

Poly(ethylene terephthalate)/Carbon Black Composite Fibers Prepared by Electrospinning

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Abstract Poly(ethylene terephthalate) (PET)/carbon black (CB) composite fibers with improved mechanical properties in tensile modulus and tensile strength are prepared by electrospinning. Stable dispersions suitable for electrospinning are obtained by dispersing melt pre-compounded PET/CB composites in hexafluoroisopropanol. The fiber morphology and CB dispersion are investigated by FESEM and TEM. The addition of CB has no obvious effect on fiber diameter, and the average fiber diameters for all the samples are around 2–3 μm . CB in the fibers is in the form of submicron-sized clusters. The thermal properties of the PET/CB composite fibers are evaluated by DSC, showing almost unchanged melting temperature and crystallinity. Uniaxial tensile tests are used to measure the mechanical properties of the PET/CB composite fiber mats. The fiber mats containing 1 wt%–8.5 wt% CB have significantly improved tensile modulus compared to neat PET fiber mat, showing reinforcing effect of CB. The electrical conductivity of the fiber mats has also been tested.

Keywords: Electrospinning; Carbon black; Mechanical properties; Morphology; Dispersions.

INTRODUCTION

Polymer/carbon black (CB) composites have been widely used in industry for many years as reinforcing, conductive, antistatic, weather-resistant and black-colored materials because CB has good mechanical properties, electrical conductivity, light-absorbing ability and color-stability. With the rapid evolution of the electrospinning technique, polymer/CB composite fibers have gained interest^[1–12] because more application fields and superior properties are expected from their unique structure such as high specific surface area, high aspect ratio and high porosity.

Some polymer/CB composite fibers^[1–12] have been prepared by electrospinning with interesting properties such as improved mechanical properties or electrical conductivity as compared to the corresponding neat polymer fibers and the CB content can be from 1 wt%^[2] to 62.5 wt%^[11]. Hwang *et al.*^[1] and Chuangchote *et al.*^[2] reported dramatic increases in tensile modulus for electrospun polyurethane (PU)/CB and poly(vinyl alcohol) (PVA)/CB composite fiber mats. Tiwari *et al.*^[3] investigated the use of electrospun poly(ϵ -caprolactone) (PCL)/CB fibrous strips as flexible strain sensors using the principle that the conductive fibrous strips become non-conductive at sufficiently high strains, and they also proposed a two-dimensional layered-percolation model to explain the increase in electrical resistance with stretching. Based on polyacrylonitrile (PAN)/CB-related electrospun webs, Im *et al.*^[4,5] investigated carbon fiber/CB webs as electromagnetic shielding materials and gas sensors, and Wang *et al.*^[6] reported electrode materials. Polycarbonate (PC)/CB, poly(ethylene oxide)/CB, poly(methyl methacrylate)/CB, polypichlorohydrin/CB, polyisobutylene/CB, polyvinylpyrrolidone/CB,

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poly(vinyl chloride)/CB, polyaniline/CB, butyl rubber/CB and chitosan (CS)/CB electrospun mats were also prepared^[7–12].

PET is widely used in industry for making soft-drink bottles, thin films for photography or food packaging, bearings, gears, housings for small appliances, *etc.* It is also a commonly used fiber-forming polymer, known as polyester fibers, extensively used in textile industry. Because of its excellent mechanical and thermal properties^[13], PET has been electrospun into fibers by both solution and melt electrospinning for various applications such as filtration, charge storage, phase change materials and vascular graft materials^[13–27]. However, the mechanical properties of polymer electrospun fibers are generally weak, limiting their applications. Adding rigid fillers to prepare composite fibers with improved mechanical properties is certainly beneficial for their applications. PET/multi-walled carbon nanotube (MWCNT) composite fibers have been prepared by electrospinning^[14, 15]. Mazinani *et al.*^[14] reported an electrical percolation threshold around 2 wt% MWCNT and significant improvement in mechanical properties through adding MWCNT for random PET fiber mats. Compared to the MWCNT, CB is much cheaper and widely used, but to the best of our knowledge, the research on PET/CB electrospun fibers is still lacking. An intriguing question then arises, whether PET/CB composite fibers might have interesting properties. This paper gives a full account of our studies on the preparation and characterization of PET/CB composite fibers.

EXPERIMENTAL

Materials

PET was provided by XinJiang Blue Ridge Tunhe Chemical Industry Joint Stock Co., Ltd. (China) with an intrinsic viscosity $[\eta]$ of 0.825 dL/g and dried in a vacuum oven at 80 °C for 8 h before use. CB (VXC-605), with a primary particle diameter of 25 nm, a dibutyl phthalate (DBP) absorption of 1.48 cm³/g, and an iodine absorption of 90 mg/g was purchased from Cabot (Shanghai), and hexafluoroisopropanol (HFIP) (purity > 99.5%) was purchased from Dongyang Biology Production Co. Ltd. (Yancheng, China).

Melt Compounding of PET/CB

PET/CB composites containing 1.0 wt%, 3.5 wt%, 6.0 wt%, 8.5 wt% and 16.0 wt% of CB were prepared by melt mixing. Thus, desired amounts of PET and CB were manually premixed and then fed into the chamber of a torque rheometer (RM 200A, Hapro Electrical Technology, Harbin, China). The screw speed, mixing temperature and mixing time were 60 r/min, 250 °C, and 10 min, respectively. The samples are denoted as PET/*x*% CB, where *x*% is the wt% of CB in the composite.

Preparation of Electrospinning Dispersions

Dispersions for electrospinning were prepared by dissolving the PET/CB composites obtained from the melt mixing process in HFIP at room temperature with magnetic stirring for 4 days. For comparison, neat PET solution was prepared by dissolving the commercial PET pellets in HFIP at room temperature, and two PET/CB dispersions containing 6 wt% CB were prepared by direct solution compounding with or without sonication, denoted as PET/6% CB-S1 and PET/6% CB-S2, where “S” means solution compounding, “1” represents no sonication, and “2” with sonication. For PET/6% CB-S1, PET pellets and CB were stirred together in HFIP for 4 days at room temperature. For PET/6% CB-S2, firstly PET pellets were dissolved in HFIP at 40 °C for 4 days to obtain a PET solution with a solution concentration of 15 wt%, and CB in HFIP with a concentration of 3.8 wt% was treated with sonication for 1.5 h and then stirred until use; then the two “solutions” were combined in an appropriate proportion. The concentration in all the dispersions is 12 wt%.

Electrospinning

The electrospinning dispersion was placed into a 10 mL glass bottle capped with a 9-gauge blunt end needle. The potential from a high voltage (15 kV) power supply was applied to the needle *via* an alligator clip. A square (12.5 cm × 12.5 cm) piece of aluminum foil bundled around a grounded metal rotary drum (diameter: 8 cm, rotating rate: 500 r/min) was used as a rotating collector. The collecting distance was kept at 15 cm and the flow rate was 1 mL/h. All the samples were dried in a vacuum oven at 40 °C for 48 h to remove the residual solvent.

Characterization

Field emission scanning electron microscopy (FESEM)

The morphology of the electrospun fibers was observed using a field emission scanning electron microscope (JEOL JSM 7401, Japan) operating at an accelerating voltage of 3 kV or 1 kV. The diameters of the electrospun fibers were determined using JEOL software (SMILEVIEW). For a better observation, all the samples were coated with Au.

Transmission electron microscopy (TEM)

In order to investigate the dispersion of CB in the electrospun fibers, a small amount of cetyltrimethylammonium bromide (CTAB) (0.5 wt%) was added into the PET/CB dispersion to obtain thinner fibers for TEM observation. The fibers were directly electrospun onto Cu grids covered with an ultra-thin carbon layer, and investigated by a Hitachi H-800 transmission electron microscope (Japan) at an accelerating voltage of 80 kV.

Differential scanning calorimetry (DSC)

DSC was carried out on the electrospun fiber mats to study the thermal properties of different samples using a Q100 calorimeter (TA Instruments, USA). The samples were heated to 330 °C at a heating rate of 10 K/min in nitrogen atmosphere. The temperature at which half the increase in heat capacity has occurred is defined as the glass transition temperature (T_g).

The enthalpy of fusion of the crystals formed during electrospinning was calculated as follow:

$$\Delta H_{f,e} = (\Delta H_f - \Delta H_{cc}) / (1 - w_{CB}) \quad (1)$$

where Δ_f and ΔH_{cc} is the enthalpy of fusion and enthalpy of cold-crystallization occurring around 115 °C in DSC curve, w_{CB} is the weight ratio of CB in the composite.

Then, the degree of crystallinity of the electrospun mat can be calculated as follow:

$$X_c = \Delta H_{f,e} / \Delta H_f^0 \quad (2)$$

where ΔH_f^0 is the enthalpy of fusion of perfect crystalline structure of PET at equilibrium thermodynamic melt temperature T_m^0 and was taken as 140 J/g^[14].

Tensile tests

Specimens (5 cm × 1 cm) with thickness of approximately 0.1 mm were cut carefully from the electrospun fiber mats. Before tensile tests, all specimens were conditioned at 25 °C for 72 h under a relative humidity of 50%. A TCS-2000 tensile tester (Gotech) was used to determine the tensile properties of different samples, with a tensile speed of 5 mm/min and a fixture distance of 10 cm.

Electrical resistivity

For bulk samples obtained from melt mixing, disk samples with a diameter of 30 mm and a thickness of 2.5 mm (Style A) or a diameter of 75 mm and a thickness of 0.38 mm (Style B) were prepared for low- and high-resistivity measurements, respectively. Samples with higher electrical resistivity ($> 10^8 \Omega \cdot \text{cm}$) were measured by the ZC-36 resistivity test (Shanghai Cany Precision Instrument). For more conductive samples ($< 10^8 \Omega \cdot \text{cm}$), the electrical resistivity was measured using a four-point test measuring instrument (KDY-1, Guangzhou Kunde Co., Ltd).

The electrical resistivities of the PET/CB fiber mats were tested by four-point method. PET/16%CB fiber mats pressed under a pressure of 1.6 MPa at room temperature, 160 °C and 250 °C for 10 min were also tested by the four-point method.

RESULTS AND DISCUSSION

Morphology of PET/CB Fibers

The key problem in electrospinning of polymer/inorganic composites is the homogeneous dispersion of

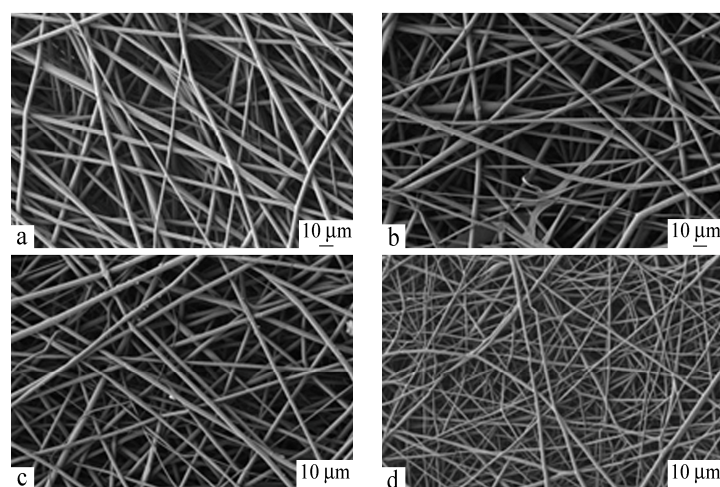
inorganic particles in electrospinning solutions. Melt pre-compounding followed by dissolution has been shown to be an effective way to resolve this problem^[28, 29]. Thus, PET and CB were pre-compounded by melt mixing at 250 °C in a rheometer to get CB dispersed in PET. The pre-compounded composites can disperse in HFIP at room temperature into homogeneous and stable black suspensions. No obvious precipitation of CB was observed after storage for at least three days. Upon electrospinning, dark-colored fiber mats were obtained, as contrasted to the white color of neat PET fiber mat. The color of PET/1% CB fiber mat is grey, all other samples with more CB are black. Pedicini *et al.*^[10] reported white fiber mats from black polymer solutions containing CB such as PC/2% CB solution. The phenomenon is attributed to light scattering produced by the porous mat which effectively “mask” the appearance of CB. According to the authors^[10], the condition for obtaining white fiber mats from black polymer/CB solutions is the fibrous morphology with fiber diameters in submicron size. In our work, the average fiber diameters for all the samples are around 2–3 μm (Table 1, averaged from 100 fibers), which do not meet the condition for obtaining white fiber mats, and CB plays efficiently a role of black pigment.

Table 1. Average diameters of the different fibers (μm) with standard deviation

Entry	PET	PET/1% CB	PET/3.5% CB	PET/6% CB	PET/8.5% CB	PET/16% CB	PET/6% CB-S1	PET/6% CB-S2
Fiber diameter*	2.2 ± 0.5	2.8 ± 0.6	2.7 ± 0.6	2.6 ± 0.5	2.4 ± 0.6	2.3 ± 0.6	3.2 ± 0.7	2.6 ± 0.6

* Averaged from 100 fibers for each sample

The FESEM micrographs of PET/CB composite fibers containing different amounts of CB (0 wt%, 1 wt%, 3.5 wt%, 6 wt%, 8.5 wt% and 16 wt%) at two different magnifications are shown in Fig. 1 and Fig. 2. At low magnification, cylindrical fibers were observed for all the samples except the one with 16 wt% CB where some elongated beads appear due to presumably reduced viscosity of the electrospinning dispersion. In the design, the concentration of PET/CB dispersion is kept constant. With a high CB content like 16 wt%, PET content is considerably reduced, as a result, the solution viscosity considerably reduced. The average fiber diameters for all the samples are similar, regardless of CB content (shown in Table 1). At high magnification, homogeneously-distributed clusters of CB in the size of submicron range were observed on PET/CB composite fiber surfaces even for PET/1% CB. With increasing CB content, more CB clusters were observed. In the literature^[14, 30, 31], beads-on-string structure or ridge-like structure with inorganic particles in the beads or ridges were often observed in polymer/inorganic composite fibers when the dispersion of inorganic particles is poor. In this work, almost no obvious beads-on-string structure or ridge-like structure with CB in the beads or ridges were observed, although CB exists in the form of clusters, because the fiber diameter is much bigger than the size of the clusters.



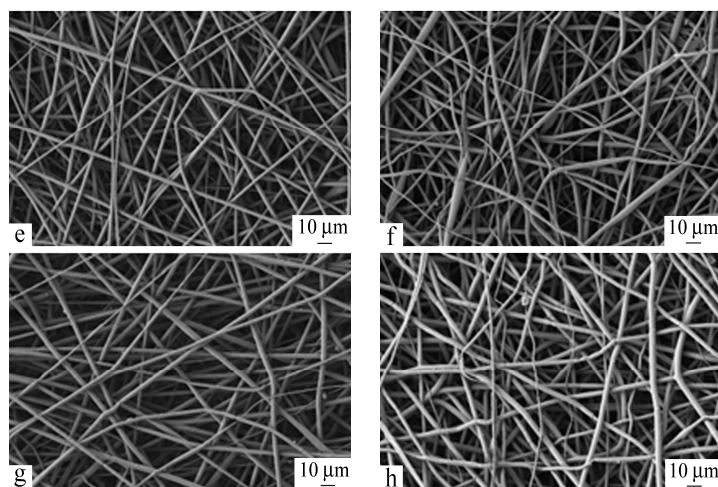


Fig. 1 FESEM micrographs of the electrospun PET/CB fibers with different carbon black contents (low magnification): (a) 0 wt%, (b) 1 wt%, (c) 3.5 wt%, (d) 6 wt%, (e) 8.5 wt%, (f) 16 wt%, (g) PET/6% CB-S1, and (h) PET/6% CB-S2

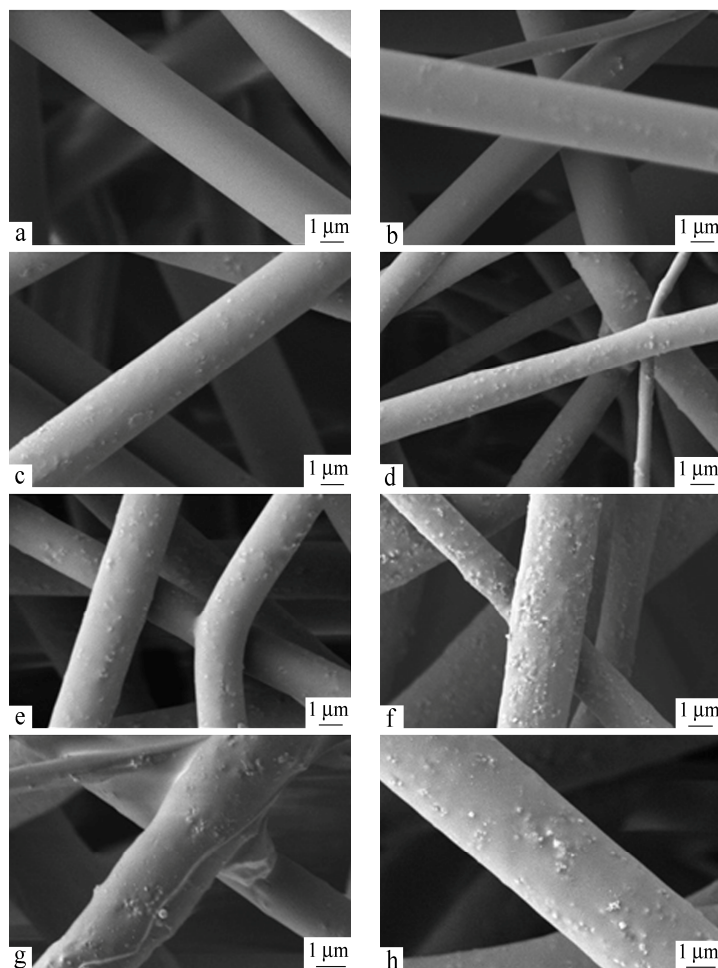


Fig. 2 FESEM micrographs of the electrospun PET/CB fibers with different carbon black contents (high magnification): (a) 0 wt%, (b) 1 wt%, (c) 3.5 wt%, (d) 6 wt%, (e) 8.5 wt%, (f) 16 wt%, (g) PET/6% CB-S1, and (h) PET/6% CB-S2

Dispersion of CB in the Fibers

Because FESEM micrographs only give information on the dispersion of CB localized on the fiber surface, TEM was envisaged to further investigate the dispersion of CB in the composite fibers, and the micrographs are shown in Fig. 3. Clearly, CB particles are observed as submicron-sized clusters in all the fibers regardless of CB content. It is hard to see any primary particles. This is typically the feature of CB particles^[1, 3, 32, 33]. TEM results are in agreement with FESEM results discussed above in view of CB dispersion, basically retaining the dispersion state in melt-compounded PET/CB composites (Figs. 3e and 3f).

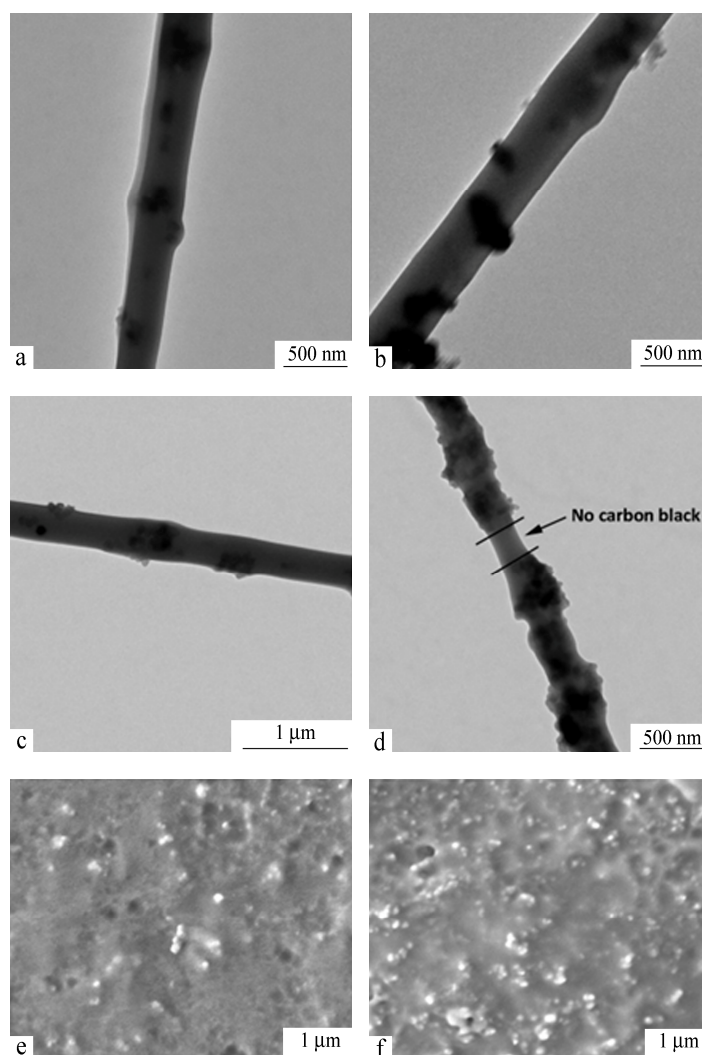


Fig. 3 TEM micrographs of the electrospun PET/CB fibers and FESEM micrographs of melt-compounded PET/CB bulks with different carbon black contents: (a) 1 wt%, (b) 3.5 wt%, (c) (e) 6 wt% and (d) (f) 16 wt%

Thermal Properties of PET/CB Fiber Mats

Thermal properties of the materials are important for their usage and also affect their mechanical properties. In this work, DSC was used to investigate the thermal behavior of the PET/CB composite fibers, and the thermograms are shown in Fig. 4.

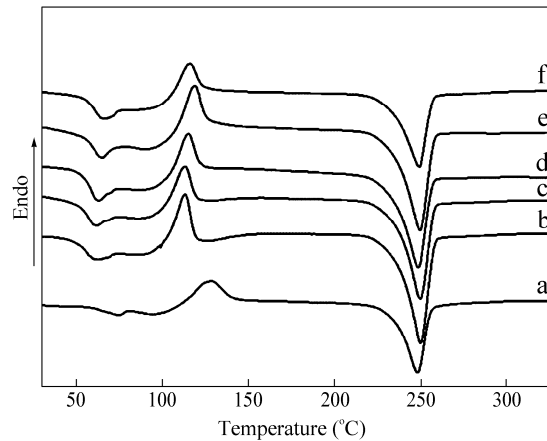


Fig. 4 DSC curves of the electrospun PET/CB fibers: (a) PET, (b) PET/1% CB, (c) PET/3.5% CB, (d) PET/6% CB, (e) PET/8.5% CB and (f) PET/16% CB

Glass transition, cold crystallization and melting are obvious in all the curves, showing typical heating behavior of PET. Compared to neat PET fibers, PET/CB composite fibers have lower glass transition temperature (T_g) and lower cold crystallization temperature (T_{cc}), indicating degradation of PET during melt compounding. Neat PET fibers were prepared by dissolving the commercial PET resin in HFIP without being heated in the rheometer. As a general rule, T_g increases with molar mass when it is below the critical value. The segments have bigger mobility when molar mass is lower, leading to the decrease of T_{cc} . However, as seen from Table 2, for PET/CB composite fibers the melting temperature (T_m) is all around 249 °C and the enthalpy of melting is all around 25 J/g, which are similar to those of neat PET fibers, indicating almost unchanged degree of crystal perfection and crystallinity. It is noted that the variation of CB content has no obvious effect on thermal properties of the PET/CB composite fibers.

Table 2. Thermal properties of the PET/CB composite fibers with different CB contents

Entry	T_g (°C)	T_m (°C)	ΔH_{fe} (J/g)	X_c (%)
PET	62.4	248.2	22.6	16.1
PET/1% CB	56.3	249.9	27.4	19.6
PET/3.5% CB	57.5	249.8	27.9	19.9
PET/6% CB	59.0	248.7	23.2	16.6
PET/8.5% CB	61.2	249.7	23.8	17.0
PET/16% CB	61.4	249.2	24.2	17.3

Mechanical Properties of PET/CB Fiber Mats

Uniaxial tensile tests were used to evaluate the mechanical properties of PET/CB fiber mats. The results are given in Table 3, and the typical stress-strain curves are shown in Fig. 5.

Table 3. Mechanical properties of the PET/CB composite fiber mats

Entry	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PET	63.3 ± 12.9	3.3 ± 0.2	512 ± 88
PET/1% CB	98.4 ± 8.8	3.5 ± 0.2	259 ± 41
PET/3.5% CB	103.5 ± 5.2	3.3 ± 0.2	291 ± 55
PET/6% CB	98.1 ± 9.1	3.9 ± 0.3	185 ± 33
PET/8.5% CB	98.2 ± 8.1	3.2 ± 0.1	206 ± 47
PET/16% CB	61.0 ± 5.4	2.2 ± 0.1	152 ± 14
PET/6% CB-S1	59.4 ± 6.5	2.5 ± 0.2	190 ± 47
PET/6% CB-S2	93.1 ± 9.8	3.8 ± 0.1	458 ± 77

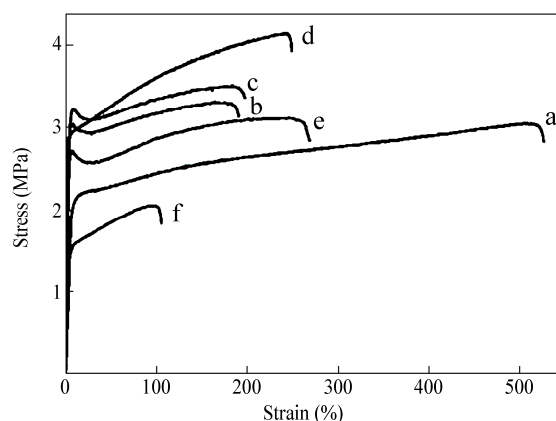


Fig. 5 Representative stress-strain curves of PET/CB fiber mats: (a) PET, (b) PET/1% CB, (c) PET/3.5% CB, (d) PET/6% CB, (e) PET/8.5% CB and (f) PET/16% CB

The tensile moduli of the PET/CB composite fiber mats containing 1 wt%–8.5 wt% CB are significantly greater than that of neat PET (98–103 MPa versus 63 MPa), an increase of 55%, despite of the degradation of PET during melt pre-compounding. The tensile modulus of the PET/16% CB sample is only 61 MPa, much lower than those of samples containing less CB, due to severe aggregation of CB particles and also the imperfect fiber morphology (elongated beads-on-string structure presents as seen from Fig. 1). As to tensile strength, only PET/6% CB sample shows moderate increase compared to neat PET, although CB dispersion is reasonably good. In general, the tensile strength is not only affected by filler dispersion, but also affected by the interfacial interaction between polymer and filler. Because no special surface treatment of CB was taken, the weak interfacial interaction is not beneficial for the increase of tensile strength.

Chuangchote *et al.*^[2] reported a 100% increase in tensile modulus for PVA/CB composite fiber mat containing 8 wt% CB (to PVA), and decreases of both tensile strength and elongation at break upon the incorporation of CB. Hwang *et al.*^[11] found a 400% increase in tensile modulus for PU/CB composite fiber mat containing 9.5 vol% CB and a decrease of elongation at break. Schiffman *et al.*^[11] showed a better conductivity but no improvement in mechanical properties for CS/CB composite fiber mats. In fact, many factors could affect the mechanical properties of the composite fiber mats, including the composition of the composite, interfacial interaction between the components, nature (such as type and crystallinity) of the base polymer, fiber diameter, porosity of the mat, bond structure between fibers, orientation of the fibers, dispersion of the filler, *etc.*, making analysis of the mechanical properties very complicated. In our work on PET/CB composite fiber mats, the increase of tensile modulus is less than that of the cases of PVA/CB and PU/CB fiber mats mentioned above, but it is still significant, meaning that the incorporation of CB to PET fiber mat can increase the stiffness of the material, *i.e.* the ability against fiber orientation in the initial stage of loading^[34].

Non-conductivity of PET/CB Fiber Mats

The electrical resistivities of all the PET/CB composite fiber mats were measured by the four-point method^[35], and all the samples are non-conductive with a very high electrical resistivity ($\lg \rho_v = 17.8$) even for the sample containing 16 wt% CB. For comparison, the electrical resistivity-CB content curve for PET/CB composites prepared by melt mixing is given in Fig. 6, and the percolation threshold calculated from power law is 8.3 wt% CB.

The non-conductivity of the PET/CB composite fiber mats could be attributed to three reasons. 1) Huge inter-fiber pores: The pores of electrospun fiber mats are generally in micron size^[36]. They certainly unfavor the formation of conductive paths. 2) Big distance among CB clusters: It's commonly known that electrospinning process involves very high elongation rates (1000 s^{-1}) and jet cross-sectional area reduction by six orders of magnitude^[3], so the distance among CB clusters is certainly much bigger than in bulk sample. Besides, the

distance between two neighboring CB clusters could be much bigger than the average distance due to inhomogeneous distribution of CB clusters, as evidenced in Fig. 3(d). 3) Lack of bond structure: As evidenced by Fig. 1, no fiber-to-fiber bond structure was observed for all the PET/CB fiber mats due to fast evaporation of the electrospinning solvent HFIP. The interface resistivity among fibers is huge.

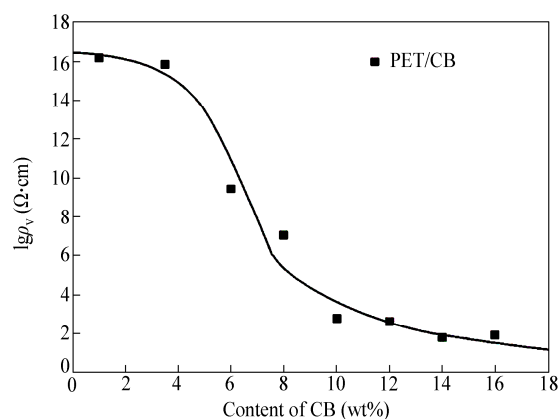


Fig. 6 Electrical resistivity as a function of CB content for PET/CB composites prepared by melt mixing

To support this point, the PET/16% CB fiber mat was melted at 250 °C in a hot press without mixing to destroy the fibrous structure and pores. After cooling, the obtained bulk sample is conductive ($\lg \rho_v = 1.9$); while it is still non-conductive ($\lg \rho_v > 10$) after cold pressing at room temperature or 160 °C which minimizes the porosity but still keeps the interfaces among fibers.

Conductive PU/CB, CS/CB and PCL/CB composite fiber mats have been reported by Hwang *et al.*^[1], Schiffman *et al.*^[11], and Tiwari *et al.*^[3] It is noted that neat PU and neat CS fiber mats are already conductive with $\lg \rho_v$ of 7 and 8, and after the incorporation of CB the electrical resistivity is 4–5 orders of magnitude lower; while the $\lg \rho_v$ of PCL/CB fiber mats can only be lowered to 6–7 (to the antistatic range). In PU/CB fiber mats, a high density of bond structure presents^[1]; while in PCL/CB fiber mats, the dispersion of CB is fairly homogeneous^[3], facilitating the formation of conductive paths.

Fiber Mats from Differently-prepared Electrospinning Dispersions

The way of preparing electrospinning dispersions is important in view of CB dispersion, which is a decisive factor affecting electrospinning and the properties of the final composite fiber mats. Therefore, the current preparation method is compared with direct solution compounding with or without sonication using the composition of PET/6% CB. No tip blockage caused by CB was observed during electrospinning regardless of sonication, indicating that the dispersion of CB in such-prepared dispersions is acceptable for electrospinning process. Compared to the sample PET/6% CB obtained from the melt pre-compounding method, the average fiber diameters of the two samples (PET/6% CB-S1 and PET/6% CB-S2) (Fig. 1 and Table 1) have no much difference; the dispersion of CB is similar in the case of sonication, but clearly poorer without sonication, indicating the necessity of ultrasonic treatment in the direct solution compounding methods; the degree of crystallinity has almost no change for both samples; the mechanical properties are comparable in the case of sonication, but significantly lower without sonication due to the poor dispersion of CB (Fig. 1). Thus, melt pre-compounding followed by dissolution is a viable approach for preparing the electrospinning dispersions having reasonably good dispersion of CB, producing fiber mats having similar morphology, crystallinity and mechanical properties to sonication method. The advantage of melt pre-compounding method is the suitability to large scale preparation.

CONCLUSIONS

PET/CB composite fiber mats containing 0 wt%–16 wt% CB can be prepared by dispersing melt pre-compounded PET/CB composites in HFIP and subsequent electrospinning. CB in the fibers is in the form of submicron-sized clusters. The average fiber diameter and crystallization behavior of PET during electrospinning do not vary obviously with the change of CB content. All the composite mats are electrically non-conductive even the one with 16 wt% CB, being much greater than the percolation threshold of the bulk sample. The tensile moduli of the composite fiber mats containing 1 wt%–8.5 wt% CB increase significantly compared to that of neat PET fiber mat. Excessive amount of CB such as 16 wt% is not favorable for the improvement of mechanical properties due to severe aggregation of CB particles. PET/CB composite fiber mat having 6 wt% CB is found to be a proper composition to have the best mechanical properties with 55% increase in tensile modulus and 20% increase in tensile strength.

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