Fibers of Polyimide with pendant biphenyl ester group :Spinning Morphology and Crystallization Control[*]

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Abstract:

A new segmented polymide has been synthesized from 4,4'-oxydianiline(ODA), 3,5-diamino-benzonic-4'-diphenylester(DABBE)and4,4'-oxydiphthalicanhydride(ODPA). This polyimide is soluble in m-cresol, allowing fibers to be spun from isotropic solution using a dry-jet wet spinning method. Control of the internal morphology of as-spun fibers has been achieved by varying the rate of polymer coagulation through adjustments in nonsolvent/solvent miscibility of the coagulation bath .SEM pictures show that filament internal morphologies ranged from very porous-like to fully solid, WAXD shows that as-spun fibers are amorphous structure, When the solvent content is less than 2%(w/w), annealed fibers are always amorphous, when the solvent content is about 10%(w/w) and the annealed temperature is $60°C \sim 130°C$ under tension, the annealed fibers are crystalline and their WAXD diffractions have two kinds of peak patterns which have different influence by the draw ratios. These results imply that there have two crystallization phase in PI morphology structure, one phase results from the main chains, the other results from the mesgon side-chain.

Keywords: Polyimides; dry-jet wet spinning ; morphology; crystallization

Introduction

High-performance polymeric fibers with high-strength, high-modulus and high-temperature properties have undergone significant growth and development in the last two decades. Linear aromatic polyimides are found increasing usage in industrial and aerospace applications due to their excellent chemical resistance, low density, radiation resistance, high modulus and strength, and high temperature stability. However, these polyimides have the disadvantage of poor solubility, which makes them difficult to process. Thus fibers with aromatic links in the molecular chains were made commercially available in the mid-1960s by the two-step poly-condensation technique[1,2]. The first step consists in acylation of diamine with tetracarboxylic dianhydride in an organic solvent and yields the soluble intermediate polymer (i.e., polyamic acid), fibers are made from this precursor polymer. In the second step, the polyamic acid is converted into polyimide by dehydration and cyclization in dehydrating agents[3,4], heating, or by the combination of chemical and thermal treatments. It is well known that water is released during the conversion reaction of PAAs into PIs during heating, so it is difficult to prevent voids from the polyimide fibers.

Recently, it has been found that the soluble polyimides to form strong fibers can be produced in a single step[5,6,7], when 3,3',4,4'-biphenytetra carboxylic dianhydride(BPDA) is allowed to react in a phenolic solvent with aromatic diamines. The conversion to polyimides is completed in solution without producing precipitation. Polyimides fibers can be produced directly by spinning of this solution. Following spinning, a fiber is treated by annealing at high

temperature under tension. Generally speaking, the heat treatment is applied to improve the fiber strength and /or modulus. From a molecular point of view, various spinning methods and heated treatment processes affect the chain orientation, crystallinity, and morphologies in the fibers. However, the establishment of relationships between structure, properties and processing conditions is still an unfinished task in high performance fibers.

In this paper, we report recent works in our group on polyimide fibers. An soluble polyimide was synthesized from 4,4'-oxydianiline(ODA), 3,5-diamino-benzonic-4'-diphenyl ester (DABBE) containing pendant biphenyl unit and 4,4-oxydiphthalic anhydride (ODPA) in NMP.[8,9] It's chemical structure is as below:
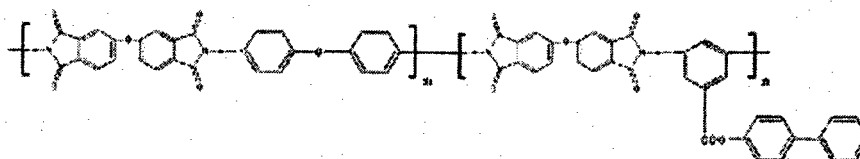
The as-spun fibers produced from isotropic solutions by dry-jet net spinning, annealed fibers display different degree of crystallinity, crystallization behavior and crystal size have been observed with different annealed process.

Experimental

Preparation of Polyimide.[10,11]

ODA, 8.6400g (0.0432 mol) and DABBE, 3.2830g (0.0108 mol) were dissolved in 150.0g of NMP in a four-necked 500ml flask equipped with a stirrer, nirogen inlet, and outlet tubes. After the mixture had been stirred at 25°C for 1.0h, ODPA, 16.7398g(0.0540 mol) was added, and the reaction mixture was kept at room temperature for 24h with stirring under the flow of dry nitrogen.Then 23.0 g acetic anhydride and 14.0g pyridine were added to convert the PAAs to PIs, after stirring for 24h the reaction mixture was heated at 65°C for 3h to complete the conversion to PIs. There no precipitation took place throughout the entire stage of reaction. Then, the solution was slowed to cool and poured into a large quantity of methanol in which the polyimide deposited as a yellow power. The precipitate was separated by filtration, washed, and vacuum dried at 200 °C .A 95% yield of polymer with an inherent viscosity of 1.15dL /g was obtained.

Preparation of As-spun Fibers.

A schematic of the spinning apparatus is shown in Figure1. Fibers from isotropic solutions of 15% polymer in m-cresol were dry-jet spun into a coagulation bath. The as-spun fibers were drawn at different temperature and different draw ratios in air.
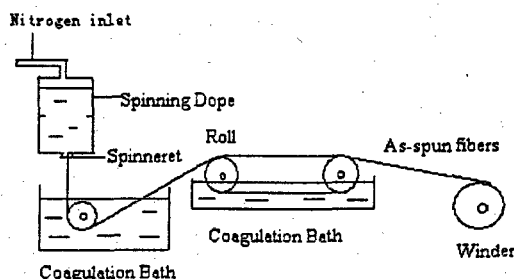

Fig.1   A schematic of the spinning apparatus

Annealed Fibers

One end of as-spun fibers was fixed on the top of heated-oven, the other end was hung weights to ensure that fibers was under tension.

Characterization

Inherent viscosity was determined using an ubbel-hode viscometer and polymer solutions at 0.5% solids(w/w)in NMP at 30℃.

Cross-sectional shapes of fibers were determined by an optical or scanning electron microscope (SEM)

Fiber tensile properties were measured using a Instron Testing System, according to ASTMD2101-82, at ambient humidity and temperature.

Crystal crystallinity measurements based on the WAXD data .

Determination of the crystal size in the fibers by use of the Scherrer equation: $L=K \lambda /[(\beta^2-b^2)^{\frac{1}{2}}]$, where β and b are, respectively, the halfwidth and broadening factor (b=0.105), and K is a geometry-dependent constant that is assumed to be unity. Used K-Alphal wavelength(Å): $\lambda =1.54056$[12].

Results and Discussion

Spinning Morphology

In a recent modeling study on polymer coagulation, Termonia[13] showed that as nonsolvent/solvent miscibility decreases the diffusion coefficient also decreases. Essentially, as the miscibility decreases the solvent and polymer molecules become more similar in relation to the coagulant. This produces the effect of slowing the outward and inward diffusion rates of the solvent and coagulation should facilitate the formation of more dense morphology polymer. In this respect, solvent consideration must take into account not only polymer solubility but also the nonsolvent/solvent miscibility. Similarly, the coagulation bath must account for both the nonsolvent/solvent miscibility and the coagulant's precipitation strength.

If coagulation bath is 100% water, the PI dope can't solidify to fibers, because m-cresol solvent isn't miscible with water, the diffusion within m-cresol and water can't take place. so we choose EtOH-water as coagulation bath, Fig.2 shows a series of fibers spun from m-cresol dope into various EtOH-water coagulation baths. These SEM pictures indicate that by decreasing the miscibility(increasing water content of baths),the morphology reverts back to being slightly porous. When coagulation consistent 85%EtOH and 15% water, the as-spun fibers are completely voids-free . This implies that miscibility is important in this case , as Termonia's rule, the miscibility controls the rate at which the coagulation front advance within the fiber. A slow rate of advance by both the coagulation front and the diffusing nonsolvent allows a polymer rich skin to grow by slowing squeezing out the solvent molecules, yielding a more solid structure. This also shows that it is important to control the rate of phase separation.

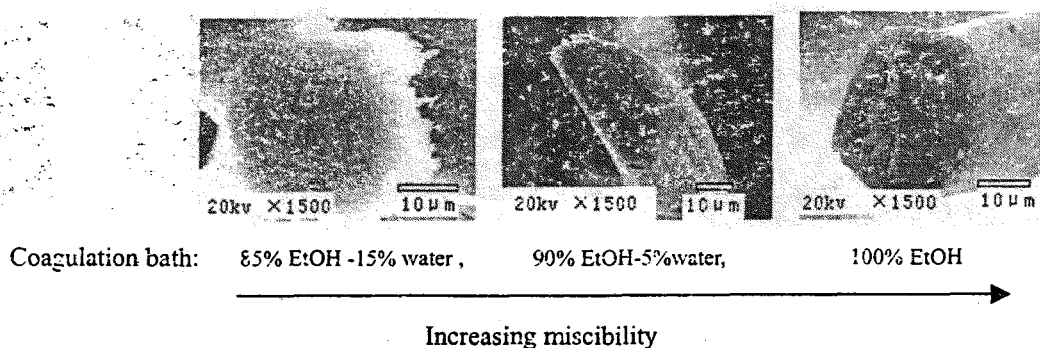| Coagulation bath: | 85% EtOH -15% water , | 90% EtOH-5%water, | 100% EtOH |

Increasing miscibility

Fig.2   Cross-sectional SEM of as-spun fiber

The tensile strength of annealed fibers are 120~280Mpa, as one would expect, the tensile strength increase as porosity decreases.

Solvent and Drawing-Induced Crystallization[14]

From molecular views, ODA +DABBE(8/2,mol ratio)/ODPA crystallization should be difficult, because of it's unsymmetrical molecular structure.　Figure 3 can prove it.
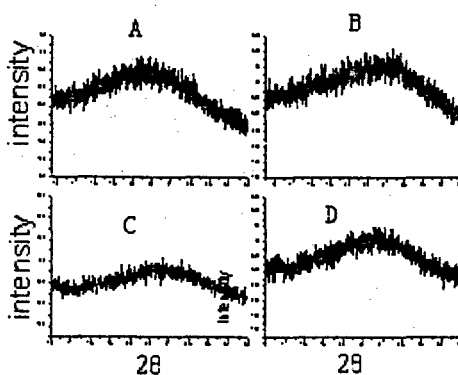

Figure 3　WAXD of annealed fibers

A: annealed process: continuously arising temperature from R.T to 350℃under tension

B: annealed process: 350℃ for 30 min under tension

　A, B:　as-spun fibers(containing 10% degree solvent)

C: annealed process: 60℃~130℃ under tension for 3h

D: annealed process: 350℃ for 6h under tension

　C, D :　as-spun fibers (degree of solvent less than 2%(w/w))

From a review of literature[15], PI as-spun fibers is amorphous, then hot drawing of the fibers above Tg will usually result in crystallization. But in ODA+DABBE/ODPA system, hot drawing of the as-spun fibers (degree of solvent less than 2%(w/w)above Tg (270℃) can't achieve crystallinity. Only a s-spun f ibers (degree of s olvent more t han 8 % (w/w)) under t ension at 60℃~130℃ for long time can result in crystallization. The crystallinity are up to 47.4%. As shown in Table 2.

Two Phase Crystallization
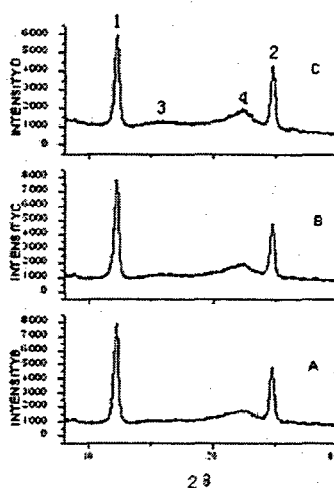
Group I :peak 1, 2

Group II :peak 3, 4

d-spacing of peak 1: 7.2338

d-spacing of peak 2: 3.5911

A: Under 5.0g tension　　B: Under 15.0g tension　　C: Under 50.0 g tension

Fig.4 WAXD of annealed fibers under different tension

(Annealed temperature: 60℃, 1h, 130℃, 3h, degree of solvent in as-spun fibers: 10%(w/w))

As Fig.4 WAXD shows, there are two different kinds of peak patterns in each of our samples. One kind is reflected by a group of sharp peaks (designated as group I), which show a perfect crystalline . The other (designated as group II) which is characterized as typical macromolecular crystalline is demonstrated by a group of blunt peaks. These two kinds of peaks originate from the same molecular structure, so their crystallization kinetics are consistent. Meanwhile, the two sharp peaks(1,2) of group I have d-spacing value of 7.2338 and 3.5911 respectively, which show that the two peaks belong to different crystal face in the same crystal cell. As shown in table 1 the half-peak-width, crystal size of group I are independent of drawing behavior. However, the peaks pattern designated by group II changes from amorphous structure to semi-crystalline, as the drawing ratios increase, their half-peak-width, crystal size, degree of crystalline are affected readily by drawing behavior. As illustrated by Table 2, drawing induces the group II to crystallize, the crystallinity increases with the increase of drawing ratios.

Table 1   The crystallization parameter of Group I

Annealed tension, g	5.0	15.0	50.0
Half-peak-width	0.2132	0.2079	0.2150
Crystal size, Å	740	768	726

Table 2   The crystallization parameter of Group II

Annealed tension, g	5.0	15.0	50.0
Half-peak-width	1.3325	0.7557	0.4480
Crystal size, Å	/	163	112
Crystallinity, %	0	31.4	47.4

According to the changes of crystallinities, crystal size and half-peak-width, we believe there are two crystallization phases in PI fiber of ODA-DABBE/ODPA. Group II phase is formed by chain backbone, whose crystalline structure has many defects and the crystalline is induced by drawing, this phase possess the properties of macromolecular crystallization. Group I phase, we believe, is formed by mesogen side chain, this phase is readily to crystallize and bears the same characters as low-mollecular-weight molecule, and its crystalline is independent of drawing, which is consistent with the position of the side chain among the macromolecule.

Summary

As-spun polyimide fibers was spun by using m-cresol as solvent, ethanol/water (90/15 w/w) as coagulation, through adjustments in nonsolvent/solvent miscibility of the coagulation bath , voids-free as-spun fiber can be product.

The solvent residue of as-spun fibers was more than 8%(w/w). By drawing and heating, semi-crystalline polyimide fibers were produced.

There are two crystallization phase among PI fiber of ODA-DABBE/ODPA structure, formed by backbone and mesogen side chain, respectively. The crystallinity (up to about 47.4%), half-peak-width, crystal size of the former phase are affected by drawing, however the other phase are independent of drawing.

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含有联苯酯侧链聚酰亚胺纤维纺丝形态及其结晶行为的控制[*]

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摘要：采用4，4′－二苯醚二胺，3，5－二胺基苯甲酸－4′－联苯酯和4，4′－二苯醚二酐为原料，共聚合成了一种新型可溶性聚酰亚胺。其间甲酚均相原液通过干/湿法纺丝获得了该聚酰亚胺纤维，通过调节凝固浴的非溶剂/溶剂的比例，可控制纺丝过程中纤维的凝固速率；其SEM照片表明纤维的内部形态随着凝固速率的不同，可由大量孔隙演变到致密的结构，WAXD也表明该原丝结构为非晶结构。在原丝的热处理过程中，当原丝的残留溶剂量小于 2％（W/W），其热处理后的纤维始终是非晶结构；但当原丝的残留溶剂量在 10％（W/W）左右，在张力、热处理温度为 60℃-130℃的情况下，热处理后的纤维是半晶型结构，且其 WAXD 衍射图具有两种不同形式的衍射峰，拉伸作用对这两种衍射峰的影响也各不相同。其结果表明在该聚酰亚胺纤维的结晶体系存在着两相结构，其一是大分子主链的结晶结构，另一相则是侧链介晶基元的结晶结构。