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Toughness improvement of tetrafunctional epoxy resin by using hydrolysed poly(ether imide)

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Toughened epoxy resins were prepared by dissolving poly(ether imide) (PEI) in the EPON HPT 1071 based resin with EPON HPT 1061M as a curing agent. Open tension tests showed an increase in fracture toughness with PEI content, from 0.61 GPa m$^{1/2}$ in the pristine resin to 1.32 GPa m$^{1/2}$ at 15 wt% PEI. Similar results were obtained for the flexural properties of the epoxy resin. In order to improve the fracture toughness of epoxy resins, increasing the interfacial adhesion strength between the dispersed PEI phase and tetrafunctional epoxy resin was necessary. Improved interfacial adhesion of the modified epoxy resin was obtained through the hydrolysis of PEI. At a concentration of 5 wt% PEI, hydrolysed PEI/epoxy resin had 40% more fracture toughness than the unhydrolysed PEI/epoxy resin. The effect of PEI hydrolysis on the flexural properties of the cured epoxy resins was also studied. Scanning electron microscopy was used to investigate the relationship between the morphological study of the fractured epoxy resins and mechanical properties of the modified epoxy resins.

(Keywords: tetrafunctional epoxy resin; fracture toughness; poly(ether imide))

INTRODUCTION

Recently, the use of tetrafunctional epoxy resins has been increasing in applications for advanced composite materials in the aerospace and aircraft industries[1–5]. Well balanced tetrafunctional epoxy resins, which retain high modulus and high strength at relatively high temperatures, make the material suitable for these applications. However, these resins have the major drawback of brittleness, due to their tightly crosslinked structure.

In the past decade, a second component, such as reactive liquid rubber, has been incorporated in the liquid epoxy system before curing, in order to improve the toughness of cured epoxy resins. The most commonly used reactive liquid rubber is poly(butadiene-*co*-acrylonitrile) with reactive end groups of either carboxyl (CTBN) or amine (ATBN) functionality[6–11]. Rubber toughening of thermosetting resins depends upon the deformation in the resin matrix, which is usually accompanied by cavitation within the rubber particles[12,13], and consequent stress whitening of the yield zone. Therefore, the rubber toughening technique is effective for difunctional epoxy resins such as diglycidyl ether of bisphenol A (DGEBA). However, tetrafunctional epoxy resin has a high crosslink density and these resins become even less ductile. Rubber particles become progressively blunt in the process of improving the fracture toughness of high performance epoxy resin. The relationship between crosslink density and the mechanical properties of cured resins has been explained by Pearson and Yee[14].

When shear yielding deformation is constrained due to the increased crosslink density of epoxy resin, the improved fracture toughness of the cured epoxy resin can not be obtained effectively. Consequently, the rubber toughening technique is not effective for tetrafunctional epoxy resins. The development of a new toughening technique, which has efficient energy absorption irrespective of matrix ductility, is required[15].

High performance thermoplastics, such as poly(ether imide) (PEI) and poly(ether sulfone) (PES), have been used to improve the fracture toughness of tetrafunctional epoxy resin systems[16–20]. Toughness improvement of cured epoxy resin, especially using high performance thermoplastics, has the additional advantage of causing no reduction of thermal and mechanical properties.

In this paper, PEI is used as a toughener to increase the fracture toughness of tetrafunctional epoxy resin. In order to improve the fracture toughness, optimization of interfacial adhesion between the dispersed PEI phase and resin matrix has been studied as a function of the hydrolysis time of PEI.

For improving the fracture toughness of the cured epoxy resin, PEI is hydrolysed to form new functional groups which react with tetrafunctional epoxy resin during the cure reaction. In addition, the relationship between the mechanical properties of modified epoxy resins and the morphology of the fractured surface of the cured epoxy resin is investigated in the present work.

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EXPERIMENTAL

Materials

The epoxy resin used was *N*,*N*,*N*′,*N*′-tetraglycidyl-α,α′-bis-(4-aminophenyl)-*p*-diisopropylbenzene (EPON HPT 1071, abbreviated to HPT 1071) supplied by Shell Chemical Company.

The curing agent was α,α′-bis-(4-aminophenyl)-*p*-diisopropylbenzene (EPON HPT 1061M, abbreviated to HPT 1061M curing agent) also supplied by Shell Chemical Company. These materials were used as supplied without further purification. The structures of HPT 1071 resin and HPT 1061M curing agent are illustrated in *Figure 1*. In addition, *Table 1* presents the physical properties of these materials.

PEI (ULTEM 1000) supplied by the General Electric Co. was used as a thermoplastic toughener. The number average molecular weight ($\bar{M}_n$) of PEI was 20000. Its structural formula is also presented in *Figure 1*. In addition, *Table 2* presents the physical properties of PEI.

PEI (10 g) was dissolved in 200 ml of methylene chloride/dioxane cosolvent and precipitated in 1000 ml of n-hexane. This powder (untreated PEI, abbreviated to UPEI) was dispersed in distilled water and maintained at 70°C, while adding NaOH solution. The PEI hydrolysis reaction is shown in *Figure 2*. Hydrolysis times of PEI were 30, 60, 90 and 180 min. Modified PEI (abbreviated to MPEI) was filtered and dried *in vacuo* at 80°C.

Methods

Three tetrafunctional epoxy resin systems, that is HPT 1071/HPT 1061M, HPT 1071/HPT 1061M/UPEI and HPT 1071/HPT 1061M/MPEI, were cured by melt casting. In each case, the amine/epoxy ratio was fixed at 0.71.

In the case of the HPT 1071/HPT 1061M system, molten resin was prepared at 170°C by mixing with a mechanical stirrer, and was subsequently degassed in a vacuum oven under 50 mmHg at 175°C. This molten resin was poured into the steel casting moulder and cured for 2 h at 150°C and for 4 h at 200°C.

Melt cast specimens of the HPT 1071/HPT 1061M/UPEI system were obtained by first dissolving HPT 1071 resin and UPEI in methylene chloride, followed by removing the solvent under a vacuum of 100 mmHg at 170°C. The HPT 1061M curing agent, which melted at 180°C, and the molten HPT 1071/UPEI mixture were

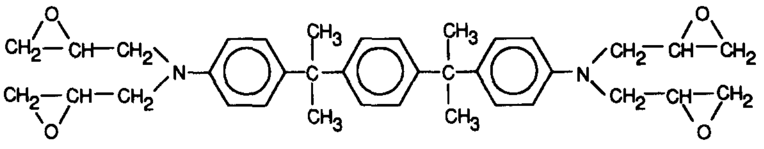
Table 1 Typical properties of EPON HPT 1071 resin and EPON HPT 1061M curing agent

	Resin	Curing agent
Physical form	Dark	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	22.8°C (d.s.c.)	

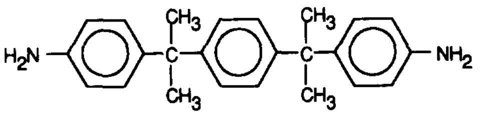
[a] ASTM D3461, Mettler, 1°C min^{-1}
[b] Brook Field viscometer

Table 2 Physical properties of poly(ether imide) (ULTEM 1000) at room temperature

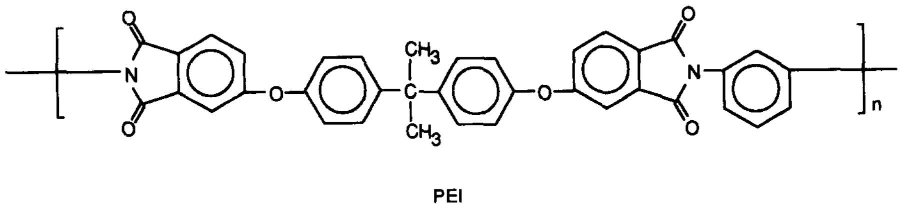
Molecular weight ($\bar{M}_n$)	20000
Tensile strength	104.88 MPa
Flexural modulus	3.3 GPa
Flexural strength	150 MPa
Fracture energy	2.5 kJ m^{-2}



EPON HPT 1071



EPON HPT 1061M



PEI

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

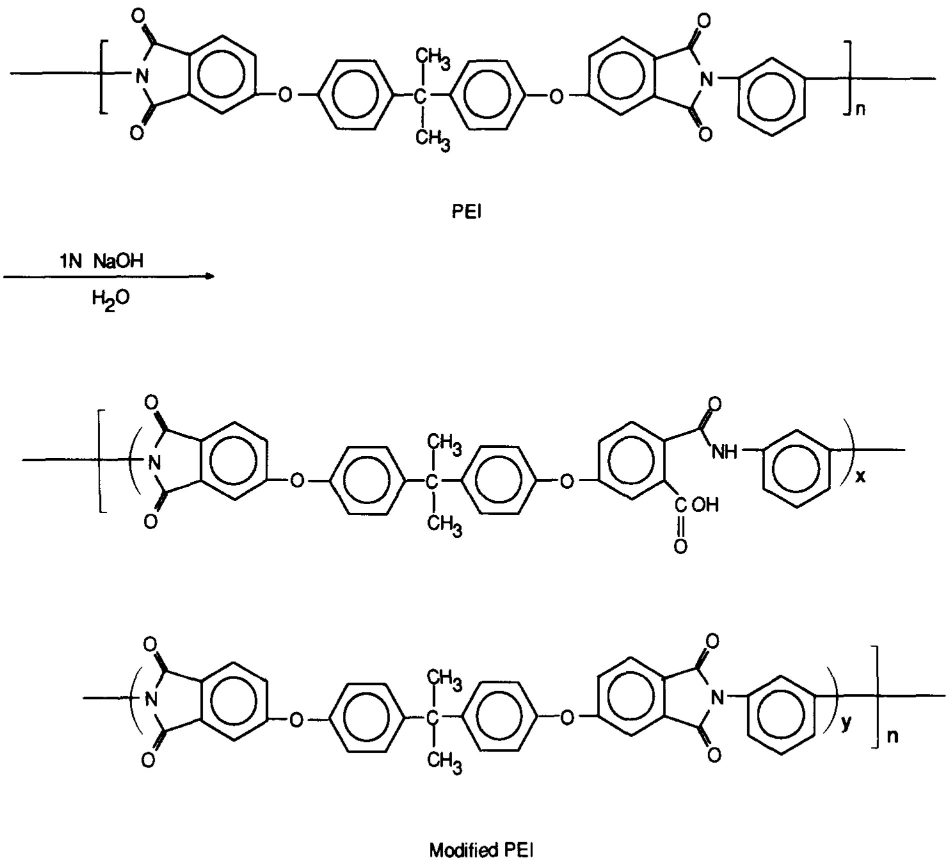


Figure 2 Schematic diagram of PEI hydrolysis reaction

mixed thoroughly by a mechanical stirrer and degassed in a vacuum oven at 190°C under 25 mmHg. This molten mixture was cast and cured for 2 h at 180°C and for 4 h at 200°C.

In the case of the HPT 1071/HPT 1061M/MPEI system, HPT 1071 resin and MPEI were dissolved in dimethylformamide, and the solvent was subsequently removed under a vacuum of 100 mmHg at 170°C. Molten HPT 1061M curing agent was added to the HPT 1071/MPEI mixture and mixed by a mechanical stirrer. This procedure was repeated for the HPT 1071/HPT 1061M/UPEI system.

Measurements

A Fourier transform infra-red spectrophotometer (Perkin–Elmer 1725-x), with a liquid-nitrogen cooled MCT detector, was used at a resolution of 2 cm^{-1} with coaddition of 64 scans. KBr pellets were used for the analysis of PEI, and the spectrophotometer was purged with dry air to remove atmospheric moisture.

Differential scanning calorimetry (d.s.c.) measurements were conducted using a Perkin–Elmer DSC7 with a microprocess controller. The temperature and powder calibration of the DSC7 were optimized for the temperature range of 20–300°C by using high purity indium as the standard calibration.

Flexural properties of the cured epoxy specimens were measured by a three-point bending test (ASTM D790) using an Instron 4201 Universal Testing Machine. The crosshead speed was 1.0 mm min^{-1}. The gauge length was 50 mm. In a fracture test, rectangular compact tension specimens were prepared by ASTM STP 381. A sharp crack was formed by carefully tapping a fresh razor blade. The notch tip radius was 0.0018 mm. The crosshead speed was 1.0 mm min^{-1} and seven specimens were tested for this study.

Scanning electron microscopy (Jeol model JSM-35CF) was used to study the morphology of epoxy resin. The accelerating power was 15 kV.

RESULTS

Mechanical properties of PEI modified tetrafunctional epoxy resins are compared with those of the pristine epoxy resins. Results for the chemical modification of PEI, fracture toughness of the cured epoxy resin and morphology of the PEI toughened tetrafunctional epoxy resins are described below.

Chemical modification of PEI

Figure 3 shows the transmission spectra of MPEIs. As the hydrolysis time of PEI increased from 30 to 180 min (*Figure 3B–E*), a new broad band at 3600–3200 cm^{-1} appears due to the OH stretching mode of carboxylic acid. A newly formed amide also appears at 3600–3200 cm^{-1} and it is difficult to distinguish its stretching peak from the OH stretching peak due to overlap between the peaks. D.s.c. thermograms of UPEI and MPEI are shown in *Figure 4*. These data indicate that the glass transition temperature (T_g) of PEI decreases slightly with increasing hydrolysis time. The explanation for this is that hydrolysis causes chain mobility of PEI.

Fracture toughness

When a compact tension test is performed, fracture

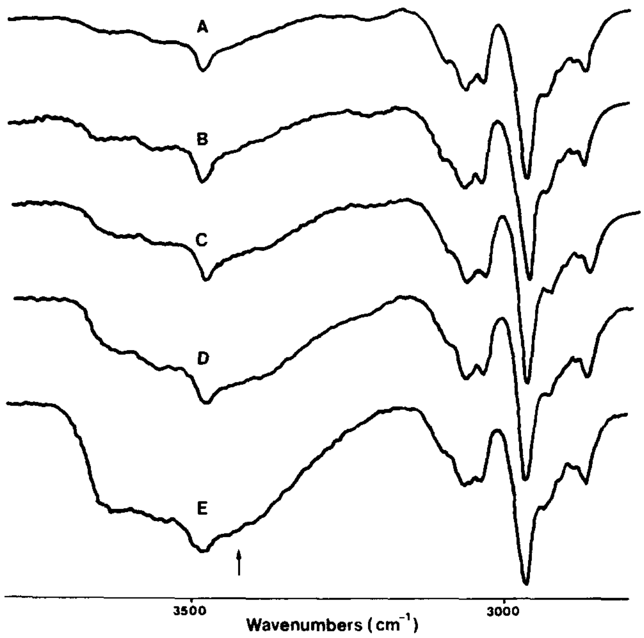


Figure 3 Transmission spectra of hydrolysed PEI as a function of hydrolysis time: A, control; B, 30 min; C, 60 min; D, 90 min; E, 180 min

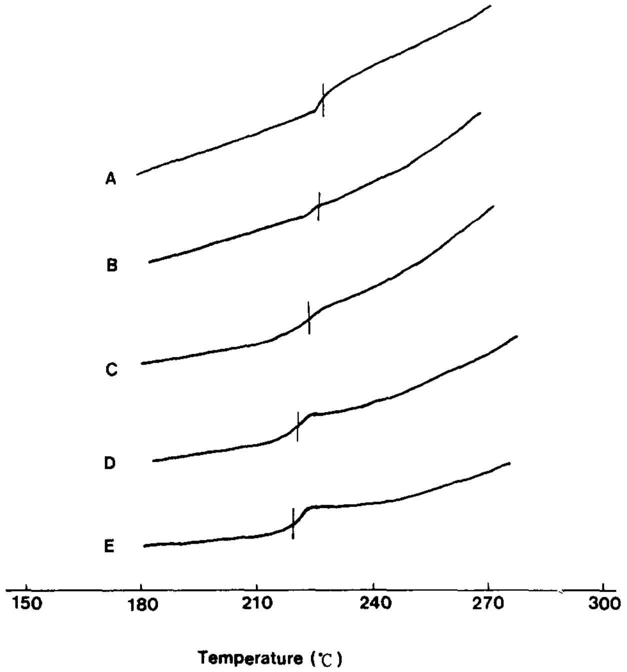


Figure 4 D.s.c. thermograms of PEI with different hydrolysis times: A, control; B, 30 min; C, 60 min; D, 90 min; E, 180 min

toughness (K_{Ic}) may be calculated as follows:

$$K_{Ic} = \frac{P_c Y a^{1/2}}{BW}$$

where P_c is the critical load for crack propagation, a is the crack length, and Y is the geometric factor. The recommended design of a compact tension rectangular specimen is shown in *Figure 5*.

Figure 6 shows the fracture toughness, K_{Ic}, of the HPT 1071/HPT 1061M system as a function of UPEI content. This figure shows that fracture toughness increases with the increase of UPEI content. When compared with the pristine epoxy resin, the cured epoxy resin has 180% fracture toughness improvement at 2 wt% UPEI.

In order to study the effect of hydrolysis of PEI, the MPEI content is fixed for the HPT 1071/HPT 1061M system. *Figure 7* shows the fracture toughness of the HPT 1071/HPT 1061M/MPEI system with 5 wt% MPEI. MPEI/epoxy resin systems show a higher fracture toughness value than UPEI/epoxy resins. The maximum fracture toughness value of the MPEI/epoxy resin system appeared at 30 min of treatment time for MPEI. *Figure 7* illustrates that further hydrolysis of PEI gradually reduces the fracture toughness.

Mechanical properties

Figures 8 and *9* exhibit the flexural strength and modulus, respectively, of the HPT 1071/HPT 1061M/UPEI system with variations of UPEI content. The

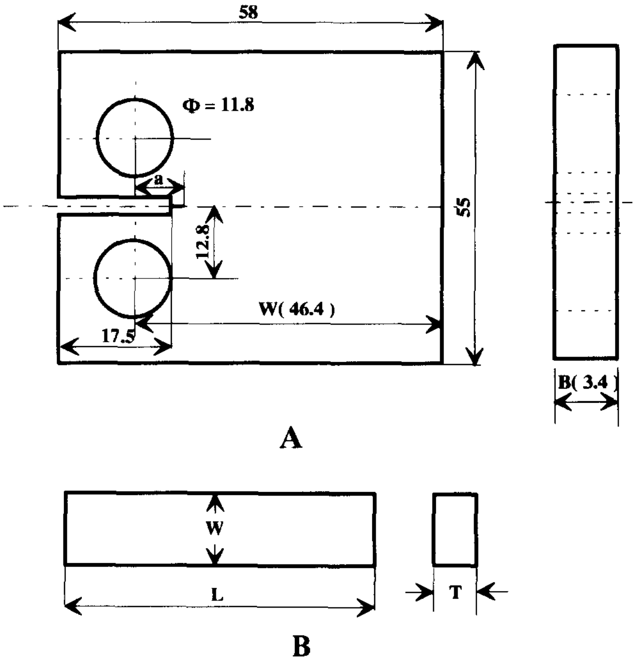


Figure 5 Specimens for the test of fracture toughness (A) and flexural properties (B)

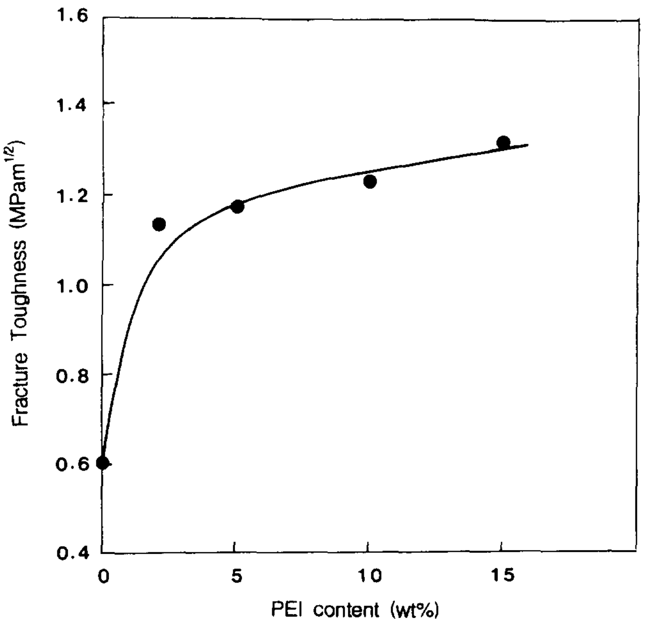


Figure 6 Fracture toughness of HPT 1071/HPT 1061M/UPEI system as a function of UPEI content

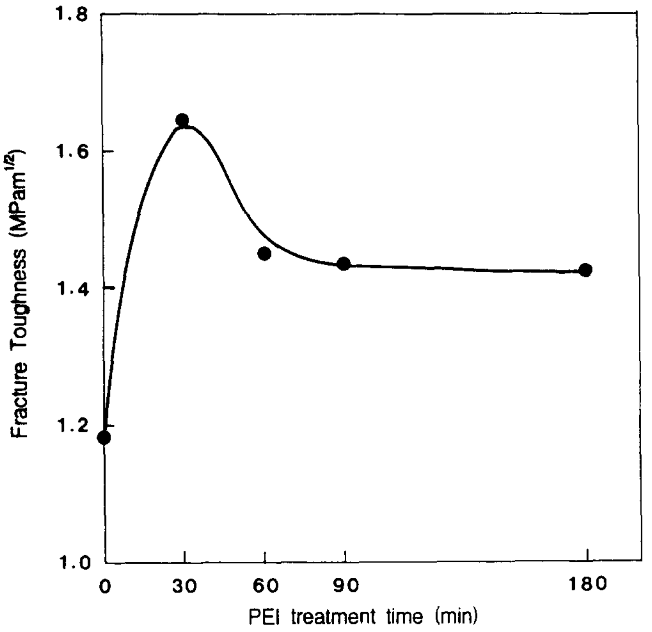


Figure 7 Fracture toughness as a function of PEI hydrolysis time for the HPT 1071/HPT 1061M/MPEI system with 5 wt% MPEI

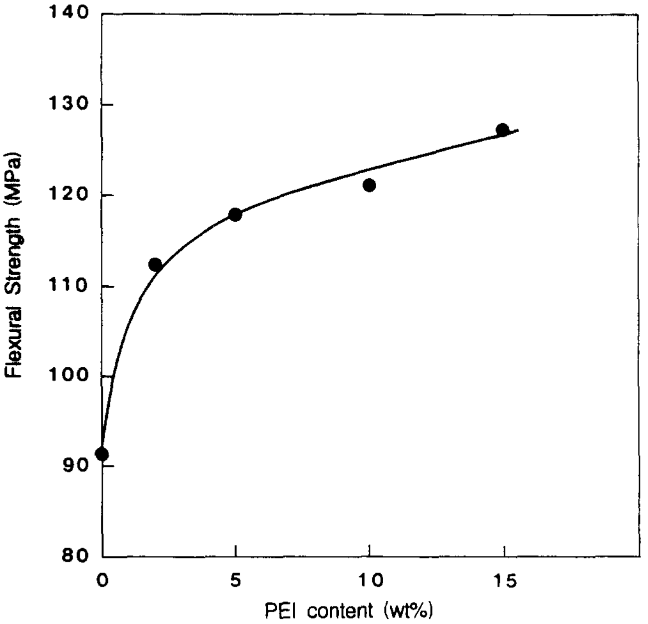


Figure 8 Flexural strength of HPT 1071/HPT 1061M/UPEI system as a function of UPEI content

flexural strength and modulus of cured epoxy resins increase as the UPEI content increases. These results follow the rule of mixtures as a general rule in composite material. The flexural strength of the MPEI/epoxy resin system with 5 wt% MPEI is plotted against the PEI treatment time in *Figure 10*. It shows that the flexural strength of the modified MPEI/epoxy resin has a maximum value at a PEI treatment time of 30 min. It also indicates that the flexural strength of the modified epoxy resin decreases slightly as the PEI treatment time increases up to 180 min.

The flexural modulus of the MPEI/epoxy resin system with 5 wt% MPEI is illustrated as a function of PEI treatment time in *Figure 11*. This shows that flexural modulus is independent of PEI treatment time.

Morphology

SEM micrographs for UPEI/epoxy resins are shown in *Figure 12a–e*. The micrographs show that the size and number of the dispersed UPEI phase increases as the concentration of UPEI in the epoxy resin increases. Several holes and voids between the dispersed UPEI particles and epoxy matrix are also observed.

Figure 13a–d demonstrates the fracture surface of MPEI-toughened epoxy resin, with the PEI content fixed at 5 wt%. These figures show that the size of the dispersed MPEI phase is reduced as the hydrolysis time of PEI increases. The fracture surface of the MPEI-toughened epoxy resin system at 30 min treatment time is shown in *Figure 13a*. It is observed that the boundary between the MPEI phase and the continuous epoxy phase has strong interfacial adhesion unlike the UPEI-toughened cases.

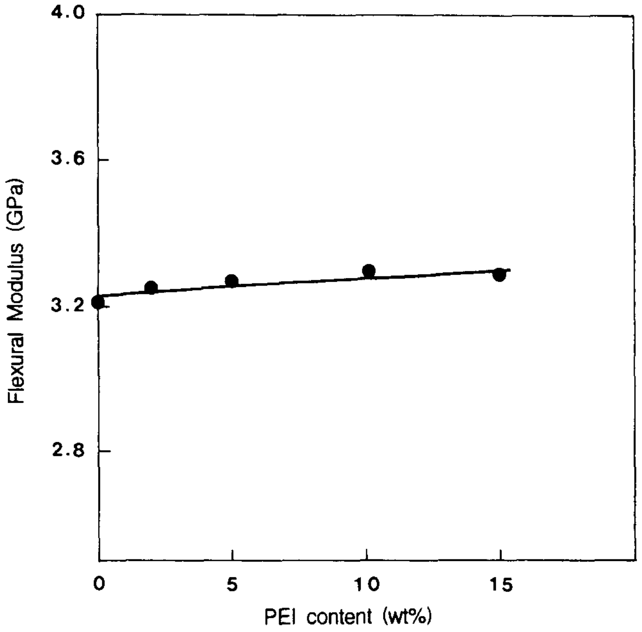


Figure 9 Flexural modulus of HPT 1071/HPT 1061M/UPEI system as a function of UPEI content

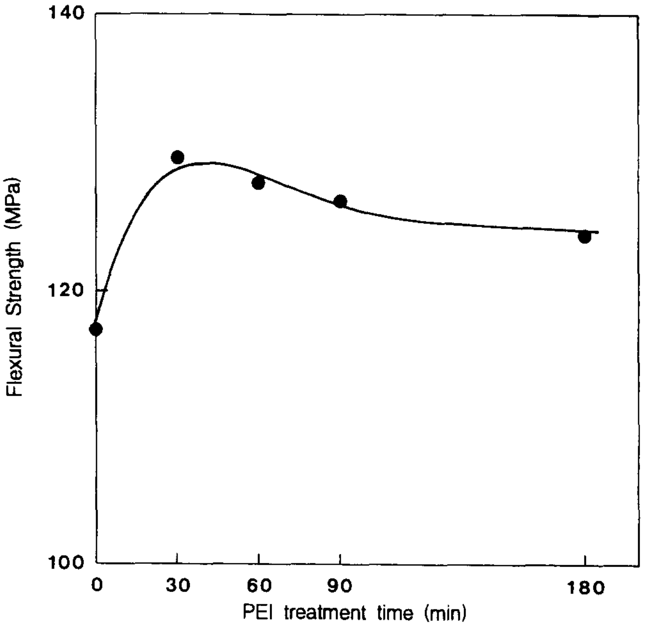


Figure 10 Flexural strength as a function of PEI hydrolysis time for the HPT 1071/HPT 1061M/MPEI system with 5 wt% MPEI

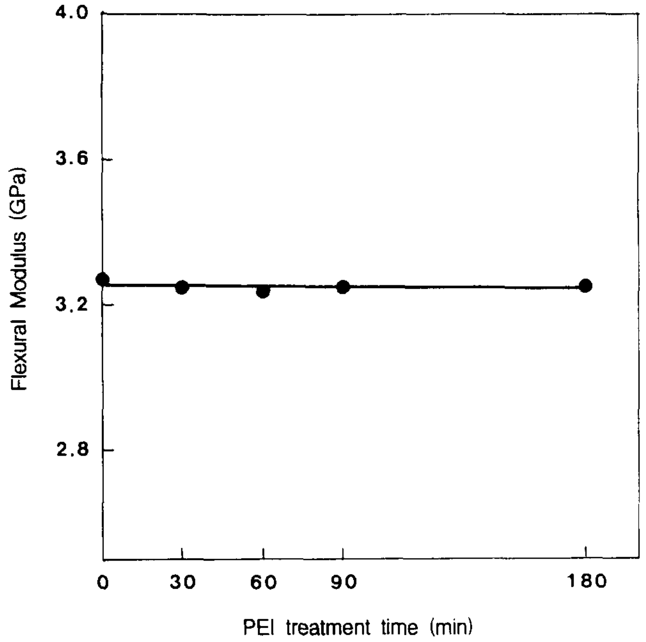


Figure 11 Flexural modulus as a function of PEI hydrolysis time for the HPT 1071/HPT 1061M/MPEI system with 5 wt% MPEI

DISCUSSION

This paper has shown that addition of PEI can substantially increase the toughness of tetrafunctional epoxy resins such as HPT 1071. When a modified PEI is introduced in a high performance epoxy resin system, fracture toughness of the cured epoxy resin is improved considerably.

The toughness of an epoxy resin/thermoplastic blend strongly depends on the phase separation of the cured epoxy resin. SEM micrographs show that there is relatively little miscibility between the two components during the later stages of curing.

During phase separation, semi-IPN (interpenetrating polymer network) structure is formed at the UPEI–epoxy interface by the interdiffusion process. UPEI, which diffuses into epoxy resin, improves the plasticity of epoxy resin around the UPEI dispersed phase. These diffused UPEI particles can induce stress relaxation by way of local shear deformation. Furthermore, deformation energy is absorbed by the ductile drawing process of UPEI dispersed phase. This phenomenon occurs when stress is transferred to the UPEI phase through the semi-IPN structure.

However, it is reasonable to expect that the local increase of the resin plasticity due to the diffused UPEI is not a major factor in toughness improvement. The improvement is due to the interdiffusion process being constrained by the great polarity difference between the UPEI and epoxy resin and the high crosslink density of the cured epoxy resin. Therefore, the ductile drawing process of UPEI is a major process in fracture toughness improvement of the modified epoxy resin.

Figure 6 shows that fracture toughness increases smoothly with increasing UPEI content. As the amount of UPEI increases in the tetrafunctional epoxy resin, the increment of UPEI domain size decreases in the cured epoxy resin system. This phenomenon is verified from SEM micrographs in *Figure 12a–e*. From these results, it can be concluded that a large amount of UPEI is miscible with epoxy resin when the UPEI content is more than 10 wt%.

Since the mechanical properties of UPEI are greater than those of pristine epoxy resin, the technique of thermoplastic modification can prevent the loss of mechanical properties of toughened epoxy resin. From *Figures 8* and *9*, it is known that the mechanical properties of the cured epoxy resin system depend on UPEI content. The flexural modulus of the modified epoxy resin shows little increase with increasing UPEI content. This can be explained by the difference in flexural modulus between the pristine epoxy resin and UPEI being small.

In this case, interfacial adhesion between the UPEI dispersed phase and epoxy resin may be poor, because the two materials have different polarities and UPEI has no functional group which can react with the epoxy resin. When stress is transferred to the UPEI phase, which has poor adhesion towards epoxy resin, the ductile drawing process does not occur effectively.

In order to maximize the fracture toughness of the modified epoxy resin system, it is necessary to optimize the interfacial strength between the UPEI phase and epoxy resin. In this study, formed functional groups of PEI are used for the enhanced interfacial adhesion of the modified epoxy resin system.

Considering the spectrum analysis, new carboxylic acid and amide groups are formed at the backbone of PEI during the hydrolysis reaction, and the amount of these functional groups increases with increasing PEI hydrolysis time. The formed functional groups of PEI participate in the curing reaction of epoxy resin.

During hydrolysis, PEI particles undergo a ring opening reaction in NaOH solution. In alkali solution, the carboxylic acid group exists as a carboxylate anion. It is expected that main chain scission cannot occur in this PEI hydrolysis reaction due to the charge repulsion between carboxylate anions and hydroxide ions. *Figure 4* illustrates that variation of the T_g of PEI with different hydrolysis time is very small.

The effect of modification of PEI on fracture toughness is well demonstrated in *Figure 7*. Compared with the UPEI/epoxy resin system, the MPEI/epoxy resin system shows considerably improved fracture toughness. This phenomenon is explained as follows.

When MPEI is introduced into the tetrafunctional epoxy resin, an IPN structure is formed at the MPEI–epoxy interface and improved interfacial strength is also obtained because new functional groups of MPEI form chemical bonds with the epoxy resin at the interface. Since the chemical bonds exist at the interface between the MPEI and epoxy resin, fracture stress is transferred to the MPEI dispersed phase more effectively than to the UPEI dispersed phase. Therefore, the MPEI dispersed phase follows a ductile drawing mechanism in the cured epoxy resin system very effectively. In addition, MPEI particles diffuse into the epoxy resin more easily than UPEI, due to their increased hydrophilicity. As a result, the plasticity of the epoxy resin around the MPEI dispersed phase increased considerably compared to the UPEI/epoxy resin system. These results show that MPEI has improved the fracture toughness of cured epoxy resin more than UPEI. Furthermore, *Figure 7* also shows that the fracture toughness of the modified epoxy resin system

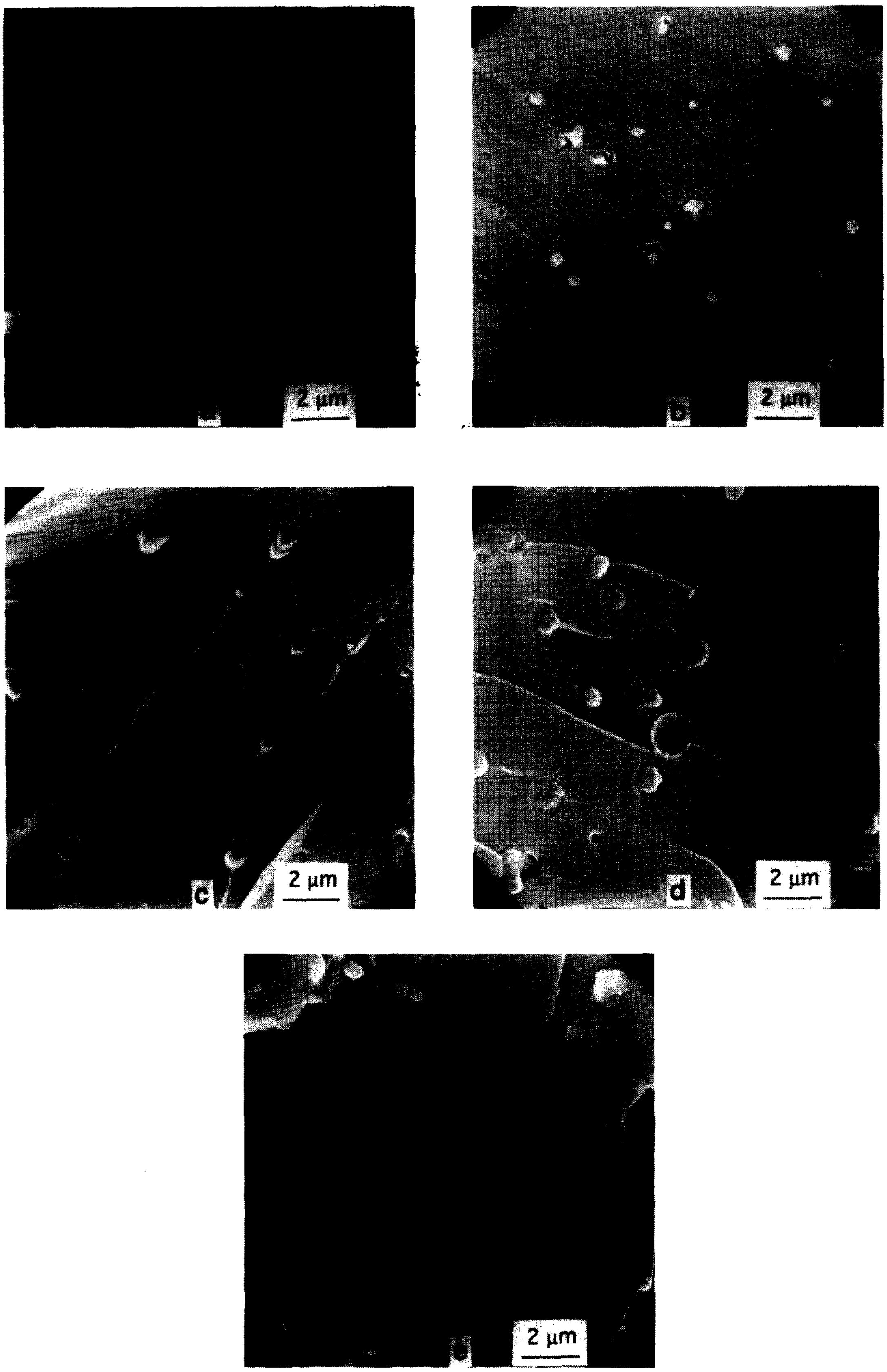


Figure 12 Scanning electron micrographs of the HPT 1071/HPT 1061M/UPEI system with various UPEI contents: (a) control; (b) 2 wt%; (c) 5 wt%; (d) 10 wt%; (e) 15 wt%

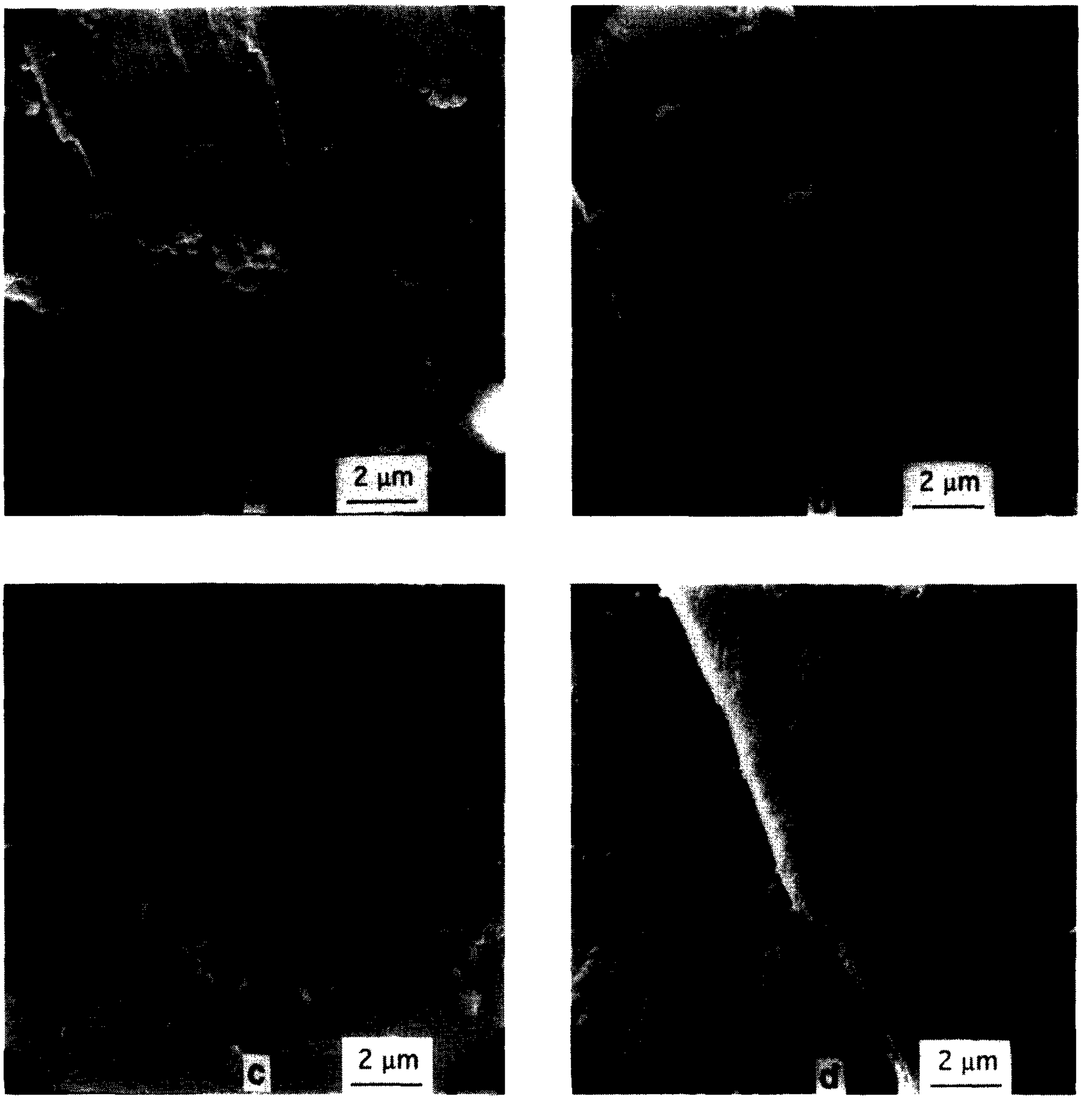


Figure 13 Scanning electron micrographs of the HPT 1071/HPT 1061M/MPEI system with 5 wt% MPEI content, at various hydrolysis times: (a) 30 min; (b) 60 min; (c) 90 min; (d) 180 min

decreases as PEI hydrolysis time increases. This result can be explained as follows. As the number of functional groups introduced on PEI particles increases with increasing treatment time, a large amount of MPEI particles forms an adduct with the epoxy due to chemical reaction. Due to the existing amount of MPEI, the dispersed phase reduces and the fracture toughness of the cured epoxy resin consequently decreases. This phenomenon is also observed in SEM micrographs of the fracture surface of MPEI-toughened epoxy.

Improved interfacial adhesion and increased miscibility must be considered for the modification of PEI. In this experimental region, maximum fracture toughness of the MPEI/epoxy resin system is obtained at 30 min of PEI hydrolysis time.

CONCLUSIONS

When tetrafunctional epoxy resin is toughened with PEI, it shows improved fracture toughness without sacrificing other mechanical properties of the cured epoxy resins. However, there is poor interfacial adhesion between the PEI dispersed phase and the epoxy resin. To improve the toughening effect of a high performance epoxy resin, interfacial adhesion between the two materials must be controlled. Optimum interfacial adhesion between MPEI and epoxy resin has been studied as a function of PEI hydrolysis time. The more hydrolysed the PEI, the more miscible it becomes with epoxy resin. Therefore, it is difficult to optimize the particle size and the distribution of PEI. The number of PEI particles which exist as a discrete second phase is reduced with increasing hydrolysis time of PEI in the cured epoxy resin system. Subsequently, it is important to determine the optimum hydrolysis time of PEI. In this paper, the optimum hydrolysis time of PEI was 30 min.

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