

# Study of Ionic Polymer Toughening Epoxy Resin

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**ABSTRACT:** In this study, PEL [copolymer of poly(propylene) oxide (PPO) and poly(ethylene) oxide (PEO)] toughening epoxy resin with ionic charge was used to produce an interpenetrating action between the cross-linking network structure of the epoxy resin and the PEL additive. Fourier transform infrared (FTIR) analysis of the toughening epoxy resin revealed that  $\text{—NCO}$  disappeared at  $2400\text{ cm}^{-1}$ ,  $\text{—NH}$  appeared at  $3300\text{ cm}^{-1}$ , and  $\text{—C=O}$  appeared at  $1750\text{ cm}^{-1}$ . These results indicate that a urethane bond was produced. Dynamic mechanical analysis (DMA) and mechanical testing results indicated that as the level of PEL increased, the compatibility between the epoxy resin and PEL also in-

creased. In addition, the compatibility was improved because the addition of cornate hardener produced a graft phenomenon. The tensile property, impact strength, and fracture toughness of PEL toughening epoxy resin all had a tendency to improve. The tensile strength, impact strength, and fracture toughness ( $K_{IC}$  value) were most improved when 30 phr cornate was added. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3740–3751, 2002

**Key words:** toughness; resins, interpenetrating polymer network; fracture; toughness value, ionic polymer

## INTRODUCTION

In the past, brittle epoxy resin systems were usually toughened with a liquid elastomer; for examples, carboxyl-terminated butadiene acrylonitrile (CTBN) or the interlinking elastomer, etc.<sup>1,2</sup> However, when the toughness was fully enhanced, the modulus of the hardened epoxy resin and the glass transition temperature ( $T_g$ ) were reduced. Therefore, in addition to using rubber as the toughener in the elastomer toughening epoxy system, many minerals (e.g., aluminum, carborundum, barium titanite, and aluminum hydroxide) were also added to the resin to increase the heat conductivity and  $T_g$  of the system and reduce the shrinkage degree.<sup>3</sup> This procedure also improved the rigidity and fracture toughness. However, the presence of these fillers increased the process difficulty of the toughened resin.

More recently, researchers have suggested the use of high-performance thermoplastic material [i.e., polysulfone (PSF),<sup>4,5</sup> polyether sulfone (PES),<sup>1,6–9</sup> and polyimide (PI)<sup>10</sup>] to toughen epoxy resin by mixing. This procedure produces a complementary effect on the mechanical structure, but the improvement in

toughness was effective only when the high-performance thermoplastic accounted a high ratio.

Other researchers brought forward using the principle of an IPN (interpenetrating polymer network) to toughen the epoxy resin.<sup>11–14</sup> Semi-IPN (semi-interpenetrating polymer network) technology mixes two kinds of polymers that have no chemical bond between them, and the semi-IPN structure is the homogeneous mixture of the epoxy resin (matrix) and the thermoplastic material, or the thermoplastic material scattering among the epoxy resin particles when the incompatible polymers linkage. IPN and semi-IPN technology are both effective methods that use only a little thermoplastic material to modify the epoxy resin.<sup>14</sup>

In this study, PEL [copolymer of poly(propylene) oxide (PPO) and poly(ethylene) oxide (PEO)] with ionic charge was added to the epoxy resin in different proportions. A simultaneous poly-reaction produced the *in situ* effect between the cross-linking network structure of the epoxy resin and the PEL additive<sup>15,16</sup> that improved the toughness of the epoxy resin.

## EXPERIMENTAL

### Preparation for material and sample

The study materials included the following: the radical material diglycidyl ether bisphenol A (DGEBA; Ciba-Geigy Company); the liquid double functional

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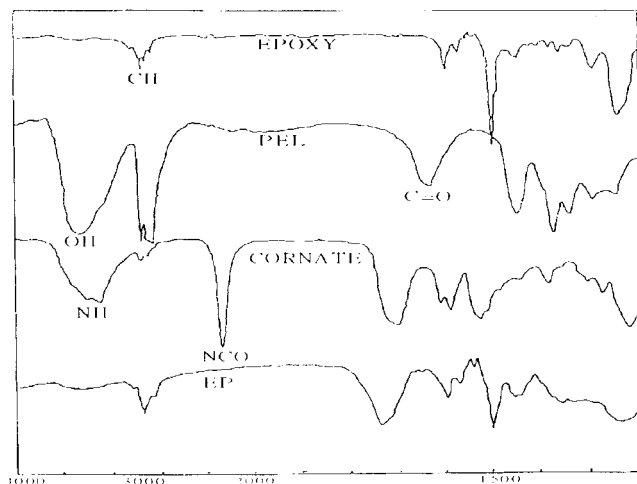
group epoxy resin (Epoxy resin) with an epoxide equivalent between 171 and 177; the acid anhydride hardener nadic methyl anhydride (NMA); the accelerant benzylimethylamine (BDMA); the accelerant PEL-20 (Japan Carlite Company), which is a copolymer of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) that contains 20 wt %  $\text{LiClO}_4$  ionic polymer inside; and cornate (Japanese PU Industrial Company), which contains  $\text{—NCO}$  as the hardener of PEL.

The liquid epoxy resin (DGEBA) that had been added with the hardener (NMA) was mixed in a four-opening separate round reaction tank, and then the mixture with PEL (that had been added with the hardener cornate) was mixed to a homogeneous phase. According to the mixing proportion in Table I, there were P-type, N15-type, N30-type, and N40-type mixtures. These homogeneous mixtures were put into the vacuum oven to remove air and casted into the warm-up flat mold after complete debubbling. The test specimen was heated at  $120^\circ\text{C}$  for 4 h and then heated at  $160^\circ\text{C}$  for 2 h to harden. After the mold was cooled completely, the test specimen was taken out of the mold and cut into the required dimension for the property to be tested.

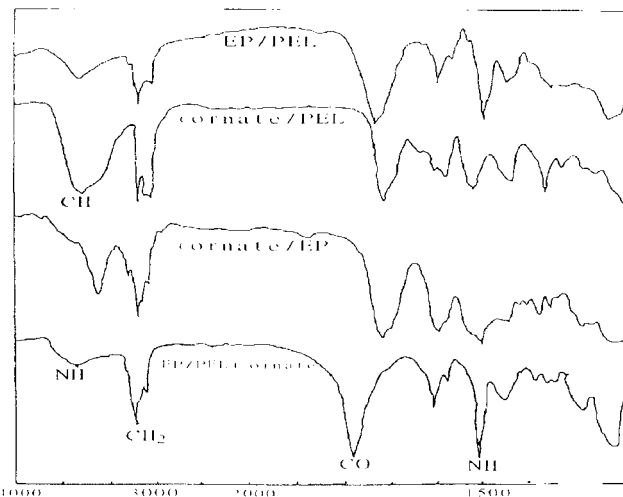
**Methods**

Fourier transform infrared (FTIR) analysis

FTIR was used to determine the property peaks of the material and the resin complex whose property has been modified. First, the material was either spread directly on the KBr salt piece or a proper amount of molded specimen was broken into pieces. Then, the samples were analyzed by FTIR with an apparatus from Japanese Spectroscopic Company (FT/IR-3 type



**Figure 1** FTIR spectra of Epoxy, PEL, cornate, and curing epoxy resin.



**Figure 2** FTIR spectra of EP/PEL, cornate/PEL, cornate/EP, and EP/PEL + cornate.

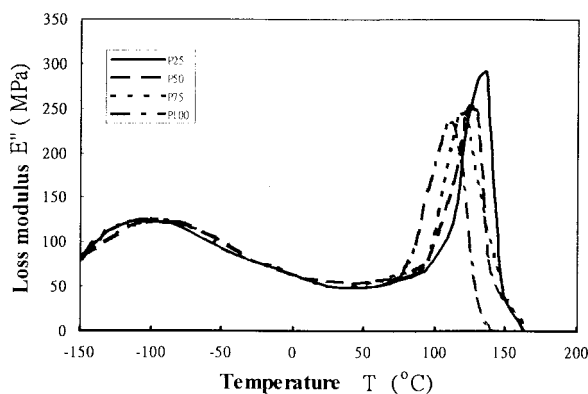
apparatus) that has a scanning scope of  $4000$  to  $400\text{ cm}^{-1}$  and scans 16 times each test.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed with an EXPLOR 150 N type dynamic thermo-mechanical analyzer from GABO Company (Germany) that has the dimensions  $50 \times 14.2 \times 2.4\text{ mm}$ . Analysis was conducted at a resonant frequency of  $20\text{ Hz}$ , a heating rate of  $5^\circ\text{C}/\text{min}$ , and a temperature range of  $-15$  to  $200^\circ\text{C}$ .

Testing of tensile strength

Tensile strength was measured with the MTS 810 type material experiment machine made by Material Testing System Corporation. Experiments were conducted



**Figure 3** Relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) for the P-type copolymer with different PEL contents.

TABLE I  
Composition of Epoxy/PEL/Cornate Resin System

Type	Content	Epoxy Resin		Ionic Polymer	
		DGEBA, phr	NMA, phr	PEL, phr	Cornate, phr <sup>a</sup>
P-type	P25	100	80	2.5	0
	P50	100	80	5.0	0
	P75	100	80	7.5	0
	P100	100	80	10	0
N15-type	N15P25	100	80	2.5	15
	N15P50	100	80	5.0	15
	N15P75	100	80	7.5	15
	N15P100	100	80	10	15
N30-type	N30P25	100	80	2.5	30
	N30P50	100	80	5.0	30
	N30P75	100	80	7.5	30
	N30P100	100	80	10	30
N40-type	N40P25	100	80	2.5	40
	N40P50	100	80	5.0	40
	N40P75	100	80	7.5	40
	N40P100	100	80	10	40

<sup>a</sup> The phr of the Cornate is compared to that of PEL.

at a stretching rate of 10 mm/min according to the ASTM D638 standards.

#### Determination of fracture toughness

The fracture toughness ( $K_{IC}$ ) was tested according to the ASTM E399-83 standards with the specimen dimension of 50 × 40 × 10 mm. The calculating expressions are as follows:

$$K_{IC} = P_{max}/B_w^{1/2}f(a/w) \quad (1)$$

where  $P_{max}$  is the maximum load,  $B$  is the specimen thickness,  $a$  is the crack length,  $w$  is the specimen thickness, and  $f(a/w)$  is a geometric factor determined by eq. 2:

$$f(a/w) = (2 + a/w)(0.886 - 4.64a/w - 13.32a^2/w^2 + 14.72a^3/w^3 - 5.6a^4/w^4)/(1 - a/w)^{3/2} \quad (2)$$

#### Determination of impact strength

The impact strength was tested with a KT7045 type impact experiment machine from High Iron Technology Company according to ASTM D256 standards.

#### Observation of fracture surface

The tensile fracture surface, toughness fracture surface, and impact fracture surface were observed with a Cambridge S360 scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

### Reactivity of PEL/epoxy admixture

The FTIR spectra of the epoxy resin (Epoxy), PEL, cornate and other materials, and the hardened epoxy resin (EP) are shown in Figure 1. These spectra indicate that Epoxy has an absorption peak of —CH at

TABLE II  
 $\alpha$ -Transition Temperature of Various Toughening Epoxy Resins with Different PEL Contents

PEL, phr	Cornate	P-Type	N15-Type	N30-Type	N40-Type
		0 phr	15 phr	30 phr	40 phr
	$T_g$ , °C <sup>a</sup>				
0		131	—	—	—
2.5		129	129	129	128
5.0		126	122	121	120
7.5		119	116	111	107
10.0		111	105	102	99

<sup>a</sup> The  $T_g$  obtained is from the characteristic peak of the  $\alpha$ -relaxation of  $E''$ .

<sup>b</sup> The phr of the cornate is compared with that of PEL.

2950  $\text{cm}^{-1}$ ; PEL has an absorption peak of  $\text{—OH}$  at 3450  $\text{cm}^{-1}$ ; cornate has an absorption peak of  $\text{—NH}$  at 3300  $\text{cm}^{-1}$  and an absorption peak of  $\text{—NCO}$  at  $\sim 2400$   $\text{cm}^{-1}$ ; and, after the epoxy resin is hardened (EP), the secondary oxyhydrogen group and the hardener reaction reduce the adsorption intensity of  $\text{—OH}$  to 3400  $\text{cm}^{-1}$ .

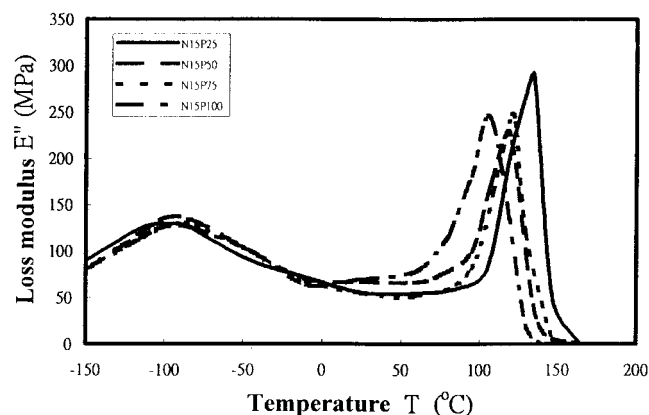
No new absorption peak is found when the EP/PEL absorption curve of the FTIR spectrum in Figure 2 is compared with the material FTIR absorption curve in Figure 1. These results indicate that neither EP nor PEL produced the urethane chemical reaction shown in eq. 3:



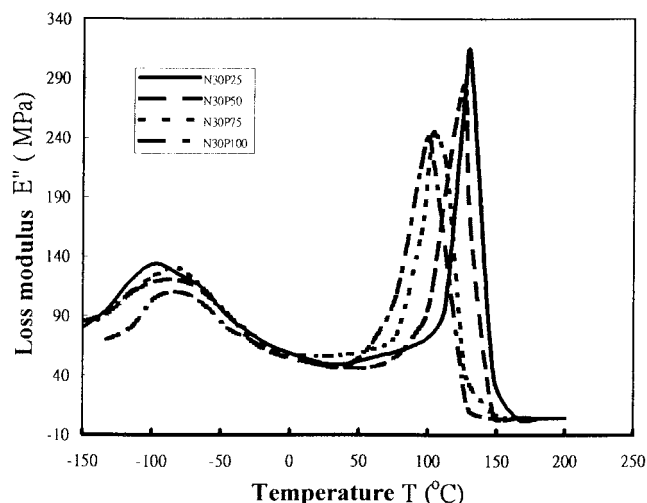
However, comparison of the curves of the hardened PEL (cornate/PEL) and cornate and epoxy resin (cornate/Epoxy) indicate that the  $\text{—NCO}$  group of cornate and the  $\text{—OH}$  group of PEL and the secondary oxyhydrogen group of epoxy resin (Epoxy) will all produce the urethane reaction. Because the  $\text{—NH}$  absorption peak was found at 3300  $\text{cm}^{-1}$  and there was a  $\text{—CO}$  absorption peak at  $\sim 1750$   $\text{cm}^{-1}$ , the cornate produces the graft phenomenon with the epoxy resin. Then, as indicated by the FTIR spectrum curve of EP/PEL+cornate, the  $\text{—NCO}$  group of cornate, the  $\text{—OH}$  group of PEL, and the secondary oxyhydrogen group of the epoxy resin produce a urethane reaction. Also, when the absorption spectrum of  $\text{—NCO}$  disappeared from the cornate spectrum at 2400  $\text{cm}^{-1}$ , a  $\text{—NH}$  absorption peak was produced at 3300  $\text{cm}^{-1}$  and there was a  $\text{—C=O}$  absorption peak at 1750  $\text{cm}^{-1}$ , which demonstrates that the toughened epoxy resin had produced a urethane bond.

### Compatibility of modified resins

The compatibility of the two polymers in an IPN is often judged by the  $T_g$ , and it is also one of the



**Figure 4** Relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) for the N15-type copolymer with different PEL contents.

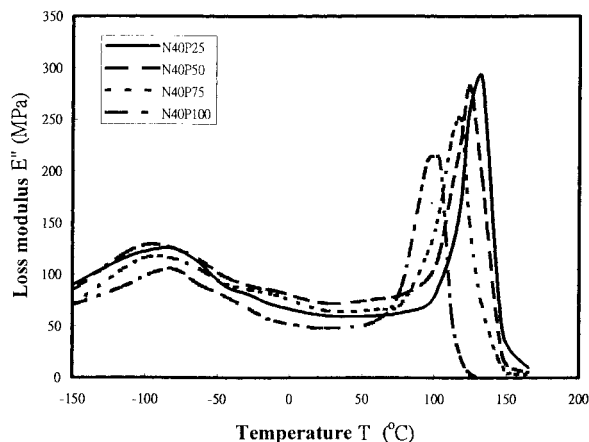


**Figure 5** Relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) for the N30-type copolymer with different PEL contents.

references to further judge the interpenetrating degree of this IPN. If two polymers are complete compatible, the  $\tan \delta$  peaks of the mixed polymers will combine to be a single peak; but if they are partially compatible or completely incompatible, the  $\tan \delta$  peaks of the mixed polymers will exist individually and the  $\tan \delta$  value will present relatively movable or unmovable phenomena according to the proportion. We used DMA testing to determine the compatibility of the polymers.

### PEL/Epoxy mixing system

The relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) of the P-type formula in which only the PEL quantity is changed and no cornate is added is shown in Figure 3. Pure PEL and EP, without addition of hardener, have the best compatibility. Therefore, the  $T_g$  point of the toughening epoxy resin will move to the lower temperature as the proportion of PEL increases, which can be seen in Table I, where  $T_g$  decreases from 131°C for P25 to 111°C for P100. Moreover, the scope of the  $\alpha$ -relaxation characteristic peaks increase as the quantity of PEL added increases and the height of the characteristic peaks decrease gradually, which shows that the rigid chain of epoxy resin causes the main chain of the whole molecule to move towards a lower temperature due to the addition of the PEL flexible chain. The results in Table II indicate that the  $\beta$ -relaxation characteristic peak moves to a higher temperature as PEL increases (from  $-94^\circ\text{C}$  for P25 to  $-83^\circ\text{C}$  for P100) and the  $\Delta T_g$  decreases. Consequently, increasing the addition proportion of PEL will improve the compatibility of PEL and the epoxy resin and enhance the interpenetrating degree of the flexible chain (PEL) and rigid chain (Epoxy).



**Figure 6** Relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) for the N40-type copolymer with different PEL contents.

#### PEL-cornate/epoxy mixing system

The relationship between loss modulus ( $E''$ ) and temperature ( $T$ ) after 15, 30, and 40 phr of cornate hardener are added to PEL is shown in Figures 4, 5, and 6, respectively. From Figure 4, we see that the  $\alpha$ -relaxation of epoxy resin moves to a lower temperature as the PEL content increases. Moreover, from Tables II and III, we find that this system has better compatibility ( $\Delta T_g$  decreases) than simply adding PEL to epoxy resin. From the  $E''$  versus  $T$  data (Figures 4–6), we find that the N15-type, N30-type, and N40-type copolymers, with added cornate of 15, 30, and 40 phr, respectively, separately all have the same tendency. From the results in Tables II and III we also find that  $\Delta T_g$  decreases as the proportion of cornate added increases. These results indicate that the addition of cornate will produce a reaction between the  $-\text{OH}$  group of PEL and the secondary oxyhydrogen group of epoxy resin to form a urethane bond. Therefore, the production of a graft phenomenon will improve the compatibility more and increase the interpenetrating degree among the molecules.

The relationships between  $E''$  and  $T$  for Epoxy, PEL, P100, and N40 P100 are shown in Figure 7. The results

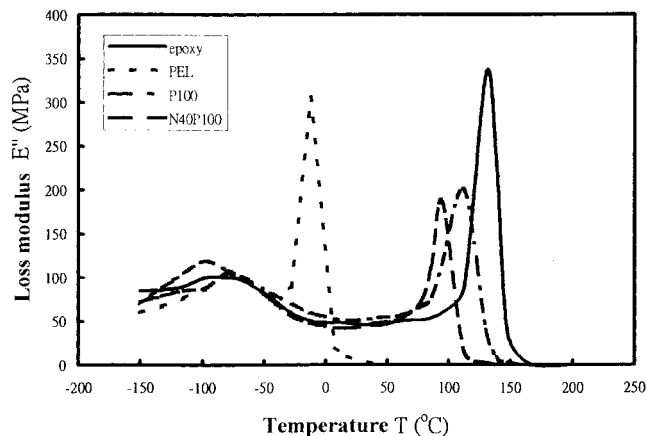
show that the  $\alpha$ -relaxation characteristic peak of PEL is  $\sim -12^\circ\text{C}$  and the  $\beta$ -relaxation characteristic peak is  $\sim -88^\circ\text{C}$ . The movement of the characteristic relaxation peak of the P100 curve indicates that the epoxy resin and PEL have good compatibility; that is, the  $\alpha$ -relaxation characteristic peak of PEL and that of the epoxy move mutually to become another more extensive independent peak. The  $\alpha$ -relaxation characteristic peaks of the two polymers also combine into one, which shows that the regularity of the rigid chain of the epoxy resin is destroyed because it is penetrated by the flexible chain of PEL when PEL is added. Moreover, because the IPN degree is very good, the moving range of the whole main chain of the molecule crank axle increases ( $\alpha$ -relaxation characteristic peak is broadened). In particular, when 40 phr cornate is added, the  $\alpha$ -relaxation characteristic peak will move to the lower temperature and the  $\beta$ -relaxation characteristic peak will move to the higher temperature. From the results in Table II we find that the  $\alpha$ -relaxation characteristic peak of P100 is  $\sim 111^\circ\text{C}$ , whereas that of N40P100 is  $\sim 99^\circ\text{C}$ . This difference is because the  $-\text{NCO}$  group of cornate produces a urethane bond with the secondary oxyhydrogen group of the epoxy resin. In addition, the  $-\text{NCO}$  group reacts with the  $-\text{OH}$  group of the PEL. The entire molecule main chain is larger and the temperature range of the molecule crank movement is broader. Consequently, the temperature of the  $\alpha$ -relaxation characteristic peak decreases, and the characteristic peak is more extensive.

The relationships between storage modulus ( $E'$ ) and  $T$  for P-type, N15-type, N30-type, and N40-type copolymers are shown in Figures 8–11, respectively. Examination of the results in these figures indicates that the  $E'$  value decreases as the addition level of PEL increases. This relationship shows that the rigidity (stiffness) of the toughening system is reduced because of the addition of PEL. The decline of the rigidity is caused because the flexible chain of PEL tangles with the epoxy resin. The relationships between  $E'$  and  $T$  for Epoxy, PEL, P100, and N40P100 are shown in Figure 12. These results show that the distribution range of the rubbery transitive section and the decline

**TABLE III**  
 **$\beta$ -Transition Temperature of Various Toughening Epoxy Resins with Different PEL Contents**

PEL, phr	$T_g$ , $^\circ\text{C}$				
	Cornate	P-Type	N15-Type	N30-Type	N40-Type
		0 phr	15 phr	30 phr	40 phr
0		-84			
2.5		-94	-91	-90	-89
5.0		-87	-87	-85	-83
7.5		-85	-84	-82	-81
10.0		-83	-81	-79	-78



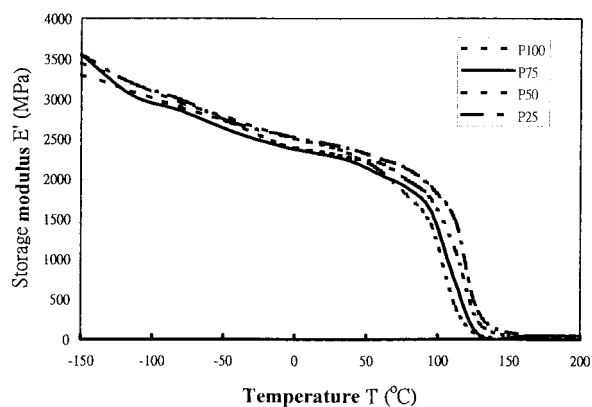


**Figure 7** Relationship between the loss modulus ( $E''$ ) and temperature ( $T$ ) for epoxy, PEL, P100 and N40P100.

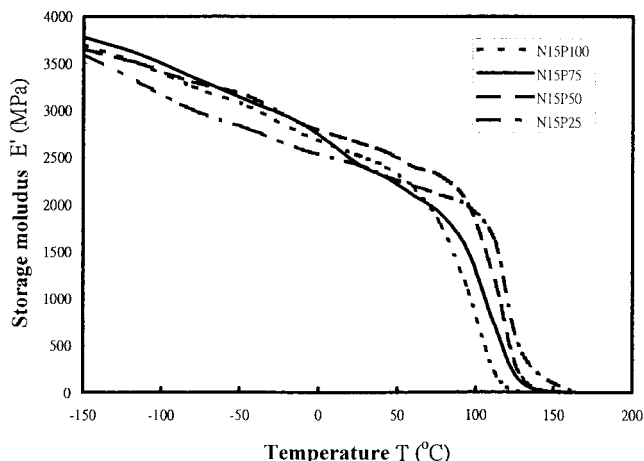
of  $E'$  plateaus with the addition of the cornate. Because the rigid main chain of the epoxy resin produces a graft effect because of the addition of cornate, the main chain becomes more flexible,  $E'$  decreases, and the distribution range of the rubbery transitive section becomes larger.

**Tensile strength of mixing resin system**

The slow stretching test results in Table IV indicate that the tensile strength and extensibility of PEL toughening epoxy resin increase when cornate is added compared with pure PEL toughening epoxy resin. The greatest increase occurs when the PEL is added at 7.5 phr, because the  $-NCO$  group reacts with the  $-OH$  group of PEL after cornate is added. Therefore, the PEL domain agglutinates to produce a tearing effect, and the  $-NCO$  group of cornate reacts with the secondary oxyhydrogen group of the epoxy resin to produce a urethane bond, as proven by the FTIR spectrum in Figure 2. However, excessive PEL



**Figure 8** Relationship between the storage modulus ( $E'$ ) and temperature ( $T$ ) for the P-type copolymer with different PEL contents.



**Figure 9** Relationship between the storage modulus ( $E'$ ) and temperature ( $T$ ) for the N15-type copolymer with different PEL contents.

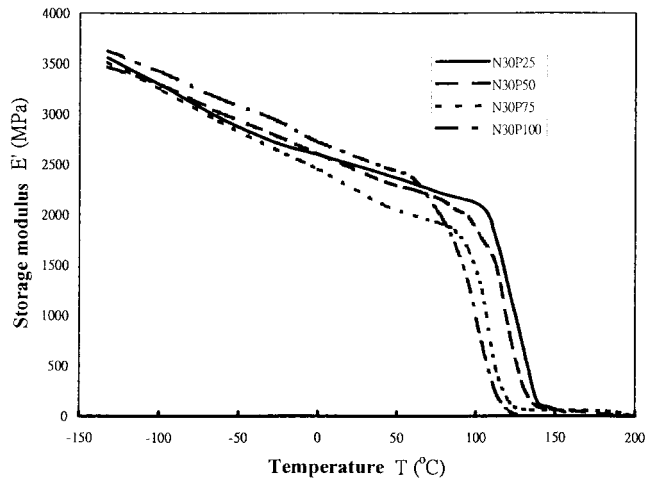
can cause structural defects. Therefore, if only 10 phr of cornate is added, there is no significant toughening effect. When 40 phr of cornate is added, the tensile strength and extensibility of this system continue to increase. However, as the PEL addition level increases, the extensibility is poorer than that when 30 phr of cornate is added because the  $-NCO$  group has fully reacted with the epoxy resin and the PEL to promote a more complete cross-linking structure.

Analysis of all systems in which cornate is added shows that the tensile strength and extensibility of each system increases as PEL increases. These increases occur because the PEL is an ionic polymer with a  $LiClO_4$  electronic charge that strengthens the compatibility of PEL and epoxy resin, enhances the interpenetrating degree, and thus increases both the tensile strength and extensibility.

Adding different proportion of cornate produces a urethane bond. Regarding the compactness of the molecule structure, IPN structures with different degrees of cross-linking are produced; these different degrees of cross-linking cause the discrepancy of the tensile strength and extensibility. For example, the 40 phr cornate system has the best tensile strength, whereas the 30 phr cornate system shows the best extensibility. These results demonstrate that the semi-gelatin condition produces a tearing of the particle during slow stretching.

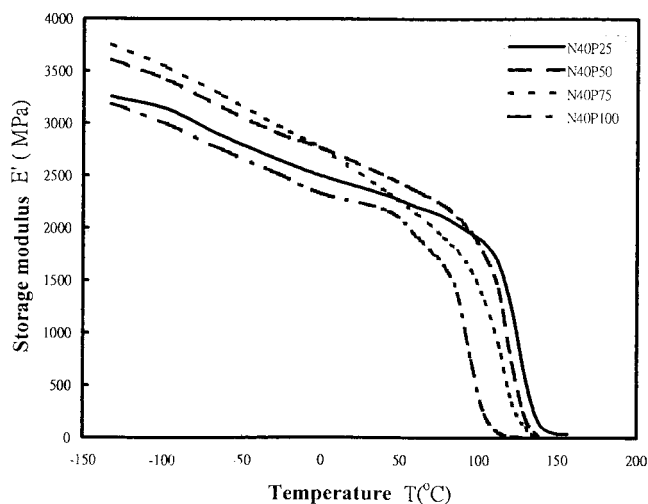
**Toughness mixing resin system**

The relationship between PEL addition level and impact strength with different cornate contents is shown in Figure 13. The impact strength of the PEL toughening epoxy resin system (P-type PEL/Epoxy) increases as the PEL addition level increases because the PEL

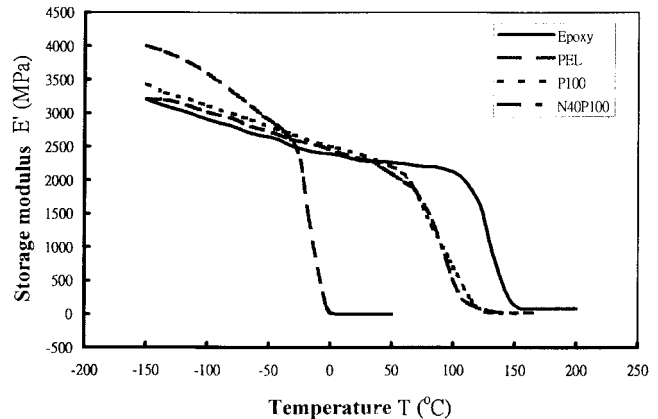


**Figure 10** Relationship between the storage modulus ( $E'$ ) and temperature ( $T$ ) for the N30-type copolymer with different PEL contents.

flexible chain tangles among the epoxy resin. When the system suffers from a high-speed cut impact fracture, the interlinking structure of the epoxy resin undergoes a de-bonding effect to endure the starting fracture of the crack. Also, the flexible chain tangled among the network is primarily responsible for enduring the development of a crack during impact fracture. The impact strength increases to the highest value when the cornate content/PEL content reaches 7.5 phr. When a hardener cornate level of 15 phr is added to PEL (N15-type cornate - PEL/Epoxy mixing system), the impact strength is poorer than that of the pure PEL toughening epoxy resin system. This result occurs because the  $\text{—NCO}$  of cornate reacts with the secondary oxyhydrogen group of the epoxy resin to



**Figure 11** Relationship between the storage modulus ( $E'$ ) and temperature ( $T$ ) for the N40-type copolymer with different PEL contents.



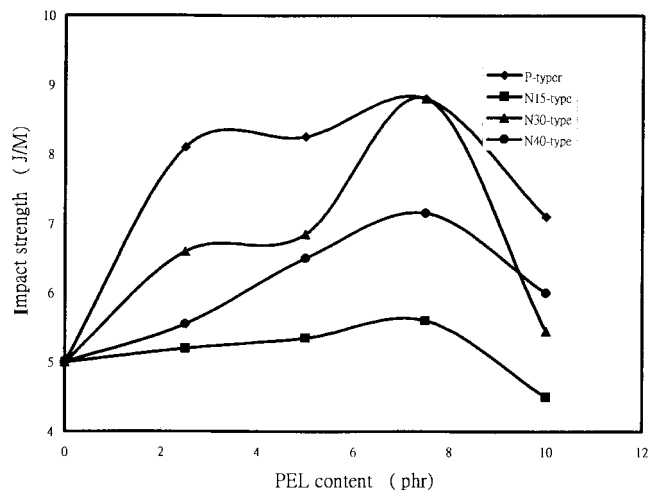
**Figure 12** Relationship between the storage modulus ( $E'$ ) and temperature ( $T$ ) for epoxy, PEL, P100, and N40P100.

produce a urethane bond, and the  $\text{—NCO}$  group also reacts with the  $\text{—OH}$  group of PEL to cause the PEL domain to coagulate and lose its good continuity. The result of adding 30 phr cornate (N30-type) is also an increase in the impact strength as PEL addition level increases, with the greatest increase occurring when the content reaches 7.5 phr. The 30 phr cornate level produces enough urethane bonds to strengthen the interpenetrating effect of the flexible chain (PEL) and rigid chain (Epoxy). In fact, the DMA results demonstrate that adding cornate helps to improve the compatibility. When 40 phr cornate is added (N40-type system), the impact strength is also improved as the PEL addition level increases. The best improvement occurs when the content reaches 7.5 phr. The aforementioned relationship between the  $E''$  and  $T_g$  (Figure 6) indicates that this system has a very good interpenetrating effect.

Therefore, from the analysis of the impact strength of the toughening epoxy resin, adding pure PEL increases the impact strength the most. The next largest increase in impact strength occurs with the N30-type with 30 phr of cornate, because the pure PEL has relatively more rubbery domains to prevent the development of cracks. However, adding the cornate forms bridge points where the stress concentrates, which

**TABLE IV**  
Stress-Strain of Various Toughening Epoxy Resins Under Different PEL Contents

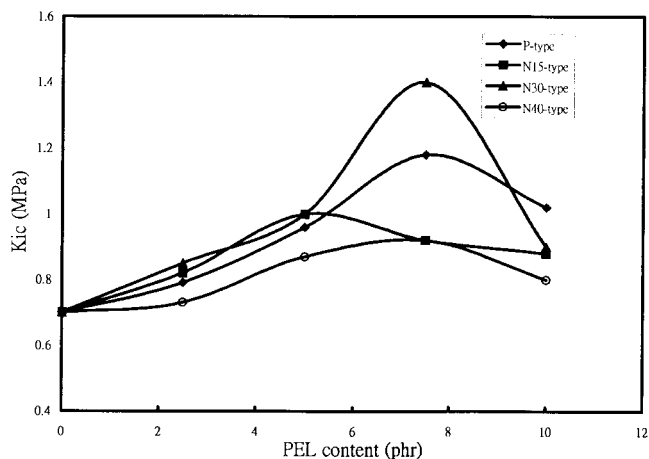
PEL content (phr)	Tensile strength (Mpa)				Elongation (%)			
	P-type	N15-type	N30-type	N40-type	P-type	N15-type	N30-type	N40-type
0	70	69.5	70	70	7.3	7.0	6.1	7.0
2.5	62	70.5	71	72	7.0	8.5	9.0	8.5
5.0	65	74.0	77	82	7.2	8.8	10.5	9.0
7.5	73	78.5	86	88	8.5	9.1	14.9	11.0
10	70	70.5	86	100	8.0	10	16.5	12.0



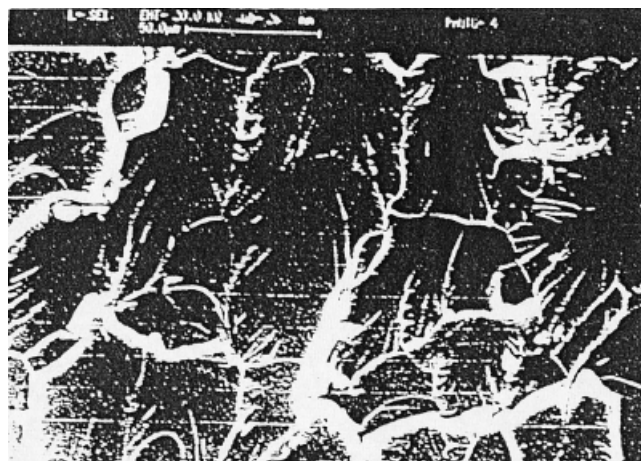
**Figure 13** Falling impact strength of P-type, N15-type, N30-type, and N40-type copolymers with different PEL contents.

causes an anti-impact property that cannot be improved effectively.

To further understand conditions that improve the toughness of each resin mixing system, the toughening effect results are shown in Figure 14 as a comparison of fracture toughness or stress intensity factor value  $K_{IC}$ . The  $K_{IC}$  value of the P-type system and the PEL toughening epoxy resin increase as the PEL content increases. The largest value of  $K_{IC}$  occurs when the PEL content is 7.5 phr; the fracture toughness value ( $K_{IC}$ ) is almost doubled. The N15-type curve is the  $K_{IC}$  value after the PEL-cornate and the epoxy resin produce interlinking when 15 phr cornate is added. This value increases the most when PEL is added to 5 phr because after the cornate is added, the —NCO group of the cornate reacts with the —OH group of PEL to scatter the rubbery domains and also



**Figure 14** Fracture toughness value of P-type, N15-type, N30-type, and N40-type copolymers with different PEL contents.



**Figure 15** Scanning electron micrographs of epoxy resin on a tensile fracture surface.

reacts with the epoxy resin to become a graft structure. However, the  $K_{IC}$  value of the N30-type system increases obviously because the cornate produces enough of an amido formate bond. The results of DMA show that the interpenetrating degree between the flexible chain and the rigid chain is relatively high. In the N40-type toughening system, when 40 phr cornate is added, the  $K_{IC}$  value increases relatively less because the interlinking of the network of the flexible chain is so complete that the interpenetrating effect with the rigid chain (Epoxy) is good. A stress situation will be produced in the bridging structure when two rigid chains interpenetrate, as shown in the DMA curve in Figure 6, which prohibits an increase in the  $K_{IC}$  value.

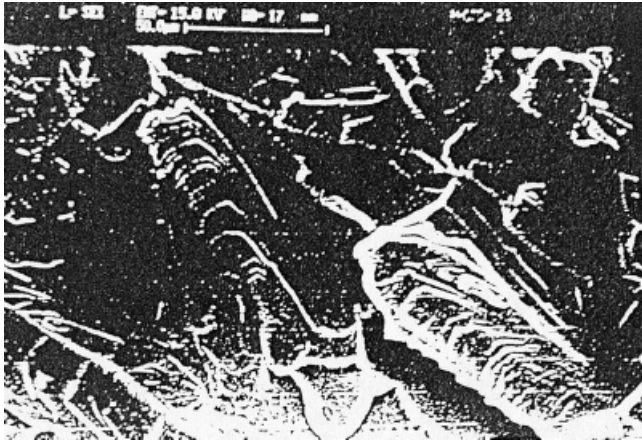
### Fracture mechanism of resin mixing system

The fracture mechanism can be explained by observing the fracture surface of tensile strength testing sam-

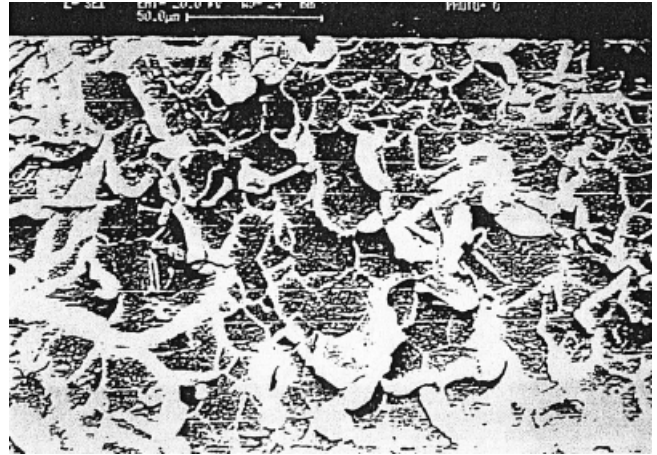


**Figure 16** Scanning electron micrographs of P75 on a tensile fracture surface.





**Figure 17** Scanning electron micrographs of N15P75 on a tensile fracture surface.

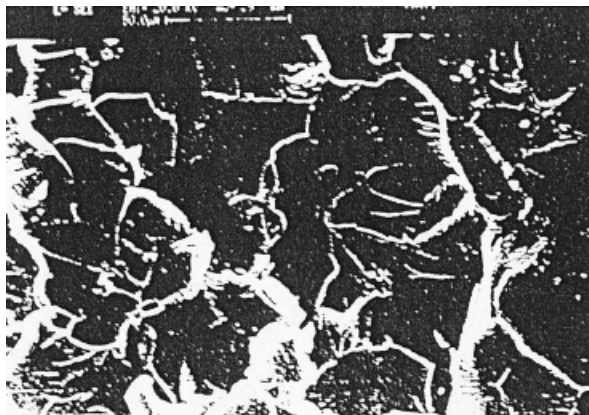


**Figure 19** Scanning electron micrographs of N40P75 on a tensile fracture surface.

ple, by testing the impact strength of the sample, and by testing the fracture toughness of the sample by SEM. Scanning electron micrographs of the fracture surface are shown in Figures 15–19. When cornate is added to the PEL toughening epoxy resin, the —NCO group of the cornate reacts with the secondary oxyhydrogen group of the epoxy resin to produce a urethane bond. Also, the epoxy resin produces a de-bonding effect during slow stretching, which in Figures 16 and 17. The de-bonding effect is more obvious at 30 phr and the wavy bright band is more obvious, producing a more shear band (Figure 18). In the 40 phr system, which has a more complete cross-linking structure, the interpenetrating effect of the PEL flexible chain and the epoxy resin rigid chain is more complete and the de-bonding effect during the destroying process is better than in 30 phr cornate system. Therefore, the flexible chain of the PEL phase in the whole system becomes relatively rigid. It can be seen in Figure 19 that the fracture surface becomes an intermittent

bright wave because of the rough fragment phase separation and the laminate structure.

The fracture surfaces of the impact testing samples are shown in Figures 20–24. The SEM of the impact fracture surface of the pure epoxy resin is shown in Figure 20. The surface is smooth because of the brittle fracture. The SEM of the epoxy resin that has been added with PEL (see Figure 21), shows the distribution of the PEL domains and the shear bands produced to prevent the crack from developing. In addition, the continual distributing condition of the PEL phase is very good. From these phenomena we conclude that the destroying energy of the semi-IPN will increase only when both the epoxy resin phase and the rubbery phase are continual but inhomogeneous. In the SEM of N15-type (Figure 22), it is evident that there are not more shear bands because the addition level of the cornate is not so large that the formed bonds are limited. Because the pure resin has a complete structure and high cross-linking degree, this system (N15-type) only produces a structural defect.



**Figure 18** Scanning electron micrographs of N30P75 on a tensile fracture surface.



**Figure 20** Scanning electron micrographs of epoxy resin on an impact fracture surface.





(a)



(b)

**Figure 21** Scanning electron micrographs of P75 on an impact fracture surface.

From the SEM of N30-type shown in Figure 23 it is evident that the shear band has a good continuity to release the partial stress; therefore, it has a good toughening effect. We can see from Figure 24 that the fracture surface is relatively homogeneous and the fibrous bright band is produced in the shear band. As the level of cornate increases, more urethane bonds



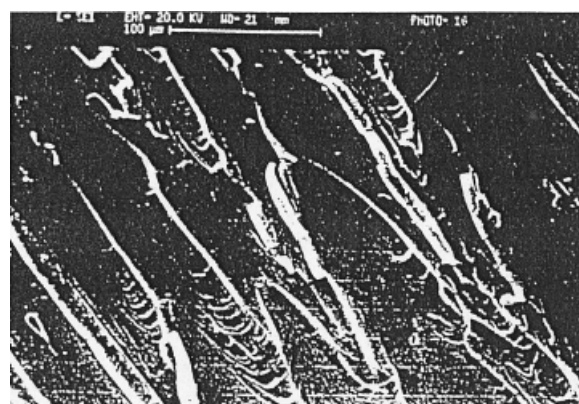
**Figure 22** Scanning electron micrographs of N15P75 on an impact fracture surface.



**Figure 23** Scanning electron micrographs of N30P75 on an impact fracture surface.

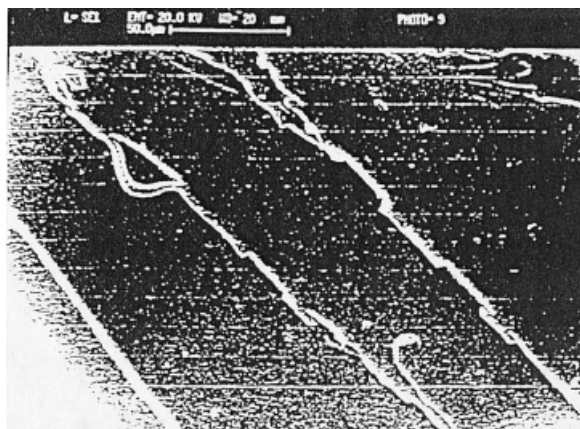
are produced and, consequently, enough de-bonding force is produced.

The SEMs of the toughness fracture surfaces are shown in Figures 25–29. In Figure 25, the rigid chain interlinking structure of pure epoxy resin cannot deposit in the rubbery section to inactivate the crack tip. However, after the PEL flexible chain molecule is added, the flexible chain will tangle in the reticulation section and produce a rubbery section to inactivate the crack. The PEL-deposited rubber has a tearing effect corresponding to high shear rate during the destroying course and drives the surrounding PEL phase to produce deformation and cause a shearing effect. We can see in Figure 26 that the distribution of the shear band is very homogeneous, which demonstrates that directly adding the PEL to the epoxy resin to form a semi-IPN structure is effective for improving the toughening effect. When 15 phr cornate is added (Figure 27), the mixing system produces a graft structure that makes the microphase separating particles not obvious and reduces the stress transition effect of the particles and the shear bands developed by the inactivated cracks. When 30 phr cornate is added, the



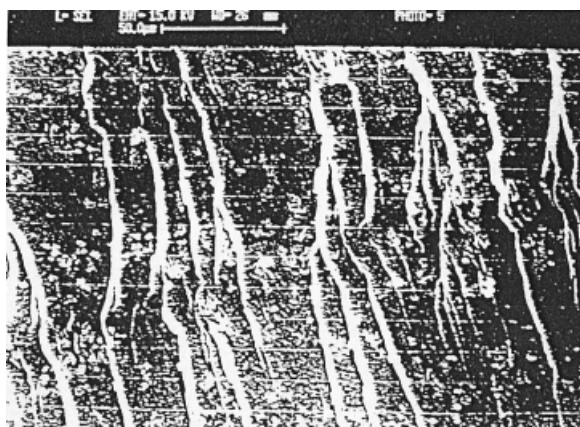
**Figure 24** Scanning electron micrographs of N40P75 on an impact fracture surface.



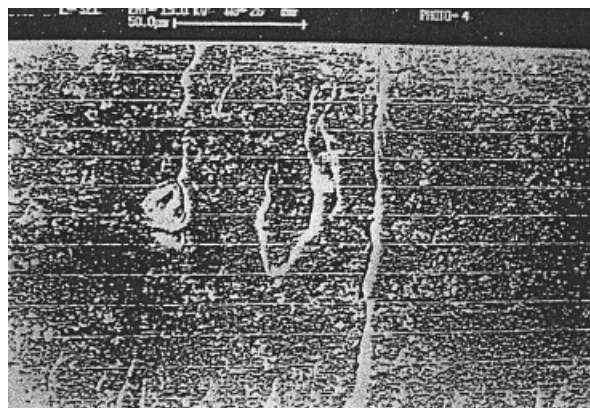


**Figure 25** Scanning electron micrographs of epoxy resin on a toughness fracture surface.

interpenetrating degree between the flexible chain and rigid chain is relatively high and the flexible chain network (PEL-cornate) enhances the tearing effect during the destroying course. However, because the rigid chain network has a de-bonding effect, the fracture structures exist mutually. Therefore, it is evident from the fracture surface in Figure 28 that the PEL particles become unclear, possibly because the increased proportion of cornate lengthens the molecule chain, which provides an opportunity to form bonds among the molecules. With 40 phr cornate, interlinking of the flexible chain network is complete, but because the flexible chain has a good interpenetrating effect with a hardened chain (epoxy) network, the interpenetrating between two rigid chains will cause a stress concentration in the bridging structure. Therefore, as shown in Figure 29, no obvious rubbery section is produced to prevent the crack from developing, so the toughening effect is not visibly enhanced.



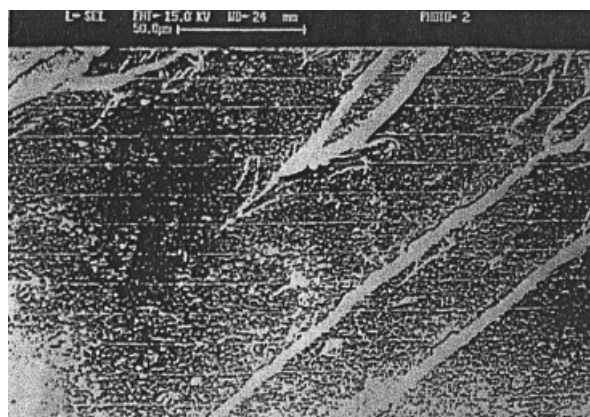
**Figure 26** Scanning electron micrographs of P75 on a toughness fracture surface.



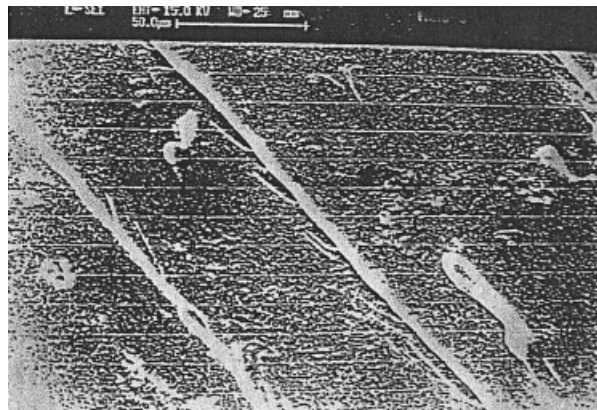
**Figure 27** Scanning electron micrographs of N15P75 on a toughness fracture surface.

## CONCLUSIONS

1. The compatibility between the epoxy resin and the PEL increases as the PEL addition level increases. It is obvious that because the PEL has the  $\text{Li}^+\text{ClO}_4^-$  electronic charge, the epoxy resin and the PEL produce a graft phenomenon after the PEL is added to the cornate hardener to promote better compatibility between the PEL and the epoxy resin.
2. After the epoxy resin is toughened by the PEL, the flexible chain interpenetrates in the rigid network to prevent the crack from developing. Therefore, both the impact strength and fracture toughness have a tendency to improve.
3. The toughness of the ionic polymer PEL with 15 phr cornate hardener declines compared with the pure PEL toughening epoxy resin. The impact strength and  $K_{IC}$  value reach the maximum values when 30 phr cornate is added because the interpenetrating of appropriate bridging flexible chain network and rigid chain network have a better toughening effect. However, when 40 phr



**Figure 28** Scanning electron micrographs of N30P75 on a toughness fracture surface.



**Figure 29** Scanning electron micrographs of N40P75 on a toughness fracture surface.

cornate is added, the stress of the bridging structure points concentrate and the toughening effect is poorer because the complete interlinking PEL and rigid network interpenetrate.

4. A 30 phr cornate level has the best effect among the three PEL-cornate/Epoxy systems studied. This result is because the PEL bridging network and the epoxy resin network caused by the ap-

propriate cornate can cause structural defects in each other during the destroying course and thus greatly improve the toughening effect.

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