Ethylene–(vinyl acetate) copolymer/carbon fiber conductive composite: effect of polymer–filler interaction on its electrical properties

Wei-hua Di,[1,2]* Guo Zhang,[1,2] Zhu-Di Zhao[2] and Yi Peng[2]

[1]*Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, People's Republic of China*
[2]*Department of Materials Science, Jilin University, Changchun 130023, People's Republic of China*

Abstract: Ethylene–(vinyl acetate) (EVA)/carbon fibre (CF) composites were prepared by changing the content of CF in the composite. To investigate the effect of the interaction between EVA and CF on the electrical properties of the composite, the CF was treated in nitric acid. The interaction between EVA and CF was examined by a solvent-extraction method. It was found that the interaction of EVA with CF was enhanced due to the chemical absorption of EVA on CF. The correlation of CF content, electrical properties and the formation of polymer–filler gel for the composite with oxidized CF was studied. Although the composites filled with treated CF exhibit a slightly higher resistivity than those filled with untreated CF at room temperature, they show the improved electrical properties, including elimination of the negative-temperature-coefficient (NTC) effect, high electrical reproducibility after thermal cycles, and independence of the conductivity on time, which improves the practical applications of positive-temperature-coefficient (PTC) materials.
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INTRODUCTION

For the last three decades, composite materials have been widely studied in fundamental research and intensively used in industrial applications,[1,2] among which, the positive-temperature-coefficient (PTC) materials filled with carbon fillers are very often investigated[3–5] because they are widely used as self-regulating heaters, switching materials, and circuit-protection devices.[6,7] The PTC effect refers to a large resistivity jump of the composite as a result of the breakage of conductive pathways due to the polymer thermal expansion when it is heated to the polymer melting temperature (T_m). However, above T_m, a negative-temperature-coefficient (NTC)[8] phenomenon appears because of the rearrangement of carbon fillers. The NTC effect refers to the decrease of the resistivity with increasing temperature. In addition, these PTC materials show poor reproducibility of resistivity[5,8] over a long period of time or when undergoing thermal cycles, which is also due to the varying dispersion of carbon fillers in the composites.

The presence of the NTC effect and the instability of electrical conductivity have an adverse influence on the application of PTC materials. Therefore, it is important that a strategy is found to eliminate the NTC effect and improve the stability of the conductivity. Consequently, many researchers have proposed and developed methods to stabilize the conductive network structure within the composite, such as using a mixture of two types of carbon black (CB) blended with polyethylene,[5] adding rubber as a mechanical stabilizer to the CB-filled composite[9] and using a very-high-viscosity polymer as one component of the composite,[10] as well as crosslinking the semi-crystalline polymer composite.[11]

The physical–chemical interaction[12] at the matrix–filler interface plays an important role in stabilizing the conductive fillers within the composite. However, there are almost no functional groups on the carbon filler surface that are able to react with matrix. Some functional groups can be generated by treating the carbon filler surface. Several methods of modifying carbon fillers have been reported, including the electrochemical, plasma treatment and the chemical methods.[13,14] These methods successfully remove weak boundary layers from the surface and produce increased surface activity with the formation of both acidic and basic moieties. Chemical treatment has

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* Correspondence to: Wei-hua Di, Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, People's Republic of China
E-mail: dwh2100@hotmail.com

been especially preferred since it affords improvement with less degradation of the filler properties.

In our work, carbon fibre (CF), which is used as a conductive filler, was chemically oxidized in nitric acid, and ethylene–(vinyl acetate) (EVA) was selected as a polymer matrix in order to better fulfill our objective. It is well known that EVA is a polymer with polar functional groups, and the fibre treated with nitric acid shows the formation of various functional groups, such as —C=O, —C—OH and —COOH. Therefore, it is very possible that the chemical bonding takes place between EVA and CF. The evaluation of the interaction between EVA and CF oxidized with nitric acid was carried out by a solvent-extraction method. The effect of the interaction between EVA and CF on the PTC/NTC behaviour and the electrical reproducibility of the composite was investigated.

EXPERIMENTAL

Ethylene–(vinyl acetate) (EVA) was used as a polymer matrix with a melt flow index of 2 g/10 min. CF is a high-strength PAN-based fibre (T300; Jilin Carbon Co, China). It is a short fibre with following characteristics: diameter, 7 μm; length, 2 mm; density, 1.6 g cm^{-3}; volume resistivity, 6×10^{-3} Ω cm at 25 °C. CF was oxidized for 1 h in 60% nitric acid at 25 °C, washed with distilled water and dried in a vacuum oven. Composites were prepared by mixing EVA with CF in a Brabender mixer at 95 °C for 10 min, and then mixing again on a two-roll mill under the same conditions. Blends were compression-moulded in a vulcanized press, then cooled in air to room temperature, and made into sheets with a radius of 1 cm and a thickness of 1.5 mm. To examine the strength of the interaction between EVA and CF, the composites were extracted with decahydronaphthalene for 24 h using a Soxhlet apparatus. Electrical resistivity was measured with a digital multimetre when it was lower than $2 \times 10^7 \, \Omega$, and a high-resistance metre was used when the resistivity exceeded $2 \times 10^7 \, \Omega$.

RESULTS AND DISCUSSION
Fourier-transform infrared spectrometry
In this section, Fourier-transform infrared (FTIR) spectrometry is used to detect the functional groups. The FTIR spectra of untreated and treated CF are illustrated in Fig 1. As shown in Fig 1, there is no particular peak on the surface of untreated CF. However, it can be seen from the spectra of treated CF that the characteristic peak of —OH appears around 3400 cm^{-1}. This reveals that CF has really been oxidized by the nitric acid and the —OH functional group forms at the surface of CF treated by nitric acid. The interaction between EVA and the treated CF will be illustrated in a later section.
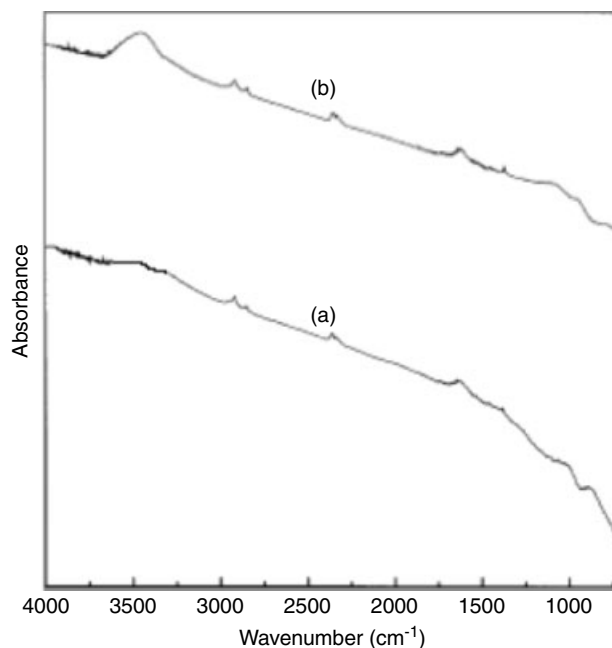

Figure 1. FTIR spectra of carbon fibre: (a) untreated; (b) treated with nitric acid.

Effect of CF treatment on the room-temperature resistivity
Figure 2 shows the effect of adding untreated and treated CFs on volume resistivity. At low concentration of CF, the composites exhibit a slight resistivity decrease with increasing CF content. However, at higher CF concentration, especially at about 14 wt%, a large reduction in resistivity is observed. This drastic change in resistivity is due to the formation of an interconnected structure of CFs and can be referred to as an electrical percolation threshold. This means that, at the percolation concentration, a very high percentage of electrons are able to flow through the composite due to the creation of an interconnecting conductive pathway. Above the percolation threshold, the composites show a slow resistivity change, as they do at low CF concentration. This suggests that once the conductive pathways are created, adding more conductive fillers cannot produce a significant influence on the conductivity level any longer. The concentration range between the point where the resistivity starts to drop greatly and the point where the resistivity starts to decrease slowly is defined as the percolation domain, as shown in Fig 2.

It is worth noting that the resistivity of treated CF-filled composite is higher than that of untreated CF-filled composite at the same filler concentration. On one hand, it is more likely that the chemical interactions of treated CF with EVA plays an important role in this difference. This interaction between EVA and CF modifies the CF distribution and makes it more uniform. Therefore, it is certain that more CFs are needed to achieve the same conductivity level as the untreated CF-filled composite for the treated CF-filled composite. On the other hand, the carboxyl content contained in
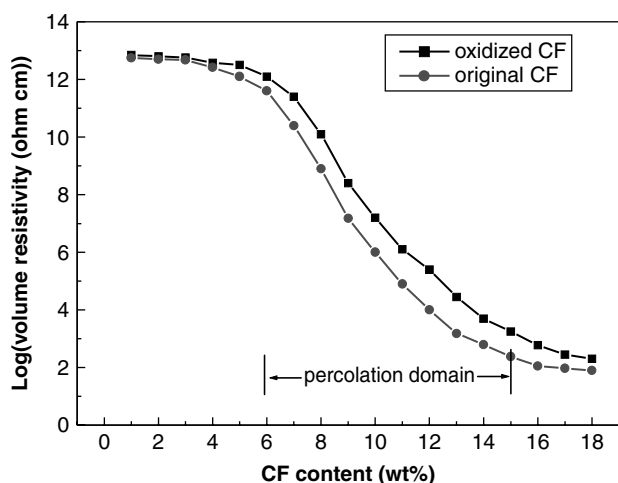
Figure 2. The resistivity as a function of CF content at room temperature.

nitric-acid-treated CF is increased, which inevitably increases the intrinsic resistance of CF[15] and improves matrix–filler interaction, leading to higher resistivity of polymer–filler composite compared with the untreated-filler filled composite at the same filler concentration.

Evaluation of the interaction between EVA and CF

The phenomenon of polymer–filler interactions has extensively been studied, since it is considered as a factor in filler-reinforced polymer composites and a measure of filler surface activity.[16–18] Wu *et al*[19] found by SEM observation that polyethylene (PE) was absorbed at cross parts or the end parts of vapour-grown carbon fibre in the polymer blends and the continuity of fillers and polymers seemed to be constructed in such a pattern with carbon fibre as a skeleton and PE as a clamp holder. Choi *et al*[20] revealed in their reports that the interfacial adhesion between carbon filler and the polymer resin was largely improved by treating carbon fibre because they observed from the SEM image that there were some holes in the untreated CF–matrix interface by pulling CF out of the matrix resin during a mechanical test, but there was seldom any hole in the treated CF-matrix interface due to the strong interaction of the polymer resin and CF. Nakajima *et al*[21,22] used tensile stress–strain, oscillatory-shear and dynamic-mechanical measurements to examine the polymer–filler interactions in the non-crosslinked polymer–filler compounds.

In our work, we attempt to adopt the solvent-extraction method for evaluation of the polymer–filler interactions. The theoretical evidence for this method is that the interaction between the polymer and filler causes a partial loss of polymer solubility. This filler-bound polymer is defined as a certain fraction of polymer strongly absorbed on the filler surface and is resistant to the absorptive action of the solvent. It is well known that decahydronaphthalene is a good

solvent for EVA. When making contact with the solvent for several hours, the polymer–filler system generally becomes divided into three parts as follows:

(I) dispersed polymer chains;
(II) dispersed filler with polymer chains absorbed on them; and
(III) coherent gel-like structure of filler particles connected through polymer chains.

The mass of polymer in these three parts are defined as m_{pI}, m_{pII} and m_{pIII}, respectively. To estimate the strength of the interaction between EVA and CF, B and G are defined as follows:

$B = (m_{pI} + m_{pII})/m_p$, fraction of filler-bound polymer;
$G = m_{pIII}/m_p$, gel, fraction of polymer not dispersed by the solvent, where m_p is the total polymer mass of the sample.

It can be seen from Figs 3 and 4 that, for the treated CF-filled samples at low CF concentration, there is only absorption of macromolecules on the solvent-dispersed filler particles and no gel forms. The gel starts to be created at higher CF concentration, which is just at the beginning of percolation domain seen in Fig 2. At high enough CF concentration, bound polymer exists primarily in gel forms, as shown in Table 1. This concentration is just at the end of the percolation domain. From these we can learn that the formation of bound polymer and gel is closely associated with the filler content that is closely linked with electrical properties. Therefore, it is necessary that filler concentration, electrical properties and the formations of bound polymer and gel are combined in considering in the treated CF-filled composite. At low filler concentration, CFs are unable to construct a continuous conductive network structure because of a large gap between fillers; hence, the composites show poor conductivity level and CF fillers with EVA absorbed on them are separated from each other, leading to only the formation of bound polymer but no gel. However, the continuity of CF starts to build up at higher CF concentration, at which the composite begins to show a drastic resistivity decrease and accordingly a gel-like structure starts to form on the action of the solvent. At high enough CF concentration, at which the gap between CFs is so small that the CF fillers with EVA absorbed on them are unable to be dispersed by the solvent, but a coherent structure called polymer–filler gel is formed, and the composite shows a high conductivity level. Narkis *et al*[5] considered that thin polymer films about a few hundreds Ångstroms in thickness was able to permit electron flow. Wu *et al*[19] came to a similar conclusion that the polymer reacted with the conductive fillers acted not only as a conductive bridge but also a mechanical bridge. Therefore, it is in the percolation domain that both the transition
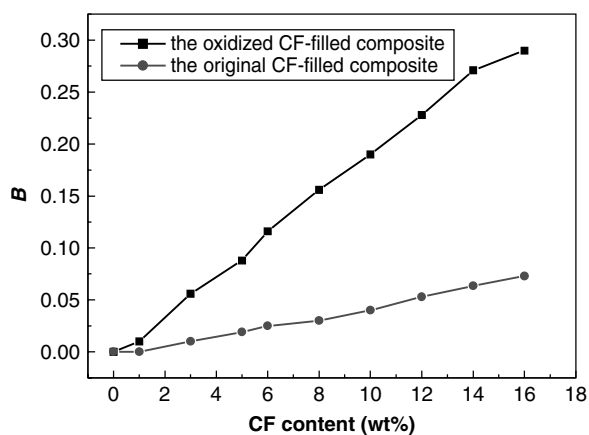
Figure 3. The bound polymer fraction *versus* CF content in the oxidized CF filled and original CF-filled composites.
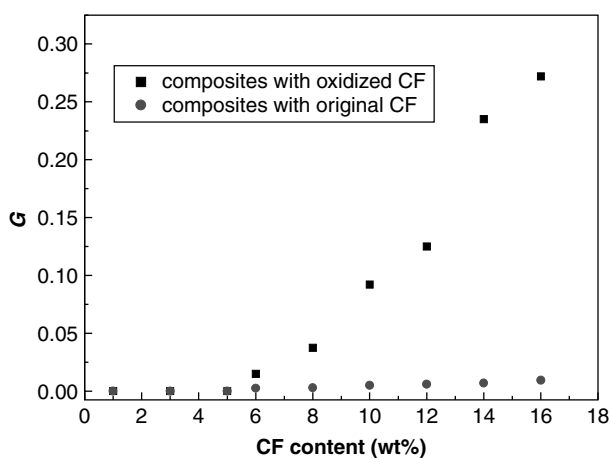

Figure 4. Polymer–filler gel fraction *versus* CF content in the oxidized CF-filled and original CF-filled composites.

Table 1. The comparison of bound polymer fraction (B) and gel fraction (G)

CF content (wt%)	B	G
14	0.271	0.235
15	0.281	0.255
16	0.29	0.272

of the insulator to conductor and the formation of polymer–filler gel occur.

The composites filled with untreated CF can only produce separated bound polymer even if at a high enough filler concentration, but almost no polymer–filler gel forms. It is supposed that the formation of bound polymer in the untreated CF-filled composites results from physical absorption and mechanical interaction between polymers and fillers, although this interaction is weak relative to the chemical bond. Roychoudhury and De[23] concluded that the formation of bound polymer is essentially a chemical process involving reactions between polymers and fillers.

Study of electrical stability

Carbon filler-filled PTC materials suffer from two main drawbacks, making them of little potential use in applications where switching properties are important. These disadvantages are (1) the lack of electrical reproducibility[24,25] due to irregular structure changes upon heating/cooling cycles, and (2) the presence of the NTC phenomenon[25,26] which may have an adverse effect on the desired switching properties of PTC materials.

In PTC systems, the expansion/contraction processes accompanying heating/cooling cycles cause the movements of conductive particles and the formations of aggregates and agglomerates. PTC composites therefore exhibit undesired NTC phenomenon and poor reproducibility of resistivity-temperature curves. Hence, it is necessary to devise a means to achieve the structure stabilization and a significant reduction of the mobility of carbon fillers in the PTC system. Narkis and Ram[11] effectively eliminated the NTC phenomenon and improved the electrical reproducibility by introduction of crosslinking forming a network to which carbon fillers were strongly attached.

It can be seen from Fig 5 that the NTC phenomenon disappears in the treated CF-filled composite, but the untreated CF-filled composites show NTC behaviour. It is suggested that the enhanced interaction in the treated CF-filled composite restricts the mobility of both CF particles and the chemically absorbed polymer chains. Thus, the elimination of NTC is believed to be the result of the reduced agglomeration of the treated CF fillers compared with that of virginal fillers.

It is interesting to find in Fig 5 that the treated CF-filled composite exhibits a lower PTC transition temperature, ie T_m, at which a maximum resistivity is achieved compared with the untreated CF-filled composite. This lower transition temperature might result from the reduced mobility of EVA chains and difficulty of crystallization due to the chemical
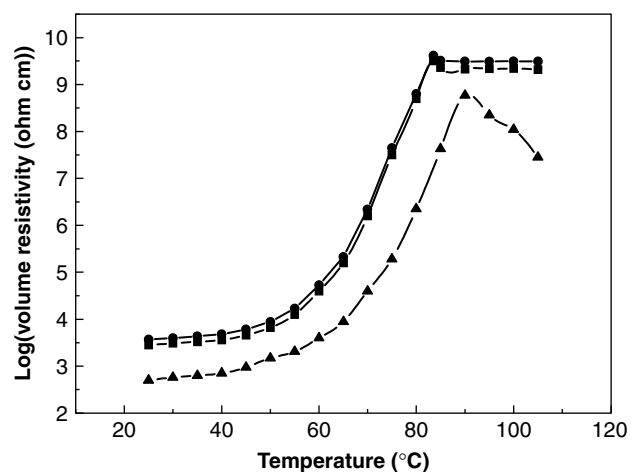

Figure 5. Log resistivity as a function of temperature in the 14 wt% CF-filled composites. ▲: the composite with original CF; ■: the composite with oxidized CF; ●: its extraction of the composite with oxidized CF.

adsorption of EVA on the CF surface. This result confirms that the reaction between EVA and CF actually takes place.

Figure 5 shows the PTC behaviour of 14 wt% treated CF-filled composite and its extracted composite, ie polymer–filler gel. They exhibit similar PTC curves. It is suggested that the thermal expansion of the absorbed polymer on CF during the entire heating process makes the main contribution to the PTC effect of the composite, but the polymer extracted by the solvent produces almost no influence on the PTC effect.

We defined the ratio of the maximum resistivity to the room-temperature resistivity as the PTC intensity. In Fig 6 it can be seen that the untreated CF-filled composites show increased room temperature resistivity and reduced PTC intensity with the increase of thermal cycles. The treated CF-filled composites show almost unchanged room-temperature resistivity and PTC intensity, even if undergoing several thermal cycles (Fig 7). It is believed that, upon heating, the 'frozen' distribution of the conductive filler will start to change in the untreated CF-filled composite. As
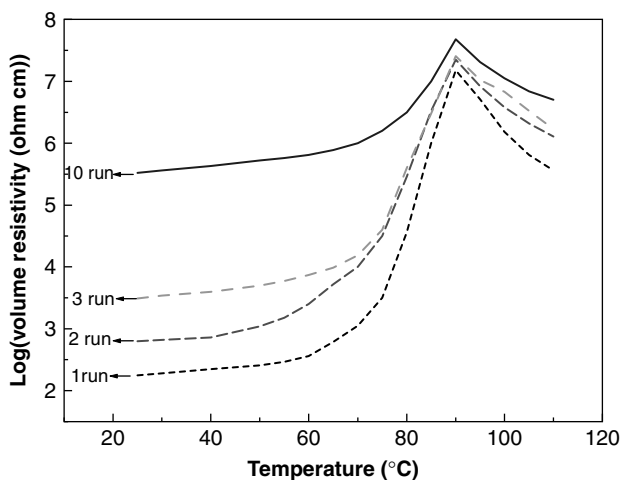
the crystallites melt and the viscosity reduces with the increase of temperature, especially when undergoing a few thermal cycles, the redistribution process results in a more uniform distribution that apparently permits additional filler to participate in the conduction process; in other words, the effective weight fraction of CF devoted to the formation of conductive pathways decreases with the increase of the number of thermal cycles, as shown in Fig 8. Hence, the increase of room-temperature resistivity and decrease of PTC intensity of the untreated CF-filled composites are ascribed to the reduced effective weight fraction of CF after undergoing the thermal cycles. Therefore, we believe that the much better stability of electrical properties for the treated CF-filled composite is attributed to the interaction enhanced by the better adhesion of polymer–filler interface which considerably restricts the mobility of the polymer chains and conductive fillers, leading to the stabilized conduction network structure during the heating/cooling processes.

Resistivity-time behaviour for the untreated CF-filled and treated CF-filled composite samples has been investigated at $75\,^{\circ}\mathrm{C}$ (below the T_{m} of EVA) and

Figure 6. Resistivity-temperature behaviour of the 15 wt% original CF-filled composite with various numbers of thermal cycles.

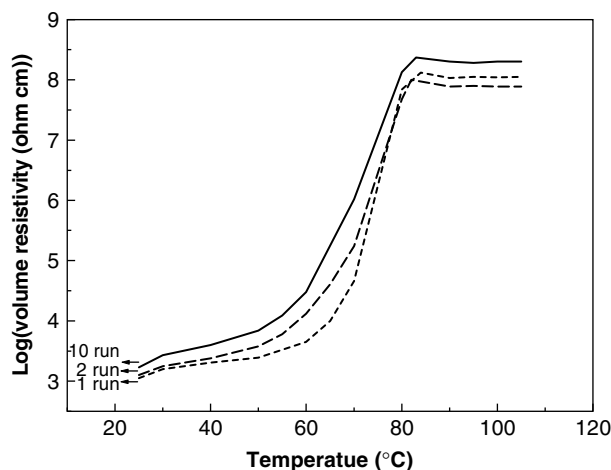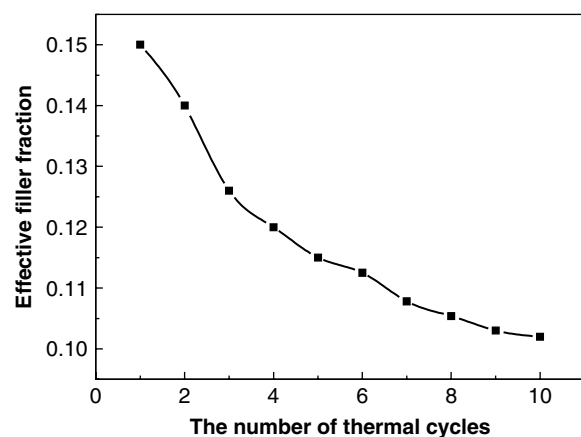**Figure 8.** Effective filler fraction of the 15 wt% original CF-filled composite with various numbers of thermal cycles.

Figure 7. Resistivity-temperature behaviour of the 15 wt% treated CF-filled composite with various numbers of thermal cycles.

Figure 9. Log resistivity as a function of time for the 14 wt% CF filled composites at $75\,^{\circ}\mathrm{C}$. ■: the composite with original CF; ●: the composite with oxidized CF.
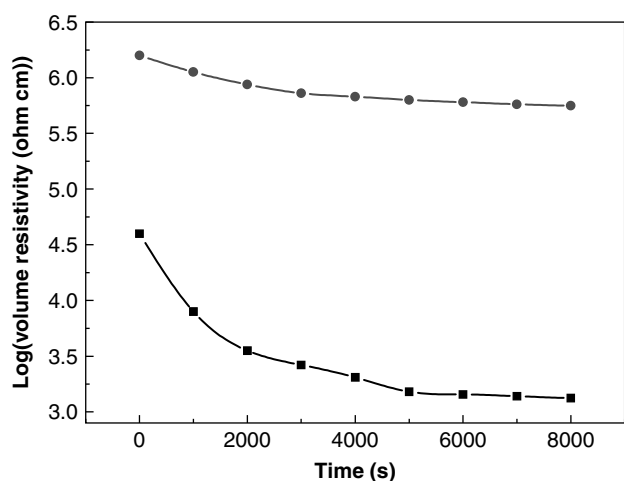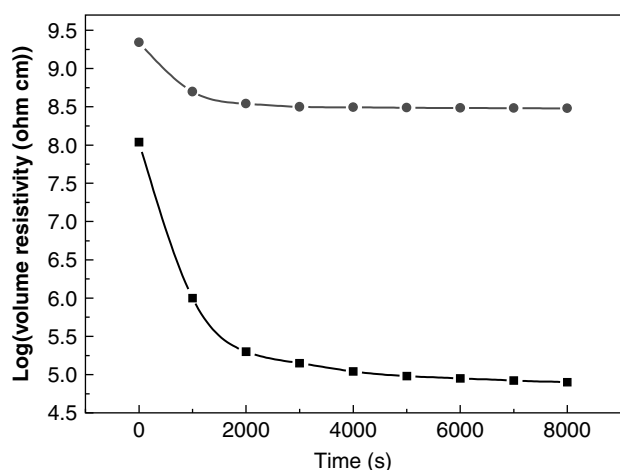
Figure 10. Log resistivity as a function of time for the 14 wt% CF filled composites at 100 °C. ■: the composite with original CF; ●: the composite with oxidized CF.

100 °C (above the T_m of EVA), as shown in Figs 9 and 10, respectively. The untreated CF-filled composites show a drastic resistivity decrease with increasing time in the initial time stage and then a low degree of decrease with further increase of time. The treated CF-filled composites exhibit a little resistivity change in the entire measured time. This phenomenon is believed to be closely associated with the polymer chains' relaxation behaviour.[27,28] For the untreated CF-filled composite at high temperature, EVA chains segments have sufficient mobility, and thus the agglomeration of CF is accompanied by the chains' segmental motion, which makes the resistivity of the sample produce a drastic decrease with the increase of time. At lower temperature, a large number of crystallites will restrict the mobility of the EVA chains and the CF particles to a certain level, resulting in a lower degree of decrease in resistivity with increasing time. However, for the treated CF-filled composite, a slight decrease of resistivity with time indicates a strong interfacial interaction between EVA and CF, which prevents the mobility of EVA chains and CF fillers, even if at high temperature.

CONCLUSIONS

CF was chemically oxidized in nitric acid and the EVA–CF composites were prepared by the conventional melt-mixing technique. The interaction between EVA and CF was evaluated by the solvent-extraction method. It was found that the interaction between EVA and CF in the oxidized CF-filled

composite was enhanced due to chemical absorption of the EVA on CF. It is concluded that the CF content is closely associated with both the electrical properties and the formation of polymer–filler gel for the treated CF-filled composite. In the percolation domain not only did the transition of the insulator to conductor occur but also the gel-like structure was formed. Although the composite with treated CF showed a slightly higher resistivity than the composite with original CF at the same filler concentration at room temperature, the enhanced interaction of EVA with CF in the treated CF-filled composite, was invariably stabilized because of which the conductive network structure, even if over a long time or by undergoing several thermal cycles. This stabilization effectively eliminate the NTC phenomenon and improved the electrical reproducibility, which are favourable for the application of PTC materials.

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