

Preparation and Characterization of Mono-endcapped PMR Polyimide Matrix Resins for High Temperature Applications

J.Y. Hao, A. J. Hu, S.Q. Gao, L. Fan, S. Y. Yang

(State Key Laboratory of Engineering Plastics and Advanced Polymer Materials Laboratory,
Center for Molecular Science, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, China)

ABSTRACT Mono-endcapped PMR-type polyimide matrix resins were prepared by two synthetic pathways. Experimental results indicated that the matrix resins were low viscous and stable homogeneous solutions with 50% solid content in ethanol, possessing good characteristics for preparation of carbon or graphite fiber prepregs or B-staged molding compounds. The thermally cured polyimide materials as well as continuous carbon fiber-reinforced composites exhibited glass transition temperature (T_g) of > 470 °C and onset temperature of storage modulus of >440 °C, being 100 °C higher than that of commercial materials.

INTRODUCTION

Carbon fiber-reinforced PMR-type polyimide composites are very important thermosetting polymer materials for high temperature applications as structural or sub-structural components in supersonic aircraft and missile airframes^[1-3]. The first generation PMR polyimide composites are usually used in long term at temperature of < 310 - 320 °C, and the second generation PMR polyimide (PMR-II) materials have an improved long-term servicing temperature of 360 - 380 °C. However, the mechanical property and mechanical strength retention of the PMR-II composites at servicing temperature are relatively low, which seriously hamper their widespread applications.

A mono-endcapped PMR-II polyimide matrix resins were prepared and characterized, which were employed to prepare carbon fiber-reinforced polyimide composites with improved mechanical property and good process ability.

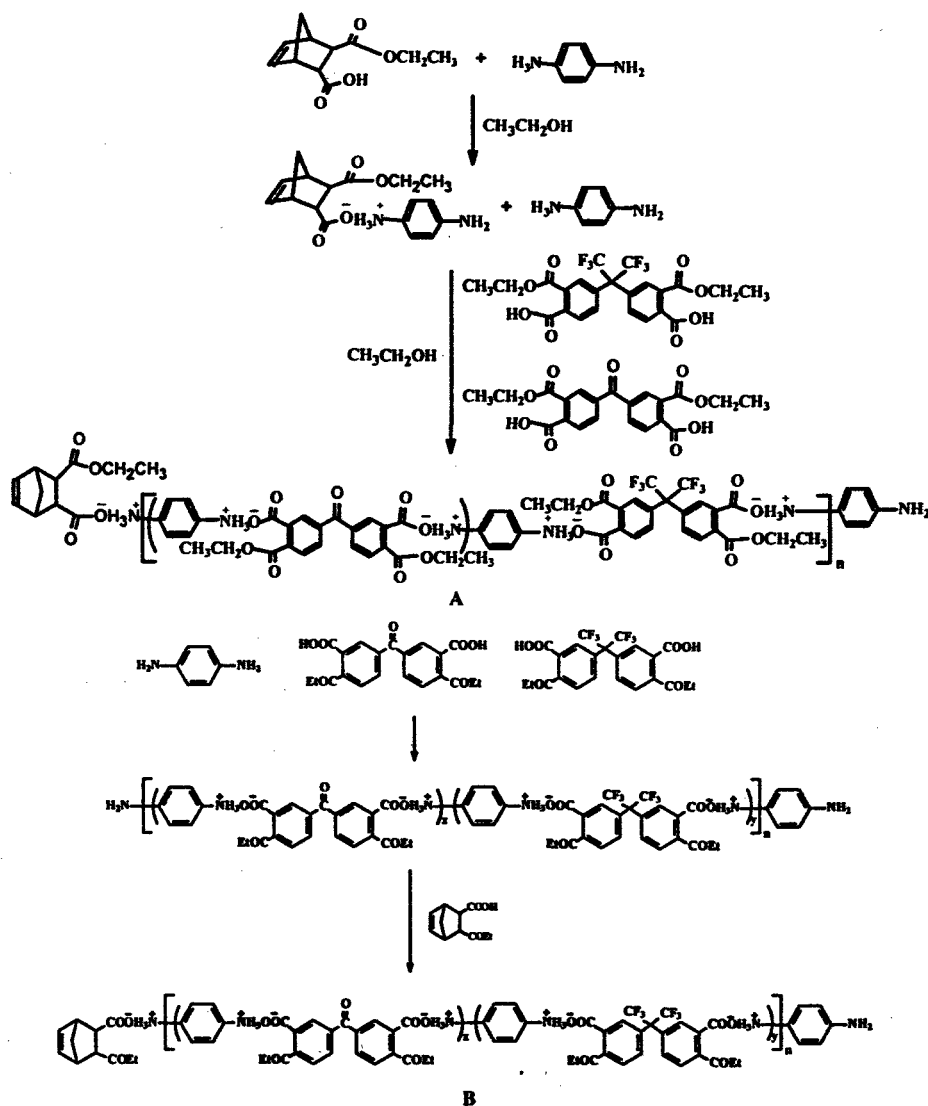
EXPERIMENTAL

A series of PMR polyimide matrix resin solution in ethanol (50 wt.%) consisted of NE, (BTDE+6FDE) and PDA with M_w of 5000 were prepared, in which BTDE content in anhydrides was formulated as 0.00 (PMR-1), 0.33 (PMR-2), 0.50 (PMR-3). After removing part of the solvents, B-staged polyimide precursor was obtained by further thermally baking the A-staged solid resin in the following schedule: 120 °C/2 hrs, 150 °C/2 hrs and then 200 °C/1 hrs. Thermally cured polyimide plates were fabricated by thermally curing the B-staged polyimide precursor at 320 °C/2 hrs, then 350 °C/2 hrs and finally 380 °C/1 hrs in a metal die by hot press technique.

RESULTS AND DISCUSSION

Preparation of matrix resins The matrix resin solution in ethanol (50 wt.%) were prepared by PMR procedure. Theoretically, there are probably three forms of oligomers existed in the matrix resin which differs from the version of end-capping. In order to explore the effect of oligomer forms on the performance of matrix resins, two preparation pathways were

employed as showed in Scheme 1. The matrix resin solutions, with $50\pm 2\%$ solid content, have absolute viscosity as low as 28-32 mPa·s at 25 °C which could be used to impregnate carbon fiber (T-300) to produce preregs. The adhesion of matrix resin to carbon fiber is good enough to ensure the prepreg laying in thermal processing.



Scheme 1 Preparation pathways of PMR matrix resins

Thermal and chemical process in processing B-staged polyimide resins were produced by thermally curing the A-staged matrix resins to 200 °C, in which two kinds of chemical reactions involved: 1) dehydration/amidization (80-150 °C); and 2) cyclization /imidization (>150 °C).

Figure 1 depicts the FT-IR spectra of A-staged and B-staged polyimide resins. New bands at $3400\text{-}3500\text{ cm}^{-1}$ (asymmetric stretching of N-H in imide group), 1780 cm^{-1} (asymmetric stretching of carbonyl bond in imide groups) and 770 cm^{-1} , were observed in B-staged polyimide resin, indicating the presence of imide groups in B-staged resin. The T_g values of the resins treated at 200 °C are ranged in 282-293 °C and the decomposition temperatures (T_d) were 550-561 °C.

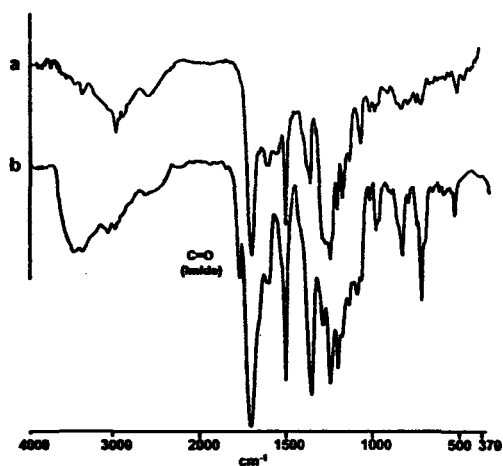


Figure 1. FT-IR spectra of PMR-3A thermally treated at different temperatures
 (a) Solid matrix resin dried at 60 °C (A-Stage)
 (b) Polyimide resins thermally treated at 200 °C (B-Stage)

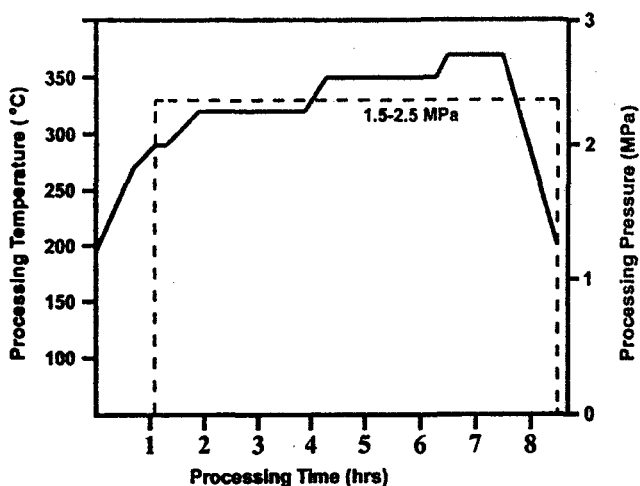


Figure 2. Thermal processing cycle of the cured polyimides

Table 1 Effect of postcuring on T_g s of cured polyimides

T_g °C \ Resin	PMR-1A	PMR-2A	PMR-3A	PMR-3B
Non-postcured	365	390	415	448
Postcured at 380 °C/10 hrs in N ₂	444	477	476	457
T_g	79	87	61	9

Thermally cured polyimide plates The B-staged polyimide resins was thermally cured to produce a crosslinked polyimide with a thermal process cycle as shown in Figure 2. It was found that the B-staged resins prepared by procedure A exhibited better process ability than that prepared by procedure B. T_g s (Table 1) of the freshly cured resins increased with increasing of carbonyl group concentration in polymer chains. The freshly prepared samples changed T_g s from 365 °C (PMR-1A) to 390 °C (PMR-2A), and 415 °C (PMR-3A). The dramatic increases in T_g values indicated that thermal curing for the freshly prepared samples are not fully completed. The freshly cured PMR-3B has a T_g of 448 °C, which increases only 9 °C for the postcured sample, implying that PMR-3B is thermally cured more mature than PMR-3A. This could be interpreted by the contribution of the endcapping morphology.

Figure 3 compares DMA curves between the mono-capped polyimide (PMR-3A) and the corresponding double-endcapped counterpart (PMR-3). The post-cured PMR-3A showed a T_g of 476 °C, which is 37 °C higher than that of the double-capped PMR-3 (439 °C) and 74 °C higher than PMR-II-50 (402 °C). Figure 4 depicts the thermal and thermo-oxidative stability of the thermally cured polyimides at elevated temperature (371 °C). In nitrogen, the cured polyimides lost its original weight of only <3.0 wt.% after isothermal aging for 550 hrs. In air atmosphere, the weight losses were in the range of 5-8 wt.% after 220 hrs of isothermal aging

and 13-18 wt.% after 350 hrs. In general, PMR-1A exhibited a little better thermal and thermo-oxidative stability than PMR-2A and PMR-3B, and the weight losses increased almost linearly with the increasing of isothermal aging time, indicating that the cured polyimide have excellent thermal and thermo-oxidative stability at 371 °C.

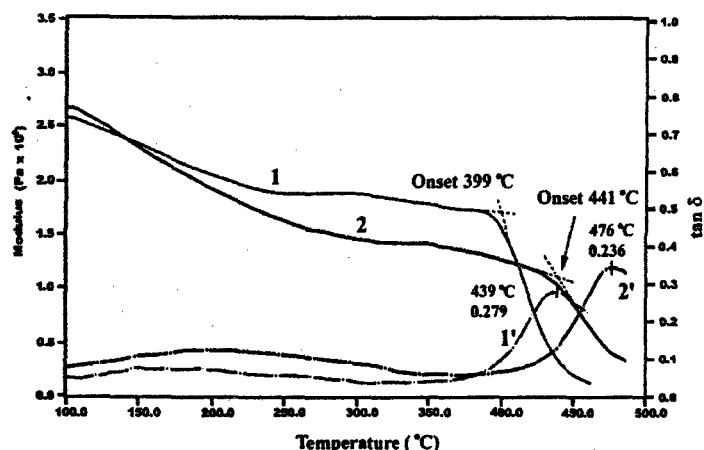


Figure 3 Comparison on DMA curves between PMR-3 and PMR-3A
 Curve 1: Storage modulus of PMR-3; Curve 2: Storage modulus of PMR-3A;
 Curve 1': tan δ of PMR-3; Curve 2': tan δ of PMR-3A.

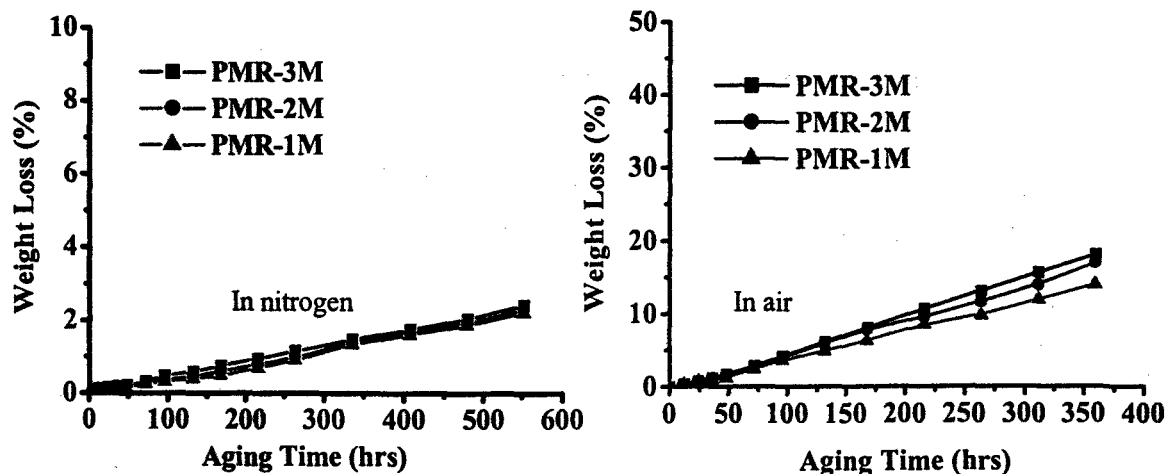


Figure 4 Thermo and thermooxidative stability of the thermally cured polyimides

Continuous carbon fiber-reinforced composites Unidirectional T-300/ PMR-3A composite laminate was fabricated by a thermal process to obtain a high quality composite laminate, with void content of <1-2%. Figure 5 depicts the DMA of the CF/PMR-3A composite laminate postcured at 371 °C for 10 hrs in nitrogen. It can be seen that the composite exhibited a very high glass transition temperature estimated at > 480 °C which is beyond the maximum detection limit of the instrument employed. A preliminary experiment was carried out to measure the mechanical strength of the T-300/PMR-3 composite laminate at 371 °C (700 °F) (Table 2). Obviously, CF/PMR-3A composite exhibits an improved mechanical property retention at 371 °C. This dramatic improvement in mechanical strength and modulus at elevated temperature could be attributed to the increase in glass transition temperature of the continuous polyimide resin phase caused by the incorporation of carbonyl groups into the polymer backbone and the rational distribution of the crosslinking sites in composites.

Table 2 Mechanical property of carbon fiber-reinforced composite laminates

Mechanical property	Composite	T-300/PMR-II-50	T-300/PMR-3A
	Flexural Strength (MPa)	R.T.	1050
371 °C		398	505
Retention		37.9%	47.7%
Flexural Modulus (GPa)	R.T.	80.0	106.7
	371 °C	43.0	99.7
	Retention	53.8%	93.4%

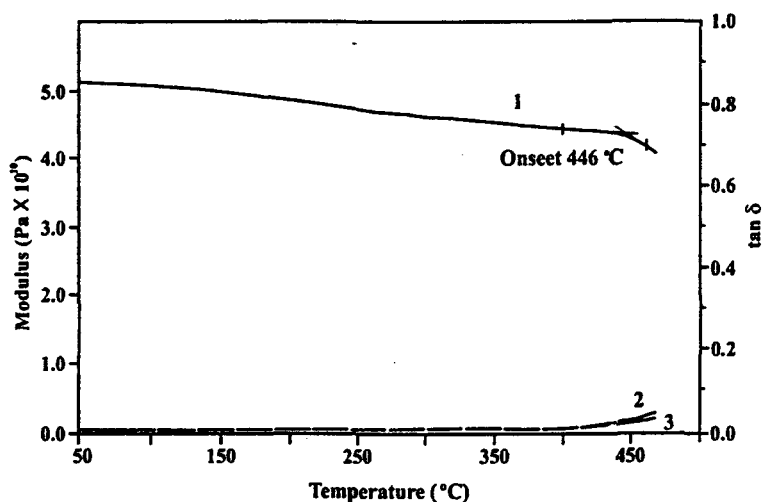


Figure 5 DMA curve of carbon fiber-reinforced PMR-3A composites
(1) Storage modulus; (2) Loss modulus; (3) $\tan \delta$

CONCLUSIONS

Mono-endcapped PMR-type polyimide matrix resins were prepared by incorporating of carbonyl groups into the polymer backbone of second generation PMR polyimide. The matrix resins have good characteristics to prepare carbon or graphite fiber prepreps or B-stage molding compounds. The thermally cured polyimide materials as well as continuous carbon fiber-reinforced composites both have glass transition temperature (T_g) of > 470 °C and onset temperature of storage modulus of > 440 °C. Preliminary results demonstrated that the composites laminate have high mechanical strength and mechanical property retention at 371 °C, superior to the commercial materials.

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