Preparation and Performance of Polyimide with Noncoplanar Structure

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***Abstract*—A series of polyimide was prepared based on 3,3',4,4'-biphenyltetra carboxylic dianhydride (BPDA) with noncoplanar, 1,2,4,5-benzenetetracarboxylicanhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA). The effect of the polymer structure and imidization temperature on the thermal stability and mechanical properties of polyimide was investigated. The results showed that the toughness of polyimide were effectively improved as the noncoplanar structure was introduced into polyimide molecular chain. The mechanical properties of polyimide reached the maximun at imidization temperature of 300℃. The tensile strength and elongation at break of polyimide were 51.84 MPa and 13.63% respectively, and the high** heat **resistance was excellent**.

Keywords-polyimide; imidization; thermal stability; mechanical property

I. INTRODUCTION

The high performance special engineering plastic can be made of polyimide by being moulded. Because of the excellent heat resistance and mechanical properties, the polyimide has been used widely, such as film, paint, fiber, foam plastics, engineering plastics and so on. At present, a lot of commercial polyimide, which was prepared from aromatic dianhydride and diamine with symmetric structure as the structure unit of polymer, are difficult to processing. But, the moulded product has the poor toughness and produced interal stress in using process. Therefore, the application of polyimide is restricted**[1-5]**. In this paper, a series of polyimide was prepared based on 3,3',4,4'-biphenyl-tetra carboxylic dianhydride(BPDA) with noncoplanar, 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) and 4,4'-diaminodiphenyl ether(ODA). The symmetry and regularity of polyimide molecular strcuture were destroyed, as a certain proportional noncoplanar structure was introduced into molecular chain. the molecular force and crystallinity were reduced and the processability and toughness of product were improved. The effect of the imidization temperature on the thermal stablity and mechanical properties of polyimide was investigated.

II. EXPERIMENTAL

A. Materials

4,4'-diaminodiphenyl ether(ODA), 3,3',4,4'-iphenyltetra carboxylic dianhydride (BPDA),1,2,4,5Benzenetetracarboxy-lic anhydride(PMDA) were all industrial grade. N,N-Dimeth-ylacetamide(DMAC), xylene and acetone were all analytical.

B. Synthesis Process of Polyimide Moulding Powder

A certain amount of ODA was dissolved in DMAC completely with stirring,then PMDA/BPDA (with the same molar ratio of ODA) were added into the solution. After 4 hours, xylene and catalyst were added into the solution, then the solution was heated to 156-160℃, dehydrated for 3 hours and obtained with a yellow powder. The powder was filtered and washed with acetone, and then dried in vacuo. The imidization of powder was performed at 260℃, 280℃, 300℃, 320℃and 340℃ for the same time, respectively. Finally, the five kinds of powder with different imidization degree were obtained.

C. Preparation of Polyimide

Moulded the above five kinds of powder into 84mm×66mm×2mm flake with pressure of 15 MPa at 410℃-430℃ for 10 min. Then the polyimide flakes were cooled and demould.

D. Characterization

Infrared (IR) spectra were obtained with a FT-IR 100 spectrometer. Thermal stability, as measured by 5% or 10% weight loss of polyimide sample, was determined on a TGA-Q50 analyzer from 50℃ to 800℃ at a heating rate of 20℃/min, under a flow of N_2. The glass transition temperature (T_g) was determined with a DMA-Q800 at a heating rate of 10℃/min and frequency of 1 Hz. The mechanical property of polyimide sample was measured according to the standard GB/T 1040-2006.

III. RESULTS AND DISCUSSION

A. Infrared Analysis

The polyamide acid was synthesized based on BPDA with noncoplanar, PMDA and ODA. Then the polyamide acid became into polyimide by the means of chemical and thermal imidization. The structure of polyimide was identified by IR spectrometer. The IR spectrum of polyimide was shown as in Fig.1.

The characteristic absorption peaks of C=O in the imide group near 1780cm^{-1}, 1720 cm^{-1} and 725 cm^{-1} appeared. The absorption of C-N at 1380 cm^{-1} appeared. The absorption of

N-H at 3500 cm^{-1} in polyamide acid disappeared. The results indicate the polyamide acid was successfully dehydrated to form polyimide.

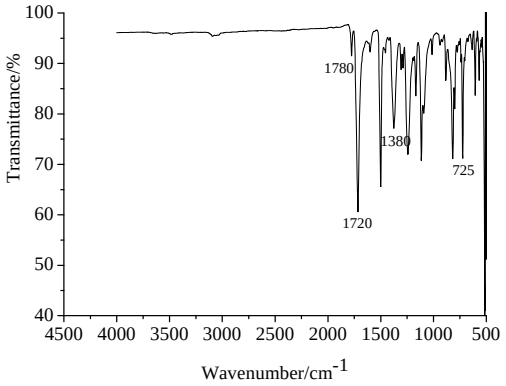

FIGURE I. INFRARED SPECTRUM OF POLYIMIDE.

B. Imidization Degree

The properties of polyimide are affected by imidization degree. If the imidization degree is low, there is water during the molding and will reduce the mechanical property of the polyimide product. The formula (1) is used to calculate the imidization rate **[6,7]**.

$$\text{imidization rate} = (S_{725}/S_{1500})_t / (S_{725}/S_{1500})_{350} \quad (1)$$

The S_{725} and S_{1500} represents the absorption peak area under the wavenumber of 725 cm^{-1} and 1500 cm^{-1}, respectively. And the 350 and t represents the imidization temperature 350℃ and t℃, respectively. The results of imidization rate were shown in the Fig.2.

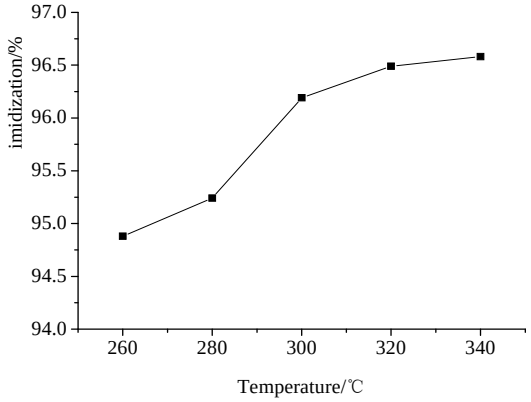

FIGURE II. EFFECT OF IMIDIZATION TEMPERATURE ON THE IMIDIZATION RATE.

The Fig.2 shows that the imidization rate reached 96.19%, and 96.49% and 96.57% at 300℃, 320℃ and 340℃, respectively. The imidization rate of polymer at 320℃ and 340℃ only increaseed by 0.3%and 0.38% than that of polymer at 300℃, so the imidization temperature of 300℃ was chosen.

C. Thermal Properties

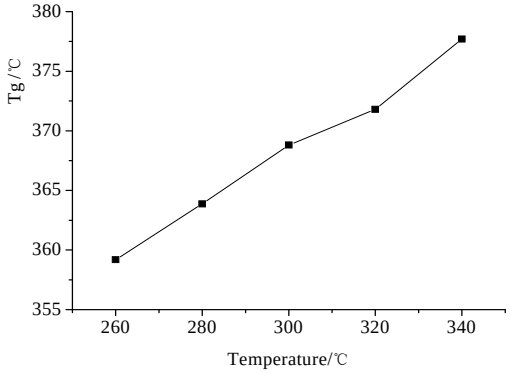

FIGURE III. EFFECT OF IMIDIZATION TEMPERATURE ON Tg.

In the Fig.3, the results show that glass translation temperature (T_g) significantly increased with the increasing temperature. The T_g of polyimide was up to 377℃.

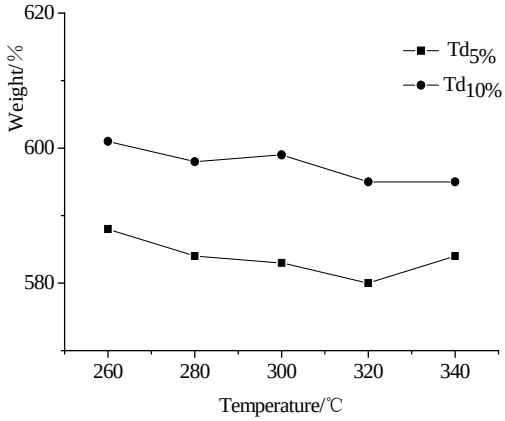

FIGURE IV. EFFECT OF IMIDIZATION TEMPERATURE ON Td.

The Fig.4 shows the temperatures of 5% or 10% weight loss of polyimide at the different imidization temperatures. The result indicates that the thermal stability of polyimide decreased slightly with the increasing imidization temperat-ure. The Td5% and Td10% of polyimide at imidization temperature of 300℃ were 583℃and 599℃, respectively, and were of excellent heat-resisting performance.

D. Mechanical Properties

The Fig.5 shows that the tensile strength and elongation at break of polyimide increased as the imidization temperat-ure rose.At the imidization temperature of 300℃, the tensile strength and elongation at break were 51.84 MPa and 13.6

%, respectively. Though the tensile strength was slightly lower,

the elongation at break is higher than the commercial polyimide. The results indicate that the toughness of polyimide was effiectively improved as the noncoplanar structure was introduced into the polyimide molecular chain.

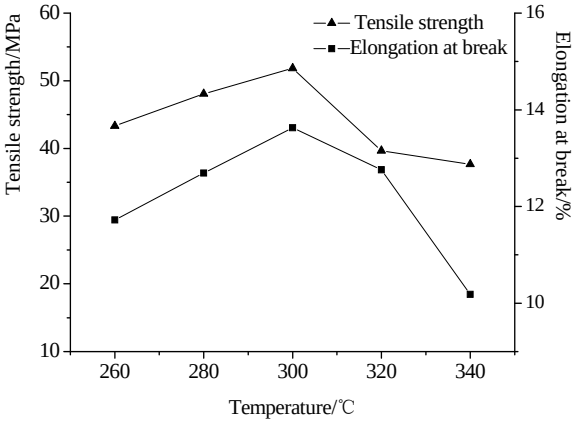

FIGURE V. EFFECT OF IMIDIZATION TEMPERATURE ON MECHANICAL PROPERTY OF POLYIMIDE.

IV. CONCLUSIONS

(1) the toughness of polyimide is effectively improved as the noncoplanar structure is introduced into the polyimide

molecular chain.

(2) It is approprite that the imidization temperature is chosen at 300℃, at which the tensile strength and elongation at break are 51.84 MPa and 13.63% respectively, and reached the maximum value.

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