene styrene copolymers (ABS) some improvement in toughness has been reported [71].

The elastomeric system which has received the greatest attention is liquid carboxyl-terminated butadiene acrylonitrile (CTBN), since small amounts of CTBN added to epoxy resin significantly increase the fracture toughness of the cured systems [72-80]. These oligomers have free carboxyl groups at the chain ends, while in some cases, the acid groups are distributed along the chains. In general toughened thermosets are characterised by an increase in impact strength and a simultaneous decrease in the glass transition temperature (Tg) and modulus [76].

These polymers are available with molecular weight ranging from 3400 to 4000 and acrylonitrile contents ranging up to 26%. The representative chemical structure of CTBN is shown below:

\[
\text{HOOC} \left[ \begin{array}{c}
\text{CN} \\
- (\text{CH}_2\text{CH} = \text{CHCH}_2)_x \\
\text{CN}
\end{array} \right]_{y} \text{COOH}
\]
There are three types of reaction which can occur between these carboxyl containing polymers and epoxy resins:

a) esterification: epoxy-acid reaction

\[
\text{esterification: epoxy-acid reaction}
\]

b) etherification: epoxy-aliphatic hydroxyl reaction

\[
\text{etherification: epoxy-aliphatic hydroxyl reaction}
\]

c) esterification: acid-aliphatic hydroxyl reaction

\[
\text{esterification: acid-aliphatic hydroxyl reaction}
\]

The more important reactions are those shown in (a) and (b). The third reaction (c) may take place to a much lower extent.

Reaction (a) can be considered as a chain extension reaction (i.e. linear condensation polymerisation of CTBN and epoxy resin) leading to a build up of molecular weight. Alvey [77], Shechter and Wynstra [78] showed with model compounds that when the reaction is base catalysed (tributylamine) reaction (a) proceeds until all the acid is consumed.

Reaction (b) is a crosslinking reaction in which the remaining epoxy groups react with pendant hydroxyl groups formed in reaction (a) to form crosslinks with the chain extended molecules. This reaction may also be considered as the curing reaction of epoxy resin alone.
2.4.1 Toughening Mechanisms for Rubber Modified Epoxy Resins

A number of theories have been proposed to explain the mechanism of rubber toughening of brittle materials.

Initially, the particle tearing theory [8,79,80] was proposed as a toughening mechanism. This theory concentrated on the rubber particle. As a crack opens and propagates, the energy required to stretch and tear the rubber particle is assumed to be responsible for the high fracture toughness of rubber modified materials. This mechanism is attractive both because it is simple and also it enables a quantitative expression to be readily developed for the fracture energy [8]:

\[ G_{IC} = \frac{K_{IC}^2}{E} = G_{ICe} \left(1 - V_f\right) + \left[1 - \frac{6}{\lambda_t^2 + \lambda_t + 4}\right] \frac{4\Gamma}{V_f} \]

where:

- \( E \) = Young's modulus of elasticity of the modified epoxy resin
- \( V_f \) = volume fraction of rubbery particles
- \( \Gamma \) = fracture (or tear) energy of the particles
- \( \lambda_t \) = extension ratio at failure of the stretched portion of the particle
- \( G_{ICe} \) = fracture energy of the epoxy matrix

The crazing theory [8] suggests that the rubber particles both initiate and control craze growth in the matrix. However, this is more likely to apply to glassy thermoplastics than crosslinked polymers. Donald and Kramer [81] have shown that in thermoplastics there is a transition from crazing to a shear yielding mechanism as the length of the polymer
chain between physical entanglements decreases. Therefore, in a cured thermosetting polymer, where the crosslink density is high (i.e. the length of chain between chemical entanglements is comparatively short), then crazing is suppressed.

The multiple crazing theory [82] suggests that under tensile stress, crazes are initiated at points of maximum principal strain, which are (in general) near the equators of the rubber particles, and propagate outwards, again following planes of maximum principal strain. Craze growth terminates when a large rubber particle is encountered or when the stress concentration at the tip falls below the critical level for propagation. The presence of rubber particles results in a large number of small crazes. However, in their absence a small number of large crazes are formed.

Shear yielding and crazing mechanisms have also been suggested by several authors [83,84] to explain toughening of epoxy resins but no direct evidence has been given. The basic idea is that, in addition to crazing, plastic flow in the matrix arises from shear yield formations and that such deformations might contribute considerably to the toughening mechanism.

Some theories [71] rely on the correlation between the morphology and the deformation mechanism, indicating that shear deformations are dominant in resins toughened with small rubbery particles (< 0.1 \( \mu m \)) and crazing is dominant in resins toughened with large particles (> 50 \( \mu m \)). Furthermore, it is proposed that maximum toughness is obtained under conditions of combined shear and craze formations. This condition is achieved when both large and small particles are present.
2.4.2 Toughening Criteria of Two Phase Blends

Many authors demonstrated that the improvement of fracture energy is dependent on particle size, volume fraction, size distribution of the dispersed phase, and on the chemical structures of the matrix and the dispersed phase.

2.4.2.1 Volume Fraction

Several studies [85-87] have suggested that the volume fraction of the rubber may be the most important factor for toughness enhancement.

In general, the fracture energy ($G_c$) increases as the volume fraction ($v_f$) of the dispersed rubbery particles increases, but the modulus and yield strength usually decrease slightly [88].

A linear relation between $G_c$ and $v_f$ was found by Bucknall and Yoshii [89]. Later, however, Kinloch and Houston [90] presented conflicting observations and showed that there is no unique relationship between $G_c$ and $v_f$. They demonstrated that at low test temperatures, the relationship between $G_c$ and $v_f$ is such that $G_c$ increases very slowly with increasing $v_f$ and reaches a plateau value. However, at high test temperatures, the relation is approximately linear. Also, the rate of increase of $G_c$ with $v_f$ is much higher than that at low temperature. The results indicated that as the epoxy matrix becomes more ductile, it responds better to the presence of rubbery particles.

2.4.2.2 Effect of Particle Size and Particle Size Distribution

Several studies [73,91] have proposed that the particle size does not appear to affect the mechanical properties significantly. However, the average particle diameter was only varied between 0.5 µm to 5 µm.
In other cases [92-94], it has been suggested that the particle size may influence the toughening mechanism and hence the toughening properties. Sultan and McGarry [85] demonstrated that different particle sizes of the dispersed phase in the epoxy matrix promote different deformation mechanisms. The authors showed that systems with only small particles (0.01-0.03 μm) exhibit shear yielding and are less effective in toughening the thermoset than the large particles (0.5-5 μm), which were suggested to cause crazing. Furthermore, Riew et al. [94] suggested that maximum toughness is obtained under conditions of combined shear band and craze deformations. This condition is obtained when there is a bimodal distribution of particle sizes in the rubber toughened resin. Some workers [95-97] have explained that the variation of particle size with cure conditions is presumably caused by the effect of temperature on the rates of nucleation and growth of the dispersed phase. At low cure temperature (i.e. high viscosity) high nucleation rate and low growth rate will produce a system with smaller but more numerous particles. On the other hand, low nucleation rate and high growth rate at high cure temperature (low viscosity) will produce a system with large but less numerous particles.

Touhsaent et al. [97] on the other hand, indicated that the precipitated particle size is controlled in part by the time of phase separation in relationship to the gel time of the reaction. They also showed that smaller particles are produced when phase separation is near or after the gel point of the total reaction. In addition, the bimodal distribution of the precipitated particles reveals that the reactions are simultaneous, since the larger particles are formed before gelation and smaller particles are formed by continued phase separation after gelation.
However, Wang and Zupko [98] gave evidence for the completion of phase separation at the point of gelation, but indicated that compositional changes continued to take place. Furthermore, Gilham and Chan [99] also stated that the phase separation is complete before gelation. Mazionne et al. [75] suggested that the two-phase structure should develop during polymerisation at a time when the system is viscous enough to prevent macroscopic phase separation, but still below the gel point.

Rowe et al. [84] demonstrated the effect of acrylonitrile content on the precipitated particles. They found that the higher the acrylonitrile content of the CTBN (carboxyl-terminated butadiene-acrylonitrile rubber), the smaller the particle size, contrary to Kunz et al. [80].

2.4.2.3 Chemical Criteria for Toughening Epoxy Resins

Drake and Siebert indicated that in any rubber-modified epoxy system, the compatibility between the rubber and the epoxy resin before and during cure is a critical chemical criterion for toughening the matrix [100].

However, Riew and his co-workers suggested that the liquid polymer modifiers should have some degree of solubility in the epoxy resin without phase separation or agglomeration before gelation [73]. Furthermore, the work of Sultan and McGarry [85], and Bucknall and Yoshii [89] proposed that initially, the rubber should be completely soluble in the epoxy resin. They also suggested that the solubility depends upon the initial molecular weight of the rubber, the chemical composition of the functional groups and the solubility parameters of the rubber and the epoxy.
Gazit [93] indicated that the rubber does not contribute to the improvement of impact strength without good initial rubber dissolution. He used poly(n-butyl acrylate) modified, methylene dianiline (MDA), cured epoxy systems in his work. Others have suggested that the overall matrix toughness is probably significant, but that poor elastomer-resin compatibility during the initial phase of crosslinking prevents development of suitable particle size [83]. Some workers have concluded that the improved toughness was related to the particle size and distribution of rubber domains [101] whereas others have indicated that the resin-rubber compatibility determined the toughness [102].

Another important chemical criterion for toughening the epoxy matrix is the reactivity of functional groups of the liquid polymers. Riew and co-workers [73] demonstrated that the terminal reactive groups are more effective than pendant groups in toughening epoxy resins. Furthermore, they concluded that the liquid modifier should have at least two functional end-groups. May [103] believed that if a number of liquid rubbers similar in chemical composition but different in reactivity are used in modifying epoxy resin, the carboxyl-terminated polymer will lead to the highest toughness of the modified epoxy system.

In addition to the reactivity of terminal groups, the selectivity of the functional groups is also very important. Riew et al. [73] indicated that the acid functional end groups such as hydroxyl, phenolic, carboxylic etc are highly selective in forming anions with amine catalysts. The order of selectivity, which is the reverse of the reactivity order, is as follows: carboxylic > phenolic > hydroxylic > mercaptan [94]. It is important to note, however, that liquid polymers with mercaptan end
groups are the most reactive but give the least improvement in toughness.

The chemical bonding between the epoxy matrix and the rubbery phase is also another important criterion for toughening of the epoxy-matrix. Baum et al. [104] explained that in the absence of sufficient adhesion, the energy of a propagating crack can tear a rubber particle from the matrix, and the crack will effectively bypass the particle. They suggested that the most commonly used method to adhere rubber to a matrix is grafting.
3. EXPERIMENTAL

3.1 MATERIALS

The materials used in this investigation are described below:

3.1.1 Epoxy Resins

Several epoxy-resins were used to investigate the possibility of producing compatible systems with perfluoropolyether oligomers and to evaluate their mechanical properties. The epoxy resins are listed below.

a) Epikote 828 (manufactured by Shell Chemical Company)

Epikote 828 is widely used in industry. It is a commercial diglycidyl ether of bisphenol A (DGEBA) of medium viscosity (about 123 Pa.s at 25°C). Epikote 828 was used for the majority of the experiments in this study because of its ease of handling, high chemical resistance and the mechanical properties of the cured product. The resin has an epoxide equivalent of 182-194 (i.e. 182-194g of resin contain 1g equivalent of epoxide).

The chemical structure of diglycidyl ether of bisphenol A is:
The resin has a molecular weight to approximately 370 and an $n$ value of approximately 0.13-0.15.

b) **Epikote 155** (manufactured by Shell Chemical Company)

Epikote 155 is a polyfunctional epoxy novolac resin of high viscosity (about 60 Pa.s at 60°C). It produces highly crosslinked compositions with high dimensional stability, chemical resistance and rigidity at high temperature.

Epikote 155 has an epoxide equivalent of 190g (i.e. 190g of resin contain 1g equivalent of epoxide).

The chemical structure of the polyfunctional epoxy novolac resin is:

![Chemical structure of Epikote 155](image)

where $n$ is approximately 1.2.

c) **Araldite CY 179** (manufactured by Ciba Geigy)

Araldite CY 179 is a cycloaliphatic liquid epoxy resin. It is generally used in electrical or low viscosity applications (viscosity is 0.35 Pa.s at 25°C).

The chemical structure of the cycloaliphatic liquid epoxy resin is:
d) Araldite MX 720 (manufactured by Ciba Geigy)

Araldite MY 720 is a liquid polyfunctional epoxy resin based on glycidylated aromatic amine, i.e. tetruglycidyl 4,4' diaminodiphenyl methane (TGDDM). It is generally used for its high temperature and chemical resistance properties.

The chemical structure of tetruglycidyl 4,4' diaminodiphenyl methane is:

![Chemical structure of tetruglycidyl 4,4' diaminodiphenyl methane](image)

3.1.2 Hardeners

a) Hardener HT 907 (manufactured by Ciba Geigy)

Hardener HT 907 is hexahydrophthalic anhydride (HHPA), a low melting point solid anhydride, having a melting point around 35°C and a molecular weight of 154. When used in epoxy resins it produces stable products with excellent mechanical and electrical properties and gives almost colourless laminates with superior weathering and anti-yellowing properties [105].
The chemical structure of hexahydrophthalic anhydride is:

\[ \text{C}\text{H}_2\text{C}\text{C}\text{CH}_3\text{C\text{CH}_2\text{C}\text{O}_2\text{C}} \]

b) Hardener HT 906 (manufactured by Ciba Geigy)

Hardener HT 906 is methylnadic anhydride, a low viscosity anhydride which is easily handled. It corresponds to methyl 4 endomethylene tetrahydrophthalic anhydride having the chemical structure shown below:

\[ \text{C}\text{H}_2\text{C}\text{C}\text{CH}_3\text{C\text{CH}_2\text{C}\text{O}_2\text{C}} \]

It has a molecular weight of 179.

c) Chlorendic anhydride (obtained from Aldrich Chemical Company)

Chlorendic anhydride is endomethylene tetrahydrophthalic anhydride i.e. 1,4,5,6,7,7' hexachloro 5 norborne 2,3 dicarboxylic anhydride. It is a white powder having a molecular weight of 370 and a melting point of 335°C.
The chemical structure of endomethylene tetrahydrophthalic anhydride is:

Due to its high reactivity, chlorendic anhydride can be considered to contain a built in acid accelerator. It is normally used as an azeotropic mixture with other anhydrides because of its high melting point. It imparts flame resistance to the cured products because of its high chlorine content.

3.1.3 Catalysts

a) Benzyldimethylamine (obtained from Aldrich Chemical Company)

Benzyldimethylamine (BDMA) is widely used in epoxy resins as a catalyst for anhydride cured systems. When HHPA hardener is used the curing is normally accelerated with 1 part by weight of BDMA per hundred parts of resin (phr) at 100°C.

The chemical structure of benzyldimethylamine is:

Its melting temperature is -75°C and its boiling point is 183-184°C.
b) Triphenylphosphine (obtained from Aldrich Chemical Company)

Triphenylphosphine (TPP) is used in this study particularly in the preparation of epoxy-extended prepolymer (~3.3.1c). 

The chemical structure of triphenylphosphine is:

\[ \begin{array}{c}
\text{P} \\
\text{P} \\
\text{P}
\end{array} \]

Its melting point is 79-81°C and its boiling point is 377°C.

### 3.1.4 Perfluoropolyethers (Fomblins)

Perfluoropolyethers (PFPE) are produced commercially by a unique method developed by Montefluos SPA (the sponsoring company for this project). This method consists of a direct conversion of perfluoroolefins to oligomeric products by photooxidation.

The first step is performed by simultaneously introducing a fluorolefin such as hexafluoropropylene (HFP), tetrafluoroethylene (TFE) or a mixture of the two and oxygen into a cold reactor (i.e. 45°C or less) equipped with an immersion light source with a frequency of 2600 Hz (wave number ~ 8700 nm\(^{-1}\)). HFP acts as its own solvent while an external solvent has to be used with TFE. The fluoroligomers produced are terminated by trifluoromethyl and fluoroformate groups, while the major byproducts of the reaction (see reaction 1) are \( \text{C}_2\text{F}_4 \) or \( \text{CF}_3 \).
1. \[ \text{CF}_2 = \text{CF}X + O_2 \xrightarrow{< -45 \degree C} \text{CF}_3\text{O} (\text{CF}_2\text{CFXO})_m (\text{CF}_2\text{CF}_2\text{OO})_p (\text{CF}_2\text{OO})_q \text{CFO} + \text{XCF}_2 \text{O} \]

where \( X = \text{CF}_3 \) or \( \text{F} \)

The relative value of the repeating units can be varied over a wide range by adjusting the conditions of the reaction. The final reaction consists of a peroxide deactivation step by fluorination and heat as follows:

\[
\text{CF}_3\text{O} (\text{CF}_2\text{CFXO})_m (\text{CF}_2\text{CF}_2\text{OO})_p (\text{CF}_2\text{OO})_q \text{CFO} + \text{XCF}_2 \text{O} \xrightarrow{\text{heat}} \text{F}_2
\]

\[
\text{CF}_3\text{O} (\text{CF}_2\text{CFXO})_m (\text{CF}_2\text{CF}_2\text{OO})_p (\text{CF}_2\text{OO})_q \text{CFO} + \text{XCF}_2 \text{O} \xrightarrow{\text{heat}} \text{F}_2
\]

where \( m \) is usually very small.

The resulting neutral perfluoropolyethers consist of two products, known commercially as Fomblin Y and Fomblin Z according to whether \( X = \text{CF}_3 \) or \( X = \text{F} \).

Furthermore, the neutral perfluoropolyethers, particularly the Fomblin Z types are converted to more versatile difunctional oligomers, according to the method described below.

In the Fomblin Z series, (i.e. when TFE is used as monomer), the photooxidation reactions lead to the formation of peroxidic perfluoropolyethers of the following formula:

\[-(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-(\text{CF}_2\text{CF}_2\text{OO})_p(\text{CF}_2\text{OO})_q-\]
The peroxide groups are chemically reduced forming functional perfluoropolyethers and capped with methyl ester groups according to the following reaction:

\[
-\text{OOCF}_2\text{O-}-(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{OO-} \xrightarrow{\text{reducing agent}} \text{CH}_3\text{OH}
\]

\[
\text{CH}_3\text{OOC-} \text{CF}_2\text{O-}-(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{O-} \text{CF}_2 \text{-COOCH}_3
\]

The perfluoropolyether produced is called "Standard Fomblin ZDEAL", its molecular weight is around 2000 and has a viscosity at room temperature in the range 1-30 Pa.s.

Using the standard Fomblin ZDEAL, a number of derivatives can be obtained, through hydrolysis or reduction, i.e. Fomblin ZDEAL is transformed to acidic Fomblin ZDIAC or alcoholic Fomblin ZDOL derivatives which in turn can be reacted with an aromatic diisocyanate, ethylene oxide or epichlorohydrin leading respectively to Fomblin ZDISOC, ZDOLTX and ZE2000. In this investigation, three perfluoropolyethers were used to prepare suitable reactive modifiers for epoxy resins. Their properties, functionalities and chemical formulae are as follows:

a) Fomblin ZDOL, hydroxyl-terminated perfluoropolyether, described by the chemical formula below:

\[
\text{HOCH}_2\text{-CF}_2\text{O-}-(\text{CF}_2\text{-CF}_2\text{O})_p\text{-}(\text{CF}_2\text{O})_q\text{-CF}_2\text{-CH}_2\text{OH}
\]

The viscosity of Fomblin ZDOL at 20°C is 14.48 Pa.s. Molecular weight = 2000.
b) Fomblin ZDOLTX, hydroxyl-terminated perfluoropolyether, having the following chemical formula:

\[
\text{HO}\cdots(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CF}_2\text{O}\cdots(\text{CF}_2\text{CF}_2\text{O})_p\cdots(\text{CF}_2\text{O})_q\cdots\text{CF}_2\text{CH}_2\text{(OCH}_2\text{CH}_2\text{)}_n\cdot\text{OH}
\]

where \( n = 1-3 \).

The viscosity of Fomblin ZDOLTX at 20°C is 25.08 Pa.s.
Molecular weight = 2000.

c) Fomblin ZE2000, epoxy-terminated perfluoropolyether having the chemical formula as follows:

\[
\text{CH}_2\cdots\text{CH}-\text{CH}_2\cdots(\text{CF}_2\text{CF}_2\text{O})_q\cdots(\text{CF}_2\text{O})_p\cdots\text{CH}_2\cdots\text{CH}-\text{CH}_2\cdots(\text{OCF}_2\text{CF}_2\text{O})_p\cdots(\text{OCF}_2\text{CF}_2\text{O})_q\cdot\text{CH}_2\cdots\text{CH}-\text{CH}_2\cdots\text{O}
\]

The average molecular weight is about 4200. The viscosity of Fomblin ZE2000 at 60°C is 2.36 Pa.s.

3.1.5 Caprolactone (obtained from Aldrich Chemical Company)

Caprolactone is an internal ester, of \( \varepsilon \)-hydroxy caproic acid. Its chemical structure is shown below:

\[
\text{O} \quad \text{C} \quad \text{O} \\
\text{CH}_2 \quad \text{CH}_2 \quad \text{H}_2\text{C} \cdots \text{CH}_2
\]
It is a liquid with a boiling point of 97°C. The most important property of caprolactone is the readiness with which its ring is opened by a variety of chemicals; it can react with hydroxyl and carboxylic acid compounds (see reactions 2 and 3 respectively), and polymerises readily to caprolactones.

\[
2. \quad \text{R OH} + \text{C}-(\text{CH}_2)_5 \rightarrow \text{R O-C-(CH}_2)_5\text{-OH}
\]

\[
3. \quad \text{R COOH} + \text{C}-(\text{CH}_2)_5 \rightarrow \text{R COO-(CH}_2)_5\text{-COOH}
\]

### 3.2 PRELIMINARY EXPERIMENTS

In order to study the compatibility of various systems some preliminary mixing trials were carried out. These involved the mixing of small amounts of the various ingredients in glass beakers at room temperature and elevated temperatures (in a thermostatically controlled oil bath). The mixtures were stirred manually at room temperature or mechanically at elevated temperatures.

### 3.3 PREPARATION TECHNIQUES

#### 3.3.1 Preparation of Precursors

Three precursor systems were prepared as outlined below. The effect of varying the reaction time required for their preparation was studied and details are given with the results.
a) **Adduct:** the reaction product of Fomblin and anhydride was prepared by mixing the two ingredients in a round bottomed flask at a temperature of 150°C in a thermostatically controlled oil bath using a variable speed mechanical stirrer.

Adducts were prepared using Fomblin ZE2000 and the acid anhydrides CA and MNA, either alone or as mixtures of the two. The soluble compositions in the ternary system of Fomblin ZE2000/CA/MNA were identified and this enabled the selection of a particular adduct to be used in the preparation of formulations.

Adducts were also prepared (at 150°C) using the Fomblins ZDOL and ZDOLTX with acid anhydrides CA and HHPA to identify the solubility regions of the ternary systems of Fomblin ZDOL/CA/HHPA and Fomblin ZDOLTX/CA/HHPA. The effect of varying the molar ratio of the Fomblin/anhydride was also investigated. A particular adduct (where complete miscibility was obtained), was selected in order to prepare a "prepolymer" as described below.

b) **Prepolymer:** the reaction product of a 1:2 molar ratio of adduct (of the hydroxyl-terminated Fomblin) and ε-caprolactone was prepared by mixing as described above. In this case, however, the round bottomed flask was fitted with a reflux condenser because of the low boiling point of ε-caprolactone (97°C) with respect to the mixing temperature which was 140°C.
c) **Epoxy-extended prepolymer**: the reaction product of the prepolymer (see above), epoxy resin and triphenylphosphine was manually mixed in a beaker for five minutes and then placed in an oven maintained at 85°C. The mixture was stirred intermittently. The same procedure was used to prepare an epoxy-extended prepolymer containing two Fomblins by pre-reacting the prepolymer (see above) with an epoxy-terminated Fomblin.

In this study the effect of varying the amount of triphenylphosphine catalyst as a function of time and at constant temperature (85°C) was also carried out.

### 3.3.2 Preparation of Formulations

As a result of the preliminary experiments detailed above, various formulations were prepared using different concentrations of the totally clear solution of precursors.

The precursors and the Epikote 828 epoxy resin were mixed vigorously in a glass beaker in an oil bath at 120°C for ten minutes. The HHPA was then added and mixed for a further ten minutes at the same temperature. Finally the BDMA catalyst was added and mixed thoroughly for five minutes.

The mixed formulation was then degassed (whilst still warm) under vacuum to eliminate bubbles entrapped during the mixing process. The degassed mixture was then cast into preheated polytetrafluoroethylene (PTFE) moulds with dimensions 12 x 1.2 x 0.25 cm.
The effect of varying the amount of BDMA from 1 to 5 phr was also studied particularly for System A and System B (see below).

Several types of formulation were prepared:

a) A control formulation containing no Fomblin additive.

b) One-phase interpenetrating polymer network (IPN) systems containing either an adduct based on epoxy-terminated Fomblin or a prepolymer based on hydroxyl-terminated Fomblin.

c) Two-phase systems: System A formulations based on a prepolymer developed using hydroxyl-terminated Fomblins. System B formulations based on a prepolymer containing both hydroxyl and epoxy-terminated Fomblins (which is prepared by prereacting the prepolymer containing hydroxyl-terminated Fomblin with Fomblin ZE2000 and then further reacting with epoxy resin in the presence of the catalyst triphenylphosphine). A third system containing adduct based on epoxy-terminated Fomblin was also prepared.

3.3.3 Curing Schedule

Curing was carried out in a thermostatically controlled air oven at a constant temperature of 120°C for 24 hours. This was followed by a post-cure operation at 150°C for 3 hours and then at 180°C for 1 hour. The cured sample was allowed to cool to room temperature and then removed from the mould.
3.4 MICROSCOPY TECHNIQUES

Various microscopes and techniques were used in the course of this work and are described below.

3.4.1 Light Microscopy
In order to assess the compatibility of the ingredients of the different mixtures a simple bench-mounted transmitted light microscope was used to examine their microstructures before curing. In addition, a more sophisticated metallurgical reflected light microscope (Reichert MeF3) enabling higher magnifications, was used to examine the microstructure of cured specimens.

3.4.2 Hot Stage Microscopy
The hot stage microscope is a simple transmitted optical light microscope equipped with a Mettler FP52 temperature controlled stage (effectively a small oven). This enables microstructural changes to be observed as a function of temperature and time. The sample to be examined took the form of a droplet of the liquid mixture on a glass slide and covered with a glass slip. This thermomicroscopic technique was also used to study the compatibility of binary systems in the temperature range from room temperature to 180°C at a heating rate of 10°C/min. In addition, it was used to monitor, as a function of time at the curing temperature of 120°C, the microstructural changes which occur during the curing process.
3.4.3 Transmitted Light Interference Microscopy

This technique was used to measure the optical path difference (OPD) and hence the refractive index of particles present in the surrounding matrix.

The principle behind transmitted light interference microscopy is shown in Figure 3.1. The light from the source (S) is divided at X to pass along two paths XAY and XBY. If the optical path lengths are equal, the waves arriving at Y recombine to give a resultant wave identical to the source (S). If, however, a particle is inserted into the path XBY there will be a phase difference between the two waves arriving at Y. The phase difference is a function of the optical path difference between X and Y which in turn is a function of the diameter and refractive index of the particle.

The refractive index of the surrounding medium was measured using the Abbe 60 refractometer (see 3.4.5) and the OPD was measured using a compensator.

![Figure 3.1 Principle of transmitted light interference microscope.](image)

\[ \text{OPD} = d \times (\Delta n) \]
where \( \Delta n = \) difference in refractive index between the particle and the surrounding medium

\[ d = \text{diameter of the particle (\mu m)} \]

### 3.4.4 Scanning Electron Microscopy (SEM)

Fracture surfaces resulting from the mechanical tests were examined using the Cambridge Instruments Stereoscan 360. This instrument can be used to examine the fracture surface topography and also to map the distribution of elements on the surface.

In order to examine the topography of fractured specimens, the fracture surfaces were coated with a thin evaporated layer of gold. The X-ray microanalysis facility is an auxiliary feature of the scanning electron microscope which enables identification of the elemental constituents of the surface of the specimen being examined. In this study the distribution of fluorine on the fracture surface was mapped. This technique necessitates the coating of the fracture surfaces with carbon.

### 3.4.5 Refractive Index Measurement

Refractive index measurement was carried out using the Abbe 60 refractometer. This technique was used to measure the refractive index of cured IPN formulations only.

The specimen of unknown refractive index is placed between two prisms and illuminated with monochromatic sodium light (wavelength = 589 nm) from below. In this technique the sample is required to have highly polished and flat surfaces which were prepared using a rotary grinder. Initially a coarse grade (240 grit size) of abrasive paper was employed to
flatten the surfaces and then increasingly fine grades of paper (400 to 1200 grit size) were used to obtain a highly polished and flat surface.

3.5 PHYSICAL CHARACTERISATION

3.5.1 Infrared Analysis

Most polymeric materials tend to absorb electromagnetic radiation in the frequency range 600 to 4000 cm\(^{-1}\), i.e., in the infrared region of the spectrum. The infrared spectrometer is used to detect the absorption of energy by a specimen which arises due to molecular transitions between vibrational states. The frequency of the absorbed energy is related to the presence of particular chemical bonds in the specimen and the absorption spectrum represents a 'fingerprint' of the material by which it may be identified. For example, the C-H bond absorbs energy having a frequency between 2880 and 2900 cm\(^{-1}\). In addition, the intensities of specific absorption bands can be used to determine quantitatively the composition of polymer mixtures.

In this work, infrared spectra were obtained using a Pye Unicam SP3-200 spectrometer in the transmission mode. The sample to be analysed was supported on a sodium chloride plate and the spectra produced were used to characterise the reaction product at different stages of the reaction. In particular, the qualitative analysis of the disappearance of anhydride groups and the appearance/disappearance of carboxylic acid groups was used to give an indication of the extent of the reaction as the reaction progressed. Some examples of the spectral regions (cm\(^{-1}\)) of interest in this work are summarised below:
<table>
<thead>
<tr>
<th></th>
<th>Frequency Band</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrides</td>
<td>1800-1775</td>
<td>strong frequency band</td>
</tr>
<tr>
<td></td>
<td>1870-1775</td>
<td>weaker frequency band</td>
</tr>
<tr>
<td>Epoxide</td>
<td>1280-1230</td>
<td></td>
</tr>
<tr>
<td></td>
<td>950-750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2990-3050</td>
<td>(CH and CH$_2$)</td>
</tr>
<tr>
<td>Fluorinated groups</td>
<td>1350-1120</td>
<td>(CF$_2$ and CF$_3$)</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>1740-1680</td>
<td>(C=O stretch)</td>
</tr>
<tr>
<td></td>
<td>1315-1280</td>
<td>(C-O stretch)</td>
</tr>
<tr>
<td></td>
<td>ca. 3000</td>
<td>very broad (OH stretch)</td>
</tr>
<tr>
<td></td>
<td>1440-1395</td>
<td>(OH deformation in plane)</td>
</tr>
<tr>
<td></td>
<td>960- 875</td>
<td>(OH deformation out of plane)</td>
</tr>
</tbody>
</table>

### 3.5.2 Viscosity Measurement

Viscosity measurements were carried out using a Haake viscometer. This is a cone and plate rotational viscometer which can be used to measure the torque as a function of the speed of rotation and the test temperature. As the torque is proportional to the shear stress ($\tau$) and the speed of rotation is proportional to the shear rate ($\dot{\gamma}$) the viscosity ($\eta$) of liquids at a given temperature can be calculated from the following formula:

$$\eta = \frac{G \times \tau}{\dot{\gamma}}$$  \hspace{1cm} [mPa.s]

where $G$ is the instrument factor

$$G = 14,200 \text{ mPa.s/scale graduation.min.}$$

The instrument factor ($G$) depends on the type of measuring head and the sensor system and relates the torque and the rotation speed to the shear stress and the shear rate respectively.
In order to get an indication of the molecular weight changes during the chemical reactions, the viscosity was calculated as described above. The test temperatures and shear rates varied depending on the nature of the specimen and the actual conditions used in each case are detailed with the results. [Note: the direct determination of molecular weight using gel permeation chromatography is not possible in this case as the systems could permanently damage the column].

3.5.3 Surface Energy Measurement
Surface energy studies were performed using a contact angle (θ) measurement system (Krauss G40 goniometer), in order to examine the interaction of liquids on solid substrates. From the contact angle measurements of sessile drops of a series of pure liquids of known surface tension on smooth solid surfaces, the critical surface tension (σc) of the solid surface can be obtained. The Zisman plot is one of the methods of determining this, i.e. by extrapolation of the plot of cosine (θ) versus surface tension of liquid to zero contact angle, i.e. cosine (θ) = 1. Theoretically the contact angle is equal to zero in the case of a liquid wetting a solid surface thoroughly.

It should be noted that the results obtained by this method are dependent on the nature of the liquids used. Therefore, in this study the same liquids (triple distilled water, ethane 1,2 diol, dimethylsulfoxide, dimethylformamide) were used in all cases in order to obtain consistent results.

3.5.4 Water Absorption Studies
The water absorption of various cured formulations and raw liquid materials was measured to compare their behaviour and to assess the
potential of the functionalised perfluoropolyethers to reduce water absorption under moist conditions.

For each of the cured formulations, five to eight specimens (dimensions 25 x 12 x 2.5 mm) were weighed on an analytical balance prior to immersion in a distilled water bath at a temperature of 85°C. After various time intervals the specimens were removed and immersed in a second distilled water bath at room temperature for 15 minutes. After removal from the second bath the surface water was removed with blotting paper before the sample was re-weighed. The samples were then returned to the water bath at 85°C and the previous steps were repeated until the weight remained constant, i.e. equilibrium was achieved. For the raw liquid materials a small quantity (approximately 1g) was placed in a nylon 6 film sachet which was sealed by welding the edges. This sachet was weighed on an analytical balance before being placed in a Fisons environmental cabinet at 80°C and 90% relative humidity. The specimens were removed from the cabinet and re-weighed at various time intervals up to 350 hours.

The water absorption behaviour of liquid Fomblin after predrying in an air oven at 100°C for one hour was also investigated by the procedure outlined for raw liquid materials.

The moisture absorption $W_t$ was determined from the weight gain of the specimens, as function of time (t) according to:

$$W_t = \frac{w_t - w_0}{w_0} \times 100 \quad [\%]$$
where \( w_0 \) = initial weight (at \( t = 0 \))
\( w_t \) = weight after an immersion time (t)

In this study, the water diffusion into unmodified and Fomblin modified epoxy resin cured formulations at constant temperature was also investigated using the Fickian diffusion process

\[
\frac{W_t}{W_\infty} = \frac{4}{b} \left( \frac{D}{\pi} \right)^{1/2} t^{1/2}
\]

where \( W_t \) and \( W_\infty \) are the percentage of moisture absorbed in the specimen at time \( t \) and equilibrium respectively.

\( b \) is the thickness of the specimen [cm]

\( D \) is the diffusion constant, and can be calculated from the slope of the curve [cm\(^2\)/s].

By rearrangement of the above equation and expressing \( t \) in seconds

\[ D = \frac{\pi}{3600} \left( \frac{bk}{4W_\infty} \right)^2 \]

where \( k \) is the initial slope (%/hours\(^{1/2}\)) of the plot \( W_t \) vs \( t^{1/2} \)

and \( D \) is the diffusion coefficient.

3.5.5 High Temperature Ageing

Some of the cured samples of different formulations were conditioned at 200\(^\circ\)C for 21 days after which mechanical tests (flexural) and microscopy examinations (SEM) were carried out.
3.6 MECHANICAL CHARACTERISATION

3.6.1 Dynamic Mechanical Analysis

Dynamic mechanical tests were carried out using the Du Pont DMA-983 instrument in which a sample was clamped and subjected to flexural deformations. A sensor detects the response of the sample to the applied forces. In this mode the applied stress subjects the sample to sinusoidal oscillations at a selected frequency and amplitude (strain). Energy dissipation due to the viscoelastic nature of the sample causes the sample strain to be out of phase with the applied stress. This phase shift or lag, defined as the phase angle ($\delta$), enables the calculation of the viscoelastic properties of the material. This calculation is complex due to the involvement of many other parameters. However, the results, e.g. Young's modulus (E), storage modulus ($E'$), loss modulus ($E''$), $\tan (\delta)$ are produced directly by the Du Pont system.

The design of the DMA-983 system, is such that the test temperature, amplitude and excitation frequency can be controlled. In this investigation the tests were carried out on rectangular bars of cast resin formulations, generally of cross-section 2.5 x 12.0 mm, in the temperature range -100°C to 180°C at a test frequency of 1 Hz and a heating rate of 10°C/min.

3.6.2 Microhardness Measurement

Microhardness measurements were performed using a Reichert MeF2 microhardness tester. The microhardness was measured by making several indentations with different loads (5g-20g) for each specimen and measuring the diagonals of the impressions. The Vickers microhardness (HV) is calculated from the following equation [106]:

46
HV = 1854.4 x P/d² [kgf/mm²]

where: \( P \) = load [gf]
\( d \) = mean diagonal length of the indentation [μm].

3.6.3 Flexural Tests

Flexural strength, modulus and strain at break of cured specimens were measured at room temperature using a J.J. Lloyd bench mounted 5 kN capacity tensile testing machine. A three-point bending system was used and the crosshead speed was 10 mm/min. At least five specimens were tested for each formulation.

The specimens used for the flexural tests had the geometry shown in Figure 3.2 and the span (S) to thickness (h) ratio used was 16:1. Flexural strength, flexural modulus and strain at break were calculated using the following formulae:

- **Flexural modulus** \( (E_f) \):
  \[
  E_f = \frac{mL^3}{4bd^3} \] [MPa]

- **Flexural strength** \( (\sigma_f) \):
  \[
  \sigma_f = \frac{3PL}{2bd^2} \] [MPa]

- **Strain at break** \( (\varepsilon_f) \):
  \[
  \varepsilon_f = \frac{6d\Delta}{L^2} \times 100 \% \]

where: \( P \) = load at break [N]
\( \Delta \) = deflection at break [mm]
\( m \) = slope at 1% strain [N/mm]
\( L \) = span [mm]
\( d \) = thickness (mm)
\( b \) = width (mm)
3.6.4 Fracture Toughness Tests

The same procedure was used as for the flexural tests (Section 3.6.3) except that the specimen used for the fracture toughness tests was a single edge notched specimen in which the notch was prepared using a Charpy notch cutter. The geometry of the specimen is shown in Figure 3.3. The span (S) to width (W) ratio was 4:1 and 8:1 depending on specimen availability. Tests were carried out which established that both ratios gave the same fracture toughness value for a particular material.
The critical stress intensity factor, $K_{ic}$, was determined as the slope of $\sigma_c$ versus $1/(\gamma \sqrt{a})$ plots, i.e. $K_c = Y\sigma_c \sqrt{a}$. The crack length was varied from 2 to 8 mm. $\sigma_c$ is the nominal stress at fracture, equivalent to the flexural strength in the presence of a small notch. $Y$ is the compliance calibration factor, which is a function of the $a/w$ ratio and is obtained directly from tables [107] (e.g. MG/E/307/67). The critical strain energy release rate then determined from the calculated values of $K_c$ and flexural modulus ($E_f$) using the formula for plane stress conditions, i.e.

$$G_c = \frac{K_c^2}{E_f}$$

![Figure 3.3: Fracture Test, 3 Point Bend Specimen Geometry](image)

### 3.6.5 Bond Strength Tests

The measurement of bond strength to mild steel was carried out for different formulations. The adherend substrates used for this study were two mild steel cylindrical bars (Figure 3.4). These bars were
machined to fit directly into a tensile testing machine and also to ensure accurate alignment of the adherends. Prior to bonding, the ground flat surfaces of the steel bars were cleaned in an ultrasonic bath of alcohol for three minutes. Sufficient adhesive was applied to the surfaces of the steel bars to produce a satisfactory bond (complete coverage of the substrate). In order to control the bond thickness, 2% by weight of ballotini spheres (0.2 mm diameter) were mixed with the resin to act as internal spacers. The adhesive bond was cured using the same conditions as those used to cure the cast resin (120°C for 24 hours followed by post-curing at 150°C for 3 hours and 180°C for 1 hour).

The joint between the faces normal to the length of the two cylindrical adherends was stressed to rupture by a uniaxially applied tensile force using an Instron universal testing machine (model TT-DM). The breaking force was recorded (for five test specimens) and the bond strength is expressed as the ratio of the breaking force to the cross-sectional area of the adherend.

FIGURE 3.4: BUTT JOINT BETWEEN TWO CYLINDRICAL BARS
4. RESULTS

4.1 FORMULATIONS DEVELOPMENT

4.1.1 Solubility of Fomblins in Commercial Epoxy Resins

Examination of the compatibility of the Fomblins (see Section 3.1.4) with several commercial epoxy resins namely Epikote 828, Epikote 155, Araldite CY 179 and Araldite MY 720 (see Section 3.1.1) was carried out using the hot stage microscope (as described in Section 3.4.2). For all the different Fomblin/epoxy resin binary systems the compatibility of the two constituents was examined throughout the entire range of concentrations. However, particular attention was paid to the two extremes of the concentration range. Physical changes in the dispersed phase were monitored and recorded by taking appropriate micrographs.

a) Solubility of the epoxy-terminated Fomblin ZE2000

Microscopic examinations showed that at the very high concentrations of Fomblin ZE2000 (> 95%), the Fomblin and the epoxy resin are incompatible over the entire temperature range studied (from 20°C to 180°C). Two distinct phases were always evident and there was no appreciable change when the temperature was increased (Figure 4.1a). On the other hand, at very high concentrations of epoxy resin (97.5 to 99%) the dispersed particles of Fomblin ZE2000 become slightly smaller in diameter with increasing temperature, indicating that some solubility occurs. The cycloaliphatic resins appear to be more miscible than the aromatic resins (Figures 4.1a and 4.1c). However, complete solubilisation was never observed even at extremely low concentrations (i.e. 1%) of Fomblin ZE2000.
As two distinct phases existed in all the binary systems, the nature of the dispersed phase was investigated. The results of optical path difference (OPD) measurement (Section 3.4.3) confirmed that the refractive index (RI) of the dispersed droplet phase was similar to one of the starting materials. This established that these droplets were not air bubbles formed during the mixing of the two ingredients.

A typical OPD calculation is shown below:

\[
\text{OPD} = d \times \Delta n \quad \quad \text{(Section 3.4.3)}
\]

where:

\[
\Delta n = \text{difference in RI between the surroundings (} n_m \text{) and the droplets (} n_d \text{)}
\]

\[
d = \text{diameter of the droplets (} \mu \text{m)}
\]

For example, in a binary system containing 97.5% Araldite CY 179 and 2.5% Fomblin ZE 2000 (Figure 4.2):

Dispersed phase diameter \(d\) = 6.83 \(\mu\)m

Measured OPD = 1.180 \(\mu\)m

\(n_d\) Fomblin ZE2000 = 1.315

\(n_m\) Araldite CY 179 = 1.501

hence \(1.180 = 6.83 \times (1.501 - n_d)\)

therefore \(n_d = 1.328\)

The calculated refractive index of the dispersed phase (1.328) is close to the refractive index of Fomblin ZE2000 (1.315) and far above the value of air for which the refractive index is close to one.
Figure 4.1: Optical micrographs of mixtures of Fomblin ZE2000 and epoxy resins (x 100)
b) **Solubility of the hydroxyl-terminated Fomblins ZDOL and ZDOLTX**

The solubility results for the hydroxyl-terminated Fomblins are similar to those obtained for the epoxy-terminated Fomblins (Section 4.1.1a). This demonstrated that the Fomblins ZDOL and ZDOLTX were not compatible with epoxy resins at any concentration.

**4.1.2 Adducts Based on Epoxy-Terminated Fomblin**

The miscibility of Fomblin ZE2000 with methylnadic anhydride (MNA) and chlorendic anhydride (CA), both individually and in combination, is shown in the Fomblin ZE2000/CA/MNA ternary phase diagram (Figure 4.3). The preparation of these adducts is described in Section 3.3.1a. The diagram shows that:
FIGURE 4.3: PHASE DIAGRAM OF TERNARY SYSTEM, FOMBLIN ZE2000/MNA/CA
a) Fomblin ZE2000 and MNA are not miscible at any concentration;
b) Fomblin ZE2000 and CA are miscible in a limited concentration range (6% to 32% CA in Fomblin);
c) Fomblin ZE2000 is miscible with the azeotropic mixture of CA and MNA in the region indicated.

On the basis of the above observations the adduct Add ZE containing 60% Fomblin ZE2000 and 40% of the azeotropic mixture of anhydrides containing 80% CA and 20% MNA was selected for the preparation of formulations (see Table 4.1).

Two methods were used to prepare the formulations as shown in Table 4.2. Method B was used for the preparation of interpenetrating polymer networks (IPNs) and method A was used for the preparation of two-phase systems.

**4.1.3 Adducts Based on Hydroxyl-Terminated Fomblins**

Initial attempts to prepare adducts (as outlined in Section 3.3.1a) by the chain extension of Fomblins ZDOLTX and ZDOL involved using a 1:2 molar ratio of Fomblin/CA. However, the results in Table 4.3 show that CA was not completely solubilised in the Fomblins, i.e. an excess remained. Furthermore, these Fomblin/CA adducts were not compatible with epoxy resin (Epikote 828) at any concentration, although the excess CA would have dissolved in the resin.

Consequently, two adducts were prepared at molar ratios 1:1 and 1:1.5. The miscibility exhibited by these binary systems is summarised in Table 4.3. It is shown that:
<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F1</td>
</tr>
<tr>
<td>Formblin ZE2000</td>
<td>3.00</td>
</tr>
<tr>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Chlorendic Anhydride</td>
<td>1.60</td>
</tr>
<tr>
<td>Methylendic Anhydride</td>
<td>0.40</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>50.25</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Methylendic Anhydride</td>
<td>44.22</td>
</tr>
<tr>
<td>Benzyldimethylamine</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Notes: A = the precursor Add ZE as described in Table 4.10
       B = base epoxy resin + hardener + catalyst
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add ZE preparation:</td>
<td>Heated at 120°C for 30 min, giving a cloudy mixture (i.e. partially solubilised)</td>
<td>Heated at 120°C for 1 hour, giving a transparent mixture (i.e. fully solubilised)</td>
</tr>
<tr>
<td>- 60% Fomblin ZE2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 40% (CA[^a]/MNA[^b])(4:1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Step 2</strong></td>
<td>Mixed at room temperature for 10 min giving a milky product at room temperature remaining milky at high temperature. (i.e. partially compatible over the working temperature)</td>
<td>Mixed at 120°C for 10 min, giving an opaque product at 120°C but transparent at room temperature (i.e. exhibiting LCST* behaviour)</td>
</tr>
<tr>
<td>Mixing of Add ZE with Epikote 828[^c]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Step 3</strong></td>
<td>Mixed at room temperature giving a partially compatible system (cloudy) at both low and high temperature</td>
<td>Mixed at 120°C for 10 min giving a totally transparent compatible system at both low and high temperature</td>
</tr>
<tr>
<td>Adding MNA to the Add ZE/Epikote 828 mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Step 4</strong></td>
<td>Mixed for 5 min at room temperature, giving a milky mixture</td>
<td>Mixed for 5 min at room temperature, giving a transparent mixture</td>
</tr>
<tr>
<td>Adding the catalyst BDMA[^d] to the mixture Add ZE/Epikote 828/MNA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^a]: Chlorendic anhydride  
[^b]: Methylnadic anhydride  
[^c]: Epichlorohydrin bisphenol A. epoxy resin  
[^d]: Benzylidimethylamine  
[^e]: Preparation of two phase formulations  
[^f]: Preparation of one-phase IPN formulations  
* Lower critical solution temperature
TABLE 4.3: PHYSICAL APPEARANCE OF THE HYDROXYL-TERMINATED FOMBLIN/ACID ANHYDRIDE REACTION MIXTURES AFTER 6 HOURS AT 150°C

<table>
<thead>
<tr>
<th>Fomblin/Anhydride Molar Ratio</th>
<th>1:1</th>
<th>1:1.5</th>
<th>1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>150</td>
<td>25</td>
</tr>
<tr>
<td>Fomblin ZDOL + Chlorendic Anhydride</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Fomblin ZDOLTX + Chlorendic Anhydride</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Fomblin ZDOL + Chlorendic Anhydride (75%) + Hexahydrophthalic Anhydride (25%)</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
</tbody>
</table>

O = Opaque
T = Transparent
* = Turns cloudy as it cools down to room temperature
a) The adduct based on Fomblin ZDOL/CA is not miscible at 1:1.5 molar ratio but at 1:1 molar ratio some solubility at high temperature is obtained.

b) The adducts based on Fomblin ZDOL and the azeotropic mixture of anhydrides (i.e. 75% CA and 25% HHPA) show complete miscibility at both molar ratios. The Fomblin ZDOL/CA/HHPA ternary phase diagram is shown in Figure 4.4.

c) The adducts based on Fomblin ZDOLTX/CA also show complete miscibility at both molar ratios.

On the basis of the observations described above, more work was carried out using 1:1.5 molar ratio of the Fomblin/anhydride adducts. The physical appearance of the adducts of Fomblin ZDOL and Fomblin ZDOLTX with the acid anhydrides CA, HHPA and an azeotropic mixture (75%/25%) of the two anhydrides at 1:1.5 molar ratio are described in Table 4.4.

In terms of visual observations made at 150°C (i.e. after the reaction) and on subsequent cooling to room temperature (25°C) these show that:

a) Fomblin ZDOLTX forms a transparent product/mixture with CA after six hours reaction time and with HHPA after ten minutes reaction time.

b) Fomblin ZDOL forms a transparent product/mixture with HHPA after six hours reaction time. However, Fomblin ZDOL does not become miscible with CA even after six hours at the reaction conditions.
**TABLE 4.4: APPEARANCE OF FOMBLIN/ANHYDRIDE SYSTEMS (1:1.5 MOLAR RATIO) AT 150 AND 25°C**

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>0 min</th>
<th>10 min</th>
<th>30 min</th>
<th>1 hour</th>
<th>6 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>150 25</td>
<td>150 25</td>
<td>150 25</td>
<td>150 25</td>
<td>150 25</td>
</tr>
<tr>
<td><strong>ZDOLTX/HHPA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>0</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T CL CL</td>
</tr>
<tr>
<td><strong>ZDOL/HHPA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>T O T T</td>
</tr>
<tr>
<td><strong>ZDOLTX/CA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>T T T T</td>
</tr>
<tr>
<td><strong>ZDOL/CA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td><strong>ZDOL/(75% CA+ 25% HHPA)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0 0 0 CL</td>
</tr>
</tbody>
</table>

Note: The system * became transparent at both 150°C and 25°C after 9 hours.

0 = opaque (i.e. two-phases)
T = transparent (i.e. one-phase)
CL = cloudy (i.e. some precipitation)
a = hexahydrophthalic anhydride
b = chlorendic anhydride
FIGURE 4.4: PHASE DIAGRAM OF THE TERNARY SYSTEM FOMBLIN ZDOL/HHPA/CA
c) Although Fomblin ZDOL appears to be miscible with an azeotropic mixture of 75% CA and 25% HHPA after six hours reaction time, the product turns cloudy on cooling to room temperature.

Furthermore, mixtures of epoxy resin (Epikote 828) with the adducts based on Fomblin ZDOLTX were not compatible for the 1:1 molar ratio adduct, whilst the 1:1.5 molar ratio adduct was partially compatible. Compatibility of epoxy resin with the adducts based on Fomblin ZDOL was not observed at any of the molar ratios studied.

4.1.4 Prepolymers Based on Hydroxyl-Terminated Fomblins

Four prepolymers based on the hydroxyl-terminated Fomblins were prepared, according to the procedure outlined in Section 3.3.1a, by prereacting the Fomblin ZDOL or ZDOLTX with the acid anhydride (or an azeotropic mixture of two anhydrides) followed by further chain extension with ε-caprolactone (see Figure 4.25). The molar ratios of these prepolymers were 1:1.5:2 Fomblin/acid anhydride/ε-caprolactone and their compositions are shown in Table 4.5.

The compatibility of these prepolymers with epoxy resin (Epikote 828) is summarised in Table 4.6. It is shown that:

Prepolymer Prep 1 (also called Prep TX) based on Fomblin ZDOLTX/CA/ε-caprolactone is fully compatible with epoxy resin at any concentration after a one hour reaction time for both the adduct and the prepolymer.
FIGURE 4.25: OPTICAL MICROGRAPHS (x100) OF REACTION MIXTURE OF PREPOLYMER 'PrepTX' (i.e. 1 ZDOLTX/ 1.5 CA/ 2 CL) at different stages:

a) Initially
b) After 1 hour at 150 °C
c) After 6 hours at 150 °C
TABLE 4.5: COMPOSITION OF PREPOLYMERS BASED ON HYDROXYL-TERMINATED FOMBLIN PERFLUOROPOLYETHERS ZDOLTX AND ZDOL

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Based on Fomblin ZDOLTX</th>
<th>Based on Fomblin ZDOL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prep 1</td>
<td>Prep 2</td>
</tr>
<tr>
<td>Fomblin ZDOLTX</td>
<td>71.93</td>
<td>81.33</td>
</tr>
<tr>
<td>Fomblin ZDOL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chlorendic anhydride</td>
<td>19.85</td>
<td>-</td>
</tr>
<tr>
<td>Hexahydrophthalic anhydride (HHPA)</td>
<td>-</td>
<td>9.39</td>
</tr>
<tr>
<td>75% CA/25% HHPA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\varepsilon)-caprolactone</td>
<td>8.20</td>
<td>9.27</td>
</tr>
</tbody>
</table>

NB: These prepolymers were produced by making first the "adduct" with molar ratio Fomblin/Anhydride 1:1.5 and then reacting the "the adduct" with \(\varepsilon\)-caprolactone, so that the final molar ratios were Fomblin 1/Anhydride 1.5/\(\varepsilon\)-caprolactone 2.
### Table 4.6: Compatibility of Prepolymers (a) with Epikote 828 at Room Temperature

<table>
<thead>
<tr>
<th>Prepolymer/Epikote 828 Ratio</th>
<th>Reaction Time (b) (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prep 1</td>
</tr>
<tr>
<td></td>
<td>1+1</td>
</tr>
<tr>
<td>10/90</td>
<td>C</td>
</tr>
<tr>
<td>20/80</td>
<td>C</td>
</tr>
<tr>
<td>30/70</td>
<td>C</td>
</tr>
<tr>
<td>40/60</td>
<td>C</td>
</tr>
<tr>
<td>50/50</td>
<td>C</td>
</tr>
<tr>
<td>60/40</td>
<td>C</td>
</tr>
<tr>
<td>70/30</td>
<td>C</td>
</tr>
<tr>
<td>80/20</td>
<td>C</td>
</tr>
<tr>
<td>90/10</td>
<td>C</td>
</tr>
</tbody>
</table>

C = compatible  
NC = non-compatible  
C* = compatibility at high shearing

a) Prepolymers as described in Table 4.5.

b) X+Y hours - means X hours reaction time for the adduct (i.e. Fomblin with anhydride) and Y hours reaction time for the prepolymer i.e. adduct with ε-caprolactone
Prepolymers Prep 2 and Prep 3 based on Fomblin ZDOLTX/HHPA/ε-caprolactone and Fomblin ZDOL/HHPA/ε-caprolactone respectively are compatible with epoxy resin at very low concentrations of the prepolymer (i.e. 10 phr), and after one hour and six hours reaction times of the adduct and prepolymer respectively.

Prepolymer Prep 4 based on Fomblin ZDOL/CA:HHPA/ε-caprolactone is compatible with epoxy resin up to 50 phr of the prepolymer. The reaction times of the adduct and prepolymer are one hour and six hours respectively.

These observations led to the development of several one-phase IPN formulations which were prepared using Prep TX (as described above) and containing different amounts of Fomblin ZDOLTX as shown in Table 4.7.

4.1.5 Epoxy-Extended Prepolymer Prep TX

The Prep TX (see above) was further chain extended with epoxy resin in the presence or triphenylphosphine (TPP) catalyst at 85°C and for various reaction times (see Section 3.3.1c). Two epoxy-extended Prep TX samples were prepared at the molar ratios 1:2 and 1:4 of Prep TX to epoxy resin. The TPP catalyst concentration was varied between 0.5 to 5 phr.

The results show that as the amount of the catalyst or prepolymer increases, the extent of the reaction increases for a given reaction time and temperature. This can lead to undesirable reaction products which phase separate into two layers. Consequently, control of the extent of reaction (chain extension) is critical. For the preparation of System A
### TABLE 4.7: IPN ONE-PHASE FORMULATIONS BASED ON PREP TX

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F5</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td></td>
</tr>
<tr>
<td>Formblin ZDOL/TX</td>
<td>3.67</td>
</tr>
<tr>
<td>Chlorendic Anhydride</td>
<td>1.11</td>
</tr>
<tr>
<td>c-Caprolactone</td>
<td>0.47</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td></td>
</tr>
<tr>
<td>Epikote 828</td>
<td>52.65</td>
</tr>
<tr>
<td>Hexahydrophthalic Anhydride</td>
<td>41.56</td>
</tr>
<tr>
<td>Benzyldimethylamine</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Notes: A = the precursor Prep TX as described in Table 4.10  
B = base epoxy resin + hardener + catalyst
type two-phase formulations (see Section 3.3.2) the 1:4 molar ratio epoxy-extended Prep TX was selected. These formulations with different Fomblin ZDOLTX contents (see Table 4.8) were prepared using epoxy-extended Prep TX reacted in the presence of 1 phr TPP. Two System A formulations were prepared using the epoxy-extended prepolymer reacted for three and five hours respectively.

4.1.6 Epoxy-Extended Prepolymer Prep TX/ZE

The Prep TX/ZE, containing a combination of the two Fomblins ZDOLTX and ZE2000 was prepared by prereacting 100 parts of Prep TX with 25 parts of Fomblin ZE2000 at 85°C for various reaction times. Twenty five parts of the reaction product, i.e. Prep TX/ZE, were further reacted with 100 parts of epoxy resin in the presence of 1 phr triphenylphosphine catalyst. The product of this reaction is called epoxy-extended Prep TX/ZE.

For the preparation of the System B type two-phase formulations (see Section 3.3.2) Prep TX/ZE and epoxy-extended Prep TX/ZE were selected after reaction times of 15 hours and 30 minutes respectively. Two System B formulations were prepared with different Fomblin contents (see Table 4.9).

Those precursors (i.e. either adducts or prepolymers) selected for use in the preparation of modified epoxy resin based formulations are summarised in Table 4.10. The characteristics of the precursors and the properties of the cured formulations are presented in the remainder of this chapter.
<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P9</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>20.86</td>
</tr>
<tr>
<td>Fomblin ZDOLTX</td>
<td>3.65</td>
</tr>
<tr>
<td>A Chlorendic Anhydride</td>
<td>1.10</td>
</tr>
<tr>
<td>e-Caprolactone</td>
<td>0.46</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>0.21</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>31.68</td>
</tr>
<tr>
<td>B Hexahydrophthalic Anhydride</td>
<td>41.51</td>
</tr>
<tr>
<td>Benzylidimethylamine</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Notes:  
A = epoxy-extended Prep TX as described in Table 4.10  
B = base epoxy resin + hardener + catalyst
TABLE 4:9 PRECIPITATED (TWO-PHASE) FORMULATIONS BASED ON EPOXY-EXTENDED PREPOLYMER CONTAINING TWO PERFLUOROPOLYETHERS (i.e. SYSTEM B)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F11</td>
</tr>
<tr>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Formblin ZDOLTX</td>
<td>2.42</td>
</tr>
<tr>
<td>Chlorendic Anhydride</td>
<td>0.73</td>
</tr>
<tr>
<td>ε-Caprolactone</td>
<td>0.30</td>
</tr>
<tr>
<td>Formblin ZE2000</td>
<td>1.24</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>18.86</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>0.19</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Epikote 828</td>
<td>33.96</td>
</tr>
<tr>
<td>Hexahydrophthalic Anhydride</td>
<td>41.73</td>
</tr>
<tr>
<td>Benzyldimethylamine</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Notes:  
A = epoxy-extended Prep TX/ZE as described in Table 4.10  
B = base epoxy resin + hardener + catalyst

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### TABLE 4.10: PRECURSOR COMPOSITIONS

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Add ZE</th>
<th>Prep TX</th>
<th>Epoxy-extended Prep TX</th>
<th>Epoxy-extended Prep TX/ZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fomblin ZDOL/TX</td>
<td>-</td>
<td>71.93</td>
<td>13.86</td>
<td>10.19</td>
</tr>
<tr>
<td>Fomblin ZE2000</td>
<td>60.00</td>
<td>-</td>
<td>-</td>
<td>5.25</td>
</tr>
<tr>
<td>Chlorendic Anhydride</td>
<td>32.00</td>
<td>19.85</td>
<td>4.20</td>
<td>3.09</td>
</tr>
<tr>
<td>Methyl nadic Anhydride</td>
<td>8.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ε-Caprolactone</td>
<td>-</td>
<td>8.20</td>
<td>1.77</td>
<td>1.30</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>-</td>
<td>-</td>
<td>79.36</td>
<td>79.36</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>0.80</td>
</tr>
</tbody>
</table>
4.2 CHARACTERISTICS OF ADDUCTS AND PREPOLYMERS OF PERFLUOROPOLYETHERS

4.2.1 Infrared Spectra

The infrared spectra of the reaction products of Fomblin ZE2000 with an azeotropic mixture (80/20) of chlorendic anhydride/methylnadic anhydride for different reaction times are shown in Figure 4.5. A comparative examination of the different spectra reveals the formation of ester groups which are characterised by the strong absorption near 1740 cm\(^{-1}\) due to the carbonyl group C=O stretching frequency and by the strong absorption involving the stretching of C-O near 1200 cm\(^{-1}\). However, it is difficult to detect the latter absorption band due to the large absorption peak of C-F masking all the regions between 1330-1050 cm\(^{-1}\). It is also difficult to monitor the disappearance of epoxide groups near 1280-1230 cm\(^{-1}\). The anhydrides are characterised by two bands in the carbonyl region: a stronger band near 1800-1775 and a weaker band near 1870-1775 cm\(^{-1}\).

The infrared absorption spectra of the adduct based on the hydroxyl-terminated perfluoropolyether Fomblin ZDOLTX and chlorendic anhydride taken at different reaction times are shown in Figure 4.6. A comparison of the spectra reveals a decrease of the free hydroxyl (-OH) band around 3400-3500 cm\(^{-1}\), and the appearance of an absorption band at around 3000-3200 cm\(^{-1}\) corresponding to the stretching of (OH) of the carboxyl (COOH) groups (see Section 3.5.1). However the disappearance of OH groups can be explained if the unreacted terminal OH groups in the Fomblin chains of prep TX react with the -COOH groups of the same chain. Hence the exact mechanism of the reactions taking place remains unknown. The formation of ester groups (-COO-)
FIGURE 4.5: INFRARED SCANS OF THE REACTION PRODUCT OF FOMBLIN ZE2000/MNA/CA SYSTEM
FIGURE 4.6: INFRARED SCANS OF THE REACTION PRODUCT OF FOMBLIN ZDOLTX/CA AT 1:1.5 MOLAR RATIO
is also revealed around 1750 cm\(^{-1}\) with an absorption band which increases as the reaction time increases.

**4.2.2 Viscosity Data**

The viscosity data show that all systems, even for the higher viscosity materials, are Newtonian (see Appendix). Figure 4.7 presents the viscosity measurements at a constant shear rate (i.e. 192 sec\(^{-1}\), chosen for convenience) of adducts and prepolymer of Fomblin ZDOLTX at different molar ratios. The viscosity of each system was measured after 6 hours reaction time at 150°C and after a storage period of three months at room temperature in order to assess the storage stability (shelf life) of these systems.

It is observed that as the molar ratio of CA/Fomblin increases the viscosity increases for both adducts and prepolymer (see Figure 4.7). The reaction with ε-caprolactone increases the viscosity of the system indicating that the reaction cannot be one of simple end capping, but also chain extension. Furthermore after a storage period of three months at room temperature the systems containing ε-caprolactone do not show any change in viscosity. This indicates that the more reactive chloroendic acid groups have probably reacted completely and that they have been replaced with the less reactive caproic acid groups. It also indicates that the reaction product is stable.

Figure 4.8 show the viscosity of adducts and prepolymer based on the combination of the two Fomblins ZDOLTX and ZE2000, as a function of reaction time. Once again, the increase in viscosity in the presence of ε-caprolactone indicates the occurrence of chain extension reactions. In addition, the adduct TX/ZE shows a gradual increase in viscosity with
Figure 4.7: Viscosity of adduct and prepolymer based on Fomblin ZDOLTX

Molar ratios:
1. 1 TX/1 CA
2. 1 TX/1 CA/2 CL
3. 1 TX/1.5 CA
4. 1 TX/1.5 CA/2 CL
5. 1 TX/2 CA
6. 1 TX/2 CA/2 CL

A = 6 hours reaction time at 150°C.
B = 6 hours reaction time at 150°C and aged for 3 months at room temperature.

Note: The viscosity measurements were carried out at 60°C and at 192 s⁻¹ shear rate.
FIGURE 4.8: EFFECT OF REACTION TIME ON VISCOSITY OF ADDUCTS AND PREPOLYMERS based on both Fomblins (ZDOLTX and ZE2000) (Temperature=60°C ; Shear rate=192 s⁻¹)

![Graph showing the effect of reaction time on viscosity of adducts and prepolymer based on Fomblins (ZDOLTX and ZE2000). The graph displays the viscosity in Pa.s against reaction time in hours. The prepolymer TX/ZE and adduct TX/ZE are compared.]
time, while the prepolymer TX/ZE displays a constant viscosity followed by a drastic increase after 15 hours reaction time. This increase in viscosity may be due to a further reaction (chain extension).

The results of viscosity measurements of epoxy-extended adducts and prepolymer based on Fomblin ZDOLTX at 25 and 50 parts per hundred parts of Epikote 828 are presented in Figure 4.9. This shows that an increase in molar ratio of CA to Fomblin causes an increase in viscosities, similar to the results for the adducts and prepolymer (see Figure 4.7). The viscosities of the epoxy extended adducts and prepolymer decrease with increasing the amount of epoxy resin used. In most cases the viscosity values for 1 hour and 4 hours reaction time are similar, indicating that possibly only end capping reactions are occurring rather than chain extension.

Figure 4.10 shows a particular example of the change in viscosity as a function of time of the epoxy-extended prepolymer ZDOLTX at molar ratio 1 ZDOLTX: 1.5 CA: 2 CL and at 25 parts of prepolymer per hundred parts of Epikote 828. This diagram shows a small reduction in viscosity after 4 hours, followed by a very rapid decrease after 5 hours. Visual inspection shows that this is the result of the precipitation of particles of Fomblin prepolymer due to the occurrence of crosslinking reactions.
FIGURE 4.9: EFFECT OF REACTION TIME ON VISCOSITY OF EPOXY-EXTENDED ADDUCTS AND PREPOLYMER BASED ON FOMBLIN ZDOLTX.
(Temperature=60°C; Shear rate=192 s⁻¹)

- 100 parts Epikote 828/25 parts adduct or Prepolymer
- 100 parts Epikote 828/50 parts adduct or Prepolymer
- 1 TX/1.5 CA
- 1 TX/1.5 CA/2 CL
- 1 TX/2 CA
- 1 TX/2 CA/2 CL
FIGURE 4.10: EFFECT OF REACTION TIME ON VISCOSITY OF EPOXY-EXTENDED PREPOLYMERS 'PrepTX'. (Temperature=60°C; Shear rate= 192 s⁻¹)
4.3 MORPHOLOGY DEVELOPMENT IN THE CURING OF IPN AND TWO-PHASE SYSTEMS

As explained in Section 3.4.2, this study was carried out on a hot stage microscope at 120°C for both one-phase and two-phase systems at 3.67% Fomblin concentration. The results are presented in Figures 4.11 and 4.12 respectively.

For one-phase IPN systems, the mixture of all the ingredients (i.e. Prepolymer ZDOLTX, Epikote 828, hexahydrophthalic anhydride and catalyst) at room temperature gave a clear solution. However, the microscopic examination (Figure 4.11a) shows some precipitated particles which dissolve at high temperature, i.e. 120°C (see Figure 4.11b). These particles appear as well formed crystals and are believed to consist essentially of HHPA, probably swollen by epoxy resin. After 4 minutes, the system is fully gelled and remains homogeneous as shown in Figure 4.11c.

For two-phase systems, Figure 4.12a shows the mixture of all the ingredients (i.e. epoxy-extended prepolymer ZDOLTX, Epikote 828, hexahydrophthalic anhydride and catalyst) at room temperature prior to curing. Small nuclei are observed before the reaction starts, evolving into spherical particles as the cure proceeds at 120°C. These particles grow in diameter until the system gels, i.e. after 4 minutes. In Figures 4.12b, 4.12c and 4.12d, the phenomenon is clearly illustrated, revealing also a substructure within each precipitated particle. Very diffuse (highly swollen) precipitated particles of epoxy-extended prepolymers are clearly seen dispersed in the surrounding of epoxy resin and HHPA mixture.
FIGURE 4.11: OPTICAL MICROGRAPHS OF THE CURING-PROCESS OF ONE-PHASE IPN SYSTEM AT 3.65% FOMBLIN ZDOLTX
a) at zero curing time, room temperature (X400)
b) at intermediate stage, 2 mins at 120°C (system not gelled) (X400)
c) After 4 mins at 120°C (system fully gelled) (X400)
FIGURE 4.12: OPTICAL MICROGRAPHS OF THE CURING AND PHASE SEPARATION PROCESSES OF A TWO-PHASE SYSTEM (SYSTEM A) AT 3.67% FOMBLIN ZDOLTX
a) at zero curing time, room temperature (X400)
b) at intermediate stage of cure (i.e. 2 mins at 120°C (X400)
c) fully gelled system (i.e. 4 mins at 120°C) (X400)
d) Fully gelled system (X800)
4.4 PROPERTIES OF CROSSLINKED UNMODIFIED AND PERFLUOROPOLYETHER MODIFIED EPOXY-RESIN FORMULATIONS

The general appearance of castings produced from both one-phase IPN and precipitated (two-phase) formulations is shown in the photograph in Figure 4.13. It is shown clearly that the IPN specimens are transparent, while the two-phase specimens are opaque, indicating that phase separation had occurred.

4.4.1 Scanning Electron Microscopy Analysis

The detailed post-failure examination of fracture specimens (see Section 3.6.4) performed using scanning electron microscopy (SEM) is summarised below.

Figure 4.14 shows the fracture surface of the unmodified epoxy-resin specimen (i.e. control specimen). It shows essentially a brittle fracture with fibrils within a coaxial two layer sheath.

For one-phase transparent specimens containing the prepolymer Prep TX based on Fomblin ZDOLTX (see Table 4.7) Figure 4.15 shows similar sharp ridges along the direction of the crack propagation, which become smoother as the amount of Fomblin ZDOLTX in the sample increases.

For two-phase opaque specimens obtained with the epoxy-extended prepolymer, based on Fomblin ZDOLTX prepolymer, and the prepolymer produced with a combination of the two Fomblins ZDOLTX + ZE2000, Figures 4.16, 4.17 and 4.18 display typical distributions of
FIGURE 4.13: PHOTOGRAPHS OF EPOXY CASTINGS CONTAINING VARIOUS AMOUNTS OF PRE-REACTED FOMBLINS, SHOWING ONE-PHASE IPNs AND TWO PHASE PRECIPITATED MICROSTRUCTURES
FIGURE 4.14: SEM MICROGRAPHS OF FRACTURE SURFACES OF UNMODIFIED EPOXY RESIN
FIGURE 4.15: SEMs of fracture surfaces of Fomblin ZDOLTX modified epoxy resin (i.e. IPNs, one phase formulations) at (A) 3.67%; (B) 8.58%; (C) 15.47% and (D) 25.82% Fomblin ZDOLTX content.
Figure 4.15 (continued)
regular particles embedded in the epoxy resin matrix. The size of the in situ formed particles ranges from 0.5 μm to larger than 20 μm diameter. However, one notes that in the first series of formulations based on Fomblin ZE2000 (see Figure 4.16) the systems were opaque right from the beginning indicating that the Fomblin ZE2000 was never fully solubilised and, therefore, contained nuclei for subsequent particle evolution, without the need to produce these through the production of an epoxy-extended adduct or prepolymer, while in the second case, Fomblin ZE2000 was fully solubilised before making the extended prepolymer. It is possible that in the latter case the Fomblin ZE2000 component of the prepolymer precipitates first and accelerates the precipitation of the component of the prepolymer based on Fomblin TX/CA/CL which develops around it. It can be seen that the size of the precipitated particles of specimens obtained from the epoxy-extended prepolymer ZDOLTX (i.e. containing Fomblin ZDOLTX) are larger than those obtained from the epoxy-extended prepolymer ZDOLTX/ZE2000 (i.e. containing a combination of the two Fomblins ZDOLTX + ZE2000). In other words, the presence of Fomblin ZE2000 seems to promote the formation of small particles.

Figures 4.17 and 4.18 indicate that the particles are densely packed and that increasing the initial amount of perfluoropolyether prepolymer does not appear to produce a proportionate increase in volume fraction of the precipitated particles.

In all of the two-phase systems, the crack runs through the particles which are clearly seen (in Figures 4.17b-4.17d) to slow down the crack propagation by a particle tearing mechanism. It seems, in fact, that in all cases the cracks form in the matrix and then propagate into the
FIGURE 4.16: SEMs OF FRACTURE SURFACES OF FOMBLIN ZE2000 MODIFIED EPOXY RESIN AT 5.80% FOMBLIN CONTENT: (A) ONE PHASE IPN SYSTEM; (B) AND (C) TWO PHASE PRECIPITATED
FIGURE 4.17: SEMs of fracture surfaces of FOMBLIN ZDOLTX modified epoxy resin (System A), observed at different magnifications: (A), (B) at 3.62% FOMBLIN and (C), (D), (E) at 5.65% FOMBLIN.
FIGURE 4.18: SEMs of fracture surfaces of Fomblin (ZDOLTX + ZE2000) modified epoxy-resin (system B), observed at different magnifications: (a), (b), (c) at 3.67% Fomblins and (d), (e), (f) at 5.65% Fomblins
Figure 4.18 (continued)
particles from the equator towards the centre. Furthermore, the particle-matrix bond appears to be perfect with no signs of debonding observed.

Figure 4.19 shows the fracture surfaces of an epoxy-extended prepolymer Prep TX modified epoxy resin cured formulation at 3.65% Fomblin ZDOLTX content. Figures 4.17a and 4.17b show the fracture surfaces of a similar formulation. However, the only difference between the two formulations is that the total reaction time of the prepolymer for the second one is five hours (i.e. one hour more than for the first) at which some precipitation had occurred.

Figure 4.19 shows agglomerations of the particles embedded in the surrounding matrix. Furthermore, the micrographs 4.19b and 4.19c in particular indicate a lack of adhesion between the agglomerates and the main matrix.

The micrograph on the right of Figure 4.20 is an X-ray map. The white spots forming dense circles correspond to the distribution of fluorine detected in the precipitated particles. There are also some white spots in the matrix which correspond to fluorine detected in the underlying particles and perhaps in the matrix.

Figures 4.21 to 4.24 show the fracture surfaces of specimens aged at 200°C for 21 days. In general, the fracture surfaces of the aged samples were less smooth than those of the non-aged samples.

The control sample, i.e unmodified epoxy resin shown in Figure 4.21, has a less fibrillar appearance than that of the non-aged sample (Figure 4.21).
FIGURE 4.19: SEMs OF FRACTURE SURFACES OF FOMBLIN ZDOLTX MODIFIED EPOXY RESIN (i.e. SYSTEM A WITH 5 HOURS REACTION TIME OF THE EPOXY-EXTENDED PREPOLYMER)
FIGURE 4.20: ENERGY DISPERSIVE X-RAY ANALYSES MAP DETECTING FLUORINE AT FRACTURED SURFACE OF FOMBLIN ZDOLTX MODIFIED EPOXY RESIN (SYSTEM A) AT 5.67% FOMBLIN CONTENT
FIGURE 4.21: SEMs OF FRACTURE SURFACES OF AGED CONTROL (UNMODIFIED) FORMULATIONS
FIGURE 4.22: SEMs of fracture surfaces of aged IPN formulations at 25.6% FOMBLIN ZDOLTX
4.14). In the case of IPN one-phase formulations (Figure 4.22), the microstructure differs slightly from that of the non-aged sample (Figure 4.15) in that the IPN microstructure appears to be more pronounced in the aged sample. These micrographs clearly show the presence of heterogeneous domains for the IPN systems dispersed in the parallel direction to the base of the specimens, however, they have a very fine and diffuse geometry, insufficient to create internal light scattering.

In the System A and System B two-phase formulations (Figures 4.23 and 4.24 respectively), the general appearance of the fracture surfaces (i.e. the number, size and the size distribution of the particles) was similar in the aged and non-aged samples. A particularly interesting feature observed only in the aged samples of System A is that a small number of particles appear to have 'pulled out' of the matrix. Such behaviour was not observed in any other samples.
FIGURE 4.23: SEMs OF FRACTURE SURFACES OF AGED SYSTEM A FORMULATIONS WITH 3.6% FOMBLIN ZDOLTX
FIGURE 4.24: SEMs OF FRACTURE SURFACES OF AGED SYSTEM B FORMULATIONS WITH 3.6% TOTAL FOMBLIN (ZDOLTX + ZE2000)
4.4.2 Water Absorption Data

The results of water absorption studies (see Section 3.5.4) on Fomblin ZE2000 and uncured epoxy resins are shown in Figure 4.27. These show that the water absorption of Fomblin ZE2000 is two orders of magnitude lower than that of epoxy resin. Further, a considerable reduction in water absorption is achieved when the functionalised oligomer is preheated at 100°C, possibly due to the removal of solvent residues.

The water absorption data for the unmodified and perfluoropolyether modified epoxy resin cured formulations are plotted (see Figures 4.28 to 4.30) as percent of water uptake versus square root of time in hours. Figure 4.28 presents the water uptake results for the control (i.e. unmodified resin) and one-phase IPN formulations containing Fomblin ZDOLTX. Initially (after 3 hours immersion) all the formulations with different Fomblin ZDOLTX contents absorb nearly the same amount of water, which is greater than for the control formulation (see Figures 4.28b and 4.31). On the other hand, as the immersion time increases to 466 hours the opposite behaviour is observed, i.e. the control absorbs more water and, as the amount of Fomblin ZDOLTX in the epoxy increases, the water uptake appears to decrease. However, the decrease is not very large (see Figures 4.28a and 4.32).

Figure 4.29 shows the water absorption of the control and that of two-phase formulations containing either the Fomblin ZDOLTX (System A) or a combination of the two Fomblins ZDOLTX and ZE2000 (System B). At short immersion times (3 hours), the control formulation absorbs more water than the two-phase formulations (see Figures 4.29b and
FIGURE 4.27: WATER ABSORPTION AT 80°C AND 90% RELATIVE HUMIDITY

- Dried Fomblin ZE2000
- Non-dried Fomblin ZE2000
- Dried Epikote 828
FIGURE 4.29: WATER ABSORPTION OF CONTROL AND TWO-PHASE CURED FORMULATIONS

(a)

(b)
FIGURE 4.30: WATER ABSORPTION OF CONTROL AND ONE-PHASE IPN CURED FORMULATIONS BASED ON FOMBLIN ZE2000
Figure 4.31: Water absorption of Control and modified cured formulations at 85°C and after 3 hours immersion time.

Figure 4.32: Water absorption of Control and modified cured formulations at 85°C and after 466 hours immersion time.
### Table 4.11: Summary of Water Absorption Data

<table>
<thead>
<tr>
<th>Content</th>
<th>Control</th>
<th>One-phase IPNs</th>
<th>Two-phase System A</th>
<th>Two-phase System B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>0</td>
<td>3.65</td>
<td>8.58</td>
<td>15.47</td>
</tr>
<tr>
<td>(wt %)</td>
<td></td>
<td>3.65</td>
<td>8.58</td>
<td>15.47</td>
</tr>
<tr>
<td></td>
<td>1.07</td>
<td>1.11</td>
<td>1.05</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.135</td>
<td>0.148</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.164</td>
<td>0.163</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>3.66</td>
<td></td>
<td></td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.141</td>
<td></td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>0.158</td>
<td></td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td></td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>W = % weight gain after 466 hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k = initial slope of graph W versus t^{1/2}, i.e. up to 17 hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D = diffusion coefficient (see Section 3.5.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.31): at long immersion times (466 hours), the control absorbs less water (see Figures 4.29a and 4.32).

In addition, Figure 4.29 indicates that the formulations based on Fomblin ZDOLTX absorb less water than those based on a combination of the two Fomblins ZDOLTX and ZE2000 (System B). Figure 4.28 also shows that the difference in the amount of Fomblin present does not significantly affect the level of water absorption.

The data in Figures 4.28a and 4.29a indicate that equilibrium water absorption is approached after about 400 hours.

Figure 4.30 shows the water absorption behaviour as a function of square root of time in hours ($t^{1/2}$) at 100°C for unmodified and Fomblin ZE2000 modified epoxy resin cured IPN formulations with 12% Fomblin content. It reveals once more that for IPN formulations at low immersion time (3 hours), the modified formulations absorb more water than the control. However, at longer immersion times a contrary behaviour is observed, i.e. the modified formulations absorb less water than the control formulation.

The obtained diffusion constants and the calculated slopes $k$ of the plot (% weight gain) versus ($t^{1/2}$), using a least-squares technique (see Section 3.5.5) are given in Table 4.11.

4.4.3 Refractive Index Data

The results of the refractive index measurements are plotted as a function of the concentration of Fomblin in the formulation in Figure
Figure 4.33: Refractive index of IPN cured formulations as function of Fomblin concentration

(a)

(b)
4.33. The plots show an almost linear decrease in refractive index as the amount of Fomblin increases.

The plots for formulations containing Fomblin ZE2000 and those containing Fomblin ZDOLTX appear to coincide (see Figure 4.33a). A closer examination at lower concentrations of Fomblins (see Figure 4.33b) however, shows a slight shift of the two plots.

Increasing the Fomblin concentration produces a reduction in refractive index from 1.5587 for unmodified epoxy resin to 1.5137 for a composition containing 25.82% Fomblin ZDOLTX.

4.4.4 Surface Energy Results
The results in Table 4.12 show that the surface energy decreases rapidly even with small amounts of Fomblin (i.e. 3.5%) for both one-phase and two-phase cured formulations based on Fomblin ZDOLTX. The results also indicate that the surface energy is uniform throughout the cured cast specimen.

4.4.5 Microhardness Results
The microhardness results which are presented in Table 7.7 (see Appendix), are plotted in Figure 4.34 as a function of Fomblin content, indicate that the microhardness of one-phase formulations containing Fomblin ZDOLTX is inversely proportional to the Fomblin content, i.e. it decreases linearly with increasing Fomblin concentration. It is interesting that the microhardness extrapolates to zero at approximately 50% Fomblin, i.e. when the material is expected to behave like a soft rubber.
<table>
<thead>
<tr>
<th></th>
<th>Fomblin Content (wt %)</th>
<th>Surface Energy (mN/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>30.3</td>
</tr>
<tr>
<td>One-phase IPNs</td>
<td>3.5</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>25.8</td>
<td>16.7</td>
</tr>
<tr>
<td>Two-phase</td>
<td>3.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.1</td>
</tr>
<tr>
<td>System A</td>
<td>3.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>3.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Calculation of the critical surface energy was made according to ZISMAN method (see appendix p.199)

a: measurements on the top surface of the casting
b: measurements on the bottom surface of the casting
c: measurements on the inner surface of sectioned casting

Surface tension of test fluids:

- Water: 72.8 mN/m
- Ethanediol: 47.6 mN/m
- DMSO: 42.6 mN/m
- DMF: 35.9 mN/m
FIGURE 4.34: MICROHARDNESS OF IPN CURED FORMULATIONS AS FUNCTION OF FOMBLIN ZDOLTX CONCENTRATION

![Graph showing the relationship between hardness and Fomblin Zdoltx concentration. The hardness decreases linearly as the concentration increases.](image)

HARDNESS (Kgf/mm²)

AMOUNT OF FOMBLIN ZDOLTX (%)
FIGURE 4.35: MICROHARDNESS TEST EXAMINATION, INDENTATIONS ON THE MATRIX AND THE PRECIPITATED PARTICLES OF SYSTEM B AT 3.75% FOMBLIN ZDOLTX + ZE2000 (X1000)
For two-phase formulations, the microhardness of the precipitated particles is lower than that of the matrix (see Table 7.7), which in turn has almost the same value as the unmodified control formulation. The microhardness of the precipitated particles suggests that these contain approximately 25% Fomblin. The micrograph in Figure 4.35 shows the larger indentation in the precipitated particles than in the matrix.

4.4.6 Adhesive Bond Strength

The results of adhesive bond strength (to mild steel) are shown in Table 4.13, and in Figure 4.36 which presents the plot of the adhesion of hydroxyl-terminated perfluoropolyether modified epoxy resin (one-phase IPN systems) as a function of the amount of Fomblin ZDOLTX used. This plot indicates that as the amount of Fomblin increases, the adhesion to mild steel increases, both with and without ballotini spheres. This is unexpected insofar as the reduction in surface energy (see Table 4.12) would suggest a deterioration in adhesion. Note, however, that the two-phase systems appear to exhibit a stronger bond than IPN systems, possibly owing to their intrinsic higher toughness.

4.4.7 Flexural Properties

Table 4.14 shows the results obtained from flexural tests on unmodified and perfluoropolyether modified epoxy resin, for all the formulations described in Section 3.6.3. Flexural modulus, flexural strength and percent strain at break are plotted as a function of Fomblin concentration in Figures 4.37, 4.38 and 4.39 respectively.

As expected, in all cases the use of the Fomblin perfluoropolyethers produces a reduction in modulus. However, for both two-phase systems A and B, increasing the Fomblin concentration causes
### Table 4.13: Bond Strength Measurements

<table>
<thead>
<tr>
<th></th>
<th>Adhesion strength (MPa)</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Without</td>
<td>With</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ballotini spheres</td>
<td>Ballotini spheres</td>
</tr>
<tr>
<td></td>
<td>Fomblin Content (wt %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Control</td>
<td>One-phase IPNs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.55 ± 3.46</td>
<td>37.50 ± 4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.02 ± 1.56</td>
<td>5.88 ± 1.00</td>
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<tr>
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<td></td>
<td>0</td>
<td>8.58</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>40.88 ± 5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.05 ± 0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>15.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42.96 ± 2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.04 ± 3.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>25.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>45.05 ± 2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.24 ± 2.86</td>
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<tr>
<td></td>
<td></td>
<td>3.67</td>
<td>11.70 ± 3.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.60</td>
<td>9.22 ± 1.50</td>
</tr>
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</table>
FIGURE 4.36: ADHESIVE BOND STRENGTH OF IPN SYSTEMS AS FUNCTION OF FOMBLIN ZDOLTX CONTENT

- Without Ballotini Spheres
- With Ballotini Spheres

ADHESION TO MILD STEEL (MPa)

AMOUNT OF FOMBLIN ZDOLTX (%)

0 10 20 30 40 50

0 10 20 30

120
### TABLE 4.14: FLEXURAL PROPERTIES OF FOMBLIN MODIFIED FORMULATIONS

<table>
<thead>
<tr>
<th></th>
<th>Formulation</th>
<th>Flexural Strength (MPa)</th>
<th>Modulus at 1% Strain (GPa)</th>
<th>Strain at Break (%)</th>
</tr>
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<tbody>
<tr>
<td><strong>Control</strong></td>
<td>0</td>
<td>76.13 ± 3.90</td>
<td>3.37 ± 0.25</td>
<td>2.65 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>131.68 ± 15.12</td>
<td>2.31 ± 0.16</td>
<td>2.90 ± 0.50</td>
</tr>
<tr>
<td></td>
<td>8.58</td>
<td>127.60 ± 20.70</td>
<td>2.71 ± 0.41</td>
<td>3.60 ± 0.60</td>
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<tr>
<td><strong>One-phase IPNs</strong></td>
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<td></td>
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<tr>
<td></td>
<td>15.47</td>
<td>107.64 ± 10.16</td>
<td>2.80 ± 0.20</td>
<td>3.00 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>25.82</td>
<td>85.82 ± 10.20</td>
<td>3.20 ± 0.20</td>
<td>3.50 ± 0.50</td>
</tr>
<tr>
<td><strong>Two-phase System A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td>81.87 ± 16.72</td>
<td>2.14 ± 0.23</td>
<td>3.76 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>3.66&lt;sup&gt;b&lt;/sup&gt;</td>
<td>94.10 ± 6.50</td>
<td>2.50 ± 0.25</td>
<td>5.08 ± 1.12</td>
</tr>
<tr>
<td></td>
<td>3.66&lt;sup&gt;c&lt;/sup&gt;</td>
<td>51.13 ± 5.70</td>
<td>1.49 ± 0.04</td>
<td>2.17 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>5.63</td>
<td>98.40 ± 13.50</td>
<td>2.16 ± 0.17</td>
<td>7.37 ± 1.70</td>
</tr>
<tr>
<td><strong>Two-phase System B</strong></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>133.20 ± 3.50</td>
<td>2.40 ± 0.33</td>
<td>8.09 ± 1.30</td>
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<tr>
<td></td>
<td>5.66</td>
<td>105.00 ± 6.80</td>
<td>2.27 ± 0.18</td>
<td>6.88 ± 1.00</td>
</tr>
</tbody>
</table>

Note: a, b and c are two-phase formulations which are modified with prepolymer Prep TX reacted for 3, 4 and 5 hours respectively.
FIGURE 4.37: FLEXURAL MODULUS OF IPN AND TWO-PHASE CURED FORMULATIONS AS FUNCTION OF FOMBLIN CONTENT

![Bar chart showing flexural modulus of one-phase and two-phase IPNs as a function of FOMBLIN content.](chart1.png)

FIGURE 4.38: FLEXURAL STRENGTH OF IPN AND TWO-PHASE CURED FORMULATIONS AS FUNCTION OF FOMBLIN CONTENT

![Bar chart showing flexural strength of one-phase and two-phase IPNs as a function of FOMBLIN content.](chart2.png)
Figure 4.40: Fracture Energy of IPN and Two-Phase Cured Formulations as Function of Fomblin Content

Figure 4.39: % Strain at Break of IPN and Two-Phase Cured Formulations as Function of Fomblin Content
reduction in modulus, contrary to one-phase IPN systems, which show an increase in modulus, after the initial drop (Figure 4.37).

It is very important to note, however, that the modified systems show much higher flexural strength than the control. For example, an IPN system exhibits a 42% increase on addition of only 3.65% Fomblin ZDOLTX to the epoxy network.

The strain at break of the modified systems is higher than that of the control, and an increase in Fomblin concentration results in an increase in the strain at break. However, the increase in strain at break is much larger for two-phase systems than for IPN systems. Furthermore, for System B, the specimens yielded but did not actually break in the test. The values presented in Table 4.14 are the maximum strains reached during the test.

The effects of ageing the specimens for two weeks at 200°C in an air oven are shown in Table 4.15 and Figures 4.41 and 4.42. These results again demonstrate the superior mechanical properties of the Fomblin modified systems. In particular the IPN systems show an increase in strain at break after ageing, proportionally to the amount of Fomblin used. This is very unusual behaviour which is rarely observed with crosslinked polymeric materials and is particularly attractive for design engineers.

The flexural properties of Fomblin ZE2000 modified formulations are presented in Table 4.16. It is shown that for both one-phase and two-phase systems, the properties are improved for small additions of Fomblin ZE2000.
Table 4.15: The Effect of Ageing on the Flexural Properties of Fomblin Modified Formulations

<table>
<thead>
<tr>
<th>Fomblin (wt %)</th>
<th>Flexural Strength (MPa)</th>
<th>Strain at Break</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Ageing</td>
<td>After Ageing</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>76.12 ±3.90</td>
<td>38.40 ±11.90</td>
</tr>
<tr>
<td>One-phase IPNs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.65</td>
<td>131.68 ±15.12</td>
<td>75.84 ±13.87</td>
</tr>
<tr>
<td>8.58</td>
<td>127.60 ±20.70</td>
<td>78.55 ±3.44</td>
</tr>
<tr>
<td>15.47</td>
<td>107.65 ±10.16</td>
<td>75.08 ±15.40</td>
</tr>
<tr>
<td>25.82</td>
<td>85.82 ±10.20</td>
<td>63.44 ±3.76</td>
</tr>
<tr>
<td>Two-phase System A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.66</td>
<td>94.10 ±6.50</td>
<td>72.54 ±7.95</td>
</tr>
<tr>
<td>5.63</td>
<td>98.40 ±13.50</td>
<td>65.93 ±5.80</td>
</tr>
<tr>
<td>Two-phase System B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.65</td>
<td>133.20 ±3.50</td>
<td>71.73 ±2.80</td>
</tr>
<tr>
<td>5.60</td>
<td>105.00 ±6.80</td>
<td>70.54 ±6.22</td>
</tr>
</tbody>
</table>
FIGURE 4.41: PROPERTIES OF TWO-PHASE CURED FORMULATIONS BEFORE AND AFTER AGEING AT 200°C FOR 21 DAYS

### Flexural Strength (MPa)

- **CONTROL**
- **SYSTEM B**
- **SYSTEM A**

<table>
<thead>
<tr>
<th>Amount of Fomblin (%)</th>
<th>Before ageing</th>
<th>After ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.65</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5.6</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3.66</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5.63</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

### Strain at break (%)

- **CONTROL**
- **SYSTEM B**
- **SYSTEM A**

<table>
<thead>
<tr>
<th>Amount of Fomblin (%)</th>
<th>Before ageing</th>
<th>After ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.65</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>5.6</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>3.66</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>5.63</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>
FIGURE 4.42: PROPERTIES OF ONE-PHASE CURED FORMULATIONS BEFORE AND AFTER AGEING AT 200°C AND 21 DAYS

- Flexural Strength (MPa)
- Strain at break (%)

Amount of Fomblin ZDOLTX (%):
- 0
- 3.65
- 8.58
- 15.47
- 25.82

Before ageing, After ageing
# Table 4.16: Flexural Properties of Fomblin ZE2000 Modified Formulations

<table>
<thead>
<tr>
<th></th>
<th>Fomblin ZE2000 (wt %)</th>
<th>Flexural Strength (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td>0</td>
<td>76.12 ± 3.90</td>
<td>2.65 ± 0.30</td>
</tr>
<tr>
<td><strong>One-phase IPNs</strong></td>
<td>3</td>
<td>120.50 ± 5.00</td>
<td>4.30 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>110.00 ± 11.00</td>
<td>4.42 ± 0.80</td>
</tr>
<tr>
<td><strong>Two-phase Systems</strong></td>
<td>6</td>
<td>139.2 ± 20.20</td>
<td>5.42 ± 0.70</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>96.22 ± 9.10</td>
<td>4.30 ± 0.23</td>
</tr>
</tbody>
</table>
### TABLE 4.17: FRACTURE ENERGY PROPERTIES FOR FOMBLIN MODIFIED FORMULATIONS

<table>
<thead>
<tr>
<th></th>
<th>Fomblin (wt %)</th>
<th>$K_C$ (MN.m$^{3/2}$)</th>
<th>$G_C$ (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td>0</td>
<td>1.15</td>
<td>0.39</td>
</tr>
<tr>
<td><strong>One-phase IPNs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>2.36</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>8.58</td>
<td>2.46</td>
<td>2.16</td>
</tr>
<tr>
<td><strong>Two-phase System A</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.66$^a$</td>
<td>2.26</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>3.66$^b$</td>
<td>2.25</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>3.66$^c$</td>
<td>1.02</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>5.63</td>
<td>2.24</td>
<td>2.32</td>
</tr>
<tr>
<td><strong>Two-phase System B</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>2.50</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>5.66</td>
<td>2.32</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Note: $a$, $b$ and $c$ are two-phase formulations which are modified with Prepolymer Prep TX reacted for 3, 4 and 5 hours respectively.
4.4.8 Fracture Toughness

Compared to the control specimens, all the modified systems exhibit a significant increase in fracture energy \( G_c \). (see Figure 4.40). The highest values are for System B with 3.65% of Fomblins ZDOLTX + ZE2000 in which \( G_c \) is about sevenfold higher than that of the control.

The effect of varying the reaction time in the preparation of the epoxy-extended prepolymer ZDOLTX of System A at low Fomblin ZDOLTX content are presented in Table 4.17. For 3 and 4 hours reaction time, the results are quite similar to the IPN systems, however, for five hours reaction time, the results present a drastic decrease in all mechanical properties. A similar behaviour was found with respect to flexural properties (Table 4.14). For this reason, the reaction time for the preparation of the epoxy-extended ZDOLTX prepolymer was kept at 3.5 hours in all cases.

4.4.9 Dynamic Mechanical Analysis

Figures 4.43 to 4.45 show the dynamic loss modulus, \( E'' \), as a function of temperature of the cured epoxy resin based formulations. They also show the effect of modification of the epoxy resin with Fomblin oligomers.

Figure 4.43 shows the effect of Fomblin content of one-phase IPN cured formulations on dynamic loss modulus, \( E'' \). In general, as the amount of Fomblin ZDOLTX increases the following features are immediately obvious:

There is a downward shift in the \( \alpha \)-transition of the epoxy resin, reducing the glass transition temperature from 150°C in the unmodified
FIGURE 4.43: DMA TRACES OF ONE-PHASE IPN FORMULATIONS AS A FUNCTION OF FOMBLIN ZDOLTX CONTENT
FIGURE 4.44: DMA TRACES OF TWO-PHASE (SYSTEM A) AS A FUNCTION OF FOMBLIN ZDOLTX CONTENT
FIGURE 4.45: DMA TRACES OF TWO-PHASE (SYSTEM B) AS A FUNCTION OF FOMBLINS (ZDOLTX+ZE2000) CONTENT
epoxy resin to around 122°C for 25.82% Fomblin content (see also Figure 4.46).

There is a gradual shift, to higher temperatures of the β-transition of the epoxy resin, normally associated with relaxations due to CH₂-CHOH-CH₂ groups.

There is a reduction in the height of the $E''$ peak at the glass transition temperature (see also Figure 4.48) and a broadening of β-transition (see Figure 4.47).

There is also a gradual increase of the loss modulus, $E''$, across the entire temperature range (-100 to 180°C).

Figures 4.44 and 4.45 show the effect of Fomblin content of the two-phase cured formulations (System A and System B respectively) on the dynamic loss modulus, $E''$.

For System A and System B there is a decrease in the height of the $E''$ peak compared to the control formulation. For System A, an increase in the Fomblin content does not reduce the Tg although it does decrease the peak height of the α-transition. For System B there is a decrease in both the glass transition temperature and the peak height.
Figure 4.46: THE GLASS TRANSITION TEMPERATURE AS FUNCTION OF FOMBLIN CONTENT OF BOTH ONE-PHASE (IPN) AND TWO-PHASE CURED SYSTEMS

[Diagram showing the glass transition temperature as a function of Fomblin content for IPNs, System A, and System B.]
FIGURE 4.47: THE HEIGHT OF PEAK (α) AS FUNCTION OF FOMBLIN CONTENT OF BOTH ONE-PHASE (IPN) AND TWO-PHASE CURED SYSTEMS
FIGURE 4.48: THE WIDTH OF PEAK ($\alpha$) HALF HEIGHT AS FUNCTION OF FOMBLIN CONTENT OF BOTH ONE-PHASE (IPN) AND TWO-PHASE CURED SYSTEMS

$W_{\alpha}$

Amount of Fomblin (%)
5. DISCUSSION

5.1 CHEMICAL MODIFICATION OF FOMBLINS

All the perfluoropolyethers examined (Fomblins ZE2000, ZDOL and ZDOLTX) are incompatible with epoxy resins. However, these findings are not surprising because of the poor compatibility in general of fluorocarbon polymers with epoxy resins [17]. This incompatibility results in a two-phase mixture which then phase separates into two bulk layers. The infrared technique confirmed that the top layer is epoxy resin and the bottom layer consists mainly of Fomblin. This is due to the denser nature of Fomblin.

Several workers [60] have indicated that in any rubber modified epoxy system, the compatibility between the modifier and epoxy resin before cure is an important chemical criterion for toughening of the matrix.

In an attempt to improve the compatibility of the Fomblin and epoxy resin, the next objective in this work was to chemically modify the perfluoropolyether. Several workers approached this type of problem by modifying either the resin or the modifier itself. In general, chemical pre-reaction of the modifier has been the preferred route and several examples are discussed below.

Liquid PBDs (carboxyl-terminated and hydroxy-l-terminated liquid polybutadienes) were used by Dusek and co-workers [108] to modify diglycidyl ether of bisphenol A (DGEBA) epoxy resin. They too observed poor compatibility of the modifier (functional PBD) with epoxy resin and
miscibility was increased by: (a) pre-reaction of the carboxyl (-COOH) groups with epoxy groups of the resin and (b) by attaching a polyester block, formed by an in situ reaction of monoepoxide and cyclic anhydride (such as HHPA) to the OH or COOH groups of the PBDs.

The use of a fluorocarbon elastomer (Viton GF) to modify epoxy resin (DGEBA) was investigated by Mijovic and co-workers [17]. Once again poor compatibility was observed and the Viton GF was modified, in an attempt to improve the compatibility, by the introduction of a double bond into the main chain followed by the addition of various polar groups on the double bond. However full miscibility was not achieved.

In this present work, since the Fomblin/epoxy resin system has to be crosslinked by the addition of hardener, the first attempt to improve its compatibility was to pre-react the Fomblin with the hardener. For this particular study anhydride hardeners were selected rather than the amine types which tend to adversely affect the colour of the fluoropolymer.

5.1.1 Epoxy-Terminated Fomblin

The original aim of the sponsoring company (Montefluos) was to investigate the use of Fomblin ZE2000 (i.e. epoxy-terminated perfluoropolyether) to modify commercial epoxy resins for use in high-performance applications (e.g. aerospace).
As a result of extensive investigation into the compatibility and reactivity of Fomblin ZE2000 it was found that the reaction product of Fomblin ZE2000 with an excess of the azeotropic mixture of chloroendic anhydride and methylnadic anhydride (i.e. approximately three times the molar amount required to produce acid-terminated groups) improved the compatibility with epoxy resin. This reaction product was called Add ZE.

Throughout this study, azeotropic mixtures of anhydrides were used in order to reduce the high melting point of chloroendic anhydride (i.e. 335°C) and therefore to increase the rate of dissolution in the perfluoropolyether. The curing of the Fomblin ZE2000 modified epoxy resin based formulations resulted in either a one-phase interpenetrating polymer network (IPN) or a two-phase structure, depending upon the initial solubility of the anhydride mixture in the Fomblin (see methods A and B in Table 4.2) and the reaction product of Fomblin/anhydride (Add ZE) in the epoxy resin. In other words, when this initial solubility was not obtained then the final cured product was opaque.

The cured Fomblin ZE2000 modified formulations have better mechanical properties (see Table 4.16) but their water absorption behaviour was not improved (see Figure 4.30). However, the use of Fomblin ZE2000 presented three major problems:

a) the mixture of epoxy resin and prepolymer based on Fomblin ZE2000 was not stable during storage at 23°C, i.e. the viscosity increased and eventually led to gelation;
b) a maximum of approximately 20% prepolymer (i.e. 12% Fomblin ZE2000) could be incorporated into the epoxy resin in view of its high reactivity leading to crosslinking during mixing.

c) subsequent batches of Fomblin ZE2000 oligomers behaved differently due to the difficulty of obtaining the same degree of epoxidation. The prepolymers so produced showed very low compatibility with epoxy resin (i.e. approximately 5%). These difficulties made it necessary to seek a different approach to the production of the prepolymer modifiers.

5.1.2 Hydroxyl-Terminated Fomblins

The new route was based on the alternative modifiers Fomblin ZDOL and Fomblin ZDOLTX which are hydroxyl-terminated perfluoropolyethers. These Fomblins were first reacted directly with a suitable anhydride and subsequently chain extended with ε-caprolactone to increase their solubility in epoxy resin whilst maintaining their acid functionality. The anhydrides used were: chlorendic anhydride (CA); hexahydrophthalic anhydride (HHPA) and the azeotropic mixture of the two anhydrides (i.e. 75% CA/25% HHPA). In this study HHPA was used in preference to MNA as it has been suggested by previous workers [109] that HHPA results in better mechanical, electrical and thermal properties and an almost colourless cured product (compared to the yellowish product obtained using MNA).

In order to achieve ideal chain extension, i.e. extension from both ends of the Fomblin chain, a 1:2 molar ratio of Fomblin to anhydride is required. In this work, a 1:2 molar ratio plus a 10% excess of anhydride was used with the aim of obtaining carboxyl (COOH) end
groups. This molar ratio should give rise to higher molecular weight adducts through polycondensation.

However, the adduct formed was not compatible with epoxy resin (at any concentration) even after further reaction (chain extension) with \(\epsilon\)-caprolactone.

In order to prepare either one-phase or two-phase formulations, it is necessary for the starting materials to be totally compatible before curing. Otherwise, phase separation into two bulk layers is observed before curing (as discussed earlier). Therefore, further work was carried out using the different Fomblin/anhydride molar ratios 1:1 and 1:1.5 (plus 10% excess of anhydride), with the view of obtaining lower molecular weight acid functionalised oligomers. The adducts so formed were further chain extended with \(\epsilon\)-caprolactone. Pre-reacting these Fomblins with acid anhydrides at different molar ratios (see Section 4.1.3) revealed that those anhydrides used (CA, HHPA and the azeotropic mixture of 25% HHPA and 75% CA) were more miscible and reactive with the Fomblin ZDOLTX than with the Fomblin ZDOL. It is believed that the difference observed is related to the chemical structure since Fomblin ZDOLTX contains not only hydroxyl (OH) end groups but also the repeat unit (-O-CH\(_2\)-CH\(_2\))\(_n\) where \(n = 1.5\). These should promote solubilisation of anhydrides in the Fomblin.

Furthermore, the mixture of the pre-reacted Fomblin/anhydride with standard DGEBA epoxy resin exhibits only partial physical compatibility and produces unstable systems owing to chemical reaction during storage. Further chain extension with \(\epsilon\)-caprolactone induced total compatibility (i.e. at any concentration) of the prepolymer.
based on Fomblin ZDOLTX with the epoxy resin. However, only up to 50 phr of prepolymer based on Fomblin ZDOL was compatible with the epoxy resin. Therefore more work was performed on the prepolymer based on Fomblin ZDOLTX (i.e. Prep TX) at the molar ratio of 1:1.5:2 of Fomblin ZDOLTX: chlorendic anhydride: ε-caprolactone.

The idealised reaction sequences (Reactions 4 and 5) and the chemical formulae of the copolymers formed are depicted below. Reaction 4 of the hydroxyl-terminated Fomblin with acid anhydride to produce an adduct and subsequent Reaction 5 of adduct with ε-caprolactone to produce a prepolymer.

Reaction 4: the reaction of hydroxyl-terminated Fomblin with acid anhydride to produce an adduct by the mechanisms of end capping by chlorendic anhydride and polycondensation.
Reaction 5: reaction of the adduct with \(\varepsilon\)-caprolactone to produce a prepolymer by the mechanism of end capping with \(\varepsilon\)-caprolactone.

\[
\text{(B)} + 2 \quad \overset{\text{O}}{\text{C}} - (\text{CH}_2)_5 \rightarrow \overset{\text{O}}{\text{C}} - \text{Perfluoropolyether chain} - \overset{\text{O}}{\text{C}} - (\text{CH}_2)_5 \overset{\text{O}}{\text{OH}}
\]

The infrared analyses and the viscosity data together indicate clearly that chemical reactions (as described in Section 3.3.2b) took place by not only end capping but also chain extension (see Sections 4.2.2a and 4.2.2b). An increase in the molar ratio of Fomblin ZDOLTX to CA increased the viscosity of the Prep TX due to the production of high molecular weight species. It is inferred that the compatibility achieved was a direct consequence of the chemical modification and the molecular weight of the perfluoropolyether. In this work it was found that the compatibility decreases with increasing molecular weight of the modifier (Prep TX). The optimum molecular weight (the molecular weight at which complete miscibility with DGEBA epoxy resin is achieved) is obtained using a molar ratio of 1:1.5:2 of the Prep TX.

However, above or below this optimum molecular weight (i.e. at molar ratios 1:2:2 and 1:1:2) a non-compatible and a partially compatible pre-reacted Fomblin/epoxy resin system are obtained respectively. In the first system (i.e. at 1:1:2 molar ratio) it is possible that insufficient
conversion of the terminal OH groups in the perfluoropolyether chains took place. However in the second case (i.e. at 1:2:2 molar ratio) where total conversion of the terminal OH groups is expected, the solubility decreased. This decrease is probably due to the high molecular weight of the pre-reacted Fomblin chains.

The first section of this discussion has considered the chemical modification of the Fomblins in order to overcome their incompatibility with epoxy resin. This involved extensive mixing trials and subsequent characterisation of the reaction products. This work resulted in the development of suitable modifiers (pre-reacted Fomblins as summarised in Table 4.10) which were used in the preparation of epoxy based formulations. The physical and mechanical properties of the cured formulations are discussed in the second part of this chapter.

5.2 MORPHOLOGY DEVELOPMENT DURING CURE

A combination of techniques such as optical microscopy, scanning electron microscopy (SEM), and dynamic mechanical analysis (DMA) gave useful insights into: compatibility in the various systems; phase separation processes; structure development in one-phase IPN and two-phase systems.

The hot stage microscope examinations allowed morphological developments to be followed at the curing temperature (120°C). The observations were indicative of the morphological changes which occur during the curing of bulk samples. The phase separation process in two-phase systems (see micrographs in Figure 4.12) shows clearly that the development of morphology proceeds by a classic nucleation and
growth mechanism from an initially homogeneous system. The nucleation process, which was characterised by the segregation of domains from the matrix, was observed after two minutes at 120°C. These domains appeared as regular spherical particles which continued to grow until the degree of conversion of the system was close to the gel point (four minutes). It should be noted that the reported times at which segregation (two minutes) and the gel point (four minutes) occur may not indicate the actual times required for curing of the bulk samples (castings) because the hot stage microscope technique necessitates the use of relatively small samples. However, phase separation during the first few minutes of curing was also observed by Chan and Gillham [110] who monitored changes in the level of light transmission as the curing reaction proceeded. They also observed a small degree of phase separation after gelation.

The cure of an initially homogeneous solution consisting of epoxy resin, curing agent and rubber generally involves the sequential processes of phase separation, gelation and vitrification [75,111,112]. During cure, phase separation of the rubber occurs as a result of the increase in molecular weight which lowers the compatibility of the rubber with the epoxy system. However, at later stages in the curing process, separation is prevented by the high viscosity of the resin which accompanies gelation and subsequent vitrification. It has also been suggested [113] that two factors can cause phase separation: precipitation induced by the curing agent and the increase in the molecular weight of the rubber-epoxy molecules.

In this study, there was some indication that varying the concentration of the catalyst BDMA affected the morphology development of the
precipitated particles. At low BDMA content (i.e. between 0.5 and 2 phr) the two-phase cured systems contained a small number of large particles which were more or less oval in shape. This is due to a low nucleation rate and a high growth rate. On the other hand, increasing the BDMA content (i.e. from 2.5 to 5 phr) gave rise to a large number of smaller particles which indicates a high nucleation rate and a low growth rate. Consequently, the amount of BDMA catalyst has an important effect on the rates of nucleation and growth of the dispersed phase. As reported elsewhere [96] increasing the curing temperature has an opposite effect, i.e. at high curing temperatures a system with large but less numerous particles is produced.

It should be noted that the final size of the dispersed particles also depends on whether phase separation takes place before or after gelation. If gelation takes place before phase separation the crosslinks will tend to hold the domains together and the pre-existing network will limit the size of the domains. If, on the other hand, the phase separation takes place before gelation the crosslinks will tend to hold the phase domains apart and the domains are likely to be larger. In fact, the rather large domains observed (see Figures 4.17d and 4.18f) strongly suggest that phase separation or at least some degree of phase separation precedes gelation. If this were not the case the domain size would be controlled by the network and would probably produce small (1 μ) domains as reported elsewhere [114].

In general, the two-phase formulations (System A and System B) appear to have bimodal distributions of particle size which are indicated by the presence in large numbers of small (<1 micron diameter) and large (> 20 micron diameter) particles. The large particles may be agglomerates of
small primary particles (ca. 1 micron diameter) as has also been observed for CBTN modified epoxy resins [115]. However, the difference in size between the large and the small particles is more pronounced in System B than System A.

Siebert and Riew [8] suggested that the size range of the particles formed may be dependent on the balance of two complementary processes: the aggregation of particles and the chain extension process. However, Sayre et al. [116] indicated that the rubber precipitates and agglomerates to form large particles during curing. At the same time, more particles of different sizes may be formed through either precipitation or molecular weight increase.

In this study it is surprising to note that the particle size and the volume fraction of the precipitated particles did not appear to increase in direct proportion to the increase in the concentration of perfluoropolyether, contrary to results reported elsewhere [116]. This is probably due to the fact that some Fomblin perfluoropolyether remains dissolved within the epoxy resin as a result of the high compatibility of pre-reacted Fomblin and epoxy resin or that the particles are so small that they cannot be seen. The X-ray emission analyses showed clearly that the precipitated particles contain fluorine and also gave an indication that the matrix contained some fluorine (see Figure 4.20). It is possible that the fluorine detected in the matrix is due to precipitated particles underlying the surface and not to the dissolved Fomblin in the matrix. However, the observed depression of the glass transition temperature with the increase of Fomblin content, (as determined by DMA) indicated the presence of some Fomblin in the matrix network.
Similar results have been obtained by Mijovic et al. [17] who modified thermosetting resins using fluoroelastomers.

The observed high volume fraction of the precipitated phase relative to the initial amount of the modifier suggests a large degree of epoxy sub-inclusion in the precipitated particles of the two-phase systems. This can be confirmed for System B in Figure 4.18f which shows some inclusions of a material within the precipitated phase which have an appearance similar to that of the matrix. This is probably due once more to the high compatibility of the epoxy-extended prepolymer and epoxy resin.

5.3 PROPERTIES OF CURED EPOXY RESIN BASED FORMULATIONS

The scanning electron micrographs of the fracture surfaces of the cured perfluoropolyether modified epoxy resin based formulations reveal clearly:

a) the one-phase nature of the structure of IPN cured formulations;
b) the particulate nature of the precipitate in two-phase cured formulations.

The fracture surface of the unmodified anhydride cured formulation (i.e. the control) shows a fibrillar structure which is typical of brittle fracture of unmodified epoxy resin based formulations as shown by Dusek et al. [116]. This brittle behaviour is due to the high crosslink density of the cured system. A similar fibrillar structure was obtained by Ting [117] who related this to the tearing of ligaments which are the result of crack

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propagation. Also, he suggested that the tearing marks are along the
direction of crack propagation.

For modified IPN one-phase formulations, similar marks were observed.
However, the marks in this case were not as pronounced as in the
control samples and their appearance became less noticeable as the
Fomblin content increased.

For two-phase formulations cracks grew until their propagation was
slowed down or stopped by a tearing mechanism in the precipitated
phase particles as shown clearly in Figures 4.16c, 4.17b and 4.17e.

For aged specimens of the two-phase systems a similar structure to that
of non-aged samples was observed. However, in System B some
particles appear to have been pulled out of the matrix. There are signs
of debonding due to poor adhesion between the matrix and the rubber
particles. This suggests that there is some weakening of bonds in the
vicinity of the interface and an embrittlement of the matrix, both
resulting in poor mechanical properties (see later).

On the other hand, for IPN aged systems, the structure shows some fine
lamellae less than 0.5 \( \mu \text{m} \) thickness which are not apparent before
ageing.

In contrast to the results of previous workers, the water absorption data
shown that the halogen containing modifiers (based on Fomblin) did not
significantly affect the water absorption (at equilibrium) of the epoxy
resin. It has been shown that the introduction of halogen containing
groups reduces the water absorption and that the greatest reduction is obtained for fluorine containing systems [15,55].

One of the factors which may affect the water absorption of Fomblin modified epoxy based formulations is the formation of a less dense network, as indicated by the broad E" curves, which allows the water molecules to penetrate more easily to reach the highly polar OH, and possibly COOH, groups to form strong H-bonding associations.

This hypothesis finds some support from the calculated diffusion coefficients which show clearly that water diffused more readily into the IPN systems than into the two-phase systems. Table 4.12 also indicates that at short immersion times (three hours), the rate of water absorption by IPNs is higher than that by the two-phase systems. However, the opposite behaviour is observed at long immersion times (466 hours) showing that the rate of water absorption by the two-phase system is higher than that by the IPNs. This may be due to the presence of the precipitated particles which may contain microvoids to act as reservoirs for the absorbed water after an extended period of immersion.

The considerable reduction in water absorption of the predried perfluoropolyether oligomer compared to the non-dried one is linked to the observed development of turbidity and subsequent regaining of its water-clear appearance during the heat treatment. It can be inferred that some hygroscopic residual contaminants are present in the functionalised Fomblin. These precipitate out at first and then either volatilise or react with the Fomblin.
The perfluoropolyether modified formulations present other interesting properties. The most important ones are the increases in fracture energy, flexural properties and adhesive bond strength to mild steel. However, there was some decrease in other properties such as modulus and the glass transition temperature. The properties of unmodified (control) and perfluoropolyether modified formulations including one-phase IPNs and two-phase systems (System A and System B) are compared below. Unless indicated otherwise the comparisons are based on systems containing about 3.5% total Fomblin.

The fracture energy ($G_c$) was increased the most, i.e. by 453% for IPN systems and by 566% for two-phase System A and by a minimum of 613% for the two-phase System B. It was also observed that the increase in $G_c$ was more dependent on Fomblin concentration than on precipitated particle size (see Table 4.17).

For the two-phase formulations, the difference between the fracture energies of System A and System B is attributed to their modifiers, i.e. epoxy-extended prepolymer Prep TX and epoxy-extended prepolymer Prep TX/ZE respectively. These modifiers have different chemical properties such as molecular weight, chemical structure and reactivity. The chemical properties in turn affect both the morphological (i.e. phase precipitation, particle size, particle size distribution, interfacial bonding etc.) and the mechanical properties of the cured modified systems. The chemical composition of the precipitated particles (dispersed phase) depends upon the prereacted modified Fomblin-epoxy extended precursor adduct which can chain-extend further and crosslink with additional epoxy resin, hardener and catalyst during curing.
Many workers have reported that carboxyl-terminated butadiene acrylonitrile (CTBN) rubber, which is a reactive liquid rubber, constitutes one of the more effective elastomers for toughening epoxy-resins. McGarry and Sultan [118] reported an eight fold increase in fracture energy (from 175 to 1548 J/m$^2$) by the incorporation of 10 phr of CTBN rubber. Later, Rowe and co-workers achieved a fifteen fold improvement in fracture energy by the addition of 5 phr of CTBN [66]. In this particular study the highest fracture energy was obtained for System B, i.e. the formulation modified by the combination of two Fomblins (Fomblin ZDOLTX and Fomblin ZE2000), containing about 3.6% total Fomblin. A seven fold increase in the fracture energy ($G_f$), i.e. from 390 to 2680 J/m$^2$ was observed (Table 4.16). This is obviously due to the presence of the precipitated particles dispersed in the matrix which blunt the crack tip. The mechanism is likely to be somewhat different from that obtained with CTBN insofar as the particles are not rubbery but softer than the matrix and are probably capable of yielding.

The flexural strength was also improved by 73% for IPN systems, 23% for two-phase System A and 75% for two-phase System B at the concentration exhibiting maximum fracture toughness. Furthermore, the strain at break increased by 94% for IPN systems, 92% for two-phase System A and 200% for two-phase System B. Moreover, specimens of System B yielded but did not break in the flexural tests and the value quoted above represents the strain at which the specimen was pushed out of the support (see Table 4.14).

The modulus at 1% strain decreased by 32.4% for IPN systems, 26% for two-phase System A and 29% for two-phase System B (see Table 4.13).
reduction in modulus with increasing Fomblin content. However, this finding is not surprising due to the fact that the modulus of the precipitated particles is lower than that of the epoxy phase.

In general, an increase in Fomblin content increased the strain at break and fracture energy ($G_f$). These increases were more marked in the case of IPN systems. An opposite effect was observed for the two-phase systems i.e. the fracture energy and the particle size of the precipitated particles depend on the molecular weight of the modifier (epoxy-extended prepolymer or adduct) which in turn is strongly affected by reaction time and temperature.

For the two-phase System A, optimum properties of the cured product correspond to a optimum viscosity (which is directly related to the molecular weight) of the epoxy-extended Prep TX reacted for four hours at 85°C. A gradual precipitation of the prepolymer began to take place at longer reaction times. Incorporation of such a prepolymer into epoxy resin led to the deterioration of all mechanical properties of the cured system. On the other hand, at shorter reaction times, a one-phase structure was obtained with the typical properties of IPN systems (see Tables 4.15 and 4.17).

For the systems pre-reacted at optimum conditions, it was established by examination of SEM micrographs that there was good adhesion between the matrix and the precipitated particles as a result of the chemical reactivity of the pre-reacted Fomblin modifier. Good adhesion between the matrix and the rubber is necessary in order to promote toughening and this is particularly important for systems containing a bimodal particle size distribution [119].
Poor interfacial adhesion between the matrix and the precipitated particles was only observed for two-phase System A (see Figure 4.36) with five hours pre-reaction time of the modifier. In this particular case the modifier was not chemically bound to the epoxy resin and consequently all the mechanical properties of the above system were adversely affected. Strain at break is a typical example. The ratio of strain at break of the above system to that of unmodified epoxy was 0.8 compared to 1.92 for the four hours pre-reacted Fomblin modified formulations. This significant difference is an indication of the importance of attaining adequate interfacial bonding which in turn depends on the selection of appropriate pre-reaction conditions (see Section 5.1.2).

Similar observations on the nature of the interfacial bonding were made by Chan et al. [15] who investigated the effect of modification of neat epoxy resin systems with unmodified CTBN. The authors concluded that to obtain strong interfacial chemical bonds, the modifier (i.e. liquid rubber) should be reactive.

In general, the flexural properties of all systems (modified and control) decreased after ageing at 200°C for 21 days but the residual properties (after ageing) of the modified systems were never inferior to those of the non-aged control samples. However, one interesting observation is the increase in strain at break of the IPN systems after ageing and also as the amount of Fomblin increased. In order to explain this behaviour further work is required.

The DMA data gave a quite clear indication of what is occurring at the microstructural and molecular level within the material. The dynamic
mechanical properties of the crosslinked anhydride cured diglycidyl ether of bisphenol A exhibit, in addition to an α-transition at about 150°C, a quite broad secondary β-transition at around -50°C which is associated with motions of hydroxyether groups shown below:

\[
\text{-O-CH}_2\text{-CH-CH}_2\text{-OH}
\]

In IPN systems, the concurrent downward shift of the epoxy α-transition (reducing to around 120°C for 25.8% Fomblin modified epoxy resin) and the increase in magnitude and breadth of the β-transition (see Figure 4.43) is due to an increase in the compatibility of Fomblin ZDOLTX and epoxy resin. Furthermore, the observed reduction in the height of the α-transition peak with increasing Fomblin content is related to the absence of discrete particles and the formation of very fine continuous phases morphology, which also explains the downward shift of the epoxy α-transition.

In addition, the increase in \( E'' \) across the temperature range from -100°C to 180°C with increasing Fomblin content reinforces the suggestion that a greater degree of miscibility occurs, in a similar fashion to the findings of Wolfe and co-workers [120], who studied the effect of acrylonitrile level and overall rubber content on the dynamic mechanical properties of CTBN toughened epoxy resin. This compatibility caused the modified Fomblin to remain diffused in the epoxy resin and therefore plasticising to some extent the matrix and causing the observed reduction in the glass transition temperature.

In IPN systems, as the amount of Fomblin was increased the fracture energy \( (G_c) \) increased. However, even with increasing \( G_c \), the reduction
in Tg may constitute a disadvantage for certain applications. Since high Tg values are associated with the degree of crosslinking (i.e. molecular weight between crosslinks) and the interchain attractive forces, it would be necessary to modify the formulations to achieve a tighter network, this would at the same time reduce also the water absorption.

In the two-phase systems, the β-transition was much lower than that of the IPN systems (i.e. -75°C compared to -50°C). Furthermore, as the total Fomblin content increased, this β-transition remained fairly constant, while the α-transition decreased slightly without any appreciable decrease in peak height. These together indicate the presence of distinct phase separation between the precipitated phase and the epoxy resin which is clearly seen in the micrograph (Figures 4.17 and 4.18).

The presence of fluorine, or more precisely the -CF₂- segments, within the Fomblin modified systems results in one of the desirable properties of PTFE i.e. a lower surface energy. A typical example shows that a small amount (3.5%) of Fomblin ZDOLTX reduces considerably the surface energy from 30.3 mN/m² for the control formulations to about 15 mN/m² for System A modified formulations. This would indicate a possible deterioration in the adhesion behaviour. On the contrary, however, the bond strength of the Fomblin modified epoxy increased as the amount of Fomblin was increased, varying from 6.02 MPa for the control formulation (i.e. zero Fomblin content) to 22.24 MPa for IPN formulations containing 25.87% Fomblin ZDOLTX.
The refractive index of the modified cured formulations decreases as the amount of Fomblin increases. However this reduction may not be sufficiently large to be of industrial interest for fibre optics coatings.

The observed improvement of the adhesion bond strength to mild steel of the pre-reacted Fomblin modified epoxy-resin based formulations (i.e. IPN and two-phase systems) can be explained by the toughening and flexibilising effects (as evidenced above) of adding pre-reacted Fomblin to epoxy resin. The relatively low bond strength to mild steel of the unmodified epoxy resin is probably due to its brittle nature which produces failure of the adhesive joint. Furthermore, increasing the total Fomblin content induced an increase in the bond strength of the system. It is interesting to note that the incorporation of a low level of Fomblin (i.e. about 3.6% Fomblin ZDOLTX) in the two-phase system (System A) increased the adhesive bond strength by 94% over that of the unmodified system.

These results are somewhat unexpected due to the fact that the presence of Fomblin reduces the surface energy of these systems. The observed improvement is probably the result of complex interactions between the interfacial characteristics of the joint and the toughness of the resin in the interlayer.
6. CONCLUSIONS

The conclusions that can be derived from this study are shown below.

6.1 CHEMICAL MODIFICATION OF FOMBLINS

1. The Fomblins examined are totally incompatible with epoxy resins in the temperature range from room temperature to 180°C. However, compatibility can be induced by chemical modification of the Fomblins. This modification involves reaction with acid anhydride(s) followed by further chain extension with ε-caprolactone to obtain a prepolymer.

2. Viscosity measurements and infrared spectroscopy results together demonstrate that not only end capping but also chain extension reactions occur during the modification of Fomblin.

3. The adduct based on Fomblin ZE2000 is highly reactive and unstable during storage. The high reactivity of this adduct restricts its use. This coupled with the vast batch to batch variations for the starting oligomers limits the scope of further developments.

4. Prepolymers based on Fomblin ZDOLTX of different molecular weight can be produced by varying the molar ratio of their constituents. This in turn affects the solubility in the epoxy resin. An optimum molecular weight of the prepolymer for which
complete miscibility with epoxy resin is obtained at the molar ratio 1 Fomblin: 1.5 anhydride: 2 \( \varepsilon \)-caprolactone. Complete miscibility is not achieved above or below this molar ratio.

5. The chlorendic and hexahydrophthalic anhydrides are more soluble in the Fomblin ZDOLTX than in the Fomblin ZDOL.

6. The prepolymer based on Fomblin ZDOLTX is compatible with epoxy resin at all concentrations. However, the one based on Fomblin ZDOL is only compatible up to 50 phr of prepolymer.

7. The viscosity and hence the molecular weight of the epoxy-extended prepolymer strongly depends on its pre-reaction time and temperature. This in turn affects the morphological and mechanical properties of the modified cured systems.

6.2 MORPHOLOGY OF FOMBLIN MODIFIED EPOXY RESINS

1. The microscopic studies reveal the presence of an apparently one-phase structure in IPN systems and precipitated spherical particles dispersed in the matrix of the two-phase systems. Thus it is possible to control the morphology of the cured modified formulations such that either totally transparent (IPN) or opaque (two-phase) systems are produced.

2. Modification of epoxy resin with a prepolymer based on Fomblin ZDOLTX (Prep TX) produces IPN one-phase systems. On the other hand modifications with epoxy-extended prepolymers (either containing Fomblin ZDOLTX alone to produce System A or a
combination of two Fomblins ZDOLTX + ZE2000 to produce System B) results in a two-phase structure.

3. The development of morphology in the two-phase systems follows the nucleation and growth mechanism. This particle nucleation and domain growth is related to cure rate.

4. The particle size distribution is bimodal with large particles averaging ca. 20 μm diameter and small particles in the region of 1 μm. The volume fraction of the precipitated particles is higher in System B than System A for the same total Fomblin content. There is good interfacial adhesion between the matrix and the particle for both systems.

5. The results of dynamic mechanical tests and SEM analysis reveal that the extent of plasticisation is low for all Fomblin modified composites, with IPN systems showing a slightly higher level of plasticisation than the two-phase systems. Furthermore, the ageing studies have shown that the IPN systems consist of fine lamellae.

6.3 PROPERTIES OF MODIFIED FORMULATIONS

1. The use of fluorinated modifiers does not reduce the equilibrium water absorption at 85°C of either IPNs or two-phase systems. The diffusion coefficient is higher for the IPN than for the two-phase systems.
2. The mechanical properties at room temperature of IPNs, System A and System B cured formulations show that even small amounts of Fomblin are sufficient to improve dramatically the mechanical properties of epoxy resin, for instance, with only 3.6% Fomblin content:

a) the fracture energy is improved by ca. 450% for IPNs, 570% for System A and by ca. 600% for System B;

b) the flexural strength is also improved by ca. 70% for IPN systems, ca. 24% for System A and ca. 75% for System B;

c) the strain at break is increased by ca. 9.0% for IPN systems, ca. 92% for System A and ca. 200% for System B;

d) the modulus at 1% strain decreases by ca. 31% for IPN systems, 25% for System A and ca. 28% for System B.

The best overall improvement in mechanical properties is exhibited by the two-phase System B which contains a combination of two Fomblins (ZDOLTX + ZE2000).

3. Although the flexural properties of IPN, System A and System B samples aged at 200°C for 21 days deteriorate, the residual properties (i.e. after ageing) are still superior to those of the non-aged control samples, while the strain at break of IPN systems increases. The latter is a very unusual occurrence in the field of thermosets.
4. The adhesive bond strength to mild steel increases as the total amount of Fomblin in the formulation increases. With a 26% Fomblin content the adhesive bond strength increases by about 270% compared to that of the control formulation. To improve the adhesive joint strength of epoxy resin it is important to toughen the epoxy resin without reducing its thermal and mechanical properties.

5. The incorporation of even a small amount of Fomblin (i.e. about 3.6%) reduces considerably the surface energy of the modified cured formulations.

6. In those samples having poor mechanical properties, agglomeration of the precipitated particles and poor interfacial adhesion between the matrix and the precipitated particles are evident. These defects are influenced by the prereaction conditions used to prepare the modified Fomblin.

SUGGESTIONS FOR FURTHER WORK

In order to obtain a better understanding of the systems studied it is suggested that the following experiments are carried out:

1. Study of the chemical composition of the precipitated particles using the FTIR technique combined with the optical microscope.

2. Increase the crosslink density of the epoxy resins formulations by using a tetrafunctional resin and measure the water absorption.
3. Optimise the particle size and the particle size distribution of the cured systems by studying in more detail the effect of catalyst concentration in the formulation and also the effect of varying the curing temperature.

4. Investigate the use of higher Fomblin contents in the two-phase formulations and study the effect on the mechanical properties.

5. Study the possibility of mixing IPN and two-phase systems to achieve a combination of the relatively high ageing resistance of IPNs and the high toughness of two-phase systems.
REFERENCES


SEM micrographs were used to determine the morphological parameters which were calculated as follows [121]:

1. Average diameter (D) of particles:

\[ D = \frac{\Sigma (n \times d)}{\Sigma n} \]  \hfill (1)

2. Volume fraction (%) of dispersed phase:

\[ V_f = \frac{\pi}{4} \times \frac{\Sigma (n \times d^2)}{A_r} \times 100 \]  \hfill (2)

where \( A_r \) is the area (\( \mu m^2 \)) of the micrograph region under analysis and \( d \) is particle diameter (\( \mu m \)).

Equation (2) assumes that the volume fraction is an isotropic property and hence, values determined in the plane are the same as in the volume.
Example calculations of the average diameter and volume fraction of the dispersed phase particles of System A and System B at 5.6% total Fomblin content:

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>System A</th>
<th></th>
<th>System B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number</td>
<td>Distribution</td>
<td>Number</td>
<td>Distribution</td>
</tr>
<tr>
<td>1.5</td>
<td>15</td>
<td>48.4</td>
<td>50</td>
<td>65.1</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>32.2</td>
<td>17</td>
<td>22.1</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>9.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>3.9</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2.6</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>6.45</td>
<td>4</td>
<td>5.2</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>1.6</td>
<td>0.5</td>
<td>0.65</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>1.6</td>
<td>0.25</td>
<td>0.32</td>
</tr>
</tbody>
</table>

System A

\[ D = \frac{(15 \times 1.5) + (10 \times 5) + (3 \times 8) + (2 \times 20) + (0.5 \times 30) + (0.5 \times 50)}{31} \]

Therefore \( D = 5.7 \mu m \)

\[ V_f = \frac{\pi}{4} \times \frac{(15 \times 1.5^2) + (10 \times 5^2) + (3 \times 8^2) + (2 \times 20^2) + (0.5 \times 30^2) + (0.5 \times 50^2)}{A_r} \]

where \( A_r = 21840 \mu m^2 \).

Therefore \( V_f = 10.7\% \)
System B

\[ D = \frac{(50 \times 1.5) + (17 \times 5) + (3 \times 10) + (2 \times 15) + (4 \times 20) + (0.5 \times 30) + (0.25 \times 50)}{76.75} \]

Therefore 

\[ D = 4.26 \text{ \mu m} \]

\[ V_f = \frac{\pi}{4} \times \frac{(50 \times 1.5^2) + (17 \times 5^2) + (3 \times 10^2) + (2 \times 15^2) + (4 \times 20^2) + (0.5 \times 30^2) + (0.25 \times 50^2)}{A_T} \]

where \( A_T = 21840 \text{ \mu m}^2 \).

Therefore 

\[ V_f = 14.25\% \]
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(For 25 parts Adduct TX or Prepolymer TX per 100 parts Epikote 828)

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Viscosity$^a$ (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adduct TX (TX:CA)$^b$</td>
</tr>
<tr>
<td></td>
<td>1:1.5</td>
</tr>
<tr>
<td>1</td>
<td>46.60</td>
</tr>
<tr>
<td>4</td>
<td>44.30</td>
</tr>
</tbody>
</table>

$^a$ Viscosity at 60°C and at a shear rate of 192 s$^{-1}$

$^b$ TX:CA = Fomblin ZDOLTX to chlorendic anhydride molar ratio

$^c$ TX:CA:CL = Fomblin ZDOLTX to chlorendic anhydride to $\varepsilon$-caprolactone molar ratio
TABLE 7.2: THE EFFECT OF REACTION TIME AND MOLAR RATIO ON THE VISCOSITY OF EPOXY-EXTENDED ADDUCT AND PREPOLYMER BASED ON FOMBLIN ZDOL TX
(For 50 parts Adduct TX or Prepolymer TX per 100 parts Epikote 828)

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Viscosity$^a$ (Pa.s)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adduct TX (TX:CA)$^b$</td>
<td>Prepolymer TX (TX:CA:CL)$^c$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1:1.5 82.10</td>
<td>1:1.5:2 177.50</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:2 181.94</td>
<td>1:2:2 175.30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>1:1.5:2 177.50</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1:2 84.31 184.15</td>
<td>1:2:2 142.00</td>
<td></td>
</tr>
</tbody>
</table>

a) Viscosity at 60°C and at a shear rate of 192 s$^{-1}$
b) TX:CA = Fomblin ZDOLTX to chlorendic anhydride molar ratio
c) TX:CA:CL = Fomblin ZDOLTX to chlorendic anhydride to ε-caprolactone molar ratio
<table>
<thead>
<tr>
<th>Reaction Time (hrs)</th>
<th>Viscosity (^a) (Pa.s)</th>
<th>(\text{Adduct TX/ZE})</th>
<th>(\text{Prepolymer TX/ZE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.40</td>
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<tr>
<td>2</td>
<td>35.50</td>
<td>88.50</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>53.50</td>
<td>88.75</td>
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<tr>
<td>5</td>
<td>57.70</td>
<td>88.75</td>
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</tr>
<tr>
<td>15</td>
<td>63.40</td>
<td>142.00</td>
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</tbody>
</table>

\(^{a}\) Viscosity at 60°C and at a shear rate of 192 s\(^{-1}\)
TABLE 7.4: VISCOSITY CHANGES WITH REACTION TIME FOR EPOXY-EXTENDED PREPOLYMER PREP TX

<table>
<thead>
<tr>
<th>Reaction Time (hr)</th>
<th>Viscosity (Pa.s)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>57.68</td>
</tr>
<tr>
<td>2</td>
<td>57.68</td>
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<td>5</td>
<td>53.25</td>
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<tr>
<td>6</td>
<td>30.02</td>
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</table>

Note: Viscosity at 60°C and shear rate of 192 s⁻¹
TABLE 7.5: THE REFRACTIVE INDEX OF IPN FORMULATIONS CONTAINING FOMBLIN ZDOLTX

<table>
<thead>
<tr>
<th>Fomblin ZDOLTX Content (wt %)</th>
<th>Refractive Index</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1.5587</td>
</tr>
<tr>
<td>3.67</td>
<td>1.5522</td>
</tr>
<tr>
<td>8.58</td>
<td>1.5547</td>
</tr>
<tr>
<td>15.47</td>
<td>1.5290</td>
</tr>
<tr>
<td>25.82</td>
<td>1.5137</td>
</tr>
<tr>
<td>100.00</td>
<td>1.3132</td>
</tr>
</tbody>
</table>

Note: The refractive index of raw Fomblin ZDOLTX is 1.3132.
TABLE 7.6: THE REFRACTIVE INDEX OF IPN FORMULATIONS CONTAINING FOMBLIN ZE2000

<table>
<thead>
<tr>
<th>Fomblin ZE2000 Content (wt %)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5602</td>
</tr>
<tr>
<td>3.00</td>
<td>1.5570</td>
</tr>
<tr>
<td>5.80</td>
<td>1.5507</td>
</tr>
<tr>
<td>12.98</td>
<td>1.5340</td>
</tr>
</tbody>
</table>

Note: The refractive index of Fomblin ZE2000 is 1.3150
<table>
<thead>
<tr>
<th>Case</th>
<th>Fomblin Content (% by weight)</th>
<th>Microhardness (HV)* [kgf/mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>19.98 ± 0.41</td>
</tr>
<tr>
<td>One-phase IPNs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.67</td>
<td>18.78 ± 0.31</td>
<td></td>
</tr>
<tr>
<td>8.58</td>
<td>17.05 ± 0.47</td>
<td></td>
</tr>
<tr>
<td>15.47</td>
<td>14.71 ± 0.39</td>
<td></td>
</tr>
<tr>
<td>25.82</td>
<td>10.71 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>Two-phase System A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.67 Precipitated Particle</td>
<td>11.63 ± 0.45</td>
<td></td>
</tr>
<tr>
<td>3.67 Matrix</td>
<td>20.97 ± 0.46</td>
<td></td>
</tr>
</tbody>
</table>

* Vickers hardness number
### Table 7.8: Water Absorption Data for One-Phase IPN Cured Formulations

<table>
<thead>
<tr>
<th>Immersion Time (hr)</th>
<th>Weight Gain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% Formblin</td>
</tr>
<tr>
<td>1</td>
<td>0.148±0.039</td>
</tr>
<tr>
<td>3</td>
<td>0.302±0.033</td>
</tr>
<tr>
<td>7</td>
<td>0.380±0.038</td>
</tr>
<tr>
<td>17</td>
<td>0.590±0.026</td>
</tr>
<tr>
<td>41</td>
<td>0.840±0.039</td>
</tr>
<tr>
<td>113</td>
<td>0.950±0.062</td>
</tr>
<tr>
<td>218</td>
<td>1.036±0.051</td>
</tr>
<tr>
<td>466</td>
<td>1.070±0.034</td>
</tr>
</tbody>
</table>

**Notes**

1. IPN formulations based on Formblin ZDOLTX (Table 4.7)
2. Water absorption test was carried out at 85°C (see Section 3.5.4)
3. These data are plotted in Figure 4.28
<table>
<thead>
<tr>
<th>Immersion Time (hr)</th>
<th>0% Fomblin (±)</th>
<th>3.65% Fomblin (±)</th>
<th>5.66% Fomblin (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.148 ± 0.039</td>
<td>0.094 ± 0.030</td>
<td>0.085 ± 0.011</td>
</tr>
<tr>
<td>3</td>
<td>0.302 ± 0.033</td>
<td>0.282 ± 0.015</td>
<td>0.242 ± 0.022</td>
</tr>
<tr>
<td>7</td>
<td>0.380 ± 0.038</td>
<td>0.342 ± 0.026</td>
<td>0.312 ± 0.019</td>
</tr>
<tr>
<td>17</td>
<td>0.590 ± 0.026</td>
<td>0.562 ± 0.041</td>
<td>0.547 ± 0.042</td>
</tr>
<tr>
<td>41</td>
<td>0.840 ± 0.039</td>
<td>0.835 ± 0.055</td>
<td>0.814 ± 0.048</td>
</tr>
<tr>
<td>113</td>
<td>0.950 ± 0.062</td>
<td>1.000 ± 0.016</td>
<td>0.955 ± 0.033</td>
</tr>
<tr>
<td>218</td>
<td>1.036 ± 0.051</td>
<td>1.137 ± 0.037</td>
<td>1.130 ± 0.037</td>
</tr>
<tr>
<td>466</td>
<td>1.070 ± 0.034</td>
<td>1.273 ± 0.028</td>
<td>1.266 ± 0.021</td>
</tr>
</tbody>
</table>

Notes:
1. System A contains Fomblins ZDOLTX (Table 4.8)
2. Water absorption test was carried out at 85°C (see Section 3.5.4)
3. These data are plotted in Figure 4.29.
### TABLE 7.10: WATER ABSORPTION DATA FOR TWO-PHASE SYSTEM B CURED FORMULATIONS

<table>
<thead>
<tr>
<th>Immersion Time (hr)</th>
<th>0% Formblin</th>
<th>3.66% Formblin</th>
<th>5.63% Formblin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.148 ± 0.039</td>
<td>0.085 ± 0.016</td>
<td>0.097 ± 0.030</td>
</tr>
<tr>
<td>3</td>
<td>0.302 ± 0.033</td>
<td>0.247 ± 0.027</td>
<td>0.270 ± 0.018</td>
</tr>
<tr>
<td>7</td>
<td>0.380 ± 0.038</td>
<td>0.342 ± 0.023</td>
<td>0.345 ± 0.038</td>
</tr>
<tr>
<td>17</td>
<td>0.590 ± 0.026</td>
<td>0.581 ± 0.026</td>
<td>0.615 ± 0.041</td>
</tr>
<tr>
<td>41</td>
<td>0.840 ± 0.039</td>
<td>0.925 ± 0.025</td>
<td>0.904 ± 0.021</td>
</tr>
<tr>
<td>113</td>
<td>0.950 ± 0.062</td>
<td>1.015 ± 0.019</td>
<td>1.080 ± 0.048</td>
</tr>
<tr>
<td>218</td>
<td>1.036 ± 0.051</td>
<td>1.235 ± 0.050</td>
<td>1.220 ± 0.060</td>
</tr>
<tr>
<td>466</td>
<td>1.070 ± 0.034</td>
<td>1.360 ± 0.070</td>
<td>1.370 ± 0.020</td>
</tr>
</tbody>
</table>

**Notes:**

1. System B contains Formblins ZDOLTX + ZE2000 (Table 4.9)
2. Water absorption test was carried out at 25°C (see Section 3.5.4)
3. These data are plotted in Figure 4.29.
<table>
<thead>
<tr>
<th></th>
<th>Formblin Content (wt %)</th>
<th>Glass Transition Temperature (°C)</th>
<th>Width at Peak Half Height</th>
<th>Height at Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>150</td>
<td>10</td>
<td>62.5</td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>156</td>
<td>10</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>8.58</td>
<td>140</td>
<td>14</td>
<td>35.5</td>
</tr>
<tr>
<td></td>
<td>15.47</td>
<td>135</td>
<td>15</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>25.82</td>
<td>122</td>
<td>25</td>
<td>29.5</td>
</tr>
<tr>
<td>One-phase IPNs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two-phase System A</td>
<td>3.66</td>
<td>138</td>
<td>10</td>
<td>61.5</td>
</tr>
<tr>
<td></td>
<td>5.63</td>
<td>140</td>
<td>5</td>
<td>50.0</td>
</tr>
<tr>
<td>Two-phase System B</td>
<td>3.65</td>
<td>142</td>
<td>8</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>5.60</td>
<td>133</td>
<td>9</td>
<td>49.0</td>
</tr>
</tbody>
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## LIST OF FIGURES IN APPENDIX

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page No</th>
</tr>
</thead>
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<td>193</td>
</tr>
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<td>Particle size distribution of the two-phase cured formulation (System A) at 5.6% Fomblin ZDOLTX content</td>
<td>194</td>
</tr>
<tr>
<td>7.3</td>
<td>Particle size distribution of the two-phase cured formulation (System B) at 5.6% Fomblin (ZDOLTX + ZE2000) content</td>
<td>194</td>
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<tr>
<td>7.4</td>
<td>Infrared scan of MNA</td>
<td>195</td>
</tr>
<tr>
<td>7.5</td>
<td>Infrared scan of Fomblin ZE2000</td>
<td>196</td>
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<tr>
<td>7.6</td>
<td>Infrared scan of 75% CA/25% HHPA</td>
<td>197</td>
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<tr>
<td>7.7</td>
<td>Infrared scan of Fomblin ZDOLTX</td>
<td>198</td>
</tr>
</tbody>
</table>
FIGURE 7.1: TORQUE VERSUS SPEED OF ADDUCT AND PREPOLYMERS
FIGURE 7.2: PARTICLE SIZE DISTRIBUTION OF THE TWO-PHASE CURED FORMULATION (SYSTEM A) AT 5.6% FOMBLIN ZDOLTX CONTENT

FIGURE 7.3: PARTICLE SIZE DISTRIBUTION OF THE TWO-PHASE CURED FORMULATION (SYSTEM B) AT 5.6% FOMBLIN (ZDOLTX+ ZE2000) CONTENT
FIGURE 7.4: INFRARED SCAN OF MNA
FIGURE 7.6: INFRARED SCAN OF 75% CA/25% HHPA
FIGURE 7.7: INFRARED SCAN OF FOMBLIN ZDOLTX
Determination of the critical surface tension according to Zisman

Two-phase (System A) cured formulation at 3.6% Fomblin ZDOLTX content

IPN cured formulation at 3.6% Fomblin ZDOLTX content