SYNTHESIS AND CHARACTERIZATION OF SHORT CARBON FIBER-REINFORCED PMR POLYIMIDE COMPOSITES

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ABSTRACT

Short carbon fiber-reinforced polyimide composites were prepared by wet impregnating chopped short carbon fibers with PMR type polyimide matrix resin solution followed by evaporating the solvent with strong stirring. The processing properties of the composites molding powders were investigated. The mechanical properties and thermo-oxidative stability of the composite laminates fabricated were also studied. Experimental results demonstrate that the short fiber filled molding powders exhibit good melt resin flowing characteristics and can be proceed by hot press molding technique to produce small-size, complicated composite structures which are difficulty to be produced using long fiber reinforced composite prepregs by autoclave technique.

KEY WORDS: Polyimides Carbon Fibers Composites Hot Press Laminates

1. INTRODUCTION

Thermosetting PMR polyimides which were synthesized using the process known as *in-situ* Polymerization of Monomer Reactants (PMR) are easier to process high quality composite structures than the corresponding thermoplastic polyimides(1-4). Carbon fiber-reinforced polyimide composites were usually produced by impregnating reinforced carbon fibers with PMR matrix resin followed by polymerization through crosslinking of the nadic end-capped groups and cyclodehydration to produce imide rings in polymer chains. The superior processability combined with great mechanical properties and excellent retention of mechanical properties at elevated temperature make them very attractive thermo-oxidative stable materials used at temperature as high as 320-400 °C for the application in advanced aeropropulsion systems(5-8). However, PMR polyimide composites has some notable shortcomings which severally limit their applications. One of them is the infeasibility to fabricate complicated structures due to the inadequate melt flowing properties of the prepregs. Thick, cylindrical structures are also difficulty to process due to the poor thermal conductivity of the molten fluid. To overcome these drawbacks, chopped short carbon fibers has been investigated in this laboratory as the reinforcing materials in replacing of the corresponding long carbon fibers in PMR polyimide composites, in which the short fibers were expected to be flowing easily with the molten matrix resins in the

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thermal curing process so that hot press molding technique may be suitable for the fabrications of some complicated parts.

The purpose of this study was to investigate the formulations of PMR type polyimide composites reinforced with short carbon fibers and to determine the effect of the formulations on processing characteristic, mechanical properties and thermo-oxidative stability of the composites.

2. EXPERIMENTAL

2.1 PMR Neat Resin Chemistry a PMR matrix resin solution (KH-304) was prepared using PMR process at room temperature by mixing the monomer solutions in anhydrous ethyl alcohol to form a 50 % solid solutions (Figure 1). The monomers employed are monoethyl ester of 5-norbornene-2,3-dicarboxylic acid(NE), 4,4'-methylenediamine (MDA), and diethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid(BTDE) which was prepared by refluxing a suspension of the corresponding dianhydride in anhydrous ethyl alcohol until all solids had been dissolved and then continuing for an additional two hours. The mole ratios of reactants NE:BTDE:MDA for PMR matrix resin is 2.000:2.087:3.087 which yields theoretically an oligomer with a calculated molecular weight of 1500.

Neat resin molding powder was prepared by placing matrix resin solution (100 g) into an air circulating oven set at 120 °C until almost all solvent had been evaporated and then dried at 220 °C at vacuum for 2 hrs to complete the imidization of the end-capped prepolymer.

2.2 Preparation of Composite Molding Powders 7.5 g of chopped T300 carbon fiber (length: 5-10 mm, diameter of 7-8 μm) was added to 85 g of 50 wt. % KH-304 matrix resin solution. Then the mixture was stirred mechanically for 2 hrs at room temperature in nitrogen. The solvent (ethyl alcohol) was distilled with strong stirring to produce a viscous materials in which about 15% of ethyl alcohol remained. The viscous materials was then dried in an air circulating oven at 100 °C for 4 hrs, 140 °C for 2 hrs, 200 °C for 4 hrs and 220 °C for 2 hrs, successively, to yield an imidized prepolymer molding powder with 15 wt. % of T300 fibers (Abbr. KH304-15).

KH304-7.5 and KH304-30 molding powders which contain 7.5 wt. % and 30 wt. % of T300 carbon fibers, respectively, were also prepared in the same procedure.

2.3 Melt Flowing Index(MFI) Melt flowing index of the composite molding powders were measured with XRT400 melt resin flowing index instrument in accordance with GB3682-83/ ASTM D1238-73, in which the diameter of mould exit in the sample tube was ∅1.18 mm and the loading was 7.056 kg.

2.4 Composite Laminate Fabrication The imidized prepolymer molding fine powder (50g) was placed into a 10 cm diameter metal 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 MPa was applied; After 1 min., the pressure was released to ensure the trace of low molecular weight molecules being escaped. The pressure was applied again after 10 seconds. This pressure releasing/applying cycles repeated three times. Then the die temperature increased at a rate of 3 °C /min. to 320 °C under a pressure of 3-4 MPa. After curing of 2 hrs at 320 °C , the die was allowed to cool under pressure to 200 °C, then the

pressure was released. The composite laminate was removed from the die at room temperature.

2.5 Laminate Evaluation Prior to testing, all laminates were inspected for porosity using either ultrasonic C-scan inspection or photomicrographs of the cross sections. Flexural tests were performed on 0.600 cm wide specimens in accordance with GB1449-87 at span to depth ratios of 15-16 at rate of 1.0 mm/min.. Tensile strength tests were performed on 0.600 cm wide specimens in accordance with GB1447-83 at rate of 5.0 mm/min.. Impact strength with un-notched specimens were carried out on Izod instrument in accordance with GB1451-83.

2.6 Isothermal Aging of Composite Laminates The laminate samples (0.6 x 0.4 x 6.0 cm^3) were placed in a circulating air oven at 320 °C with an inlet air flow of 100 ml/min. All samples were weighed after aging for scheduled time intervals.

3. RESULTS AND DISCUSSIONS

3.1 Preparation of the Composite Molding Powders Figure 1 shows the chemistry for synthesis of PMR-15 polyimides. The solvent used in this study was a mixture of ethyl alcohol with some additives instead of methyl alcohol for the health and environmental concerns arising from the use of methyl alcohol. Ethyl alcohol as the solvent of PMR-15 usually causes phase separation of the resin solution, especially in winter season, due to its inadequate dissolubility. This problem can be resolved by adding some additives in ethyl alcohol. The key feature for preparing short carbon fiber-reinforced PMR polyimide composites was to impregnate matrix resin on the fiber surface uniformly. Hence, fiber aggregation or cluster due to the different gravities between carbon fibers and matrix resin solution should be avoided in the impregnation process. The method employed in this study was to immerse the chopped short fiber into the resin solution and then to remove the solvent by evaporation with mechanical stirring. A homogeneous viscous material is obtained after removing of 80-85% of the solvent, in which no phase separation occur. A series of composite molding powders were prepared from PMR-15 resin and T300 fibers. Figure 2 shows the SEM photographs of the molding powders (KH304-15). It can be seen that the single short carbon fibers were coated completely with the matrix resin and no fiber clusters or aggregation was observed.

3.2 Melt Flowing Characteristic of the Molding Powders PMR polyimide neat resins possess good melt flowing properties which ensure them outstanding processing characteristics(1). The molding powders comprised of short carbon fiber and PMR polyimide resin also exhibit good melt flowing characteristic. Figure 3 shows the effect of temperature on MFI of the molding powder (KH304-15) in the range of 270-295 °C. The experimental results demonstrate that the melt flowing behaviors was influenced intensively by temperature. First, the rate of MFI increases when temperature increases. For instance, it needs 7 minutes for the molding resin to reach a maximum MFI value at 270 °C while the time at 295 °C is only 1 minute. The higher the temperature employed, the shorter the time to reach the maximum MFI. Second, the summit width of the curve which corresponds with the lifetime of melting resin with good flowing characteristic reduced as temperature increased. MFI were determined by two factors: the melting of the matrix resin and the crosslinking of the endcap groups. MFI increases with the resin melting and decreases with

the progress of the crosslinking. Third, the maximum MFI which corresponds to the lowest viscosity of the molten resin increased from 0.7 at 270 °C to an almost constant values of 3.3-3.5 above 280 °C (Figure 4), indicating that the molding powders melted completely at temperature of above 280 °C. Hence, the suggested temperature used in the composite processing is in the range of 280-290 °C where the MFI of the resin is high and the lifetime of molten resin with high MFI values is long enough so that it is easy to control the processing.

3.3 Composite Laminate Processing. Two factors which must be considered in the laminate processing are temperature and pressure. As suggested above, the temperature in the composite laminates fabrication was started at 280-290 °C and completed at 320 °C. The temperature lower than 280 °C can not produce a molten resin with high flowing character to fill the whole die, while the temperature above 290 °C will accelerate the crosslinking of the end-capped groups so that a proper pressure is difficulty to be applied. The factor that when and how much a pressure being applied in the molten fluid is also important in the processing. Inadequate pressure application may cause either the spillover of the molten resin from the die or the composite laminate produced with high void contents. The pressure employed in the processing of KH304-15 is 3-4 MPa in the method as described in Experimental section.

3.4 Laminate Studies Ultrasonic C-scanning of the composite laminates revealed that all the laminates reinforced with T300 fiber from 7.5-30 wt % were of adequate quality and showed least amount of void formation (< 2%). Table 1 lists the mechanical properties of the three laminates: KH304-7.5, KH304-15 and KH304-30 along with PMR-15. KH304-15 laminate exhibits the balanced mechanical properties: flexural strength: 130 MPa; flexural modulus: 7.7 GPa; tensile strength: 98 MPa, tensile modulus: 3.9 GPa. DMA experiment indicates that KH304-15 laminate has a glass transition temperature (Tg) of 355 °C. The density of the laminate is 1.55 g/cm^3.

Figure 5 shows the 320 °C thermo-oxidative stability(TOS) in flowing air (100 ml/min.) of the three composite laminates along with the chopped neat T300 fiber and PMR-15 neat resin. It can be seen that the TOS of the laminates increases with T300 loadings. The weight losses of the laminates with 15 and 30% of T300 fibers are 4.3 and 3.8 %, respectively, after 240 hrs air exposure at 320 °C, while that of neat T300 fiber and neat PMR resin are 6.5 and 6.0, respectively, under the same conditions. The results that the composites exhibit better TOS than that of either the fiber or the resin may be explained by the synergistic effect of matrix resin with reinforced materials in composite. A new region was formed in the interface region between polymer matrix resin and reinforced fibers in the composite, which impacts the thermo-oxidative stability of the composite. When the strength of fiber-resin bonds in the interface region is strong, air is difficulty to permeate into this region, hence the composite can withstand a long period of oxidative degradation. This is in accordance with the result reported by Bowles and Nowak(9), in which PMR-15/Celion 6K composite losses weight at a lower rate than either the matrix resin or the reinforced fibers.

Figure 6 is the SEM photograph of cross section of the laminate (KH304-15), in which the fibers were surrounded with a continuous matrix resin phase. The length to diameter(l/d) ratios of the short fiber in composite laminate was measured in the range of 30-35, which exceed the critical l/d ratio value of 20 for carbon fibers being as reinforced material in composites that ensures the effective transference of stress from matrix resin into carbon fibers.

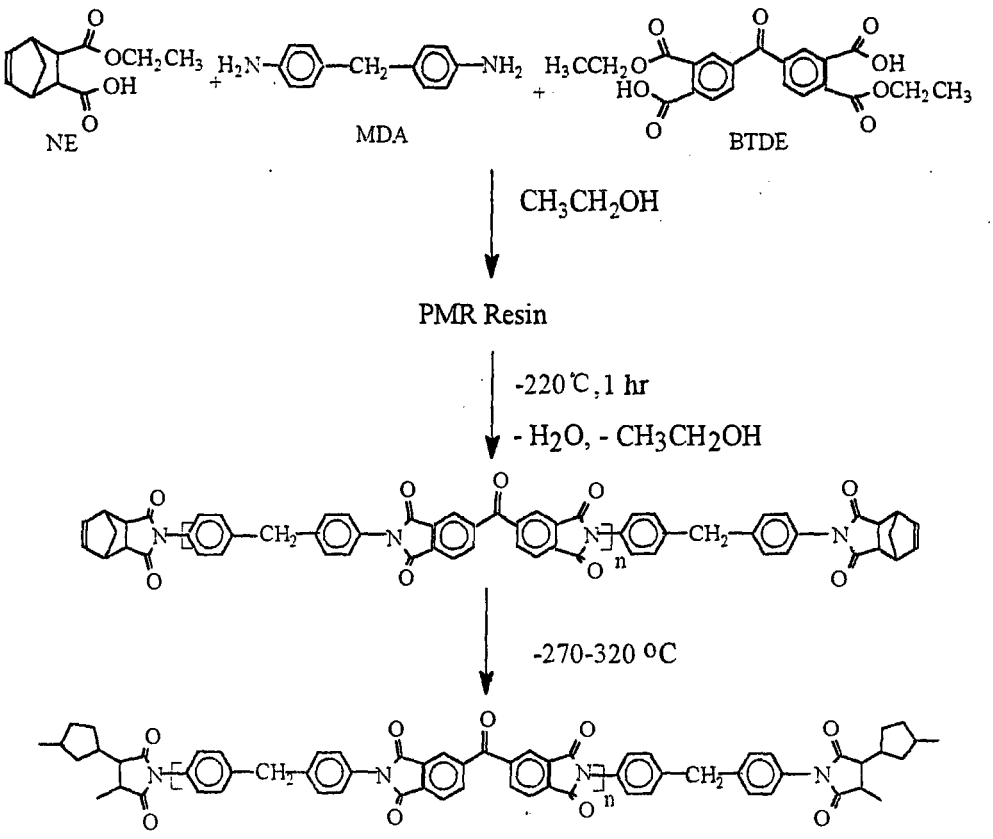

Figure 1 The chemistry of PMR-15 polyimide

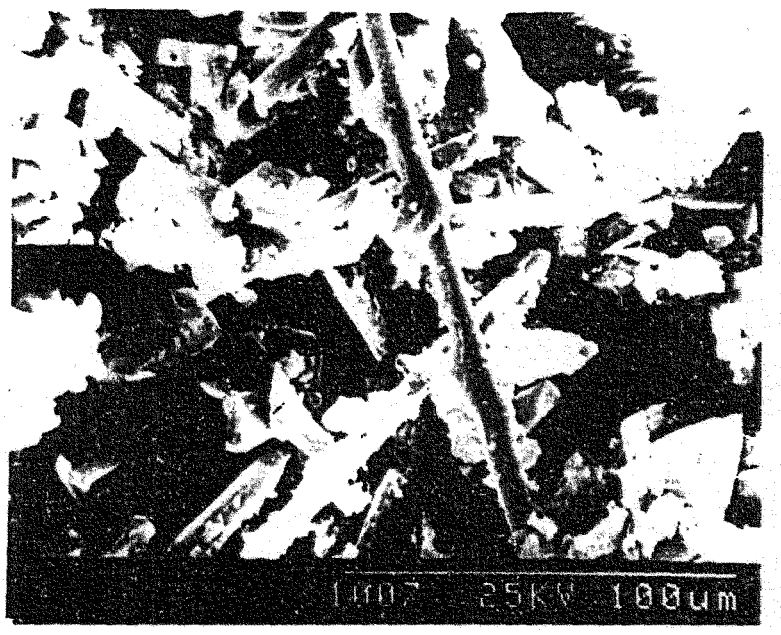

Figure 2 SEM photograph of the molding powder prepared from PMR-15 and short T300 fiber (KH304-15)

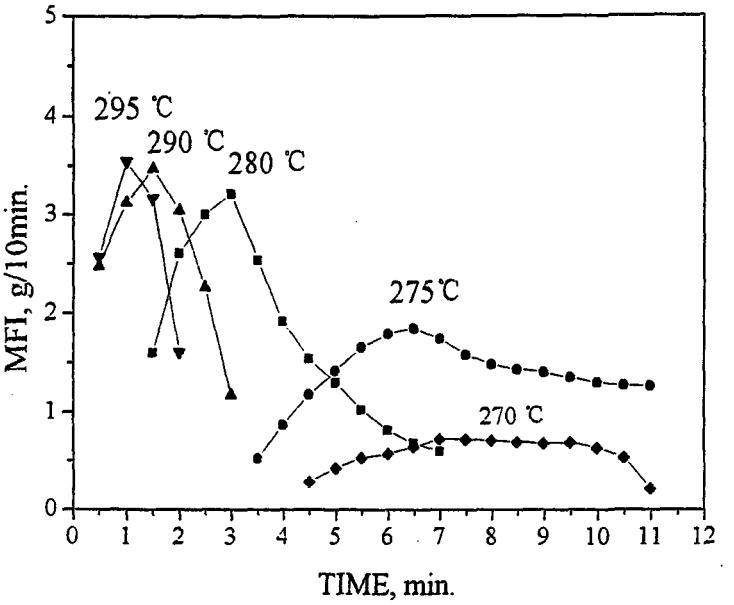

Figure 3 Melt flowing index of molding powder prepared from PMR-15 and 15 wt. % of short carbon fiber(KH304-15)

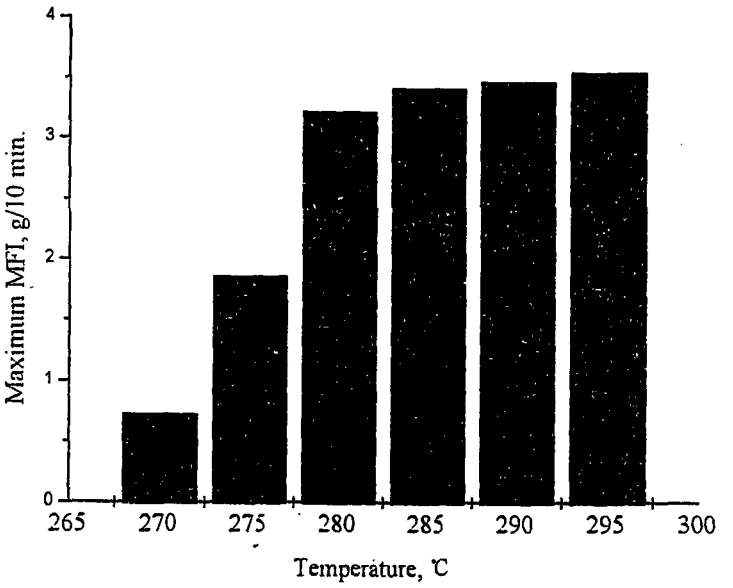

Figure 4 Effect of temperature on maximum MFI of molding powder prepared from PMR-15 and 15 wt.% of short carbon fiber(KH304-15)

Table 1 The physical properties of short carbon fiber-reinforced PMR-15 composites

	PMR-15	KH304-7.5	KH304-15	KH304-30
Decomposition temperature, °C	>400	491	497	490
Decomposition temperature at 5 wt.% of weight loss	466	490	495	505
Flexural Strength, MPa	-	106	130	117
Flexural Modulus, GPa	-	5.1	7.7	8.1
Tensile Strength, MPa	39	73	98	54
Tensile Modulus, GPa	3.9	2.4	3.9	3.3
Elongation at Breakage	-	3.4	2.7	2.3
Impact Strength, KJ/m^2	2	11	11	4.5
Weight loss in air, %				
110 hrs/1 atm	4.1	3.6	2.0	1.9
250 hrs/1 atm	5.5	5.3	4.5	3.8
CTE, x 10^{-6}/°C (20-250 °C)	43-46	46-54	52-58	48-53
Density, g/cm^3	1.33	1.45	1.55	1.76
Tg, °C	284	321	328(TMA) 355(DMA)	332

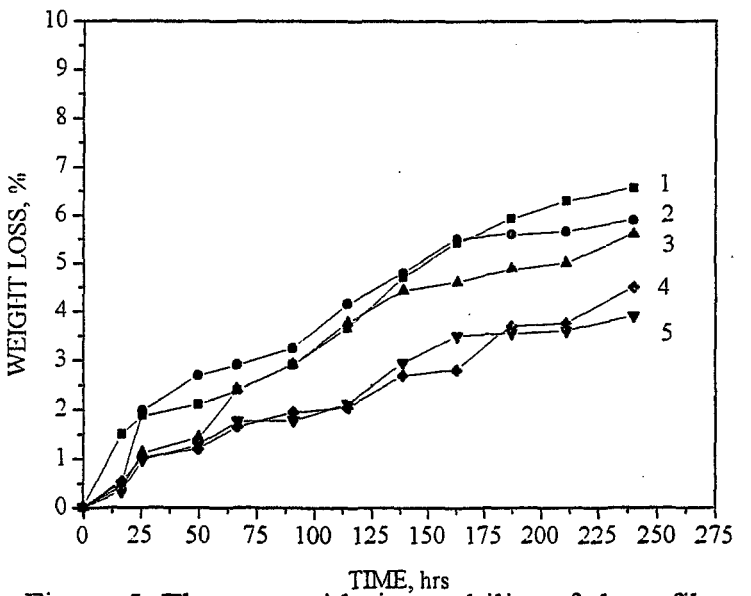

Figure 5 Thermo-oxidative stability of short fiber-reinforced PMR-15 polyimide composite laminates during 320℃ air exposure

1: T300 fiber; 2: PMR-15; 3: KH304-7.5
4: KH304-15; 5: KH304-30

Figure 6 SEM photogragh of the cross section of the composite laminate (KH304-15)

4. Conclusion

Uniform PMR polyimide composite molding powders, prepared by impregnating the chopped carbon fiber with PMR matrix resin solution and followed by removing the solvent with strong mechanical stirring, possess good melt flowing characteristics and processing properties. Composite laminates fabricated by hot press molding technique exhibit outstanding mechanical properties and good thermo-oxidative stabilities.

5. REFERENCES

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