

Modifying the poly ether ester antistatic agent by carbon nanotubes, the antistatic effect on polypropylene fibers^{*}

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Abstract A new antistatic fiber is investigated using carbon nanotubes (CNTs) to enhance the antistatic ability of polymer fibers based on the mechanism of the discharging process of polarity macromolecule. Composite antistatic agent (CAA), prepared by dispersing CNTs in an organic antistatic agent carrier containing metallic ions in their main chains, is copun with polypropylene (PP) to prepare CAA/PP fibers. It is indicated through analyzing the measured dynamic tribo-electrostatic voltages that CNTs can promote the discharging process of polarity macromolecule of antistatic agent carrier and further improve the antistatic ability of PP fibers. It is also indicated that the antistatic effect promoted by CNTs is better than that by conductive carbon black. Moreover, the antistatic effects of the CNTs treated by different methods are also compared.

Keywords: carbon nanotubes, polypropylene fiber, antistatic agent, tribo-electrostatic voltages.

Electrostatic property of synthetic fibers leads to attraction of dust, intertwisting, electric shocks and damages in electronic machines. When it is necessary to provide polymer fibers with antistatic properties, manufacturers have two choices; either adding the antistatic agents to the polymeric material or applying them onto its surface^[1~4]. Because inner antistatic agents are more durable than outer antistatic agents, they become major research directions of plastics antistatic agents^[2]. Traditional ways to make antistatic fibers are: (1) Filling conductive particles, such as carbon black (CB), graphite powder and metal powder^[5,6], by which static is dissipated by an electron transfer path between the particles; (2) filling inorganic salts^[6], by which static is dissipated by the deliquescence of inorganic salts; (3) incorporating some kinds of macromolecules, such as polyethylene glycol, polyether and their derivatives^[4], for their polar radical groups orientate to the surface of polymer fibers and attracting a conductive film of atmospheric moisture, so the resistivity of the material's surface is reduced and static is dissipated. If the surfactants are lost by wash or friction, the antistatic effects can be continued due to the migration of the additive from the inner to the surface of the polymer fibers; and

(4) incorporating special macromolecules containing metallic ions in their main chains, such as metal-locenes, the copolymers of alkyl carbonates and some kinds of poly ether esters, as these macromolecules provide a low energy transfer of electrons between adjacent aromatic layers^[7].

Since their discovery in 1991^[8], carbon nanotubes (CNTs) have shown attractive properties in the area of engineering material reinforced by nanophase, semiconductor material, catalyst carrier etc.^[9]. It is possible to apply CNTs to antistatic polymers due to their nanometer diameters, unique structure, high chemical stability and conductance property^[10]. One of the above approaches should be considered if a study is aimed at enhancing the antistatic ability of polymer fibers by CNTs. The drawbacks of the first approach lie on large quantities of conductive particles being needed to form transmission paths, so the reduction of the optical transparency and alteration of the mechanical properties often limit the application range. The drawback of the second approach lies in the corrosion behavior of inorganic salts on metal material devices. Moreover, bad hand feeling and extrinsic features of the polymer

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fibers may be caused by the filled inorganic salts. For the third approach, the durability may be also not enough because most of antistatic agent molecules will be lost after wash and friction of a long time.

Our study is based on the fourth antistatic approach. The molecules of the employed poly ether ester antistatic agent contain metallic ions in their main chains. The antistatic process is called "polarized discharging principle of polarity macromolecule"^[6]. Experimental result showed that the composite antistatic agent (CAA) prepared by dispersing CNTs in antistatic agent carrier had superior antistatic effect on PP fibers to the pure antistatic agent and pure CNTs. Moreover, the antistatic effect promoted by CNTs was compared with that by conductive carbon black. The antistatic effects of the composite antistatic agents prepared by dispersing the differently treated CNTs in antistatic carrier on PP fibers were also studied.

1 Experimental procedure

1.1 Preparation of CNTs

CNTs were prepared by catalytical pyrolysis of ethane ($\text{CH}_2=\text{CH}_2$) with Ni particles as the catalyst. Hydrofluoric acid and nitric acid treatment were employed to remove diatomite and metallic catalysts. A transmission electronic microscopy (TEM, JEOL-200CX) image of thus prepared carbon nanotubes is shown in Fig. 1. The prepared multi-walled CNTs are several micrometers in length and 20 ~ 30 nm in diameter.

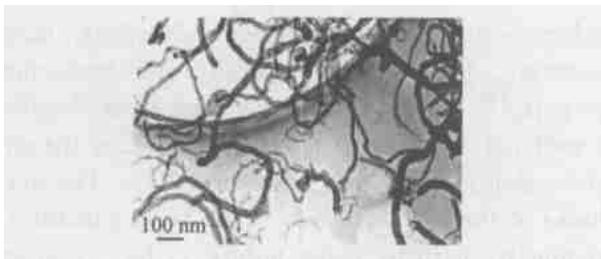


Fig. 1. The transmission electronic microscopy (TEM) of carbon nanotubes.

1.2 Carbon black

A conductive carbon black (HG-1P, made in Shandong HuaGuang CB Plant, China) was used for referenced test. The diameter of the CB particles is about 40 nm.

1.3 CNTs treatments

Heat treatment: The CNTs were heated at 2200 °C, under 4 atm in an inert gas shield for 4 h in an apparatus of HIGH MULTI5000 sintering furnace (made in Japan). The corresponding heat-treated CNTs are called "HCNTs".

Air activation: The tube of the resistance furnace (SK-2-12), 60 mm in diameter and 1.0 m in length and with the two ports open, was initially set to 600 °C. Then a quartz tube carrying 25 g of HCNTs was placed in the center of the furnace tube. Temperature was kept at 600 °C for 20 min, while the quartz tube was rotated at the rate of 25 r/min with a quartz rod so that the HCNTs could be in full contact with air. The corresponding air-activated HCNTs are called "HCNTs-1".

1.4 Preparation of antistatic fibers and the measurement of antistatic ability

1.4.1 Preparation of composite antistatic agents (CAAs)

An organic antistatic agent (AA), "PMME", was prepared by the copolyreaction of diethylester terephthalate and a fatty acid polyethylene glycol ester whose molecules contain metal ions^[11]. This AA was employed as the antistatic carrier. One part of CNTs, HCNTs, HCNTs-1 or CB was mixed with 9 parts of the antistatic carrier (in distilled water) and scrambled at a low speed through water bath heating, then toasted and milled, forming CAAs (CNTs/AA, HCNTs/AA, HCNTs-1/AA or CB/AA) antistatic filler grains.

1.4.2 Preparation of antistatic fibers

Antistatic filler grains and polypropylene (PP) pieces (PC932, Himont Company) were mixed up, then cospun by Model Filature Device at temperature of 227 ~ 230 °C, and at a speed of 200 m/min. Tension temperature and tension multiple were respectively 65 °C and 4; and forming temperature and forming duration were 120 °C and 15 min respectively. Model Filature Device was assembled of domestic makes, viz, XRZ Melt Flow Speed Meter, single-hole spinning jet and JB 50-D Gearshift Electric Mixer, by our own laboratory.

Dynamic tribo-electrostatic voltage was taken as the standard of antistatic ability and its measurement

was performed following the standard proposal “ZBW 04009-89” of the National Textile Ministry^[6]. QF2292 Digital Electrostatic Voltmeter was used for measuring the dynamic tribo-electrostatic voltage.

2 Results and discussion

2.1 Antistatic effects of composite antistatic agent of CNTs/ AA on PP fibers

Fig.2 shows the antistatic abilities of PP fibers filled with pure CNTs, pure AA and CAA (CNTs/AA). It is indicated that PP fibers filled with pure CNTs (CNTs-PP) have almost no antistatic ability at the CNT content of 0 ~ 2%. The antistatic mechanism of filling CNTs, as conductive particles, in PP fibers lies in that static is dissipated by a conductive network of CNTs. But large quantities of conductive particles should be needed, as stated above. Theoretical calculation showed that only when the average distance between dispersed CNTs is smaller than 10^{-8} m could a transmission path be formed and the CNT content has to be over 15%. While PP fibers can hardly be spun with such a high CNT content.

As for the fibers prepared by cospinning PP and pure AA (AA-PP), definite antistatic ability can be generated. Tribo-electrostatic voltage drops as the content of AA increases, approaching 1000 V at the AA content of 2%, as shown in Fig.2.

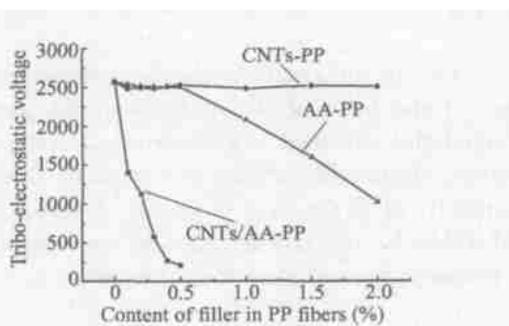


Fig. 2. Tribo-electrostatic voltages of CNTs-PP, AA-PP and CNTs/AA-PP fibers (ambient temperature: 19.5 °C, relative humidity: 39%).

We observed that phase separation occurred between the antistatic agent and the polymer matrix during the cospinning process. Antistatic agent became a discontinuous “island” phase, PP matrix became a continuous “sea” phase, as shown in Fig. 3. Their antistatic mechanism is “polarized discharging principle of polarity macromolecule”^[11]. When fibers are frictionized to be charged, electric field is generat-

ed. Electrons are definitely moving and “islands” are polarized in the ambient electric field. Discharge will occur between adjacent “islands” and the charges are delivered when polarizations are heavily accumulated.

From Fig.2 we can see that the antistatic effect is further enhanced when pure AA is substituted by CAA (CNTs/AA). Tribo-electrostatic voltage drops from 2570 V to 210 V at the CAA content of 0.5%. The result suggests that the added CNTs further promoted the antistatic effect of the organic antistatic agent. For the conductivity of CNTs they constructed the electric pathways inside AA phases, promoted the transmission of electrons, made discharging process of polarity macromolecule more accessible and further improved the antistatic ability of fibers.

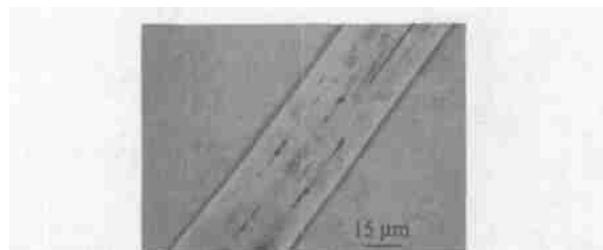


Fig. 3. Transmission optical microscopy (TOM, Nikon, Japan) of the polypropylene fiber cospun with CAA.

When the polymer fibers are concerned, their antistatic ability can be regarded as qualified if the tribo-electrostatic voltage is below 1000 V, and their antistatic ability can be regarded as superior if the tribo-electrostatic voltage is below 500 V^[6]. For the AA-PP fibers prepared by cospinning PP and AA, they have the qualified antistatic ability when the AA content is above 2%; for the CNTs-PP fibers prepared by cospinning PP and CNTs, they have no antistatic ability when the CNT content attains 2%; and for the CNTs/AA-PP fibers prepared by cospinning PP and CNTs/AA, they have the superior antistatic ability at the CAA content as low as 0.5% (in which the content of CNTs is only 0.05% because CAA contains 10% of CNTs).

2.2 Comparison of antistatic effects between CNTs and carbon black

Fig. 4 shows the measured tribo-electrostatic voltage of CB/AA-PP fibers (prepared by cospinning PP and CB/AA) and CNTs/AA-PP fibers. The tribo-electrostatic voltage of CNTs/AA-PP fibers is much lower than that of CB/AA-PP fibers, and the difference between the two samples becomes more and

more obvious as the content of CAA fillers increases. At the CAA filler content of 0.5%, tribo-electrostatic voltage of CNTs/AA-PP fibers is lower than that of CB/AA-PP fibers by about 75%, suggesting that CNTs created greater antistatic effect than CB did, though the powder specific resistance of CB is obviously lower than that of CNTs, as listed in Table 1. The powder specific resistance was measured by constant current way under a pressure of 5 MPa. The employed apparatus was GM-1 Powder Resistivity Instrument, made in Institute of Coal Chemistry, CAS.

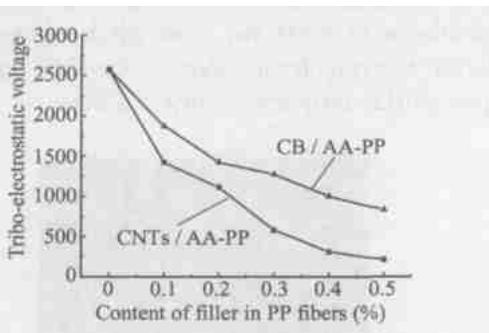


Fig. 4. Tribo-electrostatic voltages of CNTs/AA-PP fibers and CB/AA-PP fibers (ambient temperature: 19.5 °C, relative humidity: 39%).

Table 1. Some characteristics of CB, CNTs, HCNTs and HCNTs-1

	CB	CNTs	HCNTs	HCNTs-1
Powder specific resistances ($\Omega \cdot \text{cm}$)	0.221	0.451	0.245	0.247
Specific area (m^2/g)			121.45	148.92

CB (which is roughly spherical) is a low aspect ratio (length to diameter ratio) additive, and CNTs are a high aspect ratio additive. Longer particles (CNTs) cover a greater distance of the conductive pathway, while spheroidal CB has to form a chain of particles to cover the distance that a fibre-shaped CNT will cover by itself. This means that up to the same level of conductivity, the required loading of CB should be many times more than that of CNTs for the reason that a great deal of CB is wasted compared to the state that these CB particles could be placed in the optimum positions to form long chains with the minimal loading. Thus CNTs created greater antistatic effect than CB did.

2.3 Antistatic effects of the treated CNTs

Fig. 5 shows the typical Raman spectrum (measured by RM2000 Fiber Confocal Raman Spectroscopy) of CNTs and the heat-treated CNTs. The

spectrum presents two sharp peaks characteristic of the graphite structure at approximately 1350 cm^{-1} and 1580 cm^{-1} , respectively. The peak at 1580 cm^{-1} can be identified as the G peak of crystalline graphite arising from zone-center E_{2g} mode, and the peak at 1350 cm^{-1} as the D peak assigned to an A_{1g} zone-edge phonon induced by the disorder due to finite crystalline size¹². The origin of the D peak of CNTs has been explained as disorder-induced features that were formed during the preparation of CNTs¹³. Some parts of nanotube walls were composed of small size graphene sheets that were roughly parallel to the tube axis. Moreover, the stack of the graphene layers might not be uniform along the circumference of the tube in the curvature places and at the tube ends. These uneven microstructures might induce a higher free energy and should be removed by high temperature and pressure¹³.

The intensity of the G-line in comparison to the D-line becomes higher after heat treatment, indicating an increased crystallinity in the material. During the heat treatment, with the diffusion of carbon atoms, growth of the graphene sheets began along their original orientations (the axial and circumferential directions), and the growing graphene sheets might join together to form bigger sheets. Moreover, in order to decrease the free energy, the graphene sheets tended to the uniform stack, a configuration of CNTs.

Due to the graphene sheets growing, joining together and forming the uniform stacks, many grain boundaries vanished and electron scattering that occurred at grain boundaries was weakened, thus the conductivity of CNTs was obviously elevated. As listed in Table 1, the powder specific resistance of CNTs obviously dropped after heat treatment.

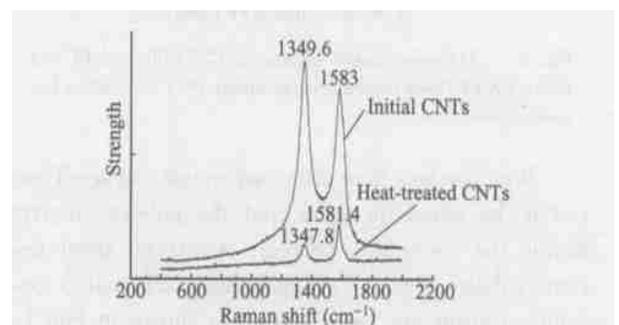


Fig. 5. Raman spectrum of CNTs before and after heat treatment.

The antistatic effect of the heat-treated CNTs

was measured and compared with that of initial CNTs. As shown in Fig. 6, the tribo-electrostatic voltage of HCNTs/AA-PP fibers is obviously lower than that of the CNTs/AA-PP fibers. At the CAA filler content of 0.5%, the tribo-electrostatic voltage of HCNTs/AA-PP fibers is lower than that of CNTs/AA-PP fibers by about 48%. From this experimental result, we know that due to the conductivity of CNTs being obviously elevated after heat treatment, they created stronger antistatic effects compared to initial CNTs. This result also demonstrated that one of the main reasons that CNTs can enhance the antistatic effect of the used AA lies in their conductance property.

Fig. 6 also indicates that the tribo-electrostatic voltage of HCNTs-1/AA-PP fibers is further decreased compared to that of the HCNTs/AA-PP fibers. Their tribo-electrostatic voltage drops from about 2570 V at the CAA filler content of 0% to about 59 V at the CAA filler content of 0.5%. The reason may lie in the dispersity of CNT powder being improved after air activation. During the air activation process, the curvature sites of nanotubes could be first attacked by oxygen molecules due to their relatively high reactivities^[14, 15], resulting in breaking of nanotubes. Many entangled nanotubes were disassembled and the dispersity of CNT powder was enhanced. As listed in Table 1, the specific area (measured by BET method in "SORPTOMATIC1990 (Thermo Quest, Italia) S. P. A".) of HCNTs-1 is higher than that of HCNTs. The reason lies in the CNT surfaces being exposed after the entangled CNTs being dispersed, thus demonstrating that the dispersity of CNT powder was enhanced after air activation.

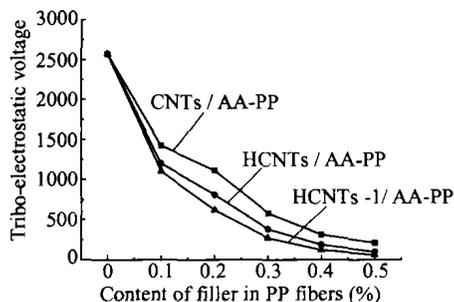


Fig. 6. Tribo-electrostatic voltages of CNTs/AA-PP, HCNTs/AA-PP and HCNTs-1/AA-PP fibers (ambient temperature: 19.5 °C, relative humidity: 39%).

resistance of HCNTs and HCNTs-1 is basically equivalent, but due to the dispersity of HCNTs-1 being higher than that of HCNTs, HCNTs-1 should be distributed more uniformly in the antistatic carrier. Thus the antistatic ability of HCNTs-1/AA-PP fibers is better than that of HCNTs/AA-PP fibers.

2.4 Crystallinity, orientation birefringence and mechanical properties of antistatic fibers

As listed in Table 2, the crystallinity (measured by D/Max- γ BX X-Ray Diffractometer, Japan) of every CAA-PP fiber sample is basically not changed compared to that of PP fiber sample, which might be due to the CAA filler content being low. The orientation birefringence (measured by XP 1820282 Polarization Microscope) of every CAA-PP fiber sample is slightly decreased compared to that of PP fiber sample. In order not to further affect the orientation birefringence of the fibers, the maximal content of the CAA filler added was 0.5% in this work.

Table 2. The properties of PP fibers and CAA (0.5 wt. %)-PP fibers

Sample (fiber)	Crystallinity (%)	Orientation birefringence ($\Delta n \times 10^3$)	Breaking elongation (%)	Breaking strength (cN/dtex)
PP	41.8	38.8	32.0	4.40
CB/AA-PP	41.1	31.4	30.8	4.10
CNTs/AA-PP	41.3	33.5	34.5	4.58
HCNTs/AA-PP	41.5	33.9	43.7	5.67
HCNTs-1/AA-PP	41.4	34.2	43.5	5.50

From Table 2 we may see that the mechanical properties (measured by YG 001A Fiber Electric Strength Apparatus) of CNTs/AA-PP fibers are superior to that of PP fibers, but the mechanical properties of CB/AA-PP fibers are not as good as that of PP fibers. The reason for that is CNTs are linear nano-material, with a high aspect ratio and the specific area, thus they can effectively transfer internal stresses, inhibit the expansion of microcracks and strengthen the matrix materials. Whereas CB is a low aspect ratio additive, and does not possess these merits that CNTs possess.

After heat treatment, the degree of crystallinity of nanotube-walls became increased, resulting in the mechanical properties of nanotubes being enhanced, thus the mechanical properties of HCNTs/AA-PP fibers and HCNTs-1/AA-PP fibers are superior to that of CNTs/AA-PP fibers.

It is indicated in Table 1 that the powder specific

3 Conclusion

In this work, the antistatic effects of CNTs on PP fibers were investigated.

Based on the antistatic mechanism of “polarized discharging principle of polarity macromolecule”, CNTs can effectively promote the antistatic ability of PP fibers when they are carried by an organic antistatic agent, and the antistatic effect of CNTs is higher than that of CB.

The antistatic effects of CNTs can be enhanced when their conductivity is elevated through heat treatment and their dispersity is elevated by air activation.

In summary, due to the nanometer diameters, unique structure, superior mechanical properties and conductance property of CNTs^[9, 10], not only the antistatic ability of polymer fibers can be further enhanced by CNTs, but also the physical performances and spinning process of polymer fibers are secured. As shown in Fig. 3, the diameters of the spun PP fibers are about 30 μm , whereas the diameters of the dispersed “island” phases formed by antistatic agent may be under 1 μm . CNTs can be freely distributed in the “island” phases because they have nanometer diameters, while the other conductive particles are generally by far larger.

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