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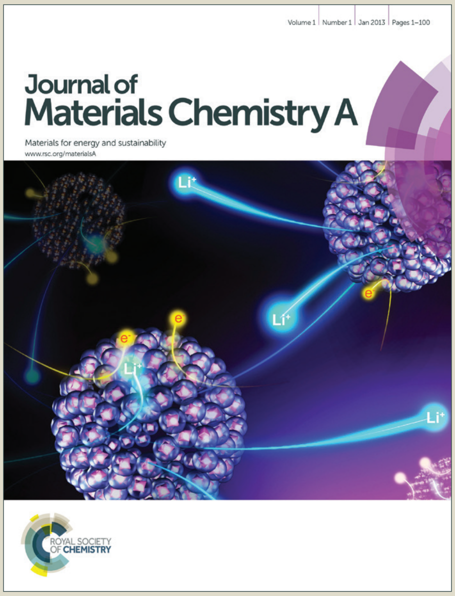

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Construction of PANI/cellulose Composite Fibers with Good Antistatic Properties

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For the first time, novel polyaniline (PANI)/cellulose filament fibers have been successfully spun from hydrophobic PANI and hydrophilic cellulose complex solution dissolved in aqueous containing 7 wt% NaOH/12 wt% urea as solvent by wet-spinning. The composite fibers had a circular cross-section and homogenous surface structure, as a result of a good miscibility between PANI and cellulose associated through hydrogen bonding. Moreover, at low PANI content, the composite fibers realized a transition from an insulator to semiconductor. This work has provided a simple and eco-friendly avenue for the production of PANI composite fibers that have a great potential application in the antistatic textile and military industries.

Electrically conducting polymers have been considered to be a class of “synthetic metals” that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors,[1-4] and driven many advances in materials science, electronic theory, nanoscience and technological application.[5-7] Polyaniline (PANI) has been under intensive research and development in both academic and electronics industrial areas. Until now, a number of methods for producing a promising PANI materials have been reported, such as chemical polymerization,[8] electrochemical polymerization,[9] and template synthesis polymerization.[10] With the rapid emergence of nanoscience and nanotechnology, the nanomaterials including nanofibers,[11] nanotubes,[12,13] nanosheet,[14,15] nanospheres[16] and nanonetworks[17] have been synthesized and found applications as nanoelectronic devices, such as sensors, energy management, memory, eletrochromic devices, actuators.[18-23] Traditionally, PANI has been successfully utilized by forming blends and composites with a conventional polymer, which still have a great advantage in processing and to combine the mechanical properties of the conventional polymer and the functional properties of PANI. The most straightforward approaches towards processing polymers include fabricating the composites to films,[24] hydrogels[25,26] microspheres[27] and fibers.[28]

Spinning including wet-spinning, melt-spinning and electro-spinning, is the technique most used for constructing fibers with diameters in the range of micrometers to nanometers. Recently, many kinds of conventional polymers including poly(ethylene oxide),[29] polyimide,[30] nylon 6,[31] poly(L-lactide)[32] have been prepared as composite fibers with PANI using electro-spinning method.[33,34] However, the preparing of the conductive polymer/ biopolymer composite filaments with wet-spinning has been scarcely reported. Nowadays demands for new functional fibers based on natural polymers has been increasing which are sustainable and environmentally friendly.[35,36] A worthwhile endeavor would be to construct cellulose-based complex fibers from hydrophilic cellulose and hydrophobic PANI.

In previous work, PANI doped with acidic phosphate ester has been dissolved in cellulose solution rapidly, forming the PANI/cellulose supramolecular complex through hydrogen bonds between hydrophobic PANI and hydrophilic cellulose in NaOH/urea solution at low temperature.[37] This homogeneous composite solution can remain in a liquid state for a long time in the temperature range of 0 to 8 °C.[38] Additionally, the films and hydrogels have been fabricated from the PANI/cellulose complex solution, showing good conductivity and electromechanical actuation.[39] In the present study, PANI/cellulose composite fibers were spun from the PANI/cellulose solution through the wet-spinning technique. The structure, morphology and properties of the composite filaments were investigated. This work may open up a novel pathway for the development of high value–added materials in today’s textile industry.

Fig. 1 Photographs of the wet PANI/ cellulose multifilament fibers in distilled water (left) and the dried PANI/cellulose multifilament fibers (right) spun from PANI/cellulose solution.

The PANI/cellulose solution remained a stable liquid state in the whole process of wet-spinning, which makes the system suitable for both foundational research and industry processing.[38] The dark green composite fibers were spun directly from the PANI/cellulose solution, and regenerated by coagulating with 10 wt% H_2SO_4 via a simplified laboratory spinning frame (Fig. S1 in Supporting Information). It was noted that this process did not require external doping to render the fibers conductive. According to the mass percentage of PANI (x wt %) in PANI/cellulose fibers, a series of PANI/cellulose fiber samples were coded as PCx, such as PC02, PC15. Figure 1 shows photographs of the freshly prepared PANI/cellulose filaments (PC15) in distilled water and at the dry state. The dried PANI/cellulose fibers were flexible, and had lustrous surface. Moreover, there was no vaporization of the chemical agents during the processing, and the PANI /cellulose fibers were regenerated directly from their composite solution by physical gelation, similar to cellulose multifilament fibers produced by the same solvent system.[40] This pathway was completely different from the traditional PANI fiber processing spun from organic solutions.[41] Therefore, the fabrication of the PANI/cellulose composite filaments were successfully realized by using a simple and essentially non-polluting process.

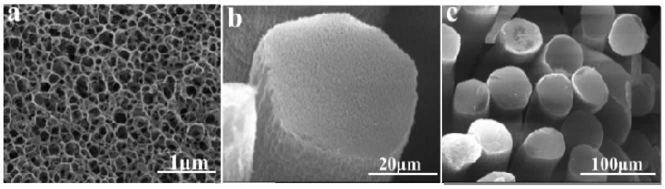

Fig. 2 SEM images of (a) the cross-section, (b) surface and (c) a bound of filaments for the PANI/cellulose filaments at the drawing ratio of -0.31 in freeze-dried state.

Figure 2 shows the SEM images of the cross-section and a bound of the PANI/cellulose filaments at the drawing ratio of -0.31. Clearly, the cross section of PANI/cellulose fibers was circle, which was similar to Lyocell fibers and pure cellulose filaments regenerated by physical process.[40,42] A homogenous porous structure as shown in Figure 2 (a) indicated that the composite PANI/cellulose fibers had a good compatibility between PANI and cellulose. Additionally, with an increase of the PANI content, the pore diameter at the surface was increased slightly (Fig. 2S). This could be explained that the hydrophobic nature of the PANI/cellulose complexes, composed of hydrophilic cellulose and hydrophobic PANI, led to the formation of surface tension. Therefore, the more the amount of PANI chains was, the greater the surface tension was, resulting in a larger hole in coagulation process.

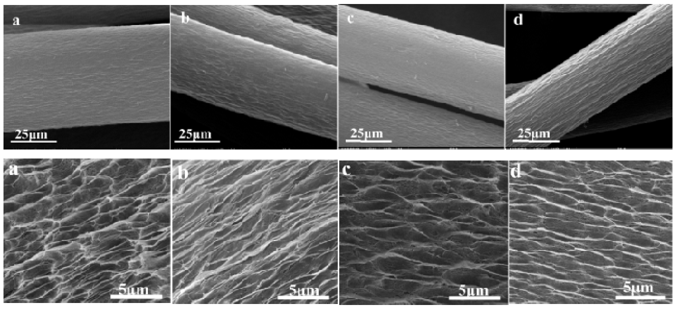

Fig. 3 SEM images of the surface (top) and cross-section (bottom) for the P15 PANI/cellulose fibers obtained by different drawing ratio: (a) -0.54, (b) -0.46, (c) -0.39, (d) -0.31.

Figure 3 shows the SEM images of the surface of the PANI/cellulose (PC15) composite filament under the different drawing ratios. Because a simple wet-spinning machine was applied, the drawing of the PANI/cellulose composite fibers could not be oriented sufficiently. The speed of collection roller was set at 24, 28, 32 and 40 rpm to obtain the different drawing ratio and the speed of metering pump was fixed at 20 rpm. With an increase of the drawing ratio, the diameter of the composite filaments fibers decreased from 55 to 35μm, and the fibers exhibited a more uniform and denser surface texture, indicating that the orientation of the fabrics occurred and could be modulated by varying the drawing process. In addition, the pore size of the cross section of PANI/cellulose fibers decreased slightly with drawing progress (Fig. S3). As shown in XRD patterns (see Fig. S4), the peak area of the PANI/cellulose fibers was slightly smaller than that of regenerated cellulose fibers, and the characteristic peak of PANI disappeared in the composite fibers. These results suggested that the dissolution of PANI in a cellulose solution resulted in limited re-crystallization, and the entanglement between PANI and cellulose chains through intermolecular hydrogen bonds led to the reduced crystalline level of cellulose.[37] This further confirmed that a good miscibility existed between PANI and cellulose chains in the complex fibers, which was in favour of the wet-spinning.

Table. 1 The tensile strength (σ_b) and breaking elongation (ε_b) of PANI/ cellulose filaments and regenerated cellulose filaments (RC) under different drawing ratio.

Filament No.	D (drawing ratio)	σ_b (cN/dtex)	ε_b (%)
PC15/RC	-0.54	0.91/0.71	25.4/22.1
PC15/RC	-0.46	1.10/0.85	20.6/19.7
PC15/RC	-0.39	1.18/0.87	19.2/18.8
PC15/RC	-0.31	1.27/1.05	18.8/16.9

The tensile strength (σ_b) and elongation at break (ε_b) of the PANI/cellulose composite filaments in different drawing ratios are summarized in Table 1. The σ_b values of the composite filaments increased from 0.91 to 1.27 cN/dtex when the speed of collection roller enhanced from 24 to 40 rpm. It can be predicted that the tensile strength of PANI/cellulose composite fibers will be improved significantly through suitable drawing orientation. The PANI in the matrix may play a role of plasticizer to some degree, leading to the enhancing of the mechanical properties of the PANI/cellulose fibers on the whole. It is possible that the mechanical properties of the PANI/cellulose fibers could be further improved after further optimization of the spinning process and the machine.

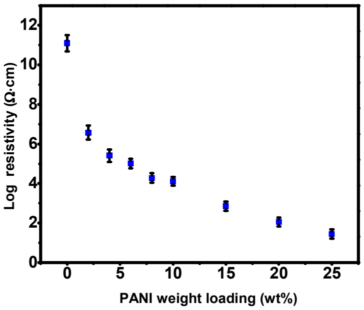

Fig. 4 Resistivity of the PANI/cellulose composite filament fibers as a function of PANI content.

The plot of resistivity of the PANI/cellulose composite filaments as a function of the PANI content is shown in Figure 4. The resistivity of the regenerated cellulose fibers was about 10^{11} Ω·cm corresponding to the magnitude of an insulator. However, with an increase in PANI content, the electrical resistivity of the composite fibers significantly decreased. It was noted that the resistivity can be as low as 10^6 Ω·cm at the lower PANI loading of 2 wt%, which exhibited a transition from an insulator to semiconductor. This result suggests that a conductive network was formed at 2 wt% PANI content in the cellulose matrix which can be considered to be the percolation threshold. Interestingly, the value of the percolation threshold was lower and the resistivity decreased sequentially against the increase of the PANI content, which were difference from the results reported in literature.[43,44] This phenomenon could be explained by the fact that the entanglement of PANI and cellulose chains ensured a larger aspect ratio and nanoscale dimension of the PANI in the cellulose matrix, leading to the formation of conductive network at low PANI loading.

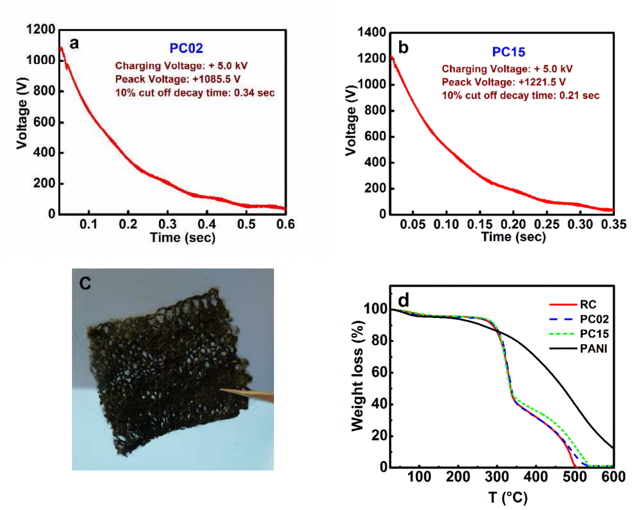

Fig. 5 Static decay curves of (a) PC02 and (b) PC15, and (c) Photograph of PANI/cellulose fabric for the static charge dissipation tests. (d) TGA plots of RC, PC02, PC15 and PANI powder at a heating rate of 10°C min^{-1} under an air atmosphere.

In order to further describe the ability of a material to dissipate or decay charge on its surface, the static charge decay measurements were made with the voltage of 5.0 kV. The static decay curves of the PC fabrics are shown in Figure 5a, b. All of the charge decay curves exhibited exponentials character. The decay time of initial surface voltage decaying to 10% of RC fabric was 2.2 s (Fig. S5),[45-47] which is still higher than the limiting time of 2.0 s. However, the values of decay time of PC02 and PC15 were 0.34 and 0.21 s, respectively, indicating that the PC fabrics passed the antistatic criteria of 2.0 s. It was worth noting that the decay time decreased with an increase of PANI loading, suggesting the higher conductivity can be beneficial to charges dissipation. Therefore, the fabrics would have the satisfactory values of decay time by using the low PANI content, showing good antistatic properties. Additionally , the higher initial surface potential of the samples was observed here, which may be due to the larger internal between the conductive fibers and irregular surfaces,[48,49]as the results of the handing woven fabrics here as shown in Figure 5c. In view of the importance of thermal stability in many applications of fabric materials, thermogravimetric behaviours of the RC fibers, PC fibers and PANI powder were investigated under an air atmosphere. The results are shown as Figure 5d. In the TGA curve of the pure cellulose fibers, the small weight loss occurred in the temperature range of 25 to 120°C and 120 to 275°C, respectively, due to the loss of absorbed moisture and dehydration process.[50,51] The decomposition commenced at 275°C and increased rapidly at 350 °C up to 60% of weight loss. Within the temperature range, the PC fibers displayed nearly identical curves with the RC fibers. However, the decomposition rate of PC fibers slightly slowed with an increase of PANI loading above 350°C, indicating that thermal stability of PC fibers was slightly improved by the additive of PANI. Therefore, the PANI/ cellulose composite filaments had good antistatic properties and thermal stability, which can be used as anti-static wire and in military industries.[52]

Conclusions

The PANI/cellulose composite filament fibers were successfully spun from the PANI/cellulose supramolecular complex solution by wet- spinning. The composite filaments had a circular cross-section and homogeneous structure, as a result of the good miscibility of the two components. The PANI composite fibers did not require external doping to render the conductivity, leading to non-toxic and simple pathway for fabrication of new conductive fibers. By combing the advantageous properties of cellulose and PANI, the composite fibers exhibited good antistatic properties and mechanical strength. This work is important for the fabrication and application of functional fibers in the anti-static textile and military industries.

Experimental Section

Materials

Cellulose (the cotton linter pulp) with α-cellulose content of more than 95% was supplied by Hubei Chemical Filament Co., Ltd. (Xiangfan, China). Its weight-average molecular weight (M_w) was determined by laser light scattering in a 4.6 wt% LiOH/15.0 wt% urea aqueous solution to be 9.8×10^4.[53] The cellulose sample was dried under vacuum at 55 °C for 24 h to remove any moisture before use. Polyaniline (PANI) doped with acidic phosphate ester was supplied by Changchun Institute of Applied Chemistry (Chinese Academy of Sciences in China). Its M_w value was determined in N-methyl-2-pyrrolidone (NMP) solvent with laser light scattering to be 3.0×104.[54,55] All of the other chemical agents of analytical grade including NaOH, urea and H_2SO_4 were purchased from commercial sources in China and were used without further purification.

Preparation of PANI/cellulose composite filaments

A mixture solution with NaOH/urea/H_2O ratio of 7:12:81 by weight was pre-cooled to -12 °C. 4.2 g cellulose was immediately dispersed into the solvent system (100 g) under vigorous stirring for 4 min to obtain a transparent cellulose solution. Subsequently, PANI doped with acidic phosphate ester pre-cooled to 0 °C was immediately dropped into the cellulose solution under vigorous stirring for 3 min to form a dark blue PANI/cellulose solution at ambient temperature, and then was subjected to centrifuge to degas at 7200 rpm for 20 min at 8 °C. The composite solution was employed as a spinning dope for wet-spinning filaments. Wet-spinning of the fibers was worked out on a small and simple homemade wet-spinning apparatus (Fig. S1, see Supporting Information), in which a spinneret with 75 orifices (diameter, 120 μm) and the ratio of nozzle length to diameter of 20 was used. The spinning dope was into a coagulation bath composed of 10 % H_2SO_4. The composite filaments from the spinneret were passed through the coagulation bath and rolled on Nelson-type rollers connected to a motor. Finally, the composite filaments were immersed in distilled water for 2 days to remove residue. A series of fibers consisted of hydrophilic cellulose and hydrophobic PANI were spun from the composite PANI/cellulose solution by coagulating with 10 wt% H_2SO_4, and coded as PC02, PC04, PC06, PC08, PC15, and PC25, corresponding to 2, 4, 6, 8, 15 and 25 wt% PANI content in the dried PANI/cellulose fibers, respectively.

Characterization

Scanning electron microscopy (SEM) measurements were carried out on a FE-SEM (FE-SEM, FEI SIRION-200) by using an accelerating voltage of 20 kV. Wide-angle X-ray diffraction (XRD) measurement was carried out on a XRD instrument (XRD-6000, Shimadzu, Japan) with Cu Kα radiation (λ = 0.15406 nm). The mechanical properties of the PANI/ cellulose filaments (PC) and regenerated cellulose filaments (RC) were measured out on a tensile tester (XQ-1, Shanghai Textile University, China) according to ASTM method D2256-80, The values of the tensile strength (σ_b) and breaking elongation (ε_b) presented the average of 20 measurements. Electrical resistivity was measured using the four-probe technique (RTS-8, Shenzhen Four Probes Tech Co. Ltd, China) and high resistance meter (6517A, Keithley, USA). The textiles were wove using fibers by manual operation. The size of samples was 4.5 cm × 5 cm. Static charge decay was measured at 17.8 °C and 40% RH on ME-268A instruments (Monroe, USA). HDO4104 high definition oscilloscope (Teledyne LeCroy, Taiwan) were used for the measurement and curve analyses. Thermogravimetric analysis (TGA) was carried out on TGA Q500 equipment (TA instruments, USA) at a heating rate of 10°C min^{-1} under in an air atmosphere (40 ml min^{-1}).

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