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Conducting carbon black filled EPDM vulcanizates: assessment of dependence of physical and mechanical properties and conducting character on variation of filler loading

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Abstract

The effects of incorporation of different extents of extra conducting carbon black as filler on some selected physical and mechanical properties, aging behavior and DC electrical conducting character of vulcanizates of ethylene-propylene diene monomer (EPDM) based compounds have been studied. Increasing carbon black loading caused a monotonic increase in density and hardness and in tensile strength with a leveling off trend for carbon black filler loading >40 phr. Elongation at break of the initial EPDM vulcanizates, however, passes through a maximum corresponding to 20 phr carbon black loading; the position of the maximum shifts to 30 phr carbon black loading on aging of the vulcanizates at 135°C for 7 days. DC electrical conductivity measurements of the filled EPDM vulcanizates indicate a percolation concentration range over 15–30 phr of conducting carbon black loading. Trends of change in voltage (V) developed with increase in the current (I) applied for the carbon black filled EPDM vulcanizates at different temperatures commonly indicate ohmic behavior for application of current up to a critical level. Beyond the critical current (I_C), the developed voltage becomes practically insensitive to large enhancements in the applied current; the filled vulcanizates, thus, exhibit non-ohmic character for $I > I_C$. An attempt has been made to analyze and interpret the observed effects. Electromagnetic interference (EMI) shielding effectiveness (SE) generally increases on increasing the carbon black loading. Vulcanization substantially contributes to enhancement in the EMI SE of the filled EPDM compounds.

1. Introduction

Studies on electrically conducting polymer composites prepared by incorporation of metallic powders, flakes, whiskers, and other conducting fillers such as carbon black, graphite, etc. have attracted wide attention due to their effectiveness in such applications as electromagnetic interference (EMI) shielding [1–9], electrostatic charge dissipation [4] and sensors for vapours and chemicals [5]. Among the filled conducting polymer composites, however, those based on the use of different grades of carbon black [6–10] and carbon fibre [11] as filler have grown more in importance in respect of their physical, mechanical, conducting and noncorrosive property balance.

Recent investigations on conducting polymer composites have led to some important revelations relating to attainable electrical conductivity range and trends

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of change in the conductivity parameter with variations in: (i) the loading level [4,12], (ii) nature of the matrix polymer [13,14], (iii) degree of filler dispersion [4,15] and (iv) temperature [16,17].

The present paper reports results of our studies relating to assessment of some physical and mechanical properties and aging behavior, and of electrical conducting character of conducting carbon black filled vulcanizates based on compounds from ethylene-propylene diene monomer (EPDM) system; the main objective of the studies relate to ascertaining how the said properties would vary with variation in the extent of loading of the carbon black filler.

2. Experimental

2.1. Materials

Elastomer selected for the present studies is an EPDM system containing 4% hexadiene (Nordel 1040E, from Du Pont, USA) having a density of 0.90 g/cm^3 and Mooney viscosity ML_{1+4} of 40 at 125°C. Extra conducting (furnace) carbon black, Vulcan XC-72, from Cabot Corporation, USA (having density of 1.84 g/cm^3, average particle diameter of 30 μm, dibutyl phthalate absorption value of 200 cm^3/100 g and iodine absorption value of 270 mg/g) was used as the filler. A peroxide, viz., 1,3-bis(tertiary butyl peroxy isopropyl) benzene (Perkadox 14/40, containing 40% active ingredient and 60% granular calcium carbonate) and polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (Pilnox-TDQ) each obtained from Akzo Chemie, Netherlands, were used as the curing agent and antioxidant, respectively, for EPDM elastomer. A fixed low dose of a process oil (Sunpar 2280) obtained from ICI India was commonly used in the rubber compounding.

2.2. Methods

2.2.1. Compounding of EPDM

The mixing or compounding of EPDM with the selected peroxide curative (0 and 6 phr) and other additives was carried out in a laboratory two-roll mill at a temperature of 75 ± 2°C, following the conventional technique [18]. An overall mixing time of 15 min was allowed in each case to ensure uniform and efficient dispersion of the carbon black filler particles in the elastomer matrix. Carbon-black loading was selectively varied from 0 to 60 phr as detailed in Table 1.

2.2.2. Vulcanization of EPDM

The vulcanization or curing characteristics of the filled EPDM compounds were studied in a Monsanto Rheometer (Model-R-100) at 160°C and the optimum cure time was obtained from torque–time curves (not shown) given by the rheometer.

Vulcanizates from the appropriately compounded elastomers were prepared in a compression moulding machine under a pressure of 80 kgf/cm^2 and at a temperature of 160 ± 2°C over a time period corresponding to the optimum cure time as revealed by torque rheometry.

2.2.3. Evaluation of physical and mechanical properties of the EPDM vulcanizates

The density and hardness (shore A) of unfilled and conducting carbon black filled EPDM vulcanizates were determined at 25°C following the methods [19,20] described in BS 2782 and ASTM 2240, respectively. Tensile properties (both initial and after aging at 135°C for 168 h in air) of the vulcanizates were measured on a universal tensile tester (Blue Star, Germany, model No. 2132) according to ASTM D412-83 test method [21].

Table 1
Compound recipe for EPDM vulcanizates[a]

Ingredients (phr)	Compound code									
	EM^*_0	EM^*_{10}	EM^*_{15}	EM^*_{20}	EM^*_{25}	EM^*_{30}	EM^*_{35}	EM^*_{40}	EM^*_{50}	EM^*_{60}
EPDM	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Antioxidant (Pilnox-TDQ)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Process oil (Sunpar-2280)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Highly conducting carbon black (Vulcan XC-72)	0.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	50.0	60.0
Curing agent (Perkadox 14/40)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0

[a] In compound code, EM indicates EPDM, asterisk (*) indicates vulcanized product and numerals attached indicate carbon black loading in phr. For the unvulcanized EM compounds having no curing agent (0 phr of Perkadox 14/40) and coded without asterisk (not shown), the ingredients used and their loading levels are the same as for the corresponding vulcanizates shown.

2.2.4. Evaluation of electrical properties

2.2.4.1. Measurement of volume resistivity (ρ). The room temperature (25°C) volume resistivities (ρ) for unfilled and conducting carbon black filled vulcanizates having different filler loading were measured according to ASTM D991-85 method [22] using a resistivity cell from Hewlett–Packard, USA (model 160084) and a high resistance meter from Hewlett–Packard (model 4329A). The reciprocal of the measured volume resistivity (ρ) in each case was taken as the DC electrical conductivity (σ) of the corresponding sample.

2.2.4.2. Measurement of DC electrical conductivity (σ). We also made use of a programmable DC voltage/current generator (Advantest Corporation, Japan, model-R6142) along with a precision digital voltmeter (Schlumburger, UK, model 7071) for measurement of voltage generated on application of a known current on filled EPDM vulcanizates having relatively high conductivities due to the presence of a relatively high dose (≥30 phr) of the conducting carbon black filler. The said measurements were made at different temperatures (25–200°C) for each such filled vulcanizate following the four probe van der pauw technique [23], and the observed data were then utilized for calculation of DC electrical conductivities of the respective samples.

2.2.5. Evaluation of EMI shielding effectiveness (SE)

The effectiveness of EMI shielding of the conducting carbon black filled unvulcanized and vulcanized EPDM compounds and variation of the said property with variation in carbon black phr were studied. The SE is defined as the ratio of the incident power (P_I) to the transmitted power (P_T) of the microwave passing through the sample and is generally expressed [24] in decibel (dB) as:

$$\mathrm{SE} = 10\log_{10}\left(\frac{P_I}{P_T}\right) \tag{1}$$

To measure the SE, samples having the shape of a rectangular block (sample dimension, 22.5 × 10 × 5.5 mm) was placed inside a sample holder (cell) of similar dimension located at the end of a waveguide. As a source of microwave (X-band, frequency range, 8–12 GHz) a sweep oscillator (model 8620) from Hewlett–Packard, USA was used. The power of the incident wave (P_I) was measured with the help of a power meter (Markoni Instrument, model 6460/3, UK); similarly, the power of the transmitted wave (P_T) was also measured with the help of another power meter of the same make. Finally, the SE value was calculated using Eq. (1).

2.2.6. Scanning electron microscopy (SEM)

SEM studies of some selected conducting carbon black filled EPDM samples appropriately gold coated following a sputter coating technique were done on a Hitachi S-415A electron microscope employing an accelerated voltage of 25 kV.

3. Results and discussions

Results based on studies of physical and mechanical properties, DC-electrical conductivity, EMI SE, etc. of unfilled EPDM and filled EPDM vulcanizates are shown in Figs. 1–14 and in Table 2.

3.1. Density and hardness of EPDM vulcanizates

Density and hardness (shore A) of EPDM vulcanizates by and large followed a monotonically increasing trend with increase in carbon black loading as shown in Figs. 1 and 2, respectively. Analysis of plots point to a carbon black loading range (15–35 phr) as a transition zone over which a relatively sharp change in the two physical property parameters is clearly indicated. Filled EPDM vulcanizates having carbon black loading up to 25 phr are lighter than water; however, carbon black loading ≥30 phr makes the EPDM vulcanizates heavier than water.

Fig. 1 further shows the calculated density values of the studied carbon black filled EPDM composites. Experimental density values, being measurably lower than the calculated density values for the carbon black filled composites, point to the existence of considerable amount of microvoids in the highly porous and high structured conducting carbon black filler which were

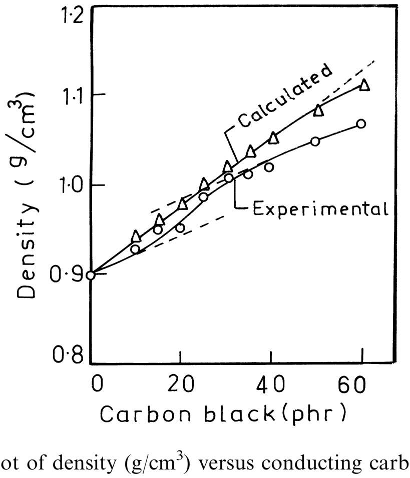

Fig. 1. Plot of density (g/cm^3) versus conducting carbon black loadig (phr) at 25°C for EPDM vulcanizates; △ — calculated, ○ —experimental.

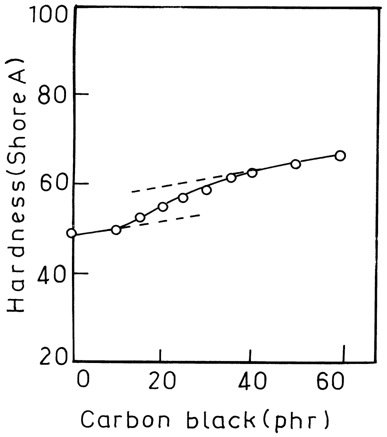

Fig. 2. Plot of hardness (shore A) versus conducting carbon black loading (phr) at 25°C for EPDM vulcanizates.

not completely filled or occluded by the elastomer chain segments in the composites. The difference in calculated and experimental density values, Fig. 1, gets somewhat narrowed down near the upper limit of the percolation threshold. Use of still higher doses of carbon black leaves progressively higher levels of microvoids due to progressively incomplete occlusion of segments of the matrix polymer in the pores of the filler particles and thereby causing a widening of the gap between the experimental and calculated density values.

3.2. Tensile strength (TS) and elongation at break (EB %)

Values of TS for the initial unfilled and carbon black filled vulcanizates having different extents of filler loading and of the corresponding heat aged (135°C for 168 h) samples, Fig. 3, also indicate increasing trends with increase in the extent of carbon black loading. A transition zone corresponding to (20–40 phr) loading of carbon black is clearly indicated. Over a comparatively high carbon black loading range (≥30 phr), TS values tend to follow a levelling off trend. However, the plot of the EB (%) versus carbon black phr for the EPDM vulcanizates, Fig. 4 passes through a maximum over the said transition zone with positioning of the peak for the aged system at a somewhat higher carbon black loading than that for the unaged system.

A sharp dropping trend in the EB for use of carbon black loading > 30–35 phr indicates development of a sharply enhanced physical stiffening effect of carbon black filler just above the said loading level.

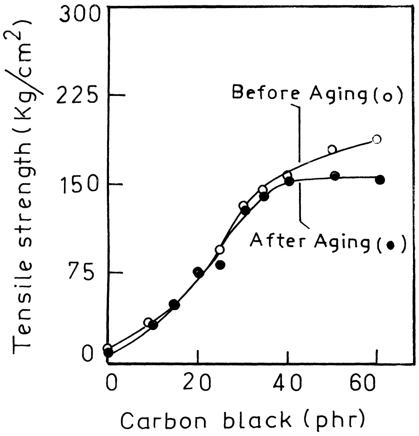

Fig. 3. Plot showing variation of tensile strength of EPDM vulcanizates with variation in conducting carbon black filler (phr); ○, before and ●, after aging.

3.3. Electrical conductivity

Electrical conductivity data for EPDM vulcanizates having different amounts of carbon black loading (0–60 phr) are shown in Fig. 5. The conductivity (σ) value undergoes a sharp transition over a carbon black loading range of 20–35 phr which is taken as the percolation concentration range. The numerical figures shown near different points in Fig. 5 indicate shore A hardness values of the vulcanizates having corresponding carbon black loadings.

For low carbon black loading (≤ 15 phr) of EPDM, the conducting carbon black particles in the elastomer

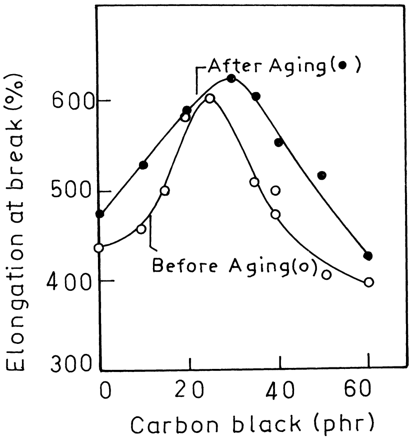

Fig. 4. Plot showing variation of elongation at break (%) of EPDM vulcanizates with variation in conducting carbon black filler (phr): ○, before and ●, after aging.

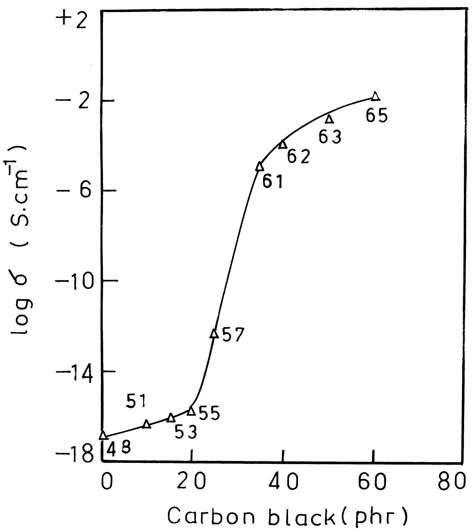

Fig. 5. Plot showing variation of DC electrical conductivity of EPDM vulcanizates at 25°C with variation of conducting carbon black loading.

matrix are relatively widely separated. Large gap-widths between the conducting filler particles stand as physical barriers to flow of electrons through the elastomer matrix, thereby resulting in a relatively low level of electrical conductivity. Over the percolation concentration zone (20–35 phr), as the carbon black particle concentration increases (leading to effective and progressive lowering in the gap width [9] between the conducting filler particles), the barrier or hindrance to electron mobility drops sharply. This causes a sharp rise in the electrical conductivity with enhancement in filler loading over the percolation zone. On further increase in conducting carbon black filler loading, the increase in conductivity value follows a gradual levelling off trend over this zone. Successive increase in carbon black loading over the high filler loading zone contributes to progressive narrowing or may be even limited elimination of the gap widths, thus facilitating much improved electrical conduction.

It is interesting to further note that the trends of variation in the physical (density and hardness), mechanical (TS) and electrical (DC electrical conductivity) properties of the EPDM vulcanizates with change in carbon black loading are somewhat similar or parallel in nature.

3.4. Filler threshold, filler networking and polymer-filler interactions

The trends of results described above arise as a consequence of the following four factors, viz, (i) enhanced stiffening effect of the carbon black filler particles that sharply comes to much greater prominence from the threshold filler loading of 15–20 phr due to a fast developing trend in filler particle networking [25–28], (ii) increasing restriction in the mobility of EPDM polymer chains due to enhanced degrees of filler-polymer interfacial interactions [29–31], (iii) limited degree of possible chemical anchorage [29,32,33] of the segments of polymer on the active sites (such as –OH, >C=O, –COOH, etc.) of the filler particles and (iv) more and more occlusion [34,35] of rubber chain segments into the void space of the porous conducting carbon black particles. A sharp or notable jump in experimental density, hardness and electrical conducting character from or above 15–20 phr carbon black filler incorporation tends to finally level off beyond 40 Phr carbon black incorporation, apparently due to attainment of levelling off effects in the filler networking process via factor (i), much as a consequence of enhanced filler rubber contacts via factors (ii), (iii) and (iv) mentioned above.

3.5. Voltage–current characteristics

Some typical V–I plots for carbon black filled EPDM vulcanizates at 25°C are shown in Fig. 6. In each case, the V–I plot is linear, showing a positive slope, indicating ohmic behavior. The critical applied current (I_C), corresponding to the point of the advent of a sharp change in the slope of each V–I plot beyond which the filled vulcanizate turned non-ohmic [36], Fig. 6, is different for different carbon black loading. The observed I_C value at a given temperature is higher for an EPDM composite of a higher carbon black loading, Table 2 and Fig. 7 and for a given composite, the I_C value is higher for measurement at a higher temperature, Table 2. A big jump in the magnitude of I_C is commonly exhibited for measurements at all temperatures (low or high) for carbon black content ≥50 phr, Fig. 7 and Table 2.

Table 2
Data for critical current (I_C) at different carbon black loadings and temperatures

Temperature (°C)	Critical current, I_C (mA)				
	EM^{*}_{30}	EM^{*}_{35}	EM^{*}_{40}	EM^{*}_{50}	EM^{*}_{60}
25	0.005	0.014	0.201	0.85	9.00
50	0.005	0.061	0.202	1.00	8.50
75	0.006	0.150	0.350	1.50	10.50
100	0.010	0.452	0.501	2.50	12.50
150	0.015	0.501	0.502	3.00	17.00
175	0.024	0.501	0.801	4.00	25.00

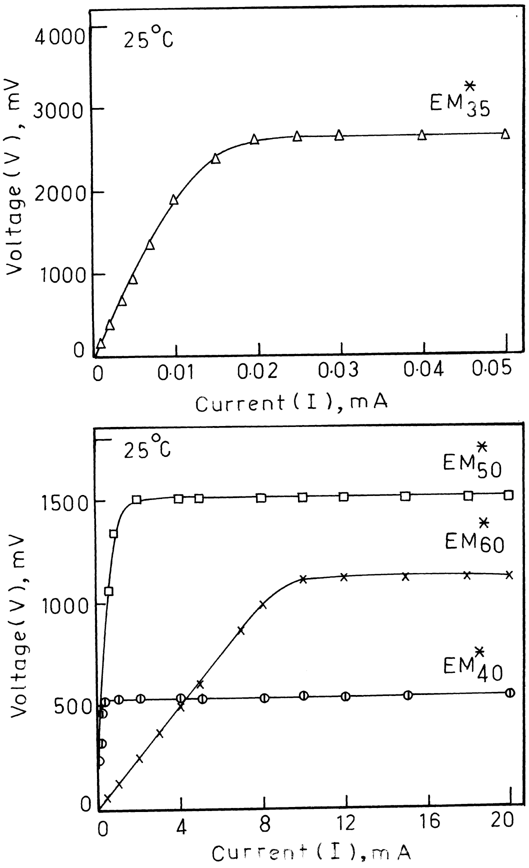

Fig. 6. Voltage (V)–current (I) characteristics at 25°C of some selected EPDM vulcanizates filled to different extents (phr) using conducting carbon black.

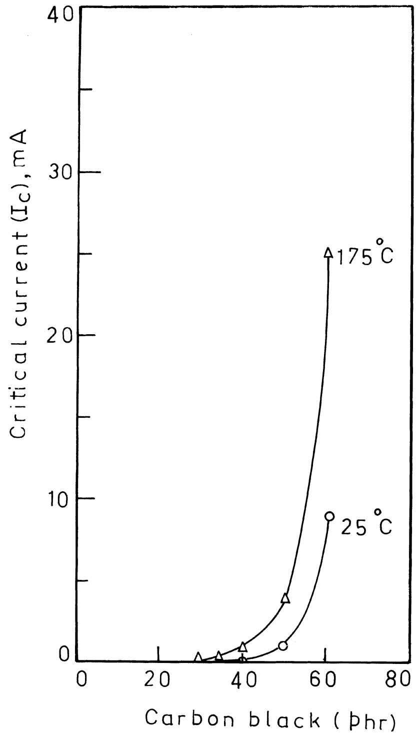

Fig. 7. Plots showing variation of I_C for EPDM vulcanizates with variation in conducting carbon black loading (phr).

The room temperature V–I plots for each EPDM composite in the electrical unloading (descending current) cycle is usually the retrace of the corresponding V–I plot obtained in the preceding electrical loading (ascending current) cycle. The odd deviation from ohmic behavior for $I > I_C$ is believed to be the consequence of a failure phenomenon somewhat like though much different from dielectric break down [9] that is commonly experienced at a much higher current or voltage range. The observed odd breakdown phenomenon may be explained on the basis of the following considerations.

Besides the voltage (V) that develops in proportion to the applied current (I), there will be thermally generated electric field across the gap between the conducting carbon black particle agglomerates. Thermal fluctuations in the material would lead to voltage fluctuations across a gap. For low capacitance of the junction, as obtains in the carbon black filled EPDM system, the thermally generated electric field across the gap can, in fact, be very high; a situation may then arise leading to an odd electric breakdown as observed and outlined here.

In the heat insulating EPDM matrix, the heat generated at a typical junction between two carbon black agglomerates due to passage of the applied current cannot possibly be balanced [37] by the heat loss from the junction by the normal process; this may ultimately cause a runaway situation leading to the observed odd effects causing the field strength to remain apparently steady and insensitive to large enhancements in the applied current.

In filled composites prepared with particulate conducting carbon black as filler as in the present studies, a number of uncertain factors may come in operation to influence their physical properties such as electrical conductivity and its dependence on the matrix material, loading level and temperature of observation. In conducting carbon black composites, long continuous conducting path between a pair of attached electrodes is rare or nil. Therefore, to exhibit a finite DC conductivity, electrons must hop from conductor to conductor and they may also occasionally do so by tunneling through the insulating (matrix) barrier. The extent of hopping and tunneling as they are commonly understood [9,38,39] would depend on the gap-width between the conducting particle aggregates and, hence, on the extent of filler loading. Use of progressively higher extents of loading over the percolation threshold and beyond contributes to progressive narrowing of the gap-width, causing some degree of tunneling to be also effective along with the prevalent hopping mechanism for electrical conduction as opposed to near exclusive prevalence of high activation-energy [40] hopping mechanism for carbon black loading less than the percolation threshold. For conducting carbon black loading less than or equal to the percolation threshold, little or very limited establishment of continuous conducting pathways through a test sample would result and its conductivity would then appear to be very sensitive to crack or flaw that may develop in the test specimen. For much higher carbon black loadings, however, multitudes of conducting pathways in parallel are expectedly established and, therefore, loss of a pathway by development of a crack on flaw does not really cause perturbation or catastrophic drop in DC electrical conductivity.

Further, for application of $I > I_C$, the filled system is apparently incapable of transmitting additional electrons in proportion to the excess current ($\Delta I = I - I_C$), thus giving rise to accumulation of high density of electrons at the cathode end, giving rise to what is known as the space charge region [41,42]. The advent of the electron dense negative space charge region for $I > I_C$ is manifested in the voltage developed becoming unsusceptible to large increase in the applied current above I_C. The space charge region, thus, developed limits the passage of total number of electrons from cathode to anode at any instant of time such that it does not exceed the limiting number corresponding to passage of I_C. Electrons admitted in excess of this number for $I > I_C$ are expectedly returned to the cathode by some obscure mechanism.

A higher temperature would lead to two opposing effects in such filled conducting systems. Mostly hopping [9] and limited tunneling current would tend to increase at a higher temperature because the enhanced thermal fluctuation would lower the potential barrier between the carbon black aggregates. In competition with this effect, the thermal expansion of the insulating elastomeric polymer matrix material expectedly enlarges the gap-widths between the carbon particle aggregates [38]. It is known that the thermal expansion coefficient of EPDM-like elastomers [43] ($\sim 600 \times 10^{-6}/°C$) are usually much higher than that of the conducting carbon black [38] ($3–5 \times 10^{-6}/°C$). At an intermediate stage in the temperature scale, the initial increasing trend in conductivity (σ) may, therefore, get subdued and a levelling off trend in σ may then follow.

Data shown in Fig. 8 and the observed odd variations in trends of change in the electrical properties (covering (i) percolation threshold, (ii) dependence of conductivity on the extent of carbon black loading and on temperature and (iii) the odd variation of trends in the V–I plots) can all be understood and interpreted in the light of the points discussed above.

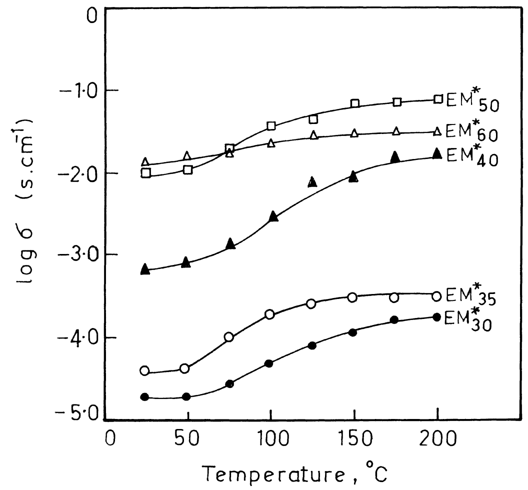

Fig. 8. Temperature dependence of DC electrical conductivity for selected EPDM vulcanizates.

3.6. Temperature dependence of DC electrical conductivity

For practical reasons, we focused our attention on the conducting character of the filled vulcanizates having carbon black loading greater than the percolation threshold. Plots of conductivity against temperature for filled EPDM vulcanizates show ‘S’ shaped curves, Fig. 8. A notable feature is that the difference between

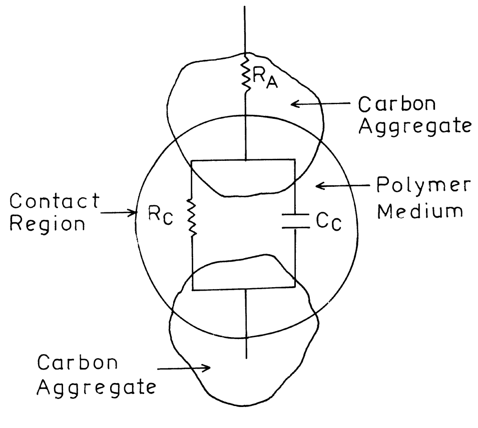

Fig. 9. Equivalent resistor–capacitor circuit in the contact region of carbon black filler aggregates in an elastomer compound.

the low temperature (25°C) and high temperature (200°C) conductivity levels tends to get narrower as the carbon black loading increases. It is notable that the conductivity values over a wide range of temperature for a vulcanizate having a relatively high carbon black loading (60 phr) becomes relatively much less sensitive to wide changes in temperature.

With increase in carbon black loading, the filler particle aggregates get more tightly packed and more intensely pressed against each other. This leads to a net reduction in the internal contact resistance R_C, Fig. 9, and, therefore, the net resistance $(R_C + R_A)$ decreases [9] with increase in the loading level; here, R_A indicating resistance within the conducting particle aggregate is in series with the contact resistance, R_C. The gaps between conducting particle agglomerates at high filler loading becomes very small or negligible and the net resistance becomes practically equal to R_A. This would usually happen for high enough loading using a conducting filler; with further increase in the conducting filler loading, the conductivity is not likely to vary substantially, if it varies at all. In such a situation, conduction predominantly takes place via 'through going chains' as distinct from hopping or tunneling. The evidence for conduction via through-going chain mechanism is commonly revealed by low or little dependence of conductivity on temperature above 125–150°C. Thus, we believe that for the filled EPDM system in the present studies, the conducting mechanism prominently shifts from hopping or tunneling to 'through going chains' for EPDM composites having carbon black loadings > 35 phr, more so, for carbon black loading ≥60 phr.

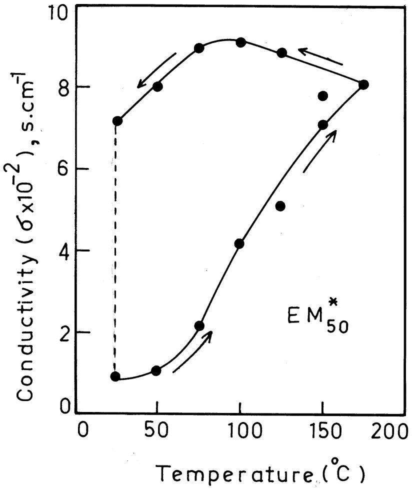

Fig. 10. Variation of DC electrical conductivity with variation of test temperature over a single heating and cooling cycle for EPDM vulcanizate (EM^*_{50}).

3.7. Conducting hysteresis

Conductivity data for a filled EPDM vulcanizate having a conducting carbon black loading of 50 phr (compound EM^*_{50}) at different temperatures (25–175°C) over a heating cycle followed by a cooling cycle are graphically shown in Fig. 10. The conductivity (σ)–temperature (T) plot obtained in the cooling cycle distinctly passes much over the 'S' shaped conductivity (σ)–temperature (T) plot obtained in the preceding heating cycle. Higher conductivity observed in the return cycle apparently results from a frozen-in or stabilizing effect of the orientations of the conducting carbon black chain agglomerates being cooled in successive stages to lower and lower temperatures. Initially, heating of the filled vulcanizates resulted in orientation of the carbon black chain agglomerates by thermo-mechanical extensional effect. Cooling in stages during the cooling cycle caused the relatively high orientations of the filler particles at a relatively high temperature to get set, frozen-in or stabilized, thus causing the test specimen exhibit a relatively high electrical conductivity over the cooling cycle as shown in Fig. 10.

This odd thermal hysteresis in the conducting character appears to be a rare observation, and it stands in contradiction to some relevant data reported in the literature for carbon black filled polychloroprene rubber [44] and metal-filled poly(vinyl chloride) [45].

The room-temperature conductivity for a given EPDM vulcanizate at the end of the cooling cycle, however, followed a slow dropping trend over days or a week or so, finally approaching the initial room temperature conductivity value observed at the beginning of the initial heating cycle. It is likely that a good degree of stress gets retained or accumulated in the test specimen due to extended cycles of initial heating and subsequent cooling and consequent expansion and contraction over the successive thermal cycles. Relaxation of the accumulated thermo-mechanical stress at ambient temperature over a long time period at the end of the cooling cycle apparently imparts a notable time-dependent deorientation effect on the initially oriented carbon black particle aggregates. The said time-dependent deorientation effect is eventually manifested by a time-dependent dropping trend in the electrical conductivity level as in Fig. 10. The thermo-mechanical stress relaxation over a long time period at the ambient temperature at the end of the cooling cycle also causes relaxation or lowering in the conducting level of the composite due to associated time-

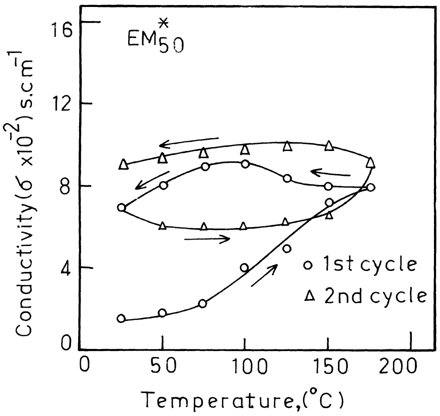

Fig. 11. Variation of DC electrical conductivity with temperature over two successive heating and cooling cycles for EPDM vulcanizate (EM^*_{50}).

dependent deorientation of the initially oriented carbon black aggregates.

The nature of change in the conductivity over two successive heating and cooling cycles for 50 phr carbon black loaded EPDM vulcanizate is shown in Fig. 11. The conductivity versus temperature curves over the second heating and cooling cycles are placed on the upper side of the same observed in the first heating and cooling cycles. The conductivities in the thermal loading–unloading cycle suffer much less drastic change and they appear somewhat more steady over the major part (25–150°C) of the second cycle as shown in Fig. 11.

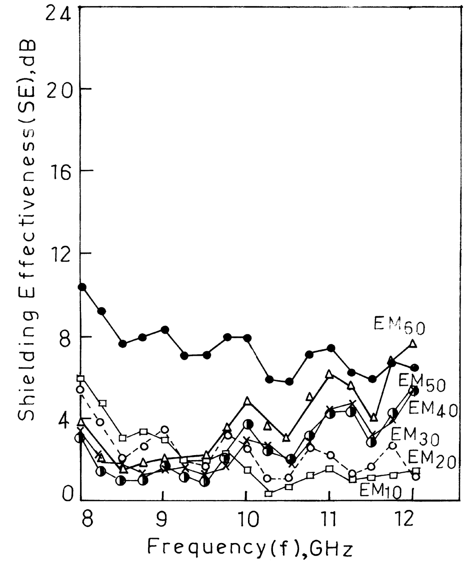

Fig. 12. Plot showing electromagnetic interference (EMI) shielding effectiveness (SE) as a function of frequency for unvulcanized EPDM having different loadings (phr) of conducting carbon black.

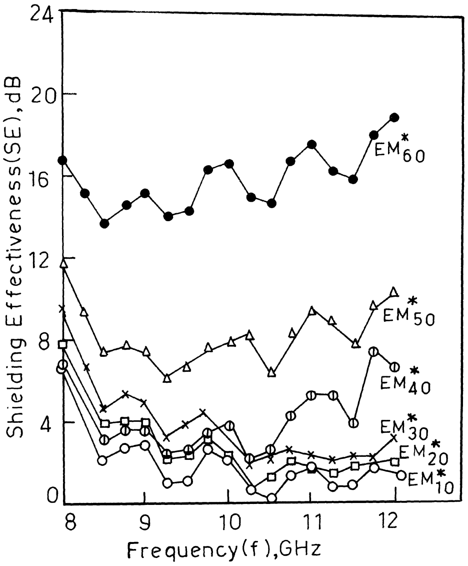

Fig. 13. Plot showing electromagnetic interference (EMI) shielding effectiveness (SE) as a function of frequency for vulcanized EPDM having different loading (phr) of conducting carbon black.

3.8. Electromagnetic interference (EMI) shielding effectiveness (SE)

EPDM vulcanizates of different carbon black loadings were examined for their EMI shielding property at different applied frequencies (*f*, in GHz) and relevant SE–*f* plots for both unvulcanized and vulcanized systems are shown in Figs. 12 and 13, respectively. There are small differences in the SE values of the unvulcanized and vulcanized EPDM when the carbon black loading is relatively low ≤ 30 phr. The DC electrical conductivities for EPDM vulcanizates having low carbon black loading are also relatively low. For carbon black loadings $\geq$30–40 phr, the SE values tend to rise sharply much in tune with sharp rise in their DC electrical conductivity values as detailed earlier (Fig. 5). For high EMI SE, therefore, vulcanizates having ≥ 50 phr conducting carbon black loading are indicated to be quite effective and useful.

3.9. Scanning electron microscopy (SEM)

SEM micrographs for some EPDM vulcanizates having different carbon black loadings (10–50 phr) are shown in Fig. 14. SEM micrograph (a) of a low carbon black loading (10 phr) shows closely packed, broad

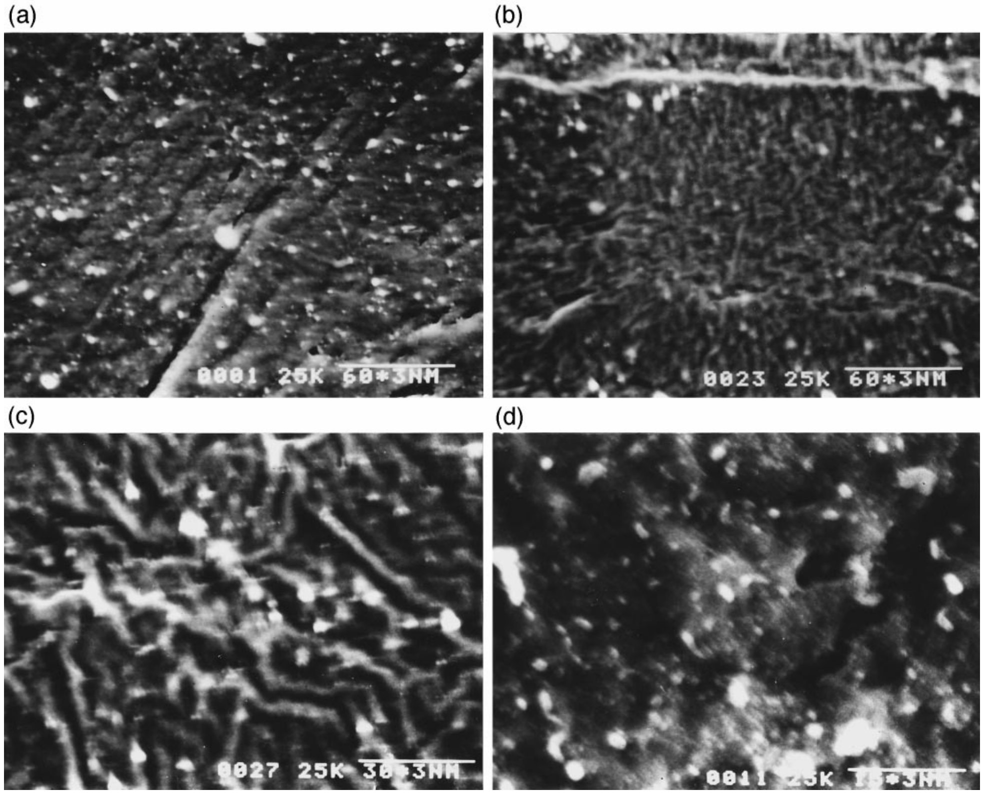

Fig. 14. Scanning electron micrographs of some EPDM vulcanizates having conducting carbon black loadings of (a) 10 phr, (b) 20 phr, (c) 35 phr and (d) 50 phr.

and nearly parallel strands or clusters of the EPDM phase interspaced with the distributed carbon black phase accommodated in narrow discontinuous crevices between them with different degrees of discontinuity. As the carbon black loading is increased over the percolation concentration range (20–35 phr or slightly beyond) the distribution of the carbon black phase becomes more uniform through break down of the parallel strands and clusters of the EPDM phase into finer strands with carbon black particles pressed between them along different directions infusing higher degree of isotropy uniformity and continuity in phase morphology; a certain trend of development of a filler-matrix co-continuous phase morphology, micrographs (b) and (c), with increase in carbon black phr over the percolation concentration range is noticeable. For carbon black loading (50 phr) much above the percolation concentration range, micrograph (d), however, the phase morphology becomes notably different indicating masking, interpenetration and overlapping of the two phases. The observed trends in the variation in DC electrical conductivity and of some mechanical properties on variation of conducting carbon black phr in the EPDM vulcanizates detailed earlier in the paper can be better appreciated considering the above trend of variation in their phase morphology as revealed by SEM.

3.10. Properties threshold as commonly understood by percolation concept and kinetical aggregation model

Carbon black as a particulate filler is well known for its ability to reinforce [46] rubber and related polymer systems. The reinforcement is manifested mainly through physical interactions or interfacial attachments via operation of surface forces between them and perhaps by some minor degree of chemical interactions too through anchorage of the rubber chains on the reactive sites of the filler particles. The physical and chemical interactions may together explain the overall reinforcing effects [46,47]. The dependence of physical, mechanical and electrical properties of EPDM vulcanizates on the conducting carbon black loading level, as outlined and detailed in this paper, however, points to a developing trend in filler-particle networking. The effect of filler networking on the property parameters can be understood on the basis of (i) percolation concept (PC) [48] and (ii) a kinetical cluster–cluster aggregation (KCCA) model [49–51].

The PC is based on pure geometrical considerations and it is understood as a simple case of formation of chain like clusters on a lattice resulting from random placement or positioning of the filler particles to the adjacent/nearby lattice sites which, however, admits of some variations in the number of particles in a cluster and in the structure and size distribution of the clusters, ultimately leading to filler networking. Filler networking through the PC does not really depend much on the nature of the polymer matrix because pure geometrical arguments are considered. For the KCCA model, however, the structure parameters of the matrix polymer as well as the size of the filler particles or particle networks also become important. The KCCA model considers fluctuation of the colloidal filler particles or their clusters around their mean position in the elastomer matrix that behaves much like a liquid [51]. The fluctuating particles are clustered together on contact and the particles, thus, growing in size are held in the cluster irreversibly in view of their adhesive energy being much larger than their thermal energy; in this way, continued cluster–cluster fluctuation leads to formation of larger clusters and finally, to cluster networking in all directions. The network growth continues until all particles within a distance smaller than the average entanglement spacing are aggregated. It is possible that chemical anchorage between the filler and elastomer and occlusion of the matrix elastomer within the pores of the filler particles may pose as physical hindrances to or may even impede further cluster growth and networking under a given set of conditions of time, temperature, shearing and filler loading level. A levelling off effect in the trends of change in the property parameters indicating reinforcement of the matrix elastomer with increase in conducting carbon black loading level may be understood and interpreted on the basis of the above considerations.

4. Conclusions

Results presented in this paper point to the existence of a carbon black loading threshold range of 15–35 phr, that is taken as the percolation threshold range over which, due to the developing filler networking trend as discussed above, the properties of the EPDM vulcanizates i.e., density, hardness, tensile strength, elongation at break and DC electrical conductivity are seen to pass through relatively sharp changes when plotted against the conducting carbon black loading level. It is also interesting to note that for carbon black loading greater than the percolation threshold, the phase morphology of the filled EPDM turns more uniform and isotropic with a developing trend in filler-matrix phase co-continuity and with a mutual masking effect, more so for carbon black content of ≥50 phr; some interpenetration and overlapping of phases also become more consequential at relatively high filler loadings; this trend of change of filler-matrix phase morphology forces a levelling off trend in the enhancement in physical, mechanical and electrical properties of the filled vulcanizates as the conducting carbon black filler content is increased beyond the percolation zone. The property parameters and their changes with variation in conducting filler loading level can be well understood on the basis of the filler networking concepts outlined above.

The time-dependent decay in electrical conductivity of a filled specimen after it has been cooled to room temperature following heating to a relatively high temperature can be explained on the basis of the following successive events: (i) extensional (orientational) effect of heating, (ii) freezing of the filler orientations attained at a higher temperature on immediate cooling and (iii) notable accumulation of associated thermo-mechanical stress in the filled test specimen. Relaxation of the accumulated thermo-mechanical stress on storage of the cooled specimen at room temperature leads to time-dependent deorientation of the thermally oriented conducting filler agglomerates resulting in the decay of the electrical conductivity to the initial (equilibrium) value.

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