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ORIGINAL ARTICLE

The effect of silica on the properties of marble sludge filled hybrid natural rubber composites

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Abstract Hybridization of natural rubber (NR) filled marble sludge (MS) and silica composite was prepared by adding various weight ratios of MS and silica. Compounding was carried out on a two-roll mill with total filler loading of 60 parts per 100 rubbers (phr). The composites were vulcanized at 140 °C. The effects of partial or complete replacement of MS with silica on physical characterization such as curing characteristics, mechanical and swelling parameters of composites were examined. Mechanical properties of composites, including tensile strength, elongation, modulus, tear strength, hardness, swelling parameters such as swelling ratio, volume fraction, crosslink density and shear modulus before and after aging, were analyzed. Results indicate that minimum torque, maximum torque, tensile strength, modulus, tear strength, hardness, and crosslink density volume fraction increased while elongation at break, swelling ratio and shear modulus decreased with the increasing silica loading in MS/NR/Silica hybrid composites. The aging test of corresponding hybrid composites was also evaluated at two different aging temperatures. The results in this work recommend that MS from marble processing industrial waste could be used as filler for cost savings in NR compounds.

1. Introduction

Within the last decade, the effects of different types of fillers of Natural Rubber compounds have been evaluated. This is done for the improvement in overall physical and mechanical properties. Among these fillers carbon black (Salaeh and Nakason, 2012; Ismail et al., 1995), silica (Ismail and Freakley, 1996; Luginsland et al., 2002), calcium carbonate, clays (Ghari and Shakouri, 2012), titanium oxide (Ochigbo and Luyt, 2011) and magnesium hydroxide (Zhang et al., 2004) etc., are mostly used in rubber compounds. The addition of fillers to rubber compounds has a strong impact on the static and dynamic behavior of rubber (Morton, 1995). Fillers have an important direct action on the physical properties of rubber compounds. It is well known that in the filled rubber compounds, the efficiency of reinforcement depends on a complex interaction of

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filler related parameters, such as filler structure, size, shape, dispersion, surface area, surface reactivity, and bonding quality between fillers and rubber matrix (Frohlich et al., 2005).

Seo et al. (2008) conducted a study on non black fillers like silica that shows the enhancement in reinforcing properties. The performance of silica proves the capability as reinforcing material for the manufacturing of highly stable rubber products such as tire. The significant enhancement of tensile strength was achieved due to the physical entanglements of rubber molecules with the networks formed by silica particles. The dispersion of the networked silica in a rubber molecule is expected to be good because its surface is covered with organic materials. The openings formed in the networked silica additionally contribute to improve its dispersion by penetration of rubber molecules into it. They also investigated the advantages of networked silica in compounds as follows: (i) high performance as a reinforcing filler to enhance tensile strength; (ii) the high dispersion of silica in rubber compounds; and (iii) no emission of alcohol during rubber processing. Both carbon black and silica fillers are quite expensive commercially. There is a need, therefore to develop cheaper fillers from other natural resources. Recently, the application of fillers those obtained from industrial or agriculture wastes has attracted interest due to their low cost, and environment friendly nature. These include agricultural waste such as agricultural byproduct (Imanah and Okieimum, 2003), ground wood floor waste (Ichazo et al., 2006), bamboo (Ismail et al., 2002), white rice husk (Alan et al., 2011), etc., used as fillers for rubber and industrial wastes such as marble sludge from marble cutting industries and fly ash from power plants. Marble sludge is produced in the marble processing industry in Karachi city Pakistan during the cutting/polishing process of marble blocks. Attempts have been made using marble sludge waste for various purposes such as in cement and construction industries (Binici et al., 2007) ceramic tiles (Montero et al., 2009) and asphalt concrete (Karasahin and Terzi, 2007) but rarely it has been used as a filler in natural rubber compounds (Agrawal et al., 2004; Ahmed et al., 2012a,b, 2013c).

Thus, it was the aim of this contribution to assess the potential of the utilization of marble sludge in natural rubber compounds. So, the objective of the present investigation was to develop hybrid composites by partially or completely replacing 10 μm size particles of marble sludge powder by frequently used commercial fillers such as silica and to test the rheological, mechanical, swelling and the aging behavior of NR composites. The mechanical properties include tensile strength, 100% and 300% modulus, elongation at break, tear strength and hardness. Swelling test was conducted by measuring the swelling ratio, crosslink density and shear modulus of MS/NR/Silica hybrid composites.

2. Experimental

2.1. Materials and sample preparation

The materials used for the preparation of the compounds were:

Natural rubber (NR) ribbed smoked sheet (RRS) Sadao P.S. Rubber Co., Ltd. Thailand and precipitated silica (Zeosil-175) by Rhodia were obtained from Rainbow rubber industry. Marble sludge (MS) waste (waste product from marble cutting industry) was collected from local marble cutting industry. The marble sludge waste was dried in oven at 80 °C for 24 h and ground into fine particles and passed through a 10 μm sieve. Zinc oxide was use as an activator, stearic acid, tetra methylthiuram disulfide (TMTD) as an accelerator, bis-(3-triethoxysilylpropyl)-tetrasulfane (Si-69) as coupling agent, 3-dimethylbutyl-N-phenyl-p-phenylenediamine as antioxidant and sulfur as vulcanizing agent. All materials were used as received and purchased from local market.

2.2. Preparation of sample

Rubber was compounded according to the formulation given in Table 1, on a laboratory two-roll mill (16 × 33 cm). Mixing was done according to ASTM D 3182 (2001). The NR was masticated on the mill and the total amount of the filler was incorporated into the rubber (60 parts per 100 of the rubber, phr) with 10 μm size of MS, Silica (Si-69, 2% w/w based on the filler) and a different ratio of MS/Silica. The compounding ingredients were added in the following order: activators, filler, accelerators, and then sulfur. After mixing, the rubber compound was passed through the tight nip gap for 2–4 min and finally sheeted out. The sheeted rubber compound was conditioned at 25 °C for 24 h prior to cure assessment.

2.3. Cure characteristics

The cure characteristics of the mixture were studied using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM method D 2084. Samples of the respective compounds were tested at a vulcanization temperature of 140 °C for 20 min. The torque was noted at every 30 s. The cure time, measured as t_{90}, scorch time as t_{S2}, maximum torque, minimum torque, etc., were determined from the rheograph.

The cure rate index, which is a measure of the rate of cure is calculated according to the equation given below (Dannenberg 1975) (Eq. (1)).

$$\mathrm{CRI} = \frac{1}{t_{90} - t_{S2}} \tag{1}$$

The CRI results given in Table 3, reveal that there was no significant effect on the CRI properties with the increase in silica ratio in MS/NR/Silica hybrid composites. Curing rate (C_R) was calculated according to the following (Eq. (2)).

$$C_R = \frac{M_{90} - M_{S2}}{t_{90} - t_{S2}} \tag{2}$$

where M_{90} is the torque at t_{90} and M_{S2} is the torque at time t_{S2}.

2.4. Vulcanization process

The compounded rubber stock was then cured in a compression molding machine at 140 °C and at an 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. Rheometer tests at 140 °C showed that 90% crosslinking occurs at the corresponding cure time for each MS/NR/Silica hybrid composites. All samples were cured at this temperature for the specific cure time and stored in a cool dark place for 24 h before testing.

Table 1 Compound recipe of marble sludge/silica hybrid natural rubber composites.

Ingredient	Compound recipe							
	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[a]	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Antioxidant[b]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
MS[c]	00	60	50	40	30	20	10	00
Silica	00	00	10	20	30	40	50	60
Si-69	00	1.2	1.2	1.2	1.2	1.2	1.2	1.2

[a] Tetra methylthiuram disulfide.
[b] 3-Dimethylbutyl-N-phenyl-p-phenylenediami.
[c] Micro size of MS particle, 10 μm.

2.5. Mechanical properties

The properties of MS/NR/Silica hybrid composites were measured with several techniques based on ASTM. The tensile strength, elongation at break, modulus, and tear strength were measured by Tensile tester (Instron 4301), according to ASTM-412 and ASTMD-624. Samples were punched out from the molded sheets with a dumbbell-shaped die for tensile strength and angular specimens for tear strength. The cross-head speed was maintained at 500 mm/min at room temperature. The hardness of the sample was determined using the Shore hardness tester, according to ASTM D 2240.

2.6. Swelling property

The chemical crosslink densities of MS/NR/Silica hybrid composites were determined by the equilibrium swelling method according to ASTM D 471. A sample weighing about 0.2–0.25 g was cut from the compression-molded rubber sample. The samples were soaked in pure toluene at room temperature allowed to reach diffusion equilibrium. After 5 days, the test pieces were taken out one by one and the adhered liquid was rapidly removed by blotting with filter or tissue paper, and the weight after swelling was measured immediately. It was then dried under vacuum at 80 °C up to constant weight and the desorbed weight was taken. The swelling ratio of the sample was calculated from the following equation (Unnikrishnan and Thomas, 1994) (Eq. (3)).

$$SR = \frac{W_2 - W_1}{W_1} \tag{3}$$

W_1 is the weight of the test piece before swelling and W_2 is the weight of test piece after swelling. The chemical crosslink densities of the composites were determined by the Flory–Rehner equation by using swelling value measurement (Flory and Rehner, 1943) according to the relation (Eq. (4)).

$$v = \frac{-ln(1 - V_r) + V_r + \chi V_r^2}{\rho_0 V_s \times V_r^{1/3} - V_r/2} = \frac{1}{M_C} \tag{4}$$

where V_r is the volume fraction of rubber in the swollen gel, V_s is the molar volume of toluene (106.2 cm^3 mol^{-1}), χ is the rubber–solvent interaction parameter (0.38 in this study) (Mathai and Thomas, 1996), ρ_0 is the density of the polymer, v is cross-link density of the rubber and M_C is the average molecular weight of the polymer between cross-links and is related to the shear modulus (G) by the following expression (Aigbodion et al., 2000).

$$G = \frac{RT\rho_r}{M_C} \tag{5}$$

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 (Eq. (6)).

$$V_r = \frac{W_{rf}/\rho_1}{W_{rf}/\rho_1 + W_{sf}/\rho_o} \tag{6}$$

where W_{sf} is the weight fraction of solvent, ρ_0 is the density of the solvent, 0.867 g/cm^3 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 was taken as 0.9125 g/cm^3 for NR in this case.

2.7. Thermal aging

The thermal aging of the MS/NR/Silica hybrid composites was done for 96 h at 70 °C and 100 °C as per ASTM D 573. The properties of accelerated aging were measured after 24 h of aging test. Tensile strength, modulus, elongation at break, tear strength, hardness, resilience, abrasion loss and compression set of the MS/NR/Silica hybrid composites after aging were calculated to estimate aging resistance. Percentage of retention in properties of the specimen is calculated as bellow (Eq. (7)).

$$\%\,\text{Retention} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100 \tag{7}$$

3. Results and discussion

3.1. Characterization of marble sludge

Surface area of the silica and marble sludge dry powder was determined by the Brunauer, Emmett and Teller (BET) adsorption technique applying nitrogen isotherm on a Micromeritics

Table 2 Surface area of the marble sludge and silica samples.

Sample #	Item	Surface area, m^2/g
1	Marble sludge dry powder	13
2	Silica	178

Table 3 Quantitative analysis of marble waste using WDX-ray fluorescence spectrometer.

Components	Weight %
CaO	68.6
MgO	22.13
SiO_2	3.89
Al_2O_3	2.785
Fe_2O_3	0.603
Cr_2O_3	0.24
ZnO	0.20
TiO	0.549

Tristar 3000, surface area and porosity analyzer. The following relation was used to find out the surface area: (Eq. (8))

$$S\text{BET} = 4.353 \times Vm \tag{8}$$

where S BET is the surface area in m^2/g and Vm is the molar volume of adsorbate gas (N_2) at STP.

Table 2, gives the BET adsorption results of the commercial silica and marble sludge dry powder. From the table it is clear that silica has a higher surface area than that of marble sludge dry powder. So higher the surface area, lower the particle size.

The chemical composition of MS was determined using WDX-ray fluorescence spectrometer (model S4 pioneer Bruker AXS, Germany) as shown in Table 3. It is evident from the results that chemically MS composed of calcium and magnesium compounds in large amounts. Silica, aluminum oxide and iron oxide are also present in small amounts. The values obtained from the relative metal component of marble sludge of atomic absorption spectroscopic study is in close proximity to those obtained from X-ray florescence spectrometer study.

The above observation shows that the marble powder is basically composed of calcium carbonate, magnesium carbonate with small amounts of silicate, aluminum oxide and iron oxide.

3.2. Cure characteristics

Cure characteristics such as minimum torque, maximum torque, cure time, scorch time, cure rate index and cure rate of MS/NR/Silica hybrid composite at 140 °C are shown in Table 3. The addition of silica in composites resulted in an increase in the minimum torque and maximum torque. Both the torques mainly depend on the extent of crosslinking and reinforcement by filler particles in the polymer matrix (Abdul Kader and Changwoon, 2004). The reduced macromolecular mobility is often due to the reinforcing effect of the filler composition as silica-filled rubber has a higher viscosity than an unfilled or partially filled compound in MS/NR/Silica hybrid composite. It is also clear that the various weight ratios of MS/silica gradually improved the interaction between filler and the NR matrix. Minimum torque is an indirect measure of the viscosity of the compound (Wolff and Wang, 1992). The increase in minimum torque found in these MS/NR/Silica hybrid composites is simply due the physical stiffness of the compound. The value of scorch time and cure time with increasing amounts of silica is also evident from Table 3. Both the scorch time and cure time of MS/NR/Silica hybrid composite decreases with the addition of silica.

The cure properties of the MS/NR/Silica hybrid composition were noticeably better than those of the unfilled NR compound. The reduction in scorch time and cure time might be the results of shear heating, which is more pronounced in the MS/Silica ratio with high silica content filled MS/NR/Silica hybrid and Silica/NR compounds. It was also attributed to the presence of a high number of crosslinks in the hybrid composite.

The cure rate results in Table 4 show that curing rate increases with the addition of silica in hybrid composite. It is observed that for curing temperature 140 °C the initiation period is very short, the vulcanization is very fast and the process ends with reversion. This means that curing at high temperature decreases the mechanical property. The results indicate that silica is more beneficial in terms of cure properties for MS/NR/Silica hybrid composite as compared to MS/NR composite this may be due to the surface area of silica which is greater than MS.

3.3. Mechanical properties

The composite containing 60 phr of silica has the maximum tensile strength as expected. This suggests that this is the opti-

Table 4 Data for the minimum torque, maximum torque, cure time, scorch time, cure rate index and cure rate from cure characteristics of marble sludge/silica hybrid natural rubber composites at 140 °C.

Properties	MS/Silica ratio, phr							
	Unfilled	60/00	50/10	40/20	30/30	20/40	10/50	00/60
Min. torque, dNm	0.25	0.43	0.45	0.47	0.56	0.68	0.82	1.12
Torque at $t_{S2,}$ dNm	0.79	1.04	1.06	1.12	1.19	1.31	1.38	1.52
Torque at $t_{90,}$ dNm	2.13	3.36	3.41	3.60	3.72	3.81	3.96	4.07
Max. torque, dNm	2.63	3.85	3.93	4.06	4.22	4.46	4.76	5.26
Cure time $t_{90,}$ min	4.38	4.86	4.78	4.60	4.53	4.41	4.23	4.15
Scorch time t_{S2}, min	2.47	1.76	1.74	1.69	1.65	1.59	1.56	1.51
CRI, min^{-1}	0.523	0.323	0.329	0.343	0.347	0.354	0.374	0.378
Cure rate, dNm min^{-1}	0.701	0.748	0.773	0.852	0.878	0.886	0.966	0.966

Table 5 Mechanical properties of marble sludge/silica hybrid natural rubber composites before aging.

Hybrid ratio	Mechanical properties					
	Tensile strength, MPa	100% Modulus, MPa	300% Modulus, MPa	Tear strength, N/mm	% Elongation at break	Hardness, Shore-A
00/00	5.08	0.73	1.51	15.96	952	30.00
60/00	11.64	1.48	2.41	24.90	620	47.00
50/10	12.28	1.63	2.83	25.83	583	52.00
40/20	13.98	1.66	2.87	28.00	570	53.00
30/30	17.10	1.80	3.00	29.95	518	59.00
20/40	20.38	1.94	3.25	34.00	440	63.00
10/50	21.75	1.98	3.38	38.25	405	70.00
00/60	23.12	2.04	3.77	42.00	311	74.00

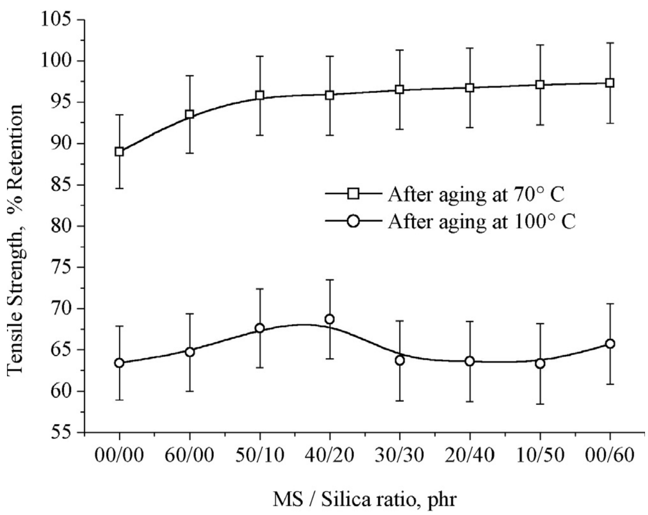

Figure 1 Percentage retention V/S marble sludge/silica loading on tensile strength of hybrid natural rubber composites.

mum tensile strength. Influence of silica content replacing with MS on the tensile strength of the NR composites is shown in Table 5.

It shows the variation of tensile strength with the weight increase of silica in total filler content. The composite containing only silica has the highest tensile strength where as the composite containing only MS exhibits the lowest value. As mentioned earlier, silica has higher aspect ratio in comparison with MS. Thus, by increasing the amount of the silica in the hybrid composites, the tensile strength improves. This suggests that the tensile strength of the NR composite is dependent more on the weight of silica than MS, which could be due to good filler–rubber interaction. Strong rubber–filler interaction would increase the effectiveness of the stress transferred from the rubber matrix to filler particles dispersed in the rubber matrix (El-Nashar et al., 2006). The dependence of the reinforcement of the silica content can be seen in their mechanical behavior, especially in the ultimate tensile values.

Percent retention of tensile strength is shown in Fig. 1. Thermal aging of the MS/NR/Silica composites caused the tensile strength to deteriorate, especially at 100 °C for 96 h (Bhowmick and White, 2002). It was observed that percent retention of tensile strength at 70 °C slightly increased up to some extent with the varying composition of MS/Silica up to 50/10 and remains almost constant at a higher concentration of silica in the Tensile strength of hybrid NR composites. Percentage retention at 100 °C increases till 40/20 composition and then decreases after further replacing the MS by silica at 30/30, 20/40, and 10/50 compositions. There is slight increase in percentage retention in 00/600 composition. This is explained that both aging temperatures show lower retention (below 100%), after thermal aging. However, aging at 70 °C for 96 h of MS/NR/Silica hybrid composites shows a higher retention of tensile strength after thermal aging compared to that of 100 °C for 96 h as illustrated in Fig. 1. This could be due to the better thermal stability at a lower temperature.

The effect of silica on the 100% and 300% modulus of the MS/NR/Silica hybrid composites before and after aging are depicted also in Table 5, and percent retention of 100% and 300% modulus is shown in Figs. 2 and 3, respectively. Before aging, the results show that as the silica weight increased, in

Table 6 Swelling data of marble sludge/silica hybrid natural rubber composites before aging.

Hybrid ratio	Swelling data		
	Swelling ratio	Crosslink density × 10^{-4} mol/cm^3	Shear modulus, MPa
00/00	4.29	1.258	0.285
60/00	2.53	2.090	0.473
50/10	2.35	2.428	0.550
40/20	2.26	2.569	0.582
30/30	2.13	3.025	0.685
20/40	2.07	3.233	0.732
10/50	2.03	3.410	0.772
00/60	1.91	3.856	0.873

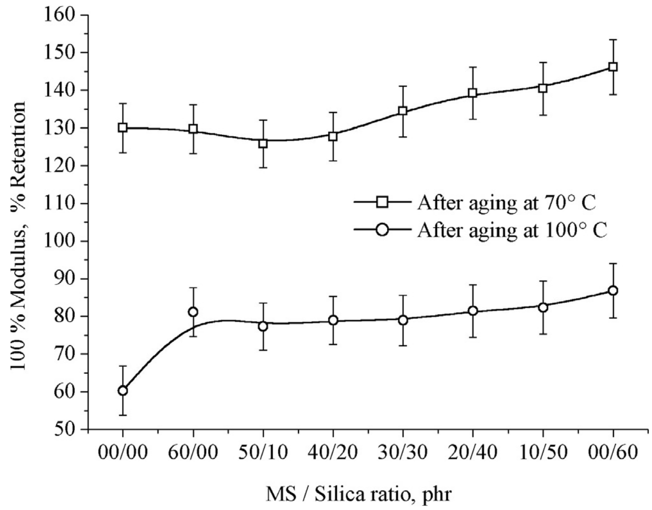

Figure 2 Percentage retention V/S marble sludge/silica loading on 100% modulus of hybrid natural rubber composites.

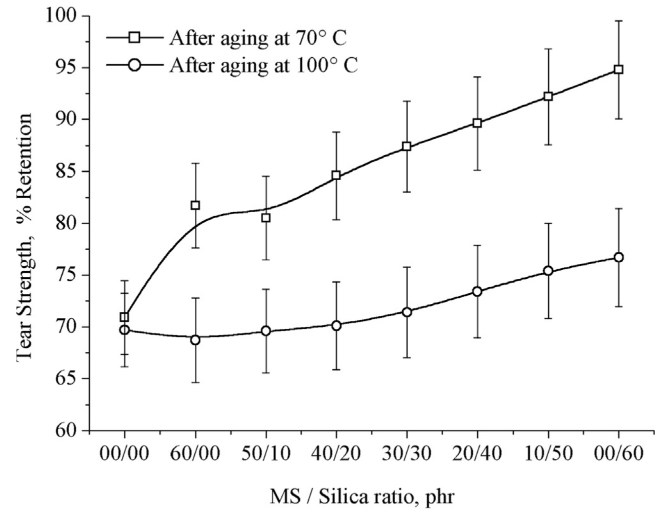

Figure 4 Percentage retention V/S marble sludge/silica loading on tear strength of hybrid natural rubber composites.

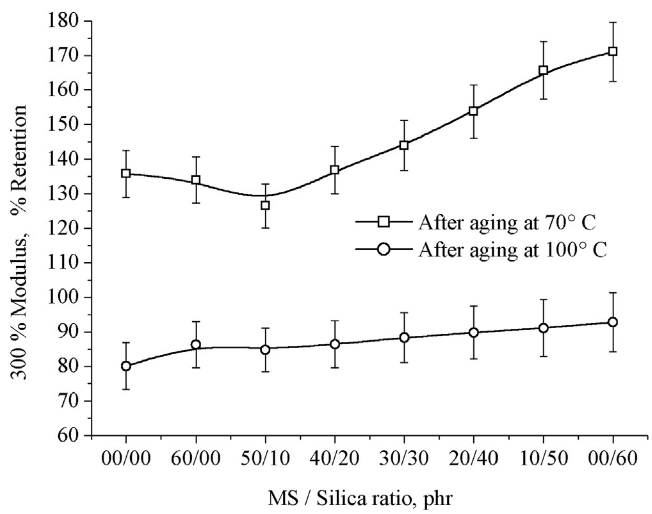

Figure 3 Percentage retention V/S marble sludge/silica loading on 300% modulus of hybrid natural rubber composites.

replacement of MS , the 100% and 300% modulus increased, which indirectly shows that the MS/NR/Silica composites become harder and stiffer. It may be due to the silica–rubber interaction which reduces the elasticity of rubber chain, creating a more rigid compound. The higher retention in both moduli (more than 100%) is shown at 70 °C for 96 h after thermal aging which might be due to the post crosslinking of the rubber composites. However at 100 °C for 96 h shows the lowest retention in individual modulus (less than 100%).

Ahagon et al. (1990) and Baldwin et al. (2005) in their studies of accelerated aging of rubber compound observed the modulus increase and later reduction, depending on aging mechanism. At 90–110 °C the rate of modulus increase, decreases with increasing aging temperature. However at 70–90 °C the rate of modulus increases with a 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 change in property may cause polymer chain scission which results in reducing molecular weight and molecular entangling with a high crosslink density of MS/NR/Silica hybrid composites. This phenomenon is post curing effect which tends to increase aging temperature. Clarke, (Clarke et al., 2006), studied the fractional rate law which was applied to evaluate the kinetics of aging in terms of its effect on the modulus of natural rubber compound. He also shows that both crosslinking and scission reactions increase with increase in aging temperature in rate of reaction. The scission reaction has higher activation energy than crosslink reaction. Hence 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 decreases. The rate of crosslink at 70 °C is dominated and at 100 °C effected by rates of both crosslinking and scission reactions. The percent retention of 100% and 300% moduli somewhat increases with increasing silica weight ratio in MS/Silica hybrid NR composites. This may be due to increasing crosslink density of the vulcanizates with the progress of aging after keeping at 70 °C and 100 °C for 96 h. At 70 °C of aging the extent of main chain scission is less and the effect of cross-linking predominates but at 100 °C the reverse situation happens resulting in lower % retention of 100% and 300% moduli.

The tear strength of MS/NR/Silica hybrid composites before and after aging is given in Table 5. It follows the same trend as that of tensile strength. This suggests that the tear strength of the composite is dependent more on the weight of silica than MS, which is due to good filler–rubber interaction. The result of percent retention of tear strength is represented in Fig. 4. The results showed that silica incorporated in MS/Silica hybrid NR composite has better retention after aging. According to the outcome the highest percentage retention of tear strength after aging is reported at 70 °C, the action of oxygen on natural rubber is activated by heating.

Table 5 shows the influence of silica content on elongation at break before and after aging. It is clear that the values of elongation at break decrease with increasing amounts of silica. This may be because of the adherence of the filler to the polymer, which leads to the stiffening of the polymer chain and hence show resistance against stretching when strain is

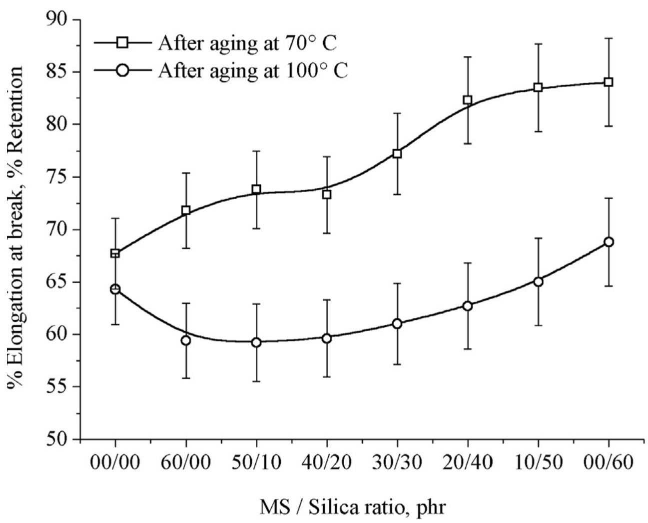

Figure 5 Percentage retention V/S marble sludge/silica loading on % elongation at break of hybrid natural rubber composites.

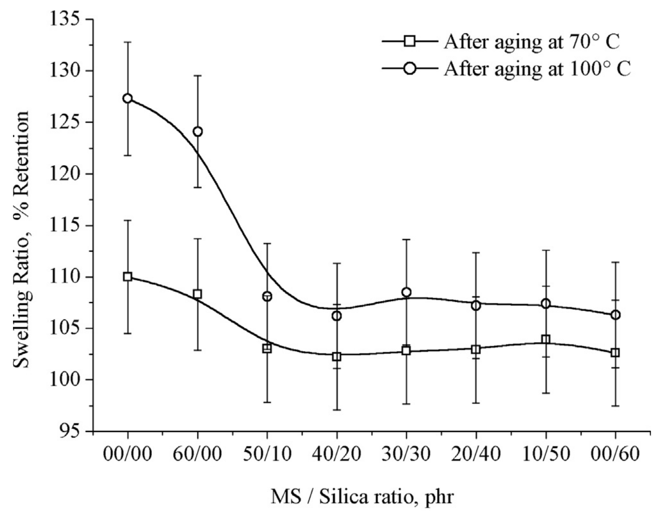

Figure 7 Percentage retention V/S marble sludge/silica loading on swelling ratio of hybrid natural rubber composites.

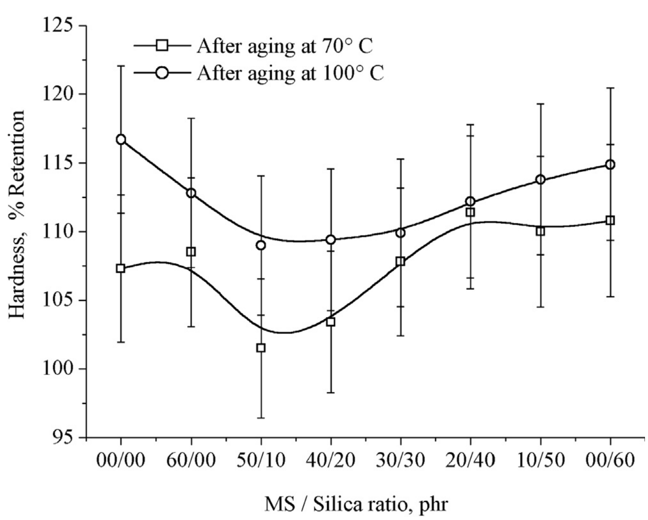

Figure 6 Percentage retention V/S marble sludge/silica loading on hardness of hybrid natural rubber composites.

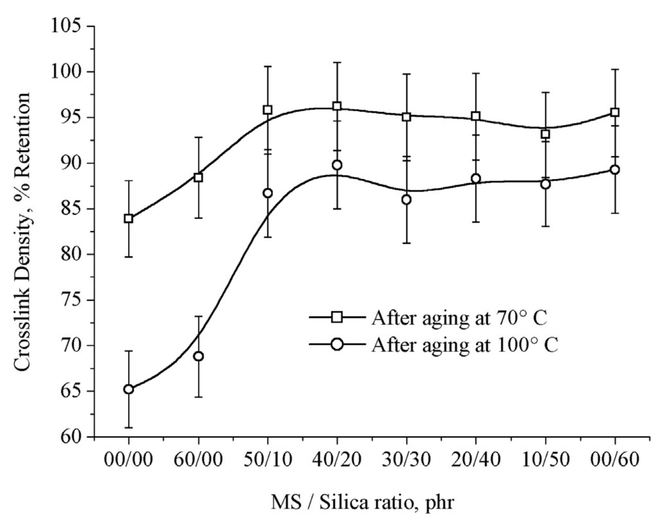

Figure 8 Percentage retention V/S marble sludge/silica loading on crosslink density of hybrid natural rubber composites.

applied. The percent retention of elongation at break for various hybrid systems at different silica weight ratios after aging is demonstrated in Fig. 5. But percent retention of elongation at break values at a higher silica content in MS/Silica hybrid system increases considerably at 70 °C as compared to 100 °C, this is a result of both thermo-oxidative degradation and post vulcanization.

The influence of hardness before and after aging on the replacement of MS by silica is also shown in Table 5. It is seen that the hardness increases with the increasing silica amount. An increase of 157.4% is obtained for the composite with 60 phr of silica. Moreover, hardness reaches to 74 from 47 Shore-A when the amount of silica increased in MS/Silica ratio. When compared, it is observed that hardness obtained from MS filled composite is lower than the corresponding silica containing composites. The percentage retention of hardness is revealed in Fig. 6. The percent retention value of hardness decreases with increasing silica weight ratio and further addition shows a little increase or to be a plateau in hybrid system. With the progress of aging the composites become stiff therefore hardness increases, which was due to the agglomeration of silica particles.

All these mechanical properties indicate that the technique for partial replacement of MS by silica in hybrid composites is ideal for the rubber industry.

3.4. Swelling properties

A swelling test is performed to observe the swelling ratio, volume fraction, crosslink density and shear modulus of the cured rubber. The effect of silica replacement on swelling ratio is shown in Table 6.

The obtained results show a decreasing trend in swelling ratio after replacing MS by silica. It showed that the penetration

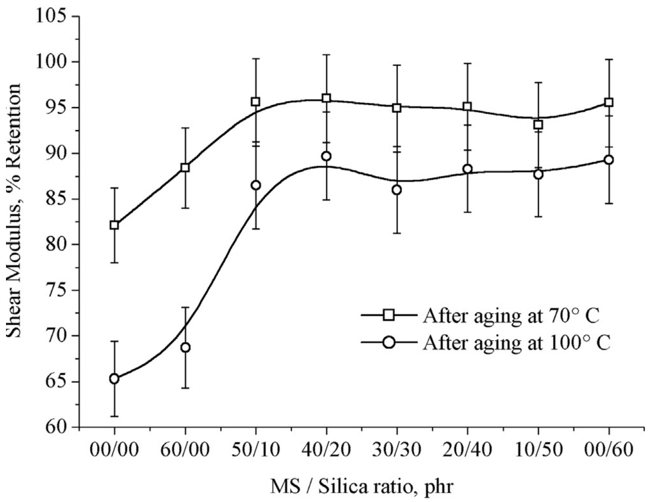

Figure 9 Percentage retention V/S marble sludge/silica loading on shear modulus of hybrid natural rubber composites.

of toluene into MS/NR/Silica hybrid composites was reduced by the increasing silica content. This means that higher amount of silica restricted the penetration of toluene in composites. It can also be seen that there is a lower swelling ratio associated with fully replaced MS by silica in hybrid composites as compared to other gradually silica filled hybrid composites. This is due to the better dispersion of filler in NR, thus promoting better filler–rubber matrix interaction in composites. The changes of percentage retention of swelling ratio of the MS/Silica hybrid NR composite is shown in Fig. 7. The results showed that the addition of silica decreased the parentage retention of swelling ratio with increasing the content of silica. It was due to the presence of good dispersion of filler and the strong interaction between silica and the NR matrix.

After the calculation of crosslink density of MS/NR/Silica hybrid composites, the data obtained are also shown in Table 6. The cross-link density of polymer is the average molecular weight between the cross-links, was determined from swelling. The cross-link density, v, is defined as the number of elastically active network chains totally included in a perfect network, per unit volume. A clear linear increase of the apparent cross-link density with the silica content in the MS/NR/Silica hybrid composite was observed. This shows as the major contributor of strong interaction between the NR and the filler leading to strong physical cross-links.

Fig. 8 shows the percentage retention of crosslink density values for different MS/Silica ratio hybrid NR filled and unfilled composite in toluene. The lower percentage retention value is exhibited by the unfilled NR compound. The percentage retention increases with increasing the amount of silica in hybrid system till 40/20 hybrid ratio and further addition of silica led to a plateau barely increasing percentage retention (Table 6).

When the silica content increases the crosslink density was also increased. It may be due to the increasing amount of silica restricts the molecular movement of the rubber and makes it more difficult for toluene to penetrate through the rubber matrix. The 40/20, 10/50 and full replacing MS by silica containing hybrid composites have better performed as compared to other hybrid composites. The average molecular weight between crosslinks is inversely proportional to the crosslink density thus M_C for 60 phr silica containing composite was very small. The above swelling results are to some extent supported by the observations of the curing characteristics. The maximum and minimum torque, change significantly with the silica content as shown by the values.

The shear modulus of hybrid composites before aging is given in Table 6. The shear modulus also follows the same trend as that of crosslink density. The shear moduli of hybrid composites before and after aging are given in Fig. 9. The shear modulus also follows the same trend as that of crosslink density.

The percent retention of shear modulus of MS/Silica hybrid NR composites is illustrated in Fig. 9. It is seen that at both aging temperatures the shear modulus increases with increasing weight ratio of silica in MS/Silica hybrid NR composites. The percentage retention of shear modulus was closely related to the crosslink density percentage retention value.

4. Conclusion

From the present investigation the following conclusion can be drawn:

1. The increased weight ratio of silica in hybrid composites continuously increases the minimum torque and maximum torque while the scorch time and cure time were reduced by the addition of silica which is due to the filler–rubber interaction.
2. Addition of silica in MS/NR/Silica hybrid composites rather than MS increases mechanical properties such as tensile strength, modulus, tear strength and hardness as it can interact strongly with natural rubber.
3. The increased weight ratios of silica into the desired hybrid composites reduce the elongation at break value.
4. Swelling ratio decreases with increasing silica ratio, while crosslink density and shear modulus increases with the addition of silica in hybrid composites.
5. The reduction in mechanical properties after aging is found, at both temperatures. However, the effect becoming very pronounced when the MS/NR/Silica hybrid composites were aged at 100 °C
6. The results of this study clearly support the use of the higher characteristic ratio of silica for increasing the strength of hybrid composites. Taking the overall properties of hybrid composites into account, we believe that MS could be used as an extender for cost saving.

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