

Characterization of epoxy–bismaleimide network matrices

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This study investigated intercrosslinked networks formed by co-curing two thermosets: a tetra-functional epoxy/amine and a bismaleimide formulation. The mechanical properties and phase behaviour of the intercrosslinked networks were compared with the corresponding neat epoxy and bismaleimide systems. In addition, the reaction scheme of the epoxy–bismaleimide resin mixtures was investigated using differential scanning calorimetry. A homogeneous structure for the networks was suggested by the results of both dynamic mechanical analysis and scanning electron microscopy. In contrast to most epoxy systems modified with rubbers or thermoplastics, phase separation was not observed in these intercrosslinked epoxy–bismaleimide networks.

1. Introduction

Modification of epoxy matrix resins by incorporating other components is an important technique for tailoring properties to meet end-use performance. In past years, there have been considerable efforts in the search for techniques for toughening and improving the performance of epoxies [1–5]. It has become increasingly important to modify an epoxy using either thermoplastics [1, 2], or conventional rubbers or elastomers. For the latter case, interpenetrating network structure is generally cited as a most likely network form when both components are capable of crosslinking [6]. The network microstructure and phase behaviour are the fundamental building blocks for understanding the morphology, which is expected to play an important role in determining the mechanical properties of a material.

In the present study, a combination of both a bismaleimide and an epoxy forming an “intercrosslinked” network was examined as a model system. Here, the term “intercrosslinked” was used to embody the cases of interpenetrating, interlocking, and possibly some inter-reactions through co-polymerization between the epoxy and bismaleimide components. The epoxy polymer, tetraglycidyl 4,4'-diamino diphenyl methane (TGDDM, Ciba-Geigy MY720) cured with 25 p.h.r. (parts per hundred of resin) 4,4'-diamino diphenyl sulphone (DDS, Ciba-Geigy HT976), was co-cured with various amounts of a bismaleimide formulation (Kerimid DI-3651, Rhone-Poulenc) whose high-temperature performance is well established [7, 8].

This work describes the preparation of network mixtures from these two components and characterization of the phase behaviour of the mixed resins, before and after cure, using differential scanning calorimetry (DSC), dynamic mechanical analysis, and optical and scanning electron microscopy. The pos-

sible reaction scheme of the epoxy–bismaleimide resin mixtures was explored with a series of DSC measurements. Finally, the thermal decomposition behaviour of the epoxy–polyimide intercrosslinked networks was compared to that of the individual networks.

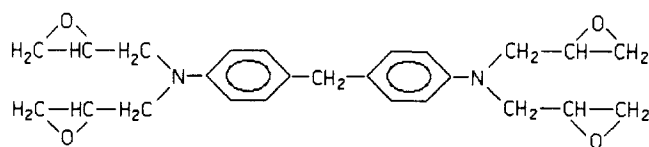
While bismaleimide resin systems are generally used for high-temperature applications, a problem with them is their brittle nature. Epoxy resin systems are excellent in many aspects, but their T_g values drop dramatically in a hot wet environment and, as a result, their mechanical properties suffer greatly. The objective of the modification by blending was to balance the advantages and disadvantages of both the epoxy and the bismaleimide components. Collectively, this work represents a first step in understanding interactions between epoxy and bismaleimide resins which have already been utilized in practice with commercial systems for processing and property modifications.

2. Experimental procedure

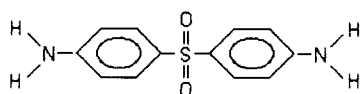
2.1. Materials and preparation

The epoxide resin and amine hardener, TGDDM (MY720) and DDS (HT976), respectively, were obtained from Ciba-Geigy Co. Standard formulation was used for the epoxy in which 25 p.h.r. DDS was mixed with TGDDM. The mixing of DDS with TGDDM was done using our well-established melt mixing method [9]. The bismaleimide prepolymer was a developmental resin, Kerimid DI-3651, which was supplied by Rhone-Poulenc, Inc. [7]. It is a mixture of two kinds of bismaleimide (BMI), diphenylmethane-BMI and tolylene-BMI, with a weight ratio of 60 to 40. The formulation contains an imidazole catalyst (0.6%). Although another Kerimid formulation, FE-70003, contains diphenylsilanediol as a toughener, and triallyl isocyanurate (TAIC) as a processing aid, these components were not used in the mixture for

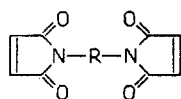
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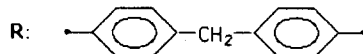
**Tetraglycidyl 4,4'-diamino diphenyl methane
(TGDDM)**



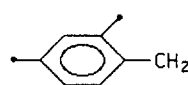
**4,4'-diaminodiphenyl sulphone
(DDS)**



Bismaleimide (BMI)



Diphenylmethane-BMI



Toluene-BMI

Figure 1 Chemical structures of materials used in this study.

this study. Fig. 1 shows the chemical structures of the epoxy and bismaleimide materials used in this study.

After dissolving DDS into TGDDM by mechanical stirring, the bismaleimide prepolymer (which had already been degassed under vacuum at about 80°C for about 10 min) was added gradually to the TGDDM–DDS melt mixture at 135°C. Mixing by mechanical stirring was continued for about five more minutes until a clear melt was obtained. The bismaleimide resin readily dissolved in the epoxy resin without any difficulty. Three epoxy–bismaleimide resin mixtures were prepared, each containing 25, 50 and 75 wt %, respectively, of the bismaleimide resin in the epoxy formulations.

Uniform film samples for dynamic mechanical studies were obtained by curing the melt mixtures of the epoxy–bismaleimide resin in a steel mould coated with Frekote, a silicone release agent, and separated with a shim stock. The thickness of the films was between 0.04 and 0.08 cm. The resin mixtures were cured at 177°C for two hours followed by post-curing at 220°C for various lengths of time from 2 to 15 h. The samples turned from amber to black upon completion of post-curing at 220°C for longer than 10 h, indicating some degradation of the epoxy component.

2.2. Thermal analysis

DSC was used for investigating cure reactions of the resin mixtures. In addition to that, homogeneity and compatibility of the epoxy–bismaleimide resin mixtures was characterized using the glass transition temperature as a criterion for compatibility. A DuPont DSC 910 supported by the 9900 thermal analysis system was used. A heating rate of 5 or 10°C min⁻¹ was used.

A Dupont 951 thermogravimetric analyser (TGA) was used to investigate the decomposition behaviour

of the intercrosslinked networks. A heating rate of 5°C min⁻¹ was used for TGA.

2.3. Dynamic mechanical measurements

Dynamic mechanical analysis (DMA) was performed on crosslinked network film samples between –120°C and the glass transition temperatures of the samples using a Rheovibron (Model DDV-II) dynamic viscoelastometer (Toyo Baldwin Co.). The frequency was 11 Hz and a heating rate of approximately 1°C min⁻¹ was used. To ensure obtaining more accurate modulus values of the samples, error corrections for quantitative data acquisition were performed with the procedures of Wedgewood and Seferis [10].

2.4. Optical and scanning electron microscopy

The resin mixtures were examined using a Nikon polarizing microscope. Microscopy examination on the mixtures during cure was monitored using the microscope equipped with a hot stage with the capability of temperature ramping, and an on-line video tape recorder was used to record the change during cure.

Cured samples of the intercrosslinked epoxy–bismaleimide networks were fractured at ambient temperature. The fracture surface was subsequently coated with gold vapour deposition. In contrast to rubber-modified systems, the technique of osmium tetroxide stain could not be applied because, when fully cured, there was no unsaturated part of the bismaleimide molecules. An ISI mini-electron microscope was used for examining the fracture surfaces at 5000 × magnification.

3. Results and discussion

3.1. DSC results

Fig. 2 shows the DSC traces of five resin samples, the neat epoxy and bismaleimide resins, and the three

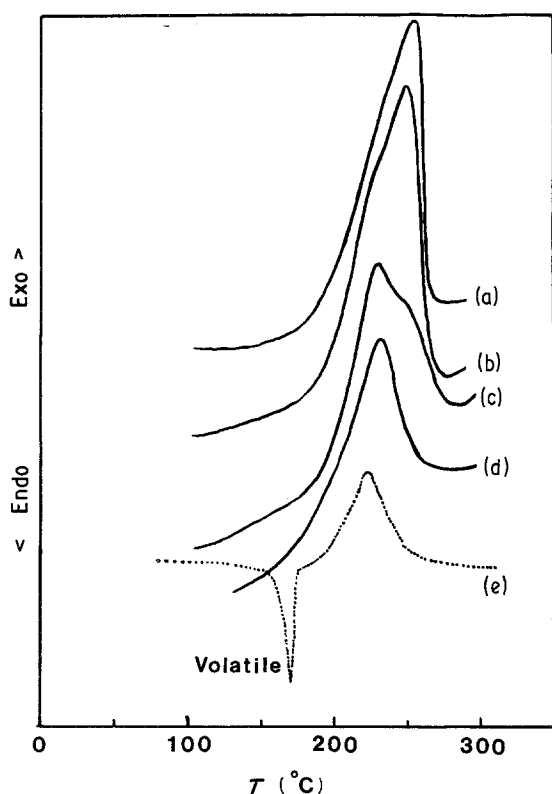


Figure 2 DSC scans (at $5^{\circ}\text{C min}^{-1}$) of epoxy-bismaleimide resin mixtures during cure: (a) pure epoxy, (b) 75:25, (c) 50:50, (d) 25:75, (e) pure bismaleimide.

epoxy-bismaleimide mixtures of different compositions. An exothermic reaction peak that may be attributed to the pure epoxy system was observed at 255°C , while that of the bismaleimide system was observed at a lower temperature of 220°C . In addition, as can be seen, the bismaleimide also exhibited an endothermic peak at 175°C in the DSC trace, which has been attributed to evaporation of the minor additives in the bismaleimide resin formulation [7]. Except for the mixture sample which contains 75 wt % of bismaleimide, the cure exotherm of the other two mixture samples containing 50 and 25 wt % of the bismaleimide resin exhibited two peaks, indicating two reaction regimes. The first exothermic peak, located at about 230°C , may be associated with the bismaleimide cure reaction. It appears merely as a shoulder on the lower-temperature side in the mixture containing 25 wt % of bismaleimide, while the epoxy exothermic peak, located at about 250°C , is the predominant one. However, in the mixture containing 50 wt % of bismaleimide, the first peak becomes the predominant peak and the epoxy peak appears as a shoulder on the higher-temperature side. These observations suggest that the bismaleimide and epoxy reactions are well separated and resolved, except for the resin mixtures containing bismaleimide contents higher than 75 wt %.

If the two reactions are independent and well resolved, a three-dimensional intercrosslinked network may be visualized. The intercrosslinked structure is similar to that of an interpenetrating network (IPN). Idealized reaction schemes for the resin mixtures will be that the bismaleimide molecules react separately from the epoxy at earlier stages of cure. The

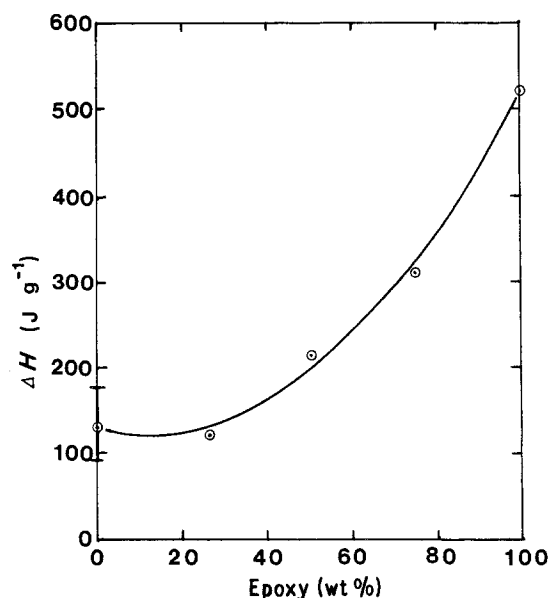


Figure 3 Heats of reaction of epoxy-bismaleimide resin mixtures as a function of composition.

bismaleimide molecules do not react with either the epoxide or the amine molecules. At later stages of cure, but before gelation of the matrix caused by the bismaleimide crosslinking reaction, the epoxy reaction starts. Together, these two reactions reach the vitrification stage simultaneously, and an idealized intercrosslinked network similar to an IPN is formed.

Fig. 3 shows the heats of reaction of the resin mixtures as a function of composition of the epoxy in the mixture. The composition is expressed in terms of the weight percentage of the TGDDM-DDS epoxy formulation in the epoxy-bismaleimide mixtures. The heat of reaction for the neat epoxy (TGDDM cured with 25 p.h.r. DDS) is 525 J g^{-1} . By comparison, the heat of reaction for the bismaleimide resin is quite low, about 120 J g^{-1} , because the crosslinking reaction for the bismaleimide involves only the energy difference between a double and a single bond. Due to the weight loss from evaporation of volatiles, the heat of reaction for the pure bismaleimide resin could not be calculated accurately. The error bar on this data point indicates this inaccuracy. If the two reactions were completely independent, a linear plot should have resulted. The non-linearity suggests that some level of co-polymerization (i.e. a reaction between the bismaleimide and epoxy components) may be taking place.

3.2. Phase behaviour of resin mixtures

3.2.1. Uncured samples

The melt-mixed resins of epoxy and polyimide were clear, though appearing amber in colour. They also appeared homogeneous. To confirm that the mixed resins were indeed single-phase mixtures, the glass transition temperature was used as a criterion for phase homogeneity of the mixture [11].

Fig. 4 shows the DSC traces for the mixed resins (before cure). In addition, thermograms indicated that the glass transitions of the epoxy and bismaleimide resins were observed at 5 and 56°C , respectively. For each of the epoxy-bismaleimide mixtures only a

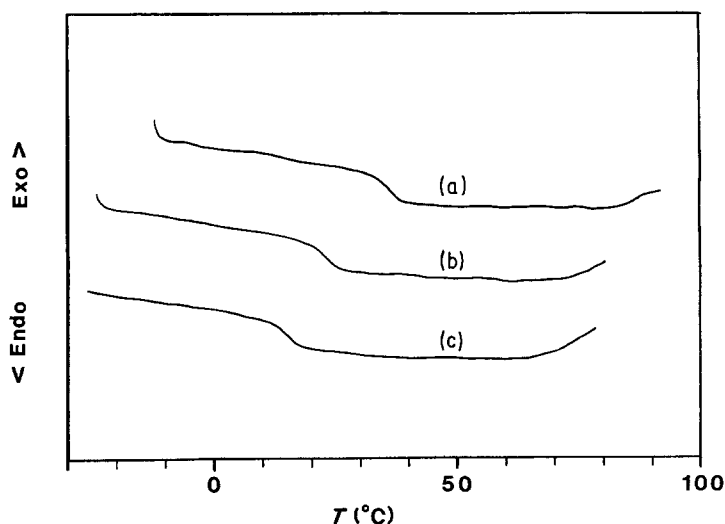


Figure 4 DSC thermograms ($10^{\circ}\text{C min}^{-1}$) of epoxy-bismaleimide resin mixtures of three different compositions: (a) 25:75, $T_g = 32^{\circ}\text{C}$; (b) 50:50, $T_g = 20^{\circ}\text{C}$; (c) 75:25, $T_g = 12^{\circ}\text{C}$.

single glass transition was observed, which increased as a function of the weight percentage of bismaleimide component in the mixtures. The single and composition-dependent glass transition temperature indicates phase homogeneity of the mixed resins.

The compatibility of the resin mixtures before cure may originate from the combination of low molecular weights and a match of solubility parameters. The match of solubility parameters can be well explained by the fact that there is some similarity in segments of the molecules of these two components.

3.2.2. Cured samples

For cured samples, the glass transition was not detected by the DSC technique. The intercrosslinked network structure was examined using dynamic mechanical analysis. In Fig. 5, the dynamic mechanical data are shown for the two network samples with 50 and 75 wt % of bismaleimide. As can be seen, homogeneity of the epoxy-bismaleimide networks is suggested by the single and sharp dynamic mechanical transitions (E'' peaks).

The transition temperatures of the cured networks are plotted in Fig. 6 as a function of composition (wt % of bismaleimide in the mixtures). A fully cured neat epoxy has a glass transition temperature of 260°C , while a cured bismaleimide has a glass transition temperature above 400°C , which could not be observed directly with DMA since it reached the limit

of the heating capacity of the heater in the Rheovibron and was close to the decomposition temperature. The glass transitions (defined here as the peak of the loss modulus curve) of the two samples with 75:25 and 50:50 epoxy-bismaleimide compositions, respectively, are sharp and well defined, indicating that the intercrosslinked networks are homogeneous.

It should be noted that the intercrosslinked network samples started to decompose at temperatures above 350°C . However, the glass transition of the network samples examined is well defined and not broadened, indicating that the phase domains are smaller than the size of the segments that are responsible for the primary molecular relaxations [11]. Although the relatively high density of the mechanical interlocks in the network may be primarily responsible for the phase homogeneity, there may exist a possibility of reactions between the bismaleimide and epoxy segments, which inherently enhances miscibility between these two components.

By curing the mixtures of the epoxy and bismaleimide resins, an intercrosslinked network is formed. During cure, the molecules grow in size, and the entropy contribution to the free energy of mixing decreases. As a result, phase separation tends to occur. However, formation of mechanical interlocks between the molecules of the two components in the network may counter that trend and essentially enhance phase homogeneity. This is a highly crosslinked system

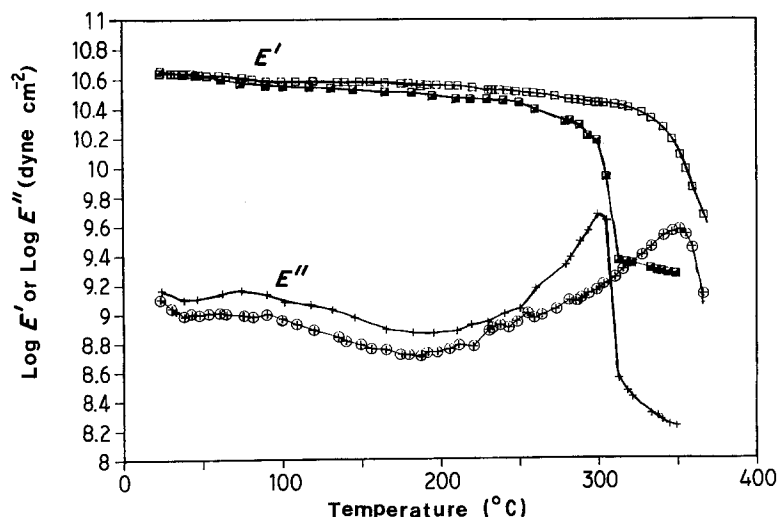


Figure 5 Dynamic mechanical properties of intercrosslinked epoxy-bismaleimide networks: (\square , \oplus) 25:75; (\blacksquare , $+$) 50:50. 1 dyne = 10^{-5} N .

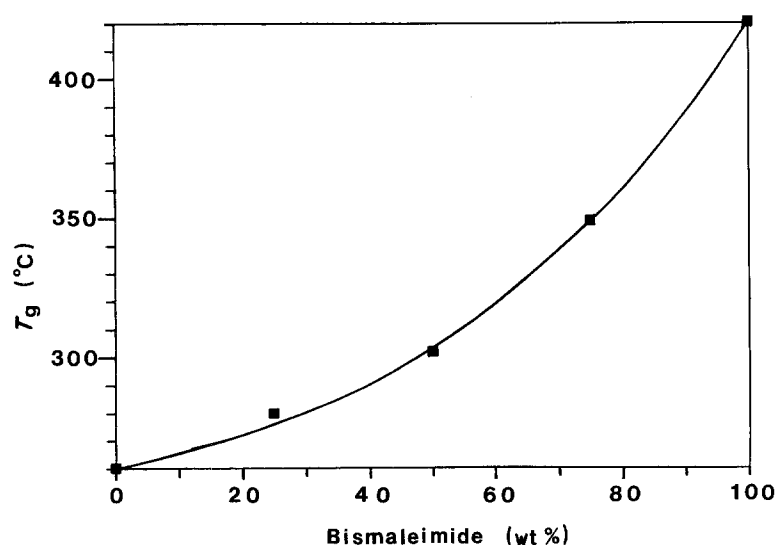


Figure 6 Glass transition temperatures measured by dynamic mechanical properties (E'' peak) as a function of composition for intercrosslinked epoxy-bismaleimide networks.

with dense interlocks that can be viewed as a three-dimensional (3-D) copolymer. The difference between an intercrosslinked network and a hypothetical 3-D copolymer is that the segments are "locked" by mechanical interlocks in the former but actually linked by covalent bonds in the latter.

It can be argued that there may be co-polymerization between the epoxy and the bismaleimide components. It is a good possibility although it is not proved unambiguously in this paper whether there is indeed co-polymerization or not. However, co-polymerization is not to be expected to contribute significantly to phase homogeneity. It is known that in some rubber-modified epoxy systems, carboxyl-terminated butadiene nitrile (CTBN) liquid reactive rubbers can co-polymerize with an epoxy [12]. However, an originally miscible CTBN-epoxy resin mixture may develop separated phases when the molecular weights of the rubber and epoxy components increase during cure [13]. For epoxies modified with either lightly crosslinked CTBNs or thermoplastics, phase separation is apt to occur when the molecular weights increase. For the present intercrosslinked networks, it is mainly high-density interlocks, not necessarily covalent bonds, that maintain phase homogeneity.

3.3. TGA results

Figs 7 and 8 show the TGA data for the pure bismaleimide, the pure epoxy, and the intercrosslinked networks with a composition of 25, 50 and 75 wt % of bismaleimide. The pure epoxy sample started to degrade at 375°, but the pure bismaleimide sample did not exhibit significant degradation until 500°C. The intercrosslinked network samples exhibited a somewhat intermediate behaviour. Fig. 8 shows that as the bismaleimide content of the samples increases, the percentage weight loss due to degradation at the same temperature proportionally decreases. All these data suggest an average type of decomposition behaviour typical of a blend.

It can be seen that the temperature at which the intercrosslinked networks start to decompose was not raised significantly by incorporating the polyimide structure. The two components, epoxy and bismaleimide, seem to undergo degradation independently.

3.4. Microscopy results

3.4.1. Optical microscopy

The phase behaviour of the mixed resins during curing was examined using the optical microscope. One of the uncured resin mixtures, 50 wt % in the bismaleimide resin, was examined using the microscope equipped

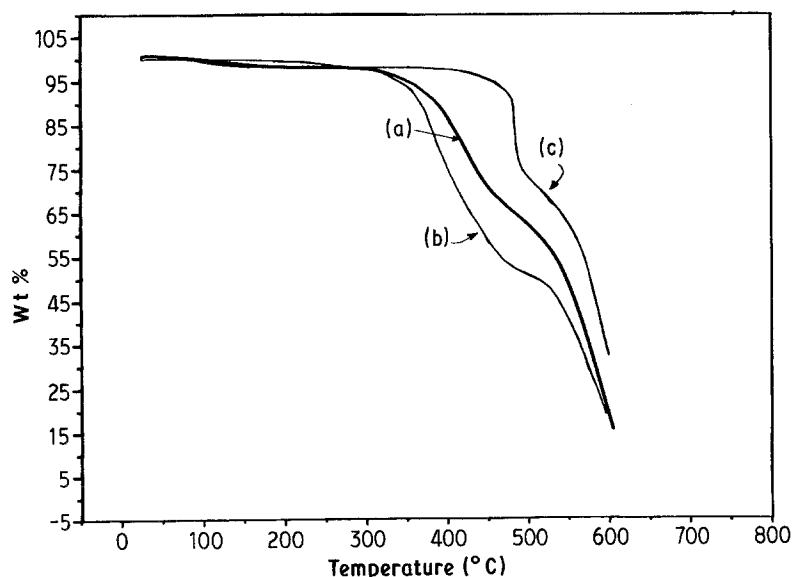


Figure 7 TGA thermograms ($5^{\circ}\text{C min}^{-1}$) for (a) an epoxy-bismaleimide 25:75 intercrosslinked network and its comparison to (b) neat epoxy and (c) neat bismaleimide networks.

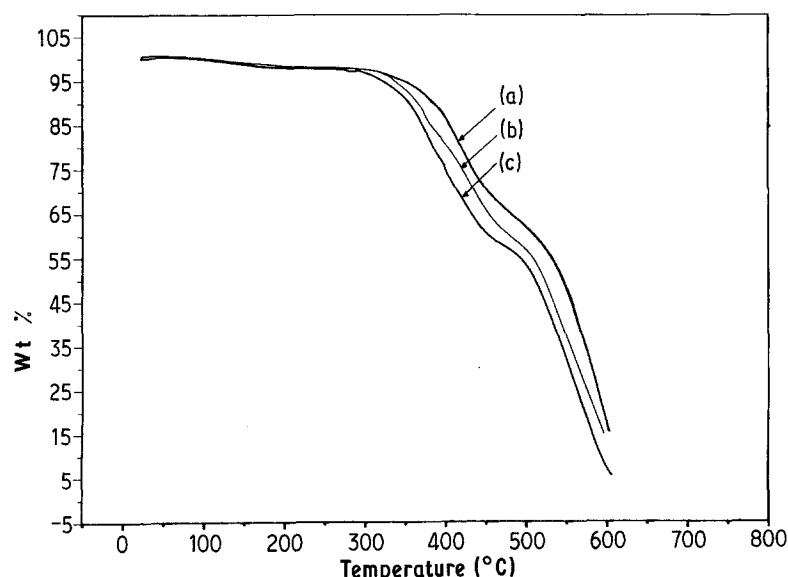


Figure 8 TGA thermograms showing decomposition characteristics of three epoxy-bismaleimide networks. Ratio of epoxy to bismaleimide (a) 25:75, (b) 50:50, (c) 75:25.

with a heating stage. The phase behaviour was continuously monitored while the sample was subjected to dynamic heating from the ambient temperature to 400°C at a heating rate of 10°C min⁻¹. Microscopic examination at 400× showed that no phase heterogeneity could be detected for the resin mixture.

Fig. 9 shows the fracture surfaces examined using scanning electron microscopy (SEM). The neat epoxy exhibits a typical fracture surface of a homogeneous material without any plastic deformation. By comparison, the micrographs of the intercrosslinked networks with 25, 50 and 75 wt% epoxy indicate that all fracture surfaces are similar and do not show phase domains of two components. Thus, again, SEM suggests the formation of homogeneous networks.

4. Conclusions

This paper demonstrates an interesting case of a compatible blend of a matrix thermosetting epoxy (TGDDM-DDS) with a thermosetting polyimide (bismaleimide). Both systems were capable of forming highly crosslinked networks independent of each other. When their mixtures were co-cured, an intercrosslinked network was formed.

Based on the results of dynamic mechanical analysis and microscopy, no phase separation was detected in the two-component intercrosslinked networks. TGA thermal decomposition measurements, which are associated with the chemical nature of the network mixtures, were only slightly affected by the modification, which may be viewed as mechanical interlocks formed in the networks.

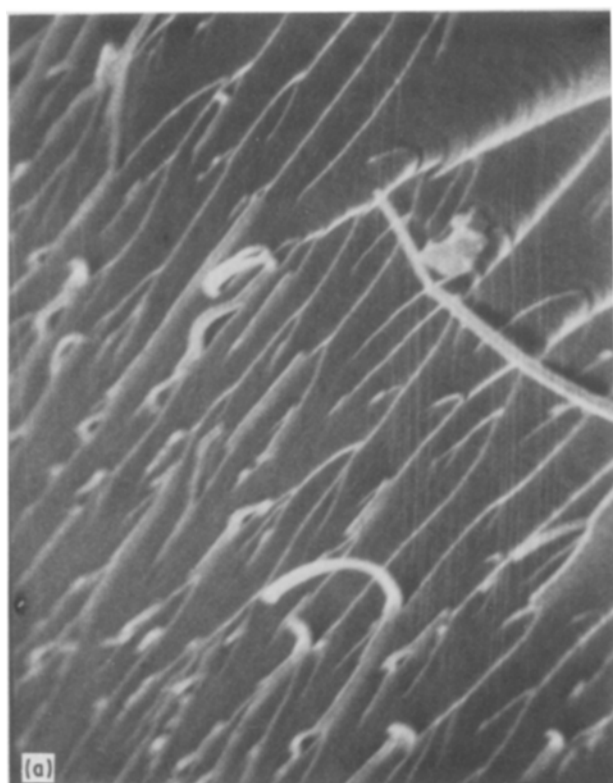


Figure 9 SEM micrographs (× 5000) showing fracture surfaces of (a) neat epoxy; and intercrosslinked epoxy-bismaleimide networks (b) 25:75, (c) 50:50, (d) 75:25.

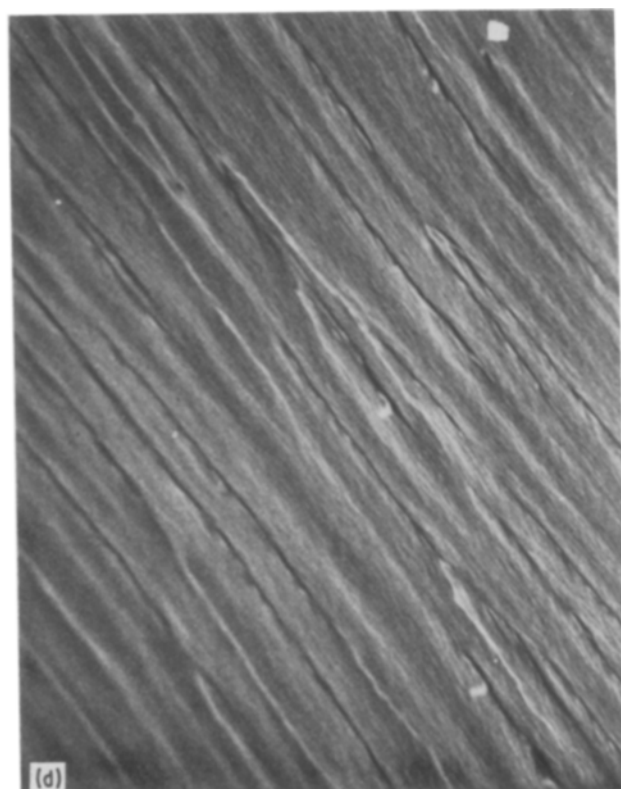


Figure 9 Continued.

Before cure, the epoxy and the bismaleimide resins form a homogeneous mixture, most likely because of a match of their solubility parameters. Upon curing, the molecular weights increase but phase separation does not occur, primarily because of high-density mechanical interlocks.

In summary, an important homogeneous matrix material blend has been formulated whose temperature capability is between those provided by the individual constituents. Since the individual constituents are widely used as matrices for high-performance composites with different service temperatures, this blended matrix offers an intermediate service temperature that can be tailor-made to meet specific end-use requirements.

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