

Allylamine-Adducted Bismaleimide Resins. II. Their Physical/Mechanical Properties and Morphology

KING-FU LIN* and JIN-SING LIN

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10764, R.O.C.

SYNOPSIS

Physical/mechanical properties of various cured allylamine-adducted bismaleimides (A-BMI), such as allylamine-adducted 4,4'-bismaleimidodiphenylmethane (A-BDM), and allylamine-adducted 4,4'-bismaleimidodiphenylether (A-BDE) were investigated and correlated to their morphology. In the previous study, two types of the curing reactions were found: one is the homopolymerization through the opening of double bonds in the maleimide groups and the other is the reactions between allyl groups and benzene rings. Dynamic mechanical analysis and scanning electron microscopy of cured A-BMI indicate that the network produced by homopolymerization is immiscible with that produced by the other reactions. The glass-transition temperature (T_g) of the former network is lower than that of the latter. In addition, the 50%A-BDM prepared by reacting BDM with 50 mol % allylamine has the optimal physical/mechanical properties after cure, such as the highest T_g and the highest flexural strength and modulus among the A-BDM. Moreover, the decomposition temperature of 50%A-BDM is 450°C, only about 40°C lower than that of the pure BDM. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The cured bismaleimides (BMI) are extremely brittle because of the highly cross-linked structure. To improve their toughness and processability, the cross-linking density of BMI was reduced by using the diamine as a chain extender through the Michael addition.¹⁻⁵ However, the chain extension usually induced the side effects on the properties of cured BMI, such as poor thermal stability.¹ The other excellent approach⁶ was to use the *o,o'*-diallylbisphenol A as a toughening agent for 4,4'-bismaleimidodiphenylmethane (BDM) resin, which not only improves the toughness and processability of BDM but can also still maintain its great thermal stability. The reaction between *o,o'*-diallylbisphenol A and BDM was suggested as through the "ene" reaction and Diels-Alder reaction between the ally groups and maleimide groups.⁷

Nevertheless, to further upgrade the BDM resins for composite application, two processing problems

remain to be overcome. One is that BDM is a crystalline solid with a melting point close to the initial cure temperature of the BDM-*o,o'*-diallylbisphenol A mixture.⁸ It often incurs partial curing during the preparation of a hot melt resin system. The other is that BDM tends to recrystallize from the mixture during ageing.⁹ As a result, the hot melt-type BDM-*o,o'*-diallylbisphenol A mixture often showed inconsistent properties.

Allylamine contains both an amine group and an allyl group and can react with BMI through the Michael addition and the reaction between allyl groups and benzene rings as well.¹⁰ A series of allylamine-adducted BMI (A-BMI), such as allylamine-adducted BDM (A-BDM) and allylamine-adducted 4,4'-bismaleimidodiphenylether (A-BDE), were prepared by reacting BMI with various molar ratios of allylamine to reduce the crystallinity of BMI, to improve the toughness of its cured resin, and to maintain its great thermal stability. In the first part of this study,¹⁰ two types of curing reactions for the A-BMI resins were found: the homopolymerization of A-BMI resins through opening of the residual double bonds in maleimide groups and the reactions between allyl groups and benzene rings

* To whom correspondence should be addressed.

in the BMI portion. In the second part of the study, we found that the domains produced from different types of curing reactions were immiscible. Therefore, the physical/mechanical properties of cured A-BMI resins were investigated in terms of their inhomogeneous morphology.

EXPERIMENTAL

Sample Preparation

The A-BMI samples, such as A-BDM and A-BDE prepared by reacting BMI with various molar ratios of allylamine, are listed in Table I. A detailed description of the preparation method was given in the first part of the study.¹⁰ Curing of the A-BMI samples was conducted in a hot press by the following cure cycle: 2 h at 180°C plus 5 h at 220°C under 1.38×10^7 Pa pressure.

Analytical Techniques

The flexural properties of cured A-BMI were measured by the three-point bending test according to ASTM D-790. The support span for the three-point bending test is 4 cm. Tests were performed in an Instron TM tensile tester at a crosshead speed of 0.5 cm min⁻¹.

Dynamic mechanical analysis (DMA) of cured A-BMI was performed in a DuPont model 983 DMA. Tests were run at a heating rate of 10°C min⁻¹.

The surface morphology of cured A-BMI was investigated by scanning electron microscopy (SEM). The fresh surfaces were made by fracturing the specimens immediately after they were quenched in liquid nitrogen. The fractured surfaces were gold-

sputtered and investigated in a JEOL JWM-5200 model SEM.

Thermogravimetric analysis (TGA) of the BMI and A-BMI was conducted in a Perkin Elmer TGA-2 model thermogravimetric analyzer by heating from 50 to 800°C at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties and Morphology

Dynamic mechanical analysis of the cured A-BMI was studied first. A broad glass-transition temperature (T_g) peak at 186°C was found in the loss modulus curve of cured 10%A-BDM [Figure 1(a)]. In addition, a β relaxation peak was found at -62°C. As the amount of allylamine was increased to 50 mol % for preparing the 50%A-BDM, the T_g peak was shifted from 186 to 330°C as shown in Figure 1(b). The intensity of the β relaxation peak was substantially increased and a small additional peak appeared at 127°C.

For the 10%A-BDM cured mainly by homopolymerization through the opening of double bonds in maleimide groups,¹⁰ the broad T_g peak should be contributed by the α relaxation of the homopolymerized network. Because of the fact that the amount of double bonds in 50%A-BDM is less than in 10%A-BDM, the molecular weight of the homopolymerized network in the former resin would be smaller than in the latter, indicating that the small additional relaxation peak found at 127°C is contributed mainly by the homopolymerized network. In that case, because only two types of reactions, homopolymerization and the reactions between allyl groups and benzene rings, were found during cure of the A-BMI,¹⁰ the T_g peak at 330°C should be associated with the network produced by the latter reaction.

The DMA results of cured A-BDE shown in Figure 2(a,b) are, in general, similar to those of cured A-BDM. However, the T_g of cured 50%A-BDE is 340°C, higher than that of the cured 50%A-BDM. The intensity of the additional peak contributed by the homopolymerized network in the cured 50%A-BDE is also higher than its counterpart in the cured 50%A-BDM, implying that the former resin has higher content of the domains contributed by the homopolymerized network than the latter. Thus, based on the DMA results, both cured 50%A-BDE and 50%A-BDM should have the inhomogeneous structure where the homopolymerized network and the network produced by the reaction between allyl groups and benzene rings are immiscible. To provide

Table I A-BMI Samples Prepared by Reacting BMI With Various Molar Ratios of Allylamine

Allylamine (mol%)*	A-BMI	
	% A-BDM	% A-BDE
10	10	10
50	50	50
100	100	100
150	150	150
200	200	200

* The molar percentage is calculated by dividing the moles of allylamine by the moles of BMI.

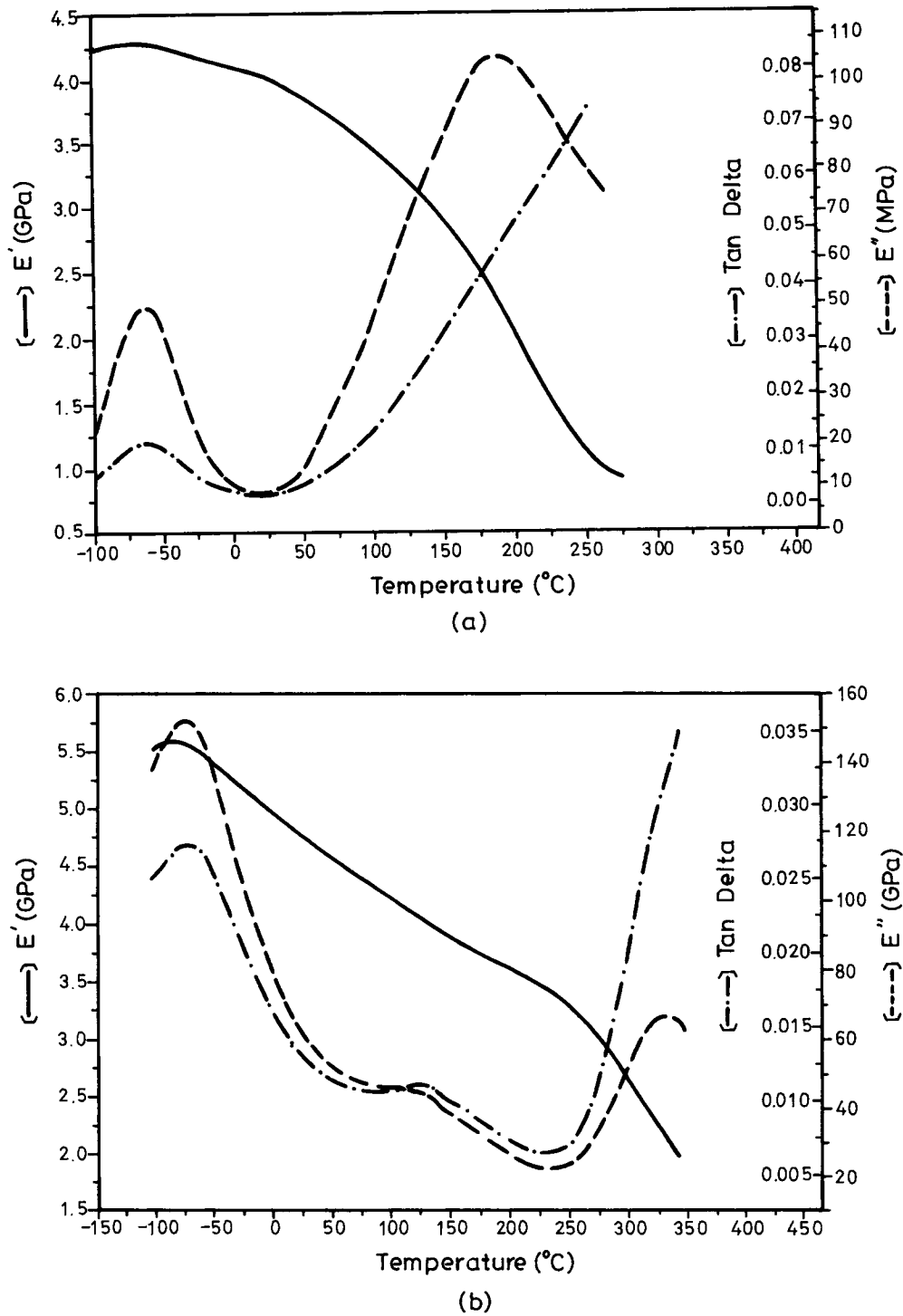


Figure 1 Dynamic mechanical spectra of the cured (a) 10%A-BDM and (b) 50%A-BDM.

the direct evidence for the inhomogeneous structure, we employed SEM to investigate their fracture surface.

The fracture surface of both cured 10%A-BDM

and 10%A-BDE shows a homogeneous structure as seen in Figures 3(a) and 4(a) which is consistent with the DMA results. As the amount of allylamine was increased to 50 mol %, the fracture surface of

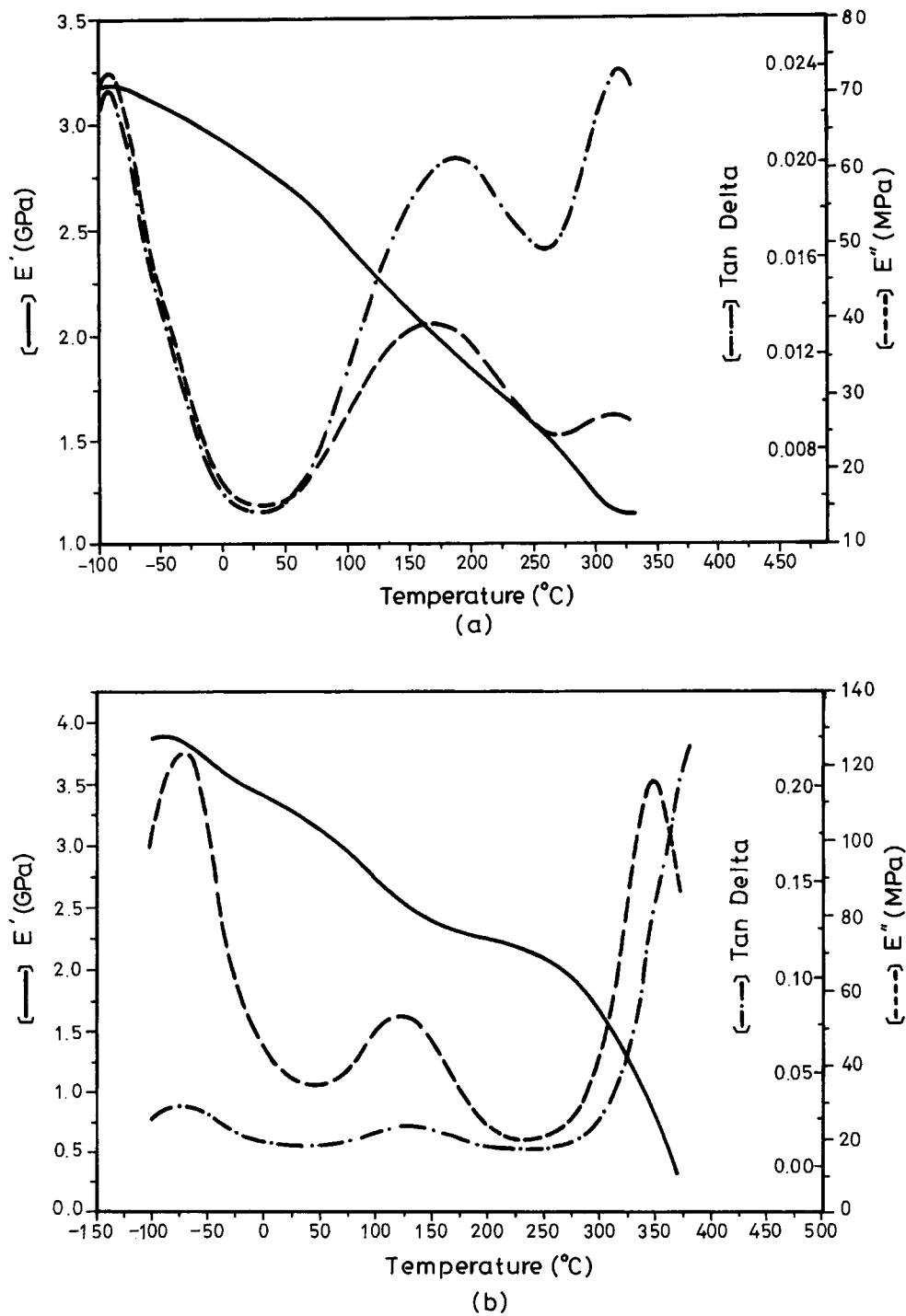
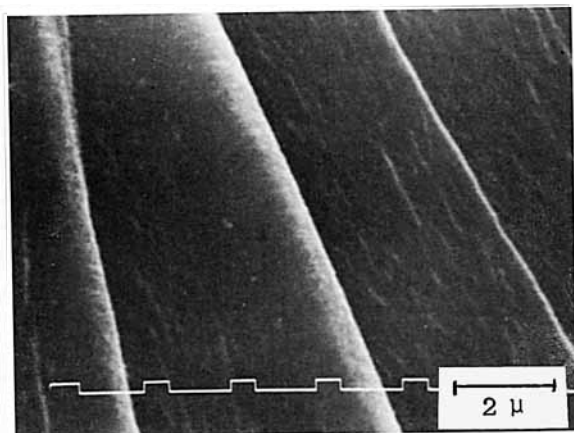


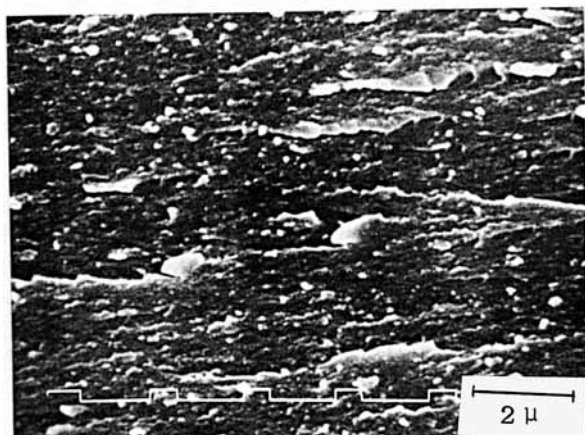
Figure 2 Dynamic mechanical spectra of the cured (a) 10%A-BDE and (b) 50%A-BDE.

cured 50%A-BDM shows only roughness instead of two-phase morphology as seen in Figure 3(b), whereas the fracture surface of cured 50%A-BDE shows a clear two-phase morphology with a dispersed phase in a size range of 1–40 μm as seen in Figure 4(b). Two-phase morphology found in the

cured 50%A-BDE instead of the cured 50%A-BDM might be due to the fact that the molecular chains containing ether groups in the former resin are more flexible than those containing $-\text{CH}_2-$ groups in the latter, leading to the higher mobility of the molecular chains for phase separation.



(a)

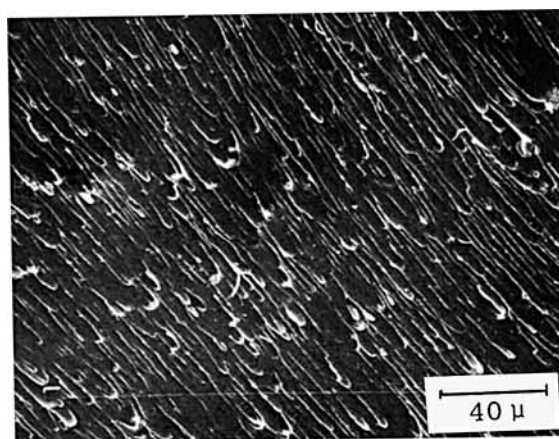


(b)

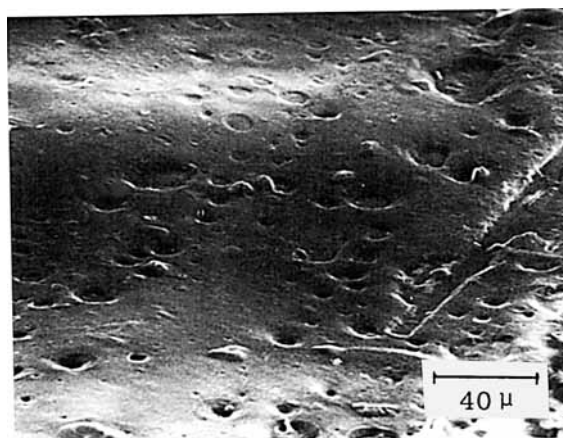
Figure 3 SEM photographs of the cured (a) 10%A-BDM and (b) 50%A-BDM.

Figure 5 shows the T_g of cured A-BDM and A-BDE measured from the loss modulus curve as a function of the molar ratio of allylamine used for monomer preparation. In general, the trend of change in T_g is similar between the cured A-BDM and A-BDE. It reached the maximum as the molar ratio of allylamine reached 50 mol % and then the T_g decreased. The initial increase in T_g came from the higher T_g of the network produced by the reaction between allyl groups and benzene rings compared to the homopolymerized network. As the molar ratio of allylamine was over 50 mol %, the decrease in T_g might be due to the fact that more aliphatic chain segments are introduced into the cured network.

In addition, the β relaxation peak appeared at -100 to -50°C range as shown in Figures 1(a,b) and 2(a,b), is associated with the local molecular motions in the glassy state.¹¹ However, the exact type of molecular motion is not clear. The intensity of the β relaxation peak in the loss modulus curve of cured A-BDM and A-BDE as a function of the molar ratio of allylamine used to prepare their monomers is shown in Figure 6. The highest intensity of β peak was found in the cured 50%A-BDM and 50%A-BDE specimens, respectively. It was indicated that nearly all glassy polymers with high impact strength have prominent β relaxation,¹² sug-



(a)



(b)

Figure 4 SEM photographs of the cured (a) 10%A-BDE and (b) 50%A-BDE.

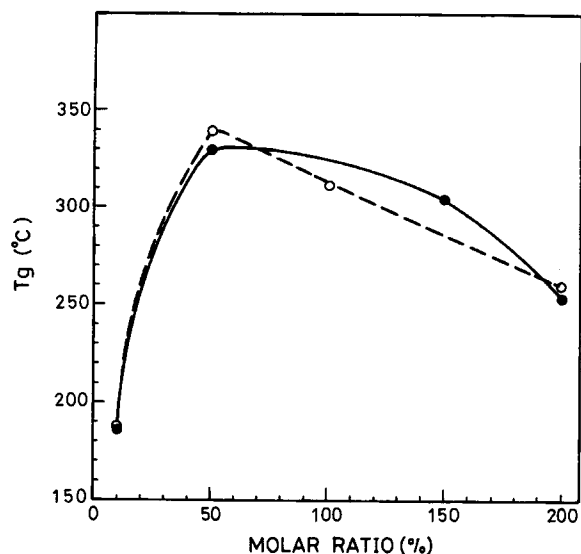


Figure 5 T_g of the cured (●) A-BDM and (○) A-BDE as a function of the molar ratio of allylamine used for monomer preparation.

gesting that the toughness of cured 50%A-BDM and 50%A-BDE might be the highest among all the cured A-BDM and A-BDE samples. The detailed discussion on the mechanical properties of cured A-BMI is provided in the following section.

Mechanical Properties and Decomposition Temperature

The change in flexural strength of the cured A-BDM and A-BDE as a function of molar ratio of allylamine used to prepare the monomers shown in Figure 7, is almost parallel to the change in the intensity of β peak as seen in Figure 6. The unmodified BDM and BDE after cure were too brittle to measure the flexural strength. When they were modified by reacting with 10 mol % allylamine, although the flexural strength of cured 10%A-BDM and 10%A-BDE could be measured, they were still brittle. Presumably, the cross-linking density provided by homopolymerization through opening of the double bonds is rather high. A significant increase in flexural strength was found as 50 mol % allylamine was used to modify the BDM and BDE. It might be due to the fact that large amounts of the double bonds have been opened by allylamine so that the cross-linking density provided by homopolymerization is reduced. Besides, the flexural strength of cured 50%A-BDE is higher than that of the cured 50%A-BDM. When the amount of allylamine used was over 50 mol %, the flexural strength of both cured A-BDE and A-BDM

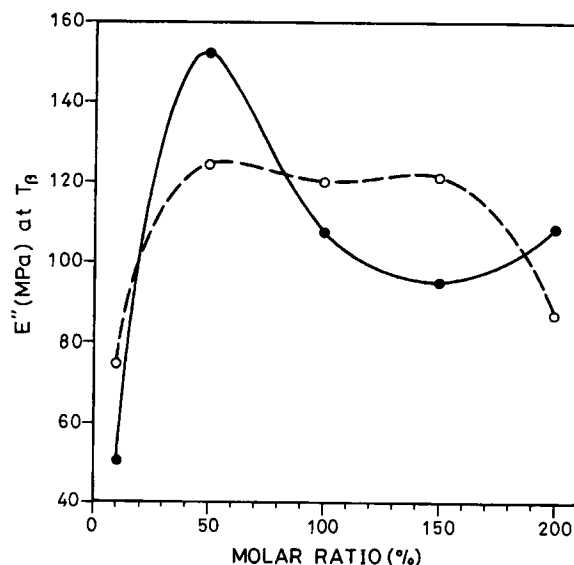


Figure 6 Intensity of β relaxation peak of the cured (●) A-BDM and (○) A-BDE as a function of the molar ratio of allylamine used for monomer preparation.

was decreased and their morphology turned to a single phase mainly contributed by the reaction between allyl groups and benzene rings. Thus, the highest flexural strength of cured 50%A-BDM and 50%A-BDE among the cured A-BDM and A-BDE resins, respectively, might be attributed to their two-phase morphology.

Furthermore, although the flexural strength of

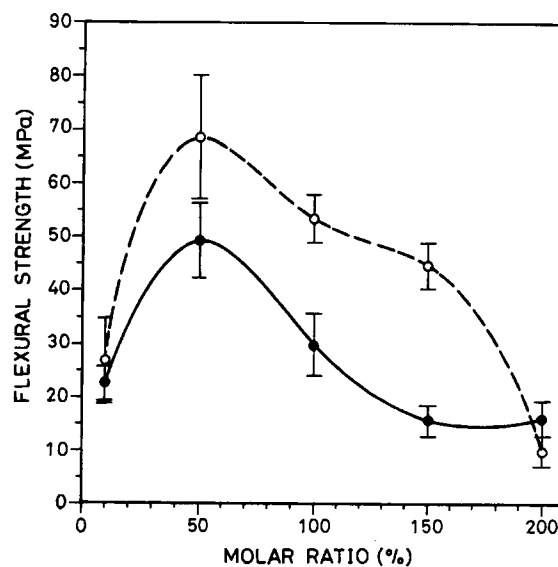


Figure 7 Flexural strength of the cured (●) A-BDM and (○) A-BDE as a function of the molar ratio of allylamine used for monomer preparation.

cured A-BDM and A-BDE is roughly parallel to the change in the intensity of β peak (Figs. 6, 7), the correlation between the flexural strength and the intensity of the β peak is not clear. However, it was indicated that some type of β relaxation appears to decrease notch sensitivity so that the polymer is able to sustain tensile loads.¹² It was also reported that as the intensity of the β peak is increased for the impact-modified polypropylene, its drop weight impact value is also increased, suggesting that a suitable calibration curve can be developed to predict the toughness by the intensity of the β peak.¹³

The change in flexural modulus of cured A-BDM and A-BDE as a function of molar ratio of allylamine used to prepare the monomers is shown in Figure 8. For the cured A-BDM, the highest flexural modulus was found in the cured 50%A-BDM. However, for the A-BDE, the highest flexural modulus was found in the cured 10%A-BDE. The modulus of polymeric materials in the rubbery and leathery states is directly related to the cross-linking density. However, in the glassy state, the resins are frozen to glass so that the cooperative motions of chain segments are prohibited.¹⁴ Consequently, the modulus is measured in the elastic region where the Van Der Waals attraction among the chain segments was affected. Thus, the modulus is not directly related to the cross-linking density but dependent on the packing density or concentration of the chain segments in the glassy state. For the cured A-BDM, the maxi-

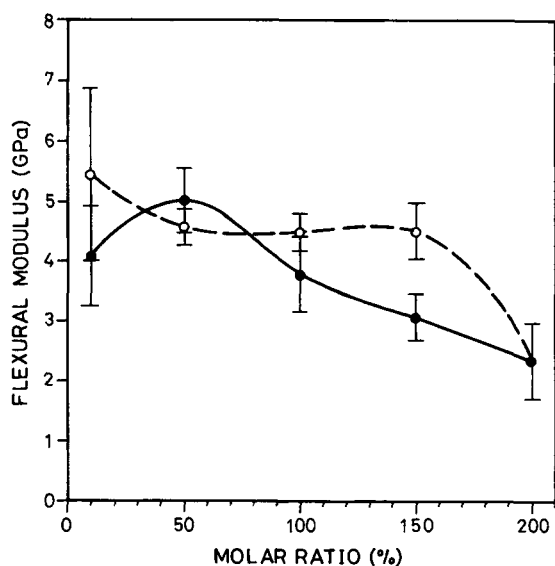


Figure 8 Flexural modulus of the cured (●) A-BDM and (○) A-BDE as a function of the molar ratio of allylamine used for monomer preparation.

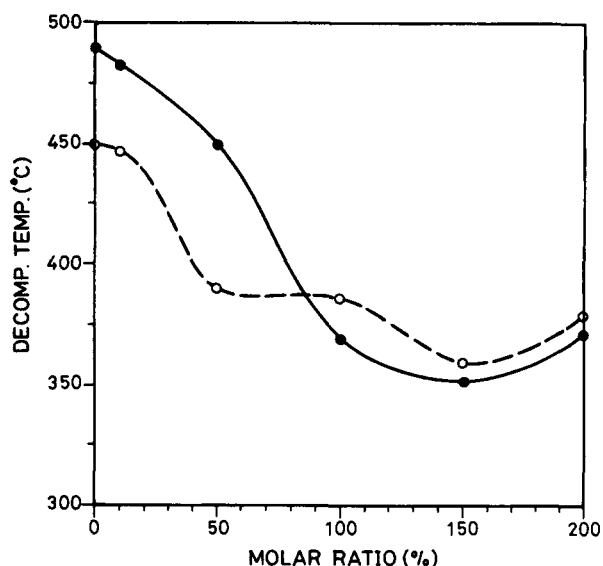


Figure 9 Degradation temperature of (●) A-BDM and (○) A-BDE as a function of the molar ratio of allylamine to react with BDM and BDE, respectively.

imum flexural modulus found in the cured 50%A-BDM might be due to the fact that the network produced by homopolymerization and that produced by the reactions between allyl groups and benzene rings are more compatible and might interpenetrate with each other, resulting in the increase in packing density of the molecular segments in view of less phase separation compared to the cured 50%A-BDE.

The degradation temperature (T_d) of BDM, A-BDM, BDE, and A-BDE at the 5 wt % loss of materials measured by the thermogravimetric analysis is shown in Figure 9. The T_d of pure BDM is 490°C with 50 wt % char yield at 800°C. When it was modified by 50 mol % allylamine, the T_d only dropped to 450°C. But with a further increase of the amount of allylamine to 100 mol %, the T_d dropped to 369°C with 48 wt % char yield. On the other hand, the T_d of pure BDE is 450°C with the same char yield as BDM at 800°C. When it was modified by 50 mol % allylamine, the T_d dropped at 390°C with the char yield maintained at 50 wt %. With a further increase in the amount of allylamine, the T_d was not significantly changed. In summary, the T_d of A-BDM was substantially decreased as the amount of allylamine was increased from 50 to 100 mol % and then leveled off; whereas the substantial decrease in T_d of the A-BDE took place earlier. However, the char yield for both A-BDM and A-BDE was only slightly changed by increasing the amount of allylamine.

Finally, according to the experimental results, the

cured 50%A-BDM not only has the highest T_g and the highest flexural strength and modulus among the cured A-BDM, but it still has high degradation temperature. In addition, its processability is better than that of the unmodified BDM in view of the low crystallinity and melting point.¹⁰ Thus, its application to the composite materials as a resin matrix is promising and will be studied in the near future.

CONCLUSIONS

During cure of the A-BDM and A-BDE, the network produced by homopolymerization through the opening of double bonds in maleimide groups is immiscible with that produced by the reactions between the allyl groups and benzene rings. Due to the fact that the former network has much higher T_g than the latter, the T_g of cured BDM and BDE was significantly increased by the presence of the network produced by the latter reactions. Among the cured A-BDM, the cured 50%A-BDM has the optimal physical/mechanical properties, such as the highest T_g , the highest intensity of β relaxation, the highest flexural strength and modulus, and still has high degradation temperature. On the other hand, although the T_g , the intensity of β relaxation, and flexural strength of cured 50%A-BDE are the highest among the cured A-BDE, its degradation temperature is rather low.

Financial support of this work by the National Science Council in Taiwan, R.O.C., through Grant NSC81-0405-E002-09 is gratefully acknowledged.

REFERENCES

1. J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1185 (1973).
2. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Polym. Chem. Ed.*, **20**, 283 (1982).
3. D. K. Kumar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 245 (1983).
4. I. K. Varma, Sangita, and D. S. Varma, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1419 (1984).
5. C. D. Giulio, M. Gautier, and B. Jasse, *J. Appl. Polym. Sci.*, **29**, 1771 (1984).
6. J. King, M. Chaudhari, and S. Zahir, *Proceedings of the 29th National SAMPE Conference*, **29**, 392 (1984).
7. M. Chaudhari, T. Galvin, and J. King, *SAMPE J.*, **21**, 17 (1985).
8. J. Mijovic and B. Schafran, *SAMPE J.*, **26**, 51 (1990).
9. H. D. Stenzerberger, W. Roemer, M. Herzog, S. Pierce, M. Canning, and K. Fear, *31st Intl. SAMPE Symp.*, 920 (1986).
10. K.-F. Lin and J.-S. Lin, to appear.
11. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley, New York, 1980, p. 437.
12. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Vol. 1, Marcel Dekker, New York, 1974, p. 215.
13. R. Hassel, private communication.
14. P. Meares, *Polymers: Structure and Bulk Properties*, Van Nostrand, Princeton, New Jersey, 1965, p. 251.

Received December 21, 1992

Accepted July 1, 1993