

Physico-mechanical and electrical properties of conductive carbon black reinforced chlorosulfonated polyethylene vulcanizates

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Abstract. The present work deals with the effect of conductive carbon black (Ensaco 350G) on the physico-mechanical and electrical properties of chlorosulfonated polyethylene (CSM) rubber vulcanizates. The physico-mechanical properties like tensile strength, tear strength, elongation at break, compression set, hardness and abrasion resistance have been studied before and after heat ageing. Up to 30 parts per hundred rubber (phr) filler loading both tensile and tear strength increases beyond which it shows a decreasing trend whereas modulus gradually increases with the filler loading. Incorporation of carbon black increases the hysteresis loss of filled vulcanizates compared to gum vulcanizates. Unlike gum vulcanizate, in filled vulcanizates the rate of relaxation shows increasing trend. The bound rubber content is found to increase with increase in filler loading. Dielectric relaxation spectra were used to study the relaxation behavior as a function of frequency (100 to 10⁶ Hz) at room temperature. Variation in real and imaginary parts of electric modulus has been explained on the basis of interfacial polarization of fillers in the polymer medium. The percolation limit of the conductive black as studied by ac conductivity measurements has also been reported.

Keywords: rubber, dielectric properties, fillers, crosslink density, reinforcement

1. Introduction

Electrically conductive CSM composites are widely used in electronic sectors in power distribution, audio, and telephone application, as packaging and semi conductive polymeric materials due to their good weather resistance, good electrical properties and good ageing resistance. The systematic study of the CSM rubber particularly filled with highly conductive carbon black has not received much attention till today. Literature study reveals that very few research works dealing with CSM rubber have been reported [1–4]. The preparation of electrically conductive polymer composites filled with conductive fillers has already been reported by several researchers [5–7]. The relation between electrical and mechanical properties of conductive

polymer composites [8] has also been subject of recent research. Very recently electrical relaxation dynamics in polymer matrix-ceramic composites has been reported by Psarras *et al.* [9, 10].

The incorporation of filler in to a rubber for instance CSM, not only enhances the mechanical properties of the final product but also decreases the cost of the end product. The reinforcement of an elastomer by filler is associated with a strong interaction between a rigid phase and a soft solid phase, which may be of physical or chemical type. However the nature of interaction and the significance of carbon black surface chemistry for reinforcement of polar rubbers have not been reported in the literature. It is widely accepted that the surface area and the concentration of functional groups present

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on the surface of filler plays an important role towards the degree of reinforcement. It has been reported earlier that CSM has a great affinity towards polar sites on carbon black surface [11, 12]. The crosslink density is also influenced by the structure and surface chemistry of carbon black [13, 14]. Present study uses a newly generated highly conductive carbon black (Ensaco 350G) having very high surface area and exhibiting very high conductivity. In this work the cure characteristics, physico-mechanical properties, bound rubber measurement and electrical properties of conductive black reinforced rubber compound having an accelerated sulfur cure system have been studied.

The elastomer filler interactions are often characterized by the content of apparent ‘bound rubber’ which is determined as the amount of insoluble part of rubber matrix adhering to the dispersed carbon black aggregates before vulcanization. The bound rubber depends upon characteristics such as surface area, structure, morphology and surface activity of filler. With respect to the polymer, the chemical structure (saturated or unsaturated and polar or non polar) also affects the bound rubber content. Though the bound rubber is a parameter that is simple to measure but the factors that influence test results are complicated. The polymer filler interaction leading to formation of bound rubber involves physical adsorption, chemisorptions and mechanical interaction. In the present work the variation of bound rubber content with variation of filler loading has been studied taking three different solvents such as toluene, tetrahydrofuran (THF) and chloroform. The relaxation behavior of CSM vulcanizates has been studied as a function of frequency (100 to 10^6 Hz). Electric modulus formalism has been used to study the dielectric characteristics of the rubber vulcanizates. Percolation limit of the filler as obtained from the ac conductivity study has also been reported.

2. Experimental

2.1. Materials

Details of the compositions of the mixes are given in Table 1. CSM rubber ((Hypalon-40), 35% chlorine content, Mooney viscosity ML_{1+4} at $100^\circ\text{C} = 56$) manufactured by DuPont Limited, Delaware, USA, was used. The conductive filler used in this study was highly conductive carbon black, Ensaco

Table 1. Compositions of unfilled and Ensaco 350G filled CSM vulcanizates in phr (parts per hundred rubber)

Mix designation	G ₀	HB ₁	HB ₂	HB ₃	HB ₄
CSM	100	1 00	100	100	100
MgO	4	4	4	4	4
Ensaco 350G	0	10	20	30	40
DOP	0	1	2	3	4
MBTS	0.5	0.5	0.5	0.5	0.5
DPG	0.5	0.5	0.5	0.5	0.5
Tetrone-A	0.75	0.75	0.75	0.75	0.75
Sulfur	1	1	1	1	1

350G having a Brunauer-Emmett-Teller (BET) nitrogen surface area, $770\text{ m}^2/\text{g}$, pH-8, manufactured by Timcal Corporation, Belgium. The plasticizer used was dioctyl phthalate (DOP), pharmaceutical grade processing oil with B.P 340°C , supplied by C.D. Pharmaceuticals, Calcutta, India. Magnesium oxide was of analytical grade, with a specific gravity of 3.8 g/cm^3 , which was supplied by E. Merck Limited, Bombay, India. Sulfur of chemically pure grade, with a specific gravity of 1.9 g/cm^3 was supplied by M/S Nice chemicals Private limited Cochin, India. Dibenzothiazyl disulfide (MBTS), diphenyl-guanidine (DPG) and dipentamethylenethiuram tetrasulfide (Tetrone-A) were supplied by M/S ICI limited, Hoogly, India which were used as curatives. Other compounding ingredients used were procured locally.

2.2. Sample preparation

The mixing was carried out in a two roll mixing mill ($325\text{ mm}\times 150\text{ mm}$) at a friction ratio of 1: 1.19 according to ASTM D 3182 standards with careful control of temperature, nip gap, mixing time and uniform cutting operation. The curing characteristics of the compounds were determined by Monsanto Rheometer (R-100) according to ASTM D 2084 and ASTM D 5289 procedures. After mixing, moulding was done in an electrically heated hydraulic press having ($300\text{ mm}\times 300\text{ mm}$) platens at 150°C at a pressure of 4.0 MPa. Vulcanization was done to optimum cure (90% of the maximum cure) using different molding conditions determined from torque data obtained from Monsanto Rheometer. The test specimens were punched out from test sheets.

3. Characterization and testing

3.1. Physical test method

Curing characteristics of the compounded stocks were determined by using an oscillating disc Rheometer with an arc of oscillation of 3°. Tensile strength, modulus at 100% (M100), 200% (M200), and 300% (M300) extension and elongation at break were determined according to ASTM D-412 using dumbbell specimen in a Hounsfield 1145 universal testing machine. Tear strength was also determined by using Hounsfield 1145 according to ASTM method D-624 using a die C specimen. Measurement of hysteresis is also carried out in the same machine. The hardness of the vulcanizates was measured using a Shore-A durometer as per ASTM D 676-59T. Molded sheets were heat aged at 100°C for 72 hours in an electrically heated air oven for ageing study. Compression set was carried out by compressing the specimen to 25% of its original thickness for 22 hours at 70°C according to ASTM D395-85. Abrasion loss in cubic centimeter per hour [cm³/h] was measured by Dupont abrader according to BS-903.

3.2. Chemical test methods

The resistance to solvent was obtained by swelling test. The volume fraction of rubber (V_r) in the vulcanizate was determined by equilibrium swelling in toluene, using the method reported by Ellis and Welding [15]. The relationship used for calculating V_r is represented by Equation (1):

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad (1)$$

where T is the weight of the test specimen, F is the weight fraction of the insoluble components in the sample, D is the de-swollen weight of the test specimen, A_0 is the weight of absorbed solvent, corrected for swelling increment, ρ_r is the density of the rubber. The number of effective network chains per unit volume of rubber is denoted as ν which was calculated using Flory-Rehner equation (Equation (2)) [16, 17]:

$$\nu = \frac{-1}{V_s} \cdot \frac{\ln(1-V_r) + V_r + \mu V_r^2}{V_r^{1/3} - \frac{V_r}{2}} \quad (2)$$

where ν is the number of effective network chains per unit volume of rubber, V_s is the molar volume of the solvent and μ is the polymer-solvent interaction parameter (Flory-Huggins's interaction parameter), which was found to be 0.401 [18].

3.3. Bound rubber measurement

The contents of bound rubber (BdR) were determined by extracting the unbound materials such as the ingredients and free rubber with three different solvents for seven days followed by drying for two days at room temperature. The weights of the samples before and after extraction were measured, and the BdR contents were calculated using the Equation (3):

$$\text{BdR}[\%] = 100 \cdot \frac{w_{fg} - w_i \left(\frac{m_f}{m_f + m_r} \right)}{w_i \left(\frac{m_r}{m_f + m_r} \right)} \quad (3)$$

where BdR is the bound rubber content; w_{fg} the weight of filler and gel, w_i the weight of the sample, m_f the weight fraction of the filler in the compound and m_r the weight fraction of the rubber in the compound.

3.4. Dielectric relaxation spectra

The dielectric and electrical properties of the conductive black reinforced CSM vulcanizates were obtained using a computer-controlled impedance analyzer (PSM 1735) on application of an alternating electric field across the sample cell with a blocking electrode (aluminum foil) in the frequency range of 10²–10⁶ Hz at room temperatures. The test cell comprises of two electrodes and a voltage of 30 mV (V_{rms}) was applied across the cell. The parameters like dielectric permittivity (ϵ') and dielectric loss tangent ($\tan\delta$) were obtained as a function of frequency. The ac conductivity (σ_{ac}) was calculated from the dielectric data using the relation given in Equation (4):

$$\sigma_{ac} = \omega\epsilon_0\epsilon'\tan\delta \quad (4)$$

where ω is equal to $2\pi f$ (f is the frequency) and ϵ_0 is vacuum permittivity and ϵ' dielectric permittivity which is determined according to Equation (5):

$$\epsilon' = \frac{C_p}{C_0} \quad (5)$$

where C_p is the observed capacitance of the sample (in parallel mode) and C_0 is the capacitance of the cell. The value of C_0 is calculated using the expression $(\epsilon_0 A)/d$, where A and d are the area and thickness of the sample respectively.

4. Results and discussion

4.1. Rheometric characteristics

The Rheometric characteristics of the unfilled and conductive carbon black filled CSM vulcanizates are given in Table 2. The respective Monsanto rheographs are shown in Figure 1. From the table it is observed that with increase in filler loading both minimum and maximum torque increases. This may be due to increase in crosslink density with increase in filler loading [19]. With incorporation of filler cure rate (slope of cure curve) gradually increases and scorch safety (time to scorch) decreases [20, 21]. The optimum cure time decreases with increase in filler loading.

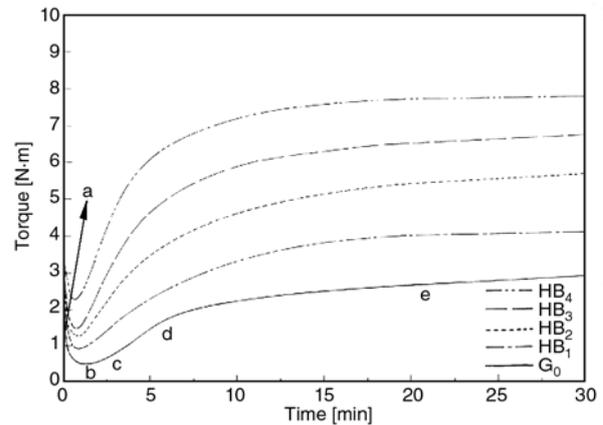


Figure 1. Representative rheographs of unfilled and Ensaco 350G filled CSM vulcanizates: effect of filler loading. a – initial viscosity, b – minimum torque, c – scorch time, d – cure rate (slope of cure curve), e – maximum torque

4.2. Physico-mechanical properties

The Physico-Mechanical properties of CSM vulcanizates reinforced with conductive carbon black (Ensaco 350G) at different filler loading have been determined. From Table 3 it can be observed that tensile strength, tear strength and modulus increases up to 30 phr filler loading beyond which tensile strength and tear strength decreases but modulus increases. Since modulus is a function of crosslink density it increases with increase in num-

Table 2. Rheometric characteristics of unfilled and Ensaco 350G filled CSM vulcanizates

Mix designation	Initial viscosity [N·m]	Minimum torque [N·m]	Maximum torque [N·m]	Scorch time [min]	Cure rate [min ⁻¹]	Optimum cure time [min]
G ₀	1.9	0.525	2.9	3.0	6.89	17.5
HB ₁	2.3	0.85	4.1	2.50	7.40	16.0
HB ₂	2.9	1.3	5.7	1.75	8.16	14.0
HB ₃	3.2	1.5	6.7	1.5	9.09	12.5
HB ₄	4.1	2.2	7.8	1.25	11.40	10.0

Table 3. Physico mechanical properties of unfilled and Ensaco 350G filled CSM vulcanizates

Properties	G ₀		HB ₁		HB ₂		HB ₃		HB ₄	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
Tensile strength [MPa]	27.3	28.6	29.3	31.0	31.4	32.0	33.5	34.0	32.3	32.4
M100% [MPa]	1.7	1.9	3.4	3.6	6.9	7.1	11.4	11.8	15.6	15.7
M200% [MPa]	2.3	2.7	8.1	8.3	16.9	17.0	25.6	25.7	–	–
M300% [MPa]	3.3	3.7	14.1	14.2	22.1	22.1	–	–	–	–
Elongation at break [%]	874.0	770.0	570.0	545.0	390.0	365.1	268.0	250.6	190.2	182.8
Tear strength [N/mm]	28.0	29.1	57.3	58.2	64.0	64.8	67.0	67.8	54.2	54.6
Hardness IRHD	50	51	58	61	67	69	70	72	82	85
Compression set 22 hrs at 100°C [%]	6.8	5.6	5.0	3.9	3.4	3.3	3.0	3.0	1.6	1.5
Abrasion loss [cc/hr]	0.37	0.33	0.25	0.24	0.15	0.14	0.10	0.09	0.13	0.12
Crosslink density ($\nu \cdot 10^3$) [mol/cc]	2.0	2.3	3.0	3.2	3.8	3.9	4.2	4.2	4.8	4.8

ber of crosslinks. Increase in moduli is due to stronger carbon black-rubber rigid interactions which are confirmed by bound rubber measurement. At 30 phr filler loading CSM gives the highest value of tensile strength, which means that at this loading polymer-filler interaction is maximum whereas at higher filler loading filler-filler interaction predominates. Unlike conventional carbon black conductive carbon black possess high structure and very high surface area and this complex structure of the branched filler aggregates attributes to a strong surface polymer interaction leading to higher bound rubber content. Incorporation of fillers is a major source of energy dissipation there by increasing the tensile strength of carbon black vulcanizates. On addition of filler like conductive carbon black to the vulcanizates, free space between the chains is filled up thus depriving the chains to straighten thereby reducing elongation. The higher the filler loading the more is the reinforcement and the more crosslinks are formed during vulcanization, thereby trapping the free ends of polymer chains. As the degree of crosslinking increases, the hardness progressively increases. The more compact the networks, the shorter are the molecular segments between the crosslinks and hence the tighter is the network, which causes increase in hardness [22]. Very high value of hardness is due to highly reinforcing conductive black having very high surface area. Compression set property is also a function of crosslink density, which increases with increase in crosslink density. Very good abrasion resistance may be due to chemically bound flexible chains with the carbon black, which provide a coupling action between carbon black surface and rubber molecules thus retarding the polymer to be abraded out from the surface. With increase in filler loading the bound rubber value increases which decreases the abrasion loss gradually. Above 30 phr filler loading decrease in tensile strength and tear strength is observed which may be due to agglomeration of filler particles at the highest filler loading. At lower filler loading cross-linking density decreases which may also cause increase in elongation at break whereas at higher filler loading cross linking density and viscosity both increases which causes decrease in elongation at break. Like tensile strength, tear strength also increases up to 30 phr but at 40 phr it decreases. This may be due to increase in crosslink-

Table 4. Hysteresis loss in J/m^2 of unfilled and Ensaco 350G filled CSM vulcanizates at 100% elongation

Mix designation	1 st cycle	2 nd cycle
G ₀	0.107	0.049
HB ₁	0.152	0.061
HB ₂	0.390	0.146
HB ₃	0.645	0.226
HB ₄	1.610	0.606

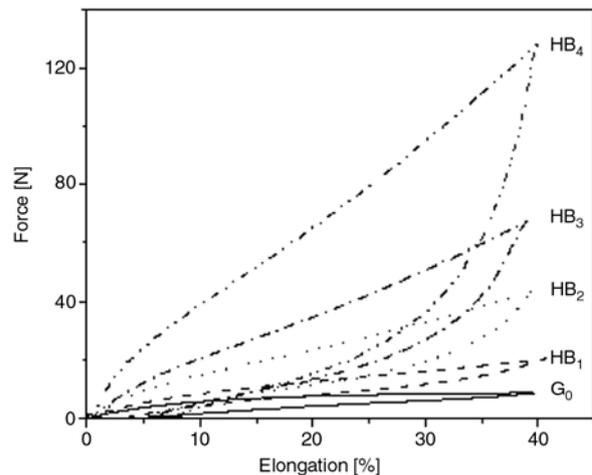


Figure 2. Hysteresis loss plots of unfilled and Ensaco 350G filled CSM vulcanizates

ing density at higher filler loading. It may be concluded that around 30 phr of Ensaco 350G is optimum filler loading for hypalon 40. The hysteresis loss values of different vulcanization at 100% elongation are given in Table 4. Figure 2 shows the plot of hysteresis loss of unfilled and filled vulcanizates. The result exhibits that the incorporation of Ensaco 350G filler causes an increase in the hysteresis loss. The low hysteresis loss of gum vulcanizates can be attributed to low energy absorption characteristics of the rubber matrix, which can act as an elastic body and is incapable of dissipating energy. The stress relaxation behavior of CSM vulcanizates is determined by stretching the samples at constant strain level of 100%. Figure 3 shows the decay of stress with time of unfilled and Ensaco 350G filled vulcanizates. The nature of decay is almost same for gum and filled vulcanizates. The stress relaxation phenomenon in the unfilled vulcanizate may be associated with a number of elementary processes like rearrangement of broken chains, crosslinks and entanglements. Unlike gum vulcanizate, in filled vulcanizates the rate of relaxation increases due to breaking-up of carbon black structure and distorted broken carbon elastomer linkage

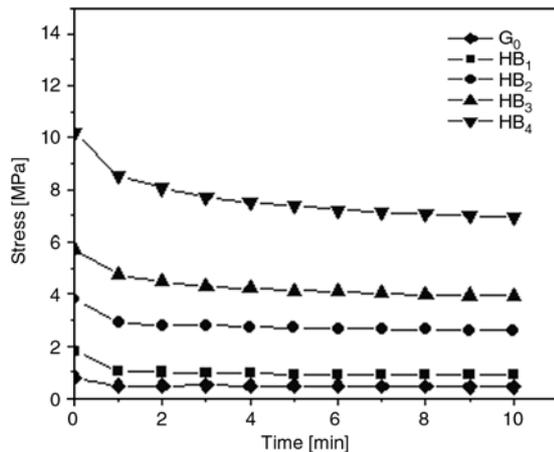


Figure 3. Stress relaxation behavior of unfilled and Ensaco 350G filled CSM vulcanizates

[23]. CSM rubber having no unsaturation sites possesses excellent resistance to heat, weather, ozone and chemicals. Enhancement of tensile strength after ageing in all cases may be due to post vulcanization. It can be clearly observed that crosslink density gradually increases on ageing for 72 hrs. Since CSM rubber has no reactive sites prone to oxygen attack it shows very good resistance to heat ageing. It has been observed that as the cure progresses tensile strength, hardness increases while compression set, elongation at break decrease. The significant increase in tear strength after ageing for 72 hrs is expected to be related to the formation of excessive cross-linked structure, which may be due to post curing effect. Increase in hardness value after aging may be due to increase in crosslink density, which agreed well with the increase in 100, 200, and 300% modulus after thermo-oxidative ageing process. Compared to gum vulcanizate in filled vulcanizates the increase in tensile strength after ageing is not so much pronounced which may be due to increase in inelastic nature of the rubber matrix. In case of higher filler loading the tensile strength after ageing remains almost same.

4.3. Bound rubber

Bound rubber can be defined as the rubber portion of uncured compound, which cannot be extracted by a good solvent due to adsorption of rubber molecules on to the filler surface. Bound rubber measurement plays an important role in determination of surface activity of the filler and the degree of reinforcement. It is widely accepted that the formation

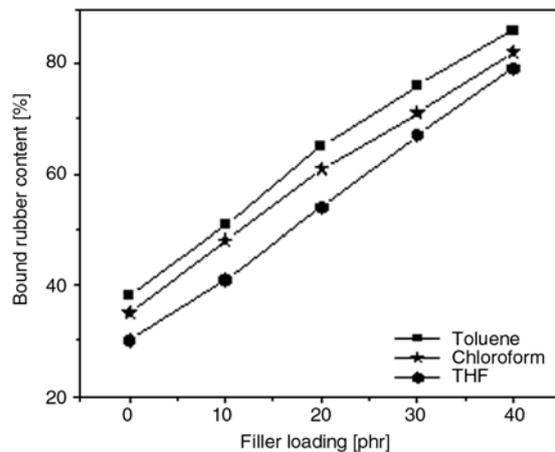


Figure 4. The variation of the bound rubber content for different solvents as a function of filler loading in CSM vulcanizates

of bound rubber in a compound involves physical adsorption, chemisorption and mechanical interaction of which chemisorption is considered as the crucial one. The adsorption of polymer molecules onto the filler surface leads to two phenomena, which are: the formation of bound rubber and a rubber shell on the filler surface. Many studies have been carried out on the mechanisms and factors affecting the formation of bound rubber [24–30]. The physico-chemical characteristics of the filler surface and filler morphology has a profound effect on the bound rubber content in a compound. The variation of bound rubber content with filler loading has been studied with three different solvents like toluene, tetrahydrofuran (THF), and chloroform. Figure 4 shows the variation of the bound rubber content with the filler loading for CSM vulcanizates. Irrespective of the nature of solvent bound rubber content increased with filler loading which may be due to increase in degree of reinforcement. The high percentage of BdR content is attributed to high surface area, high structure and high concentration of oxygen containing surface functional groups. With increase in the structure of conductive carbon black the breakdown of the aggregates during mixing is greater which results in an increase in filler-polymer interface. High bound rubber values in sulfur added compounds have been reported earlier by Gessler [31]. During mixing of rubber and carbon black, free radicals are generated which results in instantaneous interactions between carbon black and the rubber chain end. Gessler explained the phenomenon of forma-

tion of bound rubber as a two step theory: the reaction of sulfur with black and the reaction of this sulfur modified black with the polymer. The functional groups on carbon black surface react with sulfur and cure accelerators as a result $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed [32]. The surface activity, which can be related to different chemical groups on the black surface such as carboxyl, quinonic, phenol, and lactonic groups, dominates polymer-filler interactions, filler aggregate interactions, as well as filler-ingredient interactions. The surface of conductive carbon black (Ensaco 350G) has a number of hydroxyl groups, which results in strong filler-filler interactions. High bound rubber content in case of CSM vulcanizates does not necessarily mean a large amount of polymer-filler interaction. The strong polar groups present in filler surface may lead to both polymer-filler interaction as well as filler-filler interaction.

4.4. Effect of solvents

The nature of the extracting solvent is important in bound rubber formation. For bound rubber measurement the uncured rubber compound is exposed to a solvent capable of totally extracting the polymer in the absence of any polymer-filler bonding. These solvents for polymers may or may not interact with conductive carbon black. The solvents, which are poorly interacting with conductive carbon black, cannot disrupt the filler network to release the trapped polymer chain [33]. In regard to interaction with black, tetrahydrofuran (THF) is found to be the best solvent, followed by chloroform and toluene. Bound rubber content decreases with increasing solvation of carbon black. Solvents with more interaction with the polymer tend to show lower bound rubber value.

4.5. Dielectric relaxation spectra

One of the most valuable tools for characterizing the relaxation behavior of polymer composites is dielectric relaxation spectroscopy (DRS). Dielectric spectroscopy is a useful complement to the most customary mechanical methods of probing the viscoelastic properties of polymers. Though there have been many studies on the dielectric relaxation behavior of conductive black reinforced rubber vul-

canizates [34] but it has never been reported in CSM rubber vulcanizates. Dielectric spectroscopy offers advantages to study the high frequency dynamics of polymers. Dielectric spectra reflect the same chain motions as the mechanical modulus; however it has reduced interference due to symmetry from shorter time process making it more accurate than the traditional dynamic mechanical analysis [35]. The ‘electric modulus’ formalism first introduced by McCrum *et al.* [36] and extensively used for the investigation of relaxation phenomena in polymer composites by Tsangaris *et al.* [37, 38] can be defined as the inverse quantity of complex permittivity and is given by the following expression (Equation (6)):

$$M^* = \frac{1}{\epsilon^*} = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + j \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} = M' + jM'' \quad (6)$$

where M^* is the complex electric modulus, M' is the real and M'' is the imaginary part of electric modulus, ϵ' and ϵ'' are the real and imaginary parts of permittivity.

M^* characterizes the dynamic aspects of the charge motion in conductors in terms of relaxation in an electric field [39]. Figure 5 shows the variation of the real part of the electric modulus as a function of frequency in conductive carbon black loaded CSM vulcanizates. From the figure it can be observed that irrespective of the amount of filler in the composite, the value of M' is nearly zero at low frequencies indicating that the electrode polarization gives a negligibly low contribution to M' and can be ignored [40]. After this initial low value, M' increases steeply in the range of 10^3 – 10^5 Hz for all

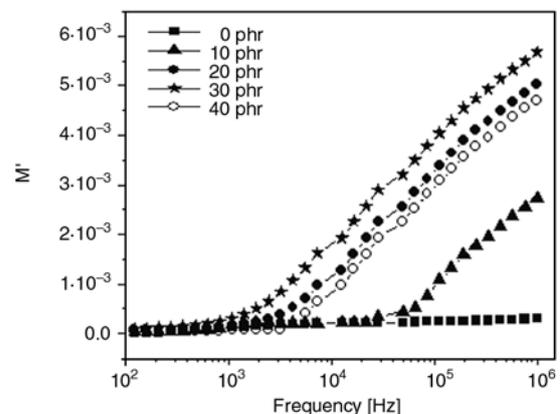


Figure 5. The variation of the real part of the electric modulus (M') as a function of frequency in CSM vulcanizates at increasing filler loadings

filler loadings. From the figure it can be observed that with increasing filler loadings there is an increase in modulus values up to 30 phr beyond which it decreases. This may be due to agglomeration of filler particles in the polymer matrix. The increase in real part of the electric modulus with filler loading can be explained on the basis of the viscoelastic properties of cross linked multiphase polymeric materials, which depend upon molecular relaxation processes and the morphology of the composites. Although these relaxations can usually be associated with each component, their appearance depends upon the chemical and physical interactions between the phases (filler and polymer matrix). Conductive carbon black like Ensaco 350G shows high interaction with the polymer matrix, because of their high surface activity, thereby leading to the formation of a weak interphase compared to other carbon blacks. The thickness of the interphase is inversely proportional to the interfacial tension between the polymeric phases. The interphase formed between the filler and the polymer matrix has distinct properties that differ from the bulk. A polymer layer having higher stiffness than the bulk polymer in the vicinity of the dispersed phase surface is created from restricted molecular mobility that is attributable to interactions between phases.

Figure 6 shows the variation of the imaginary parts of the modulus as a function of frequency at increasing filler loadings. It can be observed that with increase in filler loading, M'' peaks in general exhibit increasing peak heights and peak maximum shifts to higher frequencies. It can be explained on

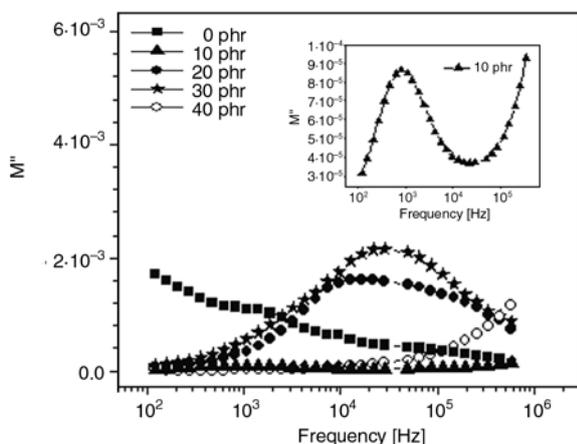


Figure 6. The variation of the imaginary part of the electric modulus (M'') as a function of frequency in CSM vulcanizates

the basis of Maxwell-Wagner-Sillars polarization. The broad nature of the M'' peaks can be interpreted as being the consequence of distributions of relaxation time. At low filler loadings, the value of M'' reaches a peak in the range of 1000 Hz for 10 phr and around 10 000 Hz in case of 20 phr and 30 phr filler loaded samples. Further increase in filler loading shifts the peak value towards higher frequency region and could not be found due to instrumental limitations.

The Cole-Cole plots plotted as M'' vs. M' (imaginary part of electric modulus vs real part of electric modulus) for all filler loadings are shown in Figure 7. The advantage of M'' vs. M' is that it offers better resolution than ϵ'' vs. ϵ' plots (imaginary part of electric permittivity vs. real part of electric permittivity). From the Figure 7 it can be clearly observed that with increasing filler loadings the semicircle nature of the peak is reducing and at higher filler loadings the semi-circle become more skewed which can be explained on the basis of interfacial polarization. The filler particles are electrically charged by fixed or adsorbed ions or polar molecules and are surrounded by small counter-charges (probably of the polymer matrix), forming an electrical double layer. The resulting medium frequency relaxation is caused primarily by interfacial polarization due to the build-up of charges on boundaries and interfaces between materials with very different electrical properties [41]. Imposition of an external AC field causes polarization of large colloidal particles and creates perturbation in a miniature double layer on each particle, which then behaves like a macro-ion [42]. Under the influence

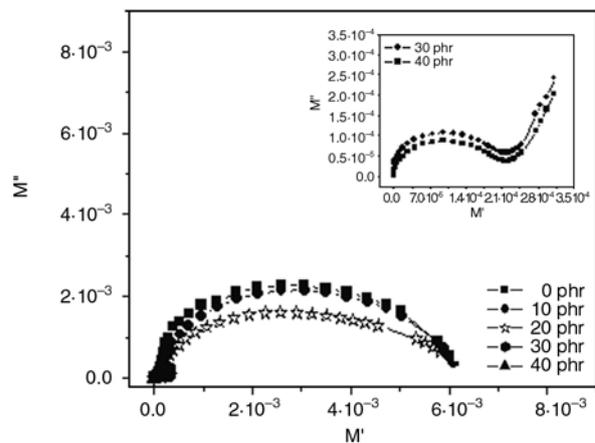


Figure 7. Cole-Cole plots of CSM vulcanizates reinforced with Ensaco 350G conductive carbon black

of an external electric field, the counter-ions become redistributed along the surface of a filler particle, and the double layer becomes deformed and polarized, leading to interfacial polarization and the resulting relaxation or dispersion.

Percolation

Many studies have been done on the percolation phenomenon in carbon black reinforced polymer composites. But no research work related to percolation phenomenon in CSM vulcanizates has been reported so far. Figure 8 shows the effect of filler loading on the conductivity of Ensaco 350G reinforced vulcanizates at 10^6 Hz. At low levels of filler loading the conductivity of the composite is slightly higher than that of the base polymer as the filler particles are isolated from each other by the insulating polymer matrix. As the filler loading is increased, mutual contacts between the filler particles are developed and at a critical loading of the filler a sharp increase in conductivity is observed, indicating the ‘percolation limit’. Depending upon the type of filler, the occurrence of percolation varies. In Ensaco 350G reinforced CSM vulcanizates the percolation region is occurring at 30 phr loading of the filler. According to Medalia [43] percolation is due to the tunneling of electrons and the conductivity is controlled by the gaps between the carbon black aggregates. Many questions regarding the actual mechanism of conduction through such heterogeneous materials are still prevalent. Interpretation of dielectric and conductivity performance of such materials has been analyzed through percolation theory [44]. According to Das *et al.*

[45] the variation of conductivity with filler loading can be divided into three regions (Figure 8). In region I the ‘inductive region’, a small increase in conductivity of the composite with increasing filler loading can be attributed to the transportation of the small number of charged particles through the system without having any continuous conductive path. Region II is referred as ‘percolation region’ where conductivity increases sharply due to a continuous conductive path developed in the polymer matrix. In region III, further addition of filler has marginal effect on conductivity. Carbon blacks are widely used as reinforcing agent in elastomers because of their high surface to mass ratio, molecular-scale forces, and their interactions with the polymer matrix. Due to van der Waals forces, flocculation of carbon black particulates in the polymer matrix occurs which results in the formation of secondary structures whereas electrostatic charges or steric effects lead to a stabilization of the dispersion. The percolation phenomenon may be of lattice percolation or continuum percolation. This involves two processes: randomly adding or removing particles from a simple lattice space till an infinite cluster is not formed. It has been recognized that the conductivity of polymer composites not only depends on the geometry of filler particles but also on the processing of the materials [46]. Due to high surface activity of conductive black (Ensaco 350G) and high surface area, agglomeration of the filler particles occurs in the polymer matrix, which results in the formation of clusters.

5. Conclusions

Irrespective of the solvent the bound rubber contents increase with increase in the carbon black content. Very high value of bound rubber is due to high reinforcement obtained due to high structure and high surface area of conductive black. Both maximum and minimum Rheometric torque increase with increase in filler loading which may be due to increase in viscosity. Cure rate and scorch rate increase with increase in filler loading. Tensile strength and tear strength increase with filler loading up to 30 phr beyond which it decreases whereas modulus increases at high filler loading. Elongation at break gradually decreases with filler loading. With filler loading hardness also gradually increases which may be due to increase in crosslink

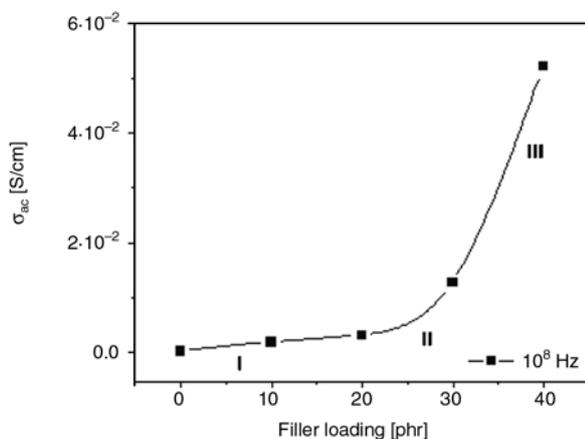


Figure 8. Variation in ac conductivity (σ_{ac}) with filler loading in CSM vulcanizates

density. Compression set property gradually increases with filler loading whereas abrasion loss shows gradual decrease which may be due to increase in stiffening property. The hysteresis loss increases with increase in the filler loading, which may be due to the inelastic behaviour of the rubber matrix. The stress relaxation behavior shown by gum vulcanizates follows nearly the same trend as filled vulcanizates. Increase in tensile strength, hardness, tears strength and decrease in elongation at break, compression set is observed after ageing which may be due to post curing effect. It is concluded that 30 phr Ensaco 350G can be taken as an optimum filler loading, which exhibits better physical and mechanical properties. The dielectric relaxation spectra of the composites showed an additional relaxation in the frequency range of 10^3 to 10^5 Hz. This has been explained on the concept of formation of interphase layer between the filler and the polymer matrix. From the conductivity studies percolation limit of the conductive carbon black (Ensaco 350G) in the polymer matrix has been found to be 30 phr, which is in good agreement with the physico-mechanical results.

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References

- [1] Smith D. A.: Thermal stability of chlorosulfonated polyethylene. *Polymer Letters*, **2**, 665–670 (1964).
- [2] Nersasian A., King K. F., Johnson P. R.: Novel curing systems for chlorosulfonated polyethylene. *Journal of Applied Polymer Science*, **8**, 337–354 (1964).
- [3] Maynard J. T., Johnson P. R.: Ionic crosslinking of chlorosulfonated polyethylenes. *Journal of Applied Polymer Science*, **7**, 1943–1950 (1963).
- [4] Mukhopadhyay S., De S. K.: Miscibility of self-vulcanizable rubber blend based on epoxidized natural rubber and chlorosulphonated polyethylene: Effect of blend composition, epoxy content of epoxidized natural rubber and reinforcing black filler. *Polymer*, **32**, 1223–1229 (1991).
- [5] Jana P. B., De S. K.: Short carbon fiber filled polychloroprene. *Plastics Rubber and Composites Processing and Applications*, **17**, 43–49 (1992).
- [6] Sau K. P., Chaki T. K., Khastgir D.: Electrical and mechanical properties of conducting carbon black filled composites based on rubber and rubber blends. *Journal of Applied Polymer Science*, **71**, 887–895 (1999).
- [7] Pramanik P. K., Khastgir D., Saha T. N.: Electromagnetic interference shielding by conductive nitrile rubber composites containing carbon fillers. *Journal of Elastomers and Plastics*, **23**, 345–361 (1991).
- [8] Micusik M., Omastova M., Prokes J., Krupa I.: Mechanical and electrical properties of composites based on thermoplastic matrices and conductive cellulose fibers. *Journal of Applied Polymer Science*, **101**, 133–142 (2006).
- [9] Patsidis A., Psarras G. C.: Dielectric behaviour and functionality of polymer matrix-ceramic BaTiO₃ composites. *Express Polymer Letters*, **2**, 718–726 (2008).
- [10] Kontos G. A., Soulintzis A. L., Karahaliou P. K., Psarras G. C., Georga S. N., Krontiras C. A., Pisanias M. N.: Electrical relaxation dynamics in TiO₂-polymer matrix composites. *Express Polymer Letters*, **1**, 781–789 (2007).
- [11] Roychoudhury A., De P. P.: Elastomer-carbon block interaction: Influence of elastomer chemical structure and carbon black surface chemistry on bound rubber formation. *Journal of Applied Polymer Science*, **55**, 9–15 (1995).
- [12] Roychoudhury A., De S. K., De P. P., Ayala J. A., Joyce G. A.: Chemical interaction between carbon black and elastomer: Crosslinking of chlorosulfonated polyethylene by carbon black. *Rubber Chemistry and Technology*, **67**, 662–671 (1994).
- [13] Cotton G. R.: The effect of carbon black surface properties and structure on rheometer cure behavior. *Rubber Chemistry and Technology*, **45**, 129–144 (1972).
- [14] Chen C. H., Koenig J. L., Shelton J. R., Collins E. A.: The influence of carbon black on the reversion process in sulfur-accelerated vulcanization of natural rubber. *Rubber Chemistry and Technology*, **55**, 103–115 (1982).
- [15] Ellis B., Welding G. N.: Estimation, from swelling, of the structural contribution of chemical reactions to the vulcanization of natural rubber Part I. General method. *Rubber Chemistry and Technology*, **37**, 563–570 (1964).
- [16] Flory P. J.: Principles of polymer chemistry. Cornell University Press, Ithaca, USA (1953).
- [17] Flory P. J., Rehner J.: Statistical mechanics of cross-linked polymer networks II. Swelling. *Journal of Chemical Physics*, **11**, 521–526 (1943).
- [18] Braton A. F. M.: Handbook of solubility parameters and other cohesion parameters. CRC Press, Boca Raton, USA. (1983).
- [19] Basfar A. A., Abdel-Aziz M. M., Mofti S.: Influence of different curing systems on the physico-mechanical properties and stability of SBR and NR rubbers. *Radiation Physics and Chemistry*, **63**, 81–87 (2002).
- [20] Devlin E. F.: The effect of cure variables on cis/trans isomerization in carbon-black-reinforced cis-1, 4-polybutadiene. *Rubber Chemistry and Technology*, **59**, 666–692 (1986).

- [21] Roychoudhury A., De P. P., Dutta N. K., Choudhury N., Roychoudhury N., Haidar B., Vidal A.: FTIR and NMR studies on crosslinking reaction between chlorosulfonated polyethylene and epoxidized natural rubber. *Rubber Chemistry and Technology*, **66**, 230–241 (1993).
- [22] Chakraborty S. K., Bhowmick A. K., De S. K.: Mixed cross-link systems in elastomers. *Polymer Reviews*, **21**, 313–332 (1981).
- [23] Dutta N. K., Tripathy D. K.: Effect of plasticizer concentration on the hysteresis, tear strength and stress-relaxation characteristics of black-loaded rubber vulcanizate. *Colloid and Polymer Science*, **269**, 331–342 (1991).
- [24] Wolff S., Wang M-J.: Carbon black reinforcement of elastomers. in 'Carbon Black: Science and Technology' (eds.: Donnet J. B., Bansal R. C., Wang M. J.) Marcel Dekker, New York, USA, 289–345 (1993).
- [25] Kraus G.: Reinforcement of elastomers. Wiley Interscience, New York (1965).
- [26] Stickney P. B., Falb R. D.: Carbon black-rubber interactions and bound rubber. *Rubber Chemistry and Technology*, **37**, 1299–1340 (1964).
- [27] Sircar A. K., Voet A.: Immobilization of elastomers at the carbon black particle surface. *Rubber Chemistry and Technology*, **43**, 973–980 (1970).
- [28] Wolff S., Wang M. J., Tan E. H.: Filler-elastomer interactions. Part VII. Study on bound rubber. *Rubber Chemistry and Technology*, **66**, 163–177 (1993).
- [29] Kraus G.: Reinforcement of elastomers by carbon black. in 'Advances in Polymer Science' (eds.: Bunde A., Havlin S.) Springer Berlin, Heidelberg, Vol 8, 155–237 (1971).
- [30] Donnet J. B., Rigaut M., Frustenberger R.: Study by electronic paramagnetic carbon black resonance treats by the azodiisobutyronitrile in absence of oxygen. *Carbon*, **11**, 153–162 (1973).
- [31] Gessler A. M.: Evidence for chemical interaction in carbon and polymer associations: Extension of original work on effect of carbon black structure. *Rubber Chemistry and Technology*, **42**, 858–873 (1969).
- [32] Sridhar V., Gupta B. R., Tripathy D. K.: Bound rubber in chlorobutyl compounds: Influence of filler type and storage time. *Journal of Applied Polymer Science*, **102**, 715–720 (2006).
- [33] Roychoudhury A., De P. P., Roychoudhury N., Vidal A.: Chemical interaction between chlorosulfonated polyethylene and silica -Effect of surface modifications of silica. *Rubber Chemistry and Technology*, **68**, 815–823 (1995).
- [34] Mahapatra S. P., Sridhar V., Chaudhary R. N. P., Tripathy D. K.: AC conductivity and positive temperature coefficient effect in microcellular EPDM vulcanizates. *Polymer Composites*, **29**, 1125–1136 (2008).
- [35] Roland C. M., Bero C. M.: Normal mode relaxation in linear and branched polyisoprene. *Macromolecules*, **29**, 7521–7526 (1996).
- [36] McCrum N. G., Read B. E., Williams G.: Anelastic and dielectric effects in polymeric solids. Wiley Interscience, London (1967).
- [37] Tsangaris G. M., Psarras G. C., Kouloumbi N.: Electric modulus and interfacial polarization in composite polymeric systems. *Journal of Materials Science*, **33**, 2027–2037 (1998).
- [38] Psarras G. C., Manolakaki E., Tsangaris G. M.: Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles. *Composites Part A: Applied Science and Manufacturing*, **33**, 375–384 (2002).
- [39] Han M. G., Im S. S.: Dielectric spectroscopy of conductive polyaniline salt films. *Journal of Applied Polymer Science*, **82**, 2760–2769 (2001).
- [40] Lee H-T., Chuang K-R., Chen S-A., Wei P-K., Hsu J-H., Fann W.: Conductivity relaxation of 1-methyl-2-pyrrolidone-plasticized polyaniline film. *Macromolecules*, **28**, 7645–7652 (1995).
- [41] Schwarz G.: Dielectric relaxation of biopolymers in solution. *Advanced Molecular Relaxation Processes*, **3**, 281–295 (1972).
- [42] Grimnes S., Martinsen O. G.: Bioimpedance and bioelectricity basics. Academic Press, New York (2000).
- [43] Medalia A. I.: Electrical conduction in carbon black composites. *Rubber Chemistry and Technology*, **59**, 432–454 (1986).
- [44] Lux F.: Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials. *Journal of Materials Science*, **28**, 285–301 (1993).
- [45] Das N. C., Chaki T. K., Khastgir D., Chakraborty A.: Electrical and mechanical properties of conductive carbon black filled EVA, EPDM and their blends. *Kautschuk, Gummi, Kunststoffe*, **55**, 300–306 (2002).
- [46] Halperin B. I., Feng S., Sen P. N.: Differences between lattice and continuum percolation transport exponents. *Physical Review Letters*, **54**, 2391–2394 (1985).