

# Positive Temperature Coefficient and Time-Dependent Resistivity of Carbon Nanotubes (CNTs)/Ultra-high Molecular Weight Polyethylene (UHMWPE) Composite

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**ABSTRACT:** The carbon nanotubes/ultra-high molecular weight polyethylene (CNTs/UHMWPE) conductive composite with a low percolation threshold had been successfully fabricated, and CNTs were only dispersed in the interface of matrix particles. Some factors, including CNTs concentration, processing temperature, and the time of isothermal treatment, which could exert influence on the positive temperature coefficient effect of the composite, were investigated. Similar with negative temperature coefficient effect, the resistivity decreased during isothermal treat-

ment above the melting point of UHMWPE, which could be thought to be a relaxation process originated from movement of molecular chains. This relaxation, also a process of CNTs aggregating to reorganize the conductive network, was testified as a function of time, temperature, filler concentration, and heating rate. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1002–1010, 2009

**Key words:** CNTs/UHMWPE composite; temperature; CNTs concentration; thermal treatment; PTC; NTC; relaxation

## INTRODUCTION

The PTC and NTC effect are typical resistivity-temperature behaviors of carbon black (CB)<sup>1–10</sup> filled conductive polymer composites, which are very often investigated because they are the basis of popular applications such as overcurrent, overtemperature protection devices, self-regulating heaters, etc. Sudden increase in electrical resistance with a rise in temperature occur when the melting point of the polymer matrix is approached, which is called PTC phenomenon. Above the region of PTC, a decrease of resistivity is often observed, which is defined as NTC effect. Many models, including volume expansion, conduction pathway theory, tunneling effect theory, etc., have been put forward to interpret PTC and NTC effect.<sup>11–22</sup> Nevertheless, the mechanisms for understanding the resistivity-temperature behaviors are still incomplete. One major reason is that too many factors can affect PTC and NTC effects in

very complex manners. Hirano et al.<sup>23</sup> discovered the magnitude of the PTC effect for the conductive composite thin films consisting of conductive ceramic filler dropped with decreasing the heating rate, and the resistivity nearly became a constant when the heating rate decreased below  $0.1^{\circ}\text{C min}^{-1}$ , both of which, according to the authors' view, was strongly related to the thermal strain rate of the matrix. Luo et al.<sup>24</sup> found that the PTC intensity enhanced with increased crystallinity for the polyethylene/CB system, which can be attributed to the increased lamellae size. Xu et al.<sup>25</sup> suggested inhomogeneous surface microstructure and the large size were responsible for the anomalous attenuation of the positive temperature coefficient of resistivity in a CB-filled polymer composite with electrically conductive in situ microfibrils. Yi et al.<sup>26</sup> supposed that crosslinking could induce the formation of a CB-rich, interlinked conductive structure in the amorphous intergranulate region, which decreased the PTC intensity, and found the PTC intensity was reduced as the the crosslinking degree became higher. Narkis et al.<sup>16</sup> found the selectively distribution of CB on the interfaces of poly(4-methyl pentene-1)(TPX)/crosslinked ultra-high molecular weight polyethylene(XL-UHMWPE)/CB composites led to a double PTC behavior. Chan et al.<sup>27</sup> studied the influence of the weight ratio of CB/polypropylene (PP)/ultra-high molecular weight polyethylene (UHMWPE) composites on double PTC effects, and suggested when the PP/UHMWPE weight ratio was

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larger than 3/7, the PTC and NTC effects are very similar to those of a CB-filled neat PP composite, but when the PP/UHMWPE weight ratio equals or is smaller than 3/7, the PTC effects of the composites are similar to those of a CB-filled neat UHMWPE composite. He et al.<sup>28</sup> prepared the MWNT/HDPE composites by a solution-precipitation process, and observed that the composites exhibited an obvious PTC effect in the vicinity of  $T_m$  of HDPE. The NTC effect of the composite at temperature above the  $T_m$  of HDPE is relatively weak and can be eliminated after 80 kGy g-ray irradiation.

With regard to the NTC effect, it is generally attributed to the formation of conductive network, which is caused by the reaggregation of conductive particles above the polymer melting point; Hence, crosslinking using either physical or chemical techniques, which can restrict the movement of conductive fillers, is often utilized to eliminate the NTC effect and improve the reproducible behaviors. Zhang et al.<sup>29</sup> chose UHMWPE as matrix, which possesses high melt viscosity, to eliminate the NTC effect in the CB filled UHMWPE composites even at temperatures much higher than the melting point of the polymer. But Chan et al.<sup>30</sup> elucidated that the negative temperature coefficient (NTC) that was observed in the CB/HDPE/tetrafluoroethylene-ethylene (ETFE) composites could not have been caused by the formation of flocculated structures because the size of the CB-filled HDPE particles was significantly large, so that their mobility was extremely limited even at high temperatures. If the conductive composites are exposed to the temperature above the melting point or the glass transition temperature for thermal treatment, the resistivity could also decrease, which is very similar with the NTC effect. Wu<sup>31-34</sup> suggested CB particles in a polymer matrix actually require time to move to form the conductive network, namely a dynamic process. By means of isothermal annealing at a temperature higher than the glass transition temperature of a polymer matrix, they confirmed that percolation is delayed by the bulk mobility of polymer layers between CB particles. The increase in thermodynamic interactions between CB and the polymer matrix causes a large reduction in polymer mobility and thus influences the dynamic percolation.

It should be noted, however, that most of the earlier studies were focused on the PTC effect of the CB filled polymer composites, and few studies are referred to conductive composites based on CNTs. As it is well known, CNTs have been more and more utilized as a kind of excellent conductive filler in polymer matrix, and such systems can potentially be useful as structural materials, electromagnetic and heat shields, conducting plastics, sensors, biocatalysts, etc. The special properties of CNTs, such as

nano-size, large aspect ratio, intrinsic supereminent electrical performances and so on, can exert a strong influence on the PTC and NTC effects. Therefore, studies on the PTC effects of CNTs-polymer composites are of high importance. For NTC, the effect of relaxation of the matrix which is factually the origin of the movement of conductive filler in polymer melt, is seldom taken into account, so it is essential to explore the relationship between the reaggregation of conductive fillers and relaxation of matrix mainly determined by the time, temperature, filler concentration, heating rate, and so on.

In our previous work, we had successfully fabricated CNTs/UHMWPE conductive composites in which CNTs were only dispersed in the interface of matrix particles.<sup>35</sup> The composite with such a segregated architecture shows a low percolation threshold. The aim of this article is to gain more insight into how some factors influence the PTC effect and the isothermal resistance relaxation with time for the CNTs/UHMWPE conductive composite.

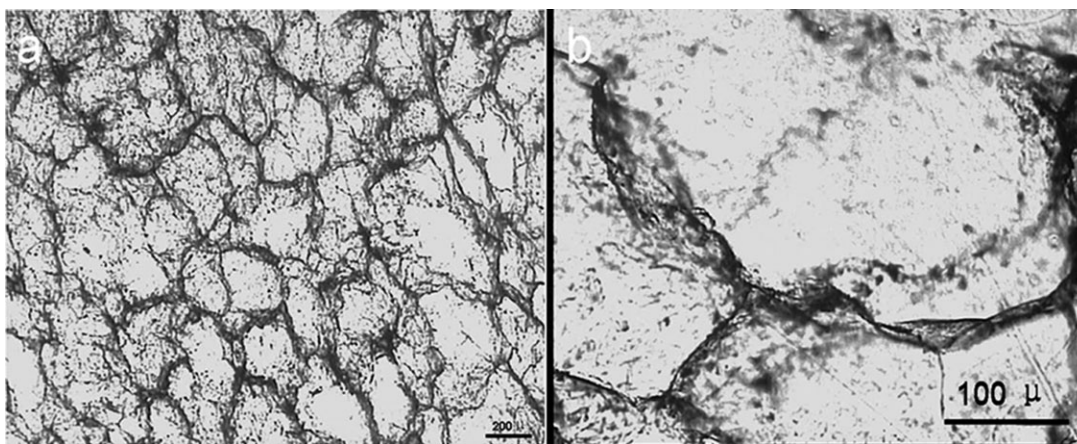
## EXPERIMENTAL PART

### Materials

The main materials used in this experiment included multiwalled carbon nanotubes (MWNTs) and ultra-high molecular weight polyethylene (UHMWPE) in powder. CNTs were purchased from Chengdu Organic Chemicals, Chinese Academy of Science, with a diameter 20–40 nm and a length 50  $\mu\text{m}$ , and were grown via the chemical vapor deposition method. The UHMWPE, a product from Beijing No.2 Auxiliary Agent Factory, China, has the following features: density  $\rho = 0.94 \text{ g/cm}^3$ , melting temperature  $T_m = 137^\circ\text{C}$  and volume resistivity  $R = 10^{17} \Omega\cdot\text{cm}$ .

### Preparation of the CNTs/UHMWPE conductive composite

The alcohol assisted dispersion was employed to achieve uniform dispersion of CNTs. The CNTs were fed into alcohol to form a suspension, and then the intense dispersion process was conducted using ultrasonication for 45 min and followed by high-speed mechanical stirring for 45 min before the UHMWPE was added into the suspension. Half an hour later, the alcohol was completely evaporated. The UHMWPE particles covered with a layer of CNTs were obtained. Subsequently, the CNTs covered powders were compression molded into  $10 \times 10 \times 2 \text{ mm}^3$  board at  $200^\circ\text{C}$  for 5 min with a pressure of 10 MPa after preheating for 15 min. All the sheets were cooled to room temperature by cold compression molding for 5 min.



**Figure 1** Optical micrographs of compression molded CNTs/UHMWPE composite film with CNTs content: 0.085 vol %.

### Morphological observation

The sample, a 100  $\mu\text{m}$  thick film, was used for optical microscopy observation.

### Thermal property test

Thermal analyses were carried out by a Netzsch DSC 200 differential scanning calorimeter. The samples experiencing different thermal treatment time were heated to 180°C at 2°C/min.

### Resistivity-temperature behaviors test

The sample ( $2 \times 10 \times 100 \text{ mm}^3$ ), which was immersed in silicone oil of a temperature-controlled apparatus to avoid oxidation, was heated from room temperature to 180°C at 2°C/min. Some samples were directly put into the silicone oil with the temperature being 140°C, 160°C, 180°C, 200°C, and 220°C, respectively. Several samples were heated from room temperature to 140°C at different heating rates (1°C/min, 2°C/min, 5°C/min), and the time dependence of electrical resistivity was real time traced using an automatic measurement system.

## RESULTS AND DISCUSSION

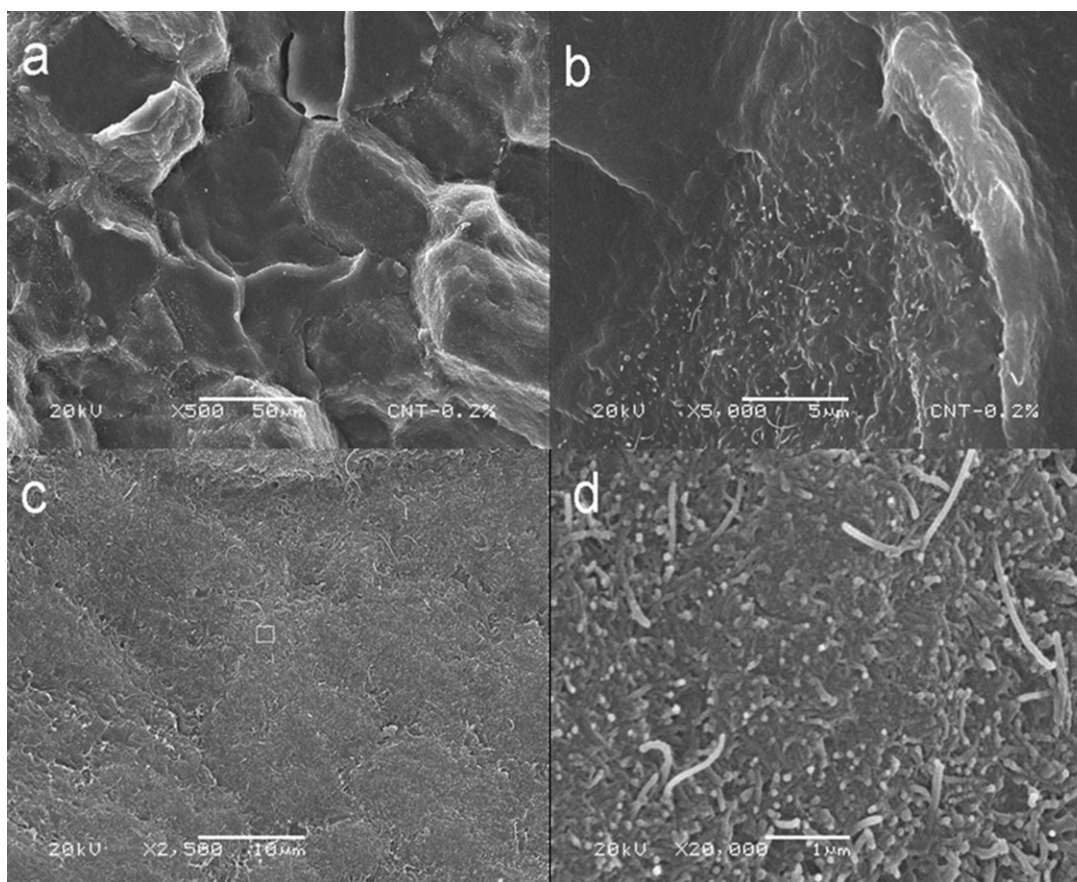
### Morphology observation of the CNTs/UHMWPE composite

To thoroughly understand the resistivity temperature behaviors of the CNTs/UHMWPE composites, it is necessary to resurvey their typical morphology. Figure 1 indicates that a segregated structure has been successfully achieved, in which CNTs are mainly localized in the interfacial regions of UHMWPE particles. Figure 2 shows SEM micrographs of the fractured surface of the CNTs filled composites with CNTs content of 0.085 vol %, which

well portrays the microcosmic distribution of CNTs in the composite.<sup>36</sup> The darker parts in Figure 2(a) were interior section of the matrix after the composite is fractured, and obviously, there are no CNTs inside the matrix. Figure 2(b) depicts the morphology of interface of the composites, and there are a lot of CNTs uniformly staying at the interface of polymer particles. Figure 2(c) describes the surface morphology of the composites, corresponding to lighter parts in Figure 2(a), and the surface of UHMWPE particles is covered with numerous individual CNTs connected each other. This morphology can be more clearly observed in Figure 2(d), which is the magnified image of the chosen region in Figure 2(c). CNTs aggregate to form conductive channels throughout the composites, and a small amount of CNTs particles are enough to establish the conductive networks in such segregated systems, resulting in very low percolation threshold. In addition, because of high melt viscosity of UHMWPE, the CNTs cannot immigrate inside the particles when the samples are heated from room temperature to 180°C or isothermally treated above the melting point (134°C), only diffusing partly near the surface of the matrix particles. As a result of this, the PTC effect and time-dependent resistivity of CNTs/UHMWPE composite must be associated with this special morphology and structure features.

### Resistivity-temperature behaviors

Here, we are focused on how several crucial parameters, including the CNTs concentration, the processing temperature, and the time of thermal treatment, influence the resistivity-temperature behaviors. The PTC intensity,  $I_{\text{PTC}}$  mentioned below, is defined as  $I_{\text{PTC}} = \log(\rho_p/\rho_{\text{RT}})$ , where  $\rho_{\text{RT}}$  and  $\rho_p$  are the resistivity at room temperature and the maximum resistivity in PTC region, respectively.<sup>25</sup> The temperature



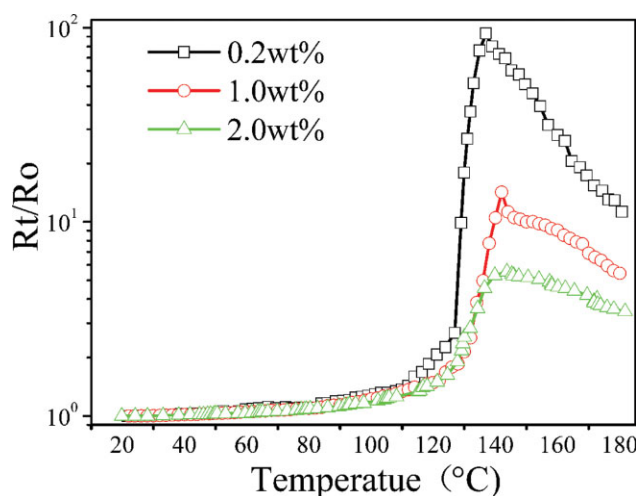
**Figure 2** SEM micrograph of the fractured surface of the CNTs filled composites with CNTs content: 0.085 vol %.

at which the peak resistivity emerges during heating is marked as  $T_p$ . To understand the curves of resistivity-temperature and resistivity-time behaviors better, the vertical axis is changed to the ratio of the resistivity upon heating or isothermal process ( $R_t$ ) to the room-temperature resistivity of the original samples ( $R_0$ ), which is defined as the relative resistivity.

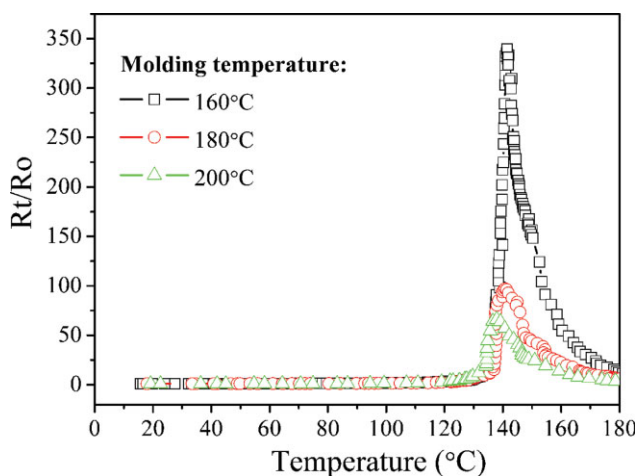
#### Effect of CNTs concentration on the resistivity-temperature behavior

Figure 3 shows the dependence of resistivity-temperature behaviors of the composites on the CNTs concentration.  $I_{PTC}$  is 1.971, 1.021, and 0.743, respectively, at 0.2%, 1%, and 2% of CNTs concentrations, showing a decreasing tendency of PTC strength with CNTs concentration. Furthermore,  $T_p$  jumps from 136.9°C to 143.7°C with increasing the CNTs concentration from 0.2% to 2%. Ying et al.<sup>15</sup> found that a higher carbon fiber content in LMWPE-UHMWPE blend caused a smaller PTC intensity and the PTC temperature, which could be attributed to the fact that the smaller inter-fiber distance in the composites became narrower with increasing CF content and the higher temperature was required to break off all contacts of carbon fibers. Being similar

with Ying's study, when the CNTs concentration increases, the conductive network of CNTs/UHMWPE composite becomes more perfect, because more conductive paths are formed. This can alleviate the breakage of the conductive network occurring as



**Figure 3** The dependence of resistivity-temperature behaviors of the composites on the CNTs concentration. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** The dependence of resistivity-temperature behaviors of the composites on the processing temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the crystalline region melts around the melting point of matrix, thus resulting in a lower PTC intensity. Different CNTs concentration may cause different viscosity on the surface of the matrix. As the CNTs concentration rises, the viscosity near the surfaces of the UHMWPE particles increases, so the energy needed into break down the conductive network is higher, corresponding to a higher  $T_p$ . After the PTC effect takes place, the NTC effect appears, which generally follows PTC, and it gradually attenuates with increasing concentration, which is also originated from the better conductive network at a higher CNTs concentration.

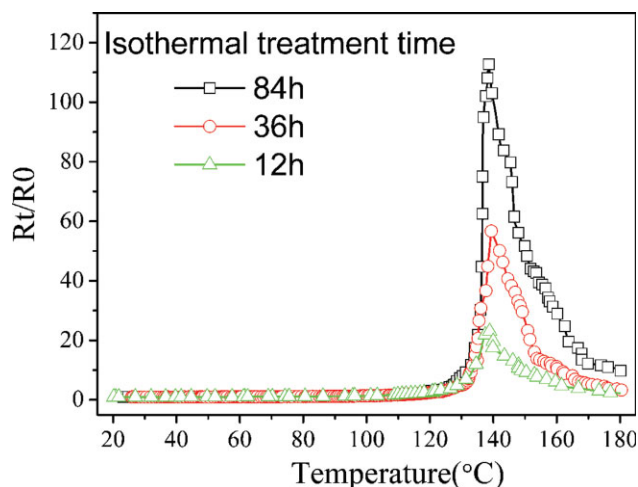
#### Effect of processing temperature on the resistivity-temperature behavior

The composites were hot compaction molded above the melting point of UHMWPE and frozen by cold compression at the room temperature, naturally, the molding temperature affects the viscosity and morphology, and further the resistivity-temperature behaviors of the samples.<sup>29</sup> Figure 4 presents the dependence of resistivity-temperature behaviors of the composites on the molding temperature. It is clear that the PTC effect at higher processing temperature is weaker. The  $I_{PTC}$  is declined from 2.53 to 1.82 as the molding temperature rises from 160°C to 200°C. As mentioned above, CNTs are only located on the surface and interface of the UHMWPE particles to form conductive pathways during processing. As the molding temperature rises, the UHMWPE particles have a relative lower viscosity and expand more violently, and CNTs become closer, which leads to more compact and perfect conductive network. The composite molded at a higher tempera-

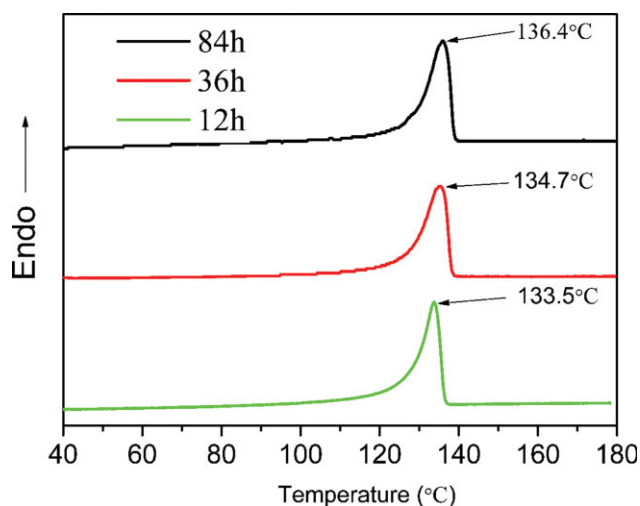
ture, hence, suffers little damage around the melting point of the UHMWPE, corresponding to a lower  $I_{PTC}$ .

#### Effect of thermal treatment time on the resistivity-temperature behavior

A thermal treatment (e.g. annealing) below the melting point of a polymer is demonstrated to be an effective means of modifying polymer properties. The size effect of polyethylene (PE) and the change of its crystallinity during annealing have been much reported.<sup>37-41</sup> Generally, PTC effect does not appear in amorphous polymer composites filled with conductive particles, which can be attributed to no sharp volume expansion from crystalline form to amorphous form.<sup>20,21</sup> UHMWPE is, however, a crystalline polymer, and its crystallinity and crystalline microstructure can be changed during thermal treatment, which more or less influences the resistivity-temperature behaviors. Figure 5 displays the dependence of resistivity-temperature behaviors of the composites on the thermal treatment time at 100°C. Obviously, the PTC intensity increases as the thermal treatment time rises. Figure 6 shows DSC scans of composites with different thermal treatment time. The DSC results illustrates that the fusion heat of the matrix increases from 133.6 J/g to 151.2 J/g as the thermal treatment time rises from 12 h to 84 h, indicating a increase in crystallinity. The  $I_{PTC}$ , together with the fusion heat of the matrix obtained from DSC measurement, are listed in Table I. Because crystallization of the polymer matrix tends to be more perfect with the increase in annealing temperature, the volume fraction of the amorphous



**Figure 5** The dependence of resistivity-temperature behaviors of the composites on the time of thermal treatment. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** DSC scans of composites with different thermal treatment time at a heating rate of 2°C /min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

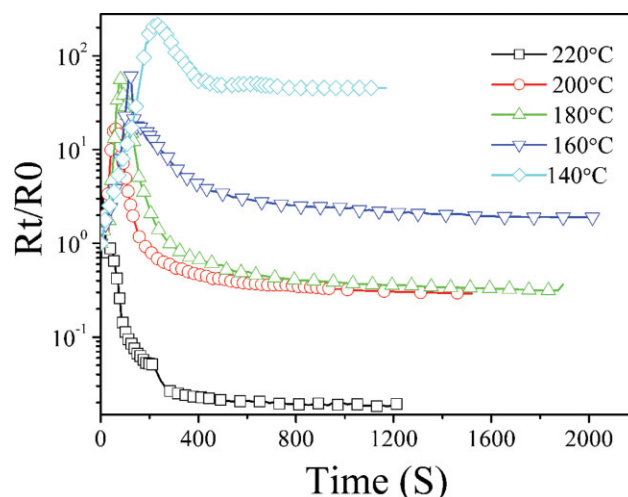
region is reduced. The larger crystallinity of the matrix can lead to a more sharply volume expansion of the system; More CNTs are separated from each other, and the whole conductive network is damaged more severely, resulting in a high  $I_{PTC}$ , and this is also coincided with Luo' conclusion on CB/PE system.<sup>24</sup>

#### Relaxation of resistivity of the composites during thermal treatments above the melting point of UHMWPE

The NTC effect usually appears after the PTC effect, which reflects the reorganisation of conductive network in the polymer melt. In fact, the reaggregation of conductive particles always occurs at any temperature above the melting point, which results in reduction of resistivity, being very similar with the NTC effect. The movement of conductive fillers and the reconstruction of conductive network stem from the movement of polymer molecules, which can be thought as a process of adjustment of molecular chains or relaxation. Except polymer's properties themselves, the movement of polymer matrix molecules is also determined by time, temperature, filler concentration, heating rate, etc. Wu et al.<sup>31-34</sup> sug-

**TABLE I**  
The Dependence of  $I_{PTC}$  on the Time of Thermal Treatment

The time of thermal treatment (h)	12	36	84
$I_{PTC}$	1.37	1.75	2.05
Fusion heat (J/g)	133.6	141.2	151.2



**Figure 7** The change of  $R_t/R_0$  with time after the sample was directly put into the silicon of different temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

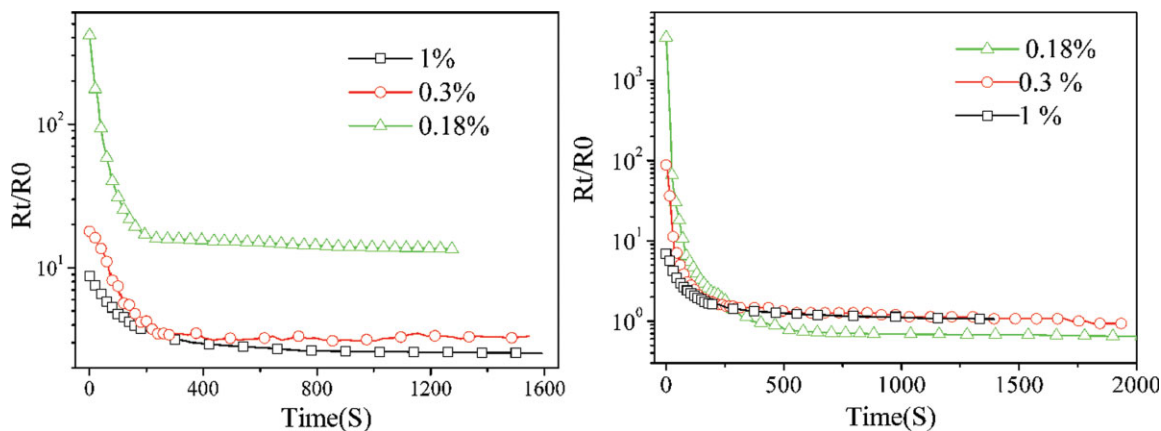
gested that the resistivity during isothermal treatments was almost unchanged, and percolation was delayed by the bulk mobility of polymer layers between CB particles. CB particles in a polymer matrix actually require time to move to form the conductive network, namely a dynamic process. It had been observed that the dynamic percolation curves maintained the same shape and shift to a shorter percolation time with increasing annealing temperature and filler concentration. However, during annealing above the melting point, the resistivity of CNTs /UHMWPE composite decreases very sharply at the initial stage, then the reduction slows down, and finally the resistivity reaches an equilibrium state. Interestingly, according to the experimental data, the attenuation of the resistivity of the CNTs/UHMWPE composites during thermal treatment can be described using a relaxation equation:

$$R_t/R_0 = R_\infty/R_0 + (R_m/R_0 - R_\infty/R_0)e^{-t/\tau} \quad (1)$$

where  $R_t$  is the resistivity at time  $t$ ,  $R_0$  is the initial resistivity before the experiment,  $R_\infty$  is the resistivity after the resistivity reaches an equilibrium state,  $R_m$  is the maximal resistivity after the sample is put into the silicon oil, and  $\tau$  is the time constant called relaxation time.

**TABLE II**  
The Results of  $R_t/R_0$  vs  $t$  in Figure 6

Temperature (°C)	140	160	180	200	220
$t_0$ (s)	234.3	120.2	81.1	48.1	6
$I_{PTC}$	2.33	1.81	1.75	1.22	0.51
$\tau$ (s)	69.57	52.44	33.98	28.11	24.24



**Figure 8** The dependence of the isothermal change of resistance with time on CNTs concentration at 180°C (a) and 220°C (b). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

#### Influence of isothermally thermal treatment temperature on the relaxation of resistivity

Figure 7 exhibits the change of  $R_t/R_0$  with time after the sample is directly put into the silicon of different temperature. Initially, the resistivity increases sharply after the sample is directly immersed into the silicon, which can be regarded as a rapid PTC process. This is reasonable because the temperature of the sample is suddenly jumped to the set temperature. After arriving at the maximal resistivity, the resistivity starts to decline.  $t_0$ , which is defined as the time that the resistivity reaches the maximum, becomes lower as the thermal treatment temperature rises.  $I_{PTC}$  and  $\tau$  share the same characteristics of dependence on temperature with that of  $t_0$ . The data of  $t_0$ ,  $I_{PTC}$ , and  $\tau$  are listed in Table II. When the composite is immersed into the silicon of high temperature, the polymer matrix expands fiercely because of linear thermal expansion and phase transition (melting), and the conductive network existing on the surfaces and their interfaces of the UHMWPE particles encounters a sudden damage, resulting in a quick rise of the resistivity. But, the conductivity could be compensated from the reaggregation of CNTs in the polymer melt above the melting point. The possibility of reaggregation depends on the temperature. Higher temperature means that the movement of matrix molecules becomes more violent, so the reaggregation of CNTs takes place more easily, resulting in a lower  $I_{PTC}$ .  $t_0$  drops as the temperature increases, because the conductive network reaggregates faster at a higher temperature. The similarity in shape of the curves for various thermal treatment temperatures strongly suggests that the primary characteristic of formation of the conductive network does not change with the annealing temperature. The values of  $\tau$  are obtained by fitting the data points into the eq. (1). The least square method is held during the fitting. The error for  $\tau$  is found neg-

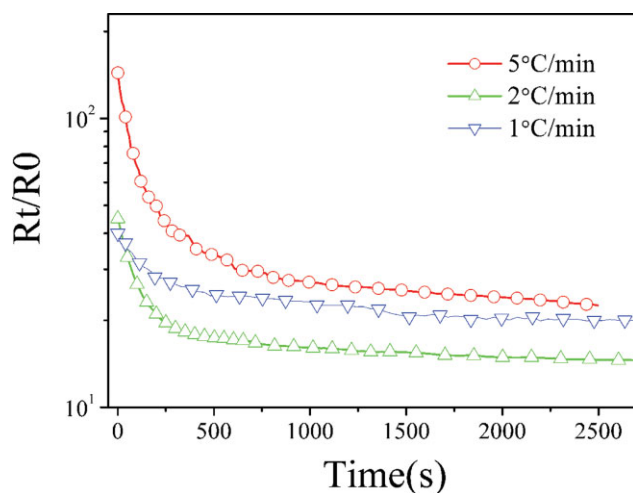
ligible, indicating the relationship between resistance and isothermal annealing time is a time relaxation process, following eq. (1), which is the result of the movement of polymer molecules.  $\tau$  strongly depended on the annealing temperatures; It drops from 69.57s at 140°C to 24.24s at 220°C. The reorganisation of the conductive network is supposed to be the contact processes among CNTs to achieve lower surface energy for the composite system. Higher treatment temperature leads to a lower polymer matrix viscosity and a stronger movement of molecule chains, which can accelerate the reorganisation of the conductive network, giving rise to a lower  $\tau$ .

#### Influence of CNTs concentration on the relaxation of resistivity

CNTs concentration influences both electrical property and the resistivity-temperature behavior of the sample, which has been discussed above. In our experiment, we choose three typical CNTs concentrations around the percolation threshold (0.18 wt %), a little higher than the percolation threshold (0.30 wt %), and much higher than the percolation threshold (1.00 wt %) for investigation. Figure 8 depicts the change of resistivity of the samples with different CNTs concentrations at 180°C and 220°C, the fitting results are presented in Table III. It is found that  $\tau$  increases as CNTs concentration rises, and for example,  $\tau$  falls down to 7.7 s with the concentration 0.18% at 220°C, being equal to 1/7 of that

**TABLE III**  
The Dependence of  $\tau$  on the CNTs Concentration

CNTs concentration (wt %)	0.18	0.3	1
$\tau$ (s, 180°C)	25.8	73.4	103.4
$\tau$ (s, 220°C)	7.7	15.4	54.7



**Figure 9** The dependence of the isothermal change of resistance with time on heating rate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

with concentration 1%. In the composite, CNTs are distributed on the surface of the UHMWPE particles, and the ability of CNTs reaggregation on the surface mainly depends on the viscosity determined by the temperature and filler concentration. The composite with a larger CNTs concentration possesses a higher viscosity which will prevent the movement of polymer molecules, and thus it takes more time for CNTs to reaggregate, leading to a larger  $\tau$ . In addition, the higher the isothermal temperature is, the shorter the  $\tau$  is, which accords with the conclusion above.

#### Influence of heating rate on the relaxation of resistivity

Heating rate influences the movement of polymer matrix, and consequently, also affects the relaxation process of the isothermal change of resistivity, which is shown in Figure 9. Based on the fitting results,  $\tau$  is 135.2 s, 123.6 s, and 69.6 s as the heating rate is set at 1°C/min, 2°C/min, and 5°C/min, respectively. To explain this phenomenon, the concept of thermal stress is introduced. Because of the difference of the thermal expansion coefficient between polymer matrix and conductive fillers, with the change of temperature, thermal residual stress develops in the interface<sup>24</sup> which contains sufficient CNTs. The expansion stress of the matrix at the filler/matrix interface grows smaller at a lower heating rate, and the conductive network survives more perfectly, so, it needs more time to make the network more perfect during isothermal treatment, corresponding to a higher  $\tau$ , which is a little similar with Yi's<sup>42</sup> study on Time-dependent resistance of CB-loaded high-

density polyethylene composites during the isothermal course.

## CONCLUSION

The CNTs/UHMWPE conductive composite with a low percolation threshold has been successfully fabricated, and the CNTs are only dispersed in the interface of matrix particles. Some factors, including CNTs concentration, processing temperature, and the time of thermal treatment, are investigated to demonstrate their influences on the PTC effect. Larger CNTs concentration leads a smaller  $I_{PTC}$  and higher  $T_{Pr}$ , processing temperature has negative effects on the  $I_{PTC}$ , and the  $I_{PTC}$  rises with the enhancement of crystallinity of the matrix, which could be realized by increasing the time of thermal treatment. Like NTC effect, the resistivity decreases during isothermal treatment above the melting point of UHMWPE, which could be thought to be a relaxation process originated from movement of molecular chains. This relaxation is testified as a function of time, temperature, filler concentration, and the heating rate. The relaxation time  $\tau$  increases as the isothermal temperature and the heating rate drop, and the filler concentration rises.

## References

1. Frydman, E. U. K. Patent Spec 1945, 604, 195, 1718, 14S.
2. Kohler, F. U. S. Pat 1966, 324, 375, 329.
3. Voet, A. Rubber Chem Technol 1981, 54, 42.
4. Meyer, J. Polym Eng Sci 1974, 14, 706.
5. Meyer, J. Polym Eng Sci 1973, 13, 462.
6. Ohe, K.; Natio, Y. J Appl Phys 1971, 10, 99.
7. Jia, W. T.; Chen, X. F. J Appl Polym Sci 1997, 66, 1885.
8. Carmona, F.; Mouney, C. J Mater Sci 1992, 27, 1322.
9. Mather, P. J.; Thomas, K. M. J Mater Sci 1997, 32, 171.
10. Jia, W. T.; Chen, X. F. J Appl Polym Sci 1994, 54, 1219.
11. Yi, X. S.; Wu, G. Z.; Ma, D. L. J Appl Polym Sci 1998, 67, 131.
12. Yi, X. S.; Wu, G. Z.; Pan, Y. Polym Int 1997, 44, 117.
13. Bin, Y.; Xu, C.; Zhu, D.; Matsuo, M. Carbon 2002, 40, 195.
14. Manuela, H. B.; Franciose, E. D. Carbon 2001, 39, 375.
15. Ying, X.; Hisako, I.; Yue, Z. B.; Masaru, M. Carbon 2001, 42, 1699.
16. Mironi-Harpaz, I.; Nakis, M. J Polym Sci Part B: Polym Phys 2001, 39, 1415.
17. Wu, T. M.; Cheng, J. C.; Yan, M. C. Polymer 2003, 44, 2553.
18. Yui, H. S.; Wu, G. Z.; Sano, H. N.; Sumita, M.; Kino, K. Polymer 2007, 47, 3599.
19. Kimura, T.; Asano, Y.; Yasuda, S. Polymer 1996, 37, 2981.
20. Tang, H.; Piao, J. U.; Chen, X. F. J Appl Polym Sci 1994, 51, 1159.
21. Wan, Y.; Wen, D. Smart Mater Struct 2004, 13, 983.
22. Di, W.; Zhang, G.; Xu, J.; Peng, X.; Xie, Z. J Polym Sci, Part B: Polym Phys 2003, 41, 3094.
23. Hirano, S.; Kishimoto, A. Appl Phys Lett 1998, 73, 3742.
24. Luo, Y. L.; Wang, G. C.; Zhang, B. Y.; Zhang, Z. P. Eur Polym J 1998, 34, 1221.
25. Xu, X. B.; Li, Z. M.; Dai, K.; Yang, M. B. Appl Phys Lett 2006, 89, 032105.
26. Yi, X. S.; Zhang, J. F.; Zheng, Y. J Appl Polym Sci 2000, 77, 494.



27. Feng, J. Y.; Chan, C. M. *Polymer* 2000, 41, 4559.
28. He, X. J.; Du, J. H.; Ying, Z.; Cheng, H. M. *Appl Phys Lett* 2005, 86, 062112.
29. Zhang, C.; Ma, C. A.; Wang, P.; Sumita, M. *Carbon* 2005, 43, 2544.
30. Feng, J. Y.; Chan, C. M. *Polymer* 2000, 41, 7279.
31. Wu, G. Z.; Asai, S.; Zhang, C.; Miura, T.; Sumita, M. *J Appl Phys* 2000, 88, 1480.
32. Wu, G. Z.; Asai, S.; Sumita, M. *Polymer* 2001, 42, 3271.
33. Wu, G. Z.; Asai, S.; Sumita, M. *Macromolecules* 2002, 35, 1708.
34. Tai, X. Y.; Wu, G. Z.; Yui, H.; Asai, S.; Sumita, M. *Appl Phys Lett* 2003, 83, 3791.
35. Gao, J. F.; Li, Z. M.; Meng, Q. J.; Yang, Q. *Mater Lett* 2008, 62, 3530.
36. Gao, J. F.; Li, Z. M.; Peng, S.; Yan, D. X. *Polym-Plast Technol* 2009, 48, 478.
37. Statton, W. O. *J Appl Phys* 1961, 32, 2332.
38. Peterlin, A.; Corneliussen, R. J. *J Polym Sci Part A-2: Polym Phys* 1968, 6, 1273.
39. Maeda, M.; Miyasaka, K.; Ishikawa, K. J. *J Polym Sci Part A-2: Polym Phys* 1970, 8, 355.
40. Zhang, M. Y.; Jia, W. T.; Chen, X. F. *J Appl Polym Sci* 1996, 62, 743.
41. Tang, H.; Chen, X. G.; Luo, Y. X. *Eur Polym J* 1997, 33, 1383.
42. Tao, X. L.; Pan, Y.; Zheng, Q.; Yi, X. S. *J Appl Polym Sci* 2001, 79, 2258.