Preparation and characterization of PA6/titania conductive fibres

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The surface activity of TiO_2 has been modified by using sodium hexametaphosphate to improve its dispersibility in matrix. The modified TiO_2 nanoparticles have been mixed with polyamide 6(PA6) into granulation, and then white conductive fibres are prepared using different weight ratios by melt spinning. The as-spun fibres are characterized by using high insulation resistance meter, scanning electron microscopy, X-ray diffraction and differential scanning calorimeter. The results show that the treated conductive TiO_2 material is well dispersed in the PA6 matrix with good compatibility and that the electrical conductivity of as-spun fibres is excellent. Considering the mechanism of its electrical conductivity, it is concluded that the conductive mechanism is tunnel when the TiO_2 content is less than 5%, the mechanism is composition of both tunnel and ohmic when TiO_2 content is between 10% and 15%, and it is ohmic conductive mechanism if the TiO_2 content is more than 15%.

Keywords: Conductive fibres, Conductive TiO_2, Electrical conductivity, Polyamide, Surface modification

1 Introduction

Conductive fibres have become more and more important in many applications due to their electronic conductivity and corona discharge. Since last few years, many efforts have been carried out to prepare carbon or coated conductive fibres. Nowadays, a great attention is given to the white conductive fibres because they combine the features of both polymers and conductive fillers, such as easy processing and the high conductivity [1-3]. In order to improve conductivity of the fibres, many kinds of inorganic conductive fillers are introduced into the matrix, such as mica powder[4], titanium pigment[5], barite[6] and quartz powder[7]. Titanium dioxide (titania, TiO_2) has been used widely due to its small powder size, whiteness, excellent weather resistance and anti-aging advantages[8,9].

Electrical conductivity of the fibres is mainly dependent on the conductive chains or networks produced by the fillers, and the high conductive performance could be obtained by adding high fraction of fillers. However, high fraction of fillers deteriorated the mechanical properties of the filled fibres. Dispersion stability, which is very important property for the nano-particles dispersion, has been widely studied. Seekkuarachchi[10] reported that nano-aggregates are made up of particle-particle collision in inertia sub-range and orthokinetic cluster-cluster collision in viscous sub-range.

In this work, the conductive nano TiO_2, modified in its Sb_2O_5 doped SnO_2-coated conductive layer by chemical co-precipitation method[11,12], have been used as conductive fillers to prepare polyamide 6-based conductive fibres by a twin-screw extruder. Effects of fibres weight ratio on the conductivity, phase structure, crystalline and thermal properties have been studied to provide guidance for the preparation of fibres with high conductivity and good performance. The main contribution is to solve the problems of industrialization of the white conductive fibres.

2 Materials and Methods

2.1 Materials

Titanium dioxide (TiO_2, rutile structure), supplied by Sinopharm Chemical Reagent Co., Ltd., was used as the conductive fillers. Polyamide 6(PA6) with lightness was used as matrix, this was supplied by Sinopec Baling (China). Antimony trichloride($SbCl_3$) and crystalline tin tetrachloride($SnCl_4 \cdot 5H_2O$), supplied by Sinopharm Chemical Reagent Co., Ltd.(China), were chosen as coating materials on the surface of TiO_2. The properties of TiO_2, PA6, $SbCl_3$ and $SnCl_4 \cdot 5H_2O$ are shown in Table 1.

2.2 Preparation of Conductive Titania

An amount of 30g of nano TiO_2 was dispersed in deionized water and stirred. The *p*H value of the

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mixture was adjusted at 1.5 through addition of HCl solution. The mixture was then transferred into four-necked flask at 65-70°C. Hundred mililiter solution of $SnCl_4$ and $SbCl_3$ ($SnCl_4$:$SbCl_3$=12:1) was added drop-wise during constant stirring, while a few drops of HCL were used to maintain the constant pH. The stirring was continued for 60 min, and then the colloidal solution was filtered followed by washing with deionized water. Once the process was finished, the particles were dried in a DZF-6090 vacuum oven (Shanghai Yiheng Scientific Instrument Co., Ltd.) and placed calcined in a GSL1600X muffle furnace (Hefei Kejing Materials Technology Co., LTD) at 850°C for 6h. The contents were finally cooled in a vacuum chamber for 1 h at room temperature[13].

2.3 Surface Treatment of Particles

In order to improve the binding quality of PA6/TiO_2 interface, the conductive TiO_2 particles were subjected to a surface treatment using sodium hexametaphosphate. The coupling agent was mixed with alcohol (Sinopharm Chemical reagent Co., Ltd.) evenly, then the solution was added to the particles and stirred with double cone mixer (Wuxi Xinbiao Powder Machinery Co. Ltd., China) followed by heating at 50 °C and kept for 35 min. The mixture was then cooled, filtered and washed repeatedly. The particles were subsequently dried in a vacuum oven at 85°C for 10 h.

2.4 Conductive Fibres Preparation

Dried the PA6 slice at 90 °C for 24 h, and mixed the surface-treated TiO_2 conductive material together with functional additives in a high speed mixer at a certain mixing ratio. Master batch was spun by twin-screw extruder at the temperature (15-35°C) higher than the melting point of PA6 (215 °C).

Before blending, conductive TiO_2 and PA6 were dried at 90 °C in the vacuum oven for 24h to remove the moisture. The PA6/TiO_2 conductive fibres were manufactured by a CET35 twin-screw extruding machine [Coperion (Nanjing) Machinery Co., Ltd.] at a screw speed of 30Hz and melt temperature of 245°C. The screw diameter in the extrude machine was 36mm. Firstly, conductive TiO_2 and PA6 were

mixed by the weight ratio and then the mixture was added to the twin-screw extrude machine through feed system **1** and spun from solid conveying zone **2** to melt conveying zone **4** (Fig 1). The weight fraction of the conductive TiO_2 was ranging from 0% to 40%. Finally, the conductive fibres were obtained which were dried at 90°C for 5 h.

2.5 Characterization

To calculate conductivity, the resistance against constant voltage of 100V was measured with a resistance meter (ZC-90G high insulation resistance meter from Subotica Electric Company, China) at room temperature (25 °C) according to ASTM C1113/C1113 M-09 for the melt-spun filaments. The electrical current was applied between two clips at a distance (L) of 100mm. The conductivity was calculated from the measured resistance R using the following equation:

$$C = 1/\rho = L/RS \qquad \qquad \dots (1)$$

where ρ is the resistivity; and S, the cross-section. Each sample was tested five times and the mean values were reported.

Scanning electron microscope (SU1510 Hitachi, Japan) was used to observe the distribution of conductive TiO_2 in the fibres after the surface modification. The accelerating voltage was 20 kV. The samples to be used for investigating the cross-sections were refrigerated in liquid nitrogen for 3h after coating with resin and curing. All the samples were dried and sprayed gold before testing.

The crystalline properties of conductive TiO_2 nanoparticles were analyzed by D8 X-ray diffractometer (XRD) (German Brooke AXS Co., Ltd) before and after the surface treatment, as well as after blending with PA6 slice. A scanning rate of scintillation probe was Bragg angle 3 deg/min.
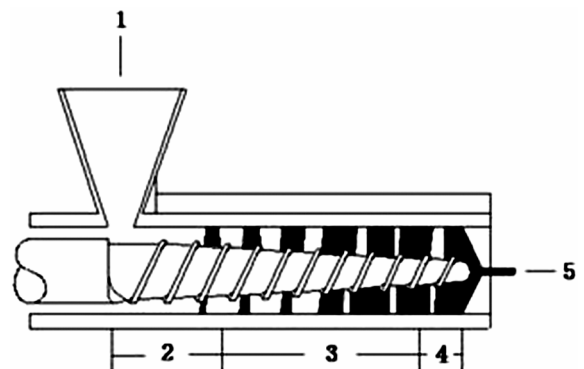
Table 1—Properties of TiO_2, PA6, $SbCl_3$ and $SnCl_4 \cdot 5H_2O$

Property	TiO_2	PA6	$SbCl_3$	$SnCl_4 \cdot 5H_2O$
Density, g·cm^{-3}	4.2	0.28	3.14	2.26
Purity, %	≥98.0	≥90.0	≥99.0	≥99.0
Diameter, μm	0.09	0.0024-0.0048	-	-
Molecular weight	79.87	-	228.12	350.6

Fig. 1—Simple cross profile of the extruder barrel part

Analysis on differential scanning calorimeter (DSC) was carried out on Waters Technology Q200 Spectrometer to test thermal properties of the fibre samples. Aluminum crucibles (40 µL) were used for the samples. About 3-5 mg of the sample was heated from room temperature to $300^{O}C$ at a heating rate of 10 ^{O}C /min followed by cooling to the room temperature at the rate of $30^{O}C$ /min with the nitrogen flow rate of 50 ml/min. Samples from pure PA, conductive TiO_2 with mass fraction of 5% and the conductive TiO_2 with mass fraction of 40% were prepared.

3 Results and Discussion
3.1 Conductivity of Fibres

Table 2 shows conductivity of the fibres with different contents of conductive TiO_2. For a given weight fraction, conductivity of the fibres changes with the increasing content of TiO_2. The conductivity of the fibres without TiO_2 is 4.00×10^{-12} S·cm^{-1} in the study. With the additon of TiO_2 particles, the conductivity of the as-spun PA6/TiO_2 improves. It is observed that the change in resistivity is very small when the TiO_2 content in the fibre is less than 5%. There has been a sudden drop of resistivity while the ratio is between 5% and 10% or 10% and 15%, then it tends to decline steadily, which illustrates the fact that conductive sites are produced by TiO_2 particles in the fibres.

The conductivity of polymer-based conductive fibres is due to the conduction mechanism interaction of ohmic conductive, tunnel conductive and field emission[14,15]. There has been less probability of forming a chain passage when the conductive particles content is 5% or lower. At this time, tunneling effect plays a major role in conducting the tunnel but it is weak. Finally, there is a smaller difference compared to the resistivity of pure PA6. Part of conductive particles contact

Table 2- Conductivity of fibres with different amounts of conductive TiO_2

TiO_2, wt%	Conductivity, S·cm^{-1}
0	4.00×10^{-12}
5	3.10×10^{-11}
10	1.40×10^{-8}
15	2.70×10^{-6}
20	5.60×10^{-6}
25	1.02×10^{-5}
30	2.63×10^{-5}
40	4.00×10^{-5}

with each other to form paths by the ohmic conductive when the content of conductive TiO_2 is 5- 10%. At this time, a portion of conductive particles which is not dispersed in the fibre matrix still can form a current path through tunneling. The two parts are combined into the overall conductivity due to ohmic conductive and Tunnel conductive phenomenon. As the content is more than 15%, the conductive particles could form a chain of basic path because of its large aspect ratio, so that ohmic conductivity plays a major role.

The effective conductivity of polymer fibres mainly depends on the interactions and connections among particles. The conductive TiO_2 particles will produce conductive chains or networks in the PA matrix as the concentration of TiO_2 is up to a level. Theoretically, the incremental content of conductive TiO_2 can improve the conductivity of PA fibres. However, the larger amount of TiO_2 does not mean the perfect conductivity of PA6 fibres after the TiO_2 volume attains the critical point. Meanwhile, the higher volume of TiO_2 causes some issues that affect the fibre properties adversely, like the poor mobility in spinning, difficulty in spinning and texturing, even the mechanical properties are also deteriorated, along with the rise in fibre costs. Therefore, from the actual need, spinnability and economic point of view, the proportion of the conductive TiO_2 of about 15% is found to be a relatively ideal ratio.

3.2 Surface Morphology

The properties of fibres can be normally controlled by the dispersion of nanoparticles in the polymer matrix. The dispersion of fillers becomes the bottle neck problem for the performance of nanofibres. Therefore, a lot of studies are focused on this area [16,17]. In this study, the grafted polymer layer consisting of coupling agent on the conductive TiO_2 surface could be completely miscible with the surrounding PA6 medium. By this way, polymer detachment is prevented due to the covalent attachment of polymer chains to the matrix. This also leads to a better stability of the dispersion.

The surface morphology of conductive TiO_2 is presented in Fig 2 after surface treatment. It can be observed that the conductive TiO_2 is rod with a certain aspect ratio, and the average length of conductive TiO_2 is approximately 5µm, which is more beneficial to form a conductive path in the matrix. The surface modification is

effective to improve the dispersion and the interface adhesion of TiO_2 to the PA6 matrix. When the conductive TiO_2 is added to the matrix, the nanoparticles are used to enhance the conductive chains and networks, which plays an important role as a conductive bridge to connect the nanoparticles with each other.
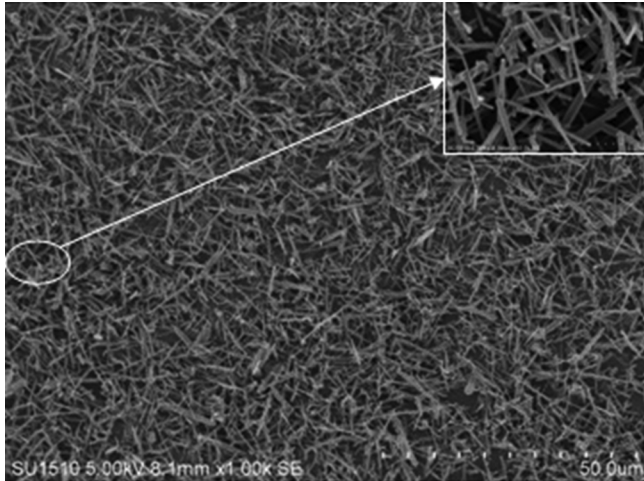
Figure 3 shows the distribution of different proportions (5, 10, 15 and 30%) of conductive TiO_2 in the PA6 matrix. The conductive TiO_2 is observed to be immersed into PA matrix which explains that conductive TiO_2 and PA matrix have a good compatibility. Figures 3 (a) - (c) reveal that conductive TiO_2 is homogeneously dispersed in the matrix and some of the nanoparticles can connect with each other and have very little aggregates. Each connected TiO_2 forms the conductive chamel due to the ohmic conductive mechanism and under the tunnel effect, non-connected TiO_2 can also form the current pathways. Figure 3 shows the poor dispersion of TiO_2 in the polymer matrix if the ratio is too large, along with the poor mobility in spinning, thereby causing problems in spinning, and deterioration in mechanical properties.

3.3 Crystalline Properties of Fibres

Figure 4 shows a comparison in X ray diffractograms, which evaluates the crystalline fraction of the conductive TiO_2 before and after the surface treatment, along with the fibres. The crystalline structure with diffraction peaks of 2θ angle of the samples is shown at $28.17°$.
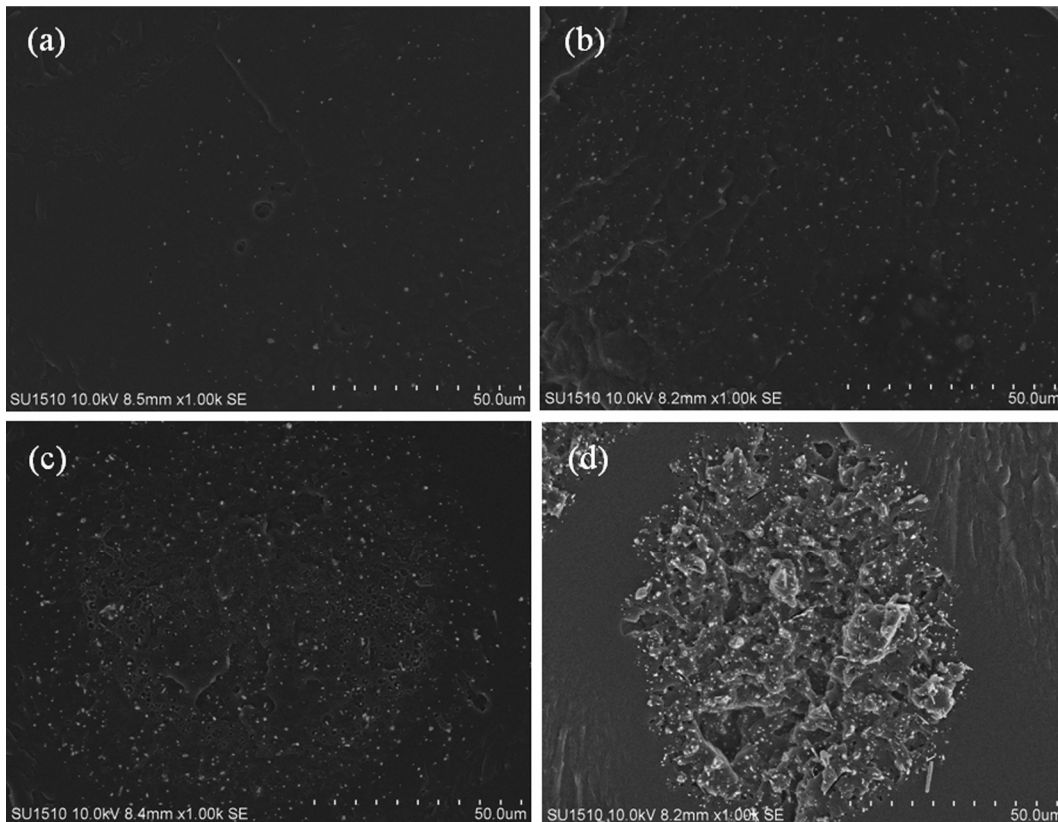
Fig. 2—SEM of conductive TiO_2 nanoparticles

Fig. 3— SEM of cross-sections of PA6/TiO_2 conductive fibres with different ratios of conductive TiO_2[(a)5%, (b)10%, (c)15%, and (d)30%
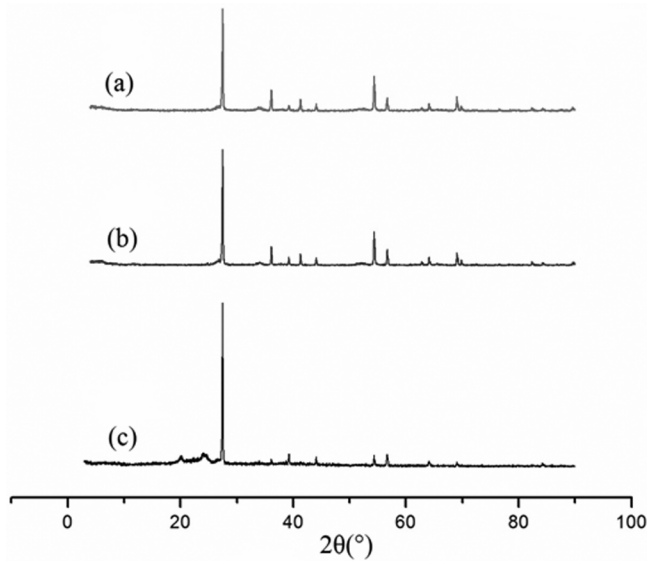
Fig. 4— XRD pattern of (a) conductive TiO_2, (b) conductive TiO_2 after surface treatment, and (c) the as-spun PA6 fibres with treated conductive TiO_2

The comparison of Figs 4 (a) and (b) curves demonstrates that the location of the two curves and intensity of diffraction peaks are similar. Also, it shows that the surface treatment does not cause any damage to the conductive properties of TiO_2. It can be observed from the comparison of X-ray curves in Figs 4 (b) and (c) that the conductive TiO_2 absorption peak is present in blended fibre. The drop in thermal decomposition temperature of the conductive fibres also demonstrates this phenomenon. Therefore, diffraction pattern of the fibres is the same as that of conductive TiO_2. This result means that PA6 adsorbed on the surface of TiO_2 nanoparticles has no effect on crystallization performance of conductive TiO_2.

3.4 Thermal Properties of Fibres

Figure 5 shows the differential scanning calorimetric (DSC) results of fibres with varying amounts of conductive TiO_2. The thermograms indicate that melting points of the as-spun fibres decline with increasing the amount of conductive TiO_2. The thermogram[Fig 5 (a)] shows that the as-spun fibre exhibits a melting point of 221 °C, whereas the fibres produced with varying amounts of conductive TiO_2 exhibit the melting points at about 220 °C. The melting point shifts towards lower value with 5% conductive TiO_2 compared to the as-spun fibre sample, while it remains the same with 15% of conductive TiO_2. As the hot melt is
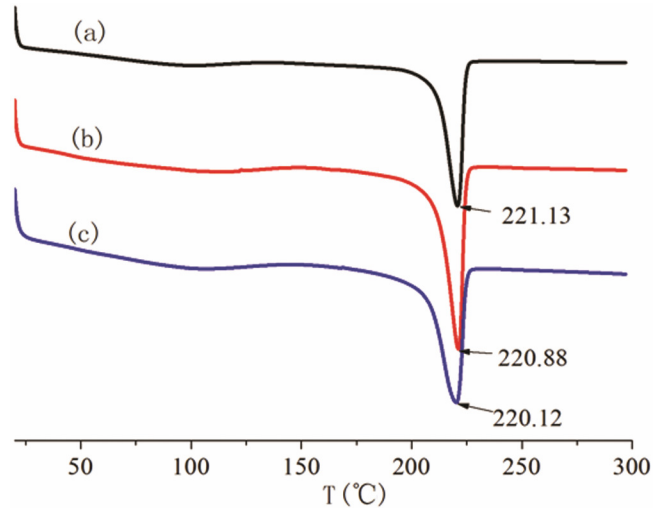

Fig. 5— DSC curves of fibres with conductive TiO_2 of (a) 0%, (b) 5%, and (c)15%

the necessary energy for crystalline polymer to be randomness, the crystallinity of blend will depend on the temperature. Additionally, the degree of crystallinity determines the crystallinity and melting point (Tm). The regularity will be damaged with the addition of conductive TiO_2, also the orderliness and tight of PA macromolecules and the crystallinity of molecules itself will reduce. The process of crystallization is nucleation process[18,19]. From the micro perspective, this appearance belongs to heterogeneous nucleation. Hetrogeneous nucleation is a physical reaction that occurs on serface of impurities. As the PA6 is mixed into a portion of conductive TiO_2, conductive particles will act as the foreign impurities, and each of the conductive TiO_2 particles may form a nucleus, so that the number of nuclei will grow with increasing the number of the conductive TiO_2. However, there are many scattered grains, and it becomes more difficult to form a large grain size regular. As the size and regularity grow, nucleus may absorb more energy. More importantly, few regularity grains are easily damaged.

According to Figs 5 (a) and (b), the location and intensity of diffraction peaks of two curves are similar. The treated conductive TiO_2 with a stronger intensity describes the fact that surface treatment does not change the crystal structure, as well as the properties, but remains more orderly. It should be noted that the characteristic peaks of conductive TiO_2 can be found in blends [Figs 5 (a) and (c)], indicating that the mixture of conductive TiO_2 and PA6 does not destroy the crystal structure of conductive TiO_2.

4 Conclusion

The result of conductivity characterization shows that the presence of the conductive TiO_2 influences the resistivity–it would be the tunnel conductivity when TiO_2 content is less than 5%; it would be the composition of ohmic conductive and tunnel conductive when TiO_2 content is 10 - 15%, and resistivity has a dump; and it would be the ohmic conductivity when content is greater than 15%. Therefore, the resistance has a mutation and there is also a certain tunnel effect. Our findings are useful for providing some practical guidance for the preparation of white fibres with high conductivity and good performance.

Acknowledgement

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