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Toughening of epoxy resin modified with in situ polymerized thermoplastic polymers

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Abstract

A thermoplastic polymer modification was tried for the purpose of simultaneously improving the heat resistance and toughness of a cured epoxy resin. The thermoplastic polymer was formed during the cure process of the epoxy resin in order to avoid any increase in the viscosity of the resin at the time of mixing. When 24 wt% of the phenylmaleimide/benzyl methacrylate/styrene monomers with a molar ratio composition of 5/5/3 was added to epoxy and phenol resins, the resin viscosity at mixing fell to about 1/8 of an unmodified resin. The epoxy and phenol resins were cured, forming a thermoplastic polymer by radical polymerization of these monomers. The glass transition temperature (T_g) of the cured resin was improved by about 10°C and the value of the fracture toughness was also improved by about 2.5 times that of the unmodified resin. This is attributed to the formation of the semi-interpenetrating polymer networks (semi-IPN) composed of the epoxy network and linear thermoplastic polymer. © 2001 Published by Elsevier Science Ltd.

Keywords: Polymer alloy; Semi-IPN; Toughening

1. Introduction

Epoxy resins are widely used in the electronics industry because of their superior thermal, mechanical and electrical properties. As applications of epoxy resins spread into the advanced technical fields, such as printed wiring boards and plastic IC packages, high performance resins have been demanded. Improvements in heat resistance and toughness are highly desired features. In most cases, enhancement of these characteristics is not achieved by improving only the structure of the epoxy resins. Therefore, modifications by elastomers (rubbers) or thermoplastic polymers have been investigated.

The modification of epoxy resins with reactive liquid elastomers, such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) or crosslinked-elastomers, have been investigated as a successful means of enhancing the fracture toughness of brittle epoxy resins [1–10]. In general, the effective improvement in toughness of elastomer-toughened epoxy resins can be achieved when the elastomer particles are dispersed on a micro-level. However, toughness improvements in most elastomer-modified epoxy systems usually result in a significant decrease in the modulus and the glass transition temperature (T_g) of the cured epoxy resins.

Recently, many attempts have been made to modify epoxy resins with high-performance engineering thermoplastic polymers that have high T_g and toughness, such as polysulfone (PSF) [11,12], poly(ether sulfone) (PES) [13–16], poly(ether imide) (PEI) [17–19] and polyimide (PI) [20]. An effective improvement in toughness in only obtained at high fractions of the engineering thermoplastic polymers, where the thermoplastic polymer forms a continuous phase with the epoxy spherical domain or the thermoplastic polymer and the epoxy form a co-continuous phase. However, the viscosity of the epoxy resins modified with high fractions of the engineering thermoplastic polymer drastically increases, which causes a decrease in handling. In addition, the T_g of the resins modified with the thermoplastic polymer is equal to or only slightly higher than that of the unmodified resin, due to the formation of the phase-separation morphologies.

On the other hand, attempts have been made to homogeneously dissolve the linear thermoplastic polymers in the epoxy resins [21–23]. This is a semi-interpenetrating polymer network (semi-IPN) technique that blends two polymers by entangling the molecular chain of thermoplastic polymer to an epoxy network without chemical bonding between them. The formation of the semi-IPN structure makes it possible to homogeneously blend the

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epoxy matrix and the thermoplastic polymer, or, to microscopically disperse the thermoplastic polymer in the epoxy matrix in a combination of immiscible polymers. We may expect that the semi-IPN structure blend combine the properties of two polymers because of the composite at a molecular level. The IPN or semi-IPN technique is one of the most effective modifications for epoxy resins with low fractions of the thermoplastic polymer [16,23].

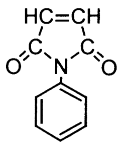
We also investigated the effect of the phase structures of the cured epoxy resins on heat resistance and toughness by modifying the thermoplastic polymer, polyethersulfone (PES) [16]. The change in the molding temperature made it possible to control the phase morphology of the cured resins from the homogeneous phase to the heterogeneous phase that has a particulate phase or a co-continuous phase. The following conclusion can be drawn from this study: the cured resin with a homogeneous morphology, which forms a semi-IPN structure composed of the epoxy matrix and linear thermoplastic polymer, can improve the heat resistance and toughness of cured resins with a very small amount of thermoplastic polymer. However, the viscosity of the resins modified with a very small amount of thermoplastic polymer is still insufficient to apply this technique to industry.

In summary, an attempt was made to simultaneously improve the heat resistance and toughness of a cured epoxy resin, reducing resin viscosity at mixing. Then, the monomers that constituted the thermoplastic polymer were added to the epoxy resin, the thermoplastic polymer was formed during the cure process of an epoxy resin by radical polymerization (in situ polymerization), and, finally, the cured epoxy resin modified with thermoplastic polymer was obtained. The effect of the modification of the epoxy resin by in situ polymerized thermoplastic polymer on the thermal and mechanical property of a cured resin was discussed. In addition, the toughening mechanism was investigated in detail using optical and electron microscope techniques.

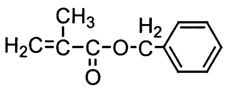
2. Experiments

2.1. Materials and preparation of samples

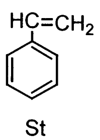
The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA: Epikote 828; Yuka-Shell Epoxy). The curing agent used was the *p*-xylylene phenol resin (XL225-3L; Mitsui Toatsu Chemicals). 1-Isobutyl-2-methylimidazol (IBMI; Yuka-Shell Epoxy) was added as an accelerator. The thermoplastic polymer was prepared by the radical copolymerization of *N*-phenylmaleimide (PMI), benzyl methacrylate (BzMA) and styrene (St) monomers. In the PMI/BzMA or PMI/St system, the thermoplastic polymers were prepared in the 5/5 molar ratios, respectively. The concentration of the added monomers varied from 0 to 30% by weight. In the PMI/BzMA/St system, the thermoplastic polymers were prepared in the 5/5/*x* molar ratio of the PMI/BzMA/St monomers. The total content of the PMI and BzMA monomers was fixed at 20 wt%, and the St monomer was then added to the blend so that the St composition became $x = 0$–6 molar ratio. 2,5-Dimethyl-2,5-bis(benzoyl peroxy)hexane was used as an initiator 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 epoxy resin was stoichiometrically compounded with the curing agent, with one epoxy group per one hydroxyl group of curing agent. The compounds were stirred at 100°C until every monomer homogeneously dissolved in the epoxy and phenol resins. As soon as the accelerator (0.25 phr) and initiator (0.2 wt% of total monomers) were added to and homogeneously dissolved in the mixture, 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 6 h, except for the PMI/BzMA system. Only the PMI/BzMA system was cured at 100°C for 25 h followed by 180°C for 6 h because it took 20 h or more at 100°C to polymerize their monomers.



PMI



BzMA



St

2.2. Measurements

The morphology of the fracture surfaces was observed using a scanning electron microscope (SEM: JSM-T20, JEOL). The fracture surfaces were coated with a gold layer about 200 Å thick.

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

The T_gs of the thermoplastic polymers were measured by a differential scanning calorimetry (DSC-3100, MAC Science) at a heating speed of 10°C/min.

The fracture toughness of the cured epoxy resins was evaluated from the critical value K_c of the stress intensity factor for the initiation of crack growth, which was determined from 3-point bent specimens ($5 \times 15 \times 75$ mm with a span of 59 mm) according to ASTM E 399-78. Careful tapping with a fresh razor blade formed a sharp pre-crack. The specimen was loaded at a constant crosshead speed (0.5 mm/min). Five specimens were tested for each sample.

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 were used at a span of 48 mm to measure the flexural properties. Again, five specimens were tested for each sample.

The subsurface damage was also examined using a transmission optical microscope (OM: BH-2, Olympus). The specimens for the OM-observations were prepared with a petrographic polishing technique described by Holic et al. [24]. The thickness of the specimens was less than 35 μm. These sections were inspected using transmitted light with and without crossed polarizers, because Yee [7] demonstrated that the crossed Nicol technique is useful for observing deformations near the crack tip, which induce birefringence.

An ultra-thin section of the modified epoxy resins was examined using a transmission electron microscope (TEM: JEM-1200EX, JEOL) to observe the microstructure. The specimens for the TEM-observations were stained with ruthenium tetroxide(RuO_4).

3. Results and discussion

3.1. Polymerization of the vinyl monomers in the epoxy/phenol resins

In a previous paper [16], we reported that a cured resin with a homogeneous morphology, which formed a semi-IPN structure, could simultaneously improve the heat resistance and toughness of the cured epoxy resins. Therefore, vinyl monomers which form a thermoplastic polymer were selected on the basis of the following concepts: (1) the thermoplastic polymer needs to have a high T_g from the point of the improvement of the heat resistance of the cured epoxy resin; and, (2) the thermoplastic polymer is compatible in the epoxy matrix. The introduction of a rigid ring structure such as an imide ring into the thermoplastic polymer is effective for improving the T_g. Therefore, the PMI monomer was used as a basic monomer, and the copolymerization of PMI and other monomers was examined. The BzMA and St monomers were examined as a copolymerization monomer of the PMI monomer.

The GPC profile of the polymerization process of the PMI and the BzMA monomers in the epoxy and the phenol resins (molar ratio: PMI/BzMA = 5/5 content: 20 wt%) is shown in Fig. 1A. Here, in order to investigate the polymerization action of these monomers in the epoxy and the phenol resins, polymerization was carried out without adding the accelerator. A broad peak of the phenol existed on the high molecular weight side, and a peak of the epoxy resin with a shoulder existed on the low molecular weight side (Fig. 1A (a)). The monomer peaks of PMI and BzMA overlapped each other on the low molecular weight side, lower than that of the epoxy resin (Fig.1A (b)). When the initiator was added to the blend and these monomers were polymerized at 100°C, these monomer peaks decreased. Each monomer peak almost disappeared after 20 h at 100°C and a GPC peak of the thermoplastic polymer was observed on the high molecular weight side (Fig. 1A (c)). Thus, in the PMI/BzMA system, it took 20 h at 100°C to polymerize these monomers. The GPC profile of the polymerization process of the PMI and the St monomers in these resins (molar ratio: PMI/St = 5/5, content: 20 wt%) is shown in Fig. 1B. When the initiator was added to the blend and these monomers were polymerized at 100°C for a 0.5 h period (Fig. 1B (b)), each monomer peak disappeared and a GPC peak of the thermoplastic polymer was observed on the high molecular weight side. No change in the GPC profile was observed even after a long time (Fig. 1B (c)). In the PMI/St system, the polymerization of the monomers proceeded rapidly in these resins. These thermoplastic polymers, which were polymerized in the epoxy and the phenol resins, were extracted from the uncured blend, and their properties are shown in Table 1. The molecular weight (M_w) of the thermoplastic polymer composed of the PMI/St was 36 000

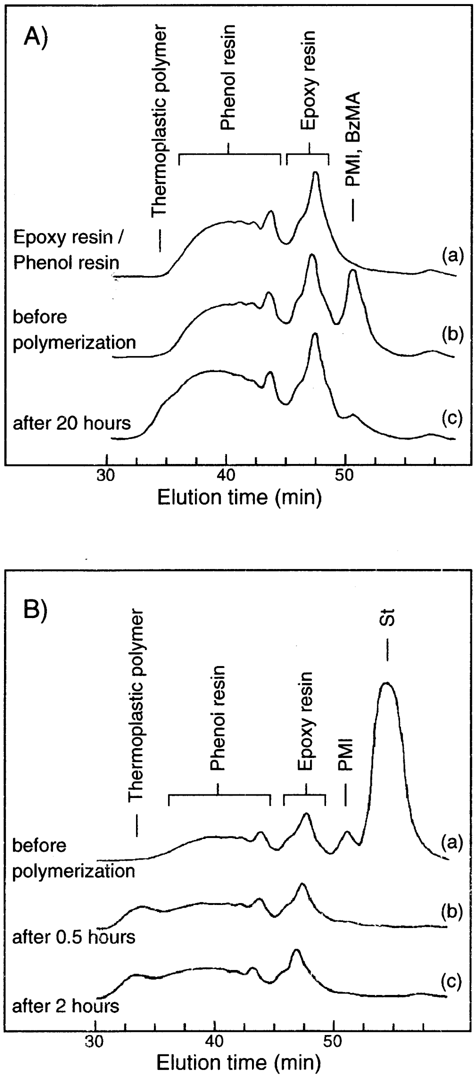


Fig. 1. GPC profiles of polymerization process of vinyl monomers in epoxy and phenol resin. Composition of vinyl monomers: (A) PMI/BzMA = 5/5, (B) PMI/St = 5/5 in molar ratio. Content of vinyl monomers: 20 wt%.

Table 1
Characterization of the thermoplastic polymers

Composition (molar ratio)	M_w	M_n	M_w/M_n	T_g[a] (°C)
PMI/BzMA = 5/5	17 000	7800	2.2	101
PMI/St = 5/5	36 000	9900	3.7	206

[a] Measured by DSC.

and its T_g was 206°C. Therefore, the St monomer was effective for rapid polymerization with the PMI monomer and for improving the T_g of the thermoplastic polymer formed from these monomers.

Next, the epoxy and the phenol resins were cured, forming thermoplastic polymer composed of the PMI/St or the PMI/BzMA by radical polymerization of these monomers. The fracture, toughness and T_g of these cured epoxy resins were measured, the results of which are shown in Figs. 2 and 3. Here the T_g values of the cured resins are measured by DMA. Fig. 2 shows the fracture toughness and T_g as a function of the PMI/BzMA content. In this system, the fracture toughness increased with an increase in the PMI/BzMA content. When 20 wt% of the PMI/BzMA was added, the fracture toughness was about 1.7 times higher than that of the unmodified resin. Thus, the fracture toughness of the cured epoxy resins was greatly improved by the addition of the PMI/BzMA. However, the addition of 30 wt% of the PMI/BzMA led to a drastic decrease in the fracture toughness. The T_g of the unmodified resin was 114°C. The improvement of T_g in this system was small. Only 6°C improvement was obtained by adding 10 wt% of the PMI/BzMA. The addition of more than 10 wt% of the PMI/BzMA reduced the T_g of the cured resins. Every cured resin in the PMI/BzMA system had a single tan δ-peak, which indicates that the thermoplastic polymer dissolved in the epoxy matrix. The low T_g of the thermoplastic polymer in this system and the drastic decrease of the fracture toughness with higher PMI/BzMA content seem to be responsible for the low copolymerizability of these monomers in the epoxy and the phenol resins. Fig. 3 shows the fracture toughness and T_g as a function of the PMI/St content. In the fracture toughness of this system, only slight improvement was obtained on the addition of 10 wt% of the PMI/St, and the fracture toughness decreased lower than that of the unmodified resin in the region of the higher PMI/St content. However, the T_g of these cured resins shifted towards higher temperatures, reaching a maximum when 10 wt% of the PMI/St was added. The observed T_g shift of the cured resin with 10 wt% of the PMI/St relative to the unmodified resin was 10°C. Thus, the addition of the PMI/St effectively improves the T_g of the cured epoxy resin. Further addition of the PMI/St caused a decrease of T_g. Two tan δ-peaks appeared in the cured resins with high PMI/St content, indicating that the cured resins have a phase-separation morphology. The low fracture toughness in this system seems to be responsible for the low compatibility with the epoxy matrix.

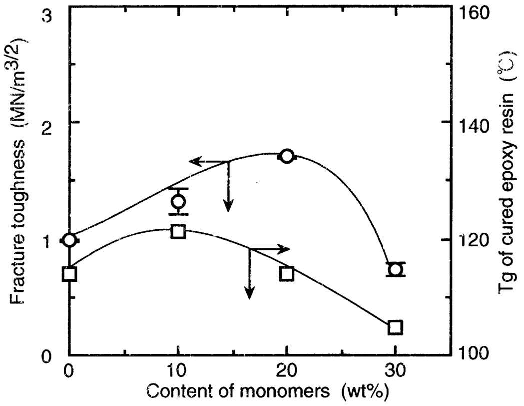


Fig. 2. Effects of addition of the PMI/BzMA on the fracture toughness and the T_g of the cured epoxy resins. Monomer composition: PMI/BzMA = 5/5 in molar ratio, ○: the fracture toughness, □: the T_g.

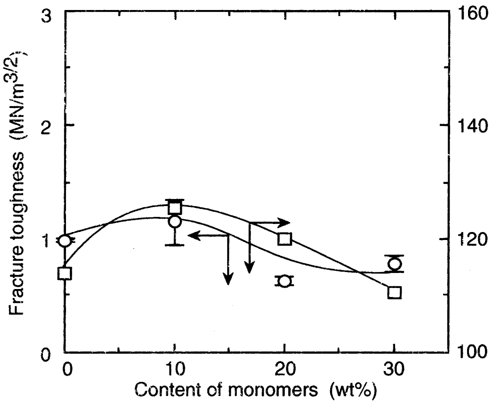


Fig. 3. Effect of addition of the PMI/St on the fracture toughness and the T_g of the cured epoxy resins. Monomer composition: PMI/St = 5/5 in ratio, ○: the fracture toughness, □: the T_g.

The morphologies of these cured resins were observed using a SEM. The results are shown in Fig. 4. In these pictures, the thermoplastic polymer was removed by extracting the samples with tetrahydrofuran (THF) prior to the SEM examination. The morphology of the cured resin with the thermoplastic polymer composed of the PMI/BzMA showed a homogeneous phase (Fig. 4(a)). In contrast, the cured resin with the thermoplastic polymer composed of the PMI/St exhibited a phase-separation morphology (Fig. 4(b)). The results of these SEM observations were consistent with the results obtained by the DMA. Therefore it can be concluded that the thermoplastic polymer composed of the PMI/BzMA has a high compatibility with the epoxy matrix, whereas that composed of the PMI/St has a low compatibility.

Thereafter, the monomer composition was fixed at 20 wt% addition of PMI/BzMA = 5/5 in molar ratio, whose fracture toughness was improved most, and St was further added to this compound in order to improve the T_g of the cured epoxy resin.

The GPC profile of the polymerization process of the

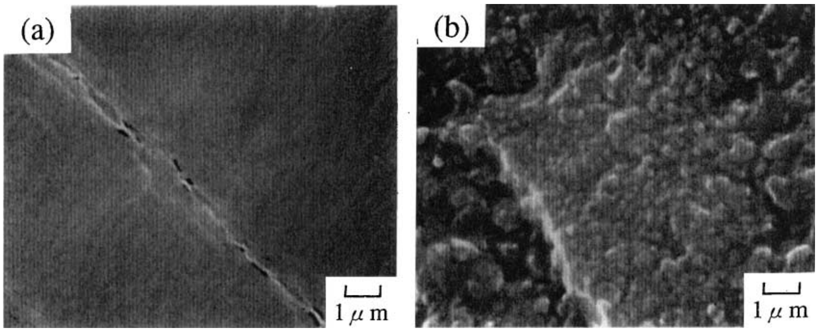


Fig. 4. Scanning electron micrographs of the fractured surfaces for the cured epoxy resins containing the thermoplastic polymer. Composition of the thermoplastic polymer: (a) PMI/BzMA = 5/5, (b) PMI/St = 5/5 in molar ratio. Content of the thermoplastic polymer: 20 wt%.

PMI/BzMA/St monomers (molar ratio: PMI/BzMA/St = 5/5/3, content: 23.6 wt%) in the epoxy and the phenol resins is shown in Fig. 5. The accelerator was not added in order to investigate the polymerization action of these monomers in the epoxy and the phenol resins also here. From the side of lower molecular weight, the peak of the St monomer and the overlapped peak of the PMI and BzMA monomers were observed (Fig. 5(a)). In the epoxy and the phenol resins, these monomer peaks decreased with time (Fig. 5(b)), and each monomer peak completely disappeared after 2 h (Fig. 5(c)). With the polymerization of these monomers, a GPC peak for the thermoplastic polymer was observed on the high molecular weight side. The molecular weight (M_w) of the thermoplastic polymer extracted from the uncured resin was approximately 27 000 (Fig. 5(d)). Thus, the PMI, BzMA, and St monomers are quickly polymerized in the epoxy and phenol resins and form thermoplastic polymer.

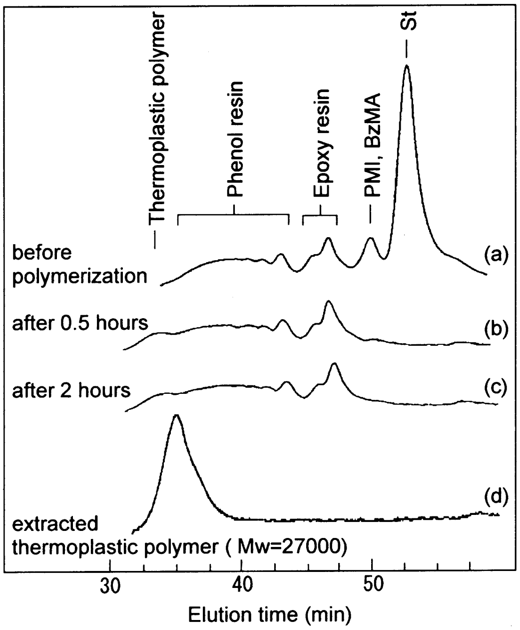


Fig. 5. GPC profiles of polymerization process of vinyl monomers in epoxy and phenol resin. Composition of vinyl monomers: PMI/BzMA/St = 5/5/3 in molar ratio. Content of vinyl monomers: 23.6 wt%.

3.2. In situ polymerization of PMI/BzMA/St monomer during the cure process of the epoxy resin

The GPC profile of the polymerization process of the PMI/BzMA/St monomers (molar ratio: PMI/BzMA/St = 5/5/3, content: 23.6 wt%) during the cure process of the epoxy and the phenol resins is shown in Fig. 6. In order to examine the copolymerization action of these vinyl monomers during the cure process of the epoxy and the phenol resins, an accelerator was added to the blend. During the cure process of the epoxy and the phenol resins, the copolymerization of these monomers progressed quickly (Fig. 6(b)), and each monomer peak disappeared after 2.5 h (Fig. 6(c)). The molecular weight (M_w) of the thermoplastic polymer extracted from the cured resin after it was cured completely (100°C/6 *h* + 180°C/6 h) was approximately 20 000 (Fig. 6(d)). Thus, it was confirmed that the polymerization behavior of these monomers during the cure process of the epoxy and the phenol resin is almost the same as the behavior without curing, except for a decrease of

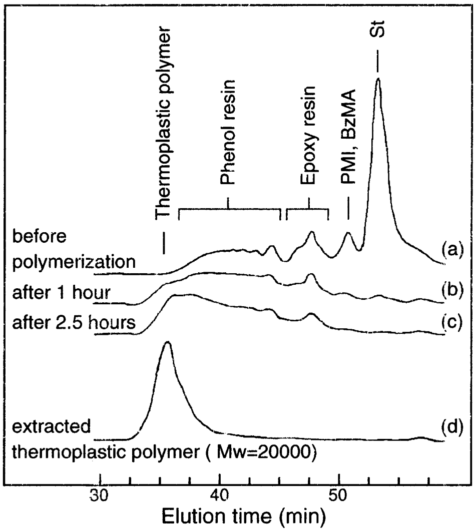


Fig. 6. GPC profiles of in situ polymerization process of vinyl monomers during cure process of epoxy and phenol resin. Composition of vinyl monomers: PMI/BzMA/St = 5/5/3 in molar ratio. Content of vinyl monomers: 23.6 wt%.

some molecular weights of the thermoplastic polymer which is finally formed because of the hindrance of the polymerization by the increase in the viscosity of the resin.

The characteristics of the thermoplastic polymer extracted from the cured epoxy resin after it was cured completely are shown in Table 2. Here, the T_gs of the thermoplastic polymer were measured by DSC. The T_g of the unmodified resin was 91°C. The T_g of the thermoplastic polymer composed of PMI/BzMA was also 91°C. However, the T_g of the thermoplastic polymer increased with an increase in St content. The T_g of the thermoplastic polymer reached more than 130°C when the molar ratio of the St became more than 3 mol, and the value was about 40°C higher than that of the unmodified resin. Therefore, the thermoplastic polymer containing high St content can be expected to improve the heat resistance of the cured epoxy resin. An elemental analysis of the CHN of these thermoplastic polymers was performed, the results of which are shown in Table 3. The composition mole ratio of the thermoplastic polymer calculated from the elemental analysis result is shown in Table 4. Since the thermoplastic polymer formed was composed of CHNO element, a calculation of their composition ratio was performed noting that the element except CHN was oxygen element O. The composition of the thermoplastic polymer of the system that added only the PMI/BzMA differed from the calculated value, and had a low PMI content under the composition. However, the compositions of the thermoplastic polymer with the St agreed well with each calculated value.

Although there has been little information reported about the copolymerization of the PMI/BzMA, the copolymerization of the PMI/MMA, and the PMI/St has been reported on [25]. In the copolymerization of the PMI (M_1)/MMA (M_2), the two monomer reactivity ratios are different ($1 > r_1 = 0.183$ and $1 < r_2 = 1.022$). Since the MMA is more reactive than the PMI, the MMA composition in the thermoplastic polymer becomes richer than the PMI one. Considering that the BzMA is the derivative of the MMA and that the molar fractions of the PMI in the thermoplastic polymer showed the low value 29–50 mol% of the molar fractions of the PMI in the monomer feed in the PMI/BzMA system, it is assumed that the copolymerization curve of the PMI/BzMA will show almost similar polymerization curve to that of the PMI/MMA. In the copolymerization of the PMI/BzMA, therefore, the thermoplastic polymer will have a tendency to contain more BzMA than PMI, since the terminal PMI radical adds the BzMA monomer more easily and the BzMA monomer reacts approximately similarly to both propagating species. In contrast, the copolymerization of the PMI/St leads to an alternate copolymer regardless of the monomer feed composition. That is, the St adds the PMI easily into the thermoplastic polymer. Consequently, the quantity of the PMI incorporated into the thermoplastic polymer was increased by the addition of the St to the PMI/BzMA system, which brought the composition of the thermoplastic polymer close to the calculated value.

Next, the pre-curing viscosity of the resins was evaluated. Fig. 7 shows the viscosity of the resin composed of the epoxy and the phenol resins, the resin containing monomers (molar ratio: PMI/BzMA/St = 5/5/3, content: 23.6 wt%) and the resin modified with a thermoplastic polymer which had been previously polymerized so as to have approximately the same molecular weight as the one obtained by the in situ polymerization (molar ratio: PMI/BzMA/St = 5/5/3, $M_w = 27\,000$, content: 23.6%). The viscosity of the resin composed only of the epoxy and the phenol resins was 0.55 Pa s at 100°C. When the thermoplastic polymer was added to the mixture of the epoxy and the phenol resins using conventional techniques, the viscosity of the resin became very high. This value was about 28 Pa s at 100°C. In contrast, when the monomers were added to the epoxy and the phenol resins, the viscosity of the resin before the polymerization of these monomers decreased. The viscosity of the resin containing these monomers was 0.065 Pa s at 100°C, decreasing to one-eighth compared with that of the resin composed only of the epoxy and phenol resins. Thus, if the monomers are added to the epoxy resin and thermoplastic polymer is formed during the cure process of the epoxy resin, the viscosity of the resin at the time of mixture can be greatly reduced.

Table 2
Characterization of the in situ polymerized thermoplastic polymers

Composition (molar ratio)	M_w	M_n	M_w/M_n	T_g[a] (°C)
Unmodified resin				91
PMI/BzMAI/St = 5/5/0	14 000	5400	2.6	91
PMI/BzMAI/St = 5/5/2	17 000	7100	2.4	119
PMI/BzMAI/St = 5/5/3	20 000	7400	2.7	130
PMI/BzMAI/St = 5/5/6	55 000	16 000	3.4	139

[a] Measured by DSC.

Table 3
Result of the elemental analysis of the in situ polymerized thermoplastic polymers (unit: %)

Composition (molar ratio)	C	H	N
PMI/BzMAI = 5/5	74.22	6.00	2.21
PMI/BzMAI/St = 5/5/3	76.13	5.90	2.95
PMI/BzMAI/St = 5/5/5	76.96	5.87	2.96

Table 4
Composition of the in situ polymerized thermoplastic polymers (unit: mol%)

Composition (molar ratio)		PMI	BzMA	St
PMI/BzMAI = 5/5	Anal. value	28.9	71.1	
	Calcd. value	50.0	50.0	
PMI/BzMAI/St = 5/5/3	Anal. value	32.8	40.2	27.0
	Calcd. value	38.5	38.5	23.1
PMI/BzMAI/St = 5/5/5	Anal. value	31.9	35.2	32.9
	Calcd. value	33.3	33.3	33.3

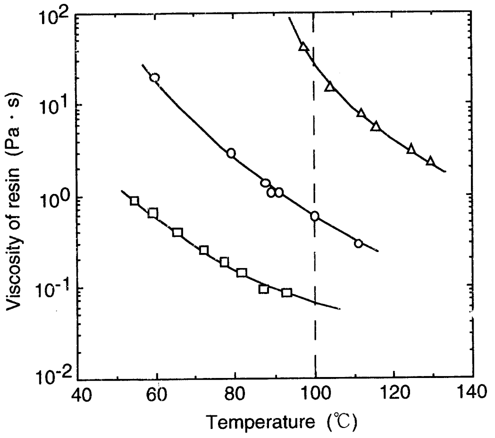


Fig. 7. Effect of addition of vinyl monomers or thermoplastic polymer on viscosity of the epoxy resins before curing. Sample: ○: unmodified resin, □: resin containing vinyl monomers (composition: PMI/BzMA/St = 5/5/3 in molar ratio; content: 23.6 wt%), △: resin modified with the thermoplastic polymer (composition: PMI/BzMA/St = 5/5/3 in molar ratio; content: 23.6 wt%; $M_w = 27\,000$).

3.3. Effect of addition of PMI/BzMA/St on thermal and mechanical properties

A dynamic viscoelastic analysis provides information on the microstructure of cured resins. Fig. 8 shows the DMA measurement of the cured resins containing the thermoplastic polymer composed of the PMI/BzMA/St. The unmodified resin produced a single tan δ-peak based on the T_g of the epoxy matrix at 114°C. The cured resin containing the thermoplastic polymer whose composition was PMI/BzMA/St = 5/5/3 in molar ratio showed a single tan δ-peak which was analogous to the unmodified resin. Thus, the thermoplastic polymer formed during the cure process was compatible in the epoxy matrix. The T_g of this system shifted about 10°C higher than that of the unmodified resin. The thermoplastic polymer formed in this study does not have any functional groups that are reactive with the epoxy resins and is not incorporated into the epoxy networks. This is confirmed by the fact that the thermoplastic polymers formed during the cure process of these resins could be extracted from the cured epoxy resins (Fig. 6(d)). Consequently, the increase in the T_g in this system was attributed to the formation of the semi-IPNs composed of the epoxy network and linear thermoplastic polymer. The cured resin containing the thermoplastic polymer with high St content (PMI/BzMA/St = 5/5/6 in molar ratio) showed two tan δ-peaks: One peak was based on the T_g of the epoxy matrix at 120°C; the other was the shoulder peak, which was based on the T_g of the thermoplastic polymer at about 160°C. This result indicates that the thermoplastic polymer phase-separated from the epoxy matrix. It appears that this is attributable to the decrease in compatibility of this thermoplastic polymer to the epoxy matrix because of the increase in its molecular weight with the increase in St content. However, it can be assumed that the semi-IPN structure is partly formed in this system, considering that the T_g of this system was slightly higher than that of the unmodified resin.

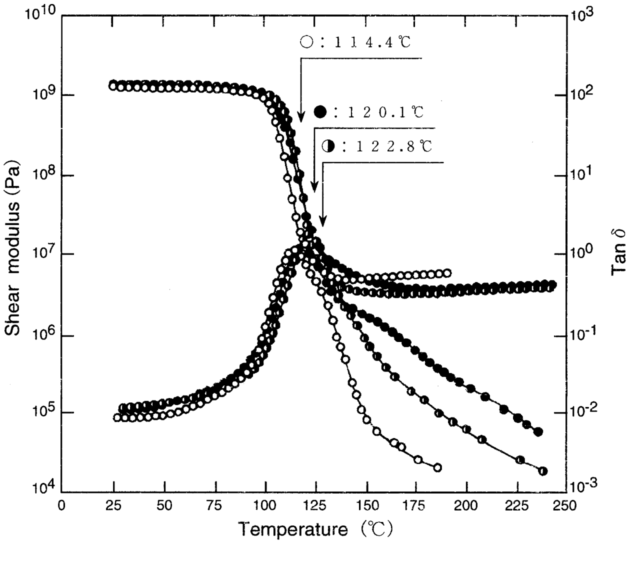


Fig. 8. Dynamic mechanical properties of the cured epoxy resins containing the thermoplastic polymer. Sample: ○ unmodified resin, ◨●: cured epoxy resins containing the thermoplastic polymer; composition and content of the thermoplastic polymer: ◨ PMI/BzMA/St = 5/5/3 in molar ratio, content: 23.6 wt% ● PMI/BzMA/St = 5/5/6 in mole ratio, content: 27.2 wt%.

Fig. 9 shows the T_g (measured by DMA) of the cured resins containing the thermoplastic polymer composed of the PMI/BzMA/St as a function of the St content. The T_g of the cured resin containing the thermoplastic polymer composed only of the PMI/BzMA was almost equal to that of the unmodified resin. This seems to be responsible for the fact that the T_g of the thermoplastic polymer formed in this system was equal to that of the unmodified resin, based on previous DSC measurement results (Table 2). The T_g of the cured resins containing the thermoplastic

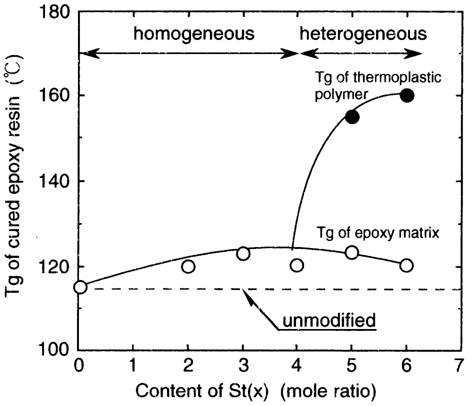


Fig. 9. Effect of St content on the T_g of the cured epoxy resins containing the thermoplastic polymer. Composition of the thermoplastic polymer: PMI/BzMA/St = 5/5/x (x = 0–6) in molar ratio; content: 20–27.2 wt%.

polymer composed of the PMI/BzMA/St increased with a corresponding increase in St content. The T_g of the cured resin shifted 10°C higher than that of the unmodified system when the molar ratio of PMI, BzMA and St was 5, 5 and 3, respectively. Thus, modification of the epoxy resin by in situ polymerization of the vinyl monomers made it possible to lower the viscosity of the resin during mixing and to improve the heat resistance of the cured epoxy resins. However, the T_g values of the cured resins decreased in the region of higher St content. The cured resins with lower St content showed a single tan δ-peak on the dynamic viscoelastic analysis, which indicates that the thermoplastic polymers formed in these systems were compatible in the epoxy matrix, and that the semi-IPN structure was formed in these cured resins. In contrast, the cured resins with higher St content showed two tan δ-peaks, which indicates that the cured epoxy resins have a phase-separation morphology. Consequently, it is believed that the decrease in T_g on the cured resins with high St content is attributable to the phase-separation of the thermoplastic polymer.

We measured the mechanical properties of these cured epoxy resins containing the thermoplastic polymer. Fig. 10 shows the fracture toughness as a function of the St content. The fracture toughness of the cured resin containing the thermoplastic polymer composed only of the PMI/BzMA was about 1.7 times higher than that of the unmodified resin, as previously stated. The fracture toughness in the PMI/BzMA system was increased further by adding the St. The maximum improvement in the fracture toughness was obtained when 3 mol of St were added, achieving a value about 2.5 times higher than that of the unmodified resin. As stated previously, the fracture toughness in the PMI/BzMA system decreased extremely when the amount of addition exceeded 20 wt%. However, such a tendency was not seen in the PMI/BzMA/St system, even if the amount of addition exceeded 20 wt%. It is thought that this is due to the following two factors: (1) that the copolymerizability of these monomers has been improved by adding the St in the PMI/BzMA system; and (2) that the thermoplastic polymer dissolved in the epoxy matrix and formed the semi-IPN structure. This indicated that the formation of a semi-IPN structure could improve the fracture toughness of the cured resins as well as their heat resistance. However, the fracture toughness of the cured resins decreased when St content in the thermoplastic polymer became higher and the thermoplastic polymer phase-separated from the epoxy matrix.

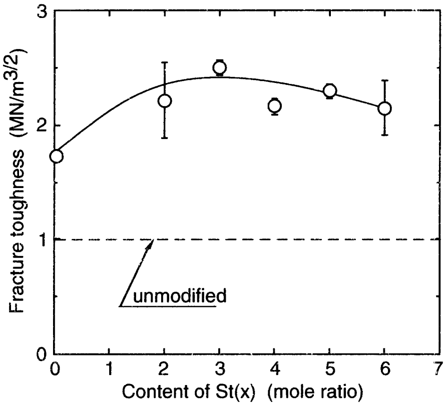


Fig. 10. Effect of St content on the fracture toughness of the cured epoxy resins containing the thermoplastic polymer. Composition of the thermoplastic polymer: PMI/BzMA/St = 5/5/x (x = 0–6) in molar ratio; content: 20–27.2 wt%.

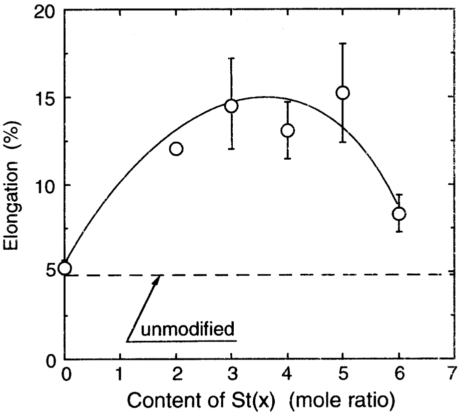


Fig. 11. Effect of St content on the elongation at break of the cured epoxy resins containing the thermoplastic polymer. Composition of the thermoplastic polymer: PMI/BzMA/St = 5/5/x (x = 0–6) in molar ratio; content: 20–27.2 wt%.

Next, we measured the flexural properties of these cured epoxy resins. Fig. 11 shows the relationship between the elongation and the St content. As to the flexural strength of these cured resins containing the thermoplastic polymer composed of the PMI/BzMA/St, every value was about 1.2 higher than that of the unmodified resin independent of St content. However, the elongation of the cured resins, as shown in Fig. 10, was quite dependent on it. In the cured resins with lower St content, which formed the semi-IPN structure, the elongation increased with an increase in St content in the thermoplastic polymer. However, when St content in the thermoplastic polymer became higher and the thermoplastic polymer phase-separated from the epoxy matrix, the elongation decreased. This significant increase in the fracture toughness in the cured resins containing the thermoplastic polymer composed of the PMI/BzMA/St with lower St content is likely attributable to the increase in the intrinsic ductility of the epoxy matrix due to the formation of the semi-IPN structure. As mentioned above, modification of the epoxy resin by in situ polymerization of PMI, BzMA and St could improve the thermal and mechanical properties of the cured resin while lowering the viscosity of resin during mixing.

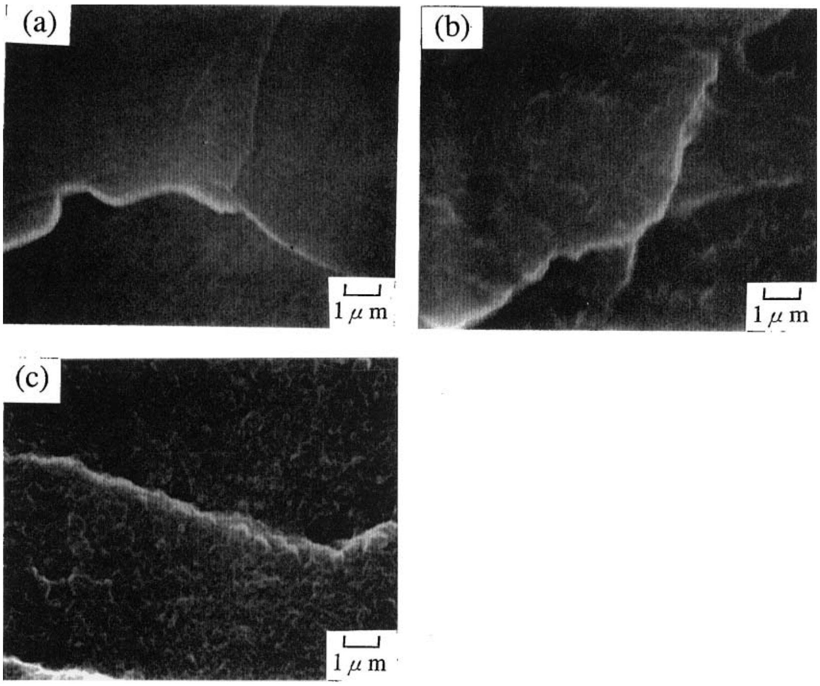


Fig. 12. Scanning electron micrographs of the fractured surfaces for the cured epoxy resins containing the thermoplastic polymer. Sample: (a) unmodified resin; (b), (c) cured epoxy resins modified with the thermoplastic polymer: composition and content of the thermoplastic polymer: (b) PMI/BzMA/St = 5/5/3 in molar ratio; content: 23.6 wt%; (c) PMI/BzMA/St = 5/5/6 in molar ratio; content: 27.2 wt%.

3.4. Toughening mechanism for the cured resins modified with the in situ polymerized thermoplastic polymer

In order to uncover the reason why the fracture toughness of the cured resins containing the thermoplastic polymer improved, the morphologies of these cured resins were observed with the SEM, the results of which are shown in Fig. 12. In these pictures, the thermoplastic polymer was removed by extracting the samples with THF prior to the SEM examination. The morphology of the cured resins containing the thermoplastic polymer composed of the PMI/BzMA/St with lower St content (Fig. 12(b)) showed a homogeneous phase, analogous to the unmodified resin (Fig. 12(a)). In the cured resin containing higher St content (Fig. 12(c)), unevenness was observed on the surface, though distinct phase-separation morphology was not observed. The phase structures of these cured resins were therefore observed in detail with a TEM. The results are shown in Fig. 13. In these micrographs, the epoxy matrix is black because the samples were stained with RuO_4. The entire photograph was black in the unmodified resin (Fig. 3(a)). In the cured resin containing the thermoplastic polymer with lower St content (Fig. 13(b)), the domain of the thermoplastic polymer, whose diameter was about 50 nm, was finely dispersed in the matrix. However, the dynamic viscoelastic analysis determined that the thermoplastic polymer of this composition was compatible with the epoxy matrix and that the semi-IPN structure was formed. Consequently, it can be concluded that the thermoplastic polymer was dispersed with its chain entangled in the epoxy network. In the cured resin containing the thermoplastic polymer with higher St content (Fig. 13(c)), it was observed that the phase-separation of the thermoplastic polymer proceeded and that the domain of the thermoplastic polymer grew into relatively large particles with a diameter of about 100 nm. This difference in the microstructure of the cured resins seems to represent a gap in toughness.

To reveal the fracture mechanism of these cured resins, a thin section perpendicular to the crack plane was observed using an optical microscope (OM) with or without crossed polarizers.

The transmission optical micrographs are shown in Fig. 14. In the unmodified resin, the crack proceeded in a straight manner in the bright field view (Fig. 14(a)) and there was a slight bright region in the view using crossed polarized light (Fig. 14(b)). In the cured resin containing the thermoplastic polymer with lower St content, the photograph viewed in the bright field (Fig. 14(c)) revealed that there were a few crack branches near the crack tip. Moreover, using crossed polarized light (Fig. 14(d)); a very bright region near the crack tip was observed. The bright region observed under crossed polarized light represents the region where the matrix had a shear deformation. Consequently, it was confirmed that a region existed in which a shear deformation in this resin occurred, resulting in the drastic improvement in toughness. It may be concluded, therefore, that the increase in the intrinsic ductility of the epoxy matrix induced by the formation of the semi-IPN structure permitted the shear deformation of the epoxy matrix. In the cured resin containing the thermoplastic polymer with higher St content, many crack branches near the crack tip were observed in the photograph viewed in a bright field

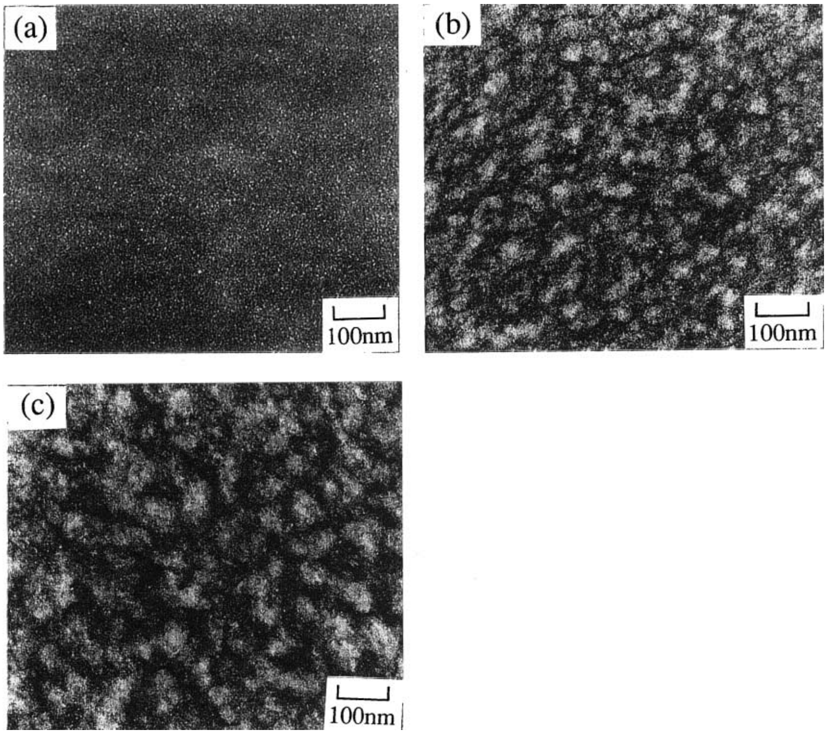


Fig. 13. TEM micrographs of the fractured surfaces for the cured epoxy resins containing the thermoplastic polymer. Sample: (a) unmodified resin; (b), (c) cured epoxy resins containing the thermoplastic polymer: composition and content of the thermoplastic polymer: (b) PMI/BzMA/St = 5/5/3 in molar ratio; content: 23.6 wt%; (c) PMI/BzMA/St = 5/5/6 in molar ratio; content: 27.2 wt%.

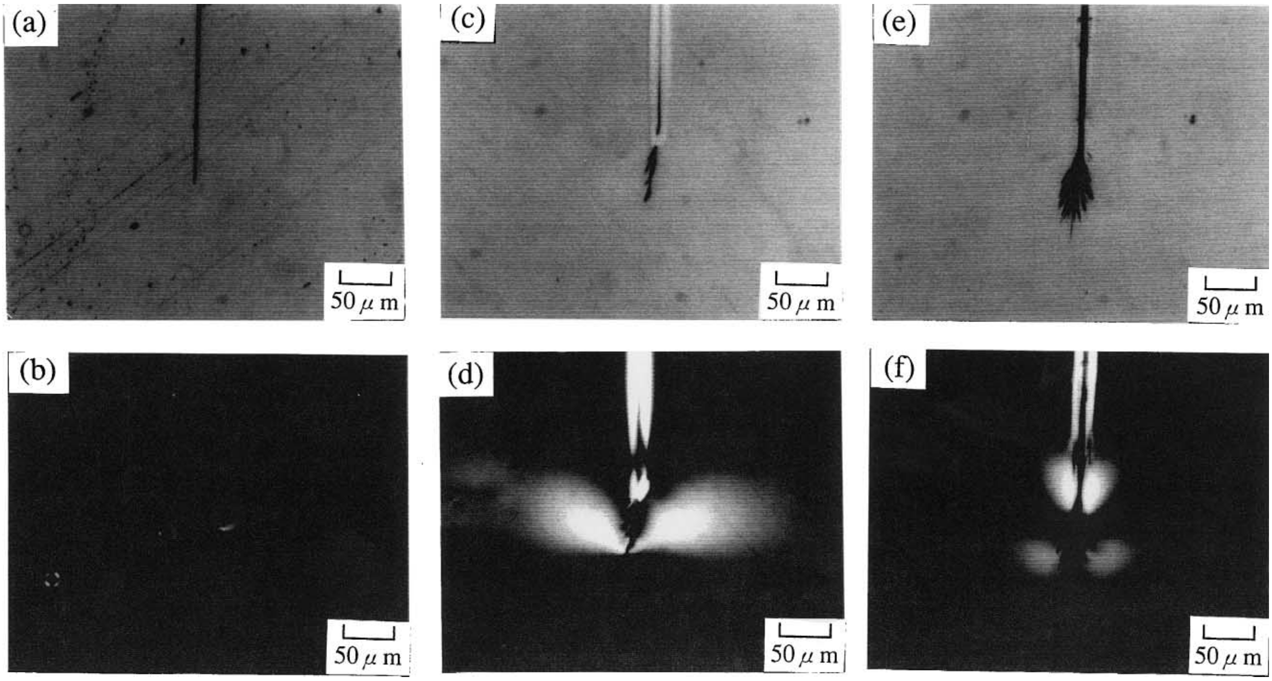


Fig. 14. Micrographs of sub-fractured surfaces in the cured epoxy resins containing the thermoplastic polymer taken under bright field ((a), (c), (e)) and crossed polarized light ((b), (d), (f)). Sample: (a), (b) unmodified resin; (c)–(f) cured epoxy resins containing the thermoplastic polymer: composition and content of the thermoplastic polymer: (c), (d) PMI/BzMA/St = 5/5/3 in molar ratio; content: 23.6 wt%; (e), (f) PMI/BzMA/St = 5/5/6 in molar ratio; content: 27.2 wt%.

(Fig. 14(e)). However, the bright region of this cured resin in the micrograph, viewed using crossed polarized light (Fig. 14(f)), was smaller than that of the cured resin with lower St content (Fig. 14(d)), which led to the small increase in toughness.

4. Conclusions

In order to simultaneously improve the heat resistance and toughness of a cured epoxy resin, and reduce the viscosity of the resin at the time of mixing, modification of a thermoplastic polymer was performed. The thermoplastic polymer was formed during the cure process of the epoxy resin by radical polymerization of vinyl monomers. The following results were obtained.

1. When 24 wt% of the PMI/BzMA/St monomers with composition of 5/5/3 by the molar ratio was added to epoxy and phenol resins, the resin viscosity at mixing fell to about 1/8 of an unmodified resin.
2. The T_g of the cured resin shifted to about 10°C higher than that of the unmodified resin when the thermoplastic polymer was formed by in situ polymerization of these vinyl monomers during the cure process of the epoxy resin. The fracture toughness also increased about 2.5 times that of the unmodified resin. Thus, the improvement in the heat and mechanical properties is attributed to the formation of the semi-IPN composed of the epoxy matrix and the thermoplastic polymer.

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