

Synthesis and Properties of PMR Type Poly(benzimidazopyrrolone-imide)s

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ABSTRACT: PMR type poly(benzimidazopyrrolone-imide) or poly(pyrrolone-imide) (PPI) matrix resin was synthesized using the diethyl ester of 4,4'-(hexafluoroisopropylidene)-diphthalic acid (6FDE), 3,3'-diaminobenzidine, *para*-phenylenediamine, and monoethyl ester of *cis*-5-norbornene-endo-2,3-dicarboxylic acid (NE) in anhydrous ethyl alcohol with *N*-methylpyrrolidone. The homogeneous matrix resin solution (40–50% solid) was stable for a storage period of 2 weeks and showed good adhesion with carbon fibers, which ensured production of prepregs. The chemical and thermal processes in the polycondensation of the monomeric reactant mixture were monitored by Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy, etc. Thermosetting PPI as well as short carbon fiber-reinforced polymer composites was accomplished at optimal thermal curing conditions. The polymer materials, after postcuring, showed excellent thermal stability, with an initial decomposition temperature > 540°C. Results of MDA experiments indicate that the materials showed > 70–80% retention of the storage modulus at 400°C and glass transition temperatures as high as 440–451°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1600–1608, 2001

Key words: poly(pyrrolone-imide); PMR; high-temperature polymers

INTRODUCTION

Polybenzimidazopyrrolone and polypyrrolone have been considered as promising high-temperature heteroaromatic polymer materials because of their excellent thermal and chemical stabilities.^{1–6} However, the poor processability caused by the rigidity of polymer backbone limits their practical application in advanced technology. Improvement in the processability of polypyrrolones was attempted by polycondensation of biphenyl or bridged biphenyl

dianhydrides with corresponding aromatic tetraamines to yield semi-ladder structures,^{3,5–8} or by incorporation of imide or imidazole segment into polymer backbone to produce linear poly(benzimidazo-pyrrolone-imide)s.^{3,9,10} The copolymer consisting of pyrrolone and imide segments resulted in, to some extent, improvements in solubility without sacrificing thermal and mechanical properties. However, the problem of processability was still an unanswered question, and there is a great need for further research.

The PMR process (*in situ* polymerization of monomer reactants), which was successfully employed in the preparation of high-performance polyimide composites,^{11–14} was employed in this

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laboratory to synthesize poly(benzimidazopyrrolone-imide) by copolycondensation of diethyl ester of 4,4'-(hexafluoroisopropylidene)diphthalic acid (6FDE), monoethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NE), 3,3'-diaminobenzidine (DAB), and para-phenylenediamine (*p*-PDA) in ethyl alcohol/*N*-methylpyrrolinone (NMP) solution to yield an end-capped oligomer, which was then polymerized and crosslinked by thermal curing to produce a thermosetting polymer materials. The synthesis and properties of the polymer materials will be described in this article.

EXPERIMENTAL

Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA; Hoeschter Celenase, 99%) was vacuum dried at 160°C for 2 h prior to use. 3,3'-Diaminobenzidine (DAB; Acros Organics, 99%) was used as received. 1,4-Phenylenediamine (*p*-PDA, 99%) was obtained from Chemical Reagent Corp. in Beijing and was sublimed prior to use. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (NA, 99%) was purchased from Nanxiang Chemical Corp. in Shanghai and was sublimed prior to use. *N*-Methylpyrrolinone (NMP) and anhydrous ethyl alcohol (EtOH) were purchased from Chemical Reagent Corp. in Beijing and were distilled before use.

Characterization

Fourier-transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FT-IR-2000 spectrophotometer. Thermogravimetric analysis (TGA) curves were carried out using a Perkin-Elmer 7 series thermal analysis system in nitrogen at a heating rate (β) of 20°C/min. Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC 25 instrument at a β of 20°C/min in air. Dynamic mechanical analysis (DMA) was performed in nitrogen with a Perkin-Elmer 7 series thermal analyzer with a β of 5.0°C/min. Scanning electron microscopy (SEM) was carried out with a Hitachi S-530 scanning electron microscope.

Synthesis of PMR Type Poly(pyrrolone-imide) (PPI) Matrix Resins

6FDA (50.50 g) and ethyl alcohol (500 mL) were placed in a 1000-mL flask fitted with magnetic

stirrer and reflux condenser. The mixture was refluxed for 2 h with stirring to yield the diethyl ester of 6FDE solution. The monoethyl ester of NE solution was prepared by refluxing a mixture of NA (6.22 g) and EtOH (25 mL) for 3 h. To a solution of DAB (16.22 g) and *p*-PDA (8.21 g) in NMP (75 mL) in a 1000-mL three-necked flask fitted with stirrer, N₂ inlet, and gas outlet, 6FDE and NE solution in EtOH were added successively. The mixture was stirred for 3–5 h at room temperature to yield a homogeneous PPI-20 matrix resin solution with solid content of 40 wt %. The NE/6FDE/(DAB + *p*-PDA) mole ratio employed was 2.00 : n : ($n + 1$), which theoretically yields an oligomer with calculated molecular weight of 2000 ($n = 2.0$).

PPI-15 and PPI-30 matrix resins with calculated molecular weights of 1500 (PPI-15, $n = 1.5$) or 2500 (PPI-25, $n = 2.5$) were prepared with monomers of NE, 6FDE, DAB, and *p*-PDA at a mole ratio of 2 : n : ($n + 1$).

PPI Neat Molding Resin Powders

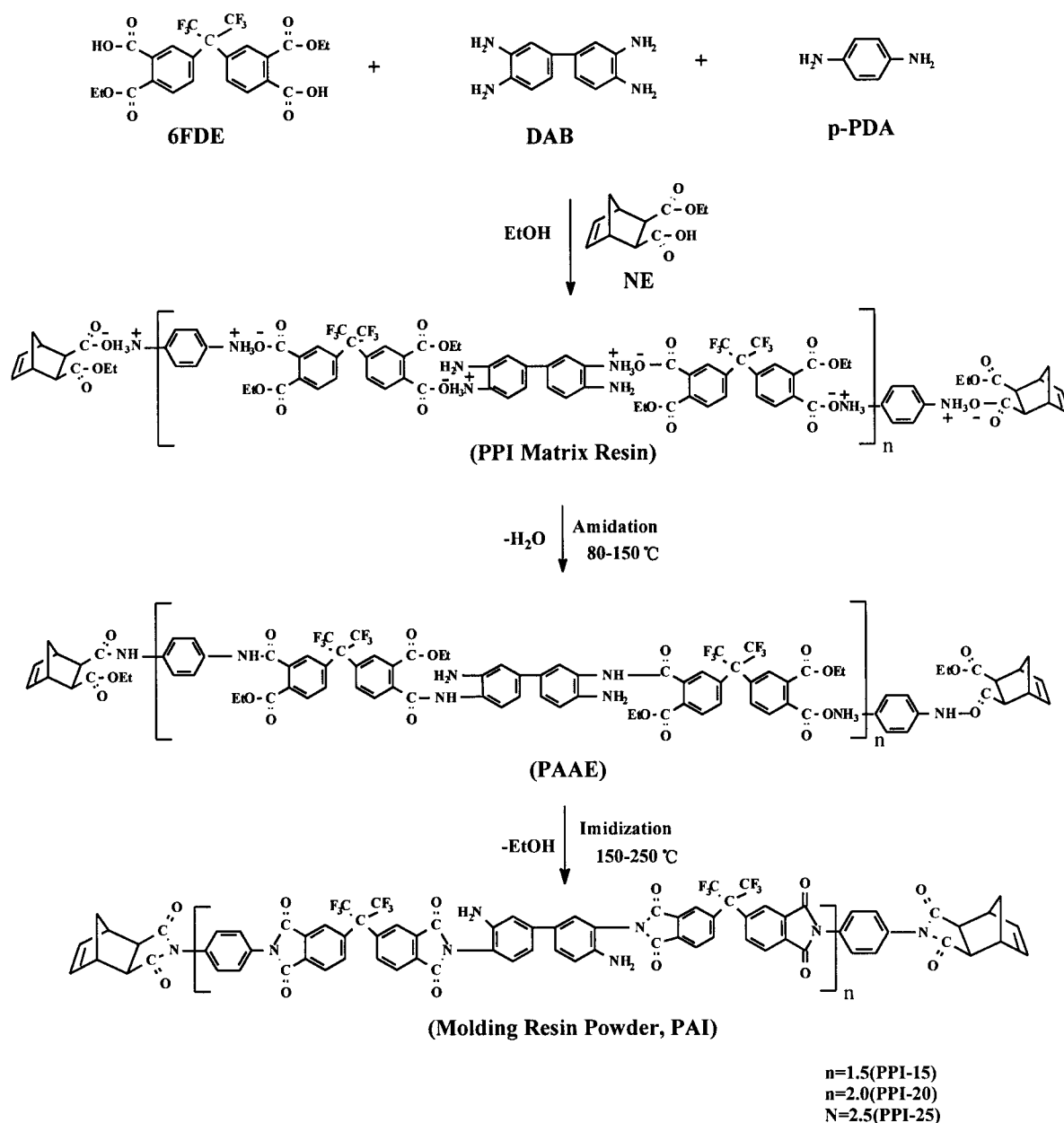
PPI-15 matrix resin solution was evaporated with a rotary evaporator at 50°C to remove some of the lower boiling point solvent and to yield a viscous liquid that was then vacuum dried at 100–120°C to produce a solid material. PPI-15 molding resin powder was obtained by thermally baking the solid to 150°C for 2 h. PPI-20 and PPI-25 molding resin powders were obtained by the same method.

PPI-20/CF Composite Molding Powders

Fifty grams of T-300 short carbon fiber (6–10 mm in length, 7–8 μ m in diameter) was mixed with 125 g of 40 w/w % PPI-20 matrix resin solution with mechanical stirring in nitrogen. The mixture was stirred mechanically for 2 h at room temperature in N₂ and then was heated to remove some of the solvent by evaporation to give a viscous material in which ~ 15–18% of solvent remained. The viscous material was then dried in an oven in vacuum at 100°C for 4 h and then at 150°C for 2 h to yield PPI-20/CF composite molding powders.

Thermal Curing of Molding Resin Powders to Molded Resin Plates

Five grams of molding powder was added at room temperature in a Φ 50-mm die that was placed in a press that had been preheated at 200°C. When the die temperature reached



Scheme 1 The chemistry of PMR type PPI matrix resins.

270°C, a pressure of 2.5–3.5 MPa was applied. The pressure was released and reapplied three times at intervals of 6 min to remove the trace of volatile evolved. The die was heated to 320°C in 15 min and kept under pressure for 3 h. Then, the temperature was increased to 340°C for 2 h under pressure. After cooling under pressure to 200°C, the pressure was released. The molded resin plate was removed from the die, which was then placed into an oven and heated in nitrogen to 350°C at a heating rate of 35°C/h for postcuring treatment.

RESULTS AND DISCUSSION

Chemistry of PPI Matrix Resins

PPI matrix resins were prepared using monomers of NE, 6FDE, DAB, and *p*-PDA at a mole ratio of 2 : 2*n* : *n* : (*n* + 1) in a mixture of EtOH and NMP at room temperature (Scheme 1). The aromatic tetramine and diamine reacted with the diethyl ester of aromatic dianhydride to yield an acid–amine salt-like oligomer that was end-capped with NE to give a matrix resin solution. A

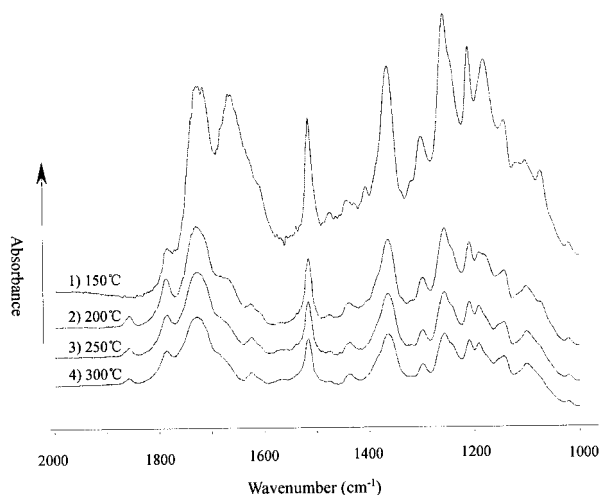


Figure 1 FT-IR spectra of PPI matrix resins baked at different temperatures.

series of matrix resins, with designed molecular weights of 1500 ($n = 1.0$, PPI-15), 2000 ($n = 1.5$, PPI-20), and 2500 ($n = 2.0$, PPI-25), were obtained. The resins showed great solubility in polar organic solvents because of the features of the polyelectrolyte. The matrix resin with 40% solid content was a homogeneous solution with an absolute viscosity of 0.10–0.12 Pa.s. This resin was stable at room temperature for a storage period of 2 weeks during which no precipitation, gelation, or phase separation was observed. The matrix resin showed good adhesion to carbon fiber, which ensures impregnation into fibers to produce prepreps for carbon fiber-reinforced composites.

PPI matrix resin undergoes a series of chemical reactions on thermal curing. Amidation occurred when temperature reached 80–150°C, with evolving a mole of H_2O per acid–amine salt segment to yield an amide bond ($-OC-NH-$) as shown in Scheme 1. Thus, an end-capped polyamide with *o*-substituted ethyl ester (PAAE) was obtained, which was then passed through a thermal cyclization/imidization reaction at a temperature of 150–250°C to produce an endcapped polyimide (PAI) with controlled molecular weight and appropriate fluidity of the melt. The dependence of FT-IR spectra of the PPI matrix resin on thermal baking conditions is shown in Figure 1. The FT-IR spectra were recorded with the matrix resin thermally cured in vacuum at 150°C/2 h (curve 1), and then at 200°C/1 h (curve 2), 250°C/1 h (curve 3), and 300°C/1 h (curve 4). The absorptions in the range 1550–1720 cm^{-1} assigned to the amide ($-OC-NH-$) and ester ($-OC-O-$)

bands of PAAE decreased gradually in intensity and split into multiple peaks with baking temperature increasing from 100 to 250°C, whereas the imide band at 1780 cm^{-1} increased in relative intensity. It is evident that the resin passed through a chemical reaction of amide with ester to yield a cyclized imide group. The TGA curves of the resin after thermal baking at different temperatures are compared in Figure 2. For the resin cured at 150°C, 9–10% of weight loss was measured by DSC when the temperature was scanned to 250°C; for the resin cured at 200°C, 4–5% of weight loss was still detected. The measured values of the weight loss are in close agreement with the calculated ones evolved in the reaction of amide with ethyl ester to yield imide group in PPI resins.

Fabrication of Molded PPI Resins

Molding powder was thermally cured under pressure by a compression molding technique to yield a crosslinked material after passing through a series of thermal chemical reactions (Scheme 2). An adequate fluidity of the melt was required, which ensured the molten fluid to fill the die. Two opposing processes affecting the flowing behaviors of the molten fluid existed in the thermal processing: one is the melting of the molding powder with a low molecular weight to yield a flowing fluid, and another is the chemical crosslinking and chain extending caused by the reaction of endcaps to reduce the flowing characters. The key features in processing were the die temperature and the applied pressure, which should be controlled carefully to ensure a high quality of molded plates. The temperature in the molded resin processing started at 280–290°C and com-

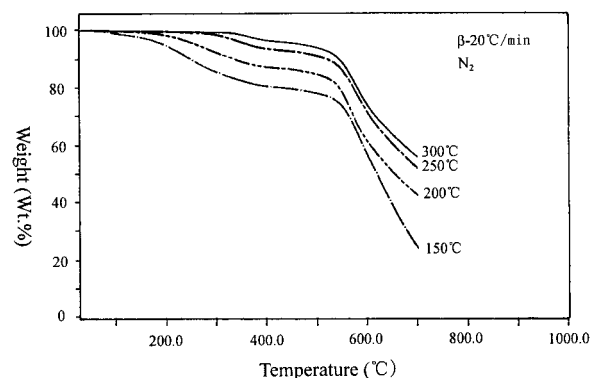
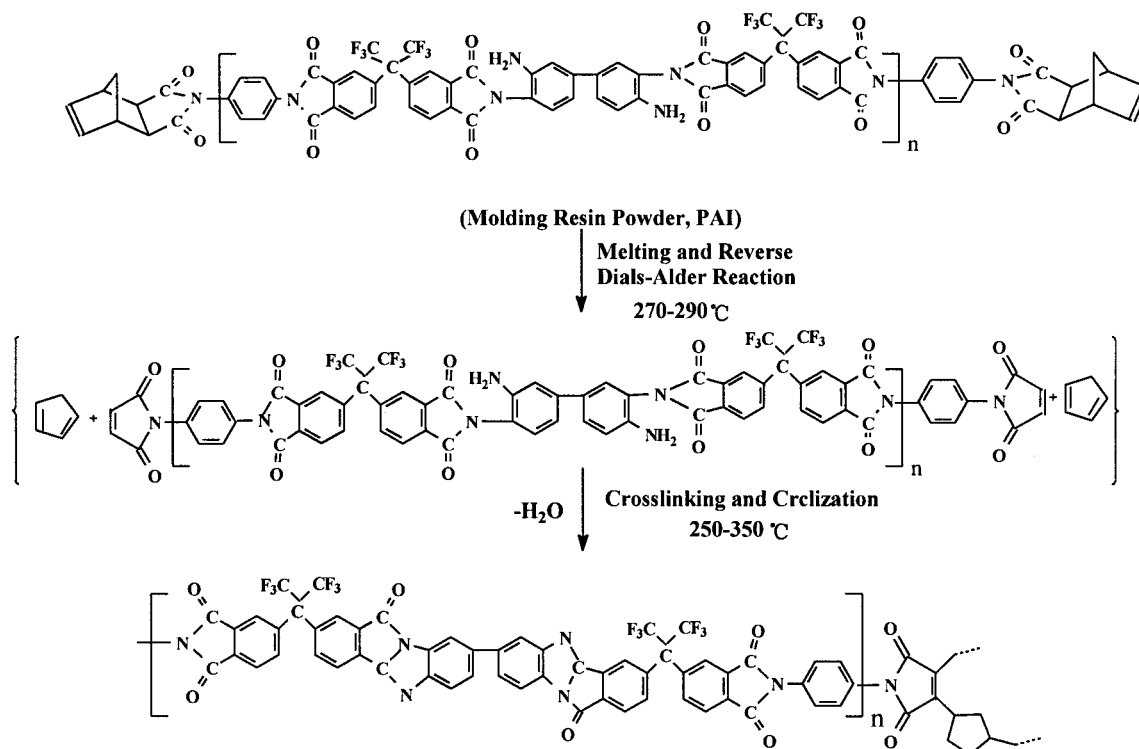


Figure 2 TGA curves of PPI-20 molding powders baked at different temperatures in a vacuum.



Scheme 2 Chemical and thermal process of PPI matrix resin in thermal curing.

pleted at 350°C. Temperatures <280°C can't produce a molten fluid resin with proper flowing character to fill the whole space of die, whereas temperatures >290°C will accelerate the crosslinking of the reactive endcaps so that the moment to apply a pressure is difficult to determine. The pressure employed in the processing of PPI molding resin (or composites) was 2.5–3.5 MPa. Experiments indicated that inadequate pressure application could cause either a spillover of molten resin from the die or a molded resin (or composite) with poor quality. In optimal conditions, PPI molded resin plate or composites were produced by thermally curing the molding powder at 270–350°C under a pressure of 2–4 MPa for 3–4 h, and then postcured at 350°C in nitrogen for 5 h.

Thermal Properties of PPI Molded Resins

The FT-IR spectra of a molded resin and the corresponding molding resin powder are compared in Figure 3. The absorption at 1600–1700 cm⁻¹ for the molding powder, which was assigned to the stretching of C—O in amide and ester, disappeared after thermal processing. The thermal properties of PPI molded resin with or without

postcuring at 350°C/20 h in nitrogen are shown in Table I. The decomposition temperatures at 5% weight loss (T_5) for molded resins with different calculated molecular weights (PPI-15, PPI-20, and PPI-25) were 426, 383, and 399°C, respectively. These temperatures increased 116–161°C after postcuring at 350°C. The decomposition temperature at 10% weight loss increased 45–

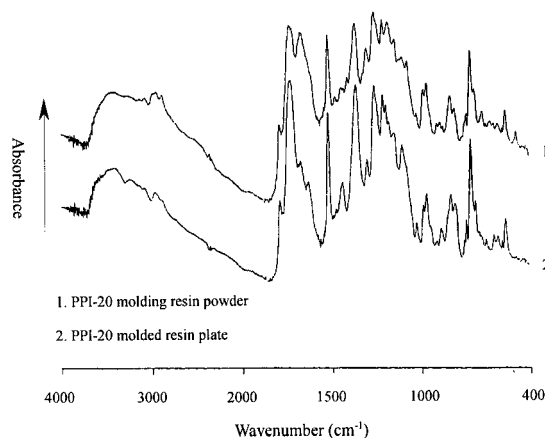


Figure 3 FT-IR spectra of molding powder and molded laminates.

Table I Thermal Properties of PPI Molded Resin Laminates^a

Sample	<i>n</i>	Pressure (MPa)	T_d (°C) ^b		T_5 (°C) ^c		T_{10} (°C) ^d	
			Non	P.C.	Non	P.C.	Non	P.C.
PPI-15	1.0	2.5	530	548	426	542	505	566
PPI-20	1.5	3.5	540	549	383	544	524	569
PPI-25	2.0	3.5	531	541	399	537	512	563

^a Non, Sample without postcuring; P.C., sample with postcuring at 350°C/10 h in N₂.

^b Initial decomposition temperature.

^c Temperature at 5% weight loss.

^d Temperature at 10% weight loss.

61°C comparing freshly molded resin with postcured resin. For instance, the T_5 value of PPI-20 (383°C) increased to 544°C after postcuring. The TGA curves of PPI-20 molded resin with and without postcuring are compared in Figure 4. For the sample without postcuring, a slow weight loss was observed when temperature was scanned from 100 to 500°C, which was attributed to the volatile evolved during thermal treatment. It could be measured that a freshly molded resin would release ~ 10% of the volatile components in postcuring, implying a more perfect cyclization and crosslinking had occurred.

The DMA spectra of PPI-20 before and after postcuring at 350°C are compared in Figure 5. The onset temperature of storage modulus (G') drop for the freshly molded resin was 350°C, which increased by 70–80°C for the postcured sample. The postcured PPI molded resin showed an almost constant storage modulus until the temperature reached 400°C, and then a rapid rise in $\tan \delta$ curve was observed. The peak temperature of the $\tan \delta$ curve was measured at 380°C for the freshly molded resin and 450°C for the post-

cured sample; these values were defined as the glass transition temperature (T_g) of the materials. The DMA data for molded resins are listed in Table II. For the samples without postcuring, retention of storage modulus (defined as the ratio of the value at elevated temperature over the value at room temperature) at 371°C for PPI-15 and PPI-20 were 58 and 28%, respectively. After postcuring, the samples exhibited remarkable increases in retention of storage modulus (78% for PPI-15 and 81% for PPI-20). At 400°C, postcured PPI-15 and PPI-20 molded resins exhibited 70% of retention of storage modulus, whereas the samples without postcuring only showed <26% storage modulus retention. In addition, postcuring yielded an increase in T_g of 47–73°C. For instance, postcured PPI-20 showed a T_g of 434°C, which was 73°C higher than the sample without postcuring. Obviously, there was a significant influence of postcuring on thermal and mechanical properties.

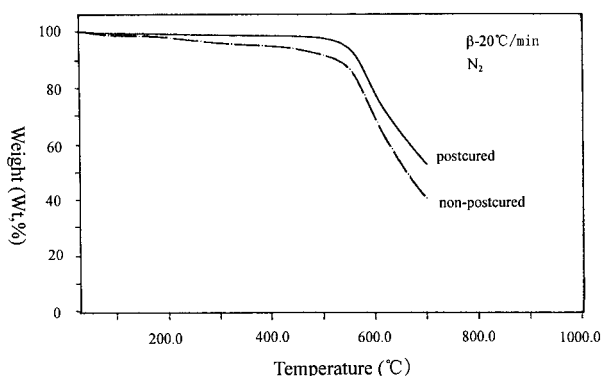


Figure 4 Effect of postcuring on TGA curves of PPI-20 molded laminates.

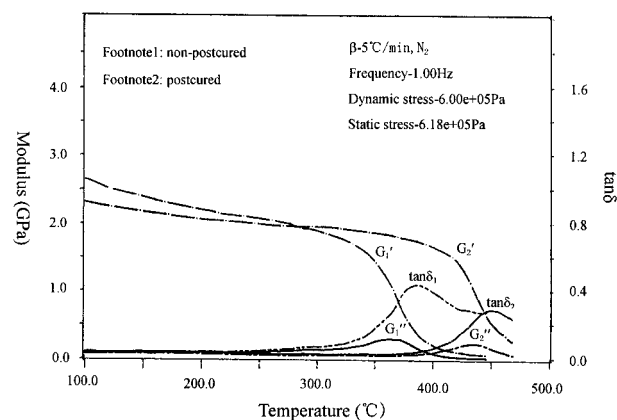


Figure 5 Comparison of DMA results of PPI-20 molded laminates with and without postcuring at 350°C/10 h in N₂.

Table II DMA Data of PPI Molded Resin Laminates

Sample	Retention of G' (%) ^a				Loss Modulus T_p (°C) ^c		Loss Tangent T_p (°C) ^c	
	370°C		400°C		Non	P.C.	Non	P.C.
	Non ^b	P.C. ^b	Non	P.C.				
PPI-15	58	78	26	70	384	431	404	448
PPI-20	28	81	11	70	361	434	387	451

^a Retention of storage modulus (G').

^b Non, non-postcured; P.C., postcured.

^c Temperature at the peak of curve.

Thermal Decomposition of Molded Resins

To understand the thermal decomposition behavior of the materials, the thermal degradation kinetics of a postcured molded plate (PPI-20) was studied by dynamic thermogravimetric analysis (DTGA), which is called Ozawa's method.¹⁵ DTGA curves were obtained at different scanning temperature rates (β ; Figure 6). The variation of the TGA curve with β value agrees with the descriptions in the literatures.^{15,16} According to Ozawa's suggestion and the approximation given by Doyle,¹⁶ the following equation was given:

$$\log F(\alpha) = \log(AE/R\beta) - 2.315 - 0.457(E/RT) \quad (1)$$

Considering the random degradation for polymer, eq. 1 can be changed to

$$\log \beta = \log(AE/R\beta_{(\alpha)}) - 2.315 - 0.457(E/RT) \quad (2)$$

where α is the conversion defined as the volatilized mass at time t divided by the initial mass; and R , A , E , and T represent the gas constant,

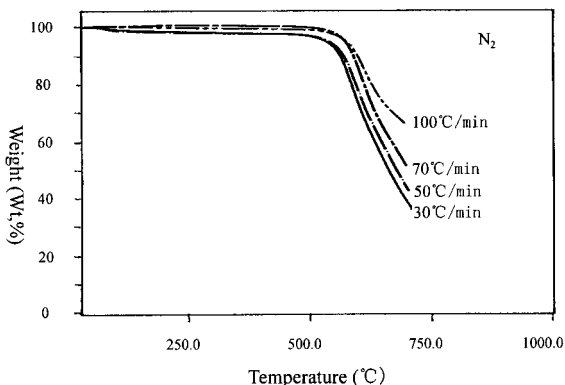


Figure 6 DTGA curves for PPI-20 molded resin laminates.

pre-exponential factor, overall activation energy, and absolute temperature, respectively. Because the curve of $\log \beta$ versus $1/T$ for a constant value of conversion would give a straight line, several curves of $\log \beta \sim 1/T$ based on various α values could be plotted, as shown in Figure 7. The parallel relationship of the straight lines for various α values indicated that the thermal degradation of PPI was in good agreement with randomly thermal initiation process.¹⁵ From eq. 1, eq. 3 was obtained:

$$\log A = 2.35 + 0.457(E/RT) - \log[E/R\beta F_{(\alpha)}] \quad (3)$$

For a random initiation model of polymer thermal degradation, eq. 4 was obtained:

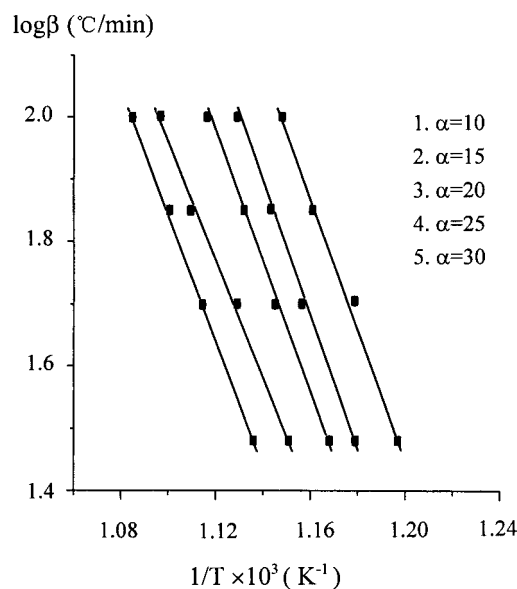


Figure 7 Ozawa's plots of $\log \beta$ versus $1/T$ at constant values of conversion for the degradation of molded PPI-20 resin laminate.

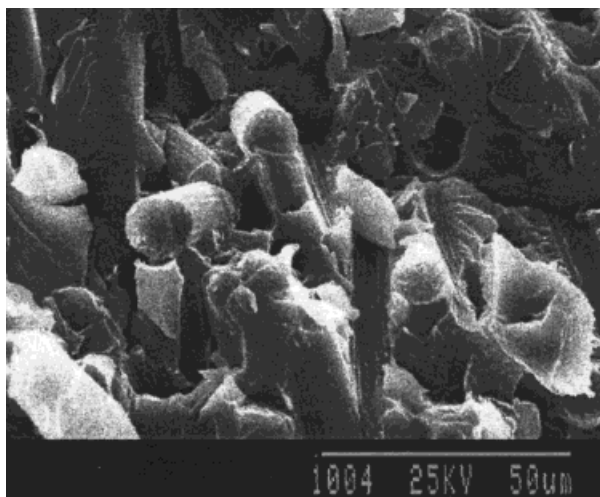


Figure 8 SEM photograph of crosssection of CF/PPI-20 composite molded laminate.

$$F(\alpha) = -\ln(1 - \alpha) \quad (4)$$

Hence, eq. 3 became

$$\log A = 2.315 + 0.457(E/RT) - \log\{E/R\beta[-\ln(1 - \alpha)]\} \quad (5)$$

According to eq. 2, a slope for the straight lines with a constant α value was $\sim 0.457 E/R$. Thus, a series of E values could be calculated from the slopes of lines, and the corresponding A values could be calculated by eq. 5 using the calculated E values and other parameters, such as T , R , β , and α . Hence, for thermal degradation of PPI molded resins, an average activation energy was 205.9 kJ/mol and pre-exponential factor is $2.14 \times 10^{12} \text{ min}^{-1}$.

Carbon Fiber-Reinforced PPI Composites

PPI composite molding powder mixed with short carbon fibers was successfully processed to yield carbon fiber-reinforced composite laminates. The SEM photographs for the crosssection of the composite laminates are shown in Figure 8. A single carbon fiber was surrounded with continuous matrix resin, showing a good interfacial adhesion between PPI-20 matrix resin and carbon fiber. The skin of the carbon fiber in the composite could even be stripped by the matrix resin in preparation of SEM sample by the freezing and split method. The DMA of the CF/PPI-20 composites before and after postcuring is shown in Figure 9, and the DMA data are

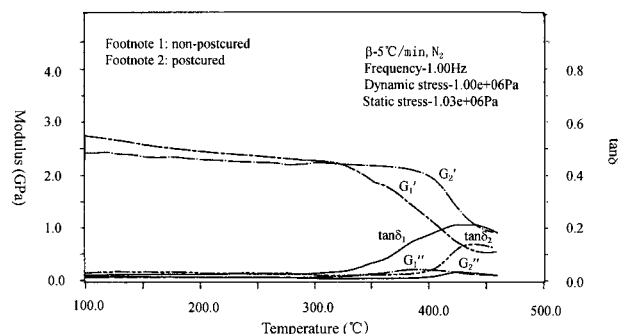


Figure 9 Effect of postcuring on DMA spectra of CF/PPI-20 composite molded laminate.

listed in Table III. The effect of postcuring on DMA parameters for CF/PPI-20 composite laminates is similar to that of PPI-20 neat molded plates (Figure 5). Postcuring can cause remarkable increases in modulus retention at elevated temperature. For instance, the composite without postcuring showed a modulus retention of 61% at 371°C, whereas the postcured composite exhibited an increased value of 93%. The retention values of storage moduli (G') for the postcured sample reached 93% at 371°C and 83% at 400°C; these values are 13–15% higher than those of the corresponding neat molded resins shown in Table 2. The improvements in modulus retention can be attributed to the reinforcing effect of carbon fibers in the composites. Composites showed similar T_g values (430°C) compared with the neat molded resins, implying that the relaxation motion of the polymer chains was not affected significantly by the presence of carbon fibers.

CONCLUSION

Processable endcapped PPI matrix resin was synthesized by a PMR process using diethyl ester of

Table III DMA Data of CF/PPI Composite Laminates

Sample	Retention of G' (%) ^a		Loss Modulus T_p (°C) ^b	Loss Tangent T_p (°C)
	370°C	400°C		
CF/PPI-20	61	44	391	433
CF/PPI-20 (Postcured) ^c	93	83	430	441

^a Retention of storage modulus.

^b Temperature at the peak of curve.

^c Postcured at 350°C/10 h in N_2 .

6FDE, DAB, *p*-PDA, and the monoethyl ester of NE in anhydrous EtOH with NMP. This precursor was stable for a storage period of 2 weeks and showed good adhesive with carbon fibers to produce prepregs. Polymer composites reinforced with short carbon fibers could be fabricated using the prepregs at optimal thermal curing conditions. The thermally cured polymer materials and composite, after postcuring, showed excellent thermal stability, with initial decomposition temperature as high as 540°C. MDA experiments indicated that the materials showed a retention of storage modulus > 70–80% at 400°C and T_g s as high as 440–451°C.

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