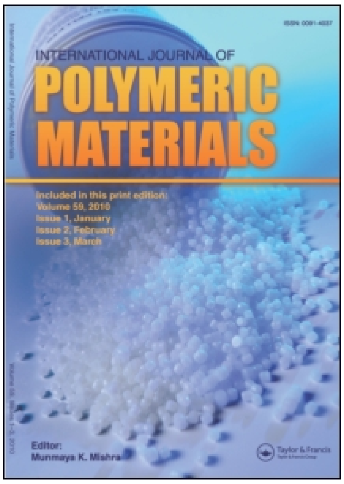

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The Effect of Rice Husk Ash as a Filler for Epoxidized Natural Rubber Compounds

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The effect of rice husk ash (WRHA) as a filler in epoxidized natural rubber compounds has been studied. The mechanical properties viz tensile and tear strength were enhanced by the addition of WRHA. The optimum level of WRHA to obtain maximum mechanical properties was achieved at 20 phr after which there was deterioration in properties. Hardness and torque increased steadily with WRHA loading while scorch and cure time, t_{90} showed the opposite trend. The presence of silane coupling agent, γ-mercaptopropyl trimethoxy silane (A-189) has increased the effectiveness of WRHA as a filler for ENR compounds.

Keywords: Rice husk ash; epoxidized natural rubber; mechanical properties; silane coupling agent; curing characteristics

1. INTRODUCTION

Epoxidized natural rubber (ENR) is made by the reaction of natural rubber with a peroxycarboxylic acid [1–4]. The success in making clean ENR under controlled conditions, coupled with the realisation that the product exhibits some unique characteristics [5–7] has prompted studies of this relatively new elastomer. Increasing epoxidation increased the glass transition temperature, decreased resilience (more damping), reduced air permeability, higher hysteresis, and better wet traction. The epoxidation also increased the polarity which brought about an improved resistance towards hydrocarbon oil [1, 5, 8].

In the last decade, cellulosic and lignocellulosic materials (e.g. jute, wood flour, baggasses, etc.) [9–12] have been used as potential supplements to common fillers in polymers, although in most cases, further treatment and modifications are still needed to obtain significant reinforcement. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. These include filler size, filler shape, filler dispersion, surface area, surface reactivity, structure of the filler and bonding quality between the fillers and the rubber matrix [13].

In this study, the potential of a relatively new type of filler that is derived from rice husk ashes (RHA) is investigated. The investigation on utilization of RHA as alternative fillers for ENR is of interest for three main reasons. First, considering the fact that ENR is known to posses unique characteristics that it could be reinforced with several types of fillers. Secondly, the nature of rice husk ash which was proven to contain both silica and carbon [14]. Rice husk ash when burnt in the open air outside the rice mill yields two types of fillers i.e. white rice husk ash (WRHA) and black rice husk ash (BRHA). The upper layer of the RHA mound is subjected to open burning in air and yields BRHA in the form of a carbonized layer. On the other hand, the inner layer of the mound being subjected to higher temperature yields WRHA. Thirdly, to date, not many studies have been reported on the subject of RHA utilization in rubber compounding. An early investigation by Haxo and Mehta [11] proved that ground RHA obtained via a special urning process is a moderately reinforcing filler for rubbers like SBR, EPDM and NR.

In this study, white rice husk ash (WRHA) was used as a filler in ENR vulcanizates and the semi-efficient sulphur vulcanization (semi-EV) system was used. The work was carried out to achieve the following objectives;

(i) To study the effect of WRHA on tensile properties, tear strength, hardness and cure characteristics of ENR compounds.
(ii) To investigate the potential of WRHA as fillers for ENR.
(iii) To determine the optimum loading of WRHA.
(iv) To study the effect of coupling agent on mechanical and curing properties of WRHA filled ENR compounds.

2. EXPERIMENTAL

2.1. Materials and Chemicals

Table I shows the materials, their manufacturer, and loadings used in this study. All materials were used as supplied. The chemical and physical properties of WRHA is given in Table II. The formulation shown in Table I was used to evaluate the cure and physical properties of ENR vulcanizates. A semi-EV system was chosen based on the previous

TABLE I Typical formulations of WRHA filled ENR 50 Compounds

Material	*Manufacturer*	*Formulation (phr)*
ENR 50	Guthrie (M)	100
Sulphur	Bayer (M) Ltd.	1.6
Zinc oxide	"	2.6
Stearic acid	"	1.5
CBS[a]	"	1.9
TMTD[b]	"	0.9
IPPD[c]	"	2.0
Silane (phr filler)*	"	2.0
WRHA	Plastic Tech. Centre, SIRIM (M)	0,10,20,30,40,50

[a] *N*-cyclohexyl-2-benzothiazole-2-sulphenamide.
[b] Tetramethylthiuram disulphide.
[c] *N*-isopropyl-*N*-phenylenediamine.
* To determine the optimum WRHA loading in ENR compounds silane coupling agent was excluded from the formulation.

TABLE II Chemical and physical properties of WRHA

Properties	*Value*
Chemical composition (%)	
CaO	0.1
MgO	0.4
Fe_2O	0.1
K_2O	1.6
Na_2O	0.1
Al_2O_3	trace
P_2O_5	trace
SiO_5	96.2
Lost on ignition (LOI)	1.6
Physical properties	
Mean particle size (μm)	5.4
Surface area (m^2/g)	1.4
Density (g/m^3)	2.2

works [15, 16] which reported that better performance for ENR vulcanizates could be obtained using such a vulcanization system. 2% w/w on filler of γ-mercaptopropyltrimethoxy silane (A-189) was applied for the treatment of the filler surface. The amount of coupling agent used was earlier found to be the best to obtain optimum properties of the vulcanizates [7]. The coupling agent was premixed with the fillers prior to mixing on the two roll mixing mill.

2.2. Sample Preparation

Mixing was carried out on a laboratory size (160 x 320 mm) two roll mixing mill. Total mixing time was kept to a minimum to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that the mill-roll temperature was not too high, i.e. exceeding the set temperatures, to avoid any crosslinking during mixing. This has been achieved by using cooling water. All compounds were vulcanized to their respective optimum cure times, t_{90} as determined by Monsanto Rheometer, model MDR 2000 at 140°C, and these times were employed to vulcanise all the specimens used in this study.

2.3. Mechanical Properties

The tensile properties and tear strength of the vulcanizates were measured on an Instron Universal Testing Machine, model 1114, according to BS 903: Part A2 and BS 903: Part A3 respectively. The cross head speed for the tensile and trouser tear tests (Method A) was set at 500 mm/min and 100 mm/min respectively. The test for hardness was carried out by using the Shore type A Durometer according to ASTM 2240. All tests were performed at room temperature (25°C).

2.4. Scanning Electron Microscope

Examination of the fracture surface was carried out using a scanning electron microscope (SEM) model Leica Cambridge S-360. The objective was to get some idea on the mode of fracture, the bonding quality between the matrix and filler surfaces and filler dispersion. All the surfaces were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

3. RESULTS AND DISCUSSION

3.1. The Effect of WRHA on ENR Compounds

3.1.1. Cure Characteristics

Table III shows the effect of WRHA loading on cure characteristics of ENR compounds. It can be seen that minimum and maximum torques and torque at 90% cure increased with increasing filler loading. The incorporation of WRHA into the rubber matrix has reduced the mobility of the macromolecular chains of the rubber and consequently increased the rubber stiffness.

Table III also indicates that scorch time and cure times decreased with increasing WRHA loading, i.e. enhancement in cure rate. The cure enhancement can be associated to the filler related parameters such as surface area, surface reactivity, particle size, moisture content and metal oxide content. In general, a faster cure rate is obtained with fillers having a low surface area, high moisture content and high metal oxide content [17]. However, in the present study, the most probable factors to account for the observed cure enhancement are surface area, particle size and metal oxide content.

3.1.2. Mechanical Properties

Figures 1 and 2 show the effect of WRHA loading on tensile and tear strength of ENR compounds. It can be seen that both properties increase with increasing WRHA loading up to an optimum level i.e. about 20% filler loading. After that, there is a deterioration of properties. As the filler loading is increased, eventually a level is reached whereby the filler particles or aggregates were no longer adequately dispersed or wetted by

TABLE III Curing characteristics of WRHA-filled ENR 50 compounds*

Properties	*% (phr)*					
	0	10	20	30	40	50
Maximum torque (dNm)	51.00	58.00	60.00	62.50	67.50	71.00
Minimum torque (dNm)	4.00	4.00	4.00	4.00	4.50	5.50
Torque at 90% cure (dNm)	46.30	52.60	54.50	56.70	61.30	64.50
t_{90} (min)	4.25	4.00	4.00	3.75	3.75	3.50
Scorch time (min)	2.75	2.50	2.50	2.14	1.75	1.64

*Monsanto Rheometer at 140°C.

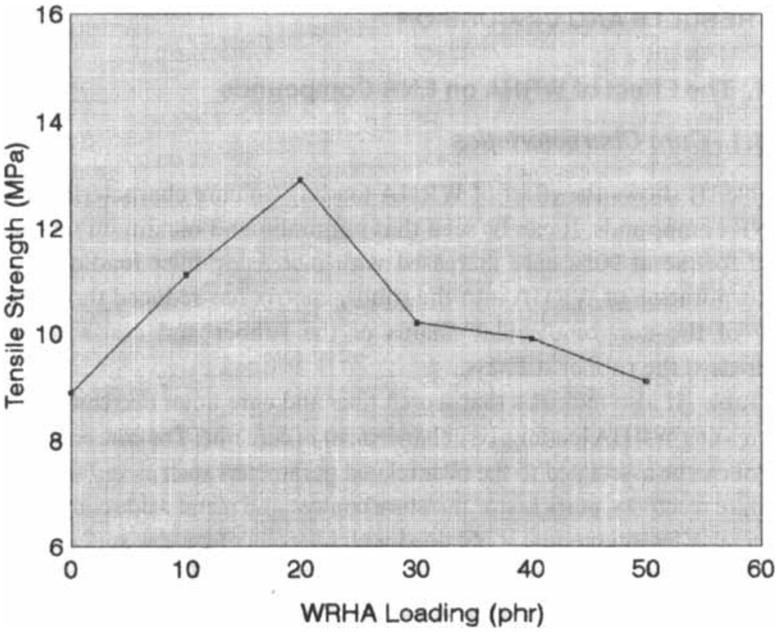

FIGURE 1 The effect of filler loadings on tensile strength of WRHA-filled ENR vulcanizates.

the rubber phase. Thus, the reduction in strength may be due to agglomeration of the filler particles to form a domain that acts like a foreign body or simply the result of physical contact between adjacent aggregates. From reinforcement point of view, a filler can be classified as reinforcing when it has the ability to increase the ultimate properties of vulcanizates such as tensile strength [15]. Thus in the present context, WRHA can be classified as a reinforcing up to 20% filler loading.

Figure 3 shows the modulus at 100% and 300% elongation. Again both modulus increased with increasing loading of WRHA up to about 20% after which further increase in filler loadings reduces the respective properties. Modulus characteristics is affected by filler structure, cross-link density, filler particle size and shape, dispersion of filler particle in rubber matrix and surface reactivity of filler [18,19]. Increment in WRHA loading has initially increased the interaction between rubber and filler and resulted in increasing modulus. However, the difficulty of filler particle to disperse and interact with rubber matrix as WRHA loading

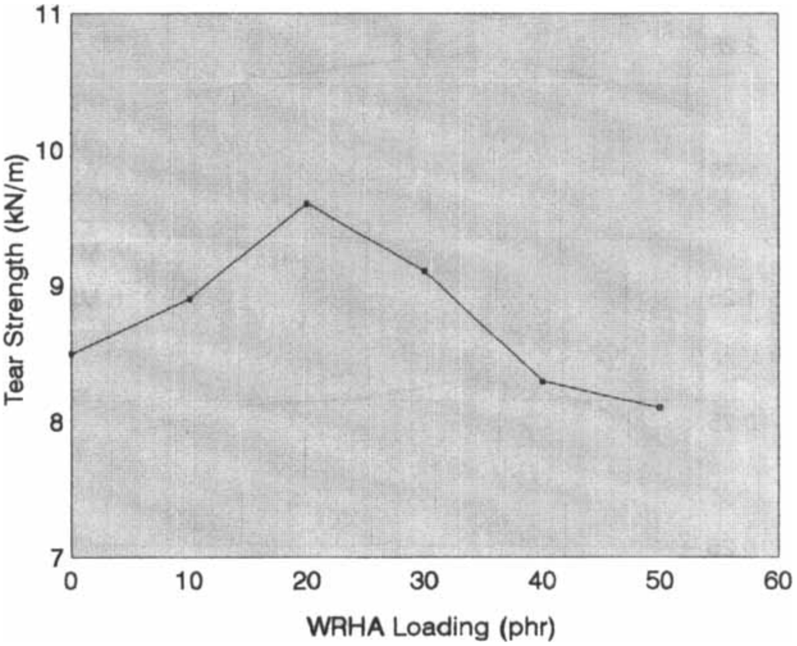

FIGURE 2 The effect of filler loadings on tear strength of WRHA-filled ENR vulcanizates.

increase beyond 20% phr has resulted in modulus reduction. A similar trend is again observed in the case of elongation at break as shown in Figure 4. Elongation at break is dependent on the quality of filler wetting by rubber matrix. Initially, the WRHA loading is increased, i.e. up to about 20% phr, the wetting effect by rubber matrix on WRHA is still efficient and resulted in increment in elongation at break. But further addition of WRHA beyond its optimum level will reduced the WRHA wetting by rubber matrix. Consequently, the rubber-filler interaction is decreased while the filler-filler interaction is increased. Once the rubber-filler interaction or the bonding quality is weaken, the applied stress can no longer be transferred efficiently from rubber to filler. Thus, after the optimum loading the elongation at break decreases with the WRHA loading.

The hardness of vulcanizates increased with increasing WRHA loading as shown in Figure 5. This result is expected because as more filler particles get into the rubber matrix the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates.

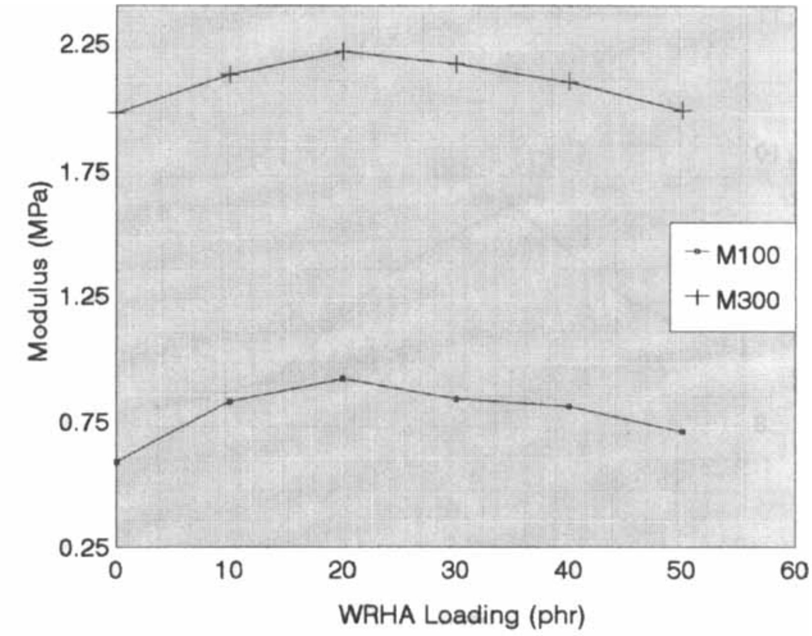

FIGURE 3 The effect of filler loadings on modulus of WRHA-filled ENR vulcanizates.

3.2. Effect Silane Coupling Agent on the WRHA Filled ENR 50 Vulcanizates

3.2.1. Cure Characteristics

Data from Table IV show that maximum torque and torque at 90% cure increased slightly with the addition of silane coupling agent (A-189), while cure time t_{90} and scorch time show the opposite trend. In the presence of silane coupling agent, WRHA-filled ENR compound exhibits cure enhancement. This may be attributed to the direct involvement of the silane during vulcanization, resulting in coupling bonds being established between the silane and both the filler and the ENR matrix. According to Wagner [17], a mercaptosilane generally enhances the cure and scorch times to a certain extent depending on the type of accelerator systems and elastomers. This effect could be partially due to the mercapto group exerting its influence as a sulphur donor in the vulcanization process.

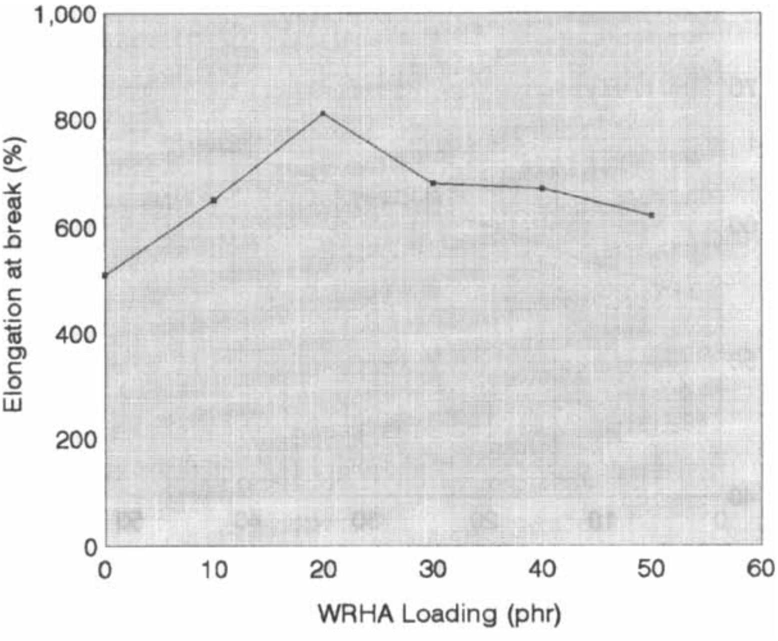

FIGURE 4 Relationship between elongation at break and filler loadings of WRHA-filled ENR vulcanizates.

Dannenberg [20] pointed out that the cure enhancement was due to silanol group on the silica surface which changed into mercaptopropylsiloxy group thereby enhanced the curing properties of rubbers. The possible mechanisms to explain the cure enhancement of silica filled rubber compounds by silane coupling agent have also been postulated by other researchers [21, 22].

3.2.2. Mechanical Properties

Table V summarises the tensile properties and tear strength of WRHA filled ENR 50 vulcanizates with and without silane coupling agent, A-189. These results indicate that there are significant improvements in the performance of WRHA filled ENR 50 vulcanizates when a silane coupling agent was added. This enhancement is expected since WRHA has a high silica content, i.e. 96.2% as shown in Table II. The addition of silane coupling agent has improved wetting and dispersion of WRHA in the rubber matrix. Figure 6a is

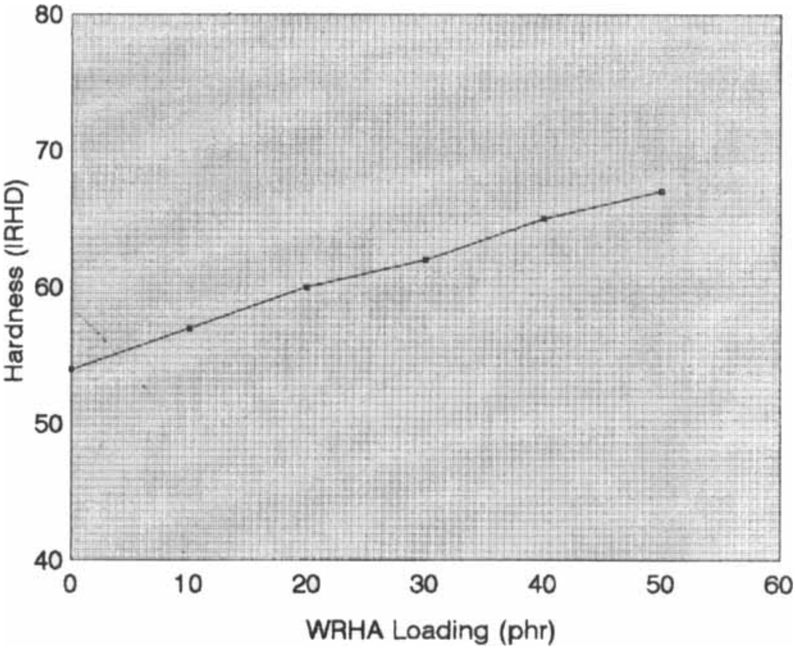

FIGURE 5 The effect of filler loadings on hardness of WRHA-filled ENR vulcanizates.

TABLE IV Curing characteristics of WRHA-filled ENR 50 compounds at optimum WRHA loading (20 phr)*

Properties	*WRHA*	*WRHA + silane (A-189)*
Maximum torque (dNm)	60.00	62.00
Minimum torque (dNm)	4.00	4.00
Torque at 90% cure (dNm)	54.45	56.20
t_{90} (min)	4.00	3.63
Scorch time (min)	2.50	2.25

*Monsanto Rheometer at 140°C.

TABLE V Mechanical Properties of WRHA-filled ENR 50 compounds at optimum WRHA loading (20 phr)

Properties	*WRHA*	*WRHA + silane (A-189)*
Tensile strength (MPa)	12.90	17.04
Modulus 100 (MPa)	0.92	0.93
Modulus 300 (MPa)	2.22	2.67
Elongation at break (%)	811	768
Tear strength (kN/m)	9.67	11.80
Hardness (IRHD)	56	60

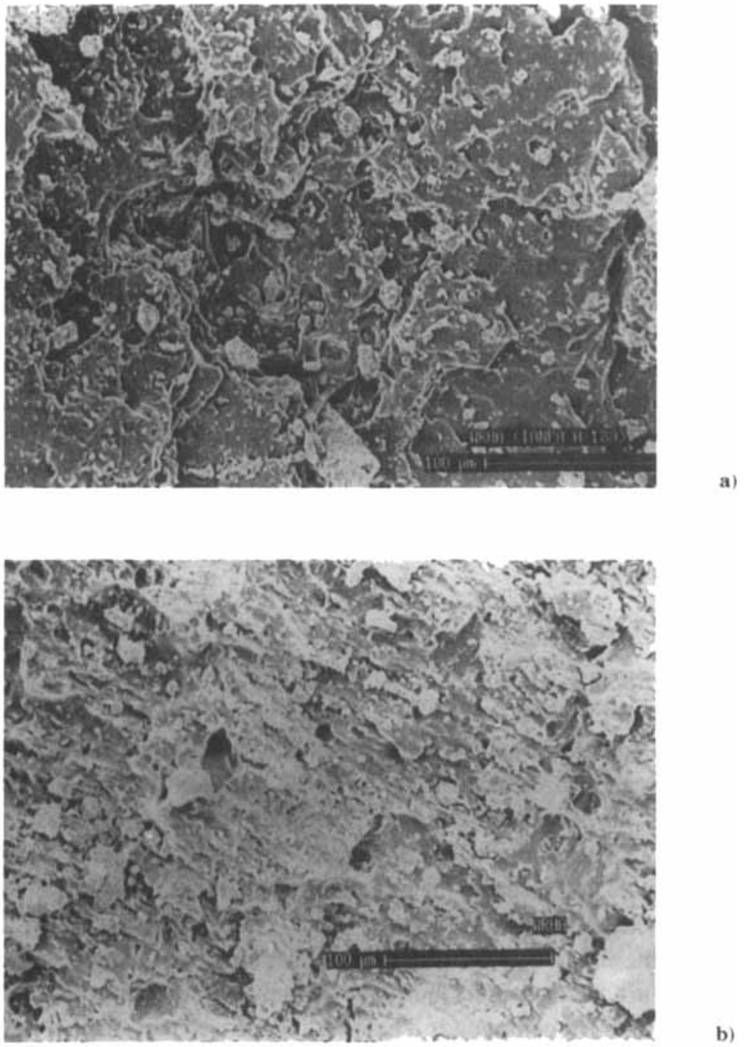

FIGURE 6 SEM micrograph of WRHA-filled ENR vulcanizates after tensile fracture at 20 phr filler loading (a) without silane coupling agent (b) with silane coupling agent (2 phr filler).

a SEM micrograph which showing the surfaces of WRHA-filled vulcanizates which are not smooth with larger particle size of WRHA fillers. The fracture plane indicates clearly the poor filler-rubber interaction. However it can be seen in Figure 6b that the fracture surfaces of vulcanizates with a silane coupling agent have better dispersion of the WRHA filler in the rubber matrix. The fracture surface is smooth and uniform compared to similar compound but without a coupling agent as shown in Figure 6a. This observation is in agreement with an earlier investigation by Nasir *et al.* [15] who reported that the addition of a 2% of silane coupling agent has enhanced the tensile and tear strength of silica-filled vulcanizates. The silane coupling agent is believed to improve the surface functionality of the fillers by changing the hydrophilic silica surface into a hydrophobic surface. This then resulted in the formation of strong chemical bond between filler surface and rubber matrix [20].

Table V shows that the presence of silane coupling agent has also increased the modulus at 300% elongation. As expected the hardness of the vulcanizates is increased while elongation at break decreased with the addition of a silane coupling agent (see Table V). The increase in hardness can also be attributed to better wetting and dispersion of the fillers. This observation is in agreement with the trend observed by other workers [20, 23, 24].

CONCLUSIONS

This investigation proved that white rice husk ash (WRHA) has a potential as a filler for epoxidized natural rubber (ENR). Addition of WRHA in ENR compounds has increased both tensile and tear properties up to an optimum level, i.e. 20 phr, after which there was a deterioration of properties. On the other hand, for hardness the increment was continuous as the WRHA loading increased. The presence of silane coupling agent, A-189 has increased the effectiveness of WRHA as a filler for ENR by improving not only the cure characteristics but also the tensile and tear properties of WRHA filled ENR compounds. These findings proved that silane coupling agent has the ability to enhance the interaction between WRHA and rubber phase.

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