

Heat Treatment-Induced Multiple Melting Behavior of Carbon Black-Filled Polymer Blends in Relation to the Conductive Performance Stabilization

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ABSTRACT: Polymer blend-based electrical conductive composites are provided with more possibilities for tailoring the performance in comparison with single polymer systems. To find an optimum heat treatment temperature of the composites, which is critical to practical applications, detailed thermal analyses of the related materials were carried out as a function of different annealing conditions. Based on the discussion of the morphological variation during treatment in terms of multiple melting behavior, it was found that an annealing temperature of 75°C is able to stabilize the resistivity of the composites within a reasonable period of time, as only solid-state crystallization of LDPE and uniformization of EVA crystalline size are involved. In contrast to treatment at a temperature higher than 75°C, the ultimate equilibrium resistivity resulting from the above annealing procedure approaches the resistivity of the composites as-manufactured. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1267–1273, 2001

Key words: multiple (double) melting behavior; conductive polymer composites; heat treatment; performance stabilization; carbon black

INTRODUCTION

The application of polymer blends instead of single polymer provides a wider processing window for the manufacturing of electrically conductive

composites.^{1,2} Owing to the effects of double percolation³ and two-step percolation⁴ resulting from the heterogeneous distribution of conductive fillers, composites with balanced performance and improved reproducibility can be obtained.

Considering that thermoplastics-based composites must undergo different thermal forming procedures, such as extrusion, injection, and compression molding, post-heat treatment of the materials is critical for the enhancement of both stability and long-term service life, especially when the composites function under inconstant temperature environment. However, heat treatment on the polyblend-based conductive composites is factually less investigated, to the authors' knowledge. Therefore, much work remains to be done in this direction.

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Table I Characteristics of the Polymers Employed

Materials	Specifications
Low-density polyethylene (LDPE)	Density: 0.912 g/cm ³ Melt flow index: 2.0 g/10 min Melting point: 108°C
Ethylene-vinyl acetate copolymer (EVA)	VA content: 10–30 wt % Density: 0.930–0.980 g/cm ³ Melt flow index: 2.0–8.0 g/10 min Melting point: 90–95°C

As one of our serial papers on carbon black-filled ethylene-vinyl acetate copolymer/low-density polyethylene composites, the present work deals with the matrix morphology variation as a function of heat treatment at different temperatures, which would furnish the basis for the selection of heat treatment conditions and the optimization of processing as well.

EXPERIMENTAL

Low-density polyethylene (LDPE) and ethylene-vinyl acetate copolymer (EVA), the matrix resins for the composites, were supplied by Yanshan Petrochemical Co. (China) and Beijing Organic Chemical Factory (China), respectively. Table I lists the specifications of these polymers. In addition, electrically conductive carbon black (CB) was used as the filler.

Polymers and CB with desired proportions (EVA/LDPE = 20/80 and a weight percentage of CB in EVA/LDPE, LDPE, and EVA always 18%) were melt mixed in a laboratory-size Brabender plasticorder model XB20-80 under standard experimental conditions, in each case at 160°C, 20 rpm and 15 min. After being removed and granulated, the blends with pre-embedded electrodes were compression-molded at 140°C and then cooled down in air to room temperature. The sheet samples (65 × 45 × 3 mm³) were rested overnight before the subsequent measurements.

Because the composites are being used as candidates for positive temperature coefficient (PTC) application, room temperature crosslinking was carried out by irradiation with a ⁶⁰Co γ -ray source in air to eliminate the undesired NTC (negative temperature coefficient) effect.

Heat treatment of the materials was conducted in an oven with the temperature kept at a preset value. The annealing time was 30 h unless other-

wise specified. After annealing, the samples were cooled inside the oven simply by switching off the electricity supply and the time needed to attain room temperature was generally about 12 h.

Thermal analyses were made by a Perkin-Elmer DSC-7C differential scanning calorimeter (DSC). Under airflow, the samples were heated to 140°C at 10°C/min, and the heat capacity versus temperature was recorded for each scan. Volume resistivity of the composites was measured with a four-lead system.

RESULTS AND DISCUSSION

In general, higher heat treatment temperature facilitates a faster relaxation of the macromolecular chains and a shorter treatment time. However, a decay of performance of the composite might occur when the filler arrangement is destroyed as a result of an extremely high temperature.⁵ Since both LDPE and EVA employed in the present work are crystalline polymers, the heat treatment temperature must not exceed the melting point of LDPE (~110°C) at most. Therefore, four annealing temperatures, 75, 80, 90, and 100°C, were chosen.

To check the effect of the heat treatment, the DSC heating scans of the composites annealed at different temperatures are shown in Figure 1 and the corresponding melting peak temperatures are listed in Table II. It is evident that multiple melting peaks can be observed. In addition, the curves become a bit sophisticated due to the contributions of the endotherms of both LDPE and EVA.

As a distinct melting behavior of crystalline polymers, multiple melting phenomenon (or double melting phenomenon) has attracted considerable attention because it is not only closely related to the microstructural details of macromolecules,^{6,7} but it also can be used as a monitoring

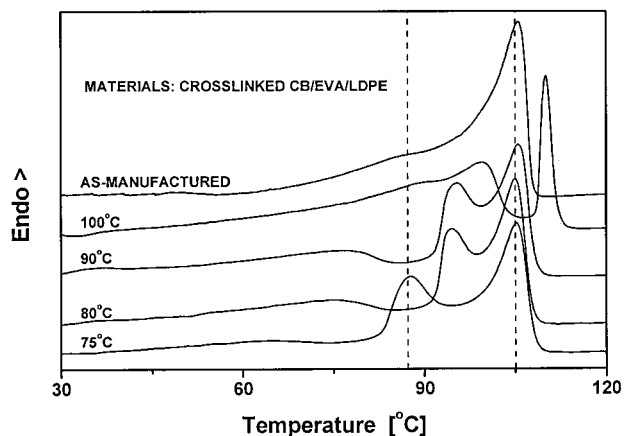


Figure 1 Melting behavior of the crosslinked carbon black/ethylene-vinyl acetate copolymer/low-density polyethylene (CB/EVA/LDPE) composites annealed at the temperatures indicated near the corresponding plots.

tool to check the phase interaction in polymer blends⁷ and even the temperature of a specific working environment.⁸ With respect to the mechanism involved, the authors of the present paper accept the explanation based on the melt, recrystallization, and subsequent remelt of the crystalline species with lower melting point.^{9,10} Figure 2 is presented as a schematic drawing, for the convenience of discussion. The dependence of multiple melting phenomena on annealing temperature is summarized as follows. When a crystalline polymer is annealed at a temperature much lower than the melting point, but higher than the glass transition temperature, two melting peaks appear on the subsequent DSC scan (curve 1 in Fig. 2). The lower melting peak corresponds to the melting of the crystalline formed during annealing, while the upper peak results from the reorganization of the lower melting crystals and the melt of the original crystalline of higher melting temperature. In fact, lower annealing temperature, T_a , means higher degree of supercooling,

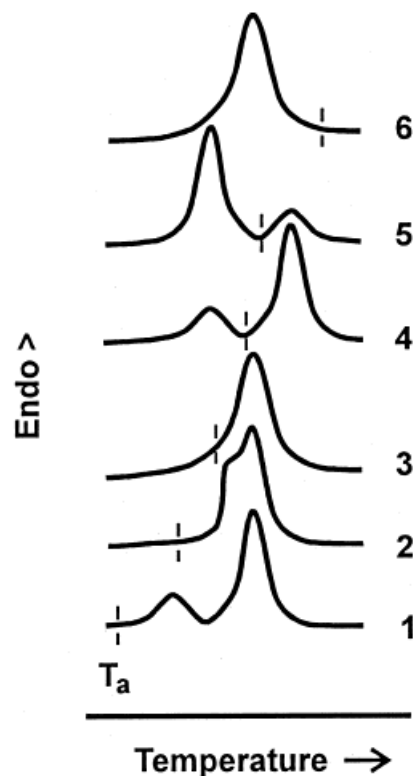


Figure 2 Simulative differential scanning calorimetry (DSC) heating plots showing the multiple melting behavior of a crystalline polymer in relation to the annealing temperature T_a .

which leads to a greater number of crystalline seeds of lower melting temperature. After annealing, the crystalline species of higher melting temperature constitute the majority with respect to total crystallinity. With the rise in T_a , the crystal nucleating density of the more perfect crystallines of higher melting temperature increases so that these crystalline species make a greater contribution to the total crystallinity. In addition, the degree of perfection and the size of the crystalline formed in the course of annealing increase as well. As a result, the lower melting peak shifts to

Table II Melting Peak Temperatures of the Crosslinked CB/EVA/LDPE Composites Annealed at Different Temperatures (The data are read out from Fig. 1)

	Annealing Temp., °C				
	75	80	90	100	As-Manufactured
Melting peak temperature (°C)	87.7, 105.2	74.6, 94.6, 105.0	77.0, 95.4, 105.6	88.1, 99.6, 110.1	86.5, 105.5

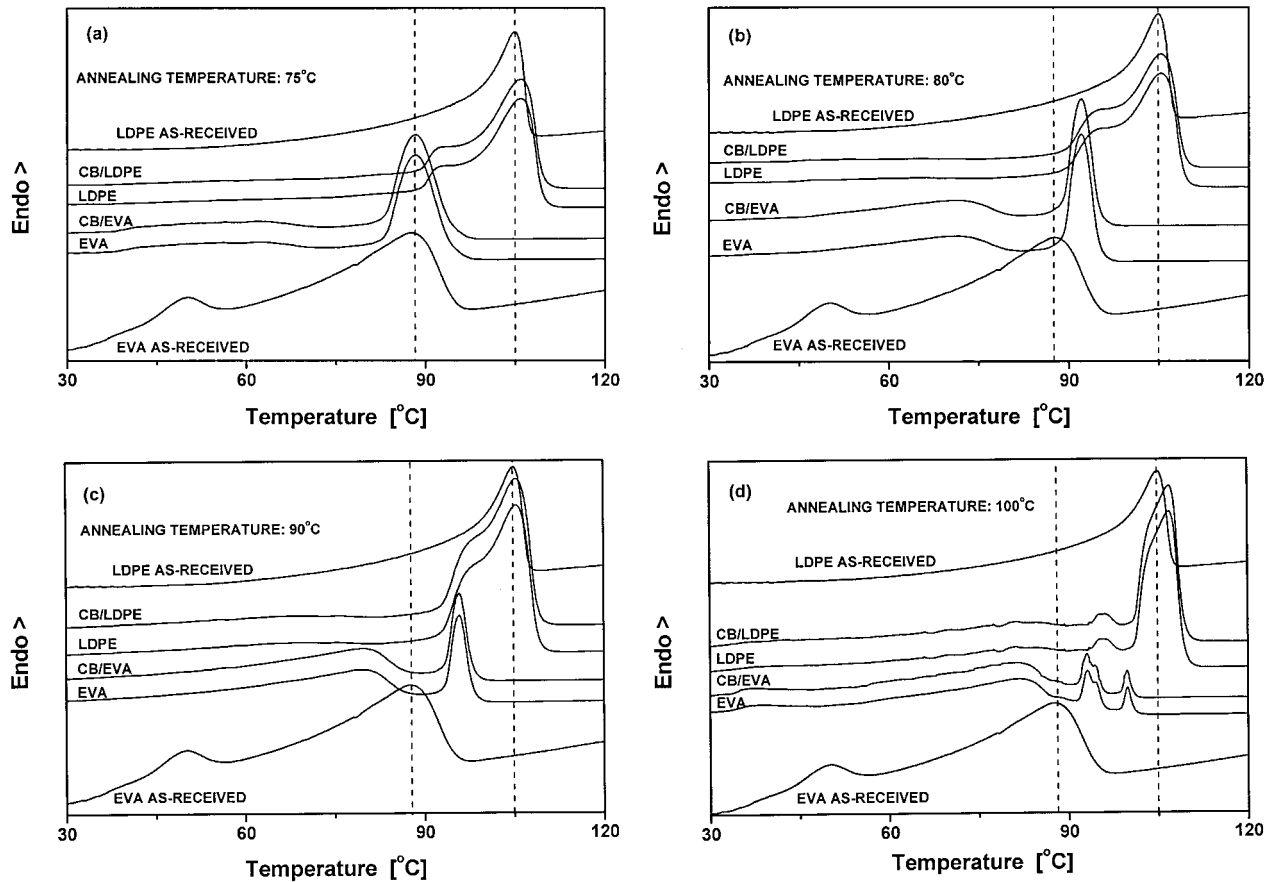


Figure 3 Melting behavior of the uncrosslinked low-density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), and their carbon black (CB)-filled composites annealed at (a) 75°C, (b) 80°C, (c) 90°C, and (d) 100°C, with the plots of unannealed LDPE and EVA as the references.

the higher temperature direction and becomes a shoulder of the upper melting peak or simply joins the upper melting peak, so that only a single peak forms (curves 2 and 3 in Fig. 2). As T_a is approaching the conventional melting point of the polymer, two melting peaks can be seen again. In this case, the lower melting peak reflects the melt of the crystalline formed (by the molten portion, which could not crystallize at the annealing temperature) when cooling down after annealing, and the upper melting peak is formed by the melt of the crystalline with a much higher degree of perfection formed during annealing (curve 4 in Fig. 2). If T_a is further increased, the crystalline portion of the lower melting peak would certainly increase, and the corresponding peak would become superior to that of the upper melting peak (curve 5 in Fig. 2). When the polymer is annealed at a rather high temperature, no crystallization will take place during annealing and the melting

curve has the same profile as the unannealed one (curve 6 in Fig. 2).

The results shown in Figure 1 can be further explained by examining the DSC traces of the uncrosslinked individual polymers, in which the filled versions, treated at different temperatures, are demonstrated in Figure 3. The melting behaviors of the polymers both with and without CB are almost the same, suggesting that CB particles are dispersed outside the lamellae, leaving the crystallites unchanged.^{11,12} As a result, the influence of the addition of CB can be neglected. With respect to LDPE, the lower melting peak presents itself as a shoulder in the case of lower annealing temperature and the peak position increases with increasing the annealing temperature. As the material is aged at 100°C, the lower melting peak appears individually and the upper melting peak is significantly higher. The results of EVA are comparatively different (Table III). The heat

Table III Melting Peak Temperatures of the Uncrosslinked Polymers and Their Filled Versions Annealed at Different Temperatures

Materials	Annealing Temp., °C				As-received
	75	80	90	100	
LDPE	92.0, ^a 105.9	94.5, ^a 105.3	97.6, ^a 105.4	96.3, 106.8	104.9
CB/LDPE	92.6, ^a 105.9	94.5, ^a 105.3	97.4, ^a 105.4	96.3, 106.8	—
EVA	88.3	71.4, 92.1	79.5, 95.8	81.5, 93.2, 94.6, 99.9	50.1, 87.5
CB/EVA	88.3	71.4, 92.1	79.5, 95.8	80.7, 93.1, 94.4, 99.8	—

The data are read out from Fig. 3.

^a Shoulder.

treatment at 75°C leads to a narrower peak at 88°C mainly owing to the uniformization of the crystallites sizes during annealing. In the case of 80 and 90°C annealing, a lower melting peak with a rather broad width and a upper melting peak, can be observed at 71–80°C and 92–96°C, respectively. They can be attributed to the melt of the crystalline formed when the sample is cooled down from the annealing temperature and the melt of the more perfect crystalline formed during manufacturing and annealing. In fact, these morphological variations follow precisely the mechanisms illustrated in Figure 2. However, the multiple melting peaks at 93–99°C of EVA annealed at 100°C can be interpreted in terms of molecular structure. That is, both the ethylene and vinyl acetate segments are arranged in disorder in the molecular chains due to the random radical copolymerization of EVA. Under sufficiently high temperature and sufficiently long time of treatment, microphase separation would take place, leading to the presence of crystallites with different ordering.

Returning to Figure 1, the two melting peaks on the DSC trace of the unannealed composite represent the LDPE (~105°C) and the EVA (~87°C) phases, as they are incompatible in both the crystalline and amorphous regions.¹ The heat treatment at 75°C produces a significant endothermic peak at around 87°C, meaning that the lower melting peak of LDPE originating from the annealing overlaps the melting peak of EVA. When the annealing temperatures are raised to 80 and 90°C, the lower melting peak of LDPE moves accordingly to the higher-temperature regime. Obviously, many of the curves in Figure 1 can be regarded as a simple superposition of the corresponding curves in Figure 3. The present crosslinking treatment does not exert detectable

influence on the melting behavior of the composites within the annealing temperatures from 75°C to 90°C, because low irradiation crosslinking of polyolefines occurs mainly in the amorphous regions and on the surface of the crystalline phases.^{13,14}

In the case of an annealing temperature of 100°C, however, the lower and upper melting peaks of LDPE appear at ~100°C and 110°C, while the melting peak position and profile of the EVA phase are the same as those of the EVA on the DSC curve of the composite as manufactured. It should be noted that the lower melting peak has a broader width and higher peak temperature and that the upper melting peak has a narrower width and higher peak temperature, as compared with the corresponding peaks of CB/LDPE in Figure 3(d). This might be explained mainly by the fact that crosslinking slightly destroys a part of the ordered structure of LDPE, which could not crystallize during annealing consequently but form the crystals of lower melting temperature as the sample is cooled. In other words, the crystals that correspond to the upper melting peak are partially transformed into less perfect crystals and only the unaffected portion having high crystallization capacity is able to crystallize at the annealing temperature. This phenomenon is invisible in the case of a lower annealing temperature due to the transition in the origination of the double melting behavior (cf. curves 2 and 4 in Fig. 2).

It can be concluded that an annealing at 100°C is not appropriate because a mechanism that leads to substantial crystalline melting of LDPE and EVA, other than that accounting for the morphological variation at lower annealing temperatures, is involved. That is, conductivity stabilization can scarcely be reached when a greater portion of the crystalline parts of a composite

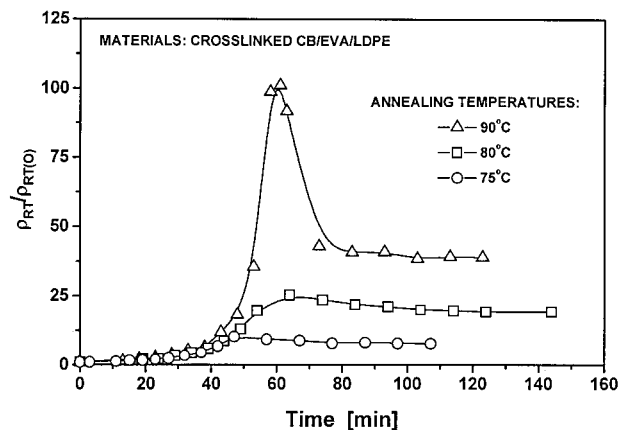


Figure 4 Room temperature resistivity of the composites annealed at different temperatures as a function of annealing time (ρ_{RT} , room temperature resistivity of the annealed composites, $\rho_{RT(0)}$, room temperature resistivity of the composites as manufactured).

remains in a state of melting under the annealing temperature of 100°C. Therefore, the composites were annealed at 75, 80, and 90°C, respectively. The resultant room temperature resistivity of the composites was measured as a function of the annealing time to examine the effect of annealing on the conductive performance (Fig. 4). Figure 4 shows that the resistivity of the composite annealed at 75°C reaches equilibrium much faster than that annealed at 80 and 90°C. In addition, the equilibrium resistivity of the former composite is close to the resistivity of the composite as manufactured, while the resistivity of the latter two composites is increased remarkably. When the composites are used as heating elements, a lower room temperature resistivity is generally desired to ensure sufficient electrothermal output.¹⁵ From the practical point of view, 75°C is a suitable annealing temperature to balance the property stabilization against annealing time.

This discussion demonstrates that the partial melting of EVA also exerts great influence on the composite performance during annealing in spite of the low fraction of EVA in the blended matrix. As shown in Figures 1 and 3, a larger portion of the crystalline phase in EVA is melted when the composites are heated to 80 and 90°C, and the process of crystallite dimension uniformization plays the leading role for the composite being treated at 75°C. Since CB is selectively dispersed in LDPE and at the interface of EVA/LDPE under the present composite composition,⁴ a volume expansion of EVA induced by crystalline melting

would certainly affect the distribution of the conductive fillers in the matrix to a great extent and hence the conduction behavior. Meantime, the affected electrical conductive networks established by the CB particles throughout the composites are frozen by the effect of crosslinking resulting from the residual free radicals (discussed in detail in a subsequent article by the authors¹⁶). Consequently, the increased resistivity attributable to the annealing process could no longer be reduced to the value of the untreated composite after the heat treatment. It is clear that an annealing bringing about much less influence on the dispersion status of CB is highly desired.

CONCLUSIONS

In summary, morphological variation in the present EVA/LDPE-based composites induced by heat treatment involves melt and reorganization of the crystallizable portions of both EVA and LDPE. Since the distribution of CB is rather sensitive to the localized deformation of the matrix, the highest possible annealing temperature would be 75°C, at which only solid-state crystallization of LDPE and uniformization of EVA crystalline size take place. As a result, a stabilized room temperature resistivity can be obtained within a reasonable time even shorter than that needed by the treatment at 80 and 90°C. After annealing, the ultimate electrical resistivity of the composites is increased slightly and thus the application and property design of the material are facilitated.

The changes in the electrical resistivity of the composites as a function of the annealing conditions (temperature and time) can, in turn, be used to monitor the morphological variation of the blended polymer matrix. This is of particular importance when in situ inspection of the materials in service is needed. Further investigation in this direction to provide more supporting evidence should be made.

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