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# Development of high performance EMI shielding material from EVA, NBR, and their blends: effect of carbon black structure

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**Abstract** The conductive composites were prepared using two different types of conductive black (Conductex and Printex XE2) filled in matrices like EVA and NBR and their different blends. The electromagnetic interference shielding effectiveness (EMI SE) of all composites was measured in the X band frequency range 8–12 GHz. Both conductivity and EMI SE increase with filler loading. However, Printex black shows higher conductivity and better EMI SE at the same loading compared to Conductex black, and this can be used as a material having high EMI shielding effectiveness value. The conductivity of different blends with same filler loading generally found to increase slightly with the increase in NBR concentration. However, EMI SE has some dependency on blend composition. EMI SE increases linearly with thickness of the sample. EMI SE versus conductivity yields two master curves for two different fillers. EMI SE depends on formation of closed packed conductive network in insulating matrix, and Printex black is better than Conductex black in this respect. Some of the composites show appreciably high EMI SE (>45 dB).

## Introduction

Electromagnetic interference shielding materials (EMI SE) are of great importance in protecting electronic instrument and communication devices from unwanted microwave radiations emitted from other nearby instruments [1–4]. Metals are commonly used as EMI shielding materials. The EMI SE property of a metal is mainly due to reflection of electromagnetic radiation from its electron rich surface. However, there are some limitations associated with metals mainly because of their high density, processing problem, lack of flexibility, and prone to oxidation. So metals are not preferred as EMI SE materials where weight is a limitation or complicated shape is wanted, or prolonged weather resistance is looked for [5]. However, the lightness of EMI SE structures can be accomplished by replacing metal by metal coated light weight materials like polymer. EMI shielding materials based on metal coatings using techniques like electroplating, electro less plating, and vacuum deposition have already been reported in the literature [6–14]. It is apparent that mainly conductive materials can serve the purpose of EMI shielding. An intrinsically conducting polymer can serve the purpose of EMI shielding material but it suffers from poor processability, environmental stability, high cost, and lack of mechanical properties [5, 15–25]. The use of extrinsically conductive composite for EMI shielding application is gaining interest where a suitable polymer matrix is filled with appropriate type and amount of conducting filler [26–36]. These conducting composites are popular because of their light weight, easy processibility, and cost effectiveness. Further such composites can easily be formed into intricate shape through common processing practices. The polymer based conductive composite is especially useful for making gasket or seal to prevent EMI leakage [37].

This study deals with EMI SE of different conducting composites made from ethylene–vinyl acetate copolymer (EVA), acrylonitrile–butadiene copolymer (NBR), and their blends filled with two different types of conducting carbon black Conductex and Printex XE2. The effect of type of conducting filler, polymer blend composition, composite thickness on EMI SE of these composites were

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investigated to understand how the conductivity and EMI SE can be co-related for such extrinsically conducting systems.

## Experimental

### Materials used

Acrylonitrile–butadiene copolymer (NBR), (33% ACN, Mooney viscosity, $ML_{1+4}$ at 100 °C = 45) (Japan Synthetic Rubber Co. Ltd). Ethylene vinyl acetate Copolymer (EVA-2806, VA-28%), (Mooney viscosity, $ML_{1+4}$ at 100 °C = 20 and MFI = 6) (NOCIL, Bombay, India). Conductive Carbon blacks, Conductex (SC Ultra bead) (Columbian Chemicals Corp., Atlanta); and Printex XE2 (PCB), (Degussa Canada Limited).

Curing agent, dicumyl peroxide (DCP), MP = 80 °C, purity of 98% (Sigma-Aldrich chemical company, USA). Co-agent for curing tri allyl cyanurate (TAC), (E. Merck India limited). Antioxidant, 1,2-dihydro 2,2,4-trimethyl quinoline (TQ, polymerized) (Lanxess India Private Ltd.)

### Preparation of blends, composites, and samples

Blending of EVA with NBR was accomplished in Brabender Plasticorder (PLE 330) under identical processing conditions where 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 with either of the neat polymers or their blends in two-roll mixing mill in a sequential manner as per formulations given in Table 1. The optimum cure time as measured from Monsanto rheometer R-100S for different composites was found to be 1 h at the experimental cure temperature 160 °C. Test specimens of various composites were prepared through curing at 160 °C under compression molding.

Different composites were designated by using alpha numerical number; for example, $E_{25}N_{75}C_{20}$ means blend composition of EVA/NBR 25/75 (wt%) containing 20 parts of carbon black by weight per hundred parts of polymer (php) and so on, where *E* stands for EVA, *N* for NBR, *C* for Conductex carbon black, and *P* for Printex carbon black.

### Testing and characterization

#### *Measurement of DC resistivity*

The DC volume resistivity of different samples was measured using either Agilent 4339B (High Resistance Meter coupled with Agilent 16008B Resistivity Cell) for samples with high resistance ($\geq 10^6$ ohm) or GOM-802 (GW Instek DC milli Ohm Meter) with home built cell for samples with low resistance ($\leq 10^6$ ohm).

#### *Measurement of electromagnetic interference shielding effectiveness (EMI SE)*

The EMI shielding effectiveness of different samples was estimated using a Scalar Network Analyzer (HP 8757C, Hewlett Packard) coupled with a sweep oscillator (HP 8350B, Hewlett Packard) in the X—band frequency range, 8–12 GHz. In general for EMI shielding measurement, samples of 5 mm thickness were used. However, to check the effect of sample thickness, samples with higher thickness were also used.

### EMI shielding theory

The spectrum of electromagnetic radiation is composed of wave with electric and magnetic components oscillating at right angles to each other. The electromagnetic shielding is a process of limiting flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material [38]. The electromagnetic interference is a disturbance caused in a radio receiver or other electrical circuit by electromagnetic radiation emitted from an external source. The shielding effectiveness is the

**Table 1** Formulations of EVA/NBR composites

| Ingredients | Composition parts by weight per hundred parts of polymer | | | | |
|---|---|---|---|---|---|
| | $E_0N_{100}$ | $E_{25}N_{75}$ | $E_{50}N_{50}$ | $E_{75}N_{25}$ | $E_{100}N_0$ |
| EVA | 0 | 25 | 50 | 75 | 100 |
| NBR | 100 | 75 | 50 | 25 | 0 |
| DCP | 02 | 02 | 02 | 02 | 02 |
| TAC | 01 | 01 | 01 | 01 | 01 |
| TQ | 01 | 01 | 01 | 01 | 01 |
| CCB | 60 | 0, 10, 20, 30, 40, 50, 60 | 60 | 0, 10, 20, 30, 40, 50, 60 | 60 |
| PCB | 50 | 0, 10, 20, 30, 40, 50 | 50 | 0, 10, 20, 30, 40, 50 | 50 |

amount of attenuation of incident radiation by a particular material and is expressed in dB [39]. An electromagnetic wave can be attenuated by absorption ($A$) inside the materials, by multiple internal reflections ($B$) inside the materials and also by reflection ($R$) from the outer surface. If the incident power density is denoted by $P_{\mathrm{inc}}$; transmitted power density by $P_{\mathrm{trans}}$ and reflected power density by $P_{\mathrm{ref}}$, then the net shielding effectiveness (SE) and loss due reflection are given by Eqs. 1 and 2, respectively.

$$\mathrm{SE} = 10 * \log_{10}(P_{\mathrm{trans}}/P_{\mathrm{inc}}) = (A + B + R)\ \mathrm{dB} \quad (1)$$

$$\text{and, } R = 10 * \log_{10}(P_{\mathrm{ref}}/P_{\mathrm{inc}}) \quad (2)$$

A mathematical relation of absorption and reflection loss with conductivity applicable to both near and far field region and to both electric and magnetic field are given as [32]

$$A = 1.32\mathrm{t}\ (G\mu f)^{1/2} \quad (3)$$

$$R = 108 + \log(G/\mu f) \quad (4)$$

where, $t$ is the thickness of sample in cm, $G$ is the conductivity of sample in mho cm$^{-1}$ relative to copper, $\mu$ is the magnetic permeability of sample relative to vacuum, and $f$ is the frequency of radiation in MHz. Above Eqs. 3 and 4 show that the absorption loss is directly proportional to the square root of conductivity and reflection loss is proportional to the log of conductivity.

## Results and discussion

### Effect of filler loading on DC resistivity

The resistivity of the present series of composites not only depends on the type and concentration of conductive additive but also to some extent on the matrix polymer. Different matrices used are either two neat polymers namely EVA and NBR or their different blends. For all composite systems, the resistivity decreases with the increase in carbon black loading. The nature of variation of resistivity (Figs. 1, 2) with filler concentration (phr) depends on type of black used. For Conductex black filled composites initially the rate of change in resistivity with filler concentration is marginal followed by appreciable decrease in resistivity especially in region of 20–40 phr loading. But with further addition of black beyond 50 phr loading the resistivity change becomes again marginal. Whereas for Printex black, the decrease in resistivity is quite sharp with initial addition of filler in polymer matrix and the rate of fall in resistivity is much faster compared to Conductex black. For Printex black also at higher loading (≥20 phr) the change in resistivity becomes marginal.

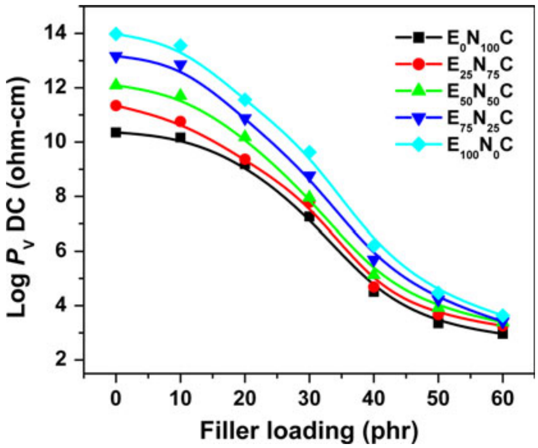

**Fig. 1** DC resistivity vs. filler loading of EVA/NBR blend composites filled with Conductex carbon black

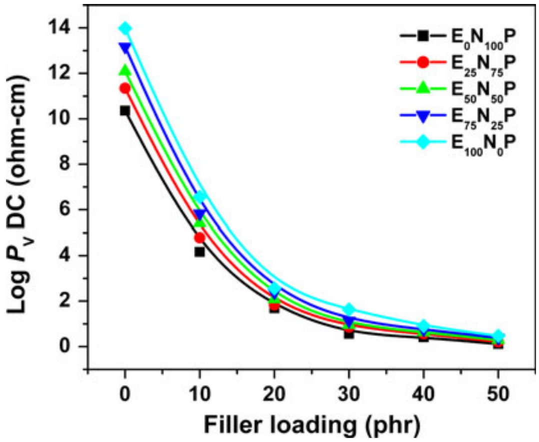

**Fig. 2** DC resistivity vs. filler loading of EVA/NBR blend composites filled with Printex XE2 carbon black

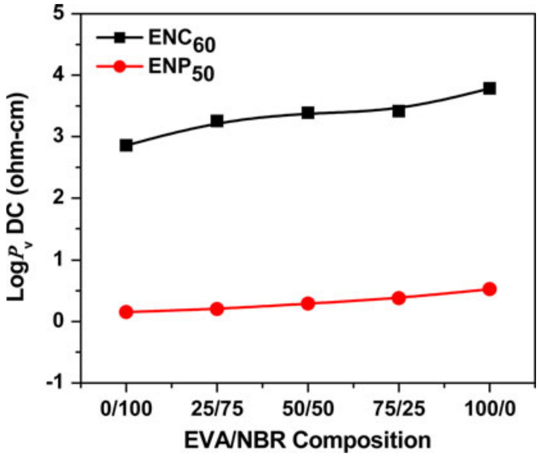

**Fig. 3** DC resistivity vs. blend compositions of $ENC_{60}$ and $ENP_{50}$ composites

The effect of blend composition on conductivity for fixed filler loading 60 phr for Conductex and 50 phr for Printex has been presented in Fig. 3. It is found that composites with Printex black exhibit much higher conductivity compared to composites with Conductex black at similar filler loading.

In any particular blend this decrease in resistivity with filler loading (concentration) can be explained in terms of general mechanism of conduction for extrinsically conductive systems [40]. The progressive addition of conductive filler like Conductex black or Printex black in an insulating polymer matrix leads to formation of discrete conductive aggregates which finally grows into a continuous conductive chain at some critical concentration known as percolation threshold. When conductive filler concentration is increased above percolation, there is only increase in the number of such chains. The large number continuous conductive chains lead to the formation of conductive network mesh. So when the first conductive chain is formed at the percolation, the system changes from insulating to conductive and an abrupt reduction in the resistivity is observed. But at loading beyond percolation only the number of such conductive chain increases so the decrease in resistivity becomes marginal. But it is noteworthy to mention here that the percolation threshold (the critical concentration) at which the continuous conductive network is first formed is very much dependent on certain characteristics of conductive filler added in the polymer. In the present investigation two different conductive carbon blacks were used, and they differ from each other in terms of structure values as given in Table 2. Carbon black particles forms strong aggregates (primary structure) and these aggregates are loosely clustered into bigger aggregates (secondary structure). The aggregate with more complex shape, size, and internal voids are termed as higher structure and vice versa [41]. The structure can be indirectly measured through quantity of DBP (dibutyl phthalate) absorbed by aggregated carbon black [42]. Carbon black with higher structure can form more easily continuous conductive network in insulating matrix. Printex black has higher structure and exhibits lower percolation threshold compared to those of Conductex black [43]. The percolation threshold for Printex is around 25 phr and that of Conductex is 45 phr.

**Table 2** General specification of Conductex SC ultra beads and Printex XE2 carbon black

| Typical properties | Conductex | Printex | Unit |
|---|---|---|---|
| Mean particle size | 20 | 35 | nm |
| Surface area, STSA | 125 | 587 | $m^2/g$ |
| Surface area, CTAB | 130 | 600 | $m^2/g$ |
| DBP absorption | 115 | 350–410 | cc/100 g |
| Volatiles at 105 °C | 1.5 | 1.0 | % |

It is observed from Fig. 3 that the resistivity has some dependence on the matrix polymer. This dependence can be attributed to viscosity of polymer matrix during mixing. If the viscosity of matrix polymer is less, then the shear stress exerted on carbon black aggregates during mixing will be less, as a result the breakdown of carbon black aggregate (structure) will be less. But if the viscosity of matrix polymer during mixing is high then there will be an extensive breakdown of carbon black structure and chain like particles aggregate will disintegrate and will be more isolated in matrix polymer. This leads to higher amount of black requirement to form conductive network and percolation threshold will be higher. The viscosity of NBR at the mixing temperature (45–50 °C) is some what lower than that of EVA, so NBR rich blends show lower percolation and lower resistivity as compared to EVA and EVA rich ones.

## Effect of frequency on EMI SE

The EMI SE of different composites containing conductive carbon black Conductex and Printex XE2 over the frequency ranges of 8–12 GHz are presented in Figs. 4 and 5, respectively. The SE of composites depends both on type and loading of filler in polymer matrix, frequency of the incident radiation, matrix composition, and thickness of the composites.

The effect of frequency on EMI SE of blends of EVA/NBR (25/75 and 75/25) filled with Conductex carbon black has been shown in Fig. 4 (75/25 composite has been shown in inset). EMI SE of all composition shows wave like variation against frequency. The variation of EMI SE against frequency is irregular and non linear, this means the shielding effectiveness fluctuates with frequency of incident ray. This may be due to irregular nature of conductive network that is formed in the matrix polymer. However,

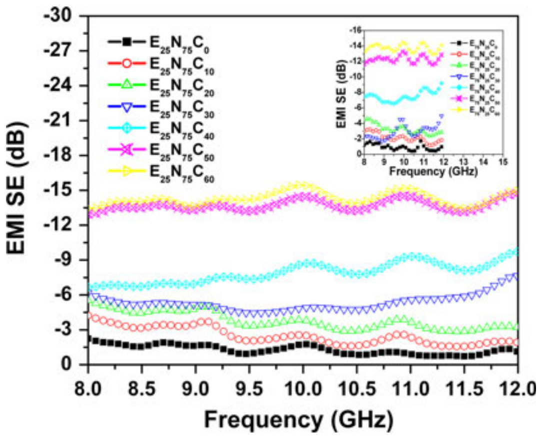

**Fig. 4** Frequency vs. EMI SE of EVA/NBR 25/75 and 75/25 (shown in *inset*) Conductex black filled composite

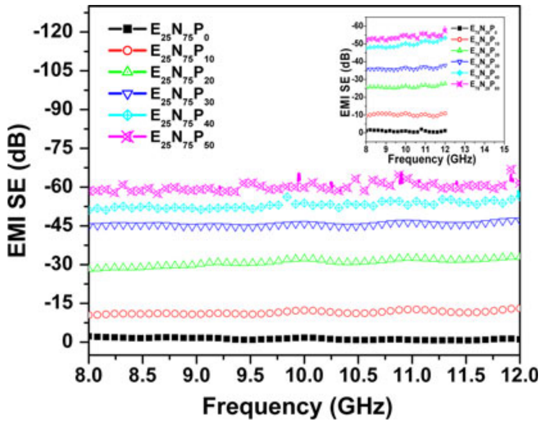

**Fig. 5** Frequency vs. EMI SE of Printex XE2 filled EVA/NBR 25/75 and 75/25 (shown in *inset*) composites

EMI SE progressively increases with filler loading at all frequencies over the frequency band of measurement.

The frequency dependency EMI SE of Printex XE2 filled EVA/NBR (25/75 and 75/25) composites (Fig. 5, 75/25 composite has been shown in inset) also show almost similar trend. These figures show that EMI SE increases with the increase in filler loading throughout the frequency range. It is also apparent when Fig. 5 are compared with Fig. 4 that composites containing the Printex black always show substantially higher EMI SE compare to composites containing Conductex black at the same loading of filler.

## Effect of filler loading on EMI SE

To check the effect of filler concentration on EMI SE, the measurement at any particular reference frequency may be taken into consideration. The shielding effectiveness at the measurement frequency of 10 GHz for composites having different filler loadings has been depicted in Fig. 6 for Conductex black, and in the inset of Fig. 6 for Printex black. Figure 7 exhibits a comparison of EMI SE against filler loading for Conductex and Printex black systems. From the frequency dependency of different composites it is clear that the EMI SE increases with filler loading and that is mainly because, with the increase in filler loading the resistivity decreases which in turn increases the EMI SE.

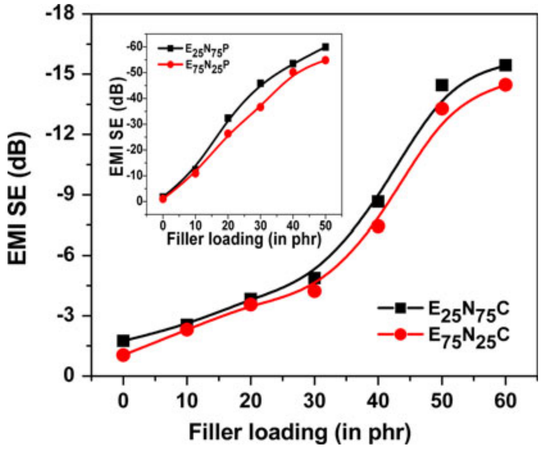

**Fig. 6** Filler loading vs. EMI SE of EVA/NBR (25/75 and 75/25) Conductex and Printex XE2 (shown in *inset*) *black filled* composites

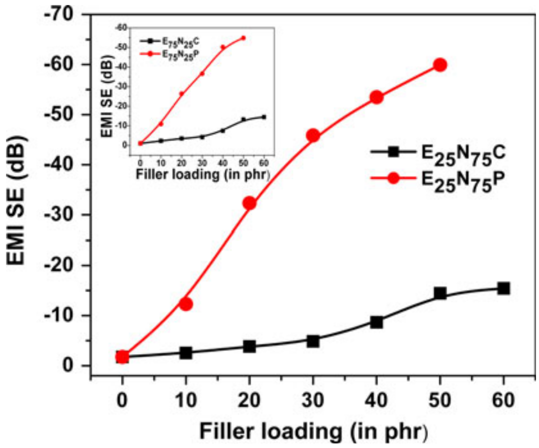

**Fig. 7** Filler loading vs. EMI SE of Conductex and Printex *black filled* EVA/NBR 25/75 and 75/25 (shown in *inset*) composites

The rate of increase of EMI SE against filler loading is initially slow up to 35–45 phr loading of Conductex black, but beyond that sharp increase is observed followed by relatively slow increase, whereas some what similar trend is observed for Printex black. But the rate of increase of EMI SE against filler loading is much faster in the case of Printex black where the sharp increase is observed beyond 15–20 phr, and EMI SE increases progressively with filler loading.

This variation of EMI SE against filler loading has some relation with the variation of resistivity against filler loading. As such insulating polymer matrix is transparent to incident radiation, the conductive networks formed due to addition of conductive particles interacts with incident ray and account for shielding effectiveness. In fact in a composite with high filler loading (at and beyond percolation), there is formation of mesh of conductive networks. With the increase in filler loading the mesh size decreases that mean conductive meshes become finer and finer with increased filler loading and their ability to absorb electromagnetic radiation increases and consequently the EMI SE increases. EMI SE of metals is due to reflection whereas EMI SE of conductive composites is mainly due to absorption [5].

The highest EMI SE value obtained for composites with Conductex black is around 14–15 dB at the highest loading (60 phr) whereas for composites with Printex XE2 black this value is around 55–62 dB at the highest loading

(50 phr). In fact if we consider the characteristics of two blacks we find that Printex black has higher particle size as compared to Conductex black that helps them to disperse more easily in the polymer matrix. But the most important characteristic of black which mainly governs the conductivity as well as EMI SE is the structure. Earlier it has been told that the structure is measured in terms of amount of DBP (dibutyl phthalate) absorption by the filler and is found to be substantially higher for Printex black compared to that of Conductex black. The structure physically signifies the number of carbon black particle fused together to form aggregates as well as the shape of these aggregates [44]. Higher structure black has larger chain like aggregation of carbon black particles. Though this structure disintegrates to some extent during mixing, but still larger part of it is retained in the polymer matrix. Because of high structure, the Printex black can form continuous conductive network more easily and at much lower concentration in polymer matrix compared to Conductex black with comparatively low structure. At higher filler loading denser conductive network is formed in the case of composites with Printex black compared to that in composites with Conductex black. This accounts for much higher EMI SE for the former compared to that for latter.

Relatively smaller contributions from other attributes can also affect the resistivity and EMI SE. The attributes like lower volatile content of Printex black (1%) indicates less concentration of functional groups on carbon black surface compared to Conductex black with volatility 1.5% (Table 2). The presence of different functional groups like >C=O, H–C=O, –OH, –COOH on carbon black surface adversely affect the electron flow, as these functional groups are electron capturing in nature. So presence of such groups on carbon black in higher concentration adversely affects the conductivity of the composites [45]. Heat treatment of carbon black can reduce the concentration of such groups.

## Effect of blend composition on EMI SE

As mentioned, in general matrix polymer being insulating in nature does not have any significant contribution towards EMI SE. However, certain characteristics like polymer viscosity during time of mixing affects conductive network formation and thus can affect EMI SE [46]. This can be easily realized when EMI shielding effectiveness is plotted against blend composition for equal filler loading. Both neat polymer NBR and EVA, and their different blends containing 60 phr Conductex black and 50 phr Printex black (shown in inset) are presented in Fig. 8, which exhibit similar trend. In case of both type of fillers, EMI SE of composites increases with increase in NBR concentration in matrix polymer (Fig. 9). This reveals that denser and more compact conductive network is formed in polymer matrix when NBR concentration is increased. Some interesting points are to be noted here, NBR is amorphous in nature whereas EVA is semicrystalline. The semicrystalline EVA consists of two phases namely, crystalline and amorphous, in crystalline phase polymer chains are parallely oriented with close packed whereas in amorphous phase polymer chains are randomly oriented with high interchain gap and are less densed. When carbon black is incorporated in semicrystalline EVA, there is every likely that black particles will be distributed mainly in the amorphous region and in the interface of crystalline and amorphous region. The distribution of carbon black particle in the closed packed crystalline region is expected to be much less compared to amorphous region of same polymer. But NBR is totally amorphous in nature with higher interchain gap and carbon black particles can be incorporated and more uniformly distributed throughout the polymer matrix relatively easily. So when carbon black is incorporated in EVA, there is always a chance of preferential distribution of carbon black especially in amorphous region of the polymer matrix. This kind of preferential distribution may help in conductive network formation at lower loading, but adversely affect the formation of uniform closed packed conductive network throughout the matrix polymer especially at higher loading. This close packed conducting network formation is essential for achieving high EMI shielding. So in NBR with carbon black loading more uniform and densely packed conductive network is formed throughout the polymer matrix. But in bi-phase EVA, the conductive network formed is relatively non uniform and less dense. The more porous conductive network in EVA is less efficient to arrest electromagnetic radiation and exhibits less EMI SE at the same level of filler loading compared to NBR.

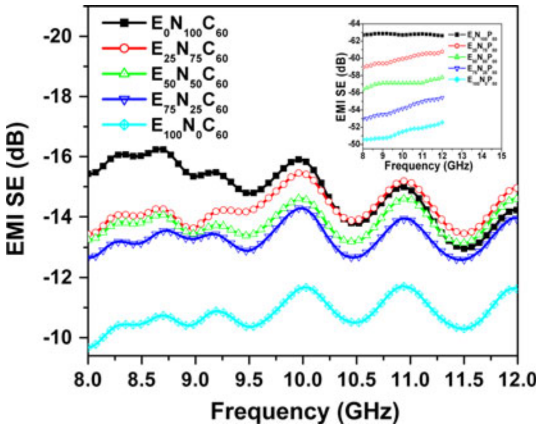

**Fig. 8** EMI shielding effectiveness vs. frequency for ENC$_{60}$ and ENP$_{50}$ blend compositions

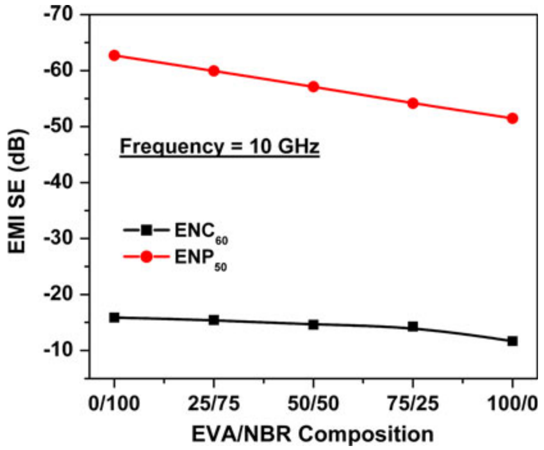

**Fig. 9** EMI shielding effectiveness vs. blend composition for $ENC_{60}$ and $ENP_{50}$ composites

The difference in distribution of carbon black particles in EVA and NBR matrices loading beyond percolation can be visualized from the TEM images shown in Fig. 10. It is clear from this figure that in EVA which is semicrystalline polymer with crystallinity in the level shows relatively non uniform distribution of carbon black in its matrix compared to amorphous NBR. The regions devoid of carbon particles are more in EVA/carbon black composites compared to those in NBR/carbon black composites. The regions without carbon black and regions with very little carbon black act as perforation in conductive network which acts as passage of electromagnetic radiation thereby reducing the EMI SE.

Same idea of distribution of carbon black in crystalline and amorphous phases can be obtained from mechanical loss tangent versus temperature plots of different filled EVA system as given in Fig. 11. In dynamic mechanical study of EVA and EVA composites two peaks in tan$\delta$ versus temperature can be identified; one at temperature region—9.5 °C and is due to glass-rubber transition of EVA phase and it is due to molecular motion of polymer chain in amorphous region. Another peak is observed at temperature 79 °C due to crystalline melting of EVA that due to molecular motion in crystalline phase. With the increase in carbon black concentration in amorphous region there is progressive reduction in tan$\delta$ peak height because of restriction imposed on polymer chain motion due to presence of carbon black. This reduction in damping measured in terms of peak height bears a linear relationship with filler loading (shown in inset of Fig. 11). However, change in peak height due to crystalline melting is much less affected by carbon black loading, and this change in peak height is also not uniform with filler loading. This signifies that mostly carbon black particles are incorporated in amorphous region and to some extent in the interfacial region in the boundary of crystalline and amorphous region.

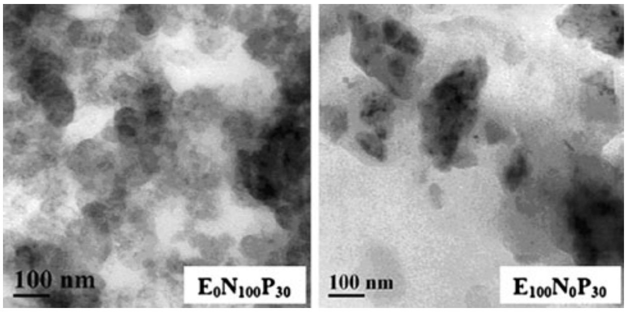

**Fig. 10** TEM image of $E_0N_{100}P_{30}$ and $E_{100}N_0P_{30}$ composites

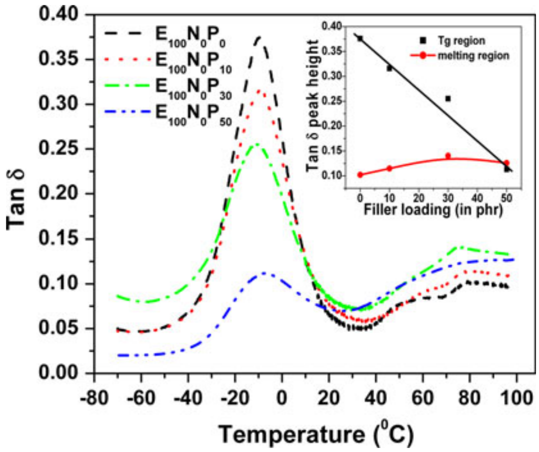

**Fig. 11** Dynamic loss tangent (tan$\delta$) against temperature, and tan$\delta$ peak height against filler loading at $T_g$ and melting region (shown in *inset*) of $E_{100}N_0P$ composite systems

## Effect of composite thickness on EMI SE

Effect of composite thickness on EMI SE has been studied at the reference frequency of 10.0 GHz for 75/25 EVA/NBR blend containing Conductex and Printex carbon blacks, and composition taken are $E_{75}N_{25}C_{40}$, $E_{75}N_{25}C_{60}$, $E_{75}N_{25}P_{10}$, and $E_{75}N_{25}P_{20}$. Plot of EMI SE versus composite thickness is presented in Fig. 12. It shows that EMI

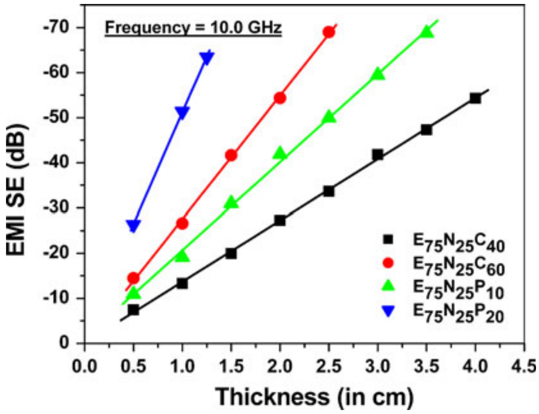

**Fig. 12** EMI SE vs. sample thickness at a frequency of 10.0 GHz for both systems ($E_{75}N_{25}C_{40}$, $E_{75}N_{25}C_{60}$, $E_{75}N_{25}P_{10}$, and $E_{75}N_{25}P_{20}$)

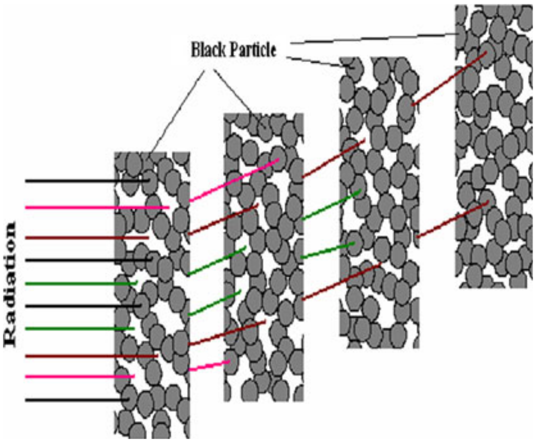

**Fig. 13** EMI absorption by different layers in case of thick sample

SE increases almost linearly with the increase in thickness. Formation of conductive mesh in the matrix intercepts electromagnetic radiation [46]. This situation can be visualized as follows: with the increase in composite thickness the number of conductive mesh increases and they are randomly placed in the system one after another in thick sample. So with continuous increase in thickness the number of mesh increases and mesh size decreases as a result EMI SE progressively increases (Fig. 13).

The linear increase in EMI SE with increase in composite sample thickness can be represented by the following straight line Eq. 5;

$$Y = B * X \tag{5}$$

where, $X$ is independent variable indicating the thickness of the sample; $Y$ is dependent variable indicating the EMI shielding effectiveness; and $B$ is a constant which represents the slope of the linear equation. In the present system, the slope which indicates the rate of increase of EMI SE with thickness is found to be the highest for $E_{75}N_{25}P_{20}$ in the system which has 20 phr Printex black followed by $E_{75}N_{25}C_{60}$, the system containing 60 phr of Conductex, 10 phr of Printex, and 40 phr of Conductex successively (Table 3).

This order of slope variation is in line with the conductivity variation of the system. The system which has the lowest resistivity shows the fastest rate of increase of EMI SE with sample thickness and the system which has the highest resistivity exhibit the slowest rate of increase of EMI SE with thickness.

This variation of resistivity versus EMI SE further corroborates our idea about the conductive network formation through black particles aggregation in polymer matrix.

## Relation between conductivity and EMI SE

The conductive materials like metals exhibit high EMI SE mainly due to reflection of radiation. Lossy dielectrics like conductive composites exhibits SE because of absorption. It is also found that EMI SE increases with conductivity of these composites. However, this relation between EMI SE and conductivity is not linear rather it is exponential in nature. This non linear relation between EMI SE and conductivity leads to a question, does EMI SE exclusively depend on conductivity or some other factor may also play an important role in controlling EMI SE of extrinsically conductive systems. The plot of EMI SE at the reference frequency of 10 GHz against conductivity for blends of $E_{25}N_{75}$ and $E_{75}N_{25}$ containing Conductex black (C) and Printex black (P) are presented in Fig. 14a–d. It can be observed that initially the increase in SE against conductivity is marginal but beyond a certain critical value of conductivity the increase is very sharp and this is true for all systems under investigation. This critical conductivity corresponds to conductivity at the percolation limit of individual filler. This seems to be logical that at and around percolation concentration, the continuous conductive network is just formed in the system which interacts with incident electromagnetic radiation. It is interesting to note that beyond percolation limit of filler loading the change in conductivity is relatively much less, but the increase in EMI SE is appreciable as shown in Fig. 15 which reflects the variation of conductivity and EMI SE of $E_{25}N_{75}P$ composite series with variation in black loading. We can calculate the relative increase in conductivity and EMI SE with filler loading after and before percolation from this figure. This relative increase is defined as follows; it is the ratio of the rate of increase in conductivity or EMI SE with filler loading after and before percolation. This relative change is 6.93% for conductivity and 46.01% for EMI SE. Very similar observations are also found for other composite systems. This reveals that after percolation, the trend in conductivity change and the trend in EMI SE change are quite different. This signifies that only conductivity is not the determining factor for controlling the magnitude of EMI SE, some other factor also plays a significant role.

**Table 3** Parameter value for Conductex and Printex XE2 filled EVA/NBR (25/75 and 75/25) systems

| Parameter | $E_{75}N_{25}C_{40}$ | | $E_{75}N_{25}C_{60}$ | | $E_{75}N_{25}P_{10}$ | | $E_{75}N_{25}P_{20}$ | |
|---|---|---|---|---|---|---|---|---|
| | Value | Error | Value | Error | Value | Error | Value | Error |
| $B$ | −13.56 | ±0.174 | −27.36 | ±0.504 | −19.502 | ±0.414 | −49.51 | ±0.434 |

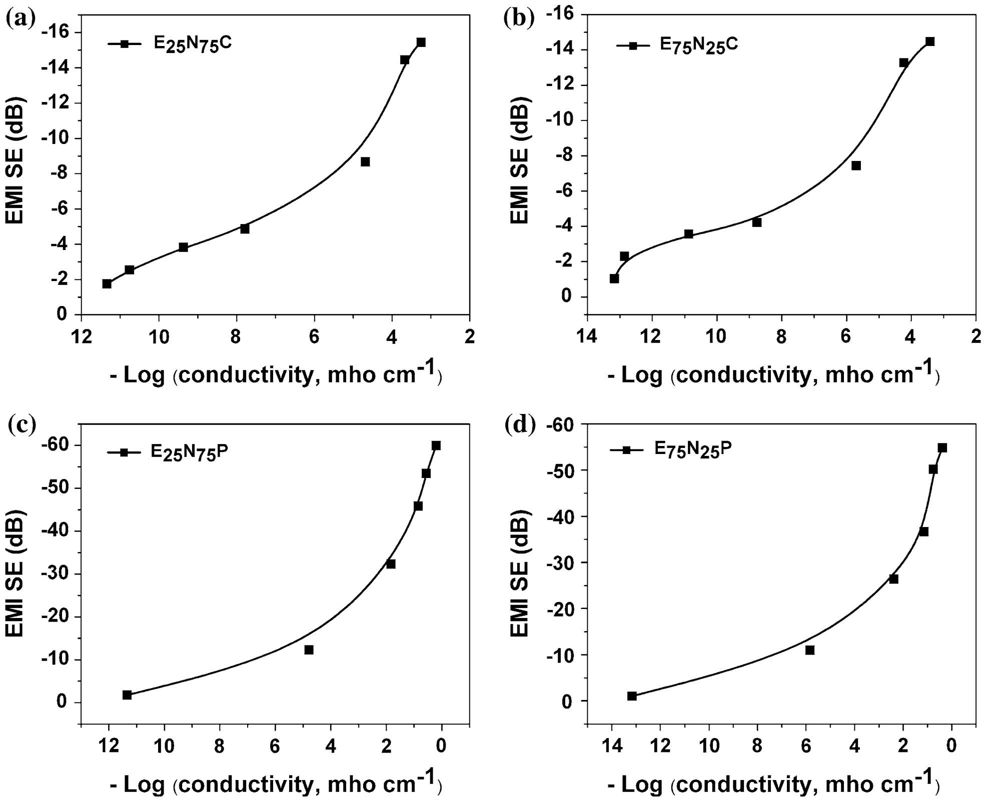

**Fig. 14** EMI SE against conductivity at a frequency of 10 GHz for blends of **a** $E_{25}N_{75}C$, **b** $E_{75}N_{25}C$, **c** $E_{25}N_{75}P$, and **d** $E_{75}N_{25}P$

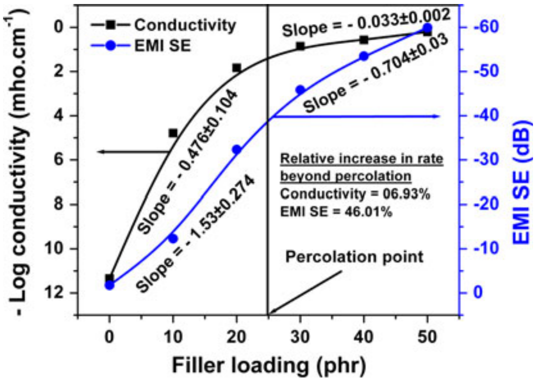

**Fig. 15** Variation of conductivity and EMI SE with respect to black loading of $E_{25}N_{75}P$ composite

Beyond the percolation, the conductive network becomes denser and more efficiently intercepts with the range of electromagnetic radiation thereby showing high EMI SE (Fig. 16a–d).

If we carefully observe Fig. 17, we will find that at the same level of conductivity, the systems containing Printex black exhibit higher EMI SE compared to that of Conductex black. The Printex black has higher structure compared to Conductex black, which helps in formation of denser network at higher filler loading and exhibits higher EMI SE compared to Conductex black.

The variation of EMI SE against conductivity can be fitted in a master curve with following Eq. 6 and its parameters values are given in Table 4.

$$Y = Y_0 + Ae^{(-x/t)} \qquad (6)$$

where, $Y$ is EMI shielding effectiveness at any point of conductivity of $x$, $Y_0$ is the offset (initial) value of EMI SE, $A$ is amplitude, and finally $t$ is decay constant. The two master curves for two different fillers reveal that EMI shielding dependence on conductivity is influenced some what by the type of conductive filler but not by matrix polymer.

## Conclusions

i. Formation of conductive network (mesh) through aggregation of conductive particles in insulating polymer matrix is the key reason for EMI SE and conductivity. Closer the conductive mesh formed better will be the EMI SE.
ii. Printex black has exhibited higher conductivity and higher EMI SE compared to Conductex black at the same loading. This behavior can be attributed to higher structure (aggregating tendency) of Printex black as compared to that of Conductex black.

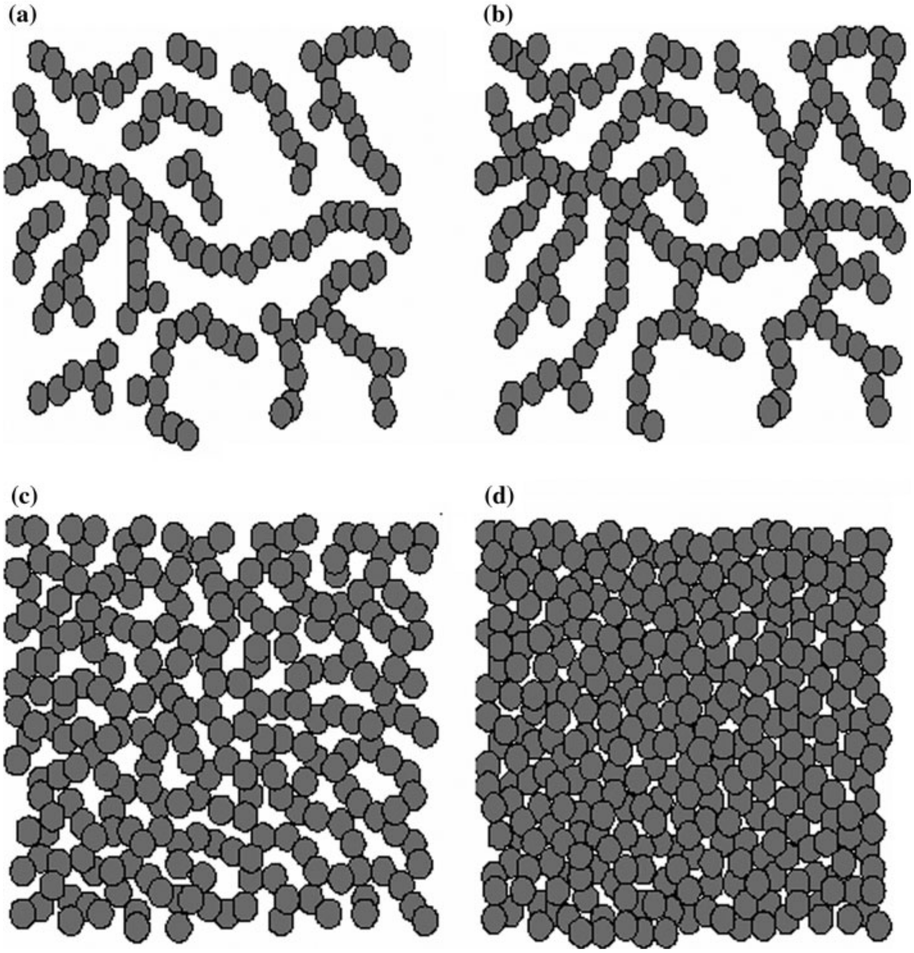

**Fig. 16** Conductive network systems **a** at percolation, **b** just above percolation, **c** above percolation, and **d** far above percolation

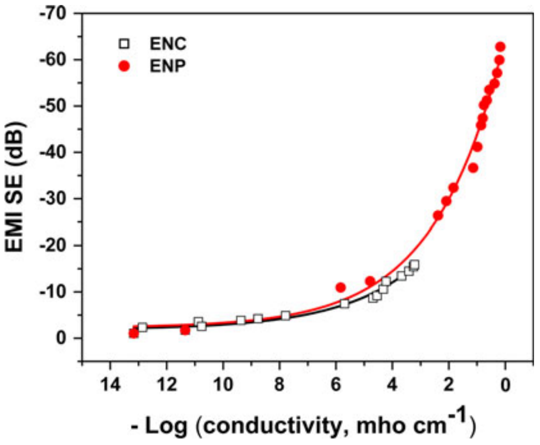

**Fig. 17** EMI SE vs. conductivity of ENC and ENP systems

iii. EMI SE exhibits linear relationship with composite thickness and an exponential relationship with logarithm of conductivity. This is in accordance with the EMI SE theory as described earlier.

iv. NBR composites exhibit higher EMI SE compared to EVA composites at same filler loading. This is due to the fact that more closely packed conductive network is formed in amorphous NBR compared to that in semicrystalline EVA.

**Table 4** Parameters value of two master curves of ENC and ENP composites

| Parameter | ENC | | ENP | |
|---|---|---|---|---|
| | Value | Error | Value | Error |
| $Y_0$ | −1.85868 | ±0.4631 | −2.26592 | ±1.39528 |
| $A$ | −45.45225 | ±6.52413 | −62.48952 | ±1.54429 |
| $t$ | 2.67699 | ±0.33061 | 2.45099 | ±0.17597 |

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