Epoxy Resins Toughened by Poly(propylene carbonate)

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ABSTRACT: Poly(propylene carbonate)(PPC) was used as a toughening agent for improving the brittleness of cured epoxy resins (EP). Methyl tetrahydrophthatic anhydride (MTHPA) was used as a curing agent. The activation energies for the reactions of PPC/MTHPA and EP/MTHPA measured by FTIR were 115.8 and 66.5 kJ/mol, respectively, while for the composite system of PPC/EP/MTHPA, the activation energy obtained from DSC was 52.9 kJ/mol. Gel contents, DMA, and DSC displayed that the cured resins of PPC/EP/MTHPA were phase-separation crosslinking systems and most of PPC could react with MTHPA or the epoxy group. The toughness of cured resins was reinforced by the addition of PPC. The optimum mechanical properties and toughness for cured resins of PPC/EP/MTHPA corresponded to the system containing 20 phr PPC, which achieved a 33% increase in tensile strength and a 45% increase in the fracture toughness at no expense of the elongation of cured resins. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2457–2465, 1997
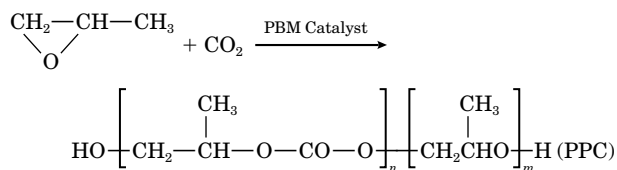
Key words: epoxy resin; poly(propylene carbonate); curing kinetics; structure and property

INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers; however, upon cure, they are relatively brittle and have poor resistance to crack propagation. The toughness of epoxy resins has been enhanced by blending with reactive liquid rubbers or terminally modified engineering thermoplastics.[1–3] Epoxide-containing rubber which can increase the fracture toughness of cured resins has also been reported.[4,5]

As a bright example of chemically fixing CO_2,

the alternating copolymer of CO_2 and epoxide is a kind of active polymer which can be extensively used as a polymer modifier[6]:

With hydroxyl-ending groups, poly(propylene carbonate)(PPC) can react with acid anhydride, epoxy resins, and isocyanate. Based on the molecular weight, PPC can be expected to be widely applied, such as in composite materials, biodegradable materials, controlled drug-releasing agents, processing aids, coating materials, and surfactants. In the present article, PPC was used

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as a toughening agent for improving the brittleness of cured epoxy resins. The structure and properties of epoxy resins toughened by PPC were studied.

EXPERIMENTAL

Materials

The epoxy resin used was a liquid bisphenol-A-type epoxy resin (EP-618, Wuxi, China, weight of epoxy equivalent [WEE] = 201 g/eq). Methyl tetrahydrophthalic anhydride (MTHPA; Chengdu, China) was used as a curing agent, and 2,4,6-tris-(dimethylaminamethyl)phenol (DMP-30), as an accelerator.

Poly(propylene carbonates) (PPC) with different molecular weights were prepared by the copolymerization of CO_2 and propylene oxide under the presence of polymer-supported bimetallic catalysts (PBM). Both the PPC and PBM were synthesized at our Institute.[7] The basic formulation for the curing resin of the EP/PPC/MTHPA system was as follows: EP: 100 phr; PPC: varied; MTHPA: 70 phr; and DMP-30: 0.5 phr.

Measurements

The IR spectra of PPC and PPC/EP mixtures were measured with an Analect FRX-65-type FTIR spectrometer. Glass transition temperatures of both PPC and the cured resins were tested by a DSC (Perkin-Elmer DSC-2C) at a heating rate of 20°C/min. Dynamic viscoelastic properties were measured with a DDV-2 type Rheometric between 150 and 250°C at a heating speed of 3°C/min and a frequency of 3.5 Hz.

Curing Procedure

A mixture of the epoxy resin and PPC was heated at 80°C to homogenize it. The curing agent (MTHPA) was added with stirring to degas it, and then the accelerator (DMP-30) was added with gentle stirring to minimize air entrapment. The resulting clear mixture was poured into a Teflon model preheated at 80°C. Then, the samples were cured at 80°C for 17 h plus at 110°C for 28 h.

The formulation of the parent epoxy resin is EP/MTHPA = 100/70 in a weight ratio.

Measurements of Mechanical Properties for the Cured Resin

The mechanical properties (tensile modulus, tensile strength at the breakpoint, and the corresponding elongation) of the samples were measured with an Instron tensile tester (Model 4201). All these properties were automatically calculated by a computer using the Instron 2412005 General Tensile Test Program. The strain rate was 5 mm/min and the tensile modulus was reported at 0.1% strain. The impact strength was tested with a WPM type of cantilever beam impact resiliometer.

RESULTS AND DISCUSSION

Kinetics of Curing Reaction

Kinetics of the curing reaction of the PPC/EP/MTHPA system was measured by the DSC method. The curing reaction in the scanning model was conducted under nitrogen and at different heating rates: 2.5, 5, 10, and 20°C/min. Figure 1 shows the curves and data for dynamic runs carried out at the four different heating rates.
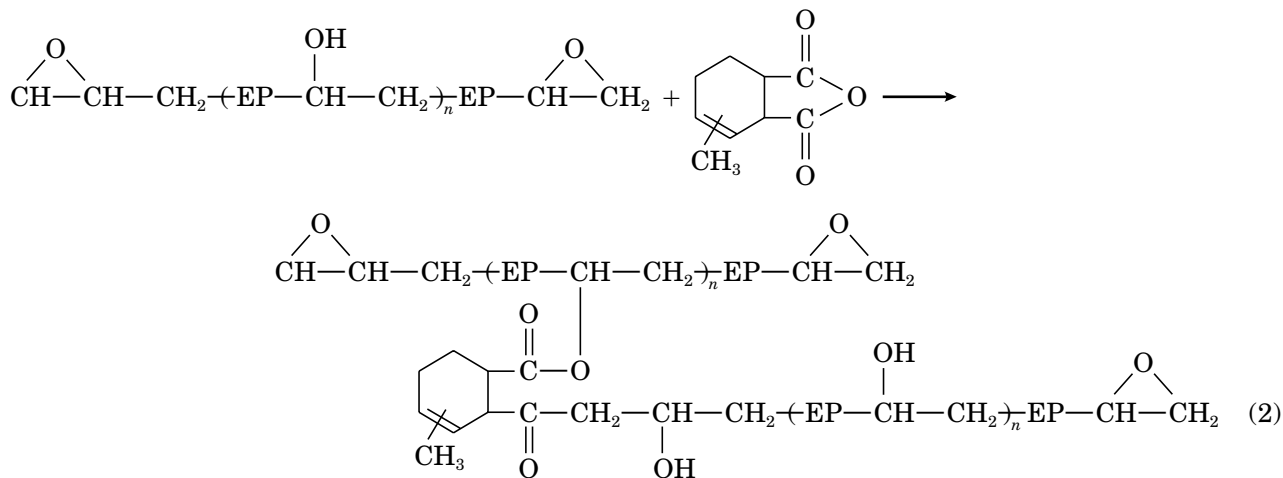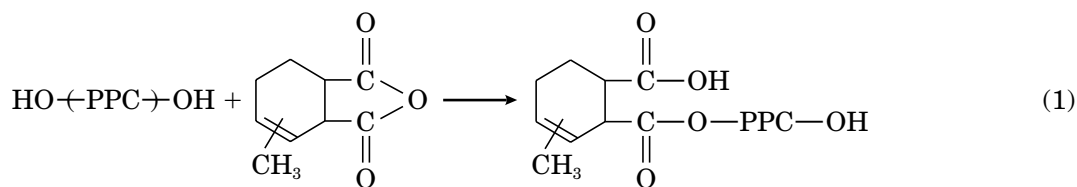
According to the Kissinger equation,[8]

$$\frac{d[\ln(\beta/Tp^2)]}{d(-1/Tp)} = -\Delta Ea/R$$

where β is the heating rate; Tp, the position of exothermic peak; R, the gas constant (8.314 J/mol K); and Ea, the apparent activation energy. A plot of $[\text{Ln}(\beta/Tp^2)]$ vs. $1/T$ was linear (shown in Fig. 2). From the slope of the linear curve in Figure 2, the apparent activation energy was obtained, i.e., $Ea = 52.9$ kJ/mol.
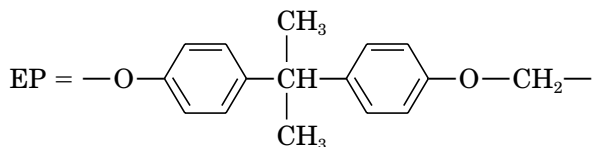
By using this Ea value to the Crane equation,[9]

$$\frac{d \ln \beta}{d(1/Tp)} = -(Ea/nR + 2Tp)$$

the kinetic order of the reaction, n, calculated from the slope of the linear plot of $\ln \beta$ versus $1/Tp$, was 0.92. In fact, the curing reaction of PPC/EP/MTHPA consists of a two binary system:

$$\text{HO} \text{--(PPC)--} \text{OH} + \text{(MTHPA anhydride)} \longrightarrow \text{(ring-opened product with C--OH and C--O--PPC--OH)} \qquad (1)$$

$$\text{CH--CH--CH}_2\text{--(EP--CH(OH)--CH}_2)_n\text{--EP--CH--CH}_2 + \text{(MTHPA anhydride)} \longrightarrow$$

$$\text{(cured network product)} \qquad (2)$$

where

$$EP = \text{--O--C}_6\text{H}_4\text{--C(CH}_3)_2\text{--C}_6\text{H}_4\text{--O--CH}_2\text{--}$$

To deduce the molecular structure of the cured resins, the FTIR method was used to trace the reaction of procedure and to measure the reaction rates of reactions (1) and (2). In reaction (1) [or reaction (2)], PPC (or EP) was mixed with the excess curing agent (MTHPA), then heated quickly to a assigned temperature and maintained at this temperature. The time dependence of the intensity of the characteristic band was recorded at every assigned temperature.

In reaction (1), the intensity of the absorption band at 1855 cm^{-1}, A1855, was used as the detected band, which corresponded to the vibration absorption of the carbonyl group on acid anhydrides, and the reference band was 1745 cm^{-1}, A1745, corresponding to the vibration of C=O on the PPC chain. The ratio of A1855/A1754 was used to characterize the fraction reacted.

For reaction (2), the detected bands were of 919 cm^{-1}, corresponding to an ending epoxy group, and of 833 cm^{-1} corresponding to the *ortho*-hydrogen on the aromatic rings of the epoxy resins. The intensity ratios of the assigned absorption bands, A1855/A1745 for reaction (1) and A919/A833 for the reaction (2), are listed in Table I.

Based on the kinetics equation,

$$\frac{d(A/A_0)}{d(t)} = k(A/A_0)^n \quad \text{and} \quad \ln\left\{\frac{d(A/A_0)}{d(t)}\right\}$$

$$= \ln k + n \ln(A/A_0)$$

the plot of $\ln\{d(A/A_0)/d(t)\}$ vs. $\ln(A/A_0)$ displays a linear curve, and the reaction rate constant, k, can be calculated from the intercept, which is shown in Table I.

According to the Arrhenius equation,

$$k = k_0 e^{-Ea/RT} \quad \ln k = \ln k_0 - Ea/RT$$

From the plot of $\ln k$ vs. $1/T$ (shown in Fig. 3), the apparent activation energy for the EP/MTHPA system can be calculated.
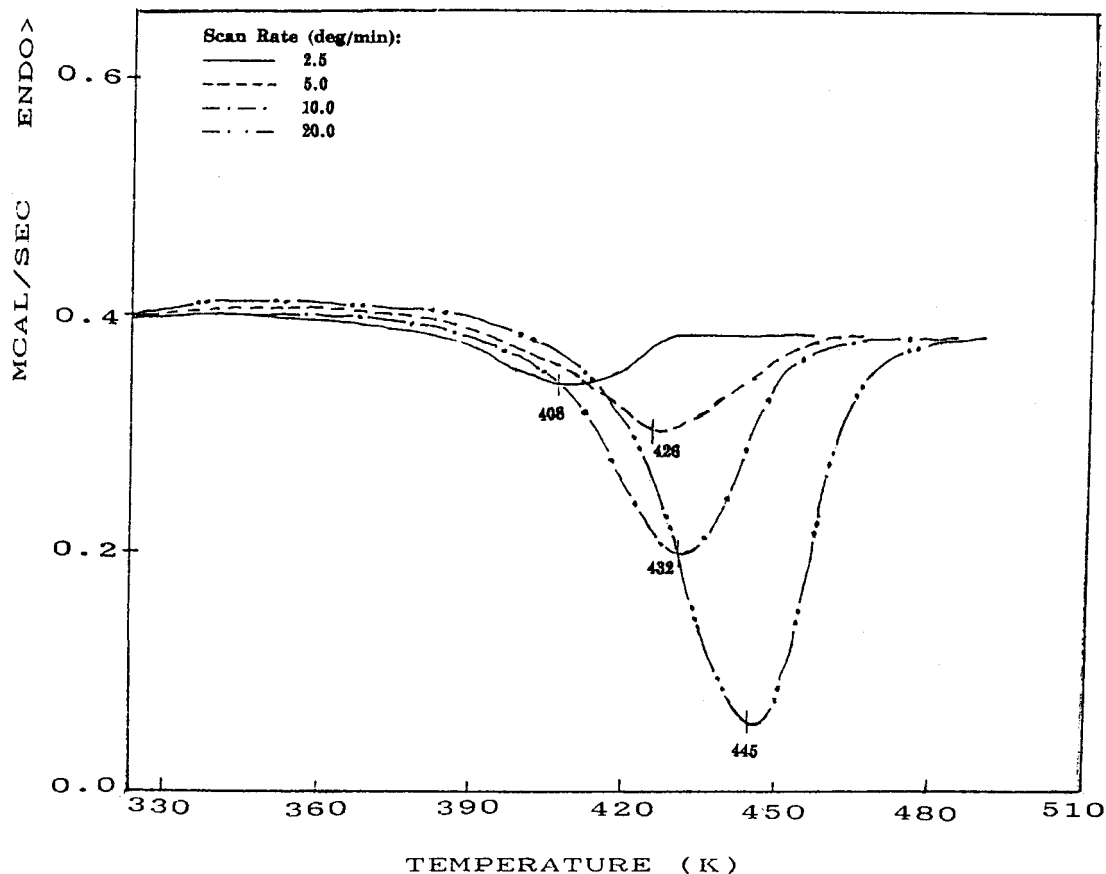
Figure 1   DSC thermogram for uncured resin of PPC/EP/MTHPA at different scanning rates. Molecular weight of PPC: 4900.

Based on the reaction rate constants listed in Table I and the following equation:
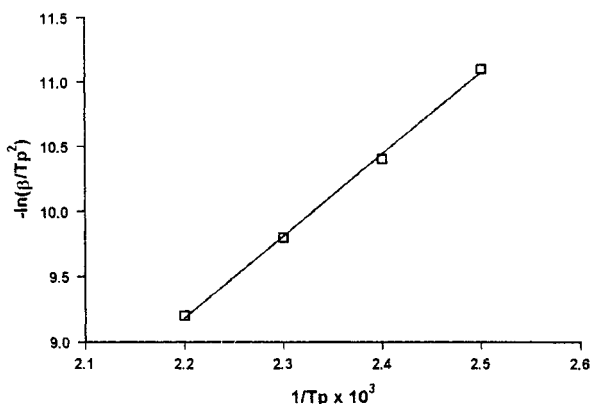
$$\ln(k_2/k_1) = -Ea/R(1/T_1 - 1/T_2) \qquad (3)$$

Figure 2   Plot of $-\ln(\beta/Tp^2)$ vs. $1/Tp$ for PPC/EP/ MTHPA system.

the Ea for the PPC/MTHPA system can be calculated. Equation (3) is only a mathematics treatment for calculating the Ea, because only two temperature ranges were measured for the PPC/MTHPA system, since at low temperature (70°C), the reaction is too slow, and at high temperature (100°C), PPC may show some decomposition. Here, k_1 and k_2 are 7.40×10^{-4} and 2.25×10^{-3}, respectively, corresponding to reaction (1) for 80 and 90°C (Table I). The reaction rate constant and the apparent activation energies for the EP/MTHPA, PPC/MTHPA, and PPC/EP/MTHPA systems are summarized in Table II. These results indicate that the EP/ MTHPA system has a lower activation energy and a faster curing rate than those of the PPC/ MTHPA system.

In comparison with the results of DSC and FTIR, it can be considered that the curing procedure for the PPC/EP/MTHPA system was deter-

Table I Kinetics Data for PPC/MTHPA and EP/MTHPA Systems

	70°C t (min)							k (min^{-1})
	0	20	40	60	80	100	120	
A919/A833	1.071	0.951	0.854	0.800	0.750	0.709	0.671	3.24×10^{-3}
	80°C t (min)							
	0	60	120	180	240	300		
A1855/A1745	0.500	0.488	0.452	0.446	0.440	0.430		7.40×10^{-4}
	t (min)							
	0	5	25	45	55	65	85	
A919/A833	1.043	1.000	0.894	0.830	0.745	0.711	0.600	6.00×10^{-3}
	90°C t (min)							
	0	10	60	120	180	240	300	
A1855/A1745	0.636	0.576	0.525	0.484	0.462	0.425	0.416	2.25×10^{-3}
	t (min)							
	0	10	20	30	40	48	55	
A919/A833	1.114	1.024	0.892	0.800	0.641	0.487	0.359	1.02×10^{-2}
	100°C t (min)							
	0	10	20	25	30	35	40	
A919/A833	1.000	0.973	0.800	0.676	0.536	0.397	0.300	1.97×10^{-2}

mined mainly by the reaction between the epoxy resin and acid anhydride. It means that the epoxy matrix formed first and the PPC chain may chemically bond to the epoxy matrix or PPC reacted with MTHPA and these resultant macromolecular chains interpenetrate the epoxy matrix.
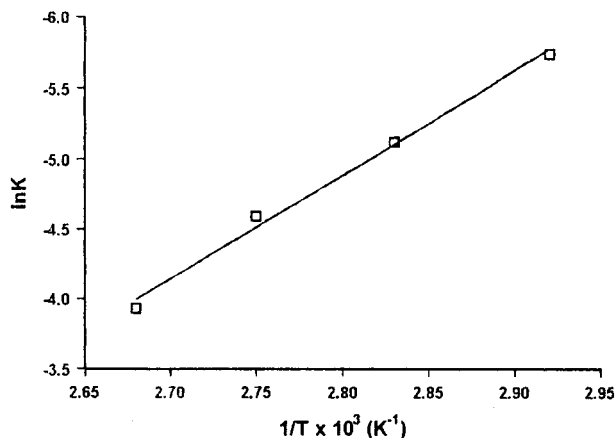
Figure 3 Plot of ln k vs. $1/Tp$ for EP/MTHPA system.

Characteristics of Modified Cured Resins

Measurement of Gel Content in the Cured Resins

To understand the degree of crosslinking of the cured resins, the cured samples were broken into small pieces and abstracted by acetone, which is a good solvent for both the uncured epoxy resins and PPC, for 72 h; the gel parts were then vacuum-dried to a constant weight. The results are shown in Table III.

It is obvious from Table III that PPC was not abstracted completely into the sol gel. FTIR analysis shows the existence of PPC in the gel components as shown in Figure 4 (sample: PPC/

Table II   Reaction Rate Constant and Activation Energies for PPC/MTHPA, EP/MTHPA, and PPC/EP/MTHPA Systems

Method	System	T (°C)	k (min^{-1})	Ea (kJ/mol)
FTIR	PPC/MTHPA	80	7.40×10^{-4}	115.8
		90	2.25×10^{-4}	
	EP/MTHPA	70	3.24×10^{-3}	
		80	6.00×10^{-3}	66.5
		90	1.20×10^{-2}	
		100	1.97×10^{-2}	
DSC	PPC/EP/MTHPA			52.9

EP/MTHPA = 60/100/70). It is obvious that the absorbing band of the carbonyl group (1744 cm^{-1}) for the PPC chain existed in the spectroscopy of the gel sample (spectroscopy 2 in Fig. 4). This confirms the suggestion that the reacted PPC chain penetrating the epoxy matrix forms physical entanglements. So, the structure of cured PPC/EP/MTHPA resins seems to be a semiinterpenetrating network (S-IPN).

Thermal Properties of Modified Cured Resins

The DSC curves (shown in Fig. 5) show that the cured resins existed at two glass transition temperatures. The lower T_g corresponding to the PPC-rich phase moved to a somewhat higher-temperature region, while the higher T_g corresponding to the epoxy-rich phase moved more to a lower-temperature region. This indicates that PPC was partially miscible with the epoxy resin and that the addition of PPC caused a sacrifice in

Table III   Gel Contents of Cured PPC/EP/ MTHPA (Variable/100/70)

Gel Contents	PPC Content (phr)			
	0	60	70	100
Experimental	100	96.9	88.3	86.6
Calculated[a]	100	62.5	58.8	50.0

[a] Assume that PPC was not crosslinked and can be abstracted into the sol gel.

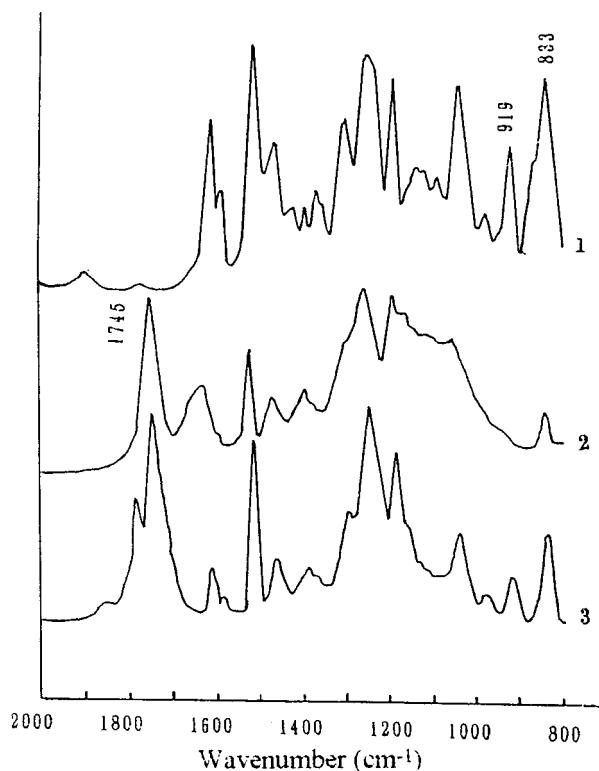the thermal properties except for the system with 20 phr of PPC.

Mechanical Properties of Modified Cured Resins

Dynamic Viscoelastic Properties: Figures 6 and 7 show the dependence of the tangent delta

Figure 4   IR spectra for cured resins: (1) parent epoxy resin; (2) after abstracted; (3) before abstracted.

Figure 5 DSC thermograms of cured resins with various PPC content. Molecular weight of PPC: 4900.
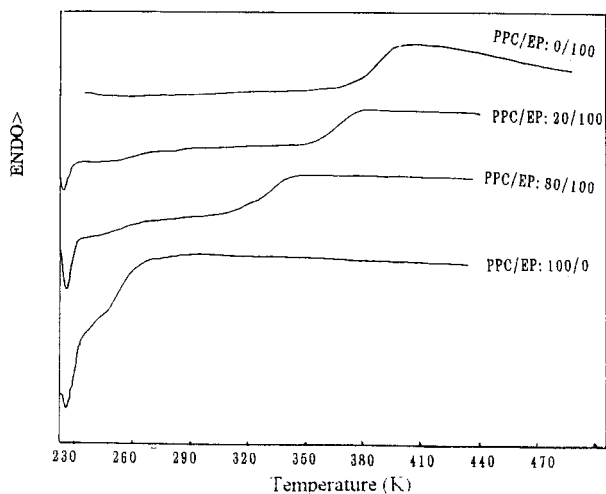

Figure 7 E' vs. temperature for cured resin with various PPC contents. Molecular weight of PPC: 4900.

(tan δ) and storage modulus (E') on the temperature for the cured epoxy resins modified with different contents of PPC (MW 4900). Two relaxation peaks, α and α' corresponding to the T_{g_1} of the epoxy-rich phase and the T_{g_2} of the PPC-rich phase, respectively, existed in each tan δ curve. This indicates that the cured resins were a ph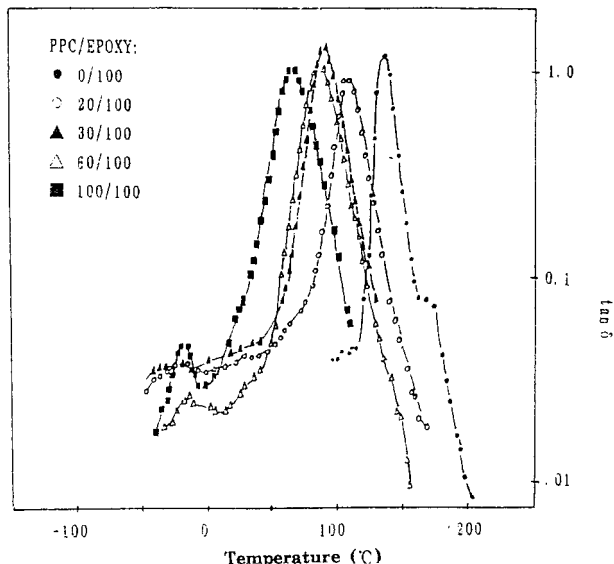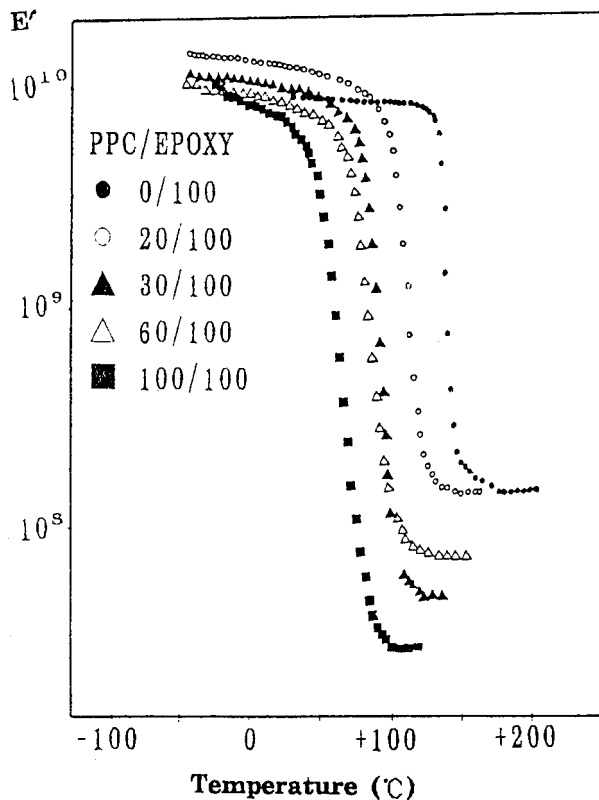ase-separated structure. All the α-relaxation peaks in the tan δ curves for the resin modified with higher PPC contents became broader than those for the parent epoxy resin (shown in Table IV). But the peak positions moved to lower-temperature regions with increase in PPC contents. The α'-relaxation peak position hardly changed by varying the PPC contents.

The E's for the cured resins with different PPC

Figure 6 Tan δ vs. temperature for cured resin with various PPC contents. Molecular weight of PPC: 4900.

Table IV Effect of PPC Contents on Half-width of α-Relaxation Peak

PPC/ EP	Half-width (°C)	T_g (EP) (°C)	T_g (PPC) (°C)
0/100	23	136.9	—
20/100	43	110.1	−24.8
30/100	45	92.2	−22.0
60/100	58	86.3	−18.9
100/100	63	68.1	−18.8
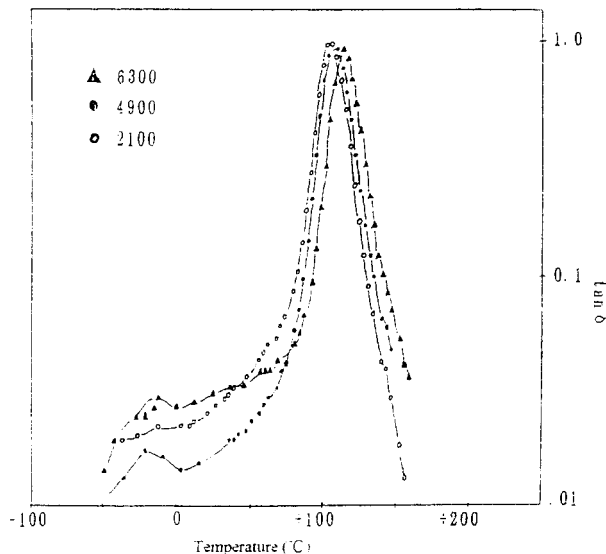
Figure 8 Tan δ vs. temperature for cured resin with different molecular weights of PPC (20 phr).

Figure 9 Tensile stress–strain curve for cured resins.

contents did not change over the temperature range lower than their α-relaxation, compared with the parent epoxy resin. This implies that the epoxy matrix was toughened by the addition of PPC at no expense of to its modulus but with a sacrifice to its thermal properties.

The dependence of tan δ curves on the molecular weight of PPC shows a slight difference in breadth of α-relaxation peaks as shown in Figure 8. It is obvious that for the cured resin with PPC of MW 2100 only an α-relaxation appeared and the sample is transparent. This implies that PPC with a low molecular weight has good miscibility with epoxy resins.

Tensile Stress–Strain Curves for Cured Resins: The dependence of stress–strain curves for the cured resins on PPC contents is shown in Figure 9. It can be seen that the stress–strain curve for the cured resin with 20 phr of PPC covers a larger area than that for the cured resins with higher PPC content. The testing results of impact strength (Fig. 10) also show that the cured resin with 20 phr of PPC has a greater impact strength. This indicates that the cured system with 20 phr of PPC was likely to absorb greater impact energies.

The measurement of mechanical properties also shows that the cured resin with 20 phr of PPC exhibited greater tensile strength and elongation at break. The data are listed in Table V.
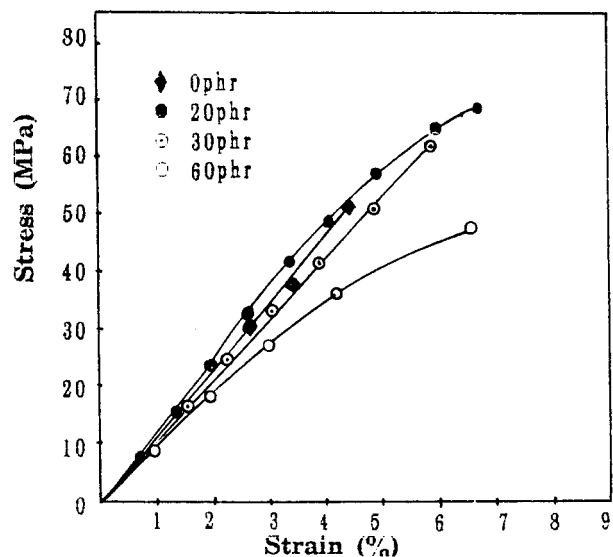
In summary, poly(propylene carbonate) was effective as a new modifier for the epoxy resin. The most suitable composition for modification of the epoxy resin contains 20 phr of PPC (MW 4900), which achieved a 45% increase in the fracture toughness and a 33% increase in tensile strength at no expense of the elongation of cured resin. The toughening mechanism of the cured resin modified by 20 phr of PPC may be due to the chemical bonding between terminal groups in PPC and the epoxy matrix.
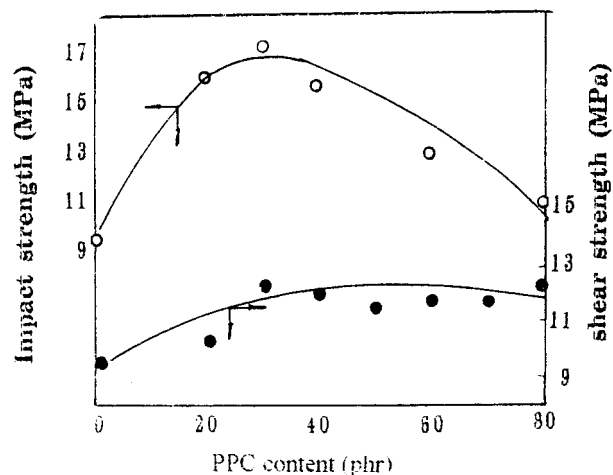

Figure 10 Effect of PPC content on impact and shear strength.

Table V   Mechanical Properties of Cured Resins

	PPC (phr)					
	0	20	30	60	80	100
Tensile strength (MPa)	51.6	67.7	62.0	48.1	8.6	23.4
Tensile modulus (MPa)	1291	1291	1316	1000	228	558
Elongation (%)	4.3	6.7	5.8	5.6	15.9	10.0
Fracture toughness[a] (J/mm^2)	0.024	0.055	0.041	0.036	0.022	0.030

[a] Fracture toughness = fracture energy/fracture area.

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