

The Curing Reaction and Glass Transition Temperature of Maleimide Resin Containing Epoxy Groups

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ABSTRACT: Investigation was made of the glass transition temperature (T_g) and the curing reaction mechanism of a new maleimide resin containing epoxy groups. It was found that the T_g of the cured product depended on the reaction temperature and a good heat-resistant product could be obtained under appropriate conditions. This T_g was above 200°C. The reaction mechanism is discussed using measured activation energy and infrared spectra. The primary reaction changed at about 180°C. Both the addition of diamine to the double bond and epoxy group occurred below 180°C. The polymerization of double bonds of bismaleimide took place simultaneously with the above-mentioned two reactions above 180°C.

KEY WORDS Maleimide / Glass Transition Temperature / Activation Energy / Curing Reaction Mechanism /

The maleimide resin formed from bismaleimide and diamine is a good heat-resistant polymer. It is suitable for use over a wide region as a composite material since it does not produce volatile byproducts which cause voids, as other conventional polyimides do. In particular, it has been applied as multilayer printed wiring boards for large-scale computers and FRP for aerospace materials.¹⁻³ Generally, though, maleimide prepolymers can be dissolved only in high boiling point solvents such as *N*-methyl-2-pyrrolidone and have a poor curability which needs a high temperature and long reaction time. Therefore they have poorer workability than epoxy or phenol resins which have also been applied to the same use.

Several years ago, we developed a new maleimide resin containing epoxy groups.⁴ This new prepolymer can be dissolved in low boiling point solvents, such as 2-methoxy-

ethanol or 2-butanone and can be final-cured at a low temperature in a short reaction time. This cured product has very good properties, similar to those of general maleimide resins.

Now, we have studied the relationship between the curing conditions and glass transition temperature (T_g) of products derived from this new prepolymer. The curing reaction mechanism of the prepolymer containing several different functional groups was also examined.

EXPERIMENTAL

Reagents

N,N'-Bismaleimide-4,4'-diphenylmethane (BMI, Mitsui Toatsu Chemical) was used as bismaleimide component. 4,4'-Diaminodiphenylmethane (DDM, Mitsui Toatsu Chemical) and 2,4-diamino-6-phenyl-1,3,5-triazine (BG, Tokyo Kasei) were used as aromatic di-

amine components. Phenol novolac type epoxy resin (DEN438, epoxide equivalent 180, molecular weight 750, Dow Chemical) was used for introducing epoxy groups into the prepolymer. The solvent for synthesis of the prepolymer was 2-methoxyethanol (Wako Pure Chemical). All these chemicals were used without further purification.

Synthesis of Aminobismaleimide Prepolymer

Three mol of BMI, 1 mol of DDM, and 7.5 mol (epoxide equivalent) of DEN 438 were mixed in 2-methoxyethanol and heated at 95°C for 90 min. After cooling to room temperature, 1 mol of BG was added to the solution with stirring. Next, the solution was dried *in vacuo* for 24 h to remove the solvent. The aminobismaleimide prepolymer containing epoxy groups was obtained as a yellow powder. The molecular weight distribution of the prepolymer obtained was measured by the gel permeation chromatography. The prepolymer contained 0.3 mol of 2:1 (BMI:DDM) product, 0.3 mol of 1:2 product, 0.1 mol of 1:1 product, and 2 mol of unreacted BMI. These products were reacted each epoxy resin molecule. It was found that there are 0.17 mol of double bonds, 0.18 mol of active hydrogens and 0.17 mol of epoxy groups in 100 g of the obtained prepolymer powder.

Apparatuses

The glass transition temperature of cured products was measured with a Thermal Mechanical Analyzer TMA-1500 (Shinku Riko). The heating rate was 2°C min⁻¹. The sample was prepared by pre-heating the prepolymer powder at 130°C for 25 min, and then forming a disk of cured product using a mold heated at the desired temperature. The disk had a diameter of 10 mm and a thickness of about 2 mm.

The curability was measured with a JSR-type Curelastmeter (Japan Synthetic Rubber). The vibration angle was 0.5 degree. The curing rate was calculated from the slope at the 50%

value in the curing curve, and the activation energy was obtained from the Arrhenius plot.

Infrared spectra were obtained using a 215 type Infrared Spectrometer (Hitachi) by the KBr method. The sample was a pressed disk containing prepolymer (2 mg) and KBr (240 mg) powders. Before the curing reaction, a spectrum was recorded to obtain an initial value (D_0). Next, the sample disk was placed in a heat-bath at the desired temperature for the curing reaction. The spectrum of the cured disk was measured (D). The ratio (D/D_0) was regarded as the degree of change caused by the curing reaction.

RESULTS AND DISCUSSION

The Glass Transition Temperature of Cured Products

The glass transition temperature (T_g) of the aminobismaleimide containing epoxy groups was measured at various reaction temperatures. The results are shown in Figure 1. When the reaction time is short, T_g has a lower value because of insufficient curing. By adequately long time curing, the T_g reaches a constant value, showing the product to be final-cured. In this case, the T_g depends on the reaction temperature and it is not higher than the

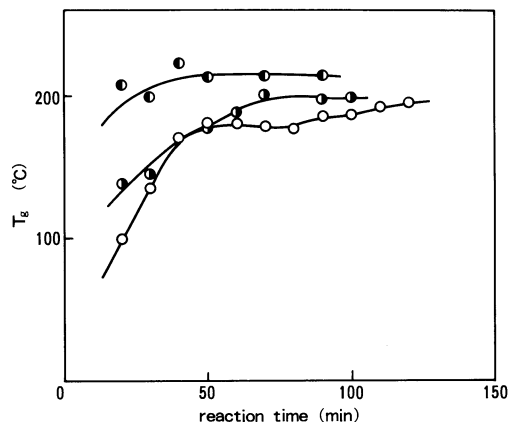


Figure 1. Effect of curing reaction time on glass transition temperature of cured products at various reaction temperatures. ○, 170°C; ◐, 180°C; ●, 200°C.

reaction temperature. Further crosslinking reaction does not occur because the mobility of the polymer chain is severely limited below T_g .

The T_g of products cured at various temperatures for 90 min are shown in Figure 2. The higher the reaction temperature, the higher is the T_g of the cured product and it reaches the curing temperature value. When the reaction temperature is under 200°C, the T_g is 10°C higher than the reaction temperature. It was considered that the sample might be experiencing a higher curing temperature than the set temperature due to exothermic crosslinking reaction. The cured product, with its high T_g , is a good heat-resistant thermosetting resin having better properties than usual

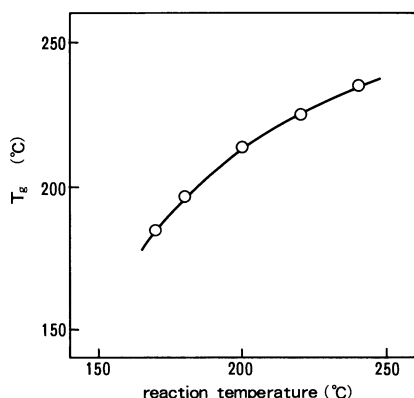


Figure 2. Relationship between glass transition temperature of cured products and reaction temperature for a 90 min curing time.

bismaleimide resins.⁵ Moreover, the curing time to obtain the final-cured product is just 40–50 min at 200°C. This is attributed to introducing epoxy groups which have a high reactivity toward the aminobismaleimide. T_0 obtained the final-cured product at 170°C, which is a comparatively low temperature, this prepolymer needs about 100 min. These are the same conditions as for conventional epoxy resins. But aminobismaleimide, without epoxy groups, shows hardly any reaction at such a low temperature. This difference is due to epoxy groups which react with diamine and form a crosslinking network in the product structure.

Reaction Mechanism

The curability of the prepolymer was measured by a curelaster. The results are shown in Figure 3. The time at the invariable curelast stress (the reaction time when the degree of curing becomes unity) is the same as the time at which T_g becomes constant as shown in Figure 1. For example, both the degree of curability and T_g are constant at about 40 min for 200°C. At this time, it seems that the curing process is completely finished. According to Figure 3, the higher the reaction temperature, the more rapid is the curing rate and the prepolymer is final-cured in a shorter reaction time.

The Arrhenius plot which represents the

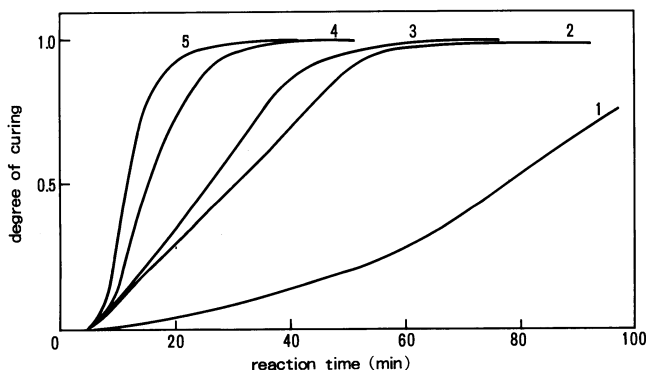


Figure 3. Curing curves at various temperatures. 1, 150°C; 2, 170°C; 3, 180°C; 4, 200°C; 5, 220°C.

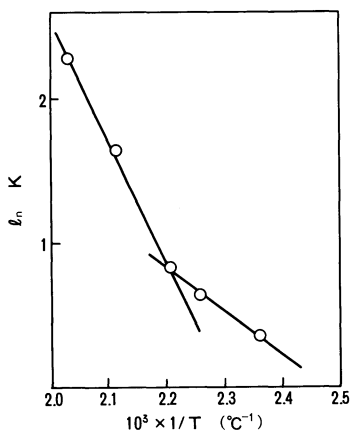
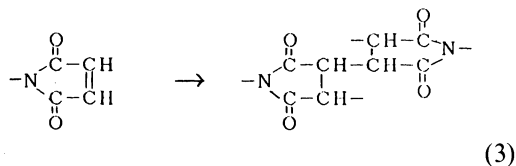
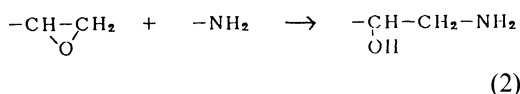
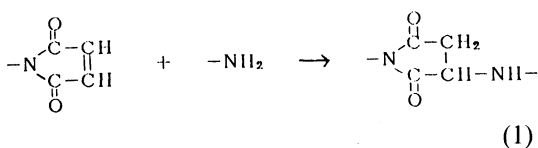


Figure 4. Arrhenius plots of curing reaction.

relationship of the curing rate and curing temperature is shown in Figure 4. The curing rate is obtained from the slope at the half-cured point in Figure 3. According to Figure 4, the activation energy (E_a) change near 180°C and there are different primary reactions for different temperature regions. At lower temperature, a reaction with lower apparent E_a (10.6 kcal mol⁻¹) occurs mainly. On the other hand, a reaction of higher apparent E_a (14.0 kcal mol⁻¹) proceeds at higher temperature. These reactions are assumed to be the following, based on consideration of the prepolymer composition.



Below 180°C, the Michael reaction which is the addition of the amino group of DDM or BG to the double bond of unreacted BMI (eq

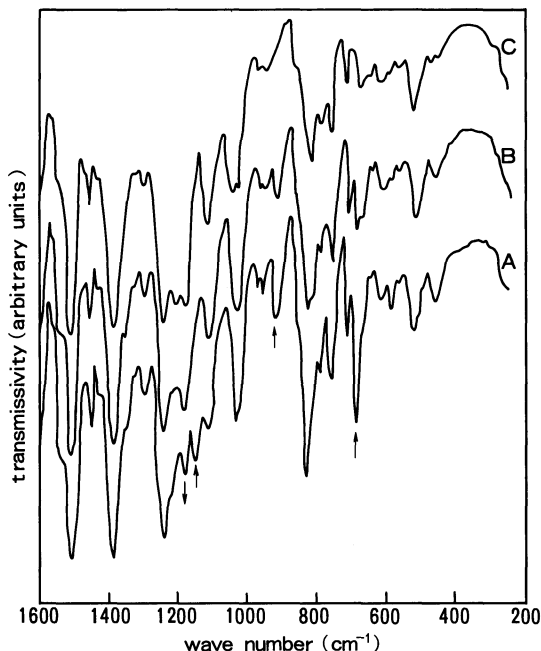


Figure 5. Infrared spectra of prepolymer (A) and products cured at 150°C (B), and 220°C (C).

1) and the ring-opening reaction of the epoxy group by the amino group (eq 2) take place simultaneously. The value of E_a at the ring-opening reaction of an epoxy compound by an aromatic amine is 10–12 kcal mol⁻¹.⁶ The Michael reaction may have a small E_a since it proceeds easily at room temperature. According to the value of E_a obtained in the present experiment, there are two curing reactions, eq 1 and 2, below 180°C. The polymerization of double bonds of BMI of aminobis-maleimide, shown as eq 3, is reported to have an E_a of 13–14 kcal mol⁻¹, as determined by differential scanning calorimetry.⁷ The E_a obtained here at high temperature agrees with the reported value and thus, the polymerization of BMI seems to occur above 180°C.

Moreover, the above-mentioned reaction scheme for the curing process is confirmed by infrared spectra of cured products. Figure 5 shows the spectra of prepolymer (A) and products cured for 90 min at 150°C (B) and 220°C (C).

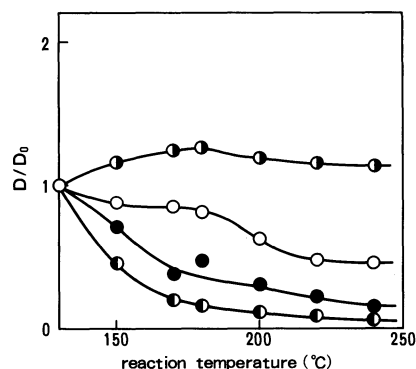


Figure 6. Effect of reaction temperature on absorbance ratio of cured products to prepolymer (D/D_0). ●, 1180 cm^{-1} ; ○, 1150 cm^{-1} ; ●, 910 cm^{-1} ; ●, 690 cm^{-1} .

The absorbance ratio (D/D_0) was measured as the degree of reaction. D_0 is the absorbance of the prepolymer, and D is the absorbance of the cured product at different reaction temperatures. The results are plotted in Figure 6. The absorbance at 1180 cm^{-1} is due to the C–NH–C bond of the secondary amine produced by the addition of the diamine to the double bond or the epoxy ring. The C–N–C bond of unreacted maleimide is represented by the absorbance at 1150 cm^{-1} . The absorbance at 910 cm^{-1} is due to the epoxy group and decreases as the ring-opening reaction proceeds. The double bond of unreacted maleimide is identified at 690, 1150, and 690 cm^{-1} , and increases at 1180 cm^{-1} . Therefore, the addition of amine to the double bond of BMI as shown in (eq 1) occurs. Additionally, the ring-opening reaction of the epoxy group as in (eq 2) occurs at the same time, based on the decreasing peak at 910 cm^{-1} . On the other hand, although the absorbance of products formed above 180°C further decreases at 1150 and 690 cm^{-1} , the absorbance at 1180 cm^{-1} changes hardly at all. This suggests that double bonds of BMI react not only to form succinimide by the addition of the amino group, such as in (eq 1), but also by a different reaction. This is assumed to be the polymerization of double bonds of BMI. Then, the polymerization reaction (eq 3) occurs simul-

taneously, and a product of high crosslinking density is obtained at the high reaction temperature. The T_g of polyaminobismaleimide containing epoxy groups varies with reaction temperature. This is caused not by only the difference in crosslinking density, but also by the difference in the cured product structure. Since absorbances at 910 and 1180 cm^{-1} do not reverse at higher temperature, we feel that the polymerization reaction (eq 3) does not interfere in the addition reaction (eq 1) and ring-opening reaction (eq 2), and these three reactions took place simultaneously over 180°C.

CONCLUSIONS

By investigating the curing reaction of aminobismaleimide containing epoxy groups, it was found that T_g of the product reaches the reaction temperature and a cured product having T_g of over 200°C is obtained under selected conditions. This product has the same heat-resistant properties as general maleimide resins, though the present prepolymer has epoxy groups. Moreover, this prepolymer has good curability, and it was final-cured after 40–50 min at a reaction temperature of 200°C. This good reactivity seems to be caused by introducing epoxy groups into the prepolymer structure.

Finally, according to activation energy obtained by curelasmeter and infrared spectra, it was found that the primary reaction changed near 180°C. At lower temperature, both addition to the double bond of maleimide and ring-opening reaction of the epoxy group by diamine occurred. Above 180°C, the polymerization of double bonds also took place, and did not interfere with the other two reactions. The polymerization reaction had a higher E_a value (14.0 kcal mol^{-1}) compared with the reactions concerning diamine, occurring at lower temperature. The scheme was confirmed by infrared spectra of cured products obtained at various curing temperatures.

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