

# High Performance Electrospun Copolyimide Nanofibers

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## Abstract

Electrospun nanofibers based on copolyimides were made aiming at finding a promising method for improving mechanical properties of electrospun polyimide nanofibers. The copolyimide had a backbone consisting of 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA), biphenylamide(BPA) and 4,4'-oxydianiline(ODA) residues. The structure and composition of the copolyimide was controlled by the ratio of rigid BPA and flexible ODA moieties. The electrospun copolyimide nanofibers were collected in the form of a belt using a rotating disc with a rim of 8 mm width. SEM, IR, X-ray scattering and Tensile Tester, DMA and TGA were used to characterize the nanofiber belts. The nanofibers have a diameter range from 80 to 300 nm, and well aligned in the belts. The nanofiber belts have a heat-resistance over 460°C. Tensile test showed that the copolyimide nanofiber belts had much better mechanical properties than either of the flexible and rigid homo-polyimide nanofiber belts. Tensile strength, modulus and elongation to break of copolyimide nanofiber belt with BPA / ODA ratio of 40/60 are respectively 1.1GPa, 6.2 GPa and 21%, compared to 459 MPa, 2.1 GPa and 41% of BPDA/ODA homo-PI as well as 384 MPa, 11.5 GPa and 3.9% of BPDA/BPA homo-polyimide. The important is that the electrospun polymer nanofibers can be made very strong by using copolyimides as spinning materials.

**Key word:** high strength; nanofibers; electrospinning, copolyimide

## 1. Introduction

High strength electrospun nanofibers are an interesting topic because of their uses or potential applications in many fields from fashion clothing, protective clothing, high performance filters, and high strength nano-fillers for polymer composites with a good interfacial contact to possible uses for solar sails, light sails and mirrors in space. Making high strength electrospun polymer nanofibers is a challenge of science and technology because traditional post-spinning stretching, which makes macromolecules highly oriented along the direction of the fiber axis, is not feasible for making high strength electrospun nanofibers due to (1) their very small diameters and (2) the complicated coiled path of the jet during the electrospinning process.

The high strength electrospun nanofiber mats were made from rigid polyimide (PI)<sup>1-2</sup> and had a tensile strength of 660 MPa, but the elongation at break of the PI nanofiber mats is less than 5%,<sup>1</sup> which might result from the rigidity of the PI molecules. Lower elongation means lower toughness and lower impact resistance. In this regards, we had a strategy to improve the elongation by using copolymer partially containing flexible or semi-flexible moieties on the rigid polyimide backbone. Experimental results are far-beyond our expectation: the aligned electrospun copolyimide nanofiber belts not only have a higher elongation but also have a very high strength. The highest tensile strength measured by using those copolyimide nanofiber belts was 1.1 GPa, and the corresponding strain was about 21%. In the present paper we report, for the first time, a detail investigation in preparation and characterization

of a series of electrospun co-PI nanofiber belts made from 3,3',4,4'- biphenyltetracarboxylic dianhydride and diamines, *p*-phenylenediamine (BPA) and 4, 4'-oxydianiline (ODA), at different ratio as well as in the influence of the rigid and flexible moiety ratio in the polymer on the mechanical properties of the electrospun nanofiber belts.

## **2. Experimental Section**

### **2.1 Synthesis of PI and co-PI Precursor**

The precursors, poly(amic acids) of BPDA/BPA (B-PAA) and BPDA/ODA (O-PAA), and co-poly (amic acid) of BPDA/ BPA/ODA (co-PAA), which were used to prepare electrospinning solutions, were synthesized by using dianhydride BPDA and two diamines, BPA and ODA. The polycondensation was performed in DMAc at  $-5\text{ }^{\circ}\text{C}$  with intense mechanical stirring for 24 h. A series of precursor solutions were formed by changing the ratio of diamines, BPA and ODA, from 0/100, 5/95, 10/90...70/30 to 100/0 in the polymerization. The concentrations of the precursor solutions were all designed to be 8% by weight of the polymer.

### **2.2 Preparation of aligned PI and co-PI precursor nanofiber belts**

Just for simplicity, the PI precursor series are called PAAs, which include co-PAA, B-PAA and O-PAA, in the following text. The co-PAA means that the molecular structure of the polymer contains BPA and ODA two kinds of diamine moieties; B-PAA and O-PAA are the co-PAA at the situation of the diamine ratio, ODA/BPA, being 100/0 and 0/100. The intrinsic viscosities of the as-synthesized PAAs were measured in DMAc at temperature of  $25^{\circ}\text{C}$ . The precursor solutions for electrospinning were prepared by using solvent DMAc to dilute the above 8% by weight precursor solution into a suitable concentration with an absolute viscosity of about 6 mPa.S. Then, 0.2% by weight dodecylethyldimethylammonium bromide (DEDAB) was mixed into the electrospinning solution to make the electrical conductivity of the solution be about  $38\text{ }\mu\text{S.cm}$ . The electrospinning process was performed using electric fields on the order of 100 kV/m, from a 15 kV electrical potential applied to a 15 cm gap between a spinneret and a rotating disc collector, which had a diameter of 0.30m and a disc rim width of 8 mm. The co-PI precursor nanofiber belts were collected on the disc collector rotated at a linear speed of 24 m/s.

### **2.3 Imidization of electrospun co-PAA nanofiber belts**

For the above same reason, the polyimide series obtained from the precursor PAAs were called PIs, which include co-PI, B-PI and O-PI. The PAA nanofiber belts were dried at  $60\text{ }^{\circ}\text{C}$  in vacuum for 2 h to remove any residual solvent, and then were converted into PI nanofiber belts by imidizing at high temperature. The imidization process was performed in a high-temperature furnace using the following protocol: 1) heating up to  $250\text{ }^{\circ}\text{C}$  at a rate of  $20\text{ }^{\circ}\text{C}/\text{min}$  in vacuum and annealing for 30 min; 2) heating up to  $370\text{ }^{\circ}\text{C}$  at a rate of  $5\text{-}10\text{ }^{\circ}\text{C}/\text{min}$ , and then annealing at  $370\text{ }^{\circ}\text{C}$  for 60 min to complete the curing process.

## **3 Results and discussion**

### **3.1 Preparation of highly aligned PI and co-PI nanofiber belts**

In order to obtain highly aligned nanofiber belts, a rotatable disc collector was used to collect electrospun nanofibers. The fibers collected on the surface of disc rim moving at a linear speed of 24m/sec have a high alignment. The alignment degree of the nanofibers in belts is about 90%, which is higher than that in mats collected on the surface of the previous reported cylinder collector,<sup>1</sup> determined by accounting the fibers with almost same stretching direction in the

SEM image. The fiber diameters range from 80nm to 300nm with a main distribution at 180-200 nm. The PI nanofibers were formed from the above precursor nanofibers by imidization at high temperature as described in experimental section. IR absorption bands from 2500 to 3600  $\text{cm}^{-1}$ , attributed to stretching vibrations of O-H in group -COOH and N-H in group -CONH-, and peaks of amide I and amide II at 1660 and 1550  $\text{cm}^{-1}$  (C=O in group -CONH-) of polyamic acids were vanished from the spectra. In the meanwhile, new IR absorption peaks appeared at 1776  $\text{cm}^{-1}$  (C=O in imide cycle, asym. stretching), 1715  $\text{cm}^{-1}$  (C=O in imide cycle, sys. stretching), 1375  $\text{cm}^{-1}$  (C-N in imide cycle, stretching) and 725  $\text{cm}^{-1}$  (C=O in imide cycle, bending). An obvious difference between B-PI and O-PI or co-PI in IR spectra is an absorption peak at 1238  $\text{cm}^{-1}$  attributed to C-O (stretching) of aromatic ether on O-PI and co-PI molecular backbone. The intensity of the peak at 1238  $\text{cm}^{-1}$  decreased with the ratio decrease of ODA moiety on the co-polyimide molecular chain.

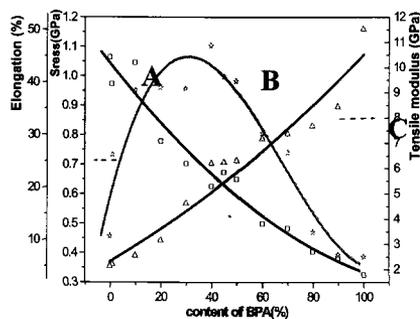
### 3.2 Mechanical properties of co-polyimide nanofiber belts

As previously reported by us,<sup>1</sup> electrospun polyimide nanofibers have a high tensile strength. The nanofiber mats, made from rigid BPDA/PPA (*p*-phyniline diamine) polyimide, had a tensile strength of 660 MPa, much higher than those of other reported polymer nanofiber mats, but the elongation at break was smaller than 5%, for which the rigidity of the BPDA/PPA polyimide molecules might be responsible. In this work reported here, a series of PI nanofiber belts were made at the same conditions, such as intrinsic viscosity, high voltage electrical fields, rotating speed of collector, imidization temperature and so on, to show how the elongation of polyimide nanofiber belts changes with the different ratios of rigid and flexible diamine moieties on the co-polyimide backbone. The elongation at break of the co-polyimide nanofiber belts increased with the increase of the flexible component on the PI molecular chain. The tensile strengths of the co-PI nanofiber belts are much higher than those of the corresponding rigid and flexible homo-PI nanofiber belts. Figure 1 shows a relationship between the tensile strengths and the co-PI compositions. The highest tensile strength 1.1GPa occurred at the ratio 40/60 of the rigid diamine BPA and flexible diamine ODA, but the corresponding flexible and rigid homo-PI belts had tensile strengths of 459 MPa and 384 MPa, respectively.

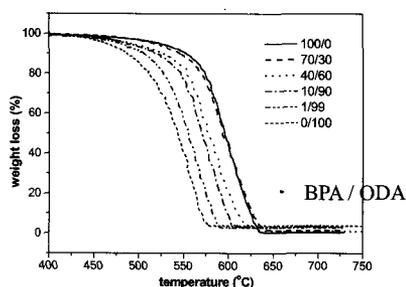
### 3.3 Thermal stability of PI nanofiber belts

Polyimides belong to a class of high thermal stable polymers, which mostly have aromatic backbones. Electrospun nanofiber belts made from B-PI, O-PI and coPI based on the backbones of B-PI and O-PI have a high thermal stability of above 460 °C. TGA curves are shown in Figure 2. Compared to B-PI, each repeat unit of O-PI contains a -O- ether bonding, which is an inherent oxidation potential to make the polymer decomposed at a lower temperature than B-PI. The belts made from O-PI decompose at 463.9°C, and B-PI belts at 523.6 °C by 5% weight loss. The thermal decomposition of co-PI nanofiber belts by 5% weight loss is in the temperature range from 463.9°C to 523.6 °C, increasing with the ratio of BPA moiety on the polymer chain (see Figure 3).

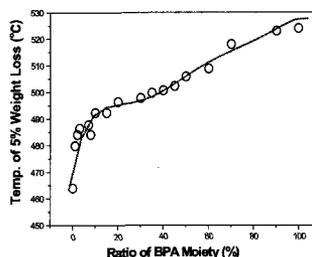
Polyimide backbone is much stiffer than most other polymer backbone. The glass transition of most polyimides is not discernible by DSC. But DMA is much more sensitive for detecting the glass transition of PI. The DMA curves of PI nanofiber belts are shown in Figure 4. The flexible O-PI nanofiber belt shows a prominent  $\alpha$  transition at peak temperature of 275 °C, which is correlated to Tg of O-PI in nanofiber belt and 10 °C lower than the previously reported Tg of 285 °C measured by using O-PI film.<sup>3-5</sup>



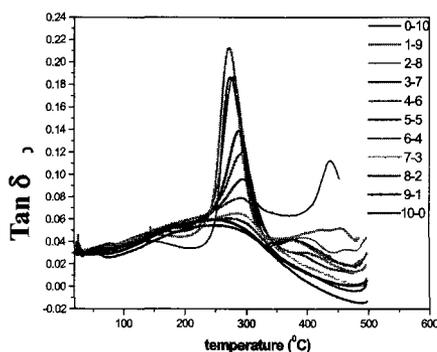
**Figure 1.** Relationships between mechanical properties and BPA moiety content in the PI polymer: curve A is strain; curve B tensile strength; curve C tensile modulus.



**Figure 2.** TGA spectra of aligned PI nanofiber belts



**Figure 3.** The decomposition temperature at 5% weight loss versus the ratio of BPA moiety in the PI polymer.



**Figure 4.**  $\tan \delta$  of electrospun PI nanofiber belts with different BPA/ODA ratios.

## Conclusion

Electrospun nanofibers were made using a class of copolyimides, the backbones of which were composed of BPDA, BPA and ODA residues. The compositions of the copolyimides were controlled by the ratio of flexible ODA and rigid BPA diamine moieties. Different ratios of the flexible and rigid diamine moieties give the copolyimide nanofibers different mechanical and thermal properties. The glass transition and decomposition temperature of copolyimide increased gradually with the increased ratio of rigid BPA moiety on the polymer backbone. The tensile strength of copolyimide nanofiber belt is much better than either of homo-O-PI and homo-B-PI nanofiber belt. The highest tensile strength 1.1 GPa, which is 2-3 times of homo-O-PI and homo-B-PI nanofiber belts, occurred at the BPA/ODA moiety ratio of about 4/6. The modulus of copolyimide is higher than homo-O-PI and lower than homo-B-PI, and that enhanced with the ratio of rigid BPA moiety, but the elongation at break of copolyimide fiber belt negatively changed with the ratio of BPA moiety and is 21% at the BPA/ODA moiety ratio of about 4/6, in company with the highest tensile strength. (next see page p269)

----End of the Proceedings-----