Relaxation Behavior of Carbon Silica Dual Phase Filler Reinforced Chlorobutyl Vulcanizates

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ABSTRACT: Dynamic mechanical analysis and dielectric relaxation spectra of carbon silica dual phase filler reinforced chlorobutyl vulcanizates were used to study their relaxation behavior as a function of temperature ($-60°C$ to $+100°C$) and frequency ($100–10^6$ Hz). Strain-dependent dynamical parameters were evaluated at dynamic strain amplitudes of 0.07–5%. The nonlinearity in tan δ and storage modulus was explained based on the concept of filler–polymer interaction and the interaggregate attraction (filler networking) of carbon black. The dynamics of chlorobutyl chain segments in the composites was explained on the basis of their connectivity. The segmental relaxation of the polymer chains in the presence of filler and crosslinking has been explained, based on conformational transitions occurring at high frequencies. The 'percolation limit' of the filler in the composites was found to be in the range of 30–40 phr loading. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4320–4327, 2006

Key words: viscoelastic properties; reinforcement; fillers; elastomers; dielectric properties; dynamic mechanical properties; Payne effect

INTRODUCTION

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 as well as in gaining detailed information on the physical behavior of existing materials. The dynamic mechanical properties of elastomers filled with reinforcing fillers such as carbon black or silica show nonlinear response in low strain regions. Medalia[1] studied this phenomenon in carbon black filled elastomers. Mechanical deformation in filled elastomers is time, temperature, and strain dependent. Processing variables (i.e., the type of filler, volume fraction of filler in the compound, the extent of interactions of filler with the polymer matrix, etc.) have pronounced influence on the dynamic viscoelastic properties of vulcanizates. The operating variables (i.e., strain amplitude, strain rate, frequency, and temperature of testing) also have a significant effect on the dynamic properties of the polymers. Despite numerous investigations on carbon black filled rubbers using different techniques, the molecular origin of the reinforcement effect is still not known. It is generally 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 carbon silica dual phase filler (CSDPF) and organically modified nano clays.[2,3] Especially, the organic clay reinforced rubber compounds have potential for tailoring unique lightweight materials with distinctly superior mechanical, thermal, and barrier properties. In view of the importance of the materials, we have carried out a systematic study of the effect of fillers on the mechanical and dynamic mechanical properties of chlorobutyl (CIIR) vulcanizates as a function of various fillers.

EXPERIMENTAL

Sample preparation

Details of the formulation of the mixes are given in Table I. The compounds were mixed in a laboratory size (325×150 mm^2) mixing mill at a friction ratio of 1 : 1.25 as per ASTM D7182 standards and at carefully controlled temperature, nip gap, time of mixing, and uniform cutting operation in the temperature range of 65–70°C. The mixture of compounds with different compositions was molded in an electrically heated

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
Filler-CSDPF	Varied

CIIR, chlorobutyl rubber manufactured by M/s Bayer GmBH, Germany; Filler, carbon silica dual phase filler (CS-DPF) with 3.2% silica manufactured by M/s Cabot corporation, USA; ZnO, zinc oxide, specific gravity 5.4; stearic acid, manufactured by E. Mark (India) Ltd., Bombay; TMTD, trimethyl thiuram disulphide, manufactured by M/s ICI Ltd., India; other compounding ingredients like ZnCl$_2$, sulfur, stearic acid were of chemically pure grade.

hydraulic press to optimum curing (90% of the maximum cure), using molding conditions determined by Monsanto Rheometer (R-100).

Testing

Dynamic mechanical properties

Dynamic mechanical parameters were obtained using a TA Instruments dynamic mechanical testing analyzer (DMTA), over a temperature range of −60°C to 100°C at a frequency of 1 Hz. Strain-dependent dynamic properties were evaluated on a Rheovibron DDV III EP of Orientec Corp., Japan, at room temperature. The dynamic strain amplitude (DSA) 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 *HiTester* 3530 LCR meter in the frequency range of 100–10^6 Hz at 30°C and 100°C.

Bound rubber measurement

Contents of bound rubber were determined by extracting the unbound materials such as ingredients and free rubber with three solvents for 7 days followed by drying for 2 days at room temperature. Weights of the samples before and after the extraction were measured, and the bound rubber contents were calculated using the following expression:

$$BdR = 100 \times \frac{\left[W_{fg} - W_1 \left[\frac{m_1}{m_1 + m_r} \right] \right]}{W_1 \left[\frac{m_1}{m_1 + m_r} \right]}$$

where *BdR* is the bound rubber content, W_{fg} is the weight of filler and gel, W_1 is the weight of sample, m_1 is the fraction of filler in the compound, and m_r is the fraction of rubber in the compound.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

Effect of temperature on loss tangent

Figure 1 shows the variation of loss tangent of the samples as a function of temperature with CSDPF loading. Increasing amount of filler in the vulcanizates has no significant effect on the temperature of location of tan δ_{max} value of glass transition, but the magnitude of the peak decreases with increase in filler loading. All the samples show the glass transition in the range of −29°C to −34°C. CSDPF is a new generation filler in rubber compounding, which has the advantage of providing improved dynamic mechanical properties compared with conventional carbon black.[2] The CS-DPF consists of a silica phase distributed in a carbon phase to reduce the carbon black networking in rubber vulcanizate, as a result good dispersion of the filler in the polymer matrix is observed.[3] It is observed that beyond glass-transition temperature, i.e., in the rubbery region, the curves of different vulcanizates crossover around a wider temperature interval. This may be attributed to the relaxation of the interfacial region of the polymer-filler in the composites. A similar behavior has also observed in carbon black filled bromobutyl[4] and styrene butadiene rubbers,[5] where the crossover was observed at a single temperature.

CSDPF has a distinct structure of finely divided silica particles interspersed in carbon phase. Since the
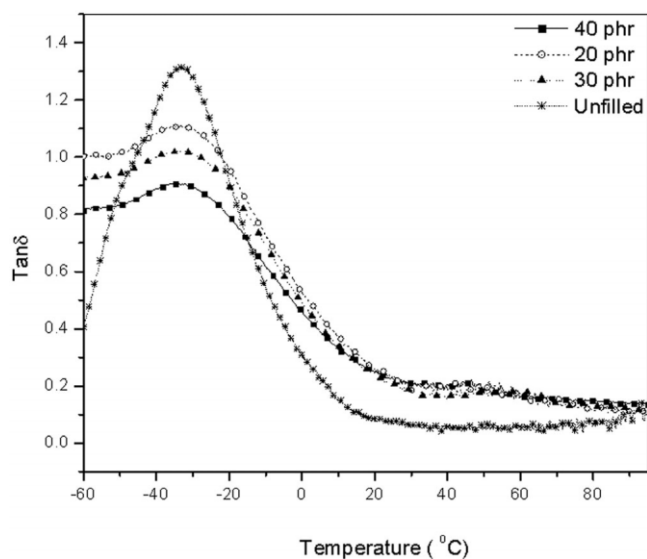

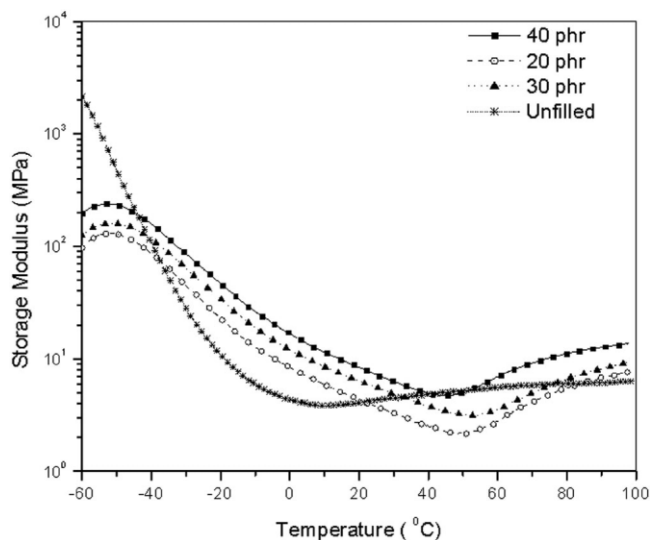**Figure 1** Variation of tan δ with temperature in CSDPF-CIIR vulcanizates at increasing filler loadings.

TABLE II
Bound Rubber of Carbon Black (ISAF, N220) and CSDPF Compounds

| Filler loading (phr)	ISAF (%)	CSDPF (%)
20	41.32	30.65
30	53.67	37.32
40	64.35	44.06
50	73.24	49.87

silica particles occupy the inner space of the carbon black fillers, there is less interaction of the polymer chain with the filler. This was confirmed by bound rubber measurements (as shown in Table II), which showed very less bound rubber in CSDPF filled compounds compared with carbon black filled compounds. The high percentage of the bound rubber in carbon black compounds can be attributed to the higher oxygen functionality of ISAF[6] when compared with CSDPF. The elastomer-filler interactions are often characterized by the content of the apparent "bound" rubber, which is determined as the amount of insoluble rubber adhering to the dispersed carbon black aggregates before vulcanization. Since the amount of bound rubber is related to the surface area and the surface activity of fillers, it is widely accepted that this phenomenon is due to multicontact adsorption of the polymer chains to the surface of the filler. Besides this, carbon blacks are porous in nature resulting in diffusion of polymer chains into the pores, which makes the polymer chain less mobile.

Effect of temperature on storage and loss modulus

Figure 2 shows the variation in storage modulus (E')

Figure 2 Variation of storage modulus with temperature in CSDPF-CIIR vulcanizates at different filler loadings.
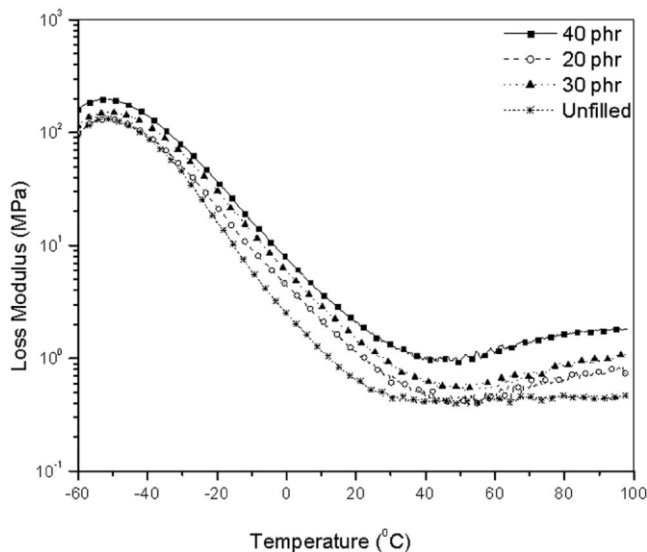

Figure 3 Variation of loss modulus with temperature in CSDPF-CIIR vulcanizates on increasing filler loadings.

for different vulcanizates over a temperature range of ($-60°C$ to $+100°C$. The characteristic sigmoidal variation of E' with temperature is apparent from the figure. In the glassy region (-60 °C to $-30°C$), the augmentation in E' with fillers can be attributed to the hydrodynamic effect of the filler particle embedded into the polymer continuum.[7] In the rubbery region (-30 °C to $100°C$), the polymer–filler and filler–filler networking(i.e., structure) and aggregate interactions have pronounced effect on the value of E'. Active fillers like carbon black and CSDPF affect the elastic properties of the vulcanizates more than the hydrodynamic reinforcement. The additional reinforcement is caused by the complex fractal structure of the active fillers.[8] At higher filler loadings, agglomeration of the CSDPF aggregates on a large scale to form filler clusters, and at filling fractions (larger than a certain threshold), the clusters form an irregular network leading to additional reinforcement.[9]

Figure 3 represents the temperature dependence of loss modulus, (E'') for various compositions. For all the compositions, a distinct transition peak (α transition) is observed at $-50°C$, which can be attributed to the confirmational transitions occuring in the polyisobutylene backbone caused by micro-Brownian motions.[10,11] The amount of filler has no significant effect on the α peak location and intensity. The amount of filler does not affect the $T^{\alpha}_{E''_{max}}$ temperature (temperature at α peak); however, the intensity of α peak increases slightly with filler loading.

Effect of strain on storage modulus and tan δ

Figure 4 shows the variation of storage modulus, E', of vulcanizates (containing an increasing concentration
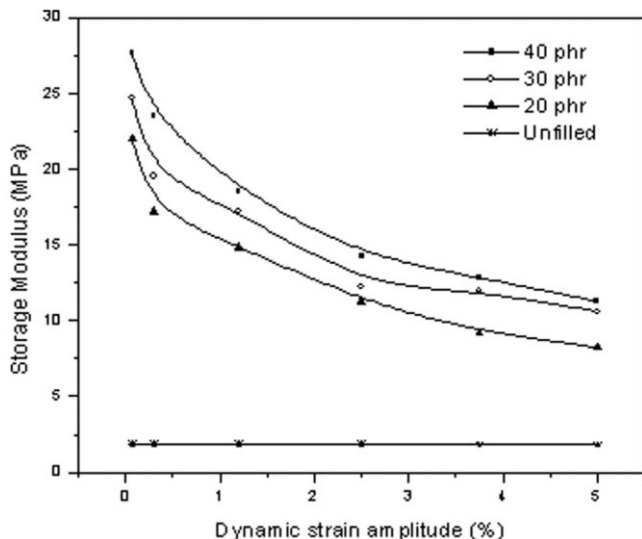
Figure 4 Variation in storage modulus with dynamic strain amplitude at different filler loading.

of CSDPF) with DSA at 30°C and 3.5 Hz. It can be observed that on increasing strain amplitude, there is a decrease in storage modulus. All the vulcanizates show highest storage modulus at the lower strain. This can be explained by the fact that increasing amplitude of oscillation causes the gradual breakdown of the secondary structure, which results in dynamic modulus reduction. At lower filler loading, this effect is low but very pronounced at higher loadings. At lower strains the three-dimensional filler-filler and filler-polymer structure act as a rigid unit against the imposed strain, and hence gives higher modulus. Low strains do not impart any significant change in network structure. The reinforcement at a moderate strain is greatly affected by a disruption of the continuous network of filler that interpenetrates the rubber matrix. On the application of strain, the molecules of smaller chain lengths between the densely packed network points get oriented and form crystallites, whereas the molecules of much longer chain length would remain in random coil states. The strong dependence of storage modulus on applied strain can be interpreted in terms of filler interparticle interaction theory in which the filler particles of the matrix interact through an interparticle potential. Since 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.

Figure 5 shows variation of tan δ with DSA for the same vulcanizates at 30°C. At lower strains (below 1%), there is a marginal variation in the tan δ value. Above this limiting value (~2% DSA), tan δ increases, which is more pronounced in vulcanizates of higher filler concentrations. 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. There is a tendency of the fillers to form a weak secondary structure when filler size becomes very small because of (a) the intricate effect of arrangement of solid particles in the elastic matrix and (b) modification of the polymer dynamics near the surface of the particles.[12] First, the arrangement of the particles (generally dispersed as fractal aggregates) contributes in a complex manner to both linear and nonlinear mechanical properties of filled rubbers. The complex interaction between the fractal aggregates and polymer matrix strongly increases the elastic modulus.[13] However, under strain there is an evolution of their fractal geometry leading to a decrease in the value of the elastic modulus.[14] 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. Second, the modification of the polymer dynamics near the surface of the fillers is not fully understood. It has been suggested that dynamics of adsorption/desorption of the polymers chains at the particle surface may be responsible for various linear and nonlinear effects, which can be attributed to the reduced mobility of the polymer chains.[15,16] A similar observation was made in strain dependent tan δ for nano clay reinforced vulcanizates at all temperatures.[12]
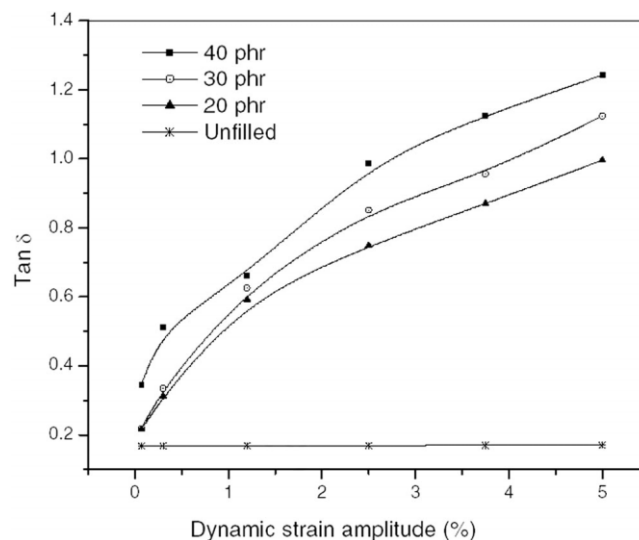
**Figure 5** Variation in tan δ with dynamic strain amplitude at different filler loading.

B dielectric relaxation spectra

Impedance analysis

One of the most valuable tools for characterizing the relaxation behavior of polymer systems is dielectric relaxation spectroscopy (DRS)]. Dielectric spectroscopy is a useful complement to the more customary mechanical methods of probing the viscoelastic properties of polymers. Dielectric spectroscopy offers advantages to study of the high-frequency dynamics of polymers. Dielectric spectra reflect the same chain motions as the mechanical modulus; however, it has reduced interference because of symmetry from shorter time processes making it more accurate than the traditional dynamic mechanical analysis.[17] The frequencies of testing in DRS correspond to the extraordinarily broad range of relaxation time associated in the polymer chains.[18,19] Although there have been many recent studies[10,11] to evaluate the relaxation phenomenon in polyisobutylene elastomers, most studies were on unvulcanized (noncrosslinked) and unfilled samples, whereas for many practical applications, a polymer is crosslinked and reinforced.

Figure 6(a,b) show the variation in the real impedance versus log of frequency as a function of CSDPF loading in CIIR vulcanizates at 30°C and 100°C, respectively. With increase in frequency, there is a gradual reduction of real impedance in all the vulcanizates. As the concentration of the filler in the composite increases, there is an increase in impedance. But this increase is possible only upto the 'percolation limit' beyond which the impedance decreases. This can be explained on the basis of the mechanical and viscoelastic properties of these crosslinked and reinforced multiphase polymeric materials. 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.[18,19] Several workers have studied the influence of the crosslinking degree on the relaxation behavior of polymers by distinct techniques, such as dielectric spectroscopy, dynamic mechanical analysis, or creep, and stress–strain measurements.[20–23] These studies reveal that increase of crosslinker concentration leads to 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. A similar trend can be observed in the system of CIIR-CSDPF, where with increase in filler concentration, there is a shift of the transition zone to lower frequencies.

Relaxation in crosslinked and reinforced polymers also depend on the chemical and physical interactions between the viscoelastic polymeric and solid filler phases. These interactions usually lead to the formation of interphase, whose thickness is inversely proportional to the interfacial tension between the two
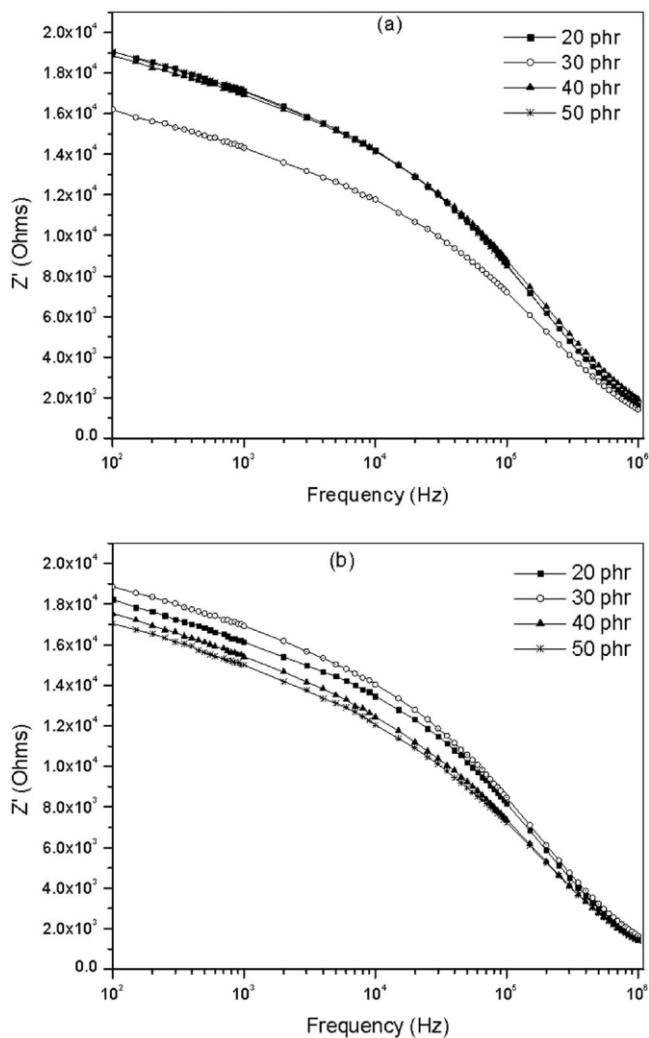
Figure 6 Effect of filler loading on real part of impedance (Z') at different frequencies in CSDPF reinforced chlorobutyl vulcanizates at 30 °C (a) and 100 °C (b).

phases. This interphase is commonly measured as "Bound rubber". The interphase formed between the filler and the polymer matrix has distinct properties, which differs from the bulk. Polymer layer having a higher stiffness compared with that of bulk polymer in the vicinity of the dispersed phase surface is created because of interactions between the filler and polymer phases[24–27] leading to different mechanical and dynamic relaxation properties resulting due to the residual thermal stresses and density fluctuations.[28]

A further proof of formation of interphase can be observed from the plots of complex impedance and log of frequency. Figure 7(a,b) show the variation of complex impedance with log frequency in CSDPF reinforced CIIR vulcanizates at 30 and 100°C, respectively. On increasing frequency, there is a rapid decrease in the complex impedance. But in the region of 10^5 Hz, there is an increase in complex impedance. Recent studies[10,11] indicate the occurrence of second-
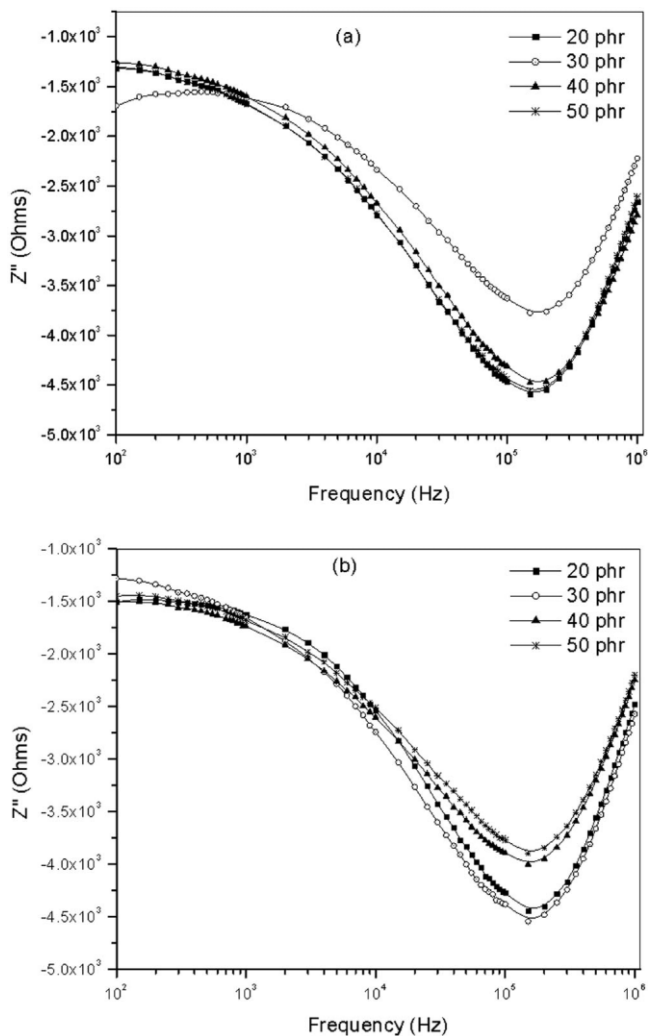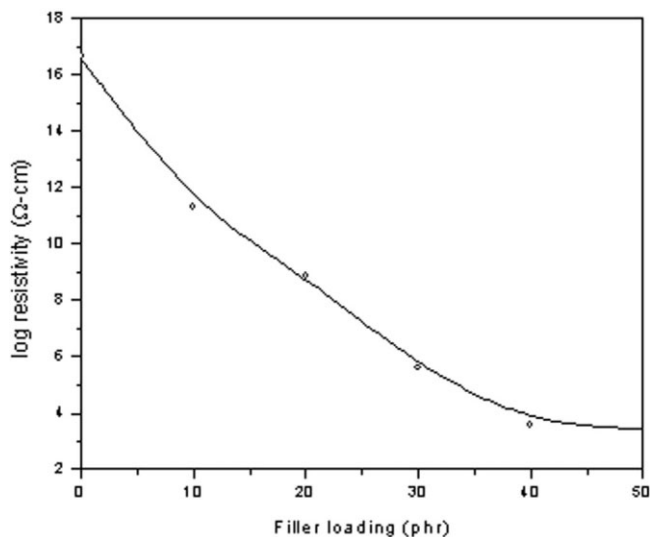
Figure 7 Effect of filler loading on complex part of imped-ance (Z'') at different frequencies in CSDPF reinforced chlo-robutyl vulcanizates at 30°C (a) and 100°C (b).

ary relaxations in the polyisobutylene chain segments at frequencies of 10^5 Hz, the so called α^* or β relax-ations. Since CIIR is 97% polyisobutylene, there may be occurrence of this secondary relaxation. However, the observation of additional damping peak in the complex impedance can also be attributed to the re-laxation of interfacial region between the polymer and the filler. Numerous examples of additional damping peaks have been cited[29–33] in the field of particulate multipolymeric systems. In system of CIIR-CSDPF vulcanizates, the effect of variation of filler loading in the composites does not have any significant effect on the frequency of location of this damping peak. All the samples show the occurrence of additional damping peak in the frequency range of 1×10^5–2×10^5 Hz. This frequency range is related to the mean relaxation time of the process and characterizes the molecular mobility (at the temperature of investigation) that de-pends on some parameters such as composition, ther-

mal treatment, and mixing with other substances.[34] The width and the asymmetry of the relaxation func-tion usually deviate from the values of Debye func-tion. In this system, as the filler loading increases, there is a decrease in the peak intensity but only until 40 phr loading of the filler above which there is grad-ual increase. There are various discussions about the physical origin of this deviation,[35,36] but it is known empirically that the effect depends on the degree of crosslinking, the polymer-filler interactions, the prop-erties of the interphase region,[37] or micro-heterogene-ity[38,39] A similar phenomenon can be observed in Figures 8(a) and 8(b), which show the complex imped-ance plot (Z'' versus Z') of CSDPF reinforced CIIR vulcanizates at 30 and 100°C, respectively.
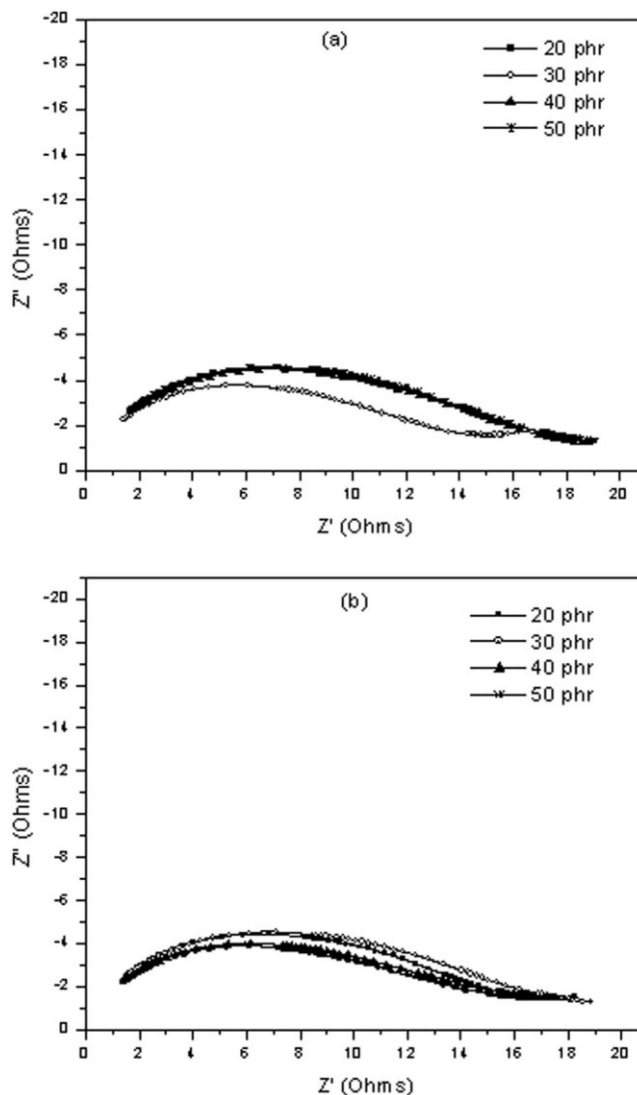
Figure 8 Complex impedance plot (Z'' versus Z') of CSDPF reinforced chlorobutyl vulcanizates at 30°C (a) and 100°C (b).

Figure 9 Effect of filler loading on resistivity in CSDPF reinforced chlorobutyl vulcanizates.

Electrical resistivity of the composites

Figure 9 shows the effect of filler loading on the volume resistivity of unfilled and CSDPF reinforced chlorobutyl vulcanizates. At low levels of filler loading, the resitivity of the composite is slightly higher than that of the base polymer because the filler particles are isolated from each other by the insulating polymer matrix, thereby decreasing the likelihood of "electron hopping". As the filler loading is gradually increased, contact between the CSDPF aggregates is established, and at particular filler loading, a sharp drop in resistivity is observed indicating the 'percolation limit'. This situation may be compared with that of increase in the conductivity because of increase in the diameter of conductive wire. The abrupt fall in resistivity at the critical concentration of the filler is due to the type of polymer matrix and filler characteristics (i.e., surface area, surface activity, particle size, etc.) In our CIIR-CSDPF system, the percolation limit is falling between 30 and 40 phr loading of the filler. There have been some studies on the percolation limit of carbon black filled elastomers,[40] but it has not been reported in CSDPF reinforced elastomers. Das[40] divided the variation of resistivity of EPDM based compounds with filler loading into two parts: (a) inductive region in which there is a small decrease in resitivity with filler loading, which is due to the transportation of the small number of charged particles through the system without having any continuous conductive network and (b) percolation region where resistivity decreases sharply.

Many questions on the actual mechanism for electrical transport through such heterogeneous materials are still prevalent. It is largely admitted that their electrical properties primarily depend on the way the filler particles are dispersed in the polymer matrix. There are several models that are supposed to describe this dispersion, usually called the mesostructure.[41,42] 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 electrical properties, it fails to predict the location of the threshold. It has long been recognized that the conductivity not only depends on the geometry of the filling particles but also on the actual processing of the materials.[43] As far as the discrepancy between actual and lattice exponents is concerned, it may be considered as a proof of the inadequacy of the lattice percolation theory to account fully the conduction through such media. However, the relationship between such models and the actual mesostructure of the materials still remains unclear. The theoretical value of the percolation threshold for randomly-dispersed, hard, and spherical particles has been determined to be about 16 vol %.[44] However, in the present system of CSDPF-CIIR composites, the percolation limit was observed in between 27 and 33 vol % of the filler. This deviation can be explained on the basis of agglomeration of the filler particles in the matrix. The addition of fractal fillers (i.e., carbon black and CS-DPF) lead to the formation of agglomerates or clusters because of their high specific activity of the chemical groups on the surface of the filler.

CONCLUSIONS

The dynamic mechanical analysis of the vulcanizates showed that the addition of the filler has no significant effect on the glass-transition temperature, T_g. However, on increasing 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 tan δ and storage modulus with strain was also studied All the vulcanizates showed a rapid decrease in storage modulus on increasing DSA while tan δ increases. The dielectric relaxation spectra of the composites showed an additional relaxation in the frequency range of 1×10^5 to 2×10^5 Hz. This was explained on the concept of formation of interphase layer between the filler and the polymer matrix. The percolation limit of the filler in the matrix as obtained by resistivity measurements showed at 30–40 phr.

References

1. Medalia, A. I. Rubber Chem Technol 1973, 46, 877.
2. Wang, M.-J.; Mahmud, K.; Murphy, L. J.; Patterson, W. J. Kautschuk Gummi Kunststoffe 1998, 5, 348.

3. Murphy, L. J.; Wang, M.-J.; Mahmud, K. Rubber Chem Technol 1998, 71, 998.
4. Dutta N. K.; Khastagir, D.; Tripathy, D. K. J Mater Sci 1991, 26, 188.
5. Smit, P. P. A. Rheol Acta 1966, 5, 277.
6. Hess, W. M.; Lyon, F.; Burgess, K. A. Kautsch Gummi Kunstst 1967, 20, 135.
7. Huber, G.; Vilgis, T. A. Macromolecules 2002, 35, 9204.
8. Vilgis, T. A.; Heinrich, G. Kautsch Gummi Kunstst 1995, 48, 323.
9. Kluppel, M.; Heinrich, G. Rubber Chem Technol 1995, 68, 623.
10. Karatasos, K.; Ryckaert, J. P.; Ricciardi, R.; Lauprete, F. Macromolecules 2002, 35, 1451.
11. Richter, D. A.; Arbe, A.; Colmenero, J.; Monkenbusch, M.; Farago, B.; Faust, R. Macromolecules 1998, 31, 1133.
12. Strenstein S. S.; Zhu, A. J. Macromolecules 2002, 35, 7262.
13. Chazeau, L.; Brown, J.; Yanyo, L.; Sternstein, S. Polym Compos 2000, 21, 202.
14. Maier, P. G.; Gortiz, D. Kautsch Gummi Kunstst 1996, 49, 18.
15. Lin, E. K.; Kolb, R.; Satija, S. K.; Wu, W.-L. Macromolecules 1999, 32, 3753.
16. Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. Phys Rev Lett 2002, 1996, 77.
17. Roland, C. M.; Bero, C. M. Macromolecules 1996, 29, 7521.
18. Runt, J. P.; Fitzgerald, J. J., Eds. Dielectric Spectroscopy of Polymeric Materials, Fundamentals and Applications; American Chemical Society: Washington, DC, 1997.
19. Matsuoka, S. Relaxation Phenomena in Polymers; Hanser: Munich, 1992.
20. Ngai, K. L.; Rendell, R. W. J Non-Cryst Solids 1991, 942, 131.
21. Kramarenko, V. Y.; Ezquerra, T. A.; Sics, I.; Balta' -Calleja, F. J.; Privalko, V. P. J Chem Phys 2000, 113, 447.
22. Casalini, R.; Fioretto, D.; Livi, A.; Lucchesi, M.; Rolla, P. A. Phys Rev B 1997, 56, 3016.
23. Glatz-Reichenbach, J. K. W.; Sorriero, L. J.; Fitzgerald, J. J. Macromolecules 1994, 27, 1338.
24. Prochazka, F.; Durand, D.; Nicolai, T. J Rheol 1999, 43, 1511.
25. Shalaby, S. W. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic Press: London, 1981.
26. Ishida, H.; Koenig, J. L. Polym Eng Sci 1978, 18, 128.
27. Mijovic, J.; Lin, K. F. Advances in Chemistry-206; American Chemical Society: Washington, DC, 1984; Chapter 19.
28. Douglas, E. P.; Waddon, A. J.; MacKnight, W. J. Macromolecules 1994, 27, 4344.
29. Nielsen, L. E.; Lewis, T. B. J Polym Sci Polym Phys Ed 1969, 7, 1705.
30. Eklind, H.; Schantz, S.; Maurer, F. H. J.; Jannasch, P.; Wesslen, B. Macromolecules 1996, 29, 984.
31. Eklind, H.; Maurer, F. H. J. Polymer 1996, 37, 2641.
32. Eklind, H.; Maurer, F. H. J.; Steeman, P. A. M. Polymer 1997, 38, 1047.
33. Colombini, D.; Martinez-Vega, J. J.; Merle, G.; Girard-Reydet, E.; Pascault, J. P.; Gerard, J. F. Polymer 1999, 40, 935.
34. Schlosser, E.; Schonhals, A. Colloid Polym Sci 1989, 267, 133.
35. Pissis, P.; Apekis, L. In Proceedings of the Conference on Relaxations in Complex Systems. Crete. June 16-23, 1991; Ngai, K. L., Ed.; J. Non-Cryst Solids 1991, 131, 95.
36. Wong, J.; Angell, C. A. Glass: Structure by Spectroscopy; Marcel Dekker: New York, 1976.
37. Bakule, R.; Havranek, A. Rubber Chem Technol 1978, 51, 72.
38. Fischer, E. W.; Zetache, A. Polym Prepr (Am Chem Soc Div Polym Chem) 1992, 33, 78.
39. Roland, C. M.; Ngai, K. L. Macromolecules 1992, 25, 363.
40. Das, N. C., Ph.D. Thesis, Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 2001.
41. Pike, G. E.; Seager, C. H. Phys Rev B 1977, 48, 5152.
42. Kirkpatrick, S. Rev Mod Phys 1973, 45, 574.
43. Janzen, J. J Appl Phys 1975, 46, 966.
44. Halperin, B. I.; Feng, S.; Sen, P. N. Phys Rev Lett 1985, 54, 2391.