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Characteristics of coupling agent blended marble/agro waste derived silica rubber composites

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Abstract
The effect of reinforcing natural rubber (NR) with industrial and agricultural waste, Marble Waste (MW) / Rice Husk derived Silica (RHS), hybrid filler on the cure characteristics, mechanical and swelling properties of the hybrid composite was investigated. Hybrid fillers were treated with silane (Si-69) as a coupling agent to enhance their dispersion property in NR matrix. This study has shown the intrinsic potential of MW/RHS as reinforcing filler revealed by the considerable improvement in mechanical properties of the NR hybrid composites. The results indicated that scorch time, cure time and elongation at break decreased but torque, tensile strength, modulus, tear strength and hardness increased. The homogenous dispersion of MW/RHS obtained with silane (Si-69) coupling agent is accountable for the substantial enhancement in the tensile strength, tear strength, modulus and hardness of NR hybrid composite. This study suggests that the use of industrial and agricultural waste in NR hybrid composite is a cost effective and smart substitute of industrial interest. Additional inducement was the social responsibility of tackling with environmental issues of both industrial and agricultural waste.

Keywords: Coupling agent (Si-69), Hybrid composite Natural rubber, Marble Waste, Rice Husk derived Silica, Mechanical properties

1. Introduction
The significance and utilization of the industrial waste material as filler in the polymer industry is rising now a days. A major reason for choosing industrial waste material for new production is to contribute in minimizing the environmental issues. Another significant fact about such fillers is their low cost as compared to other conventional fillers. Filler is responsible for the physical and mechanical properties of the ultimate invention. Carbon Black is the imperative reinforcing ingredient for the rubber compounding formulations. It improves numerous properties of these formulations by forming bonds between rubber molecule and its particle surface [1-5]. The other important reinforcing filler is silica. The surface of silica particles has hydroxyl groups, which contributes in strong filler-filler interaction by hydrogen bonding [6-8]. Carbon Black and silica both fillers are relatively costly. Therefore, there is a need to develop cheaper filler from other natural resources. These might include agriculture waste [9-12] and industrial waste such as rice husk and marble sludge respectively. Marble waste is produced in marble processing industry in Karachi Pakistan during the cutting/polishing process of marble blocks [13, 14]. Attempts have been made to use marble waste for various purposes such as in cement and construction industry [15]. However, a few experiments have been done to use it as filler in natural rubber compounds [16-20]. It is observed that the incorporation of rice husk ash in rubber leads to a significant improvement in physical properties of the composites as compared to other commercial fillers such as carbon black and silica [21]; it described the use of rice husk ash as a reinforcing agent for synthetic and natural rubbers. The purpose of this investigation is to reinforce NR with MW and rice husk derived silica, which are waste materials from industrial and agricultural industry, to achieve desired properties and to reduce the price of the finished article. To enhance the interfacial adhesion between the matrix and filler, RHS (which has 93% silica) surface was treated with Bis-(3-triethoxysilylpropyl) tetrasulphide, silane (Si-69), as coupling agent. The endeavour of the present study is to explore the opportunity of industrial and agricultural waste mainly marble sludge and rice husk derived silica for applications in the polymer industry and to examine the cure characteristics, mechanical and swelling properties. The potential of the waste as filler in rubber composites is necessary to build up economical filler. Mechanical and swelling properties were analyzed and discussed.

2. Experimental

2.1. Materials

The materials used for the preparation of the compounds were; Natural Rubber ribbed smoked sheet (RSS-1), comprising Moony viscosity (ML_{1+4} at 100 C) of 80 and Molecular Weight of 120,000 along with a density of 0.912 g/cm3, (Dirt Content 0.042 %, Ash content 0.58 %, Nitrogen content 0.63 %) origin from Thailand was acquired from the Rainbow rubber industry Karachi. Marble waste as sludge (by-product from marble processing industry) was collected. The Marble waste was dehydrated in oven at 80 ºC for 24 hours and pulverized into fine particle and passed through the 10 µm sieves (bulk density, 1.1213 g/cm^3). Zinc oxide as an activator, supplied by M/S S Chemicals Industries (PVT) Ltd. Pakistan, with Melting Point, 1775 °C, Specific gravity, 5.46 g/cm^3 and Zinc oxide content, 98.2 %. Stearic acid was supplied by Nimir (Pvt.) Ltd, Lahore (Melting Point, 67 °C and Acid number ≤ 200) and Tetramethylthiuram disulphide (TMTD) as an accelerator by Qinghai Rubber Chemicals Co. Ltd., Korea. Bis (3-triethoxysilylpropyl) -tetrasulfane (Si-69), as coupling agent, 3-Dimethylbutyl-N- phenyl-p-phenylenediamine as antioxidant and sulfur as a vulcanizing agent were purchased from the local market.

2.2. Characterization of marble sludge powder and RHS

The MW and RHS were examined by XRF spectrometer. Performed measurements done by using S4 PIONEER spectrometer. Surface area of the marble sludge dry powder and RHS was determined by the Brunauer, Emmett and Teller (BET) adsorption technique applying nitrogen isotherm on a Micromeritics Tristar 3000, surface area and porosity analyzer. The following relation was used to find out the surface area: (Eq. (1))

$$S\ BET = 4.353 \times V_m \quad (1)$$

Where S BET is the surface area in m^2/g and *Vm* is the molar volume of adsorbate gas (N2) at STP.

2.3. Silica Preparation

The silica was prepared from rice husk as described previously [20]

2.4. Preparation of Composites

The basic formulation is given in table 1. The composites were prepared as depicted earlier [22].

Table 1: Formulations recipe of studied hybrid composites.

Ingredient	Formulations recipe #							
MW/RHS	**00/00**	**60/00**	**50/10**	**40/20**	**30/30**	**20/40**	**10/50**	**00/60**
NR	100	100	100	100	100	100	100	100
ZnO	05	05	05	05	05	05	05	05
Stearic acid	02	02	02	02	02	02	02	02
TMTD	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Antioxidant	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
MW	00	60	50	40	30	20	10	00
RHS	00	00	10	20	30	40	50	60
Si-69	1.2							

2.5. Cure characteristics

The cure characteristics of the mixes were studied as in our earlier works [23].

2.6. Testing of Physical Properties

Testing on the mechanical and swelling of coupling agent blended marble/agro waste derived silica rubber composites were carried out as described previously using standard procedures [24].

3. Results and Discussion

3.1. Characterization of MW and RHS

The chemical composition of MW powder and RHS is shown in the table 2. As expected, calcium carbonate is the main ingredient in MW powder. The remaining constituents may include other carbonate minerals such as magnetite, while small quantities of SiO_2, Al_2O_3 and FeO are also present. After the analysis of MW by X-ray fluorescence spectrometer, numerous distinctive minerals are identified. The MW is consistent with the chemical examination showing a composition of around 68.6 % calcium carbonate, 22.13% magnesium carbonate, 3.89% of silica, 2.785% aluminum oxide. RHS contains the maximum amount of silica and small amount of calcium, magnesium, aluminum, iron, sodium and potassium compounds.

Table 2: Quantitative examine of MW as well as RHS through X-ray fluorescence Spectrometer.

	Weight %	
Component	**MW**	**RHS**
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

Table 3, gives the BET adsorption results of the marble sludge dry powder and RHS. From the table it is clear that RHS has a higher surface area than that of marble sludge dry powder. So higher the surface area, lower the particle size**.**

Table 3. Surface area of the marble sludge dry powder and rice husk derived silica.

Sample #	**Component**	**Surface area, m^2/g**
1.	Marble sludge dry powder	13
2.	Rice husk derived silica	153

3.2. Cure characteristics

The cure characteristics of the compounds at various mass ratios of MW and RHS compositions (60/00, 50/10, 40/20, 30/30, 20/40, 10/50, 00/60) were measured on a moving die Rheometer with and without S-69 coupling agent. The scorch time and curing time of NR hybrid compound filled with various mass ratios of marble waste and rice husk derived silica is demonstrated in figure 1. It can be observed that the scorch time and cure time of all compounds decrease with the addition of RHS. It is noted that the fall in scorch time is more pronounced in the rubber compounds with RHS loadings in comparison to MW. This is because that the larger surface area of the RHS leads to the greater rubber–filler interaction and leans to inflict additional resistance to flow of rubber molecules [25]. On the other hand, t90 for the rubber compound filled with RHS has higher values than composite with treated filler. This is correlated with the adsorption of activator such as stearic acid and zinc oxide, by the silanol groups on the RHS. Both results reveal that the values of scorch time (ts2) and cure time (t90) are a little lower for NR hybrid composites with the inclusion of Si-69. The RHS has hydroxyl group, which was better dispersed with the addition of coupling agent, and thus get better cure properties.

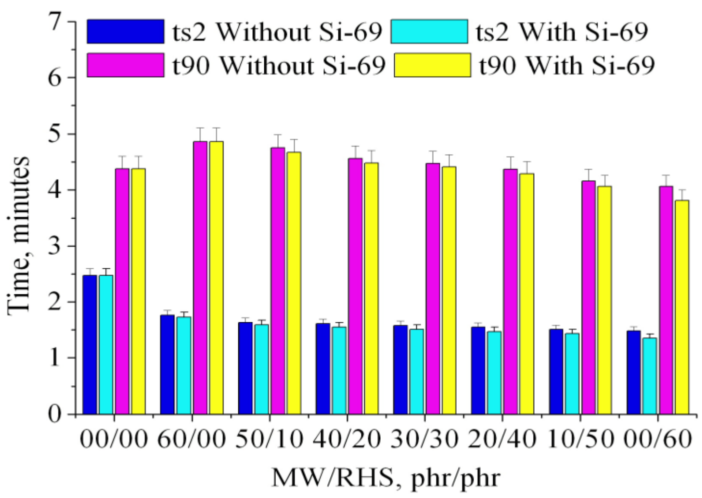

Figure 1: Scotch time and cure time -bars of MW/RHS silane (Si-69) blended hybrid NR composites.

Figure 2, defines the variation of minimum and maximum torque of the NR hybrid compound. At a similar mass ratio of marble waste and rice husk derived silica, minimum as well as maximum torques of NR hybrid compounds with Si-69 are higher than without silane coupling agent. Higher values of minimum and maximum torque of the NR hybrid compounds also point out that better rubber-filler interaction was achieved when silane coupling agent was incorporated. In the case of marble waste, it can be noted that the effect of MW content does not significantly affect the rheological behaviour of the NR compounds while the addition of treated RHS causes a sharp increase in the compound viscosity. This is due to the maximum amount of silica, which has a number of hydroxyl groups on the surface of RHS, which results in strong filler–filler interactions and thus it can aggregate more tightly as compared with MS [26, 27].

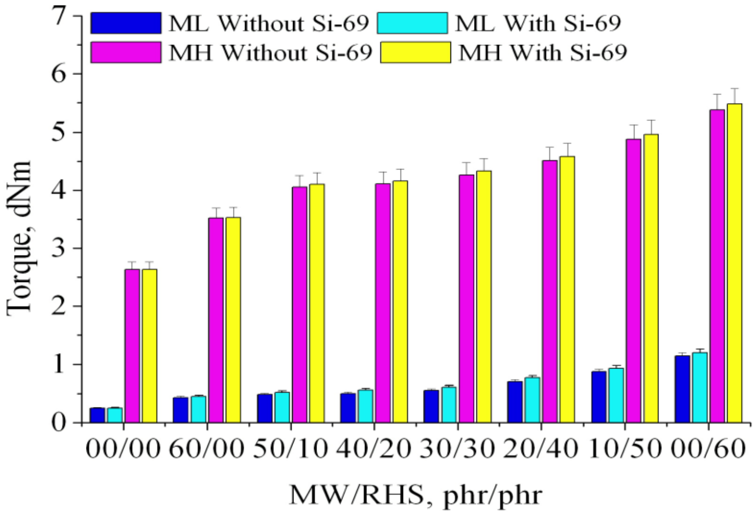

Figure 2: Torques-bars of MW/RHS silane (Si-69) blended hybrid NR composites

3.3. Testing of Physical Properties

The tensile property of various composites with and without coupling agent was shown in Figure 3. With the increase in content of RHS the values of tensile strength increases which is not observed for the unfilled and MW containing NR composite. The expected results attained in this work are likely to be due to the reinforcing effect on highest RHS content (60 phr). As for the hybrid composites, containing silane coupling agent, the tensile strength is found to be considerably higher than those of without Si-69. The silane-coupling agent Si-69 is hydrolyzed to form silanol groups which condense with hydroxyl groups on the surface of silica to form a covalent bond. This is due to the favourable molecular orientation and molecular entanglement in presence of coupling agent. However the coupling agent does not have any influence on the tensile strength of unfilled and MW (60 phr) filled NR composite. It is thought that RHS has the larger surface area as compared to MS which uniformly disperses and therefore provides a better surface area for the interfacial interaction.

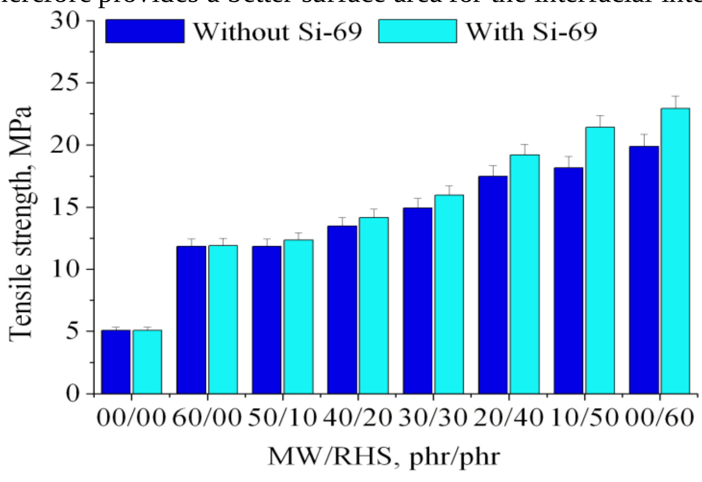

Figure 3: Tensile strength-bars of MW/RHS silane (Si-69) blended hybrid NR composites

Filler mixing into the rubber matrix plays an important role in construction of rubber composite. The hindrance in the movement of the molecular chains of the matrix, results in the stiffness of filled polymeric composite. So, if the diffusion or dispersion of the enclosures in the rubber matrix is homogeneous, the addition of filler in the matrix increases the stiffness of the composites. In this case, the modulus of treated NR composites will gradually increase with an increase of the RHS. The modulus performance has been investigated in detail among different samples, namely, unfilled NR, MW filled NR and MW with treated and untreated RHS/NR hybrid composites and is shown in Figure 4. The addition of RHS in composites resulted in an increase in modulus of approximately 50.5 % (MW 60 to RHS 60 phr). Usually, the modulus is related to the stiffness of the rubber [28]. Although the increase of RHS in composite enhances the stiffness which may cause to increase the 200% modulus of the desired hybrid composite. The effect of the coupling agent on modulus was less pronounced than their effect on tensile strength. It can be seen from the results obtained that the 200% modulus is 1.15 MPa for unfilled NR and moves to 2.18 MPa for MW (60 phr), 2.27 MPa for MW/RHS (50/10 phr), 2.45 MPa for MW/RHS (40/20 phr), 2.65 MPa for MW/RHS (30/30 phr), 2.85 MPa for MW/RHS (20/40 phr), 2.96 MPa for MW/RHS (10/50 phr) and 3.28 MPa for MW/RHS (00/60 phr). The amount of RHS added imparts a strong effect on the modulus, whereas the inclusion of a Si-69 coupling agent does not show any strong effect in changing the modulus.

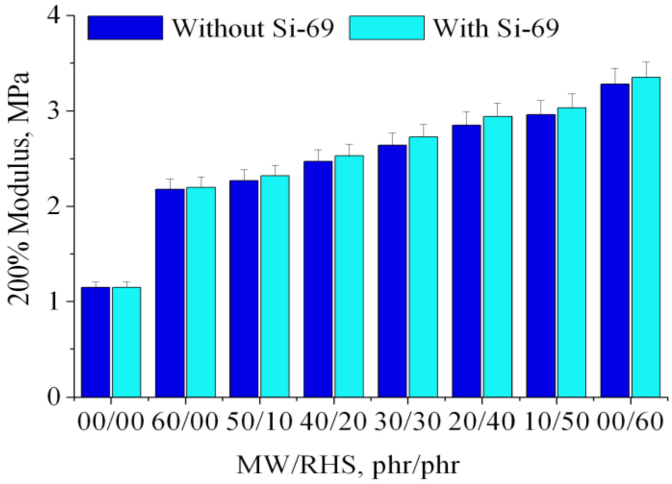

Figure 4: 200% Modulus-bars of MW/RHS silane (Si-69) blended hybrid NR composites.

Tear strength values of different composite are shown in Figure 5. The tear strength also follows the similar pattern as that of tensile strength. It is enhanced by the increment of RHS in their particular hybrid composite. The tear strength of the composites is relying more on the mass ratio of RHS than MW, which could be owing to good filler-rubber interaction. The similar behaviour is also recorded for Tensile strength with and without coupling agent. On the other hand, the presence of Si-69 coupling agent composite had higher values of tear strength over the control and without a coupling agent containing hybrid composites.

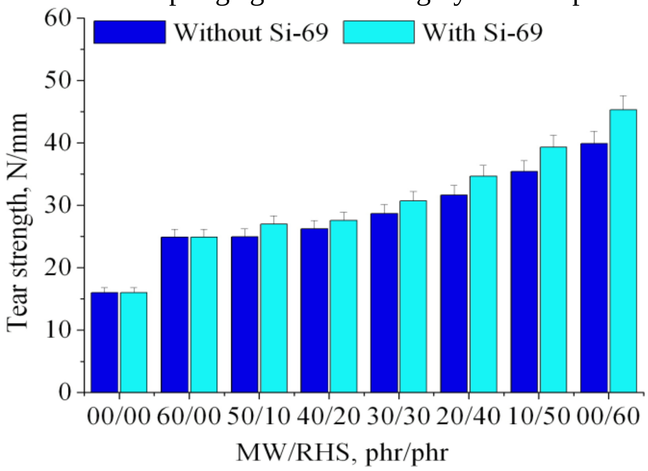

Figure 5: Tear strength-bars of MW/RHS silane (Si-69) blended hybrid NR composites.

Elongation at break of NR hybrid composites with and without a silane coupling agent is depicted in Figure 6. It is observed that with the increase in concentrations of RHS in their particular hybrid composite, the % of elongation decreases gradually. Since rice husk derived silica has a larger cover area than MW, it is expected that the interfacial adhesion between RHS and rubber matrix is better than MW and NR matrix. As the mass ratio of RHS increases in, the composite cannot resist fracture dissemination proficiently and as a result, propagate a tragic crack which lowers the % elongation at break. The elongation at break of hybrid composites with coupling agent had lower values as compared to composites without Si-69 coupling agent filled NR hybrid composites.

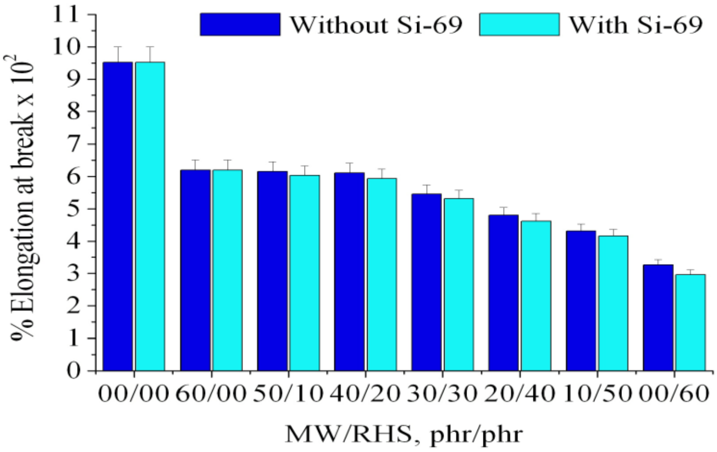

Figure 6: %Elongation at break-bars of MW/RHS silane (Si-69) blended hybrid NR composites.

The RHS interaction with coupling agent enhances the elongation at break. When the silane coupling agent was incorporated in the composites, it also enhances the drenching and dispersion of the RHS in the rubber matrix. The finding of this observation reveals that composite based on coupling agent earns lower values of the elongation at break over the other MW and RHS mass ratio combinations and also than that of the control NR sample. Average hardness value for MW and RHS along different mass ratios -filled NR composites with and without the presence of silane-69 can be seen in Figure 9. Obviously for the entire composites the hardness increased repeatedly with increasing mass ratio of the RHS in the particular hybrid NR composites. This was simply explicable because RHS is rigid as compared to MW, and thus, increasing the mass ratio of RHS furnishes to grow up the diminution of the deformable rubber in the compound; this is broadly known as the dilution effect. Furthermore, the higher hardness was found when 10/50 mass ratio of the RHS reached in MW/RHS hybrid NR composites. When Si-69 was added in the NR composites as a coupling agent, the hardness was gradually increased. The compatibility nature of RHS with rubber matrix has been improved, which was due to the enhanced interfacial adhesion between the RHS and rubber-matrix. The RHS particles adhered well to the rubber matrix in presence of coupling agent.

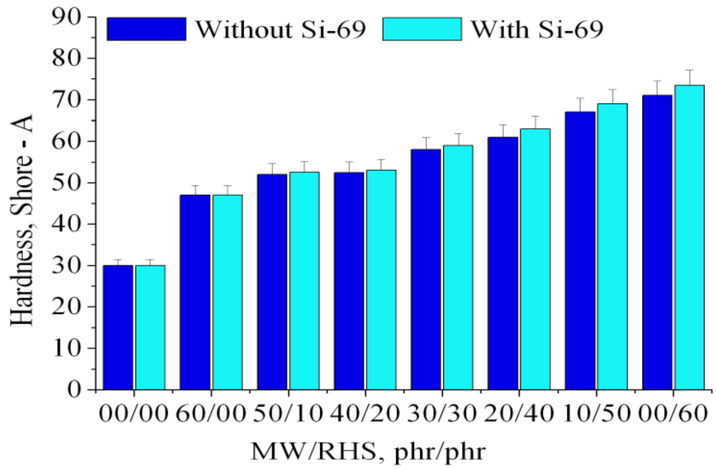

Figure 7: Hardness-bars of MW/RHS silane (Si-69) blended hybrid NR composites.

The swelling parameters versus mass ratio of the MW and RHS hybrid NR composites in toluene are represented in table 3. It can be seen that the swelling ratio of the proposed hybrid NR composite specimens decreases with the increasing RHS in MW and RHS hybrid NR composite in place of MW at room temperature. This observation might be attributed to the better dispersion of RHS in rubber matrix as compare to MW. The diffusion of toluene into the MW filled NR composites are easier compared to the RHS in recommended hybrid NR composite. Among the samples with and without silane coupling agent, the swelling ratio for hybrid composites tends to slightly decrease in the presence of Si-69 which has better resistance to the diffusion of solvent. The average molecular weight between crosslink was inversely proportional to the crosslink density. The average molecular weight of the polymer between cross-links decreased by increasing the mass ratio of corresponding hybrid composite. MW/RHS hybrid system as well as rubber matrix would lead to a stronger crosslinked network and more restriction to the entrance of the solvent. Composite with high RHS loading would form a larger interfacial area between particular filler and rubber which added to the filler rubber interaction. As a result, the entry of solvent was highly restricted in the RHS filled composites. If an enhanced bonding between the filler and the rubber matrix subsisted, a stronger crosslink would be happens. The degree of crosslink in filled composites can be reflected from the crosslink density. Si-69 containing hybrid composite has better crosslink density as compared to composites without the coupling agent. This is attributed to the enhancement in degree of filler dispersion, rubber–filler interaction and crosslink density of the desire hybrid composites

Table 3: Data for the swelling ratio and average molecular weight (M_C) of MW/RHS hybrid filler NR composites from swelling measurements**.**

Formulations #	**Swelling parameters**	
	Swelling ratio	**M_C, g mol^{-1}**
01	4.29	7646.2
02	4.26	7623.5
03	2.53	4783.5
04	2.51	4702.0
05	2.43	4273.1
06	2.39	4133.6
07	2.33	3944.7
08	2.27	3769.1
09	2.19	3528.0
10	2.13	3350.3
11	2.12	3305.6
12	2.06	3143.6
13	2.08	3186.5
14	2.00	2967.3
15	1.96	2854.1
16	1.88	2643.1

Conclusion

Natural rubber hybrid composites with different mass ratios of MW and RHS were successfully prepared. The important results were as follows. The torques of the hybrid filler composites increase with increasing mass ratios of rice husk derived silica, whereas cure time and the scorch time decreases with increasing mass ratio in their particular hybrid NR composites. Particular inquisitiveness is that such composites enhance main properties like tensile strength, tear strength, % elongation at break, modulus, and hardness. This shows that MW may be used as a co-filler with rice husk derived silica to achieve better bonding of MW and RHS hybrid filler within the natural rubber matrix resulting in better mechanical properties. The mechanical properties of MW and RHS hybrid NR composites containing Si-69 coupling agent were higher than those without silane Si-69. All results from this study showed that the RHS-natural rubber interaction was better with the addition of Si-69 into the NR hybrid composites. It can be concluded that the interaction between RHS and NR matrix can be enhanced with the incorporation of silane coupling agent into the hybrid composites. It has been noted that the products from MW and RHS hybrid composites have comparable cure characteristics, mechanical and swelling behaviour to MW filled NR composites. This allows the use of a marble waste and rice production waste in the rubber industry, reducing the environmental pollution caused by the accumulation of solid waste. This investigation suggests that the recently expanded use of industrial and agricultural waste for NR hybrid composites is a feasible cost effective, industrial imminent and smart substitute of general purpose fillers.

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