Relaxation Behavior of Conductive Carbon Black Reinforced Chlorosulfonated Polyethylene Composites

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ABSTRACT: Dynamic mechanical analysis and dielectric relaxation spectra of conductive carbon black reinforced chlorosulfonated polyethylene (CSM) composites were used to study their relaxation behavior as a function of temperature and frequency, respectively. A marginal increase in glass transition temperature has been observed upto 30 phr carbon black filled polymer composite, beyond which it decreases, which has been explained on the basis of aggregation of filler particles in the polymer matrix. The strain dependent dynamical parameters were evaluated at dynamic strain amplitudes of 0.1–200%. The nonlinearity in storage modulus increases with increase in filler loading. It can be explained on the basis of filler–polymer interaction and aggregation of the filler particulates. The frequency dependent dynamical mechanical analysis has also been studied at frequency range of 0.1–100 Hz. The variation in real and complex part of impedance with frequency has been studied as a function of filler loading. The effect of filler loading on ac conductivity has been observed as a function of frequency. An increase in conductivity value has been observed with increase in filler loading. This can be explained on the basis of formation of conducting paths between filler particulates. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2758–2767, 2010

Key words: dielectric properties; composites; dispersions; glass transition; viscoelastic properties

INTRODUCTION

Conductive polymer composites are obtained by incorporation of electrically conductive filler in to an insulating polymer matrix. These polymer composites have received considerable attention due to their technological importance in a wide variety of applications such as electrostatic charge dissipate material in pressure-sensitive sensor, transducer, EMI-shielding material, and packaging material in electronics, aircraft, telecommunications, and nuclear reactors. They are also used as antistatic materials in low temperature heaters, in energy storage devices such as batteries, fuel cells, and super capacitors and in hybrid power sources. Metal fillers, carbon fibers, and excess conductive carbon black such as Vulcan XC 72 have been used extensively.

The design of such conventional composites is based on maximizing the interaction between the polymer matrix and the filler.[1] The relaxation behavior and electrical conductivity of such composites mainly depends on the factors like polymer–filler interaction, specific surface area of the fillers, and the dispersion of the fillers within the polymer matrix. Relaxation in filled polymer composites is time, temperature, frequency, and strain dependent. Processing variables (i.e., the type of filler, volume fraction of filler in the composite) and operating variables (i.e., strain amplitude, strain rate, frequency, and temperature of testing) have a significant effect on the dynamic properties of the polymers.[2] Recently, much attention is being focused on the applicability of new generation fillers like carbon silica dual-phase filler (CSDPF),[3] carbon nanotubes,[4] conductive carbon black,[5] and nano graphite.[6]

Although there have been many studies on the effect of addition of conductive carbon black in elastomer matrices, no literature has been reported in CSM vulcanizates. Dynamic mechanical analysis of polymer composites is an important tool to study the viscoelastic behavior of the material for evaluation of its use in various engineering applications.

Some macroscopic phenomena associated with very slow relaxation processes are manifested most commonly in viscoelastic properties of bulk polymers. On the other hand, rapid relaxation processes, occurring on temporal, and spatial scale are responsible for the glass transition temperature (T_g); an important factor to understand mechanical properties of solid amorphous polymers. Therefore, understanding of local motions in bulk amorphous polymers becomes significant in designing new materials and in obtaining detailed information on the physical behavior of existing materials. It is generally

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believed that the nature and extent of interactions of the filler with the polymer matrix are important factors for the improvement of the mechanical properties of filled rubbers at a high elongation. Recently, some studies have been carried out on applicability of new generation fillers like CSDPF and conductive carbon black (Vulcan XC72). The physico–mechanical and electrical properties of Ensaco 350G filled CSM composites have been reported very recently.[7,8]

The objective of this work is to study the relaxation behavior of Ensaco 350G reinforced CSM composites as a function of temperature and frequency. The effects of variation in filler loading, temperature, and frequency on dynamic mechanical properties like loss tangent, storage, and loss modulus has been reported. The effect of dynamic strain amplitude on storage modulus and loss tangent has also been studied. The effect of frequency on dynamical parameters has also been reported. The variation in dielectric characteristics like dielectric loss tangent, real, and complex part of impedance and conductivity also form a part of this study.

EXPERIMENTAL

Materials

The following materials were used in preparation of the composite. Chlorosulfonated polyethylene rubber [(Hypalon-40), 35% chlorine content, Mooney viscosity ML_{1+4} at 100°C = 56] manufactured by Dupont Dow Elastomers was used. The conductive filler used in this study was highly conductive carbon black, Ensaco 350G having a BET Nitrogen surface area 770 m^2/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 specific gravity 3.8, which was supplied by E. Merck Limited, Bombay, India. Sulfur of chemically pure grade with a specific gravity of 1.9, supplied by M/S Nice chemicals Pvt., Cochin, India, was used. Curatives such as dibenzothiazyldisulfide (MBTS), diphenyl-guanidine (DPG), and dipentamethylenethiuram tetrasulfide (Tetrone-A) were supplied by M/S ICI, Hoogly, India.

Sample preparation

Details of the formulations of the mixes are given in Table I. The mixing of rubber and all other ingredients was carried out in a two roll mixing mill (325 mm × 150 mm) at a friction ratio of 1 : 1.19 according to ASTM D 3182 standards with optimized temperature, nip gap, mixing time, and uniform cutting operation. After mixing, molding was done in an electrically heated hydraulic press having (300 mm × 300 mm) platens at 150°C and 4.0 MPa pressure. Vulcanization was done to optimum cure (90% of the maximum cure) using different molding conditions determined from the torque data obtained from Monsanto Rheometer.[7] A fixed circular size sample (12.7 mm diameter and 2 mm thickness) was punched from the molded sheets for dielectric measurements.

TESTING

Dynamic mechanical properties

The dynamic mechanical spectra of the samples were obtained by using a Dynamic mechanical thermal analyzer (DMTA 2980 VI. 7B, TA Instrument) in a tensile mode. The linear viscoelastic (LVE) region of the CSM vulcanizates was initially determined by strain sweep test at a test frequency of 1 Hz. In the strain sweep test, strain amplitude was taken from 0.1% to 200% at a constant temperature of 30°C. The temperature sweep measurement was carried out at a constant frequency of 1 Hz, at strain of 0.06% and at a temperature range of −100°C to +100°C with a heating rate of 3°C/min. The frequency dependent dynamic properties were evaluated at room temperature. The frequency sweep test was done in the frequency range 0.1–100 Hz at strain amplitude of 0.1%.

Dielectric relaxation spectra

Dielectric relaxation spectra of the 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 10^2–10^6 Hz at room temperature. The dielectric function (dielectric constant and dielectric loss tangent) has been observed as a function of frequency. AC conductivity (σ_{ac}) has been evaluated from dielectric data.[3]

Measurement of bound rubber content

Bound rubber content (BdR) of the compound was determined by extracting the unbound materials such as ingredients and free rubber with a solvent (Toluene) for 7 days, followed by drying for 2 days at room temperature. Weights of the samples were measured before and after the extraction, and the BdR was calculated using the following expression:

$$\text{BdR} = 100 \times \frac{[w_{fg} - w_t[m_f/(m_f + m_r)]]}{w_t[m_r/(m_f + m_r)]} \qquad (1)$$

where BdR is the bound rubber content, w_{fg} is the weight of filler and gel, w_t is the weight of the

Compositions of Unfilled and Ensaco 350G Filled CSM
Vulcanizates in phr (parts per hundred rubber)

Mix designation	G_o	HB_1	HB_2	HB_3	HB_4
CSM	100	100	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

sample, m_f is the weight fraction of the filler in the compound, and m_r is the weight fraction of the rubber in the compound.

Transmission electron microscopy

The sample for TEM analysis of carbon black powder was prepared by ultrasonication method. The conductive carbon black powder was ultrasonically dispersed in toluene and deposited on microscope grid. The CSM composite sample for TEM analysis was prepared by ultracryomicrotomy using a Leica Ultracut UCT. Freshly sharpened glass knives with cutting edge of 45° were used to get the cryosections of 50–70 nm thickness. Because these samples were elastomeric in nature, the temperature during ultra cryomicrotomy was kept at −80°C (which was well below glass transition temperatures of CSM). The cryosections for individual sample (i.e., for each filler loading) were collected on sucrose solution and kept on a single copper grid of 300-mesh size. The microscopy was performed using a JEOL JEM-2010 (Japan) high resolution transmission electron microscope, operating at an accelerating voltage of 200 KV.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

Effect of temperature on loss tangent

Figure 1(a) shows the loss tangent spectra of CSM vulcanizates reinforced with increasing amounts of Ensaco 350G as a function of temperature. In this case, the location of maximum value of loss tangent (tan δ_{max}) is not significantly affected with increase in filler loading. All the samples show the glass transition temperature in the narrow range of −5.8°C to −2.1°C. A marginal increase in glass transition temperature has been observed in low filler loading (10, 20, and 30 phr), however, it decreased at 40 phr filler loading. This decrease is probably due to less interaction between the fillers and polymer matrix because of the presence of voids and poor dispersion

of Ensaco 350G in the composites.[9,10] One of the main features of reinforced elastomers is that majority of polymer chains are in contact with the filler surfaces.[11] Addition of filler into the polymer matrix induces a gradient of glass transition temperature in the polymer chains that are in the vicinity of the fillers due to the existence of strong dynamic heterogeneities.[12,13] These heterogeneities originate from thermal fluctuations of density, and the heterogeneous nature of polymer composite. When a polymer is cooled through the glass transition region, the physical properties of the polymer such as volume and enthalpy, in the nonequilibrium state (at temperature lower than T_g), gradually recover to new equilibrium values through the configurational rearrangement of polymer segments. The rate of the rearrangement or relaxation process depends on the local environment surrounding the relaxation entities, and hence, reflects the extent of environmental restriction on those entities.
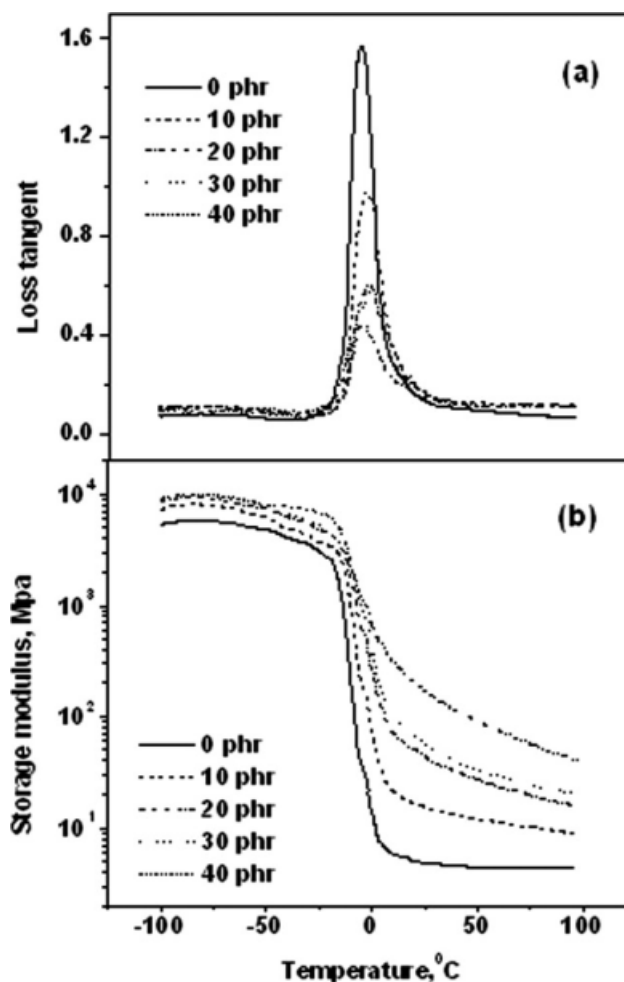

Figure 1 Effect of temperature on (a) loss tangent and (b) storage modulus of CSM vulcanizates at frequency of 1 Hz and strain of 0.06%.
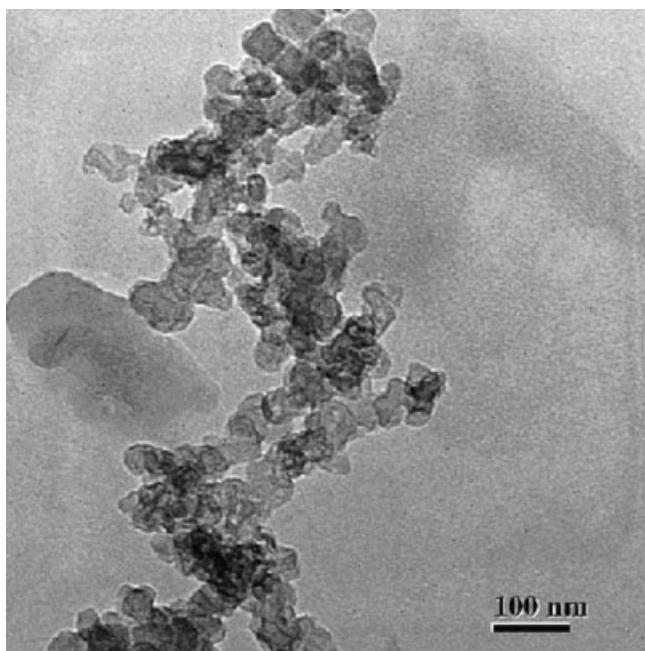
Figure 2 High resolution TEM microphotographs showing fractal aggregate structure of conductive carbon black particulate (Ensaco 350G).

Increasing filler loading shows decrease in the magnitude of the loss tangent with simultaneous broadening of the peak. The influence of filler on the damping behavior of filled polymer systems can be explained by two possible factors.[14,15] One is a decrease in free volume, which limits the mobility of molecular chains, usually in the case of elastomers, so that the damping value decreases. The other factor is the internal friction between the fillers and the polymer chains, and between the filler particles themselves over the transition range, which increases with temperature, thereby causing greater movement of molecular chains so that the damping ability increases.

Effect of temperature on storage and loss modulus

The variation in storage modulus (E') as a function of temperature ($-100°C$ to $+100°C$) is shown in Figure 1(b). Irrespective of the filler loadings all the curves show characteristic sigmoidal variation of E' with temperature. Generally, the augmentation of E' with filler in the glassy region ($-100°C$ to $0°C$) can be attributed to the hydrodynamic effect of filler particle embedded into the polymer continuum. The storage modulus increases with the increase in filler loadings in the entire temperature range [Fig. 1(b)]; however, the increase is more prominent in the rubbery region. Effect of incorporation of filler on the mechanical properties of elastomeric materials can be partially explained as follows: if particles of high elastic modulus are dispersed through a low elastic modulus matrix, the modulus of the mixture will be higher than that of the matrix. However, for a filler to be more reinforcing in nature, among many factors, the most important one is the force of adhesion of the matrix to the particle surface.[16] If the adhesion between the filler and the polymer matrix is very low, then no significant increase in modulus (except due to hydrodynamic effect) can be observed. If the particle-to-matrix adhesive force is large, then the modulus of the mixture is primarily governed a measure of the magnitude of the polymer–filler interactions.

The conductive carbon black used in this study is Ensaco 350G, which has a fractal aggregate structure (Fig. 2), having surface area of 700 m^2/g. This large surface area facilitates the adsorption of polymer chain to get immobilized on its surface. Increased filler loading leads to increase in polymer–filler interactions, thereby making a portion of the polymer matrix attached to the filler surface.[17] This explanation can also be extended to Figure 3, which shows the temperature dependence of loss modulus, E'' for various compositions. In the entire composites, distinct transition peak is observed in the temperature region of $-7°C$ to $-18°C$, which may be assigned as α relaxation related to glass transition.[18,19] The variation in filler loading has no significant effect on this peak location. Higher filler loadings result in a percolative network of filler particles that can influence relaxation on a different scale. However, recent dynamic mechanical experiments for composite solids indicate that restriction effects do in fact result from the formation of a percolation network.[20–22] Nevertheless, reports regarding the restriction effects of percolated networks on the segmental relaxation
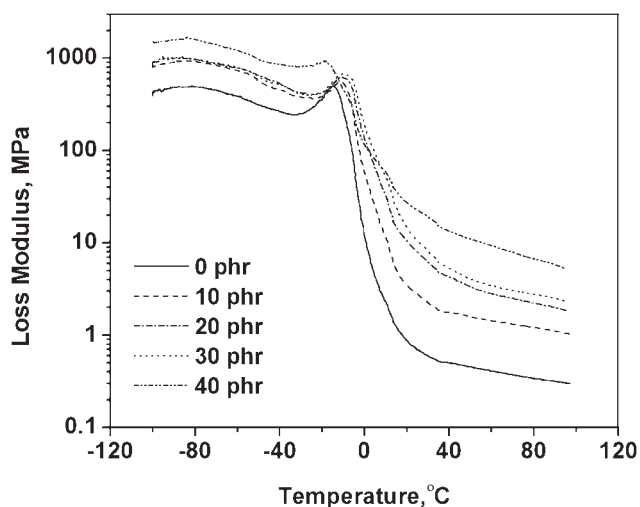

Figure 3 Variation in loss modulus with filler loading in conductive carbon black reinforced CSM vulcanizates as function of temperature at frequency of 1 Hz and strain of 0.06%.
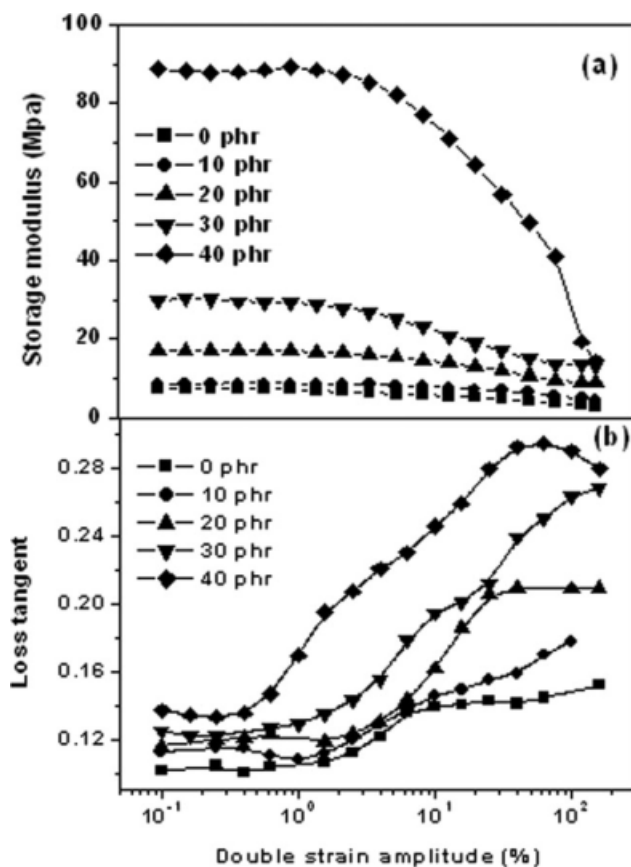
Figure 4 Effect of dynamic strain amplitude on (a) storage modulus and (b) loss tangent as a function of filler loading in CSM vulcanizates at frequency of 1 Hz and temperature of 30°C.

are not fully conclusive, and this needs more detailed and systematic study.

Effect of double strain amplitude on storage modulus and tan δ

Figure 4(a) shows the variation in storage modulus as a function of double strain amplitude (DSA) for vulcanizates with increasing filler loadings at room temperature. For all filler loadings, with increasing strain amplitude a continuous decrease in storage modulus can be observed. All the vulcanizates show highest storage modulus (E') at the lower strains. At lower strains, the three-dimensional filler–filler and filler–polymer structure acts as a rigid unit against the imposed strain, and hence, exhibits the highest modulus value.[3,23] The strain input associated at lower strains is not sufficient to cause any significant change in network structure. This can be explained from the fact that increasing amplitude of oscillation causes the gradual breakdown of the secondary structure and results in dynamic modulus reduction. At lower filler loadings, this effect is low but at higher filler loadings this effect is much pronounced.

At higher strain rates, there is a rapid decrease in storage modulus that can be interpreted in terms of filler interarticle interaction theory in which the filler particles of the matrix interact through an interparticle potential.[24,25] Because an interparticle potential is a strong function of the separation distance, this induces a steep dependence of the energy stored in the network of the particles on the macroscopic strain. Higher strains rupture this secondary networks leading to rapid decrease in the storage modulus. With increase in filler content, the strain amplitude at which nonlinearity begins moves to a lower value. This is a familiar effect[23,26] and is explained by the fact that increasing strain amplitude causes the gradual breakdown of the secondary filler aggregate network structure and results in dynamic modulus reduction. However, the effect is small at low degree of loading and is very pronounced at a higher degree of loading. The degree of nonlinearity increases continually with filler concentration, without any discontinuity in behavior. Zhu and Sternstein attributed this phenomenon to the release of trapped entanglements due to the application of strains thereby leading to the reduction in dynamic moduli.[27,28]

Figure 4(b) shows the tan δ plotted against DSA, for the same vulcanizates. It is apparent from the figure that at very low dynamic strain test condition for a particular vulcanizate, the tan δ value remains apparently constant with increasing dynamic strain. The range of strain over which tan δ remains constant is very narrow and depends on filler concentration in the sample. Above this limiting value, tan δ increases with dynamic strain for all samples. The higher the concentration of black in the sample, the steeper is the rise in tan δ value. At intermediate strain amplitude, considerable breakdown, reformation of filler aggregate structure, and desorption–reabsorption of shell rubber takes place. This can be explained on the basis of: (a) polymer–filler interaction, (b) the desorption and reabsorption of hard rubber shell surrounding the filler aggregate, and (c) breaking-reforming of effective crosslinks in the rubber forming transition zone between the bound rubber and the bulk rubber. The complex interaction between the fractal aggregates and polymer matrix strongly increases the elastic modulus.[29] However, under strain, there is an evolution of their fractal geometry leading to a decrease in the value of the elastic modulus.[30] This, so-called, hydrodynamic reinforcement effect is, however, difficult to quantitatively describe, as it requires a very precise knowledge of the particles arrangement in the composite. It has been suggested that dynamics of adsorption/desorption of the polymer chains at particle surface may be responsible for various linear and nonlinear effects, which can be attributed to the reduced mobility of the polymer chains.[31,32]
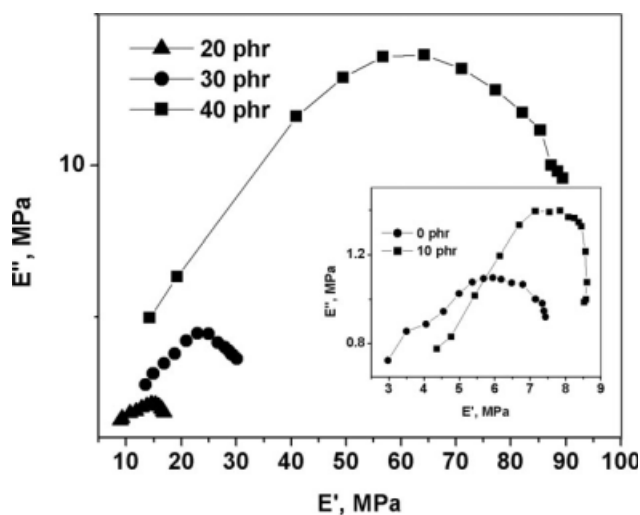
Figure 5 Loss modulus E'' as function of storage modulus E' of carbon black filled CSM composites in strain sweep at 30°C.

Figure 5 shows Cole-Cole plot for the unfilled and carbon black filled CSM composites. It is evident that the circular arc relationship of the Cole-Cole plot[33,34] holds good at high filler loadings. The unfilled and low filler loaded samples show deviation from the circular arc relationship. At high filler loading, the network entanglement contribution to the various hysteretic parameters becomes significantly high,[35] and thus a circular relationship is followed. With increase in filler loading, the area under the circular arc increases. In case of unfilled and low filler loaded samples, the departure from the circular arc relationship may be due to stress softening[36-40] and to a large extent to the lack of constituency of the modulus associated with the network slippages.[41]

Effect of frequency on storage modulus, loss tangent, and loss modulus

The effect of carbon black concentration on the frequency dependence of dynamic storage modulus at a reference temperature of 30°C is displayed in Figure 6(a). The conductive black reinforced polymer composites containing higher filler concentration show higher modulus, which increases with the increase in frequency. The behavior in the low frequency region is apparently related to the behavior at higher temperature, whereas the behavior at high frequency region is similar to low temperature characteristics. Increasing frequency reduces the configurational changes with which the polymer molecules in the elastomer matrix can respond within a cycle of deformation as a result an increase in storage modulus can be observed. A decrease in tempera-

ture means an increased resistance to molecular motions, which leads to a higher storage modulus.[42]

The higher modulus for higher filler content compared with unfilled sample is attributed to higher filler–filler interaction. It is apparent from the Figure 6(a) that the effect of frequency is more pronounced at higher (40 phr) carbon black loading [insert in
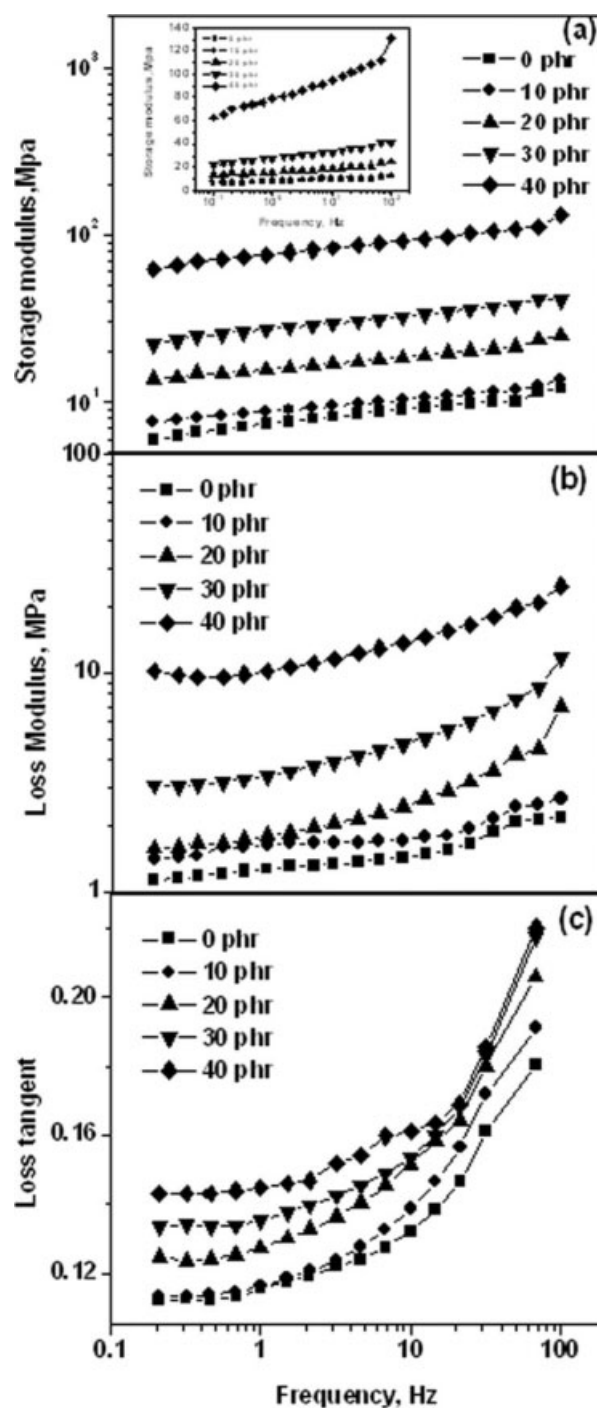

Figure 6 Effect of frequency on (a) storage modulus, (b) loss modulus, and (c) loss tangent as a function of filler loading in CSM vulcanizates at strain of 0.1% and temperature of 30°C.
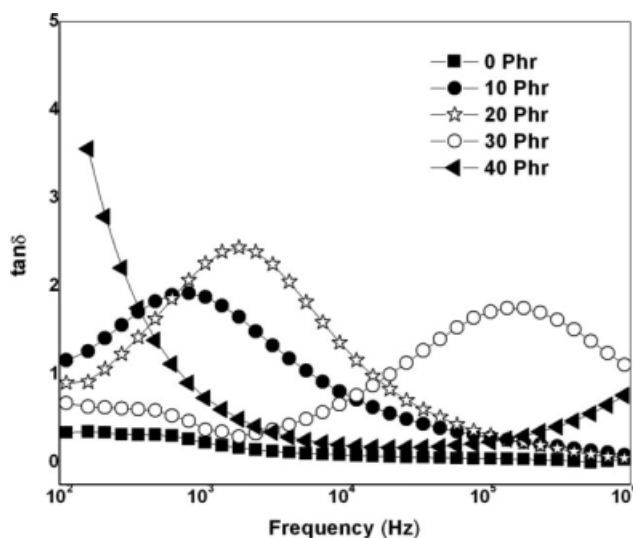
Figure 7 Variation in dielectric loss tangent (tan δ) as a function of frequency in CSM vulcanizates for different filler loading at 30°C.

Fig. 6(a) shows this more clearly]. CSM composite exhibits more elastic-like behavior as the testing frequency increases and the storage modulus tends to slope upward toward higher frequency. This is due to the fact that at low frequency, time is large enough to unraveling of the entanglements so a large amount of relaxation occur, which results in a low value of storage and loss modulus. However, when a polymer sample is deformed at large frequency, the entanglement chains do not have time to relax, so modulus goes up. The increase in loss modulus with increase in frequency as shown in Figure 6(b) is more pronounced than the storage modulus [Fig. 6(a)]. The same trend has been reflected in the loss tangent versus frequency plot [Fig. 6(c)].

Effect of filler loading on dielectric loss tangent (tan δ)

Figure 7 shows the variation in dielectric loss tangent (tan δ) with frequency in Ensaco 350G reinforced CSM vulcanizates for different filler loading. It is observed that at lower frequencies, the increase in filler loading leads to higher loss tangent values whereas, at higher frequencies, this effect is marginal. The dielectric relaxation behavior of a polymer composite mainly depends upon the distribution of filler particles in the polymer matrix. Incorporation of fillers like carbon blacks results in hydrodynamic interactions between polymer matrix and the filler surface, which leads to formation of bound rubber. Bound rubber can be defined as the amount of insoluble rubber adhering to the carbon black surface before vulcanization. The BdR can be considered as a measure of polymer–filler interactions, which mainly depends upon the surface area, and surface

activity of fillers. Conductive carbon black (Ensaco 350G) has very high surface area and high concentration of oxygen containing functional groups, which lead to higher level of interactions with the polymer matrix.[43] With increase in filler loadings, BdR is increasing which is clearly observed from Table II. With increase in filler loading, the maximum dielectric loss is shifted toward higher frequency, that is, approximately from 10^3 Hz for 10 phr to 10^5 Hz for 30 phr. In case of highest filler loading, no peak is observed in the test range (10^2–10^6 Hz). This can be explained on the basis of crosslink density, which increases with increase in filler loading. This in turn decreases segmental mobility and increases the relaxation time of segmental dipole.

Effect of filler loading on real and complex part of impedance

The effect of filler loading on real part of impedance in CSM vulcanizates is shown in Figure 8(a). The complex impedance $Z^* = Z' \pm jZ''$, where Z' and Z'' are real and imaginary parts of the complex impedance (Z^*), respectively. Z' represents the resistive part of the system and Z'' represents the reactance arising due to the capacitive or inductive nature of the system. Irrespective of the filler loading, there is a gradual reduction of real impedance with increase in frequency and at higher frequencies (10^5–10^6 Hz), the effect is marginal. With the increase in filler loading, there is a decrease in real impedance at lower frequencies but at higher frequencies effect is marginal. This can be explained on the basis of electron hopping mode of conduction, which becomes more significant at higher frequencies.

Relaxation phenomenon in crosslinked and reinforced polymers depends on the chemical and physical interactions between the viscoelastic polymeric phase and solid filler phase. Crosslinking of the polymers usually impose intermolecular constraints, which in turn play an important role in the segmental dynamics of all polymeric systems in the bulk state.[44] Incorporation of fillers like conductive carbon black (Ensaco 350G) not only results in hydrodynamic interactions but also leads to complex

TABLE II
Bound Rubber, Values of Bulk Resistance (R_B), and Centre Position (for Fig. 9) in Ensaco 350G Reinforced CSM Vulcanizates

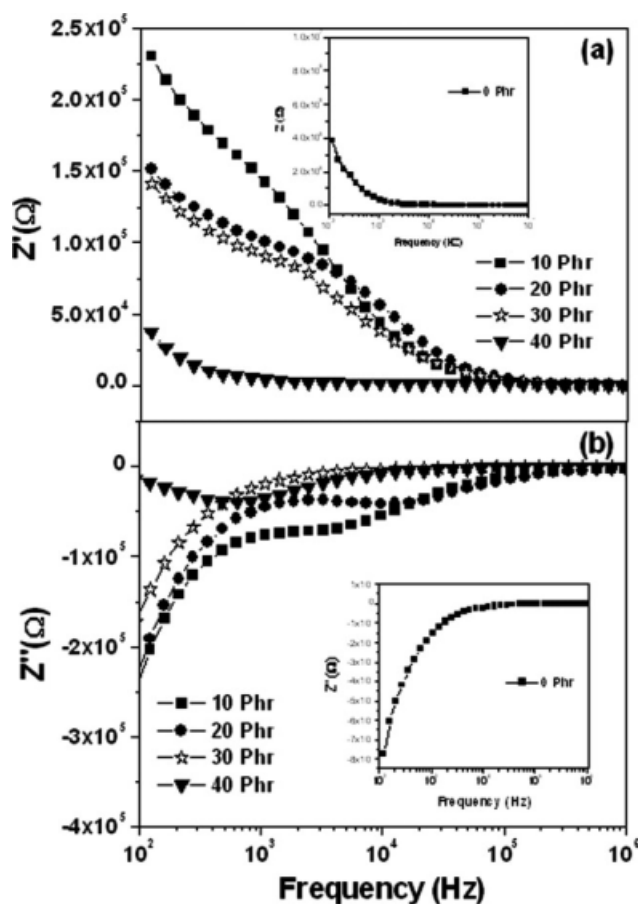| Filler loading	Bound rubber	Centre (x, 0)	R_B (x, 0)
0	33	1.5×10^6, 0	3×10^6, 0
10	41	3.85×10^5, 0	6×10^5, 0
20	54	2.5×10^5, 0	3.85×10^5, 0
30	67	1.5×10^5, 0	2.75×10^5, 0
40	79	0.5×10^5, 0	1×10^5, 0

Figure 8 Effect of filler loading on (a) real part of impedance (Z') and (b) imaginary part of impedance (Z") of CSM vulcanizates as a function of frequency at 30°C.

physico–chemical interactions between the polymer matrix and the filler surface.[45] These polymer–filler interactions are characterized by the content of the apparent "bound rubber," which is the amount of insoluble rubber adhering to the dispersed filler particles before vulcanization. Because of high surface area of the conductive carbon black (Ensaco 350G), the polymer–filler interaction is very high which leads to the formation of a strong interphase. The interphase formed between the filler and the polymer matrix has distinct properties. Polymer layer having higher stiffness than that of the bulk polymer in the vicinity of the dispersed phase surface is created from hindered molecular mobility, because of interactions between phases.[12] The variation of imaginary part of complex impedance with frequency at different filler loadings is shown in Figure 8(b). It is observed that at low frequencies, increased filler loading shows increased complex impedance. However, at higher frequencies, the effect is marginal for all filler variations. This can be explained on the basis of viscoelastic properties of crosslinked multiphase polymeric materials, which depend upon

relaxation dynamic and morphology of the polymer composites. Although these relaxations can usually be associated with each component, their appearance depends on the chemical and physical interactions between the phases (filler and the polymer matrix). Because of high surface activity of conductive black (Ensaco 350G) it shows high interaction with the polymer matrix, thereby leading to the formation of strong interphase.

Effect of filler loading on Nyquist plots

Figure 9 shows the effect of filler loading on Nyquist plots (Z' vs. Z"). It can be observed that the variation in filler loading has a sizeable effect on the real (Z') and imaginary (Z") part of complex impedance (Z*) of the system. Several attempts have been made to predict the impedance spectroscopy of polymer-filler systems on resistance-capacitance circuit model. According to Sluyters-Rehbach and Sluyters,[46] the total impedance of the cell (Z) is the series of combinations of resistors, R_B, and capacitors, C_B. In a Nyquist plot of polymer composite system, the real axis represents bulk resistance (R_B) and imaginary axis represents ω_{max} (i.e., top of the semi-circle) and is given by

$$\omega_{max} = \frac{1}{R_B C_B} \quad (2)$$

where C_B is bulk capacitance of the polymer composite. With increase in filler loading, there is a decrease in R_B, which represents increase in conductivity and less lossy response. However, with increase in filler loading, there is a gradual improvement in bulk capacitance (C_B). From Figure 9, it can be observed that at low filler loading (10 and 20
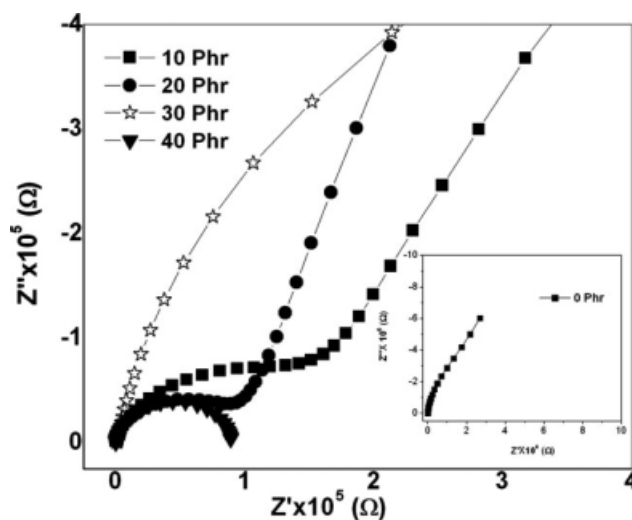

Figure 9 Nyquist plot (Z' vs. Z") for different filler loadings in CSM vulcanizates at 30°C.
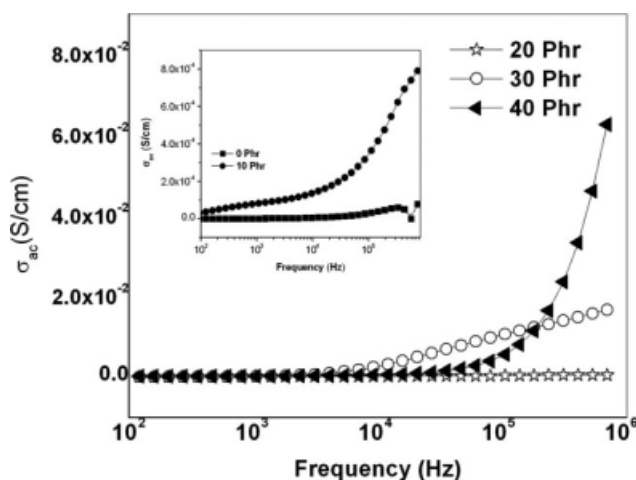
Figure 10 Variation in ac conductivity (σ_{ac}) with frequency for different filler loadings in CSM vulcanizates at 30°C.

phr) the Nyquist plot consists of a semi-circle followed by a spike. With increase in filler loading, the semi circular curve is reducing, and at 30 phr filler loading, it is completely disappearing. Beyond percolation limit (30 phr), a perfect semicircular plot has been observed. It can be explained on the basis of aggregation of the carbon black particulates to form secondary structures called aggregates.[47] Similar findings has been found by Mahapatra et al.[5] The gaps between the carbon black aggregates control the electron conduction via non-ohmic contacts between the carbon black aggregates. The centers of the semi-circle and the bulk resistance (R_B) values for all filler loading have been given in Table II. The shift in center of the semi-circle can be used as a measure of the gaps in between the aggregates of carbon black particulates. It can be observed from Table II that with increase in filler loading, the R_B value is decreasing and center of the semi-circle is also decreasing. This may be due to increase in conductivity with increase in filler loading, which agreed well with the conductivity plot (Fig. 10).

Effect of filler loading on conductivity

Figure 10 shows the variation of electrical conductivity as a function of frequency with increasing filler loading in Ensaco 350G reinforced CSM vulcanizates. Irrespective of filler loading, there is an increase in conductivity with increase in frequency, which is clearly observed in the Figure 10. The increase in electrical conductivity with frequency is more prominent in the frequency range of 10^4–10^6 Hz. The dielectric properties of polymer composite depend primarily on distribution of filler particles in the polymer matrix, which is also called mesostructure.[48] At low filler loadings, the conductivity of the

polymer composite is slightly higher than that of the base polymer as the filler particles are isolated from each other by the insulating polymer matrix, which reduces the likelihood of electron hopping.[49] As the filler loading is gradually increased, a continuous conductive path is developed due to very close contact between the filler aggregates. At particular filler loading (30 phr and above), there is a sharp increase in conductivity value, which may be called as percolation threshold. Representative TEM figures exhibiting the dispersion of the filler has been shown in Figure 11. TEM studies reveals that the dispersion of Ensaco 350G is homogeneous in the polymer matrix but aggregation takes place as filler loading is increased, which is clearly observed from the TEM photomicrographs of samples containing 30 and 40 phr filler loading. Beyond 30 phr carbon black loaded CSM composite, a continuous conductive path is developed due to close contact between the carbon black particles in the polymer matrix. This observation appears to be in good agreement with the electrical and dynamic mechanical results.

The frequency dependence of conductivity in polymer composites is due to hopping transport between localized sites. The heterogeneous dispersion of filler particles in the polymer matrix results in a wide distribution of hopping rates giving a strong dispersion of the ac conductivity. The clear-cut understanding of the conduction mechanism of such heterogeneous materials has not yet been
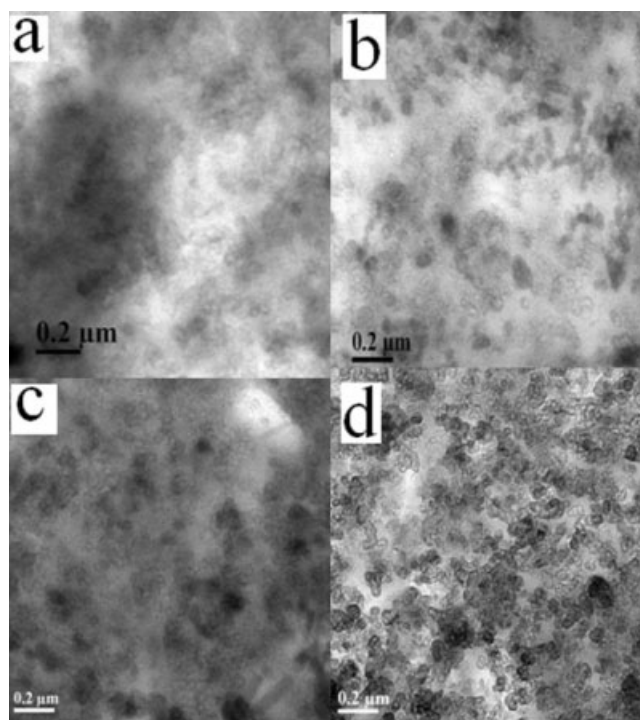

Figure 11 TEM microphotograph of CSM vulcanizates filled with various black loadings: (a) 10 phr; (b) 20 phr; (c) 30 phr; (d) 40 phr.

reached due to complexity of the polymer structure. It is widely believed that the conductivity depends not only on geometry of the filler particles but also on the actual processing characteristic of the materials.[50] The lattice percolation theory is not sufficient to account for the conduction mechanism.

CONCLUSIONS

The dynamic mechanical analysis of the vulcanizates showed that addition of the filler has no significant effect on the glass transition temperature, T_g. However, with the increase in filler loading the intensity of tan δ curve decreases. This has been explained in terms of filler–polymer interaction and interaggregate interactions. Broadening of the relaxation region was observed in the plots of storage and loss modulus with temperature. The variation in storage modulus with strain and frequency has also been studied. All the vulcanizates showed a rapid decrease in the storage modulus with increase in DSA, whereas tan δ was found to increase. Increase in storage and loss moduli with increase in frequency as a function filler loading has also been observed. This has been explained on the basis of availability of less time for relaxation. Increase in dielectric loss tangent is observed with increase in filler loading, which has been explained on the basis of viscoelastic nature of the composites. The observed variations in Nyquist plots with increasing filler loading have been explained on the basis of aggregation of the filler particles. TEM pictures revealed that the carbon black particles were homogeneously distributed in the CSM matrix, whereas beyond 30 phr filler loading, carbon black particles formed agglomerates inside the rubber matrix.

References

1. Kraus, G. Reinforcement of Elastomers; Interscience: New York, 1965.
2. Medalia, A. I. Rubber Chem Technol 1973, 46, 877.
3. Sridhar, V.; Chaudhary, R. N. P.; Tripathy, D. K. J Appl Polym Sci 2006, 100, 3161.
4. Katsuno, T.; Chen, X.; Yang, S.; Motojima, S.; Homma, M.; Maeno, T.; Konyo, M. Appl Phys Lett 2006, 88, 232115.
5. Mahapatra, S. P.; Sridhar, V.; Chaudhary, R. N. P.; Tripathy, D. K. Polym Compos 2007, 28, 657.
6. Chen, G.; Wu, C.; Weng, W.; Wu, D.; Yan, W. Polymer 2003, 44, 1781.
7. Nanda, M.; Tripathy, D. K. Express Polym Lett 2008, 2, 855.
8. Nanda, M.; Chaudhary, R. N. P.; Tripathy, D. K. Polym Compos 2010, 31, 152.
9. Stephen, R.; Thomas, S.; Raju, K. V. S. N.; Varghese, S.; Joseph, K.; Oommen, Z. Rubber Chem Technol 2007, 80, 672.
10. Choi, Y. K.; Sugimoto, K.; Song, S. M.; Gotoh, Y.; Ohkoshi, Y.; Endo, M. Carbon 2005, 43, 2199.
11. Berriot, J.; Montes, H.; Lequeux, F.; Long, D.; Sotta, P. Macromolecules 2002, 35, 9756.
12. Long, D.; Lequeux, F. Eur Phys J E 2001, 4, 371.
13. Ediger, M. D. Annu Rev Phys Chem 2000, 51, 99.
14. Trakulsujaritchok, T.; Hourston, D. J. Eur Polym J 2006, 42, 2968.
15. Li, Y.; Liu, R.; Wang, J.; Tang, X. Prog Org Coat 1992, 21, 101.
16. Mohapatra, S. P.; Sridhar, V.; Chaudhary, R. N. P.; Tripathy, D. K. Polym Eng Sci 2007, 47, 984.
17. Sridhar, V.; Xu, D.; Pham, T. T.; Mahapatra, S. P.; Kim, J. K. Polym Compos 2009, 30, 334.
18. Singh, S.; Mohanty, A. K. Comp Sci Technol 2007, 67, 1753.
19. Dutta, N. K.; Khastgir, D.; Tripathy, D. K. J Mater Sci 1991, 26, 177.
20. Angell, C. A.; Ngai, K. L.; Mckenna, G. B.; McMillan, P. F.; Martin, S. W. J Appl Phys 2000, 88, 3113.
21. Hodge, I. M. J Non-Cryst Solids 1994, 169, 211.
22. Litvinov, V. M.; Steeman, P. A. M. Macromolecules 1999, 32, 8476.
23. Payne, A. R. In: Dynamic Properties of Filler-Loaded Rubbers; Kraus, G., Ed.; Interscience: New York, 1965; p 69.
24. Shanmugharaj, A. M. Ph.D. Thesis, Indian Institute of Technology, India, 2002.
25. Shanmugharaj, A. M.; Bhowmick, A. K. J Appl Polym Sci 2003, 88, 2992.
26. Payne, A. R.; Whittaker, R. E. Rubber Chem Technol 1971, 44, 440.
27. Zhu, A. J.; Sternstein, S. S. Macromolecules 2002, 35, 7262.
28. Zhu, A. J.; Sternstein, S. S. Compos Sci Technol 2003, 63, 1113.
29. Chazeau, L.; Brown, J.; Yanyo, L.; Sternstein, S. Polym Compos 2000, 21, 202.
30. Maier, P. G.; Gortiz, D. Kautsch Gummi Kunstst 1996, 49, 18.
31. Lin, E. K.; Kolb, R.; Satija, S. K.; Wu, W. L. Macromolecules 1999, 32, 3753.
32. Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. Phys Rev Lett 2002, 1996, 77.
33. Davey, A. B.; Payne, A. R. Rubber in Engineering Practice; Maclaren and Sons: London, 1964.
34. Payne, A. R. J Appl Polym Sci 1965, 8, 2661.
35. Ulmer, J. D.; Hess, W. M.; Chirico, V. E. Rubber Chem Technol 1974, 47, 729.
36. Harwood, J. A. C.; Mullins, L.; Payne, A. R. J Appl Polym Sci 1965, 9, 3011.
37. Harwood, J. A. C.; Payne, A. R. J Appl Polym Sci 1966, 10, 315.
38. Harwood, J. A. C.; Payne, A. R. J Appl Polym Sci 1966, 10, 1203.
39. Harwood, J. A. C.; Payne, A. R. J Appl Polym Sci 1967, 11, 1825.
40. Kraus, G.; Childers, L. W.; Rollman, K. W. J Appl Polym Sci 1966, 10, 229.
41. Mullins, L.; Thomas, A. G. The Chemistry and Physics of Rubber-Like Substances; McClaren and Sons: London, 1963.
42. Eirich, F. R. Science and Technology of Rubber; Academic press: London, 1978.
43. Mahapatra, S. P.; Sridhar, V.; Tripathy, D. K.; Kim, J. K.; Kwak, H. Polym Adv Technol 2009, 19, 1311.
44. Matsuoka, S. Relaxation Phenomenon in Polymers; Hanser: Munich, 1992.
45. Xu, D.; Sridhar, V.; Mahapatra, S. P.; Kim, J. K. J Appl Polym Sci 2009, 111, 1358.
46. Sluyters-Rehbach, M.; Sluyters, J. H. Electroanal Chem 1970, 1, 4.
47. Boonstra, B. Rubber Technology; Van Nostrand: London, 1970; p 51.
48. Pike, G. E.; Seager, C. H. Phys Rev B 1977, 48, 5152.
49. Bottger, H.; Bryskin, V. V. Hopping Conduction in Solids; Academic-Verlag: Berlin, 1985.
50. Janzen, J. J Appl Phys 1975, 46, 966.