

Preparation and Characterisation of PSA/CNT/TiO₂ Nano Composites and Fibres

Abstract

Polysulfonamide/carbon nanotubes/titanium dioxide (PSA/CNT/TiO₂) nano composite spinning solutions with different CNT/TiO₂ contents were prepared using the physical blending method. The corresponding fibers were extruded through a set of wet spinning unit, and composite membranes were prepared by the spin-coating method. The performances of the PSA/CNT/TiO₂ nano fibers and membranes were investigated by means of SEM, FTIR and XRD etc. The influence of CNT and TiO₂ on the mechanical properties, thermal stability, electrical conductivity and ultraviolet resistance of PSA nano composites was also analysed in this study. The experimental results showed that low contents of CNT/TiO₂ can be distributed homogeneously in the PSA matrix; the molecular structure and chemical composition of PSA did not changed obviously; crystallisation in PSA occurred at low CNT/TiO₂ contents because it can act as a nucleation agent; the electrical conductivity and ultraviolet resistance of PSA nano composites can be improved significantly by blending CNT/TiO₂ into the PSA matrix.

Key words: nano composites, electrical conductivity, ultraviolet resistance.

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]; TiO₂ has outstanding scattering and absorption of ultraviolet. It is feasible to blend CNT/TiO₂ into PSA polymer matrix to enhance the electrical conductivity and ultraviolet resistance of PSA/CNT/TiO₂ composites.

Experimental

Materials

PSA 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, in short CNT) were blended as functional particles for improving the electrical conductivity of PSA. The CNT, with a diameter of 10 ~ 20 nm and length of 1 ~ 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 TiO₂)

with a diameter of 30 ~ 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 dissolvent in this study. The above materials were supplied by Shanghai Tanlon Fibre Co. LTD.

Preparation of PSA/CNT/TiO₂ composites

An equivalent amount of CNT and TiO₂ was dispersed in DMAC using ultrasonic vibration for 30 minutes, then added to the PSA solution. Different nano-particle contents of PSA/CNT/TiO₂ 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/TiO₂ 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/TiO₂ in the polymer matrix; the machine was operated at 10 ~ 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 (λ = 0.154 nm) at a voltage of 40 kV and current of 40 mA. The spectra were obtained at a 2θ angle range of 5 ~ 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/TiO₂ contents.

Content of nano-particles, %	PSA/g	CNT/g	TiO ₂ /g	DMAC/ml
0 wt% CNT/TiO ₂	100	0	0	0
1 wt% CNT/TiO ₂	100	0.0606	0.0606	1
3 wt% CNT/TiO ₂	100	0.1856	0.1856	3
5 wt% CNT/TiO ₂	100	0.3158	0.3158	5
7 wt% CNT/TiO ₂	100	0.4516	0.4516	7

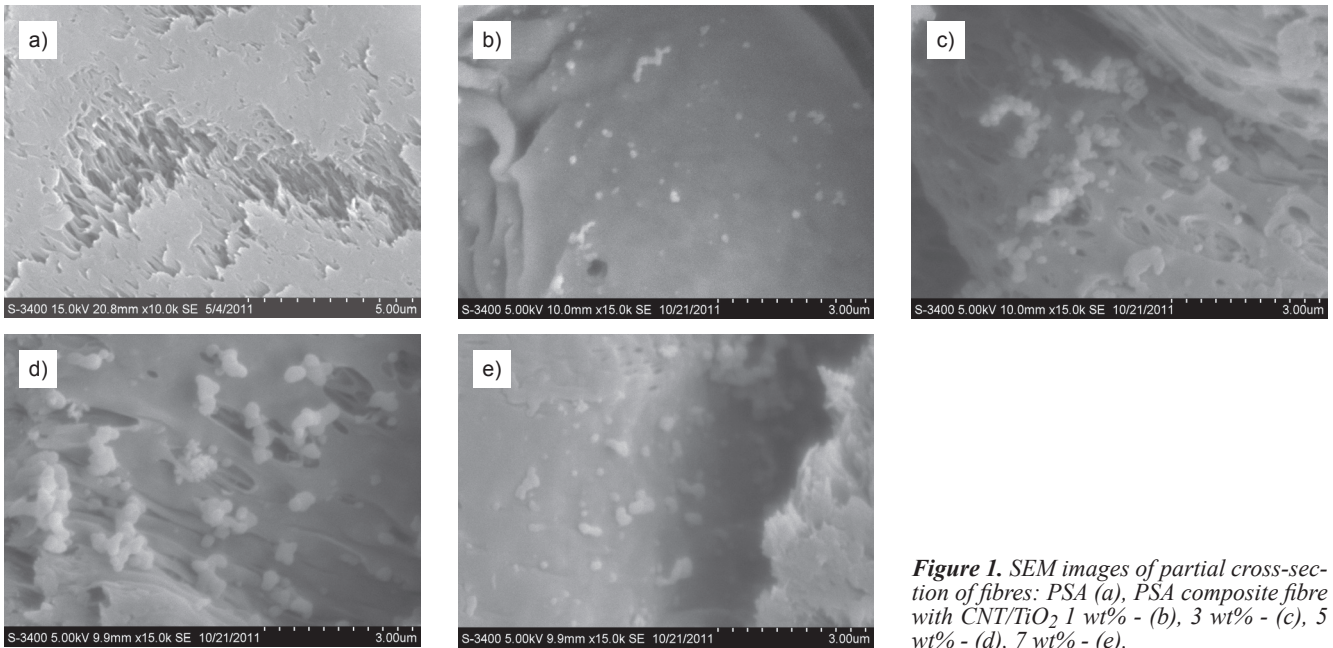


Figure 1. SEM images of partial cross-section of fibres: PSA (a), PSA composite fibre with CNT/TiO₂ 1 wt% - (b), 3 wt% - (c), 5 wt% - (d), 7 wt% - (e).

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 10² ~ 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.

Fourier transform infrared spectral analysis

As shown in **Figure 2**, the characteristic peaks of PSA composites at about 3300cm⁻¹ shift to the short-wave range compared with pure PSA. Besides this, the shape of the absorption peak at 3301.25cm⁻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

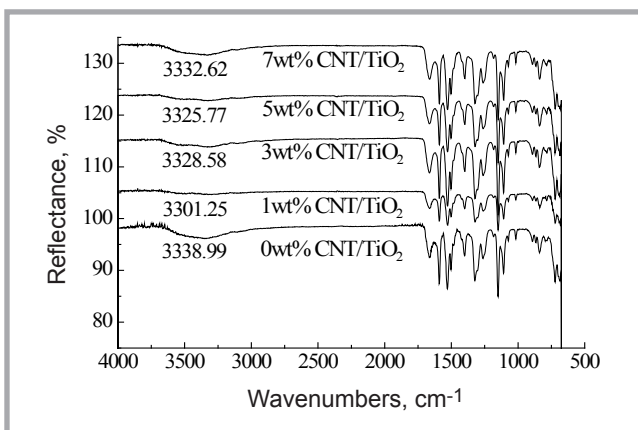


Figure 2. FTIR images of PSA/CNT/TiO₂ composite fibres with different CNT/TiO₂ contents.

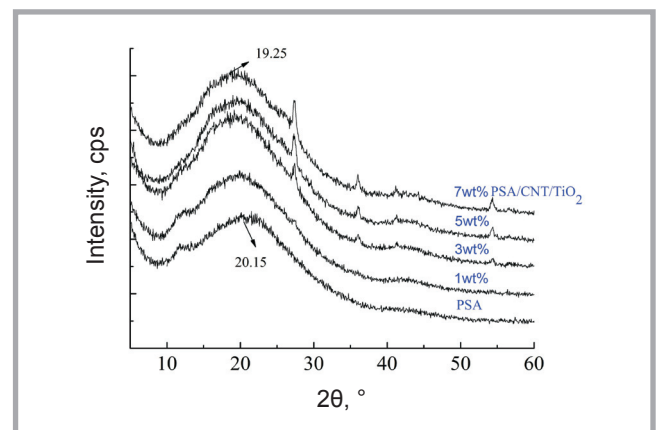


Figure 3. XRD images of PSA/CNT/TiO₂ composite fibres with different CNT/TiO₂ contents.

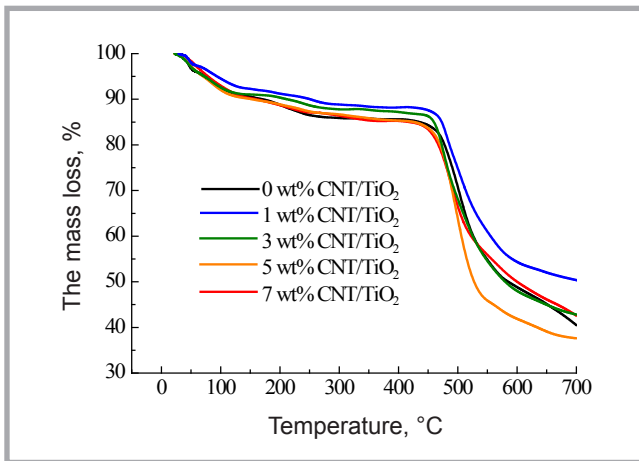


Figure 4. TG curves of PSA/CNT/TiO₂ composites with different CNT/TiO₂ contents.

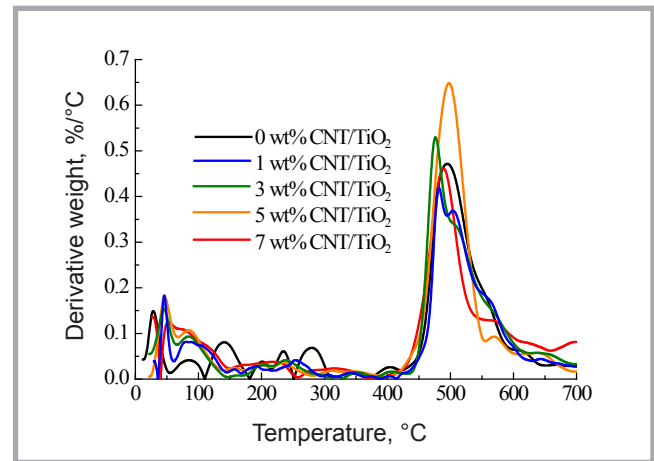


Figure 5. DTG curves of PSA/CNT/TiO₂ composites with different CNT/TiO₂ contents.

to 7 wt%, then the nano-effect can be reduced correspondingly.

X-ray diffraction analysis

Figure 3 (see page 25) illustrates that all the samples have diffraction peaks at about 20° and there is a shift excursion of PSA composites compared with pure PSA. In addition, the sharpness of the diffraction peaks at about 20° is enhanced gradually with the increasing CNT/TiO₂ contents, indicating that crystallisation in the PSA/CNT/TiO₂ composites is improved because the CNT/TiO₂ can act as a nucleation agent. Moreover **Figure 3** shows that the PSA composite fibres have diffraction peaks of rutile titanium dioxide at 27.45°, 36.15°, 41.35° and 54.40°.

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.

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 macromolecular chains tend to be more closely connected.

Thermal stability

Figures 4 and **5** present the TG curves and DTG curves of PSA/CNT/TiO₂ composites, respectively, some key parameters of which are summarised in **Table 3**. In **Figure 4**, the thermal decomposition of the composites can be divided into three sections.

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 T_{10wt} 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 T_{10wt} of the composites begins to decrease to even lower than that of PSA.

The second section is the stage of thermal decomposition (400 ~ 600 °C). According to the bond energy analysis [7],

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

Content of nano-particles, %	Tenacity, cN/dtex	Elongation at break, %	Initial modulus, cN/dtex
0 wt% CNT/TiO ₂	0.411	29.70	0.098
1 wt% CNT/TiO ₂	0.498	22.90	0.185
3 wt% CNT/TiO ₂	0.411	16.70	0.137
5 wt% CNT/TiO ₂	0.324	9.40	0.115
7 wt% CNT/TiO ₂	0.290	8.50	0.097

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; T_{10wt} - Temperature corresponding to a mass loss of 10%; T_{max} - Temperature of the maximum thermal decomposition rate.

Content of nano-particles, %	T ₀ , °C	T _{10wt} , °C	T _{max} , °C	The residual mass at 700 °C, %
0 wt% CNT/TiO ₂	460.90	170.19	495.41	40.52
1 wt% CNT/TiO ₂	470.56	251.15	481.46	50.38
3 wt% CNT/TiO ₂	460.76	212.26	476.08	42.81
5 wt% CNT/TiO ₂	466.37	153.08	497.62	37.61
7 wt% CNT/TiO ₂	462.38	159.21	488.89	42.62

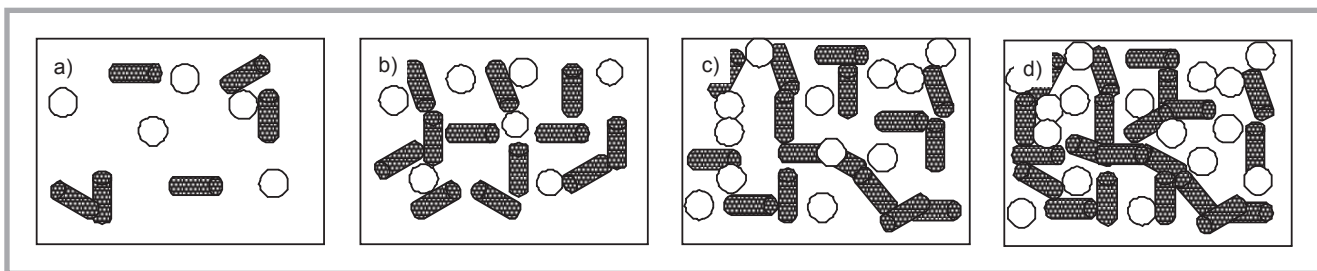


Figure 6. Sketch of the formation of an electrical conductive network in the PSA matrix; a) 1 wt%, b) 3 wt%, c) 5 wt%, d) 7 wt% CNT/TiO₂.

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.

Content of nano-particles, %	Average of surface resistivity, Ω
0 wt% CNT/TiO ₂	3.10 × 10 ¹²
1 wt% CNT/TiO ₂	8.38 × 10 ¹¹
3 wt% CNT/TiO ₂	1.84 × 10 ¹⁰
5 wt% CNT/TiO ₂	3.78 × 10 ⁶
7 wt% CNT/TiO ₂	5.98 × 10 ⁵

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 increased 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 6.a**, 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.

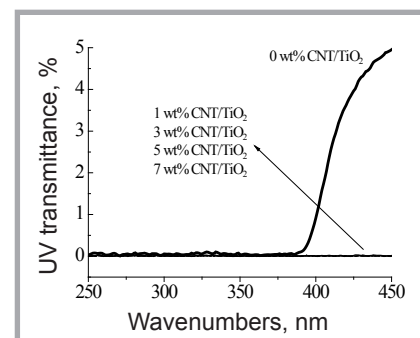


Figure 7. UV transmittance spectrum of PSA composites with different CNT/TiO₂ contents.

- 4) The breaking tenacity and initial modulus of PSA composite fibres blended with CNT/TiO₂ can be improved significantly, while its elongation at break is decreased.
- 5) The blending of CNT/TiO₂ can improve the electrical conductivity of PSA composites and the percolation threshold of the system at about 5 wt%.
- 6) The blending of CNT/TiO₂ can improve the ultraviolet resistance of PSA/CNT/TiO₂ composites significantly, with the UV transmittance almost reaching zero.

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