

# Influence of Gelling Conditions on Mechanical Properties of Simultaneous Interpenetrating Polymer Networks from Epoxy and Bismaleimide Resins

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## SYNOPSIS

Simultaneous interpenetrating polymer networks (SINs) were prepared from nadic methyl anhydride-cured epoxy resin and bismaleimide (BMI) of which the composition ratios were, respectively, comprised of 3/1 (EM-25 series) and 1/1 (EM-50 series), under different gelling conditions for both resins. Dynamic mechanical and tensile properties were measured for these SINs. Turbidity was also measured to obtain some information regarding morphology. Although the rubbery modulus was constant irrespective of a gel-time ratio ( $Gt$ ) of the epoxide resin to that of BMI for the EM-25 series, it increased with increasing  $Gt$  for the EM-50 series. The glass transition temperature ( $T_g$ ) was nearly constant at  $Gt < 1$  and then decreased with increasing  $Gt$  at  $Gt > 1$  for the EM-25 series. On the other hand,  $T_g$  was nearly constant irrespective of  $Gt$  for the EM-50 series, though the values of  $T_g$  at  $Gt < 1$  were somewhat higher than those at  $Gt > 1$ . There was an appropriate value of  $Gt$  that gave better tensile strength ( $\sigma_b$ ) or toughness evaluated by the area under a stress-strain curve. The  $T_g$  and  $\sigma_b$  were found to be correlated to the turbidity of the SINs. The above mechanical behavior can be explained in terms of the molecular mixing and morphology that vary with a change in the relative polymerization rate of both the resins.

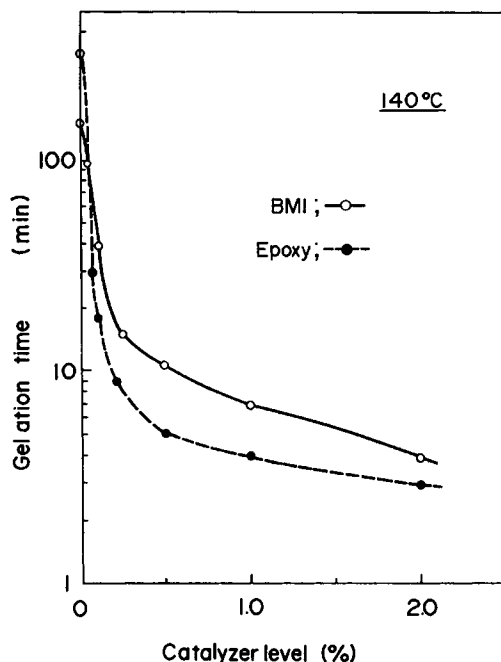
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## INTRODUCTION

Composite materials are used in a large number of electric and electronic applications. Polymeric materials having good heat resistance are needed for the composites in such applications. Polybismaleimides have high thermooxidative stability and good processability, but they are very brittle materials. On the other hand, epoxy resin is universally known as a material having moderate thermal stability but well-balanced mechanical properties. In addition, epoxy resin can be easily formulated by an appropriate curing agent so as to have a low viscosity that is desirable to easily form laminate. Accordingly, modification of epoxy resin with bismaleimide would be expected to produce a desirable polymer with high thermal stability, good mechanical properties, and processability without a solvent, of which the use seems to have deleterious effects, more or

less, on the electrical and other physical properties of composites because of inevitable residual solvent and voids. Furthermore, it is interesting that both the resins may create interpenetrating polymer networks, since they form polymer networks via different reaction mechanisms. In previous studies, simultaneous interpenetrating polymer networks (SINs) had been prepared from nadic methyl anhydride-cured epoxy resin and bismaleimide<sup>1</sup> or bismaleimide-allylester comonomer<sup>2</sup> under the same gelling conditions for both the resins. Then, these SINs exhibited an efficient increase in  $T_g$  and enhancements in mechanical and thermal properties by a synergistic effect.

In preparation of SINs, different reaction rates for both resins are known to give a material with different morphology and properties.<sup>3-7</sup> To design SINs with the most appropriate properties, it is very important to understand the influence of a condition of polymer-network formation on their properties. It was the purpose of this study to examine the me-



**Figure 1** Gelation time at 140°C vs. catalyst level for epoxy and BMI resin.

chanical behavior of the SINs as a function of gel-time ratio of epoxy resin to that of bismaleimide resin. In addition, the turbidity of the SINs was also examined to obtain information with regard to morphology.

## EXPERIMENTAL

The epoxide used was bisphenol-A-type epoxide (DGEBA, Epicote 828, epoxide equiv  $190 \pm 5$ , viscosity = ca. 130 Pois at 25°C,  $\bar{M}_n = 380$ ). The curing

agent used was nadic methyl anhydride (NMA, viscosity = ca. 2 Pois at 25°C) and the accelerator used was benzyl dimethyl amine (BDMA). Bismaleimide used was 4,4'-dimaleimide diphenylmethane (BMI, mp = 156°C). The initiator used to polymerize BMI was dicumylperoxide (Dicup). They were all chemically pure materials (i.e., special-grade reagents).

SIN samples with different gel-time ratios were prepared as follows: The epoxide resin was compounded with a stoichiometric amount of the curing agent and each amount of the accelerator. The mixture was stirred at about 60°C. Subsequently, the epoxide resin mixture was mixed with 25 and 50 wt % of BMI, respectively, with 0.5 and 1 wt % of Dicup and stirred at about 60–80°C for about 10 min. This mixture was poured between two glass plates with a silicone rubber spacer. The curing conditions were 140°C for 4 h, 200°C for 15 h, and 280°C for 1 h. The code names of the samples were designated as EM-25- and EM-50-, corresponding to 25 and 50 wt % of BMI, respectively. The last number of the code denotes the wt % of BDMA in the epoxy resin.

A gelation time was determined for both the resins with various catalyst levels at 140°C as the time until the resin did not stick on a glass rod. For only the BMI resin, a gelation time was measured in the concentration of 50 wt % BMI in the epoxy resin without BDMA. Turbidity of a film was measured at the wavelength of 800 nm with a UV-visible light spectrometer UV-260 (Shimadzu Co.). The turbidity  $\tau$  was determined by the following equation in the case of turbidity  $\gg$  absorbance:

$$\frac{I_t}{I_0} = \exp(-\tau d) \quad (1)$$

where  $I_0$ ,  $I_t$ , and  $d$  are, respectively, the intensities of incident and transmitted light and the film thick-

**Table I** Sample Preparation

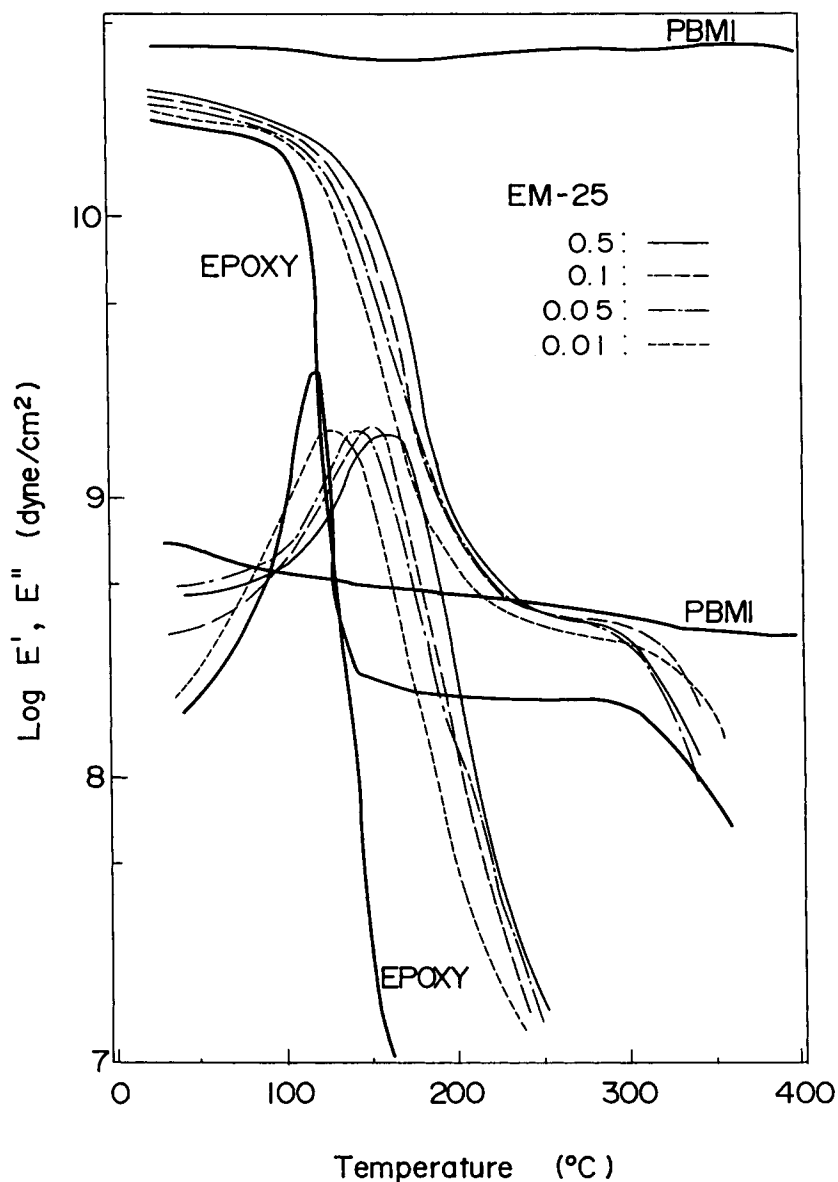
Code	BDMA (Wt %)	Dicup (Wt %)	Gel Time at 140°C		Gel-Time Ratio ( <i>Gt</i> )
			Epoxy (Min)	BMI (Min)	
EM-25-0.5	0.5	0.5	5.2	27	0.2
EM-25-0.1	0.1	↑	23	↑	0.85
EM-25-0.05	0.05	↑	56	↑	2.1
EM-25-0.01	0.01	↑	230	↑	8.5
EM-25	0.05	0.05	56	130	0.43
EM-50-1.0	1.0	1.0	5.2	11	0.47
EM-50-0.4	0.4	↑	9.0	↑	0.82
EM-50-0.2	0.2	↑	18	↑	1.6
EM-50-0.1	0.1	↑	30	↑	2.7
EM-50-0.05	0.05	↑	100	↑	9.1

ness.<sup>8</sup> Dynamic mechanical properties were measured over the temperature range from room temperature to 400°C at a frequency of 3.5 Hz using a viscoelastic spectrometer (Iwamoto Manufacturing Co., Japan). Tensile properties were measured on a Tensilon (Toyo-Baldwin Co., Japan) at the temperatures of 150 and 200°C at a crosshead speed of 4 mm/min.

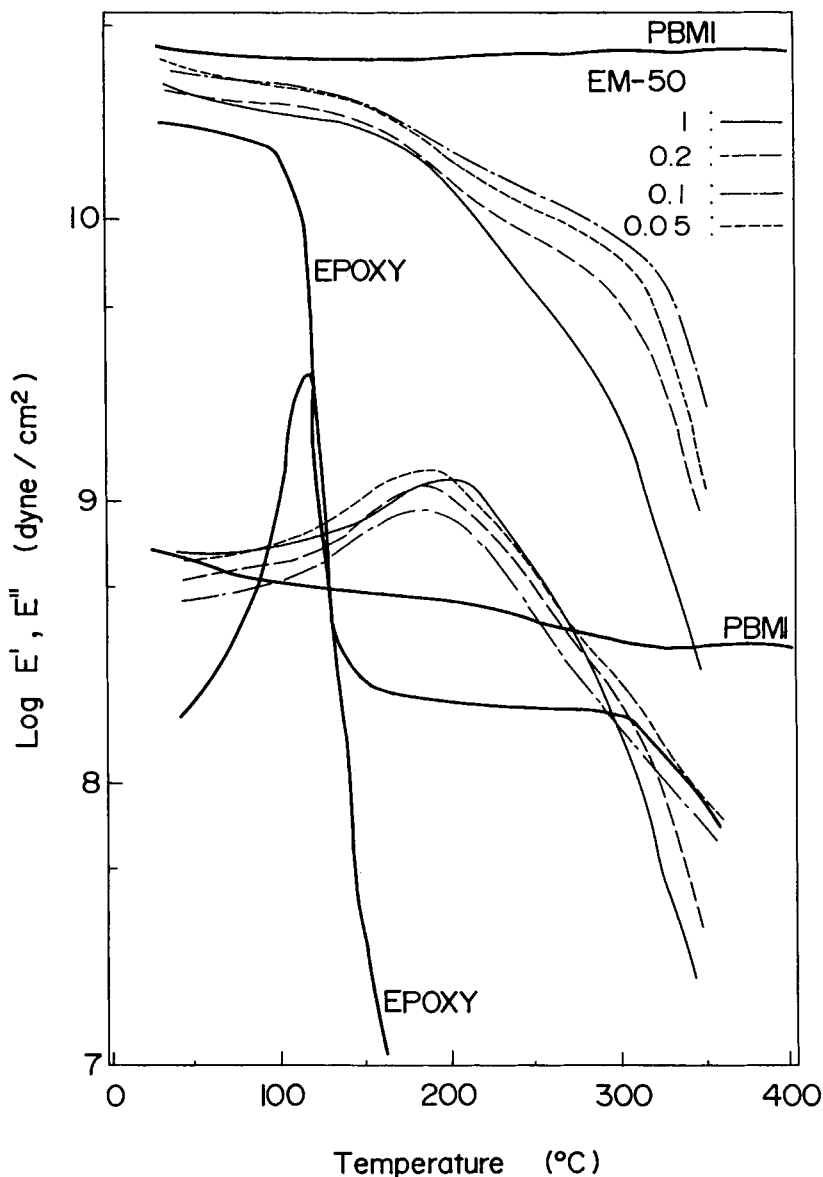
## RESULTS AND DISCUSSION

Figure 1 shows the relation of a gel-time at 140°C vs. a catalyzer level, i.e., a content of BDMA or Di-

cup, respectively, for the epoxy or BMI resin. Increasing the accelerator (BDMA) or the initiator (Dicup) considerably decreased gel times of both the resins. In the preparation of the SIN samples, the resin mixtures completed to gelation at the initial curing temperature of 140°C. Thus, a catalyzer level was chosen so that the BMI resin can be polymerized faster, slower, or at approximately the same rate as the epoxy resin, by using the data in Figure 1. Table I represents a catalyzer level, gel time, and gel-time ratio ( $Gt$ ) of the epoxy resin to that of the BMI resin. Here, the sample (EM-25 in Table I) containing a 0.05 wt % of BDMA and a 0.05 wt % of



**Figure 2** Temperature dependencies of storage modulus  $E'$  and loss modulus  $E''$  for the EM-25 series. The numbers in the figure denote wt % of BDMA.



**Figure 3** Temperature dependencies of storage modulus  $E'$  and loss modulus  $E''$  for the EM-50 series. The numbers in the figure denote wt % of BDMA.

Dicup was added for the case of 25 wt % BMI, for comparison.

Figures 2 and 3 show the temperature dependencies of storage modulus  $E'$  and loss modulus  $E''$  for the series of EM-25 and EM-50, respectively. The previous data<sup>1</sup> of the polybismaleimide and the cured epoxy resin were also cited in the same figures. The glass transition temperature,  $T_g$ , which can be ascribed to the onset of micro-Brownian motion of the chain segments, appears at about 120°C ( $E''$  max) for the cured epoxy resin. On the other hand, no dispersion is detected over the temperature range

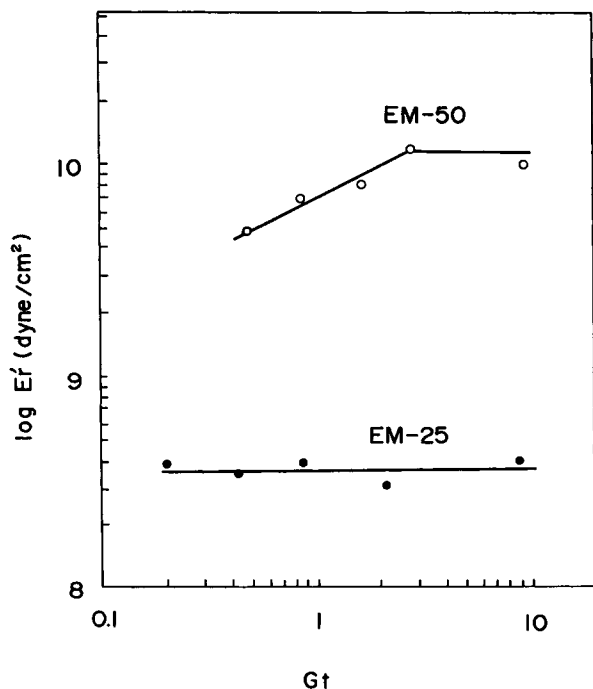
from room temperature to 400°C for the polybismaleimide. For the SINs, the  $T_g$  shifted into higher temperatures and the rubbery modulus considerably increased with loading of BMI. Moreover, storage moduli for any samples of both the series demonstrated major decreases above nearly the same temperature of about 300°C, where the cured epoxy resin starts to degrade.<sup>1</sup> Hence, such a decrease in modulus can be considered to be due to the thermooxidative degradation of the component of epoxy resin.

The viscoelastic properties manifested different behavior between the series of EM-25 and EM-50;

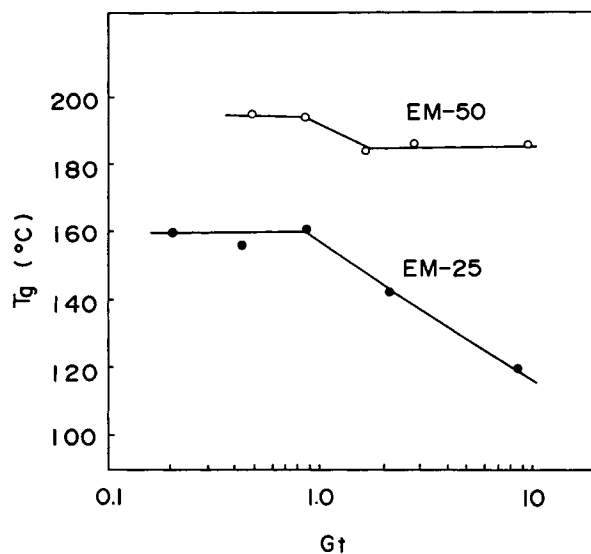
i.e., in the case of the EM-25 series, while the rubbery plateau modulus ( $Er'$ ) in the temperature range between about 200 and 300°C was nearly constant irrespective of the content of BDMA,  $T_g$  indicated an increasing tendency with increasing content of BDMA, under the condition where the content of Dicap was constant. On the other hand, in the case of the EM-50 series, the rubbery modulus in the same temperature range increased with increasing content of BDMA under the same conditions and  $T_g$  was nearly constant irrespective of the content of BDMA.

For the EM-25 series, a lower  $T_g$  was observed for a lower BDMA content. Then, the sample (EM-25) that comprised low equivalent amounts of 0.05 wt % for BDMA and Dicap was supplemented to further examine the influence of a catalyzer level on  $T_g$  and dynamic mechanical properties were observed. The  $T_g$  for this sample was about 160°C of the nearly same temperature as the case of the sample with the greatest amount of BDMA. Accordingly, the dynamic mechanical properties of the SINs can be considered to be more directly controlled by the content ratio rather than by the contents of BDMA and Dicap.

At first, the rubbery modulus  $Er'$  at 280°C was examined as a function of the logarithm of a gel-time ratio ( $Gt$ ) in place of an amount of BDMA, as



**Figure 4** Storage modulus  $Er'$  at 280°C vs. gelation time ratio  $Gt$ .



**Figure 5** Glass transition temperature  $T_g$  vs. gelation time ratio  $Gt$ .

shown in Figure 4. Although  $Er'$  was independent of  $Gt$  for the EM-25 series, it increased with increasing  $Gt$  in the region of  $Gt < 2.7$  and became nearly constant at  $Gt > 2.7$  for the EM-50 series. For the EM-50 series, the fact that the modulus changes with  $Gt$  in spite of the same composition may reflect the variation of morphology in the SIN. In the previous study,<sup>1</sup> the dependence of  $Er'$  upon composition followed nearly the Budiansky's equation that suggests the presence of phase inversion between both components.<sup>9</sup> Hence, the SIN can be considered to be composed of a dual network continuity at a midrange composition ratio. The results for the EM-50 series suggest that the network continuity for the BMI component varies with  $Gt$ , since the value of  $Er'$  for the SIN is greatly dependent on the BMI component, on account of the extraordinarily high modulus for the polybismaleimide compared with the low rubbery modulus for the cured epoxy resin, as shown in Figures 2 and 3, i.e., the network of the polybismaleimide component becomes more continuous, as the BMI resin reacts at a higher speed than the epoxy resin does. This can be supported by the observations that in a sequential IPN the morphology of the polymer network previously prepared is always composed of a continuous phase irrespective of the composition.<sup>10</sup> Moreover, in the case of the EM-25 series, the concentration of BMI was not so much that full interpenetration occurred or the continuity of the polybismaleimide network varied with  $Gt$ .

Now, to bring about further understanding as to the modulus behavior with  $Gt$ , the extent of network

continuity was examined. This can be evaluated, e.g., by comparing the observed data of the rubbery modulus with the logarithmic mixture law. The logarithmic mixture law is given by

$$\log E' = \phi_1 \log E'_1 + \phi_2 \log E'_2 \quad (2)$$

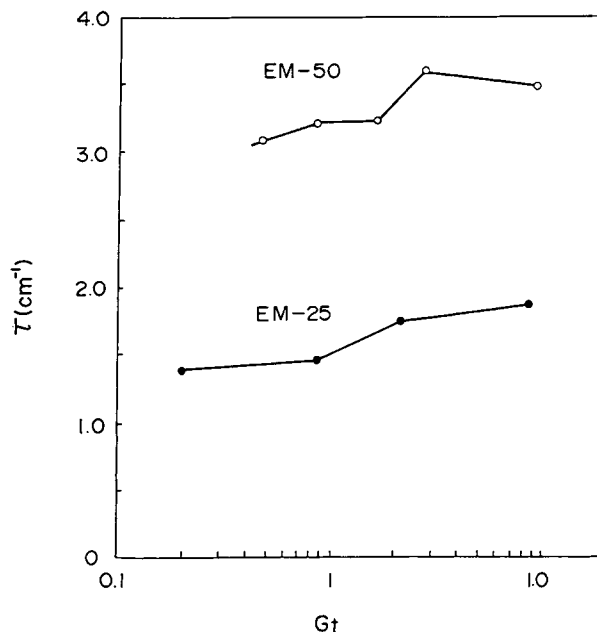
where  $\phi_1$  and  $\phi_2$  are the volume fraction of the epoxy resin and BMI, respectively, and  $E'_1$  and  $E'_2$  are the tensile moduli at 280°C of the cured epoxy resin and the polybismaleimide, respectively. The calculated values of  $\log E'$  were 8.8 and 9.5, respectively, for the 25 and 50 wt % BMI. Although the observed modulus data are slightly smaller than the calculated value for all  $Gt$  in the case of the 25 wt % BMI, they are larger for all  $Gt$  than the calculated value in the case of the 50 wt % BMI. In the case of the EM-25 series, the extent of network continuity is too small to be varied against a change in polymerization rates of both components. On the contrary, in the case of the EM-50 series, the networks are assumed to be composed from the almost continuity, which suggests the possibility of being influenced by  $Gt$ .

Next, with regard to the glass transition,  $T_g$  was plotted vs. the logarithm of  $Gt$ , because different reaction rates for both the components seem to produce a material with a different degree of molecular mixing that is associated with  $T_g$ . As shown in Figure 5,  $T_g$  can be correlated to  $Gt$  for both the series, i.e., the  $T_g$  for the EM-25 series was nearly constant at  $Gt < 1$  and subsequently decreased with increasing  $Gt$ . On the other hand, the  $T_g$  for the EM-50 series was nearly constant over the whole range of  $Gt$ , though the values of  $T_g$  at  $Gt < 1$  were somewhat larger than those at  $Gt > 1$ .

**Table II Degree of Intermixing of BMI Component to Epoxy Resin**

Code	$Gt$	$T_{g\text{obs}}$ (K)	$T_{g\text{cal}}$ (K)	Mixing Degree (%)
EM-25-0.5	0.2	432	436	94
EM-25	0.43	429	↑	88
EM-25-0.1	0.85	433	↑	96
EM-25-0.05	2.1	415	↑	60
EM-25-0.01	8.5	393	↑	16
EM-50-1.0	0.47	468	496	78
EM-50-0.4	0.82	467	↑	76
EM-50-0.2	1.6	456	↑	68
EM-50-0.1	2.7	459	↑	70
EM-50-0.05	9.1	459	↑	70

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}, \quad T_{g1} = 389 \text{ K}; \quad T_{g2} = 687 \text{ K}.$$



**Figure 6** Turbidity vs. gelation time ratio  $Gt$  for the EM-25 and EM-50 series.

In the previous study,<sup>1</sup> the truly simultaneous IPN had been prepared from the same resins under the same gelling conditions for both resins. Then, the dependence of  $T_g$  on the content of BMI was found to follow nearly the Fox equation that assumes perfect miscibility between both components.<sup>11</sup> Then, the large increase in  $T_g$  could be explained based on the hypothesis that part of the segment between junction points in the networks of polybismaleimide joins in the segmental motion of the epoxy resin. The behavior in  $T_g$  observed here suggests that a degree of molecular mixing between the epoxy resin and polybismaleimide component, which can be associated with the extent of restriction for the segmental motion, changes with  $Gt$ . Thus, the degree of intermixing of the polybismaleimide component to the epoxy resin was estimated according to the Fox equation. The Fox equation is given by

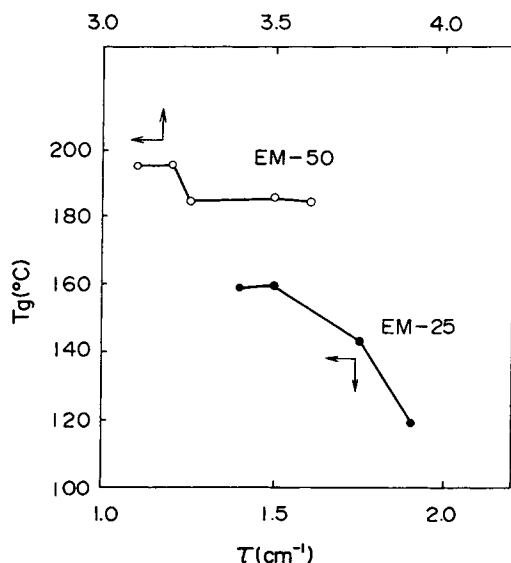
$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

where  $w$  is the weight fraction and subscripts 1 and 2 denote the cured epoxy resin and polybismaleimide, respectively. Here, the initiation temperature (= 420°C) of thermooxidative decomposition was adopted as the  $T_g$  of the polybismaleimide, since this polymer has no dispersions below 400°C. The degrees of intermixing thus derived are listed in Table II. In the case of the EM-25 series, the degree of

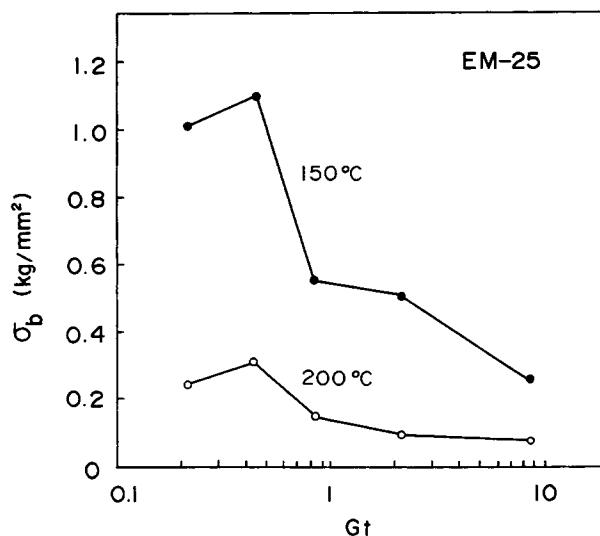
intermixing was near 100% at  $Gt < 1$  and, after that, decreased with increasing  $Gt$  and amounted to 16% at  $Gt = 8.5$ , whereas in the case of the EM-50 series, it was about 80% at  $Gt < 1$  and about 70% at  $Gt > 1$ . The larger extent of intermixing for the EM-25 series than for the EM-50 series seems to be due to the reason that the lower the concentration of BMI the more the amount of soluble BMI in the epoxy resin, because of the limited solubility.

All the present samples were translucent, irrespective of a gel-time ratio. It was reported by Sperling and Arnts<sup>3</sup> that turbidity could be correlated to mechanical properties for IPNs prepared by various methods. Then, turbidity for the SINs was examined as a function of  $Gt$ . The turbidity exhibited an increasing tendency in the region of  $Gt > 1$  for both series, as shown in Figure 6. Absorbance at a measuring wavelength can be assigned to be the same among all of the samples, even if it existed, since they have the same composition. Therefore, the variation of turbidity with  $Gt$  can be considered to have occurred because of light scattering due to inhomogeneities with larger size than wavelength. Now, the relation between  $T_g$  and  $\tau$  for both the series was examined. Although the  $T_g$  does not depend so much on  $\tau$  for the EM-50 series, the  $T_g$  decreased with increasing  $\tau$  for the EM-25 series, as shown in Figure 7. These results suggest that the  $T_g$  can be at least associated with the turbidity.

In the previous studies,<sup>1</sup> tensile strength was reported to be more enhanced by the synergistic effect at high temperatures where the cured epoxy resin



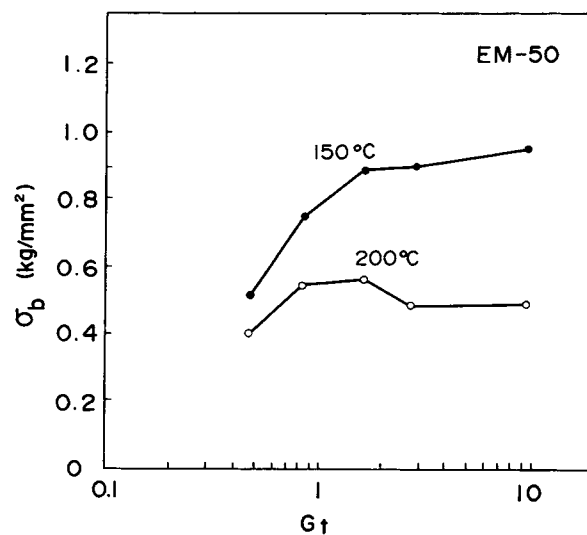
**Figure 7** Glass transition temperature vs. turbidity for the EM-25 and EM-50 series.



**Figure 8** Tensile strength vs. gelation time ratio  $Gt$  for the EM-25 series.

was in the rubbery state, compared with room temperature where both the polymers were in the glassy state. Hence, tensile properties were examined at the high temperatures of 150 and 200°C.

Figures 8 and 9 show tensile strength ( $\sigma_b$ ) at both temperatures for the series of EM-25 and EM-50. In the case of the EM-25 series,  $\sigma_b$  exhibited large values in the region of  $Gt = 0.2-0.5$  and significantly decreased with increasing  $Gt$  at  $Gt > 0.5$  at both temperatures. On the contrary, in the case of the EM-50 series,  $\sigma_b$  increased with increasing  $Gt$  and approached the upper limiting values at both tem-



**Figure 9** Tensile strength vs. gelation time ratio  $Gt$  for the EM-50 series.

peratures. These behaviors can be explained as follows: For the EM-25 series, the large  $\sigma_b$  at a lower side of  $Gt$  seems to result from the greater densification of a molecular packing, which can be assumed to be the same mechanism as the case of  $T_g$  shown in Table II. In addition, the decreasing  $\sigma_b$  at a higher side of  $Gt$  seems to be due to its lesser densification or a worse action by such impurities as voids or defects that may be liable to grow in the SIN sample when a gel time greatly differs between the two resins. In the case of the EM-50 series, strength properties depend more preferentially on the morphology, compared with the case of the EM-25 series, namely, the values of  $\sigma_b$  behave with  $Gt$  in a way similar to the case of the rubbery modulus for the EM-50 series shown in Figure 4.

Next, the relation between tensile strength and turbidity was examined as well as the case of  $T_g$ . Figure 10 shows plots of  $\sigma_b$  at 150°C vs.  $\tau$  for both series. Although  $\sigma_b$  for the EM-50 series demonstrated an increasing tendency against  $\tau$ ,  $\sigma_b$  for the EM-25 series demonstrated a decreasing tendency against  $\tau$ . In the case of the EM-25 series, such behavior seems to be reasonable. On the other hand, in the case of the EM-50 series, though the turbidity was larger compared with the EM-25 series, the rate of which it varied was rather small. Hence, in this case, the change in network continuity that is associated with modulus gives a greater contribution to the tensile strength, compared with the change in turbidity.

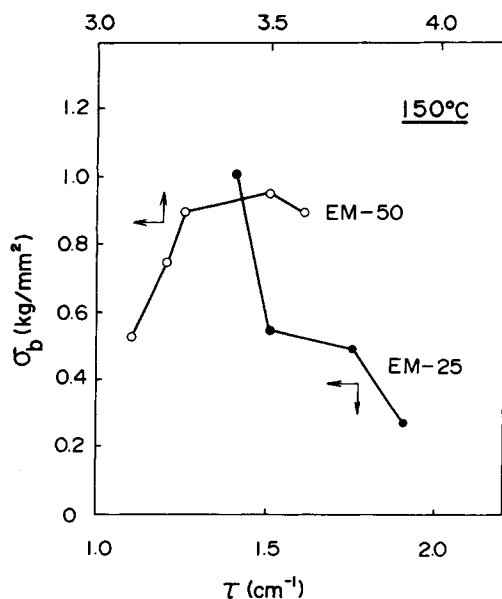


Figure 10 Tensile strength vs. turbidity for the EM-25 and EM-50 series.

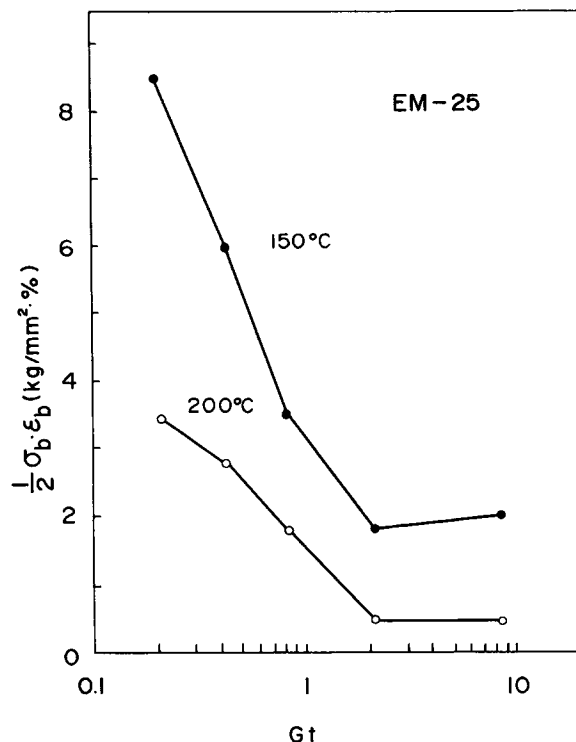


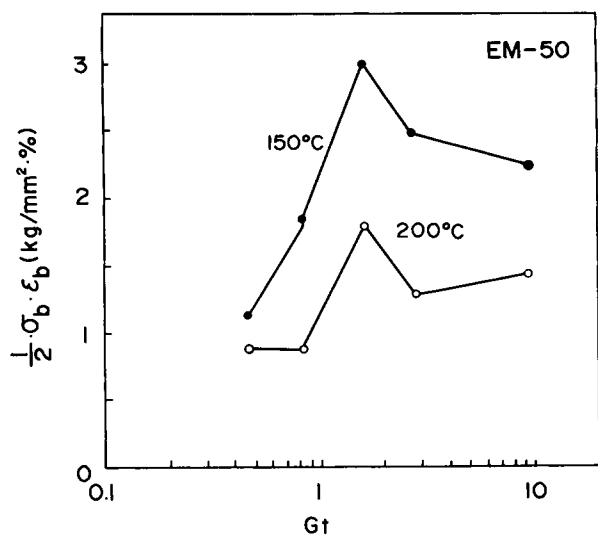
Figure 11 Toughness vs. gelation time ratio  $Gt$  for the EM-25 series.

Figures 11 and 12 show toughness evaluated by the area under a stress-strain curve. The large or maximum toughness was observed at  $Gt = 0.2$  for the EM-25 series or at  $Gt = 1.6$  for the EM-50 series, respectively, at both temperatures. The appearance of such large or maximum toughness seems to have occurred as a result of the relation between the behaviors in  $\sigma_b$  and elongation at break that monotonically decreased with increasing  $Gt$  (though not cited here).

In the case of an SIN, the degree of intermixing and morphology can be predicted to be influenced by the kinetics of a polymer-network formation in both resins. Thus, the above mechanical properties can be explained in terms of the function of the relative polymerization rate.

In the case of  $Gt < 1$ , at first, the polymer networks of epoxy resin are partially formed, and at this time, the BMI resin seems to be homogeneously melted in the gel networks of the epoxy resin at a high temperature for curing. Next, the polymer networks of BMI start to form. Thus-formed SINs would have relatively homogeneous textures. Consequently, such SINs seem to have a higher degree of intermixing, which yields enhanced  $T_g$  and  $\sigma_b$ . Next, in the case of  $Gt > 1$ , BMI polymerizes ini-





**Figure 12** Toughness vs. gelation time ratio  $Gt$  for the EM-50 series.

tially, and at this time, the BMI gels would disperse just like in the epoxy resin matrix, when the concentration of BMI is low. Subsequently, the polymer networks of the epoxy resin are formed and the gelation of the system is completed. Such derived SINs would have relatively low intermixing, which yields diminished  $T_g$  and  $\sigma_b$ . In addition, in the case of such a system as interpenetration occurs, the faster the polymerization rate is for the BMI than for the epoxy resin, the more continuous the network continuity of the former is. As a result, rubbery modulus and tensile strength seem to be enhanced on account of the higher modulus of the polybismaleimide component. The above mechanisms can also be sup-

ported by the relations derived between the turbidity and  $Er'$  or  $\sigma_b$ .

In conclusion, when an IPN is manufactured by a simultaneous polymerization method, a gelling condition that is dependent on levels of catalyzers is an important factor in order to realize an IPN possessing the most appropriate mechanical properties. Further, it remains to be proved that an optical micrography should be investigated to reveal the microstructure and to give more substance to the interpretation of the present behavior.

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