

Control of the temperature coefficient of the DC resistivity in polymer-based composites

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Abstract In this study, the roles of polymer matrices and filler additives in controlling the positive temperature coefficient (PTC)/negative temperature coefficient (NTC) behavior of DC resistivity at high temperature for semi-crystalline ethylene vinyl acetate copolymer, amorphous acrylonitrile butadiene copolymer, and their blend composites filled with different carbon fillers like Conductex carbon black, Printex carbon black, and short carbon fiber have been investigated. It is seen that the PTC/NTC behavior of resistivity depends on the characteristics of both polymer matrices and filler additives. The anomaly in the results are due to polymer crystallinity, shape and size of fillers, and their thermal expansion coefficient, that play major role in controlling the PTC/NTC of resistivity at high temperature for the composites. Finally, reproducibility of composite resistivity has been evaluated with their some proposed practical applications. These composites can be used as both PTC and NTC thermistors.

Introduction

Extrinsically conductive polymer composites, where one phase is insulating polymer matrix and the other phase is any conductive inclusion, are used in many electrical and electronic applications such as electromagnetic interference (EMI) shielding, capacitor, pressure sensitive sensor, etc. [1–10]. The conductivity/resistivity of these composites

also found to vary when subjected to elevated temperature [11, 12]. Conductive polymer composites in general exhibit either increase in resistivity with the increase temperature known as positive temperature coefficient (PTC) of resistivity or decrease in resistivity with the increase in temperature that is negative temperature coefficient (NTC) of resistivity [13]. The composites, exhibiting PTC effect of resistivity, are used as self-controlled heaters, current limiters, over current protectors and/or pyroelectric sensors [14, 15]; whereas, composites having NTC effect are useful as antistatic and shielding applications [16, 17]. Among the different conductive inclusions, carbonaceous fillers are mostly used in PTC/NTC polymer composites [18]. In many cases, the resistivity of these PTC/NTC composites varies several orders of magnitude within a very narrow temperature range so that the resistivity of these composite changes from its insulating to conducting range or vice versa upon heating/cooling [19]. The smartness of these materials not only depends on their broad PTC/NTC amplitude but also on their reversibility, adjustment at their transition temperature, etc. The broadness of PTC/NTC amplitude depends on both the nature of matrix polymer and geometry of fillers used in the composites. Polymer glass transition temperature (T_g), crystallinity, and crystalline melting point (T_m) mostly determine the PTC/NTC amplitude in polymer composites [20]. There are several parameters of particulate carbon fillers like particle size, surface area, aggregate structure, porosity, crystallinity, surface functionality, etc. affect both the base and temperature-dependent resistivity of the polymer composites [19–21]. Similarly, for fibrous fillers, aspect ratio plays a major role in controlling the base resistivity of the composite systems [1]. Carbon black with smaller particle size, low surface area, and low aggregate structure exhibits higher base resistivity and higher PTC amplitude of resistivity

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[19]. On the other hand, carbon black with smaller particle size, large surface area, and higher aggregated structure shows lower base resistivity (because of smaller separation between black particles) and lower PTC amplitude of resistivity [19]. Fiber like carbon filler, having high aspect ratio, though favors the formation of conductive networks at low percolation threshold, exhibits high PTC amplitude of resistivity [22].

Thus, from the above mentioned paragraph, it is revealed that a discussion on temperature-dependent electrical conductivity/resistivity of one amorphous and other semicrystalline polymer filled with different particulate and fibrous carbon fillers can be made. This study will be interesting if the fillers with different particle size and different structure/aspect ratio are taken in the composite to show their PTC/NTC behavior, and find out their practical applicability and reversibility. Hence, this study covers the effect of temperature on DC resistivity of composites derived from polymer matrices consists of semicrystalline neat EVA, amorphous neat NBR, and their 50/50 blend composites filled with different carbon fillers like Conductex carbon black, Printex carbon black, and short carbon fiber (SCF). The temperature was varied from 30 to 120 °C for all these composites. Conductex carbon black is having smaller particle size and lower structure; whereas, Printex carbon black is having relatively larger particle size and higher structure. The PTC/NTC behavior of the composites with respect to characteristics of polymers and fillers has been logically analyzed, and their practical applicability has been sought. In addition, the effect of heating–cooling cycle on DC resistivity (that is electrical reversibility and reproducibility) of the composites will also be studied.

Experimental

Materials and methods

Ethylene vinyl acetate copolymer (EVA-2806, VA-28 %) (Mooney viscosity, ML_{1+4} at 100 °C = 20 and MFI = 6) was procured from NOCIL, Bombay, India. Acrylonitrile butadiene copolymer (NBR) (33 % ACN, Mooney viscosity, ML_{1+4} at 100 °C = 45) was purchased Japan Synthetic Rubber Co. Ltd. Conductive carbon blacks (CCBs), Conductex (SC Ultra bead) (Columbian Chemicals Corp., Atlanta); and Printex XE2 (PCB), (Degussa Canada Limited), and conductive SCF (RK 30/12, RK Carbon Fiber Ltd., UK) were used as filler particles. The characteristics of carbon fillers have been shown in Table 1.

Dicumyl peroxide (DCP), MP = 80 °C, purity of 98 % (Sigma-Aldrich Chemical Company, USA) was used as

Table 1 General specification of Conductex and Printex carbon black and SCF

Typical properties	Conductex	Printex	SCF	Unit
Mean particle size	20	35	–	nm
Average filament length	–	–	6	mm
Filament diameter	–	–	0.0068	mm
Surface area, STSA	125	587	–	m ² /g
Surface area, CTAB	130	600	–	m ² /g
Aspect ratio (L/D)	–	–	882	–
DBP absorption	115	350–410	–	cc/100 g
Volatiles at 105 °C	1.5	1.0	–	%

curing agent along with co-agent tri allyl cyanurate (TAC) (E. Merck India limited) and antioxidant, 1, 2-dihydro 2,2,4-trimethyl quinoline (TQ, polymerized) (Lanxess India Private Ltd.).

Preparation of blends, composites, and samples

Brabender Plasticorder (PLE 330) was used for blending of EVA with NBR. All mixing were carried out at 120 °C for 6 min with 60 rpm shear rate. The conducting carbon blacks Conductex or Printex along with other ingredients (TAC, TQ, and DCP) were mixed in two-roll mixing mill in a sequential manner with either of the neat polymers or their blends as per formulations shown in Table 2. However, the mixing of EVA, NBR and their blends with SCF along with other ingredients (TAC, TQ, and DCP) was accomplished in Haake Rheocord under identical processing conditions and sequence as have mentioned earlier and shown in Table 2. Monsanto rheometer (R-100S), used for the measurement of optimum cure time for different composites, was found to be 1 h at the experimental cure temperature of 160 °C. Test specimens of various composites were prepared by curing at 160 °C under compression molding.

Table 2 Formulations of EVA/NBR composites

Ingredients	Composition parts by weight per hundred parts of polymer (php)		
	E ₀ N ₁₀₀	E ₅₀ N ₅₀	E ₁₀₀ N ₀
EVA	0	50	100
NBR	100	50	0
DCP	02	02	02
TAC	01	01	01
TQ	01	01	01
CCB	60	40, 60	60
PCB	30	10, 30	30
SCF	20	20, 30	20

Testing and characterization

DC resistivity at high temperature (30–120 °C) was measured using Agilent 34401A Digital Multimeter. The entire electrode was placed in temperature-controlled electrically heated oven (SC Dey Company) for measurement of conductivity/resistivity at different temperatures.

Differential scanning calorimetry (DSC, Q100 V8.1 series, TA Instruments) was carried out at the temperature range from –120 to +100 °C for EVA, NBR, and their 50/50 blend at the scan rate 10 °C/min in liquid nitrogen atmosphere.

Dynamic mechanical analysis (DMA, 2980 V1.7B series, TA Instruments) was studied at a constant frequency 1 Hz, static force 0.01 N and amplitude 10 in tension film clamp type modes in the temperature range +70 to +150 °C for EVA, NBR, and their 50/50 blend at a scan rate 3 °C/min in liquid nitrogen atmosphere.

The hardness of the composites was measured using Shore A durometer according to ASTM D 2240-48.

Scanning electron microscopic (SEM) study of the SCF composites was performed by JEOL JSM 5800 scanning electron microscope (Tokyo, Japan). The samples were gold coated before SEM study with a vacuum gold-sputter machine (model SC7620, Polaron Brand, Quorum Technologies Ltd, East Sussex, UK). The SEM study has been carried out on cryo-fractured and etched surface of the samples. Liquid nitrogen was used for cryo-fracture of the samples; whereas, toluene was used for etching the surface of the samples.

Transmission electron microscopy (TEM, model JEM 2100, JEOL Limited, Tokyo, Japan) of powdered Conductex and Printex black was performed at an acceleration voltage of 200 keV using a cooling-holder cryotransfer system (model CT3500, Oxford Instruments, Oxfordshire, Abingdon, Tubney Woods, UK). Before TEM analysis, the samples were ultrasonicated.

Composite designation: Example, $E_{50}N_{50}P_{10}$ means blend composition of EVA/NBR 50/50 (wt%) containing 10 parts of Printex grade CCB by weight and so on. Here, in these formulations all ingredients are taken parts by weight per hundred parts by weight of polymer (php).

Results and discussion

Effect of temperature on DC resistivity for different blend compositions and filler types

An insulating polymer matrix can be converted into a conductive composite through incorporation of conductive filler into it. When conductive filler is added to an insulating polymer matrix there is a formation of conductive

network due to filler aggregation. In fact a critical concentration of filler (percolation threshold) is needed to form one or more continuous conductive networks in an insulating polymer matrix [23, 24]. In fact when filler is added initially short discontinuous conductive chain are formed due to filler aggregation. At and above the critical concentration (percolation threshold) of filler the gap between conductive chains is reduced to a few nanometers (≤ 10 nm, almost equivalent to physical contact) which can be easily hopped by electron; thus a continuous conducting network is formed in the insulating matrix and the process of electrical conduction occurs through this continuous conductive network. The effect of temperature on DC resistivity has been studied on composites having sufficient conductivity that is composites having filler loading above percolation threshold. Accordingly, composites of EVA, NBR, and EVA/NBR (50/50) blend filled with Conductex black (60 phr), Printex black (30 phr), and SCF (20 phr) have been chosen for study. To compare the variation of DC resistivity against temperature for different composites having wide difference in resistivity, the term relative resistivity (ρ_t/ρ_0) is used, where ρ_t is the resistivity at any temperature and ρ_0 is the resistivity at starting temperature (30 °C). The variation of DC relative resistivity against temperature for these systems is shown in Figs. 1, 2, and 3.

Figure 1 shows the plots of DC relative resistivity against temperature for the composites of three matrices namely EVA, NBR, and EVA/NBR (50/50) blend containing 60 phr Conductex black. For composites based on EVA–Conductex black the relative resistivity increases sharply up to a temperature around 70 °C thereafter some decrease is observed followed by again sharp increase up to 120 °C (the highest measurement temperature). Thus, for neat EVA composite a peak in the relative resistivity vs temperature plot is observed around 75 °C which

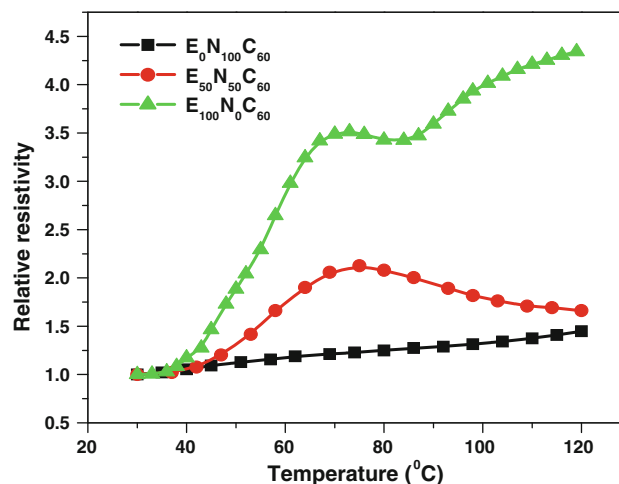


Fig. 1 Relative resistivity versus temperature of Conductex black-filled composites at different blend composition

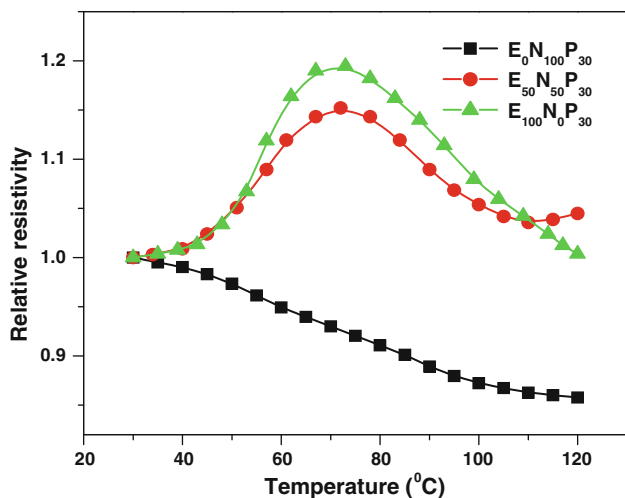


Fig. 2 Relative resistivity versus temperature of Printex black-filled composites at different blend composition

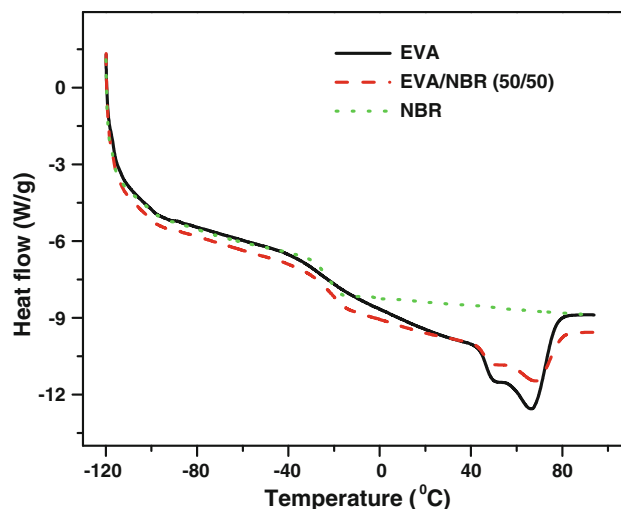


Fig. 4 DSC thermographs of EVA, NBR, and their 50/50 blend

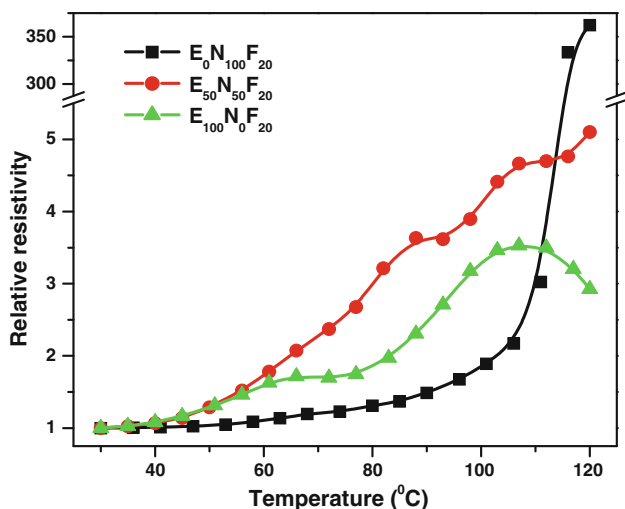


Fig. 3 Relative resistivity versus temperature of SCF-filled composites at different blend composition

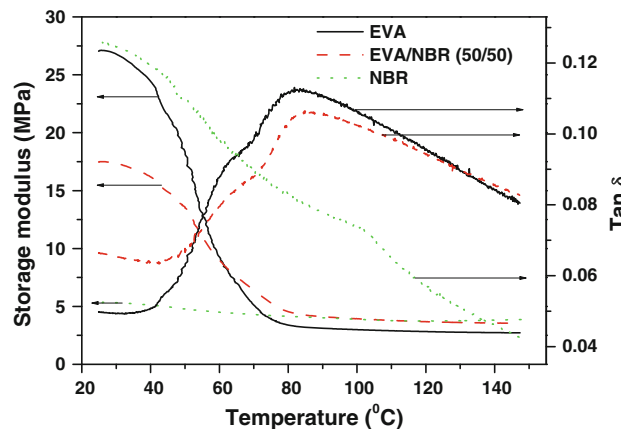


Fig. 5 DMA of EVA, NBR, and their 50/50 blend

corresponds to crystalline melting temperature of EVA polymer as seen from DSC and DMA plots of different matrices (Figs. 4, 5). Similarly EVA/NBR (50/50) blend composite containing 60 phr Conductex black shows a broad peak of relative resistivity versus temperature plot at around 70 °C. For neat NBR (100 % amorphous in nature) composite containing 60 phr Conductex black one can see slow but progressive increase in relative resistivity with rise in temperature.

Figure 2 shows the variation of relative resistivity against temperature for composite of three matrices containing Printex black. It can be seen that both neat EVA and EVA/NBR (50/50) blend containing Printex black show broad peak at around 70–80 °C but neat NBR composite shows NTC effect that is decrease in resistivity with increase in temperature. These distinct differences in

respective plots presented in Figs. 1 and 2 reflect that temperature dependency of DC resistivity not only depends on the type of matrix polymer but also on type of carbon black used. Two different matrices used in the study namely EVA, which is semicrystalline (crystalline melting point 75 °C) whereas NBR is completely amorphous in nature. Further the CCBs used have also significant influence on different relative resistivity versus temperature plots. It is observed from Table 1 that Printex black [DBP (dibutyl phthalate) absorption value 350–410 cc/100 g] has higher structure compared to Conductex black (DBP absorption value 115 cc/100 g) this means the aggregating tendency of Printex black is higher than that of Conductex black. The structure of carbon black is indirectly measured in terms of DBP absorption value absorbed by the carbon black aggregates [21]. Higher is the quantity of DBP absorption value, higher will be the structure of carbon black and consequently, easier is the formation of conductive network. With the increase in temperature there are quite a few

phenomena simultaneously operating in composites; for example, thermal expansion of matrix and conductive network, and increased thermal motion of polymer chains. As filler aggregates are well attached to polymer chain, thermal motion of polymer chain also cause some movement in filler aggregates. As a result, increase in temperature may cause both formation and destruction of conducting networks. If the formation process predominates resistivity/relative resistivity will decrease and if the destruction process predominates the resistivity/relative resistivity will increase. Initially, the PTC effect is observed for all systems containing Conductex black is mainly due to the net breakdown of conductive networks with the increase in temperature as thermal expansion of matrix polymer is substantially higher than that of carbon black (thermal expansion coefficient of EVA $\sim 160\text{--}200 \times 10^{-6} \text{ m/mK}$ [25], NBR $\sim 112 \times 10^{-6} \text{ m/mK}$ [26], and carbon blacks $\sim 7\text{--}8 \times 10^{-6} \text{ m/mK}$ [27]). This process continues up to certain temperature $\sim 75^\circ\text{C}$ for EVA and EVA/NBR (50/50) blend composites. This typical temperature is the crystalline melting temperature for EVA. At and above crystalline melting temperature the matrix polymer EVA gets substantially soft with decrease in polymer viscosity. Under this condition, polymer chains are thermally agitated resulting in progressive rearrangement of filler aggregates to form increased number of conductive network. Thus, conductive network formation process predominates over destruction process by thermal expansion and net resistivity decreases (NTC effect) so some peaks are observed in resistivity vs temperature plots for EVA and EVA/NBR composites filled with both Printex and Conductex black. But if the temperature is increased further beyond crystalline melting temperature for all EVA and EVA/NBR blend composites they show again some tendency of PTC effect at higher temperature. This PTC effect after occurrence of NTC effect at melting temperature of EVA is observed for composites which were crosslinked through curing with DCP. This presence of crosslink restricts the motion of polymer chain even after melting. The crosslink network integrity is thus preserved because of chemical crosslinking. If the system was not crosslinked then during melting of EVA molecular mobility is expected to be unrestricted, consequently filler aggregates will rearrange to form increased number of conducting network leading to decrease in resistivity as seen in the case of relative resistivity vs temperature plots for EVA/NBR (50/50) uncured blend composites (Figs. 6, 7). On the contrary, for amorphous NBR composites only PTC effect is observed for NBR–Conductex black composites due to net break down of conductive network resulting from uneven thermal expansion. However, NBR–Printex black system shows mainly NTC effect. This anomaly in the results is due to the differences in the morphology of two blacks used. As mentioned earlier and

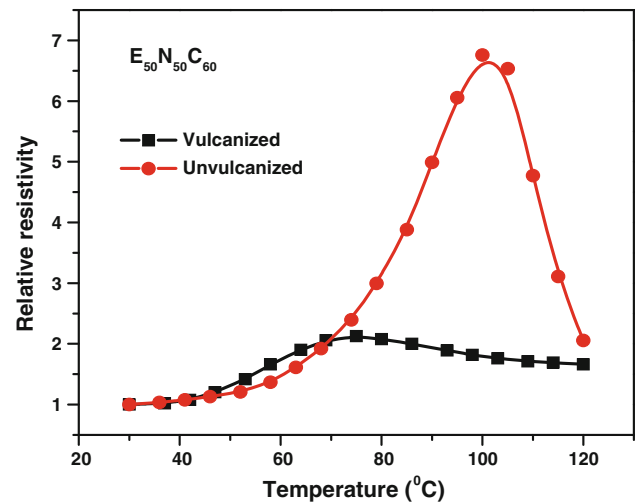


Fig. 6 Relative resistivity versus temperature of cured and uncured $E_{50}N_{50}C_{40}$ composite

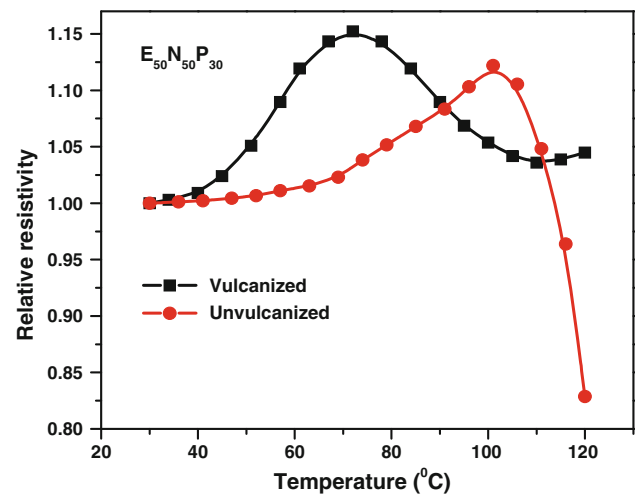


Fig. 7 Relative resistivity versus temperature of cured and uncured $E_{50}N_{50}P_{10}$ composite

also shown in Table 1 that Printex black has higher structure, higher particle size, and higher surface area compared to Conductex black; that is higher aggregating tendency of Printex black to form conductive network much more easily. The shape, size, and structure of Printex and Conductex blacks are also evident from their TEM images as have been shown in Fig. 8a, b. It is observed from Fig. 8a that the several structures of Conductex black are agglomerated where the inset picture shows the aggregation of several Conductex black particles to form a structure. Figure 8b shows that four to five carbon particles are fused together to form the aggregated structure of Printex black where the shape and size of its particle has been shown in the inset of this figure. It is interesting to see here that the size of a Printex black particle is higher compared to the size of a Conductex black particle. This is why the expansion of

polymer with the increase in temperature cannot separate the carbon particles from each other those are fused together in Printex black because of their higher aggregated structure. Thus, for this system the formation of conductive network predominates and it may be attributed to the thermal emission of electrons through the gap between the neighboring black particles separated by a distance but not equivalent to their physical contact and the rearrangement of carbon black particles during heating [28].

SCF-filled composites, however, shows somewhat different nature in relative resistivity against temperature plots compared to carbon black-filled composites. For SCF filled systems mainly PTC effect is observed for composites derived from all three base polymer matrices. This is mainly because, unlike carbon black-filled composites for SCF filled ones the conductive network destruction process predominates as carbon fiber exhibit negative thermal expansion coefficient (-1.45×10^{-6} m/mK) [29]. Further the bonding between polymer and fiber are very weak as is evident from the SEM image as shown in Fig. 8c, where the shape and size of fibers have been shown in the inset of this figure. It is seen from this figure that the fibers have separated out from the polymer creating holes on the surface. In addition, there are no traces of polymer present on the surfaces of debonded fibers. NBR–SCF composite has exhibited very high PTC amplitude. However, some tendency of NTC effect is also observed for EVA and EVA/NBR blend composites at and just beyond crystalline melting temperature of EVA. Thus, EVA and EVA/NBR composites filled with SCF show some peak in relative resistivity versus temperature plots around crystalline melting temperature. The same reason for NTC effect as mentioned for carbon black composites holds good for SCF-filled composites.

Effect of temperature on DC resistivity at different filler loading

The variation of relative resistivity against temperature at two different filler concentration has been shown in Fig. 9

for Conductex black (40 and 60 phr), in Fig. 10 for Printex black (10 and 30 phr), and in Fig. 11 for SCF (20 and 30 phr) filled EVA/NBR (50/50) composites. It is observed from these figures that the composite having lower filler loading exhibits more change in relative resistivity against temperature compare to that of one with higher loading. In fact in composites with higher loading number of conductive networks are higher in number compared to one containing less filler. Moreover, the increase in filler concentration decreases the gap among the filler particles due to their increased concentration. Thus, the probability of electron hopping is more for highly filled composites compared to one with less filler content. This increased number of conductive network and shorter inter particle gap in highly loaded sample makes them less prone to both destruction of conductive network due to differential thermal expansion (PTC effect) and network formation (NTC effect).

Effect of heating–cooling cycle on DC resistivity

The effect of temperature on DC resistivity during heating–cooling cycle for EVA/NBR (50/50) composites filled with Conductex black (40 phr), Printex black (10 phr), and SCF (20 phr), respectively, is presented in Figs. 12, 13, and 14. It is observed from these figures that the change in resistivity during heating cycle does not follow the same path as that of cooling cycle for these composites. Thus, a phenomenon termed as electrical hysteresis is observed and there exists an electrical set in resistivity at the end of the heating–cooling cycle. The electrical hysteresis is the difference in area between relative resistivity versus temperature plots during heating and cooling cycle. The electrical set is the difference between initial resistivity at the starting temperature of the composite before heating–cooling cycle and final resistivity at the starting temperature after heating–cooling cycle. The electrical hysteresis is found to be positive for particulate black (both Conductex and Printex) filled composite where there is net loss in resistivity at the

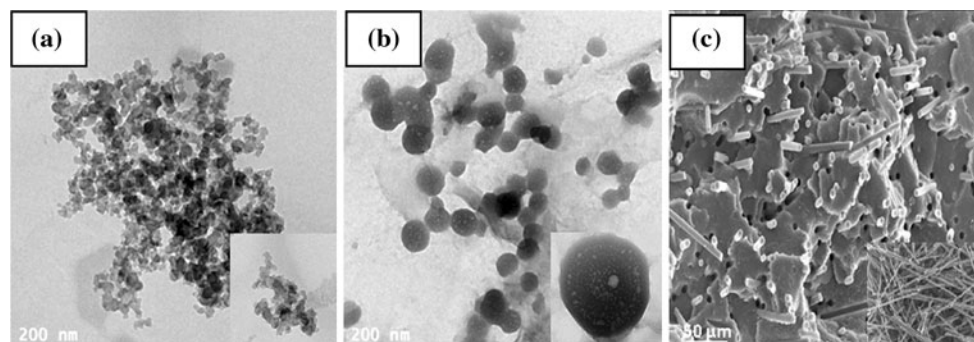


Fig. 8 **a** TEM image of agglomerate and structure (*inset*) of Conductex black, **b** TEM image of structure and particle size (*inset*) of Printex black, and **c** SEM image of EVA–SCF composite

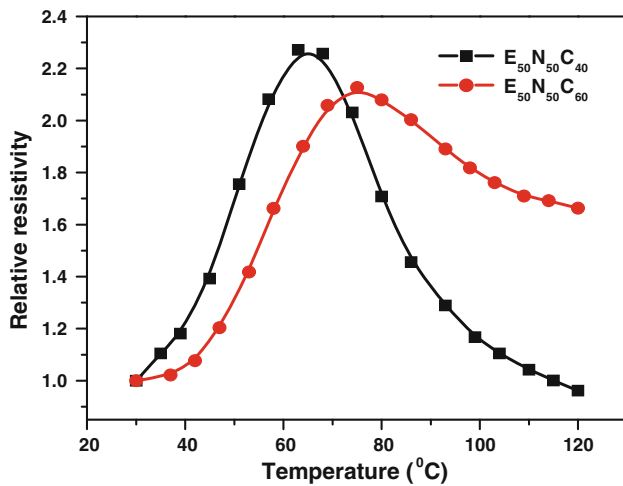


Fig. 9 Relative resistivity versus temperature of Conductex black-filled composites at different filler loading

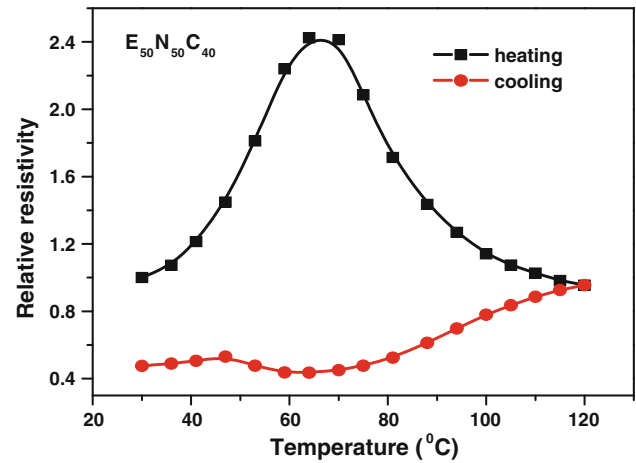


Fig. 12 Relative resistivity at heating-cooling cycle of $E_{50}N_{50}C_{40}$ composite

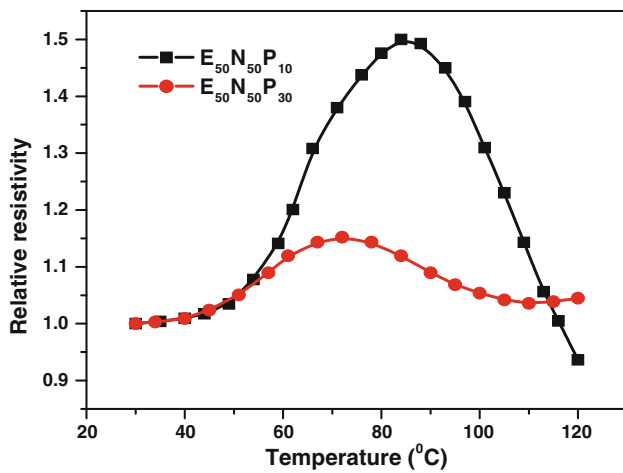


Fig. 10 Relative resistivity versus temperature of Printex black-filled composites at different filler loading

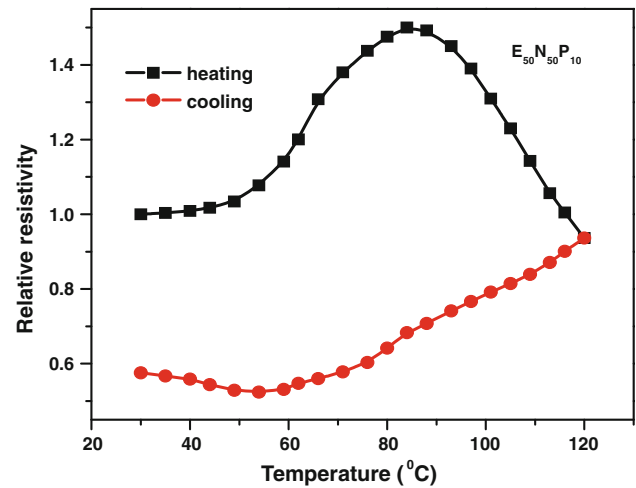


Fig. 13 Relative resistivity at heating-cooling cycle of $E_{50}N_{50}P_{10}$ composite

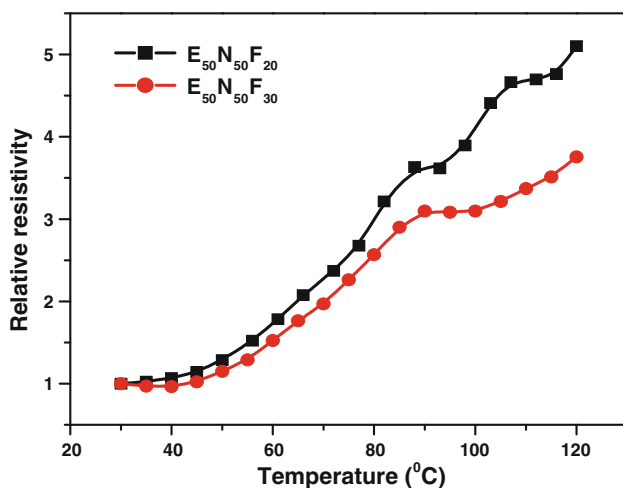


Fig. 11 Relative resistivity versus temperature of SCF-filled composites at different filler loading

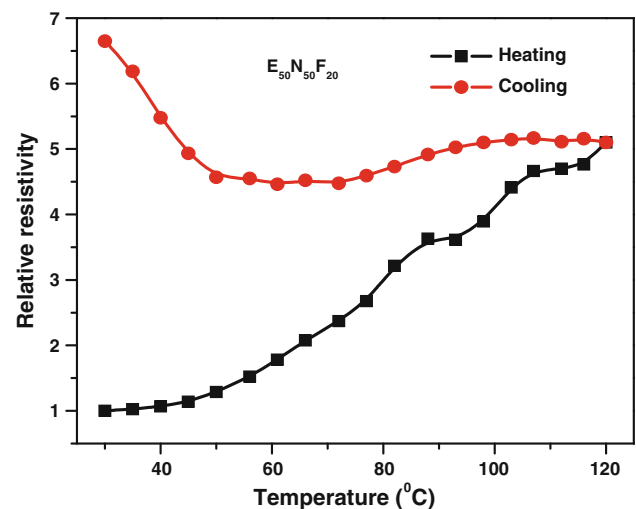


Fig. 14 Relative resistivity at heating-cooling cycle of $E_{50}N_{50}F_{20}$ composite

end of heating–cooling cycle. This difference during heating–cooling cycle is mainly due to both formation and destruction of conductive networks in an insulating matrix. The effect is more pronounced in Conductex black composites compared to that of Printex black composites. This difference in heating–cooling cycle signifies that for black filled system there is net increase in number of conductive network at the end of heating–cooling cycle. In fact during heating process some of the conducting networks undergo rearrangement due to crystalline melting on EVA where molecular rearrangements also take place. Moreover, this molecular rearrangement also happens due to crystallization process at the time of cooling. The effect of this rearrangement is more pronounced during heating process compared to cooling process. This leads to resistivity difference between the heating and cooling process. In contrast to carbon black-filled composite just opposite behavior in the variation of resistivity versus temperature plots is observed during heating–cooling cycle for carbon fiber-filled composite. In SCF-filled composites negative hysteresis is observed that is the change in resistivity during cooling cycle is higher than that during heating cycle. The close observation of change in resistivity during heating–cooling cycle reveals that for SCF filled system the breakdown of conductive network due to differential thermal expansion is the major process which causes net reduction in the number of conductive network in the system. As a result, there is a net increase in resistivity of the SCF composite at the end of heating–cooling cycle. This may be due to two reasons first for SCF systems PTC effect is highly predominant due to differential thermal expansion as discussed earlier. Further SCF unlike carbon black is not firmly attached to polymer chain (due to poor polymer–filler interaction as discussed earlier) as a result during heating–cooling movement of polymer chain does not cause efficient movement of SCF particles present in the vicinity, consequently the rearrangement of SCF to form conductive network is much less efficient.

Effect of repeated heating–cooling cycle on DC resistivity

The variation of resistivity against temperature in repeated heating–cooling cycles has been presented in Fig. 15 for Conductex black, in Fig. 16 for Printex black, and in Fig. 17 for SCF-filled composites. It is evident from the figures that the magnitude of electrical hysteresis and electrical sets in the second heating–cooling cycle is less compared to the first heating–cooling cycle for all systems.

It is observed that during heating–cooling cycles polymer matrices undergo some aging as hardness of the composites are found to increase (Table 3). Actually aging is having positive effect on conductivity [30]. The

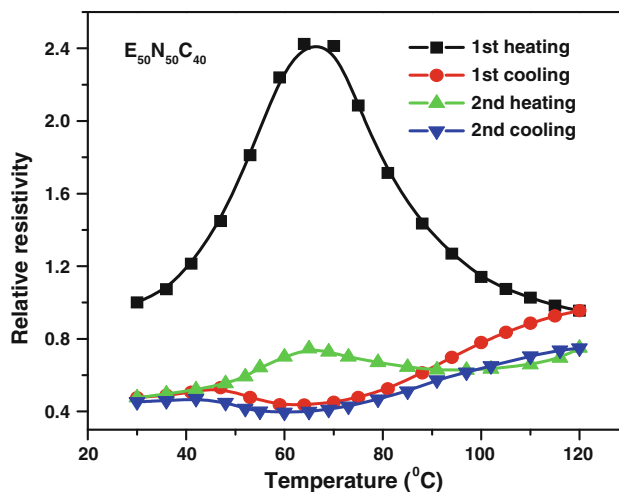


Fig. 15 Relative resistivity at repeated heating–cooling cycle of E₅₀N₅₀C₄₀ composite

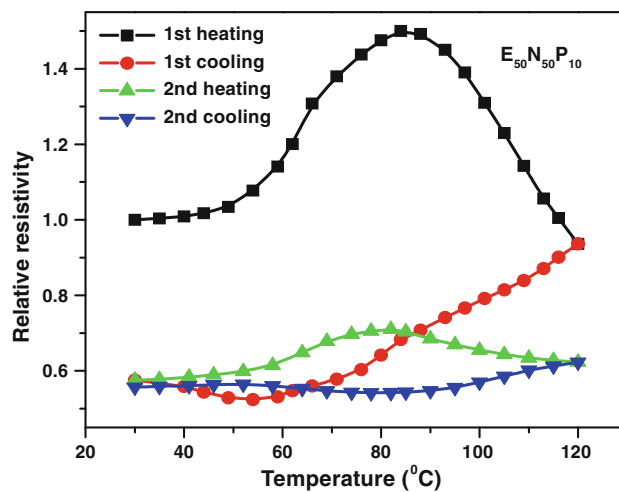


Fig. 16 Relative resistivity at repeated heating–cooling cycle of E₅₀N₅₀P₁₀ composite

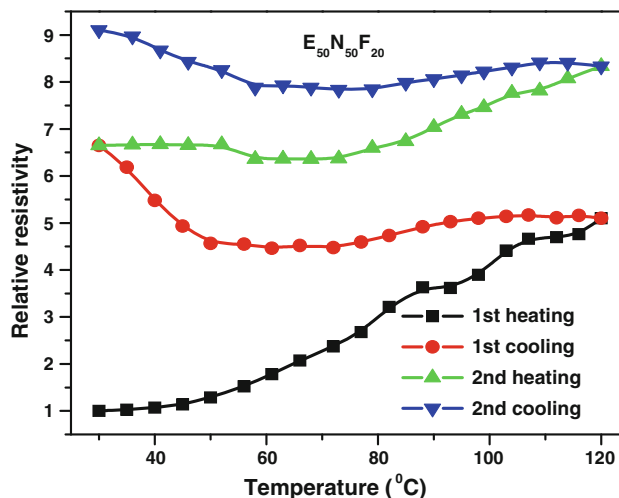


Fig. 17 Relative resistivity at repeated heating–cooling cycle of E₅₀N₅₀F₂₀ composite

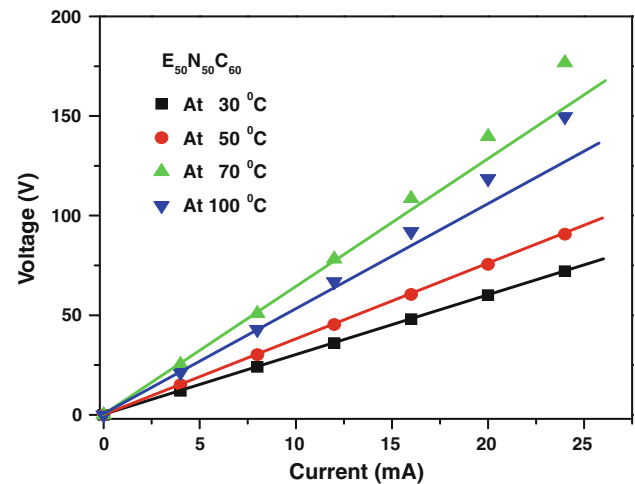
Table 3 Change in hardness after first and second heating–cooling cycles

Composition	Hardness (shore–A)		
	Initial value	After first heating–cooling cycle	After second heating–cooling cycle
E ₅₀ N ₅₀ C ₄₀	81 ± 4	87 ± 4	89 ± 4
E ₀ N ₁₀₀ C ₆₀	75 ± 3	79 ± 4	81 ± 3
E ₅₀ N ₅₀ C ₆₀	85 ± 4	90 ± 5	93 ± 4
E ₁₀₀ N ₀ C ₆₀	90 ± 5	94 ± 5	96 ± 3
E ₅₀ N ₅₀ P ₁₀	72 ± 4	79 ± 3	82 ± 4
E ₀ N ₁₀₀ P ₃₀	79 ± 3	84 ± 4	87 ± 4
E ₅₀ N ₅₀ P ₃₀	83 ± 4	88 ± 5	90 ± 5
E ₁₀₀ N ₀ P ₃₀	86 ± 5	91 ± 4	93 ± 4
E ₀ N ₁₀₀ F ₂₀	67 ± 4	73 ± 4	76 ± 3
E ₅₀ N ₅₀ F ₂₀	78 ± 3	83 ± 3	85 ± 4
E ₁₀₀ N ₀ F ₂₀	83 ± 4	89 ± 5	91 ± 4
E ₅₀ N ₅₀ F ₃₀	82 ± 4	88 ± 4	90 ± 5

composite sample is subjected to elevated temperature for prolonged period during repeated heating–cooling cycles leading to oxidation of polymer chain with the formation of groups like –OH, –CHO, –COOH, etc.

Current–voltage characteristics

The current–voltage characteristics give the idea about ohmic/non-ohmic conduction through a system. For ohmic conduction, the applied current is linearly proportional to the applied voltage; whereas, for non-ohmic conduction the current–voltage relationship deviates from its linearity. Figure 18 represents the effect of applied current on voltage at different temperature of EVA/NBR (50/50) composites filled with Conductex black. It is observed from the figure that the current is linearly proportional to the voltage when measured at 30–50 °C that means the conduction is ohmic in nature. On the contrary, at higher temperature (70–100 °C) the departures from linearity are observed for all composites due to the non-ohmic conduction. In fact at room temperature the electrical conduction is takes place through the conductive filler–filler contact and hence the conduction is ohmic in nature. On the contrary, at higher temperature due to differential thermal expansion between polymer matrices and filler particles the gaps between them are increased. This leads to a drop in electric field strength between the filler–filler particles which finally results in non-ohmic conduction through the composite systems [10]. Similar type of current–voltage characteristics has been observed for EVA/NBR (50/50) composites filled with Printex carbon black and SCF (not shown in picture).

**Fig. 18** Current–voltage characteristics of E₅₀N₅₀C₆₀ composite

Evaluation of composites on practical application point of views

It is observed from heating–cooling cycle and repeated heating–cooling cycle plots that the resistivity is not recoverable/reproducible at the entire range of measurement temperature. This is because melting of crystalline phase takes place at the switching temperature due to which rearrangements of some conductive networks takes place. Switching temperature is the temperature before which the composite exhibits PTC behavior and after which NTC behavior [13]. Most of the crystalline and semicrystalline polymers exhibit this switching effect. In practical point of views this switching effect is unwanted rather an overall PTC or NTC effect is desirable [13, 31]. So, the practical applicability of these crystalline/semicrystalline composites is restricted up to their switching temperature that is up to their PTC ranges. In this view, the PTC application limit of neat EVA and EVA/NBR blend composites filled with Conductex and Printex black is up to 70 °C, and for neat NBR composite filled with Conductex black is up to 120 °C. The proposed applications of these composites exhibiting PTC behavior are as current limiter for protection of circuits, self-controlled heaters, over current protectors, timers in degaussing coil circuit of most CRT (cathode ray tube) displays, and pyroelectric sensors. Neat NBR composite filled with SCF has exhibited very high PTC amplitude and can be used as resettable fuses. The composite of neat NBR filled with Printex black has shown overall NTC effect and can be used as NTC thermistors such as resistance thermometers to measure low temperature, inrush-current limiter in power supply circuits, coolant temperature and/or oil temperature monitor inside the engine used in automotive applications, temperature monitor of an incubator especially for storing

and preparing food used in the food handling and processing industry, proper temperature controller in toasters, refrigerators, coffee makers, hair dryers, freezers, etc. used in consumer appliance industry.

Conclusions

Conductive composites based on semicrystalline EVA and EVA/NBR blend exhibit PTC effect before crystalline melting temperature but NTC effect after crystalline melting temperature. PTC effect is due to destruction of conductive network because of uneven thermal expansion between polymer matrix and filler. NTC effect after melting is due to rearrangement of filler network because of enhanced mobility of polymer chain. Crosslinking of polymer restrict chain mobility, as a result crosslinking composites exhibit PTC effect after NTC effect beyond melting temperature; whereas, uncrosslinked composites where matrix polymer exhibit unrestricted chain mobility exhibit only NTC effect after crystalline melting. For neat NBR composites smaller particle sized, lower surface area, and lower structured Conductex black exhibit PTC effect but larger particle sized, higher surface area, and higher structured Printex black exhibits NTC effect. DC resistivity of carbon fiber-filled EVA/NBR (50/50) composites exhibit different behavior compared to Conductex and Printex black-filled composites when subjected to elevated temperature. The extent of resistivity change during heating is found to be higher for EVA-based composites when filled with Conductex and Printex black; whereas, SCF-filled composites exhibit the opposite trend. It is also observed that a composite having low loading of carbon filler exhibits relatively higher change in resistivity compared to composite with high loading of filler. The change in resistivity during heating–cooling cycle does not follow the same path for these composites. Some electrical hysteresis is observed along with electrical set. Both electrical hysteresis and electrical set are due to permanent breakdown of some conductive networks. The extent of electrical hysteresis and electrical set reduces if heating–cooling cycle is repeated more than once. Electrical conduction is ohmic in nature around room temperature and becomes non-ohmic at higher temperature. These composites can be used as both the PTC and NTC thermistors.

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