Percolation Threshold of Electrically Conductive Master Batch for Polyester Fibers Application

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ABSTRACT: In the case of the electrically conductive master batch (ECMB) for fibers application, higher filler content required to produce adequate conductivity can be accompanied by a reduction in spinnability and mechanical property of final fibers. To minimize these problems, ECMB with the character of lower percolation threshold was designed in this article. Carbon black (CB) was treated by titanate coupling agent. Polymer blend poly(ethylene terephthalate) (PET)/polyethylene(PE) was used as matrix instead of individual polymer matrix. The effects of titanate coupling agent treatment and the composition of polymer blend on the properties of ECMB have been discussed. FTIR and laser particle size distribution analyzer were employed to study the CB. Solubility tests and positive temperature effect peak were used to verify the distribution of CB in the polymer blend. These results showed that CB treated with 2 wt % titanate coupling agent and PET/PE polymer blend with the weight ratio of 60/40 appear to be an effective way to design the ECMB with a low percolation threshold. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4144–4148, 2006

Key words: carbon black; polyester; electrically conductive master batches; titanate coupling agent; polymer blend; percolation threshold

INTRODUCTION

Polyester fibers are widely used both in the textile industry and outside the classical textile fields. However, fabrics composed of polyester fibers are easy to accumulate static electricity because of its low conductivity. Thus, the development of methods for preparing the electrically conductive polyester fibers is an area of active research in the textile industry.[1–5]

There have been proposed varieties of electrically conductive polyester fibers. One of them is by means of an electrically conductive coating layer forming on the fiber substrate. Unfortunately, the coating is easily flaking during washing.[2,3] Another example is electrically conductive composite fibers, such as sheath-core and side-by-side composite fibers.[4,5] Though electrically conductive composite fibers are commercially successful, the cost is still higher due to a special process. Further, another example is produced from a polymer containing electrically conductive filler dispersed uniformly therein. To obtain desirable electrical properties, higher filler content is usually required, which is likely to be accompanied by the mechanical property of fiber getting poor.[4–6] However, we are still interested in this method because it has characters of easy operation and lower cost.

It is important to know that the filler concentration and dispersion quality in the electrically conductive master-batch (ECMB) are the main factors that have an effect on the electrical and mechanical properties of the final fibers.[7–12] Therefore, the attention to the property of ECMB is given in this article. Lowering the percolation threshold of the ECMB appears to be an effective way to reduce the amount of filler required for adequate conductivity and thereby minimize problems with mechanical properties. Today researches on ECMB or electrical conductive composite are mainly focused on thermoplastic polymer in plastic industry, for example PS, PVA, PP, EVA, PE, etc.[7–10] To our knowledge, there are few studies on ECMB for electrically conductive polyester fibers application. The aim of our research is to design a kind of ECMB with lower-percolation threshold, which meant less CB added into the ECMB, and also achieve the required volume resistivity. Thus, the processability and the mechanical property of the final fibers can be improved.

The percolation threshold of ECMB is sensitive to material factors such as the structure, aggregation, size and size distribution of filler particles and can likewise be affected by polymer matrix and the processing route used to fabricate the composite.[9] In this article, carbon black (CB) was treated by titanate coupling agent. ECMB was prepared by melt-blending with individual polymer [poly(ethylelene terephthalate) (PET), polyethylene (PE)] and PET/PE polymer blend, respectively. The effects of the titanate treat-

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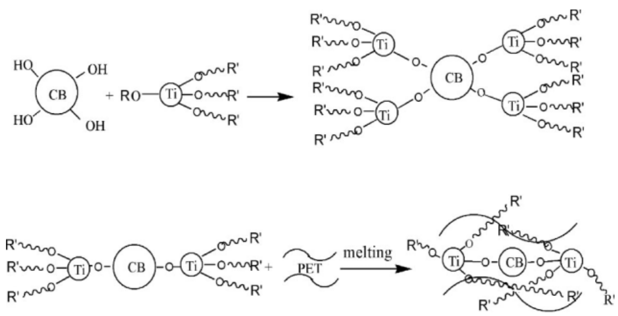


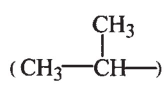
Figure 1 Schematic diagram of mechanism of titanate coupling agent treatment.

ment and PET/PE polymer blend on the percolation threshold were discussed.

EXPERIMENTAL

Materials

Electrically conductive CB beads were used as conductive filler, and were obtained from Huaguang Chemical Factory, China. The primary particle size of the obtained CB was 29 nm and DBP value was 380 mL/100 g. Poly(ethylene terephthalate) (PET) powders, $[\eta] = 0.67$ dL/g, having a density of 1.38 g/cm^3 and polyethylene (PE) powders, having a density of 0.93 g/cm^3, were supplied by Tianjin Dagang Petrochemical Company, China. Nanjing Shuguang Chemical Factory, China supplied the titanate coupling agent. General formula of titanate coupling agent in this study is: RO-Ti-(O-R′)$_3$, where the structure of R is presented as



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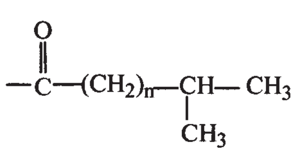

Preparation of ECMB

CB was put into drymixer and stirred at high speed for 5 min (untreated CB). Then PET, PE, and PET/PE were added to the untreated CB, respectively, and further drymixed to achieve reasonably uniform dispersion. Mixed untreated CB/polymer were subsequently passing through a conventional twin-screw extruder ($L/D = 37$, $D = 30$ mm). The polymer strands entered a water bath and a pelletizer produced CB/PET, CB/PE, CB/PET/PE ECMB. In the case of titanate coupling agent treatment, the titanate coupling agent was added into CB as alcohol solution under high-speed stirring for 5 min (titanate-treated CB marked T-CB). The amount of the coupling agent fraction on the CB basis. The alcohol in the titanate coupling agent was removed under vacuum in an oven. Then PET was added to the above T-CB and the mixer was started again to make them mixing for some time. Similarly, T-CB/PET ECMB was prepared through melt blending method. All the ECMB were dried in vacuum oven for at least 6 h before use.

Characterization

The size of CB was measured by using a laser particle size distribution analyzer (Coulter, LA-300). The infrared transmission spectra of untreated and titanate coupling agent-treated CB were recorded on a Bruker Vector-22 spectroscope.

Room temperature volume resistivity, ρ, (ohm cm) of ECMB was measured with four-point probe technique and we suppose that the effect of contact resistance is insignificant for different polymer systems in this article. The temperature dependence of ECMB resistivity was measured by heating the samples at a rate of 3°C/min.

The distribution of CB in PET/PE blends was evaluated through solubility tests using 15/80/20 and 15/20/80 (weight ratio) CB/PET/PE ECMB. A solution of 50/50 phenol/tetrachloroethane, which was selective solvent for PET, was added to the 15/80/20 ECMB at ambient temperature and left for 48 h. To the ECMB with composition of 15/20/80, xylene was added, a selective solvent for PE, at 120°C and left for 20 h.

The tensile strength of melt-spun fibers was measured by tensile instrument (PC/LLY-06, Laizhou Electron Instrument, China).

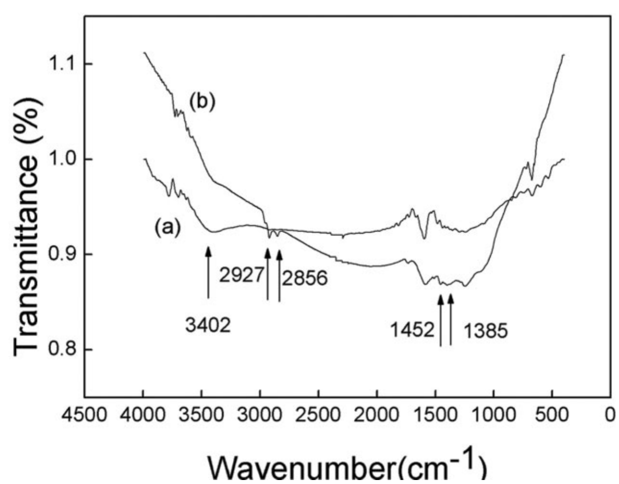

Figure 2 FTIR spectra of (a) untreated CB; (b) titanate coupling agent-treated CB.

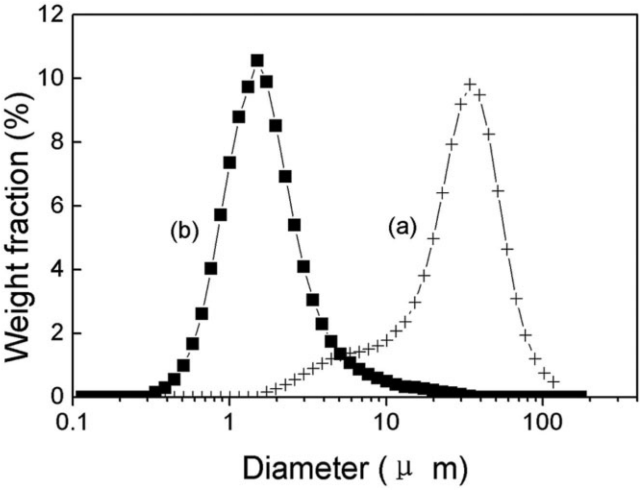

Figure 3 Size distribution of (a) untreated CB; (b) titanate coupling agent-treated CB.

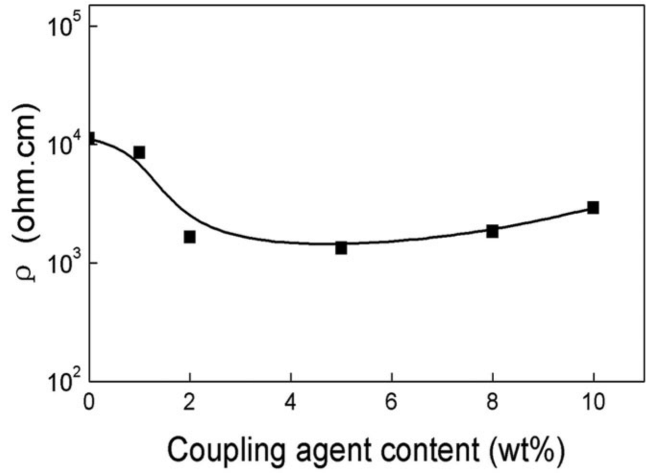

Figure 5 Effects of coupling agent content on volume resistivity of CB/PET (CB content = 15 wt %).

RESULTS AND DISCUSSION

Effect of titanate coupling agent treatment

The mechanism of titanate coupling agent treatment is represented in Figure 1. Under certain temperature, the R part of titanate coupling agent reacts with hydroxyl groups at CB surface, resulting in the formation of monomolecular layer on the CB surface. Meanwhile, when CB disperse in PET by melting process, the R′ part of coupling agent, the organic long chain, could play a part of tangling with PET chain, thereby eliminating air voids in the ECMB.[11,13]

Figure 2 shows the FTIR transmission spectroscopy of the untreated and titanate coupling agent-treated CB, respectively. The curve (a) presents that peak near 3402 cm^{-1}, which is due to vibration mode of hydroxyl groups. The result indicates that there are hydroxyl groups existing on the surface of CB particles. The curve (b) of titanate coupling agent-treated CB presents that the peak at 3402 cm^{-1} becomes weak apparently, which is attributed the hydroxyl groups on CB surface that reacted with titanate coupling agent according the above mechanism. Meanwhile, the bands near 2927, 2856, 1385, and 1452 cm^{-1} correspond to the stretching vibration and bending vibration of methylene in the R′ part of titanate coupling agent.

Figure 3 displays the size distribution of untreated CB and titanate coupling agent-treated CB, respectively. From Figure 3, it can be observed that the average size of untreated CB is 34.43 μm and has a wide distribution range, which suggests that the CB aggregates clustered into agglomerates due to their enormous surface energy. But, the average size of titanate coupling agent-treated CB decreases to 1.51 μm and the size distribution become monomodal, in-

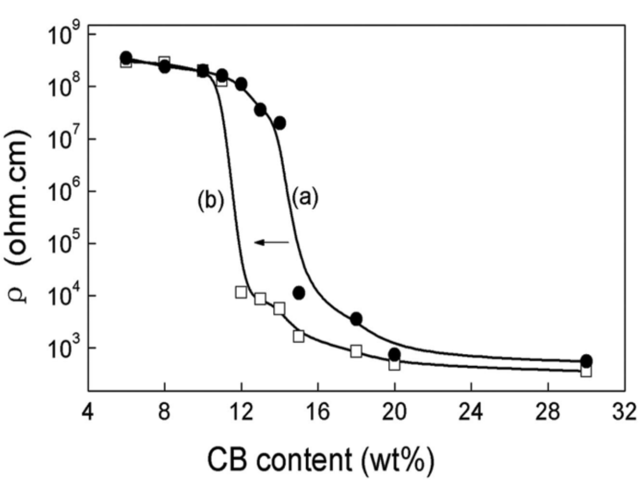

Figure 4 Plot of resistivity of ECMB against CB content: (a) CB/PET; (b) T-CB/PET.

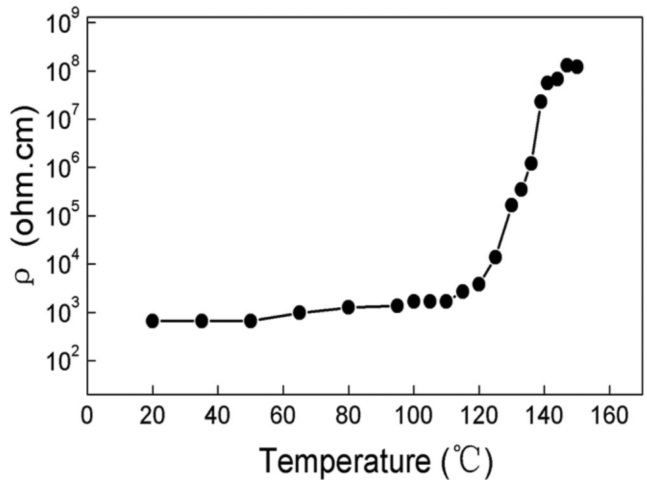

Figure 6 The positive temperature effect of CB/PET/PE ECMB.

TABLE I
Effect of Polymer Blend Composition on Volume Resistivity of CB/PET/PE ECMB[a]

Composition of CB/PET/PE ECMB	15/0/100	15/20/80	15/40/60	15/60/40	15/80/20	15/100/0
Volume resistivity (ohm cm)	8.3×10^6	4.5×10^7	5.2×10^6	2.6×10^2	1.2×10^3	1.6×10^3

[a]All compositions are expressed in wt %.

dicating that the monomolecular layers on the CB surface can prevent the broken down aggregates from clustering into agglomerates again.[11]

Figure 4 gives the dependence of volume resistivity on CB content for untreated CB and titanate-treated CB. It can be seen that there is a shift for the percolation curve toward the lower loading side when CB was treated with titanate coupling agent. The hydroxyl groups at the CB surface was found to raise the barrier potential of electrons movement from one aggregate to another, or formed an insulating shield around the CB particles.[9,13] The FTIR analysis indicates that titanate coupling agent is able to reduce hydroxyl groups fraction fixed on CB surface, which lowered the contact resistance of CB agglomerate. Meanwhile, the CB size distribution measurement results support that titanate coupling agents may be able to prevent the broken down aggregates from clustering into agglomerates again. These results show that the titanate coupling agent treatment increases the possibility of electrical network formation throughout the matrix polymer.[13,14] Therefore, the effect of titanate coupling agent is equivalently taken as a shift of percolation threshold toward lower loading region.

However, it should be noted that an excessive content of titanate coupling agent might not of benefit to lower the percolation threshold. Figure 5 shows the effect of coupling agent content on the volume resistivity of CB/PET ECMB. We can see that the volume resistivity has decreased initially and then has a increasing trend beyond 8 wt %. This is because the surface of CB are completely covered by excess coupling agent and hinder CB aggregates to form conductive networks in ECMB.[9] Therefore, the optimum content of titanate coupling agent for lowering percolation threshold is 2 wt %.

Effect of PET/PE polymer blends

Another development in the design of low-percolation threshold involves the use of immiscible polymer blends in which the conductive particles selectively reside in one of the polymer phase or along the interface. Interfacial energy constitutes one of the most important factors in determining the nonrandom distribution of filler particles in an immiscible polymer blend.[9] To design ECMB with lower percolation threshold by the measure of using PET/PE polymer blend, it is important to know which phase that CB would distribute between the two polymers. The solubility results showed that 50/50 phenol/tetrachloroethane, the solvent for PET, was white and xylene, the solvent for PE, turned to black. The result indicates that CB is presented in the PE phase. Meanwhile, positive temperature effect can also be used to confirm the CB distribution in polymer blend.[9] As shown in Figure 6, the positive temperature coefficient peak is observed around 120°C, which is the melting point of the PE, but not at 258°C, the melting point of PET. This also confirms that CB is located in the PE phase.

To design the ECMB with lower percolation threshold, it is also important to confirm the proper blend composition. Table I shows the effect of composition of PET/PE on the volume resistivity of ECMB. According to the data in Table I, the volume resistivity of ECMB is sensitive to the blend composition. The volume resistivity of the CB/PET/PE ECMB decreases by more than four orders of magnitude from 10^6 to 10^2 (ohm cm), as the concentration of PET increases from 0 to 60 wt %. The volume resistivity of CB/PET/PE exhibits a minimum in the vicinity of 60 wt % PET and then increases a little as the concentration of PET is increased further. The above phenomena can be explained by volume exclusion effects[9,15] and from the above discussion, CB are expected to reside almost exclusively in the PE matrix. In CB/PET/PE ternary

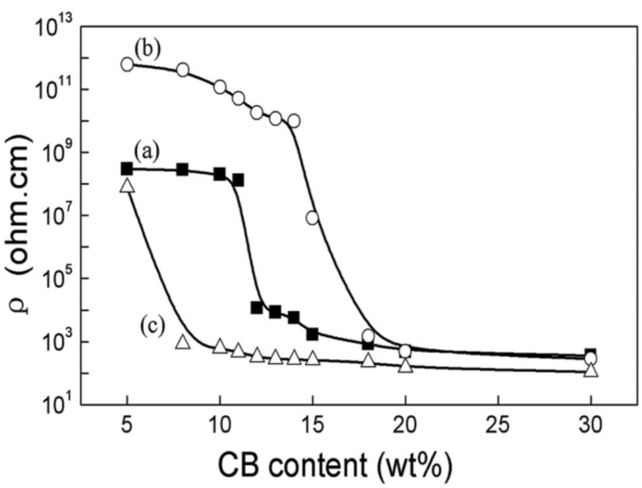

Figure 7 The effect of CB concentration on volume resistivity of (a) CB/PET; (b) CB/PE;(c) CB/60PET/40PE.

TABLE II
Mechanical Properties of the As-Spun Fibers

Fiber	PET	CB/PET (CB = 15%)	T-CB/PET (CB = 12%)	CB/PET/PE (CB = 8%)
Volume resistivity (ohm cm)	$>10^{12}$	1.9×10^4	1.9×10^4	5.4×10^3
Strength at break (cN/dtex)	1.26	0.85	0.92	1.08

composites, as the concentration of PET increases, the volume of PE-rich matrix available for CB particles to occupy decreases and the relative concentration of CB residing in continuous PE-rich channels increase, which make CB form conductive pathway more easily. So, the volume resistivity of CB/PET/PE decreases with the PET composition increasing. However, as the composition of PET is increased further, the filled PE-rich regions become increasingly discontinuous due to volume exclusion and resulting in a break up of conductive pathway. So the optimum composition of PET/PE for lowering percolation threshold is 60/40.

Figure 7 gives the dependence of room temperature resistivity on CB content for different polymer matrix (PET, PE, and polymer blends 60PET/40PE). Apparently, the addition of PE in the ECMB dramatically affects the percolation threshold. The percolation threshold value of CB/PET/PE was about 8 wt %, while the value of CB/PET and CB/PE was up to 12 and 18 wt %. At a CB loading of 8 wt %, the CB/PET/PE exhibits a volume resistivity of 8.5×10^2 ohm cm, which is ~6 and 9 orders of magnitude lower than CB/PET and CB/PE master batch, respectively. As expected, PE in the ECMB was valuable for forming the conducting paths. Therefore, comparing with the individual polymer, the polymer blend (60PET/40PE) is an effective way to lower the percolation threshold.

Mechanical property of as-spun fibers

The mechanical properties of as-spun fibers were measured and the datas were listed in Table II. From Table II, we got to know that the tensile strength at break of as-spun pure PET fiber and CB/PET are 1.26 cN/dtex and 0.85 cN/dtex, respectively. So, the lower volume resistivity of CB/PET fiber is achieved only through sacrifices in the permanence of the mechanical property of the final fiber. Compared with CB/PET fiber, T-CB/PET fiber and CB/PET/PE fiber can reach the same level or lower level of the volume resisitivity at less CB content, thus resulting in the minimized problems with the mechanical property of the final fibers. Therefore, the ECMB with the lower percolation threshold is an effective way to maintain the desirable electrical property at less CB content and lighten the problem that arise from the high CB content.

CONCLUSION

To tackle the contradiction of higher CB content required for lower volume resistivity and the negative effect of higher CB content on the processability and the mechanical property of the final fibers, the ECMB for electrically conductive polyester fibers application with the character of low percolation threshold was designed and prepared. The following statements can be made from the present investigation:

1. Treatment of CB with titanate coupling agent can reduce the hydroxyl groups fraction at the CB surface and can prevent the broken down aggregates from clustering into agglomerates again. CB treatment by titanate coupling agent is an effective way to reduce the percolation threshold of ECMB and the proper titanate coupling agent is 2 wt % on the CB basis.
2. For the PET/PE polymer blend, CB was located in the PE phase. The composition of polymer blend has an important role on the volume resistivity and the optimum PET/PE composition for lowering percolation threshold is 60/40. ECMB with lower percolation threshold could be available in the case of blended matrix, rather than a monopolymer system.

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