

An Aromatic Amine as a Co-Curing Agent in Epoxy–Bisimide Blends*

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SYNOPSIS

The structural properties of epoxy can be retained and thermal stability improved by blending epoxy with bismaleimide (BMI) and curing them simultaneously. Depending on the curing agent, the overall viscoelastic properties of the cured material can be varied. In the present work, diaminodiphenylmethane and diaminodiphenyl sulfone have been used as curing agents to prepare blends of epoxy and BMI. The blends were characterized by DSC, TG, DMA, and SEM. Results indicate that an excellent interpenetrating network forms in both the cases and that the DDM-cured system gives better thermal stability than that of the DDS-cured system. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The notable features of epoxy resins are their excellent degree of adhesion, high strength, excellent chemical and biological resistance, and good reproducibility. The conversion of the liquid epoxy resin to a tough and hard thermoset solid is generally accomplished by the addition of chemically active compounds such as anhydrides and amines. The epoxies are resistant to many environmental conditions and can be used up to 135°C on a continuous basis.

In advanced composites, where high performance in mechanical and structural properties is the main requirement, improved matrix resins are prepared by preformulating the epoxies. The center of activity, depending on the end use, is the improvement of temperature resistance, moisture resistance, toughness, and easy processibility. Even with epoxy novolacs or with tetrafunctional epoxy resins and aromatic amine-type hardeners, the epoxy matrix system has temperature stability only up to 180°C. It is also well known^{1,2} that elevated temperature

properties of epoxy–matrix resins are affected by moisture absorption due to high humidity environmental exposure. Several methods have been pursued to improve the heat deflection temperature of epoxy resins. Lauze and co-workers³ showed that cured epoxy resins based on bisphenol-S considerably increase in heat resistance over those based on bisphenol-A. Another way of improving the high-temperature performance is to incorporate a rigid backbone structure in the epoxy resin. Polyimides have good high-temperature performance and the epoxy resin possesses many desirable properties of the aromatic polyimide if it contains the phthalimide moiety. Kaplon et al.⁴ synthesized some such epoxy imide resins having good thermal stability.

Woo et al.⁵ blended a tetrafunctional epoxy resin with a bismaleimide formulation and studied the intercross-linked network formed during cocuring. Bismaleimide resins have excellent retention of mechanical properties under hot and humid conditions but their brittleness is the biggest bottleneck in addition to processing difficulties. There are two major alternatives to overcome the limitation of these matrix resins: to modify the resin backbone structure or to use blends. In the present work, we have prepared blends of epoxy–bismaleimide using 4,4-diaminodiphenylmethane (DDM) and 4,4-diaminodiphenyl sulfone (DDS) as amine curing agents. The curing characteristics were studied by dynamic differential scanning calorimetry (DSC), and the de-

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composition behavior of the intercross-linked network, by thermogravimetric analysis (TG). Fracture surfaces of the cured blend samples were observed in a scanning electron microscope for morphological information.

EXPERIMENTAL

Preparation of the Blends

The diglycidyl ether of bisphenol-A (LY-556) epoxy resin and the hardeners 4,4-diaminodiphenylmethane (DDM) (HT-972) and 4,4-diaminodiphenyl sulfone (DDS) (HT-976) received from Hindustan CIBA-Giegy Ltd., Bombay, were used. Note that DDM is carcinogenic and suitable precautions must be taken while handling this material. Bismaleimide (BMI) was synthesized in the laboratory by the acetone solvent method. The standard formulation, viz., 27 phr of DDM and 36 phr of DDS, were used with 100 parts of epoxy. The two blend compositions were cured at 140 and 180°C and finally postcured for 6 h at 200 and 220°C, respectively, for DDM and DDS.

Three epoxy-BMI blends were prepared with 25, 50, and 75% of BMI by weight per 100 g of the epoxy-BMI mixture. The mixtures were heated with stirring at 135–140°C until a clear solution was obtained and then catalyzed with the required quantity of DDM and DDS by weight of epoxy in the mixture. The curing schedule described above has been followed for these blends. Epoxy-DDS and epoxy-DDM formulations were prepared separately for comparison.

Thermal Analysis

DSC was used to study the curing characteristic of the resin mixture. The mode of transition (endothermic or exothermic) occurring during curing was the criterion for thermal analysis. A DuPont DSC module 912 supported by a 1090 thermal analysis system was used for the DSC studies, and a DuPont TGA module 951, for thermal decomposition studies on epoxy-amine castings.

The cured (cast) specimens were used to perform dynamic mechanical analysis (DMA) tests. The loss modulus and damping were studied when the sample was subjected to resonance mode at a programmed heating rate of 5°C/mt from ambient to about 350°C. A DuPont 983 DMA module was used for the above study.

Scanning Electron Microscopy

Polymer-blend samples were fractured at ambient temperature and the fracture surfaces were coated with a thin film of gold of about 400 Å thickness using a Polaron DC sputtering unit. SEM photographs of the fracture surfaces were recorded at magnifications of 200 and 2000 for most of the samples, using a JEOL 35 CF scanning electron microscope.

RESULTS AND DISCUSSION

The properties of epoxy resins can be tailored by choice of curators. Aliphatic/aromatic amines, anhydrides, BF₃-amine complexes, etc., have been commonly used as cross-linking agents for epoxy resins. The major achievement aimed at is that the hardener either increases the adhesive nature of the cured product or the temperature stability of the epoxy resin. Some of the amine-terminated bisimides have been used as curing agents for epoxy resins. The bisimide-cured epoxy exhibited a higher T_g than that of the control. The possibility of using anhydride-terminated polyimides as hardeners for epoxies has also been explored by some workers.^{6,7}

Stenzenberger et al.⁸ showed that BMI, which yields a highly brittle product on curing, can be modified by the addition of aromatic amine. This extension results in reduced cross-link density and consequent reduction in thermal stability. Nishi et al.⁹ took some hydroxyl groups containing polyimides and cocured them with epoxy resin, where the free hydroxyl group reacts to open the oxirane ring and initiates the cross-linking reaction. Woo et al.⁵ used DDS as hardener in tetrafunctional epoxy and BMI blendings, but they did not discuss the formation of the chain-extension reaction that may occur when BMI and amine are heated together. This may be because of the lower reactivity of DDS with BMI, but in the case of DDM, we observed that even if DDM and BMI are melted and mixed the extension reaction takes place. Hence, the possibility of the formation of extended BMI cannot be ruled out during the cocuring of the three compounds taken together.

From the observation of our experimental work, we are contemplating four possible reactions in this case:

1. Epoxy + BMI—adduct formation
2. Epoxy + amine—addition and cross-linking

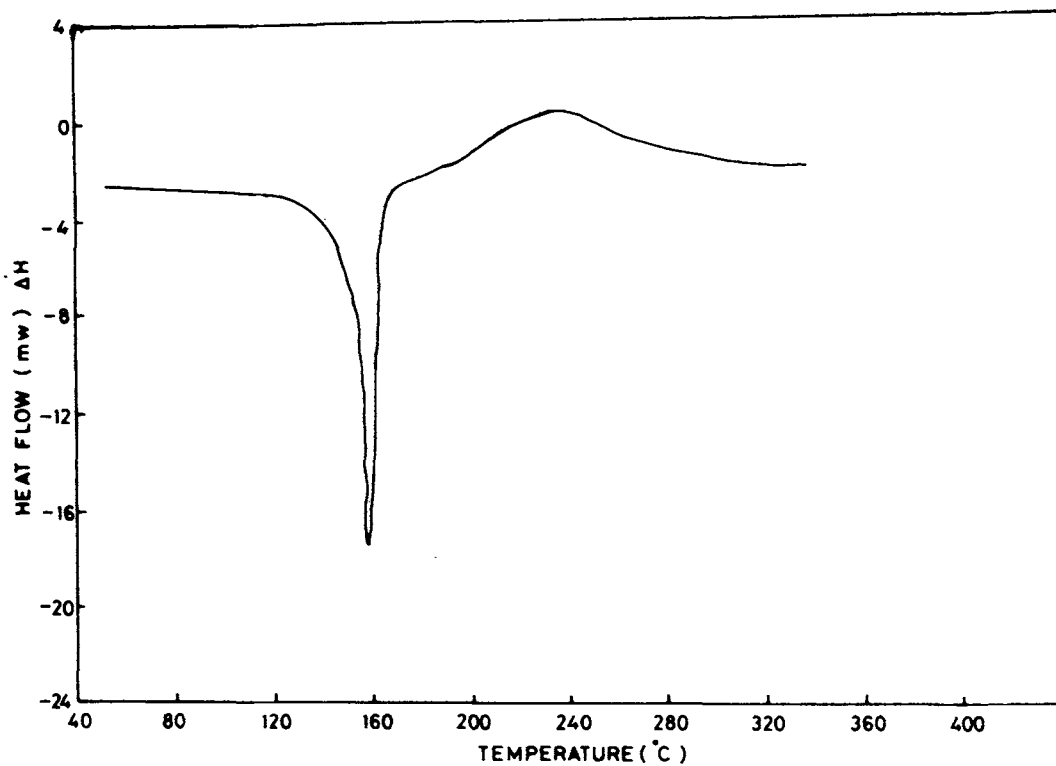


Figure 1 DSC scan of BMI at 10°C/min.

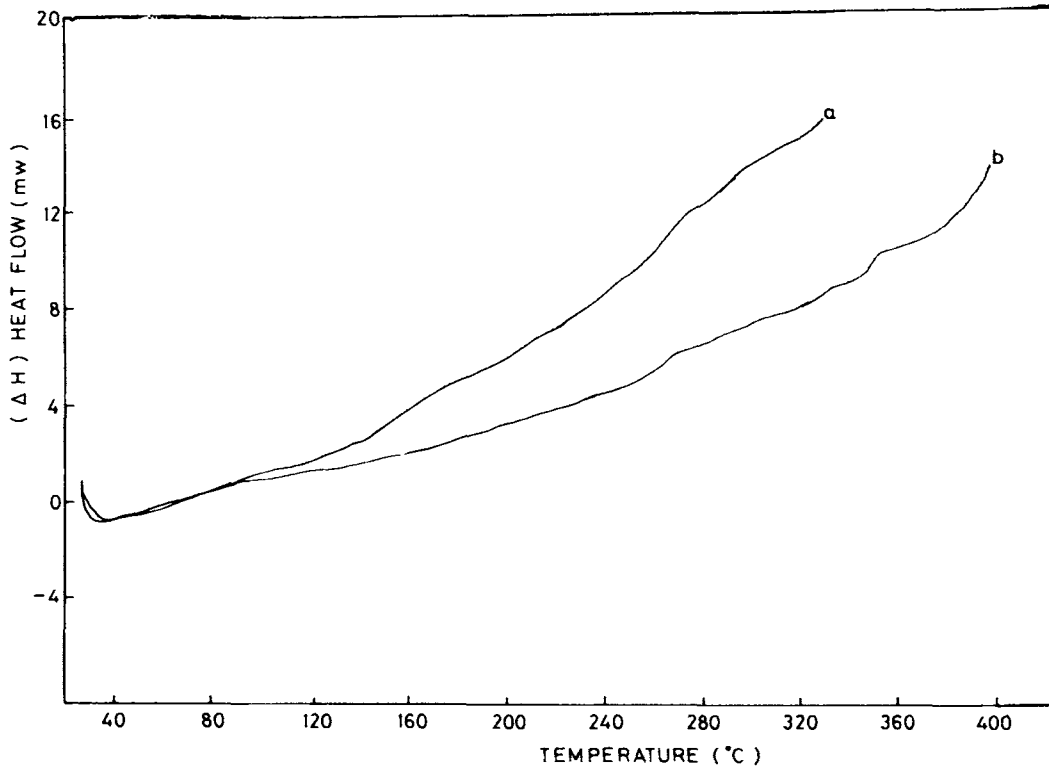


Figure 2 DSC scan of (a) epoxy + BMI and (b) epoxy + BDMA.

3. BMI + amine—extended BMI, and
4. Extended BMI + epoxy resin—cross-linking.

Differential Scanning Calorimetry

For studying the polymerization pattern of BMI and epoxy + DDM systems, DSC scans were obtained for these two systems. BMI polymerization involves an endothermic peak at 157°C, indicative of the melting of the resin followed by the polymerization initiation at 185°C with T_{\max} at 230°C (Fig. 1). This scan tallies with those obtained by other workers.¹⁰ The DDM-catalyzed epoxy system polymerizes exothermally with an initial onset at 131°C and T_{\max} at 162°C, confirming the reaction mechanism proposed for the aromatic amine hardener systems.

When BMI is added to DGEBA epoxy resin and the mixture is heated with stirring, a clear solution is obtained around 130°C. The viscosity of the solution continues increasing with time. The viscous liquid formed is soluble in MEK and acetone, indicating that cross-linking has not taken place. But when this viscous solution is heated up to 200°C and maintained at 200°C for about 4 h, a cross-linked insoluble mixture is formed. Visual examination revealed that the clarity of the blend decreased as the BMI content was increased, maximum clarity being obtained for the pure epoxy composition.

The DSC curve of epoxy + BMI (1 : 1) does not show any sharp endothermic peak (observed in BMI for its melting) and the rate of change of heat continues increasing smoothly. A similar type of curve was also obtained in a tertiary amine-catalyzed epoxy system (Fig. 2). The imide nitrogen, which has a lone pair of electrons in BMI, initiates the catalytic reaction and then autocatalyzes the epoxy-

hydroxy-epoxy cross-linking reactions. The other possibility envisaged is the reaction of the carboxylic group of amic acid species available in traces in BMI. These partially cyclized or uncyclized amic acids have also a secondary amine group attached to an electron-deficient carbonyl group at one end and an aromatic ring on the other. The reactivity of this secondary amino group will be sterically hindered, whereas the carboxylic group of amic acid that is in proximity to olefinic group becomes more mobile to react as a protonic entity with the oxirane group of epoxy resins. In both the above-mentioned possible reactions, the reactivity and the quantity of available group is too low for the reaction to follow the same characteristic pattern shown by epoxy resin catalyzed by a tertiary amine.

Epoxy and BMI were used in 75 : 25, 50 : 50, and 25 : 75 w/w proportions with an aromatic amine as hardener (Tables I and II). The quantity of DDM or DDS was stoichiometrically proportional to epoxy resin used in the mixture. The DSC scans of these compositions show two separate exothermic peaks (Fig. 3). The T_{BExo} for the first exothermic peak are at 86, 115, and 96°C, and T_{BExo} for the second exothermic peak are at 260, 235, and 236°C. The lower onset at 86°C for the first exotherm indicates that the quantity of the epoxy resin available for DDM is much lower than what is actually required due to simultaneous formation of the epoxy-BMI adduct.

In the case of the 50 : 50 epoxy + BMI blend, the increase in T_{BExo} for the first exotherm can account for the possible formation of both epoxy + BMI adduct and BMI + DDM extended adduct. But when the BMI proportion is higher than that of the epoxy (as in 75 : 25 BMI + epoxy), the T_{BExo} again reaches 96°C, which may be due to the predominance of the BMI + DDM adduct formation. T_{\max} obtained for

Table I DSC Data for Epoxy + BMI + DDM System Blends

Resin Composition	T_{BExo} (°C)	T_{\max} (°C)	T_{Exo} (°C)
BMI	185.0	231	300
DGEBA epoxy + DDM	131.0	162	238
DGEBA epoxy : BMI : DDM			
75 : 25 : 21	86.06	139	238 I transition
	260.0	286	309 II transition
50 : 50 : 13.5	115.6	164	223 I transition
	237.0	262	322 II transition
25 : 75 : 6.75	96.0	136	192 I transition
	234.0	276	313 II transition

Table II DSC Data for Epoxy + BMI + DDS System

Resin Composition	T_{Bexo} (°C)	T_{max} (°C)	T_{Eexo} (°C)
Bismaleimide (BMI)	185	231	300
DGEBA epoxy : DDS	172	220	316
DGEBA epoxy : BMI : DDS			
75 : 25 : 27	192	232	304
50 : 50 : 18	240	255	312
25 : 75 : 9	229	272	340

the three compositions are also lower than the T_{max} obtained in the case of epoxy + DDM systems, thus indicating that the initial formation of reactive groups increases the reactivity of the reaction and lowers the onset temperatures. But once the adduct formation initiates, the available distance between the reactive groups increases and, thus, the reactivity decreases. For the second exothermic reaction, even though the onsets follow the same pattern, the T_{max} temperatures are higher than those of epoxy + DDM

or BMI. This thus explains the formation of adducts and their cross-linking simultaneously, which possibly leads to a simultaneous interpenetrating network (SIN) structure.

In the case of BMI + epoxy blends cured with DDS, only a single exothermic peak was formed (Fig. 4). The above-mentioned four reactions are also possible here. In the epoxy + DDS system, the T_{Bexo} is at 172°C. This is higher than the melting point of BMI (157°C). Thus, even if the adduct of BMI + DDS is formed, these two reactions take place at lower temperatures than 172°C and, therefore, the other reactions take place simultaneously but at higher temperatures. The trend in onset temperature in both the cases, i.e., DDM-cured and DDS-cured epoxy + BMI blends, is nearly the same. Simultaneous cross-linking of the epoxy resin and BMI takes place to form a homogeneous network structure that has excellent thermal stability.

TGA Results

Thermogravimetric analysis of cured materials of BMI, extended BMI, epoxy-amine, and epoxy

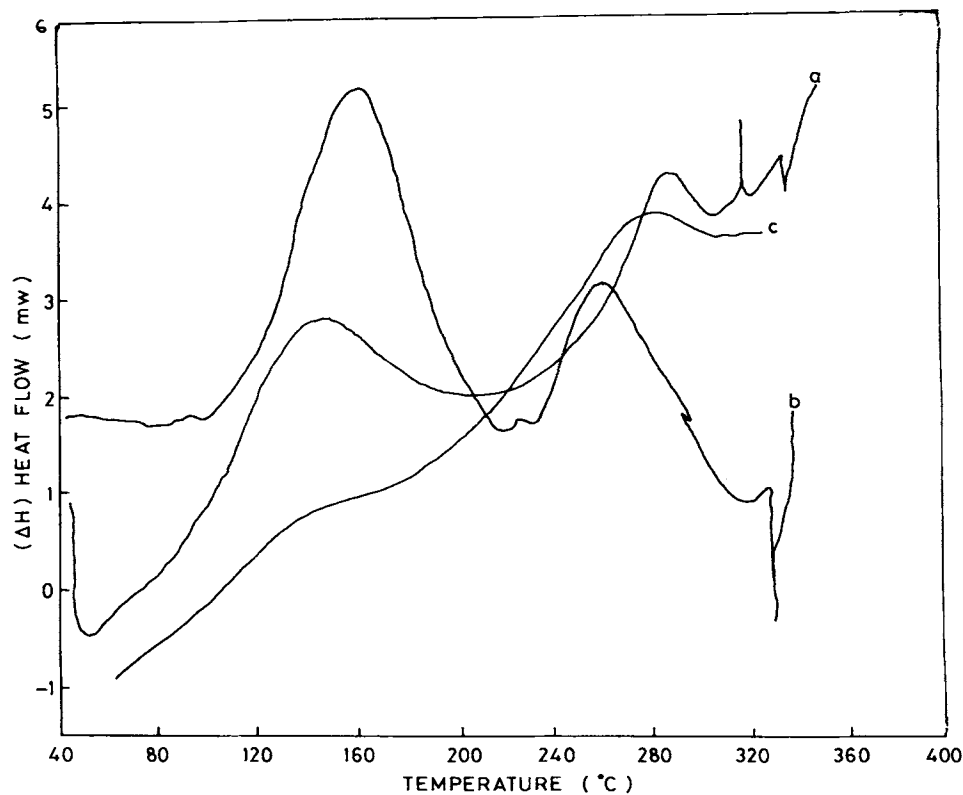


Figure 3 DSC scan of DDM cured epoxy : BMI blends: (a) 75 : 25; (b) 50 : 50; (c) 25 : 75.

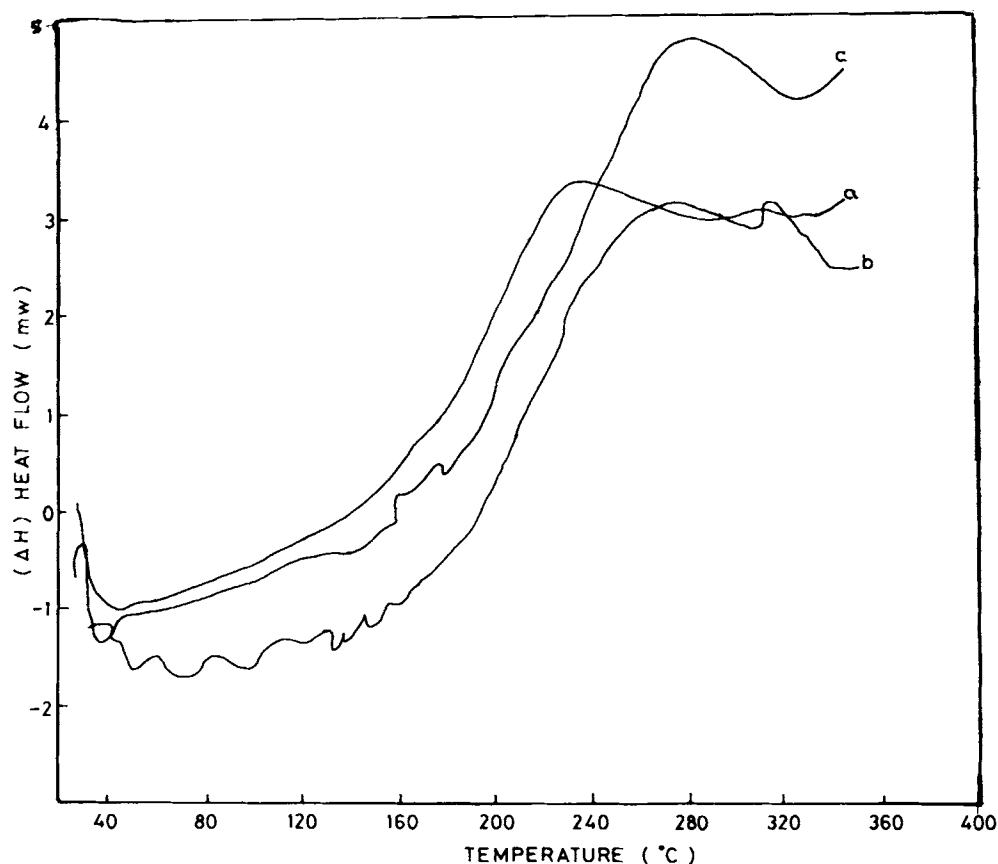


Figure 4 DSC scan of DDS cured epoxy : BMI blends: (a) 75 : 25; (b) 50 : 50; (c) 25 : 75.

+ BMI + amine systems were carried out (Tables III and IV). The degradation curves obtained indicate that BMI and epoxy + DDM systems follow single-stage degradation. But in the case of other compounds including extended BMI, it is in multistages. The extended BMI sample degrades in three stages, which shows that the polymerization reaction of extended BMI is complex and depends on the formation of the (BMI + DDM) adduct. The TGA data for the epoxy + BMI (uncatalyzed) cured product also shows three-stage degradation. The first stage indicates that the product degrading at 239°C is in a very small quantity, but the other two stages of degradation explains the formation of an additive product and cross-linking of the unutilized BMI. But the typical phenomenon of three-stage degradation observed in either extended BMI or epoxy + BMI is absent in amine-catalyzed epoxy + BMI blends. The first degradation onset was at 355°C for 25 parts, 356°C for 50 parts, and 360°C for 75 parts of BMI, respectively, as shown in Figure 5. The second

onset in all the cases around 470°C shows the formation of epoxy cross-linked by extended BMI and cross-linking of BMI as such. In general, TGA analysis confirms the two-stage reactions obtained in the thermal polymerization of the blends. Weight loss of the material during degradation was found to give an indication of an increase in the thermal stability of the blends with an increase in BMI content. At 25 parts of BMI, the loss at first stage of degradation was 52%, whereas it reduces to 36% when BMI content is 75 parts. In the case of DDS cured BMI-epoxy blends (Fig. 6), the onset temperature of polymerization was higher than that of DDM-cured blends. A similar pattern is observed from the TGA results. In the case of DDS, the onset temperature increases and the weight loss decreases with increase in BMI content in the blend. In the case of lower BMI content, catalyzation through the imide group is more predominant than is the extension reaction of BMI + DDS. The latter reaction plays a major part when BMI content goes to a 75

Table III TGA/DTG Analysis of Blends (DDM)

Composition	No. of Peak	Onset Temp (°C)	10% Loss in Weight (°C)	Inflection Temp (°C)	DTG (Maxima) (%/min)	Temp at End (°C)	% Weight Loss
Epoxy : DDM	1	383.0	390.0	395.5	21.20	423.0	75.60
BMI (100%)	1	487.8	492.5	496.9	21.20	513.0	42.97
Epoxy : BMI	1	239.0	345.0	262.8	1.50	317.5	8.60
(1 : 1)	2	332.5	—	369.7	6.50	465.0	37.06
	3	475.0	—	562.2	10.20	582.0	51.97
Epoxy : BMI : DDM	1	355.1	360.0	370.6	13.40	392.5	51.95
75% : 25% : 21%	2	470.0	—	537.2	6.50	585.8	45.98
Epoxy : BMI : DDM	1	356.0	375.0	373.6	8.30	395.0	39.23
50% : 50% : 14%	2	475.0	—	560.3	10.05	584.9	56.56
Epoxy : BMI : DDM	1	380.0	400.0	430.0	5.50	445.0	36.60
25% : 75% : 7%	2	472.5	—	611.1	6.80	652.2	60.11
BMI : DDM	1	376.8	416.0	419.2	2.40	464.0	19.53
(extended BMI)	2	470.0	—	541.3	7.60	587.0	33.65
	3	560.0	—	585.0	9.85	604.5	44.00

parts level. It is also seen that the weight loss between the onset to completion of a stage decreases with increase in the BMI content.

Dynamic Mechanical Analysis

The DMA plots of the storage modulus (G') as a function of temperature for DDM- and DDS-cured blends are shown in Figures 7 and 8, respectively.

Values of G' at temperatures from 100°C to about 300°C are shown in Table V. At 100°C, the epoxy-BMI blends cured by either DDM or DDS show higher G' than do pure epoxy cured with the respective hardeners. A similar trend is observed at 150°C, which is more predominant in the case of DDM-cured blends. It may be noticed that G' has fallen appreciably in the case of DDS blends. This behavior continues up to about 220°C, beyond which

Table IV TGA/DTG Analysis of Blends (DDS)

Composition	No. of Peak	Onset T (°C)	10% Loss in Weight (°C)	Inflection Temp (°C)	DTG (Maxima) (%/min)	Temp at End (°C)	% Weight Loss
Epoxy : DDS	1	287.0	362.5	335.5	00.6	—	03.04
	2	360.0	—	371.2	15.0	398.5	58.37
	3	442.0	—	514.3	05.4	545.0	33.77
BMI	1	487.0	492.5	496.9	21.2	513.0	42.97
Epoxy : BMI	1	239.8	345.0	262.8	01.5	305.0	08.60
(1 : 1)	2	332.5	—	389.7	06.5	465.0	37.06
	3	475.0	—	563.2	10.2	582.0	51.97
Epoxy : BMI : DDS	1	360.0	380.0	377.0	11.3	405.0	56.63
75% : 25% : 27%	2	470.0	—	533.9	06.2	576.7	42.31
Epoxy : BMI : DDS	1	299.3	365.0	323.0	07.4	445.0	37.73
50% : 50% : 18%	2	337.5	—	380.3	07.1	455.0	53.20
	3	472.5	—	552.9	04.4	582.3	25.06
Epoxy : BMI : DDS	1	366.8	400.0	409.2	04.4	455.0	25.06
25% : 75% : 9%	2	455.0	—	505.7	08.4	550.0	38.91
	3	550.0	—	596.7	06.9	624.5	34.97

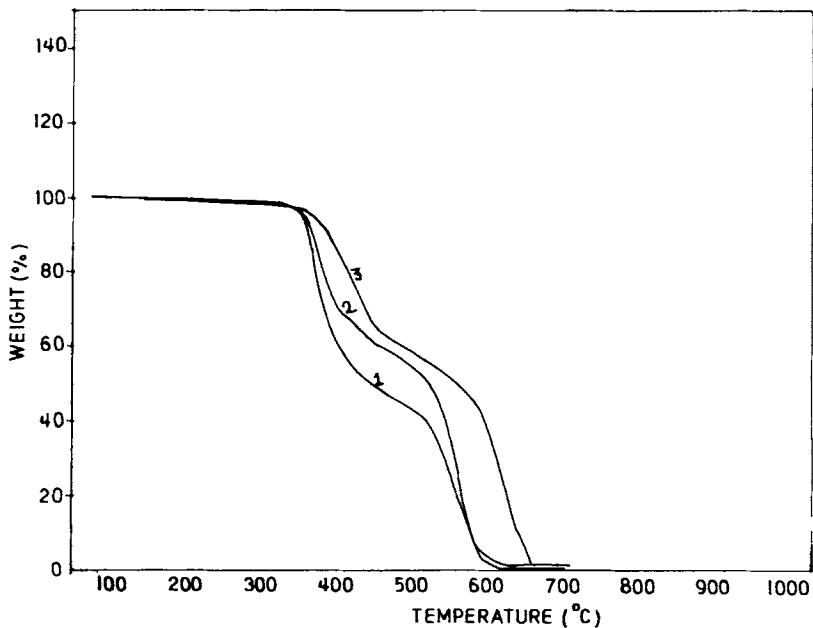


Figure 5 TGA curves for DDM cured epoxy : BMI blends: (1) 75 : 25; (2) 50 : 50; (3) 25 : 75.

G' values showed a gradual increase up to about 360°C in the case of the DDS system, whereas the increase was noticeable above 280°C for the DDM system. The increase may be due to residual cross-

linking that may be taking place under stress at elevated temperatures, as already discussed earlier regarding the DSC curves. The upward trend of G' up to 300°C indicates that the postcuring carried out

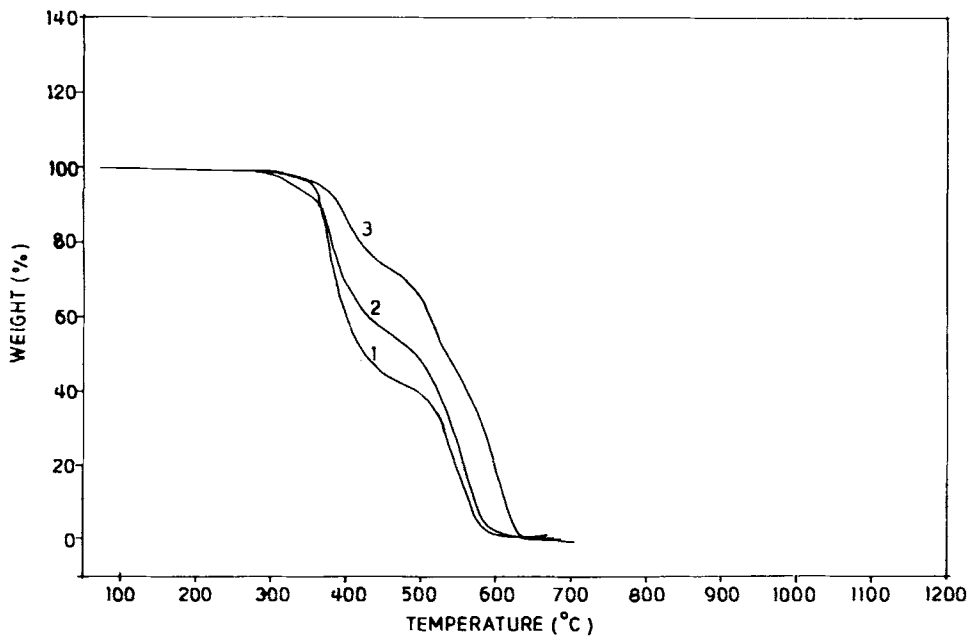


Figure 6 TGA curves for DDS cured epoxy : BMI blends: (1) 75 : 25; (2) 50 : 50; (3) 25 : 75.

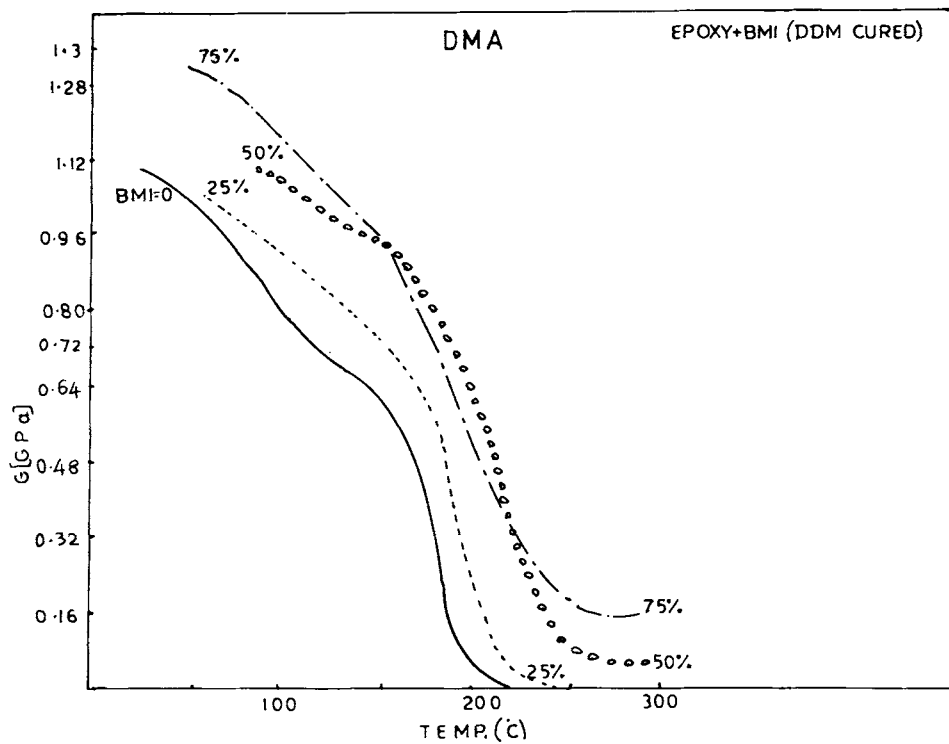


Figure 7 Shear modulus curves for epoxy and epoxy-BMI blends cured with DDM.

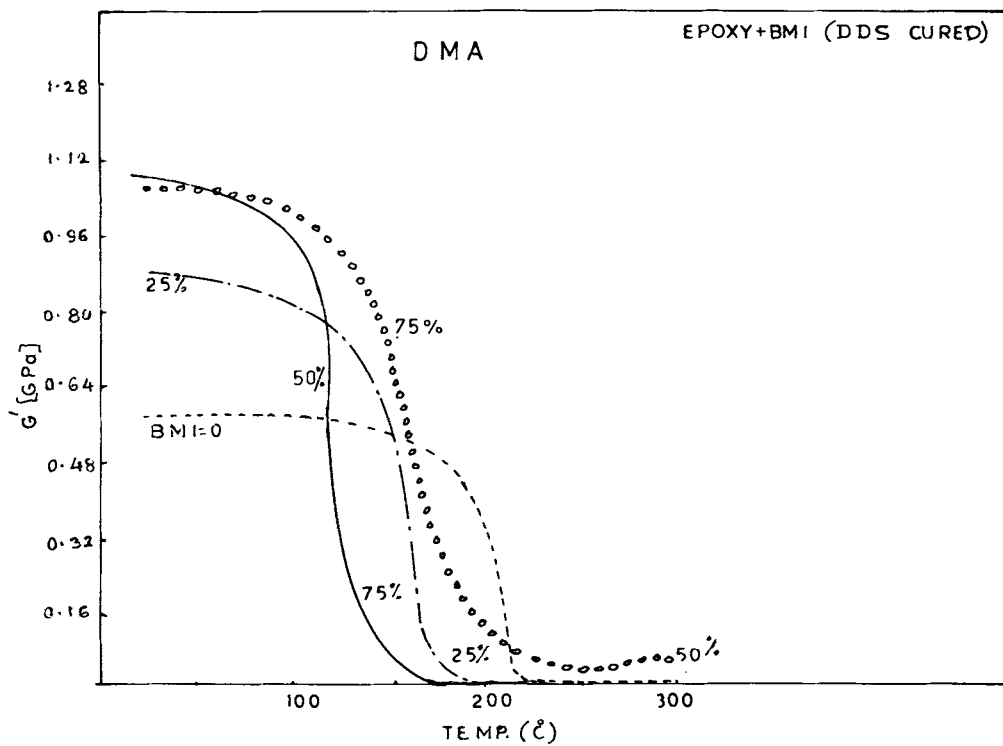


Figure 8 Shear modulus curves for epoxy and epoxy-BMI blends cured with DDS.

Table V DMA Data (Values in MPa)

	Temperature (°C)							
	100	150	200	220	240	260	280	290
EPOXY								
DGEBA : DDS	583.00	521.00	388.00	44.56	11.54	9.735	10.48	10.77
EPOXY								
DGEBA : BMI : DDS								
75 : 25 : 27	803.80	579.30	7.56	5.56	5.76	6.330	7.27	8.20
50 : 50 : 18	965.40	41.96	2.90	2.62	2.86	3.610	5.84	8.49
25 : 75 : 9	1008.00	718.80	124.70	73.14	46.57	37.270	46.20	60.90
EPOXY								
DGEBA : BMI : DDM	805.00	624.00	39.00	20.00	18.40	—	—	—
EPOXY								
DGEBA : BMI : DDM								
75 : 25 : 21	888.33	761.00	247.00	48.50	19.60	11.000	11.00	18.00
50 : 50 : 13.5	1071.60	946.00	635.00	357.00	154.00	75.000	57.00	58.00
25 : 75 : 6.75	1174.00	963.00	534.00	344.00	224.00	169.000	168.00	189.00

was insufficient and that it is imperative to investigate the effect of postcuring on the modulus, particularly for the DDS blends.

The loss tangent ($\tan \delta$) is the ratio between the shear loss modulus (G'') and the storage modulus (G'). It is related to the damping characteristics of

the material. The peak height expresses the ability of the material to dissipate energy as heat during the deformation cycle. Figure 9 shows the $\tan \delta$ curves for the DDM- and DDS-cured epoxy + BMI blends. It may be seen that the epoxy and epoxy + BMI blends cured with DDS show higher $\tan \delta$

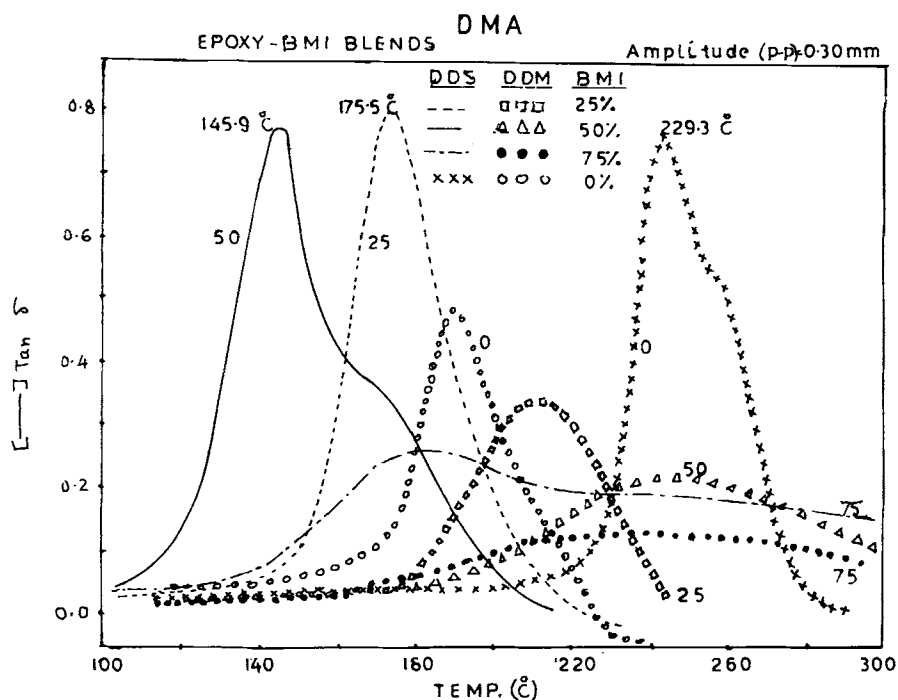


Figure 9 Tan δ curves for epoxy-BMI blends cured with (----) DDM and (—) DDS.

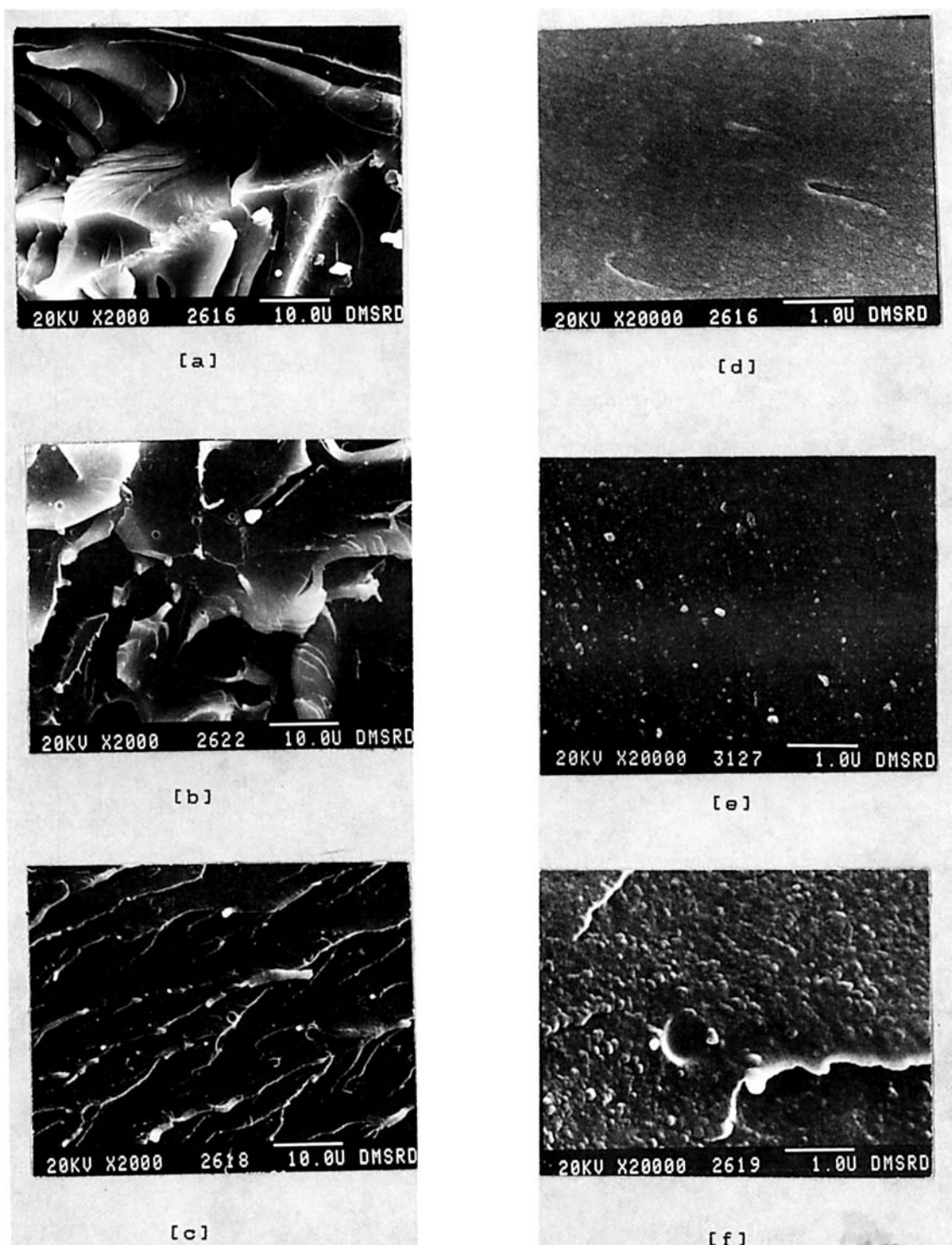


Figure 10 Scanning electron micrographs of fractured surfaces of DDM cured epoxy-BMI blends: (a) and (d) 75% epoxy; (b) and (e) 50% epoxy; (c) and (f) 25% epoxy.

values in the case of the epoxy blends with BMI content of 75% and 50% compared to the epoxy and blends cured with DDM. This indicates that the

DDS-cured blends are more flexible than are the DDM-cured ones.¹¹ In reacting epoxy resins with DDS, the addition ultimately leads to tertiary amine

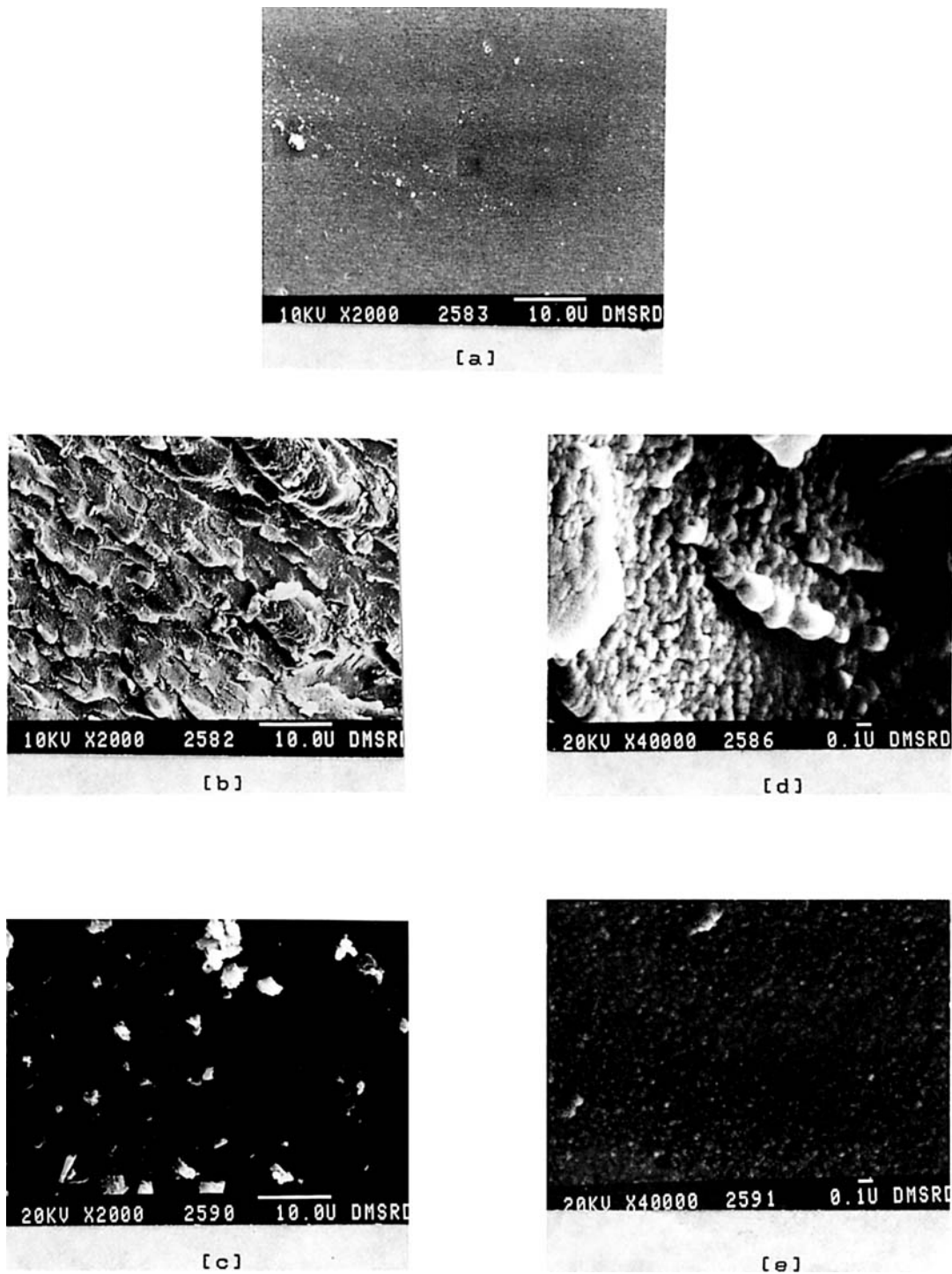


Figure 11 Scanning electron micrographs of fractured surfaces of DDS cured epoxy-BMI blends: (a) 75% epoxy; (b) and (d) 50% epoxy; (c) and (e) 25% epoxy.

formation. At elevated temperatures, this tertiary amine activates epoxy-epoxy homopolymerization that forms etherial bonds and ultimately leads to

flexibility in the structure.¹² When BMI content is only 25%, the loss $\tan \delta$ curve is sharp and clear, whereas the curve shows a small hump on the high-

temperature side for the blend with 50% BMI, which widens further for the blend with 75% BMI. The above behavior may be due to delayed residual cross-linking reactions that may be taking place. DDM-cured blends have lower $\tan \delta$ values than those of the DDS-cured blends, indicative of the higher cross-link density of the structure in the former case. A broad $\tan \delta$ peak suggests the possibility of more than one phase present in the system, and this aspect is discussed further in the following section.

Scanning Electron Microscopy

The SEM micrographs of the fracture surface of epoxy-BMI blends cured with DDM and DDS are shown in Figures 10 and 11, respectively. All the figures ($\times 2000$) show that the fracture surfaces are similar and do not show phase domains of two components, suggesting the formation of homogeneous compounds.

However, high magnification ($\times 20,000$ to $\times 40,000$) SEM micrographs shown in Figure 10(d)–(f) and Figure 11(d)–(e) for DDM and DDS, respectively, reveal uniformly distributed globules as a second phase in 50/50 and 25/75 (epoxy/BMI) blends cured with DDS and also for the 25/75 (epoxy/BMI) blend cured with DDM.

The chemistry of mixing of the epoxy and BMI has shown that an adduct of epoxy-BMI is formed. Extended BMI also forms due to the reaction of amines with BMI. These two fractions are of high molecular weight and, hence, have low cross-link density. They may appear as globules due to their higher gelation time as compared to epoxy or BMI. The size of the globules may again depend on the gelation time and the quantity of high molecular fraction present in the structure. Since DDM reacts faster with epoxy than does DDS and also since it forms a faster extension reaction with BMI, sufficient time for phase separation is not readily available with DDM-cured blends of 25 and 50% BMI content. The globular phase is seen only in blends with 75% BMI [Fig. 10(f)]. Woo et al.,⁵ observed that a homogeneous intercross-linked network of epoxide and BMI blends exhibits a sharp $\tan \delta$ peak. The sharpness of the peak also indicates that the phase domains, if present, are smaller than the size of the segments that are responsible for the primary molecular relaxation. Whereas such a sharp peak is observed for the blend with 25% BMI, for the 50% BMI, the blend shows a slightly broader peak, suggesting the possibility of a second-phase formation. SEM photographs [Fig. 10(d) and (e)] do not show

any appreciable globular features for these two cases. The cure of the compositions involves a number of reactions mentioned earlier. A broad and shallow $\tan \delta$ curve for any composition, while indicating the formation of a highly cross-linked material, also suggests that the network is heterogeneous and more than one network may form.¹³ During the cure, when enough chemical species are available, the entropy contribution to the free energy of mixing decreases. As a result, phase separation tends to increase. But the formation of the cross-links in the components that cured first may counteract that trend and may not allow the second phase to grow very large in size. Thus, for the blend with 75% BMI (DDM system) for which the $\tan \delta$ peak is shallow and very broad, globules are seen in the range of 0.01 to 0.2 μ and uniformly distributed in the blend material [Fig. 10(f)]. It may be noticed that the $\tan \delta$ curve [Fig. 9] for this composition is very broad.

In the case of DDS-cured blends, the 25% BMI blend yields a well-defined $\tan \delta$ curve with SEM showing no phase separation [Fig. 11(a)]. A broad $\tan \delta$ curve for 50% BMI and also large $\tan \delta$ value suggests that possibility of the presence of a larger second phase. The SEM photograph shown in Figure 11(d) supports the above DMA result. For the 75% BMI blend case, it is seen that the $\tan \delta$ curve has been reduced in magnitude and also has become very broad. This suggests that cross-link density is higher than for the 25% and 50% BMI blends and, hence, the globular phase is limited to a small size. The SEM photograph of Figure 11(e) shows the globular phase of about 0.05 μ uniformly distributed in the matrix.

For both the amines DDM and DDS, the composition of epoxy-25% + BMI-75% yields very small globules uniformly distributed throughout the sample. Since BMI is more dominant in these compositions, it is likely that the BMI adduct is formed in a large quantity due to the amic acid fraction and also to the amine added for extended BMI. Hence, the composition will have both fractions, namely, the epoxy-BMI adduct and the extended BMI in large quantity, which may appear as globules when the composition cures fully.

CONCLUSION

From the above experiments, it is clear that good SINs structures were formed when BMI and epoxy mix were cured with aromatic amines. SEM revealed homogeneity in the networks formed at lower mag-

nifications. But at higher magnifications, uniform microcellular structure formation is seen in blends with higher BMI content. These microglobules will perhaps enhance the mechanical properties. Further work is in progress to correlate the above two properties.

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REFERENCES

1. C. E. Browning, *Polym. Eng. Sci.*, **18**, 16 (1988).
2. C. E. Browning, G. E. Husman, and J. M. Whitney, Composite Materials: Testing Design (Fourth Conference) ASTM STP 617,487 1977.
3. J. C. Spitsbirgen, P. Lowenwrigket, C. Bluzstin, J. Sugarman, and W. L. Lauze, in *Proceedings of the 26th Annual Technical Conference on RP/comps.*, Inst SPI New York, 1971 Section 19-c.
4. S. L. Kaplan, E. L. Mitch, and A. Kazakian, in *Proceedings of the 30th Annual Technical Conference on RP/comps.*, Inst SPI New York, 1975, Section 19.A.
5. E. M. Woo, L. B. Chen, and J. C. Seferis, *J. Mater. Sci.*, **22**, 3665 (1987).
6. R. N. Gounder, J. T. Geary, U.S. Pat. 4,366,302 (1982); *Chem. Abst.*, **98**, 90559 (1983).
7. C. J. Lee, U.S. Pat. 4,487,894 (1984).
8. H. D. Stenzenberger, M. Herzog, W. Romer, R. Scheiblich, and N. J. Reeves, *Br. Polym. J.*, **15**, 2-12 (1983).
9. S. Nishi, S. Saskai, and Y. Hasuda, *Polym. Prepr.*, **28**, 2 (1987).
10. I. K. Verma, S. P. Gupta, and D. S. Verma, *J. Appl. Polym. Sci.*, **333**, 151 (1987).
11. P. I. Engelberg and G. C. Tesoro, *Polym. Eng. Sci.*, **30**, 303 (1990).
12. C. C. Riccardi and R. J. J. Williams, *J. Appl. Polym. Sci.*, **32**, 3445 (1986).
13. K. R. Carduner and M. S. Chattha, *Polym. Mater. Sci. Eng.*, **56**, 660 (1987).

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