Synthesis and Characterization of High-Temperature Fluorine-Containing PMR Polyimides

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Received July 29, 1999; Revised Manuscript Received September 15, 1999

ABSTRACT: The synthesis and characterization of novel fluorine-containing PMR polyimides derived from the diethyl ester of 4,4′-(2,2,2-trifluoro-1-phenylethylidene)diphthalic acid, *p*-phenylenediamine, and the monoethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid in low boiling solvents were described. The fluoropolyimide resin solutions are stable for several weeks at room temperatures and can easily impregnate carbon fibers to prepare prepregs. The molded resins exhibit outstanding thermal and thermooxidative stabilities at temperatures as high as 350 °C.

Introduction

PMR-15, an addition-type thermosetting polyimide synthesized by a process known as in-situ polymerization of monomer reactants (PMR), is a state-of-the-art commercial matrix resin for the fabrication of carbon fiber-reinforced composites with an upper use temperature of 316 °C (600 °F).[1,2] The requirement for polymer composites to resist thermal and thermooxidative degradation at high temperatures (350−400 °C) for applications in gas turbine engines, missiles, and high-speed civil transport has been the driving force for intensive research in this area over the past decade.[3~9] Hence, the second generation of PMR polyimides,[10−12] PMR-II, which were usually prepared from a fluorine-containing aromatic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), have been developed and successfully used in the manufacture of advanced aircraft engines.

4,4′-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic anhydride (3FDA), similar to 6FDA in chemical structure except that one of the trifluoromethyl groups (CF_3-) in 6FDA was replaced by a stable aromatic phenyl group (C_6H_5-), was first synthesized by Alston and Gratz[13] and employed to prepare linear polyimides.[13−15] It was found that these polymers exhibited high glass transition temperatures and outstanding thermooxidative stability at 371 °C in 1 and 4 atm of flowing air. Other linear 3FDA polyimides have also been prepared using 3FDA as an alternative to 6FDA.[16] It was demonstrated that 3FDA polyimides exhibit similar physical and mechanical properties to 6FDA polymers. 3FDA was also employed to replace one of the monomers, the dimethyl ester of 3,3,4,4′-benzophenonetetracarboxylic acid (BTDE), in PMR-15 resin to prepare the first generation of PMR polyimides.[14] However, few reports regarding the second generation of PMR polyimides employing 3FDA or its diester derivatives have appeared. To explore a matrix resin for more than 350 °C applications, a series of fluorine-containing PMR thermosetting polyimides using 3FDA have been synthesized and characterized in this laboratory. The chemical structures and thermal properties of the materials were intensively investigated.

Experimental Section

Materials. *p*-Phenylenediamine was obtained from the Chemical Factory of Beijing, China, and was vacuum sublimated at 115−200 °C/1−2 mmHg prior to use. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (NA) was purchased from the Chemical Factory of Nanxiang, Shanghai, China, and was vacuum sublimated at 120−125 °C/1−2 mmHg before use. Anhydrous ethyl alcohol (Chemical Factory of Beijing, China) was dried and distilled before use.

4,4′-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic anhydride (3FDA) was synthesized according to the method in the literature.[13,14] The purity of 3FDA was examined by GC-MS and found to be 99.5%.

Characterization. Differential scanning calorimetry (DSC) was performed using a Mettler DSC 25 instrument in air at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer 7 series thermal analysis system in air at a heating rate of 20 °C/min. Dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA) were carried out under nitrogen using a Perkin-Elmer 7 series thermal analysis system with a thermal analysis software (version 3.00). FT-IR spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrophotometer. ^{1}H NMR spectra were performed on a Varian Unity 200 spectrometer operating at 200 M Hz. The absolute viscosity of resin solution was measured in a NDJ-1 rotational viscometer (Shanghai Balance Instrument Corp., China) at 25 °C.

Synthesis of PMR Polyimide Resin Solutions. PMR resin solutions (50 w/w %) were prepared using the PMR process at room temperature by mixing the monomer solutions in anhydrous ethyl alcohol according to the literature.[1] The monomers employed were the monoethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NE) (prepared by refluxing a solution of NA in anhydrous ethyl alcohol), 4,4′-methylenediamine (MDA), and the diethyl ester of 3,3′4,4′-benzophenonetetracarboxylic acid (BTDE) (prepared by refluxing a suspension of the corresponding dianhydride in anhydrous ethyl alcohol). The mole ratios of reactants NE:BTDE:MDA were $2{:}n{:}(n + 1)$ which theoretically could yield oligomers with calculated molecular weights of 1500 (PMR-15, $n = 2$), 3000 (PMR-30, $n = 5$), and 5000 (PMR-50, $n = 9$).

Synthesis of 3FPMR Polyimide Resin Solutions. To a NE (13.91 g, 66.2 mmol) solution in anhydrous ethyl alcohol was added *p*-phenylenediamine (PDA) (21.47 g, 199 mmol). After the solid was completely dissolved, a solution of the diethyl ester of 4,4′-(2,2,2-trifluoro-1-phenylethylidene)diphthalic acid (3FDE) (90.07 g, 165 mmol), obtained by refluxing a solution of 4,4′-(2,2,2-trifluoro-1-phenylethylidene)diphthalic anhydride (3FDA) in anhydrous ethyl alcohol for 2 h, was added with mechanical stirring. The stirring was continued

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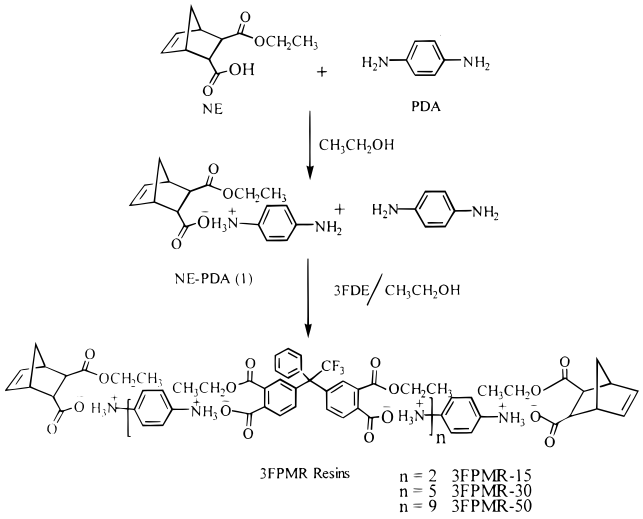
10.1021/ma991258g CCC: $18.00

Scheme 1. Chemistry of 3FPMR Resin



for 4 h at room temperature to yield a viscous resin solution (125 g, 50 w/w % solids) with absolute viscosity of 80−85 mPa·s measured by a rotational viscometer. The mole ratios of monomers NE:3FDE:PDA were 2:*n*:(*n* + 1) which yields oligomers with calculated molecular weights of 3000 (*n* = 5, 3FPMR-30)

^{1}H NMR (methanol-*d*, ppm): 4.1−4.3 (m, $-CO_2CH_2-$), 6.0−6.2 (d, $-CH{=}CH-$), 6.6−6.8 (b, $-N-C_6H_4-N-$), 7.0−7.8 (m, H on aromatic rings).

IR (KBr, cm^{-1}): 3300−3500 (−COOH, NH stretching), 2800−3000 (C−H, stretching), 2600−2650 (−OH of COOH), 1720 (C=O, stretching); 1550−1650 (C=O, stretching), 1520 (C−H in aromatic ring, stretching), 1380 (CH_3, stretching), 1270−1320 (C−F), 1080 (C−O), 820, 710 (C−H on aromatic rings).

3FPMR-15 (*n* = 2) and 3FPMR-50 (*n* = 9) with calculated molecular weights of 1500 and 5000, respectively, were also obtained by the same method.

3FPMR Polyimide Molding Powders. 3FPMR polyimide resin solution was evaporated with rotary evaporator at 50 °C to remove part of the solvent to yield a viscous liquid, which was then dried at 65 °C for 2 h in a vacuum to give a purple solid. The solid resin obtained was further heated at 120 °C for 2 h and then at 220 °C for 2 h to yield imidized molding powders.

Processing of Molding Powder into Molded Resin Plates. The imidized molding powder was placed into a 10 cm diameter die at room temperature. Then the die was placed into a press preheated at 220 °C. When the die temperature reached 280 °C, a pressure of 3−4 M Pa was applied. After 1 min, the pressure was released to allow traces of low molecular weight molecules to escape. Pressure was applied again after 10 s, and then the die temperature was increased at a rate of 3 °C/min to 320 °C under a pressure of 3−4 M Pa. After curing for 2 h at 320 °C, the die was allowed to cool under pressure to 200 °C, and then the pressure was released. The cured resin plate was removed from the die at room temperature.

Isothermal Aging. Isothermal stability studies were carried out in a circulating N_2 oven at the desired temperatures with an inlet N_2 flow of 100 mL/min. The oven temperature at three different points was recorded continuously during the run. The temperature was held constant at 350 ± 3 °C. The gas flow was controlled by a mass flow meter. Samples (2.5 × 2.5 × 1.0 mm) were placed in the oven and were weighed before and after isothermal aging for scheduled time intervals to determine weight loss. Isothermal thermooxidative stability was performed in air flow instead of nitrogen by the same method.

Results and Discussion

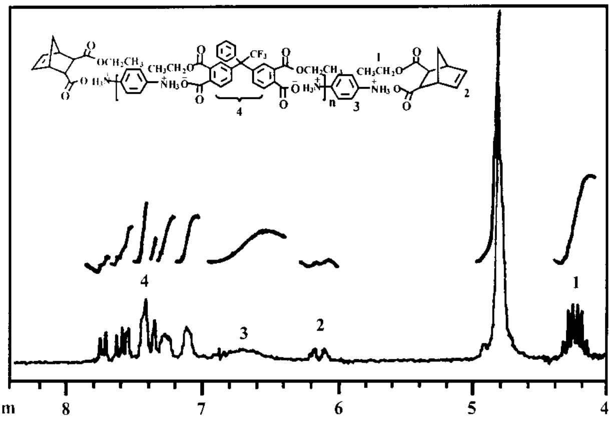


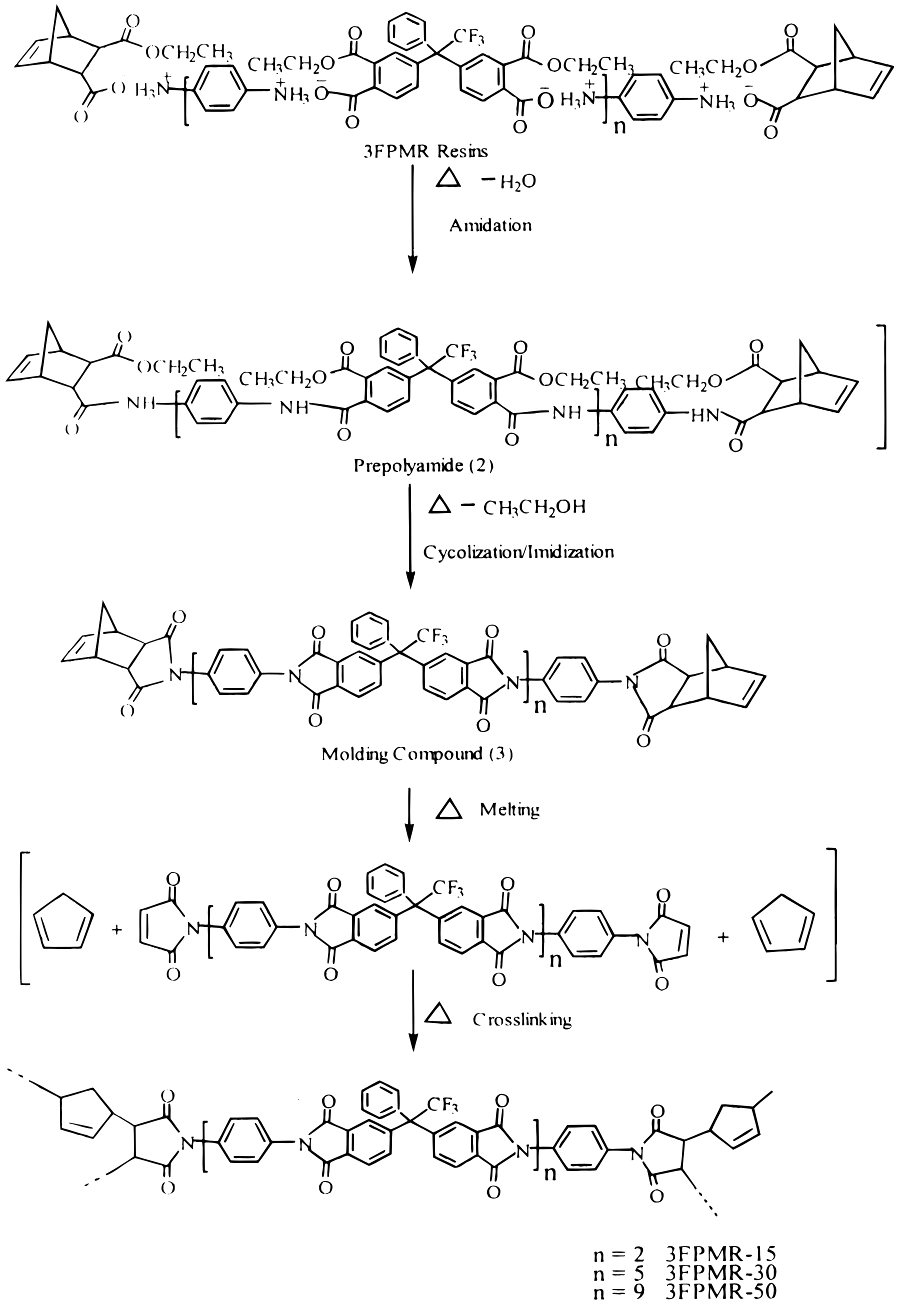
Figure 1. ^{1}H NMR spectrum of 3FPMR-30 resin in ethanol-*d*.

3FPMR Resin Solutions and the Ability to Produce Prepregs. In general, the PMR polyimide is synthesized by reacting an aromatic diamine with a dialkyl ester of an aromatic dianhydride at a calculated mole ratio in organic solvent to yield an oligomer solution which is then end-capped by adding an end-capping reagent such as the monoethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NE).[1] However, 3FPMR resins were prepared by first mixing the aromatic diamine, *p*-phenylenediamine (PDA), with end-caps (NE) at molar ratios [PDA]/[NE] > 5:1 in ethyl alcohol to yield a mixture of end-capped aromatic diamine, NE-PDA (1), with the remaining free PDA, which was then reacted with a dialkyl ester of an aromatic dianhydride (3FDE) solution to give 3FPMR resins (Scheme 1). The 3FPMR resins are presumed to be an end-capped polyamic acid−amine salt oligomer similar to PMR-15 in chemistry.[17,18] The mole ratio of NE:3FDE:PPA employed was 2:*n*:(*n* + 1). In this study, a series of 3FPMR resin formulations with calculated molecular weights of 1500 (*n* = 3, 3FPMR-15), 3000 (*n* = 5, 3FPMR-30), and 5000 (*n* = 9, 3FPMR-50) were prepared. The homogeneous resin solutions with 50 ± 2% solid contents show absolute viscosities in the range 70−85 cP, which are stable for storage of 3−4 weeks at room temperature and of more than 2 months at <4 °C. Neither phase separation nor decrease in viscosity was observed upon storing. The ^{1}H NMR spectrum indicates that 3FPMR resins were oligomers consisting of 3FDE, PDA, and NE (Figure 1).

3FPMR resins exhibit good adhesion to carbon fibers surface and are easy to produce carbon fiber prepregs. The prepregs displays good processing characteristics in the fabrication of composites. High-quality laminates can be produced from the prepregs by the hot press molding technique. The results regarding mechanical and electric properties of the carbon fiber-reinforced composites prepared using these resins will be reported elsewhere.

3FPMR Molding Powders. After most of the solvent in 3FPMR resin solutions was removed by baking in a vacuum, solid resin powders were obtained. The solid resin passed through two chemical processes to yield an imidized molding powder when heated from room temperature to 220 °C (Scheme 2). The first process is amidation of the polyamic acid−amine salt oligomers with evolution of 1 mol of water per 3FDE-PPA or NE-PPA unit to yield a polyamide backbone, prepolyamide (2), which occurs at 120−180 °C. In the DSC trace of the process, an endothermal absorption in the range 120−180 °C with a peak at 140−160 °C

Scheme 2. Chemical Reactions of 3FPMR Resins in Thermal Processing



was recorded (Figure 2). TGA results indicate that about 18−20% of weight loss for 3FPMR-30 resin dried at 65 °C was measured in the range 123−239 °C, which may be attributed partly to the escape of water (first process) on thermal treatment (Figure 3). The second one is cyclization/imidization of the amide groups with the ester in the etho-α-position of the aromatic ring to yield polyimide chains by evolving 1 mol of ethanol per polymer unit, which starts at about 180 °C and was completed at 280−300 °C. TGA results show a 7% weight loss in the range 235−350 °C, which may be assigned to the imidization process. Figure 4 compares the FTIR spectra of 3FPMR-30 solid resin dried at 65 °C and that of 3FPMR-30 molding powders precured at 220 °C. The solid resin (curve a) showed clearly the strong absorption bands due to the methyl and methylene groups in 3FDE at 3000 cm^{-1}, the carbonyl groups in amide linkages at 1720 cm^{-1}, and carboxylic acids at 2650 and 1550−1650 cm^{-1}, as well as the C−O stretch of ester groups at 1050 cm^{-1}. After thermal treatment, the FTIR (curve b) showed dramatic changes as a result of amidation and imidization processes. New bands at 1780 cm^{-1} (asymmetric stretching of carbonyl bond in imide groups) appeared while the bands at 3000, 2650, 1550−1650, and 1050 cm^{-1} disappeared, indicating that polyimide chains formed from the polyamide chains. A ^1H NMR spectrum of the sample heated at 220 °C shows only a trace resonance at 4.2−4.4 ppm (protons of $-CO_2-CH_2-$ at NE or 3FDE), implying that most of the ester groups were eliminated after imidization.

Molded Resin Plate Fabrication. 3FPMR molding powders can be processed by hot press methods similar to processing parameters of PMR-15, to yield a good quality cured resin plate. Two factors, temperature and applied pressure, must be controlled carefully. The molding powder possesses excellent melt flow characters at temperatures of 280−290 °C. Therefore,

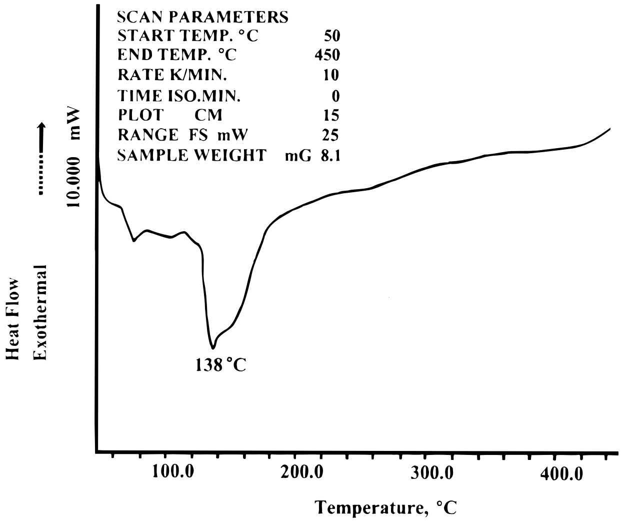


Figure 2. DSC of 3FPMR-30 resin dried at 65 °C.

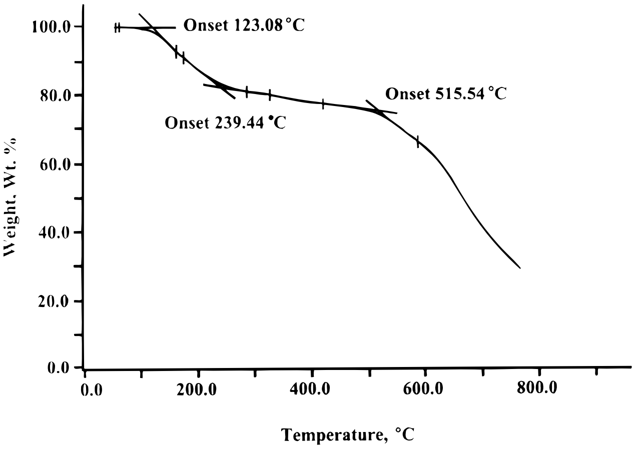


Figure 3. TGA of 3FPMR-30 resin powder dried at 65 °C in a vacuum.

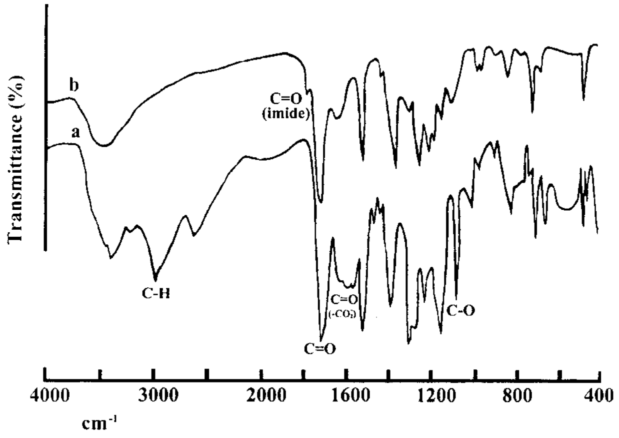


Figure 4. FT-IR spectra of 3FPMR-30 solid resin dried at 65 °C (a) and 3FPMR-30 molding powder precured at 220 °C (b).

the fabrication process was started at 280–290 °C and ended at 320–330 °C. Temperatures lower than 280 °C cannot ensure a molten resin with good flowing characteristics, while temperatures higher than 290 °C will accelerate the cross-linking of end-caps, decreasing the flow so that proper pressure is difficult to apply. Inadequate pressure application may cause either spillover of the molten resin from the die or a composite with poor quality.

Table 1. Transition Temperatures (T_g) of 3FPMR Resins Compared with PMR Resins Postcured at 371 °C in Nitrogen[a]

	postcure time, h		
resins	0	10	20
PMR-30	302	356	353
PMR-50	287	336	324
3FPMR-15	*b*	417	*c*
3FPMR-30	*b*	375	385
3FPMR-50	*b*	370	380

[a] All T_g values were determined by DSC. [b] No T_g detected by DSC. [c] Samples decomposed heavily under the postcuring conditions.

The chemical reactions in thermal processing are similar to PMR-15 resin.[19,20] A reverse Diels–Alder reaction of the norbornene end-caps probably takes place, producing maleimide end groups and free cyclopentadiene (Scheme 2). The maleic groups then reacted, to some degree, with the double bonds of the cyclopentadiene and unreacted norbornene groups to produce cross-linked structures. Thus, laminates with very low void content (<1–2%) can be produced.

Molded Resin Plate Evaluation. Prior to testing, all samples were inspected for porosity using either ultrasonic C-scan inspection or photomicrographs of plate cross sections. Table 1 shows the T_g values of the cured resin after postcure at 371 °C in nitrogen, as compared to that of PMR resins. Postcuring gives a T_g of 375 °C for 3FPMR-30 and of 370 °C for 3FPMR-50 after 10 h of curing. Increases of T_g by about 10 °C were observed if the postcuring time extended to 20 h. No glass transitions were observed in DSC for the samples without postcured. 3FPMR cured resins exhibit T_g's 30–55 °C higher than the corresponding PMR resins with the same calculated molecular weights. For instance, 3FPMR-30 with 20 h of postcuring shows a T_g of 385 °C, which is 32 °C high than that of PMR-30 (353 °C). Resins with higher calculated molecular weights exhibit lower T_g values. Thus, both 3FPMR-50 and PMR-50 exhibit lower values than 3FPMR-30 and PMR-30, respectively. These may be explained by the thermoplasticity of the long linear polymer chains in higher calculated molecular weight resins. High T_g value is one of the most desired characteristics for high-temperature polymer composites. In general, the T_g value of a high-temperature materials should be 20–30 °C over its long-term use temperature. Hence, the high T_g values of the 3FPMR resins imply that these materials may be potentially useful for >350 °C long-term applications.

Figure 5 shows the TGA of 3FPMR-30 molded resin. It can be seen that the material did not lose any weight until the temperature reaches as high as 450 °C. The decomposition temperature, given by 5% weight loss, is 536 °C and 10% weight loss at 567 °C. Table 2 shows the effect of postcuring parameters on 5% and 10% weight losses for 3FPMR-15, 3FPMR-30, and 3FPMR-50 molded resins. The 5% weight loss temperatures without postcuring were approximately 500–520 °C, and the 10% weight loss was about 550–560 °C for 3FPMR resins. After postcuring at 371 °C for 10 h, the 5% weight loss temperature increased to 525–540 °C and the 10% weight loss increases to 560–570 °C. More extended postcure time did not show obvious improvements in the thermal stability.

Figure 6 compares the dynamic mechanical analysis (DMA) curves of 3FPMR-30 molded resin with, and without, postcuring at 371 °C in nitrogen. After post-

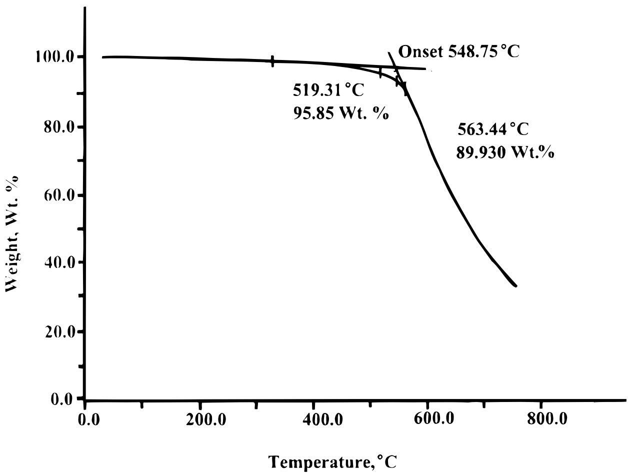


Figure 5. TGA of 3FPMR-30 molded resin.

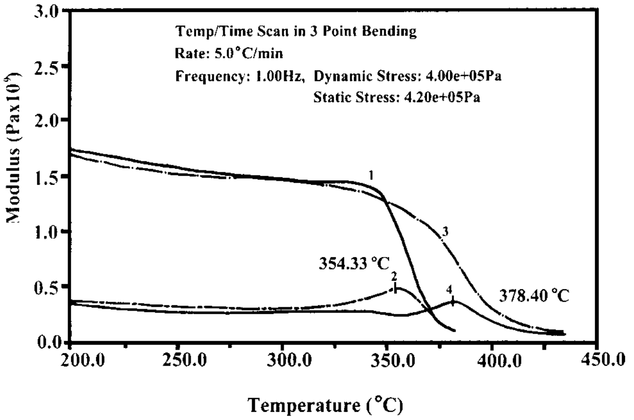


Figure 6. Comparison on DMA of 3FPMR-30 molded resins with and without postcuring. Postcuring conditions: 371 °C in N_2/24 h. Curve 1, E' of 3FPMR-30 without postcuring; curve 2, E'' of 3FPMR-30 without postcuring; curve 3, E' of 3FPMR-30 with postcuring; curve 4, E'' of 3FPMR-30 with postcuring.

Table 2. Effect of 371 °C Postcure Time on Decomposition Temperatures at 5% and 10% Weight Losses

postcure time, h	3FPMR-15		3FPMR-30		3FPMR-50	
	5%	10%	5%	10%	5%	10%
0	502	548	504	553	522	560
10	525	559	536	567	540	569
20	514	549	538	568	534	562

curing, the onset temperature of the storage modulus (E') for deteriorating increased by about 25−30 °C. T_g was also seen to increase 27−28 °C. TMA experiments indicate that 3FPMR molded resins possess coefficients of thermal expansion (CTE) in the range 40−60 × 10^{-6}/°C with an onset temperature of 340−345 °C.

Although T_g and the onset temperature of storage modulus for deteriorating were increased after postcuring, no changes in chemical structure were observed. After isothermal aging for 24 h at 371 °C in nitrogen, the FT-IR spectrum (Figure 7) shows no obvious difference in absorption.

Thermooxidative Stability Studies. Figure 8 shows the thermal stability of 3FPMR molded resins at 350 and 371 °C in flowing nitrogen (100 mL/min). At 350 °C, the materials lose only 4.0−5.2% of their original weights after isothermal aging for more than 500 h, indicating excellent thermal stability at high temperatures. The weight loss values increased linearly with the extension of isothermal aging, averaging about 0.01% of weight loss per hour. It was clear that 3FPMR-50 exhibits better thermal stability than 3FPMR-30.

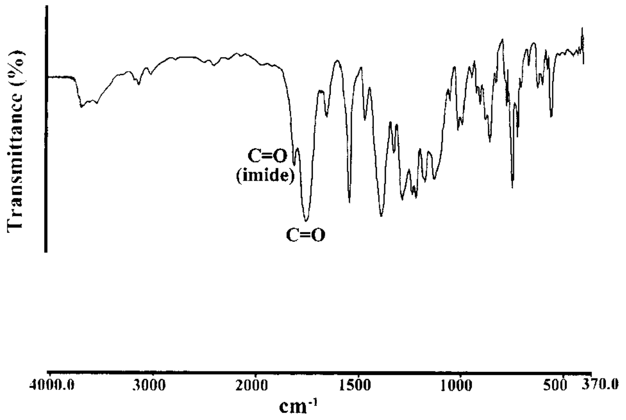


Figure 7. FT-IR spectrum of 3FPMR-30 molded resins postcured at 371 °C in nitrogen for 24 h.

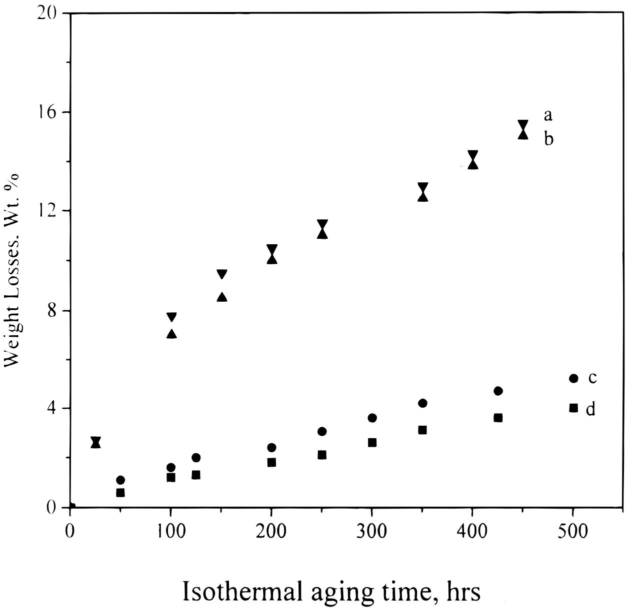


Figure 8. Thermal stability of 3FPMR resins at 350 and 371 °C isothermal aging in nitrogen: (a) 3FPMR-30 at 371 °C; (b) 3FPMR-50 at 371 °C; (c) 3FPMR-30 at 350 °C; (d) 3FPMR-50 at 350 °C.

Figure 9 compared the thermooxidative stabilities (TOS) of 3FPMR and PMR cured resin at 371 °C in air. 3FPMR-30 and 3FPMR-50 cured resins postcured at 371 °C lost 10−12% of weight in 100 h and 15−18% after aging for 175 h. In comparison, PMR-30 and PMR-50 postcured at 371 °C lost more than 28−42% of weight in 100 h, 3−4 times that of 3FPMR resins. It should be noted that 3FPMR-50 always lost less weight than 3FPMR-30 under the same conditions, indicating that 3FPMR-50 exhibits better thermooxidative stability than 3FPMR-30. This result may be attributed to the lower concentration of end-caps in 3FPMR-50 due to its higher calculated molecular weight.

In advanced aircraft engine and airframe applications, one of the critical factors considered acceptable for advanced carbon fiber-reinforced polymer composites is low weight loss at high temperature except for the mechanic properties at elevated temperatures such as flexural strength and modulus, interlaminar shear strength, etc. The result that only 4−5% of weight loss

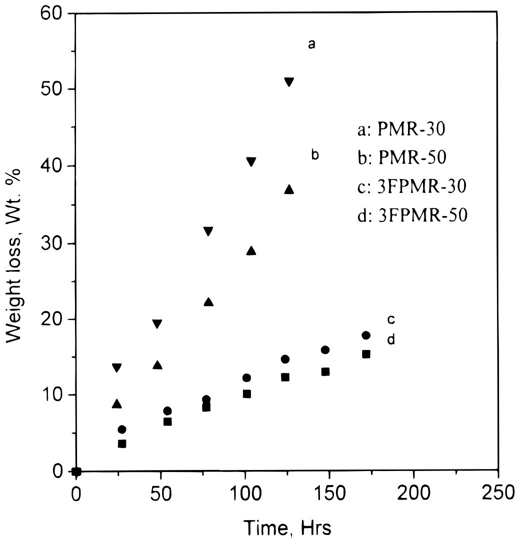


Figure 9. Thermooxidative stability of 3FPMR and PMR resin powder at 371 °C in air.

for 3FPMR resin at 350 °C in nitrogen occurs after exposure for 500 h, combined with its high T_g value, suggests that this kind of material may be a potential candidate for 350 °C applications in aeronautic and aerospace industries. Research on the mechanical properties including flexural strength and modulus, interlaminar shear strength, and SBS strength is underway, and the results will be published elsewhere.

Conclusions

Novel fluorine-containing PMR polyimide resins, 3FPMR-15, 3FPMR-30, and 3FPMR-50, were successfully prepared and characterized. The fluoro PMR polyimides display as good processing characteristics as commercial PMR-15 polyimide matrix resins. Isothermal aging experiments indicate that 3FPMR resins with high calculated molecular weights exhibit outstanding thermal and thermooxidative stabilities at temperatures as high as 350 °C, of which 3FPMR-30 and 3FPMR-50, with extended polymer chains and lower content of end-caps than 3FPMR-15, shows better thermooxidative resistance. It was suggested that these fluoropolyimides can be considered as potential low-cost candidates for 350 °C applications in aeronautic and aerospace industries.

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