

# Physico-Mechanical, Dynamic Mechanical, and Swelling Properties of Sodium Chloride Filled Chlorobutyl Vulcanizates

V. Sridhar, D. K. Tripathy\*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India

Received 9 February 2005; accepted 10 June 2005

DOI 10.1002/app.23316

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

**ABSTRACT:** The effect of addition of rigid, nonreinforcing, and noninteracting filler viz. finely ground NaCl in chlorobutyl vulcanizates on properties such as physico-mechanical, dynamic mechanical, and swelling has been studied. The nonreinforcing effect of NaCl in the system was studied by Russel and Cunnenn analysis and Kraus plots. Mechanical measurements of stress and strain at the break of filled and unfilled samples showed no appreciable change in the mechanical behavior of the system. The dynamic mechanical analysis showed that there is no change at all in the glass transition temperature with addition of NaCl filler. The damping properties showed an increase with increase in

filler loading because of the filler–filler friction. The swelling behavior of NaCl-filled CIIR was studied for a period of 60 days in four different solvents of varying chemical energy potential viz. water, chloroform, acetone, and tetrahydrofuran (THF). The degree of swelling was found to increase continuously with time in water, which is a good solvent for the filler, and in THF, which is a good solvent for the polymer matrix. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 707–714, 2006

**Key words:** vulcanizates; swelling; fillers

## INTRODUCTION

Butyl and halobutyl elastomers are widely used in vibration isolation applications because of its outstanding ability to absorb mechanical energy and excellent stability when exposed to ozone and aqueous corrosive chemicals. The properties of halobutyl elastomers that distinguish it from other low unsaturation rubbers such as EPDM include a higher impermeability to gases and vapors, much greater adhesive strength, a greater effectiveness as shock absorber over a wide temperature range of  $-10$  to  $+80^{\circ}\text{C}$ , better tear strength, and good ageing properties. The main advantage of chlorobutyl rubber over conventional butyl elastomers is the versatility of curing systems due to the presence of allylic chlorine and conjugated diene bonds. The other advantages of chlorobutyl rubber over regular butyl rubber are rapid rate of cure, with reduced curative levels, cure compatibility, and better dry heat resistance. This combination of properties makes it potentially superior base elastomer for manufacture of a variety of mechanical goods ranging from heavy duty shock absorbers to smaller sound

and vibration damping mountings, hoses, belting, and many other tire and nontire applications.

The effect of addition of rigid filler to a polymeric system is a topic of research for more than 40 years, with NaCl being the most widely used. Gessler,<sup>1</sup> Nielsen,<sup>2,3</sup> and Schwartz<sup>4</sup> have studied the effect of NaCl addition in polyurethane, natural rubber, and butyl rubbers. Bahar et al.<sup>5</sup> gave a detailed study of the swelling of butadiene elastomers of different crosslink densities with finely divided sodium chloride (NaCl) particles in water, water/acetone, and water/THF mixtures. Briggs et al.<sup>6</sup> and Edwards<sup>7</sup> reported absorption of water by butyl elastomers. They observed that crosslinked butyl elastomers absorbed significant amount of water when small amount of salts were added to the samples during crosslinking.

The present work is part of ongoing study of effects of fillers viz. carbon black,<sup>8</sup> nanoclays,<sup>9</sup> and carbon silica dual phase filler<sup>10</sup> on the physico-mechanical, dynamic mechanical, and swelling properties of chlorobutyl vulcanizates. Considering the importance of water wettability and water absorption of chlorobutyl elastomers in many practical applications, the present study is undertaken to further understand the mechanism of water absorption. Four solvents are used in this study. Cyclohexane and tetrahydrofuran (THF) are good solvents for the polymer matrix, whereas water is an excellent solvent for NaCl filler, and acetone is a poor solvent for both NaCl and the rubber.

Correspondence to: D. K. Tripathy (dkt@rtc.iitkgp.ernet.in).

\*Present address: Director, National Institute of Technology, Warangal 506004, Andhra Pradesh, India.

TABLE I  
Compounding Formulation of the Mixes

Ingredient	Phr
Chlorobutyl Rubber	100
Stearic Acid	1.0
Processing Oil	4
ZnO	5
ZnCl <sub>2</sub>	2.3
TMTD	3
S	2.6
Sodium chloride	Varying proportions

## EXPERIMENTAL

### Materials

Bayer Chlorobutyl 1240 with 1.25% chlorine content and with Mooney viscosity  $ML_{1+8}$  at 100°C = 38 was procured from Bayer AG. The diameter of NaCl particles used as filler was about 100 μm. ZnO was of chemically pure grade, with specific gravity 5.4. TMTD was supplied by ICI chemicals (Rishra, India). Other compounding ingredients (Table I) were of chemically pure grade and procured from standard suppliers.

### Experimental

ZnCl<sub>2</sub> and NaCl are highly deliquescent and were therefore dried for 7 days at 110°C before use. The compounds were mixed in a laboratory size (325 mm × 150 mm) two-roll mill at a friction ratio of 1 : 1.25, according to ASTM D 3182, by careful control of temperature, nip gap, time of mixing, and uniform cutting operations. After mixing, compounds were molded in an electrically heated hydraulic press at 160°C to the optimum cure (90% of the maximum cure), using molding conditions previously determined from torque data obtained by a Monsanto rheometer (R-100), according to ASTM D 2084 and ASTM D5289 procedures. Tensile properties and tear strength were evaluated according to ASTM D 412 and ASTM D 624 standards, respectively, using a Hounsfield H10KS Universal Testing Machine. Hydraulic grips were used to ensure line contact and to minimize slipping. Dynamic mechanical properties were carried on a TA Instruments dynamic mechanical testing analyzer (DMTA), over a temperature range of -60 to 100°C at a frequency of 1 Hz.

### Sorption experiments

Sorption experiments were performed on uniformly cut cylindrical discs of diameter 1.9 cm by immersion/weight gain method. Initially, the samples were dried overnight in a vacuum desiccator, the original weights were taken, and the thicknesses were measured within

+0.001 cm at several places. The average thickness was found to be 0.200 cm. The polymer samples were immersed in solvents having various compositions of water, water/chloroform, water/THF, and water/cyclohexane at room temperature for 60 days in specially designed air-tight bottles. At regular intervals, the test samples were removed, and the surfaces were dried between filter paper wraps, weighed immediately to nearest 0.05 mg, and placed back into the test bottles.

### Determination of crosslink density

In general, crosslink density (CLD) can be measured three different ways:

1. by stress-strain measurements and evaluation by the Mooney-Rivlin equation<sup>11,12</sup>
2. by the determination of the elastic modulus at a certain temperature in the rubbery plateau zone<sup>13,14</sup>
3. by swelling measurements using the Flory-Rehner equation.<sup>15</sup>

The values of CLD thus obtained will give different results partly because of the time scale of the measurements.<sup>6</sup> Because of the equilibrium nature of swelling measurements, the value of CLD will have lower contributions from the entanglements, as the time scale of the experiment permits disentanglement of temporary entanglements. DMTA measurements on the other hand will show much larger proportion of entanglements, as there is not enough time for disentangling.

### Characterization of molecular weights

The average molecular weight  $M_C$  of the network chains between crosslinks was obtained by two sets of experiments: (a) equilibrium stress-strain isotherms on dry unfilled networks and (b) swelling isotherms of samples in solvents. In equilibrium stress-strain method the large deformation elastic moduli were determined, and the values of  $M_C$  were calculated using the following expression:

$$M_C = \frac{1}{2} \frac{\rho RT}{[f^*]_{ph}} \quad (1)$$

where  $\rho$  is the density of dry polymer and  $[f^*]_{ph}$  is the "phantom network modulus" obtained at large deformations. The average molecular weight obtained from solvent swelling studies were calculated using the expression

$$M_C = \frac{\rho(1 - \nu_{2c})V_1\nu_{2c}^{2/3}\nu_{2m}^{1/3}}{\ln(1 - \nu_{2m}) + \chi\nu_{2m}^2 + \nu_{2m}} \quad (2)$$

**TABLE II**  
**Normalized Stress and Strain at Break Values for CIIR Vulcanizates Filled at Different NaCl Loadings**

NaCl % by weight	Stress ( $\sigma_{\text{filled}}/\sigma_{\text{unfilled}}$ )	Strain ( $\varepsilon_{\text{filled}}/\varepsilon_{\text{unfilled}}$ )	Storage modulus (MPa) at RT ( $E'_{\text{filled}}/E'_{\text{unfilled}}$ )	Loss modulus (MPa) at RT ( $E''_{\text{filled}}/E''_{\text{unfilled}}$ )	Storage modulus (MPa) at $-30^{\circ}\text{C}$ ( $E'_{\text{filled}}/E'_{\text{unfilled}}$ )	Loss modulus (MPa) at $-30^{\circ}\text{C}$ ( $E''_{\text{filled}}/E''_{\text{unfilled}}$ )
0	1.00	1.00	1.00	1.00	1.00	1.00
10	1.18	0.84	1.35	0.92	1.11	0.96
20	1.23	0.76	1.65	0.82	1.17	0.92
30	1.34	0.59	1.94	0.67	1.22	0.87

where  $\chi$  is the interaction parameter between solvent and the polymer network,  $\phi$  is the average junction functionality,  $V_1$  is the molar volume of the solvent,  $v_{2c}$  is the volume fraction of polymer during crosslinking, and  $v_{2m}$  is the experimentally determined volume fraction at equilibrium.

### Bound-rubber measurements

Bound rubber of the rubber compound was measured according to the procedure reported by Leblanc et al.<sup>16</sup>, using cyclohexane as solvent. About 0.5 g of the sample was cut into small pieces and introduced into a bottle containing 150 mL of solvent for 7 days at room temperature. The solvent was filtered out, and the remaining sample was dried for 8 h at room temperature, then for 24 h under vacuum at  $40^{\circ}\text{C}$ . Complete drying was checked by a constant final weight. The amount of bound rubber (BdR) (in percentage of initial rubber content of compound) was calculated from

$$\text{BdR} = 100 \times \frac{(M_0 - M_b) - \left[ \frac{\text{CPD}(M_0)}{100} \left( \frac{M_0}{M_c} \right) \right]}{(M_0 - M_b)} \quad (3)$$

where CPD is the total formulation [ in parts per 100 rubber (phr) ];  $M_0$  is the initial weight (bottle + unextracted sample),  $M_b$  is the empty bottle weight, and  $M_c$  is the final weight (bottle + extracted samples) when dried.

## RESULTS AND DISCUSSION

### Characterization of mechanical properties

The normalized stress-strain properties of NaCl-filled chlorobutyl vulcanizates as a function of filler loading is shown in Table II. The values of stress,  $\sigma_{\text{max}}$ , and strain at break,  $\varepsilon_{\text{max}}$ , are given in the second and third columns, respectively. These are normalized with respect to the corresponding values for unfilled samples. The ratios obtained in this manner are around unity, indicating that the inclusion of salt as filler does not produce reinforcing effects, contrary to those observed with carbon black, carbon silica dual phase filler, or

nanoclays. This was explained by Fedors<sup>17</sup> on the basis of dewetting. He postulated that the poor filler-matrix adhesion induces dilation effect in rubber, thereby triggering dewetting process, which reduces the surface area in contact with the filler, which in turn reduces the filler's efficiency in enhancing the modulus. This detrimental effect of dewetting was further studied by Nielsen,<sup>18</sup> who found an increase in dewetting with the filler loading. Schwarzl<sup>4</sup> conducted a detailed study of the addition of rock salt in polyurethane and explained the low values of tensile strength by Griffith's theory.<sup>19</sup> He explained that the stress fields in a rubber-filler matrix are independent of the size of the filler particle; however, the volume of the polymer that experiences a given value of stress concentration increases with the particle size, thereby increasing the probability of finding a large flaw within this volume. If a large flaw exists within an area of stress concentration, the tensile strength reduces. This trend is also seen in storage and loss modulus, which are discussed in detail in the subsequent sections.

The ratios obtained in this manner are around unity, which indicates that the salt added into the system is not reinforcing. The normalized values of storage and loss modulus at room temperature ( $32^{\circ}\text{C}$ ), obtained from dynamic mechanical analysis, also show the values to be around unity, thereby supporting the argument that the salt added into the system does not act as reinforcing filler.

### Evaluation of reinforcibility

According to Kraus equation<sup>20</sup> the reinforcing effect of a filler can be found by the equation

$$\frac{V_{r0}}{V_{rf}} = 1 - m \left( \frac{f}{1-f} \right) \quad (4)$$

where  $V_{rf}$  is the volume fraction of rubber in the solvent-swollen filled sample and is given by

$$V_{rf} = \frac{(d - fw)\rho_p^{-1}}{(d - fw) + A_s\rho_s^{-1}} \quad (5)$$

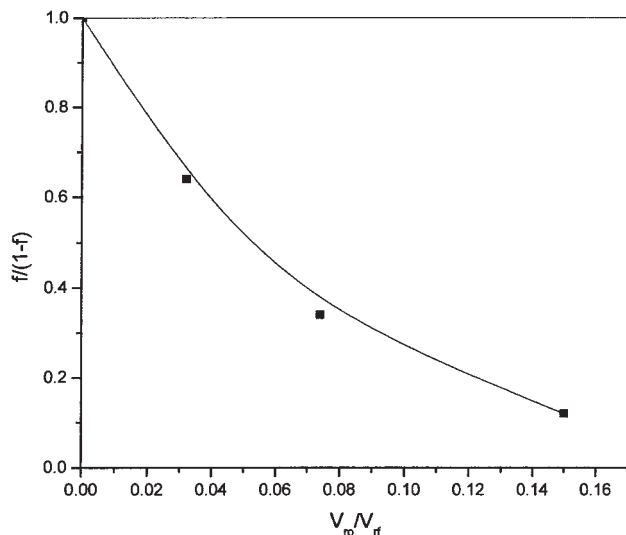


Figure 1 Kraus plot of NaCl-filled chlorobutyl vulcanizate.

where  $d$  is the deswollen weight of the sample,  $f$  is the volume fraction of the filler in unswollen sample,  $w$  is the initial weight of the sample,  $\rho_p$  and  $\rho_s$  are the densities of the polymer and solvent, respectively, and  $A_s$  is the amount of solvent absorbed after correction for the swelling increment and is given by the equation

$$A_s = A_x \frac{(1 - dx)}{100} \quad (6)$$

where  $A_x$  is the weight of the solvent absorbed after  $x$  hours of immersion, which is equal to  $(W_x - d)$  where  $W_x$  is the swollen weight of the specimen after  $x$  hours.

$$\partial x = 100 \frac{(W_s - W_g)}{W_0} \quad (7)$$

For an unfilled system, since there is no filler, volume fraction of filler  $f = 0$ . Substituting this in eq. (4), the expression for volume fraction of rubber,  $V_{r0}$ , in the solvent swollen unfilled sample is obtained. Kraus equation has the general form of straight line, where a plot of  $\frac{V_{r0}}{V_{rf}}$  against  $\frac{f}{1-f}$  gives a straight line with a slope, which is the direct measure of reinforcing ability of the filler used. Greater the reinforcing ability of filler, higher will be the will be the slope. Plots of Kraus equation for NaCl-filled chlorobutyl vulcanizate at different filler loadings for chloroform are shown in Figure 1. Cunnenn and Russel equation<sup>21</sup> is given by

$$\frac{V_{r0}}{V_{rf}} = ae^{-z} + b \quad (8)$$

where  $z$  is the weight fraction of filler used. A plot of  $\frac{V_{r0}}{V_{rf}}$  and  $e^{-z}$  gives a straight line with slope  $a$  being the measure of reinforcing ability of the filler. The plot of  $\frac{V_{r0}}{V_{rf}}$  and  $e^{-z}$  with increasing NaCl loading in chlorobutyl vulcanizates is shown in Figure 2. Both Kraus and Cunnenn–Russel analysis support the nonreinforcing nature of NaCl in chlorinated isobutylene–isoprene rubber (CIIR) matrix.

### Swelling studies

The variation of weight with time after intake of fluid for networks immersed in pure deionized water, various water/THF, water/cyclohexane, and water/acetone mixtures is shown in Figures 4–7. The degree of swelling,  $Q$ , is defined as the ratio of swollen network to dry network. Since the present network is heterogeneous finely divided NaCl particles dispersed in chlorobutyl matrix, the values of  $v_2$  were evaluated macroscopically using the method described by Erdal et al.<sup>5</sup>

### Swelling in pure water, acetone, THF, and cyclohexane

The variation of  $Q$  with time for water is shown in Figure 3. The data were fitted by B-spline method to get a smooth curve. The composite with the highest amount of NaCl showed more swelling than that of lower filler loadings. All the networks show double sigmoid shape, indicating an accelerated uptake of solvent in initial stages, and a slow down in intermediate stage, followed again by accelerated uptake.

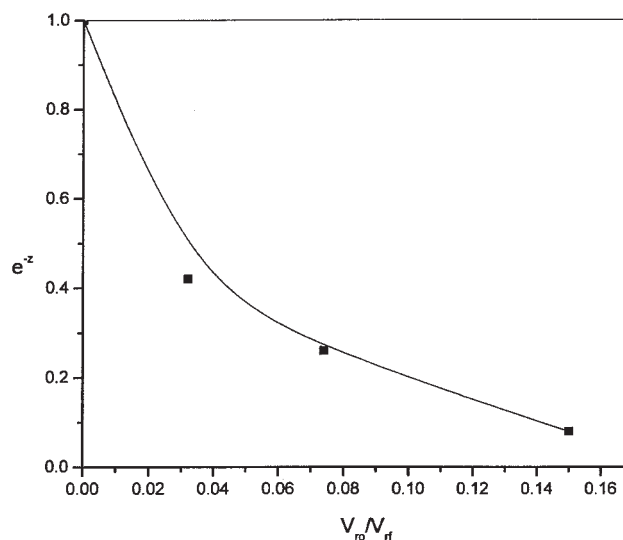


Figure 2 Russel and Cunnenn plot for NaCl-filled chlorobutyl vulcanizate.

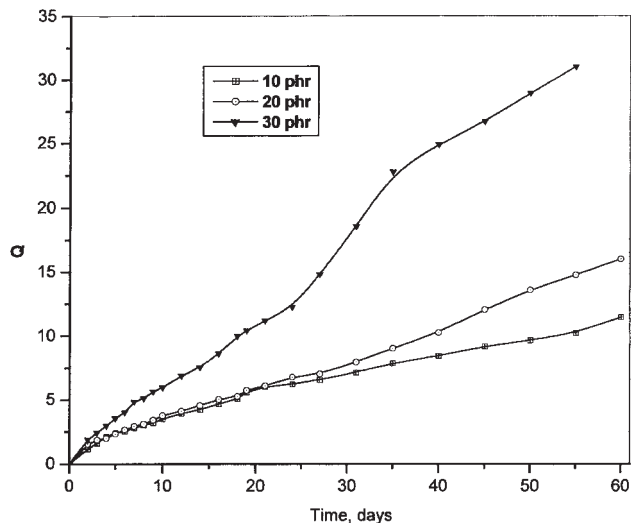


Figure 3 Swelling ratio (Q) of samples having different NaCl loadings plotted against time in deionized water.

Equilibrium degree of swelling was not obtained even after 60 days. Initially, all the networks show an accelerated uptake of water because of the absence of any chemical bonds between the filler particles and the matrix. In intermediate stage, there is a slow down in uptake due to possible leaching out of salt particles into water and eventual diffusion of salt solution inside the networks back into the surrounding solvent. After the intermediate stage, there is an increased interaction between polymer matrix and solvent which increases the solvent uptake. The variation of Q with time for THF and cyclohexane is shown in Figures 4 and 5, respectively. All the networks, irrespective of filler loading, initially show a linear increase and tend to level off later. The plateau regions of

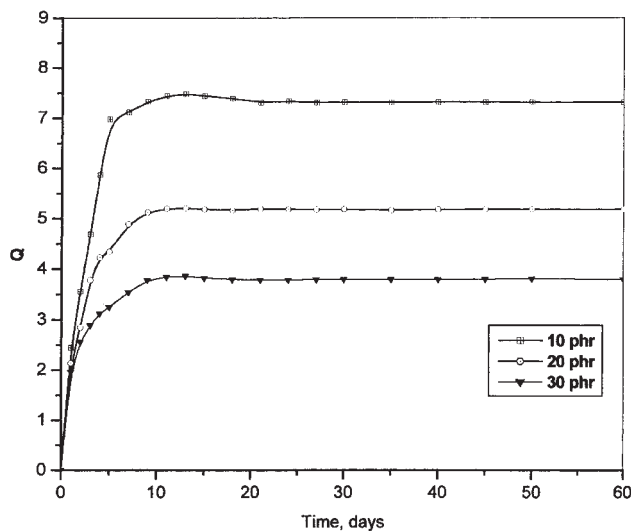


Figure 4 Swelling ratio (Q) of samples having different NaCl loadings plotted against time in THF.

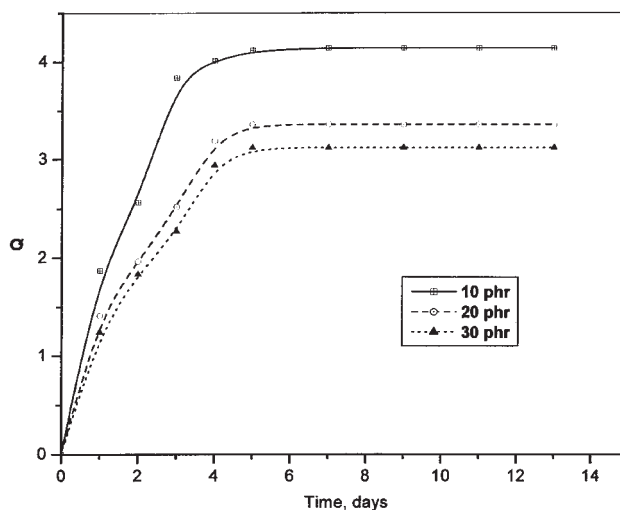


Figure 5 Swelling ratio (Q) of samples having different NaCl loadings plotted against time in cyclohexane.

curves give maximum sorption values; however, experiments were continued to ensure complete equilibration. This is a significant deviation from the data of water and acetone. Since NaCl is not soluble in either THF or cyclohexane, there is no diffusion of salt solution from networks to solvent. The degree of swelling is also small when compared with water, indicating the lack of diffusion of salt. The variable Q plotted as a function of time for acetone is shown in Figure 6. Since acetone is a poor solvent for chlorobutyl rubber, no swelling is observed, even after a significant period of time.

Dynamic mechanical properties

Tan δ

The variation of tan δ with temperature for unfilled and NaCl-filled CIIR vulcanizates is shown in Figure

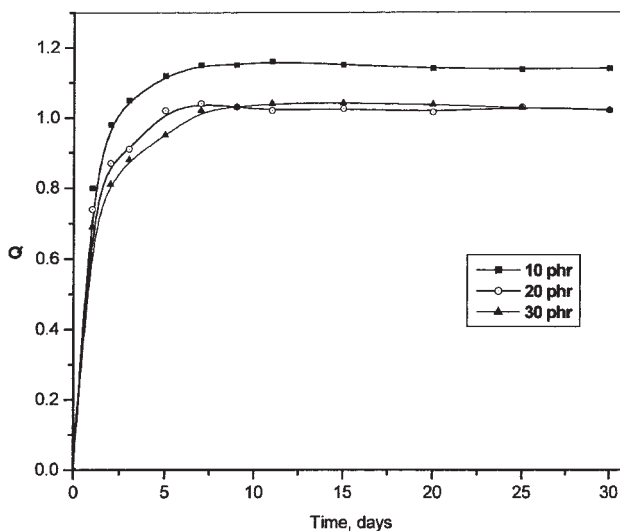
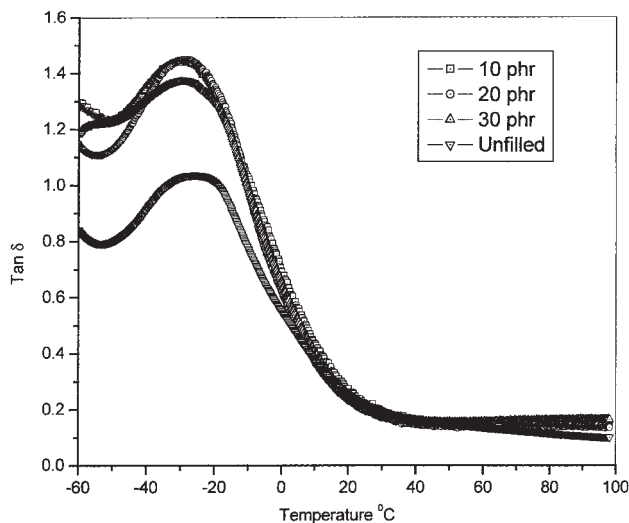


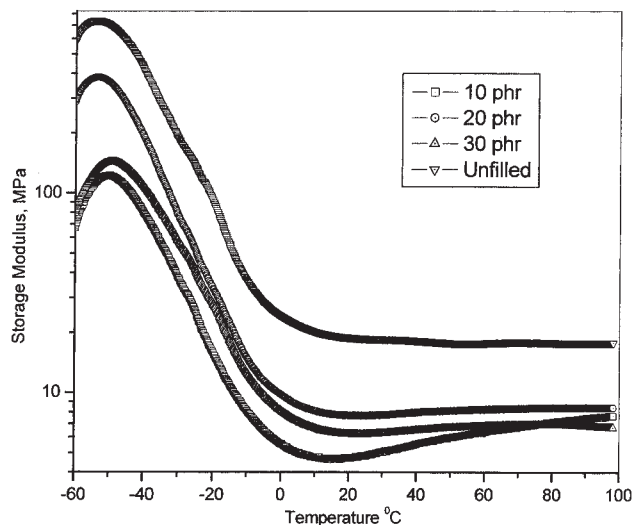
Figure 6 Swelling ratio (Q) of samples having different NaCl loadings plotted against time in acetone.



**Figure 7** Dynamic mechanical spectra of NaCl-filled CIIR vulcanizates: effect of increasing NaCl loading.

7. The maximum value of  $\tan \delta$  is occurring between the temperatures of  $-29$  to  $-30^\circ\text{C}$ , in all cases. This indicates that the addition of filler does not shift the glass transition temperature of the vulcanizates. This also indicates that no polymer chains are absorbed onto the filler surfaces, thereby causing no restriction to the mobility of polymer chains. But recent studies show that the dynamics of polymers near the immediate surface of the filler are very much different from that of the bulk.

Polymers are sensitive to the local environment, and the relaxation dynamics near the glass transition temperature,  $T_g$ , is essentially cooperative.<sup>22–25</sup> At  $T_g$ , the rate of the rearrangement or relaxation process of the polymer chain depends on the local environment surrounding the relaxation entities and hence reflects the extent of environmental restriction on those entities. Polymer chains undergo numerous modes of motion, involving a broad range of time and length scales. Segmental relaxation, associated with the glass to liquid transition, primarily involves correlated local motion of only a few backbone bonds.<sup>26,27</sup> The static structure and relaxation dynamics of polymers near rigid surfaces are believed to be fundamentally different from those in bulk materials. Substrates are for instance argued to decrease molecular configurational freedom,<sup>28,29</sup> induce collective glass like dynamics,<sup>30,31</sup> promote phase segregation,<sup>32</sup> and alter stress relaxation mechanisms available to adsorbed polymer chains.<sup>33</sup> Despite the vast literature on the subject, direct evidence of surface-induced changes in polymer properties is not available because of the difficulties associated with the visualization techniques. Besides reducing the configurational freedom of the chains, the restrictions imposed by the network junctions increase the local friction, enhancing intermolecular co-

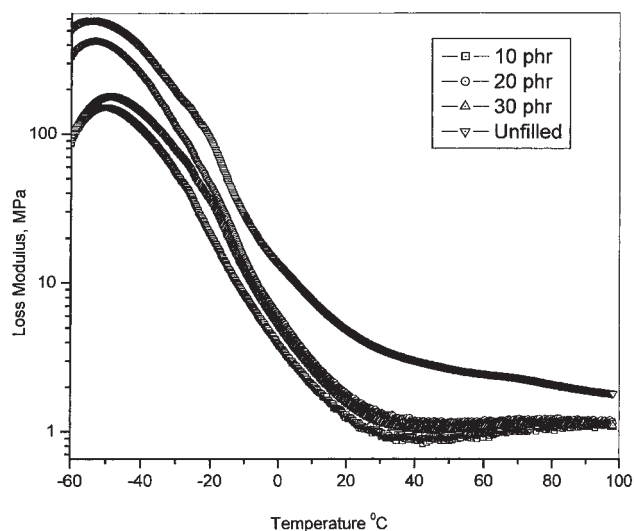


**Figure 8** Dynamic mechanical spectra of NaCl-filled CIIR vulcanizates: effect of NaCl concentration on storage modulus. Frequency, 1 Hz; strain, 0.1% DSA.

operativity as well.<sup>34–37</sup> These restrictions are in turn dependent on the degree of interaction of the polymer chains with the filler surface. Since the NaCl filler has no interactions whatsoever with the polymer chains, it is likely that it will enhance the intermolecular cooperativity, which leads to faster relaxation dynamics.

#### Storage and loss modulus

Figure 8 and 9 shows the variation of storage modulus  $E'$  and loss modulus  $E''$ , for chlorobutyl vulcanizates with increasing volume percentage of NaCl over a wide range of temperature ( $-60$  to  $100^\circ\text{C}$ ). The ap-



**Figure 9** Dynamic mechanical spectra of NaCl-filled CIIR vulcanizates: effect of NaCl concentration on loss modulus. Frequency, 1 Hz; strain, 0.1% DSA.

**TABLE III**  
**Bound Rubber Values of CIIR Vulcanizates**  
**Filled with 40 phr of Black**

Filler loading	Bound rubber (%)	Bound rubber (%) (after 30 days ageing)
0	32.15	39.58
10	34.56	42.91
20	36.97	47.62
30	39.28	50.47

plied dynamic strain amplitude and frequency test conditions were 0.1% DSA and 1 Hz, respectively. Increasing filler loading results in increase of storage modulus  $E'$  at all experimental temperatures. It is theorized that at low strains the filler is the main contributor to the reinforcing of the polymeric system. The NaCl particles dispersed in the system do not show any form of "network" because of the absence of van der Waal forces between the polymer matrix and the filler. Thus, the reinforcing effect is purely hydrodynamic in nature. There is a continuous increase in the storage and loss modulus with increasing filler loading at all the test temperatures. This increase is only due to the hydrodynamic effect. Previous studies showed that there is not much influence of crosslinking on the dynamic mechanical properties such as  $E'$  and  $E''$ . But, the amount filler loading, the filler-filler interaction, and the filler-polymer interactions play a crucial role in the dynamic viscoelastic properties of a filled polymer system. In NaCl-filled CIIR vulcanizates, there is an absence of filler-polymer interactions, and below the percolation limit, the filler particles exist only as individual particles with no agglomerations or aggregations among them.

The general effect of incorporation of rigid fillers into a polymeric system has been studied by Schwartz et al.<sup>38</sup> Fillers have a larger effect of increasing the modulus values more in the rubbery region rather than in the glassy region. This phenomenon is clearly observed from the data presented in Table III where in the normalized loss and storage modulus values are much closer to unity at  $-30^\circ\text{C}$  rather than at room temperature. With increasing filler loading, there is a clear broadening of the transition region in both storage and loss modulus curves accompanied by a slight shift to higher temperatures. This broadening is indicative of a change in relaxation mechanism as shown by Neilsen et al.<sup>39</sup> For NaCl-filled polyurethane system, Gray et al.<sup>40</sup> proposed that the incorporation of rigid fillers often increase the damping because of particle-particle friction, where particles touch another, which can be expressed by the following equation:

$$\frac{E''}{E'} = \left(\frac{E''}{E'}\right)\phi_1 + \left(\frac{E''}{E'}\right)\sigma_2 \quad (9)$$

The present system of NaCl-filled CIIR also shows increase in damping especially in the high filler loadings of 20 and 30 phr. At higher concentrations, weak agglomerates appear to form, which are easily broken up by applied stresses. As a result, the modulus is lowered, and particle-particle friction gives rise to higher damping. The other factor contributing to this effect is the large Poisson's ratio above the glass transition temperature,  $T_g$ , and the presence of induced thermal stresses below  $T_g$ . This is a significant observation, since there is increase in both storage and loss modulus without any change in glass transition temperature, thereby making NaCl-filled CIIR vulcanizates a potential candidate material for many vibration isolation applications.

## CONCLUSIONS

The present study was carried out with twin objectives of studying the effect of the addition of rigid, nonreinforcing, and noninteracting filler sodium chloride in CIIR vulcanizates.

At all filler loadings, the normalized stress-strain values are nearer to unity, which show that NaCl is nonreinforcing in nature. This was further tested by Russel and Cunnenn analysis and Kraus plots, which showed very low slopes nearer to unity. The values of normalized storage modulus and loss modulus obtained from dynamic mechanical analysis showed a larger increase in rubbery region (below  $T_g$ ) as compared with that in glassy region (above  $T_g$ ). The glass transition temperature  $T_g$  showed no change even at higher filler loadings and was found to be in between  $-29$  and  $-30^\circ\text{C}$ . The water wettability and water absorption of chlorobutyl elastomers was studied by swelling measurements using four solvents of varying cohesive energy density (CED) over a period of 60 days. THF, having higher CED, showed maximum swelling due to increased interaction between the solvent and the polymer matrix. The solvent with lower CED, water, showed no interaction with the polymer matrix, but increased interaction with the filler. The bound rubber values showed an increase with increasing filler loadings.

## References

- Gessler, A. M. *Rubber Chem Technol* 1969, 42, 850.
- Nielsen, L. E. *J Polym Sci* 1979, 17, 1897.
- Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994.
- Scharwatzl, F. R.; Bree, W. C.; Nederveen, C. J.; Van der Wal, C. W. *Rheol Acta* 1966, 5, 270.
- Bahar, I.; Erdal, S.; Erdman, B. *Polymer* 1998, 39, 2035.
- Briggs, G. J.; Edwards, D. C.; Storey, E. B. *Rubber Chem Technol* 1963, 36, 621.
- Edwards, D. C. *CHEMTECH* 1986, 10, 622.
- Sridhar, V.; Tripathy, D. K., to appear.

9. Sridhar, V.; Nayak, N. C.; Tripathy, D. K. *Polymer*, submitted.
10. Sridhar, V.; Shanmughraj, A. M.; Tripathy, D. K. *Rubber Chem Technol*, submitted.
11. Rivlin, R. S. *Rubber Chem Technol* 1992, 65, G51.
12. Mark, J. E.; Erman, B. *Rubber Like Elasticity. A Molecular Primer*; Wiley-Interscience: New York, 1988.
13. Ferry, J. D. *Viscoelastic Properties of Polymers*; Marcel Dekker: New York, 1965.
14. Collins, F. A.; Bares, J.; Billmeyer, F. W. *Experiments in Polymer Science*; Wiley: New York, 1973.
15. Flory, P. J.; Rehner, J., Jr.; *J Chem Phys* 1943, 11, 521.
16. Leblanc, J. L. *Prog Polym Sci* 2002, 27, 627.
17. Fedors, R. F.; Landel, R. F. *J Polym Sci Polym Phys Ed* 1975, 13, 579.
18. Nielsen, L. E. *J Compos Mater* 1967, 1, 100.
19. Griffith, A. A. *Philos Trans R Soc London Ser A* 1921, 221, 163.
20. Kraus, G. *J Appl Polym Sci* 1963, 7, 861.
21. Cunneen, J. L.; Russell, R. M. *Rubber Chem Technol* 1970, 43, 1215.
22. Angell, C. A. *Science* 1995, 267, 1924.
23. Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. *J Appl Phys* 2000, 88, 3113.
24. Hodge, I. M. *Science* 1995, 267, 1945.
25. Hutchinson, J. M. *Prog Polym Sci* 1995, 20, 703.
26. Adolf, D. B.; Ediger, M. D. *Macromolecules* 1992, 25, 1074.
27. Bahar, I.; Erman, B.; Kremer, F.; Fischer, E. W. *Macromolecules* 1992, 25, 816.
28. deGennes, P. G. *Macromolecules* 1980, 13, 1069.
29. deGennes, P. G. *Adv Colloid Interface Sci* 1987, 27, 18.
30. Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* 1995, 28, 3482.
31. Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* 1997, 30, 280.
32. O'Malley, J. J.; Thomas, H. R.; Lee, G. M. *Macromolecules* 1979, 12, 996.
33. Silberzan, P.; Leger, L. *Macromolecules* 1992, 25, 1267.
34. Ngai, K. L.; Roland, C. M.; Yee, A. F. *Rubber Chem Technol* 1993, 66, 817.
35. Roland, C. M. *Macromolecules* 1994, 27, 4242.
36. Ngai, K. L.; Roland, C. M. *Macromolecules* 1994, 27, 2454.
37. Roland, C. M.; Ngai, K. L.; Plazek, D. J. *Comput Theor Polym Sci* 1997, 7, 133.
38. Schwarzl, F. R.; Bree, H. W.; Nederveen, C. J. In *Proceedings of the 4th International Congress on Rheology*; Lee, E. H., Ed.; Wiley: New York, 1965; Vol. 3, p 241.
39. Nielsen, L. E.; Lewis, T. B. *J Polym Sci* 1965, 7, 1705.
40. Gray, R. W.; McCrum, N. G. *J Polym Sci* 1969, 7, 1329.