

# Synthesis and Characterization of High Performance Thermoplastic Polyimide Used the Anti-riot Bomb

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**Abstract**—Three kinds of thermoplastic polyimides (TPIs) were prepared by pyromellitic dianhydride (PMDA) and three different flexible diamines, respectively. The micromorphology, thermal properties and mechanical properties of prepared samples were tested and investigated. FTIR confirmed the successful preparation of anticipate polymers with complete imidization via an in-situ polymerization way at 300°C. DSC and TGA images showed that TPI-1 possessed the highest heat-resisting properties whose T<sub>5%</sub>, T<sub>10%</sub> and the residual carbon ratio at 800°C were 532°C, 550°C and 55.3%, respectively. The mechanical properties test results shows that TPI-1 has the highest tensile strength (76.9MPa) and tensile modulus (1.75MPa). These were the foundation of enlarging the class of polymer applying field and range.

**Keywords**—thermoplastic polyimide; flexible group; microstructure; thermal properties; mechanical properties

## I. INTRODUCTION

For the armed police force, the anti-riot bomb is the non-lethal weapon equipment with the maximum quantity and the highest utilization rate. When the anti-riot bomb is fired, most of the projectile body temperature is higher than 200°C. Therefore, it is required that higher resistance temperature properties and the mechanic properties for the plastic parts used in the anti-riot bomb. Thermoplastic polyimide (TPI) is a new generation of high performance special engineering plastic. Compared with traditional thermosetting PI, its properties are better in toughness, processing and forming ability which provides technical support for expanding the application field and scope of PI. At present, TPI has shown great application potential in national defense construction and high-tech industries such as riot control weapon, aerospace, microelectronics, etc. [1-6]

In this experiment, pyromellitic dianhydride (PMDA), which is widely used as a raw material, is used as a dianhydride monomer. 4,4'-bis(3-aminophenoxy)biphenyl(4,3-BAPOBP), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) and 1,3-bis(3-aminophenoxy-4-benzoyl)benzene (BABB) were selected as diamines monomer, respectively. TPI films were prepared by in-situ polymerization and thermal imidization methods. [3-5] The microstructures and the thermal properties of the samples were tested. At the same time, the relationship between molecular microstructure and material properties were studied and analyzed.

## II. EXPERIMENT

### A. Materials and Reagents

Pyromellitic dianhydride (PMDA, 98.5%) was obtained from Sinopharm Chemical Reagent Co., Ltd, China and dried at 130 °C for 3h before use.

N,N-dimethylacetamide (DMAc, 99.5%) was purchased from Shanghai SSS Reagent Co., Ltd, China and purified by distillation under reduced pressure and stored over 4Åmolecular sieves prior to use.

4,4-bis(3-aminophenoxy)biphenyl(4,3-BAPOBP, 98%) was supplied by Heowns Biochemical Technology Co., Ltd, China and used directly as received.

2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received.

1,3-bis(3-aminophenoxy-4-benzoyl)benzene (BABB, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received.

### B. Preparation of TPIs Hybrid Films

This test is achieved by a two-step method and the entire reaction process was carried out at room temperature in a nitrogen atmosphere.

The preparation of polyamic acid (PAA): 0.1mol 4,3-BAPOBP or BABB or BAPP was joined into a three-necked flask while owning about 30mL DMAc solvent; the mixture was stirred by ultrasonic shaking and mechanical agitator until completely dissolved. In order to prevent PMDA partial hydrolysis, PMDA was divided 6 times and added into the above mixed solution with a certain time sequence, and the mixture was stirred mechanically again for 8 h to get a yellow viscous PAA solution. [2,5]

Thermal imidization of PAA: In order to remove the bubbles in the viscous solution generated during the stirring process, the prepared PAA solution was laid for 12h under the protection of N<sub>2</sub> at room temperature; The PAA solution was casted onto the clear glass plate to form films that were then placed in a vacuum oven for 20min to remove air bubbles. The films were then heated successively at 70°C, 120°C, 180°C, 240°C and 300 °C for 1h, respectively. Finally, they were cooled to room temperature, immersed in distilled water for 2h,

and then removed from the glass plates using a razor blade. Finally, three films of TPI-1, TPI-2 and TPI-3 were obtained. The reaction mechanism is shown in Figure I, II and III.<sup>[3-4]</sup>

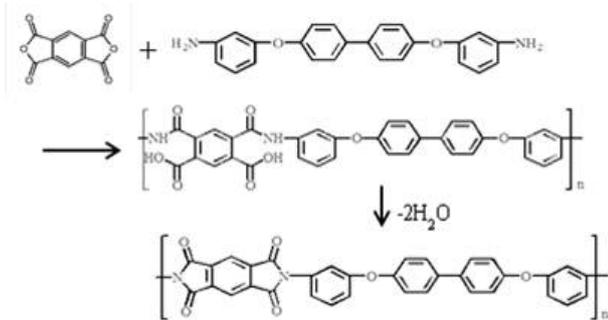


FIGURE I. SCHEMATIC REPRESENTATION OF TPI-1 REACTION MECHANISM

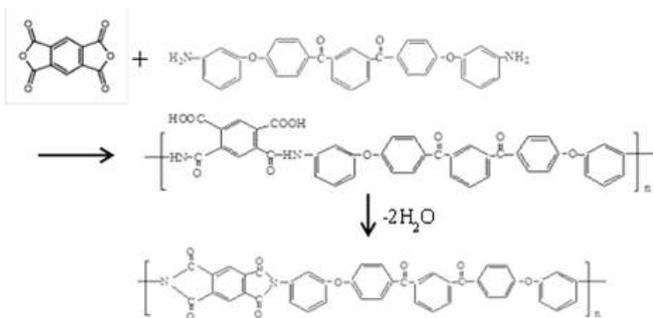


FIGURE II. SCHEMATIC REPRESENTATION OF TPI-2 REACTION MECHANISM

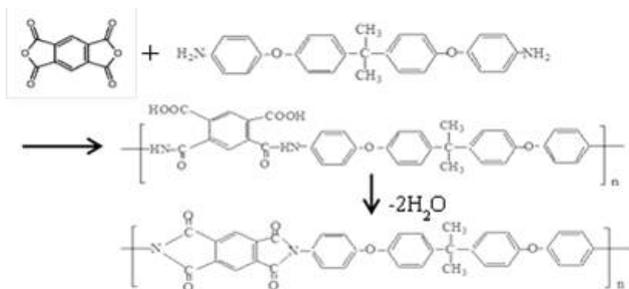


FIGURE III. SCHEMATIC REPRESENTATION OF TPI-3 REACTION MECHANISM

### C. Characterization and Performance Testing of Polymers

**X-ray diffraction(XRD):** XRD was carried out on the sample prepared was tested using a Bruker AXS D8 diffract meter at a  $2\theta$  angle of  $10-75^\circ$ , with a voltage of 40,000 volts and a current of 0.04A.

**Thermogravimetric analysis(TGA):**The test was carried out under a  $N_2$  atmosphere using a TGA Model 2050 Thermogravimetric Analyzer from TA, with a flow rate of  $100\text{ ml}\cdot\text{min}^{-1}$  and a temperature range of  $100^\circ\text{C}$  to  $800^\circ\text{C}$  and a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$ .

**Differential calorimetric scanning(DSC)analysis:** The glass transition temperature ( $T_g$ ) of the films was determined by differential scanning calorimetry (DSC) (Mettler Toledo DSC1,

USA) in a nitrogen atmosphere. The samples were heated from  $0$  to  $400^\circ\text{C}$  followed by a cooling cycle. Both the heating and cooling rates were  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

## III. RESULTS AND DISCUSSION

### A. FTIR Analysis of Polymers

Figure IV is the imidized infrared spectrum of TPI-1 at different temperatures. It indicates that the imidization degree of the sample increases with the temperature increasing, and the four distinct characteristic peaks of aromatic PI can be seen at  $1721\text{cm}^{-1}$ ,  $1778\text{cm}^{-1}$ ,  $725\text{cm}^{-1}$  and  $1373\text{cm}^{-1}$ . The strong absorption peaks around  $1721\text{cm}^{-1}$  and  $1778\text{cm}^{-1}$  are attributed to the symmetry and asymmetric stretching vibration of the imide group  $\text{C}=\text{O}$  in the TPI molecule, the peak at  $725\text{cm}^{-1}$  may be due to the out-of-plane bending vibration of the imide group  $\text{C}=\text{O}$ , and the peak near the  $1373\text{cm}^{-1}$  was caused by the stretching vibration absorption of the  $\text{C}-\text{N}-\text{C}$  in the imide bond<sup>[3-7]</sup>. At the same time, the characteristic peak of the amide group ( $\text{CONH}$ ) near  $1660\text{cm}^{-1}$  is significantly weakened with the increasing of temperature, and it is faintly visible in the curve of  $180^\circ\text{C}$ , it is almost invisible in the curve of  $240^\circ\text{C}$ , and it is not seen in the spectrum curve of  $300^\circ\text{C}$ . These results indicate that the expected TPI polymer can be obtained by in-situ polymerization and thermal imidization<sup>[5,7]</sup>.

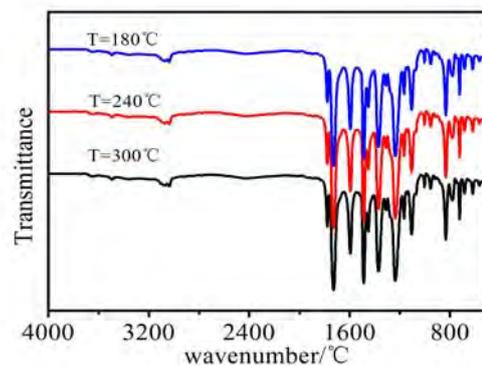


FIGURE IV. FTIR SPECTRA OF TPI-1 WITH DIFFERENT TEMPERATURE

### B. XRD Pattern Analysis of Polymers

The X-ray diffraction of the samples are shown in Figure V. It can be clearly seen that there are obvious dispersion peaks on the three curves, which indicates the formation of amorphous aggregate structure during the synthesis of TPI. In addition, the average distance between the three TPI molecular chains is  $4.92\text{\AA}$ ,  $4.98\text{\AA}$ , and  $5.09\text{\AA}$ , respectively; this is due to the fact that the diamine monomer 4,3-BAPOBP molecule used synthesizing TPI-1 has the more regular linear structure and no additional branching, so the average spacing between TPI-1 molecular chains is the smallest; the diamine monomer BAPP used synthesizing TPI-3 contains a large volume isopropyl which increases the molecular steric hindrance, so the average distance between molecules is the largest<sup>[9]</sup>.

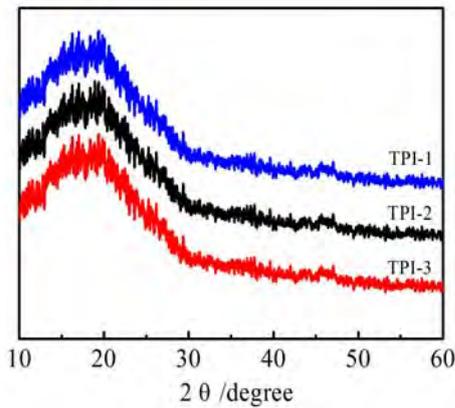


FIGURE V. XRD CURVES OF DIFFERENT TPI FILMS

C. DSC Curve Analysis of TPI Polymer

Figure VI is DSC curves of the test samples. It can be seen that the three samples have all obvious endothermic peaks, and the peak corresponding temperatures are 267°C, 225°C and 220°C, respectively. Among them, TPI-1 has the highest peak temperature and TPI-3 has the lowest peak temperature. It is not difficult to find out the reason by analyzing the difference of the each monomer structure for the synthetic sample: the diamine 4,3-BAPOBP monomer molecule used synthesizing TPI-1 has two flexible ether bonds -O- among the four benzene rings, and the amine BABB monomer used synthesizing TPI-2 has two flexible greater-volume carbonyl -CO- except the two flexible ether bonds -O- among the five benzene rings, so the density of the flexible group in the TPI-2 chain is higher than that of TPI-1 and the peak temperature of TPI-1 is higher than that of TPI-2; for the TPI-3, the diamine monomer BAPP used synthesizing TPI-3 contain not only two flexible ether bonds -O- but also a bulky isopropyl group among the four benzene rings which reduces the interaction between molecular chains and the rigidity of the molecular chain and the regularity of free packing. From the above, the rigidity of the TPI-3 molecular chain is reduced and the flexibility is enhanced, so the peak value temperature of TPI-3 is lower than that of TPI-2, which is consistent with the XRD pattern analysis results [2-3].

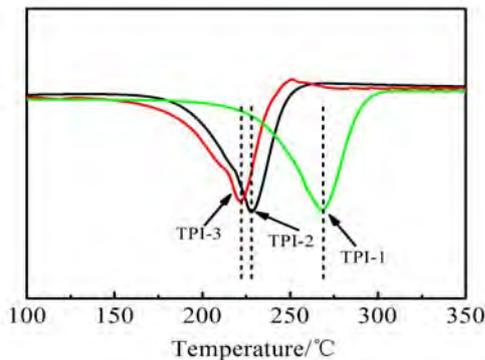


FIGURE VI. DSC CURVES OF DIFFERENT TPI FILMS

D. Thermogravimetric Analysis of TPI Films

The weight loss trends of three TPI are shown in Figure VII with temperature. The residual carbon ratios of samples T<sub>5%</sub> and T<sub>10%</sub> and 800°C are shown in Table I. It is not difficult to see from the analysis of Figure VII and Table I, for TPI-1 that thermal decomposition temperature of 5% and 10% and the residual carbon ratio at 800°C are the highest in three samples and are 532°C, 550°C and 55.3%, respectively, which indicates that TPI-1 has the best thermal stability which is the basis and guarantee for the long-term use of TPI-1 at high temperatures. There are two main reasons: firstly, the monomeric diamine 4,3-BAPOBP used synthesizing TPI-1 belongs to the biphenyl structure and has a standard symmetrical structure; secondly, the molecular chain regularity degree of the TPI-1 polymer is higher<sup>[8]</sup>.

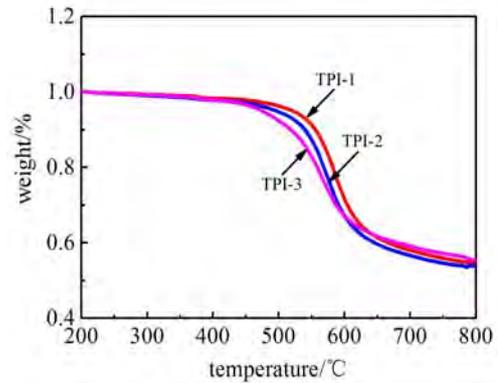


FIGURE VII. TGA CURVES OF DIFFERENT TPI FILMS

TABLE I. THERMAL PROPERTIES OF TPI FILMS

Samples	T <sub>5%</sub> (°C)	T <sub>10%</sub> (°C)	Residual weight at 800 °C (%)
TPI-1	532	550	55.3
TPI-2	523	538	54.8
TPI-3	482	513	53.6

E. Mechanical Properties of TPI Films

The tensile strength and modulus of the samples are shown in Figure VIII.

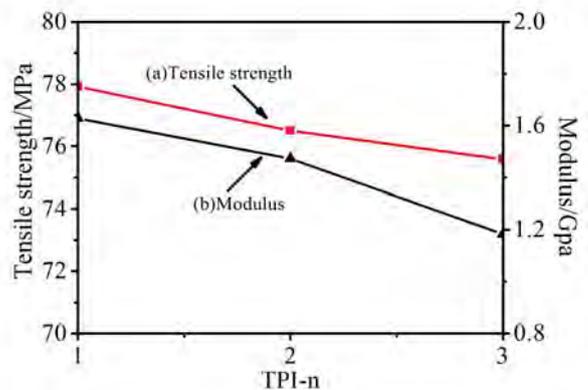


FIGURE VIII. THE CURVES OF TENSILE STRENGTH AND MODULUS OF DIFFERENT TPI SAMPLES

The tensile strengths of TPI-1, TPI-2 and TPI-3 are 76.9MPa, 75.6MPa and 73.2MPa, respectively, and the moduli are 1.75GPa, 1.58GPa and 1.47GPa, respectively. It is easy to see that the TPI-1 has the highest tensile strength and tensile modulus. It is well known that for any polymer, the most fundamental factor in determining its performance is the molecular structure; for the TPI-1, when the amic acid PAA-1 formed by the reaction of monomeric diamine 4,3-BAPOBP and dianhydride PMDA is imidized, a rigid imide ring containing high-density and structure stable rigid benzene ring was formed by dehydrating and cyclizing which allows the sample presence the stronger tensile strength under external force<sup>[5,9,10]</sup>.

#### IV. CONCLUSION

After In order to prepare and study TPIs with high temperature resistance, good processing property and mechanic properties and low cost, the homogenous benzene type PMDA with a wide range of raw materials is used as the dianhydride monomer and three diamine monomer with the flexible group were selected. The TPI samples were synthesised, the microstructure, thermal stability and mechanical properties of the prepared samples were tested and analyzed. The conclusions are as follows:

1) FTIR results show that the experiment scheme designed is scientific and feasible, and the imidized completely polymer can be prepared at 300 °C by in-situ polymerization and thermal imidization;

2) DSC and TGA test data indicate that TPI-1 has the best thermal stability, which provides a theoretical foundation for studying the relationship between structure and properties of such polymers;

3) The mechanical properties test results shows that TPI-1 has the highest tensile strength (76.9MPa) and tensile modulus (1.75MPa), which offers the basis for exploring the application fields and scope of such polymers.

#### ACKNOWLEDGMENT

Supported by Scientific Research Project Within the Military (WJ20182A020036); Supported by the Innovation Team Scientific Research Foundation of Engineering University of PAP; Supported by Basic Research Foundation of PAP (WK2016-L7); Supported by Military Application Research Foundation of PAP (WK2015-J12)

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