J. Mater. Environ. Sci. 4 (2) (2013) 205-216
ISSN : 2028-2508
CODEN: JMESCN

An assessment of Rice Husk Ash modified, Marble Sludge loaded Natural Rubber hybrid composites

Khalil Ahmed*[1], Shaikh Sirajuddin Nizami [2], Nudrat Zahid Raza [1], Shaikh Kamaluddin[1], Khalid Mahmood

[1] *Applied Chemistry Research Centre PCSIR Laboratories Complex, Karachi.75280 Pakistan*
[2] *Department of Chemistry, University of Karachi, Pakistan*

Received 22 Jan 2012, Revised 30 Sept 2012, Accepted 30 Sept 2012
*Corresponding author: Khalil Ahmed, Applied Chemistry Research Centre PCSIR Laboratories Complex, Karachi.75280 *E-mail, khalilmsrc@gmail.com

Abstract

Marble sludge (MS) and rice husk have been collected from marble industry and rice processing mill. MS was dried, ground and passed through 10µm size sieve. Rice husk was treated with hydrochloric acid solution at 105˚ C, and burned at 650˚ C for four hours, pulverize and passed through 10µm size sieve. Both powders were characterized by the X-ray fluorescence and then incorporated in the natural rubber (NR), according to recipe for various hybrid compositions. Compounding was carried out on a two-roll mill with total filler loading of 60 parts per hundred rubber (phr). The composites were vulcanized at 155º C. The effects of partial or complete replacement of MS by rice husk ash (RHA) on mechanical and swelling properties of MS/RHA/NR hybrid composites before, and after ageing were analyzed. Results show that tensile strength, 100% modulus, 300% modulus, tear strength, hardness, crosslink value, volume fraction and shear modulus increases while elongation at break, compression set, rebound resilience, abrasion loss, swelling coefficient and the average molecular weight of the polymer between cross-links decreases with increasing RHA weight ratio in hybrid composites. The ageing characteristic of corresponding hybrid composites was evaluated at 70˚ C and 100˚ C temperatures for 96 hours.

Key words; Marble sludge, rice husk derived silica, Natural Rubber, hybrid composite, mechanical properties, swelling properties

1. Introduction

The most common fillers used in polymer industry are carbon black, silica and other non black materials mainly calcium carbonate, talc etc. They assist in the improvement of physical and mechanical properties where carbon black is the most important reinforcing part of rubber compounding [1-5]. Carbon Black improves the overall properties by forming bonds between rubber molecule and particle surface of Carbon Black but now days most important reinforcing filler is precipitated Silica [6-9]. The particles of silica surface have hydrophilic silanol / hydroxyl groups, which results in strong filler-filler interaction by hydrogen bonding [10-14]. Several fillers such as wollastonite, talc, calcium carbonate with carbon black were studied by Robinson [15]. He investigated the effect of wollastonite by two different particles size with epoxy silane treatment. Furtado et al., studied the effect of mica on the fatigue life of carbon black filled elastomeric compounds. The fatigue life of Styrene Butadiene Rubber compounds increased up to certain value beyond which no significant decrease is observed [16].

Carbon Black and silica both fillers are quite expensive commercially. Therefore, there is the need to develop cheaper filler from other natural resources. These include agriculture waste and industrial waste such as marble sludge [17-19]. Marble Sludge is produced in marble processing industry during the cutting/polishing process of marble blocks. Throughout the processing of marble, water is showered on blades to cool the blades which absorb the dust produced during the cutting operation. The water is stored in pits until the suspended particles settle, and then the sludge is disposed of on the ground and left to dry and its particles become airborne causing air pollution. Attempts have been made to consume marble sludge waste for various purposes such as in cement and construction industry [20] and asphalt concrete [21] but very rare attempts have been made to use as a filler in natural rubber compounds [22]. Another major agricultural residue is rice husk. Rice being the most important food crop generates huge amount of husk as waste. It is mostly burned uncontrolled in open air or used as fuel in the rice paddy milling process. This procedure left ash behind which in turn creates environmental pollution. As both of these materials are low cost and cheap therefore the utilization of waste like marble sludge (MS) and rice husk ash (RHA) in the production of new material is a global challenge now and will also help to protect the environment. Ismail, et, al., observed that the incorporation of rice husk ash in rubber has led to a significant improvement in physical properties of the composites i. e., comparable to that imparted by other commercial fillers such as carbon black and silica [23-27]. Mehta and Haxo described the use of rice husk ash as a reinforcing agent for synthetic and natural rubbers. In this work it was observed that RHA did not adversely affect either the vulcanization characteristics or the aging of styrene butadiene rubber, natural rubber, nitrile rubber, butyl rubber, neoprene, and ethylene- propylene-diene rubber. In addition, it was concluded that RHA filler is a satisfactory substitute for carbon black and can be effectively used as a partial replacement for finer and more reinforcing black [28].

The aim of this investigation is to develop hybrid composites with industrial and agricultural waste material with zero economic value of the partially or fully replacement of the marble sludge powder by rice husk ash. The studies involved mechanical properties and swelling behavior of MS/RHA weight ratio in Marble Sludge/Rice Husk Ash/ Natural Rubber (MS/RHA/NR) hybrid composites. Mechanical properties such as tensile strength, modulus (at 100%, and 300% elongation), elongation at break, tear strength, compression set, hardness, abrasion resistance and rebound resilience were analyzed and discussed. Swelling tests were conducted by measuring the swelling coefficient, volume fraction of rubber, crosslink value, the average molecular weight of the polymer between cross-links and shear modulus of the rubber composites.

2. Material and methods

2.1. Materials and sample preparation

All materials were used as received. Natural Rubber (NR) ribbed smoked sheet (Grade RRS 3) obtained from Rainbow rubber industry Karachi. Marble Sludge (MS) dry powder and rice husk were obtained from local marble and rice manufacturing industry. Other materials, such as zinc oxide, stearic acid, tetra methylthiuram disulphide (TMTD) as accelerator, 3-Dimethylbutyl-N-phenyl-p-phenylenediamine as an antioxidant and Sulphur as a vulcanizing agent were commercial grade and purchased from local market. Toluene as a solvent was chemically pure from Merck.

Physical properties of Natural Rubber such as dirt Content, ash content, nitrogen content, volatile matter, initial plasticity, and plasticity retention index were determined by ASTM, the results are presented in table 1. Marble sludge waste (waste product from marble cutting industry) was collected from local marble cutting industry. The Marble Sludge Waste was dried in oven at 80º C for 24 hours and ground into fine particle and passed through the desire sieve to obtain selective micro size particles such as 10µm.

Table 1: Physical properties of RSS (Natural Rubber)

Parameter	**Method**	**Value %**
Dirt Content	ASTM D1278-91	0.042
Ash content	ASTM D 1278-91	0.58
Nitrogen content	ASTM D3533-90	0.63
Volatile matter	ASTM D1278-91	0.80
Initial plasticity	ASTM D2227-96	30
Plasticity retention index	ASTM D3194-04	60

2.2. Silica Preparation
Rice husk was washed with water to remove any foreign body. The cleaned husk was mixed with 0.4M hydrochloric acid in the ratio of 100 gm husk per 1 litre acid and heated until boiled for 30-45 minutes. Then the mixture was maintained at 105^o C in the oven for 3 hours. After the reaction, the acid was entirely eliminated from the husk by washing with tap water. It was then dried in an oven at 110^o C for 3-5 hours. The treated husk burnt in an electric furnace at 600^o C for 6 hours, silica was obtained as white ash. The outline of the silica is like to the shape of the husk but smaller in size. To reduce its size, a ball mill was used to grind the silica. Then ground silica passed through 10 µm sieves.

2.3. Sample preparation
The rubber was compounded on a laboratory two-roll mill (16 X 33 cm) employing the formulation given in Table 2. The mixing was done according to ASTM D 3182 (2001). The NR was masticated on the mill and the total amount of filler was incorporated into the rubber (60 part per hundred of the rubber (phr) with 10 µm size of MS and RHA then the compounding ingredients were added in the following order: activators with balance, accelerators, and then sulphur. After mixing, the rubber compound was passed 2-4 minutes through the tight nip gap and finally sheeted out.

Table 2: Compound recipe of partial or complete replacement of marble sludge by rice husk ash in MS/RHA/NR hybrid composites.

Ingredient	MS/RHA ratio (phr)
NR	100
ZnO	05
Stearic Acid	02
TMTD[a]	2.4
Antioxidant[b]	1.5
Sulphur	1.6
MS/RHS weight ratio	00/00, 60/00, 50/10, 40/20, 30/30, 20/40, 10/50, 00/60

[a]Tetra methylthiuram disulphide
[b]3-Dimethylbutyl-N-phenyl-p-phenylenediami

2.4. Vulcanization process
The compounded rubber stock was then cured in a compression molding machine at 155° C and at applied pressure of 10.00 MPa for the respective optimum cure time ($t = t_{90}$) obtained from rheographs. After curing, the

vulcanized sheet was taken out of the mold and immediately cooled under tap to stop further curing. All samples were cured at this temperature for the specific cure time and stored in a cool dark place for 24 hours.

2.5. Mechanical Properties
The properties of MS/RHA/NR hybrid composites were measured with several techniques based on ASTM. The tensile strength, elongation at break, Modulus at 100%, and 300% elongation, and tear strength were measured by Tensile Tester (Instron 4301), according to ASTM D 412 and ASTM D 624. Samples were punched out from the molded sheets with a dumbbell-shaped die and angular specimens for tear strength. The crosshead speed was maintained at 500mm/minute at room temperature. The hardness of the sample (Shore A) was determined using Shore Hardness Tester according to ASTM D-2240. Abrasion tests were conducted using ASTM D 5963 test method. The abrasion resistance has been expressed as relative volume loss mm^3. The test was conducted on Abrasion check from Gibitre Italy. Resilience was determined by the vertical rebound method according to ASTM D-2832 88, Using Rebound Check from Gibitre Italy

2.6. Swelling Properties

The chemical crosslinking density of MS/RHA/NR hybrid composites, were determined by the equilibrium swelling method. The sample is weighing about 0.2-0.25 g was cut from the compression-molded rubber sample. The sample was soaked in pure toluene at room temperature to allow the swelling to reach diffusion equilibrium. After 5 days the swelling was stopped and at the end of this period the test piece was taken out. The adhered liquid was rapidly removed by blotting with filter or tissue paper, and the swollen weight was measured immediately. It was then dried under vacuum at 80°C up to constant weight and the desorbed weight was taken. The swelling Coefficient (α) of the sample was calculated from following equation. [29]

$$a = \frac{W_2}{W_1} \times r_S^{-1} \quad (1)$$

W_1 is the weight of the test piece before swelling and W_2 is the weight of test piece after swollen.

The chemical crosslink densities of the composites were determined by the Flory-Rehner equation by using, swelling value measurement according to the following relation [30-31].

$$n = \frac{-\ln(1-V_r) + V_r + c\,V_r^2}{r_o V_s \times V_r^{1/3} - V_r/2} = \frac{1}{M_C} \quad (2)$$

where *Vr* is the volume fraction of rubber in the swollen gel, V_s is the molar volume of the toluene (106.2 cm3·mol^{-1}) χ is the rubber-solvent interaction parameter (0.38 in this study), ρ_o is the density of the polymer, ν is cross-link density of the rubber (mol·cm−3) and M_C is the average molecular weight of the polymer between cross-links (g mol^{-1}) and is related to the shear modulus (G) by following expression [32].

$$G = \frac{RT\,r_r}{M_C} \quad (3)$$

Where ρ_r is the density of rubber matrix , R is the universal gas constant and T is absolute temperature.

The volume fraction of a rubber network in the swollen phase is calculated from equilibrium swelling data as:

$$V_r = \frac{W_{rf}/r_1}{W_{rf}/r_1 + W_{sf}/r_o} \quad (4)$$

Where W_{sf} is the weight fraction of solvent, ρ_0 is the density of the solvent, W_{rf} is the weight fraction of the polymer in the swollen specimen and ρ_1 is the density of the polymer i.e. NR which is 0.9125 g/cm3. The weight of toluene uptake per gram of rubber material, Q was determined according to the following equation:

$$Q = \frac{Swellen\ Weight - Dried\ Wiegth}{Original\ Weight \times \left(\frac{100}{Formula\ Weigth}\right)} \quad (5)$$

Q is defined as the amount of solvent absorbed by 1 g of rubber.

2.7. Thermal Ageing

The thermal ageing characteristics of the MS/RHA/NR hybrid composites were studied at 70°C and 100ºC for 96 hours as per ASTM D 573. The properties of accelerated aging were measured after 24 hours of aging test. Tensile strength, 100%, modulus, 300% modulus, elongation at break, tear strength, hardness, resilience, abrasion loss and compression set of the MS/RHA/NR hybrid composites were measured after aging to estimate aging resistance. Percentage of retention in properties of the specimens is calculated as below.

$$\% \text{ Retention} = \frac{\text{Value after aging}}{\text{Value before aging}} \; X \; 100 \quad (6)$$

3. Results and Discussion

3.1. Characterization of marble sludge and rice husk ash

The chemical composition of MS and rice husk derived silica were determined using WDX-ray fluorescence spectrometer (model S4 pioneer Bruker AXS, Germany) is shown in the table. 3. It is evident from the data that marble sludge largely composed of Calcium and Magnesium compounds. Silica, aluminum oxide and iron oxide are also present in small amount. The values obtained for relative metal component of marble sludge from atomic absorption spectroscopic study are in close approximation with the results obtained from WDX-ray florescence spectrometer study where RHA contains the maximum amount of silica. The above observation shows that the marble powder is basically composed of calcium carbonate, magnesium carbonate with small amount of Silicate, aluminum oxide and iron oxide.

Table 3: Quantitative analysis of marble sludge and rice husk ash using WDX-ray fluorescence Spectrometer Model: S4 Pioneer from Braker – axs Germany.

Component	Weight %	
	MS	RHA
CaO	68.6	0.62
MgO	22.13	0.45
SiO_2	3.89	94.88
Al_2O_3	2.785	0.86
Fe_2O_3	0.603	0.24
Cr_2O_3	0.24	----
ZnO	0.20	----
TiO	0.549	----
$Na_2\ O_3$	----	0.18
K_2O	-----	1.93

3.2. Mechanical properties of hybrid marble sludge/rice husk ash/natural rubber composites.

Figure 1 shows, that incorporation of RHA to MS/NR composites increases the tensile strength. It is clear that the content of RHA increases in place of MS modified the tensile strength value, which could be due to the RHA better interaction with rubber as compared to MS. Strong rubber-filler interaction would increase the effectiveness of the stress transferred from the rubber matrix to filler particles dispersed in the rubber matrix [33]. The dependence of the reinforcement of the RHA content can be seen in their mechanical behavior, especially in the ultimate tensile values. The tensile strength increases with increasing RHA for MS/RHA/NR hybrid composite. The tensile strength data from MS/RHA/NR hybrid composite showed better results when 50 phr RHA and 10 phr of MS were used. It is noteworthy that this result is better than those shown by NR hybrid composites which contain different MS/RHA weight ratio. The natural rubber composite with 60 phr RHA has a maximum tensile strength, as expected.

It could be seen that the similar tensile strength trends are observed in samples after ageing. The result shows that tensile strength decreased at all MS/RHA ratios after ageing. Thermal ageing of the MS/RHA composites caused the tensile strength to deteriorate, especially at 96 hrs with 100ºC temperatures of ageing [34]. This is explained why, both aging temperatures show a lower retention (below 100%), after thermal ageing. However, aging at 70º C for 96 hours of MS/RHA/NR hybrid composites show higher retention of tensile strength after thermal ageing compared to that of 100ºC for 96 hours. This could be due to the better thermal stability at lower temperature.

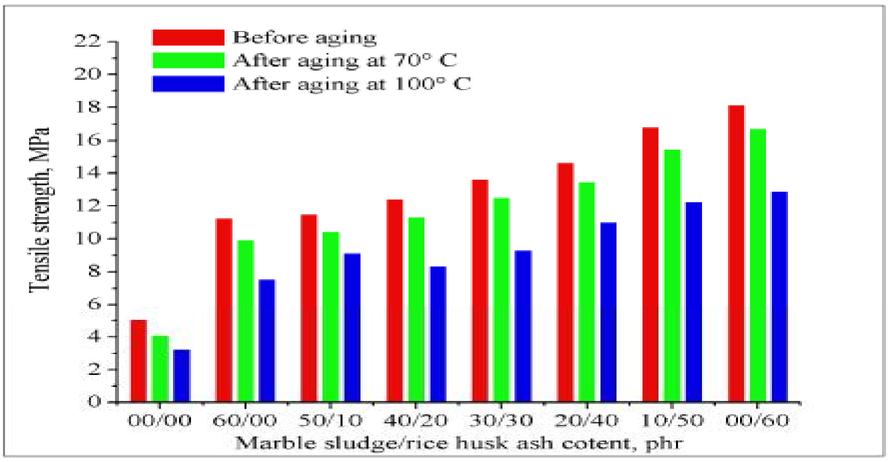

Figure 1: The effect of rice husk ash loading on tensile strength of hybrid marble sludge/rice husk ash/natural rubber composites

The effect of RHS on the 100% modulus and 300% modulus of the MS/RHA/NR hybrid composites before, and after ageing are shown in Figures 2 and 3 respectively. Before ageing, the results show that as RHA content increases, in replacement of MS , the 100% modulus and 300% modulus increases, which indirectly shows that the MS/RHA/NR hybrid composites become harder and stiffer. It may be due to the RHA more filler-rubber interaction as compare to MS, which causes the reduction in the elasticity of rubber chains, therefore it will create more rigid compound. The higher retention in 100% modulus and 300% modulus (more than 100%) MS/RHA/NR hybrid composites have been shown at 70º C for 96 hours after thermal ageing which might be due to the post cross linking of the rubber composites. However at 100º C for 96 hours show the lower retention in 100% modulus and 300% modulus (less than 100%) Ahagon et. al. [35] and Baldwin et. al. [36] in their studies of accelerated aging of rubber compound also observed the modulus increase and later reduction, depending on aging mechanism. At 90 to 110º C the rate of modulus decreases with increasing, aging temperature be expected, however at 70 to 90º C the rate of modulus increases with decrease in aging temperature.

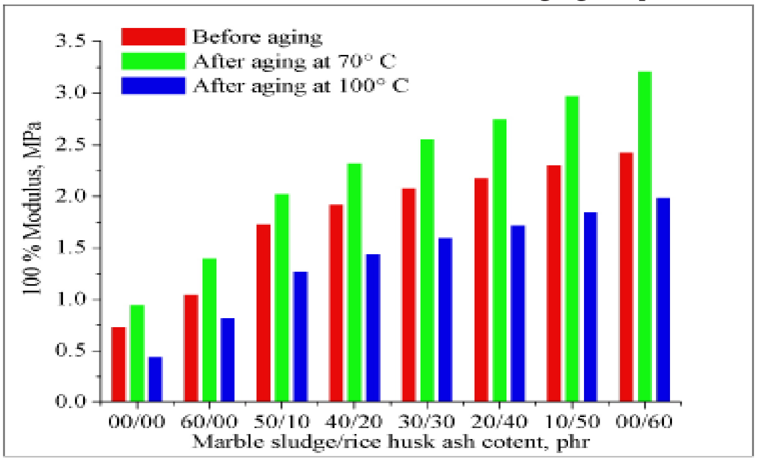

Figure 2: The effect of rice husk ash loading on 100% modulus of hybrid marble sludge/rice husk ash/natural rubber composites

The effect of aging temperature on modulus is owing to the complication of reactions taking place in cured rubber compound. Polymer chain scission causes reduction in molecular weight and molecular entangling with high cross link density of MS/RHA/NR hybrid composites. The latter results in the energy dissipation reduction via molecular mobility restriction. The crosslink density is playing an important role in tensile and tear strength properties. It is also evident from table 4 that Crosslink value of the composite continuously increases with the increasing RHA content. This phenomenon is due to post curing effect which tends to increase with aging temperature. Clarke et. el. [37] in their reported outcome on the aging kinetics of tensile strength of NR compound, also elucidate that both crosslinking reaction and scission reaction increases in the rate of reaction to rising aging temperature. The scission reaction has a greater activation energy then crosslink reaction. The rate of crosslink reaction in fact increases as temperature decreases. The more prompt, enhance in modulus would happen in lower aging temperature.

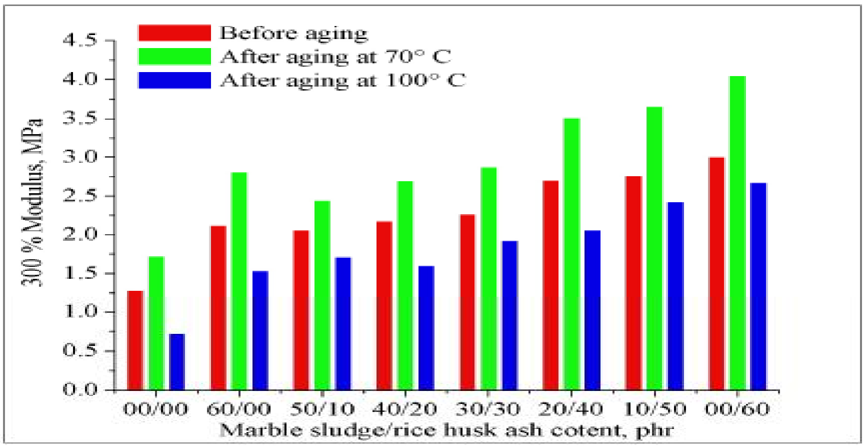

Figure 3: The effect of rice husk ash loading on 300% modulus of hybrid marble sludge/rice husk ash/natural rubber composites.

Tear strength values of MS/RHA/NR hybrid composites before, and after aging are given in figure 4. The tear strength also follows the same trend as that of tensile strength. The tear strength varies with the increase in weight of RHA in total filler content at different MS/RHA weight ratio. Evidently, it is also seen that as the content of RHA increases in place of MS the tear strength also increases. This suggests that the tear strength of the MS/RHA/NR hybrid composites is dependant more on the weight of RHA than MS, which could be due to good filler- rubber interaction, exhibits improved tear strength.

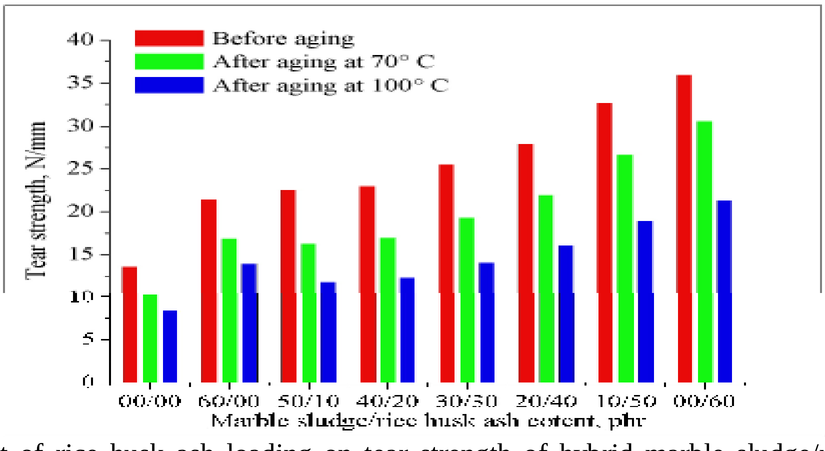

Figure 4: The effect of rice husk ash loading on tear strength of hybrid marble sludge/rice husk ash/natural rubber composites

Significant variations can be seen in the behavior of elongation at break mechanical as shown in figure 5. The incorporation of RHA into MS/NR composites decreased the elongation at break of hybrid composites. Evidently the values of elongation at break decrease with increasing amount of RHA in place of MS in MS/RHA/NR hybrid composites. This may be because of NR matrix allows more rheological flow due to good filler rubber interaction i.e. good toughing. Elongation at break for MS/RHA/NR hybrid composite decreased with increasing RHA content. This is also explained in terms of the adherence of the filler to the polymer, which leads to the stiffening of the polymer chain and hence resists against stretching when strain is applied.

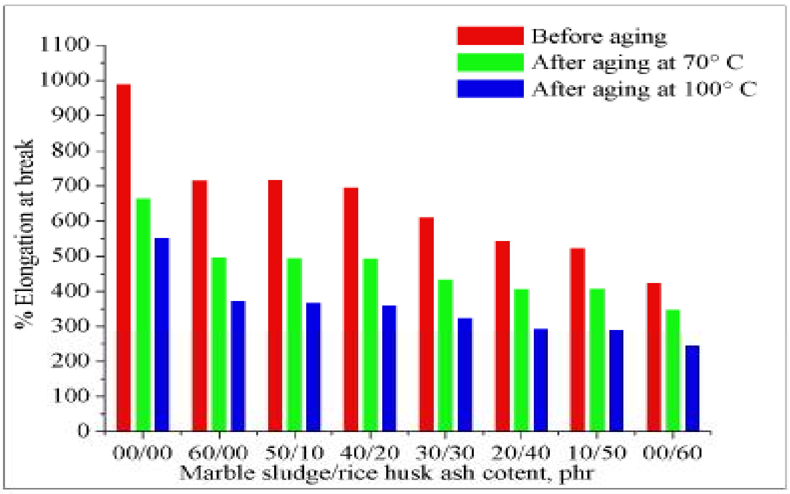

Figure 5: The effect of rice husk ash loading on % elongation at break of hybrid marble sludge/rice husk ash/natural rubber composites

The influence of hardness on the replacement of MS by RHA is shown in figure 6. It is seen that the hardness increases with the increasing RHA amount. From these results it is obvious that hardness Shore A was modified when MS replaced by RHA added to the MS/RHA/NR hybrid composites and gradually increased with the increasing RHA amount. Moreover, higher value of hardness was reached when amount of MS fully replaced by RHA. If compared to RHA, one can observe that hardness obtained from MS filled composite is lower than the corresponding value for RHA containing MS/RHA/NR hybrid composites.

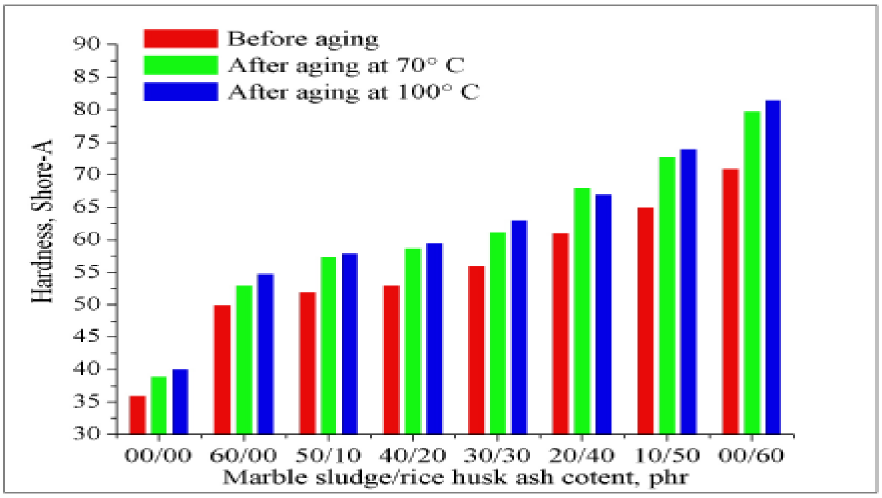

Figure 6: The effect of rice husk ash loading on hardness of hybrid marble sludge/rice husk ash/natural rubber composites.

Figure 7, shows the relationship of compression set of MS/RHA/NR hybrid composites before, and after aging. It is widely known that compression set is another property that can be used to show the degree of elasticity evidently compression set decreases with increasing RHA amount but after aging the compression set values continuously increases it means that the elasticity of the composite is reduced. [38] This phenomenon also seen in rebound resilience property of. MS/RHA/NR hybrid composites.

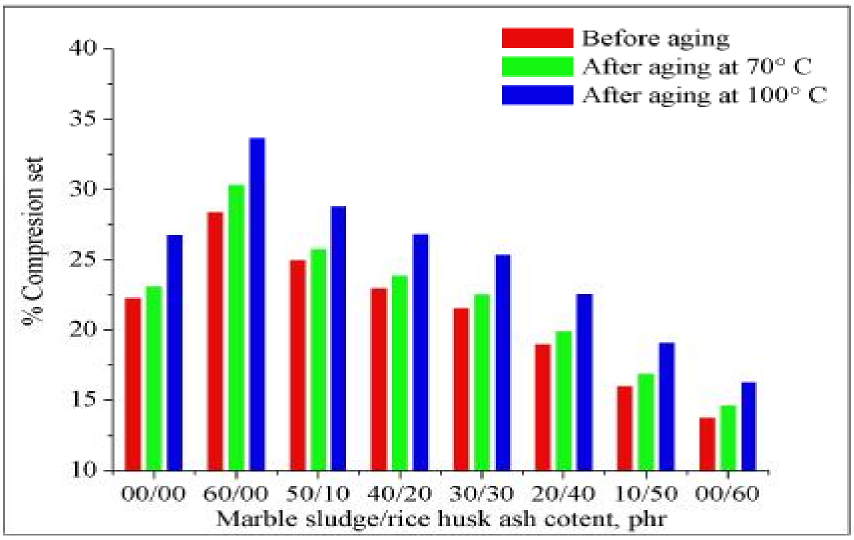

Figure 7: The effect of rice husk ash loading on % compression set of hybrid marble sludge/rice husk ash/natural rubber composites

Figure 8, shows that rebound resilience of MS/RHA/NR composites before and after aging tends to decrease. These observations highlight the fact that the incorporation of RHA amounts into the rubber composite can improve the stiffness of the compound. Rebound resilience also decreases with the addition of RHA. The reduction in resilience shows that the elasticity of the compound is reduced.

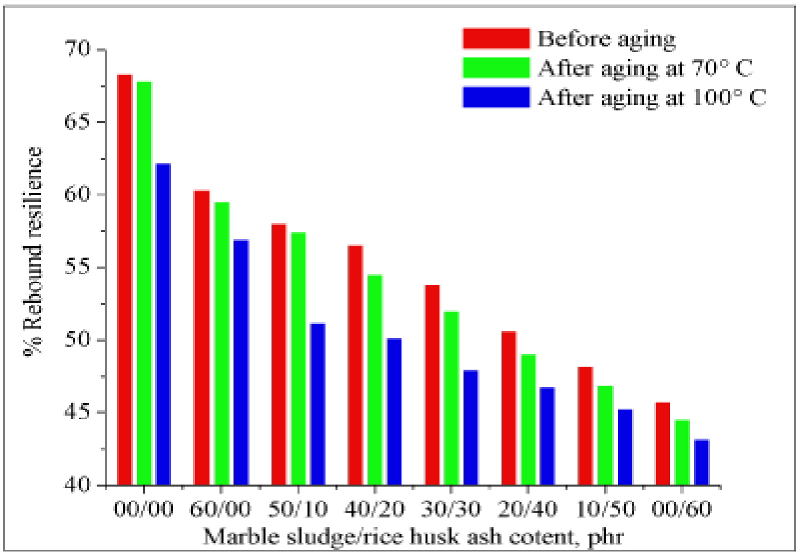

Figure 8: The effect of rice husk ash loading on % rebound resilience of hybrid marble sludge/rice husk ash/natural rubber composites

The results of abrasion loss are presented in the vertical bar shown in Figure 9. It is clear from the graph that the abrasion loss of MS/RHA/NR hybrid composites has been influenced by the addition of RHA. The addition of RHA gradually decreases abrasion loss and increases abrasion resistance of MS/RHA/NR hybrid composites.

It is well known that the abrasion resistance of filled rubber is basically determined by filler characterization, especially its morphology and surface reactivity. The lower filler- filler interaction leads to higher abrasion resistance. Therefore, addition of RHA in MS/RHA/NR hybrid composites minimizes the filler-filler interaction.

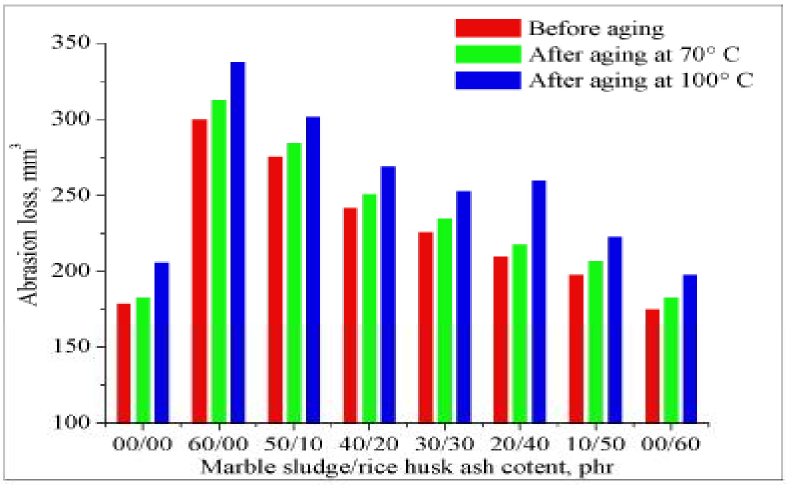

Figure 9: The effect of rice husk ash loading on abrasion loss of hybrid marble sludge/rice husk ash/natural rubber composites

3.3. Swelling properties of hybrid marble sludge/rice husk ash/natural rubber composites

Swelling test is performed to observe the swelling coefficient, volume fraction of rubber, crosslink value, and the average molecular weight of the polymer between cross-links and shear modulus. The effect of RHA on swelling coefficient of hybrid composites was determined by immersing the samples in toluene for five days. The obtained results showed a decreasing trend in swelling coefficient after replacing the MS by RHA (table 4). It is indicated that the penetration of toluene into MS/RHA/NR hybrid composites was reduced with the increasing RHA content. This means that higher amount of RHA restricted the penetration of toluene in hybrid composites. It could be also seen that there is a lower swelling coefficient associated with full replacement of MS by RHA in hybrid composites as compared to other RHA gradually filled MS/RHA/NR hybrid composites. This is due to better dispersion of RHA in NR, promoting better filler-rubber matrix interaction in composites.

A comparison of crosslink density can be measured from the reciprocal swelling values 1/Q (apparent crosslink density or crosslink value) after the calculation of crosslink value of composites as shown in table 4. It could be observed that the crosslink value increases from 10/50 to 60/00 of MS/RHA weight ratio. When the RHA content increases the crosslink value also increased. However average molecular weight of the polymer between cross-links observed decrease in their values. It may due to the increasing amount of RHA in rubber matrix. The molecular movement of the rubber reduces and makes it more difficult for toluene to penetrate through the rubber matrix. The 40/20, 10/50 and full replacement of MS by RHA hybrid composites have better performed their crosslink value as compared to others MS/RHA weight ratios composites. The average molecular weight between crosslink was inversely proportional to the crosslink density thus M_c for 60 phr RHA containing composite was very small value. The above swelling results are to some extent supported by the observations of the curing characteristics. The maximum and minimum torque changes significantly with the RHA content as indicated by the values.

Table 4, also shows the shear modulus of hybrid composites with partial or complete replacement of MS by RHA. The result shows the shear modulus values continuously increases with increasing content of RHA in MS/RHA weight ratio. The increment in rubber-filler interaction observed in MS/RHA weight ratio of hybrid composites might be due to the increment in the RHA which has higher surface activity then MS and consequently high affinity to rubber. Equilibrium swelling measurements were performed to evaluate the chemical cross-linking density in MS/RHA/NR hybrid composites.

The cross-link density of polymer i.e. average molecular weight between the cross-links was determined from swelling data. The cross-link density and the average molecular weight of the polymer between cross-links are calculated by using Flory-Rehner equation. A clear linear increase of the apparent cross-link density with the RHA content in the hybrid composite is observed from table 4. This indicates a strong interaction between the NR and the RHA lead to strong physical cross-links.

Table 4: Data for the swelling coefficient (α), volume fraction of rubber (V_r), crosslink value, Average molecular weight between the crosslink in polymer (M_C) and shear modulus (MPa) of hybrid marble sludge/rice husk ash/natural rubber composites before and after aging from swelling measurements.

MS/RHA	Swelling properties				
	Swelling coefficient ($g^{-1} cm^3$)	**Volume fraction of rubber (V_r)**	**Crosslink value**	**Average molecular weight M_C ($g\ mol^{-1}$)**	**Shear modulus (MPa)**
00/00	4.40 (4.94)[a] [6.45][b]	0.1917 (0.1745) [0.1610]	0.2412 (0.1850) [0.1950]	6444.2 (7917.1) [9457.1]	0.351 (0.286) [0.240]
60/00	2.63 (3.26) [2.88]	0.237 (0.2018) [0.2225]	0.4048 (0.325) [0.368]	3954.2 (5737.2) [4617.4]	0.573 (0.393) [0.490]
50/10	3.05 (3.12) [3.23]	0.2153 (0.2110) [0.2056]	0.3490 (0.340) [0.329]	4981.9 (5216.2) [5507.0]	0.454 (0.434) [0.411]
40/20	2.88 (2.06) [3.09]	0.2248 (0.2200) [0.2131]	0.368 (0.358) [0.344]	4512.3 (4750.2) [5079.1]	0.502 (0.477) [0.446]
30/30	2.62 (2.69) [2.86]	0.2426 (0.2380) [0.2269]	0.406 (0.395) [0.371]	3769.8 (3937.9) [4409.5]	0.600 (0.575) [0.513]
20/40	2.56 (2.60) [2.78]	0.2471 (0.2440) [0.2324]	0.415 (0.407) [0.382]	3581.8 (3716.0) [4166.0]	0.632 (0.609) [0.543]
10/50	2.51 (2.57) [2.78]	0.2507 (0.2466) [0.2326]	0.422 (0.413) [0.382]	3489.6 (3623.0) [4144.4]	0.649 (0.625) [0.546]
00/60	2.36 (2.47) [2.66]	0.2632 (0.2552) [0.2410]	0.450 (0.430) [0.398]	3093.1 (3337.0) [3573.9]	0.732 (0.678) [0.633]

Values in parentheses are present
[a] aging at 70˚ C
[b] aging at 100˚ C

Conclusion

This study explored the suitability of industrial and agricultural waste in the formulation of hybrid NR composites. Addition of RHA in MS/NR greatly enhanced the mechanical properties of the MS/RHA/NR hybrid composites, such as tensile strength, 100% modulus, 300% modulus, tear strength, hardness and abrasion resistance. However the increased ratio of RHA into the MS/RHA/NR hybrid composites reduces the elongation at break, compression set and rebound resilience. Increasing the RHA ratio in MS/RHA also raise the volume fraction of rubber, crosslink value and shear modulus while swelling coefficient and average molecular weight of the polymer between cross-links decreases in hybrid composites. The reduction in mechanical properties of NR hybrid composites after aging is established. The incorporation of MS and RHA in rubber reduces the deposition of such waste on agricultural lands and hence contributes in resolving the pollution issues and saves the ecosystem and the environment.

References

1. Chung, P. K., Funt, K. J., Quyang, G. B, *Rubb. World*, 204 (1991) 46.
2. Wang, M., *Rubb. Chem. Technol*. 72, (1999), 430.
3. Ismail, H., Anwar, A., *Polym. Test.* 19, (2000), 349.
4. Hamed , G. R., *Rubb. Chem. and Technol*. 77, (2004), 227.
5. Wampler, W. A., Gerspacher, M., Yang, H. H., *Rubb. World, 210*, (1994), 39.
6. Bertrand, P., Wang, L. T., *Rubb. Chem. Technol*. 75, (2002), 627.
7. Litvinov, V. M., Steeman, P. A. M., *Macromolecules* 55, (1999), 1095.
8. Edwards, D. C., *J. Matt. Sci*. 25, (1990), 4175.
9. Leblance, J. L., Cartault, M. J., *J. Appl. Polym. Sci.* 80, (2001), 2093.
10. Reuvekamp, L. A. E. M., Ten Brinke, J. W., Van, P. J., *Kautsch Gummi Kunstst* 53, (2002), 41.
11. Hashim, A. S., Azahari, B., Ikeda, Y., *Rubb. Chem. Technol.* 71, (1998), 289.
12. Kim, I. l. J., Kim, W. S., Dong-Hyun, L., Kim, W., Jong-Woo, B,, *J. Appl. Polym. Sci.* 117, (2010), 1535.
13. Shin Jeong, D., Hong, C. K., Lim, G. T., Seo, G., Seok, C., J. *Elast. and Plast*. 41, (2009), 353.
14. Hongsang, S., Sombatsompop, N., J. *Macromol. Sci. B*: 46, (2007), 825.
15. Robinson, S., Sheridoan, M. F., Authony, G., In: Presented at Meeting of Rubber Division, America, Chemical Society, Savannah, Georgia. (2001)
16. Furtoda, C. R. G., Lebtance, J. L., Nunes, R. C. R., *Eur. Polym. J.* 35, (1999), 1319.
17. Imanah, J. E., Okieimum, F. E., *J. Appl. Polym. Sci*. 90, (2003), 3718.
18. Ishak, Z. A. M., Baker, A. A., *Eur. Polym. J*. 31 (1995), 259.
19. Imanah, J. E., Okieimum, F. E., *J. Polym. Mat.* . 22 (2005), 411.
20. Binici, H., Hasan, K., Salih, Y., *Sci. Res. Ess.* 2 (2007), 372.
21. Karasahim, M., Terzi, S., *Const. Build. Mat.* 21 (2007), 615.
22. Agrawal, S., Mandot, S., Bandyopadhyay, S., Mukhopadhyay, R., *Prog. Rubb. Plast. Recyc. Technol*, 20 (2004) 229.
23. Ismail, H., Nasaruddin, M.N., Ishiaku, U. S., *Polym. Test.* 18 (1999) 287.
24. Ismail, H., Nizam, J.M., Abdul Khalil, H. P. S., *Polym. Test.* 20 (2001) 124.
25. Ismail, H., Nasaruddin, M. N., Rozman, H. D., Eur. *Polym. J*. 35 (1999), 1429.
26. Ismail, H., Mega, L., Abdul Khalil, H. P. S., *Polym. Int.* 50 (2001) 606.
27. Siriwardena, S., Ismail, H., Ishiaku, U. S., Perera, M. C. S., *J. Appl. Polym. Sci.* 85 (2002) 438.
28. Mehta, P.K., Haxo, H. E., *Rubb. Chem. Technol.* 48 (1975) 271.
29. Unnikrishnan, G., Thomas, S, *Polymer, 35* (1994), 5504.
30. Flory P. J., Rehner J., *J. Chem. Phys*. 11, (1943), 512.
31. Mark, H. F., 'Chemical crosslinking' Encycl. of Polym. Sci. & Technol. Inter Science Publisher John Wiley & sons Inc, NY, 4, (1966), 331.
32. Aigbodion,. A. I Menon, A. R. R., Pillai, C. K. S., ,*J. Appl. Polym. Sci.* 77, (2000), 1413.
33. El-Nashar D. E..Mansour S. S. H., Girgis E., *J. Mat. Sci.* 41, (2006), 5359,
34. Bhowmick A. K., White J. R., *J. Mat. Sci.*, 37, (2002), 5141,
35. Ahagon A., Kida M., Kaidou H., *Rubb. Chem. Technol*. 63, (1990), 683.
36. Baldwin M., Bauer D. R., Ellwood K. R., *Rubb. Chem. Technol*. 78, (2005), 336,
37. Clarke J., .Ngolemasango E. F., Bennett M., *J. Appl. Polym.. Sci,* 102, (2006), 3732,
38. Ismail H., Abdul Khalil H. P. S., *Polym. Test.* 20, (2001), 33.