

Modification of Three-Component Bismaleimide Resin by Poly(phthaloyl diphenyl ether) and Related Copolymers

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ABSTRACT: A three-component bismaleimide resin, composed of 4,4'-bismaleimido-diphenyl methane (BDM), *o,o'*-diallyl bisphenol A (DBA), and *o,o'*-dimethallyl bisphenol A (1.0/0.3/0.7 eq ratio) was used as a parent bismaleimide resin. Modification of the three-component bismaleimide resin was examined by blending it with poly(ether ketone ketone)s. 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). The PPIDE (51 mol % isophthaloyl) and PPTDE (44 mol % terephthaloyl) were more effective as modifiers for the bismaleimide resin than was PPDE. For example, the fracture toughness (K_{IC}) for the modified resin increased 30% with no deterioration in the flexural strength and modulus with a 15 wt % inclusion of PPTDE (MW 23,400) compared to the parent three-component bismaleimide resin: the K_{IC} increased 95% compared to the value for the Matrimid 5292 resin composed of BDM and DBA. The morphologies of the modified resins changed from particulate to cocontinuous phase structures, depending on the modifier structure and concentration. Toughening of the cured bismaleimide resin could be achieved because of the cocontinuous phase structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2991–3000, 2001

Key words: bismaleimide resin; modification; poly(phthaloyl diphenyl ether); fracture toughness; flexural properties; morphology

INTRODUCTION

Addition polyimide resins are among the most important thermosetting polymers. The drawbacks of the polyimide resins are brittleness and difficulty in processing. Bismaleimide resins are attractive because of their good processability, nonvolatility, high thermal stability, and mechanical properties. A two-component bismaleimide system (Matrimid 5292 A and BTM), composed of 4,4'-bismaleimidodiphenyl methane (BDM) and *o,o'*-diallyl bisphenol A (DBA), was devel-

oped by Ciba Geigy Corp. to improve the mechanical properties and processability.¹ During curing, DBA copolymerizes with BDM via an ene-type linear chain extension reaction followed by the Diels–Alder reaction. The brittleness of the cured resin was improved in comparison to the conventional two-component bismaleimide resins composed of BDM and 4,4'-diaminodiphenyl methane. Hence, the selection of comonomers is important to improve the brittleness of the cured resin in the two-component bismaleimide resin. We recently reported on the modification of the two-component bismaleimide resin by blending (meth)allyl compounds as third components.² The third components included triallyl isocyanurate, *o,o'*-dimethallyl BA (DMBA), and trimethallyl

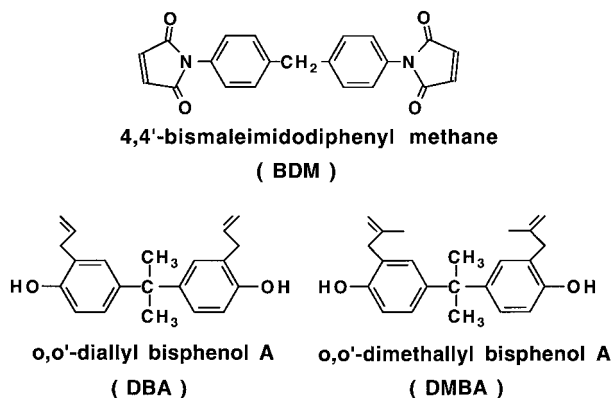
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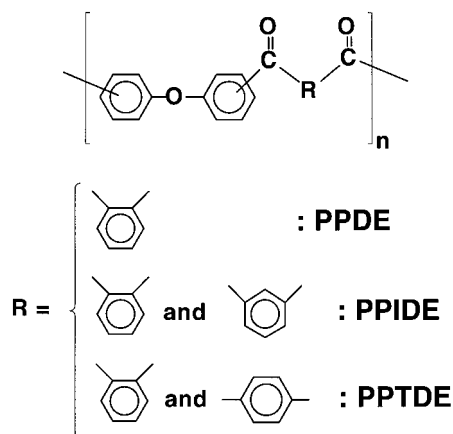
isocyanurate. The mechanical and thermal properties of the cured resins depended on the third-component structure and concentration. For example, in the ternary BDM/DBA/DMBA (1/0.3/0.7 eq ratio) blend the fracture toughness (K_{IC}) for the cured resin increased 45% with no deterioration of the flexural properties and a reduction of the glass-transition temperature (T_g , 195°C) compared to the T_g value (299°C) of the cured Matrimid resin.

The toughness of the thermosetting resins was increased by blending them with reactive liquid rubbers such as carboxyl-terminated butadiene-acrylonitrile rubbers³ or engineering thermoplastics including polysulfone (PSF) or poly(ether imide) (PEI).⁴ Engineering thermoplastics are interesting materials as modifiers for bismaleimide resins from the viewpoint of the maintenance of the mechanical and thermal properties for the matrix resins. The engineering thermoplastics used as modifiers for the bismaleimide resins included PSF,⁵ PEI,⁵⁻⁷ polyhydantoin,⁵ poly(ether sulfone),⁶ poly(ether ketone)s,^{8,9} 6F polyimide,¹⁰ and poly(arylene ether phosphine oxide).¹⁰

Modification of the two-component bismaleimide resin (the Matrimid 5292™ system) was carried out on the basis of information on the toughening of epoxies by thermoplastics in our laboratory.¹¹⁻²⁰ The thermoplastics used as modifiers for the bismaleimide resin included *N*-phenylmaleimide-styrene copolymer and related copolymers²¹⁻²³ and aromatic polyesters such as poly(ethylene phthalate).^{24,25} Further, poly(ether ketone)s (PEKKs) were reported as effective modifiers for the bismaleimide resin²⁶; high toughening can be achieved because of the cocontinuous or phase-inverted structures of the modified resins.



Scheme 1 The structures of the resin components.



Scheme 2 The structures of PEKKs.

The three-component bismaleimide resins are interesting materials to control the mechanical and thermal properties of the cured resins.² When using the three-component bismaleimide resin composed of BDM, DBA, and DMBA, the cured resin was tougher than the two-component Matrimid resin and had a higher T_g value (195°C) than that (180°C) of aromatic diamine cured diglycidyl ether of BA (DGEBA),¹⁴ although the T_g value was lower than that of the Matrimid resin (299°C). This indicated that the three-component bismaleimide resin was interesting as a parent resin for toughness enhancement by thermoplastics. Hence, this article examines the PEKK modification of the three-component bismaleimide resin composed of BDM, DBA, and DMBA. The PEKKs included 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 resin components and PEKKs are shown in Schemes 1 and 2, respectively.

EXPERIMENTAL

Materials

The three-component bismaleimide resin comprised BDM, DBA, and DMBA (1/0.3/0.7 eq ratio); the two-component bismaleimide resin composed of BDM and DBA is known as Matrimid 5292 A/B™ (Ciba Geigy Corp., Fribourg, Switzerland). The DMBA (white solid) was a gift from Toagosei Corp. (Nagoya, Japan). Dichloromethane was dried and distilled over calcium hydride. Diphenyl ether, phthaloyl chloride, and isophthaloyl

Table I Characterization of PPDE and Related Copolymers

Entry and No.	Polymer Composition	$M_{\text{GPC}}^{\text{a}}$ (10^3)	M_n^{a} (10^3)	M_w/M_n	T_g^{b} ($^{\circ}\text{C}$)
PPDE					
101	—	18.4	6.7	4.28	249
102	—	26.4	7.6	7.41	252
PPIDE					
101	IP 48	8.0	4.9	2.11	167
102	IP 48	17.4	8.4	2.71	183
104	IP 51	31.0	13.0	3.51	191
PPTDE					
101	TP 44	11.6	7.4	2.10	227
102	TP 44	23.4	12.2	3.58	241

IP, isophthalolyl unit; TP, terephthalolyl unit (mol %).

^a By GPC.

^b By DSC.

chloride were distilled under reduced pressure. Other reagents were used as received. The PEKKs were prepared by the reaction of benzenedicarbonyl dichlorides and diphenyl ether according to the procedure of a previous article.²⁶

Measurements

¹H-NMR spectra were recorded on a 90-MHz instrument (JNM-9MX 90, Jeol, Tokyo) at 60°C using CDCl₃ as a solvent and tetramethylsilane as an internal standard. The molecular weights of the modifiers were measured by gel permeation chromatography (LC-5A, Shimadzu, Kyoto, Japan) 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 K_{IC} was measured in a three-point bent geometry at a crosshead speed of 1 mm/min (ASTM E-399). The T_g values of the modifiers and the cured resin were measured as the onset temperatures by differential scanning calorimetry (DSC, DSC 60 type, Shimadzu) at a heating speed of 10°C/min under nitrogen. Scanning electron microscopy (SEM) was performed with a combined microanalyzer (JXA-8900RL, Jeol) using failed specimens in the K_{IC} tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II (Rheometrics Co., Tokyo) between -50 and 400°C at a heating speed of 5°C/min and a frequency of 1 Hz.

Curing Procedure

The PEKKs were dissolved in (meth)allyl components at 150°C without solvents. Then BDM was

added to the mixture at 130°C. The BDM and the (meth)allyl components were used in an equivalent ratio of 1:1. The resulting clean mixture was degassed *in vacuo* at 130°C. The mixture was poured into a preheated mold (140°C) to obtain 7-mm thick plaques. The mold consisted of one pair of upright, metal clip held glass plates spaced by a U-shaped silicon rubber stick. The curing cycle was 160°C for 3 h, 180°C for 1 h, 200°C for 2 h, and 250°C for 6 h. After curing the oven temperature was decreased from 250 to 50°C at a cooling speed of 25°C/h. The amount (wt %) of the modifier was calculated based on the three-component bismaleimide resin.

RESULTS

Mechanical and Thermal Properties of Cured Bismaleimide Resins

The PEKKs were prepared by the reaction of the benzenedicarbonyl dichlorides and diphenyl ether according to the previous procedure.²⁶ The PEKKs included PPDE, PPIDE, and PPTDE. The polymer compositions were determined by ¹H-NMR spectroscopy. The characteristics of the PEKKs are shown in Table I. The GPC-average molecular weight (M_{GPC}), which was obtained from the peak position of the GPC curve, was used as a measure of the molecular weight (MW) of the PEKKs in this study, because the number-average MW (M_n) is highly sensitive to the presence of a small amount of lower MW materials.

The ternary BDM/DBA/DMBA (1.0/0.3/0.7) blend system was selected as a parent resin based

Table II Physical Properties of Modified Bismaleimide Resins

Entry No.	Modifiers				K_{IC} (MN/m ^{3/2})	n	Flexural Properties			
	No. ^a	Composition (mol %)	MW (10 ³)	Concn (wt %)			Strength ^b (MPa)	Modulus ^b (GPa)	n	T_g^c (°C)
Control ^d	—	—	—	—	0.90 ± 0.03	7	222 ± 5	4.35 ± 0.12	5	195
PPDE										
30	PPDE 101	—	18.4	15	0.94 ± 0.03	7	135 ± 7	4.06 ± 0.07	5	212, (254)
33	PPDE 102	—	26.4	15	0.94 ± 0.03	7	131 ± 11	4.21 ± 0.07	6	216
PPIDE										
28	PPIDE 101	IP 48	8.0	15	0.85 ± 0.05	5	166 ± 6	4.01 ± 0.05	6	(154), 197
27	PPIDE 102	IP 48	17.4	15	0.95 ± 0.02	6	147 ± 14	3.61 ± 0.08	5	(169), 197
26	PPIDE 102	IP 51	31.0	5	1.01 ± 0.02	7	189 ± 24	4.22 ± 0.06	5	197
24	PPIDE 104	IP 51	31.0	10	1.10 ± 0.03	6	158 ± 16	4.22 ± 0.12	5	(177), 200
25	PPIDE 104	IP 51	31.0	15	1.17 ± 0.02	8	160 ± 20	3.75 ± 0.08	5	(180), 203
PPTDE										
32	PPTDE 101	TP44	11.6	15	0.85 ± 0.03	6	135 ± 7	4.06 ± 0.07	5	(182), 203
35	PPTDE 102	TP44	23.4	5	1.09 ± 0.06	5	152 ± 11	3.87 ± 0.12	5	(192), 201
34	PPTDE 102	TP44	23.4	10	1.11 ± 0.02	6	164 ± 15	3.74 ± 0.07	5	(192), 207
31	PPTDE 102	TP44	23.4	15	1.21 ± 0.08	6	200 ± 8	4.32 ± 0.04	5	(188), 203
Matrimide 5292 ^d	—	—	—	—	0.62 ± 0.06	8	200 ± 6	4.02 ± 0.11	5	299

n , The number of specimens tested.

^a The entry and number in Table I.

^b The mean ± standard deviations.

^c By DSC. The values in parentheses are based on modifiers.

^d From a previous study.²

on information of the previous study.² Table II shows the representative results for the modification of the bismaleimide resin with PEKKs. Two T_g values for the modified resin were observed in many cases, based on the matrix and the modifier. The results indicated the existence of the phase-separation structure in the modified resins. The cured unmodified bismaleimide resin was transparent whereas the modified resins became translucent or opaque, depending on the PEKK structure, MW, and concentration. The PPDE-modified resins were translucent. The PPIDE-modified resins were opaque except for a translucent 5 wt % PPIDE-modified material. The PPTDE-modified resins were also opaque except for 5 wt % PPTDE inclusion (translucent).

Figure 1 shows the PEKK MW dependence of the mechanical and thermal properties for the modified resins with a 15 wt % inclusion. The PPDE was less effective as a modifier: the K_{IC} values and flexural moduli for the modified resins were comparable to those for the cured parent resin and their flexural strength decreased by blending the PPDE. When using PPIDE [51 mol % isophthaloyl (IP) units], the K_{IC} for the modified resin increased with the increasing MW of

the PPIDE while its flexural strength and modulus decreased on PPIDE inclusion. In the modification with PPTDE [44 mol % terephthaloyl (TP) units], PPTDE with a high MW (23,400) was an effective modifier: the K_{IC} increased 30% with no loss of flexural properties and T_g values. The 20 wt % inclusion of the same modifier was difficult to process because of an increase in viscosity at 130°C of the bismaleimide/PPTDE mixture before curing.

Figure 2 shows the mechanical and thermal properties of the modified resins as a function of the modifier concentration. The K_{IC} for the modified resins increased linearly with increasing PPIDE (51 mol % IP, MW 31,000) concentration and there was a deterioration in the flexural properties. When using PPTDE (44 mol % TP, MW 23,400), the K_{IC} for the modified resins also increased linearly with increasing PPTDE concentration, and the flexural properties were restored: the flexural strength and modulus for the modified resin were comparable to those for the unmodified bismaleimide resin on a 15 wt % inclusion of PPTDE. The T_g values for the modified resins were comparable to that for the unmodified bismaleimide resin.

Microstructure of Modified Resin

Figure 3 shows SEM micrographs of fracture surfaces for the unmodified and PPIDE-modified resins. The unmodified cured resin had one phase and was featureless [Fig. 3(a)]. Inclusion of PPIDE led to a two-phase morphology. When using 5 wt % PPIDE (51 mol % IP, MW 31,000), the modified resin had a particulate structure with ill-defined domains ($\ll 1\text{-}\mu\text{m}$ diameter) [Fig. 3(b)]. The use of 10 wt % of the same modifier also led to the particulate morphology of the modified resin [Fig. 3(c)]: the number and the diameter of the modifier-rich domains increased with increasing modifier concentration. When using 15 wt % of the same modifier, the modified resin had a cocontinuous phase structure, although the contour of the modifier-rich phase was slightly obscure [Fig.

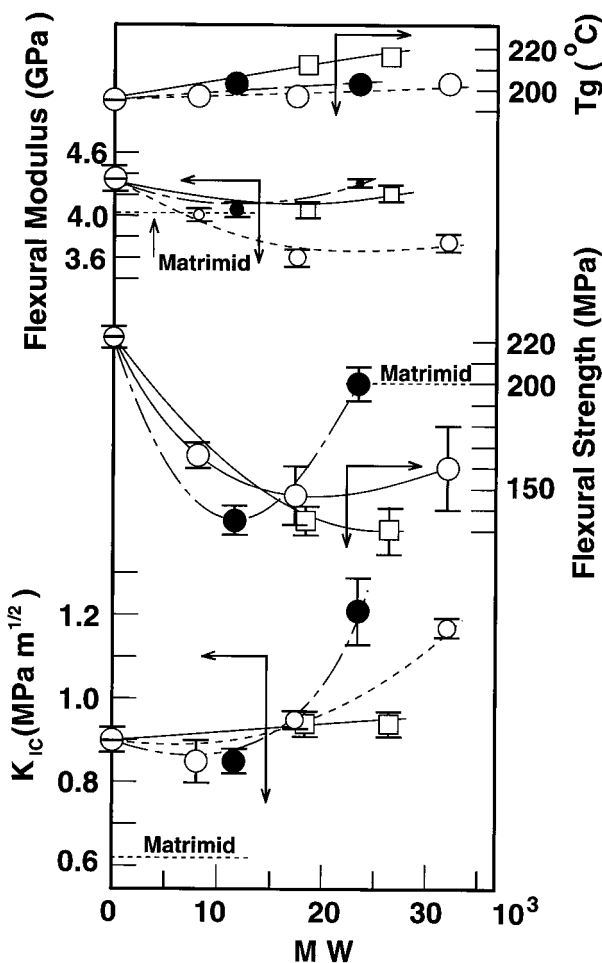


Figure 1 The dependence of the physical properties of the modified resins on the modifier molecular weight (15 wt % modifier): (\ominus) control, (\square) PPDE, (\circ) PPIDE (ca. 50 mol % IP), and (\bullet) PPTDE (44 mol % TP).

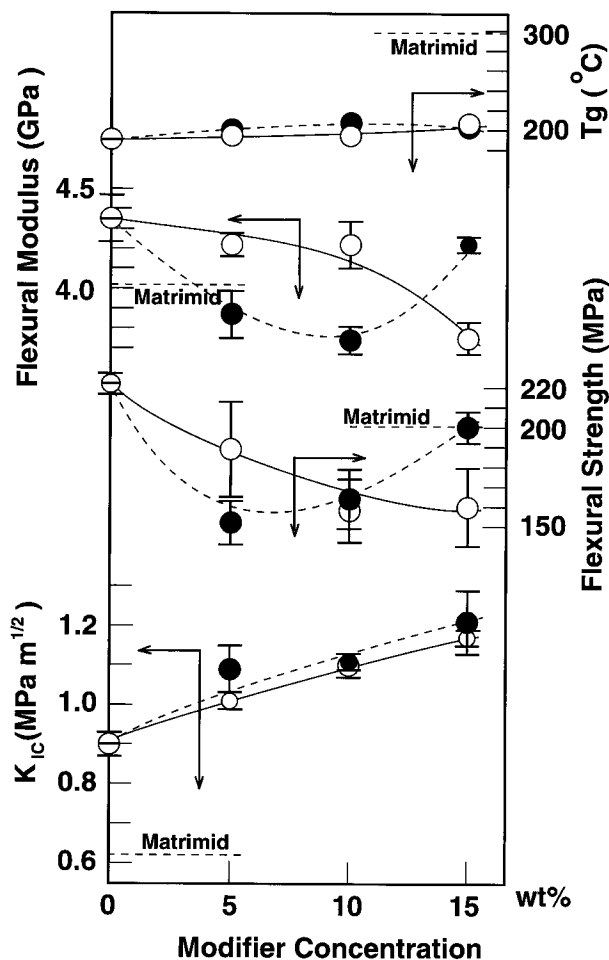


Figure 2 The physical properties of the modified resins as a function of the modifier concentration: (\ominus) control, (\circ) PPIDE (51 mol % IP, MW 31,000), and (\bullet) PPTDE (44 mol % TP, MW 23,400).

3(d): dark and flat phases were bismaleimide rich, and light and rough ones were a cluster of modifier particles. Figure 3(e) is the solvent-etched surface of the same resin (in dichloromethane for 5 days): the etched surface was rather obscure and the modifier-rich phase could not be etched out fully.

Figure 4 shows SEM micrographs of the PPTDE-modified resins. When using 15 wt % PPTDE (44 mol % TP, MW 11,600), the morphology of the modified resin was obscure [Fig. 4(a)], but the etched fracture surface showed it had a particulate structure with bimodal distribution of particle sizes [Fig. 4(b)]: larger particles (about $1\text{-}\mu\text{m}$ diameter) looked like clusters of smaller particles. On 10 wt % inclusion of PPTDE (44 mol % TP, MW 23,400), irregularly shaped domains were observed [Fig. 4(c)]. When using 15 wt % of the same modifier, a number of irregular domains

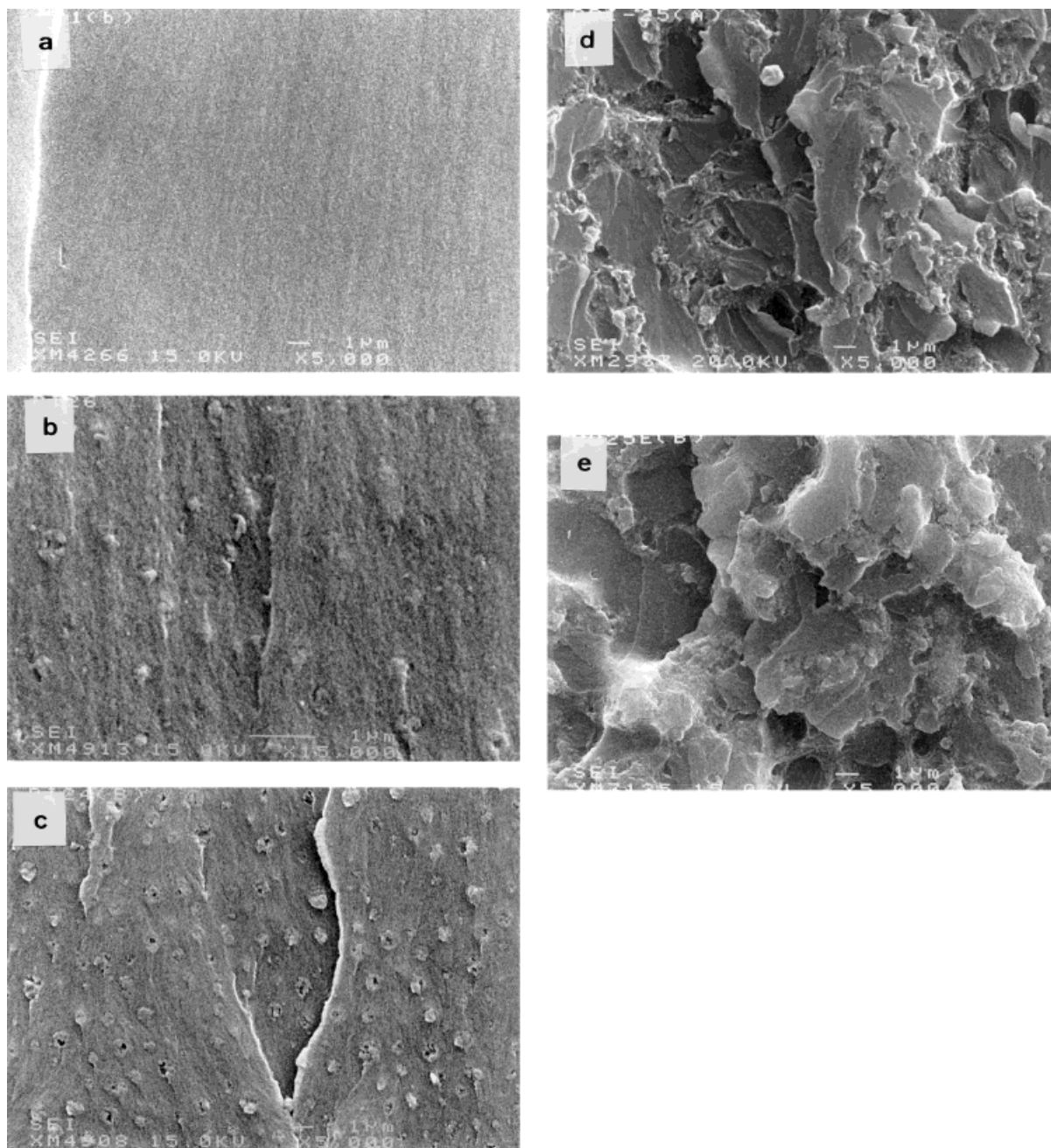


Figure 3 Scanning electron micrographs of the fracture surfaces for the PPIDE-modified resin with (a) 0 (control), (b) 5, (c) 10, (d) 15, and (e) 15 wt % (after etching) PPIDE (51 mol % IP, MW 31,000).

increased, their shape became larger, and the morphology of the modified resin became cocontinuous [Fig. 4(d)], but the PPTDE-rich domains were not etched out [Fig. 4(e)].

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 5 shows the storage modulus (G') and the damping (δ) curves for the unmodified and

PPIDE-modified resins. The peak position of the α relaxation in the $\tan \delta$ curve shifted gradually toward higher temperatures with increasing PPIDE concentration, compared with that of the cured parent resin. A new relaxation peak (α' relaxation) appeared at about 200°C as a shoulder and its magnitude became larger with increasing PPIDE concentration. The G' at room

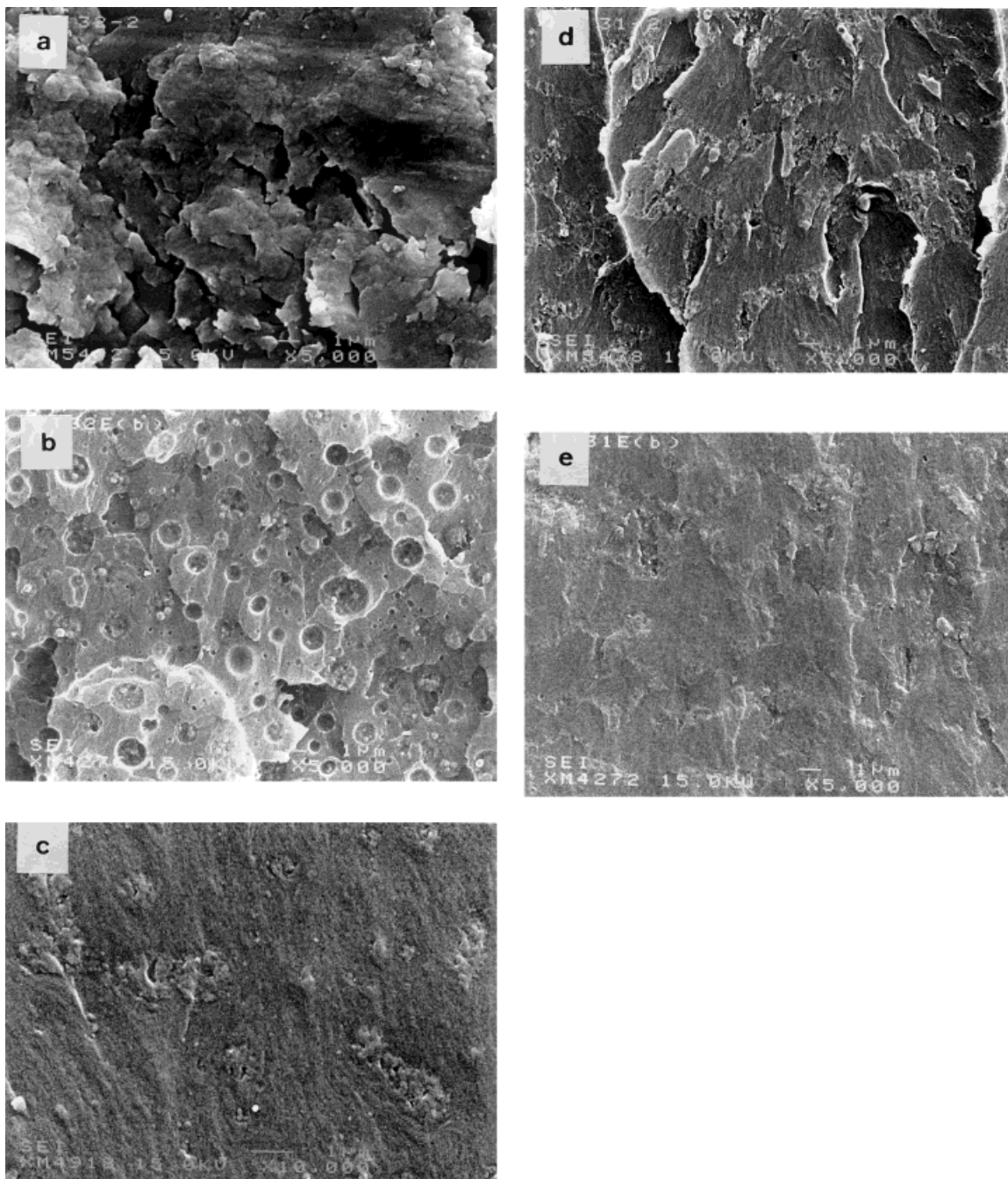


Figure 4 Scanning electron micrographs of the fracture surfaces for the PPTDE-modified resin with MWs and amounts of PPTDE (44 mol % IP) of (a) 11,600 and 15 wt %, (b) 11,600 and 15 wt % (after etching), (c) 23,400 and 10 wt %, (d) 23,400 and 15 wt %, and (e) 23,400 and 15 wt % (after etching).

temperature for the modified resins were smaller than that for the unmodified resin.

Figure 6 shows the G' and the $\tan \delta$ curves for the unmodified and PPTDE-modified resins with a 15 wt % inclusion. The peak position of the α relaxation shifted slightly toward a higher temperature

on the inclusion of PPTDE. When using PPTDE (44 mol % TP, MW 11,600), the α' -relaxation peak appeared at about 200°C as a shoulder. A 15 wt % inclusion of PPTDE (44 mol % TP, MW 23,400) caused the α -relaxation peak to become broader and the α' -relaxation peak could not be distinguished,

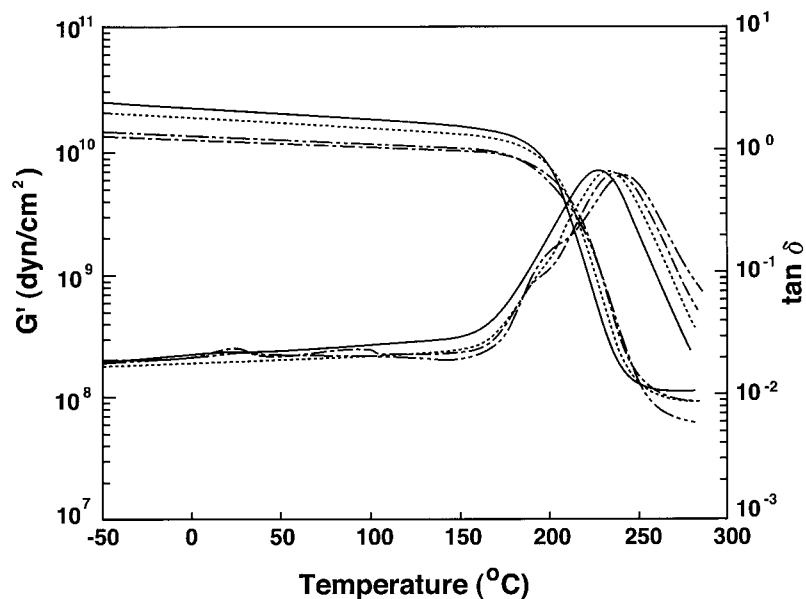


Figure 5 The dynamic viscoelastic analysis for unmodified and PPIDE-modified resins with (—) 0 (control), (---) 5, (- - -) 10, and (· · · ·) 15 wt % with PPIDE (51 mol % IP, MW 31,000).

perhaps because of overlapping of the α relaxation and the α' -relaxation peaks, although the modified resin had the cocontinuous phase structure as observed by SEM [Fig. 4(d)]. The storage moduli at room temperature for the modified resins were smaller than that for the unmodified resin.

DISCUSSION

The PPDE and related copolymers were soluble in the three-component bismaleimide resin without solvents. The PPIDE (51 mol % IP) and PPTDE (44 mol % TP) were more effective as modifiers

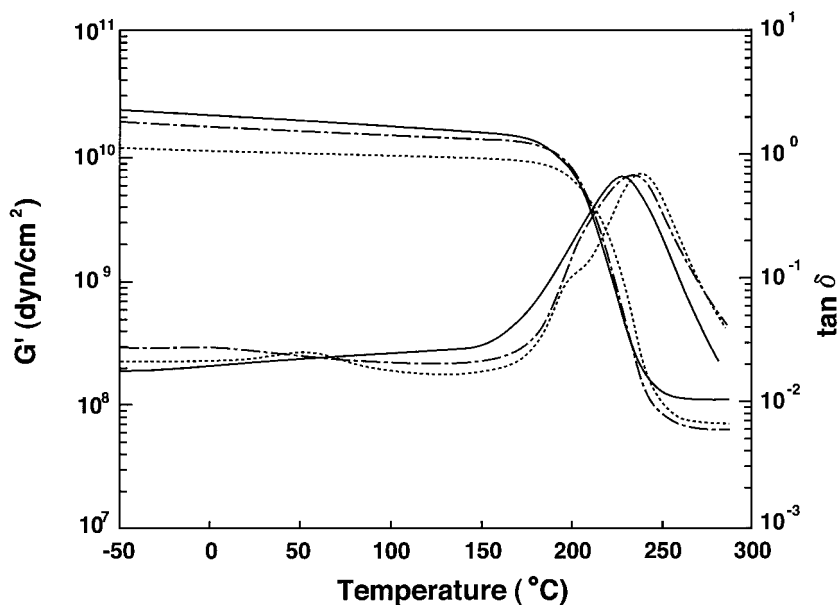


Figure 6 The dynamic viscoelastic analysis for unmodified and PPTDE-modified resins with 15 wt % PPTDE. The MWs of PPTDE (44 mol % TP) were (—) control, (---) 11,600, and (- - -) 23,400.

than was PPDE. When using 15 wt % of PPTDE (44 mol % TP, MW 23,400), the K_{IC} value for the modified resin was increased by 30% at no expense of the mechanical and thermal properties, compared with that for the cured parent material: the K_{IC} increased 95% compared with the value for the cured Matrimid resin.

In the modification of the Matrimid resin (the two-component bismaleimide resin composed of BDM and DBA) by PPDE and related copolymers the morphologies of the modified resins changed from particulate to cocontinuous phase or to phase-inverted structures, depending on the modifier structure and content.²⁶ The PPDE-modified resins had particulate structures. The morphologies of the PPIDE-modified resins changed from particulate to cocontinuous or phase-inverted structures with increasing PPIDE MW and content. The PPIDE (50 mol % IP) was more effective as a modifier than were PPDE and PPTDE (50 mol % TP). The toughness improvement was achieved because of the cocontinuous phase or phase-inverted structures. It is noteworthy that the formation of interpenetrating polymer networks (IPNs) was evidenced by high-resolution SEM with a field emission gun (FE-SEM) in the modification of the Matrimid resin by PPIDE (50 mol % IP, MW 21,800); the solvent resistance of the modified resin was also improved.

In the advanced two-component bismaleimide resin the selection of the comonomer is essential to improve the brittleness of the cured resin. The previous article examined several kinds of (meth)allyl compounds as the third component to improve the brittleness of the cured Matrimid resin.² In the curing of the Matrimid resin the ene reaction of the BDM and DBA monomers proceeds slowly in the 100–200°C range and the principle cure reaction occurs in the 200–300°C range, including the rapid ene reaction, homopolymerization of both BDM and the ene product, crosslinking by the Diels–Alder reaction of the ene product and maleimide groups of BDM, and dehydration of the phenolic hydroxyl groups.^{27–29} In the ternary blends of BDM/DBA/DMBA the mechanical and thermal properties of the cured resins were examined as a function of the resin compositions. The Diels–Alder reaction of the ene product and DMBA (methallyl component) was suppressed because of steric hindrance, compared with that of the ene product and DBA (allyl component).^{2,30} Therefore, the T_g values for the cured resins decreased with increasing DMBA content. This indicated that the crosslink density of the

network decreased because of the lower Diels–Alder reactivities of the methallylic groups in DMBA than those of the allylic groups in DBA. Despite the decrease in the T_g , the flexural strength and modulus of the cured resins were comparable to the values of the cured Matrimid resin (Table II).

The decrease in the crosslink density of the networks may act as a favorable factor for improving the toughness of the matrix in the modification by thermoplastics, because loosely crosslinked networks tend to induce plastic deformation of the matrix near propagating cracks during fracturing based on phase-separated thermoplastics. Hence, the ternary blend of BDM/DBA/DMBA (1.0/0.3/0.7) was used as the resin composition in place of the Matrimid resin in this study to enhance the toughness of the matrix by blending it with PPDE and related copolymers. In the modification by PPIDE (51 mol % IP, MW 31,000) the K_{IC} values increased, and the flexural strength and modulus decreased gradually with PPIDE concentration (Fig. 2); the morphologies of the modified resins changed from particulate to cocontinuous phase structures [Fig. 3(b–e)]. The modification behavior by PPTDE was different from that by PPIDE. When using 5 or 10 wt % of PPTDE (44 mol % TP, MW 23,400), the flexural strength and modulus for the modified resin decreased significantly, although the modified resins had two-phase morphologies with modifier-rich domains [Fig. 4(c)]. A similar decrease in the flexural strength and modulus for the modified resin having the particulate structure was also observed on 15 wt % inclusion of lower MW (11,600) PPTDE (44 mol % TP) [Figs. 1, and 4(b)]. In the previous results on the modification of the Matrimid resin by PPDE and related copolymers,²⁶ the flexural strength and modulus for the modified resins with particulate structures were not deteriorated, although the particulate structure was unsuitable to improve the brittleness. It is not clear why the flexural properties for the PPTDE-modified resins deteriorated in the present modification, despite their two-phase morphologies with the modifier-rich domains dispersed in the bismaleimide matrix. When using 15 wt % of PPTDE (44 mol % TP, MW 23,400), the K_{IC} value for the modified resin increased 30% and its flexural properties were restored compared with those of the unmodified resin, and the modified resin had a cocontinuous phase structure [Fig. 4(d)]. The PPTDE (44 mol % TP, MW 23,400) was the most effective modifier in the modification of the three-component bismaleim-

ide resin, and its 15 wt % inclusion led to an increase in toughness at no loss of the flexural properties. The toughness improvement could be achieved because of the cocontinuous phase structure in both the PPIDE and PPTDE modification systems. Furthermore, the cocontinuous phase could not be etched out fully by immersion in dichloromethane. Such high solvent resistance may have been because of the formation of IPNs, considering the previous results in the modification of the Matrimid resin by PPIDE.²⁶ The fracture toughness enhancement would be partly because of the improvement in the interfacial adhesion by the IPN structure.

However, it is doubtful whether the decrease in crosslink density might act favorably to improve the brittleness of the matrix, because the extent of toughness enhancement in the present three-component bismaleimide resin was unexpectedly small compared to the modification results of the higher crosslinked Matrimid resin by PPIDE.²⁶ In many cases the fracture toughness enhancement can be achieved because of the continuous phase or phase-inverted structures in the modification of highly crosslinked networks by the engineering thermoplastics, where some increase in plastic deformation based on some decrease in the crosslink density might be less effective to improve the brittleness of the modified resins.

CONCLUSION

The PEKKs were effective modifiers for the three-component bismaleimide resin composed of BDM, DBA, and DMBA (1.0/0.3/0.7). PPIDE (51 mol % IP) and PPTDE (44 mol % TP) were more effective as modifiers than was PPDE. Toughness improvement was achieved because of the cocontinuous phase structure in both the PPIDE and PPTDE modification systems. When using 15 wt % of PPTDE (44 mol % TP, MW 23,400), the K_{IC} value for the modified resin increased 30% at no expense of the mechanical and thermal properties compared to that for the cured parent material: the K_{IC} increased 95% compared to the value for the cured Matrimid 5292 resin.

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