

# Effect of Silica and Rice Husk Ash Fillers on the Modulus of Polysiloxane Networks

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**ABSTRACT:** The preparation of polymethylvinylsiloxane rubbers with silica (SC) and black rice husk ash (BRHA) as fillers is reported. We conducted stress-strain experiments on these vulcanized rubbers to study the reinforcement properties of the fillers. Curves showing the dependence of the stress on the reciprocal of the elongation ratio displayed, in most cases, a slow upturn starting at rather low values of the elongation ratio attributed to a rather wide distribution of chain lengths between crosslinking points. Physical crosslinks between the hydroxyl groups of SC fillers and the polymer matrix seemed to enhance the modulus. BRHA-

polymer interactions were rather weak in comparison with those occurring between SC and the polymer, presumably as a consequence of the carbon coating of the surface of the former fillers. These interactions were even less important for calcined BRHA. The absence of voids in the polymer-filler interfaces was proven by the analysis of gas diffusion across the rubbers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 421–429, 2003

**Key words:** polysiloxanes; networks; fillers; mechanical properties

## INTRODUCTION

The conformational versatility of flexible polymers is responsible for the high elasticity displayed by these materials above their glass-transition temperatures. Elastic and viscous contributions to the deformation may be comparable, and as a consequence, polymeric materials exhibit a marked viscoelastic behavior. Crosslinking molecular chains with suitable molecular agents impede flow in shearing force fields. Although high elasticity is a bonus in most applications of crosslinked rubbery materials, the low strength resistance of these substances compared with that of other materials, such as ceramics and metals, decreases their applicability. Obviously, the modulus of rubbers can, in principle, be improved by an increase in crosslinking density, but this process decreases the elasticity of these systems. Fillers are used to improve the properties of rubbers without significantly reducing their elasticity.<sup>1–22</sup> In this context, reinforcing fillers are added to rubber formulations to promote the improvement of their mechanical properties, including modulus, hardness, compression and elongation, and rupture energy. The reinforcement properties depend

on the nature and amount of particles of fillers incorporated and on the shape and size distribution of the particles.<sup>1–22</sup>

Although a great deal of work related with the development of high-performance elastomers has been reported, a quantitative understanding of the effects of fillers on the elastic properties of rubbers is still lacking. For example, the anomalously high reinforcement power of fillers is still poorly comprehended. To get a glimpse into the reinforcement mechanisms, Mark and coworkers<sup>23–26</sup> prepared polysiloxane elastomers by precipitation *in situ* of fillers. These authors found that hydroxyl groups in silica (SC) greatly enhanced the modulus of silicone rubbers.

An important issue in big rice-producing countries, such as Brazil, is the enormous disposal of rice husk.<sup>27</sup> The burning process of this substance pollutes the environment with residual ash, and therefore, this is not the best way to get rid of the huge amounts of rice husk produced every year.<sup>28–34</sup> Both white rice husk ash (WRHA) and black rice husk ash (BRHA) obtained from burning rice husk could, in principle, be used as reinforcing agents in different rubbers. In 1995, Ishak and Bakar<sup>35</sup> studied the use of rice husk ash (RHA) in the WRHA and BRHA varieties for the reinforcement of elastomers, verifying that the mechanical properties of epoxidized natural rubber were inferior to those of composites prepared with commercial fillers, a fact attributed to the relatively large size of the particles that favored only a moderate reinforcement. RHA has

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TABLE I  
Physical Characteristics of Fillers Used in the Preparation of Polysiloxane Compounds

Property	Commercial SC	Gross BRHA	BRHA-MP	BRHA-C
Particle average diameter ( $\mu\text{m}$ )	10 (5–100)	35	3.0	7.0
Specific area ( $\text{m}^2/\text{g}$ )	108 (185)	74	139	1.06
Density ( $\text{g}/\text{cm}^3$ )	1.91 (2)	1.10	1.95	2.24
pH	6.74 (6.50)	9.26	8.98	10.14

The values in parentheses are those supplied by the manufacturers.

also been used as a filler in SBR, EPDM, and NR, where it hardly altered the vulcanization process and the lifetime of these rubbers. To our knowledge, no work has been reported concerning the use of rice husk for the reinforcement of polysiloxane elastomers.

In our laboratories, we undertook a study that involved the preparation and characterization of RHA as a filler for polysiloxane elastomers. In this article, the characterization and development of polysiloxane rubbers filled with RHA is described. We obtained stress–strain isotherms with the aim of analyzing how RHA fillers affect the properties of elastomers based on polysiloxane materials. Polysiloxane compounds filled with SC were also prepared, and their elastomeric properties were measured and compared with those containing RHA.

## EXPERIMENTAL

### Materials

BRHA was obtained from Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA, Rio de Janeiro, Brazil). The characteristics of this substance are given in Table I.

Polymethylvinylsiloxane (VMQ) with a density of  $1.08 \text{ g}/\text{cm}^3$  at  $25^\circ\text{C}$  was obtained from Dow Corning do Brasil, Ltd. (São Paulo, Brazil). The vinyl residue content was 1 mol %, randomly distributed along the chains.

SC (Zeozil 175) was obtained from Rhodia Brasil S.A. (São Paulo, Brazil). The physical characteristics of this filler are shown in Table I.

2-5-Bis-*tert*-butyl-dimethylhexane peroxide (Varox, density =  $0.87 \text{ g}/\text{cm}^3$ ) was obtained from Ipiranga Comércio e Química (Rio de Janeiro, Brazil).

### Granulometric analysis

The distribution of filler particle sizes was determined with scanning electron microscopy. For this purpose, filler samples pulverized on an appropriate support were sputter-coated with a very thin layer of gold and placed into the vacuum chamber of an electronic microscope. From the images observed, the average size of the particles was determined with the Global Lab computer program. The average diameter of the par-

ticles was calculated with the Rosin–Ramlet–Bennet model, which requires the determination of the major axis of a large number of particles.<sup>36–39</sup> The results concerning the size of the particles used in this work are summarized in Table I. Sieving the ground gross BRHA reduced the particle diameter by about 92%. The notation used for the sieved ground BRHA fillers is BRHA-MP. Calcination of BRHA-MP (12 h at  $1000^\circ\text{C}$ ) to yield calcined black rice husk ash (BRHA-C) promoted the increase in the particle size. The average diameter of the particles followed the trend BRHA-MP < BRHA-C < SC. Photomicrographs of SC, BRHA-MP, and BRHA-C fillers are shown in Figure 1.

### Determination of filler specific surface areas

The specific surface area of the fillers was obtained from the adsorption of nitrogen under different partial pressures at the temperature of liquid nitrogen.<sup>39,40</sup> The method consisted of the experimental determination of physical adsorption isotherms. The evaluation of the volume of the monolayers was obtained from the isotherms with the Brunauer–Emmett–Teller equation, given by

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{p}{p_0} \quad (1)$$

where  $p$  is the reduced atmospheric pressure (mmHg),  $V$  is the adsorbed specific volume of nitrogen determined by means of a thermal conductivity detector,  $p_0$  is the saturation pressure of liquid nitrogen (mmHg),  $V_m$  is the specific volume necessary to coat the particles of filler with a monolayer of nitrogen, and  $C$  is a constant that depends on the heat of adsorption. From plots of  $p/[V(p_0 - p)]$  against  $p/p_0$ , a straight line was obtained, from whose slope and intercept  $V_m$  could be determined. Then, the specific surface area ( $A_{sp}$ ) was calculated from the expression

$$A_{sp} = A_0 \frac{V_m}{M_a} \quad (2)$$

where  $A_0$  is the area ( $\text{m}^2/\text{mol}$ ) covered by a mole of nitrogen in STP conditions and  $M_a$  is the molar vol-

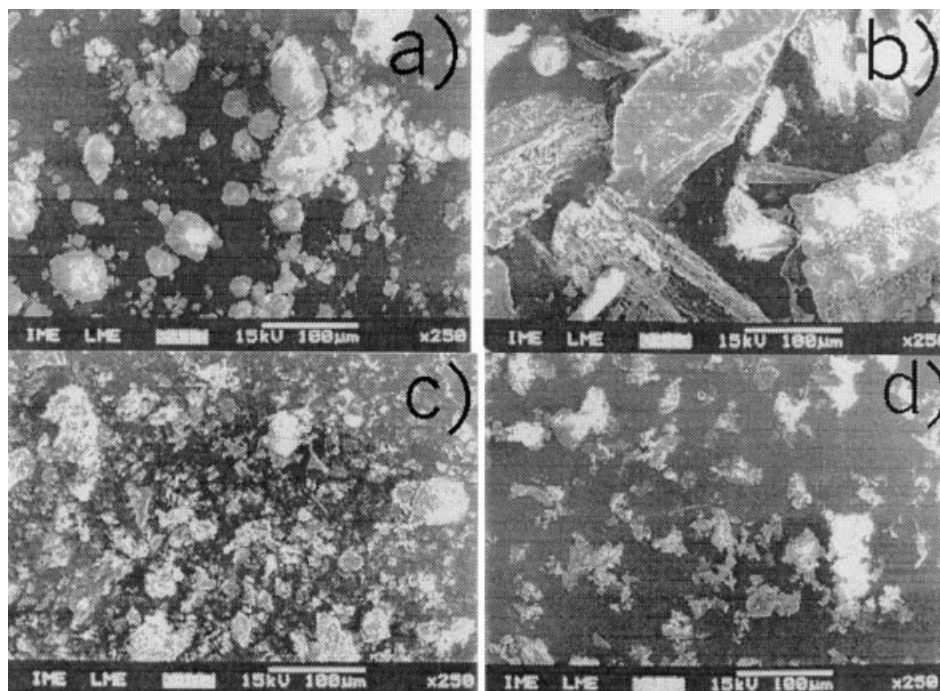


Figure 1 Micrographs of (a) SC, (b) gross BRHA, (c) BRHA-MP, and (d) BRHA-C.

ume of the gas. To obtain good results, the fillers surface must be completely dried. Therefore, just before the determination of the adsorption isotherms, the fillers were kept in an oven at 150°C for 24 h. The values of the specific areas of SC, BRHA-MP, and BRHA-C, shown in the second row of Table I, suggested that the calcination process severely reduced the specific area of the BRHA-MP fillers, presumably as a consequence of the decrease in their surface rugosity.

### Compounding process

Compounds containing the required amount in grams of filler per 100 g (phr) of VMQ were prepared in an open-roll mill with a friction ratio of 1:1.25 at  $40 \pm 5^\circ\text{C}$

with 0.8 phr of Varox-DBPH-50 (2,5-bis-ter-butyl-2,5-dimethyl-hexane peroxide) for the vulcanization process. The fillers were kept in an oven at 120°C for 24 h before they were incorporated into the compounds. An oscillating disk rheometer was used to determine the vulcanization parameters, including the optimum cure time. This test renders possible the determination of the maximum and minimum torques, the precuring time, and the optimum vulcanization time, considered as the time necessary to achieve 90% cure. Values of the maximum and minimum torques and the curing time are shown in Table II. Considering the rheometric measurements, rubber sheets were prepared by compression molding at 170°C and 3.0 MPa, where they were cured during periods of time given by the rheometer. To complete the vulcanization step, the cured,

TABLE II  
Rheometric Results for Different Rubber Compositions

Type of filler	Concentration (phr)	Minimum torque (dN m)	Maximum torque (dN m)	Optimum cure time (min)
No filler		3.6	39.9	6.2
SC	10	6.3	69.6	5.5
	20	14.2	106.2	5.0
	30	32.1	136.6	5.0
BRHA-MP	10	3.5	45.5	5.5
	20	3.9	50.8	5.5
	30	4.5	56.0	5.4
BRHA-MP-C	10	3.7	44.3	5.5
	20	3.9	48.6	5.0
	30	4.2	53.1	5.0

molded samples were subjected to a postcuring process at 200°C in an oven provided with air circulation, which allowed the elimination of products produced by peroxide decomposition. In this way, the following rubbers were prepared: VMQ, VMQ-SC-10, VMQ-SC-20, VMQ-SC-30, VMQ-BRHA-MP-10, VMQ-BRHA-MP-20, VMQ-BRHA-MP-30, VMQ-BRHA-C-10, VMQ-BRHA-C-20, and VMQ-BRHA-C-30. The numbers in the notations indicate the amount of filler in grams per 100 g of VMQ.

### Swelling experiments

Two strips with dimensions of  $2 \times 2 \times 0.3 \text{ cm}^3$  and cut from vulcanized sheets were weighed and immersed in *n*-hexane at 25°C for approximately 7 days; they were kept in darkness until a swelling equilibrium was achieved. Then, the surface of the swollen strip was gently dried with filter paper, and the sample weight was registered. From the difference in weights between the swollen and unswollen strips, the filler content, and the density of the solvent, the volumes occupied by the pure polymer in the swollen vulcanized compounds were determined.

### Diffusivity of oxygen in rubbers

A circular sheet of the pertinent rubber 800–1700  $\mu\text{m}$  thick was placed between two chambers equipped with pressure transducers. A high vacuum was made in the two chambers, and then, oxygen at a given pressure was allowed to flow to the high-pressure, or upstream, chamber. Gas diffusion across the rubbers from the upstream chamber to the low-pressure, or downstream, chamber was monitored with a Leybold (0–10 torr) pressure transducer (Germany). Before each series of measurements, the system was vacuum-calibrated by the measurement of the inlet of air into the downstream chamber. The experimental device was placed inside a thermostat, and permeation experiments were conducted at 30°C. A detailed description of the experimental device was given elsewhere.<sup>41</sup>

Once steady-state conditions were accomplished ( $t \rightarrow \infty$ ), the variation of pressure of gas in the downstream chamber with time obeyed the following expression:

$$p(t) = 0.2786 \frac{p_0 A L S T}{V} \left( \frac{Dt}{L^2} - \frac{1}{6} \right) \quad (3)$$

where  $T$  is the absolute temperature,  $p_0$  and  $p(t)$  are the pressures of gas (cmHg) at the upstream and downstream chambers, respectively,  $A$  is the area ( $\text{cm}^2$ ) of the circular sheet of rubber separating the chambers across which gas permeation takes place,  $L$  is the

thickness of the sheet (cm),  $V$  is the volume of the downstream chamber ( $\text{cm}^3$ ), and  $D$  and  $S$  are the diffusion (in  $\text{cm}^2/\text{s}$ ) and solubility [ $\text{cm}^3$  (STP)/( $\text{cm}^3$  cmHg)] coefficients, respectively, of oxygen in the networks. According to this equation, the plot of  $p(t)$  versus  $t$  is a straight line that intercepts the abscissa axis at a time  $\theta$ , called *time lag*, at which  $(D\theta/L^2) - 1/6 = 0$ . Therefore, the diffusion coefficient can be obtained from the experimentally determined time lag by means of the following expression:<sup>42</sup>

$$D = \frac{L^2}{6\theta} \quad (4)$$

### Stress-strain experiments

Dumbbell-shaped S2-type samples were fixed to two clamps, one of them fixed and the other mobile, connected to a pressure transducer (Gould Statham, UC3, USA). The elongation ratio was determined by the measurement with a cathetometer of the separation between two marks made on the undeformed strips. The clamped sample was placed inside a double-wall thermostated cylinder, and stress-strain experiments were conducted in the temperature interval 20–60°C.

## RESULTS

Stress-strain results were expressed in terms of the Mooney-Rivlin approach<sup>43–45</sup>

$$[F^*] = 2C_1 + 2C_2\lambda^{-1} \quad (5)$$

where  $2C_1$  and  $2C_2$  are constants,  $\lambda$  is the elongation ratio, and  $[F^*]$  is the reduced force or modulus given by

$$[F^*] = \frac{f}{A(\lambda - \lambda^{-2})} \quad (6)$$

where  $f$  is the elastic force and  $A$  is the undistorted cross-sectional area of the strips. Plots of the reduced force against the reciprocal of the elongation ratio for rubbery samples containing different fractions of SC are shown in Figure 2. The shapes of the curves did not resemble those reported for crosslinked rubbery materials. Actually, in most rubbers,  $[F^*]$  decreases with increasing elongation ratio until a certain value of  $\lambda$  is reached, above which the modulus increases with decreasing values of  $\lambda^{-1}$ . An increase or upturn in the modulus in polymer networks can be caused either by crystallization, as occurs in polybutadiene and natural rubber, or by the maximum extension of the chains, as happens in model polydimethylsiloxane networks.<sup>46</sup>

Mooney-Rivlin curves for VMQ-BRHA-MP and VMQ-BRHA-C networks are shown in Figures 3 and 4,

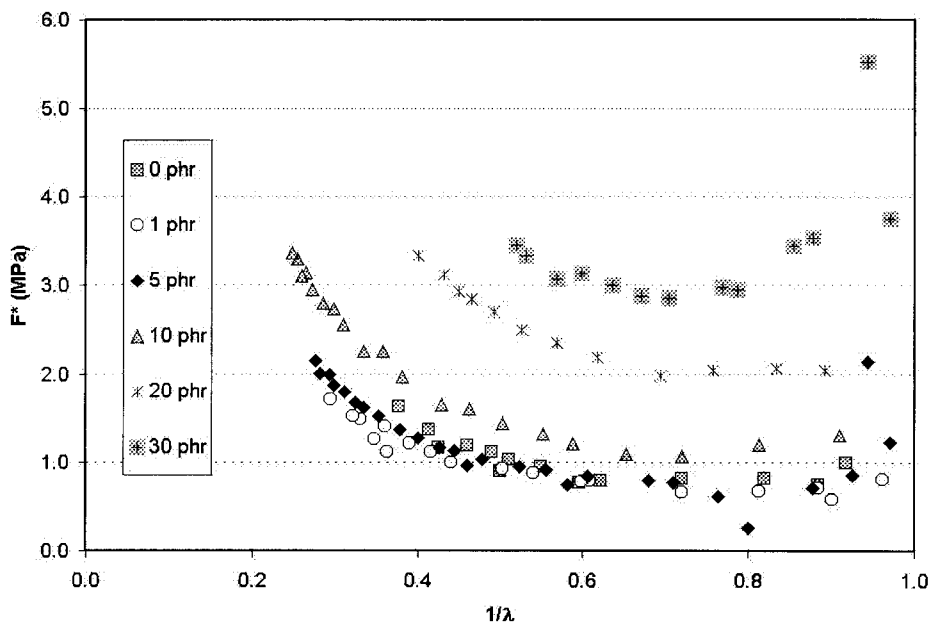


Figure 2 Mooney-Rivlin plots at 30°C for VMQ-SC. The compositions are indicated in the figure.

respectively. For comparative purposes, the isotherms corresponding to vulcanized unfilled VMQ rubbers are also shown in these figures. In general, the elongated networks relaxed very rapidly in such a way that steady conditions were reached in less than half an hour.

All the stress-strain isotherms displayed similar characteristics in the sense that the modulus either decreased or remained nearly constant at low elongations, slightly increased at moderate elongations, and underwent a rather steep growth at high elongations. The reinforcing capability of the fillers followed the trend SC

> BRHA-MP > BRHA-C. For example, the values of the reduced force (MPa) at 30°C and  $\lambda = 1.92$  were 1.001, 3.453, 1.884, and 1.165, respectively, for VMQ-0, VMQ-SC-30, VMQ-BRHA-MP-30, and VMQ-BRHA-C-30. The reduced force of silicone rubbers filled with SC and BRHA-MP augmented with the fillers content. This increase was not so effective in the case of rubbers containing BRHA-C fillers in their compositions. Tests to detect reversibility were occasionally made in the elastic experiments, which showed that the stress-strain curves displayed significant hysteresis.

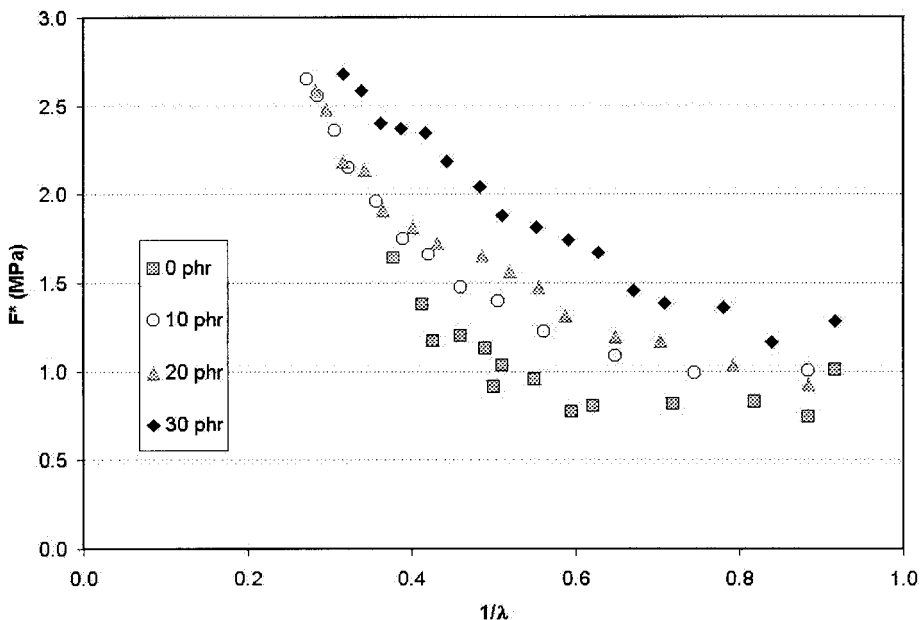


Figure 3 Mooney-Rivlin plots at 30°C for VMQ-BRHA-MP. The compositions are indicated in the figure.

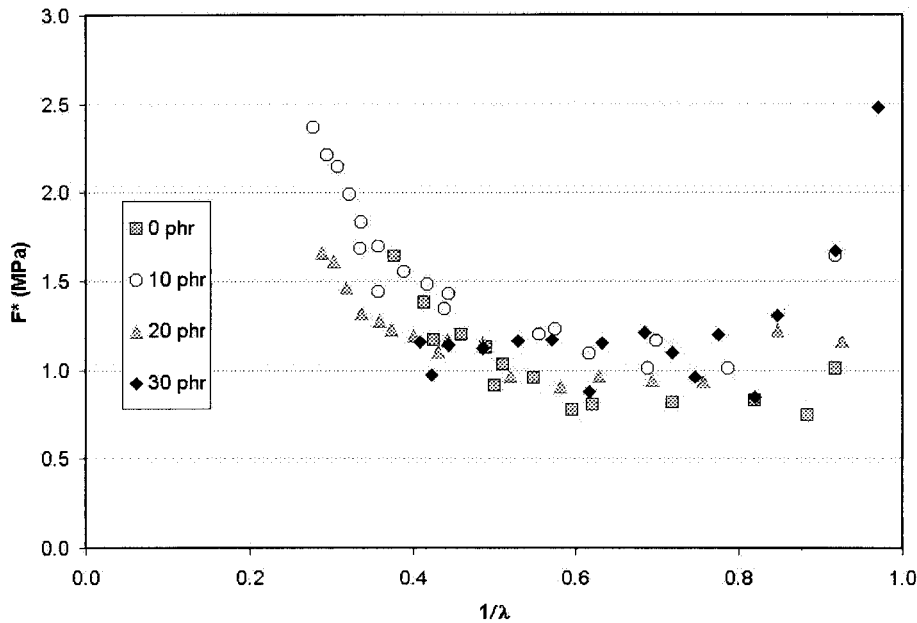


Figure 4 Mooney–Rivlin plots, at 30°C, for VMQ–BRHA–C. The compositions are indicated in the figure.

## DISCUSSION

The peculiar shape of the Mooney–Rivlin plots obtained led us to determine the average molecular weight between crosslinking points ( $M_c$ ) in crosslinked VMQ rubbers with swelling experiments in *n*-hexane. According to the Flory–Rehner theory, the density of crosslinking points ( $\nu$ ) equivalent to the number of effective elastic chains per volume unit is given by<sup>47</sup>

$$\nu = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{\rho V_1 (V_r^{1/3} - V_r/2)} \quad (7)$$

where  $V_r$  is the reduced volume of the sample equal to the ratio between the volumes of the dried (after swelling) and swollen samples,  $\chi$  is the polymer–solvent interaction parameter,  $\rho$  is the density of polymer, and  $V_1$  is the volume of the adsorbed solvent. Once  $\nu$  is known,  $M_c$  can be calculated as<sup>47</sup>

$$M_c = \frac{\rho}{\nu} \quad (8)$$

The interaction parameter was estimated through the following equation:

$$\chi = \chi_s + \chi_H \quad (9)$$

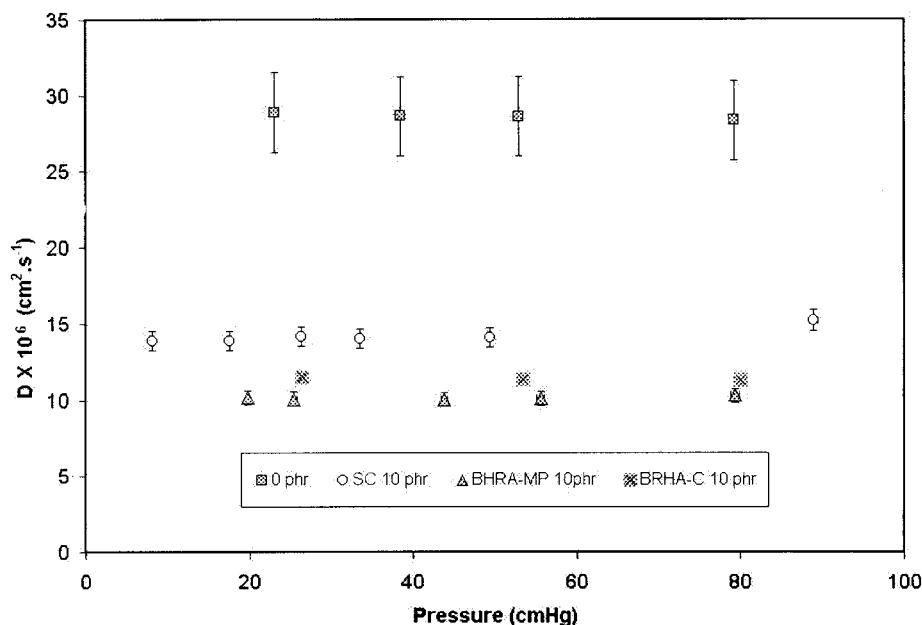
where  $\chi_s$ , whose value is<sup>46</sup> 0.34, and  $\chi_H$  are the entropic and enthalpic contributions to  $\chi$ , respectively. This latter contribution was calculated as<sup>47</sup>

$$\chi_H = \frac{A_{12} V_1}{RT} \quad (10)$$

where  $V_1$  is the volume of the adsorbed solvent,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $A_{12}$  is estimated as the square of the difference between the solubility parameters of the solvent [ $\delta_s = 7.33$  (cal/cm<sup>3</sup>)<sup>1/2</sup>] and the polymer [ $\delta_p = 7.30$  (cal/cm<sup>3</sup>)<sup>1/2</sup>]. Values of  $V_r$ ,  $\nu$ , and  $M_c$  for the VMQ network are shown in the first row of Table III. The value obtained for  $M_c$ , 2650, was the average of a presumably wide distribution of molecular weights of the chains between crosslinking points. The low value of  $M_c$  suggested that chains of very low molecular weight existed in the VMQ networks, whose more extended conformations were reached at rather low

TABLE III  
Values of  $V_r$ , the Density of Effective Elastic Chains,  $\nu$ , and  $M_c$  Obtained from the Swelling Experiments in *n*-Hexane

Rubber	Filler content (phr)	$V_r$	$10^6 \nu$ (mol/cm <sup>3</sup> )	$M_c$
VMQ	0	0.2978	377	2650
VMQ–SC	10	0.4224	510	1963
	20	0.4156	818	1222
	30	0.4544	1053	950
VMQ–BRHA–MP	10	0.3269	436	2298
	20	0.3552	538	1859
	30	0.3878	678	1474
VMQ–BRHA–C	10	0.2838	308	3250
	20	0.3229	423	2369
	30	0.3465	505	1981



**Figure 5** Values of the diffusion coefficient against the upstream pressure for VMQ elastomers containing the fillers indicated.

elongation ratios. As the elongation ratio increased, more and more elastic chains reached the extended conformations, and as a consequence, the reduced force continuously increased with increasing elongation ratio.

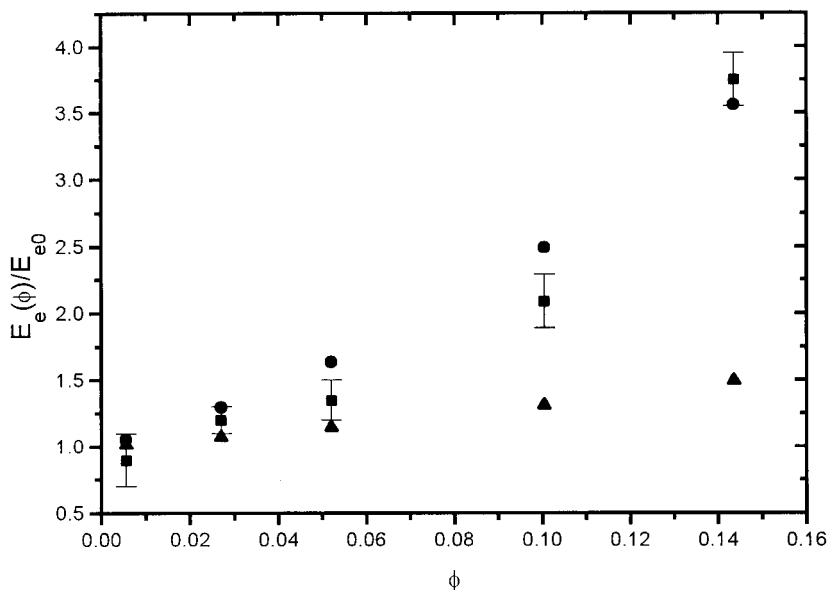
Values of the elastic parameters obtained from the swelling experiments for the rubbers filled with SC, BRHA-MP, and BRHA-C fillers are also shown in Table III. As shown in Table III, VMQ-SC rubbers displayed a larger density of effective elastic chains. The values of  $\nu$  for these rubbers increased nearly 100% when the SC content increased from 10 to 30 phr. This increase was only 55 and 64% for rubbers with BRHA-MP and BRHA-C fillers, respectively, although the number of elastic chains was higher in VMQ-BRHA-MP than in VMQ-BRHA-C rubbers. Hence, the value of  $M_c$  was lower in the former than in the latter. As occurs with VMQ-vulcanized networks, the rather wide distribution of molecular weights in the filled rubbers was presumably responsible for the continuous increase in the reduced force, starting at rather low elongation ratios.

Filler-polymer interactions increased the density of elastic chains, and for any composition, the value of  $M_c$  followed the trend VMQ-SC < VMQ-BRHA-MP < VMQ-BRHA-C < VMQ. Hence, the reduced force corresponding to a given elongation would follow the order VMQ-SC > VMQ-BRHA-MP > VMQ-BRHA-C > VMQ. The reinforcement of BRHA-C fillers was rather low for the 10- and 20-phr compositions. In fact, the values of the modulus for these compositions were similar to those found for VMQ rubbers. This behavior may have arisen from the removal of the totality of the

filler-surface hydroxyl groups during the calcination process.

The homogeneous dispersion of the fillers in the compounds is paramount to maximizing their reinforcing properties. Actually, the formation of agglomerates and bad adherence in the filler-matrix would give rise to the formation of voids in the interphase, which would decrease the mechanical properties of filled rubbers. The presence of voids in the rubbers used was investigated by the measurement of the diffusivity of gases across them. Results for the diffusion coefficient of oxygen in VMQ, VMQ-SC-10, VMQ-BRHA-MP-10, and VMQ-BRHA-C-10 rubbers are plotted against the upstream pressure in Figure 5. The diffusion coefficient was independent of the upstream pressure, and moreover, a sharp decrease on the value of this parameter by the action of fillers occurred. For example, the value of the diffusion coefficient of  $O_2$  in vulcanized VMQ at 30°C was  $28.4 \times 10^{-6} \text{ cm}^2/\text{s}$ , and this quantity dropped to about  $14.05 \times 10^{-6} \text{ cm}^2/\text{s}$  in VMQ-SC-10 rubbers. The diffusion coefficient was much lower than the volume fraction of polymer in the filled rubber times the value of this coefficient in vulcanized VMQ. Similar behavior occurred in the other rubbers. Therefore, these results suggest the absence of voids in the polymer-filler interphase that would facilitate the diffusive process. This behavior indicated good filler-polymer matrix adherence.

The fact that the enhancement of the modulus by the action of fillers was higher in VMQ-SC than in the other networks suggested that hydrogen bonding between the hydroxyl groups of the SC particles and the



**Figure 6** Dependence of the ratio between the equilibrium tensile relaxation modulus of rubbers filled with SC and that of the unfilled one: ( $\blacksquare$ ) experimental results and results obtained from eq. (11) with  $k =$  ( $\bullet$ ) 5 and ( $\blacktriangle$ ) 1.25.

polymer matrix acted as physical crosslinks in these networks. In general, an increase in temperature hardly affected the modulus. This behavior suggested that physical crosslinks between SC and VMQ were hardly affected by temperature in the interval 30–60°C. Lower strength physical crosslinks were formed between VMQ and BRHA-MP particles, presumably as a consequence of the carbon coating of the SC particles of BRHA. Carbon layers in BRHA-MP fillers presumably hindered the formation of hydrogen bonding between the hydroxyl groups of the filler and the polymer. This behavior was more marked in the BRHA-C filler.

The dependence of the equilibrium elastic modulus ( $E_{e0}$ ) on the volume fraction of fillers may be in some cases be described in terms of the empirical equation<sup>48,49</sup>

$$\frac{E_e(\phi)}{E_{e0}} = \left(1 + \frac{k\phi}{1 - \phi/\phi_m}\right)^2 \quad (11)$$

where  $E_e$  is the elastic modulus at the volume fraction of filler  $\phi$ ,  $K$  is an empirical constant, and  $\phi_m$  is the maximum volume fraction corresponding to close packing. The value of this latter quantity may lie between 0.74 and 0.80. For noninteracting rigid particles, the value of  $k$  is 1.25. The experimental values of  $E_e(\phi)/E_{e0}$  for the networks filled with commercial SC are shown in Figure 6. In the same curve and for comparative purposes, the values of  $E_e(\phi)/E_{e0}$  obtained with eq. (11) with  $k = 1.25$  and 5 are also shown. In the region of low values of  $\phi$ , the calculated results for  $E_e(\phi)/E_{e0}$  showed a low dependence of  $k$ . However, reaching an acceptable concordance be-

tween the experimental and calculated results at moderate values of  $\phi$  required postulating a relatively high value of  $k$ . It seems as though  $k$  was related to the polymer–filler interaction in such a way that the larger these interactions were, the higher  $k$  was. A qualitative analysis of the results obtained for the other fillers seemed to confirm this assumption.

## CONCLUSIONS

Interactions between the hydroxyl groups located in the surface of SC particles with the polymer matrix promoted the formation of physical crosslinks that enhanced the modulus of the rubbers. These interactions were smaller with BRHA-MP and BRHA-C fillers as a consequence of the surface of the fillers being coated with carbon from the incomplete burning process. BRHA-MP displayed better reinforcing properties than BRHA-C, presumably as a consequence of the higher specific surface area of the former filler and the total elimination of hydroxyl groups by calcination in the latter. The reduction in filler–matrix interactions for BRHA-MP did not seem to come from the formation of voids in the interphase. It seemed, however, that dimensional mobility rather than adherence of the matrix at fixed points on the surface of BRHA-MP fillers occurred. This decreased the effective density of elastic chains, and as a result, the reinforcement provided by the BRHA-MP filler was inferior to that of commercial SC.

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