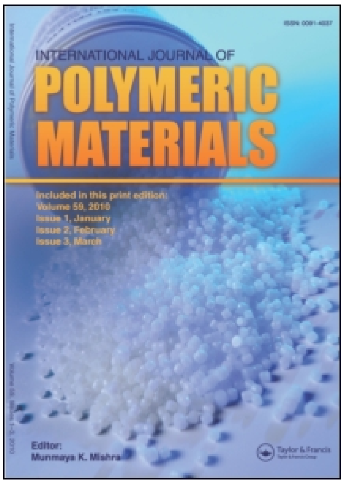

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

RICE HUSK ASH FILLED NATURAL RUBBER COMPOUNDS - THE USE OF RHEOMETRIC DATA TO QUALITATIVELY ESTIMATE OPTIMUM FILLER LOADING

H. M. Costa[a]; L. L. Y. Visconte[a]; R. C. R. Nunes[a]; C. R. G. Furtado[b]
[a] Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro [b] Grupo de Polímeros - Instituto de Qumíca/Universidade do Estado do Rio de Janeiro, Rio de Janeiro

To cite this Article Costa, H. M. , Visconte, L. L. Y. , Nunes, R. C. R. and Furtado, C. R. G.(2004) 'RICE HUSK ASH FILLED NATURAL RUBBER COMPOUNDS - THE USE OF RHEOMETRIC DATA TO QUALITATIVELY ESTIMATE OPTIMUM FILLER LOADING', International Journal of Polymeric Materials, 53: 6, 475 — 497

To link to this Article: DOI: 10.1080/00914030490450100

URL: http://dx.doi.org/10.1080/00914030490450100

International Journal of Polymeric Materials, 53:475–497, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490450100

RICE HUSK ASH FILLED NATURAL RUBBER COMPOUNDS – THE USE OF RHEOMETRIC DATA TO QUALITATIVELY ESTIMATE OPTIMUM FILLER LOADING

H. M. da Costa
L. L. Y. Visconte
R. C. R. Nunes
Instituto de Macromoléculas Professora Eloisa Mano,
Universidade Federal do Rio de Janeiro, Rio de Janeiro

C. R. G. Furtado
Grupo de Polímeros – Instituto de Química/Universidade do
Estado do Rio de Janeiro, Rio de Janeiro

White rice husk ash (WRHA) and black rice husk ash (BRHA) were incorporated as filler in natural rubber (NR) compounds. A conventional vulcanization system (CV) was chosen and cure studies were carried out on a TI-100 Curometer at 150, 160, 170 and 180°C. From the rheometric data obtained at 150°C, a specific constant related to the filler structure was evaluated that allowed predictions on how the presence of filler would affect mechanical properties such as tensile and tear resistances, and hardness. Swelling behavior and examination of the fracture surface, which was carried out on a Scanning Electron Microscope (SEM), were used to get some idea on the interaction between the rubber matrix and the filler. WRHA showed a good reinforcing potential for NR compounds and catalytic effect upon vulcanization.

Keywords: rice husk ash, natural rubber, composites

1. INTRODUCTION

Rice husk is a residue produced in significant quantities on a global basis. While utilized as a fuel in some regions, in other countries it is considered as waste, thus adding to pollution and disposal problems.

Received 19 November 2001; in final form 2 December 2001.

The authors thank LAMIN/CPRM for the chemical composition analysis and CAPES for the financial support.

Address correspondence to L.L.Y. Visconte, Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, Brazil. E-mail: lyv@ima.ufry.br

In recent years, due to growing environmental concern and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to use the resultant ash as a construction material [1]. Rice husk ash (RHA) contains a high amount of silicon dioxide and when obtained from combustion at temperatures below 600°C consists primarily of a disordered Si-O structure, which is the product of decomposition and sintering of opaline or hydrous silica without melting. Occasionally, a small amount of crystalline impurities may be present, including quartz, cristobalite and/or tridymite [2, 3].

Black rice husk ash (BRHA) or white rice husk ash (WRHA) owe their differences to the burning conditions under which they are obtained. As usually, the husks are burnt in the open air, outside the rice mills, and two types of products are formed. The upper layer of the husk mound, subjected to open burning and lower temperatures, yields BRHA in the form of a carbonized layer. However, the inner layer of the mound, being subjected to higher temperatures, yields WRHA with high silica content, easily ground into fine powder [4].

Applications of rice husk ash (RHA) as filler in polymers have been reported by Ahmad Fuad et al. [5, 6], who observed that the incorporation of this material into polypropylene has led to a significant increase in flexural modulus, comparable to that imparted by commercial fillers such as mica. Ismail et al. [7−9] reported the effect of rice husk ash as filler in epoxidized natural rubber (ENR) compounds and the effect of silane coupling agents in natural rubber, also compounded with RHA. More recently, Costa et al. [10, 11] reported RHA application in natural rubber compounds.

In this work, BRHA and WRHA were incorporated in NR compounds and their effects upon vulcanization kinetics were evaluated. From the application of rheometric data, obtained at 150°C, to suitable models, filler structure and optimum loadings were estimated. Mechanical properties and swelling behavior were studied and the fracture surface was also examined by SEM.

2. EXPERIMENTAL

Natural rubber (SMR-L) was supplied by Irwin Industrial e Comercial Ltda. 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. The compositions were prepared following the formulation presented in Table 1.

The ashes were supplied by EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária), milled, and sieved on a 325 mesh sieve before

TABLE 1 Typical Formulation

Material	Phr
Natural rubber	100
Zinc oxide	3.5
Filler	0–50
Stearic acid	2.5
CBS[a]	0.8
Aminox[b]	2.0
Sulphur	2.5

[a] N-cyclohexyl-2-benzothiazole-2-sulphenamide.

[b] Antioxidant – low temperature reaction product of diphenylamine and acetone.

analysis by Inductively Coupled Plasma Emission Spectroscopy. The chemical composition results are shown in Table 2. Particle size distribution, surface area and density for the two ashes are presented in Table 3 and were determined by using a Global Lab Image (SP0550)

TABLE 2 Chemical Composition of Rice Husk Ash

Chemical composition (%)	BRHA	WRHA
CaO	0.40	0.77
MgO	0.38	0.53
Fe_2O_3	0.13	0.25
K_2O	1.22	1.05
Na_2O	0.13	0.30
Al_2O_3	0.23	0.27
MnO	0.16	0.14
TiO_2	0.01	0.01
P_2O_5	0.96	1.00
SiO_2 (silica)	74.85	97.00
Loss on ignition (LOI)	21.00	0.20

TABLE 3 Physical Properties of Rice Husk Ash

Properties	BRHA	WRHA
Mean particle size (μm)	2.5	2.2
Surface area (m^2/g)	109	17
Micropore Area (m^2/g)	88.2	1.8
% Micropore Area	80.1	22.6
Density (g/cm^3)	1.9	2.0
pH	9.5	9.4

software package, an ASAP 2010 Accelerated Surface Area and Porosimetry System (through the BET method), and a glass pycnometer, respectively. Method ASTM D1512 was followed to measure pH.

2.1 Preparation of Mixes, Rheometry and Preparation of Test Samples

Mixing was carried out on a two-roll mill at 70°C and 1:1.25 speed ratio, according to ASTM D 3182. Rice husk ash was dried at 120°C for 24 h immediately before use. The batch mass was checked and recorded. If different from the theoretical value by more than 0.5%, it was rejected. The sheeted compound was conditioned at 25 ± 2°C for 24 h in a closed container before the determination of the optimum cure time by using a TI-100 Curometer, at different temperatures ranging from 150 to 180°C. For mechanical properties, vulcanizates were prepared by compression molding in an electrically heated press at 150°C and 3.0 MPa, appropriate specimens were cut and, after conditioning for 24 h, the properties were evaluated. All properties were measured along the grain direction. For cure studies, torque-time curves were registered at vulcanization temperatures of 150, 160, 170, and 180°C. For each temperature, three samples of each mix were analyzed and the rheometric data used to calculate the apparent activation energy.

2.2 Physico-mechanical Testing of the Samples

Stress-strain data were determined on an Instron Universal Testing Machine, Model 1101, on C-type dumbbell specimens, according to ASTM D 412. Other physico-mechanical tests were tear strength (ASTM D 624) and hardness (ASTM D 2240).

2.3 Scanning Electron Microscopy

Examination of the fracture surface was carried out on Scanning Electron Microscope (SEM) model JEOL JSM-5300. The objective was to get some idea on the fracture mode, degree of adhesion between rubber matrix and filler and filler dispersion. The fractured ends of the tensile specimens were mounted on aluminum stabs and sputter coated with a thin layer of gold, to avoid electrical charging during examination.

2.4 Swelling Tests

Small pieces, approximately 2 × 2 × 0.3 cm, were cut from the vulcanized sheets. The dry, unswollen samples were weighed from time to time until weight variations not higher than 0.0001 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 and the specimens were immediately weighed with utmost care. The swelling degree of the NR vulcanizates was then calculated.

3. RESULTS AND DISCUSSION

3.1 Effect of BRHA and WRHA on the Cure Parameters of NR Vulcanizates

Table 4 summarizes the values of optimum cure time (t_{90}), scorch time (t_{s2}), minimum and maximum torques of BRHA and WRHA-NR vulcanizates. The increment in the minimum torque with the increasing filler loadings suggests a reduced mobility of the rubber chains caused by the incorporation of these fillers. The higher values of maximum torque of the filled composites, in comparison to the unfilled one, indicate that with the addition of the ash, some sort of interaction between the filler and the rubber matrix has developed. This effect is a little higher for WRHA.

Increasing amounts of BRHA have almost the same effect on both t_{90} and t_{s2}. The scorch time slightly decreases while t_{90} is practically

TABLE 4 Cure Time (t_{90}), Scorch Time (t_{s2}), Minimum and Maximum Torque of BRHA and WRHA-Filled NR Vulcanizates

Filler loading (phr)	Minimum torque (lb.in)	Maximum torque (lb.in)	Optimum cure time t_{90}(min)	Scorch time t_{s2}(min)
0	4.5	50.0	16.3	6.6
WRHA				
10	4.7	51.7	15.5	6.2
20	5.2	53.4	15.2	7.1
30	5.6	55.7	15.1	6.3
40	6.1	56.7	14.4	6.1
50	6.5	59.0	14.0	6.3
BRHA				
10	4.6	50.5	17.3	7.3
20	4.8	51.9	17.1	6.6
30	5.0	53.3	17.1	6.3
40	5.5	55.2	16.7	6.1
50	6.1	57.1	16.6	6.1

independent of the filler content. Concerning t_{90}, WRHA and BRHA induce similar behavior, although WRHA slightly accelerates the vulcanization process when compared to pure gum. These small differences in cure characteristics may be attributed to differences in the 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 having low surface area, high moisture and high metal oxide contents [12]. In recent investigations on WRHA-NR compounds [13, 14], using a more appropriate model, a remarkable increase in the rate constant with filler loadings above 20 phr was found, when a catalytic effect with consequent decreasing of E_a values seems to exist. This fact was attributed to the smaller surface area and loss on ignition, and, mostly, to the higher oxide content present in WRHA as compared to BRHA, which might have accelerated the vulcanization process in the presence of zinc oxide.

A simple way to follow the cure process is through the cure rate index (CRI), defined by the equation: CRI = 100/(cure time – scorch time). As previously cited, the torque-time curves were registered at temperatures of 150, 160, 170, and 180°C. Figure 1 (a, b) shows the

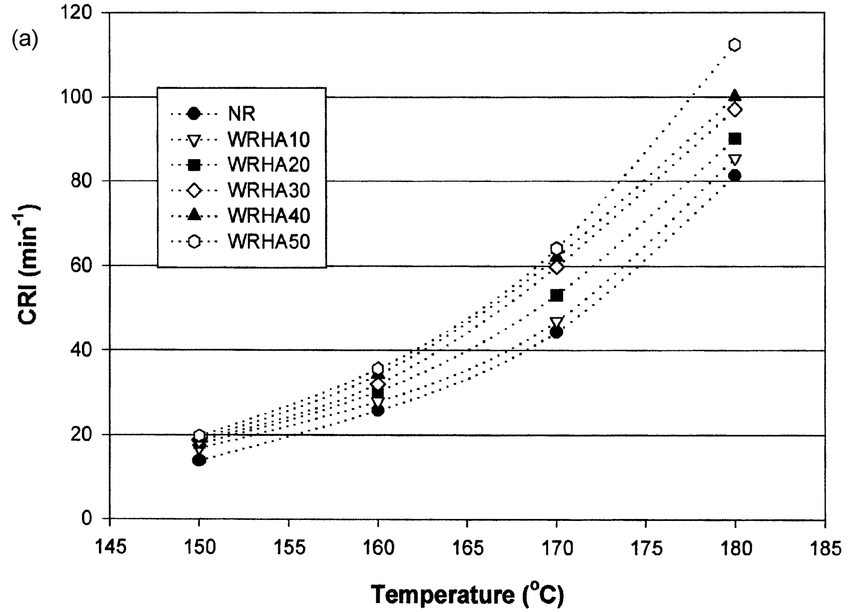

FIGURE 1 CRI variation with increasing cure temperature (a) WRHA-filled NR compounds, (b) BRHA-filled NR compounds.

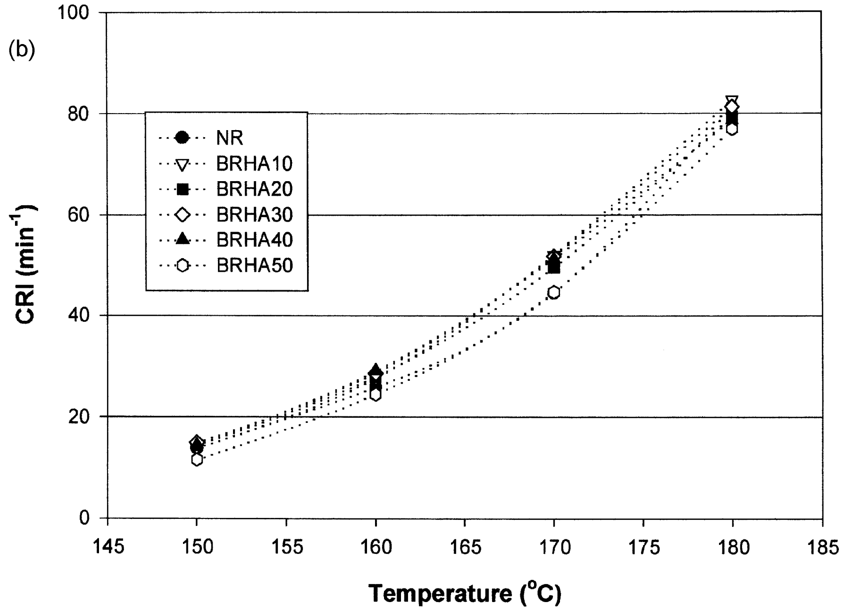

FIGURE 1 (Continued).

variation of CRI for WRHA and BRHA-filled NR compounds with the increase in cure temperature. It is observed that by increasing the temperature, the cure rate index increases for all NR compositions according to the "rule of thumb," which states that the rate of cure doubles for every 10°C increment. The BRHA compounds present a less significant increase.

Using the rheographs data for CRI and the Arrhenius equation, the apparent activation energy (Figure 2) was estimated. For BRHA compositions, the apparent activation energy does not change much up to 30 phr and then starts to increase for higher filler loadings. The dual nature of BRHA, given by the presence of both silica and carbon components, with different physical and chemical properties, may have been responsible for the reduced efficiency of this filler in rubber vulcanization. In addition, BRHA was found to be extremely porous, as seen from the discrepancy between particle size and surface area data. The presence of pores can result in cure retardation owing to an extensive adsorption and inactivation of rubber curatives entrapped in the pore cavities. For WRHA compounds, the apparent activation energy gradually decreases with the increase in filler loading. The chemical composition of WRHA (Table 2) shows that this filler is

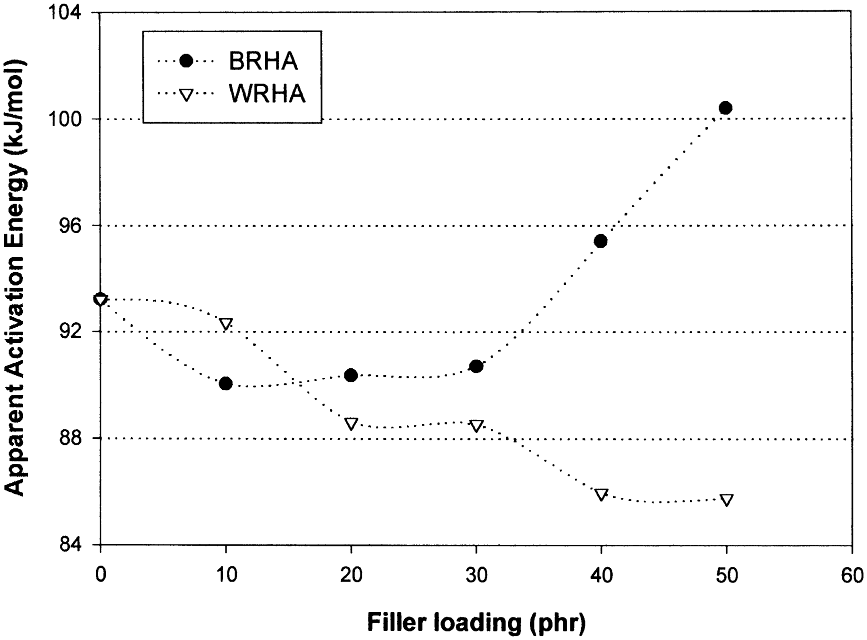

FIGURE 2 Variation of apparent activation energy for BRHA- and WRHA-filled NR compounds.

mostly silica (97%), with a very small amount of organic material, given by the low value of LOI, and oxide content 19.3% larger than in BRHA. Also, from physical properties the amount of pores is much less than in BRHA. The combination of these factors may have contributed to the catalytic effect on NR vulcanization.

3.2 Effect of BRHA and WRHA on Mechanical Properties of NR Vulcanizates, Prepared at 150°C

The mechanical performance of rubber vulcanizates is intimately related to the degree of filler dispersion and interaction between filler and rubber matrix. According to Lee [15], even well dispersed filler-rubber systems, show differences in the degree of filler agglomeration (hydrodynamic volume) in the cured and uncured state. In his study on carbon black filled BR and SBR, he assumed that $\eta_r > M_r$, where η_r and M_r are the relative viscosity (ratio of the viscosities due to loaded and unloaded elastomer) and the relative moduli (ratio of the modulus for loaded and unloaded elastomer), respectively. Lee [15] further proposed that η_r and M_r could be determined from Oscillating Disc Rheometer curves for the corresponding stocks by using the following expressions:

$$\eta_r = T^f_{min}/T^0_{min} \tag{1}$$

$$M_r = T^f_{max}/T^0 max \tag{2}$$

where T denotes torque and the superscripts f and o are related to the loaded and unloaded polymer, respectively. In his study, a new parameter L was introduced, defined as:

$$L = \eta_r - M_r \tag{3}$$

The value of L changes slowly at low filler loadings but above certain content it increases very sharply. Thus, the plot of L versus filler loading is a curve that can be approximated by two straight lines of different slopes. The abrupt rise of the index L at high filler loadings may be ascribed to the predominance of agglomerates remaining relatively undispersed in the rubber. In such a situation, it is assumed that the filler concentration has now reached the point where there is not enough rubber to fill all available voids in the filler. This may be true for carbon blacks that, on account of their high surface energies, possess a large affinity to hydrocarbon rubbers, resulting in good wetting of the surfaces. This does not seem to be the case for silicas, since the strong aggregate-aggregate interaction may cause agglomeration to occur even at low concentrations [16], when there is still more than enough rubber to fill all voids in the filler. Thus, the intersection of the tangents drawn for the two parts of the curve, at low and high concentrations of the reinforcing filler, provides an approximate idea concerning the maximum dispersion of the filler. It is expected that at this concentration, there will be very little filler agglomerates and it may be reasonably taken as the optimum loading for that particular formulation. It is supposed that at the optimum loading, the developing interaction between filler and rubber matrix is at its maximum and the vulcanizates are likely to exhibit the highest physical properties.

The same procedure has been adopted in this work for the study of the effect of BRHA and WRHA. In Figure 3, the variation of the parameter L with BRHA and WRHA concentration (0-50 phr) is shown. The magnitude of L is strongly dependent on how the filler particles disperse in the rubber matrix, and also on how the polymer interacts with the surface of the filler particle [15]. It is clear from

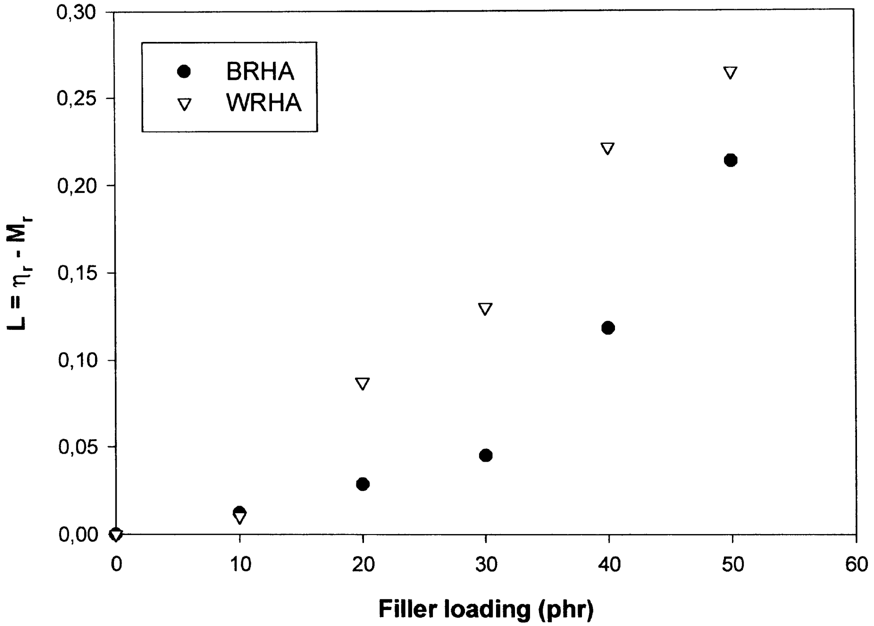

FIGURE 3 Variation of parameter L with BRHA and WRHA concentrations.

Figure 3 that L increases as the filler loading increases. The magnitude of L changes slowly at low loadings. Above a certain loading (around 10 phr for WRHA and 30 phr for BRHA), however, L increases very sharply, showing that from this point on there is a preponderance of undispersed filler agglomerates, according to Lee's theory. The particular loading at which these agglomerates start to show up is higher for BRHA, which is consistent with the chemical nature of these fillers. From the observation of Table 2, with regard to chemical composition, BRHA is more similar to carbon black while WRHA, containing 97% of SiO_2 and only 0.20% of loss on ignition, resembles silica. It is known that carbon black possesses a high dispersive component of the surface energy, which is related to a strong interaction between filler and hydrocarbon rubber. Silica, on the other hand, is characterized by a higher specific component of the surface energy, which is related to stronger interaggregate interaction [17]. From this, it may be suggested that BRHA disperses more readily in NR rubber than WRHA.

Another interesting investigation has been carried out by Wolff [18, 19], who proposed a mathematical expression also in terms of rheometric data, to characterize filler structures present in rubber vulcanizates, particularly in the case of carbon blacks. When a filler is incorporated into a compound, the maximum torque variation, $\Delta T^f = (T^f_{max} - T^f_{min})$, observed on a curometer during vulcanization, increases. The ratio between ΔT^f and ΔT^o, the torque variations for the loaded and the unloaded compound, respectively, was found to be directly proportional to the filler loading. By plotting the relative torque as a function of filler loading, a straight line is obtained whose slope was defined by Wolff [18,19] as α_F:

$$\frac{[T^f_{\max} - T^f_{\min}]}{[T^o_{\max} - T^o_{\min}]} - 1 = \alpha_F \cdot \frac{W_F}{W_P} \tag{4}$$

where W_P is the mass of polymer in the compound, W_F is the mass of filler in the compound, and α_F is a specific constant for the filler, which is independent of the cure system and closely related to the morphology of the filler. The parameter α_F represents the final structure of the filler, as it exists in the vulcanizate after all possible structure breakdowns occurred during mixing and vulcanization. It is easy to realize that the reinforcement build-up and the crosslinking reaction both take place during curing without affecting each other. The application of Equation 4 allows the definition of a filler specific constant, related to the filler structure, and also predicts whether or not crosslink density is unaffected by the presence of the filler, in which case a straight line is obtained. If no linear relationship between ΔT and filler loading is observed, then, the filler must have affected crosslink density. Equation 4 also shows that, based on a single test, α_F can be calculated from the changes in torque which occur during vulcanization of two compounds, a gum and a loaded composition.

In Figure 4, Wolff equation is applied to rice husk ash-filled NR rubber. The linear correlations shown in Figure 4 imply that α_F is independent of filler loading and that WRHA and BRHA structures remain constant over the loading range investigated. Since α_F is a measure of the in-rubber structure of fillers, the higher α_F value found for WRHA (${\alpha_F}^{WRHA} = 0.304$ while ${\alpha_F}^{BRHA} = 0.225$) would be an evidence for this filler to have a higher tendency to form agglomerates in the vulcanizates, when compared to BRHA.

The above discussion seems to suggest that BRHA is less susceptible to agglomerate in NR vulcanizates. This may not be the case and the results must be looked at with precaution since during the vulcanization process in the oscillating disk rheometer, the sample undergoes an angular movement imposed by the rotor (3° in the present work), which is equivalent to approximately 20% strain [20].

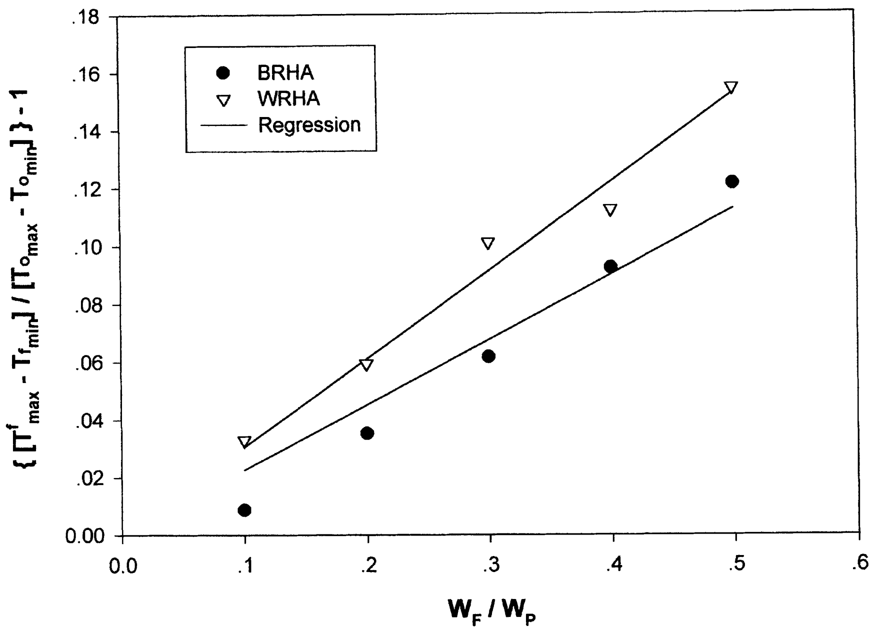

FIGURE 4 Wolff relation for rice husk ash as a function of filler loading.

At this level of strain, most of filler agglomerates may no longer exist since the networks they might have formed at higher loadings are probably too weak to withstand shear deformation. This is even more likely to occur at temperatures as high as 150°C.

The effect of BRHA and WRHA on tensile strength of NR composites is shown in Figure 5. For WRHA, increasing the filler content increases this property until a maximum value is reached at about 20 phr filler loading. Further increase in filler content reduces the tensile strength. As the filler loading is increased, more surface area is available for interaction between filler particles and rubber molecules; hence reinforcement increases with an increase in filler loading. However, maximum reinforcement level is eventually reached, at about 20 phr of WRHA, after which dilution effect occurs. From Lee's [15] treatment, as shown in Figure 3, an optimum filler concentration around 10 phr has been predicted.

Figure 5 also shows that comparing the two ashes, tensile strength for BRHA-filled NR vulcanizates is lower along the entire loading range. Up to 20 phr a more or less constant value is obtained but at higher loadings (30 phr and up) the property is badly affected. Figure 3 shows a different approach to estimate the maximum level in filler

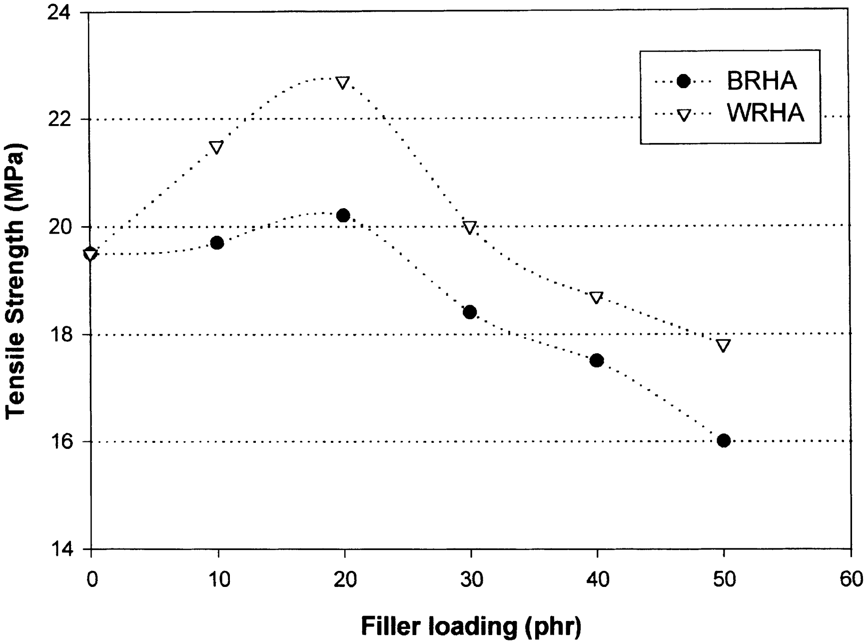

FIGURE 5 Effect of filler loadings on tensile strength of BRHA- and WRHA-filled NR vulcanizates.

loading which is allowed to be incorporated before deterioration of the property. This can be taken as the point at which an abrupt change in the slope occurs. From Figure 3, this discontinuity happens around 30 phr. So, the combination of these results with those for tensile strength, suggests that the optimum amount of filler to be used in the formulation must be somewhere in between 20 and 30 phr for BRHA, and 10 and 20 phr for WRHA. At higher loadings undispersed filler agglomerates preponderate.

The factors that influence the reinforcement of elastomers by particulate fillers are: (i) the particle size or specific surface area which, together with filler loading, determine the effective contact area between filler and polymer matrix; (ii) the structure or degree of irregularity of the filler unit that plays an essential role in restricting motion of elastomer chains under strain; (iii) the surface activity that is the predominant factor with regard to filler-filler and filler-polymer interaction. In our case, perhaps, the particle size of BRHA might be the main culprit for the low level of reinforcement. According to Fetterman [21], fillers with size in the order of 50 nm, or greater, are classified as semi or non-reinforcing. However, the superior tensile strength of the WRHA-filled vulcanizates suggests that other factors, in addition to particle size (similar for both ashes), also influence the properties of NR vulcanizates such as the surface activity and the quality of the bonding between WRHA and NR matrix.

The scanning electron micrographs presented in Figure 6 depict two distinct characteristics, i.e., filler dispersion and failure mode. The failure surface for NR gum shows a smooth topography and only a few tear lines, long and branched. This failure surface pattern is typical for gum vulcanizates cured with the conventional vulcanization (CV) system [22]. Considering now the filled vulcanizates, as previously discussed, the application of the Lee [15] analysis suggested that BRHA would disperse more readily in NR rubber than WRHA. This, however, is not completely true as seen in Figure 6. The fractured surfaces of the compounds containing this BRHA filler show a topography that is more characteristic of a coarse dispersion. To figure out the possible reasons for these conflicting results one must take into account the experimental conditions imposed on the compounds during processing and vulcanization. Filler aggregates in an elastomer matrix are known to have a tendency to form agglomerates, especially at high loading, leading to chain-like filler structures or clusters. These are generally termed secondary structures or, in some cases, filler network, even though they are not comparable to the continuous polymer network. Such a structure has a significant effect on the properties of filled rubber [23]. The photomicrographs in Figure 6 refer to BRHA-compounds with 10 and 20 phr that, according to Lee's [15] treatment, are still in the region of the curve in Figure 3 related to good filler dispersion. Data used to build this curve were measured on an oscillating disk rheometer in which the material, differently from the samples used in microscopy analysis, were submitted to a shear deformation caused by the oscillating movement of the rotor. This means that these two analyses impose different experimental conditions on the samples so that, during vulcanization in the rheometer, filler agglomerates might have been destroyed due to shearing, thus giving rise to misleading results and this apparent inconsistency.

Figure 6 also shows that, under similar loading, WRHA forms a better dispersion, with less aggregates, and minimum presence of holes on the surface. Hole formation results from detachment of filler aggregates from the rubber matrix. Usually, the presence of holes or loose aggregates on the failure surface indicates a weak filler-rubber matrix interaction. Thus, the low incidence of holes on the fractured surface, as seen in Figure 6, may account for the better performance of WRHA concerning reinforcement and tensile strength. BRHA

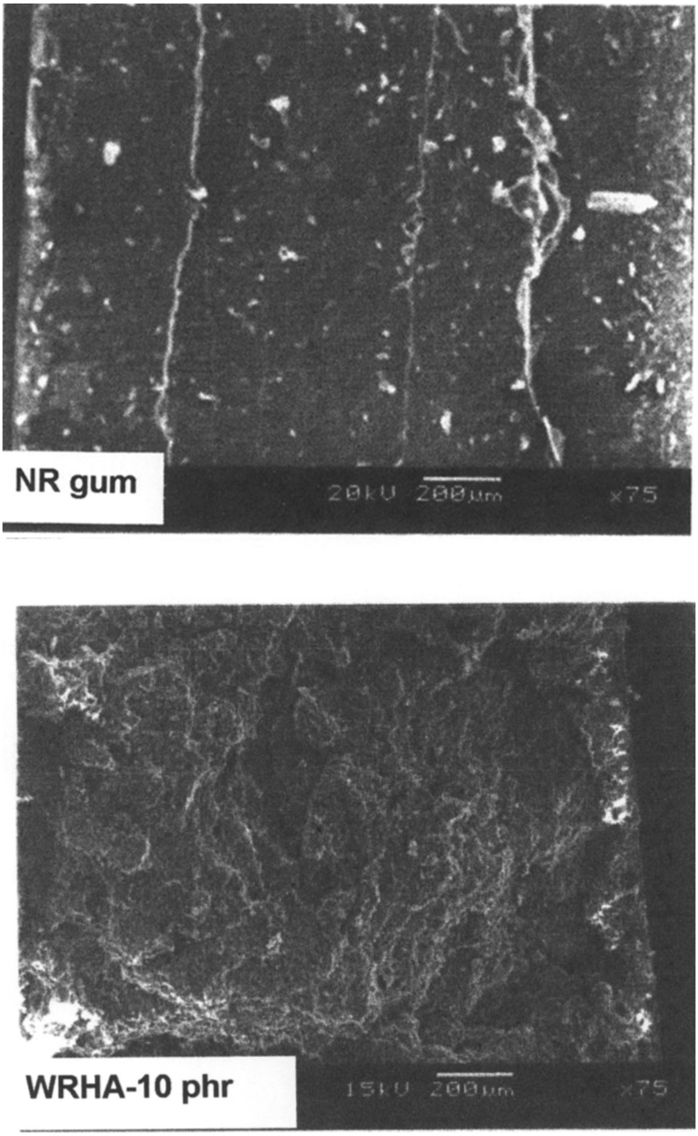

FIGURE 6 SEM photomicrographs of BRHA- and WRHA-filled NR vulcanizates after tensile fracture (x75).

compositions, on the other hand, show agglomeration and poor dispersion leading to non-reinforcing properties. The rough topography of these surfaces indicates that the fracture is a relatively slow process

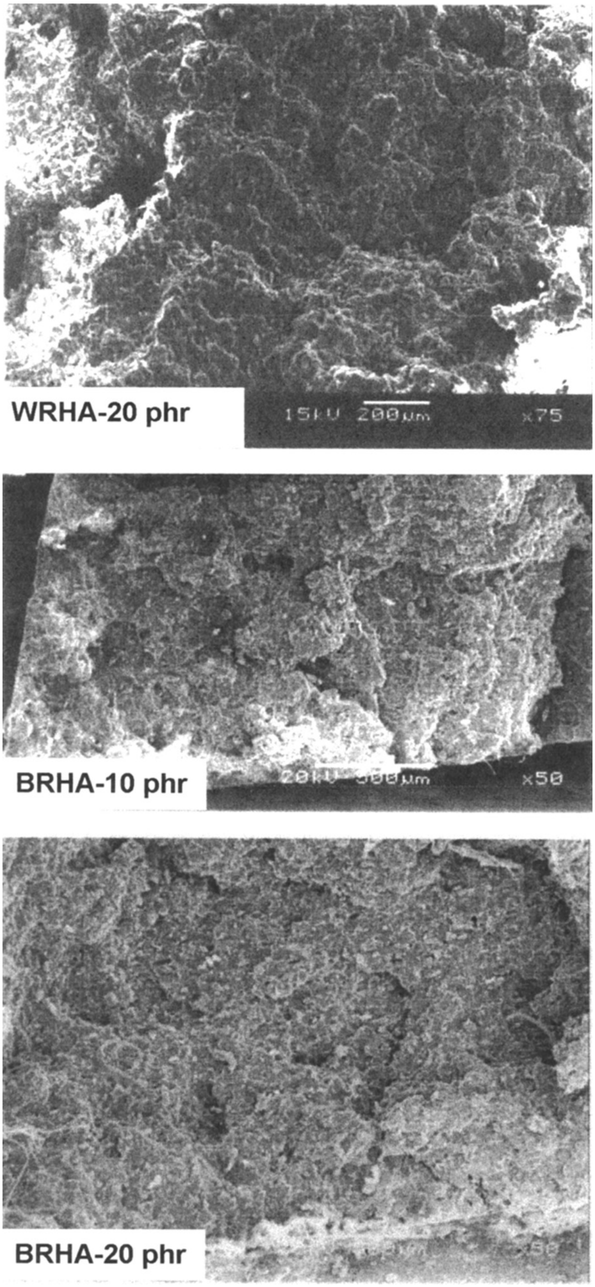

FIGURE 6 (Continued).

and that the initial stage of crack propagation can be said to be ductile. However, as failure progresses, stress distribution in the vulcanizates is no longer uniform and the samples will not offer any further resistance to crack propagation. Thus, in BRHA composites, fast and unstable crack propagation is believed to have occurred, leading to catastrophic failure.

Figure 7 shows the effect of BRHA and WRHA loading on tear strength. The addition of rice husk ash had a negative effect on this property, especially BRHA. This property also depends on the degree of adhesion between filler aggregates and rubber matrix. When tearing force is applied, high stresses occur at the interface between rubber and filler in the vicinity of the tear region [24, 25]. Thus, the presence of filler aggregate near or at the locus where tear is going to start will determine tear strength. As the tearing force becomes higher, failure would create new surfaces, leading to energy dissipation [24]. If a stronger adhesion at the filler-rubber interface does exist, more energy will be dissipated during the internal failure, thus reducing the stress concentrated near the region of tear. This internal

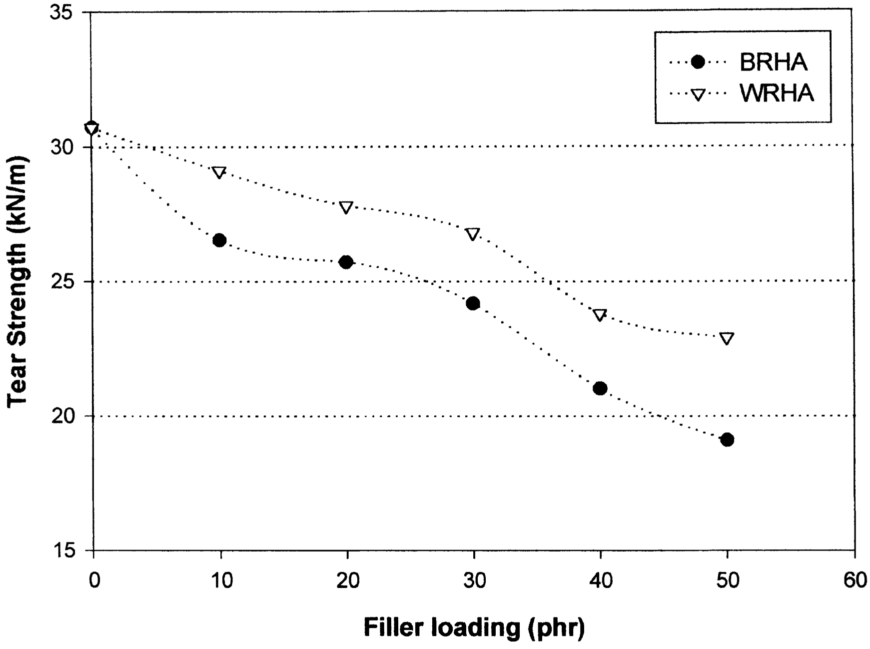

FIGURE 7 Effect of filler loadings on tear strength of BRHA- and WRHA-filled NR vulcanizates.

failure mechanism would prolong the failure process. Since good rubber-filler adhesion is a necessary condition for high tear strengths, it can be seen from the photomicrographs of Figure 6 why WRHA and BRHA did not impart good reinforcement character to the NR vulcanizates.

Values of hardness are shown in Figure 8. According to Jacques [26], hardness and modulus of vulcanizates normally increase with the use of particulate fillers, the greatest effect being obtained with the reinforcing ones. From Figure 8, it can be seen that, as expected, hardness of BRHA and WRHA vulcanizates increases with increasing filler loading. Rice husk ash is in particulate form and is a hard and stiff inorganic (not pure silica) material, so that the presence of BRHA and, mostly, WRHA in the rubber matrix would reduce flexibility of the rubber chains and, consequently, will make the vulcanizates harder and stiffer.

The effect of fillers on crosslink density in vulcanizates is determined by modulus measurements or by swelling experiments. The latter method yields interesting results since the filler solid surface

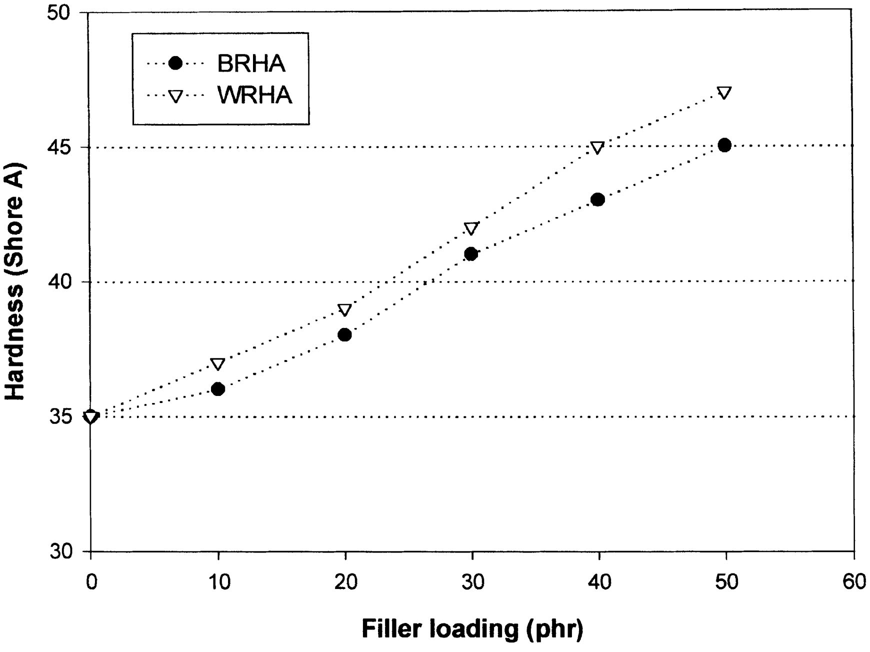

FIGURE 8 Effect of filler loadings on hardness of BRHA- and WRHA-filled NR vulcanizates.

can develop three types of interaction with the elastomer: adherence at fixed points, non-adherence, and adherence with 2-dimensional mobility over the surface of the filler. The difference in the type of interaction becomes clear upon swelling a vulcanizate in solvents of increasing swelling power and comparing the degrees of swelling with that for the unfilled vulcanizate, assuming that chemical crosslink density of the polymer has not been changed by the presence of the filler [27].

Whereas uncrosslinked rubber can be dissolved in good solvents, vulcanized rubbers can be only swollen to an extent determined by the crosslink density and the nature of the solvent. After incorporation of the filler, the volume fraction of the filled rubber in the swollen gel, V_{rf} (corrected for filler volume, since the filler is assumed not to swell in the solvent), should differ from that of the pure gum, V_{ro}. In the case of reinforcing fillers, the strong filler-matrix interaction caused by the strong physical and/or chemical adsorption can have an effectiveness equivalent to the true crosslinks. The ratio V_{ro}/V_{rf} would thus decrease with increasing filler loading. However, filler addition may change the crosslink density in the polymer matrix, since it may affect the vulcanization reaction. In cases where the crosslink density of the matrix is independent of the presence of the filler, Kraus [28] derived the following expression relating the ratio V_{ro}/V_{rf} and the loading of the adhering filler:

$$\frac{V_{ro}}{V_{rf}} = 1 - \frac{[m\phi]}{[1-\phi]} \tag{5}$$

with

$$m = 3C(1 - V_{ro}^{1/3}) + V_{ro} - 1$$

where C is a parameter characteristic of the filler, which is related to filler-polymer interaction and the filler structure in the vulcanizate. For fillers having the same structure, higher values of C suggest stronger interaction between filler and the rubber matrix.

Figure 9 shows the plot of V_{rO}/V_{rf} versus $\phi/(1-\phi)$ according to Kraus equation [28]. It can be observed that BRHA compositions exhibit large deviations in relation to the proposed linear mathematical model, as the ratio V_{rO}/V_{rf} has an initial ascendant profile and then starts to gradually decrease. In addition, the values are higher than 1 for the entire range; this means that the matrix around the filler particles will swell and as the particle is not affected by the solvent, it will keep its original volume and the swollen elastomer will

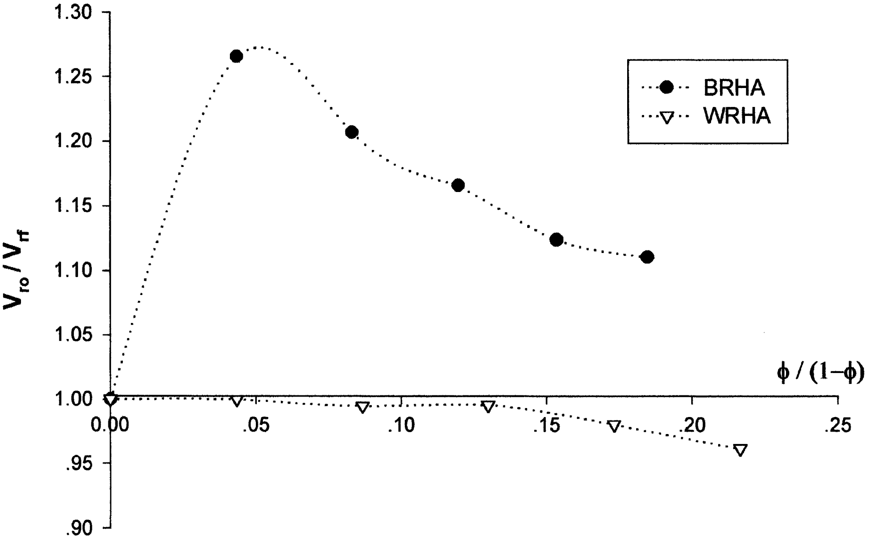

FIGURE 9 Kraus model for swelling test of vulcanizates containing rice husk ash.

separate from the particle [29]. The porosity of this filler is another point to be considered. As shown in Table 3, BRHA and WRHA have comparable particle size but the surface area for BRHA is much larger than for WRHA, due to the presence of pores. This behavior resembles that described by Voet [30] and Pal [31], who investigated the reinforcement by silica. They suggested that the deviation from linearity found in the case of this material would be related to the onset of dewetting and void formation. The spaces between the particle and the swelling vulcanizate, being filled with solvent, would no longer fulfill the conditions set forth in the Kraus model. WRHA, on the other hand, presents a larger interaction with NR matrix, since for this filler in the loading range studied, V_{rO}/V_{rf} is less than 1. Thus, comparing these results with the scanning electron micrographs, it can be seen that they are in good agreement when the vulcanizates are filled with WRHA, a more homogeneous material, with less incidence of pores. In the case of BRHA, porous particulate filler composed of an organic and inorganic phases, large deviations were found.

The problem of measuring crosslink densities in filled rubbers has not been solved despite many studies. In pure gum vulcanizates, excellent correlations have been obtained between chemically estimated crosslink densities and equilibrium modulus, or equilibrium swelling (V_r). Unfortunately, neither of these methods can be applied to filled rubbers. The equilibrium swelling is normally reduced (V_r values numerically larger) by restriction to swelling imposed by carbon black [32], but the value of this correction cannot be estimated theoretically. Similarly, considerable difficulty exists in calculating crosslink densities from equilibrium modulus values of filled stocks since these measurements must be corrected for the hydrodynamic effect of the filler and rubber-filler interaction.

Cotten [33] investigated the effect of carbon black surface properties and structure on rheometer cure behavior, and suggested that the observed increase in the rheometer torque at a given time t, ΔT, is directly related to the crosslink density, particularly if the measurements are done at relatively low frequencies. In Figure 10 the relationship between $T_{max} - T_{min}$ and V_r is shown for BRHA and WRHA-filled NR vulcanizates. Two different plots may be distinguished. BRHA gives lower V_r values at any given ΔT. This would be already expected since it was found that WRHA restricts the equilibrium swelling process, in accordance to Kraus equation, while BRHA does not impose restriction. Qualitatively $T_{max} - T_{min}$ can be

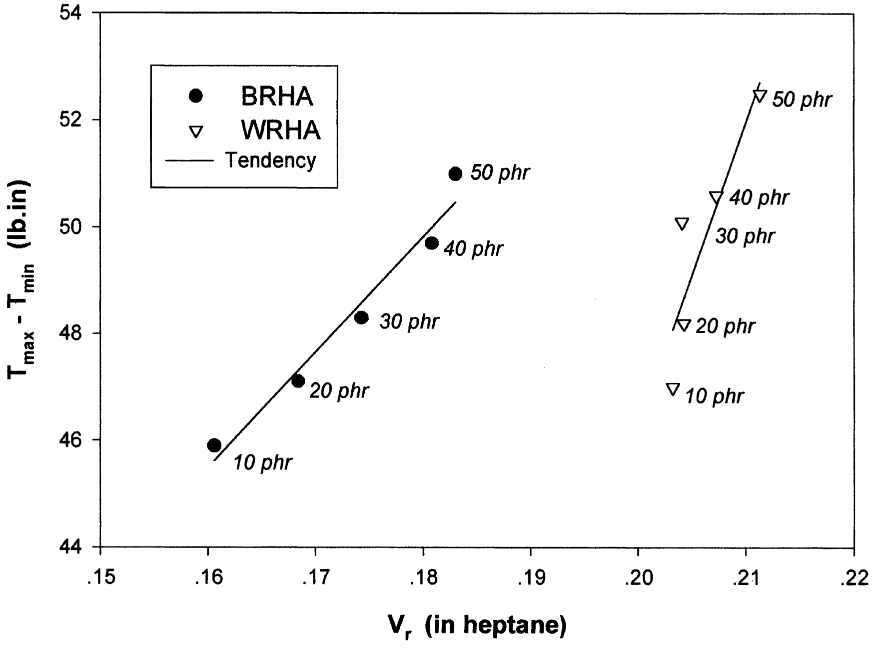

FIGURE 10 Relationship between ΔT and V_r for rice husk ash-filled NR vulcanizates.

taken as a better approximation to true crosslink density than V_r, in particular for BRHA vulcanizates. However, these $T_{max} - T_{min}$ values would have to be corrected for filler loading before deriving any quantitative relationship.

CONCLUSIONS

Rice husk ashes, BRHA and WRHA, although obtained from the same raw material, exhibit differences in chemical composition and physical properties. These differences result in superior mechanical performance in the case of WRHA-filled NR vulcanizates.

To have a better understanding of these systems, rheometric data were used to characterize filler structure present in these vulcanizates. This treatment showed evidence for a tendency of WRHA to form secondary structures at higher filler loadings. This, however, was not supported by SEM analysis. From the photomicrographs this filler was found to be better dispersed and more adhering to the rubber matrix, and less likely to form large agglomerates than BRHA, in accordance to Kraus model.

Nevertheless, before dismissing mathematical manipulations of the rheometric data, one must picture the reasons for such a discrepancy. In our case, it is believed that the method has not been able to detect BRHA secondary structures because of the shear deformation imposed on the samples by the angular movement of the rotor during vulcanization in the oscillating disk rheometer, which would be enough to destroy these structures.

REFERENCES

[1] Chakraverty, A., Mishra, P. and Banerjee, H. D. (1998). *J. Mater. Sci.*, **23**, 21.
[2] Liou, T. H. and Chang, F. W. (1997). *Ind. Eng. Chem. Res.*, **36**, 568.
[3] Sharma, N. K. and Williams, W. S. (1984). *J. Am. Ceram. Soc.,* **67**, 715.
[4] Anon, A. (1974). *Rubb. World*, **171**, 42.
[5] Fuad, M. Y. A., Ismail, Z., Mansor, M. S., Ishak, Z. A. M. and Omar, A. K. M. (1995). *Polymer Journal*, **27**, 1002.
[6] Fuad, M. Y. A., Ismail, Z., Ishak, Z. A. M. and Omar, A. K. M. (1995). *Eur. Polym. J.*, **31**, 885.
[7] Ismail, H., Ishiaku, U. S., Lu, E. S. and Ishak, Z. A. M. (1997). *Intern. J. Polymeric Mater.*, **38**, 275.
[8] Ismail, H., Ishiaku, U. S., Lu, E. S. and Ishak, Z. A. M. (1998). *Intern. J. Polymeric Mater.*, **39**, 45.
[9] Ismail, H., Nasaruddin, M. N. and Ishiaku, U. S. (1999). *Polymer Testing*, **18**, 287.
[10] da Costa, H. M., Visconte, L. L. Y., Nunes, R. C. R., Furtado, C. R. G. (2000). *J. Appl. Polym. Sci.*, **76**, 1019.

[11] da Costa, H. M., Visconte, L. L. Y., Nunes, R. C. R. and Furtado, C. R. G. (2001). *Kautsch. Gummi Kunstst.*, **54**, 242.

[12] Wagner, M. P. (1976). *Rubb. Chem. Technol.*, **49**, 704.

[13] da Costa, H. M., Visconte, L. L. Y., Nunes, R. C. R. and Furtado, C. R. G. *J. Appl. Polym. Sci.*, submitted.

[14] da Costa, H. M., Visconte, L. L. Y., Nunes, R. C. R. and Furtado, C. R. G. *J. Appl. Polym. Sci.*, submitted.

[15] Lee, B. L. (1979). *Rubb. Chem. Technol.*, **52**, 1019.

[16] Wang, M. J. and Wolff, S. (1991). *Rubb. Chem. Technol.*, **64**, 559.

[17] Wolff, S. and Wang, M. J. (1992). *Rubb. Chem. Technol.*, **65**, 329.

[18] Wolff, S. (1969). *Kautsch. Gummi Kunstst.*, **22**, 367.

[19] Wolff, S. (1970). *Kautsch. Gummi Kunstst.*, **23**, 7.

[20] Boonstra, B. B. (1982). In *Rubber Technology and Manufacture*. Second Edition, C. M. Blow and C. Hepburn, Eds., Butterworth Scientific, London.

[21] Fetterman, E. Q. (1985). *Rubb. World*, **194**, 38.

[22] Pal, P. K., Bhowmick, A. K. and De, S. K. (1982). *Int. J. Polym. Mater.*, **9**, 139.

[23] Tokita, N. and Pliskin, I. (1973). *Rubber Chem. Technol.*, **46**, 1166.

[24] Kraus, G. (1963). *J. Appl. Polym. Sci.*, **7**, 861.

[25] Mullins, L. (1960). *Rubb. Chem. Technol.*, **33**, 315.

[26] Jacques, J. E. (1982). In *Rubber Technology and Manufacture*. Second Edition, C. M. sBlow and C. Hepburn, Eds., Butterworth Scientific, London.

[27] Boonstra, B. B. (1979). *Polymer*, **20**, 691.

[28] Kraus, G. (1965). *Rubb. Chem. Technol.*, **38**, 1070.

[29] Kraus, G. (1963). *J. Appl. Polym. Sci.*, **7**, 861.

[30] Voet, A., Morawski, J. C. and Donnet, J. B. (1977). *Rubb. Chem. Technol.*, **50**, 342.

[31] Pal, P. K. and De, S. K. (1982). *Rubb. Chem. Technol.*, **55**, 1370.

[32] Boonstra, B. B. and Taylor, G. L. (1965). *Rubb. Chem. Technol.*, **38**, 943.

[33] Cotten, G. R. (1972). *Rubb. Chem. Technol.*, **45**, 129.