

Effect of Fillers on the Relaxation Behavior of Chlorobutyl Vulcanizates

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Received 10 May 2005; accepted 1 September 2005

DOI 10.1002/app.23148

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of addition of fillers (carbon black (CB), carbon silica dual phase filler (CSDPF), and nanoclays) on the relaxation behavior of chlorobutyl vulcanizates has been studied. The primary relaxation (α -transition, the glass transition) was studied by dynamic mechanical analysis as a function of temperature (-60 to $+100^\circ\text{C}$) and positron annihilation life time spectroscopy (-70 to $+110^\circ\text{C}$). Irrespective of the filler and its loading, all the composites showed the glass transition temperature in the range of -29 to -33°C , which was explained on the basis of relaxation chain dynamics of polyisobutylene in the vicinity of fillers. The secondary relaxation (α^* or β relaxation) was studied using dielectric relaxation spectra in the frequency range of 100 –

10^6 Hz. Nanoclays had a profound influence on the secondary relaxation, whereas CSDPF and CB had a marginal effect. The nonlinear strain dependent dynamical parameters were also evaluated at double strain amplitudes of 0.07 – 5% . The nonlinearity in $\tan \delta$ and storage modulus has been explained on the concept of filler–polymer interactions and the interaggregate attraction (filler networking). The “percolation limit” of the fillers in the composites has been studied by DC conductivity measurements. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3161–3173, 2006

Key words: dynamic mechanical properties; dielectric relaxation; Payne effect; fillers; percolation limit

INTRODUCTION

Fillers have a significant effect on the properties such as mechanical, dynamic mechanical, and in general on the overall performance of polymer composites. The incorporation of the fillers into a rubber is of significant commercial importance, since fillers not only enhances the mechanical properties of the final products but also decreases the cost of the end product. New generation fillers such as nanoclays and carbon silica dual phase filler (CSDPF) are challenging the domination of traditional fillers (carbon blacks (CB) and silica) of rubber industry. Especially, nanoclays dispersed as a reinforcing phase in an engineering polymer matrix are emerging as a relatively new form of useful materials. These composites exhibit a change in composition and structure over a nanometer length scale and possess remarkable property enhancements relative to pure polymer.

Understanding the local motions in bulk amorphous polymers becomes significant in designing new materials as well as in gaining detailed information on the physical behavior of existing materials. Relaxation in filled elastomers is time, temperature, frequency and strain dependent. Processing variables (i.e., the

type of filler, volume fraction of filler in the composite, the extent of interactions of filler with the polymer matrix, etc.) 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.¹ The present article deals with the dynamic mechanical properties as a function of temperature (-60 to $+100^\circ\text{C}$) and dielectric relaxation as a function of frequency (100 – 10^6 Hz) of reinforced chlorobutyl vulcanizates. The “Payne effect” (strain dependent dynamical parameters) was evaluated at double strain amplitudes of 0.07 – 5% . An attempt has been made to correlate the relaxation behavior to the free volume as measured by positron annihilation lifetime spectroscopy.

EXPERIMENTAL

Materials

Bayer Chlorobutyl 1240 with 1.25% chlorine content, Mooney viscosity ML_{1+8} at $100^\circ\text{C} = 38$ was procured from Bayer. Plasticizer was highly saturated processing oil of pharmaceutical grade, with specific gravity of 0.82, supplied by C.D. Pharmaceuticals, Calcutta, India. Zinc oxide was of chemically pure grade, with specific gravity 5.4. TMTD was supplied by ICI, Rishra, Hooghly, India, having specific gravity 1.42. Other compounding ingredients such as ZnCl_2 , sulfur, and stearic acid were of chemically pure grade pro-

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TABLE I
Compounding Formulations of the Mixes

Ingredient	Phr
CIIR	100
Stearic acid	1.0
Processing oil	4
ZnO	5
ZnCl ₂	1.3
TMTD	3
S	2.6
Fillers	Varied

CIIR, chlorobutyl rubber manufactured by M/s Bayer GmbH, Germany; filler, CB HAF (N-330), carbon silica dual phase filler and organically modified sodium nano clay (Cloisite 30B); ZnO, zinc oxide (specific gravity 5.4); stearic acid, manufactured by E. Mark, Bombay, India; TMTD, trimethyl thiuram disulphide, manufactured by M/s ICI, India; other compounding ingredients such as ZnCl₂, sulfur, and stearic acid were of chemically pure grade.

cured from standard suppliers. The fillers were CS-DPF, a two phase filler consists of a silica phase finely distributed in the carbon phase along with 90–99% elemental carbon, oxygen, and hydrogen as in traditional CB and commercialized as ECOBLACK and was supplied by M/s Cabot, USA. Microstructure of dual phase filler reveals that carbon phase is turbostratic in nature similar to conventional CB and the silica particles occupy the interstitial positions of the CB.^{2,3} The CB used is HAF, high abrasion furnace black, N-330, supplied by M/s Phillips carbon black, India. The nanoclay used in this work is organically modified sodium montmorillonite (Cloisite® 30B) purchased from Southern Clay Products, TX.

Sample preparation technique

The nanoclays were first heated in vacuum for 12 h at 100°C to remove residual water. These nanoclays were swollen in solvents for 3 days. The rubber was also swollen separately in solvent (cyclohexane). The nanoclay and the rubber solutions were then mixed under vigorous stirring. This mixture was allowed to dry for 7 days to remove the solvents. The compounding ingredients (formulation details are in Table I) were added to this rubber–nanoclay mixture on a laboratory size (325 mm × 150 mm) two-roll mixing mill at a friction ratio of 1:1.25, according to ASTM D3182 standards, by carefully controlling temperature, nip gap, time mixing, and uniform cutting operation. Mixing was done at a temperature range of 65–70°C for 12 min. The compounded material was molded in an electrically heated hydraulic press to optimum cure (90% of the maximum cure) using molding conditions determined by Monsanto Rheometer (R-100), according to ASTM D2084 and ASTM D5289 procedures. In

case of CB and CSDPF, all the ingredients (including fillers) were added during mixing on two-roll mill.

Testing

Dynamic mechanical properties

Dynamic mechanical parameters were obtained using a TA Instruments dynamic mechanical testing analyzer, over a temperature range of –60 to 100°C at a frequency of 1 Hz. Strain-dependent dynamic properties were evaluated on a Rheovibron DDV III EP of Orientec, Japan, at room temperature. The dynamic strain amplitude in tension mode was varied between 0.07 and 5% DSA.

Dielectric relaxation spectra

Dielectric relaxation spectra of the vulcanizates were obtained by a Hioki LCR meter in the frequency range of 100–10⁶ Hz in the temperature range of 30–100°C.

Positron annihilation studies

The PALS unit used was an automated EG and G Ortec fast–fast coincidence system with a ²²Na radioactive source and a resolution of 270 ps measured on ⁶⁰Co. The strength of PALS source was 15 μCi. The testing was carried out in temperature range of –70 to 110°C. PALS testing and subsequent data interpretation were carried out by the procedure given by Jean⁴ and Wang et al.⁵

RESULTS AND DISCUSSION

Dynamic mechanical analysis

Effect of temperature on loss tangent

Figure 1 shows the loss tangent spectra of chlorobutyl vulcanizates reinforced with different fillers as a function of temperature. The location of maximum value of loss tangent ($\tan \delta_{\max}$) is not significantly affected by the type of the filler. All the samples show the glass transition in the temperature range of –29 to –32°C. One of the main features of reinforced elastomers is that many polymer chains are in contact with the particle surfaces. Substrates are known to decrease molecular configurational freedom, induce collective glasslike dynamics, promote phase segregation, and alter stress relaxation mechanisms available to adsorbed polymer chains. When a polymer is cooled through the glass transition region, the physical properties of the polymer in the nonequilibrium state (at temperature lower than T_g), such as volume and enthalpy, gradually recover to new equilibrium values through the configurational rearrangement of polymer segments. The rate of the rearrangement or relax-

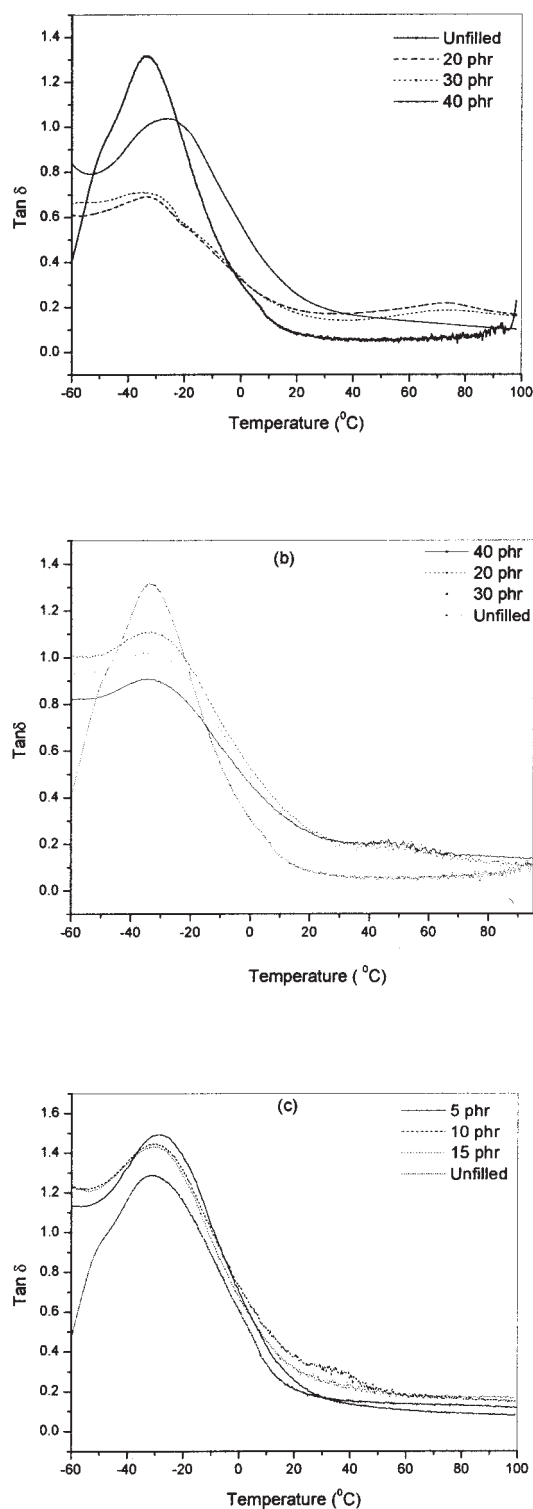


Figure 1 Variation of loss tangent with temperature in chlorobutyl vulcanizates reinforced with CB (a), CSDPF (b), and nanoclay fillers (c) at increasing filler loadings.

ation process depends on the local environment surrounding the relaxation entities and hence reflects the extent of environmental restriction on those entities. But the magnitude of T_g shift is marginal in our case.

This can be explained on the “sluggish” nature of the polyisobutylene (PIB) relaxation dynamics. The glass to liquid transition primarily involves correlated local motions of few backbone chains.^{6–8} But the segmental relaxation in PIB based elastomers is weak because of the steric hindrance by the methyl side groups. It has been suggested that low barriers to internal rotation about skeletal bonds are a contributing factor in maintaining the segmental mobility necessary for elastomeric behavior. In PIB $(-\text{C}-(\text{CH}_3)_2-\text{CH}_2-)_n$ the methyl groups bonded to alternate chain carbon atoms produce steric crowding. Although partially relieved by distortion of the $\text{C}-\text{CH}_2-\text{C}$ and $\text{CH}_2-\text{C}-\text{CH}_2$ bond angles (127° and 109° , respectively), it is still significant and hence PIB is not very flexible. As butyl and halobutyl elastomers are copolymers of 97 wt % isobutylene and 3% isoprene, the relaxation in CIIR is predominantly dominated by the PIB chains. Further, the distribution of the end-to-end distance of chain segments between topologically adjacent crosslinks plays a crucial role in relaxation process.^{9,10} As isobutylene has no chemical reactive site (unsaturated bond or double bond), and the only available reaction sites are Cl^- (1.25%) and the unsaturation of isoprene, the average chain length between the two adjacent reactive sites is very large. Consequently the vulcanization network in CIIR is expected to be more homogeneous than those in other rubbers; thereby, the glass transition is solely dependent on the PIB chain dynamics.

A significant observation is that nanoclay-reinforced systems have higher loss tangent values contrary to that of microscopic fillers (CBs and CSDPF) wherein addition of fillers leads to decrease in loss tangent. This system of nanoclay-reinforced CIIR vulcanizates has an intercalated structure. Representative TEM microphotographs are shown in Figure 2. Amount of the energy dissipated by such structures depends to a high degree on the mechanism of deformation that is induced in a viscoelastic material. The arrangement of nanoclay layers in the polymer matrix plays an important role in such systems. When layers are set in a manner wherein the nanoclay layers are aligned parallel to each other, shearing action of the polymer chains prevail in the core while face sheets undergo extension. This mechanism of dissipation of energy is called constrained layer damping.

Effect of temperature on storage and loss modulus

Figure 3 shows the variation in storage modulus (E') for different vulcanizates over a temperature range of -60 to 100°C . Irrespective of the type of filler, a characteristic sigmoidal variation of E' with temperature can be observed. But the intensity of increase in nanoclay-reinforced composites is more steeper when compared to the conventional particulate fillers (CB and

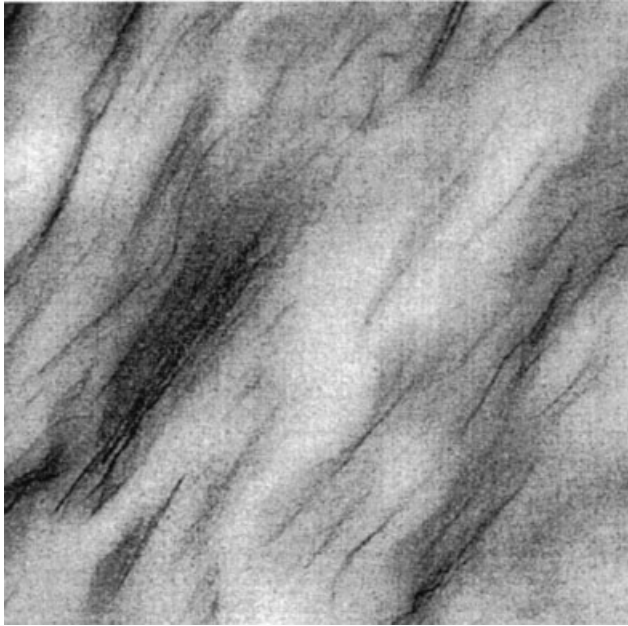


Figure 2 TEM of nanoclay-reinforced chlorobutyl vulcanizates showing an intercalated structure.

CSDPF). The effect of incorporation of a filler (be it a reinforcing filler or not) 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, it is obvious that the modulus of the mixture will be higher than that of the matrix, solely because of the decrease in volume content of matrix substance. However, for a filler to be really reinforcing in nature, many other factors come into the picture, the most important being the force of adhesion of the matrix to the particle surface plays a crucial role. If the adhesion between the filler and the polymer matrix is very low, then no significant increase in modulus (except because of hydrodynamic effect) can be observed. But if the particle-to-matrix adhesive force is large, then the modulus of the mixture is primarily determined by the magnitude of the polymer filler interactions. It has been suggested that there are three elastomer components in filled rubber samples distinguished by their characteristic molecular mobility: immobilized fraction, intermediate fraction, and mobile fraction.^{11–13} The relaxation properties of the composites are heavily dependent on the percentage of these fractions. The CB used in present study is high abrasion furnace black, HAF (N330), which has a fractal aggregate structure that is made of open, multiarmed structure that has a surface area of 250 m²/g. CBs also fall in the category of active fillers wherein the surface chemical groups on the CB surface leads to the formation of weak chemical crosslinks with the polymer matrix. A similar line of argument can be extended to CSDPF, which has a distinct structure of finely divided silica particles in-

terspersed in carbon phase. But as the silica particles occupy the inner space of the CB fillers, there is less interaction of the polymer chain with the filler. But the surface activity of CSDPF is less when compared to

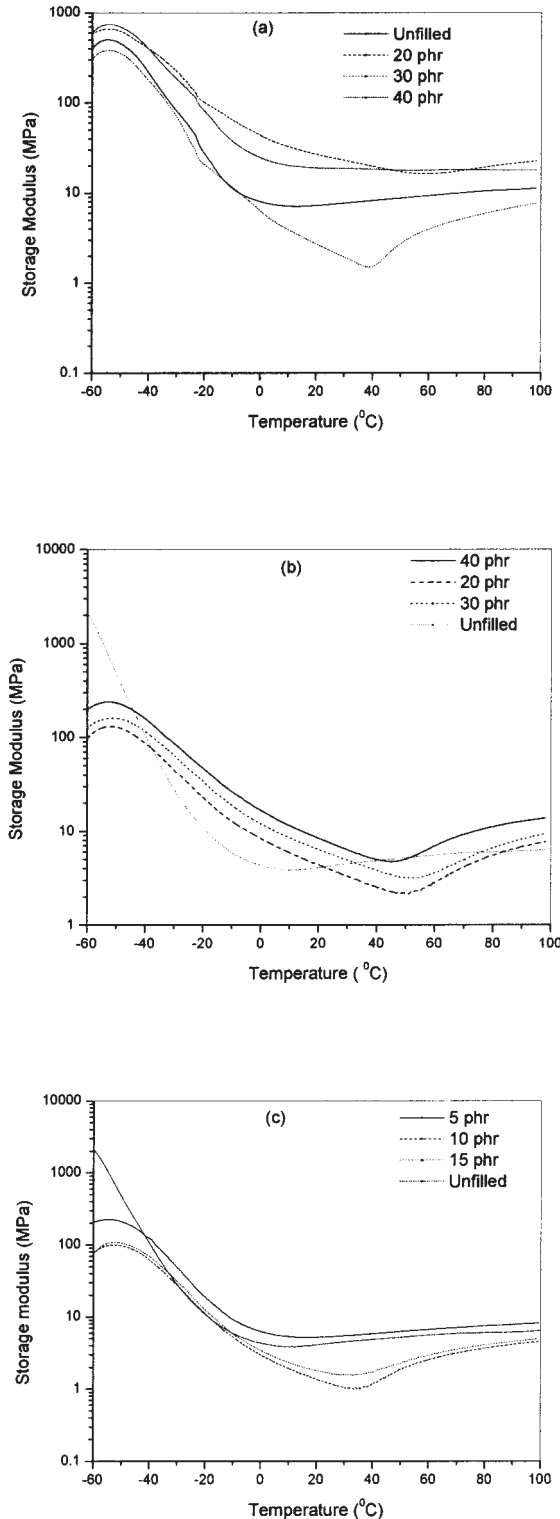


Figure 3 Variation of storage modulus with temperature in chlorobutyl vulcanizates reinforced with CB (a), CSDPF (b), and nanoclay fillers (c) at increasing filler loadings.

that of CB. Besides high surface areas (71 and 1100 m^2/g as determined by BET nitrogen adsorption, and wet surface area in aqueous solution by methylene blue adsorption¹⁴) nanoclays are also anisotropic in nature with aspect ratios of nearly 100–250, and their degree of orientation within the polymeric matrix also assumes considerable importance.¹⁵ Another reason for high reinforcing of nanoclays is the ability of the nanoclay to increase the toughness of the material resulting from the equivalence of time scales of motion for the polymer and the filler.¹⁶ This explanation can also be applied to Figure 4, which shows the temperature dependence of loss modulus, $[E(\text{dprime})]$, for various compositions. For all the compositions reinforced with nanoclays, a distinct transition peak is observed at the start of experimental region (-60°C) that may be attributed to the motion of methyl groups directly attached to the back bone of CIIR. The amount of filler has no significant effect on the α peak location and intensity. The amount of filler does not affect the $T_{E_{\text{max}}}^\alpha$ temperature (temperature at α peak); however, the intensity of α peak increases slightly with filler loading. At higher filler loadings, the result in a percolated network of filler particles can influence relaxation on a different scale. The percolation effect is usually considered to be effective for relaxation of longer time scales, such as the terminal relaxation observed in some rheological measurements. However, recent dynamic mechanical experiments for composite solids seem to indicate that restriction effects in fact do result from the formation of a percolation network.^{17–19} Nevertheless, reports regarding the restriction effects of percolated networks on the segmental relaxation are not fully conclusive, and the issue awaits more detailed and systematic study.

Effect of double strain amplitude on $\tan \delta$

Figures 5(a)–5(c) show the variation in $\tan \delta$ as a function of double strain amplitude (DSA) containing increasing concentrations of filler loadings in CB, CS-DPF, and nanoclay-reinforced chlorobutyl vulcanizates, respectively. Irrespective of the filler, at low strain rates, the $\tan \delta$ value remains almost constant. The range of strain over which $\tan \delta$ remains constant is very limited and depends on the filler concentration. Above this limiting value (about 1% DSA), $\tan \delta$ increases and this increase is more pronounced in vulcanizates of higher filler loadings. This can be explained on the basis of polymer–filler interaction, the desorption and reabsorption of hard rubber shell surrounding the filler aggregate, or breaking and reforming of effective crosslink in the rubber forming transition zone between the bound rubber and the bulk rubber. There is a tendency for the fillers to form some sort of “weak structure” when filler size becomes very small, although the exact nature of this structure is not

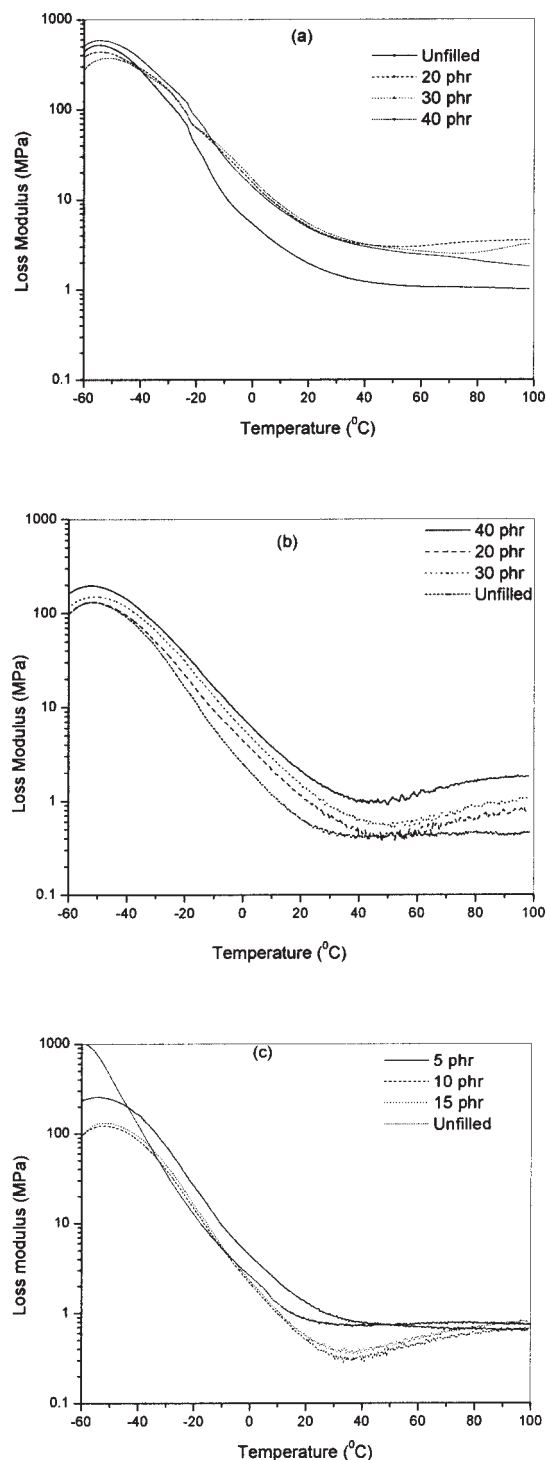


Figure 4 Variation of loss modulus with temperature in chlorobutyl vulcanizates reinforced with CB (a), CS-DPF (b), and nanoclay fillers (c) at increasing filler loadings.

clear. In case of particulate fillers such as CB and CS-DPF, the agglomeration of the filler in the matrix occurs at higher loadings wherein the mass fractal aggregates with D_m greater than half the embedding space dimension come into contact (generally at multiple points) when their centers are separated by a

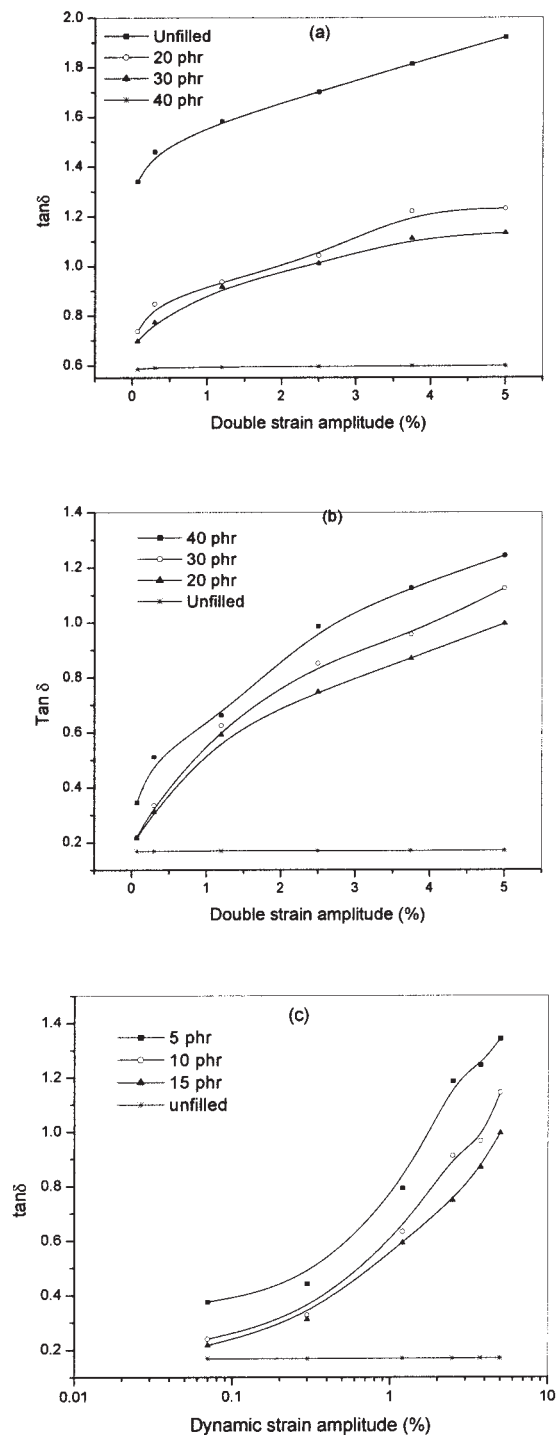


Figure 5 Effect of DSA on loss tangent in CB (a), CSDPF (b), and nanoclay fillers (c) chlorobutyl vulcanizates reinforced with increasing filler loadings.

distance less than their size.²⁰ This is mostly due to the intricate effects of the filler arrangement in the elastic matrix and of modifications of the polymer dynamics near the surface of the particles.

Another factor responsible for nonlinearity in viscoelastic properties in filled polymer systems is the sensitivity of the relaxation of polymer chains to the

local environment. Because of the characteristic long-chain molecules, polymers are sensitive to the local environment. This contention has been supported by positron-annihilation lifetime spectroscopy.²¹ (A more detailed explanation of PALS in chlorobutyl vulcanizates is given in subsequent sections.)

Effect of double strain amplitude on storage modulus

Figures 6(a)–6(c) show the variation in storage modulus as a function of double strain amplitude (DSA) for vulcanizates containing increasing concentrations of CB, CSDPF, and nanoclays, respectively. With increase in strain, it is observed that there is a decrease in storage modulus. All the vulcanizates show highest storage modulus (E') at the lower strains. This can be explained by the fact that increasing amplitude of oscillation causes the gradual breakdown of the secondary structure and results in dynamic modulus reduction. Irrespective of the type of fillers used, at lower filler loadings, this effect is low but very pronounced at higher loadings. At lower strains, the three-dimensional filler–filler and filler–polymer structure acts as a rigid unit against the imposed strain and hence will give higher modulus. The strain input associated at low strains is not sufficient to cause any significant change in network structure. The reinforcement at a moderate strains ($\sim 1.5\%$) is greatly affected by a disruption of the continuous network of filler that interpenetrates the rubber matrix. Under application of strains, the molecules of smaller chain lengths between the densely packed network points get oriented and form crystallites, whereas the molecules of much longer chain lengths would remain in random coil states. There are mainly four different mechanisms that are responsible for the reinforcing action of fillers in rubber materials: the hydrodynamic effect, rubber–filler interactions, occluded rubber, and filler networking.

In case of nanoclay-reinforced systems at higher loadings, the decrease in storage modulus with applied strain is more when compared with that in CB and CSDPF. This can be partially explained on the basis of effect of surfactant on the relaxation dynamics of polymer matrix. Polymer-coated nanoparticles are known to lead to self-assembly of nanoparticles.^{22,23} When these polymer-coated nanoparticles are dispersed in a polymer matrix, a dynamic balance between surfactant molecules adsorbed on nanoclays and the polymer matrix arises. In this dynamic balance, surfactant molecules can exist in one of three states: individual molecules in the matrix, in the gallery layers, and those adsorbed to the clay surface. But as the surfactant is primary alkylammonium amine whose affinity may be more toward the polyisoprene of CIIR (because of bisalkylation reaction) rather than

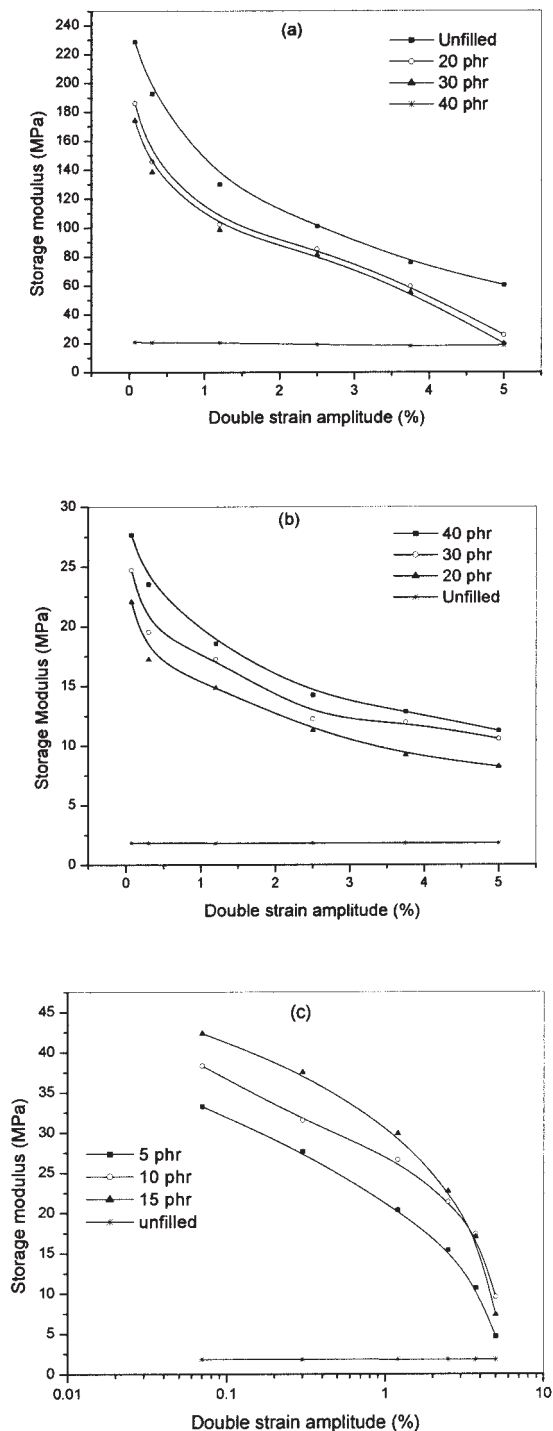


Figure 6 Effect of DSA on storage modulus in CB (a), CSDPF (b), and nanoclay fillers (c) chlorobutyl vulcanizates reinforced with increasing filler loadings.

the clay surface (because of physical absorption), this may lead to preferential anchoring of the nanoclays with the polymer matrix. Moreover at higher loadings of filler, there may not be enough polymer chains to interact with the nanoclays, which make the organically treated nanoclays to self assemble. With application of DSA, there may be rupture or breakage of these

self assemblies (analogous to structural breakdown of aggregates in CB-reinforced elastomers), thus leading to decrease in storage modulus.

Positron annihilation lifetime spectroscopy

Polymer free volume is defined as the difference between the total free volume of the material and the volume occupied by the molecules. It is a characteristic of amorphous polymers, as it is created by chain entanglements and folding. Not only does free volume in polymers has a controlling effect on the molecular mobility and the kinetic dynamic behavior in the polymer matrix, but it is also closely related to mechanical, physical, and relaxational properties of the polymers.²⁴ Mechanical properties of composites such as impact strength, fracture toughness, and loss modulus all increase as the free volume increases, because free volume facilitates the deformation of the material. The positron annihilation technique is capable of probing the free volume "holes" in polymer material based on the fact that positron annihilation lifetime and momentum correlation of annihilation photon pair are very sensitive to the surrounding electron density and distribution in localized sites.

Figure 7 shows the variation of ortho-positronium life time, (*o*-Ps) τ_3 , of chlorobutyl vulcanizates reinforced with CB, CSDPF, and nanoclay from -80 to 110°C . Far below T_g (-70 to -30°C), it can be observed that irrespective of the type of the filler, all the composite show almost similar τ_3 values. This can be explained on the basis of suppression of macro-Brownian motions in polymer matrix. At temperatures far below T_g , the composite is in "glassy state" wherein the polymer chains lack the necessary ther-

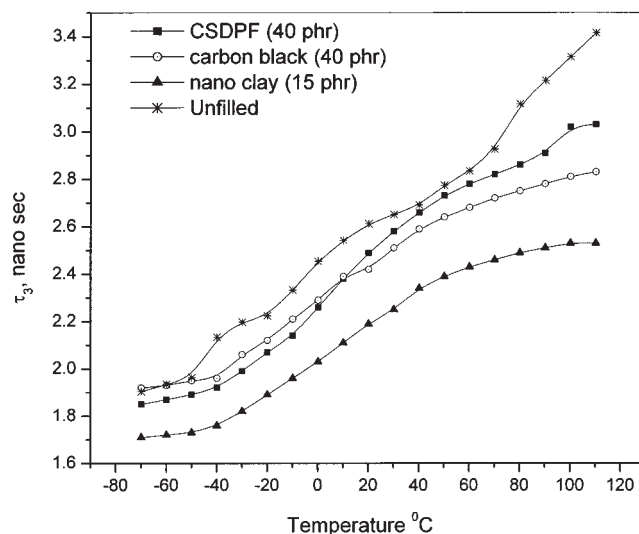


Figure 7 Temperature dependence of free volume parameter τ_3 in reinforced chlorobutyl vulcanizates.

mal energy required to move and tend to occupy lesser space. With increase in temperature, at -30°C it can be observed that there is sudden increase in values of τ_3 . This corresponds to the glass transition temperature of the composite, which was also observed using other relaxation techniques such as dynamic mechanical analysis. Increasing the temperature of the system increases the total amount of energy present within it and hence the mobility of the polymer chains. This sudden increase in the free volume near the glass transition zone (T_g) is attributed to the micro-Brownian motions because of the segmental mobility of the polymer chains. Above T_g , free volume increases rapidly with temperature, which is due to the macro-Brownian motion, i.e. the mobility of the main chain segments. However, the length of which corresponds to the chain entanglement distance. The chain molecular mobility M increases with the free volume h around the chain as defined by the following general form:

$$\ln(M) = A - B(T)/h^\gamma + \phi(T)$$

The segmental mobility M of the polymer chain in the matrix increases as the free volume increases. Many models are available to calculate the constants A and γ , and the temperature dependent functions $B(T)$ and $\phi(T)$. This is consistent with the observations of Dong and Jacob²⁵ who reported that chain alignment causes an increase in the number of larger, more elliptical free volume cavities resulting in the evolution of more broader distribution of free volume in the composites. At higher temperatures (above 70°C), it can be observed that the composites reinforced with CB and nanoclay show lower τ_3 values when compared to CSDPF reinforced systems. This can be related to the relaxation dynamics of the PIB chains in filled systems. Helfand and coworkers found that the motions of a polymer chain in the long time range are affected by the surrounding molecules, which are acting as walls, while in the short time range the motions are surprisingly similar to those observed in an single isolated chain.²³ Previous studies by Karatasos and Ryckaert²⁶ showed that PIB-based polymers show secondary relaxations about 70°C , which are related to the conformational transitions in global scale. But in reinforced polymers, these conformational transitions are localized because of the decreased degree of freedom imposed on the chains by the neighboring bonds and topological constraints. But these constraints do not completely stop their relaxation, as polymer chains are sufficiently flexible to make conformational transitions. Nanoclays (because of their higher surface area) and CB (because of their increased polymer-filler interactions) impose more constraints on the relaxation dynamics of polymer chains when compared to CSDPF systems.

Dielectric relaxation spectra

Dielectric relaxation spectroscopy (DRS) is a useful compliment to the more customary dynamic mechanical analysis for probing the viscoelastic properties of polymers.^{24,25} Dielectric spectroscopy offers the advantage to study the high-frequency dynamics of polymers. DRS reflects the same chain motions as the mechanical modulus; however, it has the advantages such as reduced interference due to symmetry arising from shorter time processes, making it more accurate.^{27,28}

Impedance analysis

Figures 8(a)–8(c) show the variation of real part of impedance as a function of frequency in CB, carbon silica dual phase, and nanoclay-reinforced chlorobutyl vulcanizates, respectively. Although there have been many recent studies to evaluate the relaxation phenomenon in PIB elastomers, most studies are made on unvulcanized (noncrosslinked) and unfilled samples; however, for most practical applications, a polymer is crosslinked and reinforced. Crosslinking of the polymers usually impose intermolecular constraints. Intermolecular constraints play an important role in the segmental dynamics of all polymeric systems in the bulk state.²⁹ Several works have studied the influence of the crosslinking degree on the relaxation by distinct techniques, such as dielectric spectroscopy, dynamic mechanical analysis, or creep and stress-strain measurements.³⁰ These studies revealed that the most striking effects caused by the increase of crosslinker concentration are the broadening of the relaxation and the slowing down of the segmental dynamics, which implies a shift of the transition zone to longer times or lower frequencies. In Figure 8, it can be observed that with increase in frequency, there is a gradual reduction in real impedance in all the vulcanizates, but the intensity of reduction is dependent on the filler type. In nanoclay systems, this phenomenon can be observed only until 10,000 Hz and beyond which the effect of frequency on real impedance is absent, whereas in CSDPF systems a continuous decrease of real impedance until the range of 10^5 Hz is observed and beyond which a further increase is observed. This can be explained on the basis of viscoelastic properties of crosslinked multiphase polymeric materials that depend on molecular relaxation processes and morphology of the 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). CSDPF because of its lower surface activity shows less interaction with the polymer matrix, thereby leading to the formation of a weak interphase when compared to nanoclays and CB. The thickness of

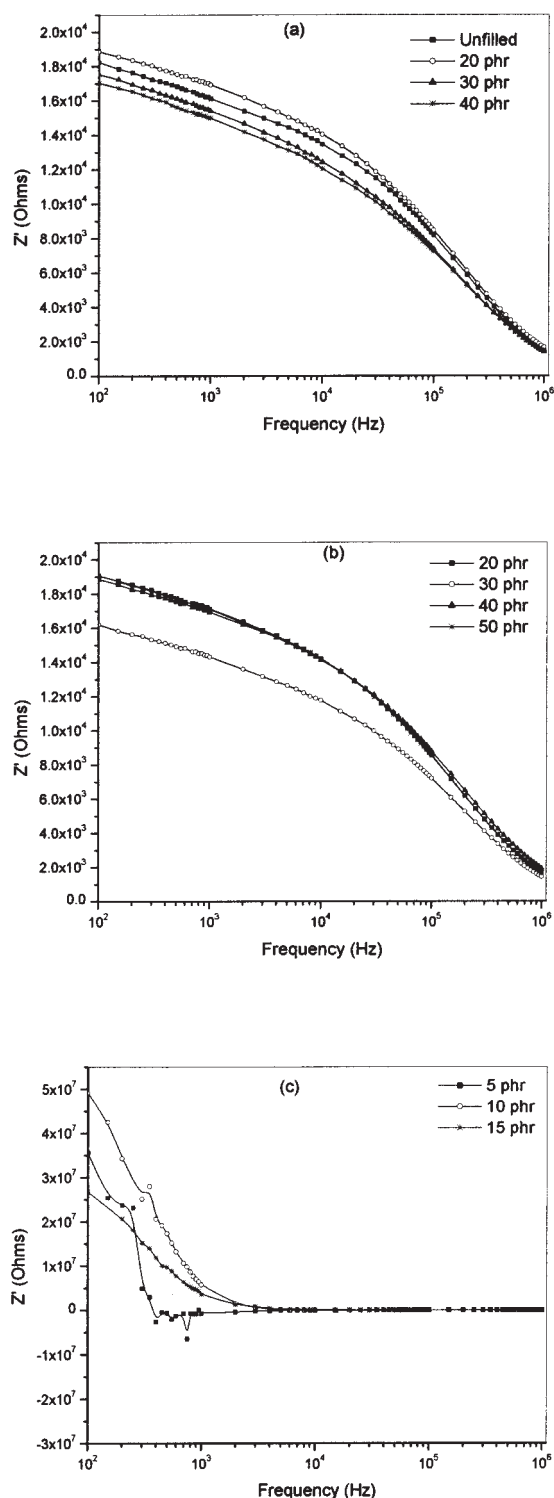


Figure 8 Variation of real part of impedance (Z') at different frequencies in chlorobutyl vulcanizates reinforced with CB (a), CSDPF (b), and nanoclay fillers (c) at increasing filler loadings.

the interphase is inversely proportional to the interfacial tension between the polymeric phases. Obviously, the properties of such an interfacial region differ from those of the pure components, and strongly affect the

overall properties of the resulting blended material. As a consequence, an interphase can be considered to have a certain volume, with its own characteristic properties or property gradients. As nanoclays have by the virtue of substantial available surface area and CBs due to their higher interactions with the polymer matrix (physicochemical-natured interactions), a substantial portion of the polymer chains are expected to be immobilized, leading to the formation of regions of spatial heterogeneities. The interphase formed between the filler and the polymer matrix has distinct properties that differ from the bulk. Polymer layer having a higher stiffness than the bulk polymer in the vicinity of the dispersed phase surface is created from restricted molecular mobility because of interactions between phases.³¹

A further proof regarding the importance of the interphase on the relaxation can be seen in Figures 9(a)–9(c) that show the variation of complex part of impedance as a function of frequency in CB, carbon silica dual phase, and nanoclay-reinforced chlorobutyl vulcanizates, respectively. In CSDPF-reinforced systems, an additional damping peak is observed in the frequency range of 10^5 Hz that can be attributed as α^* or β relaxation peak.^{32,33} The maximum frequency is related to the mean relaxation time of the process and characterizes the molecular mobility (at the temperature of investigation), which depends on such parameters as composition, thermal treatment, and mixing with other substances. The width and the asymmetry of the relaxation function usually deviate from the values because of the Debye's function. Now there is a strong discussion about the physical origin of this deviation,³⁴ but it is known empirically that this effect depends for instance on the degree of crosslinking and the level of interactions between the fillers and the polymer³⁵ or microheterogeneity.³⁶ However, in nanoclay-reinforced systems, there is total absence of these secondary relaxation peaks, which reinforces our argument that addition of nanoclays in CIIR gives rise to situations wherein the relaxation of the polymer chains is severely restricted.

Electrical resistivity of the composites

Figures 10(a)–10(c) show the variation of resistivity in CB, carbon silica dual phase, and nanoclay-reinforced chlorobutyl vulcanizates, respectively. At low levels of filler loading, the resistivity of the composite is slightly higher than that of the base polymer, since the filler particles are isolated from each other by the insulating polymer matrix. As the filler loading is gradually increased mutual contacts between the filler particles are established and at a critical loading of the filler a sharp drop in resistivity is observed indicating the "percolation limit." This abrupt fall in resistivity at the critical concentration of the filler is dependent on the type

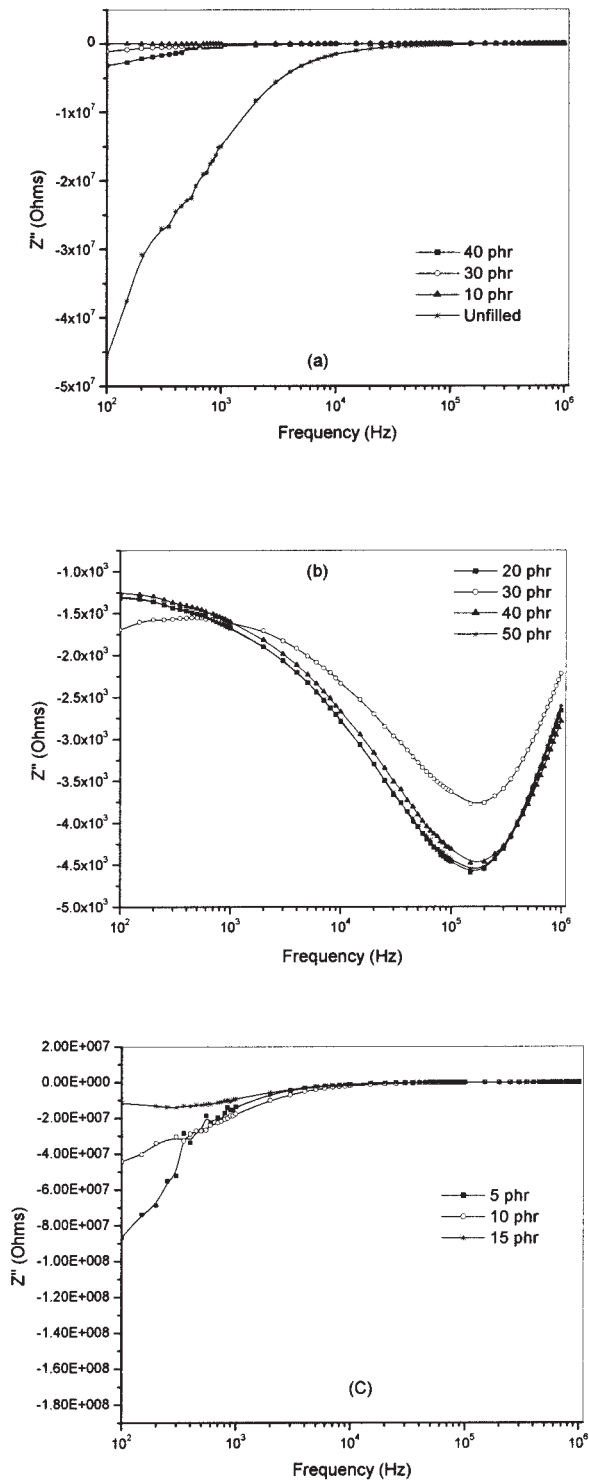


Figure 9 Variation of complex impedance (Z') at different frequencies in chlorobutyl vulcanizates reinforced with CB (a), CSDPF (b), and nanoclay fillers (c) at increasing filler loadings.

of polymer matrix and the filler characteristics such as surface area, surface activity, particle size, etc.

Depending upon the type of the filler, the occurrence of percolation limit is varying. In particulates

(CB and CSDPF) filled composites the percolation region is observed in the region of 30–40 and 40–50 phr, respectively, whereas in nanoclay-reinforced systems the percolation region is occurring between 10 and 15 phr loading of the filler. In particulate filler reinforced systems, this observation is consistent with the find-

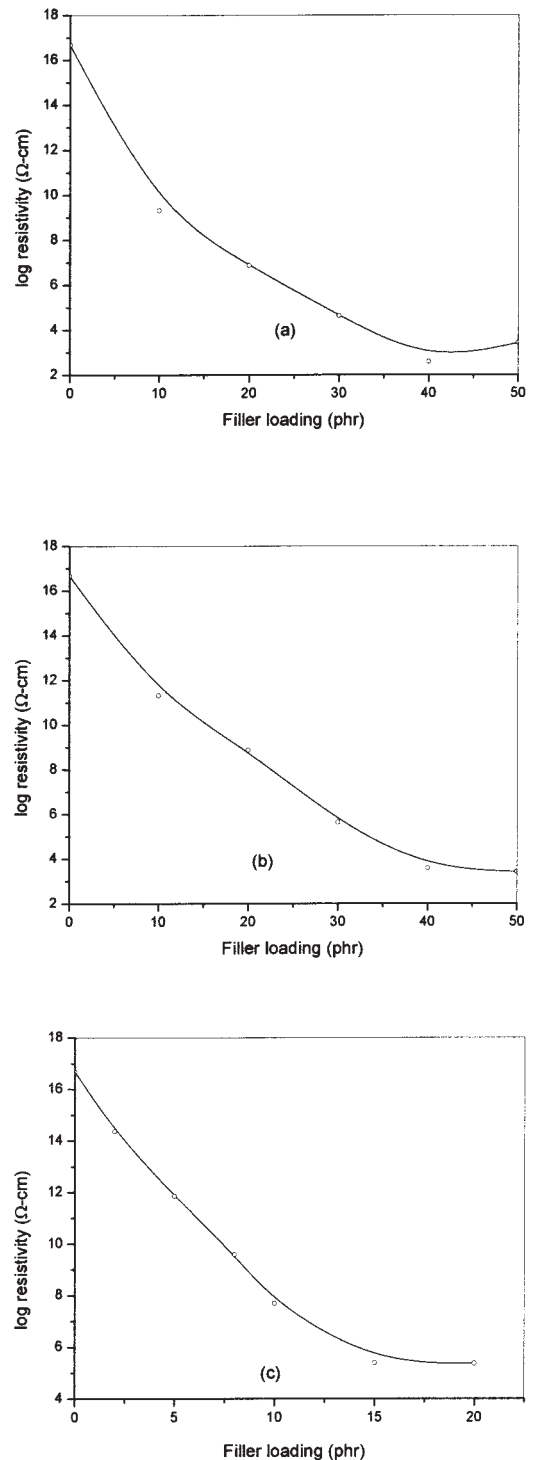


Figure 10 Effect of filler loading on resistivity in CB (a), CSDPF (b), and nanoclay-reinforced chlorobutyl vulcanizates.

ings of Das³⁷ who showed that percolation in CB-filled systems is about 40 phr. There have been many studies on the percolation limit of CB-filled elastomers, although in nanoclay-reinforced elastomers it has never been reported.

Traditionally, the variation of reinforced elastomers has been divided into three regions. In region I, the "inductive region," a small decrease in resistivity 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 network. Region II is referred as "percolation region" where conductivity increases or resistivity decreases sharply. In region III, further addition of filler has little or marginal effect on the conducting properties of the composite. In this present study (as evidenced from the plot), two distinct regions can be observed. At low nanoclay loadings (5 and 10 phr), there is a slight fall in resistivity of the composite (indicating inductive region). But as soon as the filler loading is increased to 15 phr the composite shows tremendous conductivity (almost as semiconductor), indicating the percolation limit of the nanoclay in the polymer matrix.

Many questions on the actual mechanism for electrical current transport through such heterogeneous materials are still prevalent. It is widely believed that their electrical properties depend primarily on the way the filler particles are distributed through the polymer matrix, also called as the mesostructure.³⁸ Representative SEM figures representing the dispersion of the filler have been shown in Figures 11(a) and 11(b) for CB and CSDPF. Many models that are supposed to describe this dispersion to the electrical conductivity of a composite are prevalent. The most famous one is the so-called lattice percolation theory.³⁹ However, in spite of the fact that it accounts for the existence of a conductivity threshold at some critical value of the filler concentration and for the power law dependence of some of the electrical properties, it fails to predict the location of this threshold and the observed values of the exponents sometimes depart significantly from the theoretical universal values.

The theoretical value of the percolation threshold for randomly dispersed, hard, spherical particles has been determined to be about 16 wt %.³⁹ In this case of CIIR-CB and CIIR-CSDPF reinforced composites, the percolation limit is observed about 24 and 32%, respectively. The deviation of present results with that of Lattice percolation model can be explained on the basis of dispersion, polymer–filler interactions, and agglomeration of the filler particles (at percolation) in the polymer matrix. Crosslinked polymer–filler composites are heterogeneous in nature consisting of two or more phases, which show different conductive and

dielectric properties.^{40,41} A higher concentration of filler and its distribution throughout the matrix will change the local electric field and therefore the electrical properties. The concentration of filler material influences polarization, as well as DC conduction and hopping conduction inside the material. Therefore, an increase in filler concentration will decrease the distance between filler particles, and depending on the frequency of the applied field, charges will be able to hop or tunnel between the filler particle islands. Additionally, at a critical concentration value, the filler particles form paths that connect one end of the material to the other end (percolating clusters).

In case of nanoclay-CIIR, the percolation limit is occurring about 13%. This observation is consistent with the percolation limit in single-walled carbon nanotubes (SWNT), which has percolation limits about 4–8%.⁴² However, the nanoclays that fall in between SWNT and the spherical particles (vis-à-vis surface area) should show a percolation limit in between these two values. The percolation limit of organically modified nanoclays in CIIR matrix as studied by DC conductivity measurements show the percolation at 13%. This can be explained on the basis of dipolar relaxations in nanoclay-reinforced systems. Recent studies⁴³ that compared the effect of microscopic and nanoscopic TiO₂ in epoxy resin showed a marked difference in charge accumulation in filled materials depending on whether the filler has micro- or nanometric dimensions. These studies suggest that significant interfacial polarization is implied for conventional fillers, which is mitigated in the case of nanofilled systems where a short-range highly immobilized layer develops near the surface of the nanofiller (1–2 nm). This bound layer, however, influences a much larger region surrounding the particle in which conformational behavior and chain kinetics are significantly altered. This interaction zone is responsible for the material property modifications especially as the curvature of the particles approaches the chain conformation length of the polymer. An addition of nanofiller in the host medium (polymer matrix) creates the conditions for Maxwell–Wagner–Sillars polarization, because of the difference between the intrinsic electrical properties of the media.⁴⁴

CONCLUSIONS

The dynamic mechanical analysis of the vulcanizates showed that the addition of the fillers has no significant effect on the primary relaxation, the glass transition temperature, T_g . However, in particulate fillers, increasing the filler loading the intensity of $\tan \delta$ curve decreases whereas in nanoclay systems there is an increase. This has been explained on the basis of restricted relaxation of the polymer chains

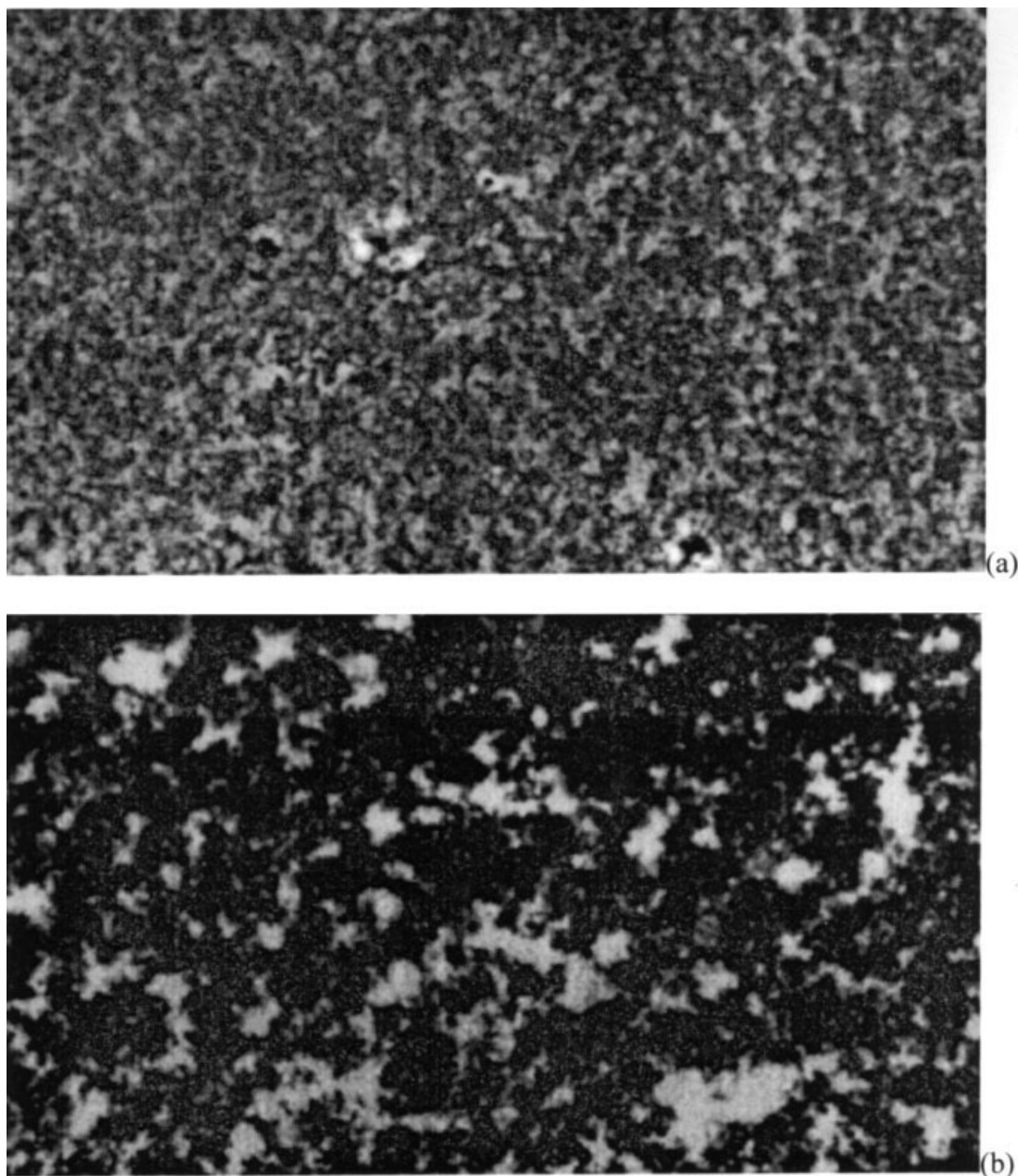


Figure 11 SEM microphotographs of (a) CB and (b) CSDPFs at percolation limit.

in intercalated nanolayers and constrained layer model. Irrespective of the type of filler, increase in filler loading in the composites lead to the broadening of the relaxation region in the plots of storage and loss modulus. The variation in $\tan \delta$ and storage modulus with strain (Payne effect) was also studied. All the vulcanizates showed a rapid decrease in storage modulus on increasing dynamic strain amplitude while $\tan \delta$ increases. The free volume as measured by positron annihilation life time spectroscopy showed that the occurrence of free volume sites in the composites is dependent on the temperature. At temperatures far below the glass transition, irrespective of the type of fillers, the available

free volume is identical in all composites, whereas at higher temperatures the free volume is more in CSDPF systems when compared with that in CB- and nanoclay-reinforced systems. The dielectric relaxation spectra of the composites showed absence of secondary relaxation peaks in nanoclay systems, whereas in CSDPF systems the relaxation was very prominent. This was explained on the concept of formation of very strong interphase layer between the filler and the polymer matrix in nanoclay and CB systems and the absence of the same in CSDPF systems. The percolation limit of the filler in the matrix as obtained by resistivity measurements showed at 30–40 in CB, 40–50 in CSDPF, and 10–15 phr loadings.

The support and help of all the members of Ferroelectrics laboratory, Dept. of Physics, Indian Institute of Technology, Kharagpur, is greatly appreciated.

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