Toughening of High Performance Epoxy Matrix Resin by Modification with Multi-block Copolymers Composed of Poly (N-phenylmaleimide-alt-styrene) and Polydimethylsiloxane or Polyoxyethylene

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Synopsis

Multi-block copolymers composed of poly(N-phenylmaleimide-alt-styrene) and flexible segments such as polydimethylsiloxane or polyoxyethylene were prepared by copolymerization of N-phenylmaleimide and styrene with macromolecular azo-initiators containing polydimethylsiloxane or polyoxyethylene segments, and used for the modification of high performance epoxy resin, which is a mixture of N,N,N',N'-tetraglycidyldiaminodiphenylmethane, dicyclopentadienyl-type epoxy resin, naphthalene-type epoxy resin and bisphenol-A diglycidyl ether, cured with 4,4'-diaminodiphenyl sulfone. The fracture toughness (Kic) and flexural strength of the modified resin were strongly dependent on both the molecular weight (Mw) and structure (composition) of the modifier, while the modulus and glass transition temperature of the modified resin were maintained in this modification system. The addition of 5 phr of poly[poly(N-phenylmaleimide-alt-styrene)-block-polydimethylsiloxane] (PMSZ) having low Mw (157,000) and high dimethylsiloxane (VPS) content (40 mol%), or high Mw (664,000) and low VPS content (11 mol%) brought about increases (ca. 70%) in Kic of the modified resin without large loss of flexural strength, compared with the control resin. The addition of 12-15 phr of poly[poly(N-phenylmaleimide-alt-styrene)-block-polyoxyethylene] (PMSE: Mw 300,000, oxyethylene content 35mol%) resulted in the largely increased Kic (210%) with rather large loss of flexural strength. PMSE was more effective for toughening of the epoxy matrix resin compared with corresponding PMSZ (Mw 371,000, VPS content 30 mol%) or poly(N-phenylmaleimide-alt-styrene) (PMS: Mw 397,000) without flexible segments. It was concluded that this is due to the high compatibility of polyoxyethylene segments in PMSE with the matrix resin. These modified resins with high Kic had the co-continuous-phase morphology. The toughening mechanism was discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified epoxy resin system.

1. Introduction

Epoxy Resins are widely used in various engineering fields because of their excellent mechanical properties, good
electrical properties and strong adhesion to other materials. They have also been used as structural adhesives and matrix resins for fiber composites. However epoxy resins are generally brittle because of their highly cross-linked structure. The toughness of epoxy resins has been increased by blending with reactive liquid rubbers, but an increase in toughness is achieved at the expense of other properties such as elastic modulus and yield strength\(^{1-3}\). An alternative approach to toughen epoxies is to employ thermoplastics as modifiers. Especially engineering thermoplastics are interesting materials as modifiers for epoxy resins from the view point of the maintenance of mechanical properties for the matrix resins\(^{4,5}\).

Various kinds of engineering thermoplastics have been reported as improving the toughness of 4,4'-diaminodiphenyl sulfone (DDS)-cured epoxy resins, including poly(ether sulfone)(PES), polysulfone, poly(ether ketone), poly(ether imide), polycarbonate, poly(butylene terephthalate)\(^{6-9}\). Commercial PES (Vicrex\(^{TM}\)) was used in the modification of polyfunctional epoxies such as tetracyclidylidiaminodiphenylmethane (TGDDM), but less effective owing both to their high cross-linking structure and to poor interfacial bonding between two immiscible phases in the cured resin\(^{10-12}\).

Terminally functionalized polysulfone (PSF) is more effective modifier than unfunctionalized PSF\(^{13,14}\).

Multi-block copolymers containing two components such as aramid or polyimide (high performance thermoplastics) and polydimethylsiloxane or butadiene acrylonitrile copolymer (flexible polymers) have been also prepared and used for the modification of epoxy resins\(^{15-17}\). These block copolymers are not only effective modifier, but also act as effective compatibilizer for the modification of epoxy resins with silicone\(^{18,19}\), liquid rubber\(^{20}\), or poly(ether imide)\(^{21}\).

In previous work we reported that N-phenylmaleimide (PMI)-styrene (St) alternative copolymer (PMS) and its derivatives such as PMI-N-cyclohexylmaleimide-St terpolymer and PMI-St-p-hydroxystyrene terpolymer were effective modifiers for epoxy resins\(^{22-26}\). In this study, multi-block copolymers composed of poly(N-phenylmaleimide-alt-styrene) (PMS) and flexible segments such as polydimethylsiloxane or polyoxyethylene were prepared and used for the modification of high performance epoxy matrix resins. It was expected that these flexible segments in the block copolymers might affect phase separation behavior or morphology of the modified system, and thereby improve the toughness of the epoxy resins.

## 2. Experimental Part

### 2.1 Materials

The epoxy resin used in this study was a mixture of liquid N,N,N',N'-tetraglycidyldiaminodiphenylmethane(TGDDM) (ELM-434; Sumitomo Chemical Industrial Co.), dicyclopentadienyl-type epoxy resin (DCPDE) (HP-7200; Dainippon Ink and Chemicals Inc.), naphthalene-type epoxy resin (NPEP) (HP-4032; Dainippon Ink and Chemicals Inc.) and bisphenol-A diglycidyl ether epoxy resin (DGEBA) (YD-128; Tohto Kasei Co.,Ltd.). 4,4'-Diaminodiphenyl sulfone (DDS) was used as curing agent. Scheme 1 shows the molecular structure of these materials.

![Scheme 1 Matrix Resins](image1)

N-Phenylmaleimide (PMI) was a commercial product (Nippon Shokubai Co.). Styrene (St) was purified in the usual way. Other reagents were used as received. Macromolecular azo-initiators, poly[polydimethylsiloxane 4,4'-azobis (4-cyanopentanamide)] (VPS-0501; Wako Pure Chemical Industries, Ltd.; molecular weight, \(M_n\) ca. 40,000) having polydimethylsiloxane moiety (molecular weight, \(M_n\) 5,000) and poly[polyoxyethylene 4,4'-azobis (4-cyanopentanoate)] (VPE-0401; Wako Pure
Chemical Industries, Ltd.; molecular weight, $M_n$ ca. 33,000) having polyoxyethylene moiety (molecular weight, $M_n$ 4,000), were used, as received, for the preparation of modifier.

2.2 Measurements

$^1$H-NMR spectra were recorded on a 270MHz instrument (JEOL EX-270) at 24°C using CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. Molecular weights of the block copolymers were determined by GPC (Tohso HLC-8020 instrument) using polystyrene standards. Mechanical properties of cured resins were measured with a Shimadzu autograph universal testing machine. Flexural tests were carried out at a crosshead speed of 2mm/min (JIS K7171). Fracture toughness, $K_{IC}$, was measured in three point bend specimen geometry at a crosshead speed 1mm/min (ASTM E-399). Glass transition temperature ($T_g$) of block polymers was measured as onset temperature by differential scanning calorimetry (TA instrument DSC 2200) at a heating speed 10°C/min. Scanning electron micrographs (SEMs) were taken with a Hitachi S-3500N instrument using failed specimens in the $K_{IC}$ tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between -150°C and 300°C at a heating speed of 5°C/min at frequency of 1Hz under the $N_2$ flow.

2.3 Preparation of poly[poly($N$-phenylmaleimide-alt-styrene)-block-polydimethylsiloxane] (PMSZ) and poly[poly($N$-phenylmaleimide-alt-styrene)-block-polyoxyethylene] (PMSE)

Poly[poly($N$-phenylmaleimide-alt-styrene)-block-polydimethylsiloxane] (PMSZ) was prepared by radical polymerization of PMI with St (molar ratio 1 : 1) using polymeric azo-initiator VPS-0501 (Scheme 2). The molecular weight of PMSZ was controlled using dodecanethiol as a chain-transfer agent. A typical procedure of PMSZ preparation is as follows:

A three necked flask was charged with PMI (17.32g, 0.10 mol), St (10.42g, 0.10 mol), acetone (200mL), toluene (100mL), polymeric azo-initiator VPS-0501 (10.0 g; amount of azo-group, 2.4 mmol). The flask was purged with $N_2$ for 0.5 h and a $N_2$ atmosphere was maintained throughout the polymerization. The polymerization mixture was stirred at 65°C for 8 h. After polymerization was over, the mixture was diluted with tetrahydrofuran (THF). Then the block polymer was isolated using methanol as precipitant and purified by reprecipitation with THF / methanol. The white solid polymer was dried in vacuo at 60°C for 30h.

Poly[poly($N$-phenylmaleimide-alt-styrene)-block-polyoxyethylene] (PMSE) was prepared by radical polymerization of PMI with St (molar ratio 1 : 1) using polymeric azo-
A typical procedure of PMSE preparation is as follows:

A three necked flask was charged with PMI (17.32 g, 0.10 mol), St (10.42 g, 0.10 mol), acetone 300 mL, polymeric azo-initiator VPE-0401 (10.0 g; amount of azo-group, 2.4 mmol). The flask was purged with N₂ for 0.5 h and a N₂ atmosphere was maintained throughout the polymerization. The polymerization mixture was stirred at 65°C for 8 h. After polymerization was over, the obtained polymer was treated in the same manner as PMSZ.

2.4 Curing procedure

The block polymer was dissolved into the epoxy resin with methyl ethyl ketone (MEK) (ca. 20%) as a solvent by heating at 60°C for 1 h. The composition of the epoxy resin was shown in Table 1.

1. Then the curing agent, DDS, was added to the mixture which was kept at 60°C for another 1 h to dissolve DDS. Consequently the mixture was poured into the tray, and was evacuated the solvent (MEK) at 60°C for 2 hour under reduced pressure. The resulting mixture was poured into the aluminum mold covered with Teflon seat. The curing temperature was raised from 25°C to 180°C at rising rate of 2°C/min, held at 180°C for 2 h, and slowly cooled until the room temperature. The amount (phr : parts per hundred parts of resin ) of the block-polymer used was based on the epoxy resin.

3. Results and Discussion

3.1 Characterization of multi-block copolymer PMSZ and PMSE

Multi-block copolymer PMSZ was prepared by the radical polymerization with macromolecular azo-initiator VPS 0501 in high yield. Table 2 shows some characteristic properties of PMSZ. The molecular weights of PMSZ could be controlled by use of dodecanthiol as chain transfer agent. The ratio of PMI-alt-St (PMS) unit to dimethylsiloxane (VPS) unit in the multi-block copolymer was measured by using 'H-NMR spectroscopy. The content of VPS unit in PMSZ [VPS / (VPS + PMS)] was a range of 11-38 mol %. The glass transition temperature (T_g) of PMSZ was similar to that of PMS (224°C) containing no VPS units, which was over the range from 200 to 213 °C. Such a block copolymer with high T_g as well as super-engineering plastics is potential modifier for the matrix resin of composites. Multi-block copolymer PMSE was also prepared by the radical polymerization with macromolecular azo-initiator VPE 0401 in high yield. The weight-average molecular weight (M_w) of PMSE was 300,000, and the content of oxyethylene (VPE) unit in PMSE [VPE / (VPE + PMS)] was 35 mol %. The glass transition temperature of PMSE could not been measured by differential scanning calorimetry. However the block copolymer as well as PMSZ might have a high T_g and is also potential modifier for the matrix resin of composites.

3.2 Mechanical and thermal properties of modified epoxy resins

The epoxy resin used in this study is a mixture of bi- and multi-functional epoxy resins, as shown in Table 1 and...
Scheme 1. Such a mixture of the epoxy resins could be used as high performance matrix resin for composites, because of high $T_g$ and flexural modulus of the cured resin. Table 3 shows the representative results for the modification of the matrix resin with PMSZ. The weight-average molecular weight ($M_w$) was used as a measure of molecular weight of PMSZ in this study. The cured parent matrix resin (control resin) was transparent but the modified resins became opaque. The modification with PMSZ-1 and PMSZ-5, which have high molecular weight ($M_w$ 656,000 and 443,000 respectively) and high dimethylsiloxane (VPS) content (35 mol% and 37 mol% respectively), gave the cured resins with marble-like appearance, namely macro-phase separated structure, and the properties of the modified resins could not been examined. The modified resin with PMSZ-8 having high $M_w$ (425,000) and moderate VPS content (28 mol%) had also macro-phase separated structure.

In the modification with PMSZ having moderate $M_w$ (157,000-295,000) and high VPS content (38-40 mol%) the micro-phase separation was observed for the modified resins (No.1, 3, 4 in Table 3). Moreover, the modification with PMSZ having high $M_w$ (371,000-664,000) and VPS content of lower than 30 mol% resulted in the formation of the resins with the micro-phase separation (No.5-13).

Fig.1 shows the same dependence of $K_{IC}$ and flexural strength for the resin modified with 10 phr of PMSZ. The fracture toughness, in analogy with the modification with 5 phr of the modifier, increased in the case of the modification that resulted in the decreased strength. The addition of PMSZ with high $M_w$ (664,000) brought out the increased $K_{IC}$ (ca. 70%), compared with the unmodified resin, without large loss of flexural strength: the strength for the resin modified with the former was a little higher than that modified with PMS (Mw 130,000) having no VPS units. PMSZ with moderate $M_w$ and VPS content (371,000, 30 mol%) gave the modified resin with high $K_{IC}$ (100 % increase) and the moderate strength compared with the control resin.

![Fracture toughness ($K_{IC}$)](A) and flexural strength (B) of the resins modified with 5 phr of PMSZ on $M_w$ and VPS content of the modifier. The fracture toughness and the strength were strongly dependent on both the molecular weight and structure (composition) of the modifier. The addition of PMSZ with low $M_w$ and high VPS content (157,000, 40 mol%) or high $M_w$ and low VPS content (664,000, 11 mol%) brought out the increased $K_{IC}$ (ca. 70%), compared with the unmodified resin, without large loss of flexural strength: the strength for the resin modified with the former was a little lower than that modified with PMS (Mw 130,000) having no VPS units. PMSZ with moderate $M_w$ and VPS content (371,000, 30 mol%) gave the modified resin with high $K_{IC}$ (100 % increase) and the moderate strength compared with the control resin.

![Fig.1](Dependence of fracture toughness ($K_{IC}$) and flexural strength (B) of the resins modified with 5 phr of PMSZ on $M_w$ and VPS content of the modifier)
and low VPS content (11 mol%), as well as PMS (Mw 397,000) without VPS units, brought about significantly increased KIC (140%) of the modified resin, though the flexural strength decreased extensively. The addition of 7.5 phr of the same modifier, however, gave increased KIC (75%) with substantial retention in the strength (see Table 3, No.12). The modification with 10 phr of PMSZ having low Mw (157,000) and high VPS content (40%) resulted in increased KIC (100%) with depression of the decrease in the strength compared with corresponding modifier PMS (Mw 130,000) without VPS units. The all modified resins maintained high flexural modulus (see Table 3). The Tg values for the modified resins were almost equal to Tg of the unmodified resin (Table 3). These results suggest that PMSZ with appropriate Mw and VPS content is effective for the toughening of the matrix resin.

Table 4 shows the results for the modification of the matrix resin with PMSE. The modified resins became also opaque. In the modification with 5-15 phr of PMSE (Mw 300,000, VPE content 35 mol%) the micro-phase separation was observed for the modified resins (No.1-5 in Table 4), whereas the resin modified with 10 phr of PMSZ having the similar molecular weight (Mw 295,000) and polydimethylsiloxane content (38 mol %) showed the macro-phase separation (see Table 3, No.2). The fracture toughness of the resin modified PMSE increased with increasing modifier contents. The addition of 10-11 phr of PMSE brought about the increased KIC (85%), compared with the unmodified resin, without large loss of flexural strength. The addition of 12-15 phr of the modifier resulted in largely increased KIC (210%) with rather large loss of flexural strength, while the modification with corresponding PMSZ (Mw 371,000, VPS content 30 mol%; 10 phr addition) containing polydimethylsiloxane and PMS (Mw 397,000; 10 phr addition) containing no flexible segments brought about less increased KIC (100-160%) with the similar or lower flexural strength (see Table 3, No.6 and 17). This result suggests that PMSE with polyoxyethylene units is more effective for the toughening of the epoxy matrix resin, compared with PMS and PMSZ. This is likely to be due to the polyoxyethylene units which have compatibility with the matrix resin (see later). The all modified resins maintained high flexural modulus. The Tg values for the modified resins were almost equal to Tg of the unmodified resin (Table 4).

3.3 Morphology of the modified resins

The morphology of the cured epoxy resins was investigated by scanning electron micrographs (SEMs). The parent matrix resin had only one-phase structure. The inclusion of PMSZ to the parent resin led to the phase-separation of the cured resins. The morphology of the modified resins changed dramatically depending on Mw and VPS content of PMSZ.

Fig.3 shows SEMs of the resins modified with PMSZ-3 (Mw 157,000, VPS
content 40 mol%). The modification with 5 phr of PMSZ-3 resulted in microscopic two-phase morphology with PMSZ-rich spherical particles dispersed in the epoxy-rich matrix: the average diameter of the particles was 1.0 μm (Fig.3a), while the morphology of the modified resin changed to the co-continuous-phase structure on the addition of 10 phr of the modifier (Fig.3b). The formation of the co-continuous structure slightly increased $K_{IC}$, though the strength decreased considerably. The addition of 5 phr of PMSZ-10 ($M_w$ 371,000, VPS content 30 mol%) induced the co-continuous phase separation (Fig.3c) similar to that observed for the resin modified with 10 phr of PMSZ-3 (Fig.3b): the former modifier as well as the latter, correspondingly to this phase structure, resulted in increased $K_{IC}$ with substantial decrease in the strength.

Fig.4 shows SEMs for the modification with PMSZ-9 having high $M_w$ (664,000) and low VPS content (11 mol%). The addition of 5-10 phr of the modifier induced the co-continuous phase separation for the modified resin. This is mainly attributed to the high molecular weight of this modifier. The resin modified with 10 phr of the modifier had more elaborate co-continuous structure, compared to that modified with 5 phr of the modifier. Such a fine structure is considered to result in more increased $K_{IC}$ for the modified resin. The resin modified with 7.5 phr of the modifier contained both fine and coarse co-continuous structures, and showed moderately increased $K_{IC}$ without large loss of the strength (see Table 3, No.12).

SEMs of fracture surfaces for the resins modified with PMS containing no silicone segments are shown in Fig.5. The addition of the modifier with low $M_w$ (130,000) gave the sea-and-island phase separation for the modified resin. The addition of 5 phr of PMS with moderate $M_w$ (397,000) also induced similar phase structure for the modified resin, while the phase structure changed to co-continuous structure on the addition of 10 phr of the modifier. Such a co-continuous structure may be effective for increasing $K_{IC}$ though the flexural strength decreased largely.

The morphology of the resins modified with PMSE containing polyoxyethylene units
was slightly different from that of the resins modified with PMSZ containing polydimethylsiloxane units. Fig.6 shows SEMs of the resins modified with PMSE (M_w 300,000, VPE content 35 mol%). The modification with 5 phr of PMSE resulted in microscopic two-phase morphology with PMSE-rich spherical particles dispersed in the epoxy-rich matrix: the average diameter of the particles was 1.0 μm (Fig.6a), while the morphology of the modified resin dramatically changed to the co-continuous-phase structure (Fig.6b-6d) on the addition of 10-15 phr of the modifier: the fracture surfaces of the resins modified with 12-15 phr of PMSE appear to be rougher than those of the resins modified with PMSZ (Fig.3b).

### 3.4 Dynamic viscoelastic analysis of modified epoxy resins

Dynamic viscoelastic analysis can give information on the microstructure of cured epoxy resins. Fig.7 and 8 show the storage modulus, G', and tanδ curve for the resins modified with PMSZ-3 (M_w 157,000, VPS content 40 mol%), and PMSZ-9 (M_w 664,000, VPS content 11 mol%) containing polydimethylsiloxane units, respectively. The peak position of the α-relaxation in the tanδ curve and the storage modulus in the glassy state for the modified resins hardly changed compared to those for the control resin. Such very small changes in the peak position of the α-relaxation are attributed to the fact that T_g of modifier PMSZ is similar to that of the control resin, as previously described. On the 10phr addition of PMSZ-9, a small peak appeared at -110°C: this tanδ peak must be the phase-separated polydimethylsiloxane moiety. A similar small peak observed in the tanδ curve for the resin modified with 10 phr of PMSZ-3 may be due to the silicone moiety.

Fig.9 shows the storage modulus, G', and tanδ curve for the resins modified with 12 phr of PMSE (M_w 300,000, VPE content 35 mol%) containing polyoxyethylene units. The peak
position of the \(\alpha\)-relaxation in the tan \(\delta\) curve for the modified resins slightly shifted towards lower temperature (5°C), in contrast to the case of the resin modified with PMSZ. Polyoxyethylene is a semicrystalline polymer with \(T_g = \text{ca.} -60^\circ\text{C}\) and \(T_m\) (melting point) = ca. 60°C \(^{29-31}\). However, the tan \(\delta\) curve for the resin modified with PMSE exhibited no peaks corresponding to the relaxation of polyoxyethylene segments in PMSE. These results are likely to indicate that a part of PMSE or polyoxyethylene segments in PMSE is miscible with the epoxy matrix, though the detailed microstructure of the modified resin can not be discussed, because the exact \(T_g\) value of PMSE is unknown.

### 3.5 Discussion on the toughening mechanism

In the modification of epoxy resins with engineering thermoplastics, the most effective results can be obtained by the formation of the modified resins with co-continuous phase structure. It is suggested that the toughening of such epoxy resins is achieved by the adsorption of fracture energy due to ductile drawing and tearing of the thermoplastic co-continuous phase \(^{7,8}\).

The epoxy resins modified with PMS had also such co-continuous phase structure and high fracture toughness \(^{22}\). In many cases, however, the modification with PMS resulted simultaneously in significantly decreased mechanical properties such as strength of the modified resins. The increased interfacial interaction between the modifier and the matrix resin, attained by the modification with functionalized PMS, brought about the increased toughness with modest or moderate loss of the strength. \(^{24,25}\).

PMSZ and PMSE, multi-block copolymers containing flexible segments, as well as PMS gave the modified epoxy resins with co-continuous phase structure and high fracture toughness. The flexible segments such as polydimethylsiloxane and polyoxyethylene in the modifier were expected to induce the formation of co-continuous phase structures with finer morphological periodic distance or with increased interaction between two co-continuous phases. In the modification of epoxy resins with terminally functionalized polyimide-polydimethylsiloxane block copolymer, the co-continuous phase structure with shorter periodic distance is reported to induce higher fracture toughness by prompted ductile tearing of the modifier-containing phase \(^{16,17,21}\). The modification of epoxy resins with PMI-St-p-hydroxy styrene terpolymer containing phenolic OH group also gave the co-continuous structure with shorter periodic distance and thereby the increased \(K_{IC}\) \(^{24,25}\).

In this study, the modified resin with PMSZ-9 had the co-continuous structure with shorter periodic distance and the higher fracture toughness with increasing the modifier content (see Fig.4). The resin modified with 10 phr of PMSZ had the co-continuous structure with shorter periodic distance compared with the resin modified with 10 phr of PMS (see Fig.4c and 5b). PMSZ contains PMS units which have solubility parameter (SP) of 26.8 (J/cm\(^3\))\(^{1/2}\) and polydimethylsiloxane units which have SP of 16.2 (J/cm\(^3\))\(^{1/2}\), calculated by Okitsu’s equation \(^{27,28}\), while the SP value of the epoxy resin containing DDS is 23.3 (J/cm\(^3\))\(^{1/2}\). These SP values indicate that the epoxy matrix is lowly compatible with PMS and PMSZ, and two segments in PMSZ are not compatible and thereby PMSZ has decreased cohesive energy compared with PMS containing no silicone segments. The shorter
periodic distance of the co-continuous phase for the resin modified with PMSZ is likely to be induced by the decreased cohesive energy of PMSZ. However, the fracture toughness of the resin modified with PMSZ is rather lower than that of the resin modified with PMS. This result must be attributed to the decreased interfacial interaction between the matrix phase and the PMSZ-containing phase, induced by the silicone segments with low SP value. In conclusion, the results on the modification with PMSZ suggest that both the co-continuous phase with fine periodic distance and the appropriate interaction (binding) between the matrix and the modifier phases are necessary to increase the fracture toughness of the epoxy matrix resin.

The SP value of polyoxyethylene contained in PMSE is calculated to be 20.5 (J/cm³)¹/², and therefore this segment is expected to increase the interfacial interaction between the matrix and the modifier phases. Polyoxyethylene or poly(ethylene oxide) is practically reported to be fully miscible with epoxy resins cured with various curing agents. Moreover, in the modification of epoxy resins with di- and tri-block copolymers composed of polyoxyethylene and polyoxypropylene segments, polyoxyethylene block has been considered to be completely or partially miscible with the cured resins. Mijovic et al. reported that blends of epoxy resins with polyoxyethylene-polyoxypropylene di-block copolymer gave the cured resins with the nanoscopic (domains of the order of nanometers) separated structure.

On the basis of their results obtained by the modification with polyoxyethylene-containing modifiers, it is concluded that in the modification with multi-block copolymer PMSE, polyoxyethylene segments in the modifier are miscible, at least in part, with the cured matrix resin and the modified resin has a similar interphase between the matrix and modifier phases. However, the modification with PMSE resulted in the formation of the cured resin not with the nanoscopic phase structure but with the microscopic (domains of the order of micrometers) structure. This must be due to differences in the structure and molecular weight between the modifiers. That is to say, di-or tri-block copolymers with well-defined structures and relatively low molecular weights were used in the previous modification, while multi-block copolymer PMSE with various different microstructures and high molecular weight was used for the modification of epoxy resin in this study. Such a multi-block copolymer must decrease the interaction of polyoxyethylene segments in PMSE with the epoxy matrix, because the segments interposed between two poly(phenylmaleimide-alt-styrene) (PMS) segments with high SP value or low miscibility with the epoxy resin are interfered to interact with the epoxy matrix.

The results obtained in this study suggest that di-or tri-block copolymers composed of poly(phenylmaleimide-alt-styrene) segments and polyoxyethylene segments can interact thoroughly with the epoxy matrix resins and therefore may be promising modifiers for toughening the epoxy resins.

4. References
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