

# Mechanical and Dynamic Mechanical Properties of Rice Husk Ash-Filled Natural Rubber Compounds

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**ABSTRACT:** A laboratory-sized two-roll mill was used to incorporate rice husk ash into natural rubber (NR). A conventional vulcanization system was used for curing and cure studies were carried out on a Monsanto rheometer. Physical testing of the NR vulcanizates involved determining tensile and tear resistances and hardness. Swelling behavior of NR compounds and scanning electron microscopy were used to investigate the interaction between rice husk ash and natural rubber. Also, dynamical mechanical thermal analysis was used to assess filler–rubber interactions in terms of storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ). For comparison purposes, two commercial fillers, precipitated silica (Zeosil-175) and carbon black (N774), were also used. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2331–2346, 2002

## INTRODUCTION

Rice is the basis of peoples' meals in Asia and is cultivated in substantial amounts in various American and European countries. The production of rice generates rice husks and straw. Chemical analysis of rice husk (RH) reveals the following typical composition (referred to as substance free from loss on ignition): 9% water, 3.5% protein, 0.5% fats, 30–42% cellulose, 14–18% pentosan, and 14–30% mineral ash. In view of the composition of rice husk, a number of suggestions have been made for its large-scale use in agriculture or industry. These suggestions relate to direct use, with or without comminution; chemical decomposition of rice husk on an industrial scale to obtain organic chemical basic materials; combustion for obtaining heat; and use of the mineral ash residue.<sup>1,2</sup>

Some studies have shown the possibility of utilizing rice husk as an alternative material for generating magnesium silicide ( $Mg_2Si$ ) semiconductors<sup>3</sup> and higher-quality solar grade silicon.<sup>4</sup> The formation of SiC whiskers from compacts of raw rice husks has also been reported.<sup>5</sup>

A filler derived from rice hulls appears to meet many of the performance and cost requirements for use in rubber compounding. The composition and structure of rice hulls make them an unusual and intriguing potential raw material from which a filler for rubber could be prepared. Although predominantly carbonaceous in nature, these hulls contain a considerable amount of silica in a hydrated amorphous form. The ash content in rice hulls is high enough to yield a filler by burning away the organic fraction. Chemical analyses show that this ash primarily is composed of very pure silica and that no metal constituents are present in sufficient quantities to cause deleterious aging effects upon rubber vulcanizates. Haxo and Mehta<sup>6</sup> described the use of rice husk ash (RHA) as a reinforcing agent for synthetic and

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natural rubbers. In their work, they observed that RHA did not adversely affect either the vulcanization characteristics or aging. In addition, RHA filler is a satisfactory substitute for medium thermal (MT) black and, in blends with blacks, it can be effectively used as a partial replacement for finer and more reinforcing blacks.

Applications of RHA as filler in polymers have been reported by Fuad et al.,<sup>7,8</sup> who observed that incorporating rice husk ash into polypropylene leads to a significant increase in the flexural modulus of the composites, one that is comparable to that imparted by commercial fillers such as mica. Ismail et al.<sup>9–12</sup> reported the effect of rice husk ash used as a filler for epoxidized natural rubber (ENR) compounds and the effect of a multifunctional additive (MFA) and silane coupling agents in natural rubber compounds filled with RHA. Overall, studies show that MFAs can partially replace Si69 without much effect on curing characteristics and mechanical properties.

Because rice husk is usually regarded as agricultural waste and, therefore, an environmental hazard, we discuss in this article the interaction between rice husk ash and natural rubber in terms of physical properties, dynamical mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), and vulcanizate swelling. For comparison purposes, the two most frequently used commercial fillers, silica and carbon black, were also investigated.

## EXPERIMENTAL

### Materials and Compounding

All materials were used as received. Natural rubber was supplied by Irwin Industrial e Comercial

**Table I Typical Formulation**

Material	phr
Natural rubber	100
Zinc oxide	3.5
Filler	0–50
Stearic acid	2.5
CBS <sup>a</sup>	0.8
Aminox <sup>b</sup>	2.0
Sulphur	2.5

<sup>a</sup> *N*-cyclohexyl-2-benzothiazole-2-sulphenamide.

<sup>b</sup> Antioxidant, low-temperature reaction product of diphenylamine and acetone.

**Table II Chemical Composition of Rice Husk Ash**

Chemical Composition (%)	BRHA	WRHA
CaO	0.44	0.75
MgO	0.54	0.60
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.24
K <sub>2</sub> O	1.23	1.28
Na <sub>2</sub> O	0.25	1.17
Al <sub>2</sub> O <sub>3</sub>	0.24	—
MnO	0.15	0.13
TiO <sub>2</sub>	0.01	—
P <sub>2</sub> O <sub>5</sub>	0.99	0.17
SiO <sub>2</sub> (silica)	41.62	77.18
Loss on ignition (LOI)	25.26	2.36

Ltda. and raw husk ash by EMBRAPA. Carbon black (N762) was supplied by Columbian Chemicals Brasil S.A. and precipitated silica (Zeosil-175) by Rhodia Brasil Ltda. The antioxidant Aminox was supplied by Uniroyal Química S.A. Other compounding ingredients, such as zinc oxide and stearic acid were standard reference materials. Sulfur was supplied by Vetec Química Fina Ltda (RJ) and accelerator by Bann Química Ltda (SP), Brazil.

Rice husk ash was milled for 5 h and sieved on a 325-mesh sieve. RHs, when burned in the open air, yielded two types of filler: white rice husk ash (WRHA) and black rice husk ash (BRHA). The upper layer of the RH mound, when subjected to open burning, yielded BRHA in the form of a carbonized layer. The inner layer of the mound, being subjected to higher temperatures, yielded WRHA.<sup>6</sup>

The formulation shown in Table I was employed to evaluate the curing and physical properties of natural rubber (NR) vulcanizates. The chemical composition was obtained with inductively coupled plasma emission spectroscopy. Particle size distribution was determined by a GLOBAL LAB Image (SP0550) software package. Surface area was calculated with the Brunauer–Emmett–Teller method on an ASAP 2010 accelerated surface area and porosimetry system. Filler density was measured in a glass pycnometer and pH was determined by the ASTM D 1512 method. The chemical and physical properties of BRHA, WRHA, silica, and carbon black are presented in Tables II and III.

### Preparation of Mixes, Rheometry, and Preparation of Test Samples

Mixing was carried out on a two-roll mill at a speed ratio of 1:1.25 at 70°C, according to ASTM

**Table III Physical Properties of Rice Husk Ash, Silica, and Carbon Black**

Properties	BRHA	WRHA	Silica	Carbon Black
Mean particle size ( $\mu\text{m}$ )	2.5	2.2	0.018	0.054
Surface area ( $\text{m}^2/\text{g}$ )	109	17	185	30
Density ( $\text{g}/\text{cm}^3$ )	1.9	2.0	2.0	1.9
pH	9.5	9.4	6.5	6.4

D 3182. RH ash was dried at 120°C for 24 h immediately before use. Optimum cure times at 150°C were obtained from a Monsanto Rheometer TM-100. Mixes were vulcanized in an electrically heated press at 150°C and 3.0 MPa. Vulcanizates were conditioned for 24 h before testing. All properties were measured in the direction of the grain.

#### Physicomechanical Testing of Samples

Stress-strain data were determined according to ASTM D 412 on an Instron universal machine using C-type dumbbell specimens. Other physico-mechanical tests were tear strength (ASTM D 624) and hardness (ASTM D 2240).

#### DMTA

The dynamic mechanical properties of rubber vulcanizates filled with BRHA, WRHA, and commercial fillers were determined with DMTA equipment (Rheometric Scientific, model MKIII; Plus V software, version 5.42). The run conditions were single-cantilever mode of deformation geometry, known as clamped-bending; temperature range from -80 to -20°C at a heating rate of 2°C/min; strain amplitude of 0.05%; and frequency of 1 Hz. To ensure uniformity of the rubber compound, three test pieces were selected from different parts of the same compression-molded sheet for each composition. Subsequently, the storage modulus ( $E'$ ) and the maximum loss tangent ( $\tan \delta_{\text{max}}$ ) were determined by averaging the three determinations.

#### SEM

Examination of the fracture surface was carried out on a scanning electron microscope, model JEOL JSM-5300. The objective was to get an insight into the fracture mode in an attempt to draw a picture of the matrix and filler surfaces

and filler dispersion. The fractured ends of the tensile specimens were mounted on aluminum slabs and sputter coated with a thin layer of gold to avoid electrical charging during examination.

#### Swelling Testing

Small pieces, approximately  $2 \times 2 \times 0.3$  cm, were cut from the vulcanized sheets. The dry unswollen samples were weighed occasionally until weight variations  $<0.0001\text{g}$  were achieved. The specimens were then immersed in heptane at 30°C and maintained in darkness. The swollen specimens were then taken out periodically, the excess liquid on the surface was wiped off, and the specimens were immediately weighed with utmost care. The swelling degree of the NR vulcanizates was then calculated.

## RESULTS AND DISCUSSION

#### Effect of BRHA, WRHA, and Commercial Fillers on the Cure Parameters and Mechanical Properties of NR Vulcanizates

Table IV summarizes the values of optimum cure time ( $t_{90}$ ), scorch time ( $t_{s2}$ ), and minimum and maximum torque of BRHA-, WRHA-, silica-, and carbon black-filled NR vulcanizates. Increased amounts of WRHA, BRHA, and carbon black had the same effect both on  $t_{90}$  and  $t_{s2}$ : scorch time slightly increased whereas  $t_{90}$  practically was independent of the filler content. Compared to pure gum, the presence of carbon black accelerates the vulcanization process but reduces scorch time. On the other hand, WRHA and BRHA ashes do not interfere with these parameters. With increasing amounts of filler, silica imparts a somewhat different behavior as both  $t_{90}$  and scorch time increase. This different trend in cure characteristics may be attributed to differences in filler properties such as surface area, surface reactivity, particle size, moisture content, and metal content. In general, a faster cure rate is obtained with fillers that have low surface area, high moisture content, and high metal oxide content.<sup>13</sup> This indeed seems to be the case as, among the fillers investigated in this work, carbon black and WRHA have the lowest surface areas and, therefore, shorter  $t_{90}$  values. The cure retardation for the silica vulcanizates can be attributed to a silica-accelerator interaction. This filler reacts with zinc oxide and subsequently reduces zinc reactivity, thus slowing the sulfur reaction.<sup>14</sup>

**Table IV** Cure Time ( $t_{90}$ ), Scorch Time ( $t_{s2}$ ), and Minimum and Maximum Torque of BRHA-, WRHA-, Silica-, and Carbon Black-Filled NR Vulcanizates

Filler Loading	Minimum Torque (dN · m)	Maximum Torque (dN · m)	Optimum Cure Time $t_{90}$ (min)	Scorch Time $t_{s2}$ (min)
0	8.3	43.2	16.3	6.6
WRHA				
10	10.0	48.0	14.5	6.0
20	10.3	48.7	15.4	6.2
30	10.7	54.5	14.4	6.5
40	10.8	57.3	14.2	6.6
50	10.9	58.3	15.1	7.1
BRHA				
10	8.4	44.7	17.1	6.0
20	10.5	48.2	17.5	6.3
30	12.2	52.1	16.3	6.5
40	13.6	54.3	17.3	6.6
50	14.2	56.8	16.5	6.7
Carbon black				
10	10.3	49.2	12.5	4.2
20	11.9	53.9	13.1	4.3
30	12.5	57.4	13.4	4.4
40	13.3	63.5	14.4	4.6
50	14.9	69.0	13.4	4.8
Silica				
10	11.6	45.3	16.6	6.4
20	14.9	48.2	18.3	7.1
30	17.6	53.2	20.0	8.5
40	19.5	57.5	22.5	9.2
50	23.9	68.8	25.1	10.4

The marked increase in maximum torque with increasing filler loadings indicates that the presence of fillers in the rubber matrix reduces the mobility of the rubber's macromolecular chains. The high values of maximum torque for carbon black and silica composites indicate that there is a high restriction to the molecular motion of the macromolecules, probably caused by the greater interaction between these commercial fillers and the rubber matrix. This seems to be a reflection of the particle size of the fillers (Table II).

Table V summarizes the mechanical properties of BRHA-, WRHA-, silica-, and carbon black-filled NR vulcanizates. In any of the studied systems, tensile strength increases with increasing filler content until a maximum level is reached at approximately 20 phr, as shown in Figure 1. A further increase in filler loadings has a deleterious effect on this property. The reduction in strength may be caused by filler particles agglomerating to form domains that act as foreign particles, or it simply may be the result of physical contacts between aggregates.

The reinforcement of elastomers by particulate fillers has been studied in depth in numerous investigations and it is generally accepted that this phenomenon is, to a large extent, dependent on polymer and filler properties and on processing. Generally speaking, the primary filler factors that influence elastomer reinforcement<sup>15</sup> are particle size, which determines surface area per unit weight and, with that, the solid-elastomer interface per cm<sup>3</sup> of compound; specific surface activity per cm<sup>2</sup> of surface area; shape and structure, as determined by void volume under standard packing conditions; and particle porosity, usually referred to as pores of very small size. These properties usually are not mutually independent; therefore their product rather than their sum determines final behavior.

As seen in Table V, the continuous addition of BRHA results in values of tensile strength that increase at the beginning, reach a maximum at 20 phr, and then start to decrease with additional amounts of filler, yet still do not show a significant variation when compared with pure gum.

**Table V Mechanical Properties of NR Mixed with BRHA, WRHA, Silica, and Carbon Black**

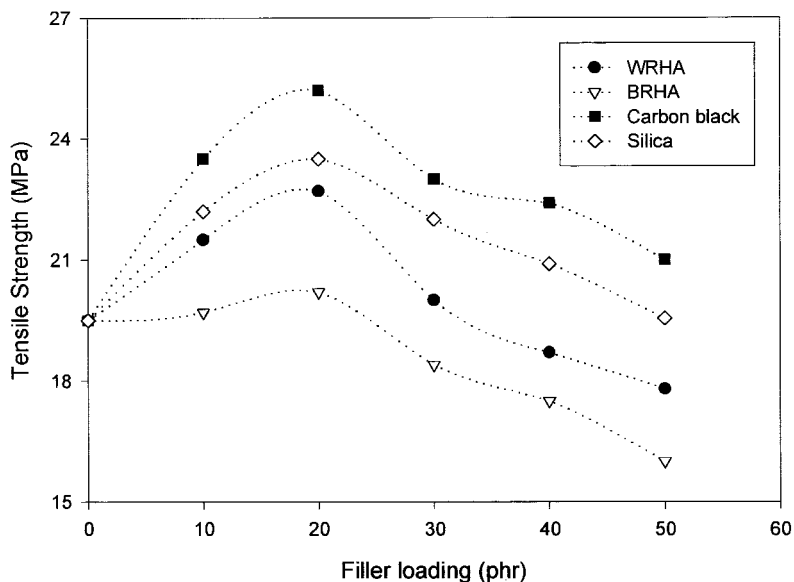
Property	Tensile Strength (MPa)	Elongation at Break (%)	Modulus at 300% (MPa)	Tear Strength (kN/m)	Hardness (Shore A)
Filler loading					
0	19.5	900	3.5	30.7	35
WRHA					
10	21.5	820	6.2	29.1	37
20	22.7	755	6.8	27.8	39
30	20.0	710	7.9	26.8	42
40	18.7	690	8.4	23.8	45
50	17.8	660	9.0	23.0	47
BRHA					
10	19.7	855	5.9	26.5	36
20	20.2	820	6.0	25.7	38
30	18.4	765	6.2	24.2	41
40	17.5	720	7.0	21.0	43
50	16.0	680	7.2	19.1	45
Carbon black					
10	23.5	750	6.0	32.7	39
20	25.2	675	8.7	35.5	44
30	23.0	620	10.4	38.9	48
40	22.4	575	11.6	42.5	52
50	21.0	530	12.5	48.7	56
Silica					
10	22.2	810	5.8	33.6	38
20	23.5	750	7.8	37.8	42
30	22.0	670	9.9	40.5	47
40	20.9	620	10.5	47.9	50
50	19.5	520	11.8	55.6	52

Perhaps the particle size of BRHA is responsible for this because, according to Fetterman,<sup>16</sup> fillers with sizes on the order of 50 nm or greater are classified as semi- or nonreinforcing. On the other hand, WRHA has a positive effect on this property, at least up to 30 phr. The superior tensile strength of the WRHA-filled vulcanizate suggests that factors other than particle size influence the properties of NR vulcanizates, factors such as, probably, surface activity and the bonding quality between WRHA and the NR matrix. In addition, the dual nature of the BRHA filler, given by the presence both of silica and carbon components, with different physical and chemical properties, may also reduce the efficiency of this filler in strengthening the rubber matrix.

From the SEM photomicrographs of BRHA-, WRHA-, silica-, and carbon black-filled NR composites shown in Figure 3, it can be seen that the fracture surface of WRHA is more uniform compared with that of BRHA. However, the lack of intensive interactions between WRHA filler and

the NR matrix is evident from these photomicrographs when they are compared with the more uniform fracture surfaces of silica and carbon black vulcanizates, which are smoother because of better filler dispersion. In addition, the larger particle size and, therefore, smaller surface area of both ash fillers, which implies poorer filler-rubber interactions, is evident on the fracture plane.

Tear strength data presented a tendency to decrease in BRHA- and WRHA-filled systems, as shown in Table V and Figure 2. Although they have similar behaviors, WRHA composites have superior values for this property, as compared with BRHA, because of their higher silica content. The formulation containing 20 phr of filler, which gave the best tensile strength results both for BRHA and WRHA, did not perform as satisfactorily as did the commercial fillers. Tear strength, like tensile strength, is affected by filler particle size and surface area. In addition, this property is controlled by the nature both of the rubber and

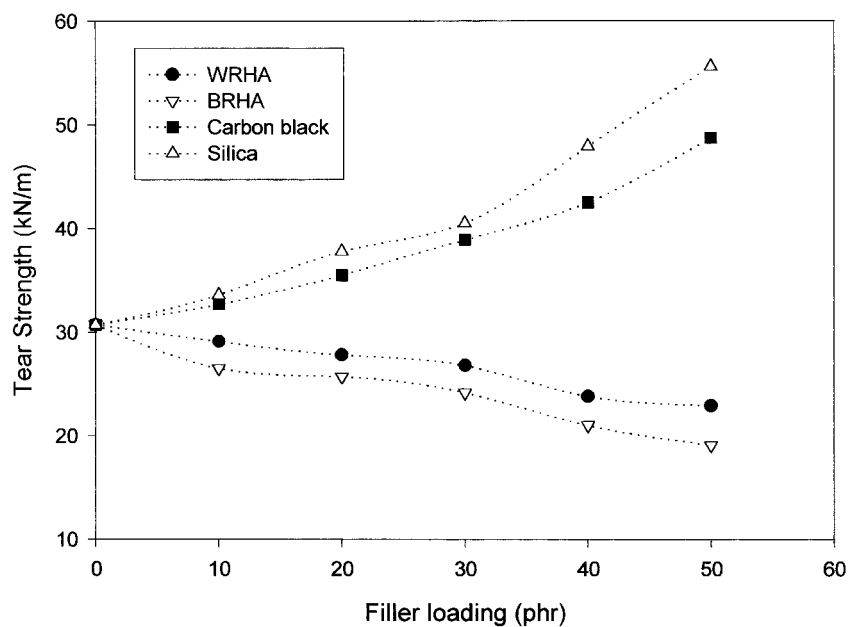


**Figure 1** Effect of filler loading on tensile strength of BRHA-, WRHA-, silica-, and carbon black-filled NR vulcanizates.

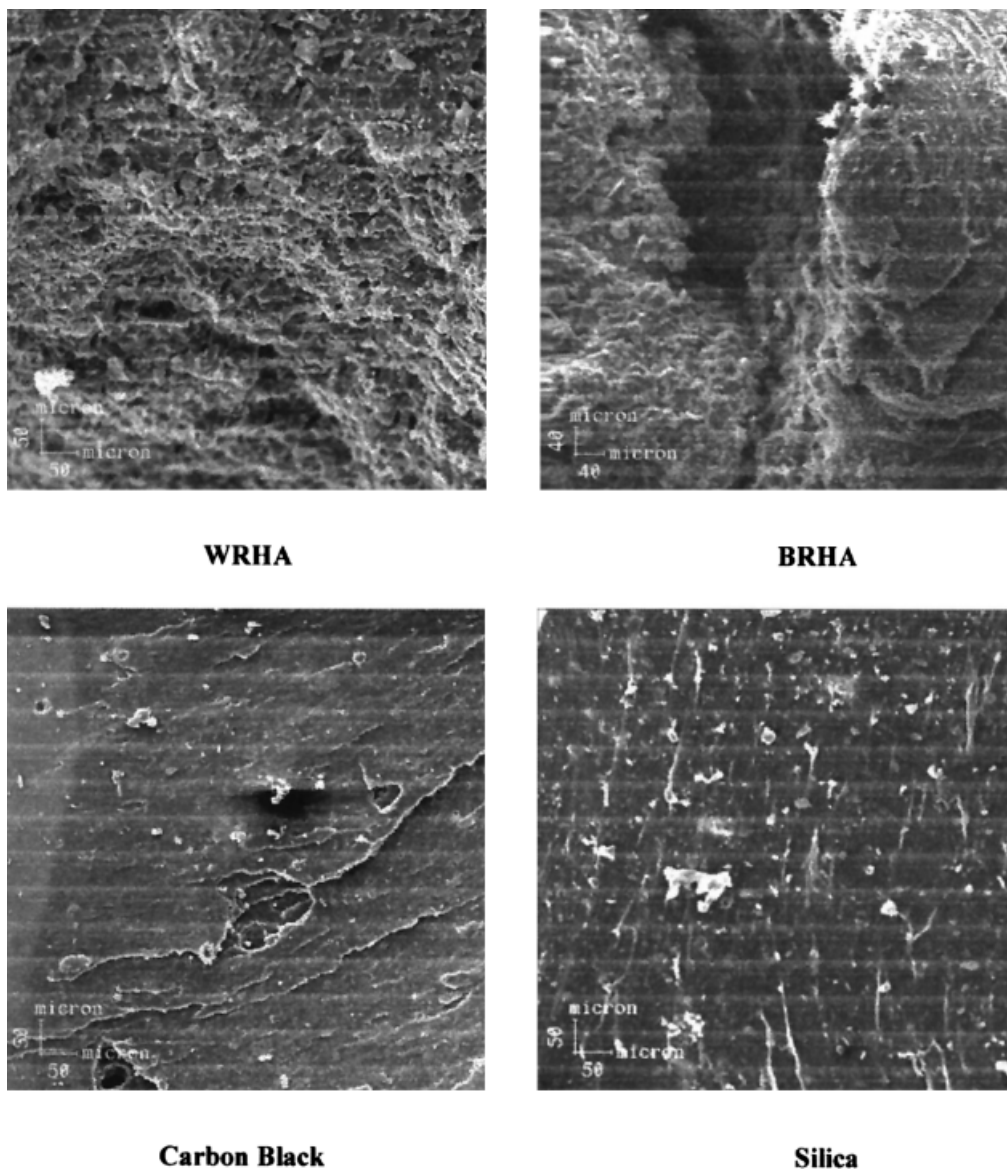
the filler, as well as by the rate and temperature of tearing.<sup>17</sup> Despite having a silica content comparable to that of commercial silicas, the WRHA-filled vulcanizates are not as tear-resistant as are those containing the commercial product. Therefore, the different performances may be the result of a much more significant influence of the nature

of the surface, particle size, and surface area of the filler used.

As for the stiffness properties, the trend observed is that which was already expected. Hardness and modulus at 300%, both for BRHA- and WRHA-filled vulcanizates, increased with increasing filler content, as shown in Table V. This



**Figure 2** Effect of filler loading on tear strength of BRHA-, WRHA-, silica-, and carbon black-filled NR vulcanizates.



**Figure 3** SEM photomicrographs of WRHA-, BRHA-, silica-, and carbon black-filled NR at 20 phr filler loading after tensile fracture ( $\times 150$ ).

result was expected because, as more filler particles are introduced into the rubber, the elasticity of the rubber chains is reduced, resulting in more rigid vulcanizates. In general, BRHA- and WRHA-filled vulcanizates have lower modulus and hardness than do the corresponding compounds with silica and carbon black. This again may be caused by differences in filler properties. The inferior stiffness of BRHA- and WRHA-filled vulcanizates may be explained by two factors. First, these fillers have larger particle sizes and, therefore, smaller surface areas. Second, WRHA and, mainly, BRHA fillers show a greater ten-

dency toward aggregation. The SEM photomicrographs shown in Figure 3 confirm that, in addition to possessing larger particle size and broad particle size distribution, the dispersion of WRHA and BRHA fillers in the rubber matrix is not uniform when compared with silica and carbon black. This poor filler dispersion reduces filler-rubber interactions and consequently decreases the ability of these fillers to restrain gross deformation of the rubber matrix.

The effect of fillers on the crosslink densities of vulcanizates is determined by modulus measurements or by swelling experiments. The latter

method yields some interesting results because the solid surface of the filler can develop three types of interaction with the elastomer: adherence at fixed points, nonadherence, and adherence with two-dimensional mobility over the surface of the filler. The difference in the type of interaction becomes clear when a vulcanizate is swollen in solvents of increasing swelling power and the degrees of swelling are compared with those for the unfilled vulcanizate. This comparison assumes that the chemical crosslink density of the polymer has not been changed by the presence of the filler.<sup>15</sup>

The degree of swelling usually is expressed in terms of the reciprocal of the fraction:

$$V_r = \frac{\text{volume of rubber/}}{\text{volume of the swollen rubber - solvent gel}} \quad (1)$$

$V_r$  is very much dependent on the swelling power of the solvent (high swelling power means low  $V_r$ ) and the crosslink density. Higher crosslink density means restraint on the network and thus results in lower swelling, that is, higher  $V_r$  (in the same solvent).

In a filled vulcanizate the important parameter is

$$V_{rf} = \frac{\text{volume of rubber in vulcanizate/}}{\text{volume of swollen rubber - gel}} \quad (2)$$

where the numerator refers to the total volume minus the filler volume and the denominator is the total swollen volume minus the filler volume. It is of interest to note that the ratio  $R = V_{rO}/V_{rf}$  ( $V_{rO}$  being  $V_r$  for the unfilled vulcanizate) with increasing filler loadings.

The Lorenz–Parks model,<sup>18</sup> represented by eq. (3), was used to investigate the swelling of filler-reinforced vulcanizates.

$$Q_f/Q_g = a \cdot e^{-z} + b \quad (3)$$

where  $Q$  is the amount of solvent imbibed per unit weight of rubber,  $f$  and  $g$  refer to filled and gum mixes, respectively,  $z$  is the weight fraction of filler in the polymer, and  $a$  and  $b$  are constants that depend on filler activity. A high  $a$  value and a low  $b$  value indicate strong polymer attachment.<sup>19</sup>

Lorenz and Parks<sup>18</sup> explain the swelling behavior of a filled stock without assuming that the

presence of filler would enhance the crosslinking efficiency of the curing agent. The filled stock is thought to be composed of  $x$  different zones that exhibit different swelling abilities. The zones nearest the filler particles would exhibit the smallest swelling ability whereas zones sufficiently far from the particles would be identical with a gum phase crosslinked to the same extent. A filled stock composed of different zones with different swelling abilities would exhibit a swelling value proportional to that of an identically crosslinked gum stock, provided that the number and the size of the zones were independent of the number of crosslinks introduced by chemical means.

In the present article, the Cunnen–Russel equation,<sup>19</sup> given in eq. (4) and originally derived by Lorenz and Parks,<sup>18</sup> was used.

$$V_{rO}/V_{rf} = a \cdot e^{-z} + b \quad (4)$$

where  $V_{rO}$  and  $V_{rf}$  are the volume fractions of the rubber in unfilled and filled vulcanizates, respectively, swollen in a solvent.

Another model used to investigate the swelling of filler-reinforced vulcanizates is the Kraus model,<sup>20</sup> given in eq. (5), which examines the consequences of the Lorenz and Parks model<sup>18</sup> and shows how to calculate quantitatively the effect on the swelling of particles either completely unbound or completely and permanently bonded to the polymer.

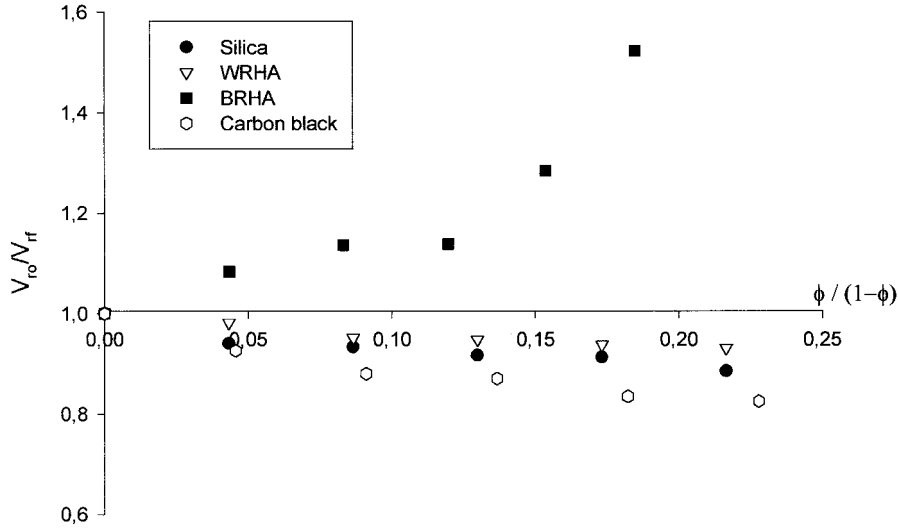
$$V_{rO}/V_{rf} = 1 - [m\phi/(1 - \phi)] \quad (5)$$

where

$$m = 3C(1 - V_{rO}^{1/3}) + V_{rO} - 1 \quad (6)$$

$V_{rO}$  and  $V_{rf}$  are the volume fractions of rubber in the solvent-swollen gum and filled vulcanizates, respectively.  $C$  is a constant characteristic of the filler but is independent of the solvent;  $\phi$  is the volume fraction of filler in the vulcanizate. The parameter  $m$ , obtained from the slope of the plot  $V_{rO}/V_{rf}$  versus  $\phi/(1 - \phi)$ , describes how much swelling is restricted for a given volume fraction of filler; it is basically a measure of the carbon–polymer interaction during the swelling process. Similarly,  $V_{rO}$  is a measure of the polymer–solvent interaction, the exact relationship being given by the Flory–Rehner theory.<sup>21</sup> If the filler swells just as much as the surrounding rubber



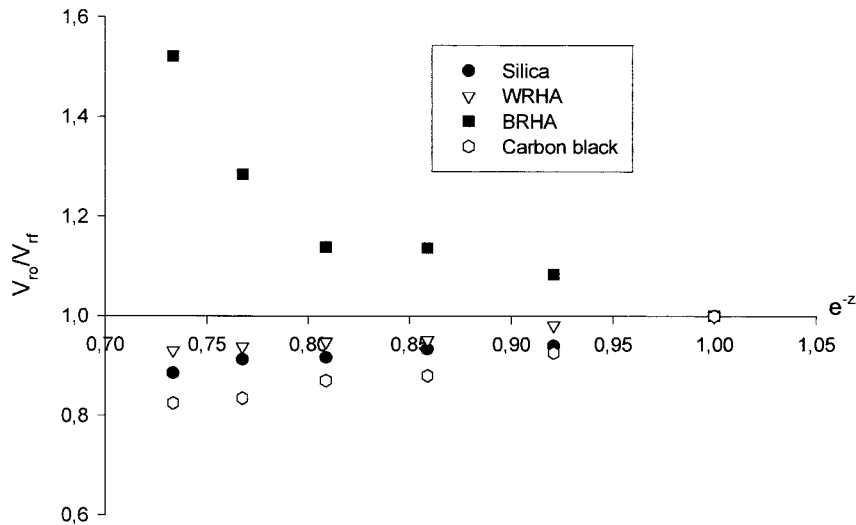


**Figure 4** Kraus equation for swelling test of NR vulcanizates containing rice husk ash and commercial fillers.

matrix, then the ratio  $V_{r0}/V_{rf}$  will be equal to unity, even with the increase in filler percentage. However, most fillers do not swell and, if the movements of the matrix are restricted because polymer segments are attached to the filler surface, the ratio  $V_{r0}/V_{rf}$  will decrease as filler loading increases. Remarkably, this ratio increases with increasing filler fraction when the filler is of the nonadhering type, as pointed out by Kraus.<sup>20</sup> The reason for this is that, in this case, a pocket filled with solvent forms around each filler particle. Because the solvent in the pocket is not taken

into account, the ratio  $V_{r0}/V_{rf}$  increases with the filler volume fraction.<sup>15</sup> Swelling results for vulcanizates containing BRHA, WRHA, and the commercial fillers are shown in Figures 4 and 5.

Kraus<sup>20</sup> suggests, for the case of carbon black, that swelling is restricted at the carbon surface but becomes normal at a distance sufficiently far from this surface. Boonstra and Taylor<sup>22</sup> suggest that the restriction of swelling by reinforcing fillers, especially carbon black, could be explained by two other mechanisms: (1) the filler has a catalytic effect on vulcanization so that different



**Figure 5** Cunen–Russel equation for swelling test of NR vulcanizates containing rice husk ash and commercial fillers.

states of crosslinking are obtained depending on whether one is dealing with filled or unfilled compositions or (2) additional crosslinks are formed on the filler surface and the carbon black particles act as giant crosslinks.

In addition, fillers can be separated into two different groups<sup>20,22</sup>: (1) those whose adhesion forces to the surrounding polymer are weak; these forces are almost negligible compared with those acting at the solvent/filler interface and those between solvent and polymer (swelling pressure) and (2) those whose adhesive forces to the surrounding polymer molecules are sufficiently strong so that these forces are not at all or not completely displaced by solvent molecules.

Figure 4 shows the plot of  $V_{rO}/V_{rf}$  versus  $\phi/(1 - \phi)$  according to the Kraus equation.<sup>20</sup> It can be observed that BRHA compositions exhibit deviations, in relation to the proposed linear mathematical model, that are greater than those for the commercial fillers. In the case of BRHA, the  $V_{rO}/V_{rf}$  ratio has an ascendant profile with values  $>1$  as filler loading increases; this means that the matrix around the filler particles will swell and, because the particle is not affected by the solvent, it will keep its original volume and the swollen elastomer will separate from the particle.<sup>20</sup> The porosity of this filler is another point to be considered. As shown in Table III, BRHA and WRHA have comparable particle sizes but the surface area of BRHA is much larger than that of WRHA, which probably is caused by the presence of pores. Voet<sup>23</sup> and Pal<sup>24</sup> investigated the reinforcement by silica and suggested that the deviation of linearity found in this material seems to indicate the onset of dewetting and void formation; the spaces between the particle and the swelling vulcanizate being filled with solvent, they no longer fulfill the conditions set forth in the Kraus model. In its turn, WRHA presents a larger interaction with the NR matrix because, for this filler, in the loading range studied,  $V_{rO}/V_{rf}$  is  $<1$ .

The systems that use the commercial fillers show not only a good fit to the Kraus model but also a more effective interaction filler/NR matrix (the ratio  $V_{rO}/V_{rf} < 1$  is an indication), mainly for the composites containing carbon black. An explanation for a deviation from the linear relationship at higher loadings may be that, because of the high viscosity imparted by these high black loadings, the mechanical breakdown of the polymer during mixing is much more intense than it is at low loadings. Therefore, the crosslinking level is not the same as it is at zero or at low black

loadings, where breakdown does not take place, and a lower  $V_{rf}$  is found.<sup>22</sup> This increases the  $V_{rO}/V_{rf}$  ratio. Another explanation for this phenomenon, put forward by Kraus,<sup>20</sup> points out that the presence of carbon affects the accelerator system so that the  $V_{rO}$  of the gum vulcanizate is no longer representative of the crosslink density attained in the presence of black.

Figure 5 shows the plots according to the Cunnen–Russel equation.<sup>19</sup> It is again observed that BRHA filler does not adhere very well to the NR matrix ( $V_{rO}/V_{rf} > 1$ ) whereas carbon black and silica develop strong interaction ( $V_{rO}/V_{rf} < 1$ ). WRHA exhibits the behavior already observed in the Kraus model.

### Effect of BRHA, WRHA, and Commercial Fillers on Dynamic Mechanical Properties of NR Compounds

The mechanical properties of filled rubbers usually are described in terms of tensile strength, stiffness, abrasion, and tearing properties. But fillers, when added to polymer, are also known to cause a considerable change in the dynamic properties, not only of the dynamic moduli, both viscous and elastic, but also in their ratios, i.e., their loss factor, which is related to the portion of energy dissipated during dynamic deformation. One method that has been used to characterize filler–rubber interactions is DMTA. This technique is particularly useful as a nondestructive test for identifying the molecular mechanisms of polymer materials.

Figures 6–9 show the dependence of storage modulus ( $E'$ ) on temperature for different concentrations of WRHA, BRHA, carbon black, and silica in the NR vulcanizates. The storage modulus decreases with increasing temperature. This tendency was proved to be very extreme around the transition region, being caused by the increasing mobility of polymer chains with increasing temperature. In the glassy region (approximately  $-80$  to  $-55^\circ\text{C}$ ), the change in the modulus  $E'$  with different filler concentrations seemed to be small. However, this effect gradually became more pronounced upon entering the transition and rubbery regions.

The variation of  $E'$  at various WRHA contents (Fig. 6) in the rubbery region is of interest here.  $E'$  decreased with increasing WRHA filler content, up to 20 phr, and then increased at higher loadings. In Figure 7 it can be seen that the behavior of  $E'$  for BRHA compounds was the same. However, for the carbon black and silica com-

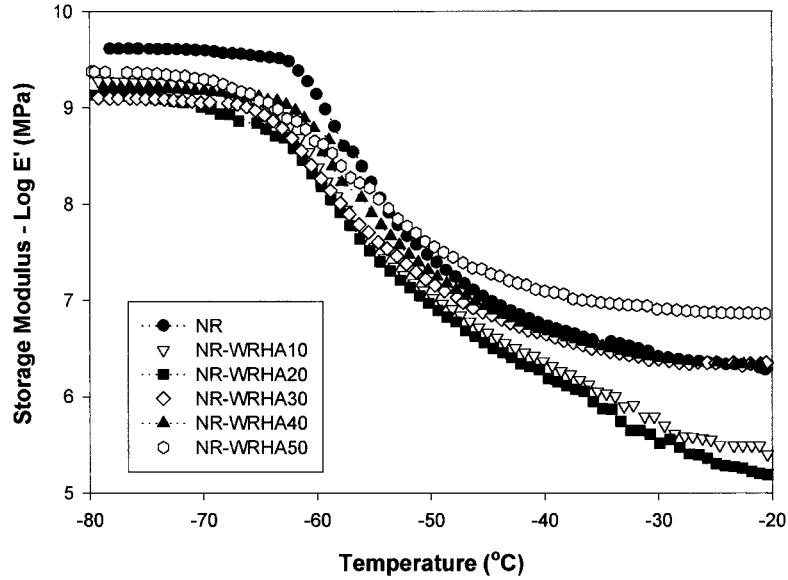


Figure 6 Influence of WRHA content on  $E'$  of NR compositions as a function of temperature.

pounds,  $E'$  increased with increasing filler content, up to 20 phr for carbon black and 30 phr for silica, and then decreased at higher loadings.

The results for WRHA and BRHA may be interpreted as the rubber being *trapped* or *caged*. With increasing filler concentration and low strain amplitude, interaggregate association (filler networks formed in the polymer matrix and kept in association by physical forces) is not bro-

ken down by straining so that the rubber trapped in the filler network or agglomerates is at least partially “dead,” losing its identity as an elastomer and instead behaving as a filler in terms of stress–strain. Therefore, the effective volume of the polymer bearing the stress imposed upon the sample is reduced by filler networking, which results in an increased modulus that is governed primarily by the filler concentration. The break-

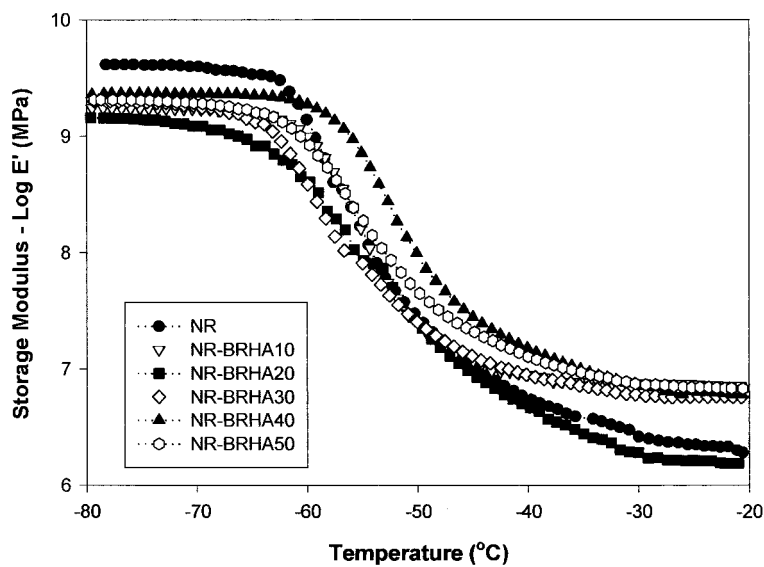
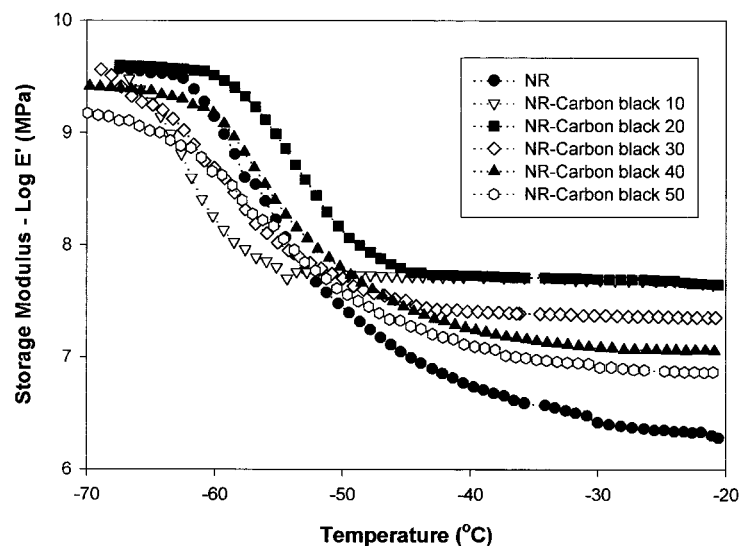


Figure 7 Influence of BRHA addition on  $E'$  of NR vulcanizates as a function of temperature.



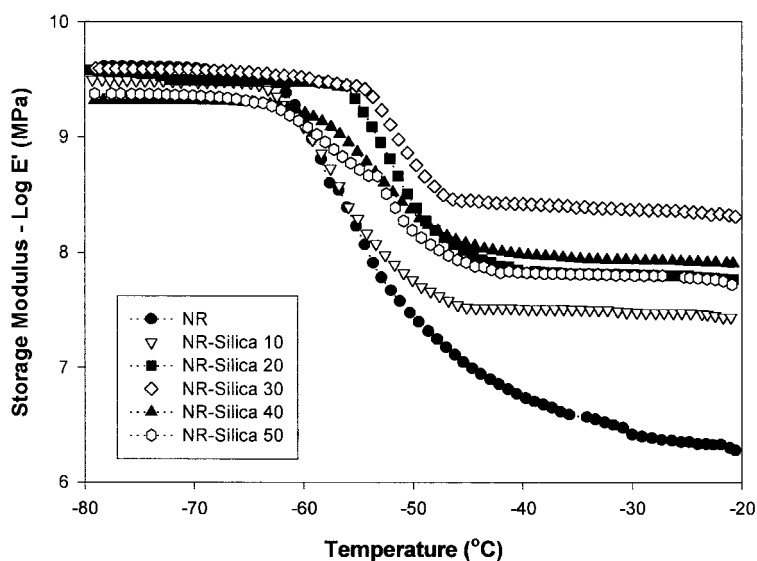
**Figure 8** Influence of carbon black content on  $E'$  of NR vulcanizates as a function of temperature.

down of the filler network by increasing strain amplitude would release the trapped rubber so that the modulus would decrease.<sup>25,26</sup>

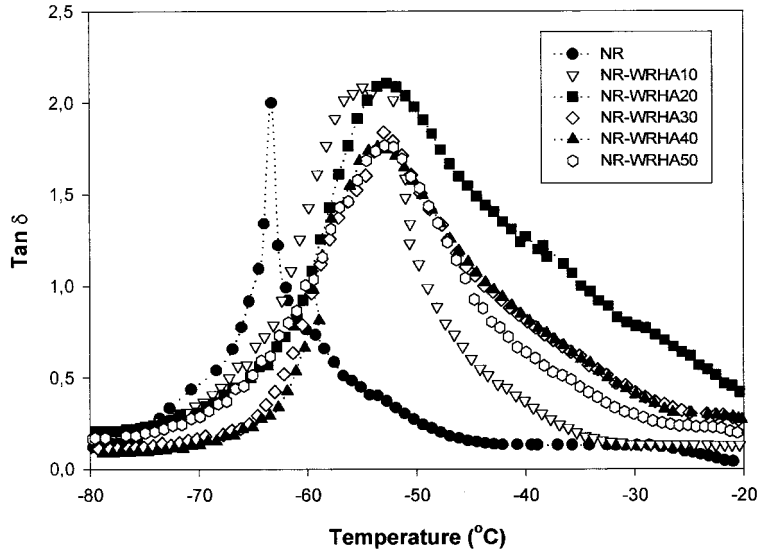
Concerning the commercial fillers, Sombatsompop<sup>27</sup> observed that the carbon black–rubber interaction is attributed to many phenomena, including (1) the formation of more stable, short polysulfide linkages (low  $x$  value in  $R-S-S_x-S-R'$  structures), which results in greater mechanical properties; (2) the formation of bound rubber, which involves the reaction of carbon black with

free radicals formed by mechanicochemical scission of the polymer; and (3) a reaction of active surfaces of carbon black formed during compounding with the rubber.

It also has been argued that, depending on the strength of the polymer–filler interaction, physical and/or chemisorption of rubber molecules might take place on the filler segments. Depending on the intensity of the filler–polymer interaction and the distance from the filler surface, the mobility of the polymer segments near the inter-



**Figure 9** Influence of silica content on  $E'$  of NR vulcanizates as a function of temperature.



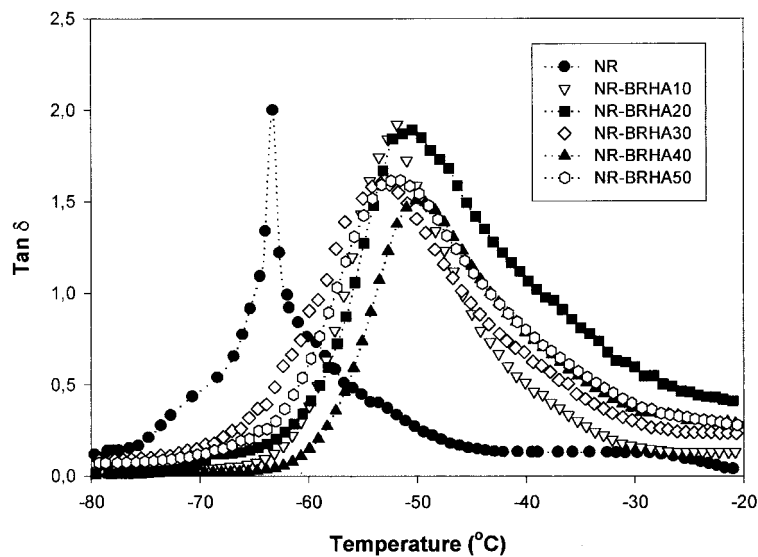
**Figure 10** Effect of WRHA content on  $\tan \delta$  of NR composites as a function of temperature.

face is less than it is in the matrix. The decrease in the modulus of the rubber vulcanizates, which was observed when higher filler loadings were added, occurred because the packing of carbon black and silica aggregates had reached a critical point where they were no longer separated by the polymer matrices. In the case of a highly polar filler, such as silica, that is incompatible with hydrocarbon rubbers, filler agglomerates may take place primarily by contact between aggre-

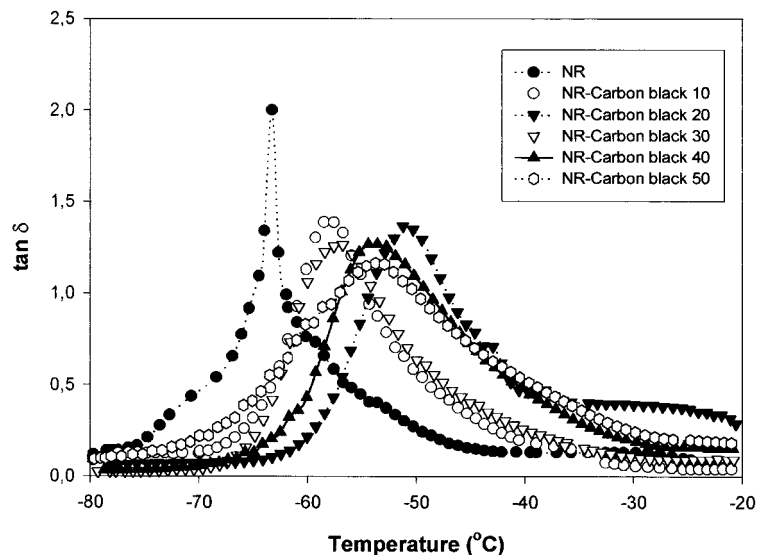
gates, in this particular case perhaps even via hydrogen bonding, to give a rigid construction.<sup>25,26</sup>

Figures 10–13 show the dependence of the damping characteristics, measured as the tangent of the phase angle ( $\tan \delta$ ) on temperature, for different concentrations of WRHA, BRHA, carbon black, and silica in the rubber vulcanizates.

It can be seen that, at sufficiently low temperatures,  $\tan \delta$  is very low because the viscosity of



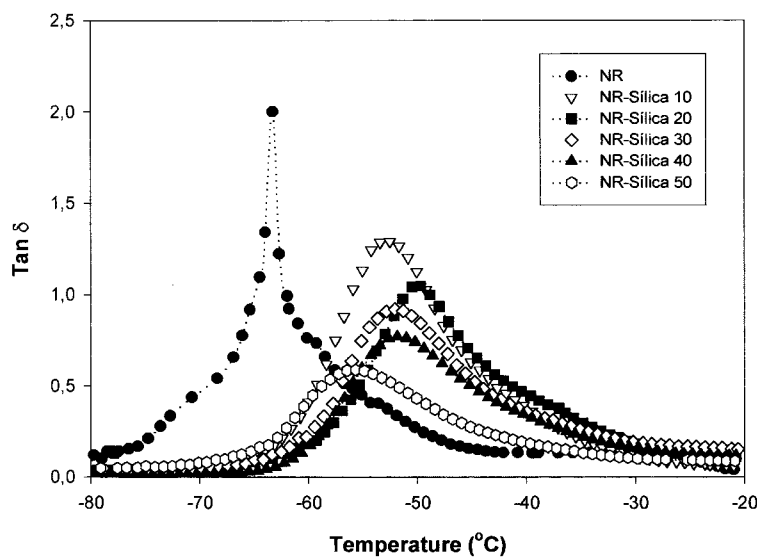
**Figure 11** Effect of BRHA content on  $\tan \delta$  of NR vulcanizates as a function of temperature.



**Figure 12** Effect of carbon black addition on  $\tan \delta$  of NR vulcanizates as a function of temperature.

the rubber is so high and the free volume in the polymer is so small that the movement of the polymer segments, and the adjustment of their relative positions, can hardly take place during the time involved in the normal dynamic experiment (frequency). This results in low energy dissipation and, therefore, low hysteresis. Under this condition, the polymer decreases in the glassy state with a very high elastic modulus.<sup>26-28</sup>

When temperature is increased, the movements of the polymer segments increase. When the temperature reaches a certain level, the free volume associated with the polymer increases more rapidly than does the volume expansion of the molecules, facilitating the segmental motion. From this point, which is known as the glass transition temperature ( $T_g$ ), the viscosity of the polymer decreases very rapidly and the molecular adjustments take place more easily so that the



**Figure 13** Effect of silica addition on  $\tan \delta$  of NR vulcanizates as a function of temperature.

elastic modulus is decreased and the energy dissipation among polymer molecules will increase with increasing temperature. This results in high hysteresis.<sup>26</sup> However, at temperatures high enough for Brownian motion to become so rapid and viscosity to become so low that, in the polymeric solid, the thermal energy is comparable to the potential energy barriers to segment rotation, the molecular adjustment is quick enough to be able to follow the dynamic strain. In this case, long-range contour changes of polymer molecules may take place that are associated with high entropic elasticity and low resistance to strain. The material falls in a so-called rubbery region that is characterized by low modulus and low energy dissipation during dynamic deformation.<sup>28</sup>

It can be seen that the  $\tan \delta$  values of rubber compounds filled with carbon black and silica (Figs. 12–13) were lower than those found in rubber gum. The  $\tan \delta_{\max}$  values of the vulcanizates decreased considerably when commercial fillers were added. The decreased value of  $\tan \delta_{\max}$  in the investigated load range suggests that a relatively high interaction of the filler and rubber was obtained. For rubber compounds with WRHA and BRHA fillers (Figs. 10–11), the decrease in  $\tan \delta$  values with increased filler content was not as intense. This again may be caused by differences in filler properties. WRHA and BRHA fillers have larger particle sizes and, therefore, smaller surface areas and show a greater tendency to aggregate, as seen in SEM photomicrographs (Fig. 3).

In addition, the results shown in Figures 10–13 lead to the conclusion that the loading effects at different temperature regions are governed by different mechanisms. It seems that, at temperatures near the  $\tan \delta$  peak in the transition zone, the presence of fillers gives a lower hysteresis for a given energy input. This may be interpreted as a reduction in the polymer fraction within the composite because the polymer per se would be responsible for the high proportion of energy dissipation whereas individual solid filler particles in the polymer matrix may not absorb energy significantly. Although this interpretation is reasonable for hysteresis in the transition zone, it may be not true at high temperatures where hysteresis is increased when filler is introduced. It has been demonstrated routinely in rubber compounds that, when the same volume fraction of fillers is incorporated into the same polymer system, fillers with different morphologies and surface characteristics have different responses

to the temperature dependency of the hysteresis.<sup>25–28</sup>

A further observation of the damping characteristics was made by considering the overall width of the loss tangent peaks. It was found that, in the presence of fillers, the peaks became clearly broadened, which indicates greater dynamic losses; this was more pronounced around the rubbery region. The losses could be caused by more mechanical energy input being converted into heat, which is generated during deformation, and more energy losses from the movements of polymer chains in the rubbery state. The  $T_g$  values of filled rubber vulcanizates shifted to higher temperatures and showed higher values than did those of the unfilled compound. The shift of  $T_g$  to higher temperatures might be caused by the presence of crosslinks, which restrict the mobility of the polymer chains, and by a slight increase in the interaction between fillers and rubber phase, which occurs principally in commercial fillers.<sup>25–28</sup>

## CONCLUSION

The main objective of this study was to verify the possibility of utilizing rice husk ash as alternative filler for NR. Concerning the mechanical properties, the results show that the tear strengths and hardnesses of BRHA-, WRHA-, carbon black-, and silica-filled NR compounds are very similar for low filler loadings; regarding tensile strength, BRHA is not as efficient as the commonly used fillers carbon black and silica. As for WRHA, in spite of parameters such as surface area and particle size, the vulcanizate with 20 phr of this filler, which gave the best results, showed physical properties not much inferior to commercial carbon black- or silica-filled vulcanizates. Furthermore, cure characteristics were not prejudiced with increased filler loading, in spite of the non-homogeneous nature of WRHA chemical composition. From the analysis of  $V_{rO}/V_{rf}$  as a function of filler loading and from the behavior found by applying the Kraus and Cunnenn–Russel models, it can be concluded that WRHA adheres better to the rubber matrix than does BRHA. However, although WRHA can have better wetting and dispersion, this was not enough to cause an enhancement in the dynamic mechanical performance of WRHA as reinforcing filler.

Nevertheless, rice husk ash can still be thought of as an alternative filler, depending on the performance desired for a given application, because

of its extremely low cost as a by-product of the rice industry. There is also the possibility of having it behave as reinforcing filler if it is obtained through controlled burning or is submitted to chemical treatment. However, the most important reason why these ashes should be given a good use of is the possibility of minimizing environmental impact by the adequate utilization of this residue (1 kg of husks produces 300 g of ash). At present, the most common method of husk ash disposal is wasteland dumping, which creates an environmental hazard through pollution and land dereliction.

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