

Effect of Diamine Structure on Properties of PMR Copolyimide Resin

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Abstract: In this paper, a series of BTDE-MDA/PPD and BTDE-MDA/MPD PMR copolyimide resin were synthesized by introducing PPD or MPD to diamine of PMR-15 system. The effect of diamine structure on resin-solution's viscosity, thermo-oxidative stability and impact intensity of the cured resins were also discussed.

Keyword: Copolyimide, PMR-15, viscosity, thermo-oxidative stability, impact intensity

1. Introduction

In the latest 30 years, advanced composites have been widely used into the fields of aeronautics and astronautics etc with perfect thermo-oxidative stability and mechanic property, using thermosetting polyimide as matrix based on PMR (Polymerization of Monomer Reactants)^[1-3]. Now, PMR-15 is the most widely used polyimide resin as composites matrix. It can be used under 316°C for a long time, but not good enough in high temperature property and mechanic property^[4,5]. To overcome the shortcoming, NASA developed PMR-II-50, V-CAP, AFR-700 etc, and some of them have perfect mechanic properties in 371°C^[6,7]. But the cost of the resins is too high because of using 4,4'-hexa-fluoro-isopropylidene dianhydride (6FDA). So one of the main directions of research is to synthesize low-cost polyimide resin without fluorine, which can be used in high temperature.

Copolymerization is a method to improve properties of resin. Based on PMR-15, p-phenylene dianiline (PPD) or m-phenylene dianiline (MPD) were introduced into diamine—BTDE, NE, MDA and PPD or MPD are used as raw materials to synthesize PMR copolyimide resin. Accounting for the dissolvable ability in alcohol, cost and common using of diamines, we chose PPD and MPD as monomer for copolymerization. And as PMR resin system is used for composites matrix, molecular weight of prepolymer cannot be too big otherwise making it difficult to shape. So the maximum molecular weight of prepolymer is 8000(calculated value) in our experiment. This paper discussed the relation between constitutes of different copolymer system and resin-solution viscosity, thermo-oxidative stability and impact intensity of cured resin. The effect of molecular weight of prepolymer on resin performance in the same copolymer system was also discussed.

2. Experimental

2.1 Materials

Raw material used: 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-methylenedianiline (MDA), p-phenylene dianiline (PPD), m-phenylene dianiline (MPD), 5-norbornene-2,3-dicarboxylic anhydride (NA) and anhydrous alcohol. All agents was tested and purified before used.

2.2 Preparation of resin solution

BTDA and NA were esterified respectively in anhydrous alcohol by heating and refluxing and produced BTDE and NE. Then BTDE and NE were moved into alcohol solution mixed with MDA and PPD (or mixed with MDA and MPD) proportionally. The mixture were mixed well and got resin solution with solid content of about 50%. Those solutions were kept in room temperature.

2.3 Measurements

Viscosity of those resin solutions were tested at 20°C by VIA-15 Faraday viscosimeter.

Thermogravimetric analysis (TGA) was used to evaluate the thermo-oxidative stability of the cured resins, using TGA-1000 with a heating rate of 10°C/min under air flow and from room temperature to 800°C. The preparation of the sample is as follows: The solvent of resin solution was removed in a vacuum circumstance, then raised the temperature to 200°C and held the temperature until the weight of the resin stops decreasing. Then the temperature was raised to 300°C and held it for 2 hours.

The impact intensity of the cured resins (the standard samples) were tested by impact testing machine ($40\text{kg} \cdot \text{cm}^{-1}$). The preparation of the sample is as follows: The solvent of resin solution was removed in a vacuum circumstance, then raised the temperature to 200°C and held the temperature until the weight of the resin stops decreasing. The outcome powder was put into mould and heat in the compressor, then impose 5MPa pressure when the temperature reached 240°C. At last, the temperature was raised to 320°C, then hold the temperature and pressure for 3 hours.

3. Results and discussion

3.1 Relation of resin structure and resin-solution's viscosity

Figure 1 shows the relation curve of the content (mol) of MPD or PPD in diamines and the resin-solution's viscosity of BTDE—MDA/PPD(for short BMP-x, $x=15, 30, 50, 80$, corresponding molecular weight are 1500, 3000, 5000, 8000 respectively) and BTDE-MDA/MPD (for short BMM-x) copolymer systems. From the figure, we can see as the molecular weight of prepolymer increases, resin-solution's viscosity increases. When the molecular weight of copolymers is same, resin-solution's viscosity will decrease with the increasing of content of MPD or PPD in diamines. Introducing MPD or PPD can increase rigidity of molecular chain and decrease the entwisting of molecules, causing resin-solution's viscosity to decrease. It is worthy noticing that in the same content of copolymer constitution, viscosity of BMM-x is smaller than that of BMP-x with the same molecular weight. This is because that the asymmetry of MPD structure makes molecules difficult to entwist and increases the space between molecules.

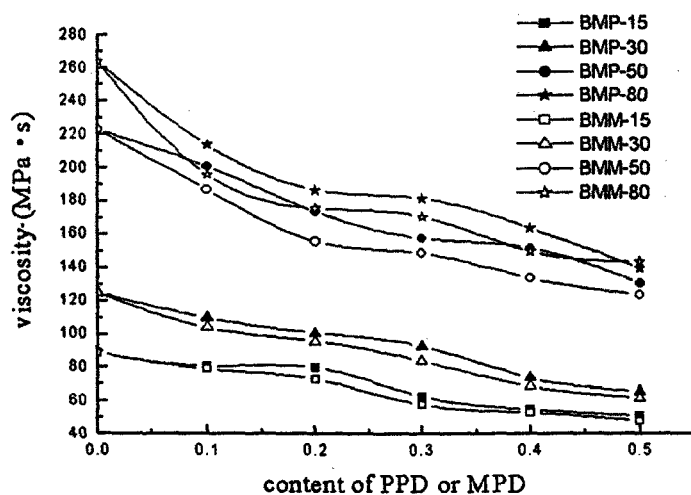


Fig.1 Viscosity vs. content of PPD or MPD

3.2 Relation of resin structure and thermo-oxidative stability

Figure 2 shows the relation between the temperature of 5% weight loss and the content of PPD or MPD of BMP-x and BMM-x copolymer system. Figure 3 shows the relation between the temperature of 10% weight loss and the content of PPD or MPD of BMP-x and BMM-x copolymer system.

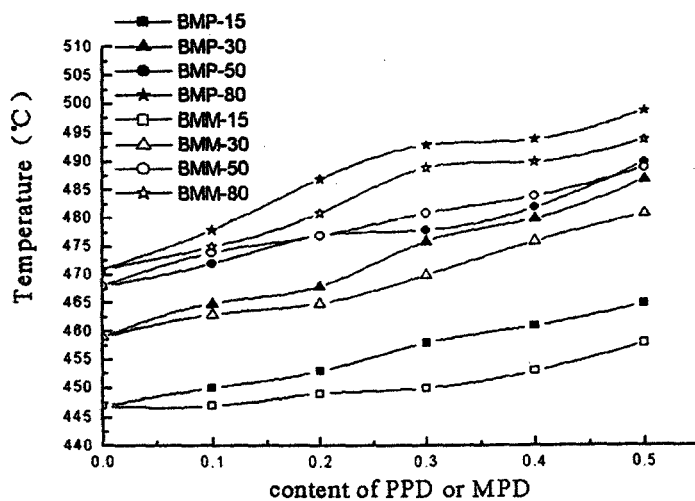


Fig.2 Temperature of 5% weight loss vs. content of PPD or MPD

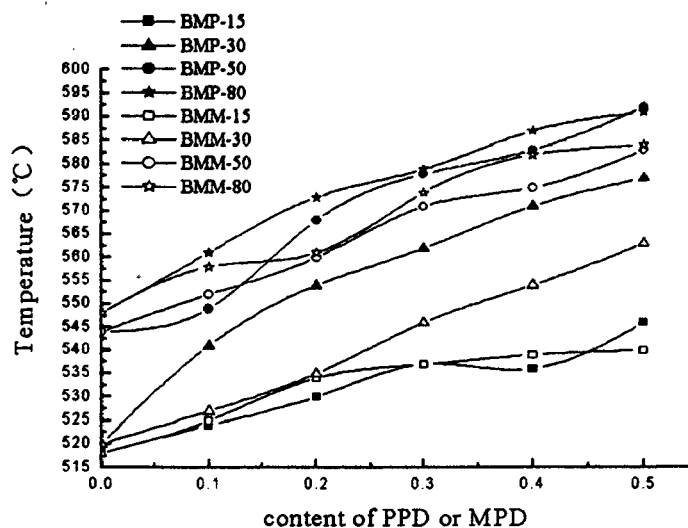


Fig.3 Temperature of 10% weight loss vs. content of PPD or MPD

From figure 2 and figure 3, we can find that the temperature of thermogravimetric increases as molecular weight of prepolymer of the same molecular structure increases. This is because that as molecular weight of prepolymer increases, content of aliphatic chain brought by NE decreases comparatively resulting in the increasing of the thermo stability. For the same molecular weight system, as the content of PPD or MPD increases, the temperature of 5% or 10% weight loss will increase greatly. Research indicates that the H atoms of methylene in MDA are the weakness of polyimide containing MDA. The H atom will disassemble to free radical or ion from methylene under high temperature resulting in chain pyrogenation. Adding PPD or MPD can decrease the content of H atom that can be disassembled, so the pyrogenation temperatures of system increase. In addition, adding PPD or MPD can also increase the density of aromatic and imide rings in the molecular chain, which can increase the thermo-oxidative stability of the system too.

We can also see from the figures that introducing PPD to BMP-x system has a more positive effect on increasing the thermo-oxidative stability than introducing MPD to BMM-x system. This is because that irregular structure of MPD makes molecular chain easy to break, making the temperature of 5% or 10% weight loss of BMM-x copolymer lower than BMP-x copolymer.

3.3 Relation of resin structure and impact intensity

Figure 4 shows the relation curve of resin impact intensity vs. content of PPD in BMP-x or of MPD in BMM-x system. If molecular weight of the system remains constantly, resin impact intensity decreases as the content of PPD or MPD increases. This is because with the introducing of phenylene dianiline, the rigidity of molecular chain increases, and the brittleness of the resin increases. With little exceptional data, when the molecular weight and content of diamine are same, impact intensity of BMP-x is higher than that of BMM-x. This is because that the structure of PPD is more regular and symmetric than MPD, which results in the chains of PPD move easier than MPD. This make BMP-x resin system more tough.

Figure 5 shows the relation curve of resin impact intensity vs. the molecular weight of BMP-x and BMM-x system. For the system of the same constitution, impact intensity increases first and then decreases as the molecular weight increases. Of all the different

molecular weight in the experimental data, when the molecular weight is about 3000, the impact intensity is the highest. There are two factors which determinate the impact intensity of resin: crosslinking density and spreading ability of molecular chain. But the two factors have contrary effect on impact intensity. Increasing crosslinking density will increase the rigidity of molecule and modulus of resin. But increasing spreading ability of molecular chain will decrease impact intensity. When the molecular weight is small, crosslinking density is high and molecular chain is short with limited ability of spreading. As molecular weight increases, crosslinking density decreases and spreading ability of molecular chain increases. When the effect of latter is bigger than the former, impact intensity increases. If the molecular weight is big enough, when the increment of the spreading ability of molecular chain can't counteract the effect made by decreasing of crosslinking density, the impact intensity of the resin will decrease.

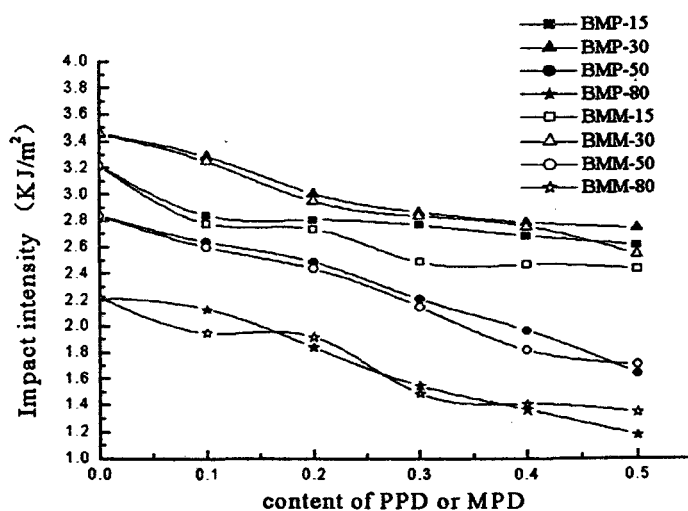


Fig.4 Impact intensity vs. content of PPD or MPD

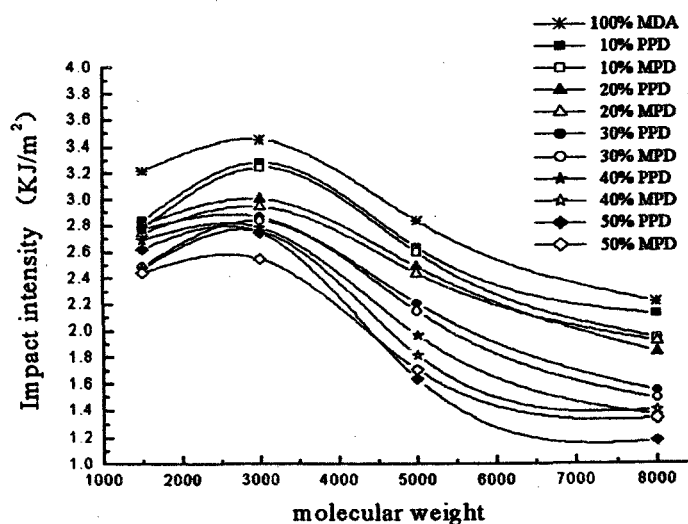


Fig.5 Impact intensity vs. molecular weight

4. Conclusions

1. Resin-solution's viscosity of BMP-x and BMM-x copolymer systems increase as

molecular weight increases. And the viscosity decrease as content of PPD or MPD increases. When the content of copolymer constitution is constant, viscosity of BMM-x is smaller than that of BMP-x with the same molecular weight.

2. The thermo-oxidative stability of PMR copolyimide resin system increases as the molecular weight increases and it also increases as content of PPD or MPD increases. PPD has a more positive effect on the stability than MPD.

3. The impact intensity of PMR copolyimide resin system decreases as the content of PPD or MPD increases. However, the impact intensity increases first and then decreases as molecular weight of prepolymer increases. Of all the different molecular weight in the experimental data, when the molecular weight is about 3000, the impact intensity is the highest.

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