

Effect of Carbon Blacks on Relaxation Phenomenon of Chlorobutyl Vulcanizates

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Received 24 August 2005; accepted 29 October 2005

DOI 10.1002/app.23640

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

ABSTRACT: The effect of the types of carbon black on the physicochemical, dynamic mechanical, and dielectric relaxation spectra in chlorobutyl vulcanizates was 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 by positron annihilation lifetime spectroscopy (-70 to $+100^\circ\text{C}$). Irrespective of the type of carbon black that was used, all composites showed glass-transition temperatures in the range of -29 to -33°C , which was explained on the basis of the relaxation dynamics of polyisobutylene chains in the vicinity of the fillers. The secondary relaxation (α^* or β relaxation) was studied using

dielectric relaxation spectra in the frequency range of 100 – 10^6 Hz. The nonlinear strain dependent dynamical parameters (Payne effect) were also evaluated at dynamic strain amplitudes of 0.07 – 5% . The nonlinearity in the $\tan \delta$ and storage modulus was explained by the concept of filler-polymer interactions and the interaggregate attraction (filler networking). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1809–1820, 2006

Key words: dynamic mechanical properties; dielectric relaxation spectroscopy; free volume; fillers; bound rubber; vulcanizates

INTRODUCTION

The majority of commercially available polymeric materials consist of a polymer matrix with properties augmented by the addition of filler materials. Carbon black is widely used as a filler in polymeric matrices to improve the mechanical properties (reinforcement) and/or to transform an insulating material (polymer) into a conducting one.¹ With the exception of thermal blacks, most carbon blacks consist of fractal aggregates of carbonaceous primary particles produced by incomplete combustion of oils. The primary particles, which are on the order of a few 10s of nanometers in diameter,² aggregate to form a mass fractal a few hundred nanometers in size with a mass fractal dimension (D_m) close to 1.8 .^{3–5}

The effects of fillers on the mechanical properties of elastomers are of great interest, primarily because the judicious use of fillers can enhance many physical properties. Fillers also strongly influence the viscoelastic properties of elastomer compounds. The dynamic properties of elastomers filled with structural fillers are influenced by factors like the type of fillers, volume fraction of filler, processing conditions, and strain history. The most fundamental feature of the reinforcement of rubbers by fillers is the size of the filler particles. Carbon blacks with nearly spherical

particles of $0.5 \mu\text{m}$ average diameter are not entirely reinforcing; their reinforcing ability depends on surface chemistry, size, and type of elastomer in which they are added. Trexler et al.⁶ reported the effects of types of carbon black on the dynamic properties of elastomers over a wide temperature range of -40 to $+40^\circ\text{C}$. They made a comparison of fillers with equal filler loading. Tripathy and Dutta^{7,8} studied the effects of the types of fillers (black and nonblack) on the physical and dynamic properties of bromobutyl vulcanizates.

The present article deals with the physicochemical and 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 dynamic strain amplitudes of 0.07 – 5% . An attempt was made to correlate the relaxation behavior to the free volume as measured by positron annihilation lifetime spectroscopy (PALS).

EXPERIMENTAL

Materials

Chlorobutyl 1240 with 1.25% chlorine content and a Mooney viscosity of 38 (ML_{1+8}) at 100°C was procured from Bayer. The plasticizer was highly saturated pharmaceutical grade processing oil (specific gravity = 0.82) supplied by C. D. Pharmaceuticals

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TABLE I
Compounding Formulations of Mixes

Ingredient	Phr
Chlorobutyl Rubber	100
Stearic Acid	1.0
Processing Oil	4
ZnO	5
ZnCl ₂	1.3
TMTD	3
S	2.6
Carbon black	40

(Calcutta, India). Zinc oxide was chemically pure grade with a specific gravity of 5.4. TMTD was supplied by ICI Ltd. (Rishra, Hooghly, India) with a specific gravity of 1.42. Other compounding ingredients were chemically pure grade and procured from standard suppliers.

Fillers

All furnace blacks were supplied by Phillips Carbon Black Ltd. (Durgapur, India). The designation and properties of the carbon blacks were as follows:

1. intermediate super abrasion furnace (ISAF): product name N-110, 18nm mean particle diameter, 142 m²/g surface area, 112 mL/100 g dibenzoyl peroxide (DBP) absorption, pH 7.8;
2. high abrasion furnace (HAF): product name N-330, 80 m²/g surface area, 104 mL/100 g DBP absorption, pH 7.6;
3. product name N-375: 18-nm mean particle diameter, 100 m²/g surface area, 114 mL/100 g DBP absorption, pH 7.0;
4. general purpose furnace (GPF): product name N-660, 67-nm mean particle diameter, 45 m²/g surface area, 91 mL/100 g DBP absorption, pH 7.6;
5. semireinforcing furnace (SRF): product name N-774, 79-nm mean particle diameter, 32 m²/g surface area, 72 mL/100 g DBP absorption, pH 7.7;
6. medium thermal (MT): product name N-990, 285-nm mean particle diameter, 24 m²/g surface area, 54 mL/100 g DBP absorption, pH 7.9.

Sample preparation technique

The details of the mixes are given in Table I. The compounds were mixed in a laboratory size (325 × 150 mm) mixing mill at a friction ratio of 1 : 1.25 according to ASTM D 3182 standards while carefully controlling the temperature, nip gap, mixing time, and uniform cutting operation. The temperature range for mixing was 65–70°C. After mixing, the elastomer com-

positions were molded in an electrically heated hydraulic press to optimum cure (90% of the maximum cure) using molding conditions determined by a Monsanto rheometer (R-100).

Test procedures

Physical test methods

The curing characteristics of the compounded stocks were determined using an R-100 oscillatory disk rheometer according to ASTM D 2084. The modulus, tensile strength, and elongation at break were determined according to the ASTM D 412 procedure at 28°C using dumbbell-shaped specimens punched out using a type D die. The tear strength was determined according to ASTM D 624 (type C). Both the tensile and tear tests were carried out using a Hounsfield H10KS universal testing machine at a crosshead speed of 500 mm/min. The hardness was measured according to ASTM D 2240.

Dynamic mechanical analysis (DMA)

DMA was carried out using a Thermal Instruments 2980 dynamic mechanical analyzer (V1.7B). The experiment was carried out over a temperature range of –60 to +100°C with a programmed heating rate of 3°C/min at an amplitude of 20 μm and a frequency of 1 Hz. The strain dependent dynamic properties were evaluated on a Rheovibron DDV III EP (Orientec Corp.) at room temperature. The dynamic strain amplitude in tension mode was varied between 0.07 and 5%.

Dielectric relaxation spectra

The dielectric relaxation spectra of the vulcanizates were obtained with a Hioki LCR meter in a frequency range of 100–10⁶ Hz.

Positron annihilation studies

The PALS unit used was an automated EG&G Ortec fast-fast coincidence system with a ²²Na radioactive source. The testing was carried out in a temperature range of –70 to 110°C.

Bound rubber

The bound rubber was measured by equilibrium swelling of the rubber compound according to the procedure reported by Leblanc⁹ using three solvents (cyclohexane, chloroform, and trichloroethylene). About 0.5 g of the sample was cut into small pieces and introduced into a bottle in 150 mL of solvent for 7 days at room temperature. The solvent was filtered

TABLE II
Physical Properties of CIIR Vulcanizates

Compound	Tensile strength (MPa)	Modulus at 300% (MPa)	Elongation at break (%)	Hardness (Shore A)	Heat buildup (°C)
C _{ISAF}	16.95	4.277	951	40	32
C _{HAF-L}	16.66	4.266	732.3	41	26
C _{HAF-H}	17.47	4.544	724.4	45	26
C _{GPF}	15.45	3.39	787.4	39	24
C _{SRF}	9.68	1.339	1398	37	22
C _{MT}	10.84	3.384	722.4	34	19

out, and the remaining sample was dried for 8 h at room temperature and then for 24 h under a vacuum at 40°C. Complete drying was checked by a constant final weight. The amount of bound rubber (BdR), which is percentage of the initial rubber content of the compound, was calculated from

$$BdR = 100 \times \frac{(M_0 - M_b) - \left[\frac{CPD(M_0)}{100} \left(\frac{M_0}{M_e} \right) \right]}{(M_0 - M_b)} \quad (1)$$

where CPD is the total formulation (phr), M_0 is the initial weight (bottle + unextracted sample), M_b is the empty bottle weight, and M_e is the final weight (bottle + extracted samples) when dried.

RESULTS AND DISCUSSION

Physicomechanical properties

Observe from Table II that the tensile strength and modulus increases with increasing specific surface area and decreasing particle size (from ISAF to MT) in carbon black fillers. The tensile strength can be regarded as catastrophic tearing of cracks initiated from accidental flaws, microvoids, dewetting, or cavitation from the filler surface.¹⁰ If the elastomeric network is capable of dissipating this input energy into heat, less elastic energy will be available to break the polymer network. Incorporation of fillers is a major source of energy dissipation, thereby increasing the tensile strength of carbon black filled vulcanizates. As the particle size decreases (from ISAF to MT) large surface areas become available. This leads to greater polymer–filler interaction and greater probability of molecular slippage that thereby dissipates more input energy as heat, thus increasing the fracture energy. There is no clear explanation or mechanism for enhancement of the elastic modulus due to filler addition by one simple theory, because several interactions and many different length scales are involved.¹¹ The rubber matrix is elastic in nature and the addition of the fillers into the rubber matrix contributes to different mechanisms, the most well known being the volume effects, which are also called hydrodynamic interactions

based on the analogy of the enhancement of the viscosity of the liquids by the addition of particles.¹² A model presented by Witten et al.¹³ for the stress–strain properties of rubbers filled with fractal aggregates such as carbon black predicts lateral compression of aggregates. In the case of carbon black filled elastomers it is widely believed that the contribution to reinforcement on small scales can be attributed to the complex structure of the branched filler aggregates as well as to a strong surface polymer interaction, leading to so-called bound rubber. (A more detailed discussion on bound rubber is given in the subsequent section.) It is widely accepted that the filler particles are coated with polymer chains, and the binding (physically or chemically) of elastomer chains to the surface of the filler particles significantly changes the elastic properties of the macroscopic material.¹⁴ When elastomers are reinforced with functional fillers like carbon black, the applied stress is transferred from the elastomer matrix to the strong and stiff mineral filler. This stress transfer will be better effected if the filler particles are smaller, because greater surface is exposed for a given mineral concentration. For a filler to be more effective, it must make intimate contact with the elastomer chains if it is going to contribute to reinforcement of the rubber–filler composite. Fillers that have a high surface area (ISAF, HAF) have a greater potential to reinforce the rubber chains. Fillers with strong chain attachments, via active sites or coupling agents, provide the most resistance to the chain extension and separation required for elongation and ultimate rupture.¹⁵

The tensile strength increases as the particle size decreases. Several possible mechanisms for this have been suggested. Decreasing particle size increases the interfacial area of the per unit volume of filler, thus providing effective dissipation of the catastrophic external forces. Another factor that also influences the higher tensile strength is the behavior of the filler particle size on the stress field. The stress field near a particle is independent of the size of the particle.¹⁶ However, the volume of the polymer that experiences a given value of stress concentration increases with the particle size, so that the probability of finding a large

flaw within this volume also increases. If a large flaw exists within this area of stress concentration, the tensile strength is greatly reduced.¹⁷

Elongation is the ability of a rubber vulcanizate to stretch without breaking. All rubbers are composed of hydrocarbon skeletons consisting of a large number of carbon atoms to form a chainlike structure. Thus, when a tensile force is applied in a uniaxial direction, these chains tend to straighten out. However, the extent to which these chains extend is limited to straightening of the C=C bond angle. The presence of small solid particles in rubber changes the stress field, increases the local strain of the chains, and leads to local heterogeneities.^{18,19} It is well recognized that the mechanical properties of these materials depend on the topology of the filler's surface and on the adsorption properties of the chains.^{20,21}

With the addition of fillers, like carbon black, to the vulcanizates, the free space between the chains is filled, thus depriving the chains of straightening and thereby reducing the elongation. This is evident from the data shown in Table II, which shows increasing elongation with decreasing particle size of the carbon black particles. The decreasing particle size of the fillers marginally decreases the elongation. The smaller the particle size is, the higher the specific surface area; more crosslinks are formed during vulcanization, thereby trapping the free ends of polymer chains. Recent studies²² using H-NMR imaging demonstrated the presence of several microvoids in the isobutylene matrix. These small voids tend to nucleate at the critical stage for crack growth, leading to lower mechanical properties. Stress-strain forces are amplified near a void, thereby creating nucleation sites for craze and crack growth. The presence of a large number of polymer microvoids leads to undesirable physical properties.

Bound rubber

Bound rubber is widely considered in the rubber industry as a measure of polymer-filler interactions. The phenomenon of bound rubber in rubber compounds has been studied extensively and is considered a typical feature of surface activity. Bound rubber can be defined as the rubber portion of an uncured compound, which cannot be extracted by a good solvent because of adsorption of rubber molecules onto the filler surface.

Table III shows the variation of bound rubber content for chlorobutyl compounds filled with 40 phr of ISAF, HAF, GPF, SRF, and MT carbon blacks extracted with cyclohexane, chloroform, and trichloroethylene. In the solvents it is evident that ISAF loaded CIIR has the highest bound rubber values and MT black filled has the lowest. The high reinforcement and the high

TABLE III
Bound Rubber of Compounds Extracted with Various Solvents

Compound	Cyclohexane	Chloroform	Trichloroethylene
C _{ISAF}	64.5	49.695	55.42
C _{HAF-H}	57.21	41.36	48.65
C _{HAF-L}	55.02	38.25	45.21
C _{GPF}	44.6	28.56	34.75
C _{SRF}	39.28	19.54	29.34
C _{MT}	19.62	9.65	11.24

percentage of bound rubber content of SAF is attributed to the small size, high surface area, and high structure whereas MT is weakest because of its comparatively large size, low surface area, and low structure. With an increasing structure of carbon black, the breakdown of the aggregates during mixing is greater, which results in an increase in filler-polymer interfaces. In addition, there is higher surface activity of a freshly built surface of carbon blacks, which results in instantaneous interactions between the carbon black and the rubber chain ends.

The high values of bound rubber are consistent with the observations of Gessler,²³ who conducted in-depth research on the bound rubber properties of isobutylene based elastomers and obtained exceptionally high bound rubber values in sulfur added compounds. He postulated that free radicals are generated by mechanical breakdown during milling of rubber and carbon black, which is responsible for the higher bound rubber content. For chlorobutyl compounds, he explained this phenomenon with a two-step theory: the reaction of sulfur with black and the reaction of this sulfur modified black with the polymer. The surface groups on carbon black react with sulfur and cure accelerators so that $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed.

Hess et al.²⁴ and Serizawa et al.²⁵ studied the bound rubber phenomenon in saturated or nearly saturated elastomers like butyl rubber and found that the oxygen functionality of the carbon blacks has a profound effect in bound rubber formation. In the case of high structured and high surface area carbon blacks like SAF and HAF, Ban et al.²⁶ demonstrated the existence of physical adsorption that results in bound rubber formation. Wolff and Wang²⁷ proposed that the rubber chains may repeatedly attach onto the carbon black surface at different sites, reducing the effectiveness of the surface because only a single attachment would render the whole molecule inextractable in a solvent. Therefore, with decreasing particle size of the carbon blacks, the probability of multiattachment of rubber chains increases, thereby showing more bound rubber values.

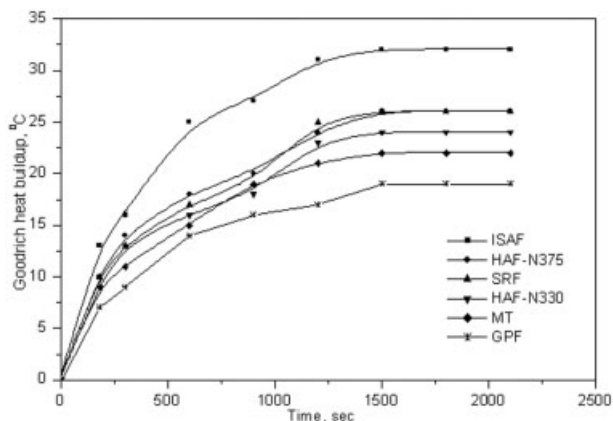


Figure 1 The effect of the dynamic compression time on the Goodrich heat build-up at 323 K with a stroke amplitude of 4.45×10^{-3} m at a stress of 0.999 MPa for CIIR vulcanizates.

Heat build-up

The values of the Goodrich heat build-up are plotted against time in Figure 1 for different samples. The temperature increases with time for all the samples until a plateau is reached. As expected, the decreasing particle size of carbon black increases the heat build-up. Heat generation in a rubber compound is not an intrinsic material property; it depends on the physical properties of the rubber size and the structure of filler particles and the nature of crosslinks in the vulcanizates. With decreasing particle size of the filler, the specific surface area increases. This leads to increased filler–filler and polymer–filler interactions, thereby increasing the heat build-up.

Dynamic mechanical properties

Effect of temperature on $\tan \delta$

Polymeric viscoelastic materials are widely used as vibration absorbers. For this function, the amplitude of the loss tangent is important (Table IV). The effect of the surface area of carbon black on the temperature dependence of $\tan \delta$ in CIIR vulcanizates is shown in Figure 2. Several studies reported that the $\tan \delta$ in-

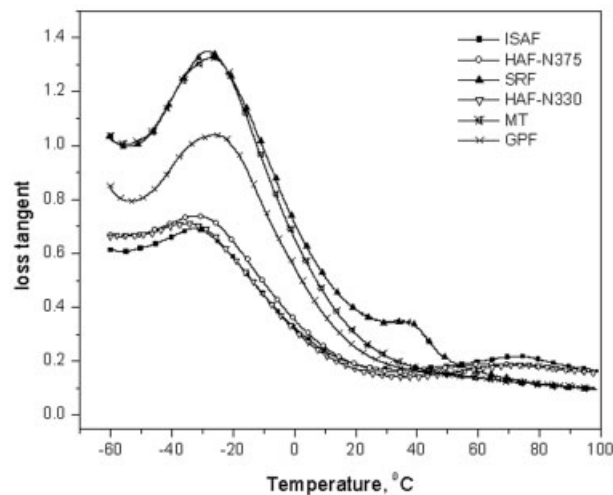


Figure 2 The variation of the $\tan \delta$ with temperature in carbon black loaded chlorobutyl vulcanizates.

creases with increased filler surface area.^{28–30} The dynamic properties of filled rubber vulcanizates are influenced by the particle size or surface area and structure. Increasing the surface area of carbon blacks at a constant loading causes an increase in the Payne effect.³¹ This increase suggests a strong tendency for agglomeration of carbon black aggregates in the rubber matrix. This phenomenon occurs at low temperatures where the vulcanizate is in rubbery state. At temperatures below the glass-transition temperature (T_g), where rubber falls in the transition zone, the $\tan \delta$ increases with decreasing surface area of fillers. The effect of the surface area of carbon black on the temperature dependence of $\tan \delta$ may be interpreted mainly by filler networking. Wolff and Wang³² studied the effect of polymer–filler and filler–filler interactions on the dynamic properties in styrene–butadiene rubber compounds. He suggested that an increased effective volume of filler loading would cause a higher $\tan \delta$ at a higher temperature and a lower $\tan \delta$ at lower temperatures. Filler–filler interactions, producing greater damping, are more likely to occur when the filler particles exist as weakly interacting agglomerates at higher filler loadings. Polymer–filler interactions can also lead to higher $\tan \delta$ values within a rubbery matrix by polymer chain segments moving past the solid filler surface. Figure 2 shows that the effect of carbon black on the $\tan \delta$ is maximum as the second plateau in the storage modulus (E') is approached and it remains large in the plateau region. Therefore, the loss modulus (E'') is a function of both the surface area and structure of the filler.

Two varieties of HAF blacks of essentially similar particle size and distribution, one with low structure (N330) and the other with high structure (N375), were used to study the effect of structure on the dynamic mechanical properties in CIIR vulcanizates. There is

TABLE IV
Dynamic Mechanical Characteristics

Sample	Temperature, $T_{\tan \delta \max}$	Loss tangent, $\tan \delta_{\max}$
ISAF	-32.44	0.69
HAF (N375)	-30.43	0.74
HAF (N330)	-31.45	0.71
GPF	-29.09	1.04
SRF	-29.79	1.23
MT	-28.34	1.33

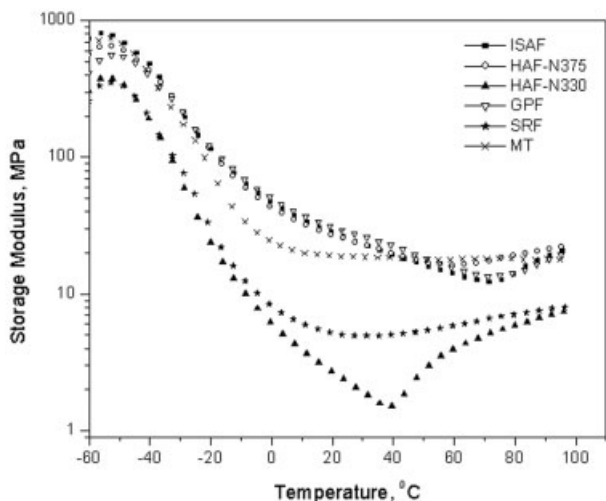


Figure 3 The variation of the storage modulus with temperature in carbon black loaded chlorobutyl vulcanizates.

little difference observed in the $\tan \delta$, with the lower structured HAF showing slightly lower values. In comparison with conventional products, carbon blacks with a broad aggregate size distribution generally give lower $\tan \delta$ values at temperatures where the rubber is in a rubbery state.

Effect of temperature on storage modulus

The variation of the E' with temperature for elastomeric composites is a very important design criterion. Nielsen et al.^{33,34} have pointed out that an elastomer composition with dynamic mechanical properties less sensitive to temperature changes is required for vibration isolation applications. Figure 3 shows the E' for different vulcanizates over a temperature range of -60 to $+100^\circ\text{C}$. The characteristic sigmoidal variation of the E' with the temperature is apparent from the plot for all compositions. Irrespective of the loading of filler, particle size, and structure, increased filler loading enhances the E' value. Tripathy and Dutta^{7,8} showed that in the glassy region the increase in E' is independent of the type, particle size, and structure of filler in BIIR vulcanizates. The effect of incorporation of a filler (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 that 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 due to the hydrodynamic effect) can be observed. However, if the particle–matrix adhesive force is large, then the modulus of the mixture is primarily determined by the magnitude of the polymer–filler interactions. Two studies suggested that there are three elastomer components in filled rubber samples that are distinguished by their characteristic molecular mobility: immobilized, intermediate, and mobile fractions.^{35,36} The relaxation properties of the composites are heavily dependent on the percentage of these fractions. Carbon blacks also fall in the category of active fillers wherein the surface chemical groups on the carbon black surface lead to the formation of weak chemical crosslinks with the polymer matrix.

At lower temperatures the finer particle black (ISAF and HAF) filled vulcanizates exhibit less temperature sensitivity. However, with an increase in temperature, the temperature sensitivity is comparable in all compositions.

Effect of temperature on loss modulus

Figure 4 represents the temperature dependence of E'' for various black filled CIIR vulcanizates. The DMA tests were carried out from a region just outside the α transition. The α peak is located in the transition region between the glassy and rubbery states. The type and loading of filler do not affect the α -peak temperature; however, the intensity of the α peak increases with increasing particle size of the filler. The crossover point was observed in the region of -50 to -45°C . In the rubbery region, E'' also shows the same trend as observed in E' , that is, E'' decreases with lower structure and lower particle size of blacks. To explain the influence of carbon black on the loss mod-

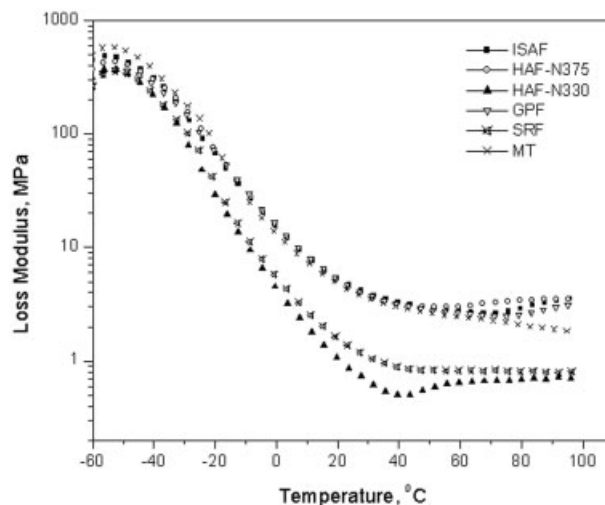


Figure 4 The variation of the loss modulus with temperature in carbon black loaded chlorobutyl vulcanizates.

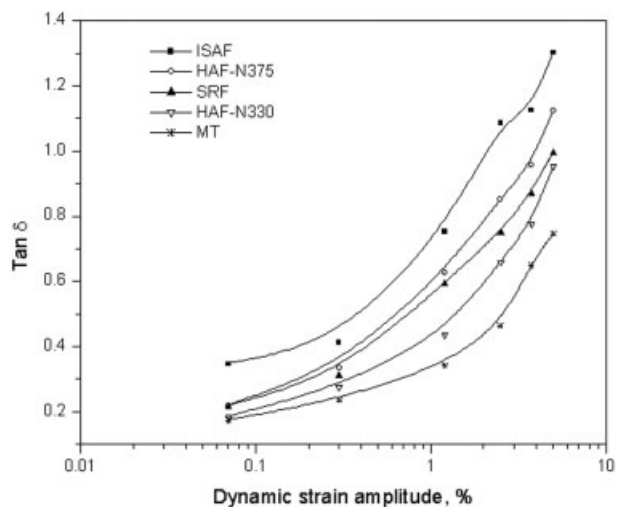


Figure 5 The effect of the dynamic strain amplitude on the loss tangent.

ulus, Kraus et al.³⁷ noted a close relationship between the decrease in storage modulus with agglomeration–deagglomeration of the primary aggregates that are formed during the process of vulcanization. Wolff and Wang³⁸ postulated that there is always a difference in the surface energy between the filler and polymer for a filled compound. Thus, even for a system in which the filler is well or uniformly dispersed in the polymer matrix, the filler aggregates tend to agglomerate during vulcanization and storage of the compound, forming a filler network. This effect is termed flocculation in a colloid system, like the filler–elastomer extensively reviewed by Bohm et al.^{39,40} Therefore, it can be said that particle size and filler–polymer interaction have profound influence on the loss modulus. This study found that N330, which has the lowest particle size, has the maximum loss modulus at all temperatures whereas MT black, because of its high particle size, has the lowest loss modulus.

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

Figure 5 shows the variation in $\tan \delta$ as a function of dynamic strain amplitude for compounds containing various types of carbon black. Regardless 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 (around 1% dynamic strain amplitude), the $\tan \delta$ 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 the hard rubber shell surrounding the filler aggregate, or breaking and reforming of the effective

crosslink in the rubber forming a 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 the filler size becomes very small, although the exact nature of this structure is not clear. In the case of particulate fillers like carbon black, 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 distance less than their size.⁴¹ This is mostly attributable to the intricate effects of the filler arrangement in the elastic matrix and 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 PALS.⁴² (A more detailed explanation of PALS in chlorobutyl vulcanizates is given in subsequent sections.)

Effect of dynamic strain amplitude on storage modulus

Figure 6 shows the variation in the storage modulus as a function of the dynamic strain amplitude for chlorobutyl vulcanizates reinforced with various types of carbon blacks. With increases in strain there is a decrease in the storage modulus. All vulcanizates show the highest E' at lower strains. This can be explained by the fact that increasing the amplitude of oscillation causes the gradual breakdown of the secondary structure and results in a dynamic modulus reduction. At

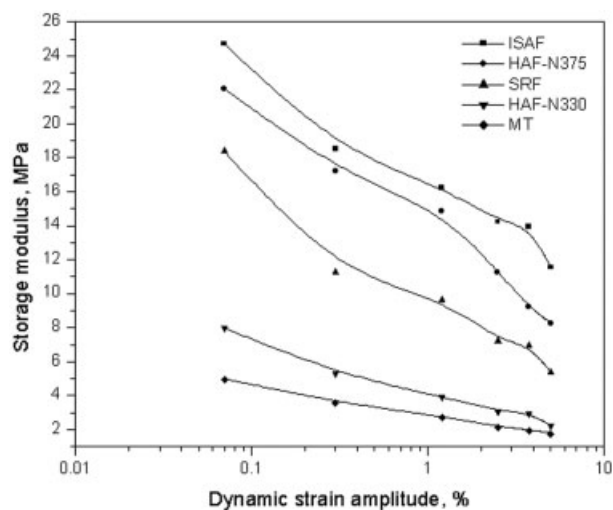


Figure 6 The effect of the dynamic strain amplitude on the storage modulus.

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 becomes 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.

The nonlinearity is less pronounced with higher particle size fillers (SRF, GPF). However, the nonlinearity is more pronounced in the vulcanizates with low particle sized fillers (ISAF, N375, N330). This can be explained on the basis of polymer–filler interaction, the desorption and reabsorption of the hard rubber shell surrounding the filler aggregate, or breaking and reforming of effective crosslinks 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 the filler size becomes very small, although the exact nature of this structure is unclear. This is mostly due to the intricate effects of solid particles arrangements in the elastic matrix and changes of the polymer chain dynamics near the surface of the particles. These two effects have been the object of various approaches. First, the generally dispersed arrangement of the particles as fractal aggregates contributes in a complex manner to both the linear and nonlinear mechanical properties of filled rubbers. The main idea is that fractal aggregates can strongly increase the elastic modulus. However, under strain there is an evolution of their fractal geometry that leads to a decrease in the value of the elastic modulus. This so-called hydrodynamic reinforcement effect is difficult to quantitatively describe however, because it requires very precise knowledge of the particles' arrangement. Second, the modification of the polymer dynamics near the surface of the particles is more puzzling. It has been suggested that the dynamics of adsorption/desorption of the polymers chains at the particle surface may be responsible for various linear and nonlinear effects. It is also difficult to separate a true size effect from agglomeration. Some researchers tend to equate "microstructure" to "agglomeration" or filler networking and therefore filler agglomeration is also widely cited for the nonlinear behavior of filled polymer melts. Many researchers showed that the chemical structure of the polymer chain has a profound influence on its relax-

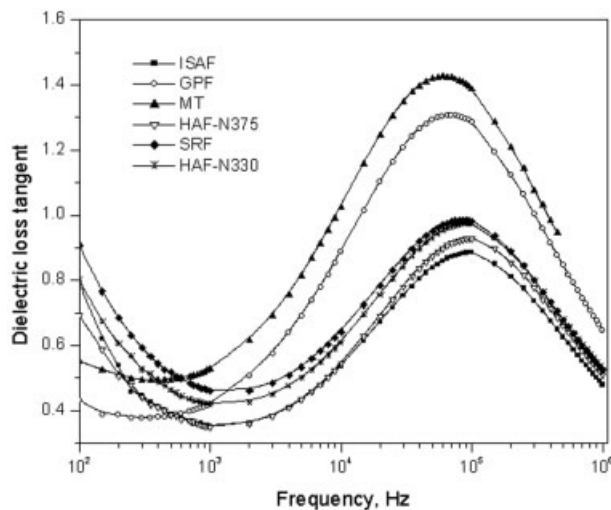


Figure 7 The variation of the dielectric loss tangent as a function of frequency in carbon black loaded chlorobutyl vulcanizates.

ation behavior. 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. Because the amount of bound rubber is related to the surface area and the surface activity of carbon blacks, it is widely accepted that this phenomenon is caused by a multi-contact chain adsorption to the surface of the filler. A number of structure–property relationships have been established between the content of bound rubber and the mechanical properties of filled rubbers.

Dielectric relaxation spectra

Dielectric relaxation spectroscopy (DRS) is a useful complement to the more customary DMA for probing the viscoelastic properties of polymers.⁴³ 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 advantages like reduced interference that is due to symmetry arising from shorter time processes, making it more accurate.⁴⁴

Figure 7 shows the variation of the dielectric loss tangent as a function of frequency in chlorobutyl vulcanizates reinforced with various types of carbon blacks. With increasing particle size the loss tangent increases, as is evidenced by the higher values in MT black and the lowest value in ISAF and HAF blacks. Between the two HAF blacks investigated, the lower structured one (N330) has lower loss tangent values. This may be attributed to the better dispersion of the filler in the matrix when compared to higher structured N375. Recent studies on carbon black reinforced

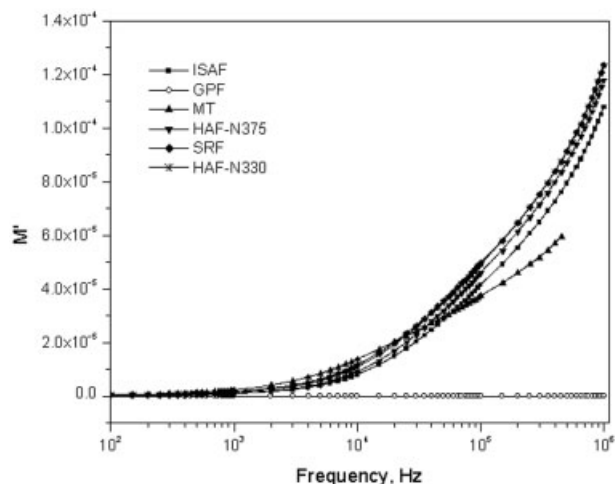


Figure 8 The variation of the real part of the electric modulus (M') as a function of frequency in chlorobutyl vulcanizates reinforced with different types of carbon black.

branched polyisobutylene⁴⁵ showed that, even though there was no significant effect of branching of the polymer matrix on the percolation limit of the filler, the intensity of the loss tangent had a definite effect.

Figure 8 show the variation of the real part of the electric modulus as a function of frequency in carbon black loaded CIIR vulcanizates. Although there have been many recent studies to evaluate the relaxation phenomenon in polyisobutylene elastomers, most studies have been made on unvulcanized (non-crosslinked) and unfilled samples; whereas for most practical applications, a polymer is crosslinked and reinforced. Crosslinking of the polymers usually imposes intermolecular constraints. Intermolecular constraints play an important role in the segmental dynamics of all polymeric systems in the bulk state.⁴⁶ Several groups have studied the influence of the crosslinking degree on the relaxation by distinct techniques, such as dielectric spectroscopy, DMA, or creep and stress-strain measurements.⁴⁷ These studies revealed that the most striking effects caused by the increase of crosslinker concentration is 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. Observe from Figure 8 that with the increase in frequency there is a gradual reduction in real impedance in all vulcanizates, but the intensity of reduction is dependent on the filler type. In systems reinforced with lower filler particle sizes, this phenomenon can be observed only until 10,000 Hz, beyond which the effect of frequency on real impedance is absent; however, in systems of higher particle size a continuous decrease of real impedance until the range of 10^5 Hz is observed, beyond which there is a further increase. This can be explained

by the viscoelastic properties of crosslinked multiphase polymeric materials, which depend on molecular relaxation processes and the morphology of the composites. Although these relaxations can usually be associated with each component, their appearance also depends on the chemical and physical interactions between the phases (filler and polymer matrix). Carbon blacks like MT, SRF, and GPF show less interaction with the polymer matrix, because of their lower surface activity, thereby leading to the formation of a weak interphase compared to other carbon blacks. The thickness of the interphase is inversely proportional to the interfacial tension between the polymeric phases. Obviously, the properties of such an interfacial region differ from those of the pure components, and they 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. The interphase formed between the filler and the polymer matrix has distinct properties that differ from the bulk. A polymer layer having a higher stiffness than the bulk polymer in the vicinity of the dispersed phase surface is created from restricted molecular mobility that is attributable to interactions between phases.⁴⁸

Further proof regarding the importance of the interphase on the relaxation can be seen in Figure 9, which shows the variation of the complex part of the electric modulus as a function of frequency. In SRF, MT, and GPF reinforced systems, an additional damping peak is observed in the frequency range of 10^5 Hz, which can be attributed as an α^* - or β -relaxation peak.⁴⁹ 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

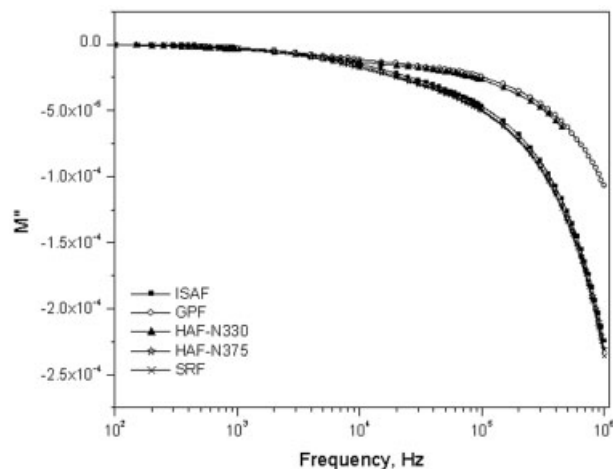


Figure 9 The variation of the imaginary part of the electric modulus (M'') as a function of frequency in chlorobutyl vulcanizates reinforced with different types of carbon black.

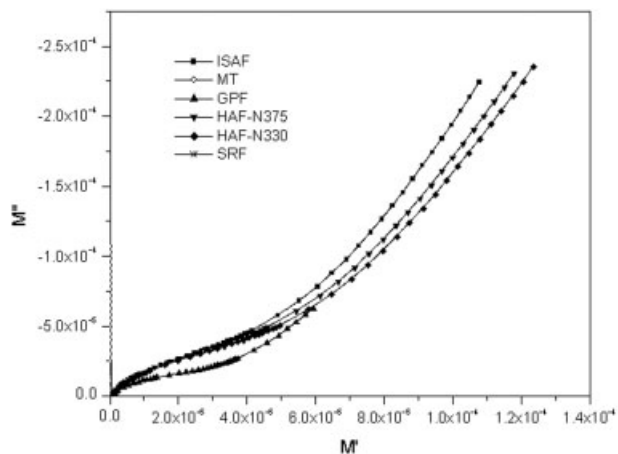


Figure 10 A Nyquist plot of chlorobutyl vulcanizates reinforced with different types of carbon blacks.

width and the asymmetry of the relaxation function usually deviate from the values because of the Debye function. There is a strong discussion about the physical origin of this deviation,⁵⁰ but it is known empirically that this effect depends on the degree of crosslinking and the level of interactions between the fillers and the polymer⁵¹ or microheterogeneity.⁵²

PALS

The polymer free volume is defined as the difference between the total free volume of the material and the volume occupied by the molecules (Fig. 10). It is a characteristic of amorphous polymers because it is created by chain entanglements and folding. Not only does the free volume in polymers have a controlling effect on the molecular mobility and the kinetic dynamic behavior in the polymer matrix, but it is also closely related to the mechanical, physical, and relaxational properties of the polymers.⁵³ The mechanical properties of composites like the impact strength, fracture toughness, and loss modulus all increase as the free volume increases, because the free volume facilitates the deformation of the material. The positron annihilation technique is capable of probing the free volume "holes" in polymer materials based on the fact that positron annihilation lifetime and momentum correlation of the annihilation photon pair are very sensitive to the surrounding electron density and distribution in localized sites.

Figure 11 shows the variation of the *ortho*-positronium lifetime (τ_3) of chlorobutyl vulcanizates reinforced with various types of carbon black from -80 to 110°C . Far below the T_g (-70°C), we observe that, irrespective of the type of the filler, all composites show almost similar τ_3 values. This can be explained by suppression of macro-Brownian motions in the polymer matrix. At temperatures far below the T_g , the

composite is in "glassy state" wherein the polymer chains lack the necessary thermal energy required to move and tend to occupy less space. With an increase in temperature, at -30°C there is a sudden increase in the values of τ_3 . This corresponds to the T_g of the composite, which was also observed using other relaxation techniques like DMA. 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 micro-Brownian motions due to the segmental mobility of the polymer chains. Above the T_g the free volume increases rapidly with the temperature, which is due to macro-Brownian motion (i.e., the mobility of the main chain segments), 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:

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

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 Jacob,⁵⁴ who reported that chain alignment causes an increase in the number of larger, more elliptical free volume cavities, resulting in the evolution of a broader distribution of free volume in the composites. At higher temperatures (above 70°C) the composites reinforced with ISAF

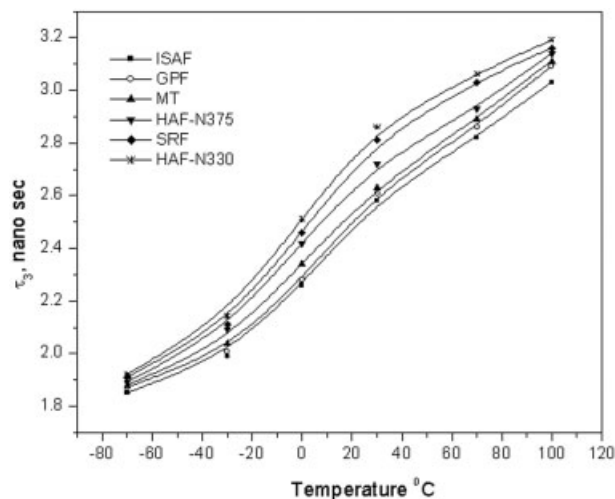


Figure 11 The temperature dependence of the free volume parameter (τ_3) in carbon black reinforced chlorobutyl vulcanizates.

and HAF show lower τ_3 values compared to other systems. This can be related to the relaxation dynamics of the polyisobutylene chains in filled systems. Helfand and coworkers found that the motions of a polymer chain in a long time range are affected by the surrounding molecules, which are acting as walls, whereas in a short time range the motions are surprisingly similar to those observed in a single isolated chain.^{55,56} Previous studies by Karatasos and Ryckaert⁵⁷ showed that polyisobutylene based polymers show secondary relaxations around 70°C, which are related to the conformational transitions in the global scale. However, in reinforced polymers, these conformational transitions are localized because of the decreased degrees of freedom imposed on the chains by the neighboring bonds and topological constraints. However, these constraints do not completely stop their relaxation, because polymer chains are sufficiently flexible to make conformational transitions. Carbon blacks like ISAF and HAF with more interactions with the polymer matrix impose more constraints on the relaxation dynamics of polymer chains when compared to other blacks like SRF, GPF, and MT. This effect is more pronounced at 100°C where the difference in τ_3 is quite noticeable.

CONCLUSIONS

The effect of the addition of various types of carbon black on the physicomechanical, dynamic mechanical, and dielectric relaxation spectra in chlorobutyl vulcanizates was studied. DMA and PALS showed that the glass-transition temperature was in the range of -29 to -33°C, regardless of the type of carbon black used. This was explained on the basis of the relaxation dynamics of polyisobutylene chains in the vicinity of fillers. The dielectric relaxation spectra (tested in the frequency range of 100–10⁶ Hz) of the composites showed additional relaxation at 10⁵ Hz, which can be attributed to the secondary relaxations of the polyisobutylene chains (α^* or β). The nonlinear strain dependent dynamic parameters (Payne effect) were also evaluated at dynamic strain amplitudes of 0.07–5%. The nonlinearity in the $\tan \delta$ and storage modulus was explained by the concept of filler–polymer interactions (as studied with bound rubber) and interaggregate attraction (filler networking).

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