

# Modification of Bismaleimide Resin by Poly(phthaloyl diphenyl ether) and the Related Copolymers

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**ABSTRACT:** Poly(ether ketone ketone)s were prepared and used to improve the brittleness of the bismaleimide resin. The bismaleimide resin was composed of 4,4'-bismaleimidediphenyl methane (BMI) and *o,o'*-diallyl bisphenol A (DBA). Poly(ether ketone ketone)s include poly(phthaloyl diphenyl ether) (PPDE), poly(phthaloyl diphenyl ether-*co*-isophthaloyl diphenyl ether) (PPIDE), and poly(phthaloyl diphenyl ether-*co*-terephthaloyl diphenyl ether) (PPTDE). PPIDE (50 mol % isophthaloyl unit) was more effective as a modifier for the bismaleimide resin than were PPDE and PPTDE (50 mol % terephthaloyl unit). Morphologies of the modified resins changed from particulate to cocontinuous and to phase-inverted structures, depending on the modifier structure and content. The most effective modification for the cured resins could be attained because of the cocontinuous phase or phase-inverted structure of the modified resins. For example, when using 10 wt % of PPIDE (50 mol % IP unit, MW 349,000), the modified resin had a phase-inverted morphology and the fracture toughness ( $K_{IC}$ ) for the modified resins increased 75% with retention in flexural properties and the glass transition temperature, compared to those of the unmodified cured bismaleimide resin. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 769–780, 1998

**Key words:** bismaleimide resin; modification; poly(phthaloyl diphenyl ether); related copolymers; fracture toughness; morphology

## INTRODUCTION

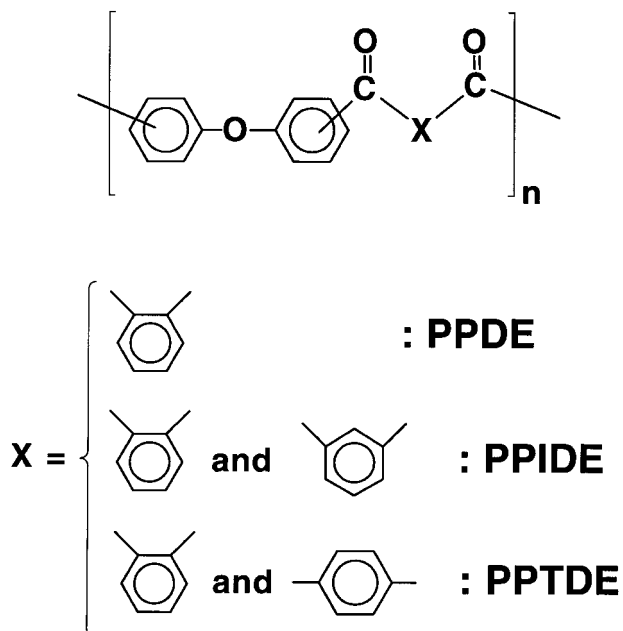
Addition polyimide resins are one of the most important thermosetting polymer groups and have received attention because of their high thermal stability and mechanical properties. The drawback of the polyimide resins is that they are brittle and difficult to process. Bismaleimide resins were also attractive because of their good processability and nonvolatility. Recently, a two-component bismaleimide system (Matrimid 5292 A and B), composed of 4,4'-bismaleimidediphenyl methane (BMI) and *o,o'*-diallyl bisphenol A (DBA), was developed by Ciba Geigy Corp. to improve the me-

chanical properties and processability.<sup>1</sup> During curing, DBA copolymerizes with BMI via the enyne-type linear chain extension reaction followed by the Diels–Alder reaction. The brittleness of the cured resin was improved compared to the conventional bismaleimide resins, but its fracture toughness is not yet sufficient for use as the advanced composite matrix.

The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN)<sup>2</sup> or engineering thermoplastics, e.g., polysulfone (PSF)<sup>3–5</sup> or poly(ether imide) (PEI).<sup>6–8</sup> Engineering thermoplastics are interesting materials as modifiers for bismaleimide resins from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Engineering thermoplastics examined as

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Scheme 1

modifiers for bismaleimide resins include PSF,<sup>9,10</sup> PEI,<sup>9,11,12</sup> 6F-polyimide,<sup>10</sup> poly(ether ketone),<sup>12-14</sup> polyhydantoin,<sup>9</sup> and poly(arylene ether phosphine oxide).<sup>10</sup>

Modification of the bismaleimide resin was carried out on the basis of information on the toughening of epoxies by thermoplastics in our laboratory.<sup>15-18</sup> In our previous articles, we reported that the *N*-phenylmaleimide-styrene copolymer (PMS) was an effective modifier for both the epoxy<sup>19,20</sup> and the bismaleimide resins.<sup>21</sup> *N*-Phenylmaleimide-styrene-*p*-hydroxystyrene terpolymers (PMSH) having functionalities were also effective modifiers for both the epoxy<sup>22,23</sup> and bismaleimide resins.<sup>24</sup> Poly(phthaloyl diphenyl ether) was an effective modifier for epoxies.<sup>15</sup>

This article reports the modification of the two-component bismaleimide resin (the Matrimid 5292 A/B system) by poly(ether ketone)s (PEKKs). PEKKs include poly(phthaloyl diphenyl ether) (PPDE), poly(phthaloyl diphenyl ether-co-isophthaloyl diphenyl ether) (PPIDE), and poly(phthaloyl diphenyl ether-co-terephthaloyl diphenyl ether) (PPTDE). The chemical structures of the PEKKs used are shown in Scheme 1.

## EXPERIMENTAL

### Materials

The bismaleimide resin was a commercial product composed of BMI and DBA (Ciba Geigy Corp.,

Matrimid 5292 A/B). Dichloromethane was dried over  $\text{CaCl}_2$  and distilled over calcium hydride. Diphenyl ether, phthaloyl chloride, and isophthaloyl chloride were distilled under reduced pressure. Other reagents were used as received.

### Measurements

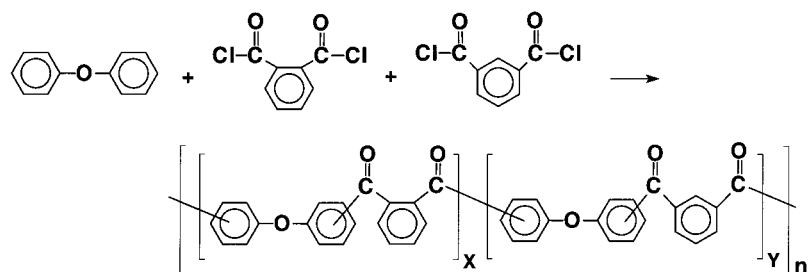
<sup>1</sup>H-NMR spectra were recorded on a 90-MHz instrument (JEOL JNM-9MX 90) at 60°C using  $\text{CDCl}_3$  as the solvent and tetramethylsilane as the internal standard. The molecular weights of PEKKs were measured by gel permeation chromatography (Shimadzu LC-5A instrument) using polystyrene standards. The mechanical properties of the cured resins were determined with a Shimadzu autograph AGS-500B universal testing machine. Flexural tests were carried out at a crosshead speed of 2 mm/min (JIS K7203). The fracture toughness,  $K_{IC}$ , was measured in a three-point bent geometry as a crosshead speed of 1 mm/min (ASTM E-399). The glass transition temperatures ( $T_g$ 's) of both the PEKKs and cured resins were measured as the onset temperatures by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating rate of 10°C/min under  $\text{N}_2$ . Scanning electron micrographs (SEM) were taken with a Hitachi SEM S-2100A instrument using failed specimens from the  $K_{IC}$  tests. For some of the modified resins, ion etching of the polished surface was carried out by a Hitachi flat milling E-3200 instrument (applied voltage 5 kV, charge current 1 mA, milling time 40 min, ion incident angle 60°), and a high-resolution SEM with a field emission gun (Hitachi FE-SEM, S-4500 type) was used. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between -50 and 400°C at a heating rate of 5°C/min at frequency of 1 Hz under  $\text{N}_2$ .

### Preparation of Poly(phthaloyl diphenyl ether) and Related Copolymers

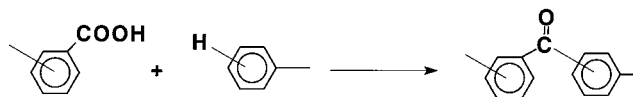
PPDE was prepared by the reaction of phthaloyl chloride and diphenyl ether according to the modified procedures of the previous article<sup>15</sup> (Scheme 2). A typical procedure was as follows.

To a 1-L four-necked separable flask equipped with a mechanical stirrer, a thermometer, and an additional funnel was added diphenyl ether 34.0 g (0.200 mol) and  $\text{CH}_2\text{Cl}_2$  500 g. After the reaction mixture was cooled to about -60°C,  $\text{AlCl}_3$ , 74.8 g (0.560 mol), was added in portions followed by

## Preparation of PPIDE



## Coupling of polymer



Scheme 2

addition of phthaloyl chloride, 40.6 g (0.200 mol), dropwise with stirring. The reaction mixtures were warmed to  $-20^{\circ}\text{C}$  in 1 h and kept at  $-20^{\circ}\text{C}$  for 6 h with stirring. The reaction mixtures were then stirred while allowing them to increase to room temperature and kept overnight. After refluxing for 30 min, the reaction mixtures were poured into ice water. The organic phase was poured into methanol. The precipitated crude polymer was filtered and dried at  $80^{\circ}\text{C}$  *in vacuo*. The crude polymer  $\text{CH}_2\text{Cl}_2$  solution was poured into methanol. The isolated polymer was refluxed in dilute HCl to remove the aluminum residue adhered to the polymer. This procedure was carried out until the chloride ion could not be detected in the filtrate. The polymer was dried at  $80^{\circ}\text{C}$  *in vacuo*. Yield, 99%;  $M_{\text{GPC}}$ , 11,100.

It was difficult to obtain higher molecular weight (MW) PPDE using the above method. The coupling of PPDE was then carried out as follows, according to the modified method of Ueda and Sato<sup>25</sup> (Scheme 2).

A 1-L four-necked separable flask was charged with the reagent PPMA (a mixture of methanesulfonic acid and phosphorus pentoxide [10 : 1 wt ratio]) and a PPDE  $\text{CH}_2\text{Cl}_2$  solution. The reaction mixtures were refluxed overnight with stirring in the presence or absence of diphenyl ether or phthalic anhydride, dependent on the terminal carboxyl content of PPDE. For example, the coupling of 40.0 g PPDE (0.342 meq/g COOH unit, MW 5300) alone with PPMA (176 g) in  $\text{CH}_2\text{Cl}_2$  (800 mL) led to a higher MW PPDE (MW 14,600; yield 93%). When using the same PPDE, 37.0 g, and phthalic anhydride, 0.21 g (1.42

mmol), the  $M_{\text{GPC}}$  of the resulting PPDE was 25,800 (yield 95%): PPMA 163 g and  $\text{CH}_2\text{Cl}_2$  800 mL.

PPIDE and PPTDE were prepared by the method similar to the PPDE preparation, but the coupling was not carried out. In the preparation of PPTDE, solid terephthaloyl chloride was used as a  $\text{CH}_2\text{Cl}_2$  solution.

## Curing Procedure

PEKKs were dissolved into DBA at  $150^{\circ}\text{C}$  without solvents. Then, BMI was added to the mixture, which was kept at  $130^{\circ}\text{C}$  to dissolve the BMI. DBA and BMI were used in a molar ratio of 1 : 1. The resulting clean mixture was degassed *in vacuo* at  $130^{\circ}\text{C}$ . The mixture was poured into a mold, preheated at  $130^{\circ}\text{C}$ , to obtain 7-mm-thick plaques. The mold consisted of one pair of upright and metal clip-held glass plates spaced by a U-shaped silicon rubber stick. The amount (wt %) of the modifier was calculated based on the Matrimid 9252 system. The curing cycle was  $160^{\circ}\text{C}/3\text{ h} + 180^{\circ}\text{C}/1\text{ h} + 200^{\circ}\text{C}/2\text{ h} + 250^{\circ}\text{C}/6\text{ h}$ . After curing, the oven temperature was decreased gradually from  $250^{\circ}\text{C}$  to room temperature and the time taken to reach  $50^{\circ}\text{C}$  was about 5 h.

## RESULTS AND DISCUSSION

## Mechanical and Thermal Properties of Modified Bismaleimide Resins

The PEKKs used in this study include poly-(phthaloyl diphenyl ether) (PPDE), poly(phthaloyl

**Table I** Characterization of PPDE and the Related Copolymers

Entry No.	Polymer Composition <sup>a</sup>	$M_{\text{GPC}}^{\text{b}}$ ( $10^3$ )	$M_n^{\text{b}}$ ( $10^3$ )	$M_w/M_n$	$T_g^{\text{c}}$ ( $^{\circ}\text{C}$ )	A.V. <sup>d</sup> (mequiv/g)
PPDE 07	—	3.4	3.7	1.6	215	0.134
23	—	5.3	3.3	2.4	—	0.342
25	—	8.3	5.5	1.8	249	0.041
13	—	11.1	7.8	2.8	277	0.210
27	—	15.2	6.1	3.9	—	0.046
23A <sup>e</sup>	—	25.8	12.0	3.8	270	0.024
23B <sup>e</sup>	—	29.0	14.5	6.2	268	0.020
PPIDE07	IP 25	10.8	6.3	2.3	207	0.019
09	25	19.0	8.8	3.3	217	—
06	50	12.5	8.0	2.6	186	0.019
01	50	21.8	10.7	4.0	189	0.022
02	50	27.3	14.2	5.4	—	0.029
05	50	34.9	18.4	8.6	198	0.019
PPTDE01	TP 25	11.2	6.4	2.4	—	—
02	50	19.4	10.5	3.1	209	—

<sup>a</sup> IP, isophthalolyl unit; TP, terephthalolyl unit mol %.

<sup>b</sup> By GPC.

<sup>c</sup> By DSC.

<sup>d</sup> Terminal carboxyl group content.

<sup>e</sup> Prepared by coupling.

diphenyl ether-*co*-isophthaloyl diphenyl ether) (PPIDE), and poly(phthaloyl diphenyl ether-*co*-terephthaloyl diphenyl ether) (PPTDE). The PEKKs were prepared in a quantitative yield. The copolymer composition was equal to the feed composition by <sup>1</sup>H-NMR spectroscopy. The characterization of PEKKs is shown in Table I. The GPC-average MW ( $M_{\text{GPC}}$ ), obtained from the peak position of the GPC curve, was used as a measure of the MW of the PEKKs in this study, because the number-average MW is highly sensitive to the presence of a small amount of lower MW materials.

Table II shows the representative results for the modification of the bismaleimide resin with PEKKs. The unmodified bismaleimide resin was transparent. All the PPDE-modified resins became translucent during curing, independent of the modifier structure and content, except for the 10 wt % inclusion of lower MW PPDE (MW 3400) (Table II, Entry No. BE01), of which the resin was transparent. PPIDE-modified resins were translucent, except for 20 wt % addition of PPIDE (25 mol % isophthaloyl [IP] unit, MW 10,800) or 20 wt % of PPIDE (50 mol % IP unit, MW 12,500), of which the resins became opaque. The PPTDE-modified resins were translucent perhaps because of lower inclusion (10 wt %) of the modifier.

Figure 1 shows the PEKKs' MW dependence of the mechanical and thermal properties for the

modified resins on 10 wt % addition. In the modification with PPDE, the fracture toughness,  $K_{\text{IC}}$ , for the modified resins increased with increasing MW with no decrease in  $T_g$ . When using PPDE with MW higher than 25,000, flexural strength decreased significantly. In the modification with PPIDE (50 mol % IP unit),  $K_{\text{IC}}$  for the modified resins increased with increase in MW with no loss of flexural properties and  $T_g$ . When using 10 wt % of PPIDE (50 mol % IP unit, MW 34,900),  $K_{\text{IC}}$  increased 75%, but the use of 15 wt % of the same modifier led to an increase in viscosity at 130 $^{\circ}\text{C}$  of the Matrimid 5292/PPIDE mixtures before curing. Fracture behavior in both PPIDE (25 mol % IP unit) and PPTDE (50 mol % terephthaloyl [TP] unit) modifications was similar to that with PPDE, so further study was not carried out. PPIDE (50 mol % IP unit) was the most effective among them.

Figure 2 shows the mechanical and thermal properties of the modified resins as a function of modifier concentration. The  $K_{\text{IC}}$  for the modified resins increased with increasing PPDE (MW 8300) concentration up to 15 wt % addition with no loss of flexural properties and  $T_g$ , but flexural strength decreased abruptly on 20 wt % addition. In the modification with PPIDE (50 mol % IP unit, MW 21,800),  $K_{\text{IC}}$  increased with PPIDE concentration. When using 15 wt % of PPIDE (50 mol %

Table II Physical Properties of Modified Bismaleimide Resins

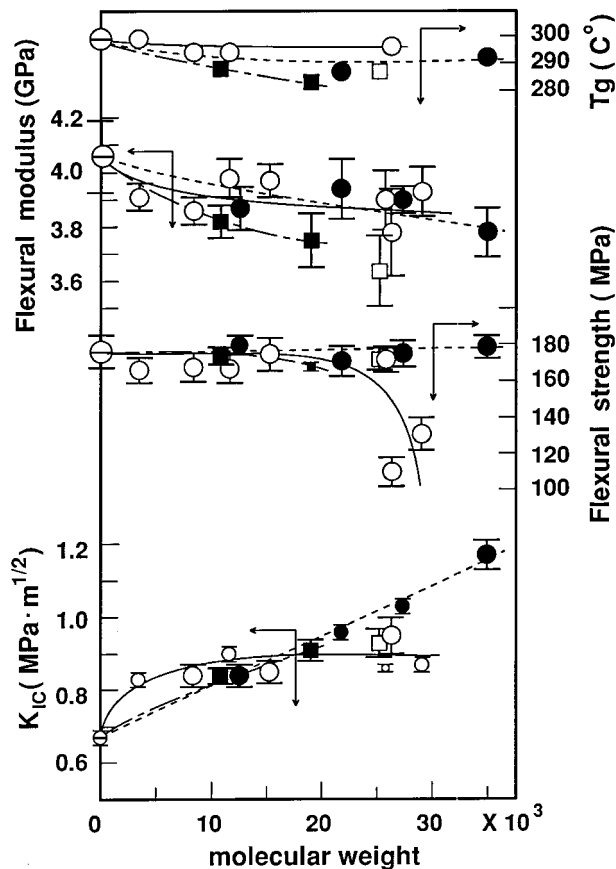
Entry No.	No.	Modifier			Flexural Properties					$T_g^c$ (°C)
		Composition <sup>a</sup> (mol %)	MW (10 <sup>3</sup> )	Content (wt %)	$K_{IC}$ (MPa m <sup>1/2</sup> )	$n^b$	Strength (MPa)	Modulus (GPa)	$n^b$	
Control		—	—	0	0.67 ± 0.02	9	176 ± 9	4.06 ± 0.13	5	289
BE01	PPDE07	—	3400	10	0.83 ± 0.02	8	166 ± 7	3.91 ± 0.05	7	289
BE07	PPDE25	—	8300	10	0.84 ± 0.03	5	168 ± 8	3.86 ± 0.05	5	294
BE02	PPDE13	—	11,100	10	0.90 ± 0.02	6	167 ± 8	3.98 ± 0.07	5	294
BE03	PPDE23A	—	25,800	10	0.86 ± 0.01	5	167 ± 7	3.90 ± 0.11	6	—
BE23	PPIDE07	IP25	10,800	10	0.84 ± 0.02	5	174 ± 9	3.82 ± 0.06	5	288
BE25	PPIDE09	IP25	19,000	10	0.91 ± 0.03	6	168 ± 2	3.75 ± 0.10	5	283
BE20	PPIDE06	IP50	12,500	10	0.84 ± 0.03	4	180 ± 5	3.87 ± 0.08	5	—
BE15	PPIDE01	IP50	21,800	15	1.13 ± 0.03	5	170 ± 8	3.90 ± 0.13	5	287
BE18	PPIDE02	IP50	27,300	15	1.06 ± 0.03	6	177 ± 11	3.78 ± 0.08	4	—
BE19	PPIDE05	IP50	34,900	10	1.17 ± 0.04	6	179 ± 6	3.78 ± 0.09	5	292
BE26	PPTDE01	TP25	11,200	10	0.79 ± 0.02	6	167 ± 4	3.77 ± 0.07	5	288
BE27	PPTDE02	TP50	19,400	10	0.93 ± 0.04	5	172 ± 6	3.64 ± 0.13	5	287

The ± x values show standard deviation.

<sup>a</sup> IP, isophthaloyl unit; TP, terephthaloyl unit mol %.

<sup>b</sup> Specimen number.

<sup>c</sup> By DSC.



**Figure 1** Dependence of physical properties for modified resins on modifier molecular weight. Modifier 10 wt % addition: ( $\ominus$ ) control; ( $\circ$ ) PPDE; ( $\blacksquare$ ) PPIDE (25 mol % IP unit); ( $\bullet$ ) PPIDE (50 mol % IP unit); ( $\square$ ) PPTDE (50 mol % TP unit).

IP unit, MW 21,800),  $K_{IC}$  increased 70% with no deterioration in flexural properties and  $T_g$ . The fracture behavior corresponds to morphologies of the modified resins as shown below.

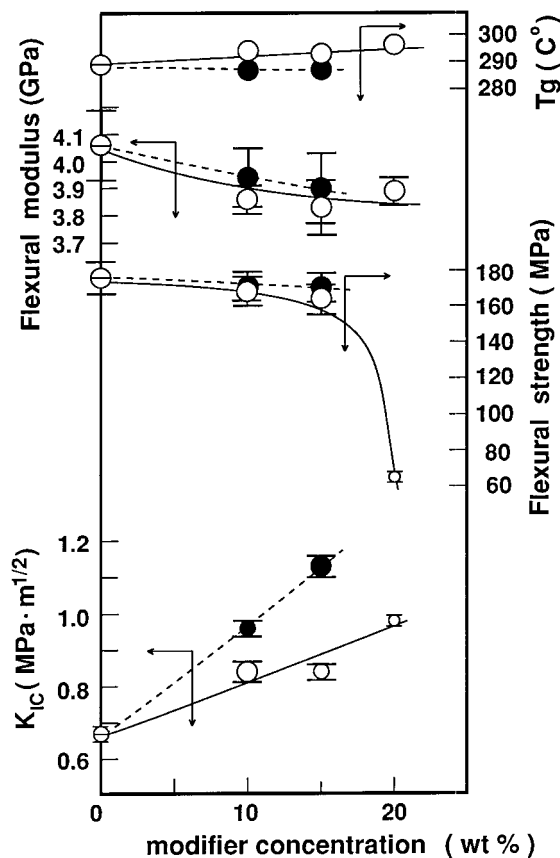
#### Dynamic Viscoelastic Analysis of Modified Resins

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 3 shows the storage moduli,  $G'$ , and  $\tan \delta$  curves for the unmodified and PPDE-modified resins. When using 10 wt % of PPDE (MW 8300), the peak position of the  $\alpha$ -relaxation shifted slightly toward lower temperature and its magnitude became higher, compared to the dynamic viscoelastic behavior for the cured Matrimid resin (Fig. 3). A new relaxation peak ( $\alpha'$ -relaxation) was observed at 250°C on 10 wt % addition of PPDE (MW 8300). The  $\alpha'$ -relaxation peak (264°C) became larger on PPDE (MW 8300) 20 wt % addi-

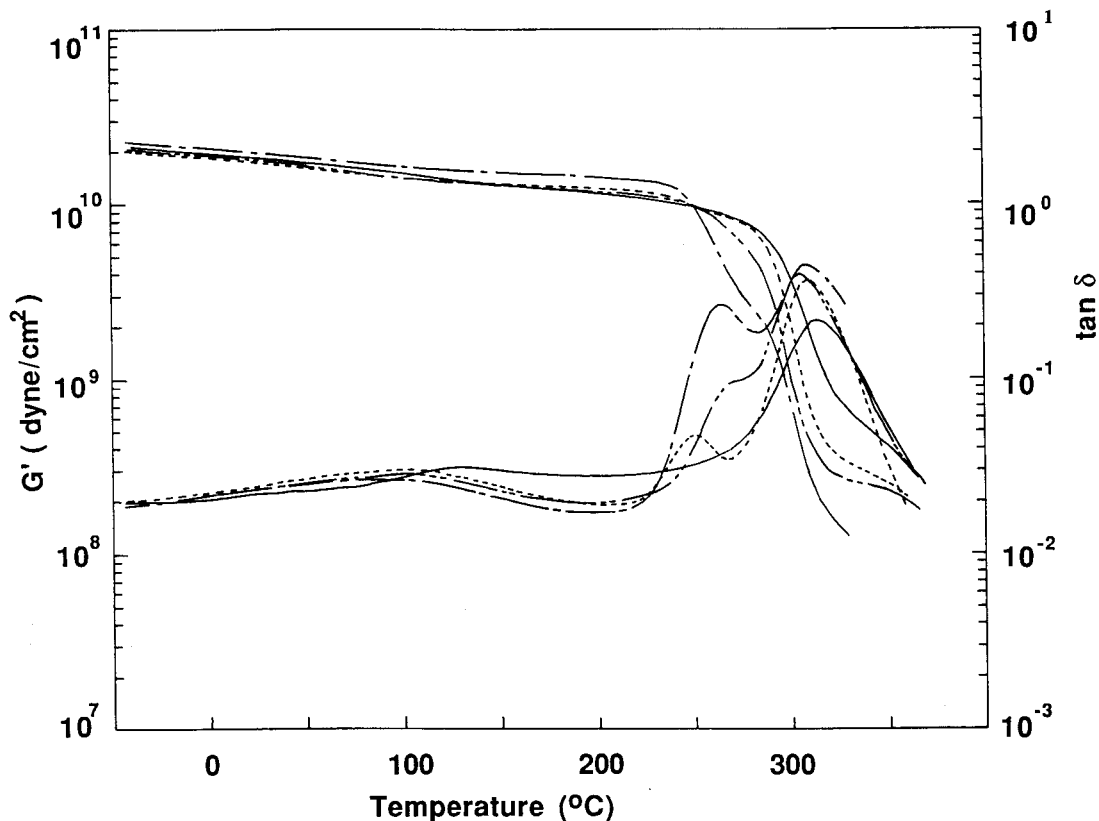
tion. In the modification with 10 wt % of PPDE (MW 25,800), the  $\alpha$ -relaxation peak position also shifted slightly toward lower temperature, the  $\alpha'$ -relaxation became the shoulder, and its position shifted to ca. 275°C, because of a higher  $T_g$  value (270°C) of PPDE compared to that (249°C) of lower MW material (MW 8300). The storage moduli at room temperature for the modified resins were equal to that for the unmodified resin.

When using 10 wt % of PPIDE (MW 21,800), the  $\alpha$ -relaxation peak position and its magnitude hardly changed, compared to that for the unmodified resin, and a new  $\alpha'$ -relaxation peak was observed at 198°C (Fig. 4). The magnitude of the  $\alpha'$ -relaxation peak became larger with increasing PPIDE content. The storage moduli at room temperature for the modified resins were comparable to that for the unmodified resin.

The appearance of the new  $\alpha'$ -relaxation peak in the  $\tan \delta$  curve indicates the existence of the phase-separated structure for the modified resin.



**Figure 2** Physical properties of modified resins as a function of modifier concentration: ( $\ominus$ ) control; ( $\circ$ ) PPDE (MW 8300); ( $\bullet$ ) PPIDE (50 mol % IP unit, MW 27,300).



**Figure 3** Dynamic viscoelastic analysis for unmodified and PPDE-modified resins: (—) 0 wt % (control); (-----) PPDE (MW 8300) 10 wt % addition; (— — —) PPDE (MW 8300) 20 wt % addition; (— · — ·) PPDE (MW 25,800) 10 wt % addition.

These results correspond to the morphological results.

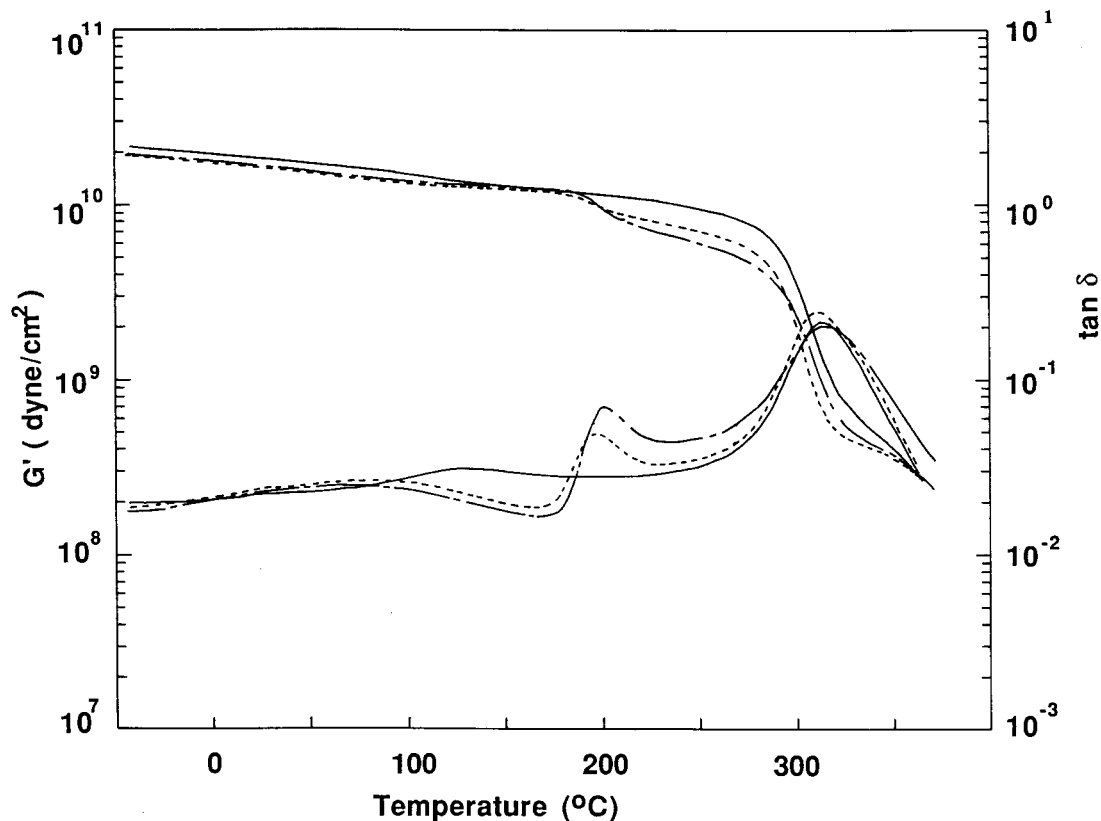
#### Morphologies of the Modified Bismaleimide Resins

The morphologies of the cured resins were investigated by scanning electron microscopy (SEM). Figures 5–7 show SEMs of the fracture surfaces for the modified resins, where etching of the fracture surfaces by dichloromethane was carried out at room temperature for 5 days except for Figure 5(C). The unmodified cured Matrimid resins had only one phase as reported previously.<sup>21</sup> Inclusion of the modifiers led to two-phase morphology. The morphologies of the modified resins depended on the chemical structure and content of the modifiers.

When using 10 wt % of PPDE (MW 8300), the modified resin had a particulate morphology and PPDE-rich phases were etched out clearly [Fig. 5(A)]; the average diameter of the particle was 0.3  $\mu\text{m}$ , and the volume fraction, 0.07. On addition

of 10 wt % of higher MW PPDE (25,800), the modified resin also had a particulate structure, but PPDE-rich phases were somewhat ill-defined spherical particles and the PPDE-rich particles were not etched out [Fig. 5(B)]; the diameter of the particles was of the order of 1.00  $\mu\text{m}$ . The particle size became larger with increasing PPDE MW. In the modification with 10 wt % of PPIDE (25 mol % IP unit, MW 19,000), the modified resin also had a particulate morphology [Fig. 5(C)].

When using PPIDE (50 mol % IP unit, MW 27,300), the morphologies of the modified resins changed from a particulate to cocontinuous and to phase-inverted structures with increasing modifier content (Fig. 6). On 5 wt % addition of PPIDE (50 mol % IP unit, MW 27,300), the modified resin had a particulate structure having light PPIDE-rich particles with an ill-defined contour dispersed in the dark bismaleimide-rich matrix [Fig. 6(A)]; the particles, composed of clusters of smaller particles, were not etched out and their diameter was the order of 1  $\mu\text{m}$ . The morphology



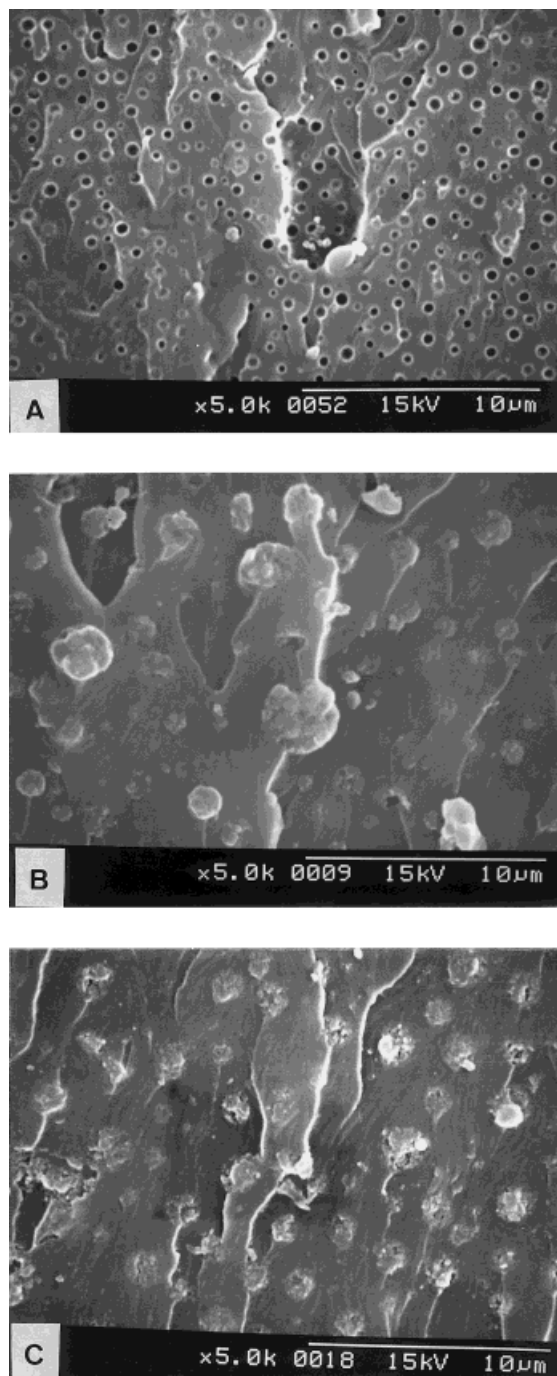
**Figure 4** Dynamic viscoelastic analysis for unmodified and PPIDE-modified resins: (—) 0 wt % (control); (-----) PPIDE (50 mol % IP unit, MW 21,800) 10 wt % addition; (- - -) PPIDE (50 mol % IP unit, MW 21,800) 15 wt % addition.

of the modified resin became a cocontinuous phase structure on 10 wt % addition [Fig. 6(B)]; light PPIDE-rich phases were composed of a cluster of irregular-shaped nodules and could not be etched out. The use of 15 wt % of the same modifier led to a development of a phase-inverted structure in the final resin, where the bismaleimide resin became a particulate phase [Fig. 6(C)]. When using lower MW PPIDE (50 mol % IP unit, MW 21,800), the modified resin had a cocontinuous phase morphology on 10% addition [Fig. 6(D)], but the morphology of the modified resin was unclear on 15 wt % addition [Fig. 6(E)]. The use of higher MW PPIDE (50 mol % IP unit, MW 34,900) led to a phase-inverted morphology even on 10 wt % addition [Fig. 6(F)].

For the cured resin modified with 15 wt % of PPIDE (50 mol % IP unit, MW 21,800), ion etching of the polished surface by  $\text{Ar}^+$  plasma was carried out and a high-resolution SEM with a field emission gun (FE-SEM) was used, where good micrographs were obtained, compared to that by

the conventional SEM [Figs. 7 and 6(E)]. The micrographs by FE-SEM were interesting to use to consider the toughening mechanism in the present modification system. The SEM micrograph for the unmodified bismaleimide resin was featureless [Fig. 7(A)]. The morphology of the modified resin had a phase-inverted structure [Fig. 7(B)] and light-etched modifier-rich continuous phases were observed under higher magnification ( $\times 10,000$ ) [Fig. 7(C)]. Interestingly, part of the dark bismaleimide-rich phase near the interface was also etched out by  $\text{Ar}^+$  plasma. This behavior became clearer under further higher magnification ( $\times 50,000$ ), where smaller, irregular dark poles (the order of 10 nm) formed by etching were observed near the periphery of the dark bismaleimide-rich particle to a greater extent [Fig. 7(D)]. This result indicates that the two incompatible phases entangle each other at their interface and form interpenetrating polymer networks (IPNs) and that their interfacial adhesion would be improved because of IPN formation.





**Figure 5** SEMs of fracture surfaces for the modified resins. 10 wt % addition of modifiers: (A) PPDE (MW 8300); (B) PPDE (MW 25,800); (C) PPIDE (25 mol % IP unit, MW 19,000).

The improvement in solvent resistance would also be perhaps because of the IPN formation. In general, it is difficult to present evidence for the presence of the IPN structure, because IPNs are often formed in the nm order. The morphological results

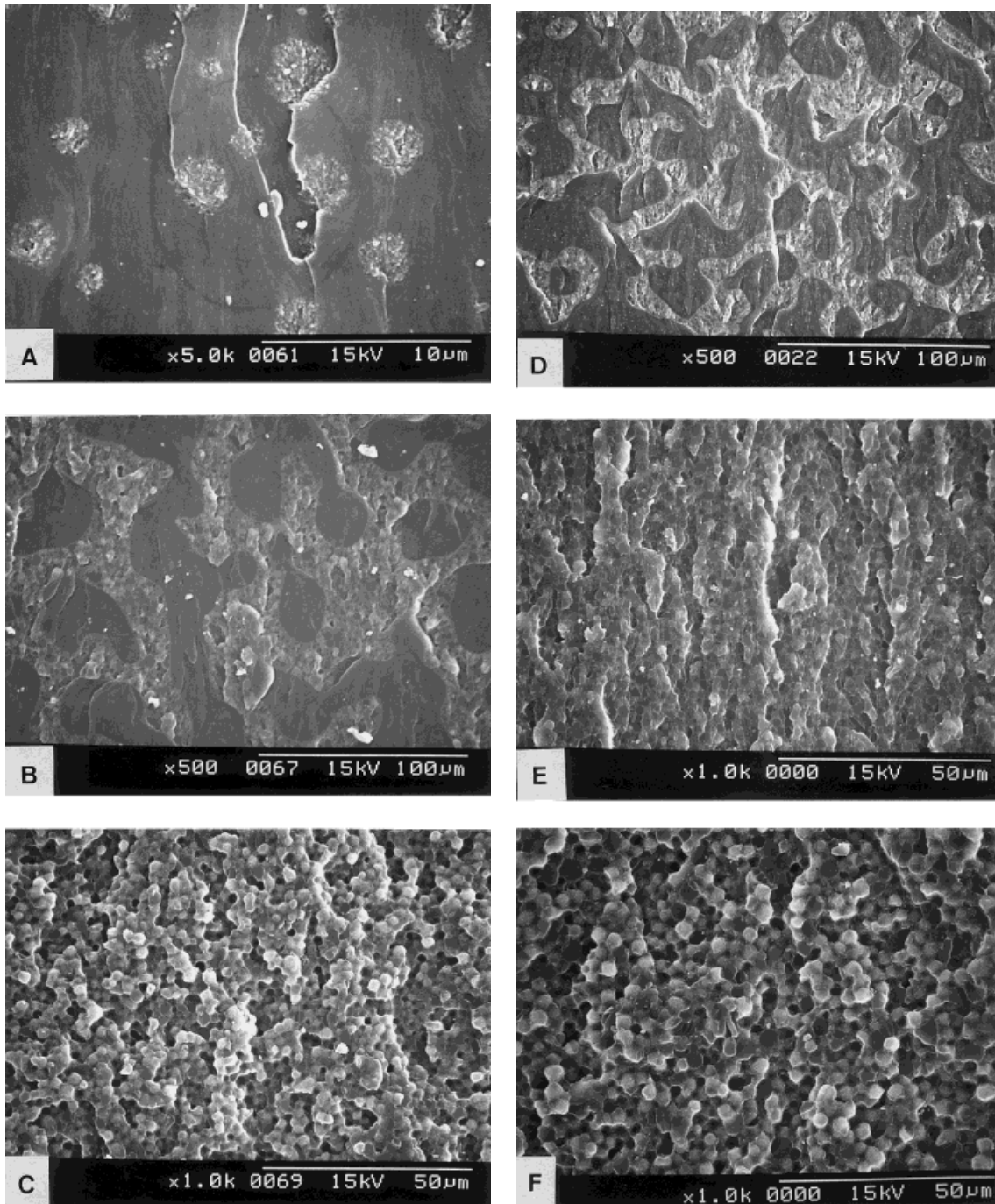
in Figure 7 indicate that FE-SEM measurements for ion-etched surfaces are useful to study the IPN structure.

#### Discussion on the Toughening Mechanism

PPDE and related copolymers were effective as the modifiers for the bismaleimide resin. PPIDE (50 mol % IP unit) was the most effective among them. The use of 10 wt % of PPIDE (50 mol % IP unit, MW 349,000) led to a 75% increase in the  $K_{IC}$  value with no expense of mechanical and thermal properties. These modifiers were soluble in the bismaleimide resin without solvents.

A commercial bisphenol A-type poly(ether ketone) (PEK) was an effective modifier for the bismaleimide resin (Technochimie Co., Compimide 796 and TM 123 system) and the modified resin had an irregular-shaped two-phase morphology on 20 wt % addition, where the interface between the two phases was ill-defined because of a good interfacial adhesion.<sup>13</sup> Reactive PEKs having pendant propenyl groups were prepared by nucleophilic aromatic substitution of 4,4'-difluorobenzophenone with mixtures of bisphenol A and 2,2'-bis(3-allyl-4-hydroxyphenyl)hexafluoropropane (6F-DABA), where allyl groups were isomerized to propenyl groups.<sup>14</sup> PEK composed of 75 mol % bisphenol-A and 25 mol % 6F-DABA was most effective for the Compimide 796/TM 123 system. The modified resin had a polyphase morphology with thermoset nodules dispersed in the PEK-rich phase on 30 wt % addition and the interfacial adhesion was improved. In the modification of the bismaleimide resin with PEK, toughening could be attained because of cocontinuous phase or phase-inverted morphologies. In both modification systems, dichloromethane was used as a solvent to prepare cured resins.

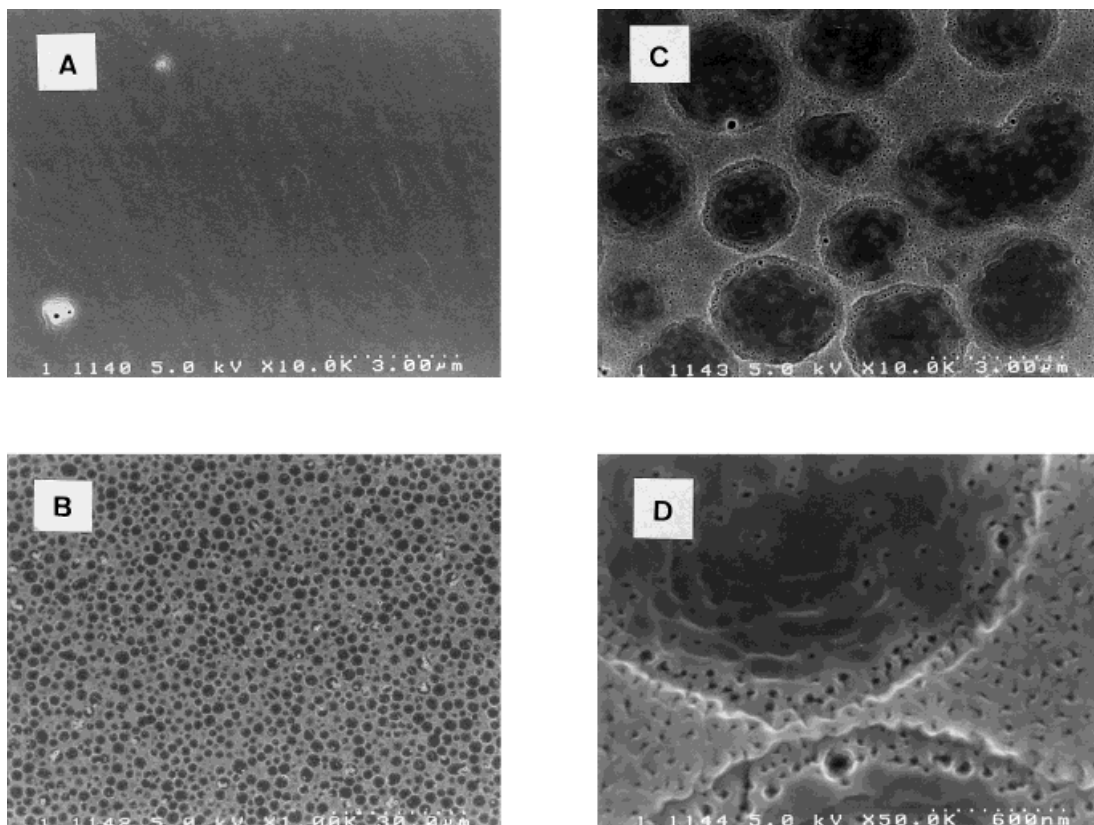
The solubility parameter (SP) is a measure for compatibility. The SP value ( $24.86 \text{ (MJ/m}^3)^{1/2}$ ) of PPDE and PPIDE is close to that ( $27.66$ ) of the Matrimid A/B resin (by Fedors' method<sup>26</sup>), indicating high compatibility of the modifiers with the Matrimid resin: The modifiers can be dissolved into the uncured Matrimid resin without solvents at an elevated temperature. In the curing of the Matrimid resin, DBA copolymerizes with BMI via the ene-type linear chain-extension reaction followed by the Diels-Alder reaction of the intermediate ene reaction product with another DBA.<sup>1</sup> During curing, the increase in MW of the bismaleimide resin initiated phase separation by spinodal decomposition.<sup>27</sup> In the present modifi-



**Figure 6** SEMs of fracture surfaces for the modified resins. MW and amount of PPIDE (50 mol % IP unit): (A) 27,300, 5 wt %; (B) 27,300, 10 wt %; (C) 27,300, 15 wt %; (D) 21,800, 10 wt %; (E) 21,800, 15 wt %; (F) 34,900, 10 wt %.

cation, morphologies of the modified resins changed from particulate to the cocontinuous phase or were phase-inverted, depending on the modifier content and structure. In the PPDE modification system, the modified resins had particulate morphologies. Morphologies of the PPIDE-

modified resins changed from particulate to cocontinuous or phase-inverted structures with increasing PPIDE MW and content. Toughness improvement for the modified resins can be achieved because of cocontinuous phase or phase-inverted morphologies. Furthermore, the fracture



**Figure 7** FE-SEMs of fracture surfaces for the modified resins: (A) control, magnification 10,000; (B) PPIDE (50 mol % IP unit, MW 21,800) 15 wt % addition, magnification  $\times 1000$ ; (C) PPIDE (50 mol % IP unit, MW 21,800) 15 wt % addition, magnification  $\times 10,000$ ; (D) PPIDE (50 mol % IP unit, MW 21,800) 15 wt % addition, magnification  $\times 50,000$ .

toughness enhancement would be partly because of the improvement in the interfacial adhesion by the IPN formation, because the interfacial adhesion is one of the most important factors to attain the effective modification.<sup>2</sup> Most of the modified resins in the present modification cannot be etched out by dichloromethane, which also indicates the good interfacial adhesion.

## CONCLUSION

PPDE and the related copolymers were effective as modifiers for the bismaleimide resin. PPIDE was most effective among them. The improvement in toughness of the modified bismaleimide resin could be achieved because of the cocontinuous phase or phase-inverted morphologies, where the interface adhesion between the two incompatible phases was improved by entangling each other at

the interface. The most suitable composition for modification of the bismaleimide resin was inclusion of 10 wt % of PPIDE (50 mol % IP unit, MW 34,900), which led to a 75% increase in  $K_{IC}$  with retention in flexural properties and  $T_g$ .

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