Introduction

The PSA fibre is a new kind of developed flame retardant material and it has excellent heat resistance and flame retardancy as well as excellent thermal stability etc [1]. However, raw PSA has high electrical resistance while poor ultraviolet resistance; these properties cause some difficulties in its manufacturing procedures and limit its application in the development of functional textile products. Therefore, it is an important work to improve the electrical conductivity and ultraviolet resistance of the PSA fibres.

It has been proved that CNT has excellent electrical conductivity, mechanical properties and thermal conductivity [2, 3]; TiO$_2$ has outstanding scattering and absorption of ultraviolet. It is feasible to blend CNT/TiO$_2$ into PSA polymer to enhance the electrical conductivity and ultraviolet resistance of PSA/CNT/TiO$_2$ composites.

Experimental

Materials

PSA was used as spinning solution with an intrinsic viscosity of 2.0 $\sim$ 2.5 dL/g and relative molecular mass of 462. Multi-walled carbon nanotubes (S-MWNT-1020, in short CNT) were blended as functional particles for improving the electrical conductivity of PSA. The CNT, with a diameter of 10 $\sim$ 20 nm and length of 1 $\sim$ 2 µm, were used after being treated with a mixed solvent of 70% nitric acid (20ml) and 98% sulfuric acid (60 ml) for 2 hours. The degree of purity of the CNT treated was about 93%. Rutile titanium dioxide (short for TiO$_2$) with a diameter of 30 $\sim$ 50 nm and rutile content of about 99% was blended as functional particles for improving the ultraviolet resistance of PSA, used without further purification. Dimethylacetamide (DMAC) was selected as a solvent in this study. The above materials were supplied by Shanghai Tanlon Fibre Co. LTD.

Preparation of PSA/CNT/TiO$_2$ composites

An equivalent amount of CNT and TiO$_2$ was dispersed in DMAC using ultrasonic vibration for 30 minutes, then added to the PSA solution. Different nano-particle contents of PSA/CNT/TiO$_2$ spinning solution were prepared after ultrasonic vibration for 2 hours. The experimental data are shown in Table 1.

The PSA fibres and corresponding composite fibres were prepared using a small-scale and single-screw wet spinning apparatus. In addition, the PSA/CNT/TiO$_2$ composite membranes were prepared using the SJT-B digital spin-coating instrument. The preparation processes of the nano fibres and membranes can be found in the previous study [4].

Characterisations

A S-3400N scanning electron microscope at a nano-scale resolution was used to characterise the dispersion of CNT/TiO$_2$ in the polymer matrix; the machine was operated at 10 $\sim$ 15 kV.

American AVATAR 370 Infrared Spectroscopy Thermo Nicolet was used to characterise the molecular structure and chemical composition of fibres; spectra data were recorded from 4000 to 500 cm$^{-1}$ with a 4 cm$^{-1}$ resolution over 32 scans and with a step size of about 1.929 cm$^{-1}$.

K780 FirmV.06 X-Ray Diffraction was used to characterise the crystalline structure of fibres using CuKα radiation ($\lambda = 0.154$ nm) at a voltage of 40 kV and current of 40 mA. The spectra were obtained at a 20 angle range of 5 $\sim$ 90° and scanning speed of 0.8 sec/step.

A YG006 electronic single fibre strength tester was used to investigate the mechanical properties of the composite fibres. The specimen gauge length was 10 mm, and the elongation speed was set at 20 mm/min. Measurements of each specimen were conducted 10 times and the average value used for result analysis.

The thermal stability of fibres was characterised by a Germany STA PT-1000 thermal gravimetric analyser. The TGA

Table 1. Sample list of PSA composites with different CNT/TiO$_2$ contents.

<table>
<thead>
<tr>
<th>Content of nano-particles, %</th>
<th>PSA/g</th>
<th>CNT/g</th>
<th>TiO$_2$/g</th>
<th>DMAC/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% CNT/TiO$_2$</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1 wt% CNT/TiO$_2$</td>
<td>100</td>
<td>0.0606</td>
<td>0.0606</td>
<td>1</td>
</tr>
<tr>
<td>3 wt% CNT/TiO$_2$</td>
<td>100</td>
<td>0.1856</td>
<td>0.1856</td>
<td>3</td>
</tr>
<tr>
<td>5 wt% CNT/TiO$_2$</td>
<td>100</td>
<td>0.3158</td>
<td>0.3158</td>
<td>5</td>
</tr>
<tr>
<td>7 wt% CNT/TiO$_2$</td>
<td>100</td>
<td>0.4516</td>
<td>0.4516</td>
<td>7</td>
</tr>
</tbody>
</table>
experiment was carried out in a nitrogen atmosphere with a gas flow of 80 ~ 100 mL/min. The 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 10⁸ ~ 10¹⁷ Ω and testing voltage of 10 ~ 100 V was used to measure the high surface resistivity of membranes. Besides this a UT70A universal digital multi-meter with a measuring range of 10⁸ ~ 10⁹ Ω was used to measure the low surface resistivity of the membranes. The specimens were conditioned at constant temperature in a humid environment for 24 hours before measurement in testing conditions of 20 ± 2 °C temperature and 35 ± 10% RH. For each specimen the measurements were conducted 10 times and the average value was used for result analysis.

An American Labsphere UV-1000F ultraviolet transmittance analyser was used to test the UV transmittance of membranes. The instrument parameters were as follows: the range of wavelength - 250 ~ 450 nm, measuring range of transmittance - 0 ~ 100%, absorbance - 0 ~ 2.5 A, scan time - 5 seconds, data interval - 1 nm and the diameter of the beam - 10 mm. For each specimen the measurements were conducted 10 times and the average value was used for result analysis.

### Results and discussions

#### Distribution of CNT/TiO₂ in PSA composites

As illustrated in Figure 1, 1 wt% CNT/TiO₂ can be distributed homogeneously in the PSA matrix system, and its size is about 30 ~ 50 nm; when the CNT/TiO₂ content is increased to 3 wt%, a little aggregation is observed, and its size is about 100 nm; with an increased CNT/TiO₂ content from 5 wt% to 7 wt%, the distribution in the PSA matrix becomes inhomogeneous, and it is hard for nanoparticles with high contents to disperse evenly in the blending system; the size of the aggregations is about 150 ~ 300 nm.

An American Labsphere UV-1000F ultraviolet transmittance analyser was used to test the UV transmittance of membranes. The instrument parameters were as follows: the range of wavelength - 250 ~ 450 nm, measuring range of transmittance - 0 ~ 100%, absorbance - 0 ~ 2.5 A, scan time - 5 seconds, data interval - 1 nm and the diameter of the beam - 10 mm. For each specimen the measurements were conducted 10 times and the average value was used for result analysis.

#### Fourier transform infrared spectral analysis

As shown in Figure 2, the characteristic peaks of PSA composites at about 3300 cm⁻¹ shift to the short-wave range compared with pure PSA. Besides this, the shape of the absorption peak at 3301.25 cm⁻¹ of PSA composite fibres with 1 wt% CNT/TiO₂ is obviously flattened, which is attributed to the quantum size effect of the nano-particles [5]. The agglomeration of CNT/TiO₂ becomes more serious with the content increasing.
to 7 wt%, then the nano-effect can be reduced correspondingly.

X-ray diffraction analysis

Figure 3 illustrates that all the samples have diffraction peaks at about 20° and there is a shift excursion of the diffraction peaks of rutile titanium dioxide (TiO2) at 27.45°, 36.15°, 41.35° and 54.40°. This indicates that the PSA composite fibres have a nucleation agent. Moreover, the content of CNT/TiO2 can act as a nucleation agent. Figure 3 shows that the PSA composite fibres have a shift excursion in the PSA/CNT/TiO2 composites is improved because the CNT/TiO2 particles have a high modulus and strength. Besides this, the CNT/TiO2 dispersed in the polymer matrix plays the role of physical cross-linking points and forms a network-like structure in the blending system [6]. Consequently, the PSA macro-molecular chains tend to be more closely connected.

Mechanical properties

As shown in Table 2, the tenacity of the 1 wt% sample is improved maximally; with the CNT/TiO2 content increased to 3 wt%, the tenacity stops decreasing and the tenacity of the 7 wt% sample is lower than that of pure PSA. Since both CNT and TiO2 have excellent mechanical properties, it is feasible to blend them into the polymer matrix to improve its mechanical behaviour. Furthermore, CNT/TiO2 particles can be distributed homogeneously in the PSA matrix at a low content to improve the tenacity of PSA composite fibres.

Table 2. Mechanical properties of PSA composite fibres with different CNT/TiO2 contents; 10 tests with a coefficient of variation of less than 10%.

<table>
<thead>
<tr>
<th>Content of nano-particles, %</th>
<th>Tenacity, cN/dtex</th>
<th>Elongation at break, %</th>
<th>Initial modulus, cN/dtex</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% CNT/TiO2</td>
<td>0.411</td>
<td>29.70</td>
<td>0.098</td>
</tr>
<tr>
<td>1 wt% CNT/TiO2</td>
<td>0.491</td>
<td>22.90</td>
<td>0.185</td>
</tr>
<tr>
<td>3 wt% CNT/TiO2</td>
<td>0.411</td>
<td>16.70</td>
<td>0.137</td>
</tr>
<tr>
<td>5 wt% CNT/TiO2</td>
<td>0.324</td>
<td>9.40</td>
<td>0.115</td>
</tr>
<tr>
<td>7 wt% CNT/TiO2</td>
<td>0.290</td>
<td>8.50</td>
<td>0.097</td>
</tr>
</tbody>
</table>

As presented in Table 2, the elongation at break of the composite fibres is lower than pure PSA. At the same time, it shows that the initial modulus of the composite fibres increases when the CNT/TiO2 content is increased from 1 wt% to 5 wt%, which is because CNT and TiO2 particles have a high modulus and strength. Besides this, the CNT/TiO2 dispersed in the polymer matrix plays the role of physical cross-linking points and forms a network-like structure in the blending system [6]. Consequently, the PSA macro-molecular chains tend to be more closely connected.

Table 3. Parameters of PSA composites with different CNT/TiO2 contents during thermal decomposition; Test with a coefficient of variation of less than 2%. T0 - Initial decomposition temperature; T10wt - Temperature corresponding to a mass loss of 10%; Tmax - Temperature of the maximum thermal decomposition rate.

<table>
<thead>
<tr>
<th>Content of nano-particles, %</th>
<th>T0, °C</th>
<th>T10wt, °C</th>
<th>Tmax, °C</th>
<th>Temperature of the maximum thermal decomposition rate, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% CNT/TiO2</td>
<td>460.90</td>
<td>170.19</td>
<td>495.41</td>
<td>40.52</td>
</tr>
<tr>
<td>1 wt% CNT/TiO2</td>
<td>470.56</td>
<td>251.15</td>
<td>481.46</td>
<td>50.38</td>
</tr>
<tr>
<td>3 wt% CNT/TiO2</td>
<td>460.76</td>
<td>212.26</td>
<td>476.08</td>
<td>42.81</td>
</tr>
<tr>
<td>5 wt% CNT/TiO2</td>
<td>466.37</td>
<td>153.08</td>
<td>497.62</td>
<td>37.61</td>
</tr>
<tr>
<td>7 wt% CNT/TiO2</td>
<td>462.38</td>
<td>159.21</td>
<td>488.89</td>
<td>42.62</td>
</tr>
</tbody>
</table>

The first section is the stage of small weight loss from room temperature to 400 °C. As shown in Figure 4, the TG curves of each sample decline sharply at the beginning and then level out as the temperature rises to 300 °C. As can be seen in Table 3, the T10wt of PSA composites with 1 wt% and 3 wt% CNT/TiO2 is higher than that of pure PSA, suggesting that it is hard for PSA composites with low CNT/TiO2 contents to decompose at this stage; and its thermal stability is significantly higher than that of PSA. However, as the particle content increased to 5 wt% and 7 wt%, the T10wt of the composites begins to decrease to even lower than that of PSA. According to the bond energy analysis [7],
the C-N section of the amide of PSA decomposes at 500 ~ 600 °C [8, 9], and the mass loss of PSA at this stage is ascribed to the production of gases such as SO₂, NH₃ and CO₂. Moreover, as shown in the data presented in Table 3, in addition to the 3 wt% sample, CNT/TiO₂ improves the T₀ of PSA composites, then the thermal stability of PSA composites can be improved.

As shown in Figure 4, the mass loss of samples begins to accelerate and each TG curve shows a rapid decomposition at about 500 °C. Corresponding to the rapid decomposition, there is a peak in DTG curve (Figure 5), and the T_{max} (presented in Table 3) can be determined according to the value of the maximum peak [10].

The third section is the stable phase of carbon formation (600 ~ 700 °C). As depicted in Figure 4, the residual mass at the terminal temperature of PSA composites with 1 wt% and 5 wt% CNT/TiO₂ tends to a steady state, while the mass loss of other specimens is decreased. As can be seen in Table 3, the residual mass of the 5 wt% sample at 700 °C is higher than the others.

Therefore it is concluded that the addition of CNT/TiO₂ with low contents can improve the thermal stability of PSA composites significantly.

**Electrical conductivity**

Table 4. Surface resistivity of PSA composite membranes with different CNT/TiO₂ contents.

<table>
<thead>
<tr>
<th>Content of nano-particles, %</th>
<th>Average of surface resistivity, Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% CNT/TiO₂</td>
<td>3.10 x 10¹²</td>
</tr>
<tr>
<td>1 wt% CNT/TiO₂</td>
<td>8.38 x 10¹¹</td>
</tr>
<tr>
<td>3 wt% CNT/TiO₂</td>
<td>1.84 x 10¹⁰</td>
</tr>
<tr>
<td>5 wt% CNT/TiO₂</td>
<td>3.78 x 10⁹</td>
</tr>
<tr>
<td>7 wt% CNT/TiO₂</td>
<td>5.98 x 10⁸</td>
</tr>
</tbody>
</table>

The content of conductive particles in a composite is one of the most important parameters to influence its electrical conductivity. Hence the electrical conductivity of PSA composite membranes can be improved gradually with an increase in CNT/TiO₂ content. Furthermore CNT has unique electrical conductivity derived from its one dimensional character and the peculiar electronic structure of graphite [11]. What is more, there are large numbers of freely movable electrons in the nanotubes. Therefore the electrical conductivity of PSA composites can be improved significantly by the blending of CNT/TiO₂.

The sketch [12] presented in Figure 6 is employed to simulate the formation of the electrical conductive network in PSA composite membranes. As can be seen in Figure 6a, 1 wt% CNT/TiO₂ can be distributed homogeneously in the PSA matrix; therefore, it is hard for the particle-polymer matrix to form a completely conductive network. With the CNT/TiO₂ content increased to 5 wt%, the distance between particles is decreased and a locally conductive network in the matrix can be basically established. Then the surface resistivity of composite membranes declines sharply, as a result of which the electrical conductivity could be improved significantly. When the CNT/TiO₂ content is increased to 7 wt%, more and more conductive particles connect directly and a closer network is established in the matrix.

As can be seen in Table 4, the electrical conductivity (reciprocal of the surface resistivity) of PSA composite membranes can be obviously improved and show an upward trend with an increase in CNT/TiO₂ content.

**Ultraviolet resistance**

As shown in Figure 7, UV transmittance in the range of 390 ~ 400 nm of PSA/CNT/TiO₂ composites almost reaches zero, while that of pure PSA is high. It is suggested that the blending of CNT/TiO₂ can improve PSA/CNT/TiO₂ composites’ scattering and absorption of ultraviolet, as a result of which the ultraviolet resistance of PSA composites can be obviously improved because PSA composites blended with CNT/TiO₂ show a gray-black colour, improving the composite’s shielding of ultraviolet. In addition, TiO₂ has excellent scattering and absorption properties at optical and ultraviolet wavelengths.

### Conclusions

PSA composite fibres and membranes with different CNT/TiO₂ contents were prepared. Experimental results of the performances of the PSA composites can be summarised as follows.

1) CNT/TiO₂ at a low content (1 wt% or 3 wt%) can be distributed homogeneously in the PSA polymer matrix; however, it is hard for CNT/TiO₂ at a high content (5 wt% or 7 wt%) to disperse homogeneously in the blending system.

2) There is less significant change to the molecular structure and chemical composition of PSA blended with CNT/TiO₂.

3) Crystallisation in the PSA occurred at low CNT/TiO₂ contents because CNT and TiO₂ can act as a nucleation agent.

![Figure 6. Sketch of the formation of an electrical conductive network in the PSA matrix; a) 1 wt%, b) 3 wt%, c) 5 wt%, d) 7 wt% CNT/TiO₂.](image)

![Figure 7. UV transmittance spectrum of PSA composites with different CNT/TiO₂ contents.](image)
4) The breaking tenacity and initial modulus of PSA composite fibres blended with CNT/TiO$_2$ can be improved significantly, while its elongation at break is decreased.

5) The blending of CNT/TiO$_2$ can improve the electrical conductivity of PSA composites and the percolation threshold of the system at about 5 wt%.

6) The blending of CNT/TiO$_2$ can improve the ultraviolet resistance of PSA/CNT/TiO$_2$ composites significantly, with the UV transmittance almost reaching zero.

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References


