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Reinforcement of natural rubber hybrid composites based on marble sludge/Silica and marble sludge/rice husk derived silica



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ABSTRACT

A research has been carried out to develop natural rubber (NR) hybrid composites reinforced with marble sludge (MS)/Silica and MS/rice husk derived silica (RHS). The primary aim of this development is to scrutinize the cure characteristics, mechanical and swelling properties of such hybrid composite. The use of both industrial and agricultural waste such as marble sludge and rice husk derived silica has the primary advantage of being eco-friendly, low cost and easily available as compared to other expensive fillers. The results from this study showed that the performance of NR hybrid composites with MS/Silica and MS/RHS as fillers is extremely better in mechanical and swelling properties as compared with the case where MS used as single filler. The study suggests that the use of recently developed silica and marble sludge as industrial and agricultural waste is accomplished to provide a probable cost effective, industrially prospective, and attractive replacement to the in general purpose used fillers like china clay, calcium carbonate, and talc.

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Introduction

Significant economic and environmental situations of the existing days promote companies and researchers to develop and improve technologies planned to reduce or decrease industrial

wastes. As a result, many attempts have been expended in different areas, including the industrial and agricultural production.

In developing countries, large amount of industrial and agricultural wastes or by-products build up each year. The recycling of these materials is of rising attention worldwide due to high environmental impact. Huge quantity of waste like marble sludge produces every day in marble processing industries in Pakistan. The marble sludge is generated as a by-product during the cutting/polishing process of marble blocks and is trashed away in the drainage system.

The rice husk is the largest waste ensuing from the agricultural processing of grains. This desecrate material is one of the problem facing rice-producing countries, which so far has no

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ultimate resolution. It is probable that the concern of the rice husk silica is about 20% by weight of the burned pelt [1–3]. It is the most important agricultural dregs and well recognized that the rice husk is a significant source of silica [2,4,5]. To reduce the quantity of these squander materials, it can be burned in the open air, which creates noteworthy environmental effluence. As a result, the use of such ash (silica) has motivated the growth of research into the value added potentialities of rice husk derived silica.

Therefore employment of marble sludge (MS) and rice husk derived silica (RHS) in the fabrication of new materials will help to protect the environment. Both waste materials are very low cost and cheap. Polymer composite could be the optimum application to use both these industrial waste to replace the conventional filler such as Carbon Black, Silica, clay and other non black materials.

Natural rubber (NR) is one of the main elastomers and widely used to prepare many rubber compounding products. NR is frequently reinforced by assimilation of filler to improve its mechanical properties like: tensile strength, modulus, tear strength, elongation at break, hardness, compression set, rebound resilience, and abrasion resistance [6,7]. For this purpose carbon black and silica are commonly used [8–11]. Calcium carbonate is also used as filler for rubber [12,13]. Effectiveness of the reinforcing filler depends on numerous factors such as particle size, surface area and shape of filler.

Now a days, there has been a growing interest in the use of industrial and agriculture waste such as products like rice husk [14–16] as fillers for rubber and their blends. The benefits of these fillers include low cost, easy availability and protection to our environment.

Information on the application of marble sludge as filler in polymers were relatively limited [17–21]. Probably, the earliest work on marble waste using up as filler in natural rubber and styrene butadiene rubber was that of Agrawal et al. [22,23] studies. They found that the marble waste with, or without chemical treatment, could be used as a cheap filler, in place of other commercial fillers like whiting in natural rubber and synthetic rubber. It is also incorporated as partial replacement of carbon black up to 10 phr.

So far, Ismail et al. observed that the incorporation of rice husk ash with additives/silane coupling agent in rubber or rubber/plastic composites enhanced the mechanical/physical properties, filler dispersion and crosslink density [24–27]. Mehta and Haxo [28] also described the use of rice husk ash as a reinforcing agent for synthetic and natural rubbers. In this work it has been observed that RHA does not negatively affect either the vulcanization characteristics or the aging of NR, SBR, NBR, CR, BR and EPDM. In addition, it was concluded that RHA filler is a satisfactory substitute for carbon black and that, in these blends, it can be effectively used as a partial replacement for finer and more reinforcing blacks. Assessment of the fatigue behavior of epoxidized natural rubber (ENR) vulcanisates [29] and the effect of partial substitute of silica by RHA in natural rubber composites was anticipated.

Though a lot of work has been done on filled NR composites the effect of partial replacement of MS by silica or RHS as hybrid NR composites on the cure characteristics, mechanical and swelling properties has not received any attention. Therefore, remarkable research and development effort are being performed to explore the opportunity to possibly use it as partially or fully replacing filler with the objective of reducing

costs with desired properties in the rubber industry. Therefore, intention of this exploration is to develop NR hybrid composite by using both industrial waste materials. The studies were involved Cure characteristics, mechanical and swelling properties of MS/Silica and MS/RHS hybrid NR composites. Mechanical properties such as tensile strength, 300% modulus, tear strength, % elongation at break and hardness were analyzed and discussed. Swelling tests were conducted by measuring the swelling coefficient, volume fraction of rubber and the crosslink density of the rubber hybrid composite materials. The effect of aging behavior of corresponding hybrid composite was also evaluated at two different aging temperatures.

Experimental

Materials

Marble sludge was collected locally mostly from the local marble cutting/processing industry. The MS was dried in vacuum oven at 80 °C for 24 h and then ground in finer form. The grounded MS was passed through sieve to obtain 10 µm with a density of 2.67 g/cm³. Natural rubber: Ribbed smoked sheet, having Mooney viscosity (ML₁₊₄ at 100 °C) of 80 and MW of 120,000 with a density of 0.9125 g/cm³, origin from Thailand was procured from the Rainbow rubber industry Karachi. Precipitated silica was from Rain bow rubber industry Rice Husk derived Silica (RHS) obtained from rice husk. All other ingredients used were of commercial grade and obtained from local markets.

Preparation of silica from rice husk

Rice husk was washed with water to remove any foreign material. Hydrochloric acid solution of 0.4 M was prepared then 100 g cleaned husk was mixed in 1 l of prepared acid solution and boiled at 100–105 °C for 30–45 min. After the reaction, the acid was completely removed from the husk by washing with tap water. It was then dried in an oven at 110 °C for 3–5 h in oven. The treated husk burned in an electric furnace at 600 °C for 6 h; silica was obtained as white ash. The shape of the silica is similar 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 sieve to obtain 38 µm sizes.

Characterization of marble sludge powder by Instrumental techniques

Marble sludge waste (waste product from marble cutting industry) was collected from local situated marble cutting industry The Marble Sludge Waste dried in an oven at 80 °C for 24 h to expel all water and then grounded in the fine micronize form and passed through the desire sieve to get 38 µm.

The characterization of marble sludge powder was carried out with a number of experimental techniques in order to confirm the composition of the sludge.

The XRF spectrometer result of marble sludge and rice husk derived silica were obtained on a S4 PIONEER with the Bruker AXS SPECTRA plus software package to analyze the chemical composition or elements present in the sample.

Thermogravimetric analysis (TGA) of MS was carried out using METTLER TOLEDO TGA/SDTA 851 under air and N₂ atmospheres from ambient temperature to 1000 °C at heating rates (10 °C min⁻¹).

Preparation of hybrid composite

The formulation of the natural rubber (NR) marble sludge (MS) composites is given in Table 1. The rubber was compounded on a laboratory two-roll mill (16 × 33 cm). 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) then the compounding ingredients were added in the following order: activators with balance, accelerators, and then sulfur. After mixing, the rubber compound was passed through the tight nip gap for two minutes and finally sheeted out.

Cure characteristics

The cure characteristics of the mixtures were studied using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM method D 2084. Samples of about 6 g of the respective compounds were tested at a vulcanization temperature of 170 °C for 20 min. The torque was noted at every 30 s. The cure time t_{90} , scorch time t_{S2} , maximum torque and minimum torque, etc., were determined from the rheograph.

Vulcanization process

The compounded rubber stock was then cured in a compression molding machine at 170 °C with applied pressure of 10.00 MPa using the optimum cure time ($t = t_{90}$). After curing, the vulcanized sheet was taken out of the mold and immediately cooled under tap to stop further curing. Rheometer tests at 170 °C showed that 90% crosslinking occurs at the corresponding cure time for each MS/Silica and MS/RHS hybrid NR composites. All samples were cured and stored in a cool dark place for 24 h.

Mechanical properties

The properties of MS/Silica and MS/RHS hybrid NR composite materials were measured with several techniques based on ASTM. The tensile strength and 300% modulus, tear strength

and % elongation at break were measured by Tensile tester (Instron 4301), according to ASTM-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 500 mm/min at room temperature. The hardness of the sample (Shore A) was determined using Shore Hardness tester, according to ASTM D 2240.

Swelling property

The chemical crosslinking density of MS/Silica and MS/RHS hybrid NR composite materials, were determined by the equilibrium swelling method. A sample 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; 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 [30]:

$$\alpha = \frac{W_S}{W_1} \times \rho_S^{-1} \quad (1)$$

Respectively, W_1 is the weight of the test piece before swelling and W_S 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 [31,32] according to the relation

$$v = \frac{-\ln(1 - V_r) + V_r + \chi V_r^2}{\rho_o V_s \times V_r^{1/3} - V_r/2} = \frac{1}{M_C} \quad (2)$$

where V_r 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, v is crosslink density of the rubber (mol cm⁻³) and M_C is the average molecular weight of the polymer between crosslinks (g mol⁻¹).

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

$$V_r = \frac{W_{rf}/\rho_1}{W_{rf}/\rho_1 + W_{sf}/\rho_o} \quad (3)$$

where W_{sf} is the weight fraction of solvent, ρ_o is the density of the solvent, 0.867 g/cm³ for toluene, W_{rf} is the weight fraction of the polymer in the swollen specimen and ρ_1 is the density of the polymer which is 0.9125 g/cm³ for NR.

Thermal aging

The thermal aging characteristics of the MS/Silica and MS/RHS hybrid NR composite were studied at 70 °C and 100 °C for 96 h as per ASTM D 573. The properties of accelerated aging were measured after 24 h of aging test. Tensile strength, 300% modulus, tear strength, % elongation at break and hardness of the MS/Silica and MS/RHS hybrid NR composite materials after aging to estimate aging resistance. Percentage of retention in properties of the specimen is calculated as below

Table 1 Compound recipe of MS/Silica and MS/RHS hybrid filler NR composites.

Ingredient	Part per hundred
NR	100
ZnO	05
Stearic acid	02
TMTD ^b	2.4
Antioxidant ^c	1.5
Sulfur	1.6
MS ^a /Silica and MS/RHS*	00/00, 60/00, 50/10, 40/20,
Hybrid filler loading	30/30, 20/40, 10/50, 00/60

^a Microsize of MS and RHS particle, 38 μm.

^b Tetra methylthiuram disulfide.

^c 3-Dimethylbutyl-N-phenyl-p-phenylenediami.

$$\% \text{ Retention} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100 \quad (4)$$

Results and discussion

Characterization of marble sludge

The chemical composition of MS marble sludge and rice husk derived silica was determined using X-ray fluorescence spectrometer (model S4 pioneer Bruker AXS, Germany) as shown in Table 2. Chemically MS composed of calcium and magnesium compound in large amount. Silica, aluminum oxide and iron oxide were 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 those obtained from X-ray fluorescence spectrometer study. XRF done for RHS shows that maximum amount of silica is present with traces of other elements.

Fig. 1 shows the thermo gravimetric curve discloses one distinctive weight loss stage for MS sample. Weight loss of 42.56% has been observed due to the evolution of carbon dioxide which signifies the presence of metal carbonates. The chemical analysis, XRF and TGA, show that marble sludge powder is mainly composed of calcium and magnesium carbonates in major quantity while alumina, silica, iron compounds and other elements in minor quantities.

Curing characteristics

This exploration reveals the a mixture of fillers affect the cure characteristics, mechanical and swelling properties of partial or full replace for MS by silica and rice husk ash filled hybrid natural rubber composites. It was also evaluated how these properties change when silica and rice husk derived silica was gradually added to replace the MS in NR hybrid composites.

The effect of the mass ratio of MS/Silica and MS/RHS hybrid NR composites on the scorch time (t_{S2}) and cure time (t_{90}) are summarized in Table 3 at 170 °C curing temperature. The result shows that the scorch time and cure time of the composites decrease with increasing silica and the RHS loading in hybrid filler arrangement. This might be due to the matrix

Table 2 Quantitative analysis of marble sludge and rice husk silica using WDX-ray fluorescence Spectrometer Model: S4 Pioneer from Braker – axs Germany.

Component	Weight %	
	MS	RHS
LOI at 750 °C	2.56	3.38
CaO	68.6	0.62
MgO	22.13	0.45
SiO ₂	3.89	93.58
Al ₂ O ₃	2.785	0.86
Fe ₂ O ₃	0.603	0.24
Cr ₂ O ₃	0.24	–
ZnO	0.20	–
TiO	0.549	–
Na ₂ O ₃	–	0.18
K ₂ O	–	1.78

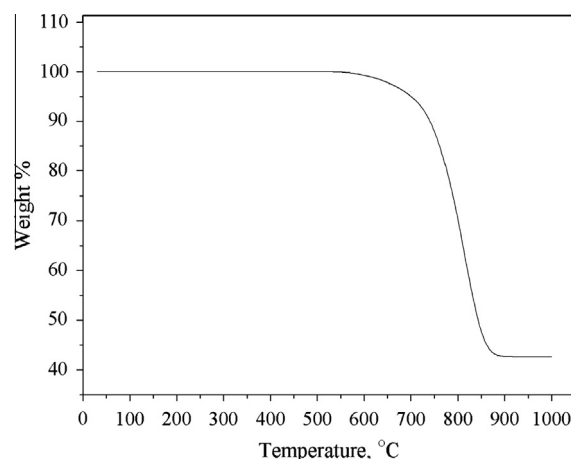


Fig. 1 Thermo gravimetric (TGA) curve of marble sludge powder.

viscosity which is constantly increasing on addition of Silica and RHS [33,34]. This interactive filler dispersion helps in effective vulcanization and results in decreasing scorch time and cure time. The same is observed for Cure Rate Index from 60/00 to 00/60 loading of MS/Silica and MS/RHS hybrid NR composites.

Table 3 also shows the minimum and maximum torque of MS/Silica and MS/RHS hybrid NR composites where minimum and maximum torque is the measurement of stiffness or shear modulus of the entirely cured samples at their vulcanize (170 °C) temperature [35]. The increase in the loading of silica and RHS in hybrid system results in the growth of the crosslinked chains which is accountable for the stiffness of composites. The maximum torque of the both hybrid composites from 50/10 to 10/50 loading of MS/Silica and MS/RHS increases from 10.65% to 29.9% for MS/Silica and from 11.17% to 43.6% for MS/RHS hybrid system compared to that of the 60 phr of MS filled NR composite. The presence of the mixture of strong fillers in the rubber matrix decreases the mobility of chains of rubber and ultimately results in the higher values of maximum torque [36].

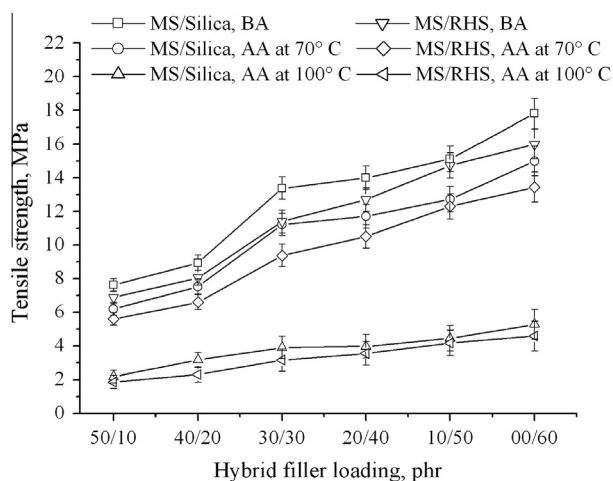
Mechanical properties

This study investigated how the filler ratios affect the mechanical properties of natural rubber composites. The mechanical properties of composites involve tensile strength, 300% modulus, tear strength, % elongation of break and hardness.

The plot of tensile strength of various hybrid composite is presented in Fig. 2. The tensile strength was determined at the break point of the specimen. Fig. 2 clearly shows the addition of silica and RHS in their particular hybrid system, results in the improvement in the tensile properties. The tensile properties of unfilled NR and single filler MS (60 phr) filled NR composites in Table 4 are compared with those of the compounds using silica and RHS as hybrid fillers. As the tensile strength increases from 15% to 133% for 50/10 to 10/50 loading of MS/Silica hybrid NR composites and 5.5–126% in the strength for 50/10 to 10/50 loadings of MS/RHS hybrid NR composites as compared to unfilled NR compound. However, the increase in the values of MS/RHS hybrid composites is less than that of MS/Silica hybrid composites.

Table 3 Data for the scorch time, cure time, minimum torque, maximum torque and cure rate index from cure characteristics of MS/Silica and MS/RHS hybrid filler NR composites.

Hybrid filler ratio	Filler system	Cure characteristics at 170 °C for 20 min				
		Scorch time t_{S2} (min)	Cure time t_{90} (min)	Min. torque (dNm)	Max. torque (dNm)	CRI (min^{-1})
00/00	Unfilled	0.86	1.59	0.43	2.81	1.37
60/00	MS-60	0.83	1.53	0.52	3.85	1.43
50/10	MS/Silica	0.82	1.48	0.56	4.26	1.51
	MS/RHS	0.80	1.45	0.57	4.28	1.54
40/20	MS/Silica	0.80	1.44	0.58	4.38	1.56
	MS/RHS	0.79	1.41	0.59	4.41	1.61
30/30	MS/Silica	0.76	1.41	0.67	4.59	1.54
	MS/RHS	0.72	1.36	0.70	4.63	1.56
20/40	MS/Silica	0.73	1.38	0.79	4.82	1.54
	MS/RHS	0.67	1.32	0.82	4.85	1.54
10/50	MS/Silica	0.70	1.26	0.93	5.00	1.78
	MS/RHS	0.63	1.21	0.98	5.07	1.72
00/60	MS/Silica	0.66	1.21	1.18	5.43	1.82
	MS/RHS	0.59	1.16	1.20	5.53	1.75

**Fig. 2** Relationship between hybrid filler loading and tensile strength of filled NR composites.

In the MS/RHS hybrid case, the reduction in strength may be caused by agglomeration of RHS particles, which increases at high filler loadings. The large RHS particles possibly interrupt matrix continuity, thereby decreasing the effective load-bearing cross-section area.

However, for maximum reinforcement, the filler particles must be of the same size or smaller than the chain end-to-end distance. The degree of filler reinforcement increases with decrease in particle size or increase in the surface area. In filled

elastomers, the fillers act as stress concentrators. Smaller the particle size of fillers, more efficient will be the stress transfer from the rubber matrix to the fillers [37].

It can be seen that the parallel tensile strength tendencies are observed in samples after aging. The result shows that tensile strength decreased at every loading of MS/Silica and MS/RHS hybrid filler arrangement. Thermal aging of composite caused the tensile strength to depreciate, particularly at 96 h with 100 °C temperatures of aging [38]. Though, aging at 70 °C for 96 h shows higher retention of tensile strength as compared to that of 100 °C for 96 h. This could be appropriate to the better thermal constancy at lower temperature.

The unfilled and MS, 60 phr filled NR compound properties like tensile strength, 300% modulus before and after aging is also shown in table 5. The effect of loading of MS/Silica and MS/RHS hybrid NR composites on modulus is summarized in Fig. 3. It can be seen that the modulus increases with the increase in silica and RHS content in the composites. Usually, the modulus is related to the stiffness of the rubber. Although the increase in silica and the RHS mass ratio of MS/Silica and MS/RHS hybrid enhances the stiffness, which may be cause to increase the modulus of the concerned composites [39]. RHS exists as crystalline in nature with the irregular shape of particles, while silica is amorphous with spherical shaped agglomerates. Having non-spherical shape [40–42], RHS particles always exceeds one. On the other hand, silica is in spherical shape and is close to one. In other words, RHS has bigger particle size than that of silica.

At a similar loading of MS/Silica and MS/RHS hybrid filler content, it is clearly observed that the modulus of MS/Silica

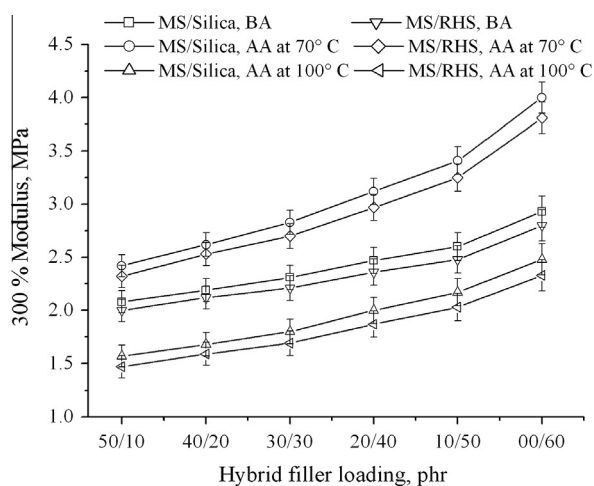
Table 4 Properties of unfilled and filled with MS, 60 phr NR composite before and after aging.

Properties	Unfilled	MS, 60 phr
Tensile strength (MPa)	3.13, {2.32} ^a , [0.79] ^a	6.50, {5.44}, [1.74]
300% modulus (MPa)	0.95, {1.24}, [0.53]	1.78, {2.25}, [1.34]
Tear strength (kg/cm)	8.39, {5.78}, [5.42]	16.80, {12.60}, [10.20]
% elongation at break	1012, {683}, [465]	885, {584}, [373]

^a Values in parentheses are at {70 °C} and [100 °C] aging.

Table 5 Correlation between hybrid filler loading and hardness of filled NR composites before and after aging.

Hybrid filler loading	Filler system	Hardness, Shore-A		
		Value before aging	Aging at 70 °C for 96 h	Aging at 100 °C for 96 h
00/00	Unfilled	38.0	42.0	43.0
60/00	MS-60	51.2	54.0	57.0
50/10	MS/Silica	50.0	56.0	56.4
	MS/RHS	49.0	54.3	52.0
40/20	MS/Silica	53.0	58.6	56.5
	MS/RHS	51.6	57.3	55.0
30/30	MS/Silica	56.0	62.4	60.3
	MS/RHS	54.0	60.0	58.0
20/40	MS/Silica	62.0	69.0	69.3
	MS/RHS	60.0	67.0	66.0
10/50	MS/Silica	65.0	73.0	72.2
	MS/RHS	64.0	72.0	71.0
00/60	MS/Silica	70.0	83.5	78.3
	MS/RHS	68.0	84.0	76.0

**Fig. 3** Relationship between hybrid filler loading and 300% modulus of filled NR composites.

hybrid NR composites is considerably higher than that of MS/RHS hybrid NR composites.

The higher retention in 300% modulus (more than 100%) for both hybrid composites have been shown at 70 °C for 96 h after thermal aging which might be due to the post crosslinking of the composites. Though at 100 °C for 96 h, the lowest retention in 300% modulus (less than 100%) is observed.

Ahagon et al. [43] and Baldwin et al. [44] in their investigation of accelerated aging of rubber compound have also observed that the modulus boosts and then drops, depending on aging mechanism. At 90–110 °C the pace of modulus increase, decreases with increasing aging temperature as expected, but at 70–90 °C the rate of modulus increase increases with decrease in aging temperature. The effect of aging temperature on modulus is due to the complexity of reactions taking place in curing rubber compound. This modification results in polymer chain scission due to which decline in molecular weight observed and molecules entangled with a high crosslink density.

Clarke et al. [45] applied a fractional rate law to assess the kinetics of aging in terms of its effect on the modulus of natural rubber compound, also show that both crosslinking and scission reaction increases with increase in aging temperature in rate of reaction. The scission reaction has a higher activation energy than crosslink reaction. Therefore with a decrease in aging temperature, the rate of scission at 70–80 °C aging temperature is lower. The rate of crosslink actually increases as temperature decrease. The rate of crosslink at 70 °C is dominated hence the increase in modulus would be fast at lower aging temperature.

Tear strength values of MS/Silica and MS/RHS hybrid NR composites before and after aging are given in Fig. 4. The tear strength also follows the same pattern as that of tensile strength. It is seen that as the content of both filler increases in place of MS the tear strength increases which owes to good filler–rubber interaction.

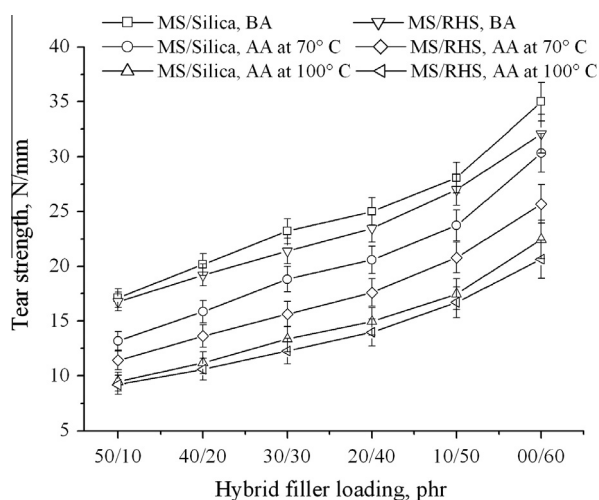
The results of % elongation at break before and after aging are shown in Fig. 5. It can be seen that % elongation at break decreases with increasing the loading of silica and RHS hybrid filler content. Since silica has smaller particle size than RHS, it is expected that the interfacial adhesion between silica and NR matrix is better than RHS. This might be as NR matrix allows more rheological flow due to excellent filler rubber interaction. As the loading of silica and RHS increases the composite cannot resist crack propagation efficiently and as a result promulgate a calamitous crack which minimizes the elongation at break.

After aging, same trend was observed for the tear strength and % elongation at break. The retained values of tear strength and % elongation at break decreased mildly at 70 °C, but at the 100 °C aging temperature other samples showed a rapid decrease in their retained tear and % elongation. This oblique that the sample with the best crosslinked structure had the greatest aging resistance.

Average hardness of these composites with different loading of silica and the RHS in hybrid NR composites, before and after aging is revealed in table. Obviously for all of the hybrid composites, the hardness increased continuously with increasing loading of silica and the RHS of their particular hybrid composites. This is comprehensible as silica and RHS are rigid as compared to MS, and thus, increasing the mass ratio

Table 6 Data for the swelling coefficient (α) and crosslink density (ν) of MS/Silica and MS/RHS hybrid filler NR composites before and after aging from swelling measurements.

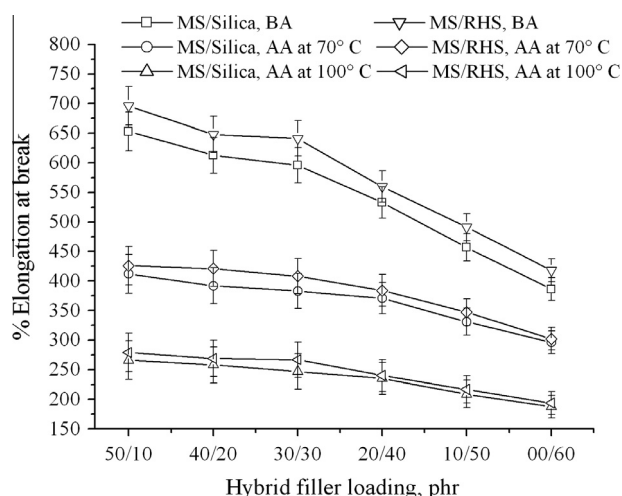
Hybrid filler loading	Filler system	Swelling coefficient ($\text{g}^{-1} \text{cm}^3$)			Crosslink density $\times 10^4$ (mole/cm^3)		
		Value before aging	Aging at 70 °C for 96 h	Aging at 100 °C for 96 h	Value before aging	Aging at 70 °C for 96 h	Aging at 100 °C for 96 h
00/00	Unfilled	4.26	6.63	6.16	1.636	0.740	0.837
60/00	MS-60	3.58	3.86	4.37	1.437	1.266	1.021
50/10	MS/Silica	3.46	3.55	3.68	1.546	1.478	1.367
	MS/RHS	3.59	3.64	3.78	1.510	1.450	1.378
40/20	MS/Silica	3.38	3.48	3.61	1.674	1.576	1.466
	MS/RHS	3.42	3.50	3.59	1.626	1.553	1.493
30/30	MS/Silica	3.00	3.09	3.23	2.109	2.001	1.854
	MS/RHS	3.15	3.27	3.41	1.843	1.768	1.638
20/40	MS/Silica	2.79	2.89	3.08	2.436	2.292	2.055
	MS/RHS	2.89	2.98	3.16	2.462	2.108	1.899
10/50	MS/Silica	2.64	2.74	2.89	2.741	2.554	2.322
	MS/RHS	2.73	2.81	3.11	2.480	2.362	1.958
00/60	MS/Silica	2.40	2.50	2.65	3.302	3.073	2.767
	MS/RHS	2.45	2.55	3.08	3.025	2.835	2.384

**Fig. 4** Relationship between hybrid filler loading and tear strength of filled NR composites.

of silica and RHS gave rise to the reduction of the deformable rubber portion in the compound this is widely known as the dilution effect [46,47]. Furthermore, the maximum hardness was found when loading of silica and RHS reached to 10/50. Results of after aging shows that all hardness values were greater than before aging due to the post curing effect, which was as per our expectations.

Swelling properties

The swelling coefficient versus mass ratio of the MS/Silica and MS/RHS hybrid NR composites in toluene are given in Table 6. It can be seen that the swelling coefficient of the proposed both hybrid NR composite specimens decreases with increasing silica and RHS in place of MS at room temperature. This observation might be attributed to the better dispersion of silica and RHS in rubber matrix. It is observed for MS/Silica filled NR hybrid composite that the swelling coefficient decreases with the increasing loading of silica.

**Fig. 5** Relationship between hybrid filler loading and % elongation at break of filled NR composites.

If an enhanced bonding between the filler and the rubber matrix existed, a stronger crosslink system would be formed. The extent of crosslink in filled composites can be reflected from the crosslink density. The diffusion of solvent in the vulcanizate was fundamentally related with the aptitude of vulcanizate to give the alley ways for the solvent to escalate in the voids [48].

Table 6 also shows the crosslink density of various composites before and after aging. MS/Silica and MS/RHS hybrid system and rubber matrix would lead to a strong crosslinked network creating restriction to the absorbance of the solvent. Consequently crosslink density is a significant parameter which helps in characterizing the reinforcing extent of filler on rubber. Both composites with high silica and RHS loadings would form a larger interfacial area between particular filler and rubber, which added a great value to filler rubber interaction. As a result, the absorbance of solvent was highly restricted in the silica and RHS filled NR composites [49].

It is also noteworthy that after aging toluene uptake increases. The increase in desired solvent uptake is due to the increase in the formation of a three dimensional network structure. The swelling results suggest and verify this conclusion, that during or after aging exposure in hot air causes polymer decrosslinking that affect the crosslink density.

Conclusions

The NR composites with MS/Silica and MS/RHS hybrid filler system were successfully prepared and introduced as a value added product to the industrial community. The examinations of cure characteristics, mechanical and swelling properties of these composites indicate that the addition of silica and RHS facilitates the vulcanization process of MS/NR composites that results in the decrease in scorch time, cure time and increases torque in the curing experiment. Furthermore, the use of the hybrid desired system at a preferable loading allows the formation of hybrid composites with maximum mechanical and proper swelling properties compared with the case where MS with only single filler was used. The addition of silica and RHS in their corresponding hybrid NR composites improves significantly the tensile strength, modulus, tear strength hardness, and crosslink density of the composites. However, MS/Silica hybrid system has the better performance as compared to MS/RHS hybrid NR composites but still we prefer the product which consumes the waste material.

Conflict of interest

The authors have declared no conflict of interest.

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