

Toughness Improvement of High-Performance Epoxy Resin Using Aminated Polyetherimide

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ABSTRACT: A tetrafunctional epoxy resin was modified with polyetherimide (PEI) to improve its fracture toughness. To improve the high-performance epoxy toughening, the effective functional groups were introduced for pristine PEI. PEI containing an ethylamine group as a functionality was obtained by reacting it with ethylenediamine. In the mode I fracture test, the K_{Ic} values of aminated PEI-toughened epoxies were higher than that of pristine PEI-toughened epoxy. The maximum K_{Ic} value was obtained when the interface between the PEI domain and the epoxy matrix was strengthened without much disturbing of the spherical domain shape. In addition, it was also observed that the toughening effect of aminated PEI depended on the amount of curing agent. The flexural strengths of aminated PEI-toughened epoxies were also higher than that of pristine PEI-toughened epoxy. However, when excessive amination was performed, the flexural strength of aminated PEI-toughened epoxy decreased due to the reduction of physical properties of PEI. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2237–2246, 1997

Key words: tetrafunctional epoxy; polyetherimide; toughening; amination

INTRODUCTION

Tetrafunctional epoxy resins have been widely used as matrices in advanced polymer composites because they have excellent properties such as high modulus and high strength at relatively high temperature and good thermal stability.^{1–6} However, these resins have a major drawback of brittleness due to their highly crosslinked structure and this drawback prevents them from enlarging their application fields.

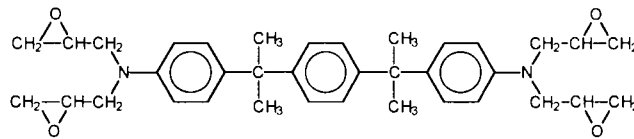
In the past decade, the common method for toughness improvement of epoxy resins was the introducing of liquid rubbers as a second component.^{7–14} However, it has been reported that the rubber-toughening method becomes less effective

as the crosslinking density of the epoxy resin increases.^{15,16} In addition, the rubber-toughening method leads to the decrease of other mechanical properties. This is an undesirable fact regarding the application fields of tetrafunctional epoxy resins. Therefore, the development of a new toughening method suitable for the tetrafunctional epoxy system was required and, consequently, the use of high-performance thermoplastics has been tried to improve the fracture toughness of tetrafunctional epoxy resins.^{17–21} Especially, toughness improvement of cured epoxy resin using high-performance thermoplastics has the additional advantage of having no reduction of thermal and mechanical properties.

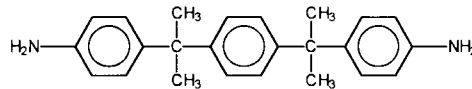
Among the high-performance thermoplastics, PEI has been widely investigated as a toughener. In this case, most articles have focused on the study of phase-separation phenomena and their relationships with mechanical properties of polyetherimide (PEI)-toughened epoxies.^{22–25} Re-

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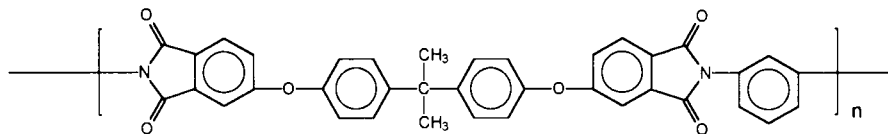
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HPT 1071 Resin



HPT 1061M Curing Agent



PEI

Figure 1 The chemical structures of HPT 1071 resin, HPT 1061M curing agent, and PEI.

cently, the effect of functional groups of a toughener on the fracture toughness becomes one of the important research subjects.^{26,27}

In this study, instead of using the pristine PEI, PEI modified with some functionality was added to epoxy resin. It was our primary objective to investigate the effect of the functional groups of PEI on the fracture toughness of the PEI-modified epoxy resin. An optimization study of the interfacial adhesion between the dispersed PEI phase and the epoxy matrix was also carried out with a viewpoint of PEI modification. In addition, the

morphological changes of modified epoxy resins due to the functional groups of PEI were also studied in this work.

EXPERIMENTAL

Materials

The epoxy resin used in this study was *N,N,N',N'*-tetraglycidyl- α,α' -bis-(4-aminophenyl)-*p*-diisopropylbenzene (EPON HPT 1071, abbreviated

Table I Typical Properties of HPT 1071 Resin and HPT 1061M Curing Agent

	Resin	Curing Agent
Physical form	Dark solid	Free flowing solid powder
Epoxy equivalent weight	150–170	
Melting point ^a	50°C	161–164°C
Melting viscosity (110°C) ^b	1.8–2.2 Pa-s	
Equivalent weight/active Hydrogen		86
T_g^c	22.8°C	

^a ASTM D3461, Mettler, 1°C/min.

^b Brook Field viscometer.

^c DSC.

Table II Physical Properties of Poly(ether imide)^a

Molecular weight (\bar{M}_n)	20,000
Tensile strength	104.88 MPa
Flexural modulus	3.3 GPa
Flexural strength	150 MPa
Fracture energy	2.5 kJ m ⁻²

^a Trade name: ULTEM 1000.

HPT 1071) and α,α' -bis-(4-aminophenyl)-*p*-diisopropylbenzene (EPON HPT 1061M, abbreviated HPT 1061M) was used as a curing agent. These materials were supplied by Shell Chemical Co. and used as supplied without further purification. The chemical structures of the HPT 1071 resin and the HPT 1061M curing agent are illustrated in Figure 1. The physical properties of these materials are represented in Table I.

Polyetherimide (ULTEM 1000), used as a thermoplastic toughener, was supplied by the General Electric Co.. The number-average molecular weight (\bar{M}_n) of PEI was 20,000. Its structural formula is also represented in Figure 1. In addition, Table II represents the physical properties of PEI.

Amination of PEI

All the PEI used in this study was purified by the reprecipitation method. Ten grams of PEI were dissolved in 200 mL of methylene chloride/dioxane (1 : 1 vol ratio) cosolvent and precipitated in 1000 mL of *n*-hexane. This precipitate was filtered and dried *in vacuo* at 60°C. The average diameter of the PEI powder used in this study was under 355 μ m.

The amination reaction was carried out with dispersing the PEI powder in acetone solvent to introduce the functional groups on the PEI powder surface and to minimize the other side reactions. The reaction scheme is as follows:

Three grams of PEI was forcibly dispersed in 300 mL of acetone at 55°C and ethylenediamine (EDA) was added to this mixture using a dropping funnel. The reaction time was fixed at 1 h. The amination reaction was carried out with mechanical stirring and the extent of amination was controlled by changing the amount of EDA. The amount of EDA was changed as follows: 5, 7.5, and 10 mL. The aminated PEI (abbreviated APEI) was filtered and dried *in vacuo* at 60°C for 1 day. The amination reaction of PEI is shown in Figure 2. PEIs treated with 5, 7.5, and 10 mL of EDA are abbreviated 5PEI, 7.5PEI, and 10PEI, respectively.

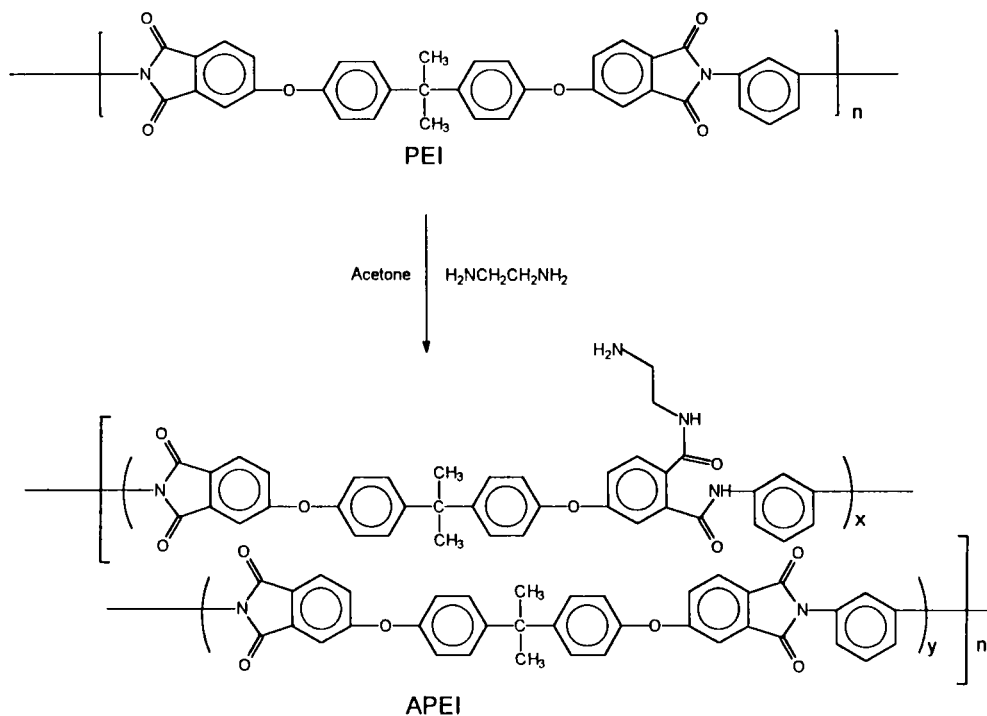


Figure 2 Schematic diagram of the amination of PEI.

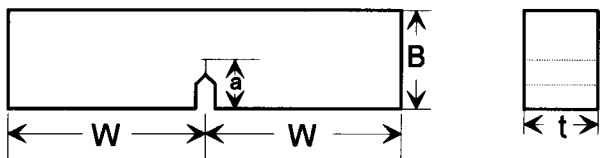


Figure 3 Specimens for the SENB test.

Sample Casting

Two kinds of tetrafunctional epoxy resin systems, i.e., the HPT 1071/HPT 1061M/PEI and HPT 1071/HPT 1061M/APEI systems, were made by melt casting. The amine-to-epoxy ratio was fixed at 0.85 and this is a commercially recommended value. Melt-casting specimens were obtained by first dissolving HPT 1071 resin and PEI(APEI) in *N,N'*-dimethylformamide followed by removing the solvent under a vacuum of 40 mmHg at 120°C, and temperature was increased to 180°C.

The HPT 1061M curing agent melted at 180°C and the molten HPT 1071/PEI(APEI) mixture was mixed thoroughly by a mechanical stirrer and degassed in a vacuum oven at 180°C, 20 mmHg. This molten mixture was cast and cured at 180°C for 2 h and at 200°C for 4 h consecutively.

Measurements

A Fourier transform infrared spectrometer (Bomem MB-100) with a deuterated triglycine sulfate (DTGS) detector was used for the PEI surface analysis. The FTIR DRIFT method was performed

for the analysis of APEI. IR spectra were obtained at a resolution of 4 cm^{-1} with a coaddition of 200 scans and the chamber was continuously purged with dry nitrogen to remove the atmospheric moisture and CO_2 .

The $^1\text{H-NMR}$ spectrum was obtained using a JEOL JNM-LA300. The excitation frequency was 300 MHz. The deuterated dimethyl sulfoxide (DMSO) was used as a solvent. The $^1\text{H-NMR}$ spectrum was obtained at 140°C.

Elemental analyses of pristine PEI and APEIs were performed with a LECO CHNS-932 elemental analyzer. Each sample was analyzed at least five times.

The inherent viscosities of PEI and APEI were determined with an automated Ubbelohde viscometer thermostatically controlled at 25°C. *N,N'*-Dimethylacetamide was used as a solvent.

Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC7 under a nitrogen flow at a constant heating rate of 20°C/min in the temperature range from 50 to 300°C. The glass transition temperatures of cured epoxies were determined by a Rheometrics Scientific Co. MKIII. The dynamic mechanical thermal analysis was performed by a bending mode with a 1 Hz frequency. Also, the heating rate was 5°C/min.

The flexural properties of the cured epoxy specimens were measured by a three-point bending test (ASTM D790) using a universal testing machine Model Instron 4201. The epoxy plaque was machined into bars with a dimension of 80 × 25

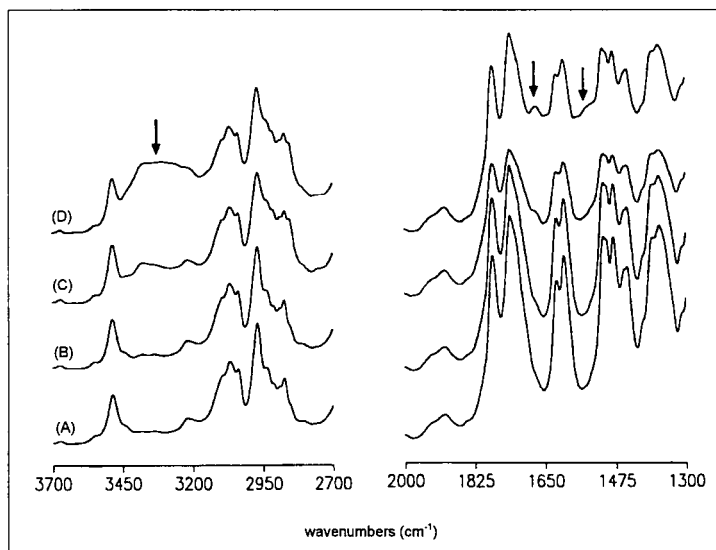


Figure 4 FTIR DRIFT spectra of aminated PEI with different amination conditions: (A) pristine PEI; (B) 5PEI; (C) 7.5PEI; (D) 10PEI.

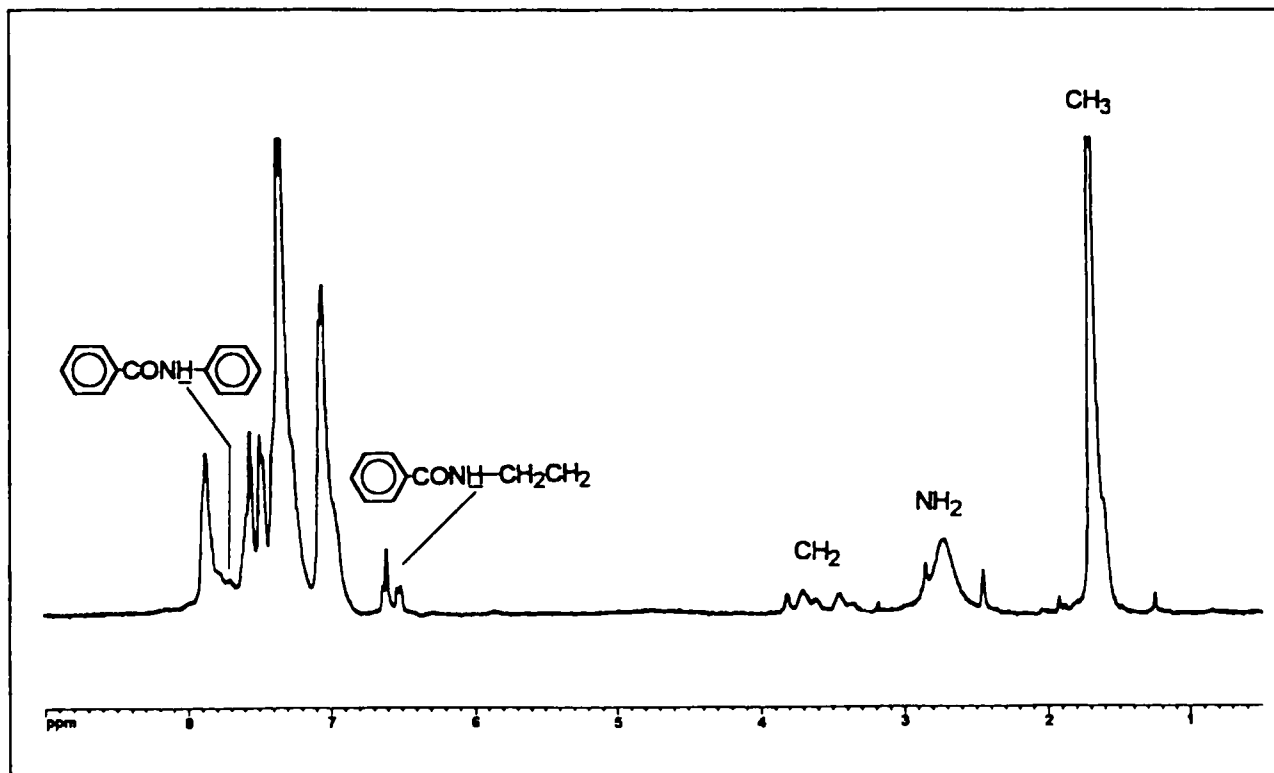


Figure 5 $^1\text{H-NMR}$ spectrum of 10PEI.

$\times 3.5$ mm. In the flexural test, the crosshead speed was 1.0 mm/min and the gauge length was 50 mm. In a fracture test, single-edge notch-bend (SENB) specimens were prepared by ASTM E399. The recommended design of the SENB specimen is shown in Figure 3. In this study, the dimension of the SENB specimen was $32 \times 7 \times 3.5$ mm. These specimens were notched with a $250 \mu\text{m}$ radius notching cutter followed by a liquid nitrogen-cooled razor blade tapping to introduce a sharp crack. The test was carried out at room temperature and the crosshead speed was 10 mm/min. Five specimens were tested for this study.

The fracture surfaces of epoxy resins were investigated with a JEOL JSM-35CF scanning elec-

tron microscope after coating with a thin layer of gold. The accelerating power was 25 kV.

RESULTS AND DISCUSSION

The mechanical properties of APEI-modified tetrafunctional epoxies were compared with those of pristine PEI-modified epoxy. Results for the amination of PEI, the relationship between the K_{Ic} values, and the corresponding morphological changes for each PEI-modified system are described below.

Table III Elementary Analysis Results and Physical Properties of Aminated PEI

Sample Code	N (Wt %)	Amine ^a (mmol g ⁻¹)	T_g (°C)	Intrinsic Viscosity
PEI	4.972	—	215.89	0.2810
5PEI	5.056	0.030	213.03	0.2150
7.5PEI	5.514	0.193	197.06	0.1450
10PEI	5.977	0.359	167.39	0.1200

^a Calculated values.

Amination of PEI

Figure 4 shows the DRIFT spectra of APEIs. As the amount of EDA increased from 5 to 10 mL, a new broad band at the 3400–3200 cm^{-1} region appears and its intensity increases due to the NH stretching mode of the amine functional group. A newly formed amide also appears at the 3600–3200 cm^{-1} region but it is difficult to distinguish its stretching peak from the NH stretching peak due to the overlap between both peaks. In the spectral region of 2000–1300 cm^{-1} , it is obviously observed that the band at 1680 cm^{-1} , corresponding to the carbonyl stretching of amide, appears. In addition, the band at 1590 cm^{-1} assigned to the NH_2 deformation peak is observed. The intensities of the above two peaks increase as the amount of EDA increases from 5 to 10 mL.

To characterize the structure of APEIs, $^1\text{H-NMR}$ analysis was performed. For brevity, only the $^1\text{H-NMR}$ spectrum of 10PEI is given in Figure 5. Although it was difficult to assign each peak due to the broadness of this spectrum, tentative assignments were performed. It could be known that APEI was obtained by EDA attacking the rigid imide ring. Considering the IR, $^1\text{H-NMR}$ spectra, the amine functional units were successfully introduced on PEI by the EDA treatment.

Because of the broadness of the NMR spectrum, it was difficult to analyze the extent of amination. Therefore, the amount of the amine functional group introduced by amination was determined by elemental analysis. The results of elemental analysis are summarized in Table III. Judging from these data, the number of amine groups increases abruptly with an increasing amount of EDA. In case of 5PEI, it has a 0.03 mmol of the amine group per 1 g, meaning that about eight of the 1000 imide rings were opened by this EDA treatment.

To examine the change of physical properties of PEI due to the amination, its glass transition temperature and intrinsic viscosity were measured. The results are presented in Table III. The glass transition temperature of APEI decreases with increasing the amount of EDA, meaning that the amination of PEI provides the chain mobility of PEI by opening the rigid imide ring. This fact is coincident with the change of the intrinsic viscosity.

The intrinsic viscosity data show that even a small amount of the ethyl amine group has a great effect on the viscosity value. This results from the fact that the opening of the rigid imide ring in-

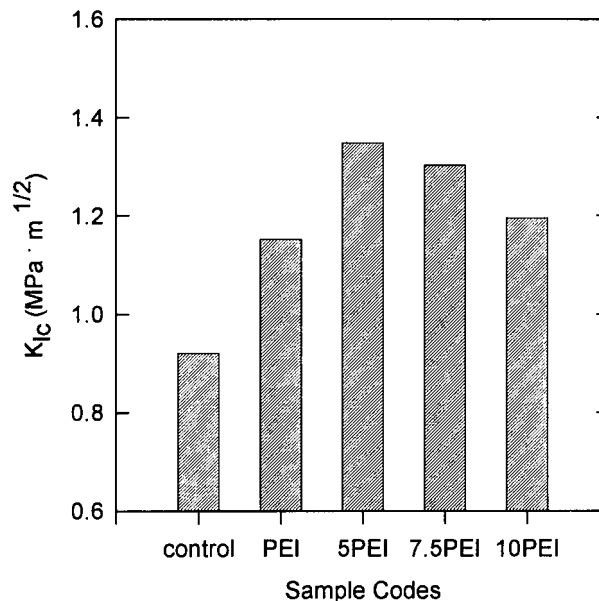


Figure 6 Fracture toughness of the HPT 1071/HPT 1061M system as a function of the amination of PEI (5 wt % PEI).

duces the large decrease of the intrinsic viscosity of PEI. In this table, severely aminated PEI(10PEI) shows much lower T_g and intrinsic viscosity value than those of pristine PEI. Therefore, it was suggested that the physical properties of PEI should be reduced in excessive amination.

Fracture Toughness and Morphology

The fracture toughness (K_{Ic}) was calculated as follows:

$$K_{Ic} = \frac{P_c S}{Bw^{3/2}} f(a/w)$$

where P_c is load at break, S is span length, and the other terminologies are presented in Figure 3. The structural factor $f(a/w)$ is given as

$$f(a/w) = \frac{3(a/w)^{1/2}[1.99 - a/w(1 - a/w) \times (2.15 - 3.93a/w + 2.7a^2/w^2)]}{2(1 + 2a/w)(1 - a/w)^{3/2}}$$

To study the effect of the amination of PEI, the PEI content was fixed at 5 wt % of the epoxy resin. Figure 6 shows the K_{Ic} values of neat epoxy and various PEI-toughened epoxies. The maximum fracture toughness value of modified epoxy resin appeared at 5PEI. The K_{Ic} values of APEI-tough-

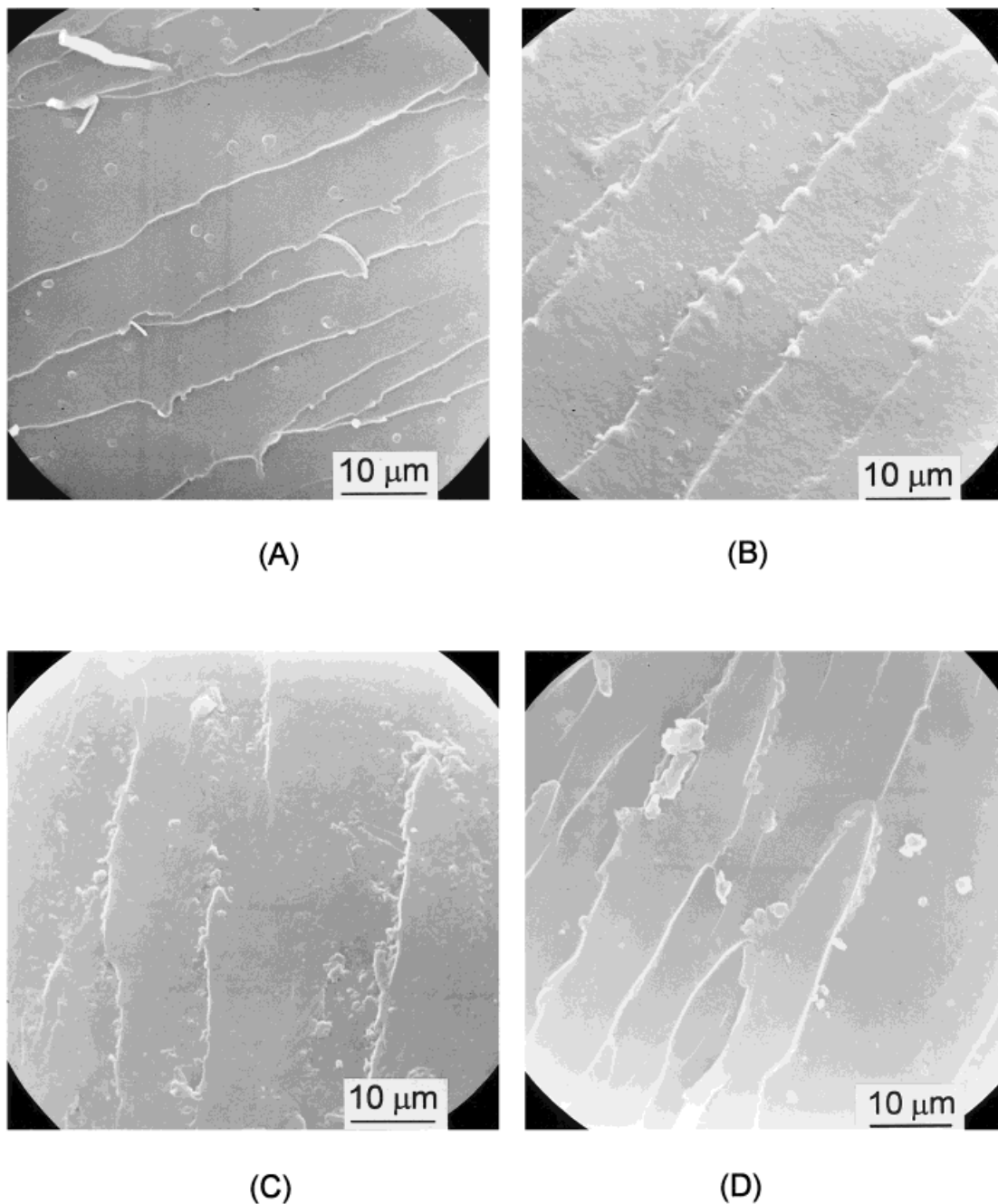


Figure 7 Scanning electron micrographs of the HPT 1071/HPT 1061M system with different PEIs: (A) pristine PEI; (B) 5PEI; (C) 7.5PEI; (D) 10PEI.

ened epoxies are higher than those of pristine PEI-toughened epoxy. Considering this figure, it could be known that the K_{Ic} value was influenced by the surface functional groups of PEI. To explain this result, a fractographical analysis was performed and the results are shown in Figure 7.

The toughness of the epoxy resin/thermoplastic blend strongly depends on the phase separa-

tion of the cured epoxy resin.²³ In the case of pristine PEI-toughened epoxy [Fig. 7(A)], its fractured surface shows finely dispersed PEI domains. These PEI domains make the crack propagation path more complex and the fracture toughness of modified epoxy resin is increased.

Compared with pristine PEI-toughened epoxy, 5PEI-toughened epoxy resin shows a similar frac-

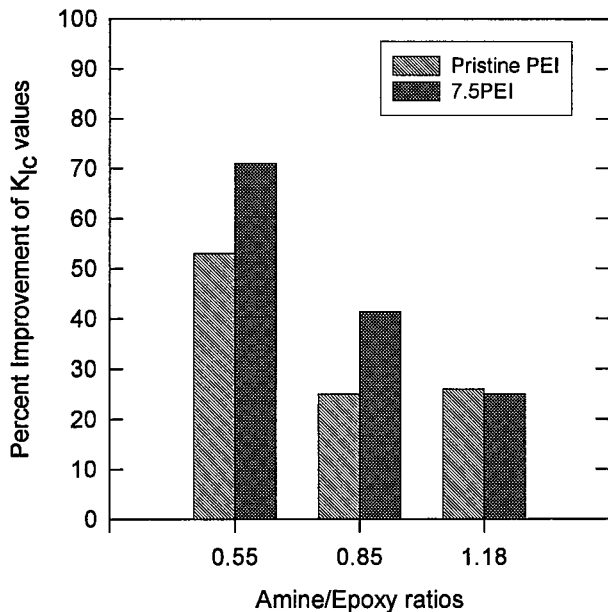


Figure 8 The percent improvement of fracture toughness of the HPT 1071/HPT 1061M system with different amine curing agent-to-epoxy ratios.

tured surface [Fig. 7(B)]. It also shows well-dispersed PEI domains. On the other hand, it shows some different features at the domain interface. Considering this figure, the interfacial adhesion of the 5PEI domain is stronger than that of pristine PEI. Therefore, some portion of the fracture energy is easily transferred to the PEI domains through this interfacial bonding. This promotes the ductile tearing of PEI. In the case of 5PEI-toughened epoxy, its improved fracture toughness comes from the finely dispersed PEI domain and the ductile drawing of PEI facilitated by the strengthened domain interface. However, the extent of improvement was not so great due to the highly crosslinked structure.

Observing Figure 7(C) and (D), the PEI domain size is reduced as the large amount of functional groups is introduced. Compared with the pristine PEI case whose average domain size is $1.44 \mu\text{m}$, the average domain sizes of 7.5PEI and 10PEI are reduced to 1.22 and $0.9 \mu\text{m}$, respectively. The decrease of the PEI domain size causes the sacrificing of the fracture mechanism induced by the PEI domain structure. This is undesirable for toughness improvement. However, the amine group of PEI is more reactive than that of the curing agent, because the former is the ethyl amine group and the latter is the aromatic amine group. Therefore, APEI can take part in the curing reaction, consequently, the PEI unit is in-

cluded in the epoxy network. This is profitable for toughness improvement because of the high fracture toughness value of PEI. Ultimately, the K_{Ic} value of highly aminated PEIs is determined by the above two conflicting factors.

Figure 8 shows the percent improvement of K_{Ic} values of epoxy resins with various amine-to-epoxy ratios using two types of PEI. It is observed that the toughening effect due to the amine functional group does not appear at an excessive amount of the amine curing agent case. The T_g 's of cured epoxy resins modified with two types of PEI are given in Figure 9. Compared with the pristine PEI-toughened case, epoxy resins with 7.5PEI show higher T_g values. The increase of T_g values due to the amination of PEI becomes smaller as the amount of curing agent increases. This implies that the participation of APEI in the curing reaction is more or less restrained as the matrix becomes highly crosslinked.

Flexural Strength

The change of other mechanical properties of APEI-toughened epoxies due to the amination was examined. The flexural strengths of various epoxies are given in Figure 10. The flexural strength also increases with modification of PEI. However, 10PEI-toughened epoxy shows a lower

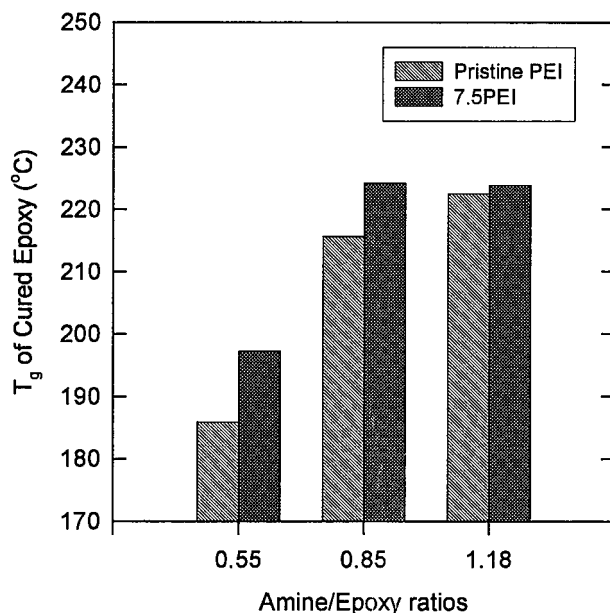


Figure 9 Glass transition temperatures of the HPT 1071/HPT 1061M system with different amine curing agent-to-epoxy ratios.

value than that of the pristine PEI case. To explain this result, the T_g 's of cured epoxies were measured by DMTA analysis. The results are presented in Figure 11. The glass transition temperatures of aminated PEI-toughened epoxy resins are higher than that of pristine PEI-toughened epoxy. As previously stated, this result comes from the reaction between APEI and the epoxy. Compared with the other APEI-toughened cases, the T_g of 10PEI-toughened epoxy was the smallest among the others in spite of many functional groups of 10PEI. Considering Table III, this result can be explained by the large reduction of T_g of 10PEI. It shows a lower T_g than that of pristine PEI by about 50°C. Therefore, the decrease of flexural strength of 10PEI-toughened epoxy is attributed to the decrease of the flexural property of PEI itself by excessive amination.

CONCLUSIONS

From this study, we can make following conclusions: First, the fracture toughness of tetrafunctional epoxy resin is successfully improved by PEI surface modification. Second, the maximum fracture toughness value can be obtained when the optimum amount of functional groups is introduced. The optimum amount of functional groups

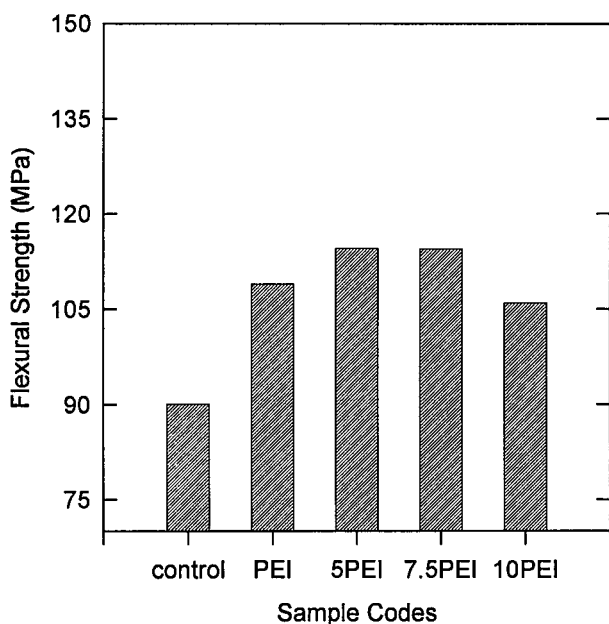


Figure 10 Flexural strengths of the HPT 1071/HPT 1061M system as a function of amination of PEI (5 wt % PEI).

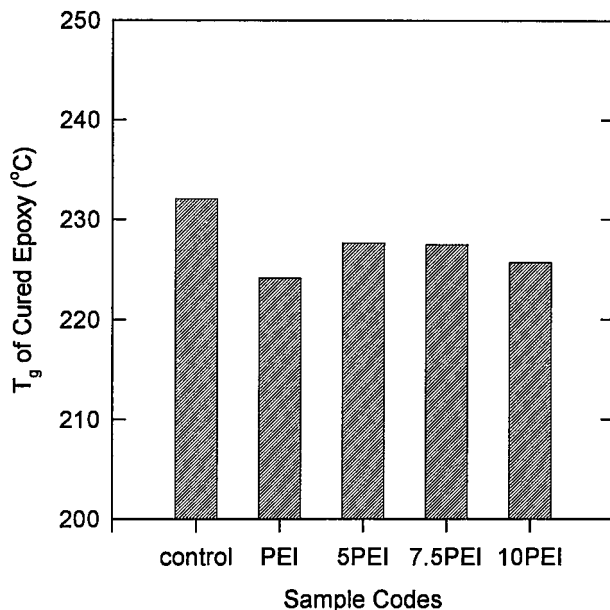


Figure 11 Glass transition temperatures of the HPT 1071/HPT 1061M system with different kinds of PEIs.

should be determined by considering the morphological change. In this study, fracture toughness was maximized when the ductile drawing of PEI is facilitated by the strengthening of the domain interface without disturbing the formation of the spherical PEI domain. The toughening effect of amination depends on the amine curing agent-to-epoxy ratios. As the amount of the amine curing agent increased, it was difficult to observe the toughening effect of APEI. In addition, the other mechanical properties of APEI-toughened epoxies was slightly increased by PEI amination except for the excessively aminated case.

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