

Performance Stabilization of Conductive Polymer Composites

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ABSTRACT: Conductive polymer composites used as candidates for positive temperature coefficient (PTC) materials are faced with performance decay characterized by gradually increased room-temperature resistivity and decreased PTC intensity. Considering that deterioration of the properties is mainly related to the capability of conductive networks established by conductive fillers to recover from the effect of repeated expansion/contraction in a timely manner, the present work introduces chemical bonding into the filler/matrix interphase. The experimental results indicate that in the composites consisting of conductive carbon black (CB), low-density polyethylene (LDPE), and ethylene-vinyl acetate copolymer, CB particles can be covalently con-

nected with LDPE through melt grafting of acrylic acid. As a result, the composites are provided with reduced room-temperature resistivity and significantly increased PTC intensity. Compared with the composites filled with untreated CB, the present composites possess reproducible PTC behavior and demonstrate stable electrothermal output in association with negligible contact resistance at the composites/metallic electrodes contacts. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2438–2445, 2003

Key words: ageing; blends; dispersions; conductive polymer composites; PTC effect

INTRODUCTION

Electrically conducting polymer composites consisting of conductive fillers and insulating thermoplastic polymers can serve as positive temperature coefficient (PTC) materials used for making self-regulating heaters, microswitches, sensors, and the like. The effect is characterized by a drastic increase in volume resistivity as the temperature approaches the melting point of the matrix. At room temperature, the conducting filler particles are in a state of close packing in close contact with the neighbors, forming conduction paths throughout the composite. During heating, the polymer expands much more than the fillers and the effect

is strongly enhanced when approaching the melting temperature of the polymer matrix. There the conducting paths established by the filler particles are obviously interrupted because of the enhanced thermal expansion of the polymer. This leads to the significant increase in the resistivity. Because the variation is reversible, the PTC-type polymer composites are regarded as promising smart materials.¹

With respect to the application of the composites as self-regulating heaters or the like, performance stability that is closely related to working life is one of the critical issues. Under the joint action of electric field and varying temperature, the composites in service have to inevitably experience severe physical and chemical aging. As a result, degradation of properties occurs as characterized by the gradually increased room-temperature resistivity and reduced PTC intensity (defined as the ratio of the maximum resistivity to the room-temperature resistivity calculated from the temperature dependency of composite resistivity). An earlier study of this problem indicates that the main influencing factors are as follows²: (1) irreversible damage of partial conductive networks, (2) oxidation degradation-induced imperfect crystallizability of the matrix polymer, and (3) increased contact resistance formed at the preembedded metallic electrodes/composites contacts.

Considering that one of the characteristic effects of PTC stabilization lies in the guarantee of the reversible

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displacement of conductive fillers during repeated heating and cooling processes, the authors of the present work strengthened the filler/matrix interaction through *in situ* grafting to improve the reproducibility. As a continuation of our studies on carbon black (CB)-filled immiscible polyblends,³⁻⁷ CB/low-density polyethylene/ethylene-vinyl acetate copolymer (CB/LDPE/EVA) composites are employed in this investigation as the target materials. Acrylic acid (AA) was incorporated into the systems as the grafting monomer. It is expected that CB can be covalently connected with the matrix by means of poly(acrylic acid) formed in the course of melt compounding. The polar monomer was chosen also because the affinity of the composites to the metallic electrodes can be enhanced to avoid the aforesaid high contact resistance resulting from poor contact. Effects of this treatment on the electrical properties of the composites are also discussed.

EXPERIMENTAL

LDPE and EVA, with identical melt-flow indices of 2.0 g/10 min, were used as the matrix polymers. An electrically conductive CB was employed as the filler. Both the grafting monomer, acrylic acid (AA), and the initiator, dicumyl peroxide (DCP), were chemically pure and used as received without further purification.

For generating chemical bonds between CB and the matrix, CB was pretreated with the alcohol solution of AA and DCP. The polymers and CB (treated or untreated) with the desired proportions (LDPE/EVA = 80/20 and the weight percentage of CB in LDPE/EVA was always 18%) were melt-mixed in a laboratory-size Brabender plasticorder Model XB20-80 at 160°C and 20 rpm. In each case, LDPE and CB were mixed for 5 min and then EVA was incorporated into the mixer for subsequent blending for 10 min. After being removed and granulated, the composites with preembedded electrodes were compression-molded at 140°C and then cooled in air to room temperature. The sheet samples ($65 \times 45 \times 3 \text{ mm}^3$) were allowed to rest overnight before the subsequent measurements.

To evaluate the variation in the chemical structure of CB before and after melt grafting, the attenuated total reflectance (ATR) mode of a Nicolet 210 Fourier transform infrared (FTIR) spectrometer (Nicolet Instruments, Madison, WI) was used. CB in the composites with the addition of AA during melt blending was isolated by extracting the unbonded matrix from the composites in a Soxhlet apparatus using dimethyl benzene for 72 h.

The volume resistivity of the composites was measured with a four-lead system. The two current electrodes made of brass net ($45 \times 5 \text{ mm}^2$) were preembedded at the ends and through the breadth of the

rectangular specimens. The two potential electrodes (a pair of brass rods 1 mm in diameter and 45 mm in length) were also preembedded through the breadth of the specimens. The center-to-center distance between a current electrode and its neighboring potential electrode was 8 mm and that between the two potential electrodes was 44 mm. In some cases, two-lead measurements were carried out by connecting the above-mentioned potential electrodes to an ohmmeter.

To examine the variation in structure-property relationship of the composites in response to alternating temperature environment, thermal-cold cycling experiments were conducted in air. In each cycle, the composites specimens were heated from room temperature to 130°C within 10 min, kept at 130°C for 5 min, and then cooled to room temperature. After certain cycles, the temperature dependency of resistivity was recorded by heating the specimens at a heating rate of 2°C/min. In addition, the specimens were also electrified to simulate the practical service situation. In this case, alternating current was applied to the potential electrodes preembedded in the specimens. The consumed power and surface temperature of the specimens were simultaneously recorded as a function of time.

Differential scanning calorimetry (DSC) studies of the composites that had experienced thermal-cold cycling were carried out on a TA DSC 2910 apparatus (TA Instruments, New Castle, DE) in N_2 atmosphere to characterize the melting and crystallization behavior. The samples were heated from room temperature to 140°C at a rate of 10°C/min and kept for 5 min to eliminate thermal history. Then, the sample was cooled to room temperature at a rate of 10°C/min. The variation in heat capacity as a function of time was recorded. Thermogravimetric analysis (TGA) of the composites was made by using a Perkin-Elmer TGA-II apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT) in N_2 atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Because the present investigation was designed to study the effect of melt grafting on the electrical behavior of the composites, variation in the chemical structure of CB particles should be known at the very beginning of the discussion. FTIR-ATR spectra of untreated and treated CB are shown in Figure 1. To eliminate the influence of homopolymers, CB with the grafting polymers used for the FTIR examination was separated from the composites in advance. In general, the surface chemistry of carbon black is rather complicated.⁸ It is considered as a series of imperfect polycyclic aromatic hydrocarbons in various states of oxidation. As shown in Figure 1, the most distinct ab-

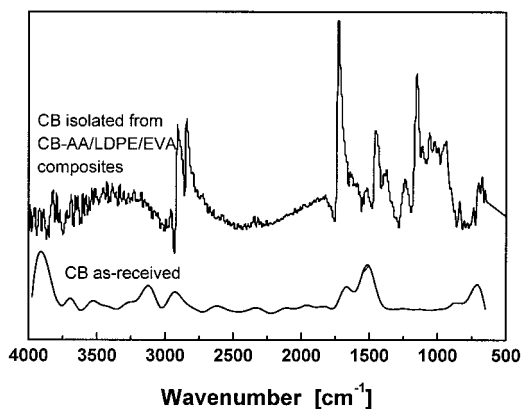


Figure 1 FTIR-ATR spectra of carbon black.

sorption of untreated CB appears at around 1500 cm^{-1} , representing the stretching mode of $\text{C}=\text{C}$ in aromatic rings. In the case of CB isolated from CB-AA/LDPE/EVA composites (denoting the composites in which AA-treated CB is added during melt compounding), a strong peak of carbonyl at 1730 cm^{-1} is perceivable. In addition, a broad band attributed to the stretching vibration of $-\text{OH}$ of carboxyl groups appears at 3500 cm^{-1} . These FTIR data suggest that acryl acid has been introduced onto the surface of carbon black as a result of melt grafting. On the other hand, analysis of the X-ray photoelectron spectra indicates that the oxygen content of the CB isolated from CB-AA/LDPE/EVA is only one half that of CB as-received⁹ evidently the result of LDPE coverage. Overall, it is evidenced that covalent bonds between CB particles and LDPE are established through the melt grafting of AA.

Figure 2 compares the effect of different sequences

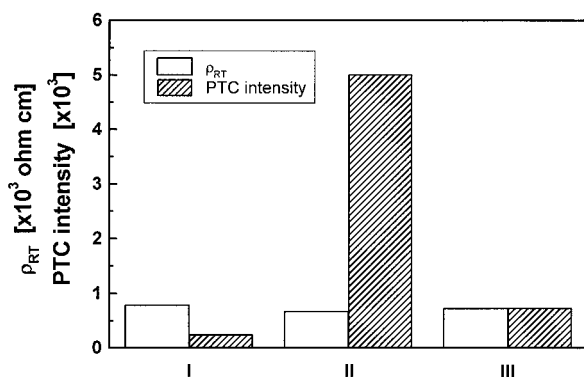


Figure 2 Effect of different ways of CB treatment on room-temperature resistivity (ρ_{RT}), and PTC intensity of CB-filled LDPE/EVA composites. I: CB was incorporated without any treatment. II: CB was pretreated with AA and DCP before melt mixing with the matrix polymers as mentioned in the Experimental section. III: LDPE was melt mixed with AA and DCP for 5 min, and then CB was added to the system and mixed for 5 min. Finally, EVA was incorporated for the subsequent blending of 10 min. AA/CB, 30 wt %.

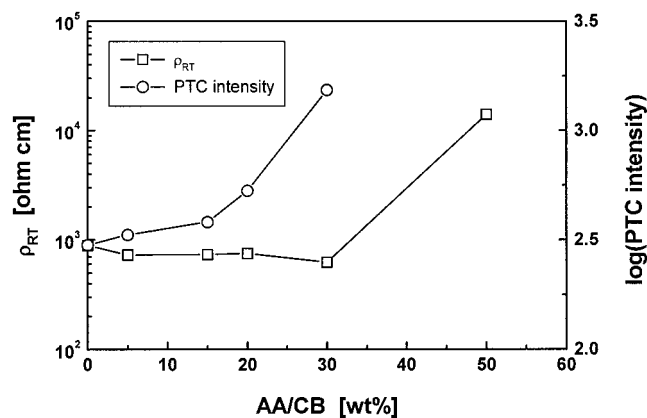


Figure 3 Room-temperature resistivity ρ_{RT} and PTC intensity of CB-AA/LDPE/EVA composites as a function of the weight percentage of AA/CB.

of CB treatment. Unlike case II where CB is pretreated with AA and DCP before melt compounding, the probability of grafting reaction is greatly lowered in case III where LDPE is melt mixed with AA and DCP before the addition of CB. The slightly increased PTC intensity (cf. cases I and III in Fig. 2) should be attributed to the interaction between carboxyl and the polar groups on CB surfaces. The results preliminarily demonstrate the important role of grafting AA onto CB.

It is worth noting that an enhanced adhesion between CB and the matrix would help to increase the stability of PTC behavior,¹⁰ but hinders the formation of conductive networks because of the insulating attachments on the CB surface leading to higher room-temperature resistivity¹¹ and thus insufficient electrothermal output. This means the amount of the grafting monomer should be optimized to reach balanced performance. As shown in Figure 3, room-temperature resistivity of the composites remains nearly unchanged with an increase in the amount of AA from 0 to 30 wt % (AA/CB) and increases to over ten times when AA/CB = 50 wt %. In contrast, there is a continuous increase in PTC intensity with increasing AA content. It is clear that the PTC effect is more sensitive to filler/matrix interfacial interaction. The presence of grafting poly(acrylic acid) not only shields CB structures from one another but also improves the homogeneity of CB dispersion in the matrix. Both factors reduce the formation probability of conduction pathways and hence the conductivity of the composites. The curve in Figure 3 also reveals that the above shielding effect would be brought into play only at a certain critical value, coinciding with the well-known percolation phenomenon. It implies that the grafting polymers also form a spatially distributed network throughout the composites when CB is pretreated with a sufficient amount of AA.

Figure 4 illustrates the temperature dependency of resistivity of the composites recorded during the re-

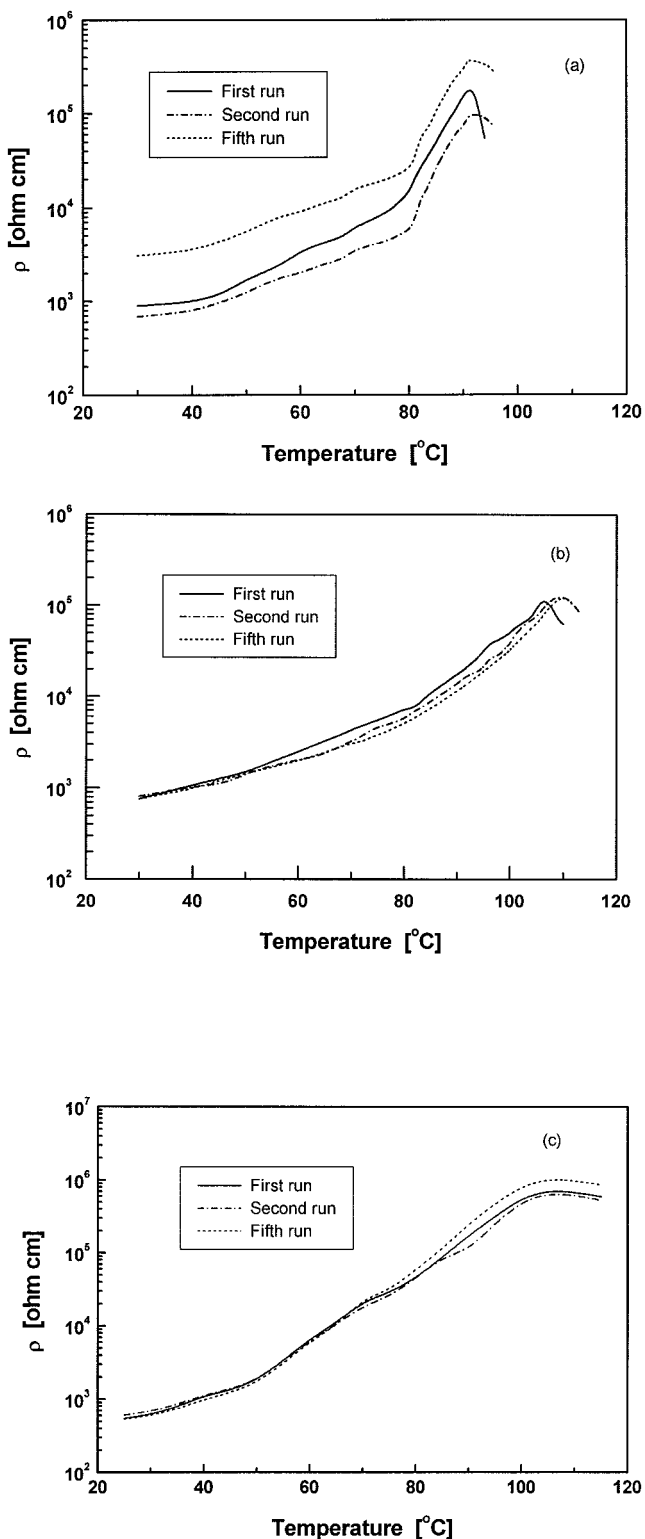


Figure 4 Temperature dependency of resistivity of (a) CB/LDPE/EVA, (b) CB-AA/LDPE/EVA (AA/CB, 20 wt %), and (c) CB-AA/LDPE/EVA (AA/CB = 30 wt %).

peated thermal-cold cycling experiments. It is found that the reproducibility of the PTC effect is greatly enhanced for CB-AA/LDPE/EVA composites as characterized by the overlapping curves [Fig. 4(b), (c)].

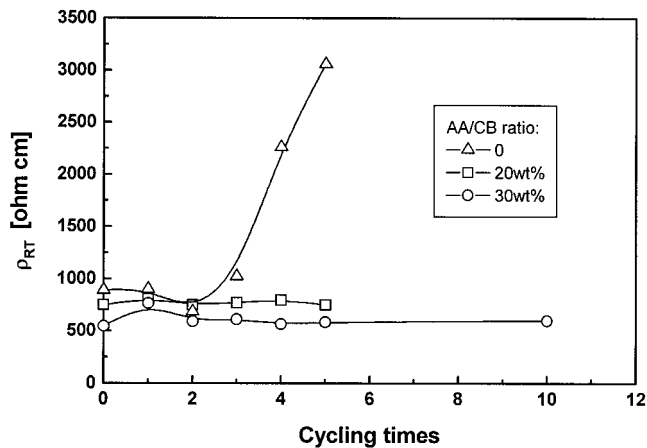


Figure 5 Room-temperature resistivity ρ_{RT} of CB/LDPE/EVA and CB-AA/LDPE/EVA composites as a function of the times of thermal-cold cycling tests.

In fact, for the short-term thermal-cold cycling experiments, the deterioration of both room-temperature conductivity and PTC intensity [Fig. 4(a)] is caused by the damage of partial electrical networks attributed to the repeated drastic volume expansion/contraction at the melting point of the matrix.² The introduction of chemical bonding into the interphase between CB and the matrix by melt grafting enhances the structural stability of the CB distributed in the composites. Figure 5 further shows the thermally induced resistivity change as a function of AA concentration. It is shown that a weight percentage of AA/CB of 30 wt % provides lower room-temperature resistivity with sufficient stability. Therefore, this ratio was used for the CB-AA/LDPE/EVA composites discussed in the following.

Figure 6 exhibits the percolation curve of CB-AA/LDPE/EVA composites at a fixed AA/CB fraction of 30 wt % compared with that of CB/LDPE/EVA composites. The two curves almost overlap within the CB

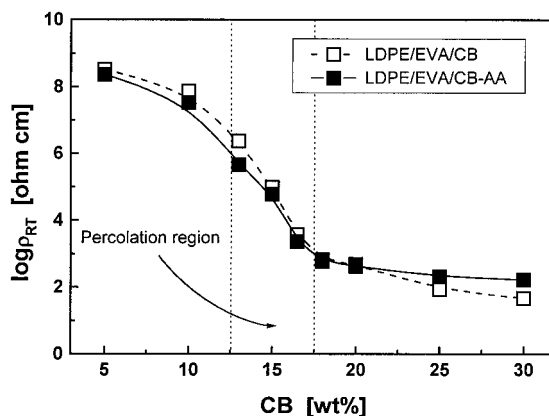


Figure 6 Dependency of room-temperature resistivity ρ_{RT} of CB/LDPE/EVA and CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites on CB content.

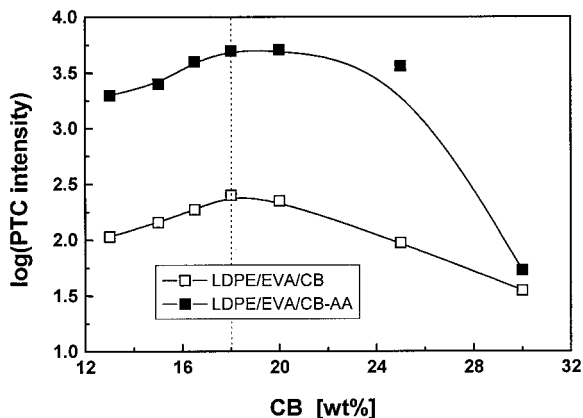


Figure 7 PTC intensity versus CB content of CB/LDPE/EVA and CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites.

concentration range of interests but there is still a slight difference. When the CB content is lower than the upper limit of the percolation region (i.e., ~ 17.5 wt %), electrical resistivity of CB-AA/LDPE/EVA is lower than that of CB/LDPE/EVA at the same CB content. It is believed that the strong interaction between CB and the matrix attributed to the effect of *in situ* grafting would lead CB agglomerates to be broken into much smaller aggregates under the action of shearing during compounding, and thus increase the formation probability of conduction networks and the composites that exhibit resistivity lower than that of CB/LDPE/EVA.

Figure 6 also shows that when the CB content exceeds 17.5 wt %, the resistivity of CB-AA/LDPE/EVA begins to be higher than that of CB/LDPE/EVA. In general, the conductivity of composites is mainly controlled by the intrinsic conductivity of the fillers rather than arrangement of the fillers when conducting pathways are built up. Because CB aggregates are partially covered by poly(acrylic acid) produced during melt grafting in CB-AA/LDPE/EVA, either the apparent resistivity of the fillers or the resistivity of the composites has to be higher. Accordingly, the PTC intensity of the composites is plotted against the CB content in Figure 7. Besides the fact that PTC intensity decreases with increasing CB content, which is observable in conventional PTC composites,¹² the PTC intensity of CB-AA/LDPE/EVA is significantly higher than that of CB/LDPE/EVA over the whole CB loading range. It again demonstrates the enhancing effect of *in situ* grafting of AA on PTC behavior of the composites.

To check how the electrothermal performance is affected by the *in situ* grafting technique, the specimens were electrified with alternating current (Fig. 8). For CB/LDPE/EVA composites, both power and surface temperature of the composites reached the maxima rapidly and then decreased with an increase in

time. An increased resistivity of the composites themselves (Fig. 5) and increased contact resistance of the composites/metallic electrodes contacts account for the phenomenon.² With respect to CB-AA/LDPE/EVA composites, their power and surface temperature remained almost unchanged with increasing time, as expected, manifesting the effect of grafting-induced structural stability.

To have a clear image of the influence of contact resistance, Figure 9 exhibits the resistivity of the composites determined by two methods before and after being electrified. So far as we know, the four-terminal method is able to remove the influence of contact resistances, and the two-terminal one cannot. Figure 9(a) indicates that before being electrified the resistivity of the composites measured by the two-lead method is close to that by the four-lead method, suggesting the contact resistance is negligible. After being electrified, the resistivity determined by the two-lead method is significantly higher than that by the four-lead method, besides the fact that the resistivity values determined by the two methods are all higher than those of the composites before being electrified. The former phenomenon has to be related to the remark-

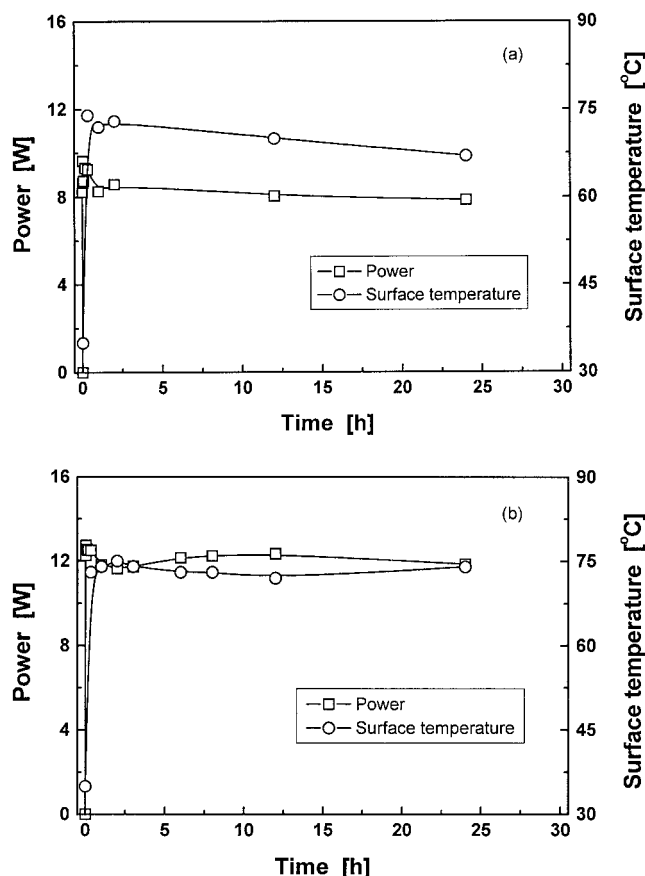


Figure 8 Time dependency of power and surface temperature of (a) CB/LDPE/EVA and (b) CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites electrified with 110 V a.c.

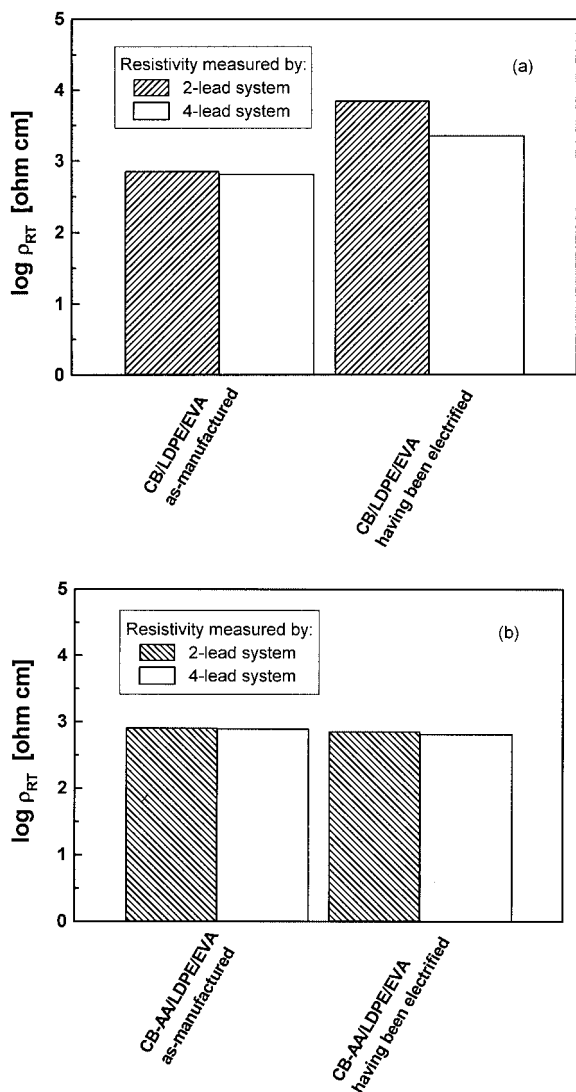


Figure 9 Room-temperature resistivity ρ_{RT} of (a) CB/LDPE/EVA and (b) CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites as-manufactured and those electrified with 110 V a.c. for 24 h.

ably increased contact resistance between the preembedded metallic electrodes and the composites, and the latter can be explained by the aforementioned structural degradation-induced increase of the composites' resistivity. In the case of *in situ*-grafted CB filled composites, however, the resistivity values measured by the two methods are almost the same regardless of the electrification history [Fig. 9(b)]. This should be the result of the improved adhesion between the composites and the preembedded electrodes, which prevents the debonding of the composites/electrodes contacts originating from the different thermal expansion coefficients of the components.

The above analysis is conducted on the basis of the short-term performance of the composites. The long-term behavior should also be studied from the engineering viewpoint. As reflected by Figure 10, although

the rates of change in room-temperature resistivity and PTC intensity of CB-AA/LDPE/EVA are lower than those of CB/LDPE/EVA at the beginning stage of thermal-cold cycling tests, the modification based on *in situ* grafting of CB cannot prevent the deterioration of performance of the composites. Our previous study suggests that under the circumstances of repeated thermal-cold cycling, the early degradation of electrical properties is mainly attributed to the irreversible variation in the dispersion status of CB particles in the matrix, whereas thermal-oxidative aging-induced destruction of crystallization characteristic of the matrix is responsible for the performance decay in the case of long operating times.² That is, the current technique is able to improve the interfacial strength of filler/matrix bonding but fails to stop the aging of the polymers themselves. This conclusion is supported by the DSC traces given in Figure 11 and Figure 12. With an increase in time, either the melting temperatures or the crystallization temperatures of the composites decrease significantly. In addition, the profiles of both the endothermic and exothermic peaks become increasingly irregular. These strongly demonstrate morphological variation of the matrix polymer irrespective of whether CB was pretreated or not pretreated with AA. The crystalline structure is gradually destroyed, leading to an increase in the amount of imperfect crystals or the amorphous portion. Because an increase in the amount of disordered region in the matrix would result in volume expansion of the composites (because the density of crystallites is always higher than that of amorphous ones), the conductive networks established by CB particles throughout the composites have to be damaged in the course of the thermal-cold cycling experiments and the room-temperature resistivity increases as a result. On the other hand, damage of the crystalline phase would also reduce the driving force for the PTC effect according

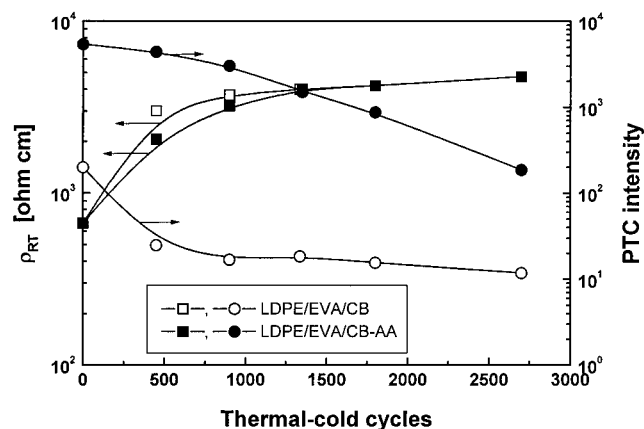


Figure 10 Room-temperature resistivity ρ_{RT} and PTC intensity of CB/LDPE/EVA and CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites versus thermal-cold cycles.

to the generally accepted theory.^{1,13} Therefore, the PTC intensity of the composites decreases with increasing the cycling times of the thermal-cold experiments.

The pyrolytic behaviors of the composites exhibited in Figure 13 also manifest that the melt grafting of AA is insufficient to prevent or retard oxidative degradation, the main cause accounting for aging of polyethylene in air and hence damage of crystalline phases.^{14,15} The decrement of pyrolytic temperature corresponding to 50% weight loss ($T_{50\%}$) of both composites is similar with respect to the same thermal-cold cycles. This is reasonable because the melt grafting of AA can neither change the backbones of the matrix nor crosslink the matrix to form three-dimensional networks. The above analysis is evidenced when the composites are exposed to an irradiation environment.⁹ Because of the appearance of irradiation-induced

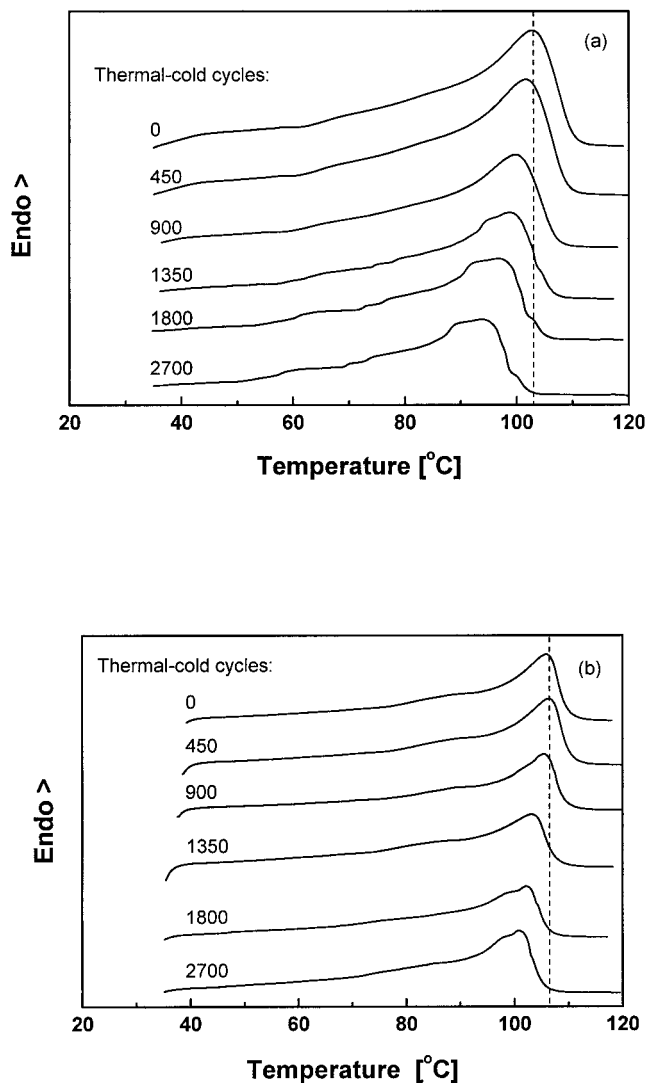


Figure 11 DSC heating traces of (a) CB/LDPE/EVA and (b) CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites at different times of thermal-cold cycling.

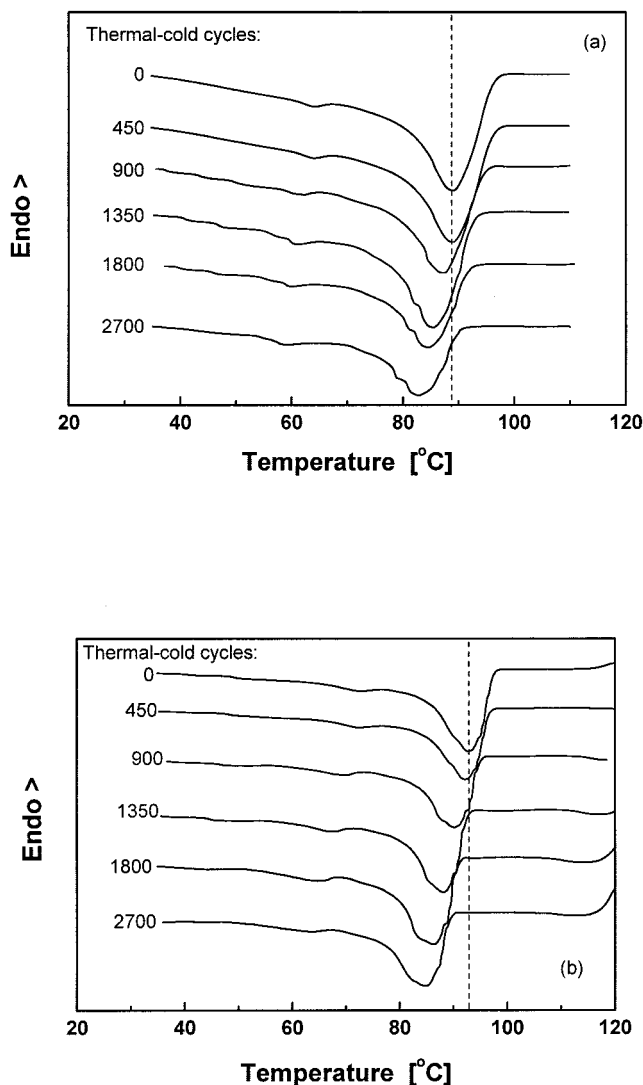


Figure 12 DSC cooling traces of (a) CB/LDPE/EVA and (b) CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites at different times of thermal-cold cycling.

crosslinking structure, the transportation of oxygen becomes difficult, leading to a higher thermal decomposition temperature.

CONCLUSIONS

1. Acrylic acid can be grafted onto CB particles and LDPE simultaneously during melt compounding, establishing covalent bonding between the fillers and the matrix. In this way, distribution of carbon black in LDPE/EVA can be stabilized. Besides a slight reduction in room-temperature resistivity of the composites, PTC intensity can be remarkably increased as a result. This conforms to the criterion of manufacturing qualified PTC-type composites.¹²

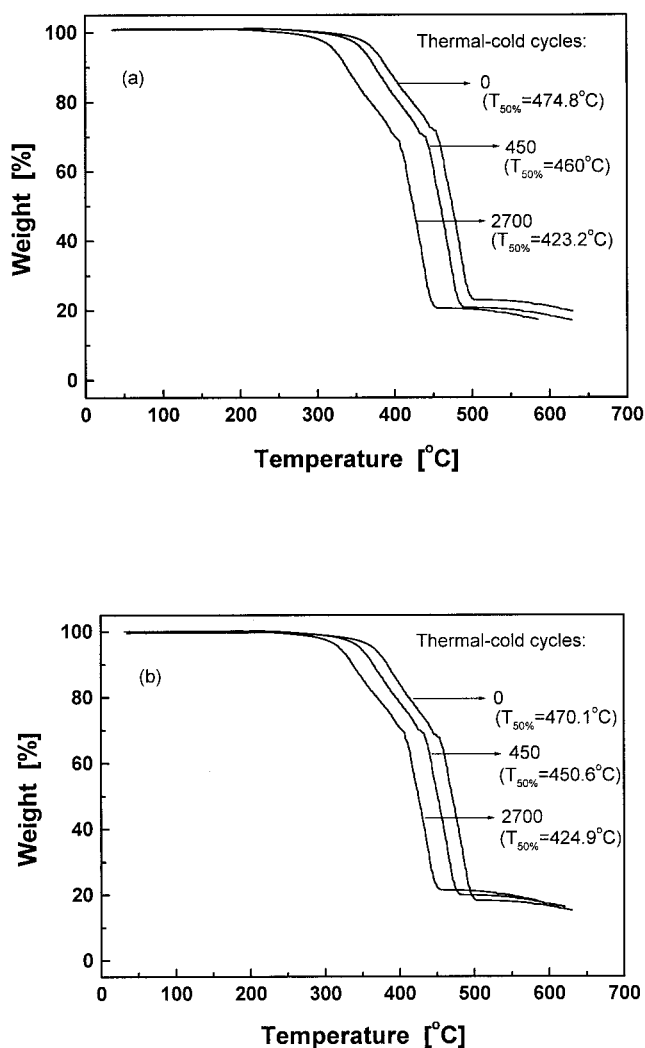


Figure 13 TGA curves of (a) CB/LDPE/EVA and (b) CB-AA/LDPE/EVA (AA/CB = 30 wt %) composites at different times of thermal-cold cycling ($T_{50\%}$ denotes the temperature corresponding to 50% weight loss).

- The *in situ* grafting of acrylic acid at the presence of both fillers and matrix can effectively improve the short-term performance stability of the composites serving as PTC materials by ensuring the

restoration of the displaced filler particles during the repeated expansion/contraction. Moreover, the contact resistance at the composites/metallic electrodes contacts is also negligible as a result of the increased adhesion between the contacts.

- The technique proposed in this work cannot be used to stabilize the long-term performance of the composites because the latter is related to the aging of the matrix itself. Other measures available for increasing aging resistance would help to solve the problem instead.

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