

Modification of Cyanate Ester Resin by Soluble Polyimides

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ABSTRACT: Soluble polyimides (PIs) were prepared as random or multiblock types with 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) as acid dianhydride components and 4,4'-bis(*m*-aminophenoxy) diphenyl sulfone (*m*-BAPS) as a diamine component by a one-pot process and used to improve the brittleness of the cyanate ester resin. Random-type PIs were more effective as modifiers than multiblock-type PIs. The morphologies of the modified resins depended on PI structure, molecular weight, and concentration. The most effective modification of the cyanate ester resin was attained because of a heterogeneous phase structure composed of a flat matrix phase and phase-inverted structures of the modified resin; a 15 wt % inclusion

of a random PI (weight-average molecular weight = 63,400) composed of 6FDA, *s*-BPDA, and *m*-BAPS (0.5/0.5/1.0 molar ratio) led to a 65% increase in the fracture toughness for the modified resin with a slight loss of flexural strength and a retention of flexural modulus and glass-transition temperature, compared with the values for the unmodified resin. Water absorptivity of the modified resin was comparable to that of the unmodified resin up to 400 h, and then, water absorption of the modified resins increased considerably. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1–11, 2003

Key words: modification; polyimides; fracture; morphology

INTRODUCTION

Cyanate ester resins are among the most important thermosetting polymers and have received attention because of their outstanding physical properties and low water absorptivity.¹ In general, the drawback of the thermosets is that they are brittle. The toughening of epoxies has been increased with a reduction in the mechanical and thermal properties by blending with reactive rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers² and epoxide-containing acrylic elastomers.³ Furthermore, reactive rubbers are rather less effective modifiers for the highly crosslinked epoxies.³ Recently, modifications of thermosets with engineering thermoplastics have been studied as alternatives to reactive rubber toughening from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Engineering thermoplastics that have been examined as modifiers for the cyanate ester resin include poly(ether imide),^{4,5} polysulfone,^{4–7} poly(ether sulfone),^{6,7} polyarylate,⁴ poly(ether ketone ketone),^{7,8} and phenol phthalein-based poly(arylene ethers).⁹

Modification of the cyanate ester resin has been carried out on the basis of information on the toughening of epoxy and bismaleimide resins by thermo-

plastics such as aromatic polyesters and *N*-phenylmaleimide–styrene copolymer (PMS) in our laboratory.^{10–18} Recently, we reported on poly(ethylene phthalate) and related copolyesters as effective modifiers for cyanate ester resin.¹⁹ PMS and related copolymers were also effective modifiers for the cyanate ester resin.^{20,21}

Poly(ether imide) (PEI; Ultem 1000, GE) was used as an effective toughener for epoxy^{22–24} and bismaleimide resins.²⁵ PEI was also used as a modifier for cyanate ester resin,^{4,5} but other polyimides (PIs) have hardly ever been used as modifiers for cyanate ester resin. Recently, modification of the cyanate ester resin by a soluble benzophenone-type PI containing an indan moiety was reported shortly as technical data.²⁶ This article reports on the modification of the cyanate ester resin by soluble PIs. The soluble PIs, random or multiblock type, were prepared from the reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) as acid dianhydride components and 4,4'-bis(*m*-aminophenoxy) diphenyl sulfone (*m*-BAPS) as a diamine component. The effects of structure, molecular weight (MW), and amount of the PIs on the toughness of the cured resins were examined.

EXPERIMENTAL

Materials

The cyanate ester resin was a commercial, bisphenol-A type material (AroCy B 10, melting temperature

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= 79°C, Ciba Geigy Corp., Fribourg, Switzerland). Other reagents were used as received.

Measurements

IR spectra were measured with a Shimadzu Fourier transform infrared type 4000 spectrophotometer (Shimadzu Seisakusho Co., Kyoto, Japan). $^1\text{H-NMR}$ spectra were recorded on a 90-MHz instrument (Jeol, JNM-9MX 90, Tokyo, Japan) at 60°C with CDCl_3 as solvent and tetramethylsilane as internal standard. The MWs of the PIs were measured by gel permeation chromatography (GPC) with an instrument equipped with an ultraviolet detector (Tosoh HLC-802UR instrument, Tokyo, Japan) with polystyrene standards: dimethylformamide elution solvent containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L), and a flow rate at 0.8 mL/min at room temperature. The mechanical properties of the cured resins were determined with a Shimadzu autograph AGS-500B universal testing machine (Shimadzu). 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 at a crosshead speed of 1 mm/min (ASTM E-399). The glass-transition temperatures (T_g 's) of the modifiers were measured as the onset temperatures by differential scanning calorimetry (DSC; Shimadzu DSC 60 type) at a heating rate of 10°C/min under nitrogen (50 mL/min). The T_g values of the cured resins were obtained by dynamic viscoelastic analysis performed with a Rheometrics RDS-II type instrument (Rheometrics Co., Tokyo, Japan) at -50 to 350°C at a heating rate of 5°C/min at a frequency of 1 Hz under nitrogen purge. Scanning electron micrographs (SEMs) were taken with a combined microanalyzer (Jeol, JXA-8900RL) with failed specimens in the K_{IC} tests.

Preparation of soluble PIs

PI was prepared by the reaction of aromatic acid dianhydride and aromatic diamine according to a reported procedure.²⁷ The typical procedure for the preparation of random-type polyimide was as follows.

6FDA [31.16 g (70.0 mmol)], *s*-BPDA [20.60 g (70.0 mmol)], *m*-BAPS [61.76 g (142.8 mmol)], and *N*-methylpyrrolidone (NMP; 435 g) were charged into a 1-L separable flask fitted with a stainless-steel anchor agitator, a Dean-Stark trap, a nitrogen inlet, and a thermometer, where the clean reaction mixtures were obtained as about a 20 wt % solution. Then, a catalyst composed of γ -valerolactone [2.80 g (28 mmol)], pyridine [4.43 g (56 mmol)], and toluene (40 g) was added. The polymerization was carried out at 180°C for 8 h by removal of the resulting water by azeotropic distillation under a stream of nitrogen. Afterward, phthalic anhydride [PA; 4.15 g (28 mmol)] was added, and the

rest of the reaction was performed at 180°C for 5 h to cap terminal amino groups. After the polymerization was complete, the polymer was isolated with methanol as a precipitant. The polymer was dried *in vacuo* at 100°C. The polymer was purified twice by reprecipitation with NMP/methanol and dried *in vacuo* at 100°C {yield = 96.5%, weight-average molecular weight [M_w] = 63,400, polydispersity [M_w /number-average molecular weight (M_n)] 1.87}.

Multiblock-type PIs were prepared via two steps. The typical procedure was as follows.

In the first step, a 1-L separable flask was charged with 6FDA [13.33 g (30.0 mmol)], *m*-BAPS [10.81 g (25.0 mmol)], NMP (92.27 g), toluene (30 g), γ -valerolactone [1.20 g (12 mmol)], and pyridine [1.20 g (15 mmol)]. The polymerization was carried out at 180°C for 2 h; the M_w value of the resulting polymer was 12,500 and its M_w/M_n was 1.47 at this step. In the second step, further polymerization was done at 180°C for 5 h, without isolation of the resulting polymer, after the further addition of *s*-BPDA [8.83 g (30.0 mmol)], *m*-BAPS [15.66 g (36.5 mmol)], NMP (93.61 g), and toluene (10 g). After the polymerization was complete, PA [1.77 g (12 mmol)] was added, and the remaining reaction was done at 180°C for 5 h to cap terminal amino groups. The final resulting polymer was isolated and purified according to similar procedures for the preparation of random-type PIs (yield = 98.2%, $M_w = 29,600$, $M_w/M_n = 1.84$).

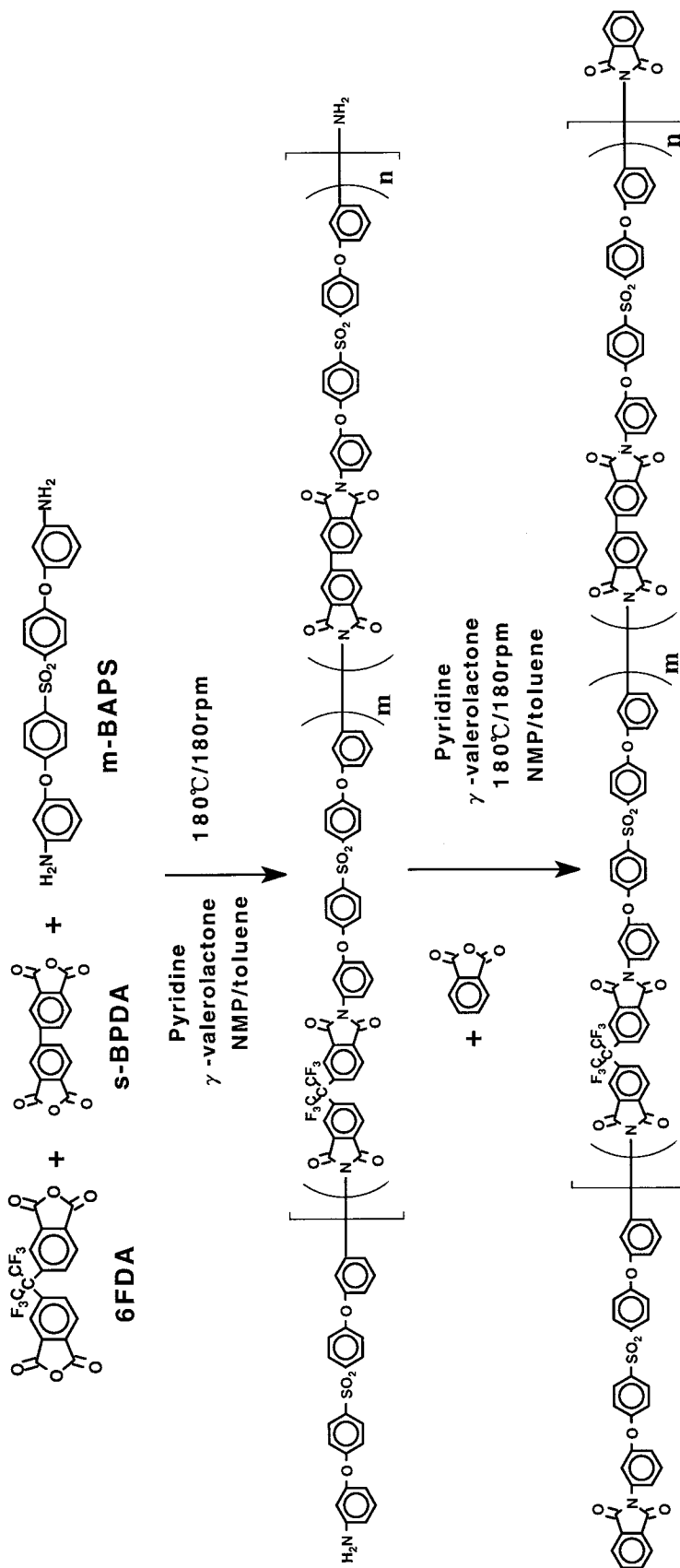
Curing procedure

PI was dissolved into the cyanate ester resin at 100–135°C without solvents, and the resulting clean mixture was degassed *in vacuo* for 15 min. The mixture was poured into a mold, preheated at 100°C, to obtain a 7-mm thick plaque. The mold consisted of one pair of upright stainless plates spaced by a *U*-shaped silicon rubber stick (8 mm). The amount (wt %) of the modifier was calculated on the basis of the matrix resin. The curing cycle was 177°C/3 h + 200°C/4 h + 250°C/4 h. After curing, the oven temperature was decreased from 250 to 50°C at a cooling rate of 25°C/h.

RESULTS

Preparation of soluble PIs

In this study, random-type PIs having various structure and MWs were prepared in quantitative yield by the one-pot process with 6FDA and *s*-BPDA as acid dianhydride components and *m*-BAPS as an aromatic diamine component in the presence of catalysts composed of γ -valerolactone and pyridine. The preparation procedure of random PIs is shown in Scheme 1. In general, PIs had amino groups as part of their terminal groups. The existence of the amino groups led to



Scheme 1 Preparation of random PI.

TABLE I
Preparation and Characterization of PIs

Entry	Feed composition (molar ratio)				Reaction time (h)		Yield (%)	M_w^b (10^4)	M_w/M_n	T_g^c ($^{\circ}\text{C}$)
	6FDA	s-BPDA	m-BAPS	PA	Polymer ^a	Capping				
Random-type series										
PI 103	0.8	0.2	1.025	0.55	2.0	8.0	77.7	1.65	1.64	207
PI 104	0.5	0.5	1.025	0.25	4.0	5.0	94.8	3.22	1.78	223
PI 107	0.5	0.5	1.025	0.25	6.5	5.0	93.7	4.40	1.73	228
PI 106	0.5	0.5	1.02	0.20	8.0	5.0	96.5	6.34	1.87	229
PI 109	0.45	0.55	1.02	0.20	8.0	5.0	91.5	4.44	2.18	228
PI 110	0.45	0.55	1.02	0.20	13.0	5.0	94.4	5.30	1.69	229
PI 108	0.4	0.6	1.02	0.20	8.0	5.0	94.6	5.06	1.95	232
Multiblock-type series										
PI 116	0.5	0.5	1.02	0.20	2.0/5.0	5.0	98.2	2.96	1.84	221
PI 117	0.5	0.5	1.02	0.20	2.0/9.0	5.0	94.6	6.24	2.07	224
PI 120	0.45	0.55	1.02	0.20	2.0/8.0	5.0	93.1	2.65	2.07	230
PI 119	0.45	0.55	1.02	0.20	2.0/8.0	5.0	95.0	3.16	2.23	229
PI 121	0.45	0.55	1.02	0.20	2.0/9.0	5.0	92.4	4.11	2.17	234
PI 118	0.4	0.6	1.02	0.20	2.0/8.0	5.0	94.6	4.12	3.04	234

^a First/second runs.

^b By GPC.

^c By DSC.

increase the viscosity of the uncured blend of the cyanate ester resin and PI at elevated temperatures because of the partial reaction of cyanate and amino groups. Hence, the PIs used here were prepared in a slight excess of *m*-BAPS, and its terminal amino groups were capped by PA. Table I reports some characteristic properties of random-type PI. The M_w was used as a measure of the MW. Miscibility of PI with uncured thermosets is one of the most important properties, when it is used as a modifier. PIs having various compositions, therefore, were prepared by control of the feed compositions of 6FDA and *s*-BPDA. The chain sequence obtained from 6FDA and *m*-BAPS was a soluble fraction of PI, and that from *s*-BPDA and *m*-BAPS was an insoluble one.

The conventional procedure of PI preparation proceeds via poly(amic acids) to result in random copolymers, but it is impossible use to prepare block-type PI because of the transamidation of poly(amic acids). Multiblock-type PIs were prepared via two steps by the method described in some detail in the Experimental section (Scheme 2). Characteristic properties of multiblock-type PIs are also shown in Table I. The T_g values of PIs used here were independent of their structure, composition, and MW.

Various kinds of PIs were used as modifiers in this study and are abbreviated as follows in this example: rPI-8-2 and bPI-5-5 represent a random-type PI having 6-FDA and *s*-BPDA units (8 : 2 molar ratio) as aromatic dianhydride components and a multiblock-type PI having 6-FDA and *s*-BPDA units (5 : 5 molar ratio), respectively.

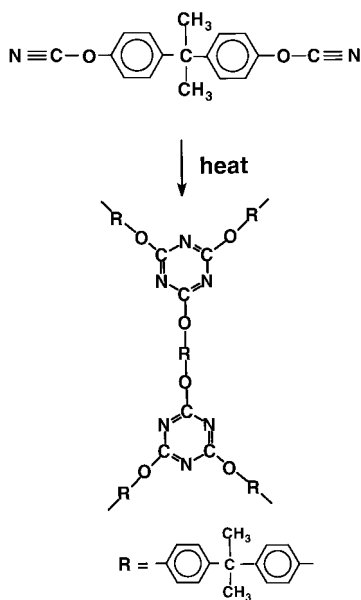
Modification of cyanate ester resin by PI

The curing reaction of the cyanate ester resin was a cyclotrimerization of the cyanate groups to form highly crosslinked polycyanurate networks in the absence or presence of the catalyst (Scheme 3).

The PIs used here were soluble in the cyanate ester resin at elevated temperatures of more than 100 $^{\circ}\text{C}$. The curing of the cyanate ester resin was carried out in the absence of the catalyst in this study, the curing behavior was examined by DSC, and the curing conditions were determined. The extent of reaction of the cyanate group was examined by IR spectroscopy with the C—H stretching band at 2983 cm^{-1} as a reference band and the C—N stretching band at 2273 cm^{-1} as the cyanate group. The degree of curing (97.5%) in the absence of the catalyst was comparable to that (97.2%) in the presence of the catalyst (2 phr) composed of copper naphthenate (8 wt % Cu^{2+}) and *p*-nonyl phenol (8.5/91.5 wt %).¹⁹

The unmodified cyanate ester resin was transparent as reported previously.¹⁹ The modified resin was transparent on the rPI-8-2 10 wt % inclusion because rPI-8-2 had high miscibility with the cyanate ester resin. The modified resins became translucent on inclusion of rPI-5-5 in every case, independent of MW and concentration of the modifier. The use of rPI-4.5-5.5 or rPT-4-6 also led to translucent cured materials. Table II shows representative results for the modification of the cyanate ester resin with a random-type PI: rPI-8-2 was less effective for improving the brittleness of the cyanate ester resin than were the others.

Figure 1 shows the physical properties of the modified resin as a function of random-type PI concentra-



Scheme 3 Cyclotrimerization of cyanate esters.

tion. K_{IC} for the modified resins increased with increasing rPI-5-5 ($M_w = 63,400$) concentration; the K_{IC} value increased by 65% on 15 wt % inclusion. Flexural strength for the modified resins decreased, and their moduli increased with increasing modifier concentration, compared with the values for the unmodified resin. The T_g values for the modified resins were comparable to that for the unmodified resin. When 15 wt

% rPI-4.5-5.5 ($M_w = 53,000$) was used, toughness enhancement of the modified resin was rather low, but the K_{IC} for the modified resin increased 60% on 17.5 wt % inclusion of the same modifier with no loss of flexural strength or modulus and a slight loss in T_g compared to those for the unmodified resin. Because rPI-4-6 with a higher BPDA unit had lower miscibility with the cyanate ester resin, the test specimen of the cured resin could not be prepared on 15 wt % inclusion.

Figure 2 shows the dependence of physical properties of the modified resins on the PI MW on 15 wt % inclusion. In the modification of the cyanate ester resin with random-type PI, rPI-5-5 with moderate MW was less effective. When rPI-5-5 with a higher MW ($M_w = 63,400$) was used, the K_{IC} for the modified resin increased abruptly. Flexural strength for the modified resins decreased on inclusion of rPI-5-5, and their moduli increased with increasing rPI-5-5 MW. In the modification with multiblock-type PI, the K_{IC} for the modified resin was independent of PI MW in this MW range. The K_{IC} value for the modified resin increased 40% on 15 wt % inclusion of bPI-5-5 ($M_w = 62,400$). Flexural strength for the modified resins decreased, and their moduli increased slightly on the multiblock PI inclusion. The T_g values for the modified resins were comparable to that for the unmodified resin in every case. The efficiency as a modifier of the random PIs was greater than that of the multiblock PIs.

TABLE II
Physical Properties of Modified Cyanate Ester Resins

Entry	PI				K_{IC} (MPam ^{1/2})	n^b	Flexural properties			
	No. ^a	6FDA/ <i>s</i> -BPDA (mol/mol)	M_w (10 ⁴)	Concentration (wt %)			Strength (MPa)	Modulus (GPa)	n^b	T_g^c (°C)
Control	—	—	—	—	0.61 ± 0.02	8	181 ± 5	3.09 ± 0.07	7	323
Random-type PI series										
CPI03	PI 103	0.8/0.2	1.65	10	0.68 ± 0.02	7	151 ± 10	2.98 ± 0.09	5	—
CPI06	PI 104	0.5/0.5	3.22	15	0.77 ± 0.03	7	133 ± 14	3.23 ± 0.13	7	303
CPI08	PI 107	0.5/0.5	4.40	15	0.75 ± 0.02	8	139 ± 14	3.25 ± 0.06	5	312
CPI15	PI 107	0.5/0.5	4.40	17.5	0.92 ± 0.05	5	159 ± 13	3.37 ± 0.12	5	—
CPI09	PI 106	0.5/0.5	6.34	10	0.77 ± 0.05	6	143 ± 10	3.22 ± 0.09	5	315
CPI07	PI 106	0.5/0.5	6.34	15	1.01 ± 0.10	8	144 ± 9	3.51 ± 0.14	5	315
CPI13	PI 109	0.45/0.55	4.44	15	0.82 ± 0.05	8	173 ± 8	3.36 ± 0.06	7	—
CPI14	PI 110	0.45/0.55	5.30	15	0.79 ± 0.04	6	162 ± 13	3.29 ± 0.05	6	—
CPI16	PI 110	0.45/0.55	5.30	17.5	0.98 ± 0.10	7	170 ± 11	3.25 ± 0.06	5	303
CPI12	PI 108	0.4/0.6	5.06	10	0.86 ± 0.06	6	140 ± 25	3.21 ± 0.08	7	303
Multiblock-type PI series										
CPI20	PI 116	0.5/0.5	2.96	15	0.85 ± 0.04	6	135 ± 16	3.23 ± 0.09	7	311
CPI21	PI 117	0.5/0.5	6.24	15	0.85 ± 0.02	7	156 ± 13	3.28 ± 0.08	7	308
CPI24	PI 120	0.45/0.55	2.65	15	0.77 ± 0.06	6	138 ± 17	3.25 ± 0.05	5	—
CPI25	PI 121	0.45/0.55	4.11	15	0.89 ± 0.03	7	126 ± 10	3.20 ± 0.07	6	—
CPI23	PI 118	0.4/0.6	4.12	10	0.78 ± 0.04	5	136 ± 18	3.09 ± 0.05	5	306

The ± x values show standard deviation.

^a Entry number in Table I.

^b Number of specimens tested.

^c By dynamic viscoelastic analysis.

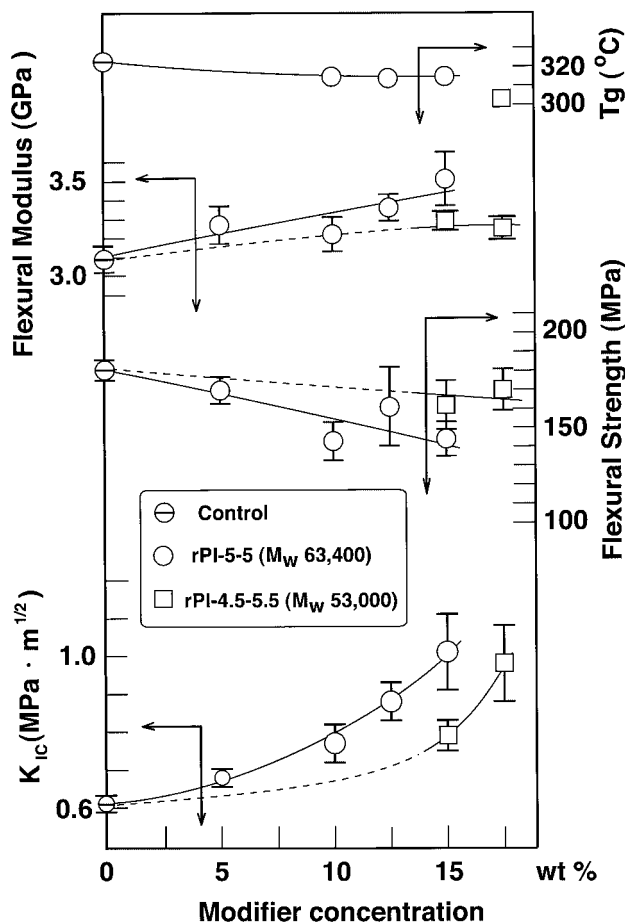


Figure 1 Physical properties of the modified resins as function of random-type PI concentration.

Microstructures of modified cyanate ester resins

Morphologies of the cured resins were investigated by the use of SEMs. Figure 3 shows the SEMs for the modified resins. The unmodified cured cyanate ester resins had only one phase, as reported previously.¹⁹ When 15 wt % rPI-5-5 ($M_w = 44,000$) was used, the fracture surface was ridgy, and PI-rich domains (about 1–3 μm in diameter) were observed, the domains were clusters of small particles, and their contours were obscure [Fig. 3(a,b)]. The modified resin had heterogeneous phase morphology composed of a flat matrix phase and phase-inverted structures on 15 wt % inclusion of rPI-5-5 [$M_w = 63,400$; Fig. 3(c,d)]. In the modification with 17.5 wt % inclusion of rPT-4.5-5.5 ($M_w = 53,000$), the morphology of the modified resin was a cocontinuous phase structure [Fig. 3(e)]. When 15 wt % bPI-5-5 ($M_w = 29,600$) was used, the modified resin also had a particulate structure with PI-rich domains [on the order of 1 μm or more in diameter; Fig. 4(a)]. The fracture surface of the modified resin was obscure when 15 wt % bPI-5-5 [$M_w = 62,400$; Fig. 4(b)] was used, but a cocontinuous phase morphology was observed in the etched-fracture surface (etched in NMP for 3 days; Fig. 4(c)).

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 5 shows the storage moduli and $\tan \delta$ curves for the unmodified and PI-modified resins. The α -relaxation in the $\tan \delta$ curve was observed at 323°C for the unmodified resin. In the use of 15 wt % rPI-5-5 ($M_w = 63,400$), the peak position (315°C) of the α -relaxation shifted slightly toward lower temperatures, and a new relaxation peak (α' -relaxation) was observed at 263°C, compared to the dynamic viscoelastic behavior for the cured cyanate ester resin. When 15 wt % bPI-5-5 ($M_w = 62,400$) was used, the α -relaxation peak (308°C) shifted further toward lower temperatures, and the α' -relaxation peak appeared at about 267°C as a shoulder peak. The existence of the α' -relaxation peak indicated the presence of a phase separation structure in the modified resin. The α' -relaxation peak of random PI-modified resin was differentiated from the α -relaxation peak, but that of multiblock PI-modified resin was observed as the shoulder peak. Furthermore, the α -relaxation peak position for the multiblock PI-modified resin shifted toward lower temperature than that for the random-type-PI-modified material. These re-

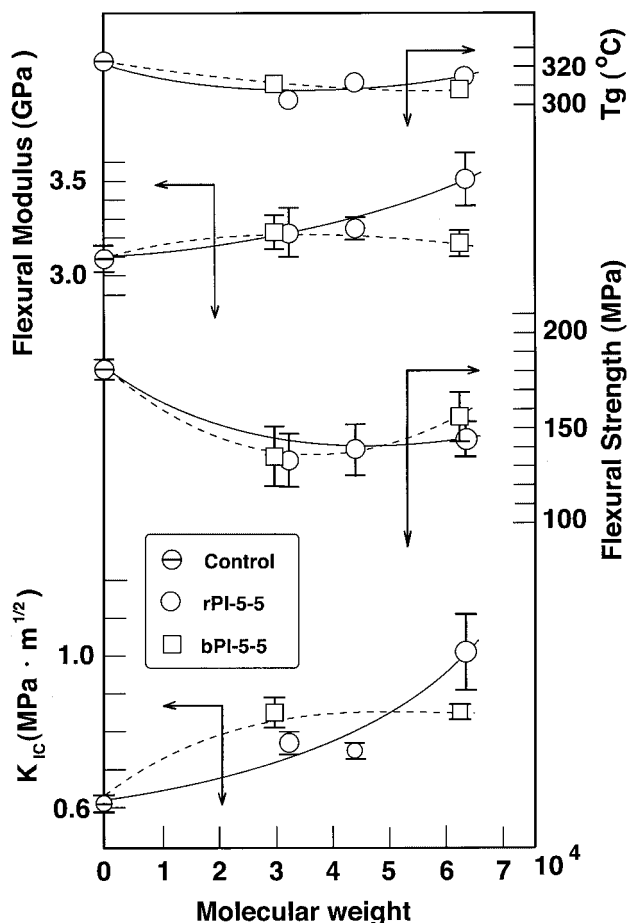


Figure 2 Dependence of mechanical properties of the modified resins on the modifier MW (15 wt % inclusion of the modifier).

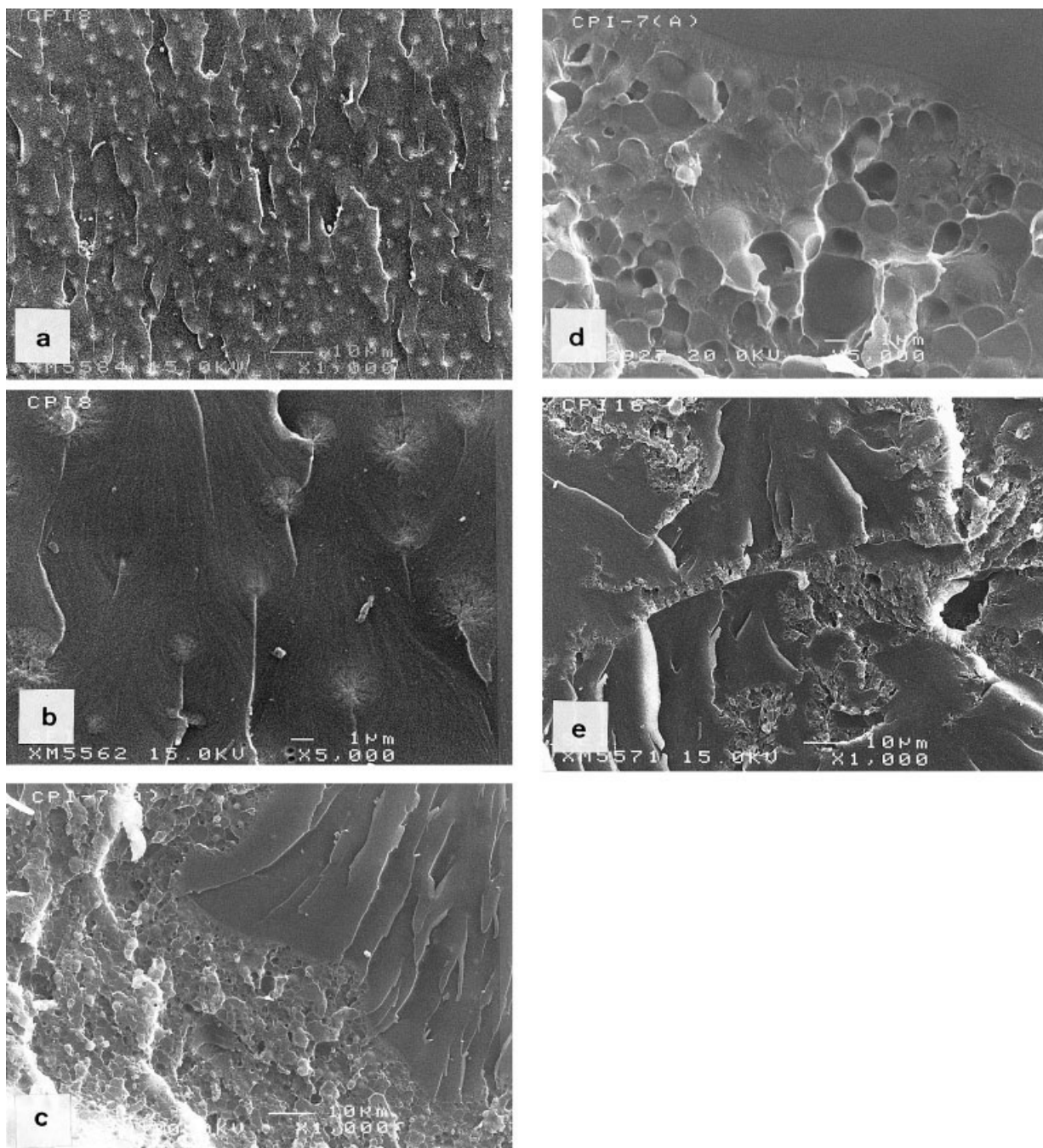


Figure 3 SEMs of the fracture surfaces for the rPI-modified resins: (a) and (b) rPI-5-5 ($M_w = 44,000$) 15 wt %, (c) and (d) rPI-5-5 ($M_w = 63,400$) 15 wt %, and (e) rPI-4.5-5.5 ($M_w = 53,000$) 17.5 wt % inclusions.

sults reveal that the multiblock-type PI had a higher miscibility with the cyanate ester resin than did the random-type PI. These behaviors also corresponded to morphologies of the respective modified resins [Figs. 3(e) and 4(c)].

Water absorptivity of the modified resin

One of the characteristics of the cured cyanate ester resin was its low water absorptivity. Water absorption

tests were carried out by immersion of the cured resins in boiling water to examine the influence of the modifier inclusion. Figure 6 shows water absorptivity of the cured resins in the modification with rPI-5-5 ($M_w = 63,400$) and bPI-5-5 ($M_w = 62,400$), with 15 wt % inclusion. Water absorption of the unmodified resin increased with time and then leveled off at less than 3.5 wt % water gain. The water gain of the unmodified resin used here was greater than that (2.5 wt %) of the unmodified materials prepared in the presence of the

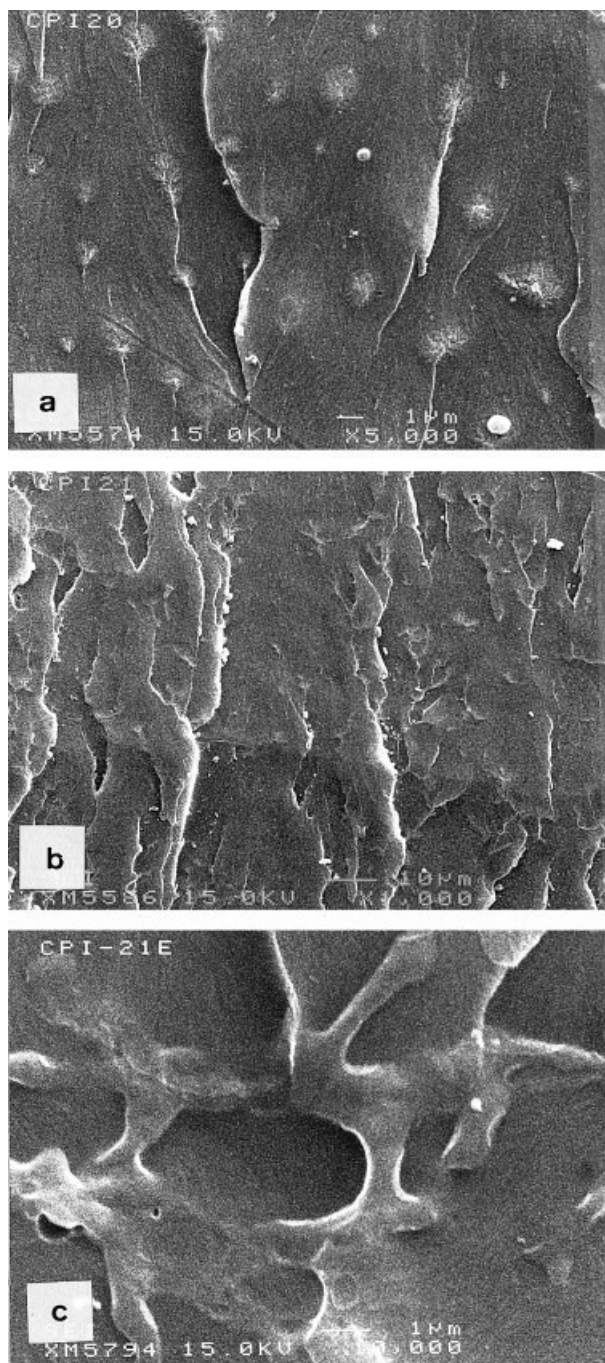


Figure 4 SEMs of the fracture surfaces for the multiblock-PI-modified resins (15 wt % inclusion of the modifier): (a) bPI-5-5 ($M_w = 29,600$), (b) bPI-5-5 ($M_w = 62,400$), and (c) bPI-5-5 ($M_w = 62,400$) after etching.

catalysts.¹⁹ Water absorptivity of the modified resin was comparable to that of the unmodified resin up to 400 h, and then, further water absorption of the modified resins occurred, where the surface of the modified resin whitened gradually with an increase in the extent of water absorption. Further increase in the water absorption of the rPI-5-5-modified resin occurred slightly faster than that of the bPI-5-5-modified material.

DISCUSSION

Aromatic PIs are interesting materials as modifiers for thermosets because of their outstanding thermal, mechanical, and electric properties. However, these polymers are difficult to process because they are often insoluble in organic solvents in the state of full imidization. Hence, they are hardly used as modifiers for thermosets. Much effort has been devoted to the synthesis of soluble PIs in fully imidized form. Various soluble PIs have been obtained by the incorporation of flexible spacers such as (perfluoro) alkylene groups or dimethylsiloxane units, bridging functional groups, and bulky substituents into the polymer backbone.²⁸ One of the most effective methods for obtaining soluble aromatic PIs is the incorporation of fluorine atoms in the polymer structure. The use of 6FDA as an acid dianhydride component of PI is one of the interesting methods for improving the miscibility of the polymer. The control of chain sequence of the polymers is also important for enhancing the miscibility of PIs. However, the conventional method for the preparation of PIs proceeds via poly(amic acid), which leads only to random-type PIs. The preparation method in this study allowed us to obtain multiblock-type PIs. Therefore, the efficiency as modifiers of multiblock type PIs was also examined, compared with that of random-type PIs. The various kinds of PIs used here were soluble in the cyanate ester resin without solvents.

In the modification of the cyanate ester resin with random-type PIs, rPI-8-2 containing larger amounts of the 6FDA/*m*-BAPS sequence was unsuitable for obtaining effective modifiers because rPI-8-2 had a high miscibility with the cyanate ester resin and phase-separation did not occur during curing. When 15 wt % rPI-5-5 ($M_w = 44,000$) was used, the modified resin had a particulate structure with PI-rich domains dispersed in the matrix [Fig. 3(a)], and its K_{IC} value increased only 20%. The use of 15 wt % rPI-5-5 ($M_w = 63,400$) led to a 65% increase in the K_{IC} value with a slight loss of flexural strength and a retention of both flexural modulus and T_g , compared with the values for the unmodified resin. The modified resin had a complicated morphology [Fig. 3(c)]. The morphology of the modified resin was composed of a flat matrix phase and a global phase-inverted structure. Morphological behaviors revealed that there was a significant MW dependence of miscibility of rPI-5-5 with the cyanate ester resin. The modification results indicated that toughening could be achieved because of the phase-inverted structure of the modified resin. However, the 15 wt % inclusion of rPI-5-5 ($M_w = 63,400$) may have been slightly too low to develop its phase-inverted structure to a greater extent, and further inclusion of the same modifier was difficult to process because of an increase in viscosity of the uncured blends at 130°C. When 15 wt % rPI-4.5-5.5 (M_w

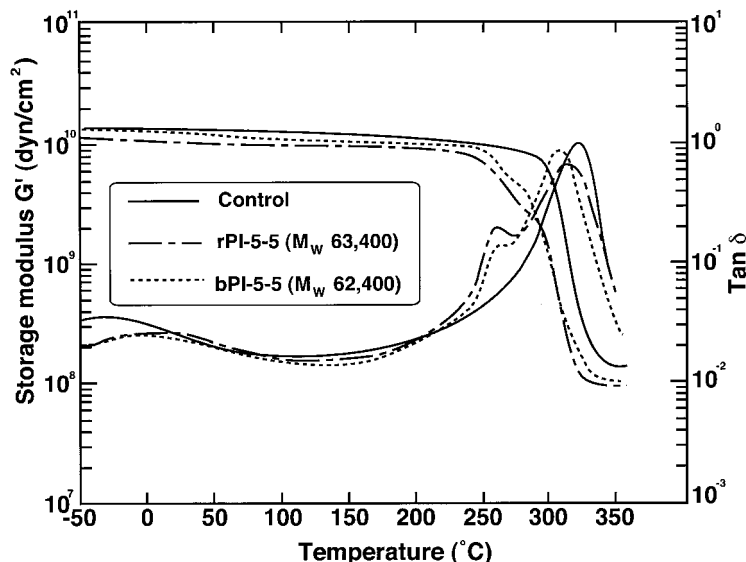


Figure 5 Dynamic viscoelastic analysis of unmodified and modified resins (15 wt % inclusion of the modifier).

= 53,000) was used, the increase in the K_{IC} value was low (30%), whereas the K_{IC} value increased by 60% on 17.5% inclusion of the same modifier, and the modified resin had a cocontinuous phase morphology [Fig. 3(e)]. The morphology of rPI-5-5 ($M_w = 63,400$)-modified resin was different from that of the rPI-4.5-5.5 ($M_w = 53,000$)-modified one [Fig. 3(c,e)]. The former modifier may have phase-separated in an earlier, lower viscous stage of the process of curing than did the latter modifier, which led to a partially aggregated phase-inverted structure of the modifier without a spread over the whole resin. rPI-5-5 ($M_w = 63,400$) contained larger 6FDA/*m*-BAPS chain sequences, and its MW was higher than rPI-4.5-5.5 ($M_w = 53,000$). An increase in the 6FDA/*m*-BAPS unit of the modifier

was favorable to enhance miscibility, a high MW was unfavorable, and vice versa. Miscibility of this PI with the cyanate ester resin might have been determined by the previous two factors: rPI-5-5 ($M_w = 63,400$) was less miscible because of its high MW than rPI-4.5-5.5 ($M_w = 53,000$).

In general, cocontinuous or phase-inverted structures are suitable morphologies for enhancement of the brittleness of the cured material in the modification of thermosets by thermoplastic polymers. In the modification of bisphenol A dicyanate ester resin by PEI, toughening could also be attained on 20 wt % inclusion because of a complicated cocontinuous phase structure having PEI nodules (2–10 μm in diameter) embedded into a continuous polycyanurate network, whereas a considerable enhancement in toughness was not obtained on 15 wt % inclusion, although its morphology was not presented.⁴ PEI was also effective in the modification of epoxy resins. Toughening was attained on 20 wt % inclusion of PEI because of phase-inverted structures.^{23,24} These results indicate that the inclusion of more than 20 wt % PEI is essential to enhance the toughness of the cured resin by a more suitable morphology.

In this modification by random-type PI, the modified resins had no fully developed phase-inverted structure on 15 wt % inclusion. To enable more than 20 wt % inclusion of the modifier, the multiblock PIs were used as modifiers with higher miscibility because the presence of block sequences of the soluble fractions, the 6FDA/*m*-BAPS units, were favorable for enhancing the miscibility of the PI used here because of aggregation of the soluble fractions. When 15 wt % bPI-5-5 ($M_w = 29,600$) was used, the modified resin had a particulate structure with PI-rich domains dispersed in the matrix [Fig. 4(a)], and its K_{IC} value

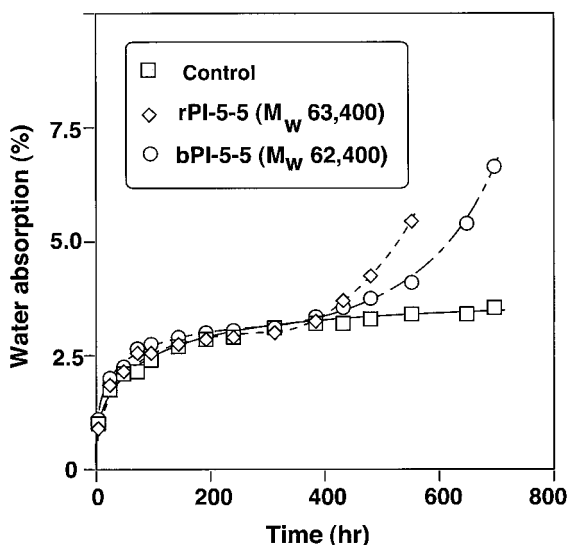


Figure 6 Water absorption of the unmodified and modified resins (15 wt % inclusion of the modifier).

increased 40%. The modified resin had a cocontinuous structure on 15 wt % inclusion of bPI-5-5 [$M_w = 62,400$; Fig. 4(b)], whereas a significant enhancement in toughness was not attained. The effectiveness as the modifier of bPI-4.5-5.5 was similar to that of bPI-5-5. The modification results indicated that the phase-inverted structure may have been more suitable for enhancing the toughness of the cured resin in this modification system. When 15 wt % random or multiblock PIs with similar compositions and MWs [rPI-5-5 ($M_w = 63,400$) and bPI-5-5 ($M_w = 62,400$)] were used, the extent of phase-separation of the multiblock-PI-modified resin was smaller than that of random-type-PI-modified materials, as shown by dynamic viscoelastic analysis (Fig. 5). The morphological behaviors also indicated that the miscibility of the multiblock PI with the cyanate ester resin was higher than that of the random PI. However, enhancement of the miscibility of bPI used here was still insufficient for preparation of the modified resin on more than 20 wt % inclusion. Hence, the efficiency as the modifier of multiblock-type PI was less than that of random-type PI.

CONCLUSIONS

Various kinds of soluble PIs, random or multiblock, were prepared with 6FDA and *s*-BPDA as acid dianhydride components and *m*-BAPS as a diamine component and used as modifiers for the cyanate ester resin. The miscibility of the PIs with the cyanate ester resin depended on the PI structure and MW. In the modification with random-type PI, rPI-8-2, containing larger amounts of the 6FDA/*m*-BAPS sequence, was noneffective because of its high miscibility. A decrease in the 6FDA/*m*-BAPS sequence of the random-type PI led to a lowering of the miscibility. When 15 wt % rPI-5-5 ($M_w = 63,400$) was used, the K_{IC} value for the modified resin increased 65% with a slight loss of flexural strength and a retention of flexural modulus and T_g , compared with the values for the unmodified resin. Toughening of the cyanate ester resin by the random-type PI could be attained because of the heterogeneous phase structure composed of a flat matrix phase and phase-inverted structures of the modified resin. Although the miscibility of the multiblock-type PIs with the cyanate ester resin was higher than that of the random-type PIs, a specimen of the cured resin could not be prepared on more than 20 wt % inclusion. Hence, the multiblock-type PI was less effective as the

modifier than the random-type PI. Water absorptivity of the modified resin was comparable to that of the unmodified resin up to 400 h, and then, further water absorption of the modified resins increased considerably.

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