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# Characteristics of epoxy resin cured with in situ polymerized curing agent

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**Abstract**

In order to improve the heat resistance of a cured epoxy resin together with reducing the viscosity of the resin composition, an epoxy resin was cured with a curing agent formed from the radical copolymerization of vinyl monomers during the cure process of the epoxy resin. *N*-phenylmaleimide and *p*-acetoxystyrene were used as vinyl monomers of the curing agent. The epoxy resin was cured by the insertion reaction of the ester group of the in situ polymerized curing agent and the epoxy group of the epoxy resin. In the cure system of the epoxy and the phenol resins, reduction of the viscosity of the resin composition was achieved by replacing some or all of the phenol resin with these monomers. When all phenol resins were replaced by these monomers, the viscosity of resin composition (0.01 Pa s at 70 °C) decreased by about 1/2000 compared with that of the system with only phenol resin (21 Pa s at 70 °C). The glass transition temperature ($T_g$) of the cured resin with no phenols was 174 °C, an improvement of 17 °C compared with that of the system cured with only phenol resin. The flexural strength of the new resins remained unchanged. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Epoxy resin; Heat resistance; Low viscosity

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## 1. Introduction

Epoxy resins are widely used in the electronic industry because of their superior thermal, mechanical, and electrical properties. During the IT (Information Technology) revolution in recent years, the accompanying electronic apparatus has made impressive technological progress. Various personal digital aids including cellular phones have also become smaller and have a great number of varied functions. Therefore, technical development has been undertaken to make various electronic products smaller and thinner. In the case of the molding material used for the semiconductor package, improvement of properties such as heat resistance and rigidity is required. In order to improve these properties, it is necessary to improve the properties of the epoxy resin used for the molding material. To do this, it is necessary to (1) improve the heat resistance and (2) reduce the viscosity of the resin composition, which will enable the filler content to be increased.

Various methods of improving the heat resistance of cured epoxy resin together with reducing the viscosity of epoxy resin composition have been made. The cycloaliphatic type epoxy resins have low viscosity and their cured resins have high glass transition temperature ($T_g$) [1]. But they are poor in mechanical elongation and toughness because of their high crosslinking density. To improve the performance of the cycloaliphatic epoxy resin, a new family of cycloaliphatic epoxy resins was discussed [2,3]. Moreover, low viscosity epoxy resins, such as biphenyl-type, [4–7], dicyclopentadiene-type [8], etc. have been examined. Thus, the method of introducing rigid structure into the resin skeleton is one effective means of improving these properties. Another method involves forming an interpenetrating polymer network (IPN) by introducing other polymer into the epoxy network. We investigated the formation of the semi-IPN structure of the epoxy resin and the thermoplastic polymer with high $T_g$ [9]. Reduction in the viscosity of epoxy resin composition was achieved by forming the thermoplastic polymer from vinyl monomers during the cure process of the epoxy resin simultaneously (in situ polymerization). In situ polymerization is very effective in reducing the viscosity of resin composition.

For further reduction in the viscosity of resin composition, we tried to form a curing agent of the epoxy resin with high $T_g$ by in situ polymerization. *N*-phenylmaleimide (PMI) and *p*-acetoxystyrene (AxSt) were used as vinyl monomers of the curing agent. The epoxy resin was cured by the insertion reaction [10] of the ester group of the in situ

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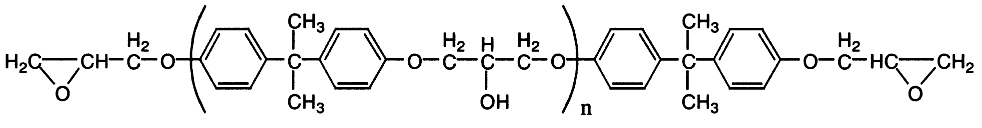
polymerized curing agent and the epoxy group of the epoxy resin. In this paper, the polymerization nature of these vinyl monomers in the epoxy resin, and the reaction of the in situ polymerized curing agent and the epoxy resin were discussed. The thermal and mechanical properties of the cured resins were also evaluated.

## 2. Experimental

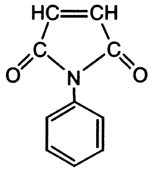
### 2.1. Materials and preparation of samples

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA: Epikote825; Japan Epoxy Resins Co., Ltd).

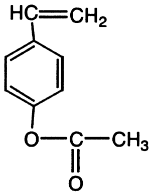


Epikote825

The curing agent used was a phenol resin (VR-9315; Mitsui Chemicals, Inc.). PMI and AxSt were used as vinyl monomers of the curing agent of the epoxy resin.



PMI



AxSt

Fractions of the AxSt monomer and the PMI monomer were blended so that their molar ratio was 1/1. The epoxy resin was compounded stoichiometrically with the curing agent: one epoxy group corresponds to one hydroxyl group of the phenol resin or to one ester group of the AxSt. The phenol resin and AxSt were blended so that their total quantity was equivalent to that of the epoxy resin. The fraction of PMI/AxSt monomers in the curing agent (phenol resin and PMI/AxSt monomers) was varied so that the AxSt monomer was 0, 0.25, 0.50, 0.75, or 1.0 equiv. to the epoxy resin. The accelerator used was 1,5-diazabicyclo[4,3,0]-5-nonene (DBN), which was added at 0.25 phr. 2,5-Dimethyl-2,5-bis(benzoyl peroxy)hexane was used as the initiator of the vinyl monomers because its decomposition temperature (110 °C) is close to cure temperature (100 °C) and it is easily melted in epoxy and phenol resins at 100 °C. The concentration of the added initiator was 0.5 wt%.

Preparation of the epoxy composition was performed as follows. An epoxy resin and phenol resin were first mixed uniformly at 135 °C. After cooling, the mixture at 100 °C, the PMI monomer and the initiator were added to the mixture and mixed until they dissolved uniformly. Then, after cooling the mixture to 40 °C, the AxSt monomer and the accelerator were added and mixed. The mixture was rapidly taken out of the apparatus and poured into glass molds. The compounds were cured at 100 °C for 6 h followed by 180 °C for 8 h.

### 2.2. Measurements

The molecular weight was measured with solvent THF using a gel permeation chromatograph (GPC:HLC-8020, Tosho Co., Ltd).

IR spectra were recorded with an FT-IR spectrophotometer (FT/IR-230, Japan Spectroscopic Co., Ltd).

The $T_g$s of the copolymers were measured by differential scanning calorimetry (DSC-3100, MAC Science Co., Ltd) at a heating speed of 5 °C/min.

The $T_g$s of the cured epoxy resins were measured by dynamic mechanical analysis (DMA) using a non-resonance forced vibration viscoelastometer (RDA, Rheometrics Co., Ltd). The frequency was adjusted to 1 Hz and the heating rate was 2 °C/min in air.

The mechanical properties of the cured epoxy resins were determined with a Shimadzu autograph AG-5000D universal testing machine. Flexural tests were carried out at a crosshead speed of 1.5 mm/min according to JIS-K 6911. Bars of $3 \times 10 \times 85$ mm$^3$ were used at a span of 48 mm to measure the flexural properties. Five specimens were tested for each sample.

## 3. Results and discussion

### 3.1. Copolymerization of the PMI/AxSt monomers in the epoxy/phenol resins

In order to investigate the copolymerization of the PMI/AxSt monomers in the epoxy and phenol resins, the copolymerization process was monitored with GPC. Fig. 1 shows the GPC profile of the copolymerization of the PMI/AxSt (1.0 equiv.) monomers in the epoxy resin when all phenol resins were replaced by the AxSt monomer. Here, in order to investigate only the copolymerization of these monomers, the accelerator was not added. Before polymerization, the monomer peaks of PMI and AxSt overlapped each other on the low molecular weight side. The GPC peak of epoxy resin with one sharp peak and two small peaks appeared on the higher molecular weight side. When the initiator was added to the mixture and the monomers were

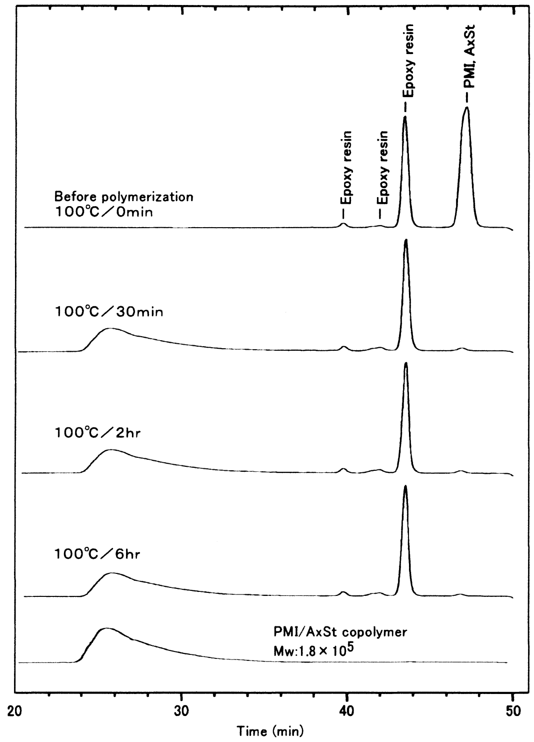


Fig. 1. GPC profiles of polymerization process of vinyl monomers in epoxy resin. Composition: epoxy resin/vinyl monomers (PMI/AxSt (1.0 equiv.) = 1/1 molar ratio).

polymerized at 100 °C, the peak of the monomers decreased. This peak disappeared after 30 min at 100 °C and a GPC peak of the copolymer was observed on the high molecular weight side. No change in the GPC profile was observed even after 2 or 6 h at 100 °C. When the PMI/AxSt monomers were polymerized for 6 h at 100 °C in the epoxy resin, the molecular weight ($M_w$) of the copolymer extracted from the uncured resin was approximately 180,000. The Q–e values of AxSt are indicated to be $Q = 1.35$ and $e = -0.8$ by Danusso and others [11]. Considering these values, it is assumed that the polymerization action of the AxSt monomer will be almost the same as that of a styrene (St) monomer. We discussed the copolymerization nature of PMI/St in epoxy and phenol resins in our previous report [9], in which we confirmed that these monomers will rapidly polymerize in these resins. Therefore, the PMI/AxSt monomers are also considered to have polymerized rapidly in these resins and to have formed a copolymer.

Fig. 2 shows the GPC profile of the copolymerization of the PMI/AxSt (0.5 equiv.) monomers in the epoxy and phenol resins (0.5 equiv.) when half of the phenol resin was replaced by the AxSt monomer. The copolymerization of PMI/AxSt monomers also progressed rapidly in the epoxy and phenol resins, completing after 30 min at 100 °C. When the PMI/AxSt monomers were polymerized for 6 h at 100 °C in the epoxy and phenol resins, the molecular weight ($M_w$) of the copolymer extracted from the uncured resin was approximately 110,000.

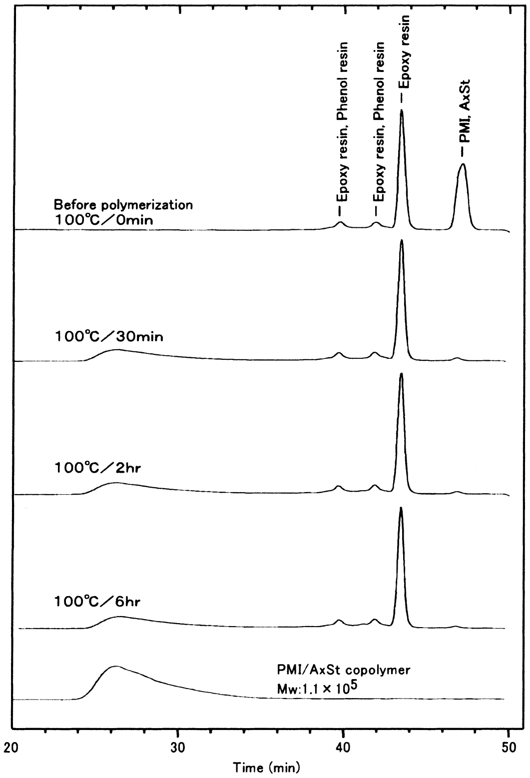


Fig. 2. GPC profiles of polymerization process of vinyl monomers in epoxy and phenol resins. Composition: epoxy resin/phenol resin (0.5 equiv.)/vinyl monomers (PMI/AxSt (0.5 equiv.) = 1/1 molar ratio).

The characteristics of the copolymers extracted from the uncured resin compositions with different content of PMI/AxSt monomers are shown in Table 1. The molecular weight of the copolymer increased with an increase in the PMI/AxSt content. This may be attributed to the lower viscosity of the resin composition with higher PMI/AxSt content, as described below. The $T_g$s of the copolymer polymerized in the resin compositions with higher PMI/AxSt content was high, since the copolymer had a high molecular weight. The $T_g$ of the copolymer polymerized in the resin composition with PMI/AxSt (1.0 equiv.) was 210 °C. Therefore, improvement of the $T_g$ could be expected in the resin composition with higher PMI/AxSt content.

As mentioned above, it was confirmed that the PMI/AxSt

Table 1
Characterization of copolymer

| Composition (molar ratio) | $M_w$ | $M_n$ | $M_w/M_n$ | $T_g$[a] (°C) |
|---|---|---|---|---|
| PMI/AxSt = 1/1 (0.25 equiv.) | 47,000 | 12,000 | 2.7 | 183 |
| PMI/AxSt = 1/1 (0.50 equiv.) | 110,000 | 19,000 | 5.7 | 199 |
| PMI/AxSt = 1/1 (0.75 equiv.) | 190,000 | 36,000 | 5.4 | 209 |
| PMI/AxSt = 1/1 (1.00 equiv.) | 180,000 | 29,000 | 6.1 | 210 |

[a] Measured by DSC.

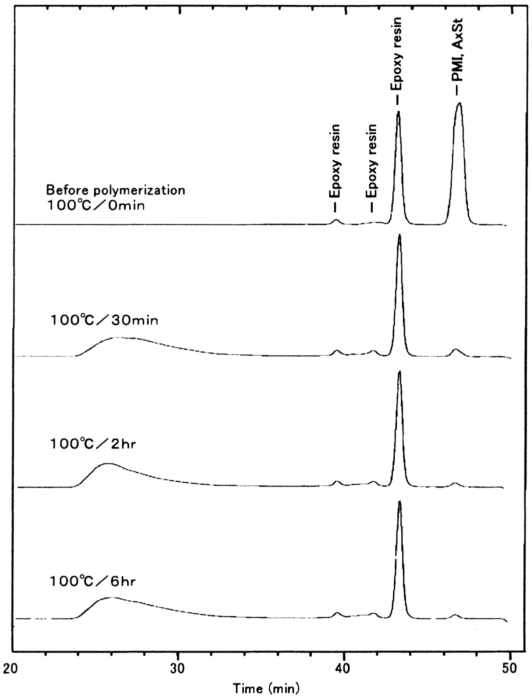


Fig. 3. GPC profiles of in situ polymerization process of vinyl monomers during cure process of epoxy resin. Composition: epoxy resin/vinyl monomers (PMI/AxSt (1.0 equiv.) = 1/1 molar ratio).

monomers polymerized rapidly in the epoxy and the epoxy/phenol resins and that copolymers with $T_g$ of 200 °C were formed.

### 3.2. *In situ polymerization of PMI/AxSt monomers during the cure process of the epoxy resin*

Fig. 3 shows the GPC profile of the copolymerization of the PMI/AxSt (1.0 equiv.) monomers during the cure process of the epoxy resin when all phenol resins were replaced by the AxSt monomer. Here, in order to investigate the copolymerization action of the PMI/AxSt monomers during the cure process of epoxy resin, the accelerator was added to the resin composition. During the cure process of the epoxy resin, the copolymerization of these monomers progressed rapidly. The monomer peak almost disappeared after 30 min at 100 °C and a GPC peak of the copolymer was observed on the high molecular weight side. Thus, it was confirmed that the polymerization behavior of these monomers during the cure process of the epoxy resin was same as the behavior without curing. However, the GPC peak of the epoxy resin was almost unchanged compared with before cure even if cured for 2 or 6 h at 100 °C. Next, in order to monitor the reaction of epoxy resin and AxSt, the IR spectrums of this composition under curing were measured. Change in the IR spectrum under curing at 100 °C is shown in Fig. 4. The –C=O peak of the acetoxy group of AxSt at 1760 cm$^{-1}$ and the peak of the epoxy group at 915 cm$^{-1}$ hardly changed. From these results, it was confirmed that the ester insertion reaction of the epoxy resin and AxSt hardly progresses during the cure process at 100 °C although the copolymerization reaction of the PMI/AxSt monomers progresses. Change in the IR spectrum under curing at 180 °C of the post-cure is shown in Fig. 5. The –C=O peak of AxSt at 1760 cm$^{-1}$ and the peak of the epoxy group at 915 cm$^{-1}$ decreased with elapse of cure time. When 8 h passed at 180 °C, their peaks almost disappeared. Instead, a –C=O peak near 1740 cm$^{-1}$ newly appeared and increased with elapse of cure time at 180 °C. It was assumed that the new peak near 1740 cm$^{-1}$ was a peak based on the –C=O peak made by the ester insertion reaction of the epoxy resin and AxSt. Here, the DMA of the system cured with only phenol resin and the system with reduced content of phenol resin of 0.5 equiv. (the PMI/AxSt monomers have not been added) were measured. The results are shown in Fig. 6. The $T_g$ of the system cured with only phenol resin was 157 °C. The $T_g$ of the system with reduced content of phenol resin of 0.5 equiv. was 90 °C which was a marked decrease. This indicated that reactions, other than the reaction of the epoxy resin and the phenol resin, such as a reaction of epoxy

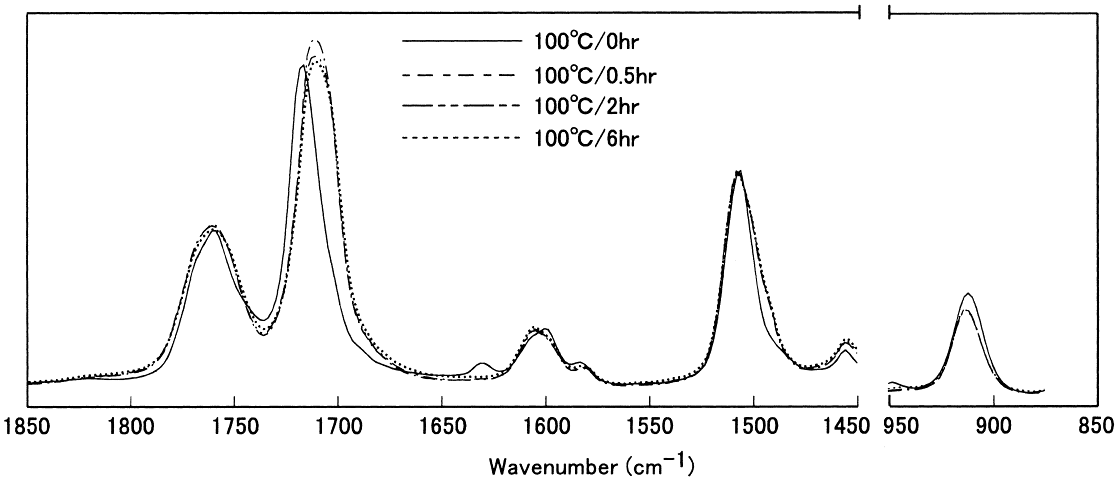


Fig. 4. IR spectra of epoxy resin containing vinyl monomers during cure process at 100 °C. Composition: epoxy resin/vinyl monomers (PMI/AxSt (1.0 equiv.) = 1/1 molar ratio).

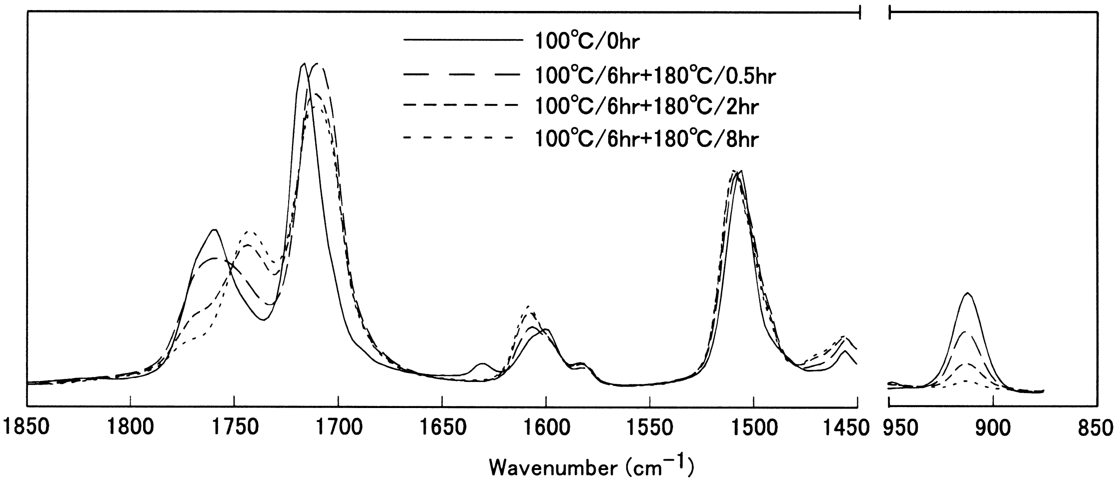
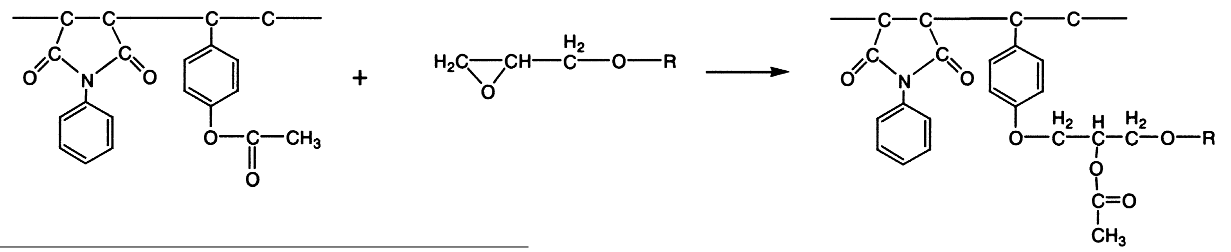


Fig. 5. IR spectra of epoxy resin containing vinyl monomers during cure process at 180 °C. Composition: epoxy resin/vinyl monomers (PMI/AxSt (1.0 equiv.) = 1/1 molar ratio).

resins, do not progress under this curing condition. Accordingly, it was concluded that the disappearance of the –C=O peak of AxSt at 1760 cm$^{-1}$ and the peak of the epoxy group at 915 cm$^{-1}$, and the appearance of the –C=O peak near 1740 cm$^{-1}$ was dependent on the progress of the ester insertion reaction of the epoxy resin and AxSt at 180 °C of the post-cure, as shown in the equation.



As mentioned above, the PMI/AxSt monomers polymerized rapidly in the epoxy resin and in the epoxy and the phenol resins. Moreover, the cured resin was formed by the

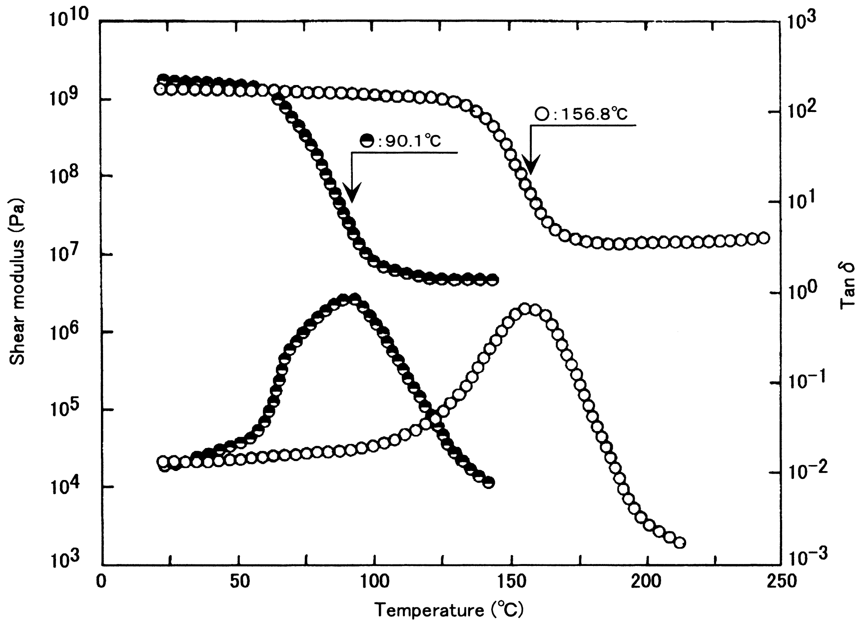


Fig. 6. Dynamic mechanical properties of cured epoxy resins. Samples: ○, epoxy resin/phenol resin (1.0 equiv.); ●, epoxy resin/phenol resin (0.5 equiv.).

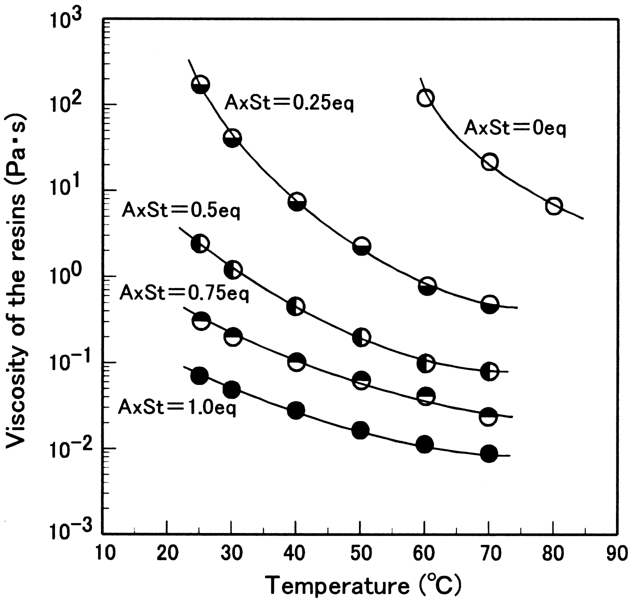


Fig. 7. Viscosity of resin compositions with PMI/AxSt monomers. Samples: ○, AxSt = 0 equiv.; ◒, AxSt = 0.25 equiv.; ◐, AxSt = 0.5 equiv.; ◓, AxSt = 0.75 equiv.; ●, AxSt = 1.0 equiv.

insertion reaction of the ester group of the polymerized copolymer and the epoxy group of the epoxy resin.

### *3.3. The material properties of the epoxy resin cured with in situ polymerized curing agent*

The viscosity of the uncured resin compositions before cure/polymerization is shown in Fig. 7. The viscosity of the resin composition decreased as the content of PMI/AxSt monomers was increased. The viscosity of the system with only phenol resin (AxSt = 0 equiv. in Fig. 7) at 70 °C was 21 Pa s. The viscosity of the system in which half the phenol resin was replaced by PMI/AxSt monomers (AxSt = 0.5 equiv. in Fig. 7) was 0.1 Pa s. The value was about 1/200 of the viscosity of the system with only phenol resin. Furthermore, when all phenol resins were replaced by the AxSt monomer (AxSt = 1.0 equiv. in Fig. 7), the viscosity of the resin composition decreased even to 0.01 Pa s. The value decreased to about 1/2000 compared with the viscosity of the system with only phenol resin. This indicated that the viscosity of the epoxy resin composition could be reduced enormously when the phenol resin was replaced by the PMI/AxSt monomers.

A dynamic viscoelastic analysis (DMA) provided information on the microstructure of the cured resins. Fig. 8 shows the DMA measurement of these cured resins. In the system cured with only phenol resin, a single tan $\delta$ peak based on the $T_g$ of the epoxy matrix was observed at 157 °C. The tan $\delta$ peak of the system with half phenol resin replaced by PMI/AxSt became considerably broad. In this case, the $T_g$ was 163 °C and shifted about 6 °C higher than that of the system cured with only phenol resin. Furthermore, for the tan $\delta$ of the system with all phenol resin replaced by PMI/AxSt, a clear peak could be observed. This system's $T_g$ value was 174 °C, which was an improvement of about 17 °C compared with that of the system cured with only phenol resin. Thus, the cure with an in situ polymerized curing agent made it possible to reduce the viscosity of the resin compositions and to improve the heat resistance of the cured epoxy resins. The modulus in the rubbery region was also investigated. In the case of the system with half phenol resin replaced by PMI/AxSt, the modulus in the rubbery region was lower than that of the system cured with only

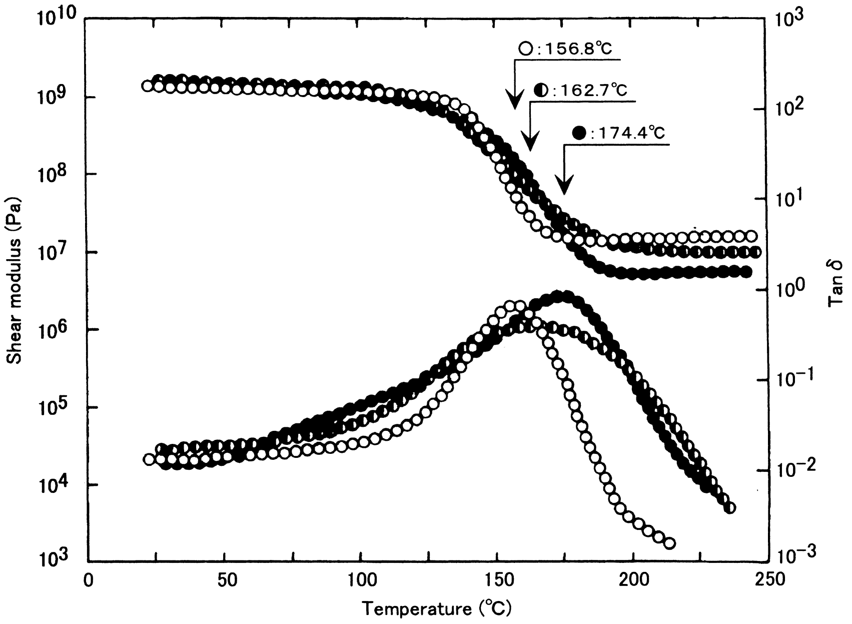


Fig. 8. Dynamic mechanical properties of cured epoxy resins. Samples: ○, epoxy resin/phenol resin (1.0 equiv.); ◐, epoxy resin/phenol resin (0.5 equiv.)/(PMI/AxSt (0.5 equiv.) = 1/1 molar ratio); ●, epoxy resin/(PMI/AxSt (1.0 equiv.) = 1/1 molar ratio).

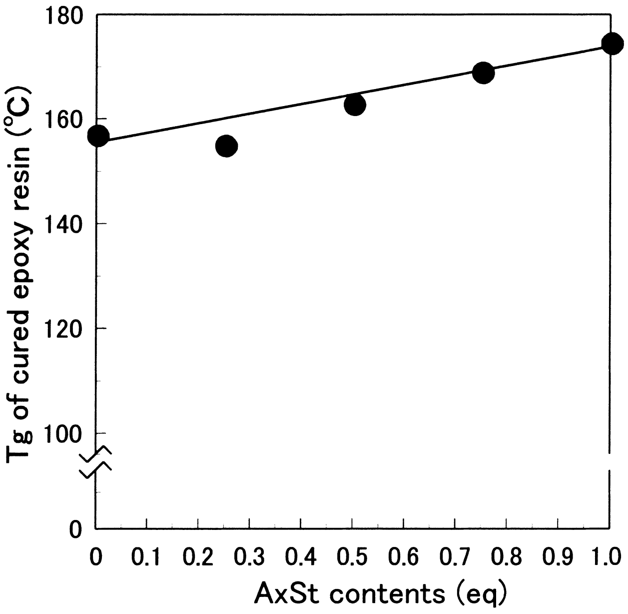


Fig. 9. Effect of AxSt contents in cured agent on $T_g$ of cured epoxy resin.

phenol resin. The modulus in the rubbery region of the system with all phenol resin replaced by PMI/AxSt decreased still further. Thus, in the systems with half or all phenol resin replaced by PMI/AxSt, it was confirmed that the crosslink density of the cured resins was lower than that of the system cured with only phenol resin. Accordingly, it was considered that the heat resistance of these systems was improved by the influence of the rigid skeleton, which reduced the crosslink density of the cured resin. Fig. 9 shows the $T_g$ of the cured resins as a function of the PMI/AxSt content in the curing agent. The $T_g$ of the cured resin increased linearly with an increase in PMI/AxSt content.

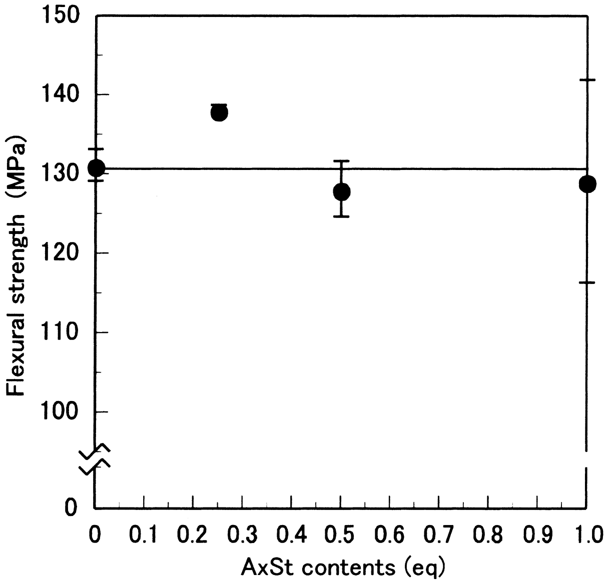


Fig. 10. Effect of AxSt contents in cured agent on flexural strength of cured epoxy resin.

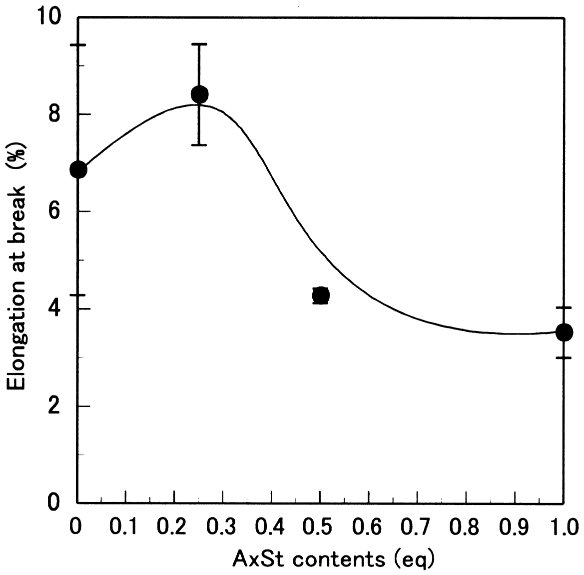


Fig. 11. Effect of AxSt contents in cured agent on elongation of cured epoxy resin.

Next, we measured the mechanical properties of these cured resins. Fig. 10 shows the flexural strength of the cured resins as a function of the PMI/AxSt content in the curing agent. The flexural strength of the system cured with only phenol resin was about 130 MPa. The flexural strength of the systems with phenol resin replaced by PMI/AxSt was equal to that of the system cured with only phenol resin, irrespective of the PMI/AxSt content. Thus, it was indicated that the replacement of phenol resin by PMI/AxSt could improve the heat resistance of the cured resin, while retaining its flexural strength.

Fig. 11 shows the relationship between the elongation of these cured resins and the PMI/AxSt content in the curing agent. The elongation of the cured resins was quite dependent on the PMI/AxSt content in the curing agent. In the case of the system with some phenol resin replaced by PMI/AxSt, the elongation of the cured resin increased. But, the elongation of the systems with half or all phenol resin replaced by PMI/AxSt decreased compared with that of the system cured with only phenol resin. In spite of the decrease of the crosslink density in these systems, the decrease of the elongation seems to be for their rigid skeleton. Accordingly, it is assumed that the fracture toughness of the systems with half or all phenol resin replaced by PMI/AxSt decreases although the system with some phenol resin replaced by PMI/AxSt increases. In future, molecular design that causes the increase of fracture toughness of the cured resin will be important.

## 4. Conclusions

In order to improve the heat resistance of the cured resin together with reducing the viscosity of the epoxy resin composition, an epoxy resin was cured with a curing agent formed from the radical copolymerization of vinyl monomers during the curing process of the epoxy resin. PMI and AxSt were used as vinyl monomers of the curing agent. The following results were obtained.

1. The PMI/AxSt monomers were polymerized rapidly in the epoxy resin and in the epoxy and the phenol resins. Moreover, the in situ polymerized curing agent cured the epoxy resin by the ester insertion reaction of the ester group of the polymerized copolymer and the epoxy group of the epoxy resin.
2. The viscosity of the epoxy resin composition decreased with an increase in the amount of phenol resin replaced by PMI/AxSt. When all phenol resin was replaced by the PMI/AxSt monomers, the viscosity of the composition was 0.01 Pa·s at 70 °C. The value decreased to about 1/2000 compared with the viscosity of the curing system with only phenol resin.
3. The $T_g$ of the system with all phenol resin replaced by PMI/AxSt was 174 °C, which was an improvement of about 17 °C compared with that of the system cured with only phenol resin. The crosslink density of the system with no phenols was lower than that of the system cured with only phenol resin. Moreover, the flexural strength of the system with no phenols was equal to that of the system cured with only phenol resin.

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