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Preparation of high temperature resistance polybenzimidazole resin

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Abstract Polybenzimidazole's (PBI) was synthesized from 3,3'-diaminobenzidine and adipic acid by melting copolycondensation. Its thermal properties have been studied. The molecular structure and thermal stability of the resulting polymers were characterized by means of FTIR, TGA and DSC. The results indicate that the melting temperature of the PBI is higher than 400°C and the polymer possesses excellent thermal stability. The onset decomposition temperature was determined to be 516°C, and the highest decomposition temperature reaches 536°C.

Keywords polybenzimidazole, melting polycondensation, thermal weight losses

Polybenzimidazole (PBI) [1] is a kind of aromatic heterocyclic polymer with benzimidazole groups in its molecules. Its structure can be represented as Fig. 1.

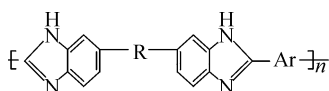


Fig. 1 The structure of PBI

PBI has excellent thermal stability due to its main chain containing aromatic heterocyclic groups. The high rigidity of its molecular chain and the interaction among the molecules makes PBI possess a high modulus, which gives it great popularity in use as fibers and circuit boards [2–5].

With the development of space exploration, especially with the increase of the space probes' speed and the improvement in efficient load and quality ratio of its

structure, advanced composite materials with high temperature resistance are becoming the foremost subjects, particularly the materials with temperature-resistance higher than 400°C. The ordinary polymers with high temperature resistance, such as BMI resin and polyimide resin cannot fulfill the requirement of practical use. PBI exhibits wonderful dynamic and electric properties under the conditions higher than 400°C. It is one of the kinds of best basic resin used to prepare composite materials with high temperature resistance higher than 400°C for use in making space probes [6].

1 Experiments

1.1 Raw materials

3,3'-diaminobenzidine(DAB, purity $\geq 97\%$) was purchased from the Shandong Taishan Mountain Dye Corporation, China. Adipic acid (AR), triphenyl phosphate (CP), anhydrous ethanol (AR) and vacuum wax were purchased from the Kelong Chemical and Industrial Factory, china.

1.2 Preparation of PBI

DAB 10.7 g (0.05 mol), adipic acid 7.3 g (0.05 mol) and TPP 0.2 g as activator were added into a strictly dried 250 mL three-necked flask. All of the air was taken out with a vacuum pump and the flask was heated to 220°C on a furnace. The water vapor was excluded to make the reactant absolutely dry and then a blender was used to mix the reactant until the temperature reached -250°C . The mixing speed was slowed gradually and stopped as the melting material became stiffer. The stiffer material was heated again to -250°C . To crystallize, it was then heated to -270°C . The pre-polymer was obtained after one hour of heating and was then cooled to room temperature with N_2 to avoid the oxidation of the product. The product was taken out and crushed, and was added into the flask under N_2 . It was heated to $\sim 330^\circ\text{C} - 350^\circ\text{C}$ for 1–2 h for

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complete cyclization of the pre-polymer. The experimental method can be represented as Fig. 2.

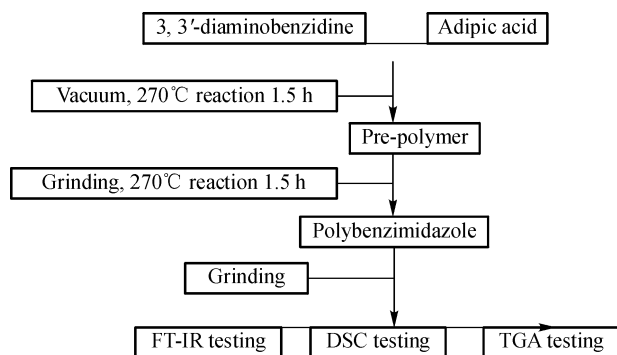


Fig. 2 The experimental flow path

2 Results and discussion

2.1 FT-IR measuring and analysis

The FT-IR spectrum of PBI is presented in Fig. 3.

According to Fig. 3, there is no residual carbonyl absorption between 1650 and 1780 cm^{-1} , suggesting the nearly complete closure of the imidazole rings under the reaction conditions. The peak assigned to the stretching modes of the aromatic C–H was detected at 3070 cm^{-1} . The 2357 cm^{-1} is the stretching mode of the imidazole ring in the state of $-\text{NH}^+$. The benzimidazole characteristic band is clearly observed at 1626 cm^{-1} (C–N stretching). The peak of 1450 cm^{-1} is the inside distorting vibration of the methylene. The 1279 cm^{-1} is the flexing vibration absorption of the imidazole ring. The 1227 cm^{-1} is the

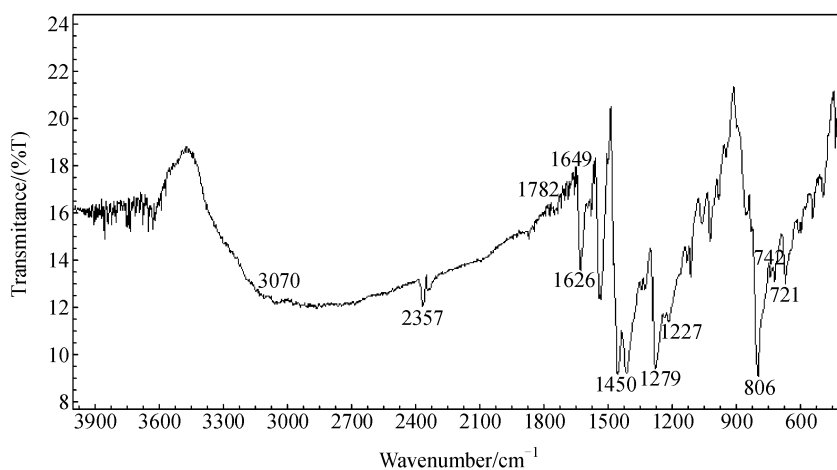


Fig. 3 The FT-IR spectrum of PBI

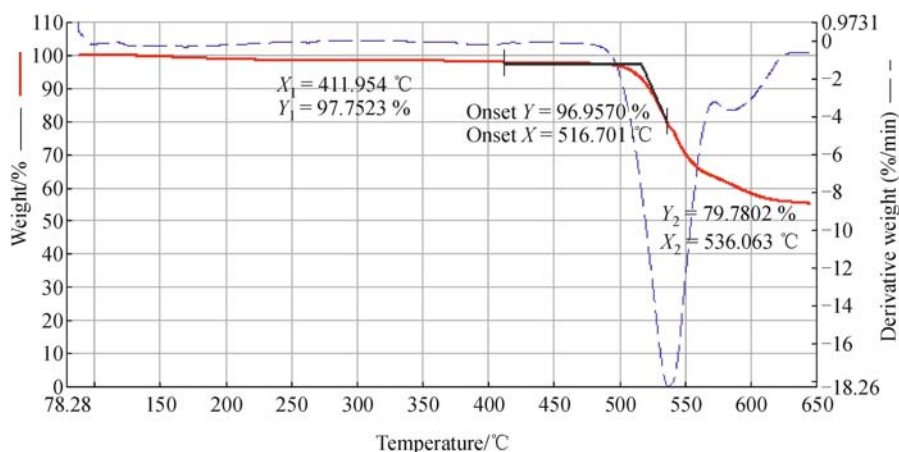


Fig. 4 The TGA plot of PBI

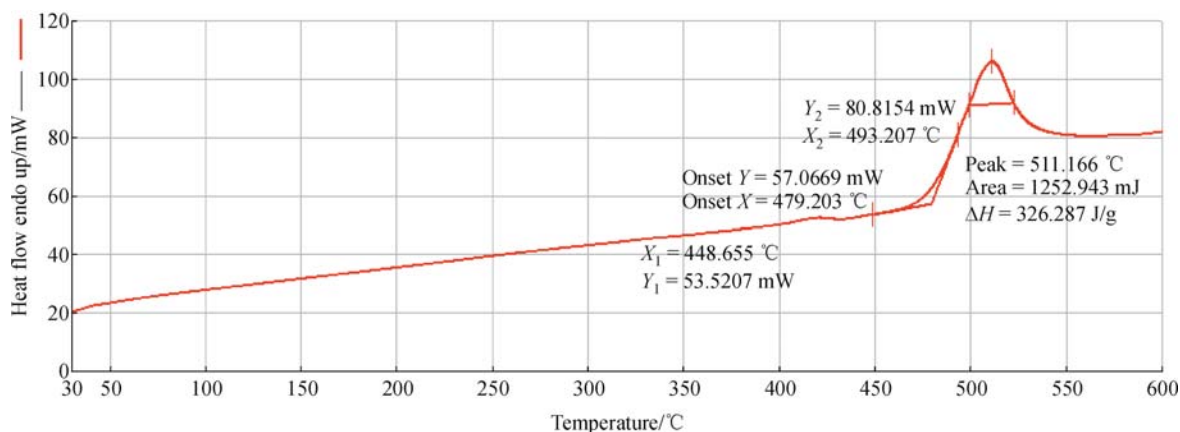


Fig. 5 The DSC plot of PBI

inside C–H cutting vibration absorption of 2,6-substitute benzimidazole and the 806 cm^{-1} is the mixed ring vibration absorption. The range of $742\text{--}721\text{ cm}^{-1}$ is the outside distorting vibration of the methylene.

2.2 TGA measuring and analysis

The TGA plot of PBI is shown in Fig. 4.

Figure 4 shows that PBI has a little weight loss in the range of -500 due to a little vaporization of the water and low-molecule reactants in the polymer when the temperature was increasing. The curve of TGA has a distinct decline at 516°C because the PBI began to decompose. The decomposition is finished at -640°C with -56% PBI remained. The PBI has the fastest speed of weight loss at -536°C . This shows that the PBI possesses excellent thermal stability.

2.3 DSC measuring and analysis

The DSC plot of PBI is presented in Fig. 5.

Figure 5 shows that a little of the PBI has been melted with decalescence but does not present the vitrifying temperature. This means that the polybenzimidazole was changing from thermoplastics to thermosetting plastics while it underwent a cyclic reaction in a too high temperature. The curve of DSC has a distinct melting change in $X_1\text{--}X_2$ with the starting temperature at 440°C and the ending temperature at 493°C . A decalescence apex occurs when the temperature is higher than the changing area of melting due to the fact that polybenzimidazole absorbs heat when it is carrying out the chaining together of molecules in the experiment.

3 Conclusion

(1) The target product PBI was produced by melting polycondensation from 3,3'-diaminobenzidine (DAB) and adipic acid.

(2) The biphenyl structure and imidazole groups in the polymer were confirmed by means of FTIR.

(3) The determination of TGA shows that the decomposition of PBI begins at -516°C and finishes at -640°C , and reaches the fastest speed at -536°C .

(4) From the DSC determination the melting temperature of the PBI starts at -440°C and ends at -493°C .

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References

- Liu A C, Zou J, Huang S H. Progress on synthesis of polybenzimidazole resins. *New Chemical Materials*, 2004, 32(5): 16–19
- Cheng Kangchen, Hu Binghuan. Aromatic all-polybenzimidazole synthesis and modified. *Chemical Engineering and Equipment*, 2006, 4: 1–4
- Pu H T, Ye S. Progress in Synthesis, Properties, and Application in Fuel Cells of Polybenzimidazole. *Polymer Communications*, 2006, 2: 9–10
- Xiao C F. Polybenzimidazole fiber and its application. *High-Tech Fibers and Application*, 2003, 28(3): 5–10
- Qing S B, Huang W, Yan D Y. Synthesis and Characterization of Thermally Stable Sulfonated Polybenzimidazoles. *Chemical Journal of Chinese Universities*, 2005, 26(11): 2145–2148
- Lu W F, Yu X H. Synthesis and application of polybenzimidazole resin. *Insulating Material Communications*, 2000, 5: 5–9