Use of Rice Husk Ash as Filler in Natural Rubber Vulcanizates: In Comparison with Other Commercial Fillers

P. SAE-OUI,[1] C. RAKDEE,[1] P. THANMATHORN[2]

[1] National Metal and Materials Technology Center, 73/1 Rama VI Road, Rajdhevee, Bangkok 10400, Thailand

[2] Faculty of Science, Mahidol University, Rama VI Road, Rajdhevee, Bangkok 10400, Thailand

ABSTRACT: Rice husk ash is mainly composed of silica and carbon black remaining from incomplete combustion. Both silica and carbon black have long been recognized as the main reinforcing fillers used in the rubber industry to enhance certain properties of rubber vulcanizates, such as modulus and tensile strength. In this study, two grades of rice husk ash (low- and high-carbon contents) were used as filler in natural rubber. Comparison was made of the reinforcing effect between rice husk ashes and other commercial fillers such as talcum, china clay, calcium carbonate, silica, and carbon black. Fourier transform infrared spectroscopy (FTIR) analysis was employed to study the presence of functional groups on the ash surface. The effect of silane coupling agent, bis(3-triethoxysilylpropyl)tetrasulfane (Si-69), on the properties of ash-filled vulcanizates was also investigated. It was found that both grades of rice husk ash provide inferior mechanical properties (tensile strength, modulus, hardness, abrasion resistance, and tear strength) in comparison with reinforcing fillers such as silica and carbon black. However, the mechanical properties of the vulcanizates filled with rice husk ash are comparable to those filled with inert fillers. The addition of silane-coupling agent has little effect on the properties of the ash-filled vulcanizates. This is simply due to the lack of silanol groups on the ash surface. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2485–2493, 2002

Key words: rice husk ash; fillers; rubber; mechanical properties

INTRODUCTION

Considerable effort has been expended to find beneficial and profitable uses for rice husk, a major by-product of the rice milling process. The main constituents of rice husk are cellulose, lignin, and sugar.[1] In addition to organic compounds, rice husk is also composed of approximately 20 wt % of amorphous silica.[2,3]

One of the major ways in which rice husks are used is as fuel. It can be a significant energy source in rice-producing countries because of its high energy content. It is considered a cellulosic biomass which can be converted into electric energy. To use the rice husks as fuel, they are simply burned. The burned rice husks produce an ash which is also used in many ways, such as a component of refractory material and as a very effective insulating material to insulate molten steel.[4]

Rice husk ash (RHA) is a by-product obtained from the electrical power plant by using rice husk as a power source. The ash mainly consists of amorphous silica and the residual carbon black, alternatively called carbonaceous siliceous material. The amount of silica and carbon black in the ash varies depending on the burning conditions. In addition to silica and carbon, the ash is also composed of the small amount of nonvolatile inorganic constituents such as oxides of the alkali elements (e.g., potassium, magnesium, sodium, and calcium). In general, RHA contains about

49–98% of silica. Frequently, the residual carbon cannot be completely eliminated because it is apparently trapped within the amorphous silica structure or completely coated with silica so that its removal by thermal processes is difficult.

Many attempts have been made to use rice husk ash as a filler for natural and synthetic rubbers. Haxo and Mehta[5] revealed the possibility of using ground RHA obtained by a special burning condition as a moderately reinforcing filler for styrene-butadiene rubber (SBR), ethylene–propylene–diene elastomer (EPDM), and natural rubber (NR). The influences of RHA incorporation on mechanical properties and fatigue behavior of epoxidized natural rubber (ENR) were also investigated.[6,7] The effects of multifunctional additive (MFA), silane coupling agent (Si-69), and the combination of the two on the properties of white RHA-filled natural rubber compounds were studied by Ismail et al.[8]. It was found that the incorporation of such additives increases cure rate and improves the mechanical properties of the vulcanizates because they enhance filler dispersion and crosslink density of the vulcanizates. In addition, the effects of coupling agent (Si-69) and chemical treatment on RHA-filled natural rubber were also investigated by Costa et al.[9] They found that the addition of silane-coupling agent results in little improvement in the performance of all vulcanizates.

The work reported herein is based upon the RHA obtained from the electrical power plant installed at the rice mill. Rice husk was burnt at 1000°C for 7 min in the combustion chamber with efficient air circulation. Attention is given to the comparison of curing and mechanical properties of NR vulcanizates filled with RHA and other commercial fillers.

EXPERIMENTAL

Materials

All mixing ingredients were used as received. Natural rubber (STR 5 L) was supplied by Union Rubber Product Corp., Ltd. (Thailand). Two grades of RHA [i.e., low carbon content (3.4%) and high carbon content (7.0%) denoted as RHA-LC and RHA-HC, respectively] were obtained from Thunyakit Nakhornprathom Rice Mill Co., Ltd. (Thailand). The ashes were milled for 2 h and sieved on a 200-mesh sieve and dried in a vacuum oven at 120°C for 3 h prior to using. Hi-Sil 233s silica (SiO_2) was manufactured by PPG-Siam Sil-

ica Co., Ltd. (Thailand) and N330 black (CB) was supplied by Thai Carbon Product Co., Ltd. Light-precipitated calcium carbonate ($CaCO_3$), china clay, talcum, and tetramethyl thiuram monosulfide (TMTM) were obtained from Kij Paiboon Chemical Ltd. (Thailand). Stearic acid, zinc oxide (ZnO), and sulfur (S) were obtained from Chemmin Corp., Ltd. (Thailand). N-cyclohexyl-2-benzothiazyl sulfenamide (CBS) was supplied by Flexsys Co., Ltd. (Belgium). Poly(ethylene glycol) (PEG) was supplied by Condea Chemica D.A.C. Co., Ltd. (Italy) and silane-coupling agent (Si-69) was supplied by JJ-Degussa (Thailand) Co., Ltd.

Characterization of Filler Properties

The surface area of fillers was determined by the Brunauer–Emmett–Teller (BET) method on the Autosorb-1. The density and mean agglomerate particle size were measured by Ultrapycnometer-1000 and Mastersizer-S, respectively. The pH was determined by the procedure described in ASTM D1512. The presence of functional groups on the surfaces of both commercial silica and ashes was verified by FTIR Perkin–Elmer System-2000. The samples (0.2 mg) were ground with 50 mg dry KBr in a mortar and then pressed to form thin disks. The disks were dried in an oven at 100°C for 24 h prior to the analysis.

Preparation and Testing of Rubber Compounds

The rubber compounds were prepared by using a laboratory-sized internal mixer (Haake Rheomix 3000p). The mixing conditions were as follows: fill factor, 0.7; chamber temperature, 40°C; rotor speed, 40 rpm; and mixing time, 12 min. The compound formulations are given in Table I. Mooney viscosity (ML1 + 4@100°C) was measured by viscometer (Monsanto-1500) and the

Table I   Rubber Formulations

Ingredient	phr[b]
NR (STR 5L)	100.0
Filler	Variable (0–60)
ZnO	5.0
Stearic acid	2.0
CBS	1.0
TMTM	0.5
S	2.0
PEG[a]	2

[a] Only in batches having silica as a filler.
[b] phr, parts per hundred of rubber.

Table II Physical Properties of the Rice Husk Ashes and Other Commercial Fillers

Filler	Mean Agglomerate Particle Size (μm)	Surface Area (m^2/g)	pH	Density (g/cm^3)
RHA-HC	20.4	22	10.5	1.7
RHA-LC	19.6	8	10.5	1.7
Talcum	18.5	8	9.5	2.6
China clay	7.1	8	5.3	2.6
CaCO$_3$	11.8	3	9.5	2.6
SiO$_2$	29.3	140	7.1	2.0
CB	20.2	84	6.8	1.8

scorch (t_{s2}) and optimum curing times (t_{c90}) at 150°C were obtained from an oscillating disk rheometer (Monsanto-100S). Tensile properties (ASTM D412) were measured along the grain direction, whereas the tear strength (ASTM D624, Die C) was measured perpendicular to the grain direction.

Both tensile and tear properties were determined on an Instron 4500 series. An Instron Shore A durometer was used to measure the hardness and a Zwick abrasion tester 6102 was used for abrasion resistance determination (DIN 53516). The degree of filler dispersion was examined by scanning electron microscopy (SEM) tech-

nique (JEOL JSM-5410). The SEM micrographs were taken on the newly exposed surface of the rubber specimens fractured immediately after embrittling in liquid nitrogen.

RESULTS AND DISCUSSION

Filler Properties Characterization

The physical properties of the fillers used in this study are given in Table II. The mean agglomerate particle sizes of all fillers are not significantly different, even though silica is found to have the largest agglomerate size because of its highly reactive surface chemistry. The BET surface area of RHAs (both low- and high-carbon contents) is considerably lower than that of highly reinforcing fillers (e.g., CB and silica) but comparable to that of inert fillers such as talcum, clay, and calcium carbonate. It has also been found that RHA has higher pH value than other fillers. This can be explained by the presence of impurities, particularly the metal oxides. Figure 1 shows FTIR spectra for silica, RHA-LC, and RHA-HC. Obviously, most functional groups found on both RHA-LC and RHA-HC are the same as those found on silica. According to Wagner's report,[10] the strong broad band at approximately 1100 cm^{-1} is assigned to Si-O vibration. The bands at 795 and
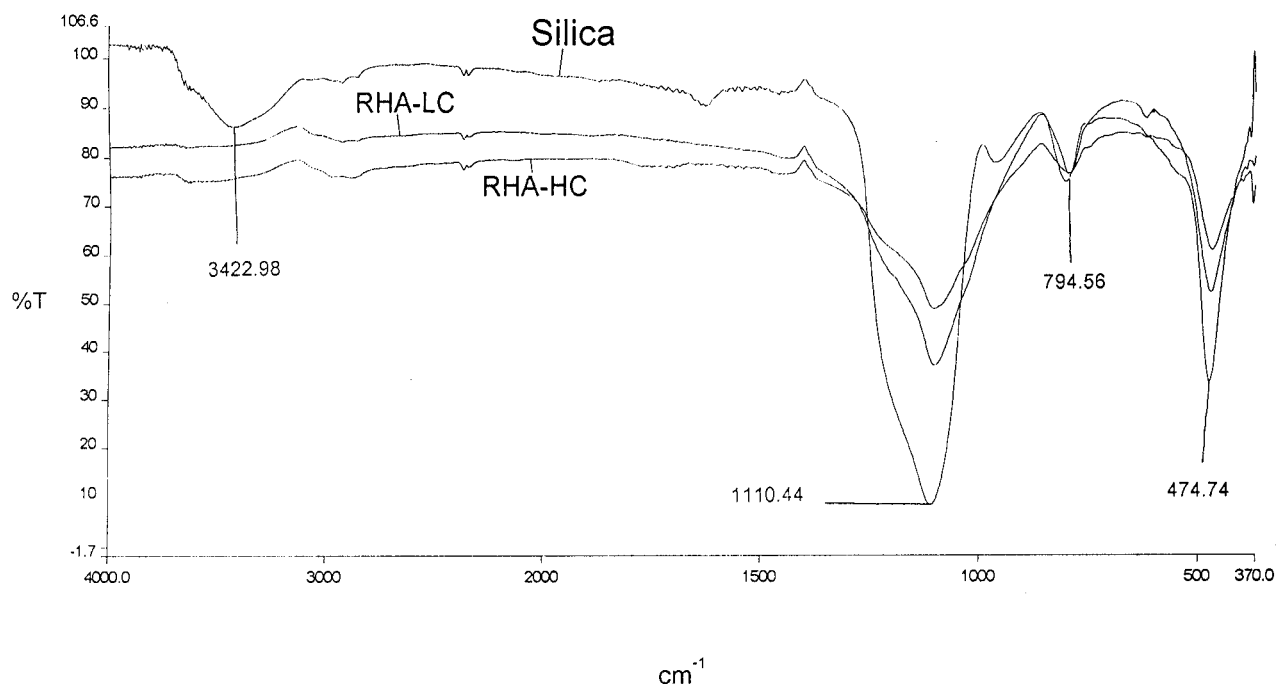
Figure 1 FTIR spectra of silica, RHA-HC, and RHA-LC.
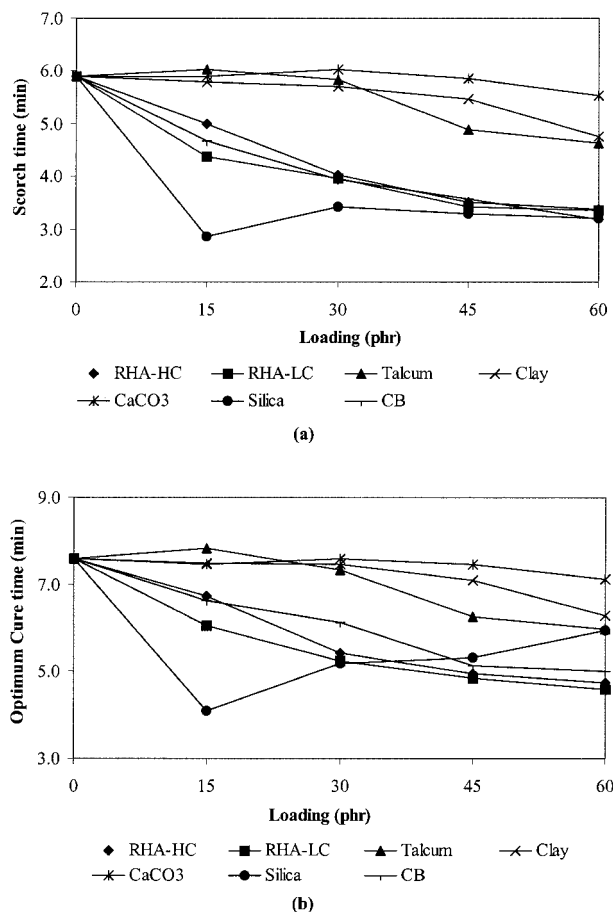
Figure 2 Cure characteristics of rubber vulcanizates (a) scorch time, t_{s2}; and (b) optimum cure time, t_{c90}.

475 cm^{-1} are the characteristic bands of amorphous silica.[11] However, the broad absorption band at 3200–3750 cm^{-1} is only found on silica. This band is attributed mainly to the vibration of silanol groups and the hydrogen-bonding interaction between water and adjacent (vicinal) silanols. It is widely known that silica surfaces are densely covered with silanol groups (four to five SiOH groups per 100 Å^2).[12] Unlike silica, the results reveal the absence of hydroxyl or silanol groups on the surface of both RHAs.

Comparison of Cure and Mechanical Properties of Filled Vulcanizates

Figure 2 represents the scorch time (t_{s2}) and the optimum curing time (t_{c90}) of the rubber compounds filled with various fillers. Generally, the addition of filler reduces not only scorch time, but also optimum curing time. The higher the filler loading, the lower the curing time. This is clearly seen in highly reinforcing filler such as CB. For silica, the curing time tends to increase slightly at very high loading. This is possibly due to the reduction of accelerator activator (zinc complex) in the rubber matrix, as it is trapped on the silica surface. However, the effect of filler loading is not very pronounced for compounds filled with inert fillers (e.g., CaCO$_3$, clay, and talc). A possible explanation of this observation is given by the thermal history of the compounds during processing. In the mixing state, large particle size and low interaction between the inert fillers and rubber give rise to lower compound viscosity (see also the Mooney viscosity results in Fig. 3), as compared to compounds filled with reinforcing fillers. The shearing force during mixing is therefore lower, leading to lower frictional heat and, hence, mixing temperature. The maximum temperature during mixing of inert fillers is in the range of 80–90°C depending on filler loading. On the contrary, the viscosity of compounds filled with highly reinforcing fillers is relatively high because of their high surface area and the strong rubber–filler interaction leading to higher mixing temperature (in the range of 90–130°C). As the viscosity and mixing temperature are directly proportional to filler loading, both the scorch time and the optimum curing time reduce with increasing filler loading. Exception is found in the compounds filled with RHA. Even though the viscosity and mixing temperature are comparable to those of other inert fillers, both scorch time and optimum curing time are significantly reduced with increasing ash loading. This is possibly due to the presence of metal oxides which could accelerate the vulcanization process.

Similar to the Mooney viscosity results, hardness of filled vulcanizates increases with filler
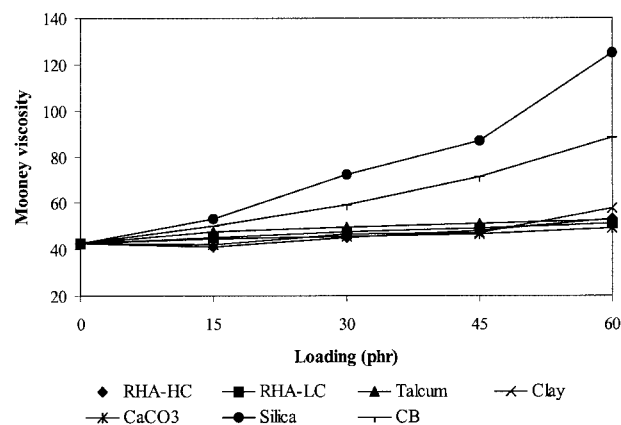
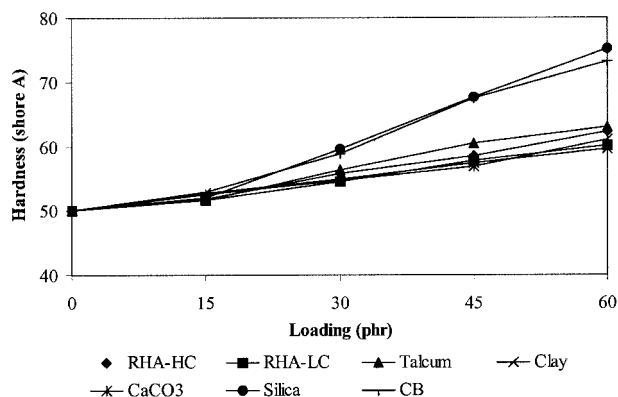**Figure 3** Mooney viscosity (ML1 + 4 at 100°C) of the rubber vulcanizates.

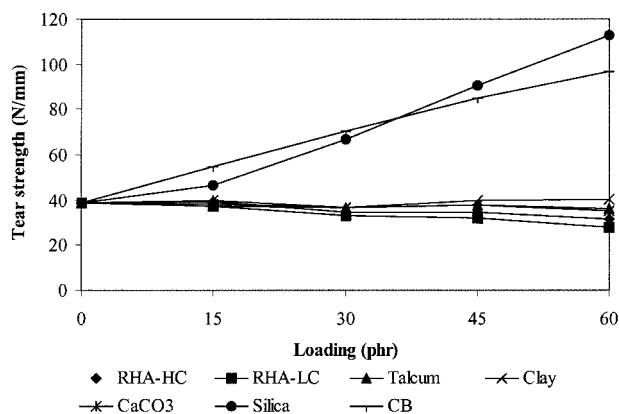**Figure 4** Hardness (shore A) of the rubber vulcanizates.

Figure 5 Tear strength against filler loading of the rubber vulcanizates.

loading, regardless of filler type, as shown in Figure 4. This is simply due to the fact that incorporation of more rigid filler particles into rubber reduces elasticity of the rubber chains leading to

more rigid vulcanizates. As expected, the addition of RHA-LC and RHA-HC causes an increase in hardness to the same degree as other inert fillers

Table III Tensile Properties of Rubber Vulcanizates

| Filler	Loading (phr)	Properties			
		M_{100} (MPa)	M_{300} (MPa)	TS (MPa)	EB (%)
None (gum)	0	1.1	3.2	25.4	628.0
RHA-HC	15	1.3	3.7	25.3	561.0
	30	1.5	4.2	23.6	516.0
	45	1.7	4.8	18.5	492.8
	60	1.9	6.2	15.0	419.7
RHA-LC	15	1.3	3.5	26.3	549.5
	30	1.4	3.7	21.0	484.3
	45	1.4	3.9	18.6	511.4
	60	1.5	4.1	15.6	468.6
Talcum	15	1.3	3.4	28.5	607.3
	30	1.5	3.8	27.7	582.0
	45	1.8	4.1	22.4	551.2
	60	2.1	4.9	20.0	517.9
Clay	15	1.5	3.9	28.4	550.9
	30	1.8	4.7	25.8	524.5
	45	2.1	5.1	24.4	519.7
	60	2.4	5.4	23.4	496.5
CaCO$_3$	15	1.4	3.6	25.9	562.8
	30	1.5	4.0	25.1	541.0
	45	1.6	4.1	23.5	533.8
	60	1.9	4.7	21.4	478.9
Silica	15	1.2	3.7	29.1	611.1
	30	1.6	4.5	29.0	623.2
	45	2.0	5.7	27.1	598.0
	60	2.2	6.6	24.2	601.6
CB	15	1.7	8.4	29.0	495.2
	30	2.7	14.4	27.8	453.9
	45	4.4	19.4	25.3	391.6
	60	6.7	21.2	21.7	310.5
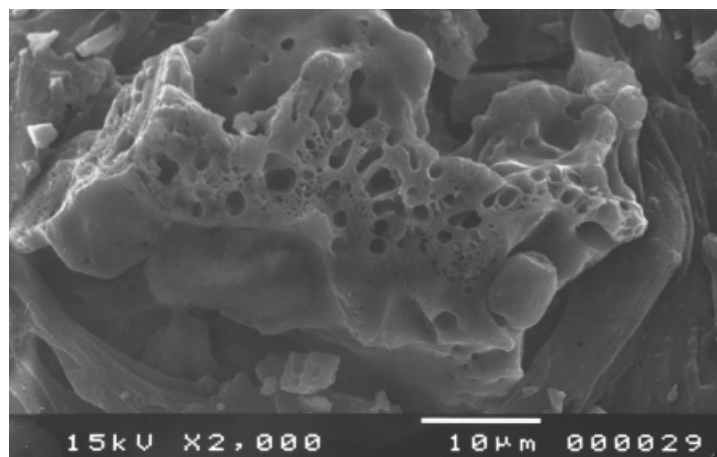
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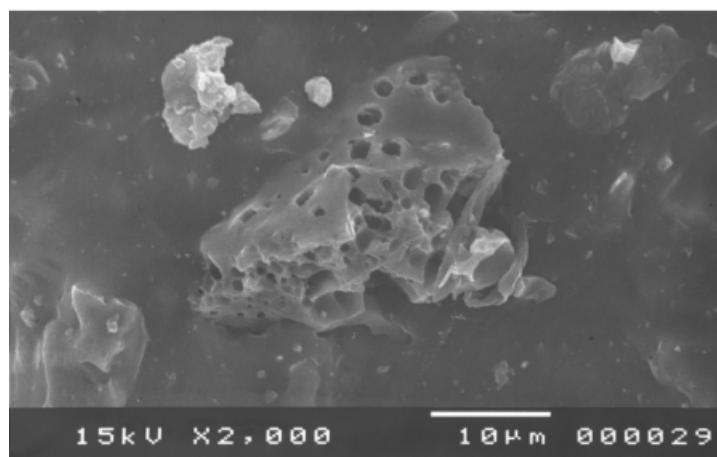
(b)

Figure 6   SEM micrographs of fillers embedded in the rubber matrix (a) RHA-HC and (b) RHA-LC.

because of their similarity in agglomerate particle size, surface area, and the lack of reactive functional groups on the surface. The effect of filler loading on hardness is even more pronounced in systems filled with reinforcing fillers. Silica gives harder vulcanizate than CB, particularly at high loadings, because of its stronger filler network.[13]

Table III summarizes the tensile properties of the filled vulcanizates. Both 100% modulus (M_{100}) and 300% modulus (M_{300}) are increased with filler loading, particularly seen in CB-filled vulcanizates. This is attributable to the strain amplification effect.[14,15] As expected, the elongation at break (E_B) reduces with increasing filler loading. Tensile strength (TS) is generally found to increase with filler loading until a maximum level is

reached (at approximately 15–30 phr depending on filler type). Again, the detrimental effect on tensile strength at high loadings may be attributed to the dilution effect.[16] It can be observed that, at any particular loading, silica-filled vulcanizate has higher tensile strength, whereas its moduli (M_{100} and M_{300}) are considerably lower than CB-filled vulcanizate. This observation reveals that surface area is the most important factor controlling the tensile strength, whereas the surface activity (rubber–filler interaction) controls the modulus (i.e., natural rubber forms stronger adsorptive bonds with CB than with silica). In the ash-filled system, the values of M_{100}, M_{300}, TS, and E_B are comparable to those of the inert fillers. However, unlike other inert fillers,
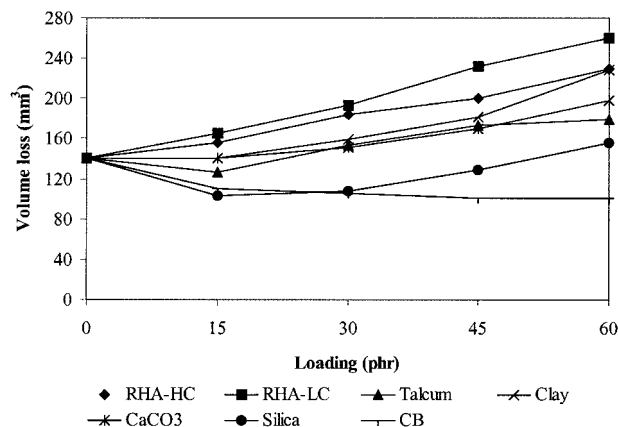
Figure 7 Abrasion resistance as a function of filler loading of the rubber vulcanizates.

the tensile strength of vulcanizates filled with RHA-LC and RHA-HC drops dramatically at high loadings. This is simply due to the ash structure which will be discussed in detail later on.

Figure 5 shows the tear strength of the filled vulcanizates. As can be seen, the addition of silica and CB increases considerably the tear strength of the vulcanizates. This is mainly attributed to the reduction of stress concentration at the crack tips in the presence of fillers, particularly the fine particle ones.[17,18] In contrast, the addition of the inert fillers reduces somewhat the tear strength of the vulcanizates. Unexpectedly, the tear strength is markedly reduced with the addition of RHA-LC and RHA-HC, particularly at high loadings. This may be attributed not only to their large particle size, but also to their highly porous structure. When incorporated into rubber, the voids are not completely filled with rubber, as

shown in SEM micrographs of fracture surface [Fig. 6(a,b)], because of low rubber–filler interaction (i.e., the lack of reactive function groups such as hydroxyl group on the ash surface). Such voids could act as initial flaws leading to localized stress concentration during deformation and finally resulting in premature failure of the vulcanizates. For this reason, both tensile and tear strengths are dramatically decreased with increased loading of the ashes.

The abrasion resistance of the vulcanizates is represented in Figure 7. As far as this property is concerned, the ashes give similar effect to other inert fillers (i.e., the abrasion resistance decreases markedly with filler loading). An inverse effect is found in the systems filled with reinforcing fillers in which the abrasion resistance is found to improve. At particular loading, reinforcing fillers impart better abrasion resistance than inert fillers and the ashes. The greater surface area and better rubber–filler interfacial adhesion could explain the obtained results.

According to reinforcement concept, the main factors governing reinforcement of elastomer, apart from filler loading, include filler-particle size or specific surface area, filler structure, and specific surface activity. Fine particles actually reflect their greater interface between the rubber matrix and the filler and, hence, provide a higher degree of reinforcement than the coarse ones. High filler structure is always associated with processing difficulty as it increases considerably the viscosity of the compound and also the modulus of the vulcanizate. The surface activity is an important factor, indicating the extent of rubber–filler interaction. With good rubber–filler interac-

Table IV Effect of Silane Coupling Agent on Properties of the Vulcanizates Filled with 45 phr of Rice Husk Ash

Properties	RHA-HC		RHA-LC	
	Without Si-69	With Si-69	Without Si-69	With Si-69
Scorch time (min)	3.5	3.0	3.4	2.6
Optimum cure time (min)	5.0	4.8	4.9	4.8
Mooney viscosity (unit)	48.0	49.5	49.0	48.0
Hardness (shore A)	58.4	57.2	57.7	58.2
M_{100} (MPa)	1.7	1.6	1.4	1.6
M_{300} (MPa)	4.8	4.2	3.9	3.8
Elongation at break (%)	492.8	511.5	511.4	520.3
Tensile strength (MPa)	18.5	16.1	18.6	17.1
Tear strength (N/mm)	34.4	34.6	32.2	31.0
Abrasion resistance (% wt loss)	10.4	10.2	9.7	10.1
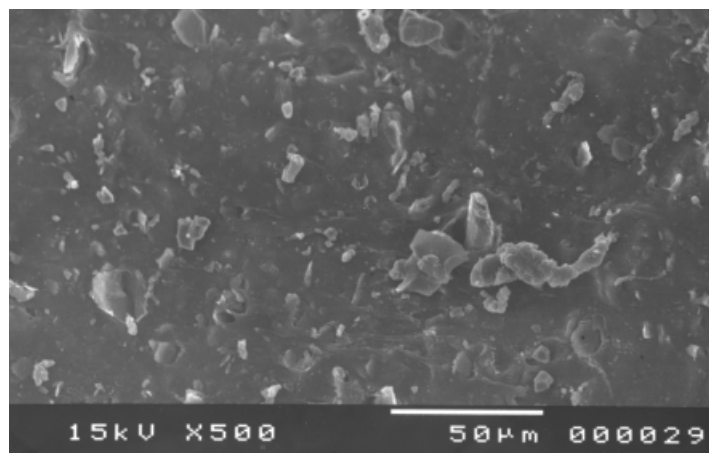
(a)
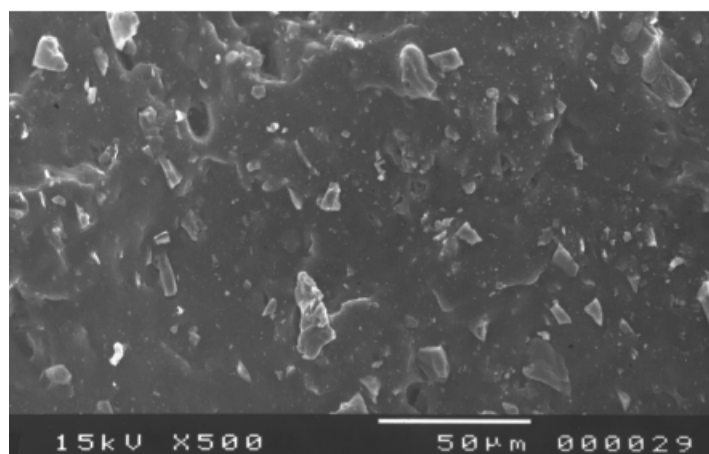
(b)

Figure 8   SEM micrographs of the ash filled vulcanizates (a) without Si-69 and (b) with Si-69.

tion, increased viscosity, modulus, and hardness, as well as other mechanical properties, result. Based on this concept, both silica and CB possess very high surface area and surface activity and thus provide noticeably greater reinforcement in comparison with the ashes and the other inert fillers, as clearly evidenced from the results of Mooney viscosity, modulus, hardness, tensile and tear strengths, and abrasion resistance. Although both RHA-LC and RHA-HC are mainly composed of silica and carbon residue, their surface area and surface activity are very low, relatively comparable to those of the other inert fillers, resulting in poor mechanical properties of the filled vulcanizates. Unfortunately, their porous structure also causes premature failure, especially at high loadings.

Effect of Coupling Agent on Mechanical Properties of the Ash-Filled Vulcanizates

In general, silane-coupling agents can be used to improve compatibility of silica with a variety of polymers. They are effective in producing increased reinforcement of rubber because they possess the functionality capable of chemically reacting with both the silica and the rubber network. The alkoxysilyl group can react with silanols on silica surface to form stable siloxane linkage, and the mercaptan can participate in sulfur vulcanization leading to the linkage with the rubber. In the present study, 2.25 phr of Si-69 was added into the compounds filled with 45 phr of the ashes. It is evident that, unlike silica in which the addition of silane-coupling agent improves notice-

ably the mechanical properties, its presence in the ash-filled vulcanizates (both RHA-HC and RHA-LC) has little effect on the compound viscosity and the mechanical properties, as shown in Table IV. A similar observation was also found by Costa et al.[9] This is simply due to the fact that there is no reactive silanol groups on the ash surface to chemically react with the organosilane. For this reason, the addition of Si-69 does not increase rubber–filler interaction and consequently no improvement in filler dispersion is obtained, as shown in Figure 8.

CONCLUSION

Due to the similarity in surface area and surface activity, the RHA (both low- and high-carbon contents) can be classified as inert filler which could be used in rubber industry for economical purposes. When incorporated into rubber, the ash, regardless of its carbon content, imparts the compound with low viscosity and faster vulcanization because of the presence of metal oxides. The modulus and hardness of the ash-filled vulcanizates are comparable to those of the vulcanizates filled with other commercial inert fillers. At low ash loadings (<30 phr), the failure properties (tensile and tear strengths), as well as the abrasion resistance of the vulcanizates, are slightly inferior to those obtained from the addition of other inert fillers. However, at high-ash loadings, such properties drop dramatically and hence are no longer comparable to those obtained from the other fillers. Premature failure and rapid deterioration of abrasion resistance are associated with the porous structure of the ash and the low rubber–filler interaction. No improvement in mechanical properties of the ash-filled vulcanizates is found in the presence of silane-coupling agent (Si-69). The lack of silanol groups on the ash surface is accounted for the results. CB and silica provide greater reinforcement than the other fillers, mainly because of their high surface area (small particle size) and high surface activity. Filler dispersion also plays an important role in reinforcement.

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