

# The Effect of Coupling Agent and Chemical Treatment on Rice Husk Ash- Filled Natural Rubber Composites

H. M. DA COSTA,<sup>1</sup> L. L. Y. VISCONTE,<sup>1\*</sup> R. C. R. NUNES,<sup>1</sup> C. R. G. FURTADO<sup>2</sup>

<sup>1</sup> Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O Box 68525, 21.945-970 Rio de Janeiro, RJ, Brazil

<sup>2</sup> Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier 524, Maracanã, Rio de Janeiro, RJ, Brazil

Received 19 March 1999; accepted 17 September 1999

**ABSTRACT:** Rice husk ash was incorporated into natural rubber (NR) using a laboratory size two-roll mill. Curing using a conventional vulcanization system (CV) was chosen, and cure studies were carried out on a Monsanto rheometer. Physical testing of the NR vulcanizates involved the determination of tensile, tear, and abrasion resistances, and hardness. Fourier transform infrared spectroscopy (FTIR) analysis was done to verify the presence of the characteristic functional groups of precipitated silica in MHA (milled husk ash) and THA (treated husk ash). The effect of the coupling agent, bis(3-triethoxysilylpropyl)-tetrasulfane (Si-69), on the curing and physical properties of the vulcanizates was investigated. A chemical treatment on a rice husk ash was done, and the effects of this procedure are also reported. For comparison, two commercial fillers, precipitated silica (Zeosil-175) and carbon black (N774), were also used. Although the presence of the silane coupling agent had not brought the expected increase in properties, treated husk ash showed exceptional performance in terms of tensile strength and abrasion resistance of the filled vulcanizates. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1019–1027, 2000

**Key words:** natural rubber, rice husk ash, filler

## INTRODUCTION

Growing population and pressure for better living standards are increasing the demand for more food, energy, and goods. Simultaneously, large amounts of wastes are generated, causing pollution of our environment and, as a consequence, the by-products resulting from the processing of agricultural products deserve the attention of those interested in their utilization. Some of these by-products are already used as raw materials for the fabrication of different materials, including

chemicals. Others, although considered potentially useful, nevertheless do not find any industrial application, because their occurrence is relatively low in certain regions.

The production of rice, one of the major food crops in the world, generates one of the major wastes; namely, rice husks and straw. Disposal of the husks is a particularly serious problem, which requires special attention because of the large quantities that can be accumulated in the vicinities of the rice mills. Efforts to use this husk waste directly have found limited results because of its highly abrasive character, low nutritional value, high resistance to degradation, low density, and high ash residue. Although the use of husk as fuel to produce the energy necessary in

---

Correspondence to: L. L. Y. Visconte.

*Journal of Applied Polymer Science*, Vol. 76, 1019–1027 (2000)  
© 2000 John Wiley & Sons, Inc.

**Table I Typical Formulation**

Material	Phr
Natural rubber	100
Zinc oxide	4
Filler	10–50
Silane	Variable
Naphthenic oil	Variable
Diethylene glycol	Variable
Stearic acid	1.5
MBTS <sup>a</sup>	0.8
TMTD <sup>b</sup>	0.2
Sulphur	2.5

<sup>a</sup> Dibenzothiazylsulfide.<sup>b</sup> Tetramethylthiuramdisulfide.

grain processing, as a substitute for oil and coal, is a feasible practice, because it allows reduction in oil expenses, other alternatives are conceivable.<sup>1</sup>

An early investigation by Haxo and Mehta<sup>1</sup> proved that ground rice husk ash obtained by means of a special burning process is a moderately reinforcing filler for such rubbers as styrene-butadiene rubber (SBR), ethylene propylene diene methylene rubber (EPDM), and natural rubber (NR). A recent study by Ahmad Fuad et al.<sup>2,3</sup> observed that the incorporation of rice husk ash into polypropylene has led to a significant increase in flexural modulus of the composites; that is, comparable to that of such other commercial fillers as mica. In addition to this, applications of rice husk ash in other fields have been reported: synthesis of zeolite, a catalyst,<sup>4,5</sup> and in structural concrete, cement, and lightweight building materials.<sup>6</sup>

This article discusses the influence of a silane coupling agent on the curing and physical properties of rice husk ash-filled NR vulcanizates. A chemical treatment on the rice husk ash was done, and the results are also presented. For comparison, two commercial fillers; namely, silica and carbon black, were used.

## EXPERIMENTAL

### Material and Compounding

All materials were used as received. Natural rubber was supplied by Irwin Industrial e Comercial Ltda. and raw husk ash (RHA) by EMBRAPA. Carbon black (N774) was supplied by Copebrás,

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

Chemical Composition (%)	MHA	THA
CaO	0.44	—
MgO	0.54	0.07
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.03
K <sub>2</sub> O	1.23	0.29
Na <sub>2</sub> O	0.25	24.26
Al <sub>2</sub> O <sub>3</sub>	0.24	0.06
MnO	0.15	—
TiO <sub>2</sub>	0.01	—
P <sub>2</sub> O <sub>5</sub>	0.99	0.20
SiO <sub>2</sub> (silica)	41.62	36.19
Lost on ignition (LOI)	25.26	49.20

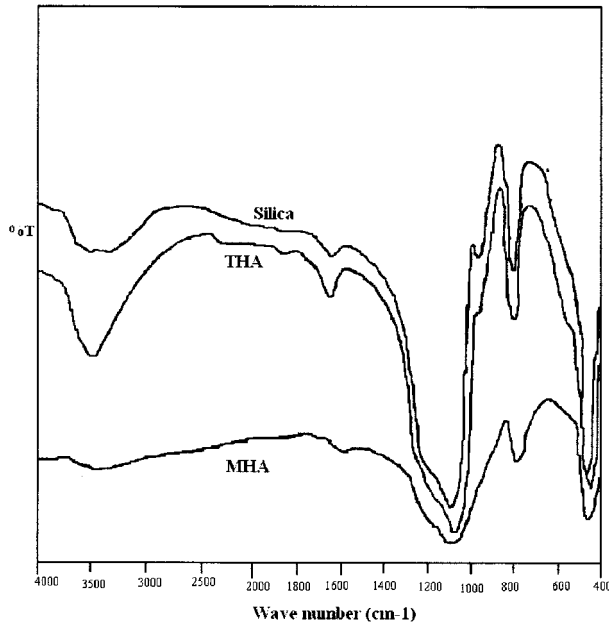
and precipitated silica (Zeosil-175) by Rhodia. Naphthenic oil was manufactured by Petroflex Indústria e Comércio. Other compounding ingredients, such as zinc oxide, stearic acid, sulphur, and accelerators were of reagent grade. The silane coupling agent, bis(3-triethoxysilylpropyl)-tetrasulfane (Si-69) was supplied by Degussa AG.

Rice husk ash was milled for 5 h and sieved on a 250-mesh sieve and is referred to as MHA (milled husk ash). Bis(3-triethoxysilylpropyl)-tetrasulfane (Si-69) 2% w/w on filler was applied for the modification of the filler surface. A chemical treatment with 20% NaOH solution and 12N HCl, under controlled conditions, was done in MHA for generation of hydrated silica, following the procedure of Louis and Banthia.<sup>7</sup> This treated husk ash form is denoted THA.

The formulation shown in Table I was employed to evaluate curing and physical properties of NR vulcanizates. The chemical composition was obtained by atomic absorption techniques. The particle size distribution was determined by using a GLOBAL LAB Image (SP0550) software

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

Properties	MHA	THA	Silica	Carbon Black
Mean particle size ( $\mu\text{m}$ )	2.9	5.5	0.018	0.054
Surface area ( $\text{m}^2/\text{g}$ )	109	12	185	30
Density ( $\text{g}/\text{cm}^3$ )	1.91	1.91	2.00	1.54
pH	9.5	8.0	5.7	6.4



**Figure 1** FTIR analysis for the fillers.

package. The surface area was calculated through the Brunauer-Emmett-Teller (BET) method, on an ASAP 2010 Accelerated Surface Area and Porosimetry System. Fillers density was measured in a glass pycnometer, based on a modified technique,<sup>8</sup> and pH was determined through ASTM D 1512 method. The chemical and physical properties of RHA, MHA, silica, and carbon black are presented in Tables 2 and 3. FTIR spectra were obtained from a Perkin-Elmer spectrometer, model 1720-X, utilizing the pellet (press-disk) technique. The sawdust sample (1 mg) was dispersed in dry KBr (300 mg), and the mixture was ground to fine particles in a mortar and then pressed to form moisture free KBr pellets. In Figure 1, the FTIR spectra of silica, MHA, and THA are shown.

#### 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 D 3182. Rice husk 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 along the grain direction.

#### Physico-mechanical Testing of the Samples

Stress-strain data were determined on an Instron using an ASTM C type dumbbell specimen, according to ASTM D 412. Other physico-mechanical tests were: tear strength (ASTM D 624), hardness (ASTM D 2240), and abrasion resistance (ASTM D 1044).

#### Scanning Electron Microscope

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 mode of fracture, the condition of the matrix and filler surfaces, and filler dispersion. The fracture 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.

## RESULTS AND DISCUSSION

#### FTIR Analysis

In Figure 1, the FTIR spectrum for silica, MHA, and THA are shown. As opposed to carbon black, which has a lot of different functional groups but in small quantities, silica has few different chemical groups but in large amounts. Silica has a high-energy surface, because of the siloxane and silanol groups. Silanols can be single or paired. Paired silanols are close enough to each other to develop such interactions as H bonds. They are either borne by the same silicon atom and said to be geminal, or borne by two adjacent silicon atoms and called vicinal. Wagner<sup>9</sup> reported that the type of silanols identified on silica surfaces, and their infrared absorption assignments, were as follows. The strong band at 3750 cm<sup>-1</sup> occurred mainly on extensively dehydrated silicas. The unequivocal assignment of this band to isolated, freely vibrating silanols (1, Fig. 2) is generally accepted. Because this is the fundamental stretching frequency, interactions with electron fields from other atoms result in lowered frequencies. Only hydrogen bonding interactions and their associated infrared absorptions were considered in Figure 2. The absorption bands for adjacent (vicinal) silanols (2) at 3660 cm<sup>-1</sup> and the water band at 3400 cm<sup>-1</sup> also met with general acceptance. Hydrogen bonding of vicinal silanols with water (3) was attributed to the 3540 cm<sup>-1</sup> and the 3607 cm<sup>-1</sup> absorption bands in the infra-

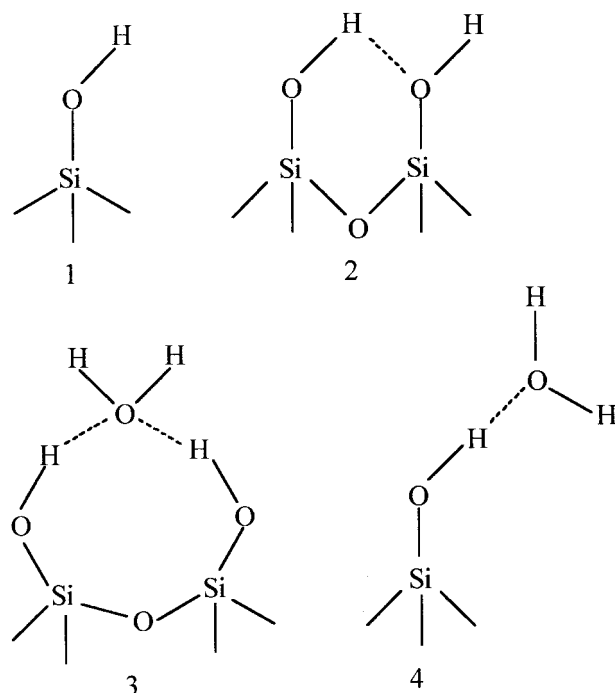


Figure 2 Hydroxyl types present in silicas.

red. The  $3550\text{ cm}^{-1}$  band also assigned to H-bonded, H-bonded vicinal silanols (2) as well as the isolated silanols (4). There are strong Si-O bands at  $830\text{--}1100\text{ cm}^{-1}$ . Vibrations for the Si-H band include the Si-H stretch ( $\sim 2200\text{ cm}^{-1}$ ) and the Si-H bend ( $800\text{--}950\text{ cm}^{-1}$ ). The Si-H stretching frequencies are increased by the attachment of an electronegative group to the silicon.

As can be seen in Figure 1, there is a correspondence between the absorptions bands of silica, MHA, and THA. The chemical treatment, which has been done on MHA, not only increased the intensity of absorption peaks in THA, but also seems to have led to an increase in the concentration of SiOH groups, because the absorption band at  $3500\text{--}4000\text{ cm}^{-1}$  is more pronounced than the present band in MHA.

#### Effect of Coupling Agent and Chemical Treatment on the Cure and Physical Properties of Filled NR Vulcanizates

Table 4 shows the values of optimum cure time ( $t_{90}$ ), minimum and maximum torque of MHA-, THA-, carbon black-, and silica-NR compositions. MHA shows a faster cure rate with increasing filler content. The most probable factors to account for this observation are such parameters as surface area, surface reactivity, particle size,

and metal oxide content.<sup>9</sup> In the presence of silane coupling agent, all filled vulcanizates exhibit lower values of  $t_{90}$ , which may be attributed to the direct involvement of silane in vulcanization, resulting in coupling bonds being established between the silane and both the filler and the NR matrix. The marked increment in the maximum torque for MHA with Si-69 can be related to an improvement of filler dispersion in NR, which reduced the mobility of the macromolecular rubber chains.

THA was incorporated only up to 30 phr (parts per 100 parts of rubber) because of processing difficulties. The chemical treatment may have caused an increase in the number of silanol groups (see FTIR spectra for THA in Fig. 1) and of adsorbed water, which might have contributed to the difficulty in achieving rapid wetting and dispersion in rubber. Although the acidic character of the hydroxyl groups in the surface has a retarding effect on vulcanization rates of the accelerated sulfur compounds, other filler properties were found to be more important to the vulcanization, because the optimum cure times for THA vulcanizates were always lower in relation to MHA, whether in the presence or not of Si-69.

For the best formulation (20 phr), which was selected from the analysis of mechanical proper-

Table IV Cure Time ( $t_{90}$ ), Minimum and Maximum Torque of MHA, THA, Silica, and Carbon Black-Filled NR Vulcanizates

Filler Loading	Minimum Torque (lb-in)	Maximum Torque (lb-in)	Optimum Cure Time $t_{90}$ (min)
0	8.2	41.1	11.5
MHA			
10	7.0 (9.8)	41.6 (49.2)	10.4 (8.1)
20	8.3 (12.0)	42.8 (54.1)	9.3 (6.3)
30	8.5 (11.6)	44.1 (55.9)	8.6 (6.4)
40	7.7 (11.4)	46.3 (57.9)	8.1 (7.3)
50	10.4 (11.0)	47.0 (58.5)	8.0 (7.1)
THA			
10	8.6	54.4	6.2
20	8.2	56.4	4.3
30	12.7	63.4	5.3
Carbon black			
20	12.7 (12.7)	57.4 (59.2)	7.4 (6.3)
Silica			
20	18.6 (16.9)	60.6 (63.5)	7.5 (7.3)

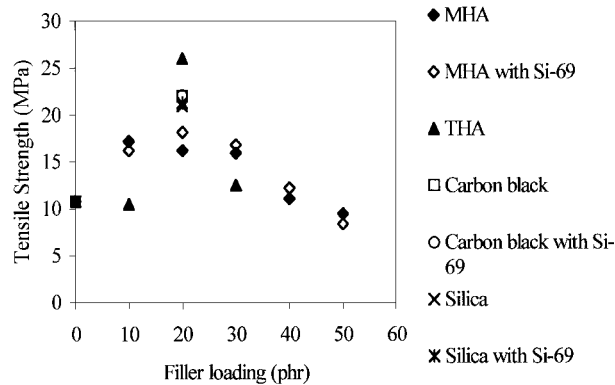
(#) Indicates the respective values in the presence of silane coupling agent.

**Table V Mechanical Properties of Mixes with MHA, THA, Silica, and Carbon Black**

Filler Loading	Property					
	Abrasion Resistance (g/1000 cycles)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus at 300% (MPa)	Tear Strength (kN/m)	Hardness (Shore A)
0 MHA	0.19	10.8	780	2.2	38.4	37
10	0.42 (0.40)	17.2 (16.2)	595 (590)	2.6 (2.5)	32.0 (39.1)	38 (38)
20	0.54 (0.84)	16.2 (18.2)	555 (585)	3.2 (3.6)	31.4 (35.8)	39 (40)
30	0.97 (0.99)	15.9 (16.8)	547 (562)	3.8 (4.0)	27.9 (30.1)	40 (41)
40	2.08 (1.28)	11.1 (12.2)	526 (492)	4.3 (4.9)	25.4 (25.3)	41 (43)
50	1.56 (1.51)	9.5 (8.4)	477 (410)	4.6 (5.4)	18.5 (15.3)	43 (44)
THA						
10	0.21	10.5	541	2.5	31.6	39
20	0.51	26.0	617	4.5	32.2	41
30	0.80	12.5	600	4.8	28.8	43
Carbon black						
20	0.01 (0.14)	22.0 (22.0)	455 (586)	4.1 (6.0)	37.0 (38.3)	43 (43)
Silica						
20	0.06 (0.01)	20.1 (21.3)	615 (642)	6.5 (4.8)	35.0 (39.1)	45 (44)

(#) Indicates the respective values in the presence of silane coupling agent.

ties,  $t_{90}$  for commercial fillers was comparable to that with MHA and Si-69. Nevertheless, silica and carbon black showed a higher  $t_{90}$  in relation to THA. The high values of maximum torque for carbon black and silica composites indicate that



**Figure 3** Effect of filler loadings on tensile strengths of MHA-, THA-, silica-, and carbon black-filled NR vulcanizates.

there is a high restriction to molecular motion of the macromolecules attributable, probably, to the greater interaction between the commercial fillers and rubber matrix, especially in the presence of coupling agent.

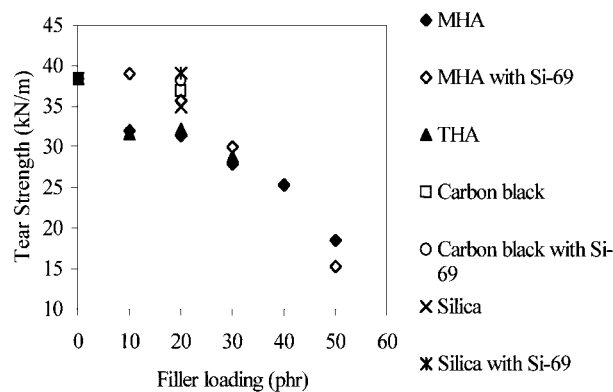
Table 5 summarizes the physical properties of MHA-, THA-, silica-, and carbon black-filled NR vulcanizates. In the THA-filled system, tensile strength increases with increasing filler content until a maximum level is reached. With MHA there is almost no change in the tensile strength up to 30 phr, as shown in Figure 3. A further increase in filler loadings has a deleterious effect on this property. The reduction in strength may be attributable to agglomeration of the filler particles to form a domain that acts as a foreign particle, or simply the result of physical contact 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 processing. Generally speaking, the primary filler factors influencing elastomers reinforcement are<sup>10</sup>: (1) the particle size or specific surface area, which, together with filler loading, determines the effective contact area between the filler and the polymer matrix; (2) the structure or the degree of irregularity of the filler unit, which plays an essential role in the restrictive motion of elastomer chains under strain; and (3) the surface activity, which is the predominant factor with regard to filler–filler and filler–polymer interaction. The results for tensile strength of MHA composites, as seen in Table 5, show that the effect of the silane coupling agent was not significant. Although Si-69 can impart a better wetting and dispersion, this was not enough to cause an enhancement in the performance of MHA as reinforcing filler. Perhaps the particle size of MHA might be responsible for this, because, according to Fetterman,<sup>11</sup> fillers with size of 50 nm, or greater, are classified as semi or non-reinforcing. On the other hand, THA-filled NR exhibits the highest tensile strength among all the fillers used, considering the best formulation (20 phr). This observation is rather unexpected, especially considering the fact that silica and carbon black are known to have a much smaller particle sizes, as shown in Table 3. Thus, the superior tensile strength of the THA-filled vulcanizate suggests that other factors, in addition to particle size, also influence the properties of NR vulcanizates such as, probably, the surface activity and the bonding quality between THA and NR matrix.

From the SEM photomicrographs of MHA, THA, silica, and carbon black (see Fig. 5), it can be seen that the fracture surface of MHA-silane is more uniform as compared to that without the coupling agent. However, the lack of intensive interactions between MHA filler and NR matrix is evident from these photomicrographs, when compared with the fracture surfaces for silica and carbon black vulcanizates, which are more uniform and smooth because of better filler dispersion. From the analysis of the fracture surface for the composite THA/NR, it can be noted that the fracture plane is smooth, similar to those for the compositions containing commercial fillers, which may be a clue to understanding of this exceptional behavior.

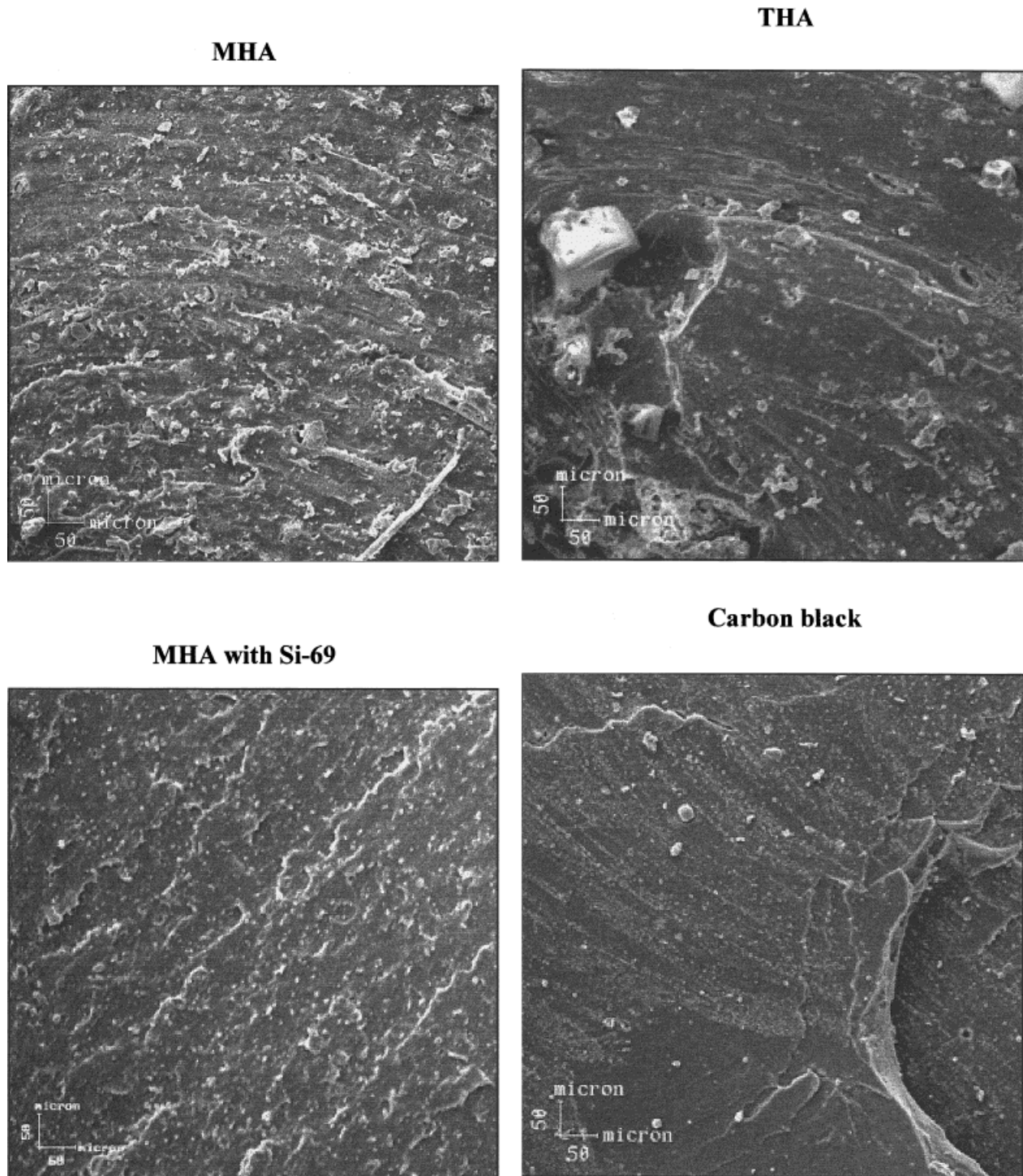
Tear strength data presented a decreasing tendency for MHA- and THA-filled systems, as shown in Table 5 and Figure 4. Although decreasing, MHA composites showed superior val-



**Figure 4** Effect of filler loadings on tear strengths of MHA-, THA-, silica-, and carbon black-filled NR vulcanizates.

ues for this property in relation to THA, when in the presence of Si-69. For the best formulation (20 phr), both MHA and THA compounds presented a performance poorer than that of the commercial fillers. Tear strength, like tensile strength, is affected by filler particle size and surface area.<sup>12</sup> In addition, this property is also controlled by the nature of both the rubber and the filler, as well as by the rate and temperature of tearing.<sup>13</sup> Therefore, the results obtained may be attributed to the nature of the surface properties, particle size, and surface area of the fillers used.

As for the stiffness properties, the trend observed is one that was expected. Hardness and modulus at 300% for both MHA- and THA-filled vulcanizates increased with the increasing filler content, as shown in Table 5. This result is expected, because as more filler particles are introduced into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates. In the presence of Si-69, the values of modulus and hardness for MHA vulcanizates were higher, and this can be attributed to better wetting and dispersion of the filler. For the best formulation, MHA-, in presence or not of Si-69, and THA-filled vulcanizates have lower modulus and hardness than the similar compounds with silica and carbon black. Again, this may be attributable to differences in the fillers' properties. The inferior stiffness of MHA- and THA-filled vulcanizates may be explained by two factors. First, these fillers have a larger particle size and, hence, a smaller surface area. Second, THA and, mainly, MHA fillers show a greater tendency towards aggregation. SEM photomicrographs shown in Fig-

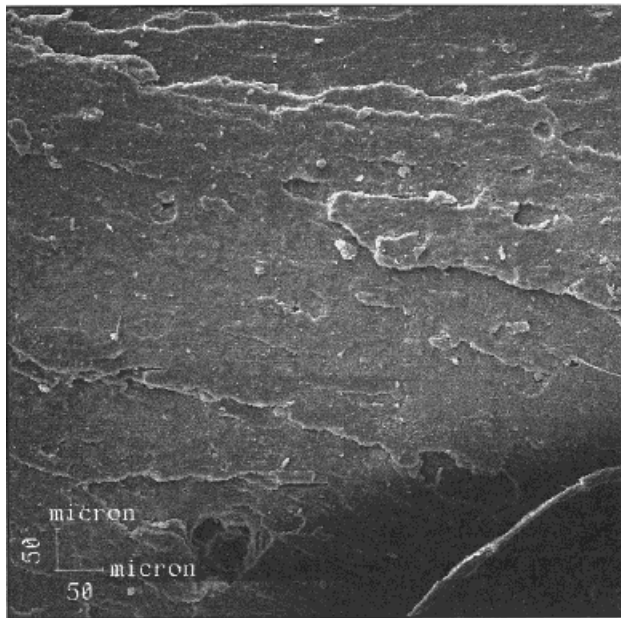


**Figure 5** SEM photomicrographs of MHA-, THA-, silica-, and carbon black-filled NR after tensile fracture at 20 phr filler loading ( $\times 150$ ).

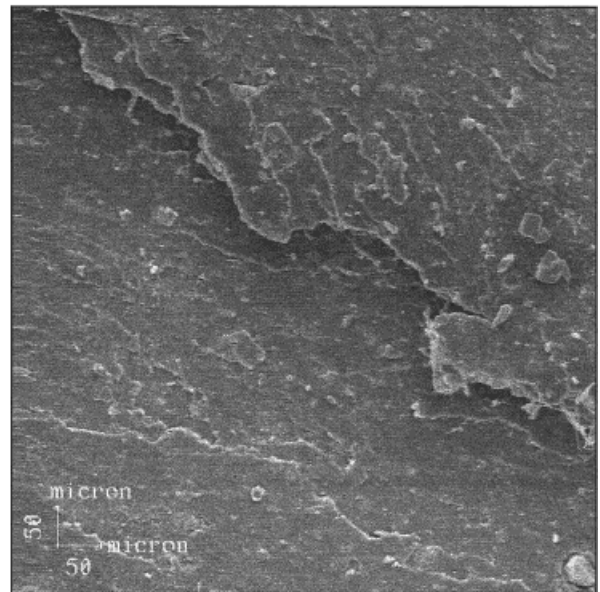
ure 5, confirm that, apart from possessing a larger particle size and broad particle size distribution, their dispersion in the rubber matrix is not uniform, if compared to silica and carbon black. This

poor filler dispersion will reduce filler–rubber interactions and consequently decrease the ability of the fillers to restrain gross deformation of the rubber matrix.

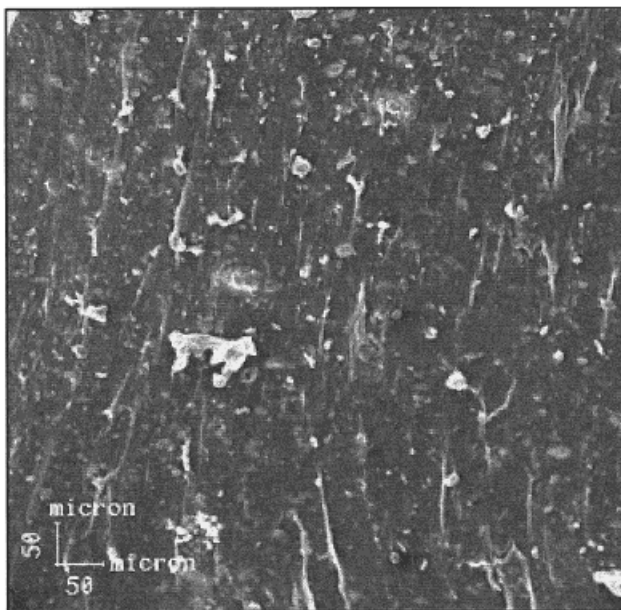
**Carbon black with Si-69**



**Silica with Si-69**



**Silica**



**Figure 5** (Continued from the previous page)

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface, as the result of mechanical action of a rubbing, scraping, or erosive nature. Table 5 shows that THA-filled NR

vulcanizates exhibit better abrasion resistances at any particular loading than MHA composites, and much lower, however, than the values for carbon black and silica compounds. The better dispersion and adhesion of the particles of silica



and carbon black in the rubber matrix could explain the obtained results.

## CONCLUSIONS

The main objective of this study was to verify the possibility of utilization of rice husk ash as an alternative filler for natural rubber (NR). It has been shown that NR compositions containing up to 30 phr of milled husk ash (MHA) exhibit practically constant values of tensile strength. Despite such parameters as surface area and particle size presented by this filler, MHA-filled vulcanizates with 20 phr, which gave the best results, show physical properties not much inferior to commercial carbon black or silica-filled vulcanizates, except for abrasion resistance. Furthermore, the cure characteristics were not prejudiced with the increasing in filler loading, despite the non-homogeneous nature of MHA chemical composition. For NR compositions with treated husk ash (THA), obtained by means of chemical treatment with NaOH and HCl, the physical properties were similar to those for MHA compositions, but, surprisingly, the value for tensile strength, considering the composition with 20 phr of filler, was slightly superior as compared to the commercial fillers. Although needing an adjustment in such reaction parameters as concentration of reagents for maximization SiO<sub>2</sub> content and control of particle size, THA can still be considered an interesting filler derived from rice husk ash and, thus, deserve more attention. The surface treatment with the addition of Si-69 silane coupling agent resulted in little improvement in the performance of all filled vulcanizates. The concentration may have been insufficient for the NR compositions with MHA and commercial fillers.

Although rice husk ash has not shown an outstanding performance as a reinforcing filler so far; nevertheless, it still presents two distinct advantages over commercial fillers. First, there is the economic advantage, because rice husk is readily available at extremely low cost as an unwanted by-product of rice mills. Second, the environmental advantage is priceless. The world is increas-

ingly sensitive to environmental issues, and the disposal of rice husk wastes poses a growing problem, because of the low bulk density nature of these husks. The annual production of rice in Brazil is estimated to be some 10 million tons, which generates approximately 2 million tons of waste husks. At present, the most common method of disposal of rice husk ash is dumping on waste land, thus creating an environmental hazard through pollution and land dereliction problems. The finding of useful applications for the rice husk ash will certainly help to alleviate the problems related to the disposal of the waste husks.

The authors are indebted to Mr. J. L. V. de Carvalho, from EMBRAPA, for providing the ashes, and to Mrs. D. M. R. Costa, from INT, for the rheometric analysis.

## REFERENCES

1. Haxo, H. E.; Mehta, P. K. *Rubb Chem Technol* 1975, 48, 271-288.
2. Fuad, M. Y. A.; Ismail, Z.; Mansor, M. S.; Ishak, Z. A. M.; Omar, A. K. M. *Polym J* 1995, 27, 1002-1015.
3. Fuad, M. Y. A.; Ismail, Z.; Ishak, Z. A. M.; Omar, A. K. M. *Eur Polym J* 1995, 31, 885-893.
4. Bajpai, P. K.; Rao, M. S.; Gokhale, K. V. G. K. *Ind Eng Chem Prod Res Dev* 1981, 20, 721.
5. Dalal, A. K.; Rao, M. S.; Gokhale, K. V. G. K. *Ind Eng Chem Prod Res Dev* 1985, 24, 465-468.
6. Fuad, M. Y. A.; Shukor, R.; Ishak, Z. A. M.; Omar, A. K. M. *Plast Rubb Proc Appl* 1994, 21, 225-235.
7. Louis, N. S.; Banthia, A. K. *Die Angew Chem* 1986, 139, 71-78.
8. Fuad, M. Y. A.; Yaakob, I.; Ishak, Z. A. M.; Omar, A. K. M. *Polym Test* 1993, 12, 107-112.
9. Wagner, M. P. *Rubb Chem Technol*, 1976 49, 704-774.
10. Morton, M. *Rubber Technology*, 3rd ed.; Van Nostrand Reinhold: New York, 1987.
11. Fetterman, E. Q. *Rubb World* 1985, 194, 38-44.
12. Kadir, A.; Thomas, A. G. *Rubb Chem Technol* 1981, 54, 15-23.
13. Mark J E.; Erman, B.; Eirich, F. R. *Science and Technology of Rubber*, 2nd ed.; Academic Press: New York, 1994.