ORIGINAL ARTICLE

Sulfonation of chlorinated polypropylene and its influence on the microstructure and the electric properties of polypropylene/chlorinated polypropylene/polyaniline composites

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Sulfonated CPP (CPP-SO₃H) was prepared by modifying chlorinated polypropylene (CPP). The results of Fourier transform infrared spectroscopy (FTIR) illustrate that the sulfonic acid group (–SO₃H) was successfully grafted onto CPP. Polypropylene (PP)/CPP-SO₃H/polyaniline (PANI) and PP/CPP/PANI composites were prepared, and the microstructures and electric properties of the corresponding composites were carefully investigated by scanning electron microscopy (SEM), FTIR, ultraviolet (UV)-vis and wide-angle X-ray diffraction (WAXD). Compared with that of the PP/CPP/PANI composite, the volume resistivity of the PP/CPP-SO₃H/PANI composites is lower. The UV-vis results show that PANI can be doped with CPP-SO₃H and that the interactional strength between PANI and CPP-SO₃H increases because of the introduction of –SO₃H. The results of WAXD show that CPP-SO₃H is more easily inserted into the interspaces of PANI-dodecylbenzene sulfonic acid and makes the layer distance increase compared with that of CPP. The addition of CPP-SO₃H can improve the crystallinity of the composites. The results of SEM show that the introduction of –SO₃H on CPP is favorable for dispersion of PANI in the PP/CPP-SO₃H/PANI composites, and that it results in an increase in the area of the conducting components, an improvement in conductive properties and the compatibility of the PP/CPP-SO₃H/PANI composites. The above results indicate that CPP-SO₃H can act as PANI's doping agent and facilitate compatibility in PP/CPP-SO₃H/PANI composites.

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INTRODUCTION

Conductive polymers are expected to yield attractive combinations of properties and are gaining increasing attention from researchers worldwide. For many years, researchers have been using these polymers to produce electronic materials,^{1–3} particularly antistatic materials, sensor materials^{4–6} and anticorrosive coatings.^{7–9} Among conductive polymers, polyaniline (PANI) has the best potential to become economically competitive because of its inexpensive materials, ease of synthesis, environmental stability¹⁰ and high electrical conductivity, which can be reversibly controlled by a change in the oxidation state and protonation of the imine nitrogen groups.¹¹

Although PANI has many merits, it is difficult to process using conventional polymer-based methods because of its strong intermolecular and intramolecular interactions.¹² Many new protonating agents, such as sulfonic acids, phosphoric acid esters^{12,13} and phosphoric acids,¹⁴ have been introduced in recent years to improve the processability of PANI. Cao *et al.*¹⁵ first introduced sulfonic acid as a protonating agent, which made it possible to process PANI in a

solvent. Another method developed to improve the processability of PANI is the blending of PANI with thermoplastic polymers due to PANI's poor mechanical properties.^{14,16–18} A unique advantage of this method lies in the combination of the electrical properties of PANI and mechanical properties of thermoplastic polymers.

In previous studies,^{19,20} we have investigated the possibility of melt processing polypropylene (PP)/chlorinated polypropylene (CPP)/PANI composites and have shown that CPP has a prominent role in determining the composite's electrical properties. We also investigated the effects of CPP on the formation of the intermolecular and intramolecular hydrogen bonds in PP/CPP/PANI composites through Fourier transform infrared spectroscopy (FTIR). The obtained results show that the introduction of CPP weakens the intermolecular and intramolecular H bond of PANI-dodecylbenzene sulfonic acid (DBSA), which is substituted by the intermolecular H-bond interaction between CPP and PANI-DBSA, and promotes the dispersion of PANI-DBSA and a decrease in the volume resistivity of the composites.

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The intermolecular H-bond interaction between CPP and PANI-DBSA through the H-bond N-H...Cl is weak. Therefore, improvement in the dispersion of PANI-DBSA is limited. In this study, the sulfonic acid group -SO₃H was introduced into CPP. As sulfonic acid can act as a protonating agent of PANI, the interaction between modified CPP and PANI may be stronger than that between CPP and PANI, and modified CPP may further improve dispersion of PANI in the composite. In this study, the influence of modified CPP on the electrical properties, morphology and microstructure of the composites was carefully analyzed by methods such as FTIR, wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM).

EXPERIMENTAL PROCEDURE

Materials

Polyaniline protonated with hydrochloric acid (HCl) was supplied by Chengdu Organic Chemicals (Chengdu, China); its electrical conductivity was $\sim 15 \text{ cm}^{-1}$.

Polypropylene (PPH-XD-045, melt-flow index=3.5 g per 10 min) was supplied by PetroChina (Lanzhou, China).

Dodecylbenzene sulfonic acid was supplied by Kewei Chemicals (Chengdu, China), and its content was $\sim 96\%$ (wt).

Chlorinated polypropylene was supplied by Sichuan Weiye Chemicals (Chengdu, China). Its chlorine content was $\sim 31\%$ (wt) and appeared yellow. The molecular weight of CPP was not clear. The viscosity of 20% (wt) of CPP in toluene solution was $\sim 700 \text{ mPa}\cdot\text{s}$ at 25 °C.

Sodium bisulfite (NaHSO₃), xylene (mixture), potassium hydroxide (KOH), acetic acid (CH₃COOH), ethanol (CH₃CH₂OH), phenolphthalein, barium chloride anhydrous (BaCl₂) and HCl were analytical reagents supplied by Kelong Chemicals (Chengdu, China).

Preparation of composites

Sulfonation of CPP. Modification of CPP was carried out in a 500-ml three-necked flask equipped with a condenser. In all, 50 g CPP and 125 ml xylene were placed into the flask under stirring for 1 h at 80 °C, and then 90 g of NaHSO₃ solution (33.3% wt)^{21,22} was dropped into the reactor. The reaction was allowed to proceed for 24 h at 100 °C and then cooled to ambient temperature. Overall, 36 g HCl was dropped into the reactor under stirring for 0.5 h. A large amount of distilled water was placed into the flask and allowed to stand for 24 h; the modified CPP was then separated from water. This procedure was repeated several times until there was no precipitation when the BaCl₂ solution (10% wt) was dropped into the separated water. The product was dried in a vacuum at 50 °C. Finally, sulfonated CPP (CPP-SO₃H) was obtained. The following is a schematic diagram of the sulfonation of CPP.

Protonation of PANI with DBSA. Polyaniline protonated with HCl was neutralized with 20% (wt) sodium hydroxide (NaOH) aqueous solution for

48 h and then filtered and washed with deionized water until the pH value of the percolate was 6–8. The obtained polyemeraldine base (PANI_{emer}) was dried under vacuum. Purified and dried PANI_{emer} was blended with DBSA, and the molar ratio of DBSA to PANI_{emer} was 0.5. The blend was stirred for 48 h at ambient temperature, thus producing PANI protonated with DBSA (PANI-DBSA).

Preparation of PP/PANI composites. The composites of PP/PANI with different CPP or CPP-SO₃H contents were prepared on a two-roll mill and then molded into 1-mm plates. Compression molding was carried out under the following conditions: preheated at 180 °C for 5 min at low pressure, compressed for 10 min at 13 MPa at the same temperature and then cooled to ambient temperature at the cooling rate of 30 °C per min in the mold at 13 MPa. Specimens with dimensions of 80×80×1 mm³ were obtained from the 1-mm plates to test their volume resistivity. The blend compositions and their corresponding sample codes are listed in Table 1.

Measurement of volume resistivity

Volume resistivity of the composites was detected using a high-resistance meter (ZC46A) produced by the Shanghai Precision Scientific Instrument (Shanghai, China). The result of each sample is the average of four measurements.

Scanning electron microscope

A JSM 5900 LV scanning electron microscope (SEM; JEOL, Tokyo, Japan) was used to observe the morphology of the PP/CPP/PANI composites. The specimens were cut from the 1-mm plates using a very sharp knife and then polished using a special polisher. By not sputtering the SEM samples with a thin conducting layer, it was possible to show the contrast between the electrically conductive and insulating parts of the material.¹⁹ The SEM images of non-sputtered samples are not based on real material contrast, but result from a contrast in the electrical conductivity between the electrically conductive fillers and insulating matrix.²³

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction measurements were carried out using a DX-2500 SSC diffractometer (Fangyuan, Dandong, China) in reflection mode. Cu K α radiation was used at 40 kV and 25 mA. Investigations were performed using two methods. First, in the range of angles 2–5°, the scan step was 0.03° (in 2 θ) with a counting time of 4 s per step. Second, in the range of angles 5–45°, the scan step was 0.06° (in 2 θ), with a counting time of 2 s per step.

To determine the mass fraction of crystallinity, WAXD curves were deconvoluted into crystalline and amorphous scattering components using the profile-fitting program JADE 6.5 (Materials data, Inc., Livermore, CA, USA). Each peak was modeled using a Gaussian-Cauchy peak shape. The degree of crystallinity was determined as the ratio of the areas of all crystalline peaks to that of total scattering. WAXD patterns were also used to evaluate the mean sizes of the crystallites. The crystallite size was estimated for planes of PP by using the Scherrer equation:

$$D = K\lambda / (\beta \cos \theta)$$

where D is the crystallite size along the direction perpendicular to the plane, β the full-width at half-maximum, the wavelength $\lambda=0.154 \text{ nm}$ and θ the Bragg angle (half of the scattering angle).¹⁴

Table 1 Composition of PP/CPP/PANI and PP/CPP-SO₃H/PANI composites (in wt)

Sample code	PP%	PANI _{emer} %	DBSA%	CPP%	CPP-SO ₃ H%	Ratio $\frac{\text{PP}}{\text{PANI-DBSA}}$
PP/CPP/PANI 0	83.70	4.10	7.79	4.41	0	7.04
PP/CPP-SO ₃ H /PANI 1	87.22	4.10	7.79	0	0.88	7.34
PP/CPP-SO ₃ H /PANI 2	86.34	4.10	7.79	0	1.76	7.26
PP/CPP-SO ₃ H /PANI 3	85.46	4.10	7.79	0	2.64	7.19
PP/CPP-SO ₃ H /PANI 4	83.70	4.10	7.79	0	4.41	7.04
PP/CPP-SO ₃ H /PANI 5	82.60	4.10	7.79	0	5.51	6.95

Abbreviations: CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene.

FTIR measurement

Specimens used for FTIR measurement were prepared by two methods. Specimens of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites for FTIR measurement were molded into very thin films. Compression molding was carried out under the following conditions: samples were preheated at 180 °C for 5 min at low pressure, compressed for 10 min at 15 MPa at the same temperature and then cooled to ambient temperature at a cooling rate of 30 °C per min in the mold at 15 MPa. CPP or CPP-SO₃H was dissolved by xylene, and the solutions were then cast into very thin films. Finally, the films were dried in a vacuum at 50 °C. FTIR analysis of specimens was conducted with a Nicolet 170× FTIR spectrometer (Nicolet, Barrington, WI, USA).

Sulfonating degree measurement

Neutralization titration was adopted to measure the degree of sulfonation of the specimens. Approximately 0.5 g of each specimen was weighed using an analytical balance, and 100 ml of xylene was placed into a conical flask with a condenser under stirring for 1.5 h at 140 °C. When the flask was cooled to 50 °C, a superfluous KOH-CH₃CH₂OH titrating solution was placed into the flask under stirring. The reaction was allowed to proceed for 0.5 h at 50 °C and was then titrated with a CH₃COOH-xylene solution, and with a solution of phenolphthalein-CH₃CH₂OH that was used as an indicator. The degree of sulfonation is the ratio of the number of -SO₃H groups in CPP-SO₃H to the number of chlorine atoms in CPP and is calculated by the following formula.

$$S = 2 \times 35.5 \times \frac{(C_1 V_1 - C_2 V_2) - N_0}{0.31 \times 1000}$$

C_1 and C_2 are the concentrations of the titrating solution of KOH and CH₃COOH, respectively (mol·l⁻¹). V_1 and V_2 are the volumes of the titrating solutions of KOH and CH₃COOH, respectively (ml), which were placed into the flask. N_0 is the number of KOH molecules (mol) consumed by CPP.

UV-vis measurement

PP/CPP/PANI and PP/CPP-SO₃H/PANI composite specimens used for ultra-violet (UV)-vis measurement were molded into very thin films. Compression molding was carried out under the following conditions: specimens were preheated at 180 °C for 5 min at low pressure, compressed for 10 min at 15 MPa at the same temperature and then cooled to ambient temperature at a cooling rate 30 °C per min in the mold at 15 MPa. The UV-vis analysis of specimens was conducted using a Hitachi U-3010 spectrometer (Hitachi, Tokyo, Japan).

RESULTS AND DISCUSSION

Characterization of the modified CPP

Figure 1 shows the FTIR spectra of CPP and modified CPP (the sulfonating degree is 1.53%). In spectrum (a), the band at 2957 cm⁻¹ is attributed to C-H stretching, and the band at 738 cm⁻¹ is attributed to C-Cl stretching. Compared with spectrum (a), spectrum (b) shows a new strong absorption band at ~1150 cm⁻¹, which is attributed to the stretching band of -SO₃H.²⁴ Thus, it can be seen that the -SO₃H group has been successfully grafted onto CPP and the method of sulfonation adopted in this study is feasible.

The volume resistivity of the PP/CPP-SO₃H/PANI and PP/CPP/PANI composites

Figure 2 shows the volume resistivity of the PP/CPP-SO₃H/PANI and PP/CPP/PANI composites. In the PP/CPP-SO₃H/PANI composites, the degree of sulfonation of CPP-SO₃H is 1.53%. Volume resistivity first decreases with increasing CPP-SO₃H content and reaches a minimum volume resistivity when the CPP-SO₃H content is lower than 4.41%; volume resistivity then increases with a further increase in the CPP-SO₃H content.

In Figure 2, the sample without added CPP-SO₃H is marked as PP/CPP/PANI 0, and its CPP content is 4.41%. The content of PANI is the same in the two kinds of composites. However, compared with the

Figure 1 FTIR spectra of CPP and modified CPP. CPP, chlorinated polypropylene; FTIR, Fourier transform infrared spectroscopy.

Figure 2 Relationship between the area of the conducting regions and the volume resistivity change with CPP-SO₃H content. CPP, chlorinated polypropylene.

PP/CPP/PANI 0 composite, the volume resistivity of the PP/CPP-SO₃H/PANI composites is lower, and that of the PP/CPP-SO₃H/PANI 4 composite decreases by four orders of magnitudes, which suggests that the introduction of -SO₃H into CPP can effectively reduce the volume resistivity of the composite.

FTIR spectra of the PP/CPP-SO₃H/PANI and PP/CPP/PANI composites

Figure 3a shows the FTIR spectra of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites. Compared with the spectrum of the PP/CPP/PANI composite, there are several altered bands in the spectrum of the PP/CPP-SO₃H/PANI composites, such as the N-H stretching region (3320–3600 cm⁻¹) and the region between 1110 and 1140 cm⁻¹. The variation of these bands indicates that the introduction of -SO₃H into CPP influences the intermolecular or intramolecular interactions of the PP/CPP/PANI composite, which will be discussed in detail according to FTIR analysis in the following sections.

The region between 3320 and 3600 cm⁻¹ is attributed to PANI's N-H stretching region,²⁵ and no band is found in this region of the FTIR spectra of PP or CPP. As the PANI_{emer} content is only 4.10% (w/w) in the composites, these bands are not particularly distinct in Figure 3a. The amplified bands of this region are presented in Figure 3b.

As shown in Figure 3b, there are at least two distinct bands. One band, at ~3345 cm⁻¹, is attributed to the hydrogen-bonded

Figure 3 FTIR spectra of the (a) PP/CPP/PANI and (b) PP/CPP-SO₃H/PANI composites in two wave number ranges. CPP, chlorinated polypropylene; FTIR, Fourier transform infrared spectroscopy; PANI, polyaniline; PP, polypropylene.

Table 2 Curve-fitting results for the N-H stretching region

Sample code	H-bonded N-H N-H...O			H-bonded N-H N-H...N N-H...Cl			
	$\nu 1\text{cm}^{-1}$	$w_{1/2}1\text{cm}^{-1}$	$S1$	$\nu 2\text{cm}^{-1}$	$\nu 3\text{cm}^{-1}$	$w_{1/2}3\text{cm}^{-1}$	$S3$
PP/CPP/PANI 0	3344.8	17.8	0.021	3368.7	3413.9	30.1	0.067
PP/CPP-SO ₃ H/PANI 1	3343.3	56.9	0.441	3371	3417.9	69.0	0.76
PP/CPP-SO ₃ H/PANI 2	3347.1	40.7	0.592	3373.1	3417.7	73.9	1.751
PP/CPP-SO ₃ H/PANI 3	3346.8	37.9	0.212	3370.2	3416.9	73.5	0.731
PP/CPP-SO ₃ H/PANI 4	3347.0	16.4	0.024	3366.5	3430.5	107.3	0.594
PP/CPP-SO ₃ H/PANI 5	3351.5	26.9	0.185	3379.6	3422.3	90.7	2.324

Abbreviations: CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene.

N-H...O;²⁵ another band, at $\sim 3420\text{cm}^{-1}$, is attributed to the hydrogen-bonded N-H...Cl and N-H...N.²⁰ With the aid of computer analysis, the curve-fitting spectra of the N-H stretching region were produced for the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites. An iterative least-squares computer program was used to obtain the best fit of the spectra of the N-H stretching region by varying the wave number (ν), width at half-height ($w_{1/2}$) and area (S) of several bands. There were two or three Gaussian bands in the N-H stretching region to be confirmed by the curve-fitting procedure. Typical examples are displayed in the inset of Figure 3b.

Table 2 lists the curve-fitting results for the spectra of the N-H stretching region. The area ($S2$) of the band of $\nu 2$ is sufficiently small to be ignored compared with the areas of the bands of $\nu 1$ and $\nu 3$. The first band is attributed to the hydrogen-bonded N-H...O; the third band is attributed to the hydrogen-bonded N-H...Cl and N-H...N. In the PP/CPP/PANI composite, the hydrogen-bonded N-H...O is the intermolecular and intramolecular H-bonded interaction of PANI-DBSA. However, in the PP/CPP-SO₃H/PANI composites, the oxygen atom of the H-bonded N-H...O may be rooted in PANI-DBSA and CPP-SO₃H, and it is impossible to separate the oxygen atom rooted in PANI-DBSA from that rooted in CPP-SO₃H. Therefore, it is very difficult to quantitatively analyze the H bond. Nevertheless, the data listed in Table 2 show the effects of CPP-SO₃H on the H bond in the composites.

Table 2 shows that compared with that of the PP/CPP/PANI 0 composite, the wave number of the H-bonded N-H...N and Cl of the PP/CPP-SO₃H/PANI composites increases significantly; for example, the increment in PP/CPP-SO₃H/PANI 4 is 17 wave numbers. However, the H-bonded N-H...O band slightly shifts, as the

sulfonating degree of CPP-SO₃H was seen to be only 1.53%. These results show that the average strength of the H-bonded N-H...N and Cl decreases and the H-bonded band shifts to a higher wave number.²⁶ The reason for this is that the H-bonded N-H...N and Cl are partially substituted by the H-bonded N-H...O because of the introduction of -SO₃H into CPP. From the shift of the H-bonded band, the interaction between CPP and PANI-DBSA is strengthened by the introduction of -SO₃H into CPP. Hence, compared with the properties afforded by the PP/CPP/PANI 0 composite, the compatibility between PP and PANI-DBSA may be increased, the dispersion of PANI may be more homogeneous in the PP/CPP-SO₃H/PANI 4 composite and the PP/CPP-SO₃H/PANI 4 composite has a lower volume resistivity.

UV-vis analysis of the PP/CPP-SO₃H/PANI and PP/CPP/PANI composites

Figure 4 shows the UV-vis spectra of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites. The UV-vis spectra of the PP/CPP-SO₃H/PANI composites are distinctly different from the PP/CPP/PANI composite spectrum, particularly at $\sim 880\text{nm}$. The band at $\sim 880\text{nm}$ is ascribed to the π -polaron transition of protonated PANI, which indicates the protonation and the degree of electron delocalization in PANI.^{27,28} The peaks were selected from this region, and the results are listed in Table 3.

From the data listed in Table 3, there is only one peak at 875 nm in the PP/CPP/PANI 0 and PP/CPP-SO₃H/PANI 1 composites. In the PP/CPP-SO₃H/PANI 1 composites, the CPP-SO₃H content is only 0.88%; therefore, the effect of CPP-SO₃H on the π -polaron transition of protonated PANI is small. However, in other PP/CPP-SO₃H/PANI

Figure 4 UV-vis spectra of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites. CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; UV, ultraviolet.

Table 3 Peak-searching results of UV-vis spectra

Sample code	Peak 1 (nm)	Peak 2 (nm)
PP/CPP/PANI 0	875	
PP/CPP-SO ₃ H/PANI 1	875	
PP/CPP-SO ₃ H/PANI 2	876	901
PP/CPP-SO ₃ H/PANI 3	875	885
PP/CPP-SO ₃ H/PANI 4	875	899
PP/CPP-SO ₃ H/PANI 5	876	901

Abbreviations: CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; UV, ultraviolet.

composites, there are two peaks: one at ~ 875 nm and another at ~ 895 nm. This suggests that due to the introduction of -SO₃H into CPP, the degree of electron delocalization and the electrical conductivity of PANI-DBSA are increased and CPP-SO₃H facilitates the role of protonation. Therefore, the introduction of -SO₃H can decrease the volume resistivity of the PP/CPP-SO₃H/PANI composites.

Morphology of the composites

Figure 5 shows SEM micrographs of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites at 200 times the normal magnification. The white regions are insulating (that is, no PANI), and the black regions are conducting. The gray regions are transitions between insulating and conducting areas. The PANI content in the gray parts is lower than that in the black parts, and the darker area indicates a higher PANI content.¹⁹ In the SEM micrograph of PP/CPP/PANI 0, the continuity of the conducting parts is bad and prone to be interrupted by insulating parts. This makes the material's ability to conduct electrons weaker. If the gray-scale intensity of the whitest region is defined to be 255 and that of the blackest region is defined to be 0 in the SEM image,¹⁹ Figure 5 can be digitally analyzed. The area of the range of the color intensity can be statistical. Although there are some parts that are gray in the intensity range of 135–255, the ability of these gray parts to conduct electrons is very weak. Hence, for statistical convenience, regions exhibiting a color range intensity of 0–135 may be regarded as conducting.

Figure 2 shows that both areas of the conducting regions and volume resistivity vary with the CPP-SO₃H content. The trendline representing the area of the conducting regions versus the CPP-SO₃H content is contrary to that of the change in volume resistivity with CPP-SO₃H content. The area of the conducting regions first increases

with increasing CPP-SO₃H content and reaches a maximum area when the CPP-SO₃H content is lower than 4.41%; the area then decreases with a further increase in the CPP-SO₃H content. In other words, all of the composites exhibit a maximum area. This result may suggest that volume resistivity is greatly influenced by the area of the conducting regions (that is, the greater the area of the conducting regions, the lower the volume resistivity). Compared with PP/CPP-SO₃H/PANI 4, the conducting area of PP/CPP-SO₃H/PANI 5 decreases significantly, and the dispersion of PANI-DBSA becomes worse; thus, its volume resistivity increases appreciably.

Figure 2 indicates that areas of the conducting regions of the PP/CPP-SO₃H/PANI composites are much greater than the area of the PP/CPP/PANI 0 composite, and the volume resistivity of the PP/CPP-SO₃H/PANI composites is much lower than that of the PP/CPP/PANI 0 composite. These results suggest that the introduction of -SO₃H into CPP can increase the area of the conducting regions of the composites, improve compatibility between PP and PANI-DBSA and decrease volume resistivity of the composites.

Wide-angle X-ray diffraction study

The lamellar-like structure of PANI. Figure 6a shows the WAXD patterns of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites using the first method over the range of 1.5–5°. The peak at $\sim 3^\circ$ is attributed to the lamellar-like structure of PANI-DBSA;^{18,29,30} the lamellar-like structure is also observed in the TEM micrograph.¹⁸ In PP/CPP/PANI 0, there is only one peak at $\sim 3^\circ$. However, in the PP/CPP-SO₃H/PANI composite, there are two peaks: one at $\sim 3^\circ$ and another at $\sim 2.5^\circ$. These indicate that because of the introduction of -SO₃H into CPP, CPP-SO₃H is more easily inserted into the interspaces of PANI-DBSA, the layer distance of PANI-DBSA increases and the aggregating domains of PANI-DBSA become loose. The increasing layer distance is beneficial to the improvement in the dispersion of PANI-DBSA in the PP/CPP-SO₃H/PANI composites and decreases the volume resistivity of the composites. These effects agree with the results of the SEM measurement.

To quantify the influence of the introduction of -SO₃H into the lamellar-like structure of PANI-DBSA in the PP/CPP/PANI composites, the WAXD curves in Figure 6a were fitted using the profile-fitting program JADE 6.5. The profile-fitting results of the WAXD curves are listed in Table 4.

Compared with the parameters of the PP/CPP/PANI 0 composite's peak, the first peak of the PP/CPP-SO₃H/PANI composites shifts to a lower angle, and its layer distance increases. For example, the first peak of PP/CPP-SO₃H/PANI 4 lies at 2.942° , and its layer distance is 30.01 Å. Moreover, the second peak of the PP/CPP-SO₃H/PANI composites lies at $\sim 2.47^\circ$, and its layer distance is ~ 35.7 Å. These may explain why the volume resistivity of the PP/CPP-SO₃H/PANI composites is lower than that of the PP/CPP/PANI composite.

The crystalline structure. Figure 6b shows the WAXD patterns of the PP/CPP/PANI and PP/CPP-SO₃H/PANI composites obtained using the second method over the range of 5–45°. In Figure 6b, the crystalline peaks at $\sim 14^\circ$, 17° , 18.5° , 21° and 21.8° are attributed to the α crystal, and the crystalline peak at $\sim 16^\circ$ is attributed to the β -crystal.³¹

To quantify the influence of the introduction of -SO₃H into the crystal structure of PP in the composites, the WAXD curves in Figure 6b were fitted using the profile-fitting program JADE 6.5. The fitting range was chosen to be 9–26° because almost all of the crystalline peaks fall within this range. Using Scherrer's law and the mass fraction crystal formula (for example, % crystallinity

Figure 5 SEM micrographs of PP/CPP/PANI and PP/CPP-SO₃H/PANI composites. CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; SEM, scanning electron microscopy.

Figure 6 WAXD patterns of (0) PP/CPP/PANI 0, (1) PP/CPP-SO₃H/PANI 1, (2) PP/CPP-SO₃H/PANI 2, (3) PP/CPP-SO₃H/PANI 3, (4) PP/CPP-SO₃H/PANI 4 and (5) PP/CPP-SO₃H/PANI 5 in two angle ranges. CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; WAXD, wide-angle X-ray diffraction.

Table 4 Profile fitting results for WAXD curves of PP/CPP/PANI and PP/CPP-SO₃H/PANI composites in the range of 1.5–5°

Sample code	Peak 1				Peak 2			
	$2\theta_1(^{\circ})$	$D(\text{\AA})$	$FWHM$	$XS(\text{\AA})$	$2\theta_2(^{\circ})$	$d(\text{\AA})$	$FWHM$	$XS(\text{\AA})$
PP/CPP/PANI 0	3.041	29.03	0.406	202				
PP/CPP-SO ₃ H/PANI 1	3.007	29.36	0.375	220	2.469	35.75	0.372	222
PP/CPP-SO ₃ H/PANI 2	2.993	29.50	0.351	236	2.467	35.79	0.335	248
PP/CPP-SO ₃ H/PANI 3	2.959	29.84	0.451	202	2.477	35.63	0.285	297
PP/CPP-SO ₃ H/PANI 4	2.942	30.01	0.377	219	2.492	35.42	0.300	281
PP/CPP-SO ₃ H/PANI 5	2.941	30.01	0.353	235	2.458	35.92	0.264	326

Abbreviations: CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; WAXD, wide-angle X-ray diffraction. ^[2]WHM: width at half-height; d : layer distance; XS: size of the lamellar-like structure.

Table 5 Structural parameters for PP/CPP/PANI and PP/CPP-SO₃H/PANI composite by means of WAXD

Sample code	X_C (%)	$d(\text{\AA})$				$XS(\text{\AA})$			
		A_{110}	B_{300}	A_{040}	A_{130}	A_{110}	B_{300}	A_{040}	A_{130}
PP/CPP/PANI 0	31.48	6.29		5.25	4.78	114		155	142
PP/CPP-SO ₃ H/PANI 1	34.97	6.28		5.25	4.78	118		147	133
PP/CPP-SO ₃ H/PANI 2	41.73	6.29	5.53	5.25	4.79	124	177	163	116
PP/CPP-SO ₃ H/PANI 3	47.22	6.29		5.24	4.78	130		153	159
PP/CPP-SO ₃ H/PANI 4	58.46	6.30	5.53	5.25	4.79	113	145	156	130
PP/CPP-SO ₃ H/PANI 5	45.76	6.28		5.24	4.78	126		157	168

Abbreviations: CPP, chlorinated polypropylene; PANI, polyaniline; PP, polypropylene; WAXD, wide-angle X-ray diffraction.

d : interplanar distance; XS: size of crystallite corresponding to appointed peak; A_{110} , A_{040} , and A_{130} : the 110, 040 and 130 crystal face of α -crystal respectively; B_{300} : the 300 crystal face of β -crystal; X_C : crystallinity index.

$=A_c/(A_c+A_n)$, where A_c is the scattering from the sharp peaks of crystalline areas and A_n the scattering from non-crystalline areas), the crystal size corresponding to the peaks and the percentage crystallinity of the composites was calculated. The profile-fitting results of the WAXD curves are listed in Table 5.

In Table 5, the most evident change is that the X_C of the PP/CPP-SO₃H/PANI composites is higher than that of PP/CPP/PANI 0. Analogously, volume resistivity of the PP/CPP-SO₃H/PANI composites is higher than that of PP/CPP/PANI 0. The X_C of the PP/CPP-SO₃H/PANI composites first increases with increasing CPP-SO₃H content and reaches a maximum X_C when the CPP-SO₃H content is lower than 4.41%; it then decreases with a further increase in the CPP-SO₃H content. The variation of X_C with the CPP-SO₃H content is analogous to that of the volume resistivity with the CPP-SO₃H content. In accordance with the abovementioned results, the formation of high crystallinity in a host polymer is favorable for a decrease in volume resistivity. Compared with PP/CPP-SO₃H/PANI 4, the X_C of PP/CPP-SO₃H/PANI 5 decreases significantly; therefore, its volume resistivity increases appreciably.

CONCLUSIONS

Chlorinated polypropylene was modified using sodium bisulfite as a sulfonating agent. The FTIR results show that -SO₃H was successfully grafted onto CPP.

Compared with that of the PP/CPP/PANI composite, the volume resistivity of the PP/CPP-SO₃H/PANI composites clearly decreases. In the PP/CPP-SO₃H/PANI composites, the average strength of the H-bonded N-H·····N and Cl decreases and is partially substituted by the H-bonded N-H·····O, and the interactional strength between PANI and CPP-SO₃H increases due to the introduction of -SO₃H.

The UV-vis results show that due to the introduction of -SO₃H into CPP, the degree of electron delocalization and the electrical conductivity of PANI-DBSA increase, and CPP-SO₃H has the role of protonation agent in the PP/CPP-SO₃H/PANI composites. The analysis of the lamellar-like structure of PANI indicates that, compared with CPP, CPP-SO₃H is more easily inserted into the interspaces of PANI-DBSA, the layer distance of PANI-DBSA increases and the aggregating domains of PANI-DBSA become loose. CPP-SO₃H can improve the crystallinity of the composites compared with CPP. The introduction of -SO₃H into CPP can increase the compatibility of the composites and the area of the conducting regions within the composites, and improve the dispersion of PANI and the conductive properties of the PP/CPP-SO₃H/PANI composites.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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