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Preparation and Characterisation of PSA/CNT Composites and Fibres

Abstract
In this paper, polysulfonamide/carbon nanotube (PSA/CNT) composite solutions with different CNT contents were prepared using the physical blending method. Corresponding composite fibers were extruded and fabricated through a set of wet spinning units, and composite membranes were prepared by the spin-coating method. The PSA/CNT composite fibers and membranes were characterised by means of SEM, FTIR and XRD among others. The mechanical, thermal and electrical properties were also analysed in this study. The experimental results show that CNT at low contents can be distributed homogeneously in the PSA matrix. Furthermore the molecular structure and chemical composition of PSA does not undergo an obvious change. Crystallisation in the PSA can be promoted at low CNT contents because the nano-particles can act as a nucleation agent. Moreover the electrical conductivity of PSA can be improved significantly by the blending of CNT.

Key words: *polysulfonamide, carbon nanotube, nano composites, thermal property, electrical conductivity.*

RESEARCH AND DEVELOPMENT

Polysulfonamide (PSA) fiber belongs to the series of poly (para-phenylene terephthalamide) (PPTA) fibers, being a new kind of high-performance synthetic fibers [1]. PSA fiber has some excellent properties such as heat resistance, thermal stability and flame retardancy etc. Therefore it can be applied to develop protective textile materials used in aerospace, high-temperature environments and civil fields with flame retardant requirements [2, 3]. PSA fibers and related products are also widely used in modern military industry.

However, pure PSA products generally demonstrate poor mechanical properties and high electrical resistivity; these properties lead to some difficulties in their manufacturing procedures and limit their application in the development of functional textiles. Therefore, it is important work to improve the mechanical properties and electrical conductivity of PSA.

It has been proved that carbonanotubes (CNT) is a promising candidate to improve the mechanical properties of composites because of its high Young's modulus (1.4 TPa) and tensile strength (above 100 GPa) [4]. Moreover, CNT is said to improve the electrical conductivity of polymer/CNT reinforced matrixes due to its unique electrical properties [5], derived from its one dimensional character and the peculiar electronic structure of graphite.
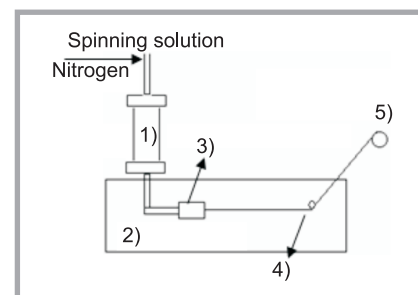
■ Experimental

Materials

PSA polymer was used as spinning solution with an intrinsic viscosity of 2.0 ~ 2.5 dL/g, and relative molecular mass of 462. Multi-walled carbon nanotubes (S-MWNT-1020, short for CNT) were blended as functional particles with a diameter of 10 ~ 20 nm and length of 1 ~ 2 μm. CNT was used after being treated with a mixed solvent of 70% nitric acid (20 ml) and 98% sulfuric acid (60 ml) for 2 hours. The degree of purity of the treated CNT was about 93%. Dimethylacetamide (DMAC) was selected as a dissolvent in this study. These materials were supplied by Shanghai Tanlon Fiber Co. LTD.

Preparation of PSA/CNT composites

A certain amount of the treated CNTs was added to a conical flask with DMAC, pre-distributed using ultrasonic vibration for 30 minutes, and then added to the PSA. Different contents of PSA/CNT composite spinning solutions were prepared after mechanical stirring for 1 hour and ultrasonic vibration for 2 hours.

Preparation process of wet spinning
The PSA fibers and corresponding composite fibers were prepared using small-scale and single-screw wet spinning apparatus (***Figure 1***).

The spinning solution was poured into a barrel and then flowed to a spinning nozzle with a hole size of (0.18 ± 0.03) mm. As shown in ***Figure 1***, the spinning trickle is forced out of the spinning nozzle under nitrogen pressure and then goes into a water bath. Nascent fibers were formed after solvent precipitation into a coagulation bath, which were then dried in an electrical blast oven for 24 hours to finish the thermosetting process and remove the residual solvent. PSA/CNT composite fibers with various contents: 0, 1, 3, 5 and 7 wt% could be obtained for systematical investigation.

Preparation of nano composite membranes
PSA/CNT composite membranes were prepared using SJT-B digital spin-coating instruments. An appropriate amount of spinning solution was spread on the substrate of the instrument so as to form a thin liquid film undertaken at a rotational speed of 2000 r.p.m. for 5 s and 4000 r.p.m. for 20 s. Then the membranes were put into water to remove the solvent. PSA composite membranes with different contents: 0, 1, 3, 5 and 7 wt% were obtained after drying in an electrical blast oven for 24 hours. The thickness

Figure 1. *Schematic diagram of the wet spinning process; 1) barrel, 2) water bath, 3) spinning nozzle, 4) guide stick, 5) winding device.*

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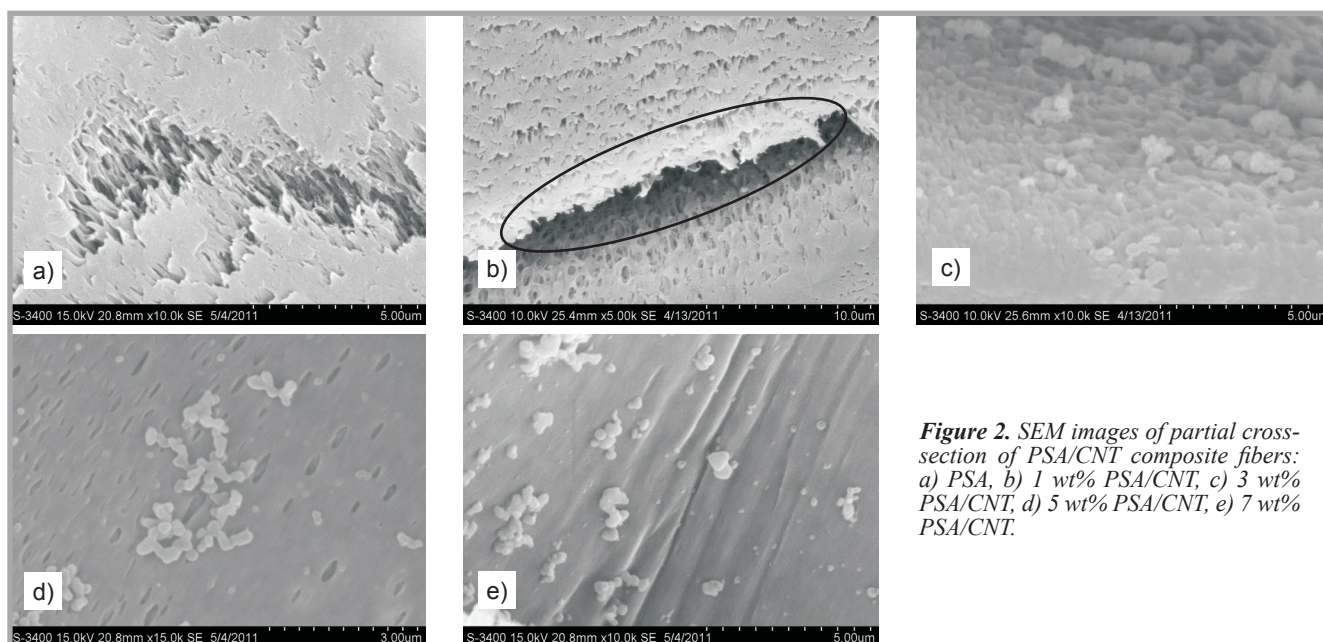
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Figure 2. SEM images of partial cross-section of PSA/CNT composite fibers: a) PSA, b) 1 wt% PSA/CNT, c) 3 wt% PSA/CNT, d) 5 wt% PSA/CNT, e) 7 wt% PSA/CNT.

of the membranes was about 1 mm, prepared for the electrical conductivity test.

Characterisations

A S-3400N Scanning Electron Microscope (SEM) with a nano-scale resolution was used to characterise the morphological surface of the PSA /CNT composites. The machine was operated at 10 ~ 15 kV.

An American AVATAR 370 Fourier Transform Infrared Spectroscopy (FTIR) Thermo Nicolet was used to investigate the molecular structure and chemical composition of the composite fibers. Spectra data were recorded from 4000 to 500 cm^{-1}, with a 4 cm^{-1} resolution over 32 scans, and a step size of about 1.929 cm^{-1}.

A k780 FirmV_06 X-Ray Diffraction (XRD) was used to characterise the crystalline structure of the composite fibers using CuKα radiation (λ = 0.154 nm) at a voltage of 40 kV and current of 40 mA. Spectra were obtained at a 2θ angle range of 5° ~ 90° with a scanning speed of 0.8 sec/step.

A YG006 Electronic Single Fiber Strength Tester was used to investigate the mechanical properties of the composite fibers. The sample gauge length was 10 mm, and the elongation speed - 20 mm/min. Measurements of each sample were conducted 10 times, and the average value was used for result analysis.

A Germany STA PT-1000 Thermal Gravimetric Analyser (TGA) was used to investigate the thermal stability of composite fibers. The TGA experiment was carried out in a nitrogen atmosphere with a gas flow of 80 ~ 100 ml/min. Samples were heated from room temperature to 700 °C at a heating rate of 20 °C/min.

A ZC36 high resistance meter with a measuring range of $10^8 \sim 10^{17}$ Ω and a UT70A Universal Digital Multi-meter with a higher limit of the measuring range of about 10^8 Ω were used to measure the surface resistivity of the composite membranes.

■ Results and discussions

Distribution of CNTs in PSA composites

As shown in *Figure 2*, a small amount of CNT (1 or 3 wt%) can be dispersed uniformly through the PSA matrix. The size of most nano-particles is about 30 ~ 50 nm; however, a little aggregation is observed, the size of which is about 100 nm. When the CNT content increased to 5 wt%, the distribution of nano-particles becomes inhomogeneous. When the CNT content is increased to 7 wt%, the agglomeration is more serious and it is hard for the CNT at high contents to disperse evenly throughout the PSA matrix. The size of the aggregated particles is about 150 ~ 200 nm.

Fourier transform infrared analysis of PSA/CNT composites

As can be observed in *Figure 3*, CNTs have no obvious influence on the shape and position of the PSA's characteristic peaks. The absorption peaks at about 3300 cm^{-1} are attributed to the amide N-H stretching vibration; the obviously narrow and sharp absorption peaks at about 1660 cm^{-1} indicate a C=C bond; at about 1590 cm^{-1} corresponds to the absorption peaks of C-N stretching vibration; absorption peaks at about 1500 ~ 1300 cm^{-1} are attributed to the plane bending vibration caused by C-H; 1300 ~ 1000 cm^{-1} corresponds to the C-C skeleton vibration, and 1000 ~ 650 cm^{-1} is the plane bending vibration of C-H. At about 1149.94 cm^{-1} is the characteristic peak of $-SO_2-$.

In *Figure 3*, except for the 7 wt% sample, the characteristic peaks of PSA composites at about 3300 cm^{-1} shift to a short-wave range compared with the pure PSA, which is attributed to the quantum size effect [6] of the nano-particles. The agglomeration of nano-particles becomes more serious as the CNT content is increased to 7 wt%, and then the nano effect is reduced.

X-Ray Diffraction analysis of PSA/CNT

It is found that all the samples in *Figure 4* show diffraction peaks at 2θ of 11.85° and 21.25°. The obviously sharp diffraction peaks of PSA composites at 11.85° suggest there is a crystalline structure in the materials [7]. In addition, the sharpening degree of the diffraction peaks at 11.85° changes significantly with an increase in CNT content from 0
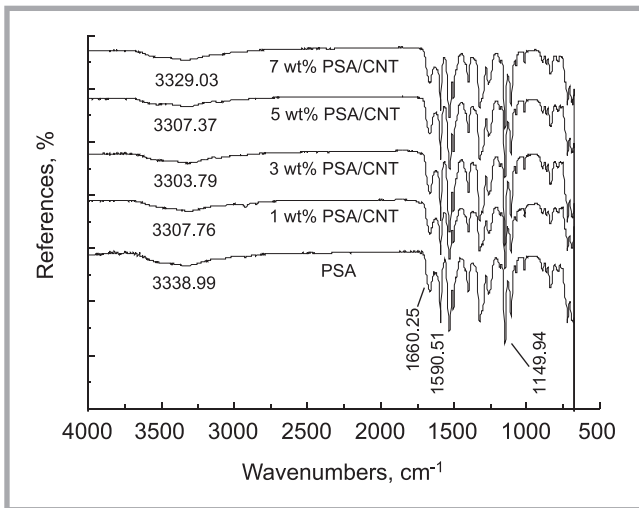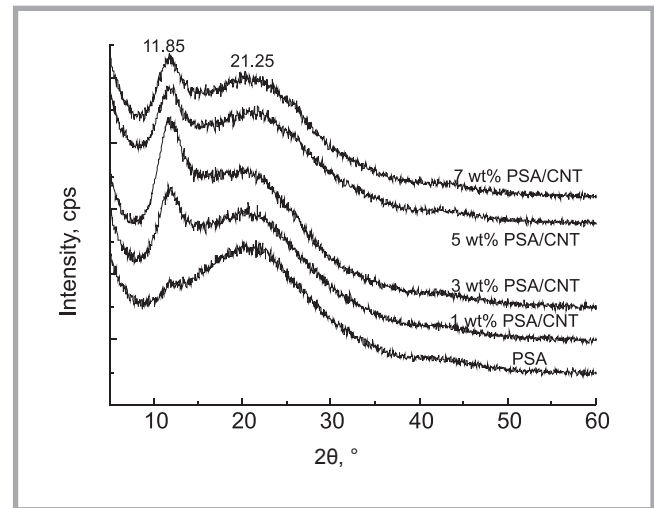
Figure 3. FTIR images of PSA/CNT composite fibers.

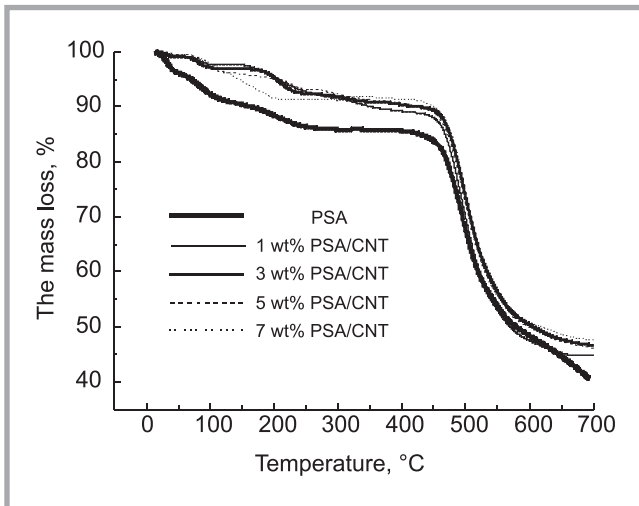**Figure 4.** XRD images of PSA/CNT composite fibers.
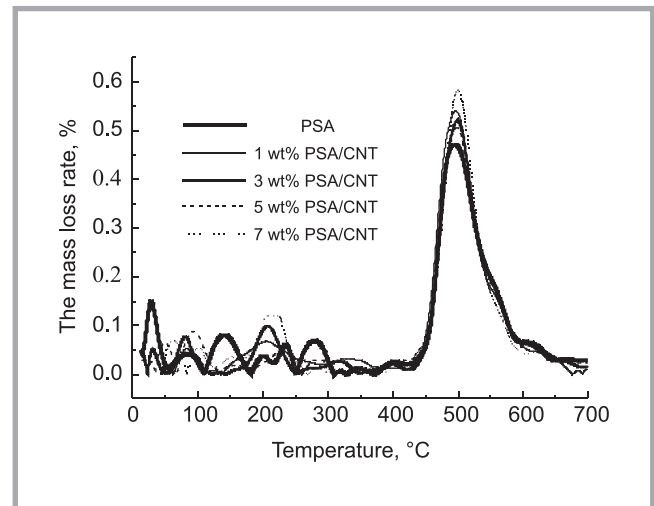

Figure 5. TG curves of PSA/CNT composites.

Figure 6. DTG curves of PSA/CNT composites.

to 3 wt%, indicating that crystallisation in PSA is promoted at low CNT contents because the nano-particles can act as a nucleation agent. What is more, the shape of the diffraction peaks at about 21.25° of PSA composites obviously broadens with an increase in CNT content, proving that the size of crystal region becomes smaller [8].

Mechanical properties of PSA/CNT

As presented in *Table 1*, 1 wt% PSA/CNT fiber has the maximum improving degree of breaking tenacity. When the CNT content is continuously increased to 3 wt%, the improvement begins to decrease, and when the CNT content is increased to 7 wt%, the breaking tenacity of the composite is lower than that of pure PSA. That is because CNT, with excellent mechanical properties, is an ideal nano-enhanced material. Besides, CNT

at low contents can be distributed homogeneously in the PSA matrix, forming a good interface with PSA.

As demonstrated in *Table 1*, the elongation at break of PSA/CNT composite fibers is lower than that of pure PSA, and the initial modulus of the composites increases with an increase in the CNT content from 1 to 5 wt%, which is attributed to the fact that CNT has high modulus and strength properties. Moreover, the CNTs dispersed in the PSA matrix can

play the role of physically cross-linking points, forming a network-like structure [9]. Therefore the PSA macromolecular chains can be closely connected.

Thermal stability of PSA/CNT

Figures 5 and *Figure 6* present the TG curves and DTG curves of PSA/CNT composites, respectively. The key parameters of the curves are summarised in *Table 2* (see page 24). In *Figure 5*, the thermal decomposition of the composites can be divided into three sections.

Table 1. Indexes of PSA/CNT composite fibers' mechanical properties; (10 tests with the coefficient of variation less than 10%).

Sample	Tenacity, cN/dtex	Elongation at break, %	Initial modulus, cN/dtex
PSA	0.411	29.70	0.098
1 wt% PSA/CNT	0.606	22.39	0.142
3 wt% PSA/CNT	0.531	15.10	0.162
5 wt% PSA/CNT	0.517	13.05	0.184
7 wt% PSA/CNT	0.310	16.42	0.060

The first section is the stage of small mass loss from room temperature to 400 °C. At this stage, the volatilisation of additives and the water bound among the molecules lead to the reduction of material's weight from room temperature to about 100 °C. With the temperature continuously increasing to 400 °C, the decomposition of oligomers with a small molecular weight leads to the mass loss of the composites.

As shown in *Figure 5* (see page 23), the change in mass loss of each PSA/CNT composite presents a similar trend, but pure PSA has a significantly high mass loss compared with the other samples. As the temperature increases to 300 °C, the TG curves of each sample begin to decrease slowly, and then reach a plateau. As can be seen in *Table 2*, the composite has a high temperature of T10wt; however, the mass loss of pure PSA reaches 10% at 170.19 °C, suggesting that it is hard for PSA blending with CNT to decompose in a high-temperature environment, hence its thermal stability can be improved significantly.

The second section is the stage of thermal decomposition (400 ~ 600 °C). In the TGA, the mass loss at high temperature can be attributed to the increasing movement rate of polymer macromolecular chains. Simultaneously the small molecules are released in the form of gases, leading to mass loss. In a nitrogen environment, the C-N in PSA decomposes at 500 ~ 600 °C [10-11]. According to the bond energy analysis [12] and structure of PSA, the mass loss at this stage is ascribed to the production of gases such as SO_2, NH_3 and CO_2.

As presented in *Table 2*, the T_o of PSA composites increases with the blending of CNT, and the thermal stability of the composites can be improved correspondingly. As can be seen in *Figure 5* (see page 23), each TG curve shows a rapid decomposition at about 500 °C. Corresponding to the rapid decomposition, there is a mass loss peak in the DTG curve (*Figure 6,* see page 23) and the T_{max} can be determined according to the value of the maximum peak [13].

The third section is the stable phase of carbon formation (600 ~ 700 °C). At this stage, most of the polymers are carbonised, and the rising temperature has less impact on the mass loss of the residues. As depicted in *Figure 5* (see page 23),
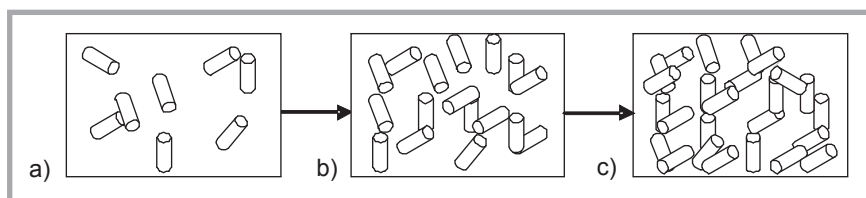

Figure 7. Sketch of formation of electrical conductive network in polymer matrix; a) 1 wt% PSA/CNT, b) 3 wt% PSA/CNT, c) 5 wt% or 7 wt% PSA/CNT.

Table 2. Parameters of different PSA composites during the thermal decomposition; (The test with the coefficient of variation less than 2%), T_o - The initial decomposition temperature; T_{10wt} - The temperature corresponding to the mass loss of 10%; T_{max} - The temperature of the maximum thermal decomposition rate.

Sample	T_o, °C	T_{10wt}, °C	T_{max}, °C	Residual mass at 700 °, %
PSA	460.90	170.19	495.41	40.52
1 wt% PSA/CNT	467.06	352.36	496.42	44.74
3 wt% PSA/CNT	467.79	425.80	498.81	46.06
5 wt% PSA/CNT	469.93	425.79	497.74	46.58
7 wt% PSA/CNT	468.47	450.38	499.75	47.48

Table 3. Surface resistivity of PSA/CNT composites in Ω.

Average	PSA	Contents PSA/CNT, wt%			
		1	3	5	7
Surface resistivity	3.10×10^{12}	1.13×10^{11}	5.96×10^6	4.70×10^5	2.10×10^4

the residual mass at the terminal temperature of the composites tends towards a steady state, while the mass loss of PSA decreases.

Electrical conductivity of PSA/CNT composite films

The content of conductive particles in the composites is one of the most important parameters influencing the materials' electrical conductivity. The CNT shows a high aspect ratio, thus it is easy for the nanotubes to establish an electrical conductive network throughout the PSA matrix. Moreover CNT has large numbers of freely moving electrons in the nanotubes. Therefore the electrical conductivity of PSA composites can be obviously improved by the blending of CNT.

The sketch [14] presented in *Figure 7* simulates the formation of an electrical conductive network in PSA/CNT composites. It is difficult for CNT at a low contents (1 wt%, *Figure 7.a*) to form a completely conductive network. With the CNT content continuously increasing to the percolation threshold (3 wt%, *Figure 7.b*), the distance among the particles begins to decrease. The local conductive network in the matrix can be basically established when the maximum distance is less than 10 nm. In this circumstance, the electrical resistivity of the composites

declines sharply and the conductivity can improve. With a further increase in CNT content, more and more conductive particles connect directly and a completely conductive network can be developed (5 or 7 wt%, *Figure 7.c*).

As can be seen in *Table 3*, the surface resistivity of PSA composites shows a downward trend with an increase in CNT content, whereby the electrical conductivity (the reciprocal of the resistivity) of the blending system can be improved significantly. This suggests that the blending of CNT can improve the electrical conductivity of PSA. However, the improving degree of electrical conductivity decreases as the CNT content continuously increases from 3 to 7 wt%, suggesting that it is difficult for high CNT contents to distribute evenly in the PSA matrix, thus impairing the outstanding electrical properties of CNT correspondingly.

■ Conclusions

PSA composite fibers and membranes with different CNT contents were prepared. The experimental results of their properties can be summarised as follows.
1) CNT at low contents (1 or 3 wt%) can be distributed homogeneously in the PSA matrix; however, it is hard for the CNT with high contents (5

or 7 wt%) to distribute evenly in the blending system.

2) There is no significant change in the molecular structure and chemical composition of PSA by blending CNT.
3) Crystallization in the PSA was promoted at low CNT contents because CNT can act as a nucleation agent.
4) Mechanical properties such as the breaking tenacity and initial modulus of PSA composites can be obviously improved by the blending of CNT; however, the elongation at break of PSA/CNT composite fibers decreases.
5) The blending of CNT can improve the electrical conductivity of PSA composites and the percolation threshold of the system at about 3 wt%.

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