

Thermal Mechanical and Dynamic Mechanical Property of Biphenyl Polyimide Fibers

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ABSTRACT: High-performance polyimide fibers possess many excellent properties, e.g., outstanding thermal stability and mechanical properties and excellent radiation resistant and electrical properties. However, the preparation of fibers with good mechanical properties is very difficult. In this report, a biphenyl polyimide from 3,3',4,4'-biphenyltetracarboxylic dianhydride and 4,4'-oxydianiline is synthesized in *p*-chlorophenol by one-step polymerization. The solution is spun into a coagulation bath of water and alcohol via dry-jet wet-spinning technology. Then, the fibers are drawn in two heating tubes. Thermal gravimetric analysis, thermal mechanical analysis, and dynamic mechanical analysis (DMA) are performed to study the properties of the fibers. The results show that the fibers have a good thermal stability at

a temperature of more than 400°C. The linear coefficient of thermal expansion is negative in the solid state and the glass transition temperature is about 265°C. DMA spectra indicate that the $\tan\delta$ of the fibers has three transition peaks, namely, α , β , and γ transition. The α and γ transition temperature, corresponding to the end-group motion and glass transition, respectively, extensively depends on the applied frequency, while the β transition does not. The activation energy of α and γ transition is calculated using the Arrhenius equation and is 38.7 and 853 kJ/mol, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1653–1657, 2004

Key words: polyimides; high-performance polymers; fibers; mechanical properties; TGA

INTRODUCTION

Aromatic polyimides have been known for their chemical resistance, excellent mechanical and electrical properties, and outstanding thermal stability. They were made into films, coatings, laminates, and even fibers in the past 4 decades by a two-step polycondensation technique. Polyimide fibers thus are expected to have attractive heat resistance and low flammability. Contrary to expectation, however, the study of polyimide fibers is rather scant. This may be due to the difficulty in finding powerful solvents for high-molecular-weight polyimides.^{1–4}

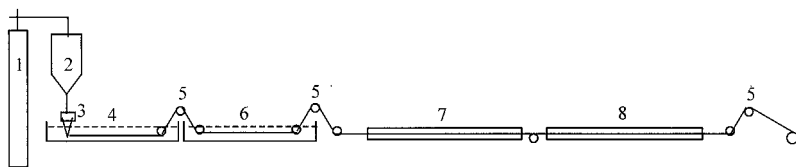
The basic technology for forming synthetic fibers includes spinning and heat treatment. As is generally known, there are three major methods of spinning: melt-, dry-, and wet-spinning processes. High-performance fibers and other functional fibers usually are spun by wet technology including wet-spinning, dry-jet wet-spinning, and gel-spinning technology. For example, aromatic polyamides (Kevlar) and high-

strength polyethylene are prepared by the two kinds of spinning processes, respectively.

Generally, polyimides are usually prepared via the reaction of a dianhydride with an aromatic diamine in a polar aprotic solvent and the reaction includes two types: two-step and one-step processes. In the two-step process, the soluble polyamic acids (PAAs) are fabricated into a product, such as fibers, film, or coating, and then are converted to the polyimide in a second process—usually by thermal imidization via heating in the vicinity of 300°C or by chemical imidization via dipping the product in a solution with acetic anhydride, pyridine, or triethylamine. The so-called two-step process is mainly a method used to prepare polyimide products including fibers in the past.^{5–7} Irwin⁸ prepared the polypyromellitimide fibers in this manner. The precursor fibers from polyamic acid solutions were thermally converted *in situ* to the corresponding polyimide fibers. The fibers showed excellent high-temperature performance, but the tenacity and initial modulus were limited to small values. The St. Clair group^{9,10} reported that PAA could be synthesized from 3,3,4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) in a solvent of DMAc and PAA fibers could be obtained by spinning the dopes into alcohol or glycol. Then the fibers were thermally imidized into polyimide fibers.

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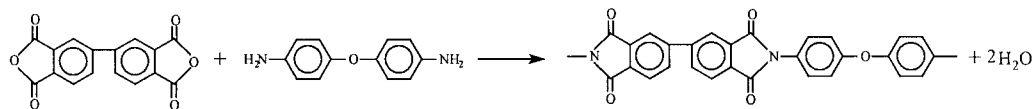
Scheme 1 Flow process diagram of spinning polyimide fibers. (1) Nitrogen gas with 0.5 Mpa; (2) polyimide solution; (3) spinning spinneret with 12 holes; (4) coagulation bath with a mixture solution of water and alcohol (1:1); (5) rollers; (6) washing bath, water; (7) heating tube with $220\pm 5^\circ\text{C}$; (8) heating tube with $340\pm 5^\circ\text{C}$; and (9) taking up.

Although the products of polyimides are mostly manufactured by the two-step technique described above, it is desirable to prepare high-molecular aromatic polyimides in the one-step process.¹¹ Kaneda et al.^{12,13} reported that the polyimide solution could be prepared in the one-step polycondensation reaction of a dianhydride with various aromatic diamines in *p*-chlorophenol and the solution dopes could be directly used for spinning polyimide fibers. The spinning, drawing, and thermal process could be conducted on one line. Cheng and co-workers^{14–16} prepared a series of polyimide fibers with high strength (26 g/d, 3.1 GPa) and high modulus (1000 g/d, 120 GPa) using one-step technology. However, in the one-step process, it is difficult to eliminate the remaining solvent inside as-spun fibers, such as *p*-chlorophenol and *m*-cresol. The research group also prepared a series of organosoluble polyimide films and studied the relax-

ation behaviors and the thermal and optical properties of the high-performance polymers.^{17,18}

As ether- or ester- groups are introduced into the main chain of polyimide, copolyimide fibers can be prepared by the melt-spinning process even though the fibers do not have good mechanical properties.^{19,20} Asahi Chem. Ind. Co. (Japan)²¹ reported that polyether-imide was spun into fibers at the temperature of 250°C . The drawn fibers with the drawing ratio of 5.5 had a tensile strength of 4.1 g/d and an initial modulus of 25 g/d. Irwin²² prepared polyester-imide at $300\text{--}400^\circ\text{C}$. The strength and modulus of the fibers were up to 13 and 400 g/d, respectively, when the as-spun fibers were thermally treated.

In this report, one type of biphenyl polyimide from BPDA and ODA is synthesized using the one-step process in *p*-chlorophenol, which is simply schemed as follows (Scheme 1).



The polymer solution is spun into fibers using the one-step process and then the fibers are drawn in two heating tubes. The studies on the thermal stability and the thermal mechanical and dynamic mechanical properties of the drawn fibers are carried out. Some transition temperatures and linear coefficients of thermal expansion along the fiber direction are investigated. Also, the active energy of α and γ transition is calculated according to the Arrhenius equation.

EXPERIMENTAL

Synthesis of polyimide

Polyimide was synthesized in our laboratory in *p*-chlorophenol at elevated temperature via one-step polymerization. The polyamic acid precursors were not isolated. In a 100-mL round-bottom flask equipped with a nitrogen inlet, a stir bar and a condenser was charged with 2 g ODA and 50 mL *p*-chlorophenol. The solution was stirred until the diamine dissolved completely, and then 2.94 g BPDA was

added into this solution slowly. The reaction was carried out at 150°C in refluxing solvent for 2 h and the water produced from the polycondensation reaction was removed from the condenser. Then, the system was heated to 200°C and continued to react for 4 h. The concentration of polyimide in the solvent was about 10% (w/v). The concentrated solution was solid at room temperature and it became viscous dopes when it was heated up to 70°C or higher.

Preparation of polyimide fibers

The polymer solution was filtrated and degassed at 100°C . Fibers were conducted on a spinning machine which was home designed as shown in Scheme 1.

The dopes at 100°C were spun into a coagulation bath by the dry-jet wet-spinning process with a gas gap of 20 mm. The composition of the bath was water and alcohol (volume ratio = 1:1). This composition of water and alcohol was helpful to form as-spun fibers with a uniform microstructure. The effect of the coag-

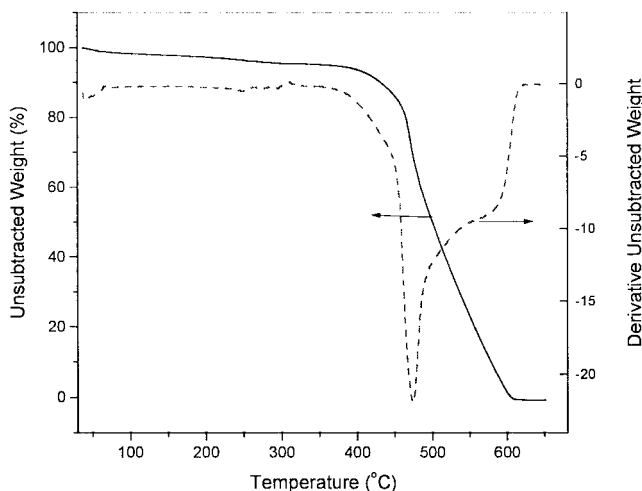


Figure 1 TGA spectra of polyimide fibers.

ulation bath composition on the as-spun polyimide fibers was described in detail elsewhere.²³ Then, the as-spun fibers were put into the second bath (washing bath, water). The drawing procedure was conducted on two heating tubes as shown in Scheme 1. The temperature of the two stainless-steel tubes was 220 ± 3 and $340 \pm 5^\circ\text{C}$, respectively.

Measurement

A Perkin–Elmer TGA 7 was employed to analyze the thermal stability of the fibers at a heating rate of $20^\circ\text{C}/\text{min}$ and the thermal mechanical properties were investigated on a Perkin–Elmer TMA 7 at a heating rate of $20^\circ\text{C}/\text{min}$. The linear coefficient of thermal expansion (CTE) of the fibers was measured according to the thermal mechanical analysis (TMA) spectrum.

The measurement of thermal dynamic mechanical behavior was carried out on a DMTA-4 Analyzer (America Rheogoniometer Co.). The heating rate was $2^\circ\text{C}/\text{min}$ in the range of $-150\sim 400^\circ\text{C}$. The frequency applied was 0.1, 1, 10, and 100 Hz, respectively. Storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta$) were recorded. The diameter of a single fiber was measured on an optical microscope with a scale.

RESULTS AND DISCUSSION

To study the thermal mechanical properties of the polyimide fibers, one must first address the thermal stability of the fibers at elevated temperature. Thermal gravimetric analysis (TGA) spectra in the range of $30\sim 600^\circ\text{C}$ in the air atmosphere at a heating rate of 20°C are shown in Figure 1. The figure indicates that the polyimide fibers of BPDA–ODA were thermally stable $\sim 400^\circ\text{C}$ before reaching a 5% weight loss. Thus, the fibers have excellent thermal stability. The obvious

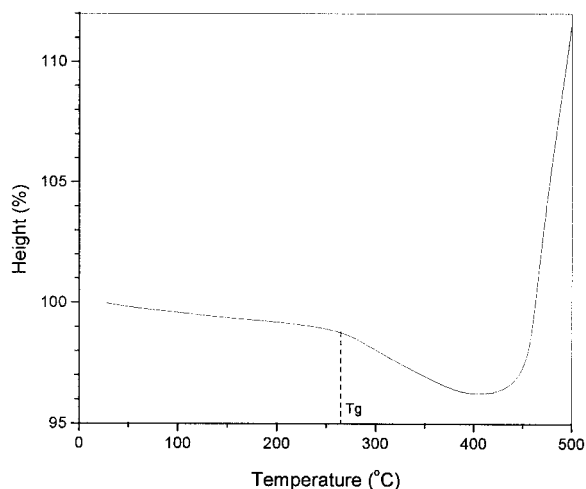


Figure 2 TMA curve of polyimide fibers.

weight loss occurs over 420°C . The plot of the derivative unsubtracted weight versus the elevated temperature indicates that the maximum rate of thermal weight loss takes place in the range of $420\sim 550^\circ\text{C}$.

Figure 2 illustrates the thermal mechanical analysis of BPDA–ODA fibers. The TMA curve shows that the linear CTE of the fibers exhibits slightly negative value from room temperature to 250°C and the CTE is $-4 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. Meanwhile, the CTE is $-2 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ in the range of $270\sim 370^\circ\text{C}$. When the temperature is up to 400°C or higher, the CTE becomes a positive value and the fibers exhibit the thermal expansion or thermal drawing at a stress. The figure also indicates that the glass transition temperature of BPDA–ODA fibers is about 265°C , which is marked T_g in Figure 2.

Figure 3 shows experimental dynamic mechanical

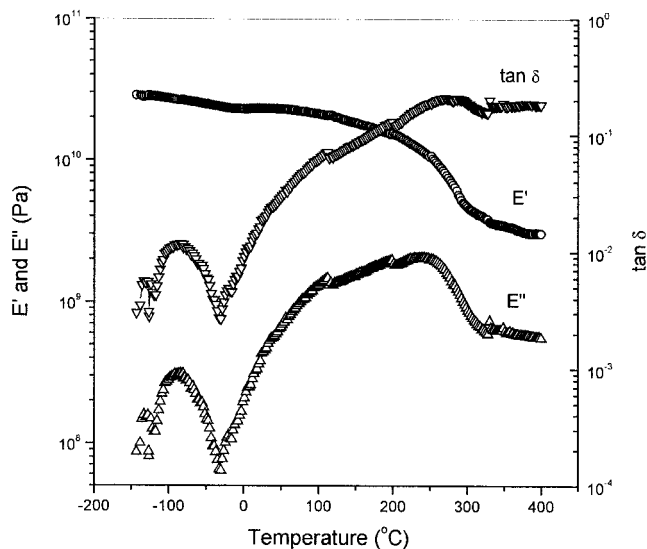


Figure 3 Dynamic mechanical data for the fibers at the frequency of 1 Hz.

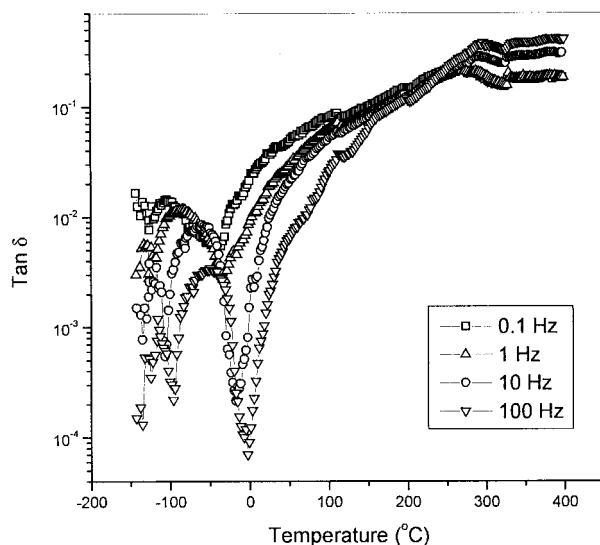


Figure 4 Changes in $\tan\delta$ of the fibers with the temperature at different frequencies.

analysis (DMA) spectra at the frequency of 1 Hz, including storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta$). In general, E' decreases with the elevated temperature, while E'' and $\tan\delta$ have some peaks. $\tan\delta$ increases with the rise in temperature. The $\tan\delta$ value is in the range of 0.005~0.2. The E' value is more than E'' by the order of magnitude of 1~2. The shape and location of the complex modulus E^* is very similar to that of E' because of $E^* = E' + iE''$.

The changes in $\tan\delta$ with the rising temperature of the biphenyl polyimide fibers at different frequencies are shown in Figure 4. The $\tan\delta$ curves have three maximum values at temperatures of -100~-40, 100, and 270°C. The three peaks correspond to γ , β , and α transitions.

The γ transition, corresponding to the end-group motion, shifts to higher temperature when the applied frequency is increased. When the applied frequency is 0.1, 1, 10, and 100 Hz, the γ transition temperature is -99, -84, -61, and -40°C, respectively. The $\tan\delta$ value is 0.003~0.015 in this temperature range, meaning that the fibers have lower viscosity. The change of the γ transition with the applied frequency f is in accordance with the Arrhenius equation. The equation is logarithmically changed as follows:

$$f = f_0 \exp \frac{-E_a}{RT} \Rightarrow \ln f = \ln f_0 - \frac{E_a}{RT}$$

Turning to the Arrhenius activation energy of the γ transition process, one can plot a relationship between logarithmic frequency and the reciprocal of the peak temperature. Linear fit with the linear relative coefficient of 0.998 is illustrated in Figure 5. The activation

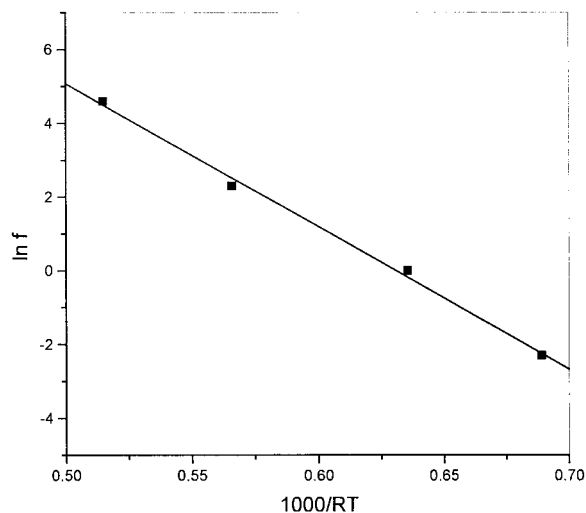


Figure 5 Relationship between logarithmic frequency and reciprocal peak temperatures of the γ relaxation.

energy E_a of the γ transition calculated from its slope is 38.7 kJ/mol.

The peak of the $\tan\delta$ (0.05~0.1) at 100°C refers to β transition, which is caused by the subglass transition. Unlike the γ transition, the applied frequency had little influence on the β transition temperature.

Another peak is the α transition, which corresponds to the glass transition (segmental motion). The applied frequency had an obvious influence on T_g . When the frequency increases from 0.1 to 100 Hz, T_g increases from 276 to 297°C. Similar to the γ transition, the relationship between logarithmic frequency and the reciprocal of the peak temperature is plotted, as shown in Figure 6. The activation energy E_a of the α transition calculated from its slope using the Arrhe-

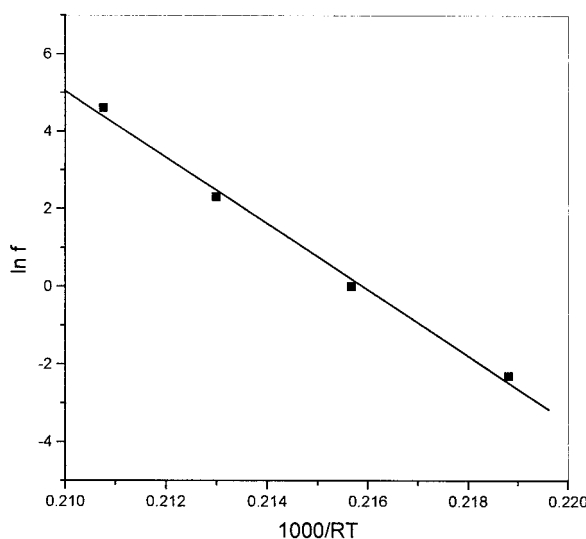


Figure 6 Relationship between logarithmic frequency and reciprocal glass transition temperatures.

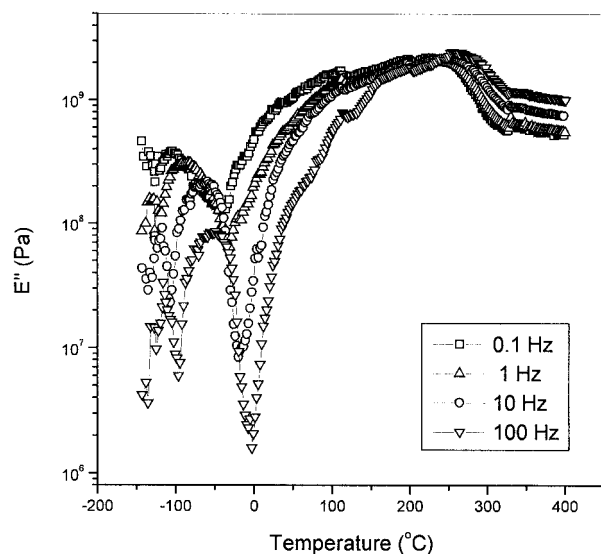


Figure 7 Changes in loss modulus of the fibers with different frequencies.

nius equation is 853 kJ/mol and the linear relative coefficient is 0.997.

The $\tan\delta$ value is more than 0.05 at the β transition temperature (100°C) or above. Moreover, when the temperature is up to T_g , $\tan\delta$ is nearly 0.5. These indicate that the viscosity of the polyimide fibers obviously increases with the elevated temperature. Thus, the response on the alternating stress is hysteretic.

Figure 7 shows the changes of E'' with the elevated temperature at the different applied frequency. Similar to the relationship of $\tan\delta$ and temperature, E'' curves also have three maximum peaks, which correspond to the γ , β , and α transitions from low to high temperatures. Either storage modulus E' or complex modulus E^* decreases with the elevated temperature, and they are little affected by the applied frequency. Thus, we do not discuss them.

CONCLUSION

Polyimide from BPDA and ODA is synthesized using one-step polymerization and the fibers are prepared by the dry-jet wet-spinning process. The fibers are measured by means of TGA, TMA, and DMA. The results indicate that the fibers have a good thermal stability and lower CTE with a negative value below 400°C. The γ , β , and α transitions can be observed on

the $\tan\delta$ curves, which correspond to the end-group motion, subglass transition, and glass transition (segmental motion). The α and γ transition temperature obviously depends on the applied frequency. The transition shifts to higher temperature with increasing frequency. Meanwhile, the Arrhenius equation can be used to calculate the activation energy of γ and α transitions, 38.7 and 853 kJ/mol, respectively. However, the applied frequency has little influence on the β transition. For the high-performance polyimide fibers, we have more work to do. For example, it is necessary to improve the mechanical properties including tensile and modulus. Therefore, we will further report our research in the future.

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