Bioinspired preparation and properties of high-whiteness polyimide ultrafine fabrics by electrospinning from organo-soluble semi-alicyclic polyimide resins

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Abstract: Ultrafine fabrics with high whiteness and good thermal stability are highly desired in modern industry. Inspired by the natural high-whiteness living beings originated from the micro-nano structure, a series of semi-alicyclic polyimide (PI) resins were synthesized from an alicyclic dianhydride, 4,4'-dihydroxybiphenyl dicyclohexanecarboxylate-3,3',4,4'-tetracarboxylic acid dianhydride (HTA-BP) and aromatic diamines, including 4,4'-bis[(4-aminophenoxy-2-trifluoromethyl)] biphenyl (6FBAB) for PI-1, 2,2'-bis[(4-aminophenoxy) phenyl] hexafluoropropane (BDAF) for PI-2, 4,4'-diaminobenzanilide (DABA) for PI-3, and 2-chloro-4,4'-diaminobenzanilide (Cl-DABA) for PI-4 via a two-step chemical imidization procedure. The derived PI resins are easily soluble in polar aprotic solvents. PI ultrafine fabrics were successfully prepared via the one-step electrospinning procedures from the PI solutions in *N,N*-dimethylacetamide (DMAc). The PI ultrafine fabrics showed high whiteness except PI-3, with the white indices more than 94 and yellow indices lower than 5.69.

Keywords: Alicyclic dianhydride, Polyimide, Electrospinning, Fabrics, High whiteness

1. INTRODUCTION

The production of white samples has been the final purpose of different industries, such as textile, paper, plastics, dentistry and paints [1]. In the current technology, mineral particles, such as titanium dioxide (TiO2), kaolin, calcium carbonate, or fluorescent whitening agents (FWAs) were added to improve the whiteness and opaqueness of the materials.

In recent years, structural white has been reported in the literature. Some nature living beings, including white beetles [2-4], butterflies [5] and poplar leaf [6], have been studied due to their white surfaces, as shown in Figure 1. It has been established the whiteness is attributed to their microstructures. For example, the whiteness of Cyphochilus beetles originates from the disordered structure of the scales. These scales are about 5 μm thick, 250 μm long and 100 μm wide. Their interiors are composed of a random network of interconnecting cuticular filaments with a diameter of approximately 250 nm. This natural phenomenon inspired researchers to produce a brilliant whiteness surface from biomimetic ideas.

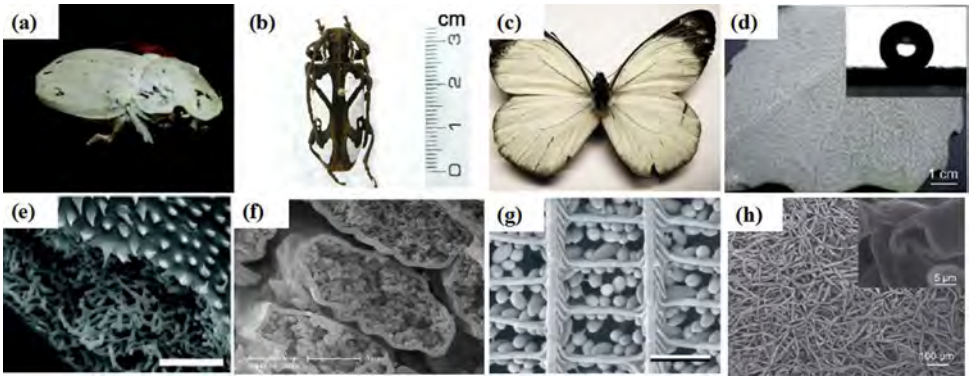

Fig. 1. Natural high-whiteness living beings originated from the micro-nano structure.
Scale bars:(e) 3 μm, (f) 5 μm, (g) 1 μm, (h) 100 μm.

Electrospinning might be the most cost-effective and straightforward method for generating random fiber network structure and the diameter of the fiber can be elaborately controlled. Yip and coworkers reported brilliant whiteness surfaces from electrospun nanofiber webs by the inspiration of *Cyphochilus* white beetles [7]. They produced an electrospun nanofiber web with a very high whiteness index, thus providing an extremely effective and efficient light shielding layer for textile and industrial applications. Zeighami, et al, also developed optically efficient nanofiber coatings with extra high whiteness and opaqueness by this biomimetic procedure [8]. They coated polyamide (nylon) and polyacrylonitrile (PAN) nanofiber layers on the surface of a paper using an electrospinning method. High whiteness and complete opaqueness were achieved even on a black cardboard by means of a thin layer of the electrospun nanofibers. Similarly, Syurik et al, fabricated large-scale and highly-scattering surfaces with exceptional whiteness from poly(methyl methacrylate) (PMMA) films by the *Cyphochilus*-inspired idea [9]. Very recently, Toivonen and coworkers achieved bright whiteness by controlling the light transport in membranes of cellulose nanofabrics (CNFs) [10]. This control was achieved by tuning the porosity and morphological features of CNFs. In summary, for polymeric microfibrous mats, high whiteness can now be achieved by structural design, such as highly disordered nanostructures induced from the biomimetic bead-like shape, rod-like scatters, micropores and so on.

Polyimide (PI) represents a class of high performance heteroaromatic polymers known as their high thermal resistance, good mechanical and dielectric properties, and excellent environmental stability [11]. However, the strong intra- and inter-molecular conjugation interactions in conventional PI chains make them exhibit deep colors from dark brown to yellow, either in the form of films or in the form of fabrics [12], which greatly limiting their applications in optical fabrication. During the past decades, various efforts have been carried out aiming at reducing the coloration of PI materials, including introduction of flexible groups, bulky substituents, aliphatic or alicyclic moieties.

In our continuous work developing low-color PI films or coatings for advanced optical applications, a series of semi-alicyclic PIs have been developed from various alicyclic dianhydrides and aromatic diamines [13-15]. The derived PI resins were generally soluble in polar solvents. Thus, based on our previous experiences in developing colorless PI films, a series of high-whiteness PI fabrics or mats were designed and developed in the current work. For this purpose, an alicyclic dianhydride containing both of rigid-rod biphenyl unit and flexible ester linkages was prepared by the method reported by Hasegawa [16]. Then, the PI resins were prepared from the dianhydride and aromatic diamines. A series of PI fabrics were fabricated via the electrospinning procedures from the developed PI solutions. The effects of molecular structure on the whiteness properties of the derived PI fabrics were investigated in detail.

2. EXPERIMENTAL

2.1. Materials

4,4'-Dihydroxybiphenyl-dicyclohexanecarboxylate-3,3',4,4'-tetracarboxylic acid diahhydride (HTA-BP) was synthesized according to a modified procedure reported in literature [16]. Aromatic diamines, including 4,4'-bis[(4-aminophenoxy-2-trifluoromethyl)]biphenyl (6FBAB), 2,2'-bis[(4-amino-phenoxy)phenyl]hexafluoropropane (BDAF), 4,4'-diaminobenzanilide (DABA) and 2-chloro-4,4'-diaminobenzanilide (Cl-DABA) were purchased from Changzhou Sunlight Pharmaceutical Co. Ltd., China and dried in vacuum at 80 ℃ overnight prior to use. N,N-Dimethylacetamide (DMAc), and other solvents were purchased from Beijing Yili Fine Chemicals, China and purified by distillation prior to use. The other commercially available reagents were used without further purification.

2.2. Polyimide synthesis

The general procedure for the synthesis of PIs can be illustrated by the preparation of PI-3. Into a 1000 mL

three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet, DABA (22.726 g, 0.1 mol) was dissolved in the newly distilled DMAc (400 g) to give a clear diamine solution. Then, HTA-BP (54.652 g, 0.1 mol) was added in one batch and an additional volume of DMAc (38.5 g) was added to wash the residual dianhydride, and at the same time to adjust the solid content of the reaction system to be 15 wt%. After stirring in nitrogen for 24 h at room temperature, a mixture of acetic anhydride (102.1 g, 1.0 mol) and pyridine (63.3 g, 0.8 mol) was then added. The reaction mixture was stirred at room temperature for another 24 h. Then, the obtained pale-brown viscous solution was diluted with DMAc and then slowly poured into an excess of ethanol to yield a white fibrous resin. The resin was collected and dried at 80 oC in vacuo for 24 h.

The other PI resins, including PI-1 (HTA-BP/ 6FBAB), PI-2 (HTA-BP/BDAF), and PI-4 (HTA-BP/Cl-DABA) were prepared according to a similar procedure as mentioned above.

2.3. Electrospinning

PI-3 resin (15 g) was dissolved in DMAc (85 g) at room temperature to afford a 15 wt% solution. The solution was filtered through a 0.45 μm Teflon syringe filter to remove any undissolved impurities. The typical electrospinning parameters were as follows: The polymer solution with a 15 wt% concentration was loaded into a 5 ml syringe as the spinneret. A syringe pump was used to squeeze out the polymer solution through a needle with an inner diameter of 0.50 mm, at the speed of 0.2 ml/h. A voltage of 15 kV was applied between the syringe and the collector. The distance between the spinneret and the grounded plate collector was 15 cm. Ultrafine PI fibers were deposited on the aluminum foil as the support medium, located on the rotating drum collector (diameter: 10 cm; length: 30 cm; speed: 100 rpm).The humidity in the electrospinning apparatus was 50±2% relative humidity. The obtained PI-3 fabric was dried at 200 ℃ for 3 h to remove the residual solvent from the fabrics.

The other PI fabrics, including PI-1 (HTA-BP/6FBAB), PI-2 (HTA-BP/BDAF), and PI-4 (HTA-BP/Cl-DABA) were prepared according to a similar procedure as mentioned above.

2.4. Measurements

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum was obtained on a Bruker Tensor-27 FT-IR spectrometer. The micromorphologies of the non-woven fabrics of electrospun PI ultrafine fibers were investigated using a Technex Lab Tiny-SEM 1540 field emission scanning electron microscopy (SEM) with an accelerating voltage of 15 KV for imaging. Pt/Pd was spattered on each film in advance of the SEM measurements. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a TA-Q series thermal analysis system at a heating rate of 10 oC/min in nitrogen.

White index (WI) and yellow index (YI) values of the PI fabrics were measured using an X-rite color i7 spectrophotometer with PI samples at a thickness of 300-400 μm in accordance with the procedure described in Chinese standard GB/T 17644-2008 “Test method for whiteness and chromaticity of textile fibres” [17]. The color parameters were calculated according to a CIE Lab equation. L* is the lightness, where 100 means white and 0 implies black. A positive a* means a red color, and a negative one indicates a green color. A positive b* means a yellow color, and a negative one indicates a blue color. The color parameters of a standard poly(pyromellitic dianhydride -oxydianiline) (PMDA-ODA) fabrics was also measured for reference. The whiteness values of the PI fabrics were calculated as equation (1).

$$WI=100-[(100-L^*)^2+a^{*2}+b^{*2}]^{1/2} \quad (1)$$

where WI standards for whiteness, L* standards for index of lightness, a* and b* stand for chromaticity coefficient.

3. RESULTS AND DISCUSSION

3.1. PI ultrafine fabrics fabrication

A series of semi-alicyclic PIs were synthesized from HTA-BP and various aromatic diamines via a two-step chemical imidization procedure, as shown in Figure 2. Four aromatic diamines were elaborately chosen for our molecular design. Two trifluoromethyl-containing diamines, 6FBAB and BDAF were utilized to reduce the coloration of the derived PI fabrics via cutting the charge transfer between the electron donating diamine moiety and the electron accepting dianhydride moiety due to the strong electronegativity of –CF3. Another two amide-bridged diamines, DABA and Cl-DABA were chosen for endowing the PI fabrics strong mechanical features originated from the polyamide (nylon).

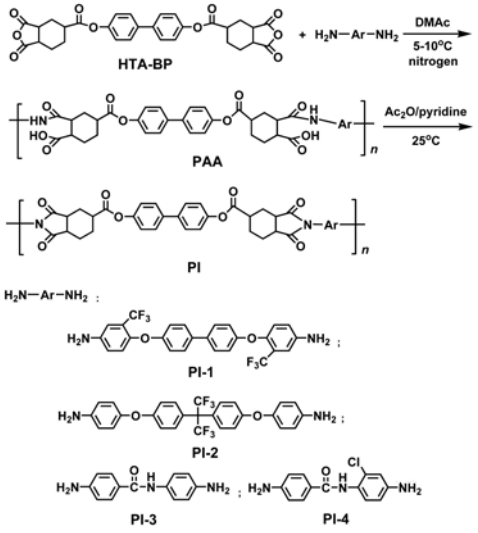

Fig. 2. Synthesis of HTA-BP-PIs

The chemical structures of PI mats were confirmed by ATR-FTIR. Figure 3 depicts the FT-IR spectra of two typical fluoro-containing PIs (PI-1 and PI-2) in the form of films. The characteristic imide group absorptions at 1789 cm-1 assigned to the asymmetrical carbonyl stretching vibrations, and those at 1716 cm-1 assigned to the symmetrical carbonyl stretching vibrations, as well as that at 1378 cm-1 due to the C–N stretching vibrations were all observed. As expected, C–F multiple stretching absorptions were also measured at 1250 and 1145 cm-1, respectively. In addition, the asymmetric and symmetric stretching vibration of the anhydride carbonyl groups absorptions in HTA-BP at 1864 cm-1 and 1750 cm-1 disappeared in the spectra of PI films. The lack of amide and carboxyl absorptions indicated that the polymers were fully imidized from the PAA intermediates.

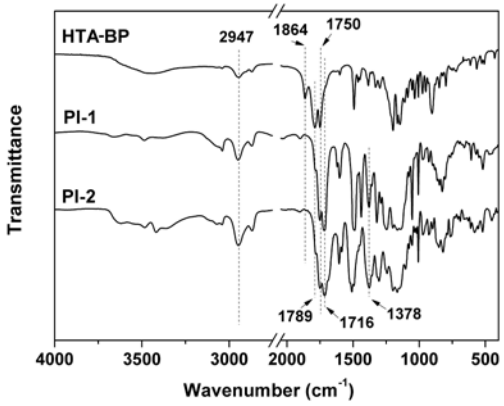

Fig. 3. FT-IR spectra of HTA-BP and the PIs.

Four flexible and tough PI ultrafine fabrics were successfully prepared by electrospinning procedures. Figure 4 presents the microscopic morphologies of typical PI-4 ultrafine fibers. The PI-4 fabric samples for the SEM measurements were dried at 200 ℃ for 3h before the tests. It can be seen that ultrafine PI-4 fibers with the average diameter of 580 nm were obtained. The surface of the fiber was smooth and little defects and fusion of filaments were detected. It can be concluded that fine PI fabrics or mats could be obtained by the current electrospinning conditions. This composition feature is propitious to efficiently scattering the visible light, resulting good whiteness for the mats.

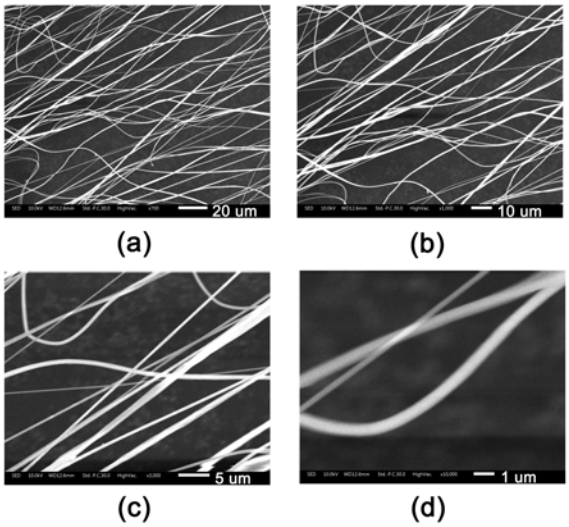

Fig. 4. SEM images of PI-4 ultrafine fibers

3.2. Optical properties

According to the Chinese standard GB/T 17644-2008, the color parameters of the PI fabrics were tested. Figure 5 exhibits the white index measurements of the PI fabrics and the color data are summarized in Table 1. It is observed that the WI values of the PI fabrics were all higher than 94 except PI-3 (84.35) and decreased according to the order of PI-2>PI-1>PI-4>PI-3. This implied that all the PI fabrics exhibited excellent whiteness except PI-3. The b* (positive b* means a yellow color) and YI values of the PI fabrics showed a similar trend of PI-2<PI-1<PI-4<PI-3. The PI fabrics showed YI values of 2.99-5.69, which were much lower than that of wholly aromatic PI-ref (YI=65.93). The fluoro-containing PI-1 and PI-2 exhibited the highest whiteness and the lowest color. This trend correlated well with their molecular structures.

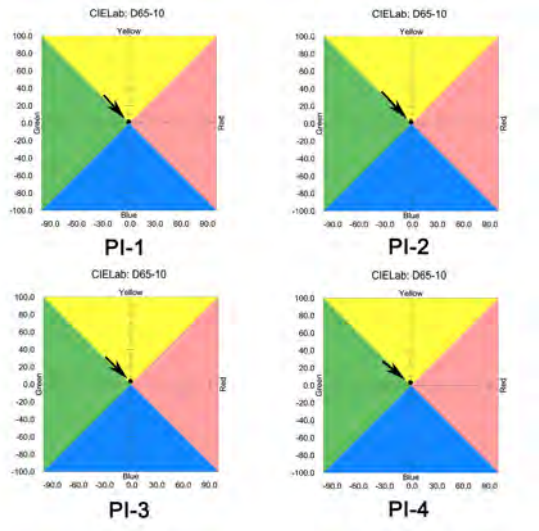

Fig. 5. White index measurements of PI fabrics.

Table 1. Optical and thermal properties of PI fabrics.

PI	Optical properties					Thermal properties [a]		
	L^*	a^*	b^*	YI	WI	T_g(°C)	$T_{5\%}$(°C)	R_{w750}(%)
PI-1	95.40	-0.43	1.99	3.57	94.97	213.8	417	28.4
PI-2	95.71	-0.23	1.66	2.99	95.39	192.9	411	20.0
PI-3	84.76	-0.23	3.55	6.58	84.35	233.3	413	25.5
PI-4	95.30	-0.29	3.17	5.69	94.32	202.2	418	27.2
PI-ref [b]	84.65	1.62	37.96	65.93	59.02	-[c]	-	-

[a] Measured by the PI fabrics after post-treatment at 200 °C for 3h; T_g: Glass transition temperature; $T_{5\%}$: Temperatures at 5% weight loss; R_{w750}: Residual weight ratio at 750 °C in nitrogen; [b] PI-ref: poly(pyromellitic dianhydride-oxydianiline) (PMDA-ODA); [c] Not detected.

In the current work, the average diameter of the current random aligned PI fibers (~580 nm) is much higher than the chitin filaments in the Cyphochilus white beetles (~250 nm), indicating that the whiteness of the current PI mats could be further enhanced by adjusting the microscopic parameters of the materials.

3.3. Thermal properties

Good thermal stability of the ultrafine fibers at elevated temperatures is of critical importance for their practical applications. The thermal stabilities of the PI fabrics were investigated by TGA and DSC measurements. Table 1 summarizes the thermal data of the PI fabrics.

Glass transition temperatures (Tg) values were obtained from the DSC measurements. All the PI fabrics exhibit good thermal stabilities with the Tg values in the range of 192.9~233.3 ℃, depending on the rigidity of the aromatic diamines. It is observed that the Tg values of the PI fabrics decreased in the order of PI-3>PI-1>PI-4>PI-2. The decreasing order of Tg is consistent with the chain flexibility of the PIs. PI-2 derived from HTA-BP and BDAF showed the lowest Tg value of 192.9 ℃ due to the increasing flexibility of the polymer chains caused by the flexible -C(CF3)2 bridges. Instead, PI-3 containing rigid-rod -CONH- unit showed the highest Tg value of 233.3 ℃ due to the strong intra-molecular interactions of the polar amide bonds. The 5% weight loss temperatures (T5%) of the PI fabrics are all higher than 400 ℃ in nitrogen. Although the thermal stability of the current PI fabrics is lower than that of common wholly aromatic PIs, it is high enough for their applications in practical applications.

4. CONCLUSION

Ultrafine PI fabrics were successfully prepared via the electrospinning fabrication of organo- soluble semi-alicyclic PI resins from HTA-BP dianhydride and aromatic diamines. The derived PI nanofibers had the average diameters of hundreds of nanometers and smooth surface. The fabrics showed high whiteness (WI>94, YI<5.69), good flexibility and toughness, and good thermal stability (T5%>400 oC; Tg> 192 oC). Good comprehensive properties make the fabrics good candidates for advanced high-tech applications.

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