Anomalous Attenuation and Structural Origin of Positive Temperature Coefficient (PTC) Effect in a Carbon Black (CB)/Poly(ethylene terephthalate) (PET)/Polyethylene (PE) Electrically Conductive Microfibrillar Polymer Composite with a Preferential CB Distribution

Kun Dai,[1,2] Yi-Chuan Zhang,[1] Jian-Hua Tang,[3] Xu Ji,[3] Zhong-Ming Li[1]

[1]*College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China*
[2]*School of Materials Science and Engineering, The Key Laboratory of Advanced Materials Processing & Mold of Ministry of Education, Zhengzhou University, Zhengzhou 450002, People's Republic of China*
[3]*College of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China*

Received 16 May 2011; accepted 21 November 2011
DOI 10.1002/app.36521

ABSTRACT: This article reports the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effects of a carbon black (CB)-filled electrically conductive microfibrillar poly(ethylene terephthalate) (PET)/polyethylene (PE) composite (FCMC). The composite contains *in situ* polymer microfibrils in the matrix of another polymer with CB particles selectively localized at microfibrils' surfaces. Anomalous attenuations of PTC and NTC intensities (I_{PTC} and I_{NTC}) of FCMC were observed during heating–cooling runs (HCRs) and long-term isothermal treatments. Particularly, when the isothermal treatment time was 32 h, the I_{PTC} decreased from 5.5 in the original sample to only 0.5, showing a tremendous attenuation ratio of up to 91%, and the NTC effect was completely eliminated. On the contrary, attenuations of PTC and NTC effects in a common conductive polymer composite (CCPC) were so weak as to be negligible through the same thermal treatments. Microstructural changes of the conductive network by Brownian motion and large size of the conductive component-CB coated PET microfibrils are both responsible for the great reductions in I_{PTC} and I_{NTC}. The present results strongly suggest that thermal field induced microstructural transformation by Brownian motion helps to reveal the origin of PTC and NTC effects. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: E561–E570, 2012

Key words: carbon black; microfibrillar blend; conductive polymer composites; positive temperature coefficient; negative temperature coefficient

INTRODUCTION

The resistivity-temperature behaviors of conductive polymer composites (CPCs) based on carbon category materials such as carbon black (CB),[1–8] carbon nanotubes,[9–11] carbon fibers[12–14] and graphite,[15,16] and semicrystalline thermoplastic have been extensively investigated due to their applications in antistatic materials,[17,18] electromagnetic interference (EMI) shielding,[19,20] overcurrent,[21] shape memory actuation materials,[22] and self-regulating heaters,[15,23–25] etc. There exist two very interesting resistivity-temperature phenomena in most CPCs: positive temperature coefficient (PTC) effect and negative temperature coefficient (NTC) effect, which are the sharp increase and the succeeding gradual decrease in resistivity respectively around the melting point of matrix polymer. These two effects are often observed and their underlying mechanisms have been explained by many researchers, such as Kohler,[26] Ohe and Natio,[27] Meyer,[28] and Voet,[29] however, due to the complicated nature of CPCs (chemical structure, crystallinity,[30] morphology of polymers;[31] size,[6] aggregate shape,[32] concentration and distribution of the conductive fillers;[3,31] etc.) and multiform testing conditions (top testing temperature,[33] and testing rate,[8,34] etc.), the origin of PTC and NTC is still in dispute.

During observing NTC and PTC, from the point of view of polymer dynamics, the viscosity and holding time, which are related to the relaxation behaviour of macromolecular chains of polymer layers surrounding conductive components,[4] affect the microstructural evolution of conductive network significantly. For a certain CPC, these two parameters are

---

Additional Supporting Information may be found in the online version of this article.

Correspondence to: Z.-M. Li (zmli@scu.edu.cn).

Contract grant sponsor: National Outstanding Youth Foundation of China; contract grant number: 50925311.
Contract grant sponsor: Nature Science Foundation of China; contract grant number: 20876099.

Journal of Applied Polymer Science, Vol. 125, E561–E570 (2012)

determined by the thermal programs predesigned for electrical properties-temperature performance measurement, whose most common form are heating–cooling runs (HCRs). Though the influence of heating rate and top temperature on HCR has been discussed,[8,33,34] the previous studies were mainly focused on the PTC and NTC effects of one or two HCRs. Systematic study of the microstructure development of the conductive network and the variation of the PTC and NTC effects in multifarious thermal fields has been barely touched up to now. If more HCRs are applied to a sample, more information about microstructural changes can be obtained. Furthermore, high temperature isothermal treatment, which can lead to drastic movement of the macromolecular chains of polymer layers surrounding conductive components, is an effective method to study the microstructures of conductive network.[4,10,14,35,36]

On the other hand, research about PTC and NTC effects is mainly limited to directly mixed CB filled single-phase or two-phase CPCs.[37] An advantage of these simple systems is a slight easier to understand the relationship between PTC, NTC, and microstructure of the conductive network, which is always common and monotonous.

In our previous work,[3,33,38–41] the concept of *in situ* microfibrillar reinforced blend was established, and a CB-filled electrically conductive *in situ* microfibrillar PET/polyethylene (PE) composite (FCMC) with a selective CB distribution was prepared, in which the CB particles assumed a gradient distribution in the outer layer of the *in situ* microfibrils.[41] Due to more perfect conductive network fabrication, a lower percolation threshold (3.8 vol %) than our previous work has been achieved.[38] The resistivity-temperature behavior of FCMC during cooling was also studied in detail, it is found the top test temperatures in HCR dominates the resistivity-temperature behaviors during cooling below 100°C. When the top test temperature is set at 140°C, the resistivity of FCMCs increases obviously during cooling below 100°C, showing cooling-induced resistivity increase. After a HCR with a top temperature of 140°C, the room-temperature resistivity of FCMC becomes four orders of magnitude higher than that of the original sample. Damage of the conductive network by the thermal residual stress occurring at the interfaces between PET microfibrils and PE matrix is the major reason.[33]

These results indicate that the subtle microstructure of FCMC, that is, the microfibrillar morphology of the dispersed phase and the particular CB distribution, is very sensitive to the external stimuli, such as the mechanical and thermal stimuli, and microstructural changes of FCMC can be induced. The unique microstructure offers a good opportunity to explore the relationship between microstructural variations and PTC and NTC effects.

In the present work, PTC and NTC effects of FCMC were studied systematically. Strong thermal treatments for eight HCRs and for long-term isothermal treatments (2, 8, 16, 24, and 32 h) at a high temperature of 180°C were applied. The same treatments were also applied to common CPCs (CCPC), i.e., CB-filled high-density PE, for comparison. After these treatments, I_{PTC} and I_{NTC} changes were studied to determine the influence of PE macromolecular chains' movement on the conductive component-CB coated PET microfibrils.

EXPERIMENTAL

Materials

The main polymers used in this work include high-density PE (HDPE) and PET. PE is 5000S, a commercial product of Daqing Petroleum Chemical Co., Daqing, China. Its melt flow rate is 0.9 g/10 min at 190°C, exerting a load of 21.6 N, and its number average molecular weight is 5.3×10^5 g/mol. PET was friendly donated by Luoyang Petroleum Chemical Co., Luoyang, China, which is a commercial grade of textile polyester with a number average molecular weight of *ca.* 2.3×10^4 g/mol. PET was dried in a vacuum oven at 100°C for at least 12 h before processing. The conductive filler, CB, model VXC-605, supplied from Cabot Co. Ltd., with a dibutyl phthalate (DBP) absorption value of 148 ± 15 cm^3/100 g, was dried at 120°C for 10 h to remove the water before use.

Preparation of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites

FCMC was prepared by the extrusion-hot stretching-quenching process, whose detailed procedures are reported in our previous articles.[33,41] A ribbon with a thickness of about 0.2 mm, in which microfibrils were generated and preserved, was finally prepared. The ribbon was pelletized and compression molded into $10 \times 10 \times 2$ mm^3 sheets at 150°C (the processing temperature of PE) for 10 min with a pressure of *ca.* 10 MPa. All these sheets were cooled to room temperature by cold compression molding for 5 min. Due to the high melting point of PET [about 257°C, by differential scanning calorimeter (DSC)],[3] the *in situ* PET microfibrils can be successfully reserved in the composite during molding. For comparison, CCPCs were also prepared by the same processes as the FCMCs except that the extrusion temperature was set at the processing temperature of PE.

Morphological observation

The specimens were frozen in liquid nitrogen for 1 h, then quickly impact fractured. Fracture surfaces were covered with a layer of gold to make them conductive, and then observed with a JEOL JSM-5900LV scanning electron microscope (SEM). In order to clearly examine the morphology of the dispersed phase, some specimens were immersed in hot xylene at about 125°C for 15 h to dissolve away the PE matrix.

Electrical properties and resistivity-temperature behaviors testing

Before electrical properties and resistivity-temperature behaviors testing, samples were annealed for 8 h at 80°C to remove effects of internal stress developed during the process history (mainly during compression molding). Four-probe method (ASTM D-991) with two multimeters and a voltage supply was used when the volume resistivity of samples is below 10^6 Ω cm. The four-probe method can effectively overcome contact resistance which affects the measurement precision. When volume resistivity is relatively low, this method is precise. When volume resistivity of samples is over 10^6 Ω cm, a high resistivity meter was used. The sample dimensions for low and high resistivity measurements were $2 \times 10 \times 100$ mm^3 and $2 \times 100 \times 100$ mm^3, respectively.

In the resistivity-temperature tests, samples of size $2 \times 10 \times 100$ mm^3, which were immersed in silicone oil in a temperature-controlled apparatus to avoid oxidation, were used. The thermal treatment journey in which a sample was heated from 20°C to 180°C at 2°C/min, held at this temperature for a predetermined time (3 min), then cooled to 20°C at the same rate, was defined as a heating-cooling run (HCR). It is well known that PTC and NTC effects occur during the heating process. In the present article, two kinds of thermal treatments were applied. Some samples were measured for eight HCRs, whose thermal treatment program is schematically illustrated in Figure 1(a) (the predetermined time, 3 min, was not shown here). To investigate the effect of thermal treatment further, other samples were isothermally treated at the top temperature 180°C for different times (2, 6, 16, 24, and 32 h); after cooled to 20°C at the same rate, 2°C/min, HCRs were also carried out to study the variations in PTC and NTC effects [Fig. 1(b), for example, here we take 2 h as isothermal treatment time]. The data were recorded online by a computer under a fixed applied voltage of 10 V.

In practice, the sample can hold its initial shape during resistivity-temperature test because PET microfibrils in the composite form a network, and remain solid state, even at 180°C.[33]

Thermal property testing

In order to study thermal behavior during HCRs and crystallinity changes before and after isothermal treatments, thermal analyses were carried out by a Netzsch DSC 204 differential scanning calorimeter. The samples were heated to 180°C at 2°C/min, held for 3 min, and then cooled at 2°C/min to room temperature. This heating-cooling journey well matches the above resistivity-temperature tests. The heat capacity versus temperature was recorded for each scan.

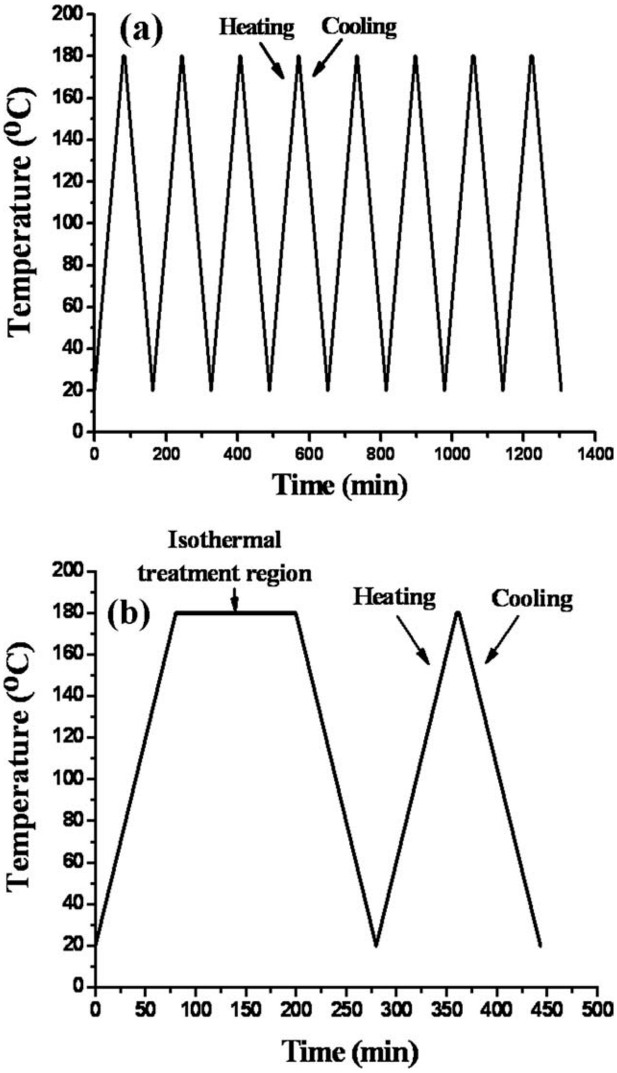


Figure 1 Thermal program for resistivity-temperature behavior test for eight runs (a) and resistivity-temperature behaviors testing after isothermal treatment (b). The isothermal treatment time is 2 h here as an example.

RESULTS AND DISCUSSION

Morphology and electrically conductive percolation

In order to better understand the resistivity-temperature behavior of FCMCs prepared in our work, it is necessary to summarize their typical morphology and percolation behavior firstly. As reported in our previous work,[33,41] PET phase assumes well-defined PET microfibrils in PE [Fig. 2(a), in which

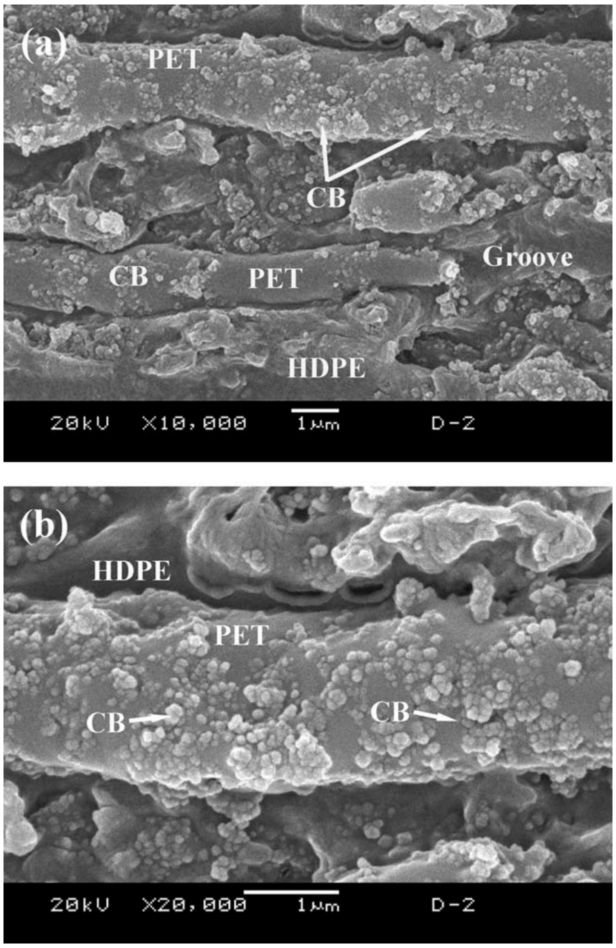


Figure 2 SEM micrographs of the cryofractured surface of FCMCs with selectively locating CB on surfaces of PET microfibrils with low (a) and high (b) magnifications. The volume ratio of PET and PE is 1 : 3.2, CB loading is 4.93 vol %.

grooves are formed by separation of PET microfibrils during the cryofracture process], and conductive CB particles are preferentially located in the surface region of the microfibrils, as shown in Figure 2(b) as an example. That is, after compression molding, the FCMC contains a conductive microfibrillar network formed by CB-coated PET microfibrils, resulting in a percolation threshold as low as *ca.* 3.8 vol % compared with a percolation threshold of *ca.* 8.5 vol % for CCPCs. In this work, the CB loading of FCMCs is fixed at 4.93 vol %, and 9.56 vol % for CCPCs, both, just beyond their respective percolation threshold to make the conductive network highly sensitive to the temperature field,[42] and make resistivity-temperature behaviors of these two composites comparable (In addition, if the CB content of FCMC is below 4.93 vol %, the PTC transition is too sharp to be recorded). Detailed descriptions of morphology and percolation behavior for these materials are available in the Supporting Information.

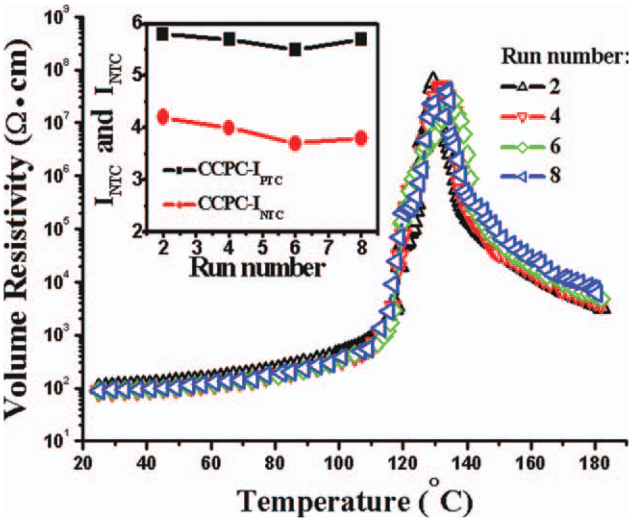


Figure 3 Resistivity-temperature relationship of common CB/PE conductive polymer composites for eight runs. For clear observation, here only the second, fourth, sixth, and eighth runs are presented. CB loading is 9.56 vol %. The insert shows the changes of I_{PTC} and I_{NTC}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Resistivity-temperature behavior during heating

First, in order to explore the effect of thermal field on microstructural change of conductive networks, eight HCRs, many more than the frequently used HCR amount in previous literature,[43,44] were applied to samples to test the temperature-resistivity behavior variation of FCMCs.

Figures 3 and 4 show the resistivity-temperature relationship of CCPCs and FCMCs respectively

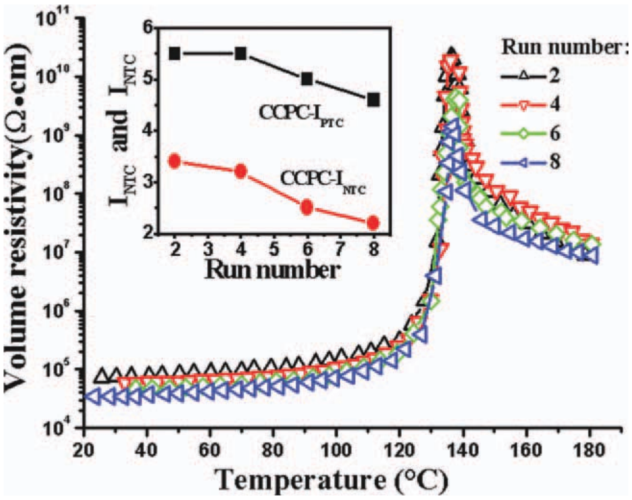


Figure 4 Resistivity-temperature relationship of FCMC for eight runs. For clear observation, here only the second, fourth, sixth, and eighth runs are shown. CB loading is 4.93 vol %. The insert shows the changes of I_{PTC} and I_{NTC}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

during eight HCRs (since the first run of CB filled CPC is always unstable and significantly different from the subsequent curves due to imperfect crystallization and internal stress generated during the process history,[16] the second run is set as the reference for next investigations in the present work. In addition, for simplification, only even number runs are presented here). In the second run, CCPCs and FCMCs display the PTC effect around the melting point, *ca.* 131°C,[33] of PE, with a 5.5 to 5.8 orders of magnitude sharp increase in resistivity. The universal thermal volume expansion theory can explain this PTC effect.[44,45] Around the melting temperature of PE, melting of crystallites results in a dramatic increase in the volume of the composite. Thermal expansion causes severe separation of previously contacted conductive elements, and thus the conductive network in the composite becomes defective, leading to a sharp increase in resistivity. Following the PTC effect region, resistivity substantially decreases with further increasing temperature, exhibiting the so-called NTC effect. Though the NTC effect mechanism is still unclear up to now, it is generally believed that the NTC effect is related to the agglomeration of filler particles in the molten matrix.[46–48] For FCMCs, the agglomeration of CB-coated PET microfibrils takes place and more contact sites are formed to produce new conductive paths.[33] The amount of the conductive paths rises with increasing temperature, leading to occurrence of the NTC effect.

To evaluate the PTC and NTC effect quantitatively, PTC intensity (I_{PTC}) and NTC intensity (I_{NTC}) are defined as follows:[49]

$$I_{\mathrm{PTC}} = \log\left(\frac{\rho_t}{\rho_{\mathrm{RT}}}\right) \tag{1}$$

$$I_{\mathrm{NTC}} = \log\left(\frac{\rho_t}{\rho_k}\right) \tag{2}$$

where ρ_t is the maximum resistivity in the heating process; ρ_{RT} is the original resistivity at room temperature; ρ_k is the resistivity at a temperature k during NTC process, so I_{NTC} matches NTC intensity at that temperature, here k is defined as 180°C. I_{PTC} and I_{NTC} of CCPC and FCMC during eight HCRs are shown in Figures 3 and 4.

For CCPC, I_{PTC} decreases from 5.8 in the second run to 5.5 in the sixth run, but returns to 5.7 again in the eighth run, showing some fluctuation in I_{PTC}, which is related to the induction period of the unstable conductive network due to small sizes of CB particles and their preferential distribution in the amorphous regions of PE matrix. As a result, from one through eight runs, I_{PTC} only decreases by 0.1 orders of magnitude. For FCMCs, the resistivity-temperature curve of the fourth run is similar to that of the second run with constant I_{PTC} of 5.5. Interestingly, by further increasing the HCR, the I_{PTC} of FCMC gradually decreases from 5.5 to 5.0 in the sixth run, and to 4.6 in the eighth run, indicating an attenuation ratio of more than 16%. As for I_{NTC}, after eight HCRs, it is reduced by 0.4 and 1.2 orders of magnitude for CCPCs and FCMCs, respectively. Similarly, the I_{NTC} attenuation of FCMCs is more than that of CCPCs.

After the same intensified thermal treatments (eight HCRs), dissimilar PTC properties of FCMCs and CCPCs, which are unavailable using less HCRs (see the first several HCRs), show up. CCPCs have only minor fluctuations of I_{PTC}, while FCMCs exhibit anomalous gradual attenuation, which is not obvious, but appreciable enough. The attenuation of I_{PTC} and I_{NTC} of FCMCs must originate from the microstructural evolution of conductive networks under thermal fields.[4,10,14,35,36] In order to reveal the relationship between resistivity-temperature behavior and the microstructure of FCMC more clearly, further information about the microstructure changes should be explored.

It is well known that the microstructural change is closely related to viscosity of polymer matrices,[42] testing temperature, and treatment time,[4,10,14,35,36] while the viscosity is dependent on temperature and time. Long-term, high temperature isothermal treatment has been considered as an effective method to tune the CPC's microstructures, which has been studied by Wu et al.[4,35,36] and Zhang et al.[10,14] in some CPCs. Naturally, this methodology is also applied to FCMC and CCPC samples. FCMC samples were treated at a high temperature (180°C, a much higher temperature than the T_m of PE matrix) for different times (2, 6, 16, 24, and 32 h) to obtain gradual change of microstructures, after cooled, I_{PTC} and I_{NTC} are measured (the thermal program is illustrated in Fig. 1).

Figure 5 shows the resistivity-temperature behavior of FCMC after different isothermal treatment times at 180°C. There is a rapid increase and decrease in resistivity around the T_m for samples with short-term thermal treatment, (e.g., below 16 h), when the thermal treatment time is relatively long (above 16 h), surprisingly, the resistivity rises very slowly, and its maximum does not appear around T_m. I_{PTC} and I_{NTC} listed in Figure 5 clearly show this dependence on resistivity. I_{PTC} decreases from 5.5 for the original sample, to only 0.5 for 32 h thermal treatment, implying a tremendous attenuation ratio up to 91%. Meanwhile, the I_{NTC} also decreases sharply. When the isothermal treatment time is beyond 16 h, I_{NTC} unexpectedly declines to zero, illustrating that the NTC effect is completely eliminated.

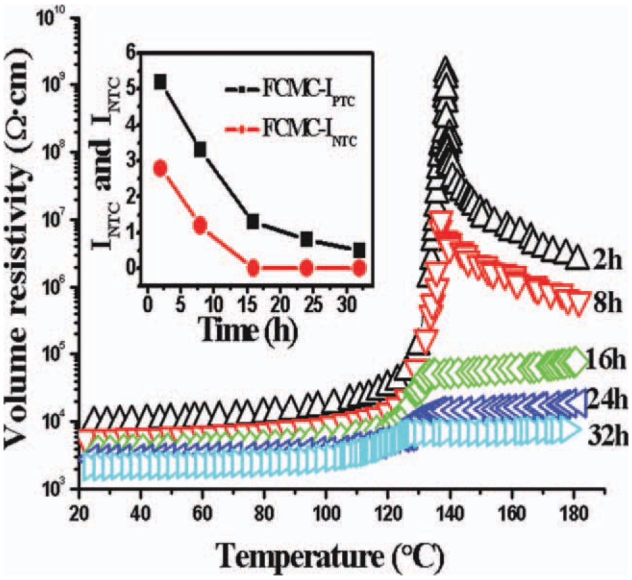


Figure 5 The resistivity-temperature behavior of FCMCs after different isothermal treatment times at 180°C, showing anomalous attenuation of PTC and NTC effects. CB loading is 4.93 vol %. The insert shows the changes of I_{PTC} and I_{NTC}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For comparison, CCPC samples were also treated at 180°C as shown in Figure 6. All the resistivity-temperature curves almost overlap. I_{PTC} and I_{NTC} inserted in Figure 6 indicate that their variations are very weak other than in FCMCs. I_{PTC} is 6.3 after 2 h isothermal treatment, while after 32 h, it becomes 6.00, only decreases by 0.3 order of magnitude, with an attenuation ratio of only 4.3%. I_{NTC} decreases by a slight 0.8 order of magnitude. These data suggest that FCMCs and CCPCs display greatly different PTC and NTC effects during the same isothermal treatment.

Mechanism of the decreasing positive temperature coefficient effect

The above results indicate that FCMCs and CCPCs have much different PTC and NTC effects through the same isothermal treatment history, that is, I_{PTC} and I_{NTC} of FCMC decrease gradually with increasing HCRs, and display a high attenuation ratio of about 91% after 32 h isothermal treatment at 180°C; however, for CCPC, the reduction of both I_{PTC} and I_{NTC} is quite minimal. Here arise two crucial problems: Why do I_{PTC} and I_{NTC} of FCMC decrease dramatically after isothermal treatment, and why do FCMCs show much higher attenuation than CCPCs?

In literature, there are some reports about decreasing PTC and NTC effects through thermal treatment by Bin et al.,[50,51] Song and Zheng,[52] and Huang et al.,[53] and the origins are concluded in detail. For example, morphology change of disperse phase[50,51] and agglomeration of conductive component-CB aggregates[52] during annealing are considered as the reasons for the decreasing PTC and NTC in the work of Bin et al. and Song and Zheng, respectively. However, due to the special morphology and unique CB distribution of FCMC, these reasons cannot be applied indiscriminately. But in the present work, PET microfibrils in FCMC form a network, and remain solid state even at 180°C,[33] i.e., the change of the disperse phase is very weak; the conductive component of this work-CB coated microfibrils is also quite different from common CB aggregates in size and morphology. Undoubtedly, the dramatic attenuation of I_{PTC} and I_{NTC} of FCMCs after different strengthened thermal treatment should be closely related to their unique conductive microstructure, i.e., the conductive microfibrillar network which must change gradually under the action of high temperature over time.

Figures 7 and 8 show the resistivity-isothermal treatment time curves of FCMCs and CCPCs at 180°C, respectively. The resistivity of FCMCs decreases gradually through the whole treatment (Fig. 7), indicating the formation of a more perfect conductive network. This can be understood by the gradual aggregation of CB-coated PET microfibrils in molten CPC through Brownian motion,[4,36] that is, the strong irregular movement of the macromolecular chains of PE layers surrounding CB-coated PET microfibrils drives the gradual movement of these CB-coated PET microfibrils. The large specific surface area of CB particles and the interaction between polar groups on their surface then drives the gradual aggregation of these CB-coated PET microfibrils

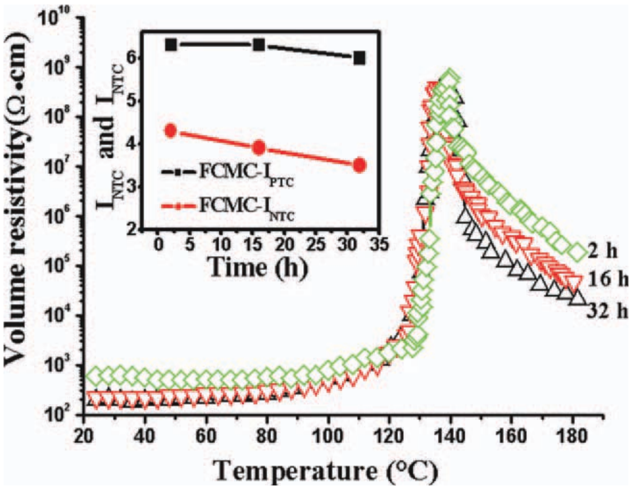


Figure 6 The resistivity-temperature behavior of common CB/PE conductive polymer composites after different isothermal treatment times at 180°C. CB loading is 9.56 vol %. The insert shows the changes of I_{PTC} and I_{NTC}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

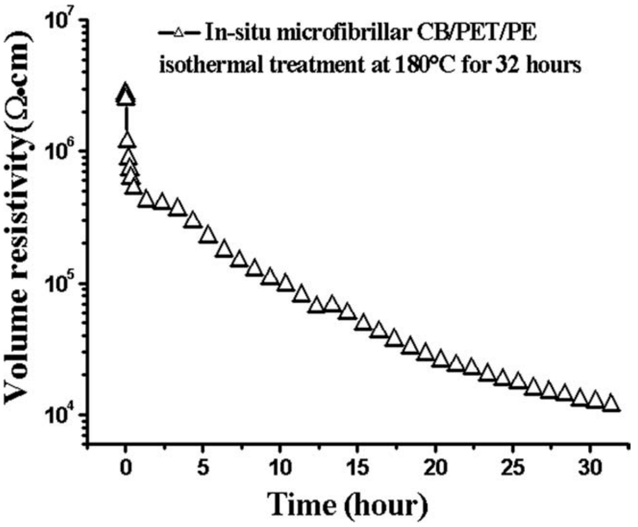


Figure 7 The resistivity-temperature behavior of FCMC with 4.93 vol % CB during 32 h isothermal treatment at 180°C.

by Brownian motion. The aggregation is intensified in the low viscosity PE matrix due to long-term treatment in the high temperature thermal field. Consequently, CB-coated PET microfibrils gradually approach each other in the thermal process.

Due to the tunneling mechanism proposed by Balberg et al.,[54–56] minute increase of the distance between conductive components results in an obvious increase in resistivity.

$$\sigma_{\text{tun}} \propto \exp\left[-\frac{r-2b}{d}\right] \qquad (3)$$

where σ_{tun} is the interparticle tunneling conductivity, r is the distance between the centers of the particles, b is the radius of the particles, and d is the typical tunneling range (or tunneling decay) parameter. Equation (3) suggests that every two particles (here assumed spherical) in the system are electrically connected, and their contribution to the conduction of the whole network diminishes as r increases and *vice versa*.

Therefore, under the action of the strengthened thermal field, aggregation of CB-coated PET microfibrils by Brownian motion[4,36] and approach of the CB particles on their surfaces lead to a reduction in resistivity of FCMCs due to smaller r. In other words, with isothermal treatment for a certain time, a much better conductive network is obtained gradually.

On the other hand, compared with CB particles, the size of CB-coated PET microfibrils is very large with diameter 1 to 3 μm and length longer than 50 μm [see Supporting Information Fig. S1(a), S2(b)], hence their movement is difficult in the PE melt. Due to the large size of CB-coated PET microfibrils, once two CB-coated PET microfibrils move close, they are hard to separate due to their poor mobility, and continuous aggregation is thus maintained. When another HCR is applied, the FCMC with perfect conductive network by gradual aggregation of CB coated PET microfibrils is not sensitive to the sharp volume expansion during melting of PE as before. In other words, the conductive network cannot be destroyed easily, resulting in a poorer PTC or attenuation of I_{PTC}. The longer the isothermal treatment time is applied, the better the conductive network that can be obtained, and consequently, the lower the PTC intensity displayed (Figs. 4 and 5). Additionally, as explained by Kopczynska and Ehrenstein,[57] properties of multiphase polymer-containing systems are largely determined by interfaces. During the long-period isothermal treatment, interfaces between CB-coated PET microfibrils will provide space for the aggregation, that is, interfaces benefit for the PTC attenuation.

As to NTC effect, it has been suggested that this phenomenon is caused by the formation of a flocculated structure when the viscosity of CPCs are sufficiently low at elevated temperatures,[7] which is also associated with the aggregation of conductive fillers. After long-term isothermal treatment, the conductive network of FCMCs is improved gradually. In the meanwhile, the tendency toward stronger aggregation of CB-coated PET microfibrils by Brownian motion in NTC region goes down, which decreases I_{NTC}. When isothermal treatment time is up to 16 h, the conductive network is so fine that in the NTC region, aggregation cannot occur any more. Contrarily, thermal volume expansion increases resistivity with maximum resistivity appearing at the end of

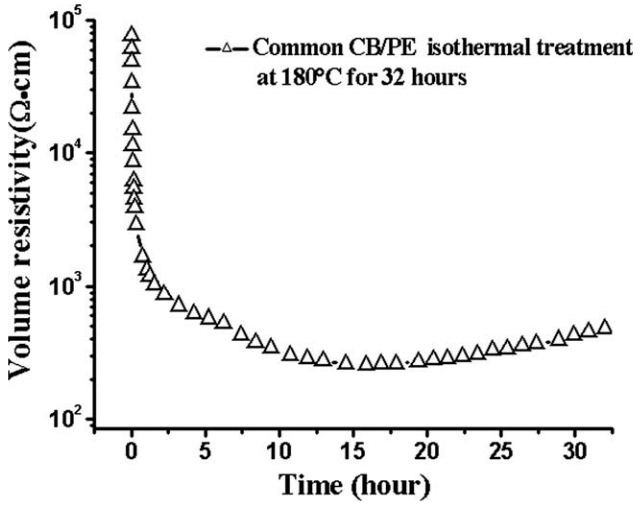


Figure 8 The resistivity-temperature behavior of common CB/PE conductive polymer composites during 32 h isothermal treatment at 180°C. The CB loading is 9.56 vol %.

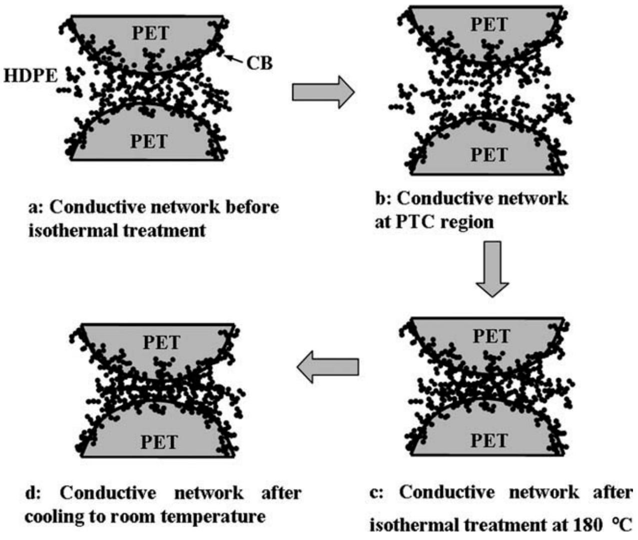
the heating process, where no NTC effect ($I_{\mathrm{NTC}} = 0$) is obtained.

The results indicate that during PTC and NTC effects detection, though the thermal field is weaker than the present work, thermal field induced microstructural transformation via Brownian motion must be performed, and it must be one of the key factors in the origin of PTC and NTC phenomena. Due to limited microstructure design and negligent study in strong thermal fields, the factor has not been pointed out up to now.

On the other hand, for CCPCs going through the same thermal journey as FCMCs, (for example, after 32 h isothermal treatment, as shown in Fig. 6), reduction of I_{NTC} and I_{PTC} is not nearly obvious. Conductive network development differences between CB/PE and FCMC must be the reason. The evolution of the conductive network of CCPCs during 32 h isothermal treatment was thus studied. As shown in Figure 8, after an initial sharp decrease, where resistivity varies very little, even as the treatment time is beyond 16 h, it shows a minimal increase. This result indicates that a stable conductive network is rapidly organized at the beginning of isothermal treatment. This is reasonable because the small size and high mobility of CB particles in the low viscosity polymer matrix allow easy reorganization of the conductive network by Brownian motion. Too much aggregation of CB particles can damage some conductive paths in the molten PE, which results in weak increase in resistivity, as observed after 16 h isothermal treatment (Fig. 8). Nevertheless, when CPCs are cooled to room temperature, in a departure from FCMC, the microstructure of the conductive network of CCPCs are largely destroyed by crystallization of PE, in which CB particles are rejected to the amorphous regions again.[58] That is, the nice conductive network cannot be preserved like FCMC. After isothermal treatment, when a HCR is applied, the samples have similar PTC and NTC effects as original samples.

A minor reduction of I_{PTC} and I_{NTC} is observed as shown in Figures 3 and 6. This is because few small CB aggregates combine into bigger ones, and the conductive network thus becomes a little more stable to the volume expansion of PE upon heating.

To explain clearly the origin of I_{PTC} and I_{NTC} attenuations of FCMC, a model for microstructural development of CB-coated PET microfibrils during the thermal treatment is schematically illustrated in Figure 9. Figure 9(a) describes the original conductive network before isothermal treatment in which adjacent CB-coated microfibrils are conductive through many contact points along the CB localized on the microfibrils' surface; when the sample approaches the PTC region, the conductive microfibrillar network is destroyed abruptly by volume expansion of the PE matrix and PTC effect can be observed [see Fig. 9(b)]; in the isothermal treatment region, due to attraction between CB particles on microfibrils and large specific surface area of CB particles, more conductive paths by aggregation of CB-coated PET microfibrils are gradually generated through Brownian motion, and a nice conductive network is achieved [see Fig. 9(c)]. Low viscosity at high temperature and a relatively long-term treatment play key roles in this microstructural transformation. In the end, after cooling, due to the large size of PET microfibrils, this more stable and perfect conductive network, which is not sensitive to sudden volume expansion as before, is maintained [see Fig. 9(d)]. In succeeding PTC and NTC testing, the weak I_{PTC} and I_{NTC} are thus obtained.



a: Conductive network before isothermal treatment

b: Conductive network at PTC region

c: Conductive network after isothermal treatment at 180 °C

d: Conductive network after cooling to room temperature

Figure 9 Illustration of the microstructural development of CB-coated PET microfibrils during thermal process. The gray domains are the cross sections of PET microfibrils with CB coating on their surfaces. The black points are carbon black particles.

Besides the effect of strong thermal field induced microstructural development by Brownian motion, it has also been reported that some factors are able to induce motion of conductive components to transform the microstructure of CPCs, including oxygen, electric field, and change of crystallinity, etc.

Meyer[28] found that the I_{PTC} decreased notably in CCPCs in the presence of oxygen after isothermal treatment at 150°C for 150, 300, 450, and 550 h. The cross-linking of PE matrix owing to oxygen adsorption, which altered either the crystalline nature of the material or the extent of its thermal expansion, was given as the reason for the observed PTC attenuation. However, in the present work, samples are all immersed in silicone oil in a temperature-controlled apparatus to avoid oxidation. So cross-linking of PE is not the main reason for the reduction of I_{PTC} and I_{NTC}.

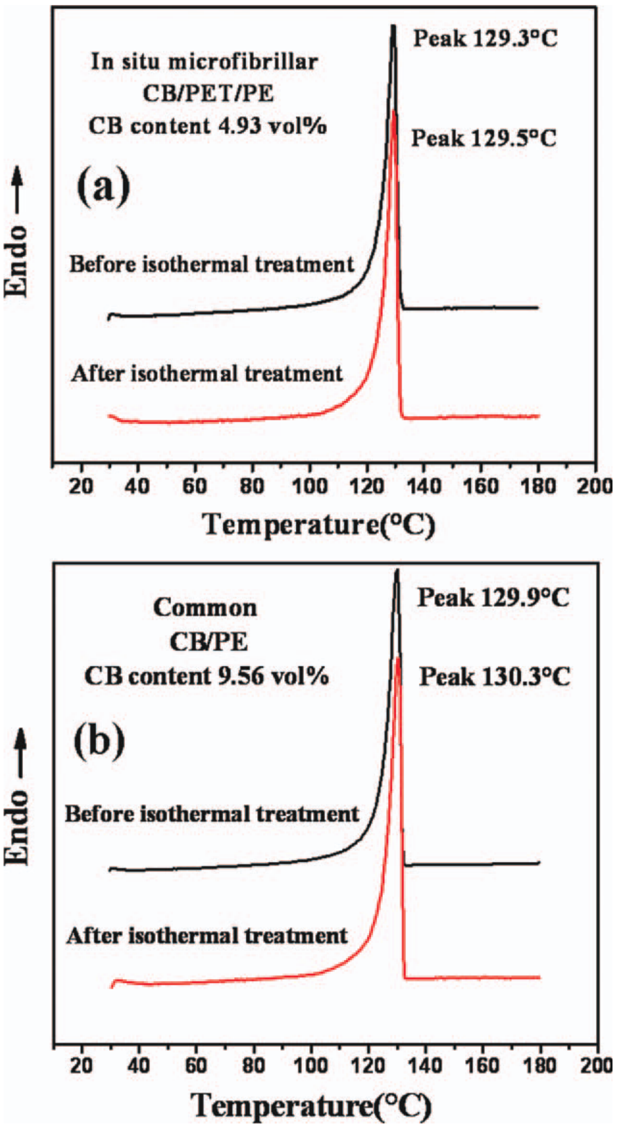


Figure 10 DSC curves of the FCMC with 4.93 vol % CB (a) and the common CB/PE composite with 9.56 vol % CB (b) in heating process before and after 32 h isothermal treatment. The heating rates are both 2°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Decreasing resistivity was studied by Tai et al., where thermodynamic analyses of electric-field-induced CB particles alignment in a nonpolar thermoplastic, low density PE were conducted.[35] The applied electric fields' strength was set as high as 500 V/mm. However, electric field strength in the present work is only 0.1 V/mm, it is much weaker. Moreover, the size of the conductive component (the CB-coated PET microfibrils) is quite large, rendering microfibrils less susceptible to this weak electric field, i.e., the effect of the electric field should not be a major factor for the microstructural changes, either.

Thermal expansion is the universal theory to elucidate PTC effect,[44,45] because sharp volume expansion and PTC effect always simultaneously occur around the melting temperature of semicrystalline polymer matrices. The crystallinity of polymer matrices dominates their thermal expansion behaviors, and is thus considered as a main element influencing I_{PTC} and I_{NTC}.[30] Thermal behaviors of FCMCs and CCPCs before and after 32 h isothermal treatment were carried out, as shown in Figure 10(a,b). The data for crystallinity listed in Table I show that both T_m and crystallinity of FCMC and CCPC change very weakly. The crystallinity of FCMC rises to 63.2% from 61.0% after 32 h isothermal treatment [see Fig. 10(a)]. Inversely, increase of the crystallinity leads to even higher PTC and NTC effects. So the effect of crystallinity is not the driving factor (in present experimental conditions). To summarize, oxygen, electric field, and change of the crysallinity may cause a minimal decrease in I_{PTC} and I_{NTC} of FCMC, however, they are not the main reasons.

CPC materials with weak PTC and no NTC have potential applications as EMI shielding or electrostatic discharge (ESD) protection materials.[3] However, CPCs manufactured by conventional technology, inevitably have NTC, and too high PTC. Increasing conductive filler loading or cross-linking of semicrystalline polymer matrix of CPCs are both usual strategies.[3] But too much conductive filler always results in poor processability, poor mechanical properties and high cost. Cross-linked composites cannot be recycled. Until now, it is still a particular challenge to suppress PTC and NTC effect of a CPC material. The isothermal treatment of FCMCs suggests a new approach to the suppression of PTC and NTC. Due to the quite simple preparation and post-treatment process of FCMC, it is believed this new CPC material with good processability, recyclability, and low cost will have very attractive prospects. The other significance of this work is that the studies about the resistivity-temperature behaviors of FCMC after strengthened thermal treatments confirms that thermal filed induced microstructural

TABLE I
Detailed Information of DSC Traces of FCMCs with 4.93 vol % CB [Fig. 10(a)] and Common CB/PE Composites (CCPCs) with 9.56 vol % CB [Fig. 10(b)] in Heating Process before and after 32 h Isothermal Treatment

Sample	T_m-onset (°C)	T_m (°C)	T_m-end (°C)	ΔH_c (J/g)	X_c (%)
CCPC	124.2	129.9	131.7	151.4	62.0
CCPC after treatment	124.8	130.3	132.1	161.5	66.1
FCMC	124.1	129.3	131.3	113.7	61.0
FCMC after treatment	124.4	129.5	131.3	117.8	63.2

T_m-onset, onset temperature on DSC endotherm; T_m, melting temperature; T_m-end, the end of the melting temperature; ΔH_c, enthalpy of crystallization; X_c, the crystallinity. Melting enthalpy of polyethylene crystal with 100% crystallinity was set as 293 J/g in this study.[52]

transformation by Brownian motion helps to reveal the origin of the PTC and NTC effects.

CONCLUSIONS

FCMC samples were prepared through a slit die extrusion-hot stretch-quenching process. With increasing HCR number, anomalous I_{PTC} and I_{NTC} attenuations of FCMC with CB loading 4.93 vol % were observed. After samples were treated in a strengthened isothermal field at a high temperature 180°C for different times (2, 8, 16, 24, and 32 h), dramatic I_{PTC} and I_{NTC} reductions were observed in the subsequent HCR testing. Finally, processable, recyclable, and low cost CPCs with weak I_{PTC} and no I_{NTC} were fabricated. Their stable resistivity in a wide temperature range makes them attractive prospects as EMI shielding or ESD protection materials.

The microstructural changes and large size of conductive component-CB coated PET microfibrils are responsible for these reductions of I_{PTC} and I_{NTC}. The microstructural changes in conductive network are achieved through the gradual aggregation of CB particles-coated PET microfibrils by Brownian motion. This microstructural evolution is continuously maintained to form a nice conductive network due to the large size of CB-coated PET microfibrils. The present results indicate that thermal filed induced microstructural transformation by Brownian motion is one of the significant origins for PTC and NTC effects. These attenuations are very weak for CCPCs due to the small size of CB particles and their selective distribution in the amorphous phases of PE.

References

1. Xu, H. P.; Dang, Z. M.; Shi, D. H.; Bai, J. B. J Mater Chem 2008, 18, 2685.
2. Brostow, W.; Keselman, M.; Mironi-Harpaz, I.; Narkis, M.; Peirce, R. Polymer 2005, 46, 5058.
3. Xu, X. B.; Li, Z. M.; Dai, K.; Yang, M. B. Appl Phys Lett 2006, 89, 032105.
4. Wu, G. Z.; Asai, S.; Sumita, M. Macromolecules 2002, 35, 1708.
5. Costa, L. C.; Chakki, A.; Achour, M. E.; Graca, M. P. F. Phys B 2011, 406, 245.
6. Feng, J. Y.; Chan, C. M. Polymer 2000, 41, 4559.
7. Feng, J. Y.; Chan, C. M. Polymer 2000, 41, 7279.
8. Hirano, S.; Kishimoto, A. Appl Phys Lett 1998, 73, 3742.
9. Byrne, M. T.; Gun'ko, Y. K. Adv Mater 2010, 22:1672.
10. Zhang, C.; Zhu, J.; Ouyang, M.; Ma, C. A. Appl Phys Lett 2009, 94, 111915.
11. Gao, J. F.; Yan, D. X.; Huang, H. D.; Dai, K.; Li, Z. M. J Appl Polym Sci 2009, 114, 1002.
12. Dang, Z. M.; Li, W. K.; Xu, H. P. J Appl Phys 2009, 106, 024913.
13. Bao, S. P.; Liang, G. D.; Tjong, S. C. Carbon 2011, 49, 1758.
14. Zhang, C.; Wang, L.; Wang, J. L.; Ma, C. A. Carbon 2008, 46, 2053.
15. Song, Y. H.; Pan, Y.; Zheng, Q.; Yi, X. S. J Polym Sci Part B: Polym Phys 2000, 38, 1756.
16. Li, Q.; Siddaramaiah, N.; Kim, H.; Yoo, G. H.; Lee, J. H. Compos B 2009, 40, 218.
17. Rizvi, R.; Kim, J. K.; Naguib, H. Smart Mater Struct 2009, 18, 104002.
18. Li, C. S.; Liang, T. X.; Lu, W. Z.; Tang, C. H.; Hu, X. Q.; Cao, M. S.; Liang, J. Compos Sci Technol 2004, 64, 2089.
19. Al-Saleh, M. H.; Sundararaj, U. Carbon 2009, 47, 2.
20. Das, N. C.; Liu, Y. Y.; Yang, K. K.; Peng, W. Q.; Maiti, S.; Wang, H. Polym Eng Sci 2009, 49, 1627.
21. Azulay, D.; Eylon, M.; Eshkenazi, O.; Toker, D.; Balberg, M.; Shimoni, N.; Millo, O.; Balberg, I. Phys Rev Lett 2003, 90, 236601.
22. Gunes, I. S.; Jimenez, G. A.; Jana, S. C. Carbon 2009, 47, 981.
23. Isaji, S.; Bin, Y. Z.; Matsuo, M. Polymer 2009, 50, 1046.
24. Song, Y. H.; Zheng, Q. J Polym Sci Part B: Polym Phys 2005, 43, 2484.
25. Song, Y. H.; Zheng, Q. Polym Int 2004, 53, 1517.
26. Kohler, F. Resistance Element. U. S. Patent 3, 243, 753, 1966.
27. Ohe, K.; Naito, Y. Jpn J Appl Phys 1971, 10, 99.
28. Meyer, J. Polym Eng Sci 1974, 14, 706.
29. Voet, A. Rubber Chem Technol 1981, 54, 42.
30. Luo, Y. L.; Wang, G. C.; Zhang, B. Y.; Zhang, Z. P. Eur Polym J 1998, 34, 1221.
31. Mironi-Harpaz, I.; Narkis, M. J Polym Sci Part B: Polym Phys 2001, 39, 1415.
32. Balberg, I. Carbon 2002, 40, 139.
33. Dai, K.; Li, Z. M.; Xu, X. B. Polymer 2008, 49, 1037.
34. Li, R. Q.; Dou, D. Y.; Miao, J. L.; Wang, W. F.; Yao, S. D.; Zeng, H. M. J Appl Polym Sci 2002, 86, 2217.
35. Tai, X. Y.; Wu, G. Z.; Tominaga, Y.; Asai, S.; Sumita, M. J Polym Sci Part B: Polym Phys 2005, 43, 184.
36. Wu, G. Z.; Asai, S.; Zhang, C.; Miura, T.; Sumita, M. J Appl Phys 2000, 88, 1480.
37. Yu, G.; Zhang, M. Q. Polym Eng Sci 1999, 39, 1678.
38. Li, Z. M.; Xu, X. B.; Lu, A.; Shen, K. Z.; Huang, R.; Yang, M. B. Carbon 2004, 42, 428.
39. Xu, X. B.; Li, Z. M.; Yang, M. B.; Jiang, S.; Huang, R. Carbon 2005, 43, 1479.
40. Xu, X. B.; Li, Z. M.; Yu, R. Z.; Lu, A.; Yang, M. B.; Huang, R. Macromol Mater Eng 2004, 289, 568.
41. Dai, K.; Xu, X. B.; Li, Z. M. Polymer 2007, 48, 849.
42. Zheng, Q.; Song, Y. H.; Wu, G.; Song, X. B. J Polym Sci Part B: Polym Phys, 2003, 41, 983.
43. Yi, S. Y; Wu, G. Z.; Pan, Y. Polym Int 1997, 44, 117.
44. Xi, Y.; Ishikawa, H.; Bin, Y. Z.; Matsuo, M. Carbon 2004, 42, 1699.
45. Shen, L.; Lou, Z. D.; Qian, Y. J. J Polym Sci Part B: Polym Phys 2007, 45, 3078.
46. Bueche, F. J Appl Phys 1973, 44, 532.
47. Chan, C. M.; Cheng, C. L.; Yuen, M. M. F. Polym Eng Sci 1997, 37, 1127.
48. Tang, H.; Piao, J. H.; Chen, X. F.; Lou, Y. Z.; Li, S. H. J Appl Polym Sci 1993, 48, 1795.
49. Feng, J. Y.; Chan, C. M. Polym Eng Sci 1999, 39, 1207.
50. Bin, Y.; Xu, C.; Agari, Y.; Matsuo, M. Colloid Polym Sci 1999, 277, 452.
51. Bin, Y.; Xu, C.; Zhu, D.; Matsuo, M. Carbon 2002, 40, 195.
52. Song, Y. H.; Zheng, Q. J Appl Polym Sci 2007, 105, 710.
53. Huang, Z. Z.; Yue, R.; Chan, H. L. W.; Choy, C. L. Polym Compos 1998, 19, 781.
54. Balberg, I.; Azulay, D.; Toker, D.; Millo, O. Int J Mod Phys B 2004, 18, 2091.
55. Grimaldi, C.; Balberg, I. Phys Rev Lett 2006, 96, 066602.
56. Rubin, Z.; Sunshine, S. A.; Heaney, M. B.; Bloom, I.; Balberg, I. Phys Rev B: Condens Matter 1999, 59, 12196.
57. Kopczynska, A.; Ehrenstein, G. W. J Mater Ed 2007, 29, 325.
58. Babinec, S. J.; Mussell, R. D.; Lundgard, R. L.; Cieslinski, R. Adv Mater 2000, 12, 1823.