Effect of Filler Treatment and Crosslinking on Mechanical and Dynamic Mechanical Properties and Electrical Conductivity of Carbon Black-Filled Ethylene–Vinyl Acetate Copolymer Composites

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ABSTRACT: Mechanical, dynamic mechanical, and electrical conductivity of conductive carbon black-filled ethylene–vinyl acetate (EVA; 28% VA) composites were investigated. The above-mentioned properties were also measured when carbon black was treated with nitric acid before addition to the EVA matrix. It was found that acid-treated carbon black exhibits a higher filler–polymer interaction and this was reflected in the improvement of the mechanical properties and the modification of electrical conductivity of these composites, especially when measured against the temperature. The effect of curing of the polymer matrix on the mechanical properties and electrical conductivity was also investigated. It was found that the introduction of crosslinks in the polymer matrix improves its mechanical properties as well as the thermal stability of its electrical conductivity. The electrical conductivity of ethylene propylene diene (EPDM) and an EVA–EPDM (50/50) blend filled with carbon black were also studied for comparison. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2073–2082, 2003

Key words: crosslinking; conductive composite; filler treatment; electron beam radiation

INTRODUCTION

Conductive polymer composites made by incorporation of different volume fractions of conductive fillers like carbon black (CB), carbon fiber, and metal powder into a polymer matrix have found many applications in the field of electronics and in electrical industries such as for electrostatic charge dissipation and electromagnetic interference shielding.[1–3] Positive temperature coefficient of resistance (PTC) composites are commonly employed in a wide range of uses, including in temperature sensors, protection circuitry, microswitches, flow meters, self-regulating heating elements, and self-resetting over current protection elements. However, the range of their technical application is restricted because most of the conductive particulate-filled polymer composites are electrically and/or dielectrically unstable with respect to thermal cycling (rise and fall in temperature) in technically useful temperature intervals. Therefore, it is necessary to determine the sources of the instability of the electrical properties filled to minimize this defect. Composite thermistors composed of highly conducting CB-filled polyethylene having room-temperature resistivity in the order of 1–100 ohm cm exhibit a PTC effect of six to eight orders of magnitude (at about 130°C, T_m for PE). These materials can easily be fabricated and are intrinsically cost-effective.[4–7]

Thermal recycling (heating–cooling cycle) of CB-filed polymer composites has been studied extensively because a large number of industrial applications are based on either their electrical properties or mechanical properties. It was found that the conductivity, in particular, changes during thermal cycling, and there is a hysteresis-type loop in the conductivity versus temperature plots during the heating–cooling cycle with some electrical set, that is, there is a permanent change in the starting value of the conductivity at room temperature after the heating–cooling cycle. Further, the conductivity versus temperature plot also changes during a repeated heating–cooling cycle. This is due mainly to the breakdown and formation of a conductive network due to CB aggregates present in the insulating rubber materials.

The PTC and negative temperature coefficient (NTC) phenomena of filled polymer composites were studied by number of authors.[8–12] In our previous work,[13] we studied the NTC and PTC effects of ethylene–vinyl acetate (EVA)-based flexible composites filled with conductive CB and carbon fiber. It is predicted that the conductive filler network undergoes two processes during an increase in temperature: One is breakdown and the other is reformation through reagglomeration of a conductive filler, especially particulate fillers. The ultimate PTC/NTC behavior of the

TABLE I
Specifications Identification of the Materials

Materials	Specifications
Ethylene–vinyl acetate copolymer, (PILENE 2806)	(EVA-28), VA content: 28 wt % Density: 9.51 kg/m^3 MFI: 6 gm/10 min Melting point approximately: 75°C
Ethylene propylene diene rubber (terpolymer of ethylene–propylene and ethyldiene norborene, ENB) (Royalene 521)	E/P: 52:48 (ethylene/propylene ratio). ML$_{1+4}$ at 100°C = 45 Mooney viscosity measured at 100°C. This is the stress experienced by a circular serrated rotor embedded in rubber at 100°C, during movement at a speed of 2 rev/min. This stress is proportional to the molecular weight of the rubber. ENB: 5% (third monomer) Density: 8.6 kg/m^3
Conductive carbon black (Vulcan XC-72)	Average particle size: 27–29 nm DBP absorption number: 178 mL/100 g CTAB, surface area: 86 m^2/g Pore area: 94 m^2/cc True density: 18 kg/m^3

composites is the net result of these two processes. Many other factors can influence these processes, such as the properties of the fillers, the filler content, and the characteristics of a polymer such as melt flow, Mooney viscosity (ML$_{1+4}$), chemical structure, crystallinity, and thermal softening. Electron-beam irradiation is often used for crosslinking rubber composites. The effect of electron-beam irradiation crosslinked rubber was used for making composites; the mechanical and electrical properties of such composites were studied by several researchers.[14–18] However, PTC composites suffer from some drawbacks, including unstable electrical reproducibility due to irregular changes in the CB aggregate structure in the polymer matrix when subjected to heating/cooling cycles during application. This gradually increases the resistivity of the composites and lowers the output power and service life as well.

It is to be noted that the performance of composites depends mostly on the starting materials and processing conditions involved in the manufacturing.[19,20] Conductive composites find wide applications in electrical and electronic industries, as mentioned earlier. To be suitable for such applications, these composites should have adequate mechanical properties as well as stable electrical conductivity; especially, the variation of the electrical conductivity against the temperature should be as minimum as possible. With this aim in mind, modifications of conductive additive CB as well as of the base polymer EVA copolymer (28% VA) were done.

EXPERIMENTAL

Materials

Conductive CB was obtained from Cabot India Ltd. (Thane, Maharastra, India). The EVA (28% VA con-

tent) copolymer was supplied by PIL (Mumbai, India). Ethylene propylene diene rubber (EPDM), grade Royalene 521, was supplied by Uniroyal (Middleburg, CT). Dicumyl peroxide (DCP) and triallyl cyanurate (TAC) were obtained from E. Merck Ltd. (Bangalore, India) and Aldrich Chemical Ltd., respectively. Table I lists the specifications and identification of these materials.

Methods

Nitric acid treatment of CB

CB was mixed with a 50% nitric acid solution, and then the solution was refluxed for 24 h. The CB slurry after filtration was thoroughly washed with distilled with water to remove all traces of the acid. Finally, the treated CB was air-dried at 50°C before use. EVA and treated carbon of different proportions (Table II) were mixed in a Brabender Plasticorder (PLE330) under the same conditions of the experiment in each case, at 130°C and ~ 60 rpm rotor speed for 5 min. CB was gradually added in the molten EVA. The mixes were sheeted out in a laboratory-size two-roll mixing mill. Compounds were then subjected to compression molding under 5 MPa pressure at 170°C for an 11-min duration to produce a rectangular sheet of approximately 2-mm thickness. All sheets were then conditioned at room temperature for 24 h, before testing.

Preparation of irradiated composites

Molded sheets of the composites were irradiated in air at a room temperature of 25 ± 2°C by an electron-beam accelerator (Model ILU-6) at the Bhabha Atomic Research Centre (BARC; Bombay, India). An irradiation dose of 5 Mrad was used.

Ingredients	E (phr)	EP 50 (phr)	P (phr)
EVA	100	50	00
EPDM	00	50	100
TAC	1.5	1.5	1.5
DCP	1.5	1.5	1.5
CB	0, 20, 30, 40, 50	0, 20, 30, 40, 50	0, 20, 30, 40, 50
Treated CB	0, 20, 30, 40, 50	—	—

Dynamic mechanical thermal analysis

Dynamic mechanical thermal properties of the samples were measured using a DMTA-IV (Polymer Laboratory Ltd., UK) under a dual-cantilever mode. The experiments were carried out at a frequency of 1 Hz. The measurements were taken over the temperature range of -50 to $100°C$, at a heating rate of $3°C/min$ and a double-strain amplitude of 64 μm. The storage modulus and the loss tangent (tan δ) were measured for all the samples under identical conditions.

Mechanical properties

The tensile strength of different vulcanized-filled composites was measured by a Zwick universal testing machine (Model 1445) according to ASTM standard D412, using dumbbell-shaped specimens.

Electrical resistivity

The volume resistivity of the composites having resistivity $\geq 10^6$ ohm cm was measured using a Hewlett–Packard high-resistance meter (Model 4329A) coupled with a Hewlett–Packard (Model 160084) resistivity cell. For composites having a low resistivity ($\leq 10^6$ ohm cm), measurements were made using the four-probe Van der Pauw method described in the literature.[21] To measure the volume resistivity at a higher temperature, the entire electrode system was placed in an oven where the temperature could be monitored and controlled. The method is based on the application of the current and measurement of the resulting voltage. The instrument used for the application of the current was a programmable dc voltage/current generator (Advantest TR 6142), and for voltage measurement, a digital precision voltmeter (Schumberger, UK, 7071) was used. The results were reproducible within 5%.

ESCA study of modified CB

XPS (ESCA) spectra were obtained using a VG Scientific, ESCA Lab MK II, spectrophotometer using MgKα (1250 eV) radiation. X-ray radiation was operated at 240 W (12 kV and 20 mA). The analyzer chamber pressure was 10^{-9} Torr. All spectra were recorded at an electron take-off angle of $90°$ with respect to the polymer surface. The concentration of different chemical groups present on the surface of the CB can be estimated from the measurement of the binding en-
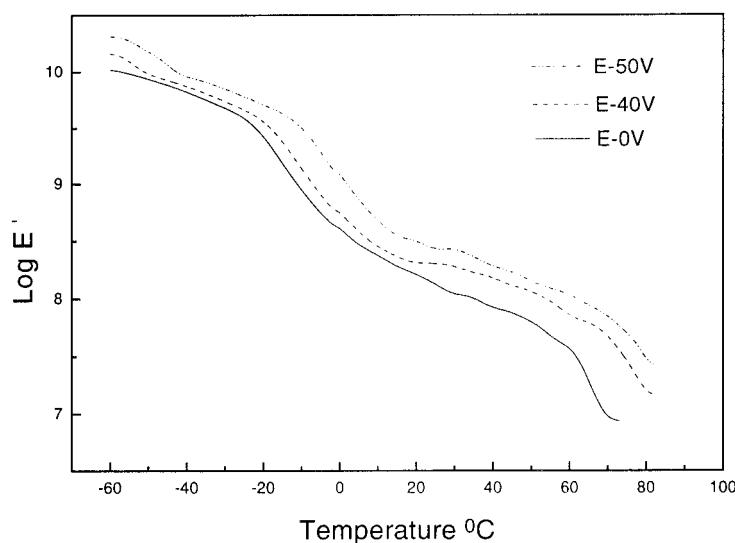

Figure 1 Effect of temperature on dynamic storage modulus of EVA–CB system.
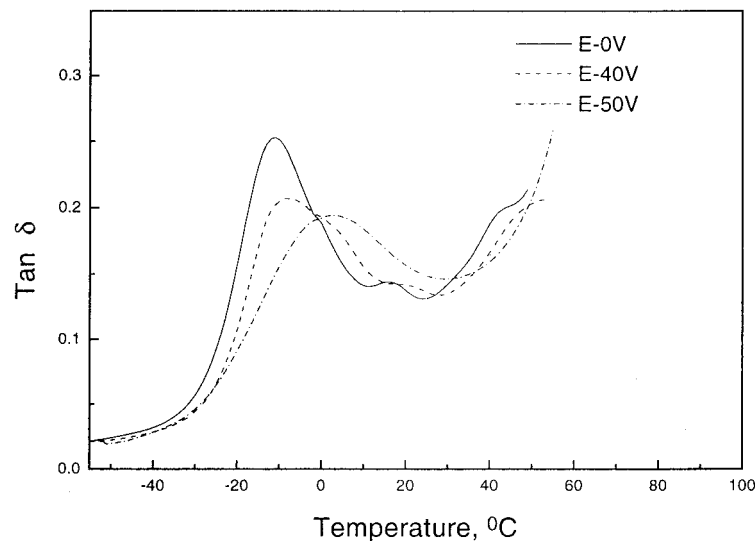
Figure 2 Effect of temperature on tan δ for EVA–CB system. E-0V, unfilled polymer; E-40V and E-50V, polymers filled with 40 and 50 phr CB.

ergy relative to each group from the ESCA analysis. The atomic concentrations of carbon and oxygen were calculated from the peak areas of C_{1s} and O_{1s} and their standard photoionization cross sections.[22] The binding energy (eV) for each chemical group involving carbon and oxygen is represented by the peak area under dotted lines, whereas the total binding energy for all the groups is represented by the area under thick lines. The concentration of each group present is again proportional to the respective binding energy. The fraction of the functional groups can be obtained from the width of these peaks. The dotted plots were obtained after deconvolution of the main plot using standard software.

RESULTS AND DISCUSSION

Mechanical and dynamic mechanical properties of CB-filled composites

EVA-28 (28% VA content) is a semicrystalline polymer, which shows a distinct crystalline melting region in DSC and a peak due to crystallinity in X-ray analysis.[23] The addition of CB to the EVA matrix increased its storage modulus (Fig. 1). It was found that the nature of the storage modulus plots against the temperature (°C) for pure EVA and EVA filled with different loadings of CB are almost alike; the storage modulus decreases with an increase in temperature. However, the decrease is slow over the temperature of
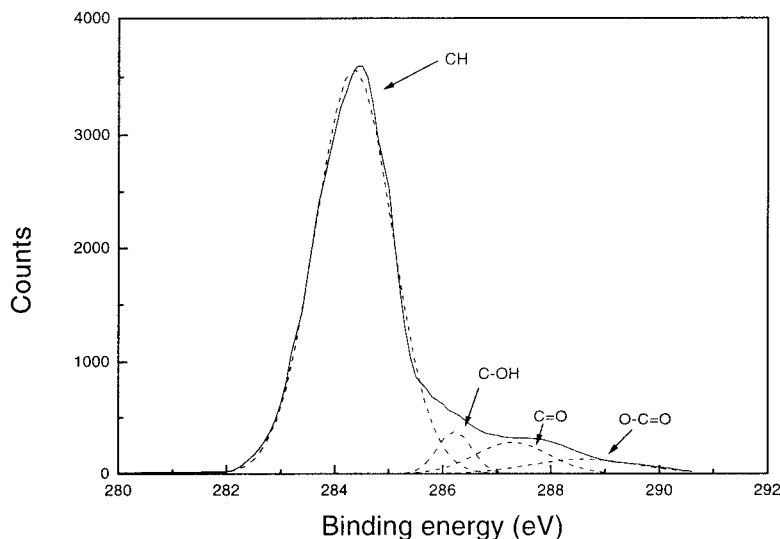

Figure 3 Typical peak resolutions for C_{1s} ESCA spectra of untreated CB.

TABLE III
Fraction of Functional Groups

CB	Functional groups		
	[C—OH]/[C—H]	[C=O, O—C—O]/[C—H]	[O—C=O]/[C—H]
Normal CB	0.15	0.078	0.055
Treated CB	0.19	0.079	0.055

−60 to −40°C and relatively sharp over the temperature of −20 to −5°C. This is because polymer chains of EVA undergo β relaxation, leading to a sharp decrease in the modulus around −15°C; again, another sharp decrease is observed above 55–75°C, which reflects the crystalline melting behavior (T_m) of EVA above the temperature region of 55–75°C. The dynamic mechanical loss tangent (tan δ) peaks for the glass–rubber relaxation (β relaxation) and the crystalline melting for pure and filled systems are also distinctly observed in the tan δ versus temperature plots (Fig. 2). However, the small increase in the peak temperature with the filler loading indicates that the viscosity of the system increases due to the incorporation of CB in the polymer matrix.

Effect of addition of treated CB on dynamic mechanical and mechanical properties of the composites

The effect of CB treatment on the dynamic mechanical properties can be seen when the loss tangent versus the temperature plots of the nitric acid-treated CB-filled system is compared with those of the untreated CB-filled ones. The treatment of CB with mineral acids like nitric acid, which is considered to be a strong oxidizing agent, changes the concentrations of different organic groups present on the surface of the CB.

The concentration ratios of the surface groups were calculated by graphical integration of the related peaks (Fig. 3) from ESCA analysis. The dotted plots were obtained after deconvolution of the main plot using the Gaussian Laurentian method to determine the chemical environment of different elements.

A comparative study of the ESCA analysis of treated and untreated CB is illustrated in Table III. Although a small but significant change in the concentration of active groups, especially the >C—OH group, is observed, the change in the concentration of other groups like >C=O, and —O—C=O is relatively marginal. The increase in the concentration of the >C—OH group on the surface of treated CB increased the low strain modulus of the EVA composites filled with treated CB compared to that of the untreated CB-filled system (Fig. 4). The increase in the concentration of the polar group, >C—OH, increased the polymer–CB interaction, which often is believed to be physicochemical in nature.[24] The treatment of CB with nitric acid also reduces the damping behavior of treated black-filled composites due to an increase in a viscous component of the system compared that of the untreated CB-filled system. There is a slight shift in the peak temperature toward the higher side; this also indicates an increased polymer–filler interaction in the case of
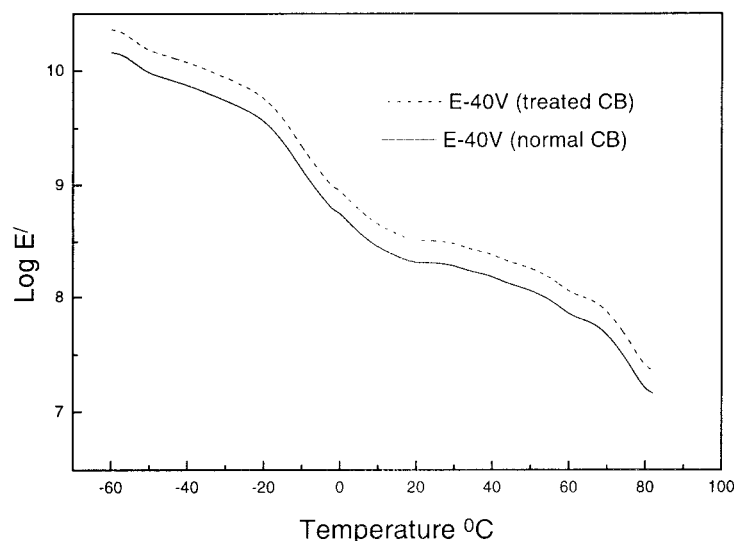

Figure 4 Effect of temperature on dynamic storage modulus normal and treated CB-filled EVA composites (E-40V-polymer containing 40 phr CB).
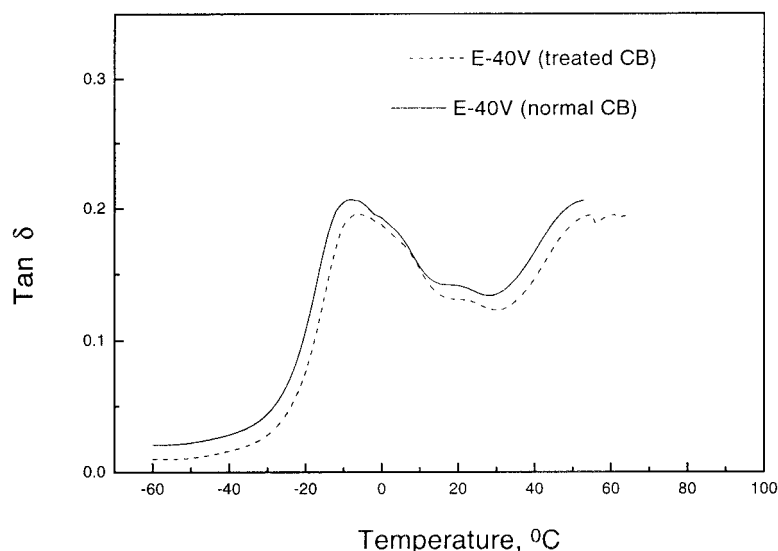
Figure 5 Effect of temperature on tan δ for normal and treated CB-filled EVA composites.

the treated CB-filled composite compared to that of the untreated black-filled one (Fig. 5).

The effect of CB treatment on the mechanical properties like the tensile strength of CB–EVA composites can be seen in Table IV. The addition of treated CB to the EVA matrix significantly increased the tensile strength at all loadings of CB compared those of untreated CB-filled ones. This result reflects that there is a significant increase in the reinforcement of the matrix due to the addition of treated CB instead of the untreated one. As expected, the increased polymer–filler interaction reduced the degree of elongation at break for the treated CB-filled system in comparison to the regular black-filled one. The reinforcement theory of a CB–rubber composite indicates that there is a formation of some kind of networks involving CB particle aggregates and a rubber chain in the composites.[25]

Effect of CB treatment on electrical conductivity

The variation of room-temperature electrical resistivity as a function of the filler content for treated and untreated CB is presented in Figure 6. It was found that, for both the filler systems at a low filler concen-

tration, the resistivity of the composites practically coincides with that of the pure polymer (EVA). This is because, at a low filler loading, the filler particles are well dispersed in the polymer matrix and they are segregated from each other. As the filler loading increases, there is a tendency of the formation of some conductive networks through the aggregation of filler particles. Thus, some continuous three-dimensional networks are formed at a certain critical concentration through particle–particle contact among filler aggregates distributed in the matrix. However, conductive networks may be formed not only due to the physical contact of particles but also due to particles being separated by a small distance (<10 nm) when an electron can hop the interparticle gap. At this concentration (known as the percolation limit), a sudden and significant drop in the resistivity is observed and the matrix changes from electrically insulating to electrically conductive.[26] However, a further increase in CB loading beyond the percolation limit does not increase the conductivity (or decrease the resistivity) significantly. The formation of conductive networks at the percolation limit may be considered as a sudden formation of continuous conductive wires through the insulating matrix. The increased filler concentration beyond percolation may be considered as a simple increase in the diameter of that wire. Consequently, an increase in the diameter will reduce the resistivity but not to as great an extent as observed in the percolation region.

It is interesting to note that the acid treatment of CB increased the concentration of certain chemical groups present on the surface of the filler, which enhanced the polymer–filler interaction and also aided in better dispersion. But better dispersion of the filler in the matrix leads to some delay in the conductive network forma-

TABLE IV
Tensile Strength of Normal and Treated CB-filled Composites

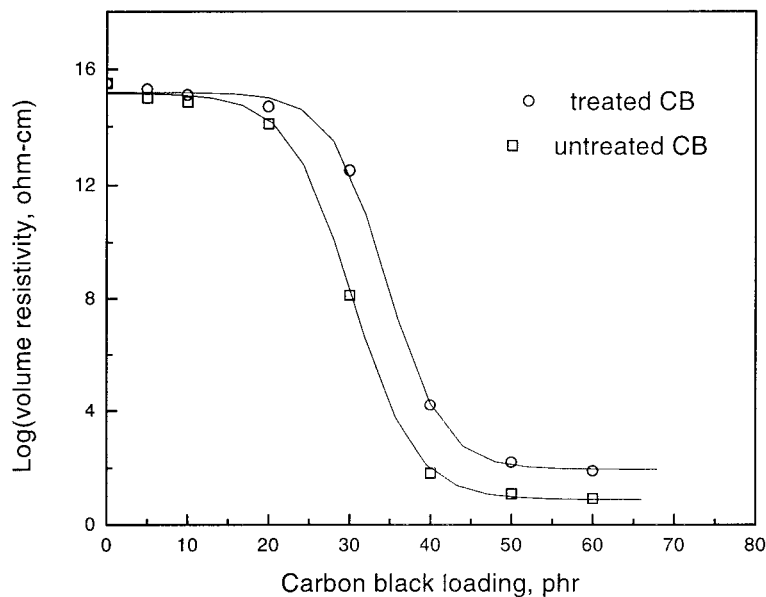|	Tensile strength (MPa)		
CB	30 phr	40 phr	50 phr
Normal CB-filled composites	18.87	18.6	17.84
Treated CB-filled composites	21.5	21.0	20.5

Figure 6 Change in volume resistivity with treated and normal black-filled EVA composites.

tion through particle aggregation. Further, some of these active chemical groups on the filler surfaces have a tendency to arrest electrons and thus increase the resistivity of the CB.[27] The treated filler increased the resistivity of the composite in comparison to the untreated filler at the some filler loadings.

Effect of temperature on electrical conductivity

The variation of resistivity against temperature is shown in the Figure 7 for EVA-28 filled with different concentrations of particulate CB (Vulcan XC-72). It is interesting to note that the resistivity of all the systems increases with an increase in the temperature to 75–

80°C (PTC effect for resistivity), but beyond 80°C, a gradual decrease in the resistivity against the temperature (i.e., the NTC effect of resistivity) was observed. The PTC effect can be explained in terms of the difference in the thermal expansion of the matrix polymer from that of conductive networks formed due to CB aggregation. With polymer expansion being greater with an increase in temperature compared to CB aggregates, the interparticle distance between the particle aggregates increases, leading to some destruction of conductive networks; consequently, there is an increase in the resistivity against temperature. But a gradual decrease in the resistivity against the temperature beyond 80°C (NTC effect) is due to the formation
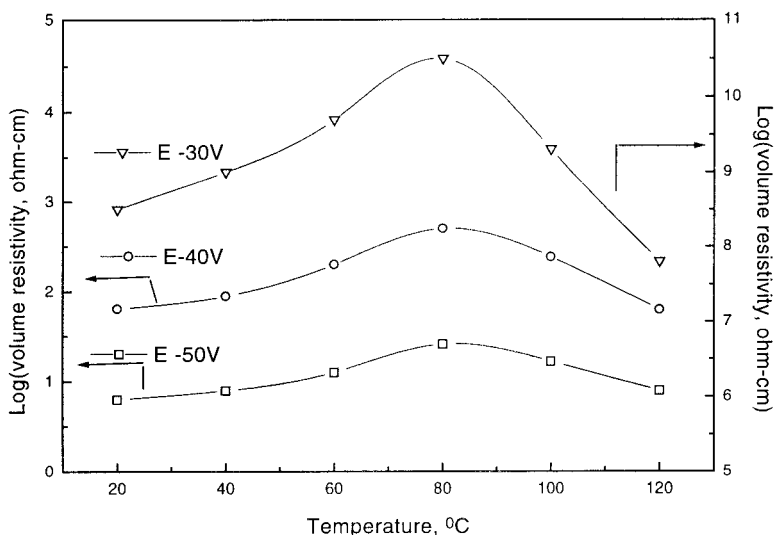

Figure 7 Effect of temperature on volume resistivity of black-filled but uncrosslinked EVA composite. E-30V and E-40V represent polymers filled with 30 and 40 phr CB.
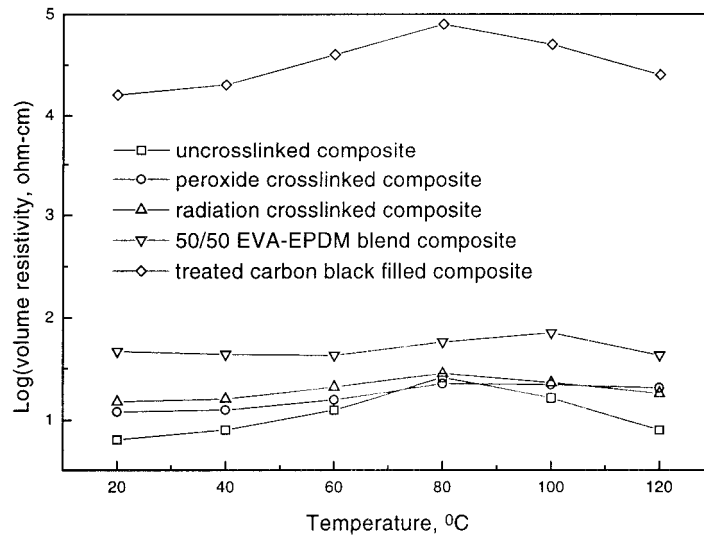
Figure 8 Effect of temperature on volume resistivity of black-filled uncrosslinked, peroxide-crosslinked, radiation-crosslinked, and treated CB-filled EVA composites.

of some extra conductive networks due to flocculation of the CB particles. This may be explained as follows: EVA-28 is a semicrystaline polymer having a crystalline melting point around 75–80°C. When polymer crystals melt, there is an appreciable decrease in the viscosity, and, consequently, an increase in the mobility of the polymer chain occurs. Now, CB aggregates are firmly attached to the polymer chain through a physicochemical increase in bonding; the polymer chain mobility leads to mobility of the aggregates, resulting in the formation of an increased number of conductive networks.

It was also found that with an increase in the CB concentration both PTC and NTC effects is insignificant. This is mainly because, with an increase in the conductive filler concentration, the number of conductive networks in the insulating matrix increase and the average interpretable distance between particle aggregates also becomes less. So, with an increase in temperature, the decrease in the resistivity due to an increased thermal expansion of the matrix also becomes less. Further, beyond crystalline melting, the effect of flocculation to form extra conductive networks is also minimized, because, as there is hardly any disconnection of the conductive network at higher filler loading, the extra network formed due to flocculation is not contributing significantly to the change in resistivity.[28]

In comparison with normal CB-filled composites, oxidized CB-filled–EVA composites exhibit higher
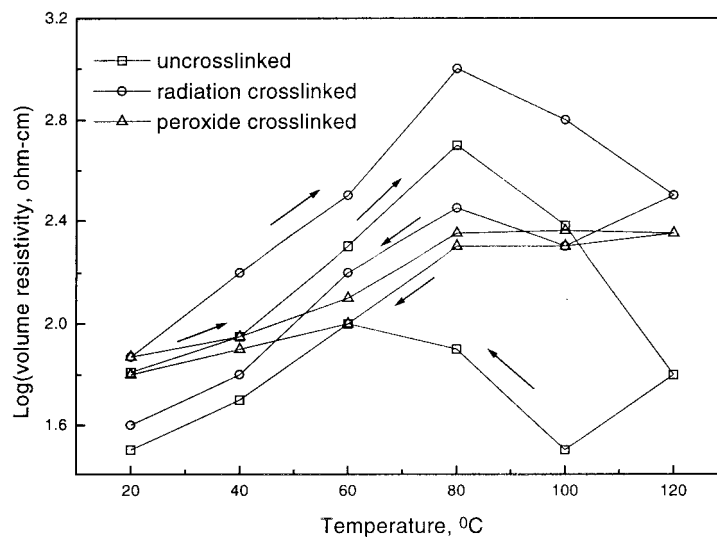

Figure 9 Effect of heating–cooling cycle on volume resistivity of CB-filled uncrosslinked, radiation-crosslinked, and peroxide-crosslinked EVA composites.
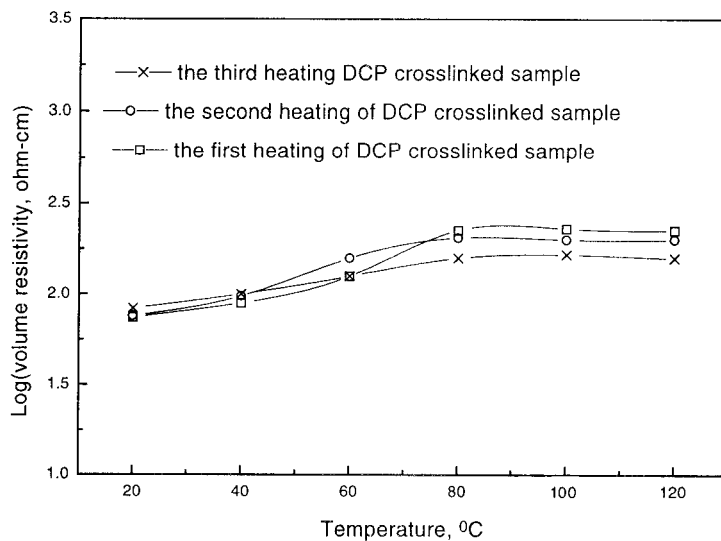
Figure 10 Effect of repeated heating on the resistivity of peroxide crosslinked, 40 phr black-filled EVA composites.

room-temperature resistivity due to the good dispersion of CB in the polymer matrix. The better interaction between the polymer and the oxidized CB reflects a strong PTC effect before crystalline melting with a reducing NTC effect beyond crystalline melting (Fig. 8). The strong polymer–filler interactions can partly prevent the tendency of the flocculation of CB aggregates during an increase in temperature beyond the crystalline melting of the polymer matrix. Therefore, the composite exhibits a weakened NTC effect beyond the melting region but the effect cannot be completely eliminated.

In our earlier communication,[26] it was found that CB–EPDM rubber composites exhibit an NTC effect throughout the temperature range of measurement (25–120°C). In fact, EPDM is an amorphous polymer. This decrease of resistivity with the temperature is attributed mainly to the predominant effect of the thermal emission of the electron through a gap between neighboring black particles and/or by re-agglomeration of small CB particles compared to the thermal expansion effect. When EVA was mixed with EPDM, the NTC effects of the EVA composites became weaker compared to those of the pure EVA-based composites (Fig. 8). The mechanism for the PTC in a semicrystalline polymer is attributed to the high degree of polymer mobility beyond its melting point, leading to the formation of an extra conductive network through conductive particle aggregation, as explained earlier. Thus, the melting behavior of the base polymers should be responsible for the PTC behavior of the composites. If we control the melting behavior through blending or incorporation of crosslinks in the matrix, the NTC behavior observed at and beyond crystalline melting point of the polymer can be arrested to a great extent.

Effect of chemical and radiation crosslinking on electrical conductivity

The presence of interchain crosslinks in a crystalline polymer like LDPE, EVA, etc., improves the thermomechanical properties of these polymers. Crosslinked LDPEs, that is, XLPE and crosslinked EVA, do not exhibit melt flow beyond their crystalline melting temperatures, but, rather, behave like a crosslinked elastomer system. Thus, the presence of crosslinks in black-filled semicrystalline EVA will also be modified. Thus, to enhance the thermal stability and to modify the temperature dependency of the electrical conductivity, CB-filled EVA composites are crosslinked with chemicals like DCP and by high-energy radiation like electron-beam irradiation. The gel fractions of the polymer cured by electron-beam irradiation and peroxide crosslinking are 82 and 93%, respectively; details of the gel fraction measurement were described elsewhere.[22]

The conductivity of these systems was measured over the same temperature range. The variations of the logarithm of the volume resistivity against temperature (°C) for 50 phr black-filled EVA composites uncured and cured by peroxide (DCP) and electron-beam irradiation are presented in Figure 8. It is found that both PTC and NTC effects have been marginalized when the composites are crosslinked as compared to uncrosslinked ones. However, the effect of the reduction of the effects of PTC and NTC is more pronounced in the case of the DCP-cured system compared to those in the radiation-cured one. This may be due to the introduction of a larger number of crosslinks in the peroxide-cured system in comparison to that in the radiation-cured one. In fact, the change in resistivity with the temperature is significantly re-

duced for the crosslinked samples, and the resistivity of these samples is somewhat higher than for that of the non-crosslinked one. The radiation-cured samples show somewhat higher resistivity compared to the DCP-cured system. This may be due to the possibility of oxidation during peroxide curing at an elevated temperature (170°C), whereas high-energy radiation curing is carried out at lower temperatures (25 ± 2°C).

The heating–cooling curves of these conductive composites exhibit two well-known phenomena, hysteresis and electrical set, as discussed earlier.[13] However, both hysteresis and electrical set become reduced due to crosslinking (Fig. 9). It was also found that repeated heating of the sample does not change its electrical characteristics significantly if the system is crosslinked either by peroxide or by electron-beam irradiation (Fig. 10). Electrical hysteresis and electrical set are due to the net result of the formation and breakdown of conductive networks present in the system due to the thermally induced mobility of the polymer chain. However, due to the presence of crosslinks, there is an increased restriction on the polymer chain mobility due to the thermal vibration; consequently, there is a decrease in the electrical hysteresis and set. This improvement of the electrical stability for the cured sample is technically important for practical applications of these composites, especially for electronic and electrical instruments.

CONCLUSIONS

1. CB treatment improves polymer–filler interaction. Thus, treated black-filled EVA composites exhibit increased strength properties and storage modulus, but reduced damping characteristics.
2. The introduction of chemical crosslinks into the polymer matrix also improves the mechanical properties and storage modulus and reduces the damping characteristics.
3. Semicrystalline EVA-based composites show the PTC effect below and the NTC effect above the crystalline melting temperature, whereas an amorphous EPDM-based composite shows only the NTC effect throughout the temperature range of measurement. The blending of EPDM with EVA also reduces both the PTC and NTC effects of EVA.

4. The variation in the electrical resistivity of the composites with the temperature can also be influenced by polymer–filler interaction. The enhanced interaction between a polymer and treated CB weakens both the PTC as well as the NTC effects of treated black-filled composites compared to those of normal black-filled ones.
5. The introduction of chemical crosslinks as well as electron-beam-irradiated crosslinks in these composites is also effective in reducing both the PTC as well as the NTC effects, thus improving the thermal stability of the electrical conductivity of these composites.
6. Both the electrical set and hysteresis property of the composites are reduced due to crosslinking.

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