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FACTORS INFLUENCING THE PROPERTIES OF EPOXY RESINS FOR COMPOSITE APPLICATIONS

By
S. Thitipoomdeja

Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology

June 1995

Supervisors: Mr. J.F. Harper
Dr. R.J. Heath

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Dedicated to

My Parents,
Brothers and Sisters
Summary

The aim of the work reported here was to determine the influence of an amine curing agent, and postcure cycle on the mechanical and thermal properties of diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The results of this initial study were then used as the basis for selecting material to obtain optimum toughness in epoxy/glass fibre systems. These basic materials were further used to make comparisons with the properties of modified resin systems which contained commercial elastomers. Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), Fourier Transform Infrared Spectroscopy (FTIR), flexural and interlaminar shear tests, Instrumented Falling Weight Impact (IFWI), visual observation, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) were all used to investigate various properties and the structures which gave rise to them. The properties of cured products were found to be affected by the amounts of curing agent, curing times and temperatures, and the structure of the elastomers. Not surprisingly the maximum thermal and mechanical properties tended to be found in the stoichiometric (standard) mix systems. However, postcuring at higher than room temperature, which was used as the basic curing temperature, led to more conversion. This effect improved the thermal and mechanical properties of both the unmodified and modified resin systems. The maximum flexural strength of 104 MPa of the unreinforced resins was found in the stoichiometric mix ratio after postcure at 150°C for 4 hr. However, the maximum flexural modulus and glass transition temperature (Tg) were found after postcuring at the same temperature for 48 hr. This was believed to be due to increased crosslinking, but unfortunately the longer curing time led to degradation of the resins. In the systems modified with ~20 phr of polyetheramine elastomers, the one modified with the lowest molecular weight (2000) was found to have the highest flexural strength (85.8 MPa) and modulus (2.5 GPa). The impact properties of all the composites with modified resin matrices were found to be higher than the unmodified resin matrix composites. The best impact properties were, however, obtained with the elastomer modifier with a molecular weight of 4000. The impact energy at maximum force increased from 11.9 to 16.4 J, and energy at failure increased from 18.7 to 21.6 J. This increase in impact properties was due to the increase in areas of phase separated elastomer particles over similar systems with lower molecular weight modifier.

Keywords: Epoxy resin; modified resins; curing agents; mechanical properties; glass transition temperature (Tg); composites; impact properties; elastomers; modifier.
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1. INTRODUCTION

1.1 Background

Epoxy resins were first prepared by Pierre Casten in Switzerland and S.C. Greenlee in United States in the late 1930s [1], but were first offered commercially in 1946 [2]. They are chemically characterised by a three-membered ring, called alternatively the epoxide, epoxy, ethylene oxide or oxirane group [2, 3] i.e.

\[ \text{C--O--C} \]

The most important commercial intermediate epoxy resin oligomer is a product of epichlorohydrin and bisphenol A [2, 4]. The ideal structure is [2],

\[ \text{CH}_2\text{CH}_2\text{OCH}(\text{CH}_3)\text{C}([\text{O}]\text{CH}_2\text{CH}-\text{CH}_2\text{OCH}(\text{CH}_3)\text{C})\text{OH}_n \]

Where \( n \), the degree of polymerisation is nearly zero \( (n \sim 0.2) \) [2].

Shell Chemical Co. and Union Carbide Corp. began research on the commonly used bisphenol-A-based epoxy resins in the late 1940s [2]. Details of the monomers for common epoxide resins are given in Appendix A.

1.2 Curing Agents of Epoxy Resins
1. Introduction

Curing agent may be classified in the following broad categories [3]: aliphatic amines; modified aliphatic amines; aromatic amines; acid anhydrides; and catalytic curing agents. Since only the first two types of amine were used in this programme, only these are described:

(a) Aliphatic polyamines.
Primary and secondary aliphatic polyamines are the most important class of room temperature activated curing agents [7], which have low viscosity [3] and little colour [2]. They have the disadvantages of needing critical mixing ratio, being rather difficult to handle, have short pot lives, high exothermic temperature during cures, high moisture absorption, and are moderately toxic and skin irritating [2, 3].

(b) Modified aliphatic amines.
These curing agents have been modified to avoid the handling and curing problems of the unmodified aliphatic amines [7]. These provide longer pot life due to the less active amine (by modification), and easier handling [3, 7] while retaining their chemical and mechanical properties [7]. They have a lower handling hazard while having higher viscosity and lower vapour pressure [7].

1.3 Reaction of Epoxy Resins

There are four types of reactions that can occur during the cure reaction of epoxy resins [7]:
(a) Epoxy resins react with crosslinking agents containing active hydrogen, e.g. amines.
(b) Self polymerisation of the epoxy resins catalysed by acid or basic groups.
(c) Hydroxy groups react with polyfunctional organic acid or anhydride crosslinking agents.
(d) Acid catalysed crosslinking of epoxy with hydroxyl groups.
Examples of reactions of epoxy with an amine curing agent and with elastomers are as follows:
(a) epoxy reacted with amine.
The reaction mechanism of epoxy resin with primary amine curing agent is [8]:
1. Introduction

This reaction \((1)\) gives amino-alcohol which has the ability to react with another epoxy oxirane group, since the amine nitrogen still has one hydrogen available for further reaction \([8]\) as follow:

\[
\begin{align*}
\text{OH} & \quad \text{CH} - \text{CH}_2 - \text{NH} \quad + \quad \text{O} - \text{CH} - \text{CH}_2 \\
\text{amino-alcohol} & \quad \text{epoxy} \quad \text{tertiary amine}
\end{align*}
\]

The hydroxyl groups so react further with epoxy to form longer chains or networks \([1, 9]\).

(b) epoxy reacted with urethanes.

Epoxy resins may be toughened with urethane based elastomers. Increasing urethane content in the epoxide not only improves impact and tensile properties but also the adhesion of the polymer to many different substrates \([10]\).
Figure 1.1 The reaction between polyurethane modified an epoxy/amine cured system [11].

The epoxy/amine cured system can be modified by polyurethane as shown in Figure 1.1 [11]. The nucleophilic groups of the primary and secondary amines react with isocyanate creating the urea groups as [12]:

\[
R-N=C=O + H_2N-R' \rightarrow R-NH-C-NH-R'
\]

1.4 Properties of Cured Epoxide Resins

Thermosetting epoxy resins have some important properties such as:
(a) Low shrinkage [1, 7, 9]:

The cure shrinkage of an unmodified epoxy resin is of the order of 2 per cent or less [1]. Therefore, it can be moulded to reproduce accurate shapes and dimensions without requiring expensive machining or other finishing [7]. Moreover, the cure reaction gives no by-products [1, 3] being by direct polyaddition/step polymerisation. In comparison, the condensation and crosslinking mechanism associated with the polyester and phenolic resins lead to higher shrinkage values [1].

(b) Toughness [1, 4].

In comparison, the toughness of cured phenolic resins is, typically, seven times less than that the epoxy resins [1]. This is attributed to the distance between the aliphatic chains and crosslinking points (i.e. proportional to cross-link density) [1] i.e. as follow:
In the oligomeric epoxide, the reactive epoxide and hydroxyl groups are relatively widely spaced, promoting relative flexibility and toughness to the resulting cured resins [6].

(c) Chemical resistance [1, 2, 3, 7, 9]:

Epoxies when properly formulated and well cured have outstanding chemical resistance [1, 3]. Ether linkages are among the most stable organic chemical structures [6]. The cured system is normally resistant to a wide range of solvents, acids and alkalis [1, 6, 7]. The stability toward organics, alkalis and acids would be expected due to C-N bond, formed during amine cure of epoxides [3].

(d) Good adhesion to a wide range of materials:
1. Introduction

The polarity of ether (R-O-R) and aliphatic hydroxyl (\(-\text{C}-\)) groups are high and thus contribute to polar adhesive bonds of high strength [1, 6, 7]. Due to their high polarity, epoxy molecules can also create dispersive bonding to the adjacent surfaces [1]. This makes epoxy resins useful as adhesives to bond with various substrates, such as many plastics, metals, rubbers and woods [7].

(e) Versatility [1]:

The epoxy resins are compatible with various types of curing agents [1]. Hence, properties of cured products can be varied as required for particular applications [1].

Epoxy resins are widely used in many industries due to the variety of properties possible. For example, consumption in the U.S.A. in 1991 was 195,000 tonnes with 84,000 tonnes (43%) used in protective coatings, and the remainder (111,000 tonnes) in structural applications such as electrical laminates, adhesives, tooling, casting, moulding, flooring and others [13].

1.5 Aims

The aim of the work reported here was to determine the influence of an amine curing agent, and postcure cycle on the mechanical and thermal properties of the diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The results of this initial study were then used as the basis for selecting materials to obtain optimum toughness in epoxy/glass fibre systems. These basic materials were then used to make comparisons with the properties of a range of modified resin systems which contained commercial elastomers.

Such comparison for the materials used in this research have not been widely published by other researchers. In particular, this present study aimed to carry out tests on both unreinforced and reinforced systems, where previous researchers have only reported studies on individual systems.

The influence of postcuring was studied in the work, since it has been reported that thermal and mechanical properties can be improved by this means, although most technical data recommends that this amine curing agent be used to cure an epoxy resin at room or lower temperature.

Visual observations of postcured specimens, which were made in this work, have not been reported by other researchers. Similarly, the molecular weight and number of functional groups in the elastomer modifier and their influence on state of cure, mechanical properties, and second phase particle sizes have not been published by many other researchers.
2. LITERATURE REVIEW

2.1 Cure Behaviour of Thermoset Resins

Low molecular weight multifunctional polymers can be converted to higher molecular weight, crosslinked networks, of infinite structure by polymerisation [14]. The physical and mechanical properties of cured systems are thought to be related to their structure which occur during cure [15]. The changes in mechanical properties related to structure may be predicted [15]. Chiao and Lyon [16] stated that material performance is directly related to the processing conditions, particularly in thermoset resin/fibre composites. With the increasing demands placed on thermoset resins used in high performance composites, for structural applications, a knowledge of structure changes during curing and processing is required [17].

Gillham [18] is a leading researcher, who has studied the relationships between time, temperature and transformation in thermoset resins during cure, since the early 1980's. Aronhime and Gillham [19] found in literature that the determination of the time to vitrification had not been widely studied. Gillham [20] defined the term "vitrification" as the formation of a glassy solid of thermoset resins, and defined the term "cure" as the overall transformation from liquid to gel to rubber to glass due to the chemical reaction.

The details of the transformation of thermoset resins during isothermal cure are shown in Figure 2.1 [21]. Where, $T_{go}$ is the glass transition temperature of the uncured resin mixture, $T_g$ is the glass transition temperature of the cured resin, $T_{gel}$ is the minimum cure temperature to form a gel, and $T_{g\infty}$ is the maximum possible glass transition temperature of a fully cured network [21, 22].

The isothermal cure of thermoset resins typically pass through two crucial events; gelation and vitrification [22, 23]. Both events control the reaction rate, rheology, density, dimensional stability, and internal stresses, which affect to all properties of the thermoset resins [24]. Gelation corresponds to the onset (incipient) of the formation of a molecular arrangement of an infinite network of crosslinked polymer molecules [22, 23]. Gelation can effect electrical, mechanical and viscoelastic properties [22]. Vitrification corresponds to the increase of molecular weight, which can occur at any state of reaction, when the glass transition temperature of the mixture reaches the cure temperature [22, 23]. This involves the transformation from a liquid or rubbery state to a glassy state [23]. Thus vitrification does not indicate complete reaction, but, it limits or quenches the reaction of the polymer stopping it reaching maximum glass transition temperature ($T_{g\infty}$) [19].
2. Literature Review

Figure 2.1 A Time-Temperature-Transformation (T-T-T) diagram for a thermoset resin under isothermal cure [21]

2.1.1 The Glass Transition Temperature (Tgs) of Cured Systems

At the first stage of crosslinking the reaction rate is high, and Tg increases linearly with the fractional conversion, but the rate of reaction is low when the fractional conversion is high, after vitrification [23]. Therefore, it is particularly helpful to measure Tg accurately at this later stage as it is very sensitive to fractional conversion [25]. The Tg also has a linear relationship with T_cure, when determined for the same cure time, which is longer than the time to vitrification, and can be expressed as [26]:

$$T_g = A + B \frac{T_{cure}}{T_{cure}}$$  \hspace{1cm} (2.1)

Where A is depends on the cure time, and B is independent of the cure time.

The relationship between the full cure temperature (T_∞) and time to full cure (t_∞) can be expressed as [26]:

$$T_\infty = a + b \log t_\infty$$  \hspace{1cm} (2.2)

Where a is the intercepts, and b is the slope of a T_∞ versus log t_∞ plot.

Similarly, the maximum temperature of a fully cured network (T_g∞) relates to the temperature at full cure (T_∞) as follows [26]:
2. Literature Review

\[ T_{g_\infty} = A + B T_\infty \] \hspace{1cm} \text{(2.3)}

The Tg of a thermoset polymer before gelation has a relationship to the number average molecular weight which can be expressed as [21, 27]:

\[ \frac{1}{T_g} = \frac{1}{T_{g_\infty}} + K_a \overline{M_n} \] \hspace{1cm} \text{(2.4)}

Where \( K_a \) is a constant parameter, and \( \overline{M_n} \) is the number average molecular weight.

The monomers of a thermoset resin have a relationship to the number average molecular weight of the reaction expressed as [14]:

\[ \frac{\overline{M_n}}{M_n} = \frac{(N_a m_a + N_b m_b)}{(N_a + N_b) - (aN_a P_a - N_{in.r})} \] \hspace{1cm} \text{(2.5)}

Where \( N_a \) and \( m_a \) are the mole and molecular weight of monomer a; \( N_b \) and \( m_b \) are the mole and molecular weight of monomer b; \( (N_a m_a + N_b m_b) \) is the total weight of the system; \( P_a \) is the fractional conversion of monomer a; \( aN_a P_a \) is the total number of groups in monomer a reacted; and \( aN_a P_a - N_{in.r} \) is the number of intramolecular reactions, which is important for crosslinking, particularly in the gel or after the gelation point [14].

The fractional conversion can be determined by using differential scanning calorimetry (DSC). For example, the fractional conversion (or extent of reaction, \( \alpha \)) of an epoxy resin/amine cured system is [21, 24]:

\[ \alpha = 1 - \frac{(\Delta H_f)}{(\Delta H_f)} \] \hspace{1cm} \text{(2.6)}

Where \( \Delta H_f \) is the residual heat of reaction, and \( \Delta H_f \) is the total heat of reaction.

For the reaction before gelation the \( N_{in.r} = 0 \), hence equation (2.5) becomes:

\[ \frac{\overline{M_n}}{M_n} = \frac{(N_a m_a - N_{smr})}{(N_a + N_b) - (aN_a P_a)} \] \hspace{1cm} \text{(2.7)}

At the crosslinking state one intramolecular bond introduces an average of two trifunctional crosslinking points; hence, [14]:

\[ N_{in.r} = \frac{1}{2} (X_{de} W) \] \hspace{1cm} \text{(2.8)}
Where $X_{dc}$ is the crosslinking density, and $W$ is the bulk mass.

The crosslinking density $(X_{dc})$ is related to the bulk mass $(W)$ by [14]:

$$X_{dc} = \frac{N_f}{W} \sum_{j=3}^{f} p^{(en)}_j \tag{2.9}$$

Where $N_f$ is the moles of monomer residues $(A_f)$, and $p^{(en)}_j$ is the probability of $j$ arms of functional group A in one $A_f$ unit.

The arms $(f)$ of the functional group A may connect to the network with $j$ arms, e.g. if 3 arms of a total of $f$ arms is linked to the network, the probability $j$ will be $(3 \leq j \leq f)$ [14]:

At a quite high degree of conversion ($\alpha > 0.58$) the reacting system of the thermoset resins can pass through the critical gel point [21]. The system can be a miscible mixture of sol and gel, and the $T_g$ can be considered to be a combination of the $T_g$ of each component in the following way [21]:

$$T_g = W_s T_{gs} + W_{gel} T_{gg} \tag{2.10}$$

Where $W_s$ and $T_{gs}$ are the weight fraction and glass transition temperature of the sol fraction; and $W_{gel}$ and $T_{gg}$ are the weight fraction and glass transition temperature of gel fraction.

The sol fraction $(W_s)$ and gel fraction $(W_{gel})$ can be determined using the following definitions [28]:

$$W_s = \frac{\text{weight of the soluble molecules/total weight of the sample}}{\text{weight of the cross-linked network, gel/total weight of the sample}} \tag{2.11}$$

$$W_{gel} = \frac{\text{weight of the cross-linked network, gel/total weight of the sample}}{\text{weight of the cross-linked network, gel/total weight of the sample}} \tag{2.12}$$

$T_{gs}$ is related to the number average molecule weight of the sol fraction $(\bar{M}_{n, sol})$ in the following way [19, 21]:

$$\frac{1}{T_{gs}} = \frac{1}{T_{gw}} + K/\bar{M}_{n, sol} \tag{2.13}$$

$\bar{M}_{n, sol}$ can be calculated from the stoichiometric balance in the sol fraction and the extension of the reaction; for example, in the reaction of diepoxy molecules and tetrafunctional amines [21]:

10
2. Literature Review

\[ \frac{M_n,\text{sol}}{M_b} = \frac{m_b + (2 / r_{\text{sol}})m_a}{1 + (2 / r_{\text{sol}}) - 4\alpha_b} \]  
\hline

Where \( m_a \) and \( m_b \) are the molecular weights of epoxy resin and amine respectively, \( r_{\text{sol}} \) is the stoichiometric balance between aminohydrogen and epoxy in the sol fraction; \( \alpha_b \) is the extent of reaction of amine in the sol fraction only.

The \( r_{\text{sol}} \) and \( \alpha_b \) can be determined from [21]:

\[ r_{\text{sol}} = \frac{\alpha_b}{\alpha_{\text{ass}}} = \frac{P^4}{(\alpha P^3 + 1 - \alpha)^2} \]  
\hline

Where \( \alpha \) is the fractional conversion or the extent of reaction of the system.

Ellis [28] suggested that the extent of reaction (\( \alpha \)) can be calculated from:

\[ \alpha = \frac{C_{\text{epo}} - C_{\text{epo}(t)}}{C_{\text{epo}}} \]  
\hline

Where \( C_{\text{epo}} \) is the initial concentration of epoxy groups, and \( C_{\text{epo}(t)} \) is the concentration of the sample at cure time (\( t_c \)).

For the stoichiometric system \( P \) can be determined from equation (2.18) [21]; (see Appendix B for the origin of this equation):

\[ P = \left( \frac{1}{\alpha^2} - \frac{3}{4} \right)^{1/2} - \frac{1}{2} \]  
\hline

Where \( P \) is the probability of finding a finite chain when looking from a random chosen molecule (\( B' \)); (see Figure 2.2 [21, 29]):

The glass transition temperature of the gel fraction (\( T_{g_g} \)) can be calculated from [17]:

\[ T_{g_g} = \frac{g_{\text{gel}}T_g + (T_{g_{\infty}} - g_{\text{gel}}T_g)[X_d]}{[X_d]_{\text{gel}}} \]

Where \([X_d]\) is the crosslinking density (see equation (2.9)), and \([X_d]_{\text{gel}}\) is the crosslinking density at complete conversion. Aronhime and Gillham [19] suggested that \([X_d]\) could be calculated from the density of polymer (\( \rho \)) and the moles of crosslinks per gram of polymer (\( N \)) by the following equation:
2. Literature Review

\[ [X_{\text{gel}}] = \rho N \]  \hspace{1cm} (2.20)

Figure 2.2 A schematic diagram of the possible reaction between diepoxide (A) and tetrafunctional amine (B) [21, 29]

The glass transition temperature of the system at the gel point, or the temperature at which the time to gel and the time to vitrify are the same \((\text{gTg})\), can be calculated from [23]:

\[ T_{\text{gTg}} = \frac{1 + (E_x / E_m - 1)X_{\text{gel}}}{1 + (F_x / F_m - 1)X_{\text{gel}}} \]  \hspace{1cm} (2.21)

Where \((E_x / E_m)\) is the ratio of the lattice energies for crosslinked and uncrosslinked polymer, \((F_x / F_m)\) is the corresponding ratio of segmental mobilities, and \(X_{\text{gel}}\) is the critical extent of reaction at the gel point. \(X_{\text{gel}}\) can be calculated from [23]:

\[ X_{\text{gel}} = \frac{1}{[r + rB(f - 2)]^{1/2}} \]  \hspace{1cm} (2.22)

Where \(r\) is the ratio of epoxide to amine hydrogen, \(B_f\) is the fraction of amine hydrogen that is part of a multifunctional reactant \((f>2)\); and \(f\) is the functionality of the branching unit, e.g. diepoxy/tetrafunctional amine system, with stoichiometric amounts \(r = B_f = 1\) and \(f = 4\) [23]:

\[ X_{\text{gel}} = \frac{1}{[1 + (4 - 2)]^{1/2}} \]  \hspace{1cm} (2.23)
2. Literature Review

\( \frac{E_x}{E_m} \) and \( \frac{F_x}{F_m} \) can be determined by fitting equation (2.24) to the \( T_g \) versus conversion (\( \alpha \)) data [25]:

\[
\frac{T_g - T_{go}}{T_{go}} = \frac{(E_x / E_m - F_x / F_m)\alpha}{1 - (1 - F_x / F_m)\alpha}
\]  \hspace{1cm} (2.24)

Where \( T_{go} \) is the glass transition temperature of unreacted material, and \( \alpha \) is the extent of reaction at the glass transition \( T_g \).

The mobility of a cross-linked unit of most polymer is expected to be zero, hence \( (F_x/F_m) = 0 \), and the ratio \( (E_x/E_m) \) may be approximated by [30]:

\[
\frac{E_x}{E_m} \approx \frac{\rho_x(M_o)x}{\rho_x(M_o)m} \left( \frac{\delta_x}{\delta_m} \right)^2
\]  \hspace{1cm} (2.25)

Where \( \rho_m, (M_o)_m, \) and \( \delta_m \) are the density, molecular weight, and solubility parameter of uncrosslinked monomer units, while \( \rho_x, (M_o)_x, \) and \( \delta_x \) are the density, molecular weight, and solubility parameter of crosslinked polymer respectively [30].

Neilsen [30] suggested from DiBennetto's work that for the styrene-divinyl benzene system the \( (E_x/E_m) \approx 1.2 \), and for many other cross-linked systems the \( (E_x/E_m) \) should be similar. Therefore, equation (2.24) can be approximated as:

\[
\frac{T_g - T_{go}}{T_{go}} \approx \frac{1.2\alpha}{1 - \alpha}
\]  \hspace{1cm} (2.26)

However, Adabbo and Williams [31] suggested that the experimental relationships between \( (T_g/T_{go}) \) or \( T_g^* \) and \( \alpha \) are consistent with \( 0 < (F_x/F_m) < 1 \). \( (F_x/F_m) \) can then be approximated from equation (2.24), if \( (E_x/E_m) \) is considered to be \( \equiv 1 \) [31]:

\[
T_g^* = \frac{1}{1 - (1 - F_x / F_m)\alpha}
\]  \hspace{1cm} (2.27)

Note: Cartmell and Fowles [32] explained that the energy required to move ions from their equilibrium position in the crystal to infinity is called "crystal or lattice energy". Oleinik [33] has modelled the structural features of crosslinking networks at all stages of their cure process as can be seen in Figure 2.3. This figure shows two possible network structures with the different probabilities of monocyclic formation in the primary and secondary amines [33].
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Figure 2.3 A computerised diagram which shows samples of network structures: (a) low and (b) high probability of monocyclization; $\rhd$ is the lattice crosslinks (aromatic amines); $\bigtriangledown$ is the unreacted ends [33]

The ability of polymer chains to rotate about single covalent bonds of chemical groups in their backbone is probably the most important motion mode [34]. However, the segmental motions of thermoset resins such as an epoxy/amine cured systems are limited by the tighter lattice [35]. At the glassy state the segmental rotation does not occur, but in the intermediate rubbery state the segmental motion is possible [34]. However, the ends of dissolved macromolecules have much more rapid segmental rotation than the chain interior [34].

2.1.2 Diffusion Control In The Cured Thermoset Resins

The isothermal curing ($T_{\text{cure}} =$ constant) of thermoset resins at a temperature lower than the maximum Tg of the resins reveals two important mechanisms: chemical reactivity and diffusion controlled [36]. The chemical reactivity controlled occurs at the cure temperature well above Tg [28], and the formation of macromolecular compounds of network structures may be considered to be accompanied by a rise in the Tg [37]. In other word, the rise in viscosity prior to gelation of the curing resin is caused by both the increase in Tg and molecular weight [28]. While the segmental motions are slowed down
2. Literature Review

as the reaction passes through the Tg, the system is controlled by these motions rather than by chemical factors [37]. As the different of temperature $(\Delta T)$ between curing $(T_{\text{cure}})$ and $T_g$, (or $\Delta T = T_c - T_g$), becomes small the curing system becomes diffusion controlled [28]. This results in a postcure schedule needing to be used to ensure the complete reaction of all reactive groups [28].

The chemical reactivity mechanism is temperature dependent as described by the Arrhenius equation [21, 38, 39]:

$$K = A \exp \left(-\frac{E_a}{RT}\right)$$

Where $K$ is the rate constant, $A$ is the constant characteristic of the particular reaction, $E_a$ is the Arrhenius activation energy, $R$ is the rate constant (i.e. 1.987 cal/mol.K), and $T$ is the temperature in Kelvin.

The diffusion controlled mechanism can be described by the Williams-Landel-Ferry (WLF) equation. The WLF equation is used to model the temperature dependence of mobility-related material properties [40] as follows:

$$\log(a_T) = \frac{-C_1(T - T_s)}{C_2 + T - T_s}$$

Where $a_T$ is the shift factor, $C_1$ and $C_2$ are the constants, and $T_s$ is the reference temperature.

2.2 Modification of Epoxy Resins

Thermoset resins show good performance at elevated temperature, and have high modulus and failure strength [41]. They also show some undesirable properties such as being relatively brittle, and poor resistance to crack initiation and growth [41]. This leads to studies of the modification of thermoset resins.

Improvements in their resistance to crack growth were first investigated in the 1960's by the used of rubber-modification with a minimum sacrifice of other desirable properties [42]. A major effort to study the failure behaviour of these materials as structural adhesives was launched in 1970 [42]. Further efforts to study the basic properties of the neat resins, and then the behaviour of adhesive and composites were
made in the 1980s [42]. A basic understanding of rubber-modified epoxy resins can be developed from these two studies [42].

Kinloch [41] reported in 1989 that epoxies, phenolics, polyesters, and polyimides can all be modified by a second phase of rubbery materials. Epoxies have been studied most extensively because of their increasing and wide use in structural adhesive and fibre composites [41]. Shaw [43] reported in 1994 that the diglycidyl ether of bisphenol A (DGEBA) epoxy resins have been studied the most, where the values of the repeating unit \( (n) \) was between 0 and 1. Although there are various types of epoxy resins available this system has a lower crosslink density in comparison with epoxies with tetrafunctional epoxide groups.

### 2.2.1 Previous works

Properties of epoxides can be changed by blending or compounding with other materials. Compounding two monomers together normally gives properties which are lower than for the individual monomers. However, it is possible to get beneficial properties with the right combination. For examples, the copolymer of monomers which would separately have brittle and flexible behaviour, might develop properties between these two extremes. This idea has been adopted in the modification of epoxy resins which are brittle materials, with very poor fracture resistance \( (K_{IC} \leq 1 \text{ MPa.m}^{1/2}) \) [44].

In an attempt to improve the fracture resistance [44] or impact resistance (toughness) of epoxy resins, reactive liquid rubbers, such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) [13, 45], have been blended into the initial reaction mass. The most convenient and effective method of enhancing epoxy toughness is by the addition of a liquid elastomer. However, other modification methods are possible [45].

Poly(phenyldiphenyl ether) (PPDE) elastomer, with an average particle size of a few microns, was dispersed and partly chemically linked by covalent bonding into a diglycidyl ether of bisphenol A epoxy resin [46]. The interfacial bonding between the two-phase structure of the resulting rubber-modified epoxy was important in decreasing the brittleness of the epoxy matrix. The overall strain required to initiate failure was increased due to the rubber particles deforming in the matrix in compression in the axial direction [44]. Troung [45] also explained that the rubbery second phase tended to stabilise crack propagation but did not have a large influence on the fracture toughness.

Epoxy-isocyanate [47, 48] and epoxy-urethane [10, 49, 50] systems have been reported. These show good resistance to many aggressive media and excellent mechanical properties, compared to other polymer systems [47]. The isocyanate group (-NCO) is extremely reactive. However, this leads to difficulties in processing and handling since is
moisture sensitive and health hazardous [49]. Its hazard and moisture sensitive are reduced by prepolymerizing with polyglycol to form an isocyanate-tipped urethane prepolymer such as [49, 51]:

(a).
\[
\begin{align*}
&\text{disocyanate} \\
&\text{diol}
\end{align*}
\]

An isocyanate group can react with available hydroxyl groups associated with epoxy oligomers to form urethane linkages; this readily occurs at relatively low activation energy such as [1, 47]:

(b).
\[
\begin{align*}
&\text{disocyanate} \\
&\text{hydroxyl}
\end{align*}
\]

An isocyanate can also react with amine groups to form urea [1, 51]:

(c).
\[
\begin{align*}
&\text{amine}
\end{align*}
\]

Therefore, crosslinked structures can result from the reactions between epoxide, amine, and isocyanate [1].

A blocked isocyanate is made by reacting a diisocyanate with any one of a number of monofunctional alcohols. Blocked isocyanates are not normally reactive at ambient but
become activated by heating at 150-200°C [53] to give free isocyanate group (i.e. deblocks). This leads to crosslinking [52]:

\[
\begin{align*}
\text{R'} - &\text{N} - \text{C} - \text{O} - \text{R'} \quad \overset{k_1}{\rightarrow} \quad \text{R'} - \text{N} = \text{C} = \text{O} + \text{R'} - \text{O} - \text{H} \\
\text{blocked isocyanate} \\
\text{R'} - &\text{N} = \text{C} = \text{O} + \text{R}-\text{XH} \quad \overset{k_2}{\rightarrow} \quad \text{R'} - \text{N} - \text{C} - \text{X} - \text{R} \\
\end{align*}
\]

Where \( X \) can be \( \text{O}, \text{N} \) or \( \text{S} \)

Catalyst can reduce the temperature of deblocking. In this project a blocked isocyanate tipped urethane prepolymer was used. Such urethane polymeric modifiers contain groups such as urea, ester, ether, and aromatic structure often along with the repeating urethane groups. A wide range of polymer properties are therefore possible because of the diversity of the polyurethane structures [53]. The aromatic and ester groups contribute moderate intermolecular forces, the urea and urethane groups contribute very strong polar intermolecular forces, while the ether and associated aliphatic groups provide relatively flexible components [53].

Drake and Siebert [54] suggested that a modified epoxy resin can be toughened when it has a rubber content between 3.5 and 20 phr, and is flexibilized when its rubber content is between 20 and 50 phr (see Table 2.1).

The toughened systems are used in various applications such as adhesive pastes, solutions, laminates (prepregs, structural panels, filament winding), powder coatings, potting and moulding, compounding electrical applications, etc. [54]. Whereas, the flexibilizing systems are used in various applications such as adhesive films, adhesive tapes, pipe coatings, flexible circuitry, coil coating, etc. [54].

The term "toughness" can be defined in various ways depending on the materials under consideration. The toughness of polymeric materials can be determined by the area under stress-strain graphs [55, 56]. The wide range of stress-strain behaviour of some polymeric materials are shown in Figure 2.4 [55].
Table 2.1 An example of the relationships between the rubber (CTBN) contents in modified epoxy resins, and the terms "toughening" and "flexibilizing" [54].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Toughening</th>
<th>Flexibilizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA epoxy resin</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Bisphenol A (Diphenyl)</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>CTBN</td>
<td>&gt;3.5&lt;20</td>
<td>&gt;20&lt;50</td>
</tr>
<tr>
<td>Continuous phase</td>
<td>epoxy</td>
<td>intermediate</td>
</tr>
<tr>
<td>Second phase</td>
<td>rubber</td>
<td>intermediate</td>
</tr>
</tbody>
</table>

Figure 2.4 Stress-strain behaviour of some polymeric materials [55]

Tough materials will absorb greater amounts of energy before failure gives rise to crack propagation, and the fracture is delayed to much higher strains [57]. In epoxy/amine cured systems the toughening can be improved by the use of chain extenders of bisphenol A, by the use of an excess-amine curing agent (50%), and by the use of high molecular weight crosslinking agents such as polyoxypropylene amines [58]. Epoxy resins can also be toughened by rubber modification, in which the toughness is a primary function of the rubber content [58, 59]. Bascom and Hunston [60] found that the fracture energy
2. Literature Review

increases with increasing rubber content. The point where the desired particle-matrix morphology becomes difficult to obtain was often at about 18% rubber [60]. However, the effects of morphological details are not clearly understood although general morphological requirements for two-phase toughened polymer are well documented [60]. While, Bucknall [61] mentioned that the highest toughness of rubber-modified epoxy resins based on CTBN rubber was obtained with acrylonitrile levels between 12 and 18 % wt.

A). Gibbs Free Energy of Mixing

An understanding of the fundamental thermodynamic factors which govern the microphase separation can be used to optimise the properties of copolymers [62]. The Gibbs free energy of mixing (ΔG_m) is normally used in this respect and is given by [61, 62]:

\[ ΔG_m = ΔH_m - TΔS_m \]

Where \( ΔH_m \) is the enthalpy of mixing, \( T \) is the mixture temperature, and \( ΔS_m \) is the entropy of mixing.

This equation can be used to determine whether the component are compatible [61]. Generally, the mixed system gives \( ΔS_m \) positive because the mixing involves an increase in disorder of the system [61]. If \( ΔH_m \) is negative or the mixed system is exothermic, the components will be miscible [61]. (The differences between inter-component and intra-component interaction effects the enthalpy of the mixing system [62]). In most cases miscibility between pairs of similar molecular weight substances is due to entropy rather than the enthalpy effects [61]. The chemical bond linking or connectivity of the monomers along the chains, which is absent in small molecules in the mixture, can cause a drastic decrease in the possible entropy gain of the mixture [62]. Polymers generally resist being surrounded by other dissimilar polymers, and this causes phase separation to occur when the entropy gain of the mixing molecules becomes very small and usually enthalpy is positive [62]. In other word, the system spontaneously phase separates when \( ΔG_m > 0 \) [62].

Note: In the case of block copolymers phase separation may be classified in two ways: microphase and the macrophase separation. When chemical linkages occur between the component blocks the size of phase separation is limited to a microscale, this is thus called "microphase separation" [62]. On the other hand, the macrophase separation generally occurs when no chemical linkages between the component blocks are present.
2. Literature Review

and thus the phase are not prevented from growing beyond sizes comparable to molecular dimension [62]. Hence, incompatible blend samples are often opaque, if the phases are large enough to scatter visible light [62].

The heat of mixing ($\Delta H_m$) of any two-component system can be given as [63]:

$$\Delta H_m = RT\chi_1 n_1 V_2$$

and the entropy of mixing disoriented polymer and solvent may be obtained from [63]:

$$\Delta S_m = -R(n_1 \ln V_1 + n_2 \ln V_2)$$

Substituting equations (2.31) and (2.32) in equation (2.30) gives [63, 64]:

$$\Delta G_m = RT((n_1 \ln V_1 + n_2 \ln V_2 + \chi_1 n_1 V_2)$$

Where $R$ is the gas constant, $T$ is the temperature, $V_1$ and $V_2$ are the volume fractions of solvent and solute respectively, $n_1$ and $n_2$ are number of solvent molecules and solute molecules in a solution, and $\chi_1$ is the interaction parameter per mole of solvent (component 1: i.e. epoxy resin) [65].

The volume fraction of each component can be written as [63]:

$$V_1 = n_1 (n_1 + V_m n_2)$$

and

$$V_2 = V_m n_2 (n_1 + V_m n_2)$$

Where $V_m$ is the ratio of the molar volume of the solute to the solvent (i.e. epoxy) or the molar volume of the liquid mixture [63].

The heat of mixing ($\Delta H_m$) can be related to the solubility parameter as [61]:

$$\Delta H_m = V_m (\delta_1 - \delta_2) V_1 V_2$$

Where $\delta_1$ and $\delta_2$ are the solubility parameters of component 1 and 2 respectively. Therefore, the $\Delta H_m$ from equation (2.31) can be written as:

$$\Delta H_m = RT\chi_1 n_1 V_2 = V_m (\delta_1 - \delta_2) V_1 V_2$$
The substitution of $\Delta S_m$ from equation (2.32) and $\Delta H_m$ from equation (2.36) in equation (2.30) gives:

$$
\Delta G_m = V_m(\delta_1 - \delta_2)^2 V_1 V_2 + R(n_1 \ln V_1 + n_2 \ln V_2) \quad \text{(2.38)}
$$

At the first stage of mixing $\Delta G_m$ should be negative if the system has good compatibility [43]. As the reaction occurs the magnitude of the molar volume of the liquid mixture ($V_m$) tends to increase due to the molecular build up [43], and results in a rise in $\Delta G_m$. The interaction parameter which effects the mixing polymers should be very small or negative in the first stage of mixing for a completely compatible mixture [61]. As the chain length increases $\Delta H_m$ tends to increase because the interaction parameter increases (equation (2.37)). Under these conditions, the rubber particles would precipitate as soon as the molecular weight began to rise [66]. The higher the free energy of mixing ($\Delta G_m$), the higher the volume fraction of rubber, in cases where the solubility parameters are the same for the same system [67]. Hence, systems with higher contents of rubber give higher phase separation [67].

The optimum phase separation is achieved when $\Delta G_m$ is very small or negative at the beginning of the reaction [66]. Whereas, poor phase separation can be improved by increasing the initial molecular weight of the resin or the rubber, or by increasing the difference in the solubility parameter between the resin and rubber ($\delta_1 - \delta_2$) [66]. The phase separation can also be influence by curing agent and curing temperature [43]. Full phase separation can be prevented by highly reactive curing agents which cause rapid crosslinking reactions and premature gelation [43]. Curing at high temperature can increase the cure rate and promote an improvement in epoxy/elastomer compatibility, but retard phase separation [43]. If the temperature is high enough to give complete miscibility up to gelation, phase separation will not be observed [64]. By adding catalyst to the mixture the polymerisation will be accelerated which results in the same effects as a temperature increase [65].

B). Particle Size

It has been found that the average rubber particle size is a maximum at an intermediate cure temperature [68]. Whereas, curing at a low temperature gave a lower in volume fraction of phase-separated rubber [68]. Therefore, overall phase separation can be expected at a maximum or intermediate curing temperature [20]. A schematic diagram of the relationship between gelation temperature and separated particles is shown in Figure 2.5 [68]. It shows a maximum volume fraction of phase-separated rubber at an intermediate temperature [68].
Two phase morphology frequently plays a critical role in toughness enhancement [43]. Rubber-modified epoxy products may fail by several mechanisms as shown in Figure 2.6 [69]. Maximum toughening is obtained under a combination of two mechanisms: shear and craze deformations [70]. Toughened resins with small rubbery particles (<0.5μm) are dominated by shear deformations. Whereas, systems with large particles (1-5μm) are dominated by crazing which is associated with polymer whitening and microvoid development [70]. Hence, polymers can achieve maximum toughening by the presence of both small and large particles in the system [70].

In epoxies toughened by an epoxy-terminated butadiene acrylonitrile rubber (ETBN), and an amino-terminated butadiene acrylonitrile rubber (ATBN), the shear deformation was considered as the major toughening mechanism [71]. The plastic shear deformation, is caused by the presence of rubber particles, and is initiated around the rubber-matrix interfaces [41]. The maximum shear stress concentration is likely to occur between the equator and the pole of the particles [41].
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Note: The shear-yielding process can also be enhanced by voids [41]. Void formation either at the particle-matrix interface or in the particles can be caused by cooling after cure [41]. The size of the particles can be varied by using different types of modifiers, and hence can be used to compare particle size effects in particular studies. Studies are reported by Riew et al. [70], and Pearson and Yee [72]. Riew et al [70] showed that an epoxy resin modified with different types of CTBN rubber gave difference particle sizes. Small particles were found to be <0.5 μm, and large particles between 1 and 5 μm. Whereas, Pearson and Yee [72] used the CTBN and carboxyl-terminated butadiene (CTB) rubbers as modifiers for an epoxy resin. They showed that the average diameter of small particles (for CTBN) was 2 μm and that large particles were 100 μm (for CTB).

2.3 Characterisation of Cured and Uncured Epoxy Resins and Composites

2.3.1 The Study of Epoxy Resins by Thermal Analysis

Figure 2.6 Crack growth mechanisms in rubber-modified polymers [69]
2. Literature Review

There are two possible events that can cause stiffening of a polymer; either crystallisation and/or cooling below its glass transition [73]. Polymeric materials become much stiffer as they cool from the rubbery state through a range of temperature [73]. Certain polymers crystallise if their cooling rates are slow enough and there is specific regularity along the length of the molecular chains to allow the formation of crystalline lamellae [73]. Many polymers, including thermosets, cannot crystallise and instead have an amorphous or liquids-like molecular structure above their Tg. As the material passes through either its Tg or Tm transition, a drastic change of macroscopic properties will be observed [73, 74]. In the narrow transition regions, properties can changed by large amounts [74]. The free volume of polymers can be reduced by up to 11% of the total volume above the glass transition temperature (Tg) [73]. Below the transition temperature a decrease in free volume and molecular mobility will be observed in a polymer resulting in a higher modulus and lower creep compliance (i.e. it is stiffer) [73].

There are several methods that can be used to determine the Tg of thermoset resins, for example; differential scanning calorimetry (DSC) (which is normally used to determine heat release or in-put); dynamic mechanical thermal analysis (DMTA) (which is normally used for viscoelastic measurements); and thermomechanical analysis (TMA) (which is normally used to measure dimension changes in thermosets) [75]. Only the first two methods have been used in this project and will be reported at this time.

**Differential Scanning Calorimetry (DSC)**

The advantage of DSC over other methods is that only a small test sample is required [73] i.e. from 1 to 10 mg, while the equipment can be used at a wide range of heating rates (0.5 to 80°C/min), and be sensitive enough to detect the heat absorption or evolution at a rate of less than 1 mcal/sec [76].

A typical thermogram of a polymeric material from a DSC scan is shown in Figure 2.7 [77]. The endothermic peak refers to heat absorbed by the sample and the exothermic peaks indicate the heat release from the sample.

The Tg of an epoxy-amine cured system has been shown to be significantly affected by relatively small variations in stoichiometry when investigated by DSC [78]. This work also showed that the maximum Tg is always observed at the stoichiometric proportion. Moreover, for increased epoxy levels the Tg values decreased more than when the amine levels were increased [79]. A diglycidyl ether of bisphenol A epoxy resin cured with an amine in a bulk reaction had a higher Tg than the same reactants mixed in a methyl ethyl ketone solution at 15°C [80]. This indicates the disadvantage of the use of diluent in the system.
2. Literature Review

DSC can also be used to study the curing behaviour of epoxy resins e.g. the degree of conversion [36, 81]. Montserrat [36] used DSC to analyse the structure relaxation process. Here the endothermic peak was analysed and with the use of the residual enthalpy technique, the degree of conversion of isothermally cured epoxy resins were studied. In a number of studies DSC has been widely used to investigate epoxy resins toughened by the incorporation of flexible materials [82-86]. For example, Iijima et al. [82] reported that the Tg of a parent epoxy resin was equal to or higher than that of a modified epoxy/terpolymer system. Whereas, Carfagna et al. [83] found that the Tg of a thermoplastic polyester modified epoxy resin was only slightly affected by the presence of a toughening polymers.

DSC has also been used to study changes in epoxy Tgs with process conditions. The Tg of an cured epoxy system was found to be significantly affected by the stirrer speed used to mix the reactants. In a study, speeds between 45 and 800 rpm were investigated and a sharp increase in Tg was found with speeds up to 300 rpm, but there was little change at higher speeds [87].

**Dynamic Mechanical Analysis**

Dynamic mechanical thermal analysis (DMTA) is one of several techniques which have been used to investigate epoxy resins and modified epoxy systems. It can be used to...
monitor the changes in molecular structure due to variation in several factors, for example, processing conditions, amounts of curing agent, and amount of modifiers. The results of these measurements are normally presented in terms of storage modulus ($E'$) or log storage modulus (log $E'$), and tangent loss angle ($\tan \delta$). These parameters can be affected by the experimental conditions used when operating the instrument. This means that the conditions used have to be consistent for a good comparison of the results.

Annealing effects can also be investigated from the results of DMTA. For example, $E'$ increases as the annealing time increases, whereas $\tan \delta$ decreases [88]. Hence, the value of $M_C$ decreases due to annealing since $E'$ is increased (equation (2.48)). The compatibility of several phase transitions can be investigated using $\tan \delta$ traces [88]. Poor compatibility is shown by the appearance of individual $\tan \delta$ peaks which are influenced by the original raw material alone. Good compatibility will occur if these two phases merge together [88].

In this technique the sample is deformed cyclically [89], and the response of the material to the frequency, vibration forces, stress and strain are monitored [90]. Information on the relaxation of the sample can be obtained from an analysis of the stress-strain relationships, it varies with changing temperature [89].

Figure 2.8 [90] shows curves of stress and strain at different frequencies. The following equations express these relationships [91]:

\[
\omega = 2\pi f \quad \text{-----------------(2.39)}
\]

\[
\varepsilon = \varepsilon_0 \sin \omega t \quad \text{-----------------(2.40)}
\]

Where $\omega$ is the angular frequency (rad/s), $f$ is the frequency (Hz), $t$ is the time (seconds), and $\varepsilon$ is the strain.

While the corresponding stress is [91];

\[
\sigma = \sigma_0 \sin (\omega t + \delta) \quad \text{-----------------(2.41)}
\]

or

\[
\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad \text{-----------------(2.42)}
\]

Where $\sigma$ is the stress, and $\delta$ is the phase angle.

Figure 2.9 [92] shows the stress and strain amplitude in a dynamic mechanical analysis, and these can be related to storage and loss modulus in the following way:
2. Literature Review

storage modulus \( E' = \frac{C}{B} \) \hspace{1cm} (2.43)

loss modulus \( E'' = \frac{D}{B} \) \hspace{1cm} (2.44)

Where storage modulus \( (E') \) is the energy stored per cycle [93], which is defined as [92]:
\[
E' = \text{in phase stress amplitude} / \text{strain amplitude} \hspace{1cm} (2.45)
\]

and loss modulus, or energy loss, which is dissipated as heat during the deformation of the material as [91, 93]:
\[
E'' = \text{out of phase stress amplitude} / \text{strain amplitude} \hspace{1cm} (2.46)
\]

Figure 2.8 Curves of strain and stress for three different frequencies [90]

The strain is in phase with the stress for completely elastic material, and the strain lags behind the stress by 90° (out of phase) for a purely viscous material [92]. Since temperature can effect the viscoelastic behaviour of polymers, the elastic-like component which is governed by the storage modulus \( (E') \) is resolved in the in-phase, and the viscous-like component which is governed by the loss modulus \( (E'') \) is resolved in the out-of-phase [92].
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The tangent of the loss angle or tan δ (damping) is dimensionless and can be calculated from [93]:

\[ \tan \delta = \frac{E'}{E} = \text{loss modulus} \div \text{storage modulus} \quad \text{(2.47)} \]

![Figure 2.9 In-phase and out-of-phase stress with respect to strain [92]](image)

The change in \( E' (\Delta E') \), is determined from the difference of the maximum and minimum values, and is directly related to tan δ. That is, \( \tan \delta \) is greater as the \( \Delta E' \) is larger [88]. \( E' \) is proportional to the molecular weight between crosslinks according to the following relationship [78]:

\[ E = \frac{3\rho RT}{Mc} \quad \text{(2.48)} \]

Where \( E \) is the elastic modulus, \( \rho \) is the density, \( T \) is the temperature in degrees Kelvin, \( R \) is the gas constant, and \( \overline{Mc} \) is the number average molecular weight of the polymer between crosslinks.

Figure 2.10 [92] shows an example of plots of storage modulus and tangent of the loss angle for a semi-crystalline polymer. Subscript \( a \) represents relaxation regions of
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amorphous, and subscript \( c \) represents relaxation of crystalline regions [92]. The \( \alpha \) peak is generally the tangent loss peak associated with the glass transition temperature [91]. \( \alpha_a \) in Figure 2.10 is the \( T_g \) of the polymer and the subsequent glassy state relaxation at lower temperatures are \( \beta, \gamma, \delta \) etc. [92]. The magnitude of the \( \alpha \) peak in the semi-crystalline polymer is much smaller than in an amorphous polymer, due to the chain segments of the amorphous polymer being freer to move [91]. DMTA can be used to determine the variation of \( T_g \) (e.g. under different strain condition), phase separation, relaxation spectra, structure or morphological change resulting from the chemical composition of polymer blends and copolymer, and processing variation [91].

![Figure 2.10 DMTA curves of semi-crystalline material: a, amorphous; c, crystalline [92]](image)

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is used to investigate the molecular structure of polymers, although at the same time it can provide other information; for example, purity, kinetics of the reactions, and quantitative analysis [94]. An infrared spectrum of a pure sample will be fairly sharp [95] but the presence of impurities will have a negative effect on the sharpness of individual bands [94]. High molecular weight materials composed of many kinds of functional groups will give poor spectra compared to more simple polymer structures [95].

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2. Literature Review

The intensity of light on passing through an absorbing medium, can be derived from Beer's and Lambert's laws as [89, 94]:

\[ A = \log \left( \frac{I_0}{I} \right) = kcd \]  

Where \( A \) is the absorbance, \( I_0 \) is the incident light intensity, \( I \) is the intensity at a depth \( d \) in the absorbing medium, \( k \) is the extinction coefficient or a constant for the material, termed the "absorbivity", \( c \) is the concentration of the absorbant material, \( d \) is the thickness of the sample.

The Fourier Transform techniques was originated by the French mathematician, Jean Fourier (1768-1830). He showed that any wave motion can be described by a sum of the waves [96]. This technique has been applied to infrared study in conjunction with a dedicated high speed computer [96]. All of the resolution elements for a spectrum are measured simultaneously by the technique [96].

2.3.3 Microscopic examinations

Microscopic studies have been widely used to investigate both unmodified and rubber modified epoxy resins.

Studies of fractured surfaces of unmodified epoxy resins have been reported by various researchers who used the scanning electron microscopy (SEM) [97, 98, 99]. For example, Cantwell and Kausch [97] showed variations in crack velocity of single edge notch specimens by comparing the roughness of fractured surfaces. They also showed the parabolic marking similar to those presented by Bandyopadhyay [98], who showed the fracture surfaces of double cantilever beam specimens. While, Ting and Moulton [99] studied fracture surfaces from the izod impact specimens, and revealed similar surfaces as shown by Bandyopadhyay [98].

The SEM has also been used to study rubber-toughened epoxy systems. Carboxyl terminated butadiene acrylonitrile rubber (CTBN) modified epoxy has been the most widely studied and reported [44, 45, 59, 72, 86, 100, 101]. However, other types of rubber have also been studied, such as urethane [102], and hydroxyl-terminated liquid elastomers [103].

Rubber-toughened epoxy systems which contain small particles of rubber can be shown more clearly by using transmission electron microscopy (TEM), as reported by Yee and Pearson [104], and Huang et al. [105]. Yee and Pearson [104] successfully showed
2. Literature Review

Particle sizes as small as 0.1 μm in TEM micrographs of CTBN modified epoxy resin systems. They suggested that it was important to observe by this method because even a small amount of rubber which remains undissolved in the epoxy could obscure the interpretation of the fracture mechanisms. While, Huang et al. [105] showed the usefulness of the TEM by presenting micrographs of a CTBN modified epoxy resin, in which the particle size was small (<0.1 μm) and could not be seen by the SEM. However, they also used the SEM to show the microstructure of the larger particle sizes (>1 μm).

Particles of rubber can be highlighted by using staining method and TEM examination. The most important staining agent for elastomeric polymer is osmium tetroxide (OsO₄) [106]. Osmium tetroxide was first developed by an English chemist, Smithson Tennant (1761-1815), in 1803 [107]. It is a pale yellow solid with a melting point of 40.6°C, a boiling point of 121.2°C, and a density of 4.906 g/cm³ [107]. It has a solubility of 7.2 per cent in water at 25°C [107]. The stained specimen will show dark and light areas on the TEM micrographs. The dark phase is the stained rubber particles, and the light phase is the epoxy resin, such as would be shown in the CTBN modified epoxy resins system [104].

2.4 Mechanical Properties and Characterisation

The mechanical properties of cured epoxies and modified epoxy systems have been examined by a large number of researchers. In studies of epoxy/amine cured systems, modulus was found to be significantly affected by variations in the amounts of curing agents [78]. The presence of a diluent in epoxy/amine systems produced a reduction in crosslinking density, with a resultant increase in the chain flexibility: as a result there was an improvement in fracture toughness [108]. The molecular weight between crosslinks of a series of cured epoxy resins has been studied by Bell [109]. He reported that the distance between crosslinks did not significantly effect the initial modulus and ultimate tensile strength. Gupta et al. [110] studied the postcuring of epoxy resins, cured with different amounts of curing agent. They found that there was a considerable increase in crosslinking and an increase in tensile strength with amount of curing agent. The greatest changes in modulus and tensile strength were observed after postcuring systems with excess epoxy (i.e. in non-stoichiometric systems) [110]. Moreover, the variations in elongation to break and the toughness within each set of samples was much higher than the variations in modulus and tensile strength [110].
2. Literature Review

Properties of cast resins are important as they can be used to predict the strength of laminates made from them [111]. The mechanical properties of glass reinforced plastics depend significantly on how strong the resins adhere to the reinforcing fibres [112]. The chemical structure of the polymeric binder is the most important variable which effects the adhesion between the polymer and the glass fibres. For example; the content of functional groups, flexibility, and the mobility of the polymeric fragments in the network structure of the thermoset resins [112]. The lowest adhesion occurs in the looser polymer structures [112].

Broutman [113] suggested that the adhesion at the glass/polymer interface could be enhanced by coupling agents, which serve as an intermediate layer between the polymer matrix and the fibre surfaces. There are several mechanisms by which coupling agent in composites can operate [113]: (1) Coupling agents can reduce voids at the interface of the polymer matrix and fibre by displacing the air by itself. (2) They can provide a low modulus and flexible layer at the interface, or, (3) coupling agent can increase the adhesive strength between the polymer matrix and fibre [113].

Dorey [114] suggested that the fibre surface condition, the size or surface finish, the fibre structure, and the matrix structure away from the interface, could all effect the failure mechanisms of the composite. A composite will not support load in shear or compression if the bond between the polymer matrix and fibre interface is too weak, and the composites will be brittle if the bond between the polymer matrix and the fibre interface is too strong [114].

Whitney and Drzal [115] reported a method for the determination of interfacial shear strength for a single fibre. The tested specimen dimensions were nominally 25 mm in length, with a cross section 3 mm wide and 1.5 mm thick, while the fibre diameter was of the order of 0.01 mm. They suggested that the value of Le, theoretically, can be determined from stress analysis, and is associated with the distance along the broken fibre required to dissipate end effects [115]. They also suggested that the interfacial shear strength (τ) can be described as:

\[
\tau = \frac{\sigma_f}{2} \left( \frac{R}{L_e} \right)
\]

Where \(\sigma_f\) is the measured fibre axial strength at the critical length as determined from tension tests performed on fibre segments, and \(R\) is the radius of the fibre [115].
2. Literature Review

Wells and Beaumont [116] reported a similar result for a brittle matrix. Stress in the fibre ($\sigma$), was related to the bond stress ($\sigma_d$) and the distance away from the debond crack ($x$). The relationships between them can be described as [116]:

$$\sigma = \sigma_d + \frac{4\tau x}{d}$$

Where $\tau$ is the frictional shear stress, and $d$ is the fibre diameter.

Debonding will continue until $\sigma$ reaches the tensile strength of the fibre ($\sigma_f$). The total debonded length will then be given by [116]:

$$l_d = \frac{d}{2\tau} (\sigma_f - \sigma_d)$$

Where $l_d$ is the total debonded length of the fibre.

Wells and Beaumont [116] suggested that the toughness of glass fibre/epoxy composites was affected by a combination of several complex interdependent material parameters. These were: (1) toughness decreases rapidly with increasing frictional shear stress ($\tau_f$), (2) toughness increases rapidly with increasing fibre strength ($\sigma_f$), (3) toughness decreases slowly with increasing interface strength and fibre modulus, and (4) toughness is approximately proportional to the square of the fibre diameter (assuming that the fibre strength is independent of diameter) [116].

The first two conditions, which are the major influence on toughness, can be related to the debonded length ($l_d$) as in equation 2.57. That is as $l_d$ decreases the frictional shear stress ($\tau_f$) increases, and $l_d$ increases as the tensile strength of the fibre ($\sigma_f$) increases.

Berg et.al. [117] and Whitney and Browning [118] suggested that the interlaminar shear test is used only for screening, and quality control, because the interlaminar shear strength test may represent the minimum shear strength value of the composite, which occurs uniformly along a segment of the beam centre, and as such is insufficient [118].

However, Roy and Kim [119] suggested that the three-point-bend test for measuring the interlaminar shear stiffness of symmetric laminates produces reliable data. They stated that the shear strain at mid-depth of symmetric laminates measured by this test are sufficiently away from the loading point. Roy and Kim [119] also suggested that an advantages of this test is the short time needed to prepare specimens, since they are have rectangular cross section.
2. Literature Review

Impact tests are alternative methods which can be used to study toughened polymer matrix/fibre composites. Lee and Zahuta [120] defined impact behaviour of composites by damage size, energy absorption, and impact force. Williams [121] concluded from a study of toughened epoxy resin/graphite fibre composites that the damage zone caused by impact can be reduced by a toughened resin systems. While, Lee and Zahuta [120] concluded that for the same damage size generated by an impact test the tougher composites required higher impact forces. However, they stated that the exact process of damage growth by impact, leading to observations of delamination size and distributions, were still unclear. Jang et.al. [122] suggested that impact energy dissipation can be affected by the matrix-fibre interfacial bonding and interlaminar cracking.

Elber [123] reported that the type and extent of impact damage is dominated by matrix toughness, and both the tougher matrix and fibres are required in tough composite systems. He also reported that the matrix shear strength controls the onset of delamination damage, and the fibre strength controls the penetration phase for both thin and thick laminates. Similarly, Morton and Godwin [124] suggested that the residual compressive strength of composites can be improved by the matrix toughness which is thought to delay the onset of matrix cracking and delamination.
3. EXPERIMENTAL PROCEDURES

3.1 Materials

3.1.1 Raw Materials

A) Epoxy Resin

An unmodified liquid bisphenol A epichlorohydrin epoxide resin i.e. Epikote 828 (ex. Shell Chemicals) was used as the main resin. Its epoxide equivalent weight is between 182 and 194 (n = 0.13) with a density at 25°C of 1.16 Kg/l [125]. Epikote 828 has medium viscosity (measured to ASTM D445) of 9 to 14 Pa.s, and can be used at room or elevated temperature without solvent diluent [125]. Its structure is believed to be:

\[
\begin{align*}
&\text{Structure Epikote 828; where } n = 0.13. \\
&\text{It is used in many applications, for example, in the electrical and electronic industries, as adhesives, surface coatings, having high resistance to mechanical and chemical attack [125], and for composites.}
\end{align*}
\]

B) Curing Agent

Ancamine MCA (ex. Anchor Chemical, UK) was used as the main curing agent in this research programme, having an amine hydrogen equivalent weight of 102. It is a product of the reaction of isophorone diamine with phenol formaldehyde. It is likely that it contains some free isophorone diamine and phenol [126]. It has high reactivity and is used since it cures under a variety of conditions, including low temperature (down to 5°C), high humidity and under water [127]. It also has low water miscibility.
and gives excellent chemical resistance to the cured epoxy [127]. Its structure is believed to be [126]:

Structure Ancamine MCA

C) Commercial Rubber Modifiers

Generally rubber modifiers are employed to increase the flexibility of epoxides (i.e. lower modulus) but also to improve impact properties.

C.1) Desmocap II was used as one type of rubbery modifier in this work. Desmocap II (ex. Bayer plc.) is a liquid urethane pre-polymer containing ether, urethane, and blocked isocyanate groups [128]. Its structure is believed to be [129]:

Structure Desmocap II

It is a solvent-free product but also has a high viscosity at 25°C of 80,000 ± 15,000 mPa.s; it is light-coloured [128]. In cured epoxides, its contribution to properties can be influenced by variation of the type of amine curing agent [129] and reaction conditions (e.g. temperature). Optimum results are obtained with cycloaliphatic diamines, e.g., Ancamine XT [128]. As determined empirically, it is considered to have an apparent epoxy equivalent of 860 to 1000 [128].

C.2) Polyamine Modifiers.

There were four types of polyamine modifiers used in this study, i.e. Jeffamine types (supplied by Huntsman Chemical, formerly Texaco U.K.). Their structures are based on a polypropylene glycol (PPG) backbone with the trifunctional amines for the T series, and difunctional amines for the D series, tipping the chain ends [130].

37
The structure of the Jeffamine T series is believed to be [130]:

\[
\begin{align*}
\text{Structure Jeffamine T series} \\
\end{align*}
\]

The structure of Jeffamine D series is believed to be [130]:

\[
\begin{align*}
\text{Structure Jeffamine D series} \\
\end{align*}
\]

They are liquids, light in colour, and low in viscosity [130]. Some important properties of these materials are shown in Table 3.1 [130, 131].

Table 3.1 Selected properties of Jeffamine modifiers

<table>
<thead>
<tr>
<th>Type of polyetheramines</th>
<th>Viscosity at 20°C mPa.s</th>
<th>Molecular weight</th>
<th>Amine hydrogen equivalent weight (AHEW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T5000</td>
<td>~911</td>
<td>~5000</td>
<td>943</td>
</tr>
<tr>
<td>T3000</td>
<td>~513</td>
<td>~3000</td>
<td>526</td>
</tr>
<tr>
<td>D4000</td>
<td>~960</td>
<td>~4000</td>
<td>1111</td>
</tr>
<tr>
<td>D2000</td>
<td>~378</td>
<td>~2000</td>
<td>500</td>
</tr>
</tbody>
</table>

D) Glass Fibres.

The glass fibres were grouped together to form strands (or yarns) which in turn were woven to produce a fabric. In this work a plain weave, which is one warp yarn interlaced over and under one weft yarn, was used. This type of fabric was chosen as it demonstrates the greatest degree of stability with respect to yarn slippage and fabric distortion. The glass fibres had the following properties:

- Tensile strength: 1750 GPa
- Young's modulus: 70 GPa
- Density: 2.55 g/m³
The fabric had the following specification (ex. Owens Corning):

- Construction: 4.5 x 4.5 tows/cm
- Weight: 193 g/m²
- Thickness: 0.18 mm

### 3.1.2 Specimen Preparation

**A) Specimens for Dynamic Mechanical Thermal Analysis**

i) Cured Resins Studied

The mixture of resin was cast in PTFE moulds to obtain a cured specimen of the dimensions 10x120x3 mm³. After cure non-postcured specimens were directly cut to a length of ~25 mm for dynamic mechanical measurements. Other specimens were postcured and cut to the testing size afterwards.

ii) Cured Composites Studied

This series of specimens were prepared from fourteen layers of woven glass fibres with different resin matrices (see section 3.1.3).

A leaky mould was used to prepare these specimens to give a composite 2 mm in thickness. The mixture of resin and hardener were mixed and poured into the female mould before a layer of glass fabric was placed on top. The resin mixture was well wetted in to the glass fabric by hand using a roller. In total 14 layers of glass fabric were used, all in the same fibre orientation. A guide of 2 mm was then used to control overall thickness of the composite. The female mould was placed on top, and was clamped in place. They were cured at room temperature for 2 days and postcured at 150°C for 4 hr. Then they were cut and sanded down to the test size of approximately 10 mm width and 25 mm length.

The fibre volume fractions of all the specimens was about 43%, which determined by using a resin burn-off technique according to the British CRAG test method 1000 [132].

**B) Specimens for Flexural Properties Determination**

i) Cured Resins Studied

Unreinforced resin specimens inclusively were prepared and tested to determine flexural properties. They were prepared from the same batch of mixed resins as used in the DMTA studies (section 3.1.2 A(i)).

After thorough mixing, each composition of about 200 g was poured into a mould treated with mould releasing agent (ex. ECL Chemical Limited). The formulations were cured at room temperature over night (16 hours), then they were...
removed from the mould. The size of each cured sheet was about 150 x 230 mm² by 3 to 5 mm thickness. Each plaque was cut with a diamond saw and polished on a linisher and then SiC paper to the required specimen sizes for flexural testing (10 ± 0.5 mm wide and 100 mm long).

ii) Cured Composites Studied
The composites were prepared in the way described in section 3.1.2 A(ii), but the final specimens for this test had dimensions of ~2x10x60 mm³.

3.1.3 The Identification of Polymers and Composites in This Programme
The following series of materials and variables were investigated in this programme.

Table 3.2 Variables studied in research programme

<table>
<thead>
<tr>
<th>Unreinforced specimens</th>
<th>Investigate the influence of curing conditions and modifiers on cured resins</th>
</tr>
</thead>
<tbody>
<tr>
<td>series 1</td>
<td>variation in Ancamine amount</td>
</tr>
<tr>
<td>series 2</td>
<td>variation in postcure time at 100°C</td>
</tr>
<tr>
<td>series 3</td>
<td>variation in postcure time at 150°C</td>
</tr>
<tr>
<td>series 4</td>
<td>variation in Desmocap amount</td>
</tr>
<tr>
<td>series 5</td>
<td>variation in Jeffamine T5000 amount: (a) RT cure; (b) postcure at 150°C for 4 hr</td>
</tr>
<tr>
<td>series 6</td>
<td>variation in Jeffamine T3000 amount: (a) RT cure; (b) postcure at 150°C for 4 hr</td>
</tr>
<tr>
<td>series 7</td>
<td>variation in Jeffamine D4000 amount: (a) RT cure; (b) postcure at 150°C for 4 hr</td>
</tr>
<tr>
<td>series 8</td>
<td>variation in Jeffamine D2000 amount: (a) RT cure; (b) postcure at 150°C for 4 hr</td>
</tr>
<tr>
<td>Reinforced specimens</td>
<td>Investigate the influence of various resin matrices on cured composites</td>
</tr>
<tr>
<td>series 9</td>
<td>variation in Ancamine amount</td>
</tr>
<tr>
<td>series 10</td>
<td>variation in Desmocap amount</td>
</tr>
<tr>
<td>series 11</td>
<td>variation in Jeffamine T5000 amount</td>
</tr>
<tr>
<td>series 12</td>
<td>variation in Jeffamine T3000 amount</td>
</tr>
<tr>
<td>series 13</td>
<td>variation in Jeffamine D4000 amount</td>
</tr>
<tr>
<td>series 14</td>
<td>variation in Jeffamine D2000 amount</td>
</tr>
</tbody>
</table>
3. Experimental Procedures

(a) Cured Systems Studied: unreinforced
The following reference systems for various formulations were adopted for each series of tests.

Series 1: Epikote 828/Ancamine MCA system (cured at room temperature for a minimum time of 7 days before testing) with various levels of Ancamine as shown in Table 3.3.

Table 3.3 Reference numbers for specimens containing various levels of Ancamine

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Ancamine MCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:35</td>
<td>35</td>
</tr>
<tr>
<td>1:45</td>
<td>45</td>
</tr>
<tr>
<td>1:55</td>
<td>55</td>
</tr>
<tr>
<td>(i.e. standard stoichiometric mix)</td>
<td></td>
</tr>
<tr>
<td>1:65</td>
<td>65</td>
</tr>
<tr>
<td>1:75</td>
<td>75</td>
</tr>
</tbody>
</table>

Series 2: Epikote 828/55 phr Ancamine MCA, was postcured at 100°C, for various times, as shown in Table 3.4.

Table 3.4 Reference numbers for specimens postcured, at 100°C, for various times

<table>
<thead>
<tr>
<th>reference number</th>
<th>postcure time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>non-postcured</td>
</tr>
<tr>
<td>2: 4</td>
<td>4</td>
</tr>
<tr>
<td>2: 8</td>
<td>8</td>
</tr>
<tr>
<td>2: 16</td>
<td>16</td>
</tr>
<tr>
<td>2: 24</td>
<td>24</td>
</tr>
</tbody>
</table>

Series 3: Epikote 828/55 phr Ancamine MCA, postcured at 150°C, for various times, as shown in Table 3.5.
3. Experimental Procedures

Table 3.5 Reference numbers used for specimens postcured at 150°C for various times

<table>
<thead>
<tr>
<th>reference number</th>
<th>postcured time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>non-postcured</td>
</tr>
<tr>
<td>3: 4</td>
<td>4</td>
</tr>
<tr>
<td>3: 8</td>
<td>8</td>
</tr>
<tr>
<td>3: 16</td>
<td>16</td>
</tr>
<tr>
<td>3: 24</td>
<td>24</td>
</tr>
<tr>
<td>3: 48</td>
<td>48</td>
</tr>
</tbody>
</table>

Series 4: Epikote 828/Ancamine MCA/Desmocap 11. The ratio of Ancamine to Desmocap was varied and mixed at stoichiometric proportions with Epikote 828. This was done by the basis of an apparent epoxy equivalent of Desmocap of 860-1000 (the value of 930 was used), as recommended by the manufacturer [128]. Testing was after 7 days at ambient, no postcure schedule was employed.

Table 3.6 Reference numbers used for the specimens containing variable amounts of Desmocap 11 in the standard epoxy system

<table>
<thead>
<tr>
<th>reference number</th>
<th>Epikote 828:Desmocap 11</th>
<th>*phr Ancamine MCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>100:0</td>
<td>0</td>
</tr>
<tr>
<td>4: 95/5</td>
<td>95:5</td>
<td>52</td>
</tr>
<tr>
<td>4: 90/10</td>
<td>90:10</td>
<td>50</td>
</tr>
<tr>
<td>4: 80/20</td>
<td>80:20</td>
<td>46</td>
</tr>
<tr>
<td>4: 70/30</td>
<td>70:30</td>
<td>41</td>
</tr>
<tr>
<td>4: 60/40</td>
<td>60:40</td>
<td>37</td>
</tr>
<tr>
<td>4: 50/50</td>
<td>50:50</td>
<td>33</td>
</tr>
<tr>
<td>4: 40/60</td>
<td>40:60</td>
<td>28</td>
</tr>
<tr>
<td>4: 35/65</td>
<td>35:65</td>
<td>26</td>
</tr>
<tr>
<td>4: 30/70</td>
<td>30:70</td>
<td>24</td>
</tr>
<tr>
<td>4: 20/80</td>
<td>20:80</td>
<td>20</td>
</tr>
<tr>
<td>4: 10/90</td>
<td>10:90</td>
<td>15</td>
</tr>
</tbody>
</table>

* phr = parts per hundred of both Epikote 828 & Desmocap 11, calculated from the formula:
3. Experimental Procedures

phr = (amine hydrogen equivalent weight x 100)/epoxide equivalent weight of resin

Series 5: Epikote 828/Ancamine MCJ/Jeffamine T5000. In this series the variable studied was the ratio of Ancamine to Jeffamine T5000, which were otherwise added at the stoichiometric proportions to Epikote 828: Two series were examined, i.e. series 5(a) cured at room temperature (Table 3.7a) and series 5(b) which included a postcure schedule of 150°C for 4 hr (Table 3.7b).

Table 3.7(a) Reference numbers used for the specimens with variable amounts of Jeffamine T5000 in the standard epoxy system: no postcure

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine T5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>0</td>
</tr>
<tr>
<td>5a: 5</td>
<td>5.4</td>
</tr>
<tr>
<td>5a: 12</td>
<td>11.8</td>
</tr>
<tr>
<td>5a: 20</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Table 3.7(b) Reference numbers used for the specimens with variable amounts of Jeffamine T5000 in the standard epoxy system: postcure at 150°C for 4 hr

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine T5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: 4</td>
<td>0</td>
</tr>
<tr>
<td>5b: 5/150/4</td>
<td>5.4</td>
</tr>
<tr>
<td>5b: 12/150/4</td>
<td>11.8</td>
</tr>
<tr>
<td>5b: 20/150/4</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Series 6: Epikote 828/Ancamine MCJ/Jeffamine T3000. The variable studied was the ratio of Ancamine to Jeffamine T3000, which were otherwise added at the stoichiometric proportions to Epikote 828: Two series were examined, i.e. series 6(a) cured at room temperature (Table 3.8a) and series 6(b) which included a postcure schedule of 150°C for 4 hr (Table 3.8b).
3. Experimental Procedures

Table 3.8(a) Reference numbers used for the specimens with variable amounts of Jeffamine T3000 in the standard epoxy system: no postcure

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine T3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>0</td>
</tr>
<tr>
<td>6a: 12</td>
<td>11.5</td>
</tr>
<tr>
<td>6a: 21</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Table 3.8(b) Reference numbers used for the specimens with variable amounts of Jeffamine T3000 in the standard epoxy system: postcure at 150°C for 4 hr

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine T3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: 4</td>
<td>0</td>
</tr>
<tr>
<td>6b: 12/150/4</td>
<td>11.5</td>
</tr>
<tr>
<td>6b: 21/150/4</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Series 7: Epikote 828/Ancamine MCA/Jeffamine D4000. The variable studied in this series was the ratio of Ancamine to Jeffamine D4000, which were otherwise added at stoichiometric proportions to Epikote 828: Two series were examined, i.e. series 7(a) cured at room temperature (Table 3.9a) and series 7(b) which included a postcure schedule of 150°C for 4 hr (Table 3.9b).

Table 3.9(a) Reference numbers used for the specimens with variable amounts of Jeffamine D4000 in the standard epoxy system: no postcure

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine D4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>0</td>
</tr>
<tr>
<td>7a: 12</td>
<td>11.8</td>
</tr>
<tr>
<td>7a: 20</td>
<td>19.7</td>
</tr>
</tbody>
</table>
3. Experimental Procedures

Table 3.9(b) Reference numbers used for the specimens with variable amounts of Jeffamine D4000 in the standard epoxy system: postcure at 150°C for 4 hr

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine D4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: 4</td>
<td>0</td>
</tr>
<tr>
<td>7b: 12/150/4</td>
<td>11.8</td>
</tr>
<tr>
<td>7b: 20/150/4</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Series 8: Epikote 828/Ancamine MCA/Jeffamine D2000. The variable studied in this series was the ratio of Ancamine to Jeffamine D2000, which were otherwise added at stoichiometric proportions to Epikote 828: Two series were examined, i.e. series 8(a) cured at room temperature (Table 3.10a) and series 8(b) which included a postcure schedule of 150°C for 4 hr (Table 3.10b).

Table 3.10(a) Reference numbers used for the specimens with variable amounts of Jeffamine D2000 in the standard epoxy system: no postcure

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine D2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55</td>
<td>0</td>
</tr>
<tr>
<td>8a: 12</td>
<td>11.5</td>
</tr>
<tr>
<td>8a: 21</td>
<td>20.5</td>
</tr>
</tbody>
</table>

Table 3.10(b) Reference numbers used for the specimens with variable amounts of Jeffamine D2000 in the standard epoxy system: postcure at 150°C for 4 hr

<table>
<thead>
<tr>
<th>reference number</th>
<th>phr Jeffamine D2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: 0/150/4</td>
<td>0</td>
</tr>
<tr>
<td>8b: 12/150/4</td>
<td>11.5</td>
</tr>
<tr>
<td>8b: 20/150/4</td>
<td>20.5</td>
</tr>
</tbody>
</table>

(b) Cured Composite Systems Studied

Composites with the following resin matrix were prepared using the procedures in section 3.1.2.
3. Experimental Procedures

Series 9: Composites with the same resin matrix as in series 1, were investigated and are shown in Table 3.11.

Table 3.11 Reference numbers used for composites with variable Ancamine levels

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>phr Ancamine MCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 35C</td>
<td>35</td>
</tr>
<tr>
<td>1: 55C</td>
<td>55</td>
</tr>
<tr>
<td>1: 75C</td>
<td>75</td>
</tr>
</tbody>
</table>

Series 10: Composites with the same resin matrix as in series 4, were investigated and are shown in Table 3.12.

Table 3.12 Reference numbers for composites with variable amounts of Desmocap 11 in the standard epoxy system resin matrix

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>Epikote:Desmocap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55C</td>
<td>100:0</td>
</tr>
<tr>
<td>4: 95/5C</td>
<td>95:5</td>
</tr>
<tr>
<td>4: 90/10C</td>
<td>90:10</td>
</tr>
<tr>
<td>4: 80/20C</td>
<td>80:20</td>
</tr>
<tr>
<td>4: 70/30C</td>
<td>70:30</td>
</tr>
<tr>
<td>4: 60/40C</td>
<td>60:40</td>
</tr>
<tr>
<td>4: 50/50C</td>
<td>50:50</td>
</tr>
</tbody>
</table>

Series 11: Composites with the same resin matrix as in series 5(a), were investigated and are shown in Table 3.13.
3. Experimental Procedures

Table 3.13 Reference numbers used for composites with variable amounts of Jeffamine T5000 in the standard epoxy system resin matrix

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>phr Jeffamine T5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: 4C</td>
<td>0</td>
</tr>
<tr>
<td>5a: 5C</td>
<td>5.4</td>
</tr>
<tr>
<td>5a: 12C</td>
<td>11.8</td>
</tr>
<tr>
<td>5a: 20C</td>
<td>19.5</td>
</tr>
<tr>
<td>5a: 29C</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Series 12: Composites with the same resin matrix as in series 6(a), were investigated and are shown in Table 3.14.

Table 3.14 Reference numbers used for composites with variable amounts of Jeffamine T3000 in the standard epoxy system resin matrix

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>phr Jeffamine T3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55C</td>
<td>0</td>
</tr>
<tr>
<td>6a: 12C</td>
<td>11.5</td>
</tr>
<tr>
<td>6a: 21C</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Series 13: Composites with the same resin matrix as in series 7(a), were investigated and are shown in Table 3.15.

Table 3.15 Reference numbers used for composites with variable amount of Jeffamine D4000 in the standard epoxy system resin matrix

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>phr Jeffamine D4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55C</td>
<td>0</td>
</tr>
<tr>
<td>7a: 12C</td>
<td>11.8</td>
</tr>
<tr>
<td>7a: 20C</td>
<td>19.7</td>
</tr>
</tbody>
</table>
3. Experimental Procedures

Series 14: Composites with the same resin matrix as in series 8(a), were investigated and are shown in Table 3.16.

Table 3.16 Reference numbers used for composites with variable amounts of Jeffamine D2000 in the standard epoxy system resin matrix

<table>
<thead>
<tr>
<th>reference number of the composites</th>
<th>phr Jeffamine D2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 55C</td>
<td>0</td>
</tr>
<tr>
<td>8a: 12C</td>
<td>11.5</td>
</tr>
<tr>
<td>8a: 21C</td>
<td>20.5</td>
</tr>
</tbody>
</table>

3.2 Characterisation

3.2.1 Differential Scanning Calorimetry (DSC)

Throughout the programme a Thermal Analysis 2000 and 910 Differential Scanning Calorimetry (ex. DuPont special Instruments), were used to determine DSC thermal behaviour with a heating rate of 10°C/min under dry nitrogen. Typically a sample of about 10 mg was used in each measurement and placed in sealed aluminium pan normally used for DSC cell.

First, the DSC was used to determine the thermal response of certain systems immediately, and some times after, mixing. These experiments were carried out on standard mix specimen reference 1: 55. The raw materials Epikote 828 and Ancamine MCA, were mixed and put in a numbers of DSC pans in order to be tested at different times after mixing. The scanning temperature range was from -75°C to +200°C. The Tg of the cured mixture was determined from the peak of the endothermic curve. It was found that the temperature determined from step transition and from the peak of endothermic curve were equivalent, as shown in Figure 3.1.

Secondly, the DSC was used to examine the thermal response of cured specimens (e.g. Tg), which were originally prepared for mechanical property determination, with variation in the amounts of curing agent (i.e. series 1). A scanning temperature from -50°C to 200°C was used to carried out the investigation.

Note: The apparent degree of conversion (α) is calculated from [36]:

$$\alpha = \frac{(\Delta H_{total} - \Delta H_{ret})}{\Delta H_{total}}$$
Figure 3.1 DSC trace of a standard mix sample, cured at room temperature.

The graph shows the heat flow (W/g) against temperature (°C). There is a distinct exothermic peak at 57.11°C.
where $\Delta H_{total}$ is the total value of the exotherm.

$\Delta H_{res}$ is the residual value of the exotherm.

The stoichiometric ratio was calculated from the following equation [5]:

$$\text{phr of amine} = \frac{(\text{Amine hydrogen eq. wt./epoxide eq. wt. of resin}) \times 100}{100}$$

where phr is the parts per hundred by weight.

### 3.2.2 Dynamic Mechanical Thermal Analysis (DMTA)

A dynamic mechanical thermal analyser, DMTA MK II, (ex. Polymer Laboratory), was used in these studies. A single cantilever beam and knife edge clamp were used with a clamp torque of about 15 cNm for the unreinforced specimens, and 30 cNm for the composites specimens. The strain level which gave the nominal peak to peak displacement of $64 \mu\text{m}$ was used. The data were collected every 4 second at the frequency of 1 Hz using a heating rate of $5^\circ\text{C/minute}$, and the temperature range was $-120^\circ\text{C}$ to $-220^\circ\text{C}$.

The DMTA experiments can be classified into two categories: studies on the cured resins and the cured composites. The first set involved tests on all the unreinforced cured epoxide based, specimens series 1 to 8. The second set tested all the glass reinforced cured epoxide based specimens, series 9 to 14.

### 3.2.3 FTIR

Infrared spectra were obtained using a "UNICAM: MARSON 300" Fourier transform infrared spectrometer. Typical operating conditions were 64 scans with the resolution at $4.00 \text{ cm}^{-1}$ and time to completion at 1.36 minutes, for the full spectrum range of 4000 to 6000 cm$^{-1}$. The crosslinking reactions and the molecular structure of cured specimens were examined with FTIR.

#### A) Development of epoxide peak with time after mixing

The cure of a stoichiometric mix formulation was followed by placing the mixture between two KBr discs. These were generally squeezed together to form a thin film. The KBr/epoxide/KBr assembly was then loaded into the FTIR equipment.

The two discs were first prepared from KBr powder (Analyse grade). They were pressed with a load of 10 ton for 15 minutes to achieve a sample disc with a diameter of $\sim13 \text{ mm}$ and thickness of $<2 \text{ mm}$. Then a mixture of Epikote and Ancamine was prepared at the stoichiometric quantities (series 1: standard). After thoroughly mixing the reactants were applied to one of the KBr discs and then sandwiched with a second KBr disc. The assembly was placed in the holder then
inserted in a FTIR instrument. The standard sample was then scanned to determine the epoxide peak height.

B) The Study of Cured Products

The various mixtures of series 1 were thoroughly mixed and cast in small polystyrene tubes (diameter ~19 mm and height ~ 5 cm).

After cure, samples were removed from the tubes and reduced to powder with a fine file. Then specimens of each cured resin were mixed with KBr. The KBr powder was first ground with an agate pestle and mortar, and the powdered resin added in a small amount (<100 mg). Next, a small disc of this mixture was made into a disc using the same conditions as in section 3.2.3(a). The ratio of KBr and cured resin powder was adjusted, when initially the FTIR spectra did not show enough detail. The final ratio used in all experiments was ~ 4:1.

3.3 Mechanical Properties

3.3.1 Flexural Properties Determination

A) Cured Resins Studied

All flexural experiments (three-point bending test) were carried out using a J.J. Lloyds tensometer (Model 2000R) with the span set at 16 times the thickness. British Standard 2782: Part 3: Method 335A was used.

Flexural stress ($\sigma_f$) was calculated from [133]:

$$\sigma_f = \frac{M}{W}$$

where $M$ was the flexural moment at load $F$ (N) and $W$ was the section modulus (mm$^3$). $M$ and $W$ was obtained from equation [133]:

$$M = \frac{FL}{4} \text{ and } W = \frac{(wt^3)}{6}$$

where $F$ was the applied load (N), $L$ was the span length (mm), $w$ was the sample width (mm), and $t$ was the sample thickness (mm).

Modulus of elasticity or flexural modulus ($E_b$) was calculated from equations [133]:

$$E_b = \left(\frac{L^3}{(4wt^3)}\right) \times m$$

where $m$ was the slope of linear load/deflection graph (N/mm).
3. Experimental Procedures

B) Cured Composites Studied

The composites in this study were those from series 9 to 14. The testing was carried out using the British CRAG test method 200 [134]. Again the J.J. Lloyds tensometer (Model 2000R) was employed. The flexural strength and modulus were calculated in the same way as for unreinforced specimens.

3.3.2 Interlaminar Shear Strength (ILSS) Determination

The specimens for interlaminar shear strength determination (ILSS) were cut from the same plaques of cure composites, as described in Section 3.1.2 B(i). The tests were carried out according the British CRAG test method 100 [135].

The interlaminar shear strength (ILSS) was calculated from:

$$\text{ILSS} = \frac{0.75P}{wt}$$

where $P$ was the load at failure (N), $w$ was the specimen width (mm), and $t$ was the specimen thickness (mm).

3.3.3 Impact Properties Determination

The specimens for impact properties determination were also cut from the same plaques of cured composites as used in section 3.1.2 B(i) and 3.3.2.

The Rosand instrumented falling weight impact test (Rosand Type 5) was used to carry out the tests at room temperature. The dropped weight, tup and drop height were constant (which gave an impact energy of 113 J). Specimens from series 9 to 14 were tested.

3.4 Visual Observations

Since samples appeared to change colour on cure, and especially post cure, it was thought important that some measurement of visible colour change be measured. Specimens from series 3, 5(a), 6(a), 7(a), and 8(a) were examined. Specimens were taken from pieces of flexure specimens. They were placed on a black line to show the transparency of each specimen and the Kodak Standard Colour Chart was used as a reference to indicate the colour variation. A photograph was taken of each of the specimens using a 35 mm camera with Kodak film 200 ISO.
3. Experimental Procedures

3.5 Microscopic Examinations

A) Scanning Electron Microscopy (SEM) [136]

The SEM was used to study various samples, as follows:

The fracture surfaces of series 3 specimens resulting from flexural testing were investigated. Specimens of series 4 were cooled down by the use of liquid nitrogen, and then they were broken by hand with two pliers. These surfaces were then coated with a thin layer of gold with a thickness of ~5-10 nm before observation in a Leica Cambridge Stereoscan S360, scanning electron microscope with a voltage of 10 KV [160]. Photomicrographs were then taken of the fracture surfaces.

B) Transmission Electron Microscopy (TEM) [137]

Examination was made of both unstained and stained specimens from series 1: 55, 5a: 20, 6a: 21, 7a: 20, 8a: 21.

A glass knife was used to produce thin sections of these specimens with a Cambridge Huxley Ultramicrotome. The microtome sections, of a thickness of ~0.1 to 0.2 μm, were floated on water and collected with copper grids [137]. The unstained specimens were then dried by using filter paper, and directly examined using the transmission electron microscope, JEOL JEM100CX, with a voltage of 100 KV. Each stained specimen was immersed in a 2 % solution of OsO₄ in water in a small tube (~13 mm in diameter, 51 mm in length), which was covered by a lid for a period of time (>2 days). Then, the chemical was washed out using distilled water, the specimen collected using a copper grid and dried by filter paper before examining under the TEM.
4. Results

4. RESULTS

4.1 Influence of Curing Agent

4.1.1 Thermal Analysis

i) Differential Scanning Calorimetry (DSC)

Table 4.1.1 and Figures 4.1.1 to 4.1.6 show the results of DSC analysis of a standard mix sample (i.e. with 55 phr Ancamine MCA).

Figure 4.1.1 is a thermogram of the mixture cured in the pan of the instrument 15 minutes after mixing. It provides several parameters including the exothermic value, glass transition temperature at a particular curing time ($T_{g_{DSC}}$), onset temperature of the exothermic peak, and exothermic peak temperature. Figure 4.1.2 shows the trace for a sample 21.3 hours after mixing.

Table 4.1.1 DSC data for a standard mix sample at various times after mixing

<table>
<thead>
<tr>
<th>Curing Time (hr)</th>
<th>Exothermic Value (J/g)</th>
<th>$T_{g_{DSC}}$ (°C)</th>
<th>Onset Temperature (°C)</th>
<th>Temp. at peak of exotherm (°C)</th>
<th>Degree of Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>308.0</td>
<td>-30.3</td>
<td>52.8</td>
<td>86.8</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>291.1</td>
<td>-26.1</td>
<td>53.4</td>
<td>94.2</td>
<td>5</td>
</tr>
<tr>
<td>1.05</td>
<td>229.0</td>
<td>-12.5</td>
<td>54.9</td>
<td>101.5</td>
<td>26</td>
</tr>
<tr>
<td>1.78</td>
<td>183.3</td>
<td>-5.7</td>
<td>55.5</td>
<td>111.3</td>
<td>40</td>
</tr>
<tr>
<td>2.53</td>
<td>150.7</td>
<td>-1.7</td>
<td>59.6</td>
<td>116.4</td>
<td>51</td>
</tr>
<tr>
<td>3.33</td>
<td>134.9</td>
<td>+6.9</td>
<td>63.1</td>
<td>117.1</td>
<td>56</td>
</tr>
<tr>
<td>4.13</td>
<td>103.9</td>
<td>+8.8</td>
<td>69.6</td>
<td>117.8</td>
<td>66</td>
</tr>
<tr>
<td>4.88</td>
<td>79.7</td>
<td>+15.9</td>
<td>74.0</td>
<td>121.7</td>
<td>74</td>
</tr>
<tr>
<td>5.62</td>
<td>64.5</td>
<td>+19.6</td>
<td>75.2</td>
<td>125.0</td>
<td>79</td>
</tr>
<tr>
<td>21.27</td>
<td>34.4</td>
<td>+40.1</td>
<td>79.5</td>
<td>136.1</td>
<td>89</td>
</tr>
<tr>
<td>45.22</td>
<td>22.8</td>
<td>+47.6</td>
<td>83.8</td>
<td>131.4</td>
<td>93</td>
</tr>
<tr>
<td>69.08</td>
<td>27.4</td>
<td>+49.1</td>
<td>90.3</td>
<td>132.3</td>
<td>91</td>
</tr>
</tbody>
</table>
Figure 4.1.1 DSC trace of a standard sample 15 minutes after mixing

-28.37°C
-26.08°C (I)
-23.39°C

94.20°C
53.35°C

0.09875 W/g
291.1 J/g
Figure 4.1.2 DSC trace of a standard sample 21.3 hr after mixing

- Heat Flow (W/g)
- Temperature (°C)

- 35.47°C
- 4.675 J/g
- 79.53°C
- 34.35 J/g
- 136.11°C
- 40.08°C

General V4.0D DuPont 2000
4. Results

Figure 4.1.3 Exotherm (heat release) vs Time After Mixing (55 phr Ancamine MCA)

Exotherm (J/g)

Time After Mixing (hr)

Figure 4.1.4 TgDSC vs Time After Mixing (55 phr Ancamine MCA)

TgDSC (°C)

Time After Mixing (hr)
4. Results

Figure 4.1.5  Degree of Conversion vs Time After Mixing (55 phr Ancamine MCA)

Figure 4.1.6  Degree of Conversion vs Tg (55 phr Ancamine MCA)
4. Results

A plot of the exothermic value against time after mixing is shown in Figure 4.1.3. Plots of $T_{g_{DSC}}$ and the degree of conversion both versus the time after mixing can be seen in Figures 4.1.4 and 4.1.5 respectively. Figure 4.1.6 shows the relationship between $T_{g_{DSC}}$ and degree of conversion.

Figures 4.1.7 to 4.1.9 were plotted by using values from the results of DSC experiments on the cured systems. The numerical values of these results are given in Table 4.1.2.

Figures 4.1.7 and 4.1.8 show variations in the endothermic and $T_{g_{DSC}}$ values with phr Ancamine MCA. A plot of exothermic value versus amount of curing agents (Figure 4.1.9) shows that the exothermic value decreased as the amount of curing agent increased. At 35 and 45 phr Ancamine MCA the exothermic values could not be measured as a maximum temperature of 200°C, at which the reaction was not completed, was used. However, it is to be expected that the exothermic value will be higher when less curing agent is used due to there being more unreacted epoxide groups.

![Figure 4.1.7 Endothermic Value vs phr Ancamine MCA](image-url)
4. Results

**Figure 4.1.8** Tg vs phr Ancamine MCA

**Figure 4.1.9** Exothermic Value vs phr Ancamine MCA
4. Results

Figure 4.1.10 is a plot of both $T_g$ (see Table 4.1.2) and $T_g$ (see Table 4.1.3) versus amount of Ancamine MCA used. Although the $T_g$ was determined at different times after mixing, the same trends were found in both experiments. This result confirmed that the method of measuring $T_g$ by DSC was acceptable.

Table 4.1.2 DSC data for stoichiometric and non-stoichiometric samples at various times after mixing

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>days</th>
<th>$T_g$ (°C)</th>
<th>Endothermic Value (J/g)</th>
<th>Exothermic Value (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>15</td>
<td>42.4</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>45</td>
<td>16</td>
<td>50.4</td>
<td>8.65</td>
<td>--</td>
</tr>
<tr>
<td>55</td>
<td>17</td>
<td>51.5</td>
<td>5.71</td>
<td>22.13</td>
</tr>
<tr>
<td>65</td>
<td>14</td>
<td>48.9</td>
<td>5.47</td>
<td>15.92</td>
</tr>
<tr>
<td>75</td>
<td>13</td>
<td>46.8</td>
<td>8.16</td>
<td>9.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>days</th>
<th>$T_g$ (°C)</th>
<th>Endothermic Value (J/g)</th>
<th>Exothermic Value (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>83</td>
<td>48.2</td>
<td>8.41</td>
<td>--</td>
</tr>
<tr>
<td>45</td>
<td>84</td>
<td>56.7</td>
<td>7.62</td>
<td>--</td>
</tr>
<tr>
<td>55</td>
<td>85</td>
<td>57.1</td>
<td>5.69</td>
<td>13.02</td>
</tr>
<tr>
<td>65</td>
<td>82</td>
<td>54.2</td>
<td>6.33</td>
<td>5.57</td>
</tr>
<tr>
<td>75</td>
<td>81</td>
<td>49.4</td>
<td>7.47</td>
<td>5.33</td>
</tr>
</tbody>
</table>
ii) Dynamic Mechanical Thermal Analysis (DMTA)

Figures 4.1.11 and 4.1.12 are DMTA thermogram of unreinforced specimens. A typical DMTA thermogram for a standard mix resin specimen is shown in Figure 4.1.11. Figure 4.1.12 shows thermogram of a series of stoichiometric and non-stoichiometric samples (series 1) studied by DMTA. The values of $\tan \delta_{\text{max}}$, $\Delta \log E'$, temperature at $E'_\text{1/2}$ and $T_g$ from these thermogram are given in Table 4.1.3. Plots of $\tan \delta_{\text{max}}$ and $T_g^{\text{DMTA}}$ versus phr Ancamine MCA using values from Table 4.1.3 are shown in Figures 4.1.13 and 4.1.14 respectively.
Figure 4.1.11 DMTA trace of 55 phr Ancamine MCA:Epikote 828
Figure 4.1.12 DMTA traces of samples containing various amounts of Ancamine MCA

Peaks
1. 52.71°C
2. 63.43°C
3. 65.69°C
4. 62.33°C
5. 58.33°C

Key
1. 35 phr
2. 45 phr
3. 55 phr
4. 65 phr
5. 75 phr
4. Results

Figure 4.1.13 $\tan \delta_{\text{max}}$ vs phr Ancamine MCA

Figure 4.1.14 $T_g$ vs phr Ancamine MCA
Figure 4.1.15 DMTA trace for a standard mix sample composite

PEAKS

1 76.66°C
### 4. Results

#### Table 4.1.3 DMTA data for stoichiometric and non-stoichiometric resins

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>days after mixing</th>
<th>tan δ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>T&lt;sub&gt;gDMTA&lt;/sub&gt; (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E'&lt;sub&gt;1/2&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>37</td>
<td>1.55</td>
<td>52.7</td>
<td>2.89</td>
<td>34.1</td>
</tr>
<tr>
<td>45</td>
<td>41</td>
<td>1.20</td>
<td>63.4</td>
<td>2.37</td>
<td>52.9</td>
</tr>
<tr>
<td>55</td>
<td>42</td>
<td>1.11</td>
<td>65.7</td>
<td>2.33</td>
<td>55.0</td>
</tr>
<tr>
<td>65</td>
<td>39</td>
<td>1.08</td>
<td>62.3</td>
<td>2.51</td>
<td>50.7</td>
</tr>
<tr>
<td>75</td>
<td>38</td>
<td>1.05</td>
<td>58.3</td>
<td>2.46</td>
<td>47.9</td>
</tr>
</tbody>
</table>

The composite specimens in series 9 were studied by DMTA and the results are shown in Table 4.1.4. Figure 4.1.15 is a typical DMTA thermogram of a composite. This sample was a composite with the standard resin matrix mix.

#### Table 4.1.4 DMTA data for Epikote 828/glass fibre composites with different amounts of curing agents

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>tan δ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>T&lt;sub&gt;gDMTA&lt;/sub&gt; (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E'&lt;sub&gt;1/2&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.48</td>
<td>71.1</td>
<td>1.34</td>
<td>57.7</td>
</tr>
<tr>
<td>55</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>75</td>
<td>0.58</td>
<td>56.0</td>
<td>1.36</td>
<td>48.0</td>
</tr>
</tbody>
</table>

#### 4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

i) Influence of Cure Time

Typical infrared spectrograms for the stoichiometric ratio of Epikote 828 and Ancamine MCA cured between KBr disc are shown in Figures 4.1.16 and 4.1.17, scanned 1 and 6.15 hours after mixing, respectively.

Table 4.1.5 gives the ratio of peak heights at wavelengths (930-910)/(2962-2853) cm<sup>-1</sup> (i.e. the ratio of the epoxide group to the C-H band stretching [15, 49, 95]. This shows the reduction in epoxide group with time after mixing. Figure 4.1.18, the ratio of peak heights against time after mixing was plotted using data from Table 4.1.5.
Figure 4.1.16 FTIR trace for Epikote 828/Ancamine MCA, cured for 1 hr
Figure 4.1.17 FTIR trace for Epikote 828/Ancamine MCA, cured for 6.15 hr
4. Results

Table 4.1.5 FTIR peak height ratios (930-910)/(2962-2853) for stoichiometric samples with varying curing times

<table>
<thead>
<tr>
<th>Time after mixing (hr)</th>
<th>Peak height ratio (930-910)/(2962-2853)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.3977</td>
</tr>
<tr>
<td>1.15</td>
<td>0.3457</td>
</tr>
<tr>
<td>2.15</td>
<td>0.2800</td>
</tr>
<tr>
<td>3.15</td>
<td>0.2375</td>
</tr>
<tr>
<td>6.15</td>
<td>0.1686</td>
</tr>
<tr>
<td>30.00</td>
<td>0.1287</td>
</tr>
<tr>
<td>97.00</td>
<td>0.1227</td>
</tr>
<tr>
<td>121.00</td>
<td>0.1213</td>
</tr>
<tr>
<td>148.00</td>
<td>0.1212</td>
</tr>
<tr>
<td>1488.00</td>
<td>0.1204</td>
</tr>
</tbody>
</table>
4. Results

ii) Influence of Ancamine MeA

The epoxide peak height of the standard mix (i.e. 55 phr) and non-stoichiometric mixes of epoxy and hardener (i.e. 35, 75 phr Ancamine MeA; see series 1) were studied using FTIR. The FTIR traces of these non-stoichiometric mixes are shown in Figures 4.1.19 and 4.1.20; they were obtained between 16 days and 21 days after mixing and curing at room temperature.

4.1.3 Mechanical Properties

i) Resins:

Flexural properties of epoxide resins reacted with different amounts of curing agent (series 1), which had been cured at room temperature for between 64 and 68 days, are presented in Table 4.1.6. The graphical representation plotted from these values can be seen in Figures 4.1.21 and 4.1.22. These are the plots of flexural strength and modulus versus phr Ancamine MeA respectively.

Table 4.1.6 Flexural strength and modulus of samples cured at room temperature with various amounts of curing agent after approximately 66 days

<table>
<thead>
<tr>
<th>phr Ancamine MeA</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.* (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>48.8</td>
<td>0.7</td>
<td>1689</td>
<td>30</td>
</tr>
<tr>
<td>45</td>
<td>63.7</td>
<td>0.8</td>
<td>3285</td>
<td>52</td>
</tr>
<tr>
<td>55</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>65</td>
<td>89.2</td>
<td>1.5</td>
<td>3041</td>
<td>66</td>
</tr>
<tr>
<td>75</td>
<td>78.6</td>
<td>1.4</td>
<td>2777</td>
<td>51</td>
</tr>
</tbody>
</table>

*standard deviation
Figure 4.1.19 FTIR trace for epoxy containing 35 phr Ancamine MCA
Figure 4.1.20 FTIR trace for epoxy containing 75 phr Ancamine MCA
4. Results

Figure 4.1.21 Flexural Strength vs phr Ancamine MCA

![Graph of Flexural Strength vs phr Ancamine MCA]

Figure 4.1.22 Flexural Modulus vs phr Ancamine MCA

![Graph of Flexural Modulus vs phr Ancamine MCA]
4. Results

ii) Composites:
Composites based on epoxy cured with various amounts of Ancamine MCA (i.e. 35, 55 and 75 phr; see series 9) were tested in flexure, and the results are shown in Table 4.1.7.

Table 4.1.7 Flexural properties of Epikote 828/glass fibre composites cured with various amounts of Ancamine MCA

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
<th>S.D. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>977.5</td>
<td>35.4</td>
<td>463.0</td>
<td>10.9</td>
<td>17841</td>
<td>499</td>
<td>4.3</td>
<td>0.2</td>
</tr>
<tr>
<td>55</td>
<td>980.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>75</td>
<td>795.2</td>
<td>10.3</td>
<td>338.4</td>
<td>15.4</td>
<td>16597</td>
<td>698</td>
<td>3.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 4.1.8 gives the results of interlaminar shear strength testing on the specimens in series 9. It shows similar trends to those found in the same set of samples tested for flexure properties.

Table 4.1.8 The interlaminar shear strength (ILSS) of Epikote 828/glass fibre composites cured with different amounts of Ancamine MCA

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Interlaminar Shear Strength (MPa)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>47.0</td>
<td>1.2</td>
</tr>
<tr>
<td>55</td>
<td>29.9</td>
<td>0.5</td>
</tr>
<tr>
<td>75</td>
<td>34.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Force/displacement curves for samples (series 9) tested by falling weight impact tests are shown in Figure 4.1.23. The peak and failure information for these tests are shown in Table 4.1.9.
### Results

Table 4.1.9 Falling weight impact data for an Epikote 828/glass fibre composite with different amounts of curing agent

<table>
<thead>
<tr>
<th>phr Anca-mine MCA</th>
<th>Peak Impact Force (N)</th>
<th>S.D.</th>
<th>Peak Impact Force at Deflection (mm)</th>
<th>S.D.</th>
<th>Energy at Peak Impact Force (J)</th>
<th>S.D.</th>
<th>Impact Energy to Failure (J)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>4607</td>
<td>122</td>
<td>4.4</td>
<td>0.2</td>
<td>9.9</td>
<td>0.7</td>
<td>17.8</td>
<td>0.4</td>
</tr>
<tr>
<td>55</td>
<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
<td>18.7</td>
<td>0.3</td>
</tr>
<tr>
<td>75</td>
<td>5268</td>
<td>127</td>
<td>4.8</td>
<td>0.2</td>
<td>11.9</td>
<td>0.8</td>
<td>19.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Figure 4.1.23  IFWI Force vs Displacement

Key
1. 35 phr
2. 55 phr
3. 75 phr
4. Results

4.2 Influence of Cure Schedule

4.2.1 Thermal Analysis

i) DSC

As shown quite clearly in Section 4.1.1 the reaction exothermic values determined by DSC, decreased with time after mixing (see Figure 4.1.3). Therefore, a sample was thermally cycled in the DSC equipment to see the effect of such treatment, and the results are shown in Figure 4.2.1. Standard mix samples were heated from -50°C to +200°C, at 10°C/min before holding at +200°C for 3 minutes in order to ensure that equilibrium was reached. This heating was followed by cooling back to -50°C, at a rate of 10°C/min before holding for 20 minutes at -50°C to again ensure equilibrium had been reached. Finally the specimen was again heated to +200°C also at 10°C/min. The result clearly showed that the endothermic peak found in the first run had disappeared in the second run. Additionally, it was noted that the exothermic peak was smoother in the second run.

ii) DMTA

a) Postcured specimens: 100°C for 0 to 24 hours (series 2).

Results for standard mix specimens postcured at 100°C for 0, 4, 8, 16 and 24 hours (series 2) determined by dynamic mechanical thermal analysis, are given in Figures 4.2.2 and 4.2.3. Table 4.2.1 lists data taken from these two figures. These values were used to plots Figures 4.2.4 and 4.2.5 for the tan δ max and Tg DMTA versus postcuring time at 100°C respectively.

Table 4.2.1 DMTA data for standard mix samples postcured at 100°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>days after mixing</th>
<th>tan δ max</th>
<th>Tg DMTA (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E' 1/2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>23</td>
<td>1.25</td>
<td>64.5</td>
<td>2.33</td>
<td>52.4</td>
</tr>
<tr>
<td>4</td>
<td>--</td>
<td>0.68</td>
<td>83.0</td>
<td>2.05</td>
<td>66.1</td>
</tr>
<tr>
<td>8</td>
<td>--</td>
<td>0.79</td>
<td>83.3</td>
<td>2.03</td>
<td>67.7</td>
</tr>
<tr>
<td>16</td>
<td>--</td>
<td>0.65</td>
<td>83.3</td>
<td>2.02</td>
<td>66.2</td>
</tr>
<tr>
<td>24</td>
<td>--</td>
<td>0.59</td>
<td>84.5</td>
<td>2.13</td>
<td>68.8</td>
</tr>
</tbody>
</table>
Figure 4.2.1 DSC curve of Standard mix sample, cooled and reheated

Heat Flow (W/g)

-0.5
-0.3
-0.1

Temperature (°C)

0 50 100 150

53.83°C
5.297J/g

106.42°C
8.761J/g

138.53°C

57.14°C

Reheating.

Initial heating.

General V4.0D DuPont 2000
Figure 4.2.2 Influence of post cure time on tan δ (DMTA)

Peaks
1. 64.45°C
2. 82.99°C
3. 83.30°C
4. 83.28°C
5. 84.51°C

Post cure time at 100°C
Key 1. 0 hr
2. 4 hr
3. 8 hr
4. 16 hr
5. 24 hr
Figure 4.2.3 Influence of post cure time on log $E'$ (DMTA)

Post-cure time at 100°C
Key 1. 0 hr
2. 4 hr
3. 8 hr
4. 16 hr
5. 24 hr

Temperature (°C)

Bending log ($E'$) (Pa)
4. Results

Figure 4.2.4 $\tan \delta_{\text{max}}$ vs Postcure Time at 100°C

Figure 4.2.5 $T_g$ vs Postcure Time at 100°C
4. Results

b) Postcured specimens: 150°C for 0 to 48 hours (series 3).

The influence of cure time at 150°C on the dynamic mechanical properties is presented in Table 4.2.2. Tan δ<sub>max</sub> and T<sub>gDMTA</sub> were plotted versus postcuring time at 150°C by using values from Table 4.2.2 and shown in Figures 4.2.6 and 4.2.7 respectively. The DMTA thermogram of these specimens (series 3) are shown in Figure 4.2.8.

Table 4.2.2 DMTA data for standard mix samples postcured at 150°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>days after mixing</th>
<th>tan δ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>T&lt;sub&gt;gDMTA&lt;/sub&gt; (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E&lt;sub&gt;1/2&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>44</td>
<td>1.07</td>
<td>67.3</td>
<td>2.27</td>
<td>55.4</td>
</tr>
<tr>
<td>4</td>
<td>--</td>
<td>0.47</td>
<td>80.2</td>
<td>1.96</td>
<td>66.3</td>
</tr>
<tr>
<td>8</td>
<td>--</td>
<td>0.42</td>
<td>85.2</td>
<td>2.05</td>
<td>71.6</td>
</tr>
<tr>
<td>16</td>
<td>--</td>
<td>0.50</td>
<td>90.5</td>
<td>2.06</td>
<td>81.0</td>
</tr>
<tr>
<td>24</td>
<td>--</td>
<td>0.48</td>
<td>93.6</td>
<td>1.96</td>
<td>82.0</td>
</tr>
<tr>
<td>48</td>
<td>--</td>
<td>0.48</td>
<td>103.6</td>
<td>2.06</td>
<td>85.4</td>
</tr>
</tbody>
</table>
4. Results

**Figure 4.2.6** $\tan \delta_{\text{max}}$ vs Postcure Time at 150°C

**Figure 4.2.7** $T_g$ vs Postcure Time at 150°C
Figure 4.2.8 DMTA tan δ traces of samples postcured at 150°C

<table>
<thead>
<tr>
<th>PEAKS</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.27°C</td>
</tr>
<tr>
<td>2</td>
<td>80.22°C</td>
</tr>
<tr>
<td>3</td>
<td>85.18°C</td>
</tr>
<tr>
<td>4</td>
<td>90.45°C</td>
</tr>
<tr>
<td>5</td>
<td>93.58°C</td>
</tr>
<tr>
<td>6</td>
<td>103.89°C</td>
</tr>
</tbody>
</table>

Key:
1. __
2. 4hr
3. 8hr
4. 16hr
5. 24hr
6. 48hr
4. Results

4.2.2 FTIR

The absorbance spectrum of a stoichiometric mix (reference number 1: 55) cured at room temperature for 19 days is shown in Figure 4.2.9. A spectrum for the same material postcured at 200°C for 24 hours is shown in Figure 4.2.10. These figures demonstrate the difference in epoxide content between postcured and non-postcured samples.

The important absorbance bands for epoxy and amine cured systems are listed in Table 4.2.3. This Table gives the number of wavelength observed per cm$^{-1}$. The smaller the wavelength the greater is the number observed per cm$^{-1}$.

<table>
<thead>
<tr>
<th>Absorption bands (cm$^{-1}$)*</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600-3350</td>
<td>hydroxyl stretching vibration or hydrogen bonded OH vibration [1].</td>
</tr>
<tr>
<td>3480-3250</td>
<td>N-H stretching vibration [1,2].</td>
</tr>
<tr>
<td>2962-2853</td>
<td>methyl C-H stretching frequencies [2,3].</td>
</tr>
<tr>
<td>1612</td>
<td>NH$_2$ deformation vibration [2].</td>
</tr>
<tr>
<td>1600, 1580, 1500, 1450</td>
<td>aromatic [1,3].</td>
</tr>
<tr>
<td>1360</td>
<td>ether methylene C-H [2].</td>
</tr>
<tr>
<td>1260, 1230</td>
<td>C-O vibration [1].</td>
</tr>
<tr>
<td>1184</td>
<td>C-C stretching [4].</td>
</tr>
<tr>
<td>1110-1100</td>
<td>small vibration of ether bond [1].</td>
</tr>
<tr>
<td>1060-1000</td>
<td>mixed ethers such as CH$_2$-O- [1].</td>
</tr>
<tr>
<td>930-910</td>
<td>epoxide (or oxirane) ring vibration [1,2].</td>
</tr>
<tr>
<td>860-820</td>
<td>1,2,4 aromatic substitution [1].</td>
</tr>
</tbody>
</table>

* Therefore, 10µ = 1,000 cm$^{-1}$ and 2.5µ = 4,000 cm$^{-1}$ [5].

The relative peak height of epoxide groups is expected to be related to the reaction of Epikote 828 and Ancamine MCA as follows [15]:

(a) primary amine + Epikote $\rightarrow$ secondary amine + hydroxyl
(b) secondary amine + Epikote $\rightarrow$ tertiary amine + hydroxyl
Figure 4.2.9 Absorbance spectrum of standard mix, cured for 19 days
Figure 4.2.10 Absorbance spectrum of standard mix, postcured at 200°C
4. Results

The actual amount of epoxide and hydroxyl groups measured would also decrease by homopolymerization of epoxide groups and reaction of the hydroxyl with Epikote. However, it has been found that the homopolymerization and reaction of hydroxyl with epoxide groups can be neglected, because the sum of epoxy conversion and hydroxyl yield is constant during cure [15]. Reaction (a) and (b) are autocatalyzed by OH [15, 108] and the rate constants of the reaction may be obtained from the following reactions [15].

\[
(1) \quad E_p + P_A + (OH) \xrightarrow{1} P_A' + (OH)
\]

\[
(2) \quad P_A + E_p + (OH) \xrightarrow{k_2} P_A' + (OH)
\]

where \( E_p \) was the epoxide, oxirane (i.e. Epikote 828)
\( P_A \) was the primary amine (i.e. Ancamine MCA)
\( P_A' \) was the secondary amine
\( P_A'' \) was the tertiary amine
\( OH \) was the hydroxyl group
and \( \frac{k_2}{k_1} \) was the rate constant

However, the rate constant for the reactions above increase as the curing temperature increases [15]. This is likely to occur when the material is used with 14 layers of glass fibre, where high temperature curing of thick samples can cause one region of the epoxy to form a glass prior to other regions, because of the temperature gradients through the thickness of the samples [138]. This will also result in stresses in the cured products [138]. In addition because of the difference in coefficients of expansion between the matrix and fillers [138] further stresses can occur. Therefore, a room temperature cure system was chosen for this study to minimise such stresses.

4.2.3 Flexural Properties

The flexural strength and modulus properties, of unreinforced samples based on a standard mix cured at 100°C for various times (4, 8, 16, and 24 hours); (series 2), are listed in Table 4.2.4. Graphs of these flexural strength and modulus values versus postcuring time at 100°C are shown in Figures 4.2.11 and 4.2.12 respectively.
4. Results

Table 4.2.4 Flexural strength and flexural modulus of standard mix samples after postcure at 100°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>93.5</td>
<td>0.6</td>
<td>2780</td>
<td>33</td>
</tr>
<tr>
<td>8</td>
<td>93.7</td>
<td>1.0</td>
<td>2867</td>
<td>43</td>
</tr>
<tr>
<td>16</td>
<td>96.5</td>
<td>1.7</td>
<td>2904</td>
<td>18</td>
</tr>
<tr>
<td>24</td>
<td>98.2</td>
<td>1.3</td>
<td>2938</td>
<td>48</td>
</tr>
</tbody>
</table>

Figure 4.2.11 Flexural Strength vs Postcure time at 100°C
4. Results

The flexural strength and modulus properties of a set of standard mix samples with no reinforcement; postcured at 150°C for various times (4, 8, 16, 24 and 48 hours; see series 3) are presented in Table 4.2.5. Figures 4.2.13 and 4.2.14 were plotted from these values. These are the plots of flexural strength and modulus versus postcuring time at 150°C respectively.

Table 4.2.5 Flexural strength and flexural modulus of standard mix samples after postcure at 150°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>8</td>
<td>104.1</td>
<td>1.7</td>
<td>3045</td>
<td>56</td>
</tr>
<tr>
<td>16</td>
<td>101.3</td>
<td>15.1</td>
<td>3119</td>
<td>92</td>
</tr>
<tr>
<td>24</td>
<td>82.0</td>
<td>29.1</td>
<td>3210</td>
<td>111</td>
</tr>
<tr>
<td>24</td>
<td>71.4</td>
<td>10.5</td>
<td>3154</td>
<td>29</td>
</tr>
<tr>
<td>48</td>
<td>45.9</td>
<td>2.6</td>
<td>3422</td>
<td>60</td>
</tr>
</tbody>
</table>
4. Results

Figure 4.2.13 Flexural Strength vs Postcure Time at 150°C

Figure 4.2.14 Flexural Modulus vs Postcure Time at 150°C
4. Results

4.2.4 Microscopic Examinations

The fracture surfaces of specimens previously tested for flexural properties are shown in Figures 4.2.15 to 4.2.18. These show the difference in smoothness of the surfaces after postcure. Figure 4.2.15 was cured at room temperature without postcuring, whereas the others were postcured at 150°C for different times, after initial cure at room temperature for the minimum time of 7 days. These are Figures 4.2.16, 4.2.17 and 4.2.18 with postcuring times of 4, 8, and 48 hours respectively.

Figure 4.2.15 Fracture surface of a standard mix sample, RT cured: fractured by flexure (x 10) at 20°C
4. Results

Figure 4.2.16 Fracture surface of a standard mix sample, postcured at 150°C for 4 hr: fractured by flexure (x 10) at 20°C

Figure 4.2.17 Fracture surface of a standard mix sample, postcured at 150°C for 8 hr: fractured by flexure (x 10) at 20°C
4. Results

4.2.5 Visual Observation

Figure 4.2.19 shows the results for standards mix specimens after postcuring at 150°C for different times (series 3). The postcure time were 4, 8, 16, 24, and 48 hr from left to right of the figure. It can be seen that the colour darkened with increasing postcuring time.

Note: The specimens were placed on a black line in order to show the transparency of these specimens. The standard colour chart was placed above the specimens to confirm the shade of the colour of the specimens which could be altered by the technique used to develop the photograph.
4. Results

Figure 4.2.19 The standard mix samples after postcure at 150°C for various times
4. Results

4.3 Influence of Liquid Urethane Modifier

4.3.1 DMTA

The results of incorporating a commercial liquid urethane polymer (i.e. Desmocap 11) into the Epikote epoxy, studied by DMTA on the unreinforced (series 4) and reinforced (series 10) systems are shown in Figures 4.3.1 to 4.3.7, and Tables 4.3.1 and 4.3.2.

Figures 4.3.1 and 4.3.2 are DMTA thermograms of the unreinforced systems which were cured at room temperature. Figure 4.3.1 is the data traces of Epikote:Desmocap in the ratio of 100:0, 90:10, 80:20, 70:30, 60:40, and 50:50. Whereas, Figure 4.3.2 is the DMTA thermograms of the same materials in the ratio of 50:50, 40:60, 35:65, 30:70, 20:80 and 10:90 respectively, (see series 4). The details of each trace are given in Table 4.3.1.

Table 4.3.1 DMTA data for Epikote modified with Desmocap, RT cured

<table>
<thead>
<tr>
<th>Epikote: Desmocap Ratio</th>
<th>tan δ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>T&lt;sub&gt;G, DMTA&lt;/sub&gt; (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E'&lt;sub&gt;1/2&lt;/sub&gt; (°C)</th>
<th>E'&lt;sub&gt;-25°C&lt;/sub&gt; (MPa)</th>
<th>tan δ at -25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>1.11</td>
<td>65.7</td>
<td>3.04</td>
<td>55.0</td>
<td>1093</td>
<td>0.02</td>
</tr>
<tr>
<td>90:10</td>
<td>1.07</td>
<td>64.6</td>
<td>3.13</td>
<td>50.7</td>
<td>1200</td>
<td>0.03</td>
</tr>
<tr>
<td>80:20</td>
<td>0.91</td>
<td>65.4</td>
<td>3.07</td>
<td>45.2</td>
<td>982</td>
<td>0.02</td>
</tr>
<tr>
<td>70:30</td>
<td>0.74</td>
<td>66.8</td>
<td>3.08</td>
<td>24.7</td>
<td>935</td>
<td>0.04</td>
</tr>
<tr>
<td>60:40</td>
<td>0.61</td>
<td>66.6</td>
<td>3.06</td>
<td>6.0</td>
<td>882</td>
<td>0.06</td>
</tr>
<tr>
<td>50:50</td>
<td>0.55</td>
<td>63.7</td>
<td>2.72</td>
<td>4.8</td>
<td>428</td>
<td>0.06</td>
</tr>
<tr>
<td>40:60</td>
<td>0.36</td>
<td>64.7</td>
<td>2.75</td>
<td>-10.1</td>
<td>432</td>
<td>0.08</td>
</tr>
<tr>
<td>35:65</td>
<td>0.28</td>
<td>61.8</td>
<td>2.78</td>
<td>-13.7</td>
<td>422</td>
<td>0.11</td>
</tr>
<tr>
<td>30:70</td>
<td>0.27</td>
<td>33.7</td>
<td>2.61</td>
<td>-11.6</td>
<td>207</td>
<td>0.12</td>
</tr>
<tr>
<td>20:80</td>
<td>0.39</td>
<td>2.4</td>
<td>2.49</td>
<td>-21.2</td>
<td>215</td>
<td>0.19</td>
</tr>
<tr>
<td>10:90</td>
<td>0.71</td>
<td>-13.8</td>
<td>2.30</td>
<td>-24.0</td>
<td>112</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Figure 4.3.1 DMTA traces for Epikote:Desmocap mixes

Peaks
1. 65.69°C
2. 64.56°C
3. 65.35°C
4. 66.80°C
5. 66.57°C
6. 63.66°C

Key  Epikote:Desmocap
1. 100:0
2. 90:10
3. 80:20
4. 70:30
5. 60:40
6. 50:50
Figure 4.3.2 DMTA traces for Epikote:Desmocap mixes

Peaks
1. -13.76°C
2. 2.42°C
3. 33.69°C
4. 61.79°C
5. 64.69°C
6. 63.66°C

Key Epikote:Desmocap
1. 10:90
2. 20:80
3. 30:70
4. 35:65
5. 40:60
6. 50:50
4. Results

A histogram, Figure 4.3.3 shows $\tan \delta_{\text{max}}$ plotted against the Epikote:Desmocap ratio, and a plot of $T_g$ values of these materials is shown in Figure 4.3.4.

A set of Epikote:Desmocap/glass fibre composites (series 10) were investigated and the general traces of some of these specimens are shown in Figure 4.3.5. The numerical data relating to these specimens are given in Table 4.3.2. The $\tan \delta_{\text{max}}$ and $T_g$ values were used to plot Figures 4.3.6 and 4.3.7 respectively.

Table 4.3.2 DMTA data for Epikote 828/glass fibre composites modified with different amounts of Desmocap 11

<table>
<thead>
<tr>
<th>Epikote: Desmocap Ratio</th>
<th>$\tan \delta_{\text{max}}$</th>
<th>$T_g^{\text{DMTA}}$ (°C)</th>
<th>$\Delta \log E'$</th>
<th>Temp. at $E'_{1/2}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>95:5</td>
<td>0.46</td>
<td>75.4</td>
<td>1.15</td>
<td>64.8</td>
</tr>
<tr>
<td>90:10</td>
<td>0.45</td>
<td>74.5</td>
<td>1.23</td>
<td>60.6</td>
</tr>
<tr>
<td>80:20</td>
<td>0.45</td>
<td>75.8</td>
<td>1.24</td>
<td>60.1</td>
</tr>
<tr>
<td>70:30</td>
<td>0.42</td>
<td>77.6</td>
<td>1.32</td>
<td>57.2</td>
</tr>
<tr>
<td>60:40</td>
<td>0.41</td>
<td>78.0</td>
<td>1.39</td>
<td>46.9</td>
</tr>
<tr>
<td>50:50</td>
<td>0.32</td>
<td>78.4</td>
<td>1.36</td>
<td>28.3</td>
</tr>
</tbody>
</table>

Figure 4.3.3 $\tan \delta_{\text{max}}$ vs Epikote : Desmocap Ratio
4. Results

Figure 4.3.4 TgDMTA vs Epikote : Desmocap Ratio

![Graph showing TgDMTA vs Epikote : Desmocap Ratio]
Figure 4.3.5 DMTA traces for Epikote:Desmocap/glass fibre composites

Key Epikote:Desmocap
1. 100:0
2. 90:10
3. 70:30
4. 50:50

Peaks
1. 74.51°C
2. 74.51°C
3. 77.16°C
4. 80.05°C
4. Results

**Figure 4.3.8** $\tan \delta_{\text{max}}$ vs % Desmocap

**Figure 4.3.7** $T_g$ DMTA vs % Desmocap
4. Results

4.3.2 Mechanical Properties

Results of flexural testing on unreinforced specimens having Epikote:Desmocap ratios from 100:0 to 50:50 (see series 4) are shown in Table 4.3.3. The flexural strength and modulus values plotted against Epikote:Desmocap ratio are given in Figures 4.3.8 and 4.3.9.

Table 4.3.3 Flexural properties of Epikote modified with Desmocap, RT cured

<table>
<thead>
<tr>
<th>Epikote: Desmocap ratio</th>
<th>phr Desmocap</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>90:10</td>
<td>11</td>
<td>77.1</td>
<td>1.9</td>
<td>2411</td>
<td>57</td>
</tr>
<tr>
<td>80:20</td>
<td>25</td>
<td>57.1</td>
<td>2.1</td>
<td>1740</td>
<td>56</td>
</tr>
<tr>
<td>70:30</td>
<td>43</td>
<td>40.4</td>
<td>1.3</td>
<td>1205</td>
<td>30</td>
</tr>
<tr>
<td>60:40</td>
<td>67</td>
<td>24.8</td>
<td>1.3</td>
<td>680</td>
<td>32</td>
</tr>
<tr>
<td>50:50</td>
<td>100</td>
<td>13.3</td>
<td>0.5</td>
<td>305</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure 4.3.8 Flexural Strength vs Epikote : Desmocap Ratio
4. Results

![Figure 4.3.9 Flexural Modulus vs Epikote : Desmocap Ratio](image)

The flexural properties of Epikote 828/glass fibre composites modified by Desmocap (series 10) are presented in Table 4.3.4. These values have been used to plot Figures 4.3.10 to 4.3.13 i.e. plots of work done producing a deflection of 5 mm (Figure 4.3.10), flexural strength (Figure 4.3.11) and modulus (Figure 4.3.12), and deflection at maximum force (Figure 4.3.13) respectively. The load/deflection curves for these flexural tests are shown in Figure 4.3.14.

Table 4.3.4 Flexural properties of Epikote 828/glass fibre composites; modified with Desmocap 11

<table>
<thead>
<tr>
<th>Epikote : Desmocap Ratio</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Max. Force (mm)</th>
<th>S.D. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>780.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>95:5</td>
<td>596.2</td>
<td>50.1</td>
<td>255.9</td>
<td>13.8</td>
<td>17296</td>
<td>658</td>
<td>2.5</td>
<td>0.4</td>
</tr>
<tr>
<td>90:10</td>
<td>570.3</td>
<td>26.2</td>
<td>226.0</td>
<td>5.1</td>
<td>14623</td>
<td>716</td>
<td>3.1</td>
<td>0.1</td>
</tr>
<tr>
<td>80:20</td>
<td>491.9</td>
<td>4.8</td>
<td>197.5</td>
<td>3.7</td>
<td>14863</td>
<td>87</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>70:30</td>
<td>480.2</td>
<td>14.7</td>
<td>183.1</td>
<td>1.6</td>
<td>13357</td>
<td>25</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>60:40</td>
<td>451.7</td>
<td>11.0</td>
<td>190.4</td>
<td>15.5</td>
<td>13533</td>
<td>176</td>
<td>2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>50:50</td>
<td>387.0</td>
<td>8.5</td>
<td>139.2</td>
<td>5.8</td>
<td>11720</td>
<td>370</td>
<td>2.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
4. Results

**Figure 4.3.10 Work to Failure vs % Desmocap (composites)**

![Graph showing Work to Failure vs % Desmocap](image)

**Figure 4.3.11 Flexural Strength vs % Desmocap (composites)**

![Graph showing Flexural Strength vs % Desmocap](image)
4. Results

Figure 4.3.12 Flexural Modulus vs % Desmocap (composites)

Figure 4.3.13 Deflection at Maximum Force vs % Desmocap (composites)
Figure 4.3.14 Load vs. Deflection (Epikote:Desmocap/glass fibre composites)

Key: Epikote:Desmocap
1. 100:0
2. 90:10
3. 70:30
4. 50:50
4. Results

The interlaminar shear strength of the above composites are shown in Table 4.3.5. Figure 4.3.15 was plotted using these values.

Table 4.3.5 The interlaminar shear strength (ILSS) of Epikote 828/glass fibre composites modified with Desmocap 11

<table>
<thead>
<tr>
<th>Epikote: Desmocap ratio</th>
<th>phr Desmocap</th>
<th>Interlaminar Shear Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Strength / ILSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>--</td>
<td>29.9</td>
<td>0.5</td>
<td>10.8</td>
</tr>
<tr>
<td>95:5</td>
<td>5</td>
<td>20.4</td>
<td>1.0</td>
<td>12.5</td>
</tr>
<tr>
<td>90:10</td>
<td>11</td>
<td>18.4</td>
<td>0.9</td>
<td>12.3</td>
</tr>
<tr>
<td>80:20</td>
<td>25</td>
<td>16.1</td>
<td>1.1</td>
<td>12.3</td>
</tr>
<tr>
<td>70:30</td>
<td>43</td>
<td>17.9</td>
<td>1.0</td>
<td>10.2</td>
</tr>
<tr>
<td>60:40</td>
<td>67</td>
<td>15.8</td>
<td>0.6</td>
<td>12.1</td>
</tr>
<tr>
<td>50:50</td>
<td>100</td>
<td>13.0</td>
<td>0.2</td>
<td>10.7</td>
</tr>
</tbody>
</table>

The values of peak force, deflection and energy of the specimens in series 10 determined by Rosand falling weight impact test can be seen in Table 4.3.6. These results were used to plot Figures 4.3.16 and 4.3.17 for the deflection at peak impact.
4. Results

force and impact energy to failure, (standardised at a deflection 7 mm) against Desmocap concentration. The force/displacement curves for the falling weight impact tests are shown in Figure 4.3.18.

Table 4.3.6 Falling weight impact data for Epikote 828/glass fibre composites, modified with Desmocap 11

<table>
<thead>
<tr>
<th>Epikote: Desmocap Ratio</th>
<th>Peak Impact Force (N)</th>
<th>S.D.</th>
<th>Deflection at Peak Impact Force (mm)</th>
<th>S.D.</th>
<th>Energy at Peak Impact Force (J)</th>
<th>S.D.</th>
<th>Impact Energy to Failure (J)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
<td>18.7</td>
<td>0.3</td>
</tr>
<tr>
<td>95:5</td>
<td>5953</td>
<td>428</td>
<td>5.4</td>
<td>0.3</td>
<td>14.3</td>
<td>1.6</td>
<td>19.5</td>
<td>0.9</td>
</tr>
<tr>
<td>90:10</td>
<td>5843</td>
<td>283</td>
<td>5.2</td>
<td>0.2</td>
<td>14.0</td>
<td>1.2</td>
<td>20.7</td>
<td>1.1</td>
</tr>
<tr>
<td>80:20</td>
<td>6014</td>
<td>209</td>
<td>5.7</td>
<td>0.3</td>
<td>15.1</td>
<td>1.2</td>
<td>20.7</td>
<td>0.7</td>
</tr>
<tr>
<td>70:30</td>
<td>5702</td>
<td>161</td>
<td>5.5</td>
<td>0.1</td>
<td>14.6</td>
<td>0.6</td>
<td>20.3</td>
<td>0.7</td>
</tr>
<tr>
<td>60:40</td>
<td>5625</td>
<td>244</td>
<td>5.8</td>
<td>0.1</td>
<td>14.7</td>
<td>0.3</td>
<td>19.2</td>
<td>0.7</td>
</tr>
<tr>
<td>50:50</td>
<td>5105</td>
<td>310</td>
<td>6.2</td>
<td>0.2</td>
<td>14.7</td>
<td>2.0</td>
<td>18.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 4.3.16 Deflection at Peak Impact Force vs % Desmocap (composites)
4. Results

Figure 4.3.17  Impact Energy to Failure vs % Desmocap (composites)
Figure 4.3.18 IFWI Force vs Displacement

Key Epikote:Desmocap
1. 100:0
2. 80:20
3. 60:30
4. 50:50
4. Results

4.3.3 Microscopic Examinations

i) Fracture Surfaces Studied by SEM

The SEM micrographs of specimens based on unmodified epoxy resin (Epikote 828) and Desmocap modified Epikote (see section 3.5 (A)) are shown in Figures 4.3.19 to 4.3.23. Figure 4.3.19 shows the fracture surfaces of the standard mix specimen (i.e. reference 1:55). While the fracture surfaces of a specimen containing 100% Desmocap (i.e. without Epikote) is shown in Figure 4.3.20. Photographs were taken using higher magnification than that used in Figures 4.3.19 and 4.3.20. These contained 0% (Figure 4.3.21), 40% (Figure 4.3.22), and 100% (Figure 4.3.23) Desmocap respectively. Figure 4.3.21 was taken from the specimen shown in Figure 4.3.19, and Figure 4.3.23 was taken from the specimen shown in Figure 4.3.20.

Note: All of these photomicrographs were taken of the central area of the fractured specimens.

Figure 4.3.19 SEM micrograph shows fracture surface of an unmodified epoxy resin at low magnification (x 75)
4. Results

Figure 4.3.20 SEM micrograph shows fracture surface of 100 % Desmocap at low magnification (x 75)

Figure 4.3.21 SEM micrograph shows fracture surface of an unmodified epoxy resin at higher magnification (x 500)
4. Results

Figure 4.3.22 SEM micrograph shows fracture surface of a modified epoxy resin containing 40% Desmocap (x 500)

Figure 4.3.23 SEM micrograph shows fracture surface of 100% Desmocap at higher magnification (x 500)
ii) Study of Thin Sections by Using TEM

Photomicrographs of microtomed sections of unmodified and Desmocap modified Epikote are shown in Figures 4.3.24 to 4.3.27.

Figures 4.3.24 and 4.3.25 are of the same specimen of the standard mixed resin (reference number 1: 55), but the former Figure is of an unstained specimen, while the latter specimen was stained with OsO₄ for 7 days. They were taken at the same magnification (i.e. 50000 x).

The specimens based on various levels of Desmocap are shown in Figures 4.3.26 and 4.3.27. The specimen in Figure 4.3.26 had the ratio of Epikote:Desmocap of 80:20 (i.e. reference 4: 80/20), whereas, in Figure 4.3.27 the ratio was 40:60 (reference 4: 40/60).

Figure 4.3.24 TEM micrograph of an unmodified epoxy resin; unstained (x 75000)
4. Results

Figure 4.3.25 TEM micrograph of an unmodified epoxy resin; after staining with OsO₄ for 7 days at room temperature (x 75000)

Figure 4.3.26 TEM micrograph of a modified epoxy resin containing 20 % Desmocap; after staining with OsO₄ for 2 days at room temperature (x 75000), 0.1 μm
4. Results

Figure 4.3.27 TEM micrograph of a modified epoxy resin containing 60% Desmocap; after staining with OsO₄ for 2 days at room temperature (x 75000), 0.1 μm

4.3.4 Visual Observations

Study of Specimens After Impact Testing

Photographs showing glass fibre composite specimens based on different ratios of Epikote and Desmocap can be seen in Figures 4.3.28 to 4.3.31. They were taken using a 35 SLR camera. The matrices of these composites contained 0 (Figure 4.3.28), 20 (Figure 4.3.29), 30 (Figure 4.3.30), and 50% (Figure 4.3.31) Desmocap.
4. Results

Figure 4.3.28 A photograph of an unmodified resin matrix composite; after impact testing (x 1.6)

Figure 4.3.29 A photograph of a modified resin matrix composite containing 20% Desmocap; after impact testing (x 1.6)
4. Results

Figure 4.3.30 A photograph of a modified resin matrix composite containing 30% Desmocap; after impact testing (x 1.6)

Figure 4.3.31 A photograph of a modified resin matrix composite containing 50% Desmocap; after impact testing (x 1.6)
4. Results

4.4 Influence of Polyamine Modifiers

4.4.1 Thermal Analysis (DMTA)

The results for Jeffamine modifier:Epikote 828 systems which had been cured at room temperature (series 5a, 6a, 7a, and 8a) and studied by DMTA are presented in Tables 4.4.1 to 4.4.4. Figure 4.4.1 is a thermogram of a modified epoxy resin containing 19.7 phr of Jeffamine D4000 (reference 7a: 20). The $\tan \delta_{\text{max}}$ and $T_{\text{g, DMTA}}$ of these modified resins, plotted against phr of modifiers, are shown in Figures 4.4.2 and 4.4.3 respectively.

Table 4.4.1 DMTA data for Epikote 828 modified with Jeffamine T5000 $R_T$ cured

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>days after mixing</th>
<th>$\tan \delta_{\text{max}}$</th>
<th>$T_{\text{g, DMTA}}$ ($^\circ\text{C}$)</th>
<th>$\Delta \log E'$</th>
<th>Temp. at $E'_{1/2}$ ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>42</td>
<td>1.11</td>
<td>65.7</td>
<td>2.33</td>
<td>55.0</td>
</tr>
<tr>
<td>5.4</td>
<td>35</td>
<td>1.00</td>
<td>67.2</td>
<td>2.29</td>
<td>55.9</td>
</tr>
<tr>
<td>11.8</td>
<td>35</td>
<td>0.90</td>
<td>65.4</td>
<td>2.20</td>
<td>49.5</td>
</tr>
<tr>
<td>19.5</td>
<td>34</td>
<td>0.72</td>
<td>67.4</td>
<td>2.18</td>
<td>50.2</td>
</tr>
</tbody>
</table>

Table 4.4.2 DMTA data for Epikote 828 modified with Jeffamine T3000 $R_T$ cured

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>days after mixing</th>
<th>$\tan \delta_{\text{max}}$</th>
<th>$T_{\text{g, DMTA}}$ ($^\circ\text{C}$)</th>
<th>$\Delta \log E'$</th>
<th>Temp. at $E'_{1/2}$ ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>42</td>
<td>1.11</td>
<td>65.7</td>
<td>2.33</td>
<td>55.0</td>
</tr>
<tr>
<td>11.5</td>
<td>43</td>
<td>0.94</td>
<td>62.7</td>
<td>2.48</td>
<td>46.2</td>
</tr>
<tr>
<td>20.6</td>
<td>44</td>
<td>0.74</td>
<td>62.8</td>
<td>2.22</td>
<td>41.3</td>
</tr>
</tbody>
</table>

Table 4.4.3 DMTA data for Epikote 828 modified with Jeffamine D4000 $R_T$ cured

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>days after mixing</th>
<th>$\tan \delta_{\text{max}}$</th>
<th>$T_{\text{g, DMTA}}$ ($^\circ\text{C}$)</th>
<th>$\Delta \log E'$</th>
<th>Temp. at $E'_{1/2}$ ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>42</td>
<td>1.11</td>
<td>65.7</td>
<td>2.33</td>
<td>55.0</td>
</tr>
<tr>
<td>11.8</td>
<td>42</td>
<td>0.92</td>
<td>64.9</td>
<td>2.32</td>
<td>49.7</td>
</tr>
<tr>
<td>19.7</td>
<td>43</td>
<td>0.89</td>
<td>64.6</td>
<td>2.38</td>
<td>49.8</td>
</tr>
</tbody>
</table>
Figure 4.4.1 DMTA trace for a sample containing 19.7 phr of Jeffamine D4000

PEAKS
1 64.41°C

Bending E' (MPa) vs. Temperature (°C)
4. Results

Table 4.4.4 DMTA data for Epikote 828 modified with Jeffamine D2000 RT cured

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>days after mixing</th>
<th>tan δ_{max}</th>
<th>T_{g, DMTA} (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E_{1/2} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>42</td>
<td>1.11</td>
<td>65.7</td>
<td>2.33</td>
<td>55.0</td>
</tr>
<tr>
<td>11.5</td>
<td>49</td>
<td>0.91</td>
<td>62.6</td>
<td>2.27</td>
<td>50.1</td>
</tr>
<tr>
<td>20.5</td>
<td>48</td>
<td>0.73</td>
<td>61.3</td>
<td>2.24</td>
<td>45.2</td>
</tr>
</tbody>
</table>

Figure 4.4.2 tan δ_{max} vs phr Jeffamine Modifier, RT cured
4. Results

The DMTA results of the Jeffamine series which have been postcured at 150°C for 4 hr (series 5b, 6b, 7b, and 8b) can be seen in Tables 4.4.5 to 4.4.8. The tan δ\(_{\text{max}}\) and T\(_{\text{gDMTA}}\) of these systems, plotted against phr of modifiers are shown in Figures 4.4.4 and 4.4.5 respectively.

Table 4.4.5 DMTA data for Epikote 828 modified with Jeffamine T5000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>tan δ(_{\text{max}})</th>
<th>T(_{\text{gDMTA}}) (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E'_1/2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.47</td>
<td>80.2</td>
<td>1.96</td>
<td>66.3</td>
</tr>
<tr>
<td>5.4</td>
<td>0.42</td>
<td>86.1</td>
<td>2.02</td>
<td>66.9</td>
</tr>
<tr>
<td>11.8</td>
<td>0.43</td>
<td>87.0</td>
<td>2.03</td>
<td>63.5</td>
</tr>
<tr>
<td>19.5</td>
<td>0.41</td>
<td>88.5</td>
<td>1.99</td>
<td>60.0</td>
</tr>
</tbody>
</table>
4. Results

Table 4.4.6 DMTA data for Epikote 828 modified with Jeffamine T3000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>tan δ_{max}</th>
<th>T_{gDMTA} (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E_{1/2} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.47</td>
<td>80.2</td>
<td>1.96</td>
<td>66.3</td>
</tr>
<tr>
<td>11.5</td>
<td>0.37</td>
<td>83.5</td>
<td>2.14</td>
<td>59.1</td>
</tr>
<tr>
<td>20.6</td>
<td>0.39</td>
<td>81.5</td>
<td>1.99</td>
<td>55.6</td>
</tr>
</tbody>
</table>

Table 4.4.7 DMTA data for Epikote 828 modified with Jeffamine D4000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>tan δ_{max}</th>
<th>T_{gDMTA} (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E_{1/2} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.47</td>
<td>80.2</td>
<td>1.96</td>
<td>66.3</td>
</tr>
<tr>
<td>11.8</td>
<td>0.40</td>
<td>86.0</td>
<td>2.04</td>
<td>60.6</td>
</tr>
<tr>
<td>19.7</td>
<td>0.42</td>
<td>87.6</td>
<td>2.17</td>
<td>58.6</td>
</tr>
</tbody>
</table>

Table 4.4.8 DMTA data for Epikote 828 modified with Jeffamine D2000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>tan δ_{max}</th>
<th>T_{gDMTA} (°C)</th>
<th>Δlog E'</th>
<th>Temp. at E_{1/2} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.47</td>
<td>80.2</td>
<td>1.96</td>
<td>66.3</td>
</tr>
<tr>
<td>11.5</td>
<td>0.43</td>
<td>79.9</td>
<td>2.11</td>
<td>60.2</td>
</tr>
<tr>
<td>20.5</td>
<td>0.41</td>
<td>77.5</td>
<td>2.06</td>
<td>51.5</td>
</tr>
</tbody>
</table>
4. Results

Figure 4.4.4 \( \tan \delta_{\text{max}} \) vs phr Jeffamine Modifier, postcured at 150 °C for 4 hr

Figure 4.4.5 TgDMTA vs phr Jeffamine Modifier, postcured at 150 °C for 4 hr
4. Results

Results for Epikote 828:Jeffamine modifiers/glass fibre composites (series 11 to 14) can be seen in Tables 4.4.9 to 4.4.12 (for composites made with the Jeffamine modifiers T5000, T3000, D4000 and D2000 respectively). Plots of tan δ max and \( T_{\text{DMPA}} \) both against quantity of Jeffamine modifiers are shown in Figures 4.4.6 and 4.4.7 respectively.

Table 4.4.9 DMTA data for Epikote 828:Jeffamine T5000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>tan δ max</th>
<th>( T_{\text{DMPA}} ) (°C)</th>
<th>( \Delta \log E' )</th>
<th>Temp. at ( E'_{1/2} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>5.4</td>
<td>0.47</td>
<td>75.9</td>
<td>1.19</td>
<td>64.9</td>
</tr>
<tr>
<td>11.8</td>
<td>0.43</td>
<td>75.5</td>
<td>1.20</td>
<td>62.1</td>
</tr>
<tr>
<td>19.5</td>
<td>0.44</td>
<td>74.4</td>
<td>1.34</td>
<td>54.8</td>
</tr>
<tr>
<td>29.2</td>
<td>0.35</td>
<td>76.6</td>
<td>1.23</td>
<td>53.8</td>
</tr>
</tbody>
</table>

Table 4.4.10 DMTA data for Epikote 828:Jeffamine T3000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>tan δ max</th>
<th>( T_{\text{DMPA}} ) (°C)</th>
<th>( \Delta \log E' )</th>
<th>Temp. at ( E'_{1/2} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>11.5</td>
<td>0.44</td>
<td>71.5</td>
<td>1.18</td>
<td>60.0</td>
</tr>
<tr>
<td>20.6</td>
<td>0.42</td>
<td>70.2</td>
<td>1.25</td>
<td>54.4</td>
</tr>
</tbody>
</table>

Table 4.4.11 DMTA data for Epikote 828:Jeffamine D4000/glass fibre composites

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>tan δ max</th>
<th>( T_{\text{DMPA}} ) (°C)</th>
<th>( \Delta \log E' )</th>
<th>Temp. at ( E'_{1/2} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>11.8</td>
<td>0.39</td>
<td>77.7</td>
<td>1.18</td>
<td>60.8</td>
</tr>
<tr>
<td>19.7</td>
<td>0.41</td>
<td>76.6</td>
<td>1.22</td>
<td>58.3</td>
</tr>
</tbody>
</table>
4. Results

Table 4.4.12 DMTA data for Epikote 828:Jeffamine D2000/glass fibre composites

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>tan δ\text{max}</th>
<th>T_{g,\text{DMTA}} (°C)</th>
<th>Δlog $E'$</th>
<th>Temp. at $E'_{1/2}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0.49</td>
<td>74.9</td>
<td>1.14</td>
<td>66.4</td>
</tr>
<tr>
<td>11.5</td>
<td>0.44</td>
<td>72.0</td>
<td>1.18</td>
<td>60.7</td>
</tr>
<tr>
<td>20.5</td>
<td>0.39</td>
<td>69.3</td>
<td>1.17</td>
<td>54.5</td>
</tr>
</tbody>
</table>

Figure 4.4.6 tan δ\text{max} vs phr Jeffamine Modifier: Epikote/glass fibre composites
4. Results

4.4.2 Mechanical Properties

a) Flexural Properties

Results for epoxy resins (Epikote 828) modified with Jeffamine modifiers and cured at room temperature (series 5a, 6a, 7a, and 8a) are presented in Tables 4.4.13 to 4.4.16. These values were used to plot Figures 4.4.8 and 4.4.9 for flexural strength and modulus respectively against quantity of Jeffamine modifiers.

Table 4.4.13 Flexural strength and modulus of Epikote 828:Jeffamine T5000, R_T cured

<table>
<thead>
<tr>
<th>phr</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>5.4</td>
<td>82.9</td>
<td>1.8</td>
<td>2523</td>
<td>24</td>
</tr>
<tr>
<td>11.8</td>
<td>70.5</td>
<td>0.8</td>
<td>2199</td>
<td>34</td>
</tr>
<tr>
<td>19.5</td>
<td>57.5</td>
<td>0.8</td>
<td>1704</td>
<td>11</td>
</tr>
</tbody>
</table>
4. Results

Table 4.4.14 Flexural strength and modulus of Epikote 828:Jeffamine T3000, \(R_T\) cured

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>11.5</td>
<td>76.1</td>
<td>0.8</td>
<td>2365</td>
<td>56</td>
</tr>
<tr>
<td>20.6</td>
<td>58.3</td>
<td>0.9</td>
<td>1722</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 4.4.15 Flexural strength and modulus of Epikote 828:Jeffamine D4000, \(R_T\) cured

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>11.8</td>
<td>72.3</td>
<td>0.6</td>
<td>2277</td>
<td>31</td>
</tr>
<tr>
<td>19.7</td>
<td>58.5</td>
<td>0.6</td>
<td>1793</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 4.4.16 Flexural strength and modulus of Epikote 828:Jeffamine D2000, \(R_T\) cured

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>89.6</td>
<td>4.8</td>
<td>3049</td>
<td>74</td>
</tr>
<tr>
<td>11.5</td>
<td>79.6</td>
<td>0.9</td>
<td>2414</td>
<td>35</td>
</tr>
<tr>
<td>20.5</td>
<td>62.9</td>
<td>0.7</td>
<td>1875</td>
<td>26</td>
</tr>
</tbody>
</table>
4. Results

Figure 4.4.8 Flexural Strength vs phr Jeffamine Modifier, RT cured

Figure 4.4.9 Flexural Modulus vs phr Jeffamine Modifier, RT cured
4. Results

The flexural properties of the same resin systems after postcuring (series 5b, 6b, 7b, and 8b) were also studied. The results are presented in Tables 4.4.17 to 4.4.20. Plots of flexural strength and modulus against quantity of Jeffamine modifier are shown in Figures 4.4.10 and 4.4.11 respectively.

Table 4.4.17 Flexural strength and modulus of Epikote 828 modified with Jeffamine T5000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>104.1</td>
<td>1.7</td>
<td>3045</td>
<td>56</td>
</tr>
<tr>
<td>5.4</td>
<td>101.1</td>
<td>2.0</td>
<td>2783</td>
<td>38</td>
</tr>
<tr>
<td>11.8</td>
<td>86.4</td>
<td>0.7</td>
<td>2470</td>
<td>29</td>
</tr>
<tr>
<td>19.5</td>
<td>71.0</td>
<td>1.0</td>
<td>2049</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 4.4.18 Flexural strength and modulus of Epikote 828 modified with Jeffamine T3000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>104.1</td>
<td>1.7</td>
<td>3045</td>
<td>56</td>
</tr>
<tr>
<td>11.5</td>
<td>90.4</td>
<td>1.5</td>
<td>2600</td>
<td>58</td>
</tr>
<tr>
<td>20.6</td>
<td>76.1</td>
<td>1.0</td>
<td>2211</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 4.4.19 Flexural strength and modulus of Epikote 828 modified with Jeffamine D4000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>104.1</td>
<td>1.7</td>
<td>3045</td>
<td>56</td>
</tr>
<tr>
<td>11.8</td>
<td>88.0</td>
<td>0.9</td>
<td>2475</td>
<td>24</td>
</tr>
<tr>
<td>19.7</td>
<td>71.6</td>
<td>0.7</td>
<td>2030</td>
<td>19</td>
</tr>
</tbody>
</table>
4. Results

Table 4.4.20 Flexural strength and modulus of Epikote 828 modified with Jeffamine D2000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>Flexural Strength (MPa)</th>
<th>S.D.</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>104.1</td>
<td>1.7</td>
<td>3045</td>
<td>56</td>
</tr>
<tr>
<td>11.5</td>
<td>97.6</td>
<td>2.0</td>
<td>2794</td>
<td>59</td>
</tr>
<tr>
<td>20.5</td>
<td>85.8</td>
<td>2.7</td>
<td>2499</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 4.4.10 Flexural Strength vs phr Jeffamine Modifier, postcured at 150 °C for 4 hr
Tables 4.4.21 to 4.4.24 show flexural test results for the Epikote 828/glass fibre composites modified with Jeffamine modifiers (i.e. series 11 to 14). Figures 4.4.12 to 4.4.15 were plotted using these values. These are plots of work at failure (Figure 4.4.12), flexural strength (Figure 4.4.13), flexural modulus (Figure 4.4.14), and extension determined at maximum force (Figure 4.4.15), all against quantity of Jeffamine modifiers.

Table 4.4.21 Flexural properties of Epikote 828:Jeffamine T5000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
<th>S.D. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>980.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>5.4</td>
<td>659.1</td>
<td>48.1</td>
<td>259.8</td>
<td>19.9</td>
<td>16804</td>
<td>440</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td>11.8</td>
<td>654.7</td>
<td>21.0</td>
<td>279.7</td>
<td>8.9</td>
<td>15916</td>
<td>582</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>19.5</td>
<td>633.5</td>
<td>29.2</td>
<td>251.9</td>
<td>6.1</td>
<td>14319</td>
<td>897</td>
<td>3.1</td>
<td>0.3</td>
</tr>
<tr>
<td>29.2</td>
<td>570.7</td>
<td>19.1</td>
<td>250.4</td>
<td>10.2</td>
<td>14788</td>
<td>562</td>
<td>2.6</td>
<td>0.2</td>
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</tbody>
</table>
4. Results

Table 4.4.22 Flexural properties of Epikote 828:Jeffamine T3000/glass fibre composites

<table>
<thead>
<tr>
<th>phr</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
<th>S.D. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>980.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>11.5</td>
<td>744.0</td>
<td>21.0</td>
<td>312.9</td>
<td>15.0</td>
<td>16674</td>
<td>1428</td>
<td>3.3</td>
<td>0.4</td>
</tr>
<tr>
<td>20.6</td>
<td>719.3</td>
<td>24.1</td>
<td>290.2</td>
<td>14.5</td>
<td>16184</td>
<td>851</td>
<td>3.3</td>
<td>0.4</td>
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</table>

Table 4.4.23 Flexural properties of Epikote 828:Jeffamine D4000/glass fibre composites

<table>
<thead>
<tr>
<th>phr</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
<th>S.D. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>980.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>11.8</td>
<td>644.7</td>
<td>40.6</td>
<td>276.7</td>
<td>16.4</td>
<td>16113</td>
<td>808</td>
<td>2.8</td>
<td>0.2</td>
</tr>
<tr>
<td>19.7</td>
<td>585.0</td>
<td>39.9</td>
<td>248.0</td>
<td>15.0</td>
<td>15270</td>
<td>896</td>
<td>2.8</td>
<td>0.2</td>
</tr>
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</table>

Table 4.4.24 Flexural properties of Epikote 828:Jeffamine D2000/glass fibre composites

<table>
<thead>
<tr>
<th>phr</th>
<th>Work to Failure (N.mm)</th>
<th>S.D. (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>S.D. (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>S.D. (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
<th>S.D. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>980.8</td>
<td>34.4</td>
<td>322.5</td>
<td>11.8</td>
<td>17285</td>
<td>1216</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>11.5</td>
<td>716.9</td>
<td>24.8</td>
<td>299.6</td>
<td>13.5</td>
<td>15893</td>
<td>1548</td>
<td>3.3</td>
<td>0.6</td>
</tr>
<tr>
<td>20.5</td>
<td>676.7</td>
<td>31.5</td>
<td>281.3</td>
<td>18.1</td>
<td>16270</td>
<td>538</td>
<td>3.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>
4. Results

Figure 4.4.12 Work to Failure vs phr Jeffamine Modifier:
Epikote/glass fibre composites

Figure 4.4.13 Flexural Strength vs phr Jeffamine Modifier:
Epikote/glass fibre composites
4. Results

Figure 4.4.14 Flexural Modulus vs phr Modifier: Epikote/glass fibre composites

Figure 4.4.15 Deflection at Maximum Force vs phr Jeffamine Modifier: Epikote/glass fibre composites
4. Results

The results of ILSS tests for the composites (i.e. for series 11 to 14) are given in Tables 4.4.25 to 4.4.28. Figure 4.4.16 was plotted from these data for the interlaminar shear strength against quantity of Jeffamine modifiers.

Table 4.4.25 ILSS of Epikote 828:Jeffamine T5000

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>ILSS (N/mm²)</th>
<th>S.D. (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>29.9</td>
<td>0.5</td>
</tr>
<tr>
<td>5.4</td>
<td>20.6</td>
<td>1.6</td>
</tr>
<tr>
<td>11.8</td>
<td>22.8</td>
<td>1.0</td>
</tr>
<tr>
<td>19.5</td>
<td>22.9</td>
<td>1.0</td>
</tr>
<tr>
<td>29.2</td>
<td>20.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 4.4.26 ILSS of Epikote 828:Jeffamine T3000

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>ILSS (N/mm²)</th>
<th>S.D. (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>29.9</td>
<td>0.5</td>
</tr>
<tr>
<td>11.5</td>
<td>26.0</td>
<td>1.3</td>
</tr>
<tr>
<td>20.6</td>
<td>23.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4.4.27 ILSS of Epikote 828:Jeffamine D4000

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>ILSS (N/mm²)</th>
<th>S.D. (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>29.9</td>
<td>0.5</td>
</tr>
<tr>
<td>11.8</td>
<td>21.7</td>
<td>2.0</td>
</tr>
<tr>
<td>19.7</td>
<td>20.9</td>
<td>1.4</td>
</tr>
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</table>

Table 4.4.28 ILSS of Epikote 828:Jeffamine D2000

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>ILSS (N/mm²)</th>
<th>S.D. (N/mm²)</th>
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</thead>
<tbody>
<tr>
<td>--</td>
<td>29.9</td>
<td>0.5</td>
</tr>
<tr>
<td>11.5</td>
<td>26.1</td>
<td>1.0</td>
</tr>
<tr>
<td>20.5</td>
<td>25.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>
b) Impact Properties

Instrumented falling weight impact test results for the above composites are given in Tables 4.4.29 to 4.4.32. A curve fit equation was used to fit the data and the results can be seen in Figures 4.4.17 to 4.4.20. These plots are of peak impact force (Figure 4.4.17), deflection at peak impact force (Figure 4.4.18), energy at peak impact force (Figure 4.4.19) and impact energy to failure (Figure 4.4.20) against phr of Jeffamine modifiers respectively.

Table 4.4.29 IFWI data for Epikote 828:Jeffamine T5000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Peak Impact Force (N)</th>
<th>S.D.</th>
<th>Deflection at Peak Impact Force (mm)</th>
<th>S.D.</th>
<th>Energy at Peak Impact Force (J)</th>
<th>S.D.</th>
<th>Impact Energy to Failure (J)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
<td>18.7</td>
<td>0.3</td>
</tr>
<tr>
<td>5.4</td>
<td>5712</td>
<td>218</td>
<td>5.4</td>
<td>0.2</td>
<td>13.7</td>
<td>1.1</td>
<td>19.8</td>
<td>0.7</td>
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<tr>
<td>11.8</td>
<td>5930</td>
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<td>0.2</td>
<td>14.5</td>
<td>1.2</td>
<td>20.1</td>
<td>0.5</td>
</tr>
<tr>
<td>19.5</td>
<td>6007</td>
<td>135</td>
<td>5.6</td>
<td>0.2</td>
<td>15.0</td>
<td>1.0</td>
<td>20.1</td>
<td>0.5</td>
</tr>
<tr>
<td>29.2</td>
<td>5618</td>
<td>190</td>
<td>5.7</td>
<td>0.2</td>
<td>14.3</td>
<td>1.0</td>
<td>18.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>
### 4. Results

**Table 4.4.30 IFWI data for Epikote 828:Jeffamine T3000/glass fibre composites.**

<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N)</td>
<td>(N)</td>
<td>(mm)</td>
<td>(mm)</td>
<td>(J)</td>
<td>(J)</td>
<td>(J)</td>
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<tr>
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<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
<td>18.7</td>
</tr>
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<td>0.1</td>
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<tr>
<td>20.6</td>
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<td>187</td>
<td>5.2</td>
<td>0.1</td>
<td>13.3</td>
<td>0.5</td>
<td>19.6</td>
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</tbody>
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**Table 4.4.31 IFWI data for Epikote 828:Jeffamine D4000/glass fibre composites**

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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N)</td>
<td>(N)</td>
<td>(mm)</td>
<td>(mm)</td>
<td>(J)</td>
<td>(J)</td>
<td>(J)</td>
</tr>
<tr>
<td>--</td>
<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
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</tr>
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<td>0.6</td>
<td>16.6</td>
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<td>21.0</td>
</tr>
<tr>
<td>19.7</td>
<td>6408</td>
<td>239</td>
<td>5.8</td>
<td>0.2</td>
<td>16.4</td>
<td>0.8</td>
<td>21.6</td>
</tr>
</tbody>
</table>

**Table 4.4.32 IFWI data for Epikote 828:Jeffamine D2000/glass fibre composites**

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N)</td>
<td>(N)</td>
<td>(mm)</td>
<td>(mm)</td>
<td>(J)</td>
<td>(J)</td>
<td>(J)</td>
</tr>
<tr>
<td>--</td>
<td>5250</td>
<td>137</td>
<td>4.9</td>
<td>0.1</td>
<td>11.9</td>
<td>0.5</td>
<td>18.7</td>
</tr>
<tr>
<td>11.5</td>
<td>5268</td>
<td>164</td>
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<td>11.3</td>
<td>0.9</td>
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</tr>
<tr>
<td>20.5</td>
<td>5080</td>
<td>205</td>
<td>4.9</td>
<td>0.1</td>
<td>11.3</td>
<td>0.5</td>
<td>18.1</td>
</tr>
</tbody>
</table>
4. Results

Figure 4.4.17 Maximum Impact Force vs phr Jeffamine Modifier

Figure 4.4.18 Deflection at Peak Impact Force vs phr Jeffamine Modifier
4. Results

Figure 4.4.19 Energy at Maximum Impact Force vs phr Jeffamine Modifier

Figure 4.4.20 Impact Energy to Failure vs phr Jeffamine Modifier
4. Results

4.4.3 Visual Observation

A photograph (Figure 4.4.21) shows the result of the visual observation of an unmodified (reference number 1: 55), and the modified epoxy resins with an elastomer content of ~20 phr (reference numbers 5a: 20, 6a: 21, 7a: 20, and 8a: 21).

Figure 4.4.21 Unmodified and modified epoxy resins with Jeffamine T5000, T3000, D4000, and D2000 respectively (from left to right)

4.4.4 Microscopic Examinations

Figure 4.4.22 shows a TEM micrograph of a thin microtomed-section of a specimen modified with 19.7 phr of Jeffamine D4000 (i.e. reference 7a: 20).

The results of stained thin-sections of Jeffamine modified epoxy resins can be seen in Figures 4.4.23 to 4.4.26; reference numbers 5a: 20 (Figure 4.4.23), 6a: 21 (Figure 4.4.24), 7a: 20 (Figure 4.4.25), and 8a: 21 (Figure 4.4.26) respectively.
4. Results

Figure 4.4.22 TEM micrograph of a modified epoxy resin, unstained, 0.1 μm

Figure 4.4.23 TEM micrograph of a Jeffamine T5000 modified epoxy resin, after staining with OsO₄ for 4.5 days, 0.1 μm
4. Results

Figure 4.4.24 TEM micrograph of a Jeffamine T3000 modified epoxy resin, after staining with OsO₄ for 7 days, 0.1 μm

Figure 4.4.25 TEM micrograph of a Jeffamine D4000 modified epoxy resin, after staining with OsO₄ for 4.5 days, 0.1 μm
Figure 4.4.26 TEM micrograph of a Jeffamine D2000 modified epoxy resin, after staining with OsO₄ for 4.5 days, 0.1 μm
5. Discussion

5.1 Influence of Curing Agent

5.1.1 Thermal Analysis

i) DSC

The mixture of Epikote 828 and Ancamine MCA, at the standard mix or stoichiometric ratio, created an exothermic reaction as can be seen from the DSC trace in Figure 4.1.1. DSC analysis was started 15 minutes after mixing and showed the greatest level of exothermic value (i.e. 291.1 J/g). This is mainly influenced by the reaction between the epoxide and amine groups. 21.3 hrs after the mixing the exothermic value was very much reduced (34.35 J/g), (see Figure 4.1.2), but had a higher Tg (see Table 4.1.1). This is shown by the endothermic curve which was not observed in the original DSC thermogram. The thermogram suggest that the second mixture had already cured. Thus the movement of the molecules in the mixture is greatly reduced and therefore a temperature higher than the Tg is required to increase the mobility of any unreacted molecules. Once above this Tg the structure started to relax and absorb some energy for restarting further reaction. An example of this can be seen in Figure 4.1.2, where a reaction exotherm could still be measured.

A plot of exothermic values against time after mixing, is shown in Figure 4.1.3. The several measurements which are presented in Table 4.1.1. TgDSC (Figure 4.1.4) and degree of conversion (Figure 4.1.5) are plotted against time after mixing, to show the relationships of these trends. Under the normal curing conditions only the reaction of the epoxide groups with the hydrogen atoms in the amine groups of curing agent is expected to occur [139]. The polyaddition reaction of these two groups can be written as [139, 140]:

\[
\begin{align*}
\text{(1)} & \quad R_1CH\overline{\text{CH}_2} + R_2NH_2 & \rightarrow & \quad R_1CH(OH)CH_2NH_2R_2 \\
\text{(2)} & \quad R_1CH\overline{\text{CH}_2} + R_1CH(OH)CH_2NH_2R_2 & \rightarrow & \quad [R_1CH(OH)CH_2]_2NR_2 \\
\end{align*}
\]

Where \( k_1 \) is the reaction rate of epoxy with primary amine [14, 15, 140].

\( k_2 \) is the reaction rate of epoxy with secondary amine group [14, 15, 140].
Levita [141] showed that the first slope of a plot of extent of epoxide reaction versus reaction time is the \( k_1 \) value and the second slope is the \( k_2 \) value (see Figure 5.1.1). The ratio \( (k_2/k_1) \) is called "the ratio of the kinetic rate constant" [14, 15]. This ratio increase is expected as the curing temperature increases and it could affect the developing of the network structure of the cured products [15]. Montserrat suggested that as the reaction proceeds the free volume of the system decreases [38] while the branching, molecular weight, and crosslinking density increases [140]. This causes a rise in \( T_g \) of the product [140].

![Figure 5.1.1 The extent of conversion of an epoxy resin/polyamine cured system; after Levita [165]](image)

A plot between degree of conversion and \( T_g \) (by DSC) is shown in Figure 4.1.6. It shows that there is a relationship between them. This relationship was found to insensitive to the kinetic constant \( (k_2/k_1) \), because the crosslinking density and the number-average molecular weight are insensitive [14].

In this research programme it was hoped to use these results to monitor the time to reach the maximum extent of the reaction for a room temperature cured system. This information was to be used to determine the curing time at room temperature before postcuring at higher temperature was considered.
5. Discussion

In the study of various cured epoxide/amine mixtures (i.e. series 1) by DSC, the influence of the amounts of curing agent has been found. The results indicate that the standard mix samples (i.e. at stoichiometric ratio) had undergone the greatest extent of reaction since they tended to have less endothermic, and also the highest Tg value. This may be due to the structure differences resulting from the mix ratio of epoxide groups and amine curing agent. That is the standard ratio gave the best network structure of crosslinking. While there was no excess amine or epoxy which would reduce the extent of reaction (i.e. crosslinking) and possibly act as plasticisers i.e. expect a reduction in modulus (i.e. Tg). The energy needed (shown as an endothermic value) to stretch or extend the structure was least for this material (Figure 4.1.7). The higher Tg possibly results from higher crosslink density which reduce the molecular mobility: therefore, the energy required to cause molecular vibrations is greater (Figure 4.1.8). The smaller value of exotherm in specimens with excess amine may be due to the presence of less unreacted epoxy (Figure 4.1.9).

Palmese and McCullough [78] reported that the crosslinking density is affected by the amount of curing agent. The lower glass transition temperature of the non-stoichiometric samples (cf. the standard mix), is due to the excess or shortage of curing agent. This leads the final structure to have a lower crosslink density [78].

The extent of curing time seemed to affect the endothermic, exothermic and Tg values of the epoxy resins as shown in Figures 4.1.7 to 4.1.9 and Table 4.1.2 (series 1). These figures illustrate that the endothermic and exothermic values decreased as the cure time increased, whereas the Tg increased. This is due to a more complete reaction occurring with longer times. This is consistent with the work of Bair [81]. He reported that a sample cured at 26°C for more than 10^5 min (>694.4 days) had the same degree of conversion and Tg as a sample cured for a shorter time at a higher temperature (i.e. 40 seconds at 105°C). He also reported that the epoxy has two distinct curing stages: those associated with rapid and slow rates. The first stage reaction (i.e. rapid rate) occurred while the curing temperature was below the eventual Tg of cured polymer. In the second stage, the reaction continued above the eventual Tg but with the rate of reaction was lower than the first stage by three orders of magnitude [81]. Because molecular diffusion is controlled by the curing temperature, particularly at low temperatures, the segmental mobility is also controlled by temperature [21, 81]. Whereas, the Tg is independent of the curing temperature of the curing stage of reaction, and is only a function of the extent of conversion [37, 81].

Tg of the same samples measured by DSC and DMTA in Figure 4.1.10 indicated the consistency of these techniques. Tg change is a more sensitive measurement of cure than others techniques, such as IR absorption bands of reactants and products or the heat of reaction [25]. It is sensitive to even a small change in
conversion and can be measured more accurately than the others [21]. Therefore, the DMTA results which provide the Tg values were used to study all cured specimens in the present work.

The peak value of the structure relaxation process or the endothermic peak [36] and the peak value of an exotherm which relates to residual curing [36], could still be measured after curing for long periods at room temperature (~83 days): see Table 4.1.2. This means that the samples in series 1, where the level of Ancamine was varied, were not completely converted since there were exothermic values (or residual values) which could be detected. It is thought that postcuring should be used to increase the conversion of the cured system.

ii) DMTA

The samples with the variations in curing agent level (i.e. series 1) showed that the standard mix specimens had the highest storage modulus at a rubbery state (i.e. above 40°C): (see Figures 4.1.11 and 4.1.12). The lowest level of curing agent (i.e. 35 phr Ancamine) had the lowest rubbery modulus (Figure 4.1.12). Again this indicates that the best crosslinking tend to occur in the stoichiometric samples. However, these specimens did not exhibit any specific trend in the variation in their storage modulus (E'), determined at -50°C. This agrees with the work of Nielsen [142] who stated that the storage modulus is little effected by crosslinking below the Tg [142]. However, Palmese and McCullough [78] showed that there were significant variations in modulus of the epoxy-amine system below Tg [78]. They explained that the molecular interactions played an important role in determining the modulus below Tg [78]. This was shown by changes in the internal energy with respect to strain in the glassy state [78]. Bellenger et.al. [78, 143] described the inverse dependence of modulus on the degree of conversion as internal antiplasticisation. Whereas Nielsen [142] reported that the glass transition increased as higher crosslink density occurred, resulting in a reduction in modulus shift to higher temperature. This theory may be used to explain E'_{1/2} values in Table 4.1.3 (series 1). It indicates that the temperature at which E' is reduced to a half, is higher with high Tg samples.

\[ \tan \delta_{\max} \text{ tended to decrease as epoxy content increased (Figure 4.1.13), which corresponds to Bell's report [109]. He suggested that this is related to the capability of the polymer to absorb energy [109], which is changed because the network structure is altered, with the rate of reaction controlled by resin/hardener ratio [144].} \]

The Tg values measured by DMTA in this research are presented in Table 4.1.3 and Figure 4.1.14. Tg is expected to be effected by the curing rate which in turn is effected by the difference in quantity of curing agent. Thus this could cause a
5. Discussion

difference in the network structure. Lewis et.al. [145] reported that a higher Tg could be obtained with a lower curing rate and that samples with the highest Tg had the maximum crosslinking.

The values of both log $E'$ and tan$\delta$ of composite samples with the standard mix ratio of the resin matrix (Figure 4.1.15) are similar to those of an unreinforced system prepared from the same mix. However, the unreinforced system showed the minimum tan $\delta$ value below and above Tg to be similar (Figure 4.1.11). Whereas, the tan $\delta$ above Tg for the composites (Figure 4.1.15) had higher values. This may be caused by the glass fibres of the composites dominating the behaviour of the composites.

The log $E'$ of the unreinforced system (Figure 4.1.12) above its Tg tended to increase. This was unexpected but it can probably be explained by errors arising from the DMTA specimen clamping jig once it was above the epoxy Tg. At these temperatures the epoxy has a higher coefficient of linear thermal expansion and will try to displace the clamps hence effecting vibration and measurement.

In addition, the increase in log $E'$ above Tg of the unreinforced system cured at room temperature, may be caused by the further polymerisation/crosslinking of the residual reactants left in the specimens. On the other hand, the log $E'$ of the composites (Figure 4.1.15) was almost unchanged above Tg. This may be caused by the glass fibres influencing the modulus of the specimen.

The unreinforced system studied by DMTA (Table 4.1.3: series 1) were cured at room temperature whereas the composites (Table 4.1.4: series 9) were postcured at 150°C for 4 hr. These two Tables show the difference in tan $\delta_{\text{max}}$, $T_{\text{g, DMTA}}$, $\Delta \text{log } E'$ and temperature at $E'$ reduced to a half. These were mainly effected by the postcuring which will be discussed in section 5.2. However, it should be noted that the Tg of these composites showed that the specimens with the lowest levels of curing agent had the greatest increase (18.4°C) after postcure, whereas, the standard mix sample had an increase of 9.2°C. These results could be influenced by the increase of crosslinking during the postcuring step. A composite with 75 phr of Ancamine MCA did not show an increase in Tg. This may be explained in that with lower levels of curing agent, there were more unreacted epoxy groups after cure at room temperature, therefore, with the increase in temperature the reaction of these groups and other groups had happened.

The standard resin matrix/glass fibre composites had the highest Tg which was also found in the unreinforced system (Table 4.1.3: series 1). Wingard and Beatty [146] also found that stoichiometric ratio of epoxy/aromatic amine hardener had an influence on the dynamic mechanical properties of both the unreinforced and
5. Discussion

reinforced systems. The optimum cure temperature was found to be a function of stoichiometry [146].

5.1.2 FTIR

The results show the usefulness of studying the cure of an epoxy resin by FTIR.

i) Influence of Cure Time

As expected the epoxide groups of the standard mix system were reduced since having reacted with the amine groups of the Ancamine, see Table 4.1.5 in section 4.1.2. The dramatic decrease in the epoxide groups indicated that the reaction was occurring rapidly in the first 30 hours (Figures 4.1.16 to 4.1.18). The slight decrease in the peak height of the epoxide groups after 30 hours may have been caused by two reactions: (a) there were not many epoxide groups remaining in the system and, (b) the material became stiffer and solidified, therefore, the polymer chains had greater difficulties in moving and finding other reactive groups.

ii) Influence of Ancamine MCA

The amounts of Ancamine were found to effect the curing system of some specimens studied in series I (reference number 1: 35, 1: 55 and 1:75). The lower the amount of Ancamine the higher the amount of unreacted epoxy groups (Figures 4.1.19 and 4.1.20). The greater the amount of Ancamine used the greater the reactive hydrogen available to react with the epoxy groups [1]. Therefore, a long cure cycle and high curing temperature is required, if lower amounts of Ancamine are used, to achieve a thoroughly crosslinked system [1]. This could help the mixture with low hardener to cure to the same degree as the mixtures with higher hardener [147].

5.1.3 Mechanical Properties

i) Resins

Differences in the flexural strength of stoichiometric and non-stoichiometric samples (Table 4.1.6: series I) are likely to be caused by their resulting network structure. Samples with excess Epikote (i.e. at 35, 45 phr Ancamine) cured at room temperature, had lower flexural strength (Figure 4.1.21) which may have resulted from the larger free volume, since there was less conversion, or degree of cure, after solidification (or vitrification). This was confirmed by the FTIR spectra (Figures 4.1.19 and 4.1.20) which showed higher peak height of the epoxy groups for a sample with excess epoxy resins (Figure 4.1.19), indicating more unreacted epoxide groups. Older literature [109] reported that a low degree of cure creates a large free volume. This is because there are more free molecular ends after completion of reaction and this leads to low tensile properties [109]. On the other hand a recent report [78] stated that

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5. Discussion

when the free volume of a cured epoxy decreases, segmental mobility also decreases; this is particularly true for non-stoichiometric mix ratio systems.

Different amounts of curing agent can cause differences in curing rate and gel time. Ohashi et al. [148] explained that with more hydroxyl methyl groups the curing rate increased. This may be caused by a reaction involving hydroxyl groups [15, 108]. This could affect the surface topology of the cured system. Gillham [20] also reported that with different gel times the surface topology of the cured specimens could be altered and result in different material behaviour.

The flexural strength of samples with excess curing agent was lower than that for the stoichiometric samples. This might be due to excess curing agents which remained in the cured products and behave like a plasticiser in the system [144]. Keenan et al. [149] has also shown that the curing system of a tetraglycidyl 4,4'-diaminodiphenyl methane epoxy (TGDDM) with a 4,4'-diaminodiphenyl sulphone (DDS) had an effect on reducing the Tg due to plasticisation [149].

It was observed that the Ancamine MCA was a brown colour, and the cured resins had a different intensity of colour depending on the amounts of curing agent used. Thus the more curing agent the more intense the colour in the cured products, with a room temperature cure. It is presumed chemical change was not associated with colour change under these cure conditions.

The flexural modulus appeared to be related to the Tg of each sample (see Figure 4.1.2 for flexural modulus and Table 4.1.3 for Tg): i.e. the higher modulus was found in high Tg samples. This agreed with Nielsen's equation [30] and a work of Palmese and McCullough [78]. Nielsen's equation is only used for a shift in Tg due to crosslinking but not for a shift in Tg due to copolymer effects:

\[ T_g - T_{g0} = \left( 3.9 \times 10^4 \right) / M_c \]

Where \( T_{g0} \) is the glass transition temperature of uncrosslinked polymer, and \( M_c \) is the number-average molecular weight of the polymer.

This equation shows that the smaller \( M_c \) the higher \( T_g \).

Palmese and McCullough [78] similarly found that the glass transition is inversely proportional to the average molecular weight between crosslink (\( M_c \)). They showed that the modulus was also related to the density of the polymer [78, 150]:

(section 2.3; equation 2.48: \( E = 3pRT / M_c \)).

These two equations can explain the trend in the modulus in this research programme. Figure 5.1.2 shows diagrams of the possible types of crosslinked networks structure [30, 151]. The differences in modulus may be caused by various of these networks, which in turn may be due to \( M_c \) varying during crosslinking.
5. Discussion

Figure 5.1.2 Possible crosslinked networks of polymers [30, 151]
ii) Composites

The flexural properties of the composites seem to be influenced by the amounts of curing agent in the resin matrix. This can be seen from Table 4.1.7 (series 9), which shows that a specimen with 35 phr Ancamine had the highest values in flexural strength and modulus, and deflection at maximum load (after postcuring at 150°C for 4 hr). This is likely to be affected by both the resin properties after heat treatment and the interaction between the resin and glass fibre surfaces. Thus more investigation was required to confirm this theory and was subsequently studied by using interlaminar shear strength testing. The same sets of specimens (series 9) examined using DMTA showed that the greatest increase in Tg was in a specimen contained 35 phr Ancamine (see Table 4.1.4), when compared to the specimens with higher amounts of Ancamine.

Riccardi [140] explained that with the increases in crosslink density, after the gel point, branching and molecular weight can raise the Tg of the epoxy resin prepared from diglycidyl ether of bisphenol A (DGEBA)/ethylenediamine (EDA). Wu [87] showed that a cured epoxy system, DGEBA/2-ethyl-4-methyl imidazole, had an increase in crosslink density of the matrix, caused by the creation of a more homogeneous system, leading to a higher Tg value. However, he suggested that the mechanical properties at the glassy state are closely related to the intermolecular forces rather than to the network structure [87].

Saldatos et al. [111] studied the effects of the distance between the active nitrogen sites in amine curing agent in an epoxy resin matrix. They found that as the distance from one reactive hydrogen to another of the amine curing agent increased, the tensile, flexural, and compressive moduli decreased. However, these properties do not depend on the type of curing agent but depend only on the distance of the active sites in the curing agent [111]. The distance between the resin matrix of the work reported here can be affected by the coupling agent on the fibre surfaces. It is likely that the specimen with 35 phr Ancamine which had more unreacted groups before heat treatment, is more likely to achieve higher orders of interfacial bonding with the glass fibre surfaces. This may cause the high flexural strength and modulus, and also the deflection at maximum load, of the cured composites.

The interlaminar shear strength (ILSS) seems to be affected by the variation in ratio of Epikote:Ancamine in composite specimens (series 9). The samples with excess Epikote (35 phr Ancamine) and excess Ancamine (75 phr Ancamine) were found to have higher ILSS than the standard mix sample (Table 4.1.8: series 9). This may be caused by the coupling agent or sizing material used on the glass-fibre surfaces, and
5. Discussion

the excess amounts of either epoxy or amine curing agent available to form interfacial bonding with the glass surfaces.

Chamis [152] suggested that the fibre-matrix interface gives fibre composites their integrity and that this area consists of the bond between fibre and matrix, and the intermediate region adjacent to the bond. Under load polymer composites require the effective transfer of stress in all parts of the composite from fibre to fibre via the glass-fibre/polymer matrix interface [153].

Besides silane coupling agent, groups of oxides such as SiO₂, Fe₂O₃ and Al₂O₃ are randomly distributed on the glass fibre surface [154]. These groups may bond to the epoxy/amine matrix through covalent and/or organometallic reactions to improve the properties of the composite.

Bascom [155] suggested that the compounds of silane coupling agent applied on the glass fibres had the general formula R-Si(OR)₃; where R is the organofunctional group, OR is the alkoxy functional group. An example of a suitable silane is NH₂CH₂CH₂CH₂Si(OC₂H₅)₃ or γ-aminopropyltriethoxysilane [155]. A model of the interaction between adhesive and adherend is shown in Figure 5.1.3 [155]. He explained that the trialkoxysilane bonds to the glass fibre surface by reaction of the alkoxy groups with surface silanols [155, 156], and bonds to the resin through interaction of the organofunctional group with the resin molecule [155].

![Figure 5.1.3 A model showing the interaction between a silane coupling agent/adhesive/adherend, after Bascom [156]](image)

These can be used to explain the interlaminar shear properties of samples cured with different amounts of curing agent (Table 4.1.8) The unreacted amine groups, after cure at room temperature of non-stoichiometric systems, may bond to the silane during the heat treatment of the composites.
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In a paper published in the 70s Plueddemann [157] reported that all coupling agents for glass fibre used with thermosetting resins would form interfacial bonds with the resins. Subsequently this statement has been proved incorrect. Chloropropylsilane coupling agent is very effective in epoxy/amine cured systems [157], and trade literature from various manufacturers suggests aminosilanes for epoxide.

Whereas, Hoh et.al.[158] explained that the important role in the interaction is the diffusion of the resin into the silane interphase. This means that the epoxy coated fibres [159] and the excess epoxy in the composites of the present work may improved their interfacial shear strength by this diffusion process.

Pitkethly [160] has used interlaminar shear strength to reveal the interfacial bond strength of post impact tested specimens. Whereas Broutman et.al. [113] suggested that the transverse strength of the composites can be determined by the interfacial strength, because when a composite is loaded either under normal or transverse to the fibre direction, the most critical factor is the interfacial fracture [113].

Many arguments from this previous work can be used to explain the flexural strength (Table 4.1.7) and the interlaminar shear strength (Table 4.1.8) determined for the same batch of samples. It was found that the higher the flexural strength the higher the interlaminar shear strength.

The peak force values from instrumented falling weight impact testing, revealed the influence of curing agent used in the resin matrix for the epoxy/glass fibre composites (Table 4.1.9: series 9). Some researcher have reported the effects of materials and loading rate on composites:

Sykes [161] reported that the failure mode and energy absorption during impact strongly depended upon the matrix chemistry. Choi and Chang [162] reported that the impact damage threshold was also found to be significantly effected by the material properties and ply orientation. The highest value in a standard mix composite may be caused by both the effects of the structure and rate of testing.

Bell [109] explained that in slow load rate testing, that used in tensile testing, the structure dissipated energy through both short and long sequences of backbone atoms. He also explained that at high loading rates only the short segments will absorb the energy [109]. This characteristic frequency corresponds to the loading rate, which causes a brief segmental motion in the structure [109]. Whereas, Jang et.al.[122] concluded that the polymer based epoxy/fibre composites exhibit a high sensitivity to rate of loading in comparison with graphite/epoxy laminate. The rate of loading depends upon the type of material being tested. Sjoblom et.al.[163] explained the word "low velocity" as the impact velocity which was low enough to justify a static analysis of the response of the structure. They also suggested that for flexible heavy structures
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the low velocity may be equal to a centimetre per second or less, and for stiff light structures with a high resonance frequency the upper limit of "low velocity" may equal tens of metre per second [163]. However, in the present work the instrumented falling weight impact test is considered as a "high loading rate", and the flexural and interlaminar shear strength tests are considered as "low loading rate", since the first test was performed at 3 m/s and the others were performed at 3 mm/s. Therefore, this could cause the deformation behaviour of specimens to differ from one test to another.

Jang et al. [122] concluded that there are three stages of deformation of a laminate: (a) indenting perforation; (b) delamination; and (c) back-surface tension cracking. The first significant break in the impact load-time curve can be found if one of these mechanism occurred [122]. They also suggested that the large absorption capability will be provided from the flexural deformation which form a dome­shape in a large diameter specimen [122].

An example of force/displacement traces from falling weight impact tests in the present work are shown in Figure 4.1.23. It shows that the standard mix resin/glass fibre composite has a higher deformation and peak force than the others. This means that it has more capability to absorb energy, which may be caused by less bonding between the resin matrix and the fibre surfaces of this specimen, as has been shown earlier in this section (flexural and interlaminar shear tests of the composites).

5.2 Influence of Cure Schedule

5.2.1 Thermal Analysis

i) DSC

As shown in section 4.1.1 (i.e. influence of curing agent studied by DSC) the endothermic and exothermic transitions were still detectable after apparent cure at room temperature for periods up to ~83 days, indicating residual reactants being activated at high temperatures. This was confirmed by an experiment using the stoichiometric mix (reference 1:55) as shown in Figure 4.2.1.

On reheating in the DSC cell to 200°C the exotherm associated with further cure was significantly reduced. This indicated that the reaction could be made to go further by postcuring: there was no residual heat of reaction detected on a further DSC scanning, after this form of postcure in the DSC. The Tg also seemed to shift to a higher temperature. Gupta et al. [110] have reported that the Tg and crosslinking density of epoxy resin cured with meta-phenylene diamine, could be increased by postcuring. Consequently, a number of postcured samples were studied in combination
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with other experiments. Post cure temperatures of 100 and 150°C at various lengths of
time, were selected to find some optimum conditions of postcure for this system.

ii) DMTA

The tan δ peak values of specimens at 100°C for all postcure times (i.e. series 2) showed shifts in Tg to higher temperatures (Figure 4.2.2), and the height of tan δmax after postcuring tended to be lower, which may be caused by the improvement in
network structure (i.e. higher crosslinking density): This may cause the higher modulus
(Figure 4.2.3). Plots of tan δmax and Tg against post-cure time are shown in Figures
4.2.4 and 4.2.5 respectively, in order to demonstrate the trends of these parameters
with postcuring at medium temperature (100°C).

Neilsen [30] suggested that one of the methods for studying network structures
is to follow the shift of Tg. He explained that the damping property of a polymer (i.e.
associated with width and height of tan δ peak) decreased as molecular weight
between crosslink (Mc) decreased. Wingard and Beatty [146] also explained that as
the molecular constraints are reduced the increasing ability of the polymer to absorb
energy is indicated by the increase in Mc and the tan δmax.

However, the values of Tg of the postcured specimens were almost the same
after post curing at 4, 8, 16 and 24 hours at 100°C (Table 4.2.1). It appears that Tg
values of this epoxy system are dependent on cure temperature. Vratsamos and Farris
[164] have also found a limiting value of Tg of a certain epoxy (DGEBA epoxy resin
and a polyamide curing agent) of 45°C, which they explained by it being cured at low
temperature (55°C) under isothermal conditions. They also suggested that this was
caused by the premature vitrification which influenced the extent of the reaction. This
may be the cause of the incomplete reaction and residual reactants in the cured systems
[164].

Lewis et.al. [145] reported that for isothermally cured epoxy resins, full cure
can only be achieved by setting the cure temperature at above the maximum Tg value
observed for the cured resins, otherwise full cure is not possible (i.e. because of
reduced chain mobilities in the last stages of cure). This is demonstrated by the results
of the present work. After postcure at 150°C for various times (i.e. series 3), the Tg
values were found to be higher than those of the samples cured at lower temperatures:
(i.e. room temperature cured, and 100°C, see Table 4.2.2). This indicated that the
maximum Tg of the fully cured resin was above 100°C.

The storage modulus thermogram of cured resins after postcuring at 100°C at
different times (Figure 4.2.3) showed the influence of postcuring. The room
temperature cured specimen had significantly lower storage modulus than the
postcured samples. This is likely to be due to these specimen cured at room
5. Discussion

temperature having a lower level of crosslinking. The change in storage modulus (Δlog E') of a room temperature cured specimen was higher than the postcured samples, which may be caused by the higher mobility of the molecules after passing through their Tg. The reduction of maximum log E' to the lowest value could reflect less crosslinked networks.

Keenan et.al. [149] explained that the material becomes softer at the higher temperature and the modulus will decrease corresponding to the increase in tan δ. This indicated that the molecular chains had more mobility [149], with the lower E' value, hence the less network structures and lower Tg.

After further increase in heating in the DMTA cell, maximum tan δ is passed and the specimen became more rubbery, tending to behave as an elastomer. Neilsen [30] explained that a polymer should not dissipate any energy as heat; if it behaves as a perfectly elastic system, damping should be zero. This can be seen from the present work (Figure 4.2.2); damping for various specimens, after reaching their rubbery state, was at the same level.

Plots of tan δ_max and Tg of specimens postcured at 150°C at various times are shown in Figures 4.2.6 and 4.2.7. The influence of postcuring at 150°C on the tan δ_max was the same as that found at 100°C; that is the height of the tan δ_max peak decreased with postcuring (Figure 4.2.6). However, Tg seemed to rise with increasing postcure times at 150°C, more than found at 100°C. This may be caused by the curing temperature (100°C), the molecular mobility of the specimens is still limited. However, when they were cured at 150°C molecular mobility increased which resulted in further crosslinking and hence higher Tg.

It is interesting to note that the width of the tan δ peak of specimens, postcured at 150°C, was wider than those postcured at 100°C or for room temperature cured samples (Figure 4.2.8). This is likely to be due to the influence of the change in structure effected by the high temperature curing. The tan δ traces of these specimens also showed a shoulder in all samples. This may be caused by some type of heterogeneity of the network structure or distribution in the molecular weight between crosslinks which will effect a broadening of the glass transition temperature [30].

5.2.2 FTIR

Figures 4.2.9 and 4.2.10 are the results for stoichiometric mixed sample; cured at room temperature for 19 days and postcured at 200°C for 24 hours respectively. They show a smoother and lower peak at 930-910 cm⁻¹ after postcuring. Whereas, Figures 4.1.16 and 4.17 (see section 4.1.2 on influence of curing agent) show an obvious epoxide peak. This implies that there were less epoxy groups left after
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postcure. Enns and Gillham [23] explained that postcure at temperatures higher than the initial curing temperature, will result in further reaction.

Bell [165] heated an Epikote 828 type epoxide (i.e. Epon 828) alone and found that there was no change in the epoxy content (i.e. no self polymerisation). This could be used to prove that the effect of postcuring (or other heat treatment), is dependent on the presence and quantity of curing agent.

5.2.3 Flexural Properties

The extent of postcure at 100°C (i.e. series 2) seemed to have only a small effect on the flexural strength of the cured epoxy. After 24 hours at 100°C the flexural strength was 98 MPa, which was a slight increase from 93.5 MPa after 4 hours postcure at 100°C. This result suggests there was a slight increase in reaction [110].

The flexural strength change (Table 4.2.4) seems to be reflected by the Tg change, determined by DMTA (Table 4.2.1), that both slightly increase after postcuring at 100°C.

The length of postcuring time at 150°C (i.e. series 3) had a very great effect on the flexural strength, especially with curing times greater than 16 hours. The flexural strengths started to decrease after a postcure of more than 4 hr, and dramatically decreased after more than 16 hr with the result showing much higher deviation. This may have been caused by a change in molecular structure due to thermal degradation.

Vallo et.al. [79] suggested that postcuring for long times at high temperatures, should be avoided, since it could cause a depolyetherification reaction. Nielsen [30] found that the tensile strengths decreased with a higher degree of crosslinking in polymers which also caused them to become very brittle. He also explained that internal stresses may have developed due to crosslinking and shrinkage. These could cause: (1) a reduction in mobility of molecular segments, and (2) submicroscopic cracks; both of which would have resulted a reduction in tensile strength [30].

In addition, Amdouni et.al. [166] concluded that the mechanical properties of a DGEBA epoxy resin and a dicyandiamide (DDA) as a curing agent, with benzyldimethylamine (BDMA) as a catalyst, were greatly dependent on crosslink density. Whereas, Gupta [110] found considerable increase in crosslinking and tensile strength when the samples was postcured.

Long et.al. [167] have also reported the influence of postcuring on flexural properties of an unreinforced cured epoxy. When the postcure temperature was too high, higher stiffness and lower strength would occur, since as the postcure temperature increased, a decrease in the strain resistance and increasing in modulus resulted [167]. Long et.al. [167] also explained that as the postcure temperature
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increased both crosslinking and chain scission reforming occurred, leading to increases in modulus. They also explained that crosslinking created stiffer material and the chain scission and reforming caused small clusters in high crosslink structures [167].

This may cause the variation in flexural properties of the epoxy systems investigated here (Table 4.2.4 and 4.2.5). Figures 4.2.11 to 4.2.14 were plotted to show the results which could be affected by the structural change, as discussed above.

5.2.4 Microscopic Examination

The fracture surfaces of specimens postcured at 150°C for various times (i.e. some of the specimens in series 3) were obtained from specimens subjected to flexural testing and are shown in Figures 4.2.15 to 4.2.18. Specimen 1: 55 showed quite smooth fracture surfaces (Figure 4.2.15), whereas the surfaces become rougher for specimens with reference number 3: 4 and 3: 8 (Figures 4.2.16 and 4.2.17). This could be caused by the structural change influenced by heat treatment.

It can be seen quite clearly that the sample cured at longest time (i.e. 48 hrs, Figure 4.2.18), had the smoothest surfaces. These surfaces are expected to be related to the polymers mechanical properties.

Cantwell and Kausch [97] have suggested that the fracture surfaces of the epoxy resin specimens from single edge notch testing, are related to the crack growth velocity during failure. They showed that the smoother surfaces had lower crack velocities than the rougher surfaces, but the patterns of the velocity profile were the same (Figure 5.2.1; after Cantwell and Kausch [97]). Figure 5.2.1 [97] shows the velocity profile of specimen (b) compared to specimen (a). After reaching the stabilized stage (determined by the sonic velocity of the material) the excess energy within specimen (b) was higher. Hence greater energy dissipation, created multiple fracture surfaces, and crack branching leading to very rough three dimensional surfaces [97].

The rougher surfaces of flexural tested specimens made for this research are also likely to be related to the energy dissipation in the specimen during failure. Figure 5.2.2 represents the traces of load versus deflection of the specimens. These can be compared with the fracture surfaces in Figures 4.2.15 to 4.2.18. The smoother surfaces (Figures 4.2.15 and 4.2.18) seem to have resulted from both smaller deflection and load (Figure 5.2.2). The rougher surfaces in Figures 4.2.16 and 4.2.17 may be caused by the higher energy dissipation, as explained in the work of Cantwell and Hausch [97]. The flexural properties data of these specimens are given in Table 4.2.5.

It should be noted that the distinct fracture surfaces in Figure 4.2.16 are similar to those found in Cantwell and Moloney's [168] work. They prepared samples from epoxy resin with an anhydride curing agent. Their samples had Tg values of 120°C, and have been tested between the temperature of 23 and 105°C. They found that the
dimensions of the smooth region in the neat resin specimen increased as a function of the test temperature. This has a relationship with the applied stress, according to the following equation [97]:

$$\sigma(r_e)^{1/2} = \text{constant}$$

Where $\sigma$ is the breaking stress, and $r_e$ is the radius of the smooth region.

![Graph](image)

Figure 5.2.1 The velocity profile of two specimens tested by single edge notch technique; after Cantwell and Kausch [97]

This could be used to explain the relationships between the fracture surfaces and stress of the present work, which has shown that the higher breaking stress gave the rougher fracture surfaces (Figures 4.2.16 and 4.2.17). On the other hand, the smaller the breaking stress the smoother the fracture surfaces (Figures 4.2.15 and 4.2.18).
Figure 5.2.2 Load vs Deflection plot obtained in flexural tests of specimens in series 3 (1: 55, 3: 4, 3: 8, and 3: 48)
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5.2.5 Visual Observation

Visible colourless light (or white light) such as sunlight, is actually a combination of several colours (light colour) which have the specific wavelength [169]. Light travelling with different frequencies can be seen by the naked eye, from the lowest frequencies, or infra-red, to the highest frequencies or ultra-violet [169].

To move the absorption from infra-red to visible may be achieved by increasing the frequency of the vibrations, as a result of the stronger bonding, tighter and shorter atoms. On the other hand, to move the absorption from ultra-violet to visible may be achieved by lowering the frequencies of the vibrations. This can be done by extending the size of the conjugated bonds in the system [170], for example, by adding electron donors or acceptor groups, or by increasing the size of the chromophore (colour bearing) which has a structure as [170]:

\[
\begin{align*}
&\text{H} & \text{H} & \text{H} & \text{H} \\
&\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\
&\text{H} & \text{H} & \text{H} & \text{H} \\
\end{align*}
\]

The chromophores contain conjugated system, which include carbon-carbon double bonds with the alternative of single and double bonds as in the azo group (-N=N-), or thio group (C=S), or nitroso group (-N=O) [170]. However, the auxochromes (colour increases) or the subsidiary groups, which can be attached to the microphores, for example, -NH₂, -NR₂, -NO₂, -CH₃, -OH, -OR, -Br, -Cl, where R represent an organic group [170], can produce the colour. These groups may behave as the electron donors or acceptors [170].

The small groups which attached to the network structure of an epoxy/amine cured system as used in the present work such as -NH₂, CH₃, -OH, -OR may lead to the coloration of the specimen. The change in amounts of these groups, therefore, could cause the alteration of the colour. This is true with the Ancamine MCA curing agent, which has a dark brown colour. The intensity of the colour of the specimens was found to be related directly to the content of Ancamine MCA, i.e. the higher its concentration the more intense is the colour in the cured system.

The influence of cure schedule on the neat resin (Table 4.2.5) can be seen clearly by colour in Figure 4.2.19. The specimens on the far left has been heat treated for 4 hr at 150°C indicated by the less intense coloration. With longer time of heat treatment, the colour of these specimens became darker. The darkest colour was found
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in a specimen which has been postcured for 48 hr. Nassau [170] described that by mixing yellow and black a wide range of browns can occur. This means that the more intense brown may be caused by more black in the specimens. This is most likely to be effected by the degradation of the specimens and lead to difference in network structure. This argument is supported by comparing mechanical properties (i.e. in Table 4.2.5: flexural properties of standard mix specimens after postcuring at 150°C: series 3). It shows that the flexural strength decreased dramatically after postcure at 150°C for 4 hr and 48 hr, to 45.9 MPa from 104 MPa. This could be used to indicate that the specimen postcured for 48 hr had the highest degradation since it had the greatest reduction in flexural strength and change in colour in the specimens. The details of these results can be seen in section 4.2.3.

Morgan [171] has recommended that the degradation of cured epoxies can be studied by FTIR. He mentioned that the decrease in the intensity of the hydroxyl bands (at wavelength 3500 cm⁻¹) in the cured epoxy resin indicates the result of network degradation when the temperature is increased in the range of 225-300°C.

This can also be found in the present work in which the peak height of the hydroxyl group (at wavelength 3600-3350 cm⁻¹) of a specimen cured at room temperature was significantly higher than that of a specimen postcured at 200°C for 24 hr. This could be used to indicate that degradation had occurred in this specimen after postcured.

5.3 Influence of Liquid Urethane Modifier

5.3.1 DMTA

The DMTA traces in Figures 4.3.1 and 4.3.2 are the results of using various mixing ratios of Epikote:Desmocap cured at room temperature. The influence of Desmocap on the thermo-mechanical properties are shown in Table 4.3.1, and a plot of tan δ max against Desmocap quantity is shown in Figure 4.3.3. Tan δ peaks of these results indicate that the Epikote and Desmocap were incompatible, since there was evidence of two peak areas of tan δ curves. However, the Epikote dominated the tan δ peak on the right at higher temperature. It can be seen that at a higher proportion of Desmocap in the system, resulted in a reduced peak height (i.e. on the right). These two materials seem to have maximum miscibility at 70 % by weight of Desmocap, because the two peaks appear to merge into a very broad peak suggesting that there was heterogeneity of the structure. The height of tan δ tends to be higher again at higher contents of Desmocap, i.e. 80 %. or more. This is an indication of the influence of the Desmocap on the modified systems. The broader the left hand peak compared to
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the right hand peak of the tan δ curves may be caused by Desmocap having higher molecular weight than Epikote. The molecular weights were ~2000 and ~380, for Desmocap and Epikote respectively.

Iijima et.al.[46] mixed poly(phathloyl diphenyl ether)s, (PPDE), in a DGEBA epoxy based resin and found an effect on the tan δ of the system. They reported that tan δ became much broader (cf the unmodified resin) when a 17000 molecular weight PPDE was mixed into the system at 10% by weight. Hentschel et.al.[172] also found that the soft segment of a system based on an epoxy (DGEBA)/reactive polyurethane resin was more distinct as the amount of the polyurethane was increased. They explained that this was seen at low temperature, being influenced by the soft polyether blocks of the polyurethane resin.

Whereas, Bucknall and Gillbert [173] studied a tetruglycidyl-4-4'-diaminodiphenylmethane (TGDDM) epoxy resin modified with polyetherimide (PEI) cured with diaminodiphenyl sulphone (DDS). They found two distinct tan δ peaks. They suggested that this was probably due to the incompatibility of the system and separation increased as the amount of polyetherimide increased [173].

The storage modulus (E') tended to be reduced as the amount of Desmocap increased, and may be caused by the greater flexibility of the Desmocap (cf that of the Epikote). This can be seen in Figures 4.3.1 and 4.3.2, with the shape of E' changing with different contents of Desmocap. The Tg value was not greatly changed at levels of Desmocap less than 65 per cent (Figure 4.3.4). The α-relaxation peak is associated with Epikote, which can be seen in Figure 4.3.1 and 4.3.2, which at less than 65% of Desmocap was influenced by Epikote rather than by Desmocap.

The dramatic change in Tg value occurred at 70% Desmocap and is directly related to the pattern of the tan δ peak which also shows significant change (Figure 4.3.2). At this level the influence of Epikote on the α-relaxation was significantly reduced. Further reduction of Tg is directly related to the Desmocap level and less effected by Epikote especially at 80% and 90% Desmocap.

Wellner et.al. [129] studied an epoxy resin system with Desmocap as a rubber modifier and found that the level of Desmocap had a significant influence on the shape of shear modulus traces. They explained that the decrease in Tg value was not only due to the heterogeneity of the end-products but also the crosslinking density in the different regions.

However, the temperature at which E' is reduced to half value (i.e. E'_{1/2}) seemed to give a better relationship, than that determined from the major peak of tan δ max (Table 4.3.1). It indicates that the temperature at E'_{1/2} decreased as the level of Desmocap increased. The E' and tan δ values determined at -25°C (E'_{-25°C} and
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tan $\delta_{25^\circ C}$ also showed the influence of Desmocap on the DMTA traces. Both were determined at this temperature because of it is closeness to the Tg of Desmocap (approximately -25°C). The $E'_{-25^\circ C}$ decreased as Desmocap levels increased (Table 4.3.1). On the other hand, tan $\delta_{25^\circ C}$ tended to increase as Desmocap increased. This is likely to be mainly affected by the Desmocap, since low Tg and modulus are normally found in all rubbery materials.

Bucknall [61], and Krause and Broutman [174] have also shown that for a polymer blend between styrene-acrylonitrile-methylmethacrylate and poly(butadiene-co-styrene) rubber the magnitude or peak height of tan $\delta$ increased as the amount of rubber increased. They also showed that the Young's modulus decreased and the height of tan $\delta$ increased due to a reduction in stiffness at temperatures above the Tg [61].

The tan $\delta_{\text{max}}$ values of the composites based on Epikote and Desmocap (Table 4.3.2) had lower values than those of Epikote:Desmocap alone (Table 4.3.1). This may be caused by both the presence of fibres and heat curing. The composites were cured at room temperature and then postcured at 150°C for 4 hr; the latter could increase the conversion of the mixture, where the reaction between the reactive ends inhibited by glassification at room temperature cure. It can be seen that there was a slight increase in Tg about 10°C (Tables 4.3.1 and 4.3.2). The fibres in composites may behave as networks and increase the stiffness of the resin matrix when it became rubbery after reaching Tg.

DMTA traces of these specimens are shown in Figure 4.3.5. It shows various thermograms of the modified resin matrix composites (series 10) as given in Table 4.3.2. Temperatures at which the storage modulus was reduced by a half ($E'_{1/2}$), show similar trends to those found for the unreinforced specimens, but the composite specimens showed greater values. While $\Delta \log E'$ increased as levels of Desmocap increased.

The results showing changes in tan $\delta_{\text{max}}$ and $T_g_{\text{DMTA}}$ with Desmocap level are shown in Figures 4.3.6 and 4.3.7. These two Figures show that as the tan $\delta_{\text{max}}$ value slightly decreased, the Tg value slightly increased as levels of Desmocap increased.

The influence of liquid urethane modifier (Desmocap 11) on the flexural properties of the modified epoxy (Epikote 828), is shown in Table 4.3.3. As expected the flexural strength and modulus decrease as the Desmocap level increases (Figures 4.3.8 and 4.3.9). This could be explained by a work of Deanian and Zgrebnak [50], who observed that most properties of epoxy/urethane random copolymers gradually change with the change in ratio of the two materials. They also suggested that the final cured products could be adjusted by changing the compositions between these two
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materials. A plot of flexural strength (Figure 4.3.8) and flexural modulus (Figure 4.3.9) versus level of Desmocap agree reasonably well with these explanations. These figures show that the decrease of the flexural properties is related directly to every 10% increase of Desmocap. However, they also suggested that the properties might not be continuously changed if they were incompatible, leading to a weak interface between the microphases. It has been shown from the DMTA results that the Epikote and Desmocap were incompatible (Figures 4.3.1 and 4.3.2), and any change in properties tended to be related to the proportion of the two materials.

The modulus (E) may be affected by the number of network chains in a mixture (Figure 4.3.9). This could be explained by an equation derived by McCrum et al. [175],

\[ G = \frac{NkT}{E/3} \]

where \( G \) is the shear modulus; \( N \) is the number of network chains per unit volume; \( k \) is a constant; \( T \) is the absolute temperature; and \( E \) is Young's modulus.

The chain ends of the Epikote modified by Desmocap will be reduced as the amount of Desmocap increases; a molecule of Epikote has more reactive ends than Desmocap, compared on a weight per cent. Consequently, the modulus (E) should be decreased as the level of Desmocap is increased, if the above equation is to agree with the formulation in this work.

5.3.2 Mechanical Properties

Table 4.3.4 shows the influence of Desmocap on the flexural properties of epoxy based resin/glass fibre composites. All properties seem to be lower as the level of Desmocap increases (Figures 4.3.10 to 4.3.13). Work done, as determined from the area under the load/deflection curve, tends to decrease with higher content of Desmocap (Figure 4.3.10). This could be caused by a change in the deformation mechanisms (Figure 4.3.14). The work done in this case was determined at a deflection of 5 mm because all tested specimens had reached a maximum load, which did not rise after the yield point.

Figure 4.3.14 shows that the maximum load found in the unmodified matrix composites, decreases as the level of Desmocap increases, which directly leads to a lower flexural strength (see Figure 4.3.11). Meanwhile, the lower modulus is caused by more deformation of the specimen as the amount of Desmocap levels increase (see Figure 4.3.12). At the same time the maximum load occurred at lower deflections as the level of Desmocap increased which may be due to the poorer load transfer between the resin matrix and glass fibre interfaces (see Figure 4.3.13). As a result less work is done at higher levels of Desmocap in the resin matrix (see Figure 4.3.10). All of these results may be caused by the lower crosslinking density of the resin matrix and the fewer bonding points to the fibre with increasing Desmocap content.
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Delmonte [176] has also reported the influence of urethane foam core laminated on mixed composites between epoxy and urethane/glass fibre composites. He explained that the decrease of flexural modulus in the composites can contribute to an improvement in ability to absorb high transient stresses. Good bonding between the cured epoxy and urethane laminate was also reported [176].

Yee and Pearson [177] reported that the ductility of an epoxy can be easily changed if the crosslinking density is altered, i.e. as the crosslinking density decreased the ductility of the matrix increased. This also affected the ductility of composites.

The greater variation in standard deviation for the flexural strength and modulus in the composites (Table 4.3.4), in comparison to the neat resins (Table 4.3.3), may be due to the fibre effects. For example, the fibre misorientation, the lamination defects, or broken fibres, could cause mechanical properties to vary from one test to the next.

Crabtree [178] suggested that in flexural and mechanical damping (i.e. tan δ) properties of composites, suffered greater scatter due to poor fibre/resin interfacial bonding and variation in fibre distribution within the specimens.

The interlaminar shear strength of the Desmocap modified Epikote/glass fibre composites seem to have a good relationship with their flexural properties. The ratio between flexural strength (Table 4.3.4) and interlaminar shear strength (Table 4.3.5) were very close in all specimens, even though they had different resin matrix ratios. A higher content of Epikote tended to give higher interlaminar shear strength (Figure 4.3.15).

Sideridis et al. [179] have studied the interlaminar shear strength of polyester/glass fibre composites and found that the interlaminar shear strength can be used to estimate the flexural strength of a composite. They also stated that composites with strong interfaces tend to have high stiffness and strength but were very brittle. On the other hand, relatively low stiffness and strength were normally found in composites with weak interfaces [179].

The present work also found that the composites with high flexural strength always had high interlaminar shear strength. This may be caused by the more brittle nature of the composites with a higher content of Epikote in the matrix.

Drzal [159] has also reported the influence of the interphases between the fibre and matrix. He explained that composites with a brittle interphase have better strength and give high modulus. Whereas, Andreevska and Gorbatina [112] stated that composites with resin of high epoxy group content had better adhesion with the surfaces of glass fibres. They also found that a high amount of glycidylether or an active diluent, created poorer adhesion of the matrix to the fibres. They explained that
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this may be due to the resins with higher diluent content causing the functional groups in the resin matrix to have less chance to bond.

Desmocap could probably act as a diluent in the systems, since the more Desmocap (and therefore less epoxy groups) the lower the adherence to the fibre surfaces. This could cause lower interlaminar shear strength at higher levels of Desmocap, as has been observed.

The impact properties of the composites based on Desmocap modified Epikote, varied with different resin ratios (Table 4.3.6). The deflection at peak impact force was plotted against level of Desmocap, as shown in Figure 4.3.16. This shows that the deflection at peak impact force tends to be greater with increasing Desmocap. This may be caused by the increasing ductility with more Desmocap content in the resin matrix.

Chivers and Moore [180] have used instrumented falling weight impact (IFWI) to study propylene copolymers and explained that the peak force corresponded to the yield point and draw behaviour. The greater the displacement determined by impact test the greater the draw length which may be due to greater ductility of the materials.

Tervet [181] explained that the beginning of significant fibre damage coincides with the peak load (of the load versus deflection curves). This could be used to show that the greater deflection indicates a delaying in the damage of the fibres. He explained that the first discontinuous trace in load/deflection curves also reveals the microcracking or delamination (incipient damage) of the composites which occurred before the peak load was reached. He also showed that the impact resistance increased in all epoxy resins after the addition of toughening agents.

The area under the force/displacement curve in the present work was determined from a displacement at 7 mm, and a plot of these results is shown in Figure 4.3.17. The typical force/displacement curves of these composites are shown in Figure 4.3.18. These could be used to indicate that these composites had higher impact resistance as level of Desmocap increased (i.e. up to 20 % Desmocap). However, Bowles [182] explained that any energy absorbed by the composites after fully failure is not useful energy. The impact damage areas of the composites was expected to be related to the maximum force, which will be discuss later in visual observation (see section 5.3.4).

Adams [183] studied polyamide (nylon 6,6) and rubber-toughened polyamide (Zytel ST801: ex. DuPont) by instrumented impact testing and found toughening greatly altered both qualitative and quantitative aspects of fracture. He explained that the left area under the curve (determined from a vertical line which was drawn from the maximum force), related to a crack-initiation energy, and the right area under the
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curve related to the propagation energy. He suggested that the energy-to-break can be determined from the sum of these two, and that brittle materials had low propagation energy.

5.3.3 Microscopic Examinations

In the DMTA thermograms, at temperatures below the materials' Tg, values of log E' were found to decrease with increasing Desmocap content. This was thought to be caused by one of a number of effects, but it was suspected that the presence of rubber domains would be largely responsible. To check this, samples were cooled in liquid nitrogen, fractured and domains were in fact, observed by TEM after staining. Figures 4.3.19 and 4.3.20 are presented to show the fracture surfaces of the pure materials (0 and 100% Desmocap). A higher magnification was needed to study details of the surface, (see Figures 4.3.21 to 4.3.23). The series of parabolic patterns shown on the fracture surfaces in Figure 4.3.21 could not be seen clearly at lower magnifications (Figure 4.3.19).

Some researchers have reported very similar patterns, as those found in Figure 4.3.21. They have found different materials have the similar fracture details. Bandyopadhyay [98], and Cantwell and Kausch [97] have found the fracture surfaces of epoxy resins to have parabolic patterns: Mills [184], Döll [185] and Kies et.al. [186] also reported the parabolic shape on the fracture surfaces of polymethyl methacrylate (PMMA). Kies et.al. [186] has shown the parabolic marking on the fracture surfaces of Lucite plate (PMMA) which could be seen quite clearly even though a magnification of x75 was used. Whereas, with this magnification the parabolic patterns is not so distinct in the present work (Figure 4.3.19).

These reports indicate that in interpreting the fracture surfaces of any material, care should be taken since even different materials can provide the same type of fracture patterns. Fracture surfaces of the specimens in the present work were created by breaking at low temperature (i.e. in liquid nitrogen). This was done because the high rubber content, the pure Desmocap systems being too ductile to break at room temperature.

Döll [185] explained that there are two crack fronts, the primary and secondary types, involved in forming these types of fracture surfaces. He explained the mechanisms using the diagram shown in Figure 5.3.1. This diagram of fracture mechanisms shows the position of primary crack front (P₁), secondary crack front (P₂), first point where the primary and secondary crack fronts meet (s), a parabolic pattern (QSO'), and distances r₁ and r₂. All of these could be presented as the following equation [185]:

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\[ r_1 - r_2 = \hat{a}t_0 = \text{constant} \]

where \( \hat{a} \) is the constant crack speed, and \( t_0 \) is the time lag in which secondary crack may start after the primary crack.

\[ \text{Figure 5.3.1 A schematic diagram of a parabolic marking (after Döll [185])} \]

Döll [185] explained that if the constant crack speed (\( \hat{a} \)) of both primary and secondary crack fronts are the same, the parabolic marking will occur, due to the difference in fracture path \( r_1 \) and \( r_2 \). On the other hand, if both crack speeds are dissimilar, for example, the primary crack speed is larger than that of the secondary crack, then ellipse patterns will occur. He also stated that the parabolic patterns of the fracture surfaces of PMMA were rougher and increased in number, if the crack speed increased from 200 m/s to 500 m/s. This may be due to the increases in the stress intensity factor, which could cause secondary fractures to be activated [185]. An example of the influence of Desmocap modifier on the fractured surfaces of modified resins can be seen in Figure 4.3.22. This specimen contained 40 % Desmocap, and it can be seen that the parabolic patterns found in an unmodified resin have disappeared and that a rougher surface exists. However, this fracture surface is smoother than that of specimen containing 100 % Desmocap (Figure 4.3.23). It is believed that the fracture mechanism was altered by the use of Desmocap, and this caused a change in fracture detail. In specimens containing 40 % Desmocap the crack growth could develop around the surfaces or directly through the particles, and create more complicated paths, resulting in rougher surfaces.

Separated phases (i.e. domains) of Desmocap modifier could not be seen in SEM micrographs, therefore, TEM was used to study this effect.

The TEM micrographs of unstained thin sections of the standard mix (1: 55) is shown in Figure 4.3.24 and that after staining with OsO_4 for 7 days in Figure 4.3.25.

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The resulting micrograph show that the OsO₄ did not have an effect on the specimens. OsO₄ would be expected to darken the soft phases based on Desmocap modifier. McGarry [187] reported that the concentration of a carboxyl terminated butadiene rubber particle was proportional to the amount of the rubber added to the system. This is also found in the present work. The specimens modified with Desmocap in Figures 4.3.26 and 4.3.27 seem to show the effect of the concentration. The dark particles scatter around the micrograph indicating areas of Desmocap in the specimens. This can be confirmed by the difference in numbers of the dark particles in both specimens (Figures 4.3.26 and 4.3.27). The number of the dark particles in Figure 4.3.26 (containing 20% of Desmocap) is less than that in Figure 4.3.27 (containing 60% of Desmocap). However, this could be used to explain that the Desmocap is incompatible with the Epikote based material. The distribution of dark particles in these pictures are very consistent although 60% Desmocap was added to the systems. These finding are supported by the DMTA traces in Figures 4.3.1 and 4.3.2 in which two peak areas of tan δ curves are observed, and indicate the incompatibility between the two polymers.

5.3.4 Visual Observation

The photographs in Figures 4.3.28 to 4.3.31 seem to show the influence of Desmocap on the damage areas of the modified resin matrix composites after impact testing. The white area in the centre of the photographs shows a hole caused by the falling weight tub pushing through the specimen. The dark areas next to the hole indicate the damaged areas of the specimens which are expected to be influenced by Desmocap in the modified resin matrix. These pictures show that higher levels of dark area are related to the specimens tested with high peak impact force (Table 4.3.6). The average peak impact force values may be matched to the pictures shown in Figures 4.3.28 to 4.3.31, and were 5250, 6014, 5702 and 5105 N respectively. This shows the highest peak impact force was recorded (i.e. 6014 N) for a specimen with a ratio of Epikote:Desmocap of 80:20, and that this specimen also had the greatest dark area (Figure 4.3.29).

The relationships between damage and force has been shown by Davies et.al.[188]. They suggested that the drop weight impact data of carbon/epoxy composites worked well with damage/force maps rather than using the damage/energy. Lee and Zahuta [120] explained that the impact damage is highly localised, and the tougher laminate could have more severe fibre breakage than the brittle laminates when tested under the same impact conditions. Whereas, O'Brien [189] used interlaminar fracture toughness to study toughened composites and reported that
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delamination resistance had improved in toughened resin composites, in comparison to
the more brittle resin composites.

Morton and Godwin [124] stated that matrix toughness is thought to delay the
delamination and onset of matrix cracking in toughened epoxy matrix/high strain to
failure fibre composites. Cantwell and Morton [190] found that the subsequent
development of damage in epoxy/carbon fibre composites was very dependent on the
ability of the composites to absorb energy by elastic deformations. Brittle polymers
usually having low energy absorption, may be due to reduced deformation once they
were impacted. Adams [183] also reported that a brittle polyamide (nylon 6 6) failed
abruptly once a maximum load was attained. This caused the polymer to have a lower
total energy than rubber-toughened nylon (Zytel ST801: ex. DuPont) [183].

The flexural properties of the Epikote:Desmocap/glass fibre composites (Table
4.3.4) can be used to indicate that the specimens with 100 % Epikote (1: 55C) were
the most brittle and the specimens with 50 % Desmocap (4: 50/50C) were the most
ductile. This result may cause the composites in Figures 4.3.28 and 4.3.31 to have less
dark areas than found in Figures 4.3.29 and 4.3.30 and can be explained from the work
of Jang et.al.[122] and Elber [123]. Jang et.al. reported that brittle fibres, such as
graphite, cause composites to have a clean penetration crack and to absorbed very
little incident energy during impact testing. Elber explained that thin plate composites
of up to 32 plies, carried no load when large deformation occurred. He also explained
that the energy absorption before the onset of the fibre failure, was very dependent
upon the toughness of the matrix. This can be seen in Figure 4.3.18. At higher %
Desmocap the onset of the force/displacement traces are likely to occur with less
slope. The lower values of peak impact force for high Desmocap contents specimens
could also be explained in this way.

5.4 Influence of Polyamine Modifiers

5.4.1 DMTA

(a) Modified Resins

The data from dynamic mechanical thermal analysis (DMTA) shown in Tables
4.4.1 to 4.4.8, shows the influence of polyamine modifiers on the Epikote
828/Ancamine MCA cured at room temperature (Tables 4.4.1 to 4.4.4), and postcured
at 150°C for 4 hours (Tables 4.4.5 to 4.4.8). A typical thermogram of the systems
modified with ~20 phr of Jeffamine modifier is shown in Figure 4.4.1.

Tables 4.4.1 to 4.4.4 were used to plot the graphs in Figure 4.4.2 and 4.4.3,
which shows that the tan δ_max of the specimens cured at room temperature decreased
as the amount of modifier increased (Figure 4.4.2). This may be caused by increasing miscibility with increasing levels of modifier in the epoxy resin. As found in the polyurethane modifier (section 5.3.1 detailing Desmocap studies) the best compatible gave the lowest tan δ peak.

Molecular weight was also found to have an influence on the various properties of copolymers. Saunders and Frisch [53] suggested that tensile strength of copolymers between vinyl chloride (86 %) and vinyl acetate (14 %) was found to rapidly increase for molecular weights from 10,000 to 14,000. However, very little increase in tensile strength was found for molecular weights beyond approximately 15,000. They also suggested that other properties, such as Tg, elongation, and elasticity have similar relations. Whereas, the brittleness, and solubility often decreased as the molecular weight approached the limiting value.

The post curing on this set of specimens had a direct effect on their dynamic mechanical properties. The tan δ max values tended to decrease as the amount of the modifier increased (Figure 4.4.4), e.g. the tan δ max of a specimen of 19.5 phr T5000 (reference 5b: 20/150/4) decreased from 0.72 when cured at room temperature to 0.41 after postcured at 150°C for 4 hr (Tables 4.4.1 and 4.4.5). This could be influenced by the high postcure temperature used, as shown in unmodified systems, where specimens with higher Tg had lower tan δ max peak values (section 4.1.1 (ii)).

The Tg values of polyamine modified Epikote systems were also found to increase after postcuring, e.g. a specimen with 19.5 phr T5000 (reference 5b: 20/150/4) had an increase in Tg of ~21°C after postcuring at 150°C for 4 hr (Table 4.4.1 and 4.4.5). The molecular weight of the modifier was found to effect the Tg, both after postcuring and in specimens cured at room temperature. Figure 4.4.5 shows that the postcured specimens had values of Tg_DMTA, in the same order found in the specimens cured at room temperature.

Hourston and Lane [191] have studied a thermoplastic, (polyetherimide (PEI)), to modify a postcured trifunctional epoxy resin. They found that postcuring had a significant effect on the Tg of PEI, which increased by about 25°C, but did not find any significant effect on the Tg of the epoxy resin. They explained that this may be caused by an increase of reaction between epoxy and PEI, resulting from postcuring, to form a graft copolymer or crosslinking at the thermoplastic.

Kemp et.al. [192] studied a modified epoxy resin with polysulphide by curing at 23°C for at least 24 hr at 50 % relative humidity and then postcuring at 120°C for 15 minutes. They found that the tan δ peak of epoxy was reduced, in both height and width, and had also shifted to a higher temperature after postcuring. However, there
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was no effect on the major tan δ peak associated with the rubber modifier. They explained that this indicated the higher degree of cure, reflecting a more tightly bound matrix.

(b) Composites based on the modified resins

The composites prepared from these resin systems and glass fibre showed similar trends to those found with the unreinforced specimens (see Tables 4.4.9 to 4.4.12). This means that the tan δ_max of the composites tended to decrease as the amount of modifier increased (Figure 4.4.6). This is most likely to be influenced by the modified resin matrix.

The Tg_DMTA values of these composites, which had been postcured at 150°C for 4 hr, were found to be similar to those using the same resin systems (unreinforced) when postcured. The molecular weight of the modifier of either functionality again influenced the Tg of the composites. As can be seen in Figure 4.4.7, the resin matrix containing T5000 had a higher Tg than that of T3000, and D4000 had a higher Tg than that of D2000. This could be due to the increased entanglement in the higher molecular weight structure, as suggested for the same resin systems (unreinforced).

However, the Tg values of the composites may be expected to show different trends, if different types of modifiers were to be used, such as shown in work by Gilwee [193]. He studied a brominated rubber as a modifier for epoxy resin and diamino diphenyl sulfone (DDS) curing agent reinforced with graphite cloth (with an epoxy resin sizing), and found that the Tg of the composites containing up to 25% of the modifier, were not adversely affected by the modifier. This means that the Tg of composites can be varied by the use of a resin matrix.

5.4.2 Mechanical Properties

(a) Flexural Properties

The flexural properties of the modified resins were also found to be influenced by the type and quantity of modifier (Tables 4.4.13 to 4.4.16). The flexural strength and modulus of specimens cured at room temperature were found to decrease as the molecular weight of the modifier increased (Figures 4.4.8 and 4.4.9). This may be due to the lower molecular weight of the modifier which contains proportionally more reactive ends, which can react in the system. As a result there was a tighter molecular structure because of the shorter bonding points in the cured system when the lower molecular weight modifier was used.

Postcuring was found to effect the flexural properties of these systems (Tables 4.4.17 to 4.4.20). Again, the effect of modifier type on the flexural strength (Figure
5. Discussion

4.4.10) and modulus (Figure 4.4.11) were similar to those observed in the room temperature cured systems. This means that both flexural strength and modulus tended to be lower with a higher content of modifier. Those systems which contained lower molecular weight modifier, also tended to have higher flexural properties than those based on higher molecular weight modifier. The flexural properties were found to increase after postcuring, e.g. flexural strength of a specimen with 20.5 phr D2000 (RT cured: reference 8a: 21) increased from 62.9 MPa to 85.8 MPa after postcure (150°C for 4 hr), and the flexural modulus of these specimens increased from 1875 MPa to 2499 MPa. The increase in flexural properties is likely to be due to the increase in conversion when the specimens were heated to much higher temperatures than their Tg. Evidence of further reaction after postcure may be evidenced by the increase of their Tg, (for 20.5 phr D2000 (reference 8a: 21) Tg increased from 61.3°C (Table 4.4.4) to 77.5°C (Table 4.4.8)) with postcure.

Chiao and Moor [194] have studied trifunctional polyether-amine-cured epoxies, cured at both room and moderate elevated temperatures (up to 70°C). They stated that these systems can be used as matrices for fibre composites. They used infrared spectroscopy to determine the degree of cure and found that the system cured at room temperature for 8 days had ~75% degree of cure with a maximum tensile strength of 52.6 MPa. After cure at the same conditions at room temperature for 8 weeks the degree of cure increased to ~90% and the maximum tensile strength increased to 64 MPa. They also found that curing at higher temperature, e.g. at 70°C for 8 hr the maximum tensile strength increased (to 72.7 MPa). These results confirmed the effect of curing schedule on the flexural properties, which increased with high temperature treatment.

The flexural properties of epoxy/glass fibre composites were also found to be influenced by these modifiers, (see Tables 4.4.21 to 4.4.24). The composite specimens with higher molecular weight modifier had lower flexural properties, and were likely to have lower work at failure (Figure 4.4.12), flexural strength (Figure 4.4.13) and modulus (Figure 4.4.14), and deflection at failure (Figure 4.4.15). These results indicate that the properties of the composites can be predicted from the properties of unreinforced systems. This can also be supported by the results of the flexural properties of the composites which contained Desmocap (section 4.3.2).

Section 4.3.2 reported that as the amount of Desmocap increased, the work at failure, flexural strength and modulus, and deflection at maximum force decreased. Thus it is anticipated that as the resin matrix properties change in this way so the composites tend to have lower work to failure, flexural strength and modulus, and deflection at maximum force values, determined by flexural testing. In a similar way, a
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Polyamine modifier with a higher molecular weight when added to an epoxy creates a more flexible material leading to composites with lower flexural properties.

(b) Interlaminar Shear Strength (ILSS)

The modified systems with higher content of modifier led to a reduction in flexural properties; this may be caused by the lower epoxy ratio of the modified resins compared with the unmodified resin matrix. The influence of the Jeffamine modifiers on the interlaminar shear strength of the composites (Tables 4.4.25 to 4.4.28) seemed to be related to the structure of the modifier. The lower molecular weight modifier tended to give the higher interlaminar shear strength (Figure 4.4.16). This is likely to be due to lower mechanical properties of the resin matrix and poorer bonding between the resin matrix and glass fibres, when the molecular weight of the modifier is high. It has been shown in section 4.3.2, that the composites with higher content of Desmocap in the matrix had lower interlaminar shear strength; this is directly comparable to the results of this section, i.e. reduction of the interlaminar shear strength, (ILSS).

Andreevska and Gorbatkina [112] reported that polymeric fragments in the network structure of a thermoset resin, for example, functional groups or mobility and flexibility of the thermoset resins, can affect the adhesion of glass fibres to the matrix. They also reported that a resin containing higher epoxy group content had greater adhesion. The higher the content of modifier in the matrix the lower the concentration of epoxy groups, therefore, smaller values of ILSS may be due to poorer adhesion between the resin matrix and the fibres.

Broutman [113] stated that the maximum stress can be transferred from the polymer matrix along the polymer/fibre interfaces if sufficient adhesive strength could be developed. This means that the network structure of the resin matrix can influence the interlaminar shear strength. Consequently, systems with poorer or no interfacial bonding between matrix and fibres are more likely to have lower interlaminar shear strength.

(c) Impact Properties

In this programme, the impact properties of epoxy resin/fibre composites were found to alter if different types of modifiers were added to the systems, (see Tables 4.4.29 to 4.4.32). These seems to be influenced by the structure variations of the modifiers. The higher molecular weight modifiers tended to enhance impact properties. This means that the greater values of maximum impact force (Figure 4.4.17), deflection at peak impact force (Figure 4.4.18), energy at maximum impact force (Figure 4.4.19) and impact energy to failure (Figure 4.4.20), were found in composites containing higher molecular weight modifiers. This would lead to a greater energy
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absorption capability of a composite, when higher molecular weight modifier was mixed in a system.

Seymour [58] suggested that impact resistance can be related to the toughness of a system. In other word, it could be said that the materials were tougher if they had higher resistance to impact forces. Whereas, Donald [57] suggested that toughness of a material is related to the amount of energy absorbed before failure. This means that a high molecular weight modifier imparts higher toughness because of the high impact resistance and energy at failure values.

As has been shown in section 4.3.2, (i.e. influence of liquid urethane modifier studied), the maximum impact force was found in a specimen containing 20% Desmocap, and the deflection at peak impact force tended to be greatest at the higher levels of Desmocap. These phenomena also tend to be found when the Jeffamine modifiers were used. The greater deflection before fracture when impact tested, was associated with systems containing higher molecular weight modifier, and may be due to the presence of softer, more flexible material. This leads to greater values of energy at maximum impact force and impact energy at failure, as mentioned earlier.

5.4.3 Visual Observations

The photograph in Figure 4.4.21 was taken using a 35 mm camera. It is shown since it was thought that the transparency of the specimens could be related to the rubbery phase content in the systems. Echte [195] has shown that the transparency of the copolymers of styrene/butadiene (so called high impact polystyrene (HIPS)), can be altered by the particle sizes of rubbery domains. He demonstrated that a HIPS specimen with the largest particle sizes (~1-2 μm) was opaque, and as the particles became smaller translucency resulted (~0.2 μm), and eventually became clear as the smallest particle size was used (<0.1 μm). He reported that the molecular weight of the matrix, interfacial bonding, phase volume ratio (i.e. type of particle, particle size and size of distribution), and rubber crosslinking density are the most important characteristics of a two phase or multiphase component. All specimens in the present work showed the same level of transparency, except specimens containing 19.7 phr of D4000 (reference 7a: 20). A scanning electron microscopy was used to investigate the presence of rubber particles in the specimens but none were detected. Therefore, microtomed sections of the cured systems were used and studied using TEM.

Light may be absorbed by materials to various extents caused by differences in transparency. Nassau [170] explained that light entering a material is equal to the sum of light scattered, reflected, absorbed, and transmitted. This is the overall balance of the energy, which may be converted into heat, or re-emitted as fluorescence when some of the light has been absorbed [170]. The material will give rise to diffuse
5. Discussion

reflection if there is enough light scattering [196]. The only translucent specimen in the present work (reference 7a: 20, 19.7 phr D4000), may be caused by the largest particle sizes, but which were still smaller than the wavelength of light: i.e. leading to the greatest scatter of light in the specimen. The transparency of the other specimens may be caused by small differences in refractive index, and for very small particle sizes, and for more miscibility in the epoxy resin. Therefore there is less light scatter.

5.4.4 Microscopic Examinations

It was found that only specimens containing ~20 phr D4000 (i.e. 7a: 20) showed the presence of rubbery particles, but resolution was poor (see Figure 4.4.22). Consequently, a staining method was used on the specimens, with the hope that it would reveal evidence of a rubbery phase.

Stained specimens based on Jeffamine modified systems seemed to indicate the presence of modifier as a second phase. The larger particle sizes, seen as dark spots, tended to be found where a higher molecular weight modifier had been used. The presence of trifunctional polyamine modifier, Jeffamine T5000 (reference 5a: 20), showed clear particles, which were well distributed in the epoxy (see Figure 4.4.23). The lower molecular weight modifier, Jeffamine T3000 (reference 6a: 21), was not presence as a distinct particle phase (Figure 4.4.24). The difunctional polyamine also showed a similar relationship between the particle size and the molecular weight of the modifier. A system based on D4000 (reference 7a: 20) had bigger and more distinct particles than that based on D2000 (reference 8a: 21), as shown in Figures 4.4.25 and 4.4.26. It was quite clear that the particle size of D4000 was the greatest (c.f. compared with those of T5000, T3000, and D2000). This may be mainly due to the length of the repeating unit of the modifiers. The repeating unit of these modifiers was \([-\text{OCH}_2\text{CH(CH}_3\text{)}_n-\) with the n value of 28, 16.7, 66.2, and 33.1 for T5000, T3000, D4000, and D2000 respectively. However, comparisons of the number of repeating units (n) in the modifier, to particle size should only be carried out relating the same functional group, such as difunctional and trifunctional groups.

It may be said that the higher the molecular weight of the modifier in the modified systems the less the compatibility achieved, because greater phase separation occurs as shown by particle sizes.
6. CONCLUSIONS

It has been shown that the properties of diglycidyl ether of bisphenol A (DGEBA) epoxy resin and an amine (Ancamine) cured systems are influenced by the amount of curing agent and cure schedule, and the presence and loading of different types of polyurethane and polyetheramine modifiers.

The glass transition temperature (Tg) of the DGEBA and Ancamine system was directly related to the degree of conversion of the reaction. The Tg of the standard (stoichiometric) mix ratio was found to be the highest in both unreinforced and reinforced systems. It is proposed that this is caused by more crosslinking at the stoichiometric mix ratio, in comparison to systems containing both an excess and a shortage of amine curing agent. In unmodified resin systems the stoichiometric mix produced the lowest endothermic value, and the greater the amounts of curing agent the smaller the exothermic value detected. This is due to the tighter network structures of the stoichiometric mix system. The flexural strength and modulus of unreinforced specimens with the stoichiometric mix (i.e. ± 10 phr) were found to be higher than the others.

The highest flexural properties and interlaminar shear strength of the reinforced systems were found in specimens with excess epoxide contents which had been postcured. By postcuring the composites, bonding between the epoxide groups in the matrix and the coupling agent on the fibre surfaces increased.

Postcuring was found to increase the properties of the systems. A greater degree of reaction achieved by postcuring resulted in an increase in Tg and also the width of the tan δ peak increased with postcuring temperature. However, tan δ_max value tended to decrease, while the temperature at E_1/2 increased after postcuring. These results were due to an increase in crosslinking after postcuring which resulted in more heterogeneity of the network structures.

The flexural strength of the standard mix materials was found to increase with postcure up to 100°C and 150°C but decreased with postcuring at the latter temperature for time greater than 4 hr. The flexural modulus continued to rise with postcure temperature: resulting from an increase in epoxy conversion. The decrease in strength was due to degradation caused by the time at high temperature, which was also indicated by a change in colour and more scatter in mechanical test results. The properties of these unreinforced specimens could be related to their fractured surface appearance: rougher surfaces were found in specimens with higher flexural strength.

Thermograms determined by DMTA of unmodified systems showed the significant effects of the addition of a polyurethane elastomer on the thermal properties.
of DGEBA/Ancamine cured systems. Tan δ curves of modified specimens prepared from epoxy and polyurethane with greater than 70 % polyurethane elastomer were dominated by the polyurethane based-material, whereas, the tan δ peak associated with the DGEBA of these specimens did not show any significant influence. The lowest value of tan δ max, and a merge of the DGEBA and the polyurethane peaks were recorded at a ratio of 30:70, which is an indication of miscibility between these materials. The Tg values of the specimens with ratios of DGEBA:polyurethane between 100:0 and 35:65 were almost identical. Therefore the Tg determined from the major peak of tan δ is not a good indicator of other changes for these modified systems. The other parameters determined by DMTA (i.e. temperature at E' 1/2, and modulus determined at -25°C) were all found to decrease as the ratio of polyurethane increased. These parameters, therefore, should be used as indicators to show the influence of the polyurethane modifier. Similar trends were found in composites prepared from these materials which contained up to 50 % polyurethane elastomer.

The mechanical properties of both unreinforced and reinforced specimens prepared with various amount of polyurethane elastomer were found to decrease as the amounts of polyurethane increased: a significant decrease occurred above 30 % polyurethane. Both the flexural strength and modulus of the unreinforced systems were found to drop by more than 50 %, in comparison to the unmodified resin matrix, i.e. from 90 MPa and 3050 MPa to 40 MPa and 1205 MPa respectively. This was due to the higher chain flexibility (i.e. due to fewer aromatic rings) and longer molecular chain length in the modified resin.

The flexural properties of the reinforced specimens prepared from the modified resins also showed a significant change at 30 % polyurethane content. The flexural strength and modulus of the composites were found to decrease by 43 and 23 % respectively and the interlaminar shear strength decreased by 40 %, as compared to the unmodified system. It is believed that this result was caused by a decrease in bond strength between the modified resin matrix and glass fibres as the amounts of the polyurethane increased, and by the resin matrix having less capability to carry load, (i.e. became more flexible).

The impact properties of these composites were also found to be influenced by variations in amounts of the polyurethane in the mixtures. However, these properties initially increased and then decreased as the amount of polyurethane changed, a peak being reached at 20 %. The higher the peak impact force and energy at peak impact force, the larger the damage area found in these composites. This result was initially caused by the resin matrix becoming tougher and more capable of absorbing energy as the polyurethane modifier content in the systems increased. However, as the
polyurethane modifier contents rose above 20%, the capability of the matrix to carry load, and the bonding between the resin matrix and the fibres become important.

Polyether-amine (Jeffamine) modifiers of different molecular weight produced variations in the thermal and mechanical properties of modified resins.

The systems modified with Jeffamine T5000 were found to have a higher Tg than those modified with Jeffamine T3000. Similar trends were found in systems modified with Jeffamine D4000 and D2000, e.g. the higher Tg was found in the system modified with the higher molecular weight Jeffamine. These results were found in both unreinforced and reinforced systems. This is believed to be caused by the greater entanglement of the structures in the systems modified with the higher molecular weight modifiers.

The flexural properties of unreinforced systems, modified with polyamine of the same type of structure, were higher when the lower molecular weight polyamine modifier was used. The flexural properties and interlaminar shear strength of composites prepared from these modified resins were found to decrease as the amounts of modifier increased. The influence of the different structure of the Jeffamine modifiers, found in the unreinforced systems, was also found in the reinforced systems. This is believed to be caused by proportionally more reactive sites being available in the resins modified with lower molecular weight modifier.

The impact properties of the composites based on polyamine, increased as the amounts of modifier increased up to ~20 phr: beyond this the impact properties decreased. These composites were found to have the higher impact properties when the matrix with the lower flexural properties were used. This indicates that the composites modified with higher molecular weight modifier (i.e. more elastomer) had more ability to absorb energy.

The higher the molecular weight and the longer the backbone structure of the modifiers the larger the area of the phase separated particle found in the cured systems. Smaller particle sizes resulted in more transparent resin systems.
7. FUTURE WORKS

7.1 Systems modified with other types of elastomer should be studied and compared. Such systems can give a range of thermal and mechanical properties, and thus more choice of the required properties.

7.2 A wider range of molecular weights of the various types of the elastomers should be used.

7.3 Particular attention should be paid to any phase separated particles which arise in the above systems and their influence on properties investigated.

7.4 The solubility parameters of the modifiers, and the cure schedules of these modified systems should be studied. Such variables can affect the formation of the rubber particles in the systems.

7.5 The viscosity of the modified resins should be studied, since it can affect the wetting of the fibre surfaces. This could be achieved by contact angle measurements.

7.6 The influence of various types of coupling agents on the fibre surfaces should be studied in relation to the modified resin systems.

7.7 Modifiers other than elastomers should be studied in the above systems.

7.8 Finally a check should be carried out to determine if the changes produced in one modified resin composite were similar in composites containing different fibres and surface treatments.
A  Monomers and Oligomers for Common Epoxide Resins

i) Epichlorohydrin

Epichlorohydrin is available commercially at 98% purity and is a colourless mobile liquid [1, 4]. Its boiling point is about 115°C [2] and can be prepared by the reaction of chlorination of propylene [1, 2, 5], followed by treatment with hypochlorous acid forming glycol dichlorohydrin, then dehydrochlorinated by sodium hydroxide [1, 2] i.e.:

(1).

\[
\text{CH}_2=\text{CH}-\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl} + \text{HCl}
\]

propylene  chlorine  allyl chloride  hydrochloric acid

(2).

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl} + \text{H}_2\text{O} / \text{Cl}_2 \rightarrow \text{Cl}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{Cl}
\]

allyl chloride  water/chlorine  dichlorohydrin

or

hypochlorous acid

(3).

\[
\text{Cl}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{Cl} + \text{NaOH} \xrightarrow{\Delta \text{H}} \text{CH}_2-\text{CH}-\text{CH}_2-\text{Cl} + \text{H}_2\text{O} + \text{NaCl}
\]

dichlorohydrin  sodium hydroxide  epichlorohydrin

ii) Bisphenol A

Bisphenol A, (or diphenyl propane (DPP) [3], or 2,2-bis(p-hydroxy phenyl) propane or dihydric phenol (mp~153°C) [1, 2, 3]) is prepared from 2 moles of phenol and 1 mole of acetone [2] at slightly elevated temperatures (50°C) in the presence of a strong acid catalyst such as 75% sulphuric acid or gaseous hydrogen chloride [2, 3]:

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Appendix

iii) Diglycidyl Ethers of Bisphenol A

Typically liquid epoxides are prepared from the reaction of two moles of epichlorohydrin with one mole of bisphenol A [6] in the presence of caustic soda (NaOH) [1]. The sodium hydroxide is used for two purposes:

(a) as a catalyst to open the nucleophilic ring of the epoxide group of epichlorohydrin on the primary carbon atom by the phenolic hydroxyl group [2, 3].

(b) as a dehydrochlorination agent for conversion of the halohydrin to the epoxide group [2, 3].

The reaction mechanisms are thought to be [2, 6].

(1).

\[
\begin{align*}
\text{HO-}\begin{array}{c} \text{C} \\ \text{OH} \\
\end{array} & + 2 \text{NaOH} \\
\text{CH}_3 & \rightarrow \\
\end{align*}
\]

(2).

\[
\begin{align*}
\text{Cl-CH}_2-\text{CH-CH}_2 & + \text{Na}^+\text{O}^- \rightarrow \\
\end{align*}
\]
Note: If the free chloride content is high (i.e. from the synthesis of chlorohydrin), it would inhibit subsequent catalytic cure by blocking the nitrogen of a tertiaryamine or by neutralising any base added to the curing reaction of an organic acid [1].

A schematic diagram of the process of the production of epoxy resins from bisphenol A and epichlorohydrin is as follows [5]:

---

1. Addition of water to the reaction mixture.
2. Formation of an intermediate compound.
3. Neutralization with sodium hydroxide.
4. Formation of the final epoxy resin product.
B. Probability of the reaction

As shown in Chapter 2: Figure 2.2, for the reaction between diepox and tetrafunctional amine, the possible reaction has been shown by Miller and Macosko [31] as:

\[
P(F_{B}^{out}) = P\left(\frac{F_{B}^{out}}{B_{\text{react}}} \right) P(B_{\text{react}}) + P\left(\frac{F_{B}^{out}}{B_{\text{does not react}}} \right) P(B_{\text{does not react}}) \quad \text{--(A1)}
\]
Appendix

When looking out from Br along —1→, it can be expressed as:

\[ P(F_{B \text{out}}) = \alpha_{B_r} P(F_{A \text{in}}) + 1 - \alpha_{B_r} \]  \hspace{1cm} (A2)

Where \( P(F_{B \text{out}}) \) is the probability of finding a finite chain when looking out from molecule B [23], \( P(F_{A \text{in}}) \) is the probability of the extent that —2→ is the start of a finite chain, and \( \alpha_{B_r} \) is the fractional conversion of the amine or B groups [23].

Looking out from A" along —3→ the chain probability, \( P(F_{A \text{out}}) \) can be [23, 31]:

\[ P(F_{A \text{out}}) = \alpha_{A_t} P(F_{B \text{in}}) + 1 - \alpha_{A_t} = r\alpha_{B_r} P(F_{B \text{in}}) + 1 - r\alpha_{B_r} \] \hspace{1cm} (A3)

Where \( \alpha_{A_t} \) is the fractional conversion of epoxy or A groups, \( r \) is the stoichiometric ratio of amino hydrogen to epoxy or (\( \alpha_{A_t} = r\alpha_{B_r} \)).

When looking out along —4→, it can be expressed as [31]:

\[ P(F_{B \text{in}}) = P(F_{B \text{out}})^{-1} \] \hspace{1cm} (A4)

In above system where \( f = 4 \), since the tetrafunctional amine is used:

\[ P(F_{B \text{in}}) = P(F_{B \text{out}})^3 \] \hspace{1cm} (A5)

Whereas,

\[ P(F_{A \text{in}}) = P(F_{A \text{out}}) \] \hspace{1cm} (A6)

By combining equations (A2), (A3), (A5) and (A6) yields [23, 31]:

\[ r\alpha^2 P(F_{B \text{out}})^3 - P(F_{B \text{out}}) - r\alpha^2 + 1 = 0 \] \hspace{1cm} (A7)

The solution for equation (A7) is 1, for the reacting system before gelation, which indicates finite chains [23]. The solution of the mixture after gelation is given as [21, 23, 31]:

\[ P(F_{B \text{out}}) = \left( \frac{1}{r\alpha^2 - \frac{3}{4}} \right)^{1/2} - \frac{1}{2} \] \hspace{1cm} (A8)

or as equation (A9) in the case of the stoichiometric mixture is used (\( r = 1 \)); and \( P(F_{B \text{out}}) \) is simply written as P [23]:
\[
P = \left( \frac{1}{\alpha^2} - \frac{3}{4} \right)^{1/2} - \frac{1}{2}
\]

---(A9)

C. Individual Results from all Tests

Table A1 DMTA data for Epikote 828/glass fibre composites with different amounts of curing agents

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>( \tan \delta_{\text{max}} )</th>
<th>( T_{\text{DGDTA}} ) (°C)</th>
<th>( \Delta \log E' )</th>
<th>Temperature at ( E'_{1/2} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.48, 0.52</td>
<td>69.1, 68.9,</td>
<td>1.31, 1.40,</td>
<td>58.0, 55.7,</td>
</tr>
<tr>
<td></td>
<td>0.46, 0.54</td>
<td>72.4, 71.8</td>
<td>1.30, 1.33</td>
<td>59.0, 58.1</td>
</tr>
<tr>
<td>55</td>
<td>0.46, 0.47,</td>
<td>76.7, 75.4,</td>
<td>1.08, 1.14,</td>
<td>69.0, 66.2,</td>
</tr>
<tr>
<td></td>
<td>0.51, 0.52</td>
<td>74.5, 72.9</td>
<td>1.17, 1.15</td>
<td>66.0, 64.3</td>
</tr>
<tr>
<td>75</td>
<td>0.57, 0.52,</td>
<td>57.4, 55.8,</td>
<td>1.34, 1.35,</td>
<td>49.2, 48.0,</td>
</tr>
<tr>
<td></td>
<td>0.60, 0.64</td>
<td>56.0, 54.9</td>
<td>1.34, 1.40</td>
<td>47.4, 47.2</td>
</tr>
</tbody>
</table>

Table A2 Flexural strength and modulus of samples cured at room temperature with various amounts of curing agent after approximately 66 days

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>48.1, 49.9, 48.2, 49.1</td>
<td>1661, 1657, 1718, 1721</td>
</tr>
<tr>
<td>45</td>
<td>64.2, 63.8, 64.4, 62.4</td>
<td>3361, 3304, 3226, 3249</td>
</tr>
<tr>
<td>55</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>65</td>
<td>90.8, 88.2, 90.9, 89.1, 87.1</td>
<td>3100, 2964, 3083, 3100, 2956</td>
</tr>
<tr>
<td>75</td>
<td>76.3, 78.3, 79.2, 78.8, 80.5</td>
<td>2734, 2699, 2809, 2812, 2829</td>
</tr>
</tbody>
</table>
### Appendix

Table A3 Flexural properties for Epikote 828/glass fibre composites cured with various amounts of Ancamine MCA

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Work to Failure (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1002.0, 922.1, 998.3, 1036.0, 979.0, 927.8, 972.8, 981.6</td>
<td>474.0, 448.5, 473.4, 467.3, 469.6, 469.0, 443.1, 459.3</td>
<td>18280, 17680, 18080, 18270, 18460, 16870, 17670, 17420</td>
<td>4.3, 3.9, 4.5, 4.1, 4.2, 4.5, 4.4, 4.5</td>
</tr>
<tr>
<td>55</td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>319.5, 336.2, 303.1, 327.5, 313.8, 335.0</td>
<td>18640, 19310, 16240, 16510, 16610, 16400</td>
<td>2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
</tr>
<tr>
<td>75</td>
<td>803.1, 794.7, 790.4, 790.1, 812.7, 780.3</td>
<td>320.1, 328.0, 331.9, 334.4, 366.6, 349.6</td>
<td>16130, 17230, 17400, 15450, 16970, 16310</td>
<td>4.0, 3.7, 3.2, 3.8, 3.7, 3.3</td>
</tr>
</tbody>
</table>

Table A4 The interlaminar shear strength (ILSS) of Epikote 828/glass fibre composites cured with different amounts of Ancamine MCA

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>46.3, 48.7, 45.9</td>
</tr>
<tr>
<td>55</td>
<td>30.5, 29.5, 29.6, 29.2, 30.6</td>
</tr>
<tr>
<td>75</td>
<td>33.2, 33.1, 34.7, 34.9, 34.7</td>
</tr>
</tbody>
</table>
Appendix

Table A5 IFWI data for Epikote 828/glass fibre composites with different amounts of curing agent

<table>
<thead>
<tr>
<th>phr Ancamine MCA</th>
<th>Peak Impact Force (N)</th>
<th>Deflection at Peak Impact Force (mm)</th>
<th>Energy at Peak Impact Force (J)</th>
<th>Impact Energy to Failure (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>4447, 4667, 4772, 4664, 4486</td>
<td>4.6, 4.6, 4.3, 4.1, 4.2</td>
<td>10.2, 11.1, 9.7, 9.1, 9.4</td>
<td>18.2, 17.7, 18.1, 17.2</td>
</tr>
<tr>
<td>55</td>
<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
<td>11.9, 12.4, 12.2, 12.4, 11.4, 11.1</td>
<td>18.6, 19.0, 18.5, 19.2, 18.3, 18.6</td>
</tr>
<tr>
<td>75</td>
<td>5123, 5468, 5228, 5399, 5253, 5136</td>
<td>4.6, 5.1, 4.8, 4.6, 4.8, 4.7</td>
<td>11.0, 13.4, 12.2, 11.1, 12.3, 11.6</td>
<td>18.7, 19.5, 18.9, 18.8, 19.3, 18.9</td>
</tr>
</tbody>
</table>

Table A6 Flexural strength and modulus of standard mix samples after postcure at 100°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>92.9, 93.0, 94.2, 93.9</td>
<td>2800, 2749, 2823, 2748</td>
</tr>
<tr>
<td>8</td>
<td>94.1, 94.5, 92.0, 93.4, 94.6</td>
<td>2871, 2800, 2908, 2841, 2917</td>
</tr>
<tr>
<td>16</td>
<td>98.3, 98.1, 93.8, 95.8, 96.7</td>
<td>2917, 2901, 2873, 2905, 2926</td>
</tr>
<tr>
<td>24</td>
<td>96.4, 98.3, 100.1, 98.7, 97.3</td>
<td>2957, 2926, 2929, 3048, 3009</td>
</tr>
</tbody>
</table>
Table A7  Flexural strength and modulus of standard mix samples after postcure at 150°C for various times

<table>
<thead>
<tr>
<th>Postcured Time (hr)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>105.4, 101.7, 105.2</td>
<td>3124, 3010, 3000</td>
</tr>
<tr>
<td>8</td>
<td>109.6, 94.6, 109.5, 109.3, 63.6, 108.9, 109.3, 106.0</td>
<td>3102, 3113, 2959, 3087, 3034, 3178, 3212, 3265</td>
</tr>
<tr>
<td>16</td>
<td>124.8, 102.0, 67.2, 60.6, 83.1, 73.6, 114.6, 29.7</td>
<td>3304, 3102, 3147, 3105, 3059, 3352, 3284, 3330</td>
</tr>
<tr>
<td>24</td>
<td>71.8, 66.1, 85.7, 54.9, 78.4</td>
<td>3162, 3104, 3143, 3191, 3170</td>
</tr>
<tr>
<td>48</td>
<td>46.3, 43.0, 49.1, 48.3, 42.9</td>
<td>3393, 3533, 3436, 3363, 3385</td>
</tr>
</tbody>
</table>
### Table A8: DMTA data for Epikote 828/glass fibre composites modified with different amounts of Desmocap 11

<table>
<thead>
<tr>
<th>Epikote 828: Desmocap 11</th>
<th>tan $\delta_{\text{max}}$</th>
<th>$T_g$ DMTA (°C)</th>
<th>$\Delta \log E'$</th>
<th>Temperature at $E'_{1/2}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>0.46, 0.47, 0.51, 0.52</td>
<td>76.7, 75.4, 74.5, 72.9</td>
<td>1.08, 1.14, 1.17, 1.15</td>
<td>69.0, 66.2, 66.0, 64.9</td>
</tr>
<tr>
<td>95:5</td>
<td>0.43, 0.49</td>
<td>75.2, 75.7</td>
<td>1.10, 1.20</td>
<td>64.7, 96.9</td>
</tr>
<tr>
<td>90:10</td>
<td>0.45</td>
<td>74.5</td>
<td>1.23</td>
<td>60.6</td>
</tr>
<tr>
<td>80:20</td>
<td>0.46, 0.45, 0.44</td>
<td>76.0, 76.3, 75.0</td>
<td>1.23, 1.19, 1.30</td>
<td>61.4, 58.7, 60.2</td>
</tr>
<tr>
<td>70:30</td>
<td>0.43, 0.42, 0.42</td>
<td>78.6, 77.2, 77.1</td>
<td>1.31, 1.32, 1.34</td>
<td>58.1, 54.9, 58.6</td>
</tr>
<tr>
<td>60:40</td>
<td>0.42, 0.41, 0.41</td>
<td>77.3, 78.7, 78.2</td>
<td>1.37, 1.37, 1.43</td>
<td>39.6, 48.6, 52.4</td>
</tr>
<tr>
<td>50:50</td>
<td>0.29, 0.30, 0.36, 0.29</td>
<td>80.1, 81.1, 74.6, 74.9</td>
<td>1.38, 1.29, 1.29, 1.49</td>
<td>25.2, 33.4, 19.3, 28.1, 35.8</td>
</tr>
</tbody>
</table>

*Appendix*
### Appendix

Table A9: Flexural properties of Epikote 828 modified with Desmocap, RT cured

<table>
<thead>
<tr>
<th>Epikote 828:Desmocap Ratio</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>90:10</td>
<td>74.4, 79.5, 76.9, 79.1, 75.7</td>
<td>2402, 2472, 2323, 2475, 2385</td>
</tr>
<tr>
<td>80:20</td>
<td>57.7, 57.6, 53.0, 58.6, 58.4</td>
<td>1752, 1761, 1631, 1790, 1764</td>
</tr>
<tr>
<td>70:30</td>
<td>42.2, 40.0, 39.1, 41.7, 39.2</td>
<td>1229, 1187, 1169, 1251, 1191</td>
</tr>
<tr>
<td>60:40</td>
<td>23.4, 23.6, 25.1, 26.9, 25.2</td>
<td>641, 654, 676, 731, 700</td>
</tr>
</tbody>
</table>
**Appendix**

Table A10 Flexural properties of Epikote 828/glass fibre composites, modified with Desmocap 11

<table>
<thead>
<tr>
<th>Epikote 828: Desmocap Ratio</th>
<th>Work to Failure (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>319.5, 336.2, 303.1, 327.5, 313.8, 335.0</td>
<td>18640, 19310, 16240, 16510, 16610, 16400</td>
<td>2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
</tr>
<tr>
<td>95:5</td>
<td>598.7, 640.6, 669.1, 600.4, 590.5, 576.9, 497.0</td>
<td>256.3, 271.6, 274.7, 258.4, 234.1, 256.4, 239.8</td>
<td>17470, 17100, 16780, 18690, 17270, 16430, 17330</td>
<td>2.8, 2.8, 3.2, 2.3, 2.1, 2.3, 2.3</td>
</tr>
<tr>
<td>90:10</td>
<td>540.0, 598.9, 560.9, 548.2, 603.7</td>
<td>226.6, 218.7, 233.9, 220.7, 224.7, 231.9, 225.8</td>
<td>15610, 15360, 15240, 13840, 14430, 14170, 13710</td>
<td>3.1, 3.0, 2.9, 3.3, 3.1</td>
</tr>
<tr>
<td>80:20</td>
<td>495.1, 495.4, 485.1</td>
<td>194.1, 202.6, 195.7</td>
<td>14880, 14960, 14750</td>
<td>2.3, 2.5, 2.3</td>
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<td>70:30</td>
<td>487.3, 493.6, 459.8</td>
<td>181.3, 185.2, 182.7</td>
<td>13330, 13390, 13350</td>
<td>2.8, 2.6, 2.4</td>
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<td>60:40</td>
<td>466.8, 447.0, 441.2</td>
<td>206.0, 169.2, 195.9</td>
<td>13310, 13740, 13550</td>
<td>2.2, 1.9, 2.9</td>
</tr>
<tr>
<td>50:50</td>
<td>375.8, 383.9, 389.0, 399.3</td>
<td>139.6, 130.2, 140.5, 146.4</td>
<td>12010, 11530, 11210, 12130</td>
<td>2.2, 1.9, 2.1, 2.3</td>
</tr>
</tbody>
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Appendix

Table A11 The interlaminar shear strength of Epikote 828/glass fibre composites modified with Desmocap

<table>
<thead>
<tr>
<th>Epikote:Desmocap Ratio</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>30.5, 29.5, 29.6, 29.9, 29.2, 30.6</td>
</tr>
<tr>
<td>90:10</td>
<td>19.2, 18.1, 18.8, 16.6, 18.7, 19.2</td>
</tr>
<tr>
<td>80:20</td>
<td>14.1, 16.6, 16.4, 17.3, 16.3</td>
</tr>
<tr>
<td>70:30</td>
<td>17.9, 19.5, 16.4, 17.4, 18.5</td>
</tr>
<tr>
<td>60:40</td>
<td>16.5, 15.9, 14.7, 16.1, 15.8</td>
</tr>
<tr>
<td>50:50</td>
<td>12.9, 12.8, 13.0, 13.3, 13.1, 12.8</td>
</tr>
</tbody>
</table>
### Appendix

Table A12  IFWI data of Epikote 828/glass fibre composites modified with Desmocap

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>100:0</td>
<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
<td>11.9, 12.4, 12.2, 12.4, 11.4, 11.1</td>
<td>18.6, 19.0, 18.5, 19.2, 18.3, 18.6</td>
</tr>
<tr>
<td>95:5</td>
<td>5460, 5411, 6183, 6381, 6332</td>
<td>5.1, 5.1, 5.5, 5.8, 5.6</td>
<td>12.6, 12.1, 15.1, 16.3, 15.4</td>
<td>19.2, 18.6, 20.7</td>
</tr>
<tr>
<td>90:10</td>
<td>5438, 5421, 5797, 6085, 6039, 5956, 6168</td>
<td>5.3, 5.2, 4.9, 5.3, 5.4, 5.1, 5.4</td>
<td>13.9, 12.1, 12.7, 14.6, 15.5, 14.0, 15.2</td>
<td>19.7, 18.5, 20.9, 21.0, 21.1, 21.9, 21.9</td>
</tr>
<tr>
<td>80:20</td>
<td>5770, 6281, 5990</td>
<td>5.6, 6.0, 5.4</td>
<td>14.4, 16.8, 14.2</td>
<td>21.3, 19.7, 21.5, 20.4</td>
</tr>
<tr>
<td>70:30</td>
<td>5702, 5963, 5724, 5458, 5665</td>
<td>5.5, 5.6, 5.3, 5.6, 5.7</td>
<td>14.6, 15.1, 13.7, 14.3, 15.2</td>
<td>19.3, 20.8, 21.2, 19.5, 20.6, 20.6</td>
</tr>
<tr>
<td>60:40</td>
<td>5502, 5407, 5966</td>
<td>5.8, 5.8, 5.8</td>
<td>14.4, 14.5, 15.2</td>
<td>19.4, 19.2, 18.0, 18.7, 18.8, 20.1</td>
</tr>
<tr>
<td>50:50</td>
<td>5631, 5158, 5077, 4989, 4672</td>
<td>6.7, 6.2, 6.1, 6.1, 6.0</td>
<td>18.2, 15.6, 13.9, 13.1, 12.6</td>
<td>17.0, 17.3, 16.7, 20.0, 19.6</td>
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**Appendix**

Table A13 Flexural strength and modulus of Epikote 828: Jeffamine T5000, RT cured

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>5.4</td>
<td>80.0, 84.2, 82.2, 85.1, 82.8</td>
<td>2501, 2566, 2498, 2527, 2525</td>
</tr>
<tr>
<td>11.8</td>
<td>69.3, 71.6, 71.1, 70.5, 70.0</td>
<td>2166, 2213, 2212, 2156, 2247</td>
</tr>
<tr>
<td>19.5</td>
<td>56.4, 57.5, 57.1, 57.5, 58.8</td>
<td>1706, 1710, 1690, 1694, 1721</td>
</tr>
</tbody>
</table>

Table A14 Flexural strength and modulus of Epikote 828: Jeffamine T3000, RT cured

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>11.5</td>
<td>75.2, 76.6, 77.1, 75.4</td>
<td>2322, 2364, 2457, 2316</td>
</tr>
<tr>
<td>20.6</td>
<td>57.9, 57.4, 59.7, 58.3</td>
<td>1702, 1701, 1771, 1715</td>
</tr>
</tbody>
</table>

Table A15 Flexural strength and modulus of Epikote 828: Jeffamine D4000, RT cured

<table>
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<tr>
<th>phr D4000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
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</thead>
<tbody>
<tr>
<td>--</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>11.8</td>
<td>72.5, 71.8, 72.0, 73.4, 72.0</td>
<td>2298, 2224, 2261, 2313, 2287</td>
</tr>
<tr>
<td>19.7</td>
<td>58.8, 57.3, 59.1, 58.4, 58.8</td>
<td>1819, 1752, 1802, 1780, 1812</td>
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### Appendix

Table A16 Flexural strength and modulus of Epikote 828: Jeffamine D2000, RT cured

<table>
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<th>phr</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>--</td>
<td>91.5, 83.1, 96.1, 87.8</td>
<td>2951, 3150, 3015, 3081</td>
</tr>
<tr>
<td>11.5</td>
<td>78.1, 79.4, 80.8, 79.7, 80.0</td>
<td>2426, 2375, 2474, 2383, 2411</td>
</tr>
<tr>
<td>20.5</td>
<td>61.8, 62.3, 63.4, 62.9, 64.0, 63.0</td>
<td>1848, 1903, 1877, 1869, 1912, 1843</td>
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Table A17 Flexural strength and modulus of Epikote 828: Jeffamine T5000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T5000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>105.4, 101.7, 105.2</td>
<td>3124, 3010, 3000</td>
</tr>
<tr>
<td>5.4</td>
<td>102.8, 98.3, 102.3, 101.6, 98.3</td>
<td>2735, 2807, 2812, 2822, 2737</td>
</tr>
<tr>
<td>11.8</td>
<td>85.4, 86.4, 87.6, 86.6, 86.0</td>
<td>2428, 2507, 2444, 2485, 2484</td>
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<td>19.5</td>
<td>69.3, 70.5, 71.4, 72.2, 71.5</td>
<td>2043, 2027, 2082, 2007, 2085</td>
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</tbody>
</table>
## Appendix

Table A18 Flexural strength and modulus of Epikote 828:Jeffamine T3000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>105.4, 101.7, 105.2</td>
<td>3124, 3010, 3000</td>
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<tr>
<td>11.5</td>
<td>89.3, 88.5, 91.7, 92.5, 90.2</td>
<td>2556, 2666, 2610, 2513, 2653</td>
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<td>20.6</td>
<td>74.5, 75.2, 77.2, 76.8, 76.8, 76.2</td>
<td>2162, 2202, 2193, 2256, 2220, 2230</td>
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Table A19 Flexural strength and modulus of Epikote 828:Jeffamine D4000, postcured at 150°C for 4 hr

<table>
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<tr>
<th>phr D4000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>105.4, 101.7, 105.2</td>
<td>3124, 3010, 3000</td>
</tr>
<tr>
<td>11.8</td>
<td>88.7, 86.9, 88.4, 89.1, 86.9</td>
<td>2470, 2441, 2508, 2495, 2459</td>
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<tr>
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<td>71.0, 72.4, 70.4, 72.0, 72.3, 71.7</td>
<td>2019, 2046, 2016, 2015, 2065, 2020</td>
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</tbody>
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Table A20 Flexural strength and modulus of Epikote 828:Jeffamine D2000, postcured at 150°C for 4 hr

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>105.4, 101.7, 105.2</td>
<td>3124, 3010, 3000</td>
</tr>
<tr>
<td>11.5</td>
<td>97.4, 99.9, 95.0, 99.8, 95.7</td>
<td>2826, 2894, 2767, 2741, 2743</td>
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<tr>
<td>20.5</td>
<td>86.7, 88.0, 88.3, 84.7, 81.1</td>
<td>2545, 2564, 2486, 2478, 2424</td>
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## Table A21 Flexural properties of Epikote 828:Jeffamine T5000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Work to Failure (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>319.5, 336.2, 18640, 19310, 2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>303.1, 327.5, 16240, 16510, 3.8, 3.9, 3.8</td>
<td>313.8, 335.0, 16610, 16400</td>
<td></td>
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<tr>
<td></td>
<td>792.7, 814.9</td>
<td>233.7, 262.5, 17740, 16470, 2.8, 3.1, 2.6, 4.4, 3.1, 2.8</td>
<td>254.0, 298.5, 16610, 16300, 3.2</td>
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<td>5.4</td>
<td>627.3, 657.1, 628.8, 739.6, 720.3, 597.7, 642.8</td>
<td>275.1, 246.4, 17010, 14960, 3.2</td>
<td>248.6, 16550</td>
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<td>628.8, 739.6, 720.3, 597.7, 642.8</td>
<td>283.2, 279.3, 15740, 16140, 2.7, 3.0, 3.2</td>
<td>300.2, 275.3, 16910, 16750, 2.8, 3.0, 3.4</td>
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<td>645.7, 623.9, 670.6, 679.5, 645.7, 688.8, 645.3, 637.8</td>
<td>270.3, 282.7, 15330, 15460, 3.2</td>
<td>271.4, 275.2, 15340, 15660</td>
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<td>670.6, 679.5, 645.7, 688.8, 645.3, 637.8</td>
<td>257.9, 249.4, 14020, 14400, 3.1, 2.7, 3.3</td>
<td>300.2, 275.3, 14440, 15960, 3.5, 3.2</td>
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</tr>
<tr>
<td>19.5</td>
<td>680.3, 625.9, 643.0, 579.8, 651.6, 639.8, 613.8</td>
<td>250.6, 257.1, 14400, 15960, 3.5, 3.2</td>
<td>259.7, 241.6, 14960, 13330</td>
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<td>643.0, 579.8, 651.6, 639.8, 613.8</td>
<td>247.0, 13120</td>
<td>242.5, 272.2, 13120</td>
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<td>528.8, 575.3, 587.9, 596.0, 563.0, 579.1, 562.7, 572.9</td>
<td>253.2, 244.0, 15080, 15160, 2.9, 2.7, 2.7</td>
<td>242.5, 272.2, 14250, 14610, 2.6, 2.2, 2.5</td>
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<tr>
<td></td>
<td>587.9, 596.0, 563.0, 579.1, 562.7, 572.9</td>
<td>248.2, 243.0, 15540, 13640</td>
<td>240.5, 259.4, 14990, 15030, 2.8, 2.6</td>
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Appendix

Table A22 Flexural properties of Epikote 828:Jeffamine T3000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Work to Failure (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>319.5, 336.2, 303.1, 327.5, 313.8, 335.0</td>
<td>18640, 19310, 16240, 16510, 16610, 16400</td>
<td>2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
</tr>
<tr>
<td>11.5</td>
<td>762.5, 765.4, 735.7, 717.0, 746.4, 718.3, 776.6, 730.4</td>
<td>332.2, 332.6, 312.0, 323.9, 308.1, 294.8, 310.3, 289.4</td>
<td>16350, 15250, 17860, 15320, 16760, 14770, 18950, 18130</td>
<td>3.3, 4.3, 2.8, 3.6, 3.3, 3.2, 2.8, 3.2</td>
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<tr>
<td>20.6</td>
<td>732.9, 729.8, 733.6, 749.7, 700.9, 666.3, 725.7, 715.2</td>
<td>273.9, 264.8, 306.4, 282.9, 304.4, 288.2, 296.6, 304.7</td>
<td>15890, 15670, 16320, 15470, 17930, 15010, 16310, 16870</td>
<td>3.3, 3.6, 3.7, 3.7, 2.9, 2.6, 3.3, 3.0</td>
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</table>

Table A23 Flexural properties of Epikote 828:Jeffamine D4000/glass fibre composites

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Work to Failure (N.mm)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Deflection at Maximum Force (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>319.5, 336.2, 303.1, 327.5, 313.8, 335.0</td>
<td>18640, 19310, 16240, 16510, 16610, 16400</td>
<td>2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
</tr>
<tr>
<td>11.8</td>
<td>617.0, 574.0, 645.4, 627.3, 675.4, 714.1, 627.3, 676.7</td>
<td>260.9, 269.8, 274.0, 279.4, 303.4, 300.8, 253.8, 271.3</td>
<td>15980, 17320, 16710, 16740, 15770, 16230, 14480, 15670</td>
<td>2.7, 2.4, 2.7, 2.8, 2.9, 3.2, 3.1, 2.8</td>
</tr>
<tr>
<td>19.7</td>
<td>565.9, 526.3, 542.4, 594.1, 602.9, 612.0, 651.3</td>
<td>232.1, 235.1, 235.9, 261.2, 236.4, 275.6, 260.9, 246.6</td>
<td>15720, 15920, 15780, 16060, 15130, 15400, 15080, 13070</td>
<td>2.9, 2.6, 2.6, 2.7, 2.6, 3.1, 3.1</td>
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</tbody>
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Appendix

Table A24 Flexural properties of Epikote 828:Jeffamine D2000/glass fibre composites

<table>
<thead>
<tr>
<th>phr D2000</th>
<th>Work to Failure</th>
<th>Flexural Strength</th>
<th>Flexural Modulus</th>
<th>Deflection at Maximum Force</th>
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</thead>
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<tr>
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<td>(N.mm)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(mm)</td>
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<tr>
<td>--</td>
<td>781.5, 821.9, 726.0, 747.7, 792.7, 814.9</td>
<td>319.5, 336.2, 303.1, 327.5, 313.8, 335.0</td>
<td>18640, 19310, 16240, 16510, 16610, 16400</td>
<td>2.7, 2.9, 3.3, 3.8, 3.9, 3.8</td>
</tr>
<tr>
<td>11.5</td>
<td>686.3, 699.9, 747.8, 733.7</td>
<td>315.3, 298.9, 310.4, 314.9, 278.0, 292.6, 286.8</td>
<td>17800, 16980, 14020, 14770</td>
<td>2.7, 2.7, 4.1, 3.7</td>
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<td>20.5</td>
<td>690.4, 627.4, 701.6, 738.1, 650.7, 662.8, 675.0, 667.6</td>
<td>272.6, 260.1, 292.2, 315.0, 260.2, 296.3, 268.5, 285.5</td>
<td>16320, 15330, 16780, 16770, 16820, 16590, 15670, 15880</td>
<td>2.8, 3.2, 3.1, 3.2, 3.1, 3.3, 3.0, 3.0</td>
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Table A25 Interlaminar shear strength of Epikote 828:Jeffamine T5000

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
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</tr>
<tr>
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<td>30.5, 29.5, 29.6, 29.9, 29.2, 30.6</td>
</tr>
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<td>5.4</td>
<td>18.6, 17.8, 21.9, 21.0, 21.0, 19.9, 22.0, 22.6</td>
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<tr>
<td>11.8</td>
<td>23.5, 23.7, 22.8, 23.8, 21.6, 23.8, 21.5, 21.7</td>
</tr>
<tr>
<td>19.5</td>
<td>24.0, 23.4, 22.2, 22.8, 24.9, 22.4, 22.3, 21.6</td>
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</tbody>
</table>

Table A26 Interlaminar shear strength of Epikote 828:Jeffamine T3000

<table>
<thead>
<tr>
<th>phr T3000</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>--</td>
<td>30.5, 29.5, 29.6, 29.9, 29.2, 30.6</td>
</tr>
<tr>
<td>11.5</td>
<td>27.7, 25.0, 28.4, 26.1, 25.0, 26.1, 25.4, 24.2</td>
</tr>
<tr>
<td>20.6</td>
<td>22.6, 23.1, 23.4, 22.8, 23.6, 24.3, 22.7, 23.9</td>
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## Appendix

### Table A27 Interlaminar shear strength of Epikote 828:Jeffamine D4000

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>30.5, 29.5, 29.6, 29.9, 29.2, 30.6</td>
</tr>
<tr>
<td>11.8</td>
<td>20.2, 20.7, 22.8, 19.4, 19.5, 22.4, 24.8, 24.1</td>
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### Table A28 Interlaminar shear strength of Epikote 828:Jeffamine D2000

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Interlaminar Shear Strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>11.5</td>
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<tr>
<td>20.5</td>
<td>25.8, 26.5, 25.6, 26.2, 27.0, 24.4, 26.7, 25.0</td>
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### Table A29 IFWI data of Epikote 828:Jeffamine T5000/glass fibre composites

<table>
<thead>
<tr>
<th>phr T5000</th>
<th>Peak Impact Force (N)</th>
<th>Deflection at Peak Impact Force (mm)</th>
<th>Energy at Peak Impact Force (J)</th>
<th>Impact Energy to Failure (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
<td>11.9, 12.4, 12.2, 12.4, 11.4, 11.1</td>
<td>18.6, 19.0, 18.5, 19.2, 18.3, 18.6</td>
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<td>5.4</td>
<td>5834, 5512, 5394, 5949, 5873</td>
<td>5.4, 5.2, 5.2, 5.6, 5.3</td>
<td>13.8, 12.5, 12.7, 15.5, 14.1</td>
<td>19.7, 19.0, 19.2, 21.0, 20.2</td>
</tr>
<tr>
<td>11.8</td>
<td>5827, 5519, 5824, 6164, 6317</td>
<td>5.4, 5.1, 5.7, 5.7, 5.8</td>
<td>13.5, 12.6, 15.4, 15.4, 15.6</td>
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<tr>
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<td>6171, 6010, 6112, 5780, 5963</td>
<td>5.7, 5.4, 5.8, 5.3, 5.8</td>
<td>15.5, 14.2, 15.8, 13.5, 16.1</td>
<td>20.4, 19.9, 20.1, 19.2, 20.7</td>
</tr>
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<td>29.2</td>
<td>5719, 5424, 5570, 5458, 5548, 5988</td>
<td>5.4, 6.1, 5.6, 5.6, 5.6, 5.7</td>
<td>13.1, 16.3, 14.0, 13.6, 14.0, 14.5</td>
<td>18.8, 19.7, 18.9, 18.4, 18.9, 18.8</td>
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### Appendix

Table A30 IFWI data of Epikote 828:Jeffamine T3000/glass fibre composites

<table>
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<tr>
<th>phr T3000</th>
<th>Peak Impact Force</th>
<th>Deflection at Peak Impact Force</th>
<th>Energy at Peak Impact Force</th>
<th>Impact Energy to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
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<td>18.6, 19.0, 18.5, 19.2, 18.3, 18.6</td>
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<td>5729, 5189, 5424, 5578, 6051</td>
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<td>18.9, 18.1, 18.1, 19.3, 19.6</td>
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<td>5683, 5973, 5707, 5443, 5468, 5480</td>
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<td>13.7, 13.3, 13.8, 12.4, 13.7, 12.7</td>
<td>19.9, 20.8, 20.0, 18.6, 19.2, 19.2</td>
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Table A31 IFWI data of Epikote 828:Jeffamine D4000/glass fibre composites

<table>
<thead>
<tr>
<th>phr D4000</th>
<th>Peak Impact Force</th>
<th>Deflection at Peak Impact Force</th>
<th>Energy at Peak Impact Force</th>
<th>Impact Energy to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
<td>11.9, 12.4, 12.2, 12.4, 11.4, 11.1</td>
<td>18.6, 19.0, 18.5, 19.2, 18.3, 18.6</td>
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<tr>
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<td>6947, 6838, 6020, 5805, 5753</td>
<td>6.6, 6.5, 5.2, 5.4, 5.3</td>
<td>20.6, 20.8, 13.5, 14.3, 13.5</td>
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<td>6156, 6557, 6774, 6151, 6403</td>
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## Appendix

Table A32 IFWI data of Epikote 828:Jeffamine D2000/glass fibre composites

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<tr>
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<td>5067, 5087, 5260, 5443, 5370, 5275</td>
<td>5.0, 5.0, 5.0, 5.0, 4.8, 4.7</td>
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<td>17.3, 18.2, 18.0, 18.4, 18.3, 18.2</td>
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