Isomeric Polyimide Resins and Their Composites

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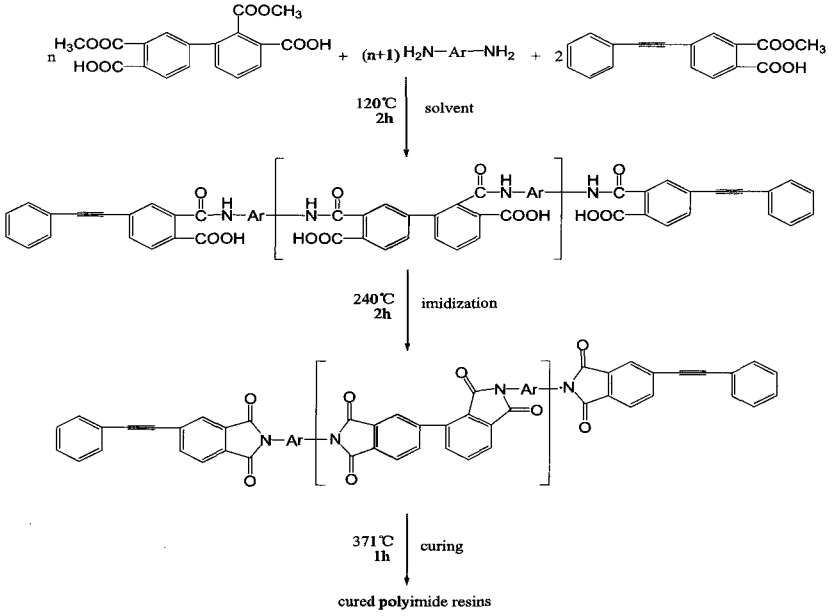
Abstract Low viscosity, high-temperature resistant isomeric polyimide resins were synthesized by modified polymerization of monomer reactants (MPMR) method. The shelf life of resin solution is more than two months. The lowest viscosity of imide resins is less than 200 Pa.s. The temperature for 5% mass loss ($T_{5\%}$) of cured resins is more than 500 °C. The flexural strength and flexural modulus of carbon fabric reinforced PI-1 composite at RT and 300℃ are 769MPa, 273 MPa and 49.1GPa, 34.3GPa; The flexural strength and flexural modulus of carbon fabric reinforced PI-2 composite at RT and 300 °C are 776MPa, 594MPa and 50.1GPa, 40.8GPa; The flexural strength of carbon fabric reinforced PI-3 composite at RT and 500 °C are 778MPa, 202MPa.

Key words: polyimide; composites; high-temperature resistant; low viscosity; mechanical properties

Experimental

Polyimide resins synthesis

Imide oligomers containing terminal phenylethynyl groups with a calculated number average molecular weight of 2000 g/mol were prepared by reacting asymmetric 2,3,3',4'-biphenyltetracarboxylic(a-BPDA) with varying mixtures of 3,4'-oxydianiline(3,4'-ODA), 4,4'-oxydianiline(4,4'-ODA), 3,5-diamino-4'-phenylethynylbenzophenone(DPEB), *m*-phenylene-diamine(*m*-PDA) and were endcapped with 4-PEPA. The appropriate molar weight of 3,4-BPDE, 4-PEPE and diamine dissolving in 1,4-dioxane were added into a reaction bottle, and the solids concentration was adjusted to 40%. The reaction mixture was stirred for 2 h at 120 °C. Imide powder was prepared by thermal imidization of the amide acid for 2 h at 240 °C, and then the cured polyimide resins were obtained through curing for 1 h at 371°C (Figure 1).



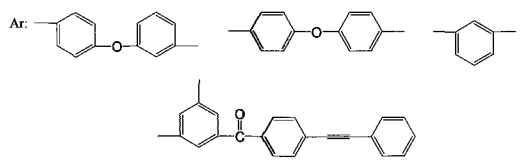


Fig.1 Synthesis of the polyimide resins

Results and Discussion

To assess the effects of aging on changes in molecular weight distribution, the MPMR solution was stored at room temperature over a ninety-day period. The effect of aging of solution on intrinsic viscosity has been displayed in Figure 2. From the data obtained at room temperature, it can be seen that the intrinsic viscosity of 40% solids solution ranged from 0.2 to 0.35 Pa.s within sixty days, after the eightieth day the intrinsic viscosity of solution increased rapidly. This phenomenon indicates that the solution prepared by MPMR method has good stability. The storage time of solution is more than two months at RT.

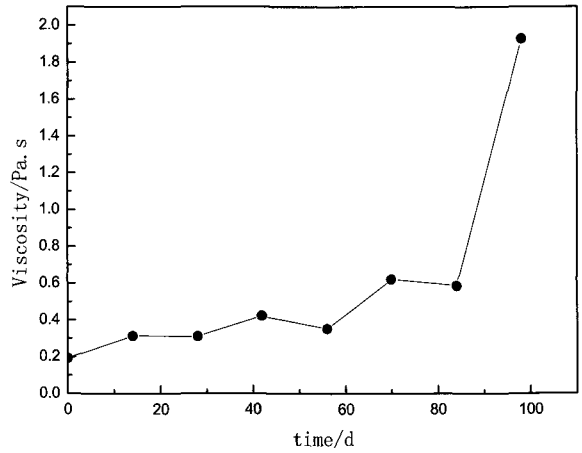


Fig.2 Stability of polyimide resin solution

The dynamic rheological curves of imide oligomers are displayed in Figure 3. Dynamic rheology behavior is employed to investigate the melt processability of the imide resins.The melt rheology was performed with an imide resin disc with a diameter of 25 mm compressed at 90 °C. The specimen was heated at a heating rate of 4 °C /min. The three resins can completely melt at 250 °C and start to cure at 350 °C, therefore, the melt temperature width is about 100 °C. The lowest viscosity of imide resins is less than 200 Pa.s, and the temperature of minimum viscosity is between 310 °C and 340 °C. The viscosity of

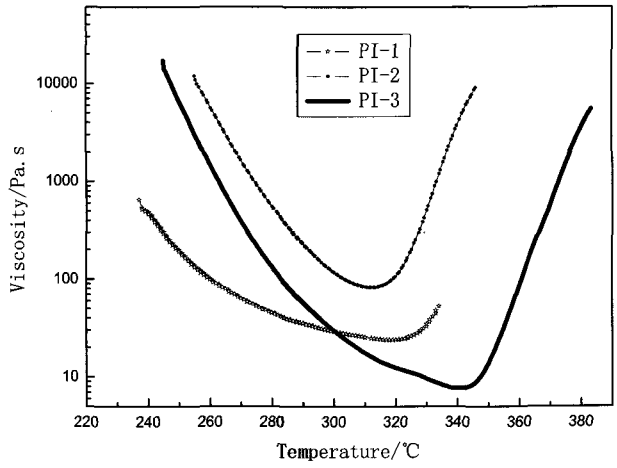


Fig.3 Viscosity curves of oligomer resins

resins increases rapidly over 340 °C due to the thermal crosslinking reaction of the terminal phenylethynyl groups.

The phenylethynyl-endcapped imide resins can be thermally cured at 371 °C for 1h to obtain thermoset polyimides, the thermal properties of the thermoset polyimides are shown in Figure 4. The TGA was performed at a heating rate of 10 °C/min in air. From TGA curves, no obvious weight loss was detected until the temperature was scanned up to 450 °C. Therefore, all products have excellent thermal stability due to their fully aromatic chemical structure. For example, the $T_{5\%}$ values of the thermoset PI-2 and PI-3 are 531 °C and 567 °C. In addition, the thermal stability of the thermoset polyimide has been improved with increasing in the calculated M_n value.

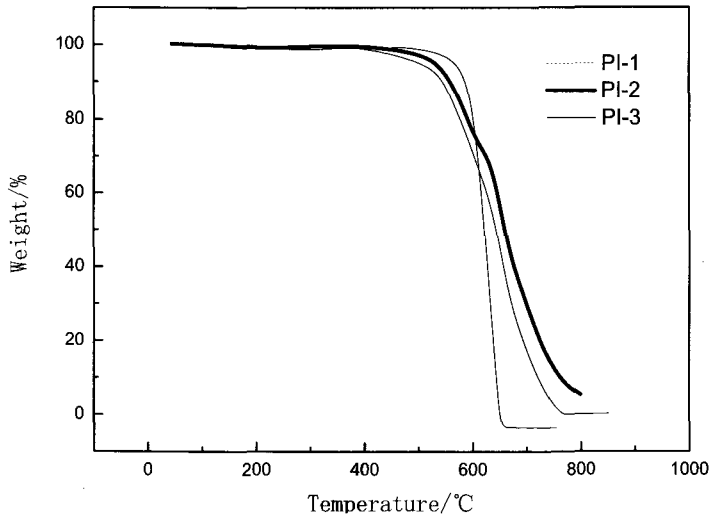


Fig.4 TGA curves of the neat resins

According to the rheological behaviour of imide resins, the processing procedure of composites is 120 °C /1h+240 °C /2h+371 °C /1h, while the elevated speed of temperature is 3-4 °C /min, 1MPa is used at 300 °C.

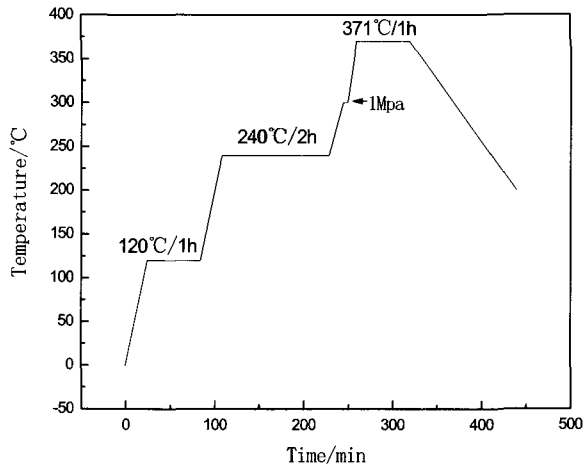


Fig.5 Processing technic of composite

Table 1 lists thermal properties and flexibility properties at room temperature and elevated temperature for carbon fabric reinforced composites based on the different formulations of PIs. It is known that composite properties are governed by many factors, such as composition and processing conditions. The laminates have fibre volumes of 60% and the processing technics are identical for the three composites. From the Table 1, it can be see that the flexural strength, flexural modulus at room

temperature are nearly equal, it indicates that changing molecular composition and the molecular weight has no significant effect on the flexural properties of composites. However, the flexural strength for PI-2 is higher than PI-1 composite at elevated temperature. This suggests that the retentivity of flexural properties of composites at elevated temperature is governed by the glass transition temperature.

Talbe.1 Flexibility properties and thermal properties for the polyimide composites

Composites	T_g/°C	Temperature/ °C	Flexural strength /MPa	Flexural modulus /GPa
fabric/PI-1	322	RT	769	49.1
		300	273	34.3
fabric /PI-2	345	RT	776	50.1
		300	594	40.8
fabric /PI-3	416	RT	778	—
		300	—	—

Acknowledgements:

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