

Novel Effect of Barbituric Acid on Glass Transition Temperature of Bismaleimide–Epoxy Resin Systems

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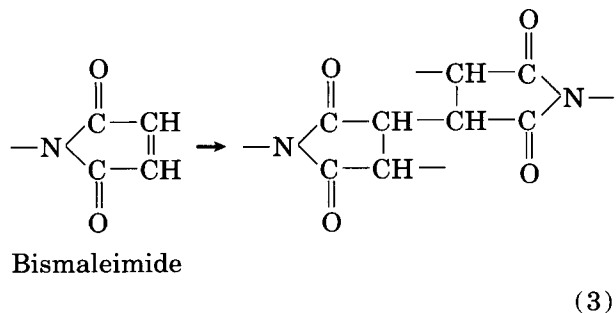
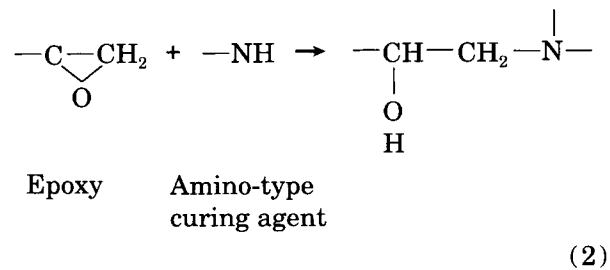
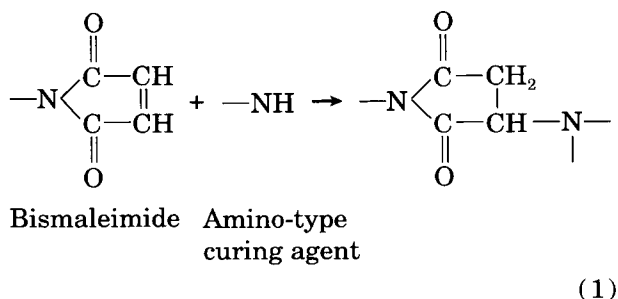
SYNOPSIS

Barbituric acid (BTA) has a novel influence on glass transition temperature (T_g) of bismaleimide (BMI)–epoxy resin systems. It causes the T_g of a BMI–epoxy resin system to rise significantly. The BTA's influence on T_g was investigated by changing the molar ratio of the reactants. In addition, the influence of benzoperoxide (BPO) on T_g was compared with that of BTA. The reaction selectivity of BTA and diamino-diphenyl sulfone (DDS) toward BMI and epoxy individually in the BMI–epoxy blended systems were studied using the DSC and GPC. By controlling the amount of DDS and BTA, epoxy and BMI could form intercrosslinking networks.

INTRODUCTION

Bismaleimides (BMIs) obtain good physical properties such as high T_g and high thermal stability, but cured BMI resins generally are very brittle.¹ Epoxies, in contrast, are much tougher, but their thermal stability and T_g are not good. Theoretically, blending them will create a high-performance resin system.² Unfortunately, the T_g of such blends has been much lower than that of a pure BMI resin system.

When a BMI–epoxy resin system is cured with an amine-type curing agent, several reactions may occur, as expressed in the following equations³:



The priority of these reactions depends on the reactants themselves, their molar ratio, and the temperature.

In our study 4,4'-diphenyl-methyl-bismaleimide was first reacted with barbituric acid. Next, epoxy (from Dow Chemical DER 331) and amine-type curing agents were added in various ratios. The T_g of the cured resin systems were measured using torsional braid analysis (TBA).

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Table I Chemical Structures of the Regents Used in Study

Chemical Name	Chemical Structure	Abbreviation
<i>N,N'</i> -Bismaleimide-4,4'-diphenyl methane		BMI
Barbituric acid		BTA
4,4'-Diamino diphenyl sulphone		DDS
4,4'-Diamino diphenyl ether		DDPE
Dicyandiamide		DICY

EXPERIMENTAL

Reagents

The chemical structures of the reagents used in this study were listed in Table I. *N,N'*-bismaleimide-4,4'-diphenyl methane (BMI, from MITSUI TOATSU CHEMICAL) was used as the BMI component and was recrystallized prior to use.

Bisphenol-A-type epoxy from Dow Chemical (DER 331) was used as the epoxy component. The barbituric acid (BTA), benzoperoxide (BPO), and amine-curing agents from Merck were used as received. The solvent for formulation was *r*-butyrolactone (Merck), which was dried with anhydrous calcium sulfate and fractionally distilled before using.

Preparation of BMI-Epoxy Resin System

BTA Included Resin System

Into a 250-mL three-necked flask fitted with a paddle stirrer, thermometer, and nitrogen inlet were added 0.1 mol BMI, various amounts of BTA, and

60 g *r*-butyrolactone. The mixture was reacted at 120°C for 0.5 h. Next, epoxy and amine curing agents were added in different molar ratios of BMI-epoxy such as 1/3, 1.5/3, and 2.143/3 at 80°C for more 0.5 h. Special effort was made to control the moles of the DDS and BTA since T_g is influenced by them.

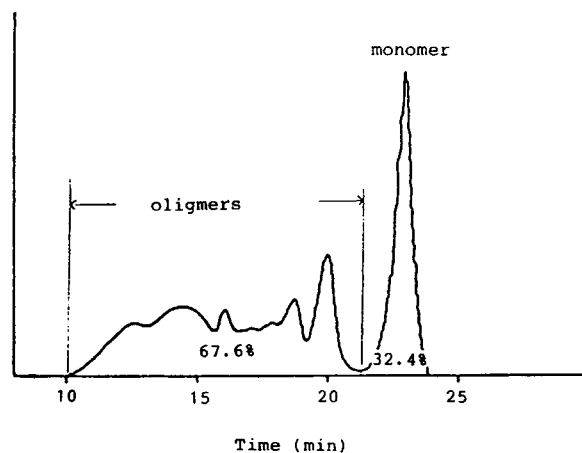


Figure 1 GPC chromatogram for molar ratio of BMI-BTA = 4/1, at 120°C reacting for 1 h.

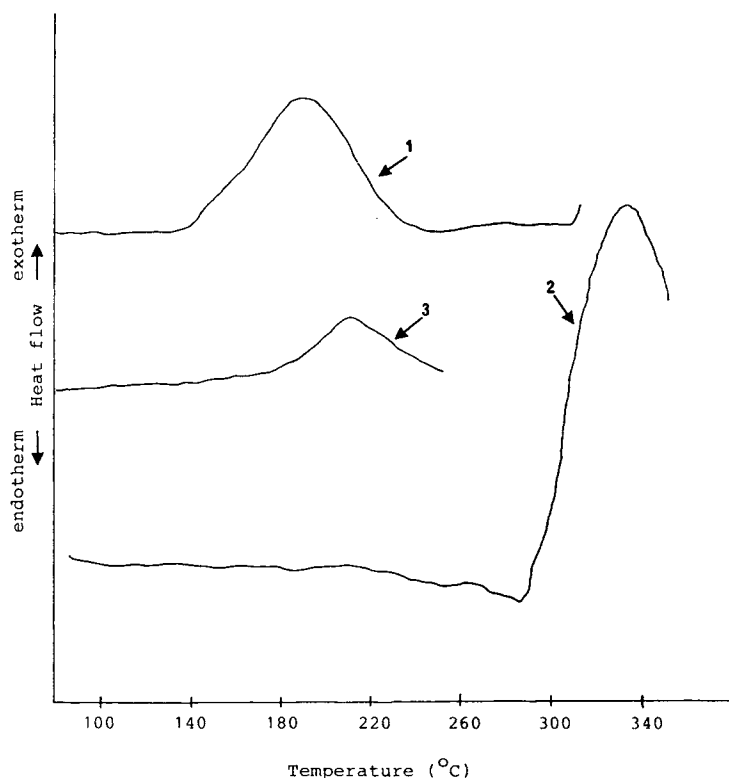


Figure 2 DSC experiments (1) DER-331/DDS = 1/4, (2) DER-331/BMI = 1/1, (3) BMI/DDS = 1/4 (in mole).

BPO Included Resin System

Dissolve BMI 5.37 g, DER-331 11.4 g, and DDS 3.1 g in 25 mL *r*-butyrolactone, then add various amounts of BPO in it at room temperature.

Apparatuses

The chromatograms were recorded on a Merck gel permeation chromatography (column number SP-4 and SP-40) and refractive index detector. DMF was used as eluent with a flow rate of 0.5 mL/min.

Thermogravimetric analysis (TGA) was carried out on a 951 TGA module at a heating rate of 20°C/min in a nitrogen atmosphere (flow rate: 20 mL/min). Differential scanning calorimetry (DSC) was done using a 910 DSC module at a heating rate of 10°C/min in a nitrogen atmosphere (flow rate: 20 mL/min). Sample size of 10 ± 2 mg were used. Thermomechanical spectrum was carried out on a TBA (Plastics Analysis Instruments) at a heating rate of 1–2°C/min in a helium atmosphere (flow rate: 10 mL/min). The sample used for measuring T_g by TBA was prepared by dipping glass braid (2-in. heat-cleaned braids for TBA from Plastic Analysis Instruments, Inc., Princeton) in the polymer

solution. After drying the braid in a 100°C oven for 24 h, it was cured at 250°C for 1 h in He atmosphere. The cured samples were then tested by TBA from 50–250°C.

RESULTS AND DISCUSSION

The DDS and BTA Influence on the BMI Curing Reaction

A 25-g sample of BMI reacted with 2.2 g BTA solving in 40 g of *r*-butyrolactone at 120°C for 1 h. Samples were taken for GPC analysis. As shown in Figure 1, 67.6% of the BMI monomers were consumed; this was determined through prepolymer molecular fraction analysis. Furthermore, if the experiment was performed at 140°C, the reaction system would quickly gel in 5 min. Hence, the BMI reactions were most certainly initiated by the free radicals that were generated by the BTA—a result consistent with the literature.^{4–6} Moreover, at 120°C, for steric hindrance, the molecule weight did not increase quickly as it did at 140°C.

When repeating the experiment with the same mole of DDS instead of BTA, the BMI precipitated

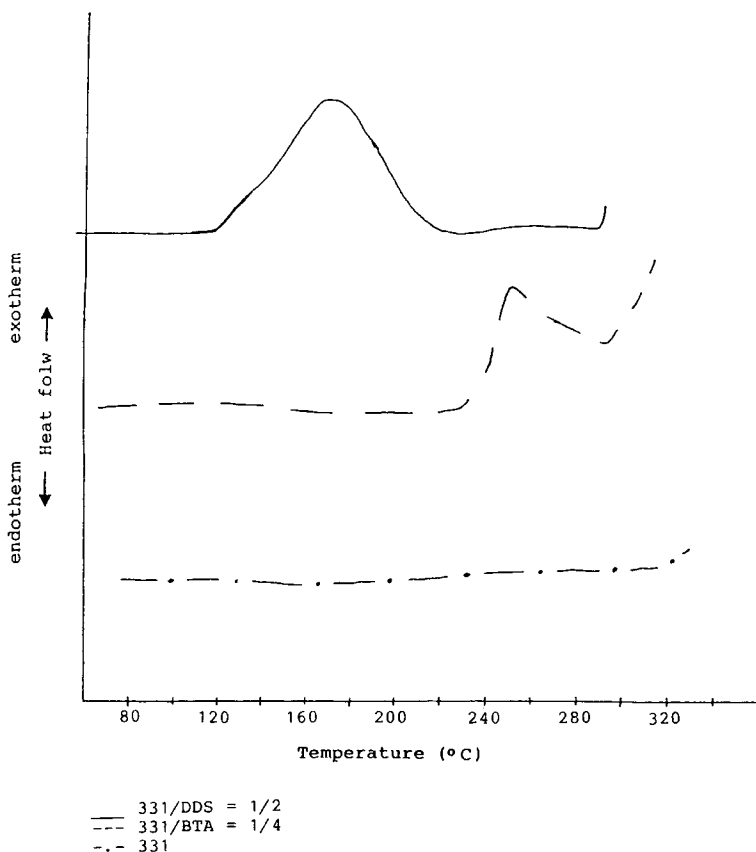


Figure 3 DSC experiments for DER 331 and curing agents.

after cooling. Furthermore, the DSC experiment (Fig. 2) revealed that the DDS could only react with BMI at temperature exceeding 180°C, which is roughly equivalent to the kick-off temperature for BMI self-polymerization. Thus, with BTA, BMI favors free radical polymerization more than it does with DDS through Michael addition.

The DDS and BTA Influence on the Epoxy Curing Reaction

As DSC (Fig. 3) and TGA (Fig. 4) experiments show, epoxy began to decompose around 300°C without self-polymerizing. Hence, for resin-containing epoxy and DDS, the exotherm peak beginning from 115°C is the reaction peak of DDS with epoxy; and for resin-containing epoxy and BTA, the exotherm peak beginning from 220°C is the reaction peak of BTA with epoxy. In other words BTA would not react well with epoxy when DDS was in the epoxy resin. After the DDS reacted completely with the epoxy, however, the BTA could then react. Furthermore, as shown in Figure 5, two curing agents were compared, one was 100% DDS and the other

50% DDS and 50% BTA. The T_g of the DDS agent was 20°C higher. Thus, epoxy resins containing BTA caused the T_g to drop.

The Effect of BTA on BMI-Epoxy Resin System

The BTA effect on T_g is shown in Table II. Its novel effects were observed for all three curing agents.

In order to study this effect in greater detail for a BMI-epoxy resin system, three cases were designed for the studies.

Case 1: If T_g was influenced by the concentration of BTA.

Case 2: If T_g was influenced by the concentration of DDS.

Case 3: If T_g was influenced by the concentration of BTA-DDS.

Case 1: The changes of T_g in correspondence with various BTA concentrations while fixing the concentrations of DDS, BMI, and epoxy are shown in Figure 6. There is a maximum T_g for an optimum BTA concentration. For molar ratios of BMI-epoxy = 1.5/3 and DDS-epoxy = 1.25/3, T_g decreased, if epoxy-BTA was greater or smaller than 3/0.5. For

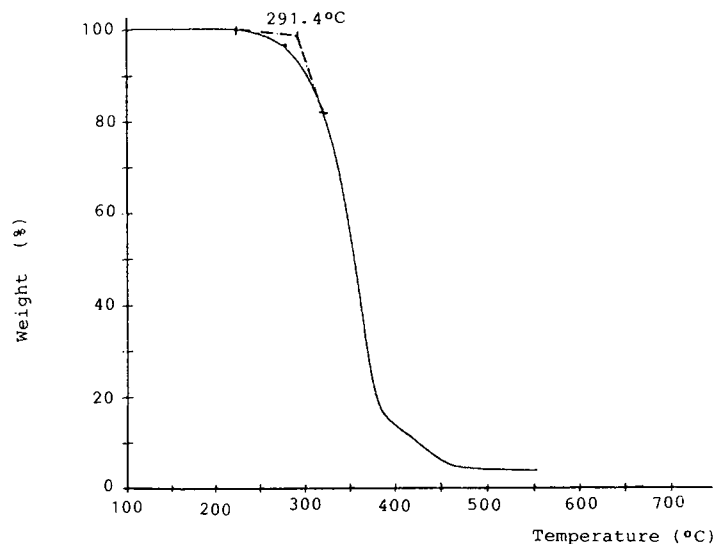
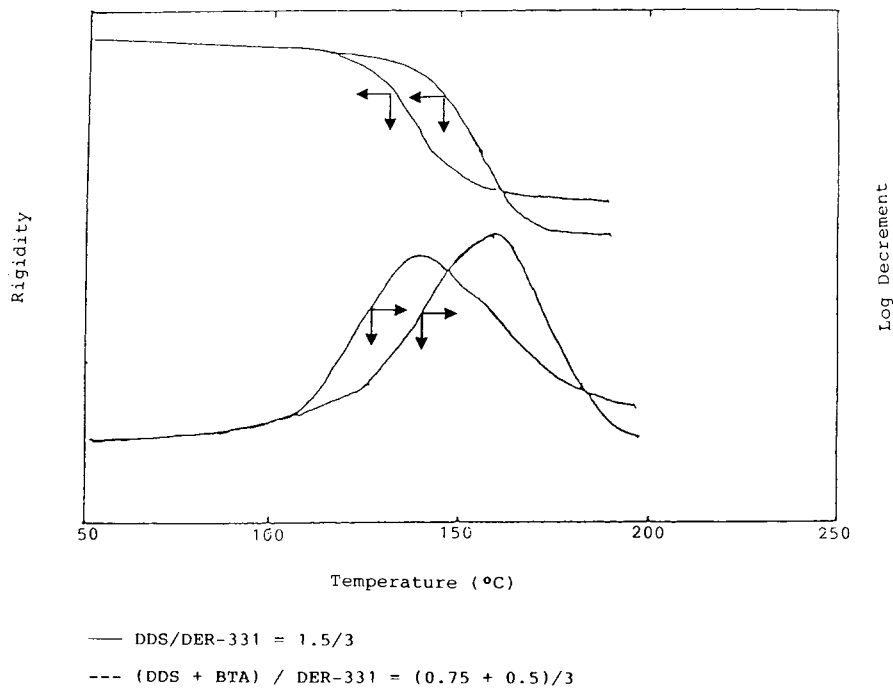


Figure 4 TGA experiment for DER-331.

molar ratios of BMI-epoxy = 2.143/3 and DDS-epoxy = 1.25/3, T_g also decreased, if epoxy-BTA was greater or smaller than 3/0.5. Theoretically, the optimum BTA concentration will occur only when the amine group within the BTA and DDS can almost fully cure the epoxy resin.

Case 2: For the resin systems that have fixed BTA, BMI, and epoxy concentrations, T_g are shown in Figure 7. In this case the extent of the BTA influence on BMI was fixed. Thus, the value of T_g depended on the amount of DDS. For the moles of DDS less than 1.25, lower T_g resulted from a not fully cured



- * 1. T_g were measured by TBA from 50-200 °C
 2. Samples were first cured at 220 °C for 1 hr under helium

Figure 5 BTA's effect on the T_g of epoxy resins.

Table II BTA's Influence on T_g

BMI-Epoxy	BMI-BTA ^a	Epoxy-Curing Agent ^a	T_g^b (°C)
1/3	1/0.5	3/2.5 (DICY)	180
1/3	1/0	3/3 (DICY)	170
1/3	1/0.5	3/2.5 (DDS)	223
1/3	1/0	3/3 (DDS)	220
1/3	1/0.5	3/2.5 (DDPE)	155
1/3	1/0	3/3 (DDPE)	140

^a Based on the moles of the amine groups.

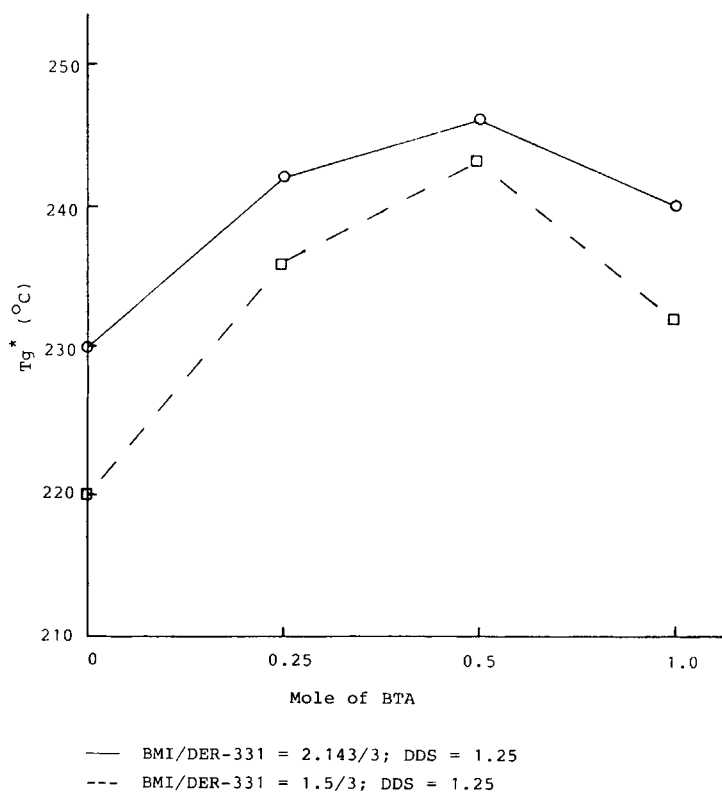
^b T_g was measured by TBA. Heating rate: 1–2°C/min, in He., samples were cured at 250°C for 1 h prior to performing the experiments.

network, meaning lower crosslinking density. On the other hand, as the moles of DDS exceeded 1.25, T_g fell dramatically due to the excess of curing agents reacting with BMI by Michael addition.^{7,8}

Case 3: The impact on T_g with various BTA-DDS ratios are shown in Figure 8. For the equivalent molar ratio of BMI/331 = 1.5/3, 331/(BTA + DDS) = 3/3, T_g decreased, if BTA-DDS was greater or

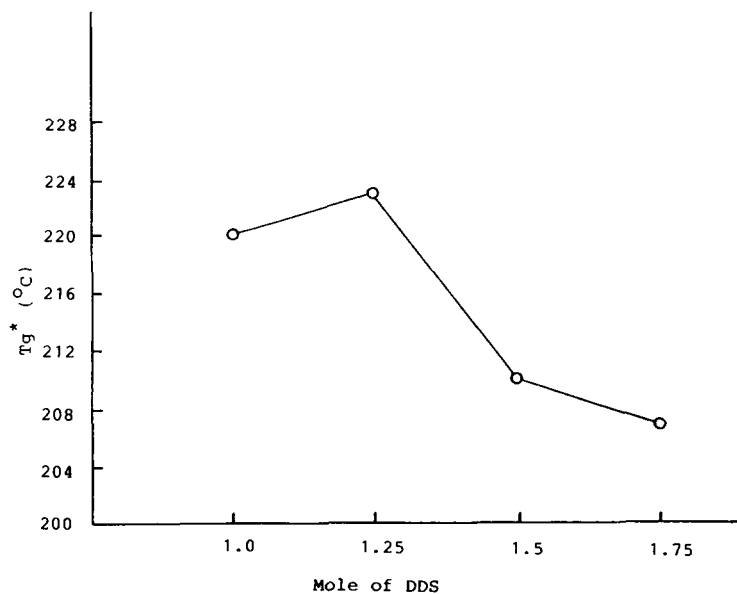
smaller than 0.5/2.5. At the equivalent molar ratio of BMI/331 = 1/3, 331/(BTA + DDS) = 3/1, T_g also decreased, if BTA-DDS is greater or smaller than 0.25/2.5. In this optimum T_g case, although the epoxy can be fully cured, theoretically, by the amine groups of DDS and BTA, an optimum concentration of BTA-DDS would still be needed to achieve maximum T_g . Thus, as proven in theory and indicated substantiated in experimentation, BTA impacts adversely on T_g .

In all these formulated cases, if the DDS mole was always controlled a little less than the required curing agent for epoxy, no more DDS could react with BMI. Epoxy was cured with DDS by a stepwise reaction; while BMI was cured by self-polymerization initiated by BTA. Hence, the cured systems formed intercrosslinking networks. From the results of case 1 and 2, it was clear that achieving maximum T_g was determined by the level of BTA and DDS that fully reacted with the epoxy. With either insufficient or excess BTA and DDS, the T_g of the BMI-epoxy resin system would descend. Thus, BTA is most likely not only the initiator for BMI free radical polymerization, but also the curing agent for



— BMI/DER-331 = 2.143/3; DDS = 1.25
 --- BMI/DER-331 = 1.5/3; DDS = 1.25
 * Samples were first cured at 250 °C for 1 hr under helium, then measuring T_g by TBA from 50–250 °C

Figure 6 The BTA effect on T_g .



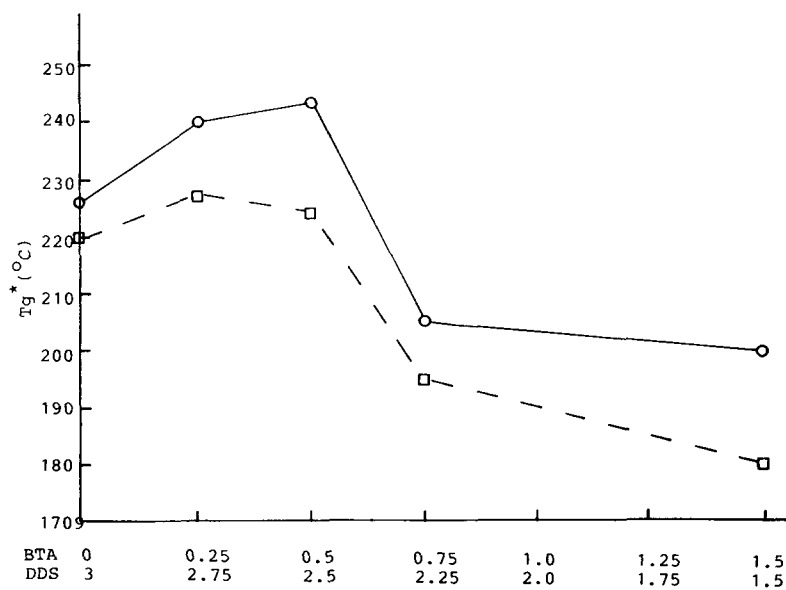
BMI/BTA = 1/0.5; BMI/DER-331 = 1/3

* Samples were first cured at 250 °C for 1 hr under helium, then measuring Tg by TBA from 50-250 °C

Figure 7 The DDS effect on T_g .

epoxy. Hence, reactions between the BMI networks and epoxy networks can occur. The novel effect of BTA on T_g may result from this phenomenon.

Through TBA experiments in Figure 9, only one T_g was observed. SEM study revealed no phase separation in Figure 10. Forming homogeneous inter-



— BMI/331 = 1.5/3; 331/(BTA + DDS) = 3/3

--- BMI/331 = 1/3; 331/(BTA + DDS) = 3/3

* Samples were first cured at 250 °C for 1 hr under helium, then measuring Tg by TBA from 50-250 °C

** Based on the equivalent moles

Figure 8 The BTA-DDS effect on T_g .

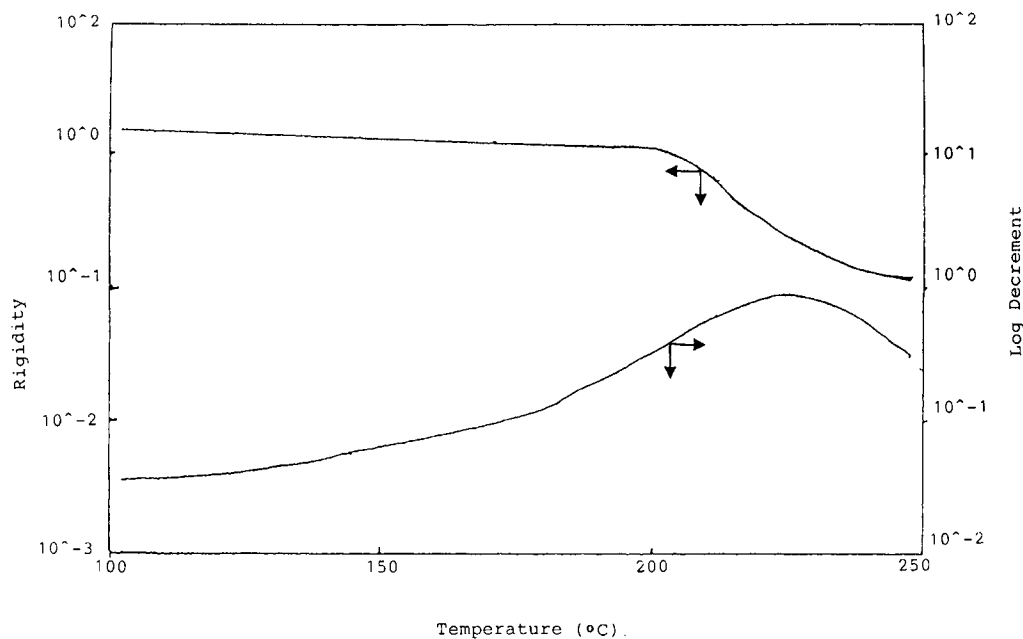


Figure 9 TBA experiment for the resin system composed by BMI/331 = 1/3, BMI-BTA = 1/0.5, 331/DDS = 3/1.25 (based on molar ratio).

crosslinking networks can, thus, be predicated. These morphology observations were consistent with the literature.^{9,10}

The BPO Influence on the BMI-Epoxy Resin System

Solid BMI powder was mixed thoroughly with BPO or BTA in a weight ratio of BMI-(BPO or BTA) = 10/1, 100/1.

As shown in Figure 11, the BPO-BMI systems had a big exotherm peak at around 110°C. In contrast, the BTA-BMI systems had no such peaks. When BMI dissolved in *r*-butyrolactone at 120°C, the solution gelled in 5 min with the addition of 1% BPO. This result confirms that BPO acts an initiator for BMI's thermal polymerization.^{11,12}

After dissolving BMI 5.37 g, DER-331 11.4 g, and DDS 3.1 g in 25 mL *r*-butyrolactone, various amounts of BPO were added at room temperature. No apparent change on T_g occurred (see Fig. 12). Hence, although BPO could be used as an initiator in BMI's initial reaction stage, it produced no novel effect like BTA on the value of T_g .

CONCLUSIONS

In the BMI-epoxy blended resin system, BMI polymerization can be easily initiated by BTA. The

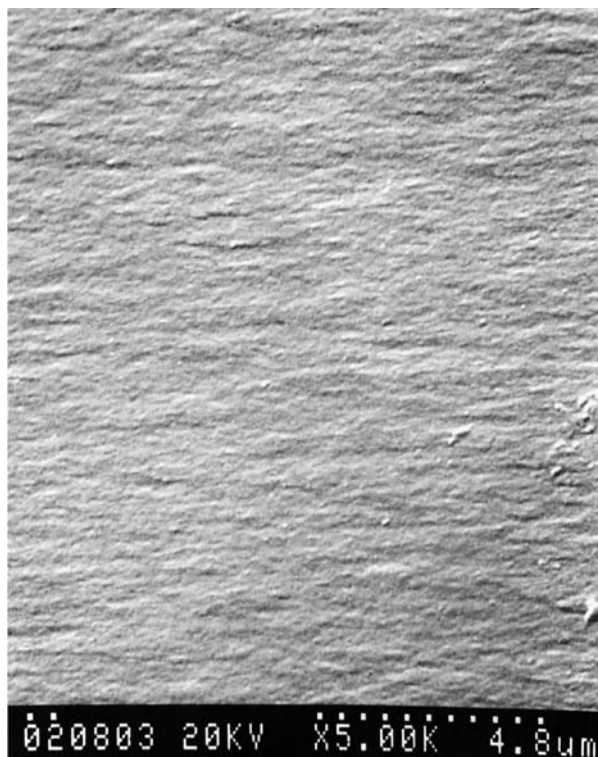


Figure 10 SEM micrograph ($\times 5000$), showing fracture surface of intercrosslinked BMI-epoxy networks composed of BMI-DER 331 = 1/3, BMI-BTA = 1/0.5, DER 331-DDS = 3/1.25 in molar ratio.

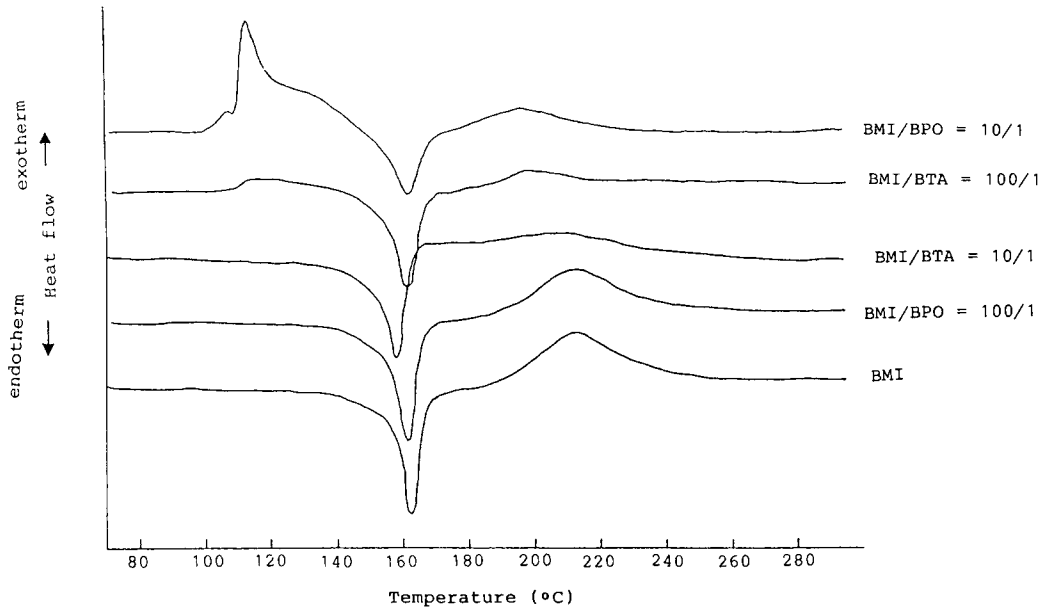
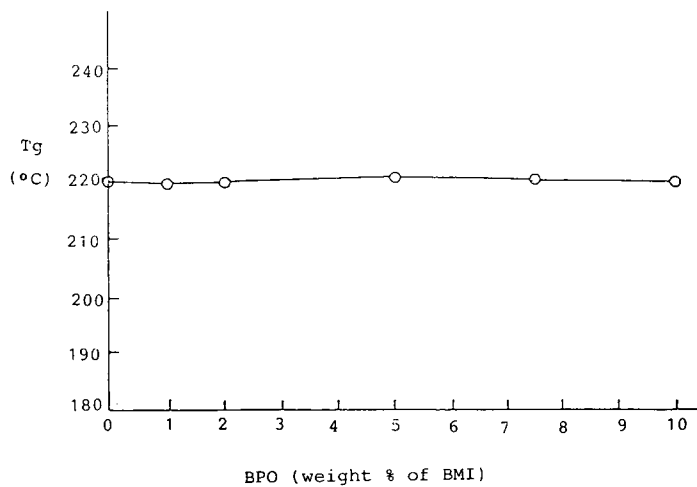


Figure 11 Comparison of DSC curves with different resin compositions.

BTA concentration can influence the final cured resin's T_g . However, the effect of BTA on softening resin networks and on initiating BMI have adverse effects on T_g . Novelty, within a certain range of BTA, the resin system will have higher T_g than it would without BTA. The optimum concentration of

BTA depended on the relative amount of BMI, epoxy, and curing agents. However, if BTA was replaced by BPO in the resin system, no such novel influence on T_g occurred. Since the selectivity of BTA and DDS reaction with BMI-epoxy were different, BMI polymerization could be controlled by



Resin system in mole: BMI/331 = 1.5/3
DDS = 1.25

- * 1. T_g were measured by TBA from 50-250 °C
- 2. samples were first cured at 250 °C for 1 hr under helium

Figure 12 The BPO effect on T_g .

free radical reaction and epoxy polymerization could be controlled by stepwise reactions. Thus, a T_g -enhancing intercrosslinking network could be formed.

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REFERENCES

1. S. J. Shaw and A. J. Kinloch, *Inter. J. Adhesion Adhesives*, **5**(3), 123 (1985).
2. William F. Graham, U. S. Pat. 4,294,743 (Oct. 13, 1981).
3. Adira Nagai, Akio Takahashi, Motoyo Wajima, and Kenji Tsukanishi, *Polym. J.*, **20**(2), 125 (1988).
4. Norio Tsubokawa, Naohiro Shibata, and Yasoo Sonne, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 425 (1983).
5. Jürgen Hüttermann, Gunnar Schmidt, and Dieter Weymann, *J. Magnet. Reson.*, **21**, 221 (1976).
6. Richard Haak and Brent Benson, *J. Chem. Phys.*, **55**(8), 3693 (1971).
7. James V. Crivello, *J. Poly. Sci. Polym. Chem. Ed.*, **11**, 1185 (1973).
8. Jerry E. White and Deborah A. Snider, *J. Appl. Polym. Sci.*, **29**, 891 (1984).
9. E. M. Woo, L. B. Chen, and J. C. Seferis, *J. Mat. Sci.*, **22**, 3665 (1987).
10. Akira Fukami, Katsuyoshi Iisaka, and Shouhei Etoh, *J. Macromol. Sci. Part B. Phys.*, **B28**(2), 251 (1989).
11. I. M. Brown and T. C. Sandreczki, *Macromolecules*, **23**(1), 94 (1990).
12. I. K. Varma, Manjeet S. Choudhary, B. S. Rao, Sangita, and D. S. Verma, *J. Macromol. Sci. Part A. Chem.*, **A21**(6&7), 793 (1984).

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