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EFFECT OF MICRO-SIZED MARBLE SLUDGE ON PHYSICAL PROPERTIES OF NATURAL RUBBER COMPOSITES

Marble waste as sludge was collected from the marble industry, as a way of solving the environmental problem of industrial waste. The sludge was dried, ground and passed through the desired sieves (10, 15, 20, 37 and 75 μ m). This powder was characterized by X-ray fluorescence and then incorporated in the formulation of NR composites with different loading of micro-sized MS particles (20, 40, 60, 80 and 100 parts per hundred of rubber, phr). The cure characteristics, mechanical properties and swelling properties of MS/NR composites were evaluated. The results indicate that minimum torque, maximum torque, tensile strength, modulus, tear strength, hardness, crosslink density increased, while the scorch time, cure time, cure rate, cure rate index (CRI), elongation at break, compression set, rebound resilience, abrasion loss, swelling coefficient, average molecular weight and filler-rubber interaction decreased with increasing MS loading.

Keywords: natural rubber, composites, marble sludge, filler, cure characteristics, mechanical properties, thermal aging.

Increasing world population and fast changing life styles are exerting pressure on natural resources and the carrying capacity of the eco-system. Environmental pollution is one of the major factors influencing the daily human life. Large quantities of marble sludge (MS) are produced daily as a by-product during the cutting/polishing process of marble blocks in marble processing industries. MS is hazardous to health and causes environmental pollution as it is emanating into the drainage system. This practice imposes threats to the ecosystem. The situation has worsened to the extent that the dumping of the sludge is becoming a problem because of the shortage of space required to accommodate the large volume of its production. It is necessary to think of an efficient use of natural resources and to use and recycle the industrial waste. Polymer composite synthesis is one of the best ways to use marble sludge in large quantities as it can help replace the conventional filler such as carbon black, silica, clay and other non-black materials. Over the

last decade, efforts have been made to utilize MS in huge quantities for road construction, land filling, asphaltic concrete and producing building materials, e.g., in cement & construction industry [1-2] but very few use it as filler in rubber composites. [3-4].

In rubber compounding, fillers are used to enhance properties such as tensile strength, tear strength, modulus, abrasion resistance, and prominently to decrease the cost of the cured compound [5].

The role of filler networking of elastomer composites has been investigated by several authors [6-9]. Filler-filler interaction is a primary mechanism in reinforcement, especially at high filler loading. These interactions depend on chemical interactions between the filler particle surfaces, physical interactions, the structure of the filler network, and filler volume fraction. The reinforcement of elastomers by fillers have been studied in depth in numerous investigations [10] and it is generally accepted that this phenomenon is dependent, to a large extent, on polymer properties, filler properties and processing [11,12].

Currently, mineral fillers are added to polymers in commercial production of low cost and improvement in stiffness [13-27]. Furthermore, among several fillers like carbon black and synthetic silica, mineral fillers can also reduce pollution. It is known that in the

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case of filled cured rubber compound, the efficiency of reinforcement depends on a complex interaction of several filler-related parameters including particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler, and bonding quality between the fillers and the rubber matrix [28].

Jalham and Ibrahim [29] presented a study on natural rubber-silica sand composite that showed the effect of loading and particle size of filler on tensile strength, elongation at break, compression set, compression stress-strain, hardness and density. It was found that the particle size for each loading is directly proportional to the hardness. It was also observed that the worst results were obtained for the silica sand filled NR composite of 75 phr loading and larger particle size. The tensile strength is inversely related to the particle size of the filler and gives the highest strength when loading was 10 phr. The elongation at break of natural rubber reduced by increasing the loading and decreasing the particle size. The best result for compression set was shown by the composite with 10 phr of smallest size filler. The elastic modulus increased with the increase of loading and particle size. The density test showed that the silica filler has no significant increase in the density of rubber especially for small particle size fillers.

The aim of this research is to obtain a recipe with the incorporation of marble sludge waste as filler in natural rubber to resolve the environmental problem and to develop cheaper filler for polymer composite. The effects of MS content with selective micro particle sizes 10, 15, 20, 37 and 75 μm were investigated. The study involved cure characteristics, mechanical tests and swelling properties. The mechanical tests include tensile strength, modulus at 100, 200 and 300% elongation, and elongation at break, tear strength, compression set, hardness, abrasion resistance and rebound resilience. Swelling tests were conducted by measuring the swelling coefficient, volume fraction of rubber chemical crosslink density and filler-filler interaction of the rubber composites.

The study also focused on the resistance of aging of the rubber composite materials.

EXPERIMENTAL

Materials

The formulation of the natural rubber (NR) marble sludge (MS) composites is given in Table 1. The Natural rubber: A ribbed smoked sheet (RSS-1), having a Moony viscosity (ML1 + 4 at 100 °C) of 80 and MW of 120,000 with a density of 0.9125 g/cm³, originating from Thailand, was obtained from the Rainbow Rubber Industry, Karachi. The MS were collected locally and were mostly from the local marble cutting/processing industry. The MS was dried in a vacuum oven at 80 °C for 24 h and then ground in finer form. The ground MS was passed through sieves to obtain five different micro-sizes of MS such as 10, 15, 20, 37 and 75 μm with a density of 2.67 g/cm³. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, tetra methylthiuram disulphide (TMTD), 3-dimethylbutyl-N-phenyl-p-phenylenediamine (Antioxidant) were commercial grade and all purchased locally. 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 (Table 1).

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

Rubber compounding

The rubber was compounded on a laboratory two-roll mill (16×33 cm) employing the formulation

Table 2. Compound recipe of marble sludge content and selective micro-size

Ingredient	Compound					
	MS-00	MS-20	MS-40	MS-60	MS-80	MS-100
NR	100	100	100	100	100	100
Marble sludge ^a	00	20	40	60	80	100
ZnO	05	05	05	05	05	05
Stearic acid	02	02	02	02	02	02
TMTD	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
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6

^aMicro-size of MS particle, 10, 15, 20, 37 and 75 μm

given in Table 2. The mixing was done according to ASTM D 3182 (2001). The NR was masticated on the mill and the MS, 50% of the total amount of filler was incorporated into the rubber (20, 40, 60, 80 and 100 parts per hundred of the rubber (phr) with selective micro-size such as 10, 15, 20, 37 and 75 μm). Then the compounding ingredients were added in the following order: activators with balance MS, accelerators, and then sulphur. After mixing, the rubber compound was passed 2–4 min through the tight nip gap and finally sheeted out.

The vulcanization characteristics of the unfilled and MS filled NR composite were determined using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM method D 2084. Samples of about 6 g. were tested at a vulcanization temperature of 140 °C for 20 min. The torque was noted every 30 s.

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. All samples were cured at this temperature for the specific cure time and stored in a cool dark place for 24 h.

Measurement of mechanical properties

The properties of the natural rubber composite were measured with several techniques based on ASTM. The tensile strength, elongation at break, modulus at 100, 200 and 300% elongation, and tear strength were measured by a 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 500 mm/min at room temperature.

Hardness

The hardness of the sample (Shore A) was determined using a Shore Hardness Tester according to ASTM D-2240.

Abrasion loss

Abrasion testing was conducted using the ASTM D 5963 test method. The abrasion resistance was expressed as relative volume loss in mm^3 . The test was conducted on a Gibitre Abrasion Check (Italy).

Resilience

Resilience was determined by the vertical rebound method according to ASTM D 2832, using a Gibitre Rebound Check (Italy). In this method, a pendulum suspended from a given height (with pendulum length 204 mm, weight 255 g, maximum oscillation arc 90° and impact speed 2.00 m s^{-1}) above the specimen was released and the rebound height was measured. The ratio of the rebound height and original height is referred to as the resilience (%).

Swelling parameters

The chemical crosslinking density of NR composite was 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 [30]. 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 to a constant weight and the desorbed weight was taken. The swelling coefficient of the sample was calculated from the following equation [31]:

$$\alpha = \frac{W_s}{W_1} \rho_{s^{-1}} \quad (1)$$

where W_1 is the weight of the test piece before swelling and W_s is the weight of the solvent absorbed test piece after swelling.

The chemical crosslink densities of the composites were determined by the Flory-Rehner equation by using swelling value measurements [32–34] according to the relation:

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

where V_r is the volume fraction of rubber in the swollen gel, V_s is the molar volume of the toluene ($106.2 \text{ cm}^3 \text{ mol}^{-1}$) 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}).

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

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

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, ρ_1 is the density of the polymer (NR) which was taken as 0.9125 g/cm^3 , and ρ_s is the density of the solvent (0.867 g/cm^3 for toluene).

To study the rubber-filler interaction, the Lorenz and Park equations were applied [35]. The f and g refer to filled and unfilled (gum) vulcanizates, respectively. Z is the ratio by weight of fillers to rubber hydrocarbon in vulcanizates, while a and b are constants. The lower value of swelling ratio (Q/Q_g) indicates better interaction between the filler and the rubber matrix:

$$\frac{Q_f}{Q_g} = ae^{-Z} + b \quad (4)$$

The weight of toluene uptake per gram of rubber material, Q , was determined according to the following equation:

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{100 \frac{\text{Original weight}}{\text{Formula weight}}} \quad (5)$$

RESULTS AND DISCUSSION

The chemical composition of MS (Table 3) was determined using a WDX-ray fluorescence spectrometer (model S4 pioneer Bruker AXS, Germany). It is mainly composed of calcium and magnesium compounds in large amounts. Silica, aluminum oxide and iron oxide are also present. The values obtained from the relative metal component of marble sludge of atomic absorption spectroscopic study are approximately the same with those obtained from X-ray fluorescence spectrometer study.

Table 3. Quantitative analysis of marble waste using WDX-ray fluorescence spectrometer model S4 Pioneer from Braker - axS Germany

Component	Weight, %
CaO	68.6
MgO	22.13
SiO ₂	3.89
Al ₂ O ₃	2.785
Fe ₂ O ₃	0.603
Cr ₂ O ₃	0.24
ZnO	0.203
TiO	0.549

The cure characteristics of MS-NR composites (Table 4) show that the maximum torque (MH) and

minimum torque (ML) increased with the addition of MS, which was in agreement with the work reported by Sezna *et al.* [36]. The torque mainly depends on both the extent of crosslinking and reinforcement by filler particles in the polymer matrix [37]. This increase indicated that incorporation of MS enhanced the viscosity of the NR matrix. The increase in minimum torque found in these NR composites is simply due to the physical stiffness of the compound. Scorch time (t_{s2}) and cure time (t_{90}) of the composites decreased with the addition of filler. The decrease in curing time is attributed to the higher energy input and greater heat buildup during mixing due to the higher viscosity, whereas the decrease in the scorch time (t_{s2}) is due to the presence of more crosslink in the NR composites [38].

The curing rate index (CRI) was calculated according to [39]:

$$CRI = \frac{100}{t_{90} - t_{s2}} \quad (6)$$

It is observed that the increase in filler loading for rubber composite shows no significant effect on the CRI properties. The curing rate (CR) was calculated according to the following equation:

$$C_R = \frac{M_{90} - M_{s2}}{t_{90} - t_{s2}} \quad (7)$$

where M_{90} is the torque at t_{90} and M_{s2} is the torque at time t_{s2} . Table 4 shows that the curing rate increased with the addition of filler. The data revealed that the rate of vulcanization depends on the ratio of the filler used. The relative minimum torque ML_{Min}^R can be calculated as a function of filler loading with the help of the Wolff and Wang expression as follows:

$$ML_{Min}^R = \frac{ML_{Min}^F}{ML_{Min}^o} - 1 \quad (8)$$

Here, the relative torque increases with filler loading due to the agglomeration of filler aggregates. This is caused by the high dispensability of the component used, which indicates strong filler-polymer interaction [40]. While *et al.* [41] expressed the activity of filler (α_f) as follows:

$$M = \frac{M_{f_{Max}} - M_{f_{Min}}}{M_{g_{Max}} - M_{g_{Min}}} - 1 = \alpha \left(\frac{m_f}{m_p} \right) \quad (9)$$

where $M_{f_{max}} - M_{f_{min}}$ is the maximum change in torque during vulcanization for MS filled NR and $M_{g_{max}} - M_{g_{min}}$ is the maximum change in torque during vulcanization for unfilled NR compound, m_f is the parts by weight of MS in the NR compound, and m_p is the parts by

Table. 4. Minimum torque, M_L (dN m); maximum torque, M_H (dN m); cure time, t_{90} (min); scorch time, t_{S2} (min); CRI (min^{-1}); cure rate (dN m min^{-1}); relative minimum torque and activity of filler from rheometric characteristics of NR composites containing MS as filler with different micro-size of particle at 140 °C

Sample	Particle size	M_L dN m	M_H dN m	Cure time t_{90} min	Scorch time t_{S2} min	CRI min^{-1}	Cure rate dN m min^{-1}	M_L^R M_{Min}	Activity of MS (α)
MS -00	Unfilled	0.22	3.00	6.14	2.67	28.82	0.680	-	-
	10	0.32	3.30	5.98	2.23	27.00	0.710	0.454	0.360
	15	0.45	3.44	5.84	2.12	27.00	0.713	1.045	0.377
MS -20	20	0.53	3.58	5.72	1.98	26.74	0.712	1.41	0.485
	37	0.58	3.70	5.60	1.71	25.70	0.670	1.636	0.611
	75	0.66	3.83	5.48	1.63	26.31	0.674	2.00	0.701
	10	0.38	3.69	5.81	1.94	25.84	0.736	0.727	0.476
MS -40	15	0.57	3.81	5.78	1.89	25.77	0.715	1.591	0.414
	20	0.66	3.88	5.69	1.72	25.20	0.725	2.00	0.395
	37	0.75	3.92	5.62	1.65	25.20	0.723	2.41	0.350
	75	0.85	4.00	5.57	1.58	25.06	0.707	2.863	0.701
	10	0.43	4.02	5.43	1.76	27.25	0.777	0.954	0.485
MS -60	15	0.76	4.13	5.39	1.69	27.03	0.773	2.454	0.353
	20	0.85	4.16	5.33	1.60	26.81	0.761	2.863	0.318
	37	0.94	4.20	5.29	1.47	26.18	0.735	3.272	0.288
	75	1.01	4.27	5.23	1.38	26.86	0.771	3.636	0.287
	10	0.67	4.25	5.23	1.48	26.70	0.797	2.045	0.360
	15	0.85	4.33	5.20	1.40	26.31	0.776	2.863	0.315
MS -80	20	0.90	4.40	5.12	1.32	26.31	0.773	3.091	0.323
	37	0.93	4.42	5.05	1.23	26.18	0.759	3.227	0.319
	75	0.96	4.47	4.98	1.16	26.18	0.759	3.363	0.328
	10	0.84	4.80	5.17	1.26	25.57	0.813	2.818	0.424
	15	0.93	4.98	5.12	1.20	25.57	0.811	3.227	0.456
MS -100	20	0.96	5.04	5.03	1.18	25.97	0.831	3.363	0.457
	37	0.99	5.09	5.00	1.16	26.04	0.833	3.500	0.475
	75	1.04	5.13	4.92	1.13	26.38	0.839	3.727	0.471

weight of NR. The calculated values of the activity of MS (α_i) for all NR compounds are shown in Table 4.

The effect of micro-sized MS on the mechanical properties of the NR composites is shown in Figure 1. The tensile strength increased with the addition of MS content and was higher than that of the unfilled NR compound. On the other hand, from 20 to 80 phr amounts of MS filling, an increase in tensile strength was observed. At 80 phr of MS with 10 μm , the composite showed the highest tensile strength, 11.85 MPa, which was about 233.2% higher than that of unfilled NR composite. The improvement of the tensile property was attributed to the fact that interactions between MS and rubber chains associated with the contact of surface of filler resulted in more effective constraint of the motion of rubber chains with improved interfacial bonding between MS and the rubber matrix [42-43]. This interaction between the filler and rubber matrix plays an important role in increasing tensile strength but further addition of MS beyond 80 phr results in

decrease in the mechanical properties of NR composites. Above 80 phr content, agglomeration occurs and thus particle-particle interaction of the MS accounts for the observed decrease in tensile strength. The formation of MS aggregates led to produce weak points in the NR phase and decreased the tensile property (7.69 MPa). The micro-sized particles of MS also influence the tensile strength and tear strength. The smallest micro-sized particle of MS (10 μm) has the greatest tensile strength as compared to other particle size MS in composite. The smallest micro-sized filler provides the biggest surface area for better interfacial interaction between filler and matrix. This is due to the high dispersion and the interaction of particle of filler in matrix.

Figures 2-4 show the relationship between MS loading and M100 stress at 100% elongation, 200% stress. At 100 phr with 10 μm particle size, the value of the composite increased by 174.3% as compared to the unfilled NR compound which was 1.05 MPa for

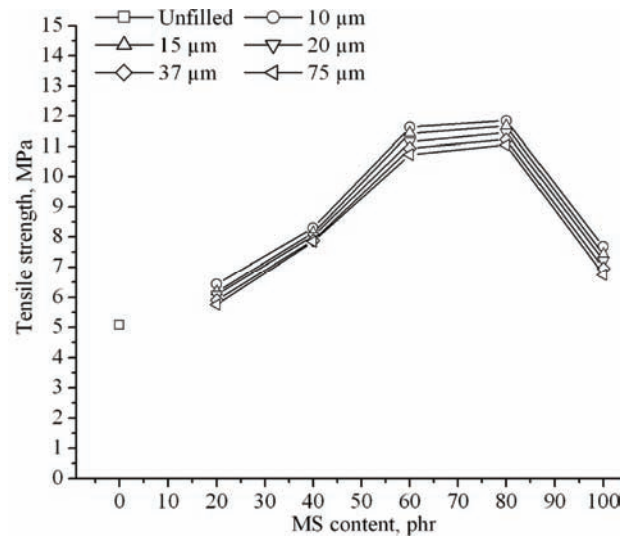


Figure 1. Effect of marble sludge content and micro-size on tensile strength of unfilled and filled natural rubber composites.

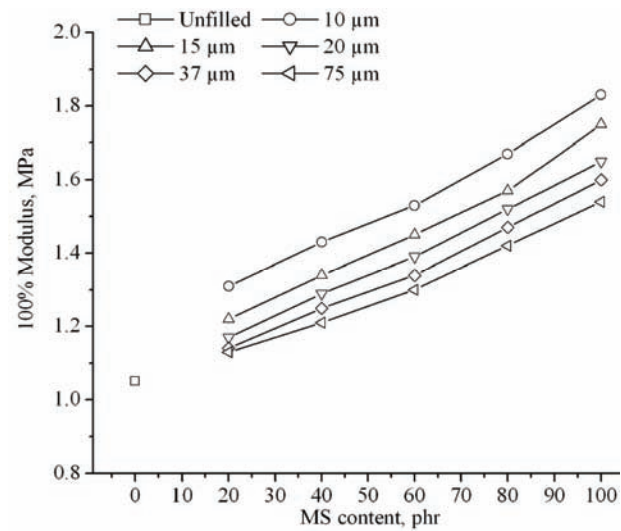


Figure 2. Effect of marble sludge content and micro-size on 100% modulus of unfilled and filled natural rubber composites.

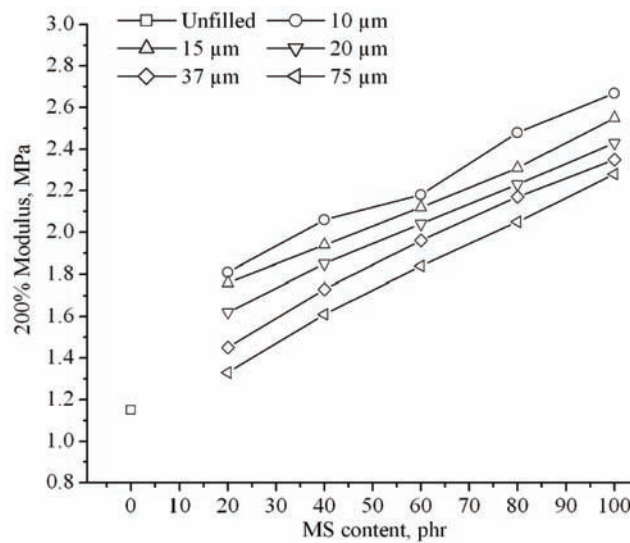


Figure 3. Effect of marble sludge content and micro-size on 200% modulus of unfilled and filled natural rubber composites.

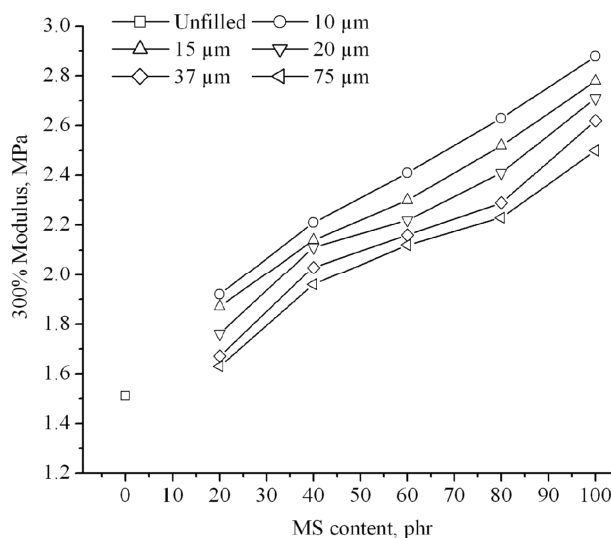


Figure 4. Effect of marble sludge content and micro-size on 300% modulus of unfilled and filled natural rubber composites.

M100, while at M200 the value observed is 2.67 MPa at maximum MS content and at M300 the value is 2.88 MPa. The remarkable enhancement of the modulus was due to the strong interaction, which effectively constrained the motion of polymer chains [44,45]. According to Poh *et al.* [46], the improvement in modulus is affected by several factors such as surface reactivity which determines the polymer-filler interaction, aggregates, size and shape of fillers, and structural and filler particle dispersion in rubber. Modulus at 100, 200 and 300% elongation of 10 μm size MS particle filled NR composites increase with increasing MS loading. It can be deduced that MS with smaller micro-size is more compatible with the rubber than the larger one. This is an indication that particles have better interaction with the rubber.

The effect of MS loading on the tear strength of filled NR composites is shown in Figure 5. It can be seen that the dependency of tear strength on MS loading is also very similar to that of tensile strength, as reported by several researchers [42–43]. Both tensile and tear strength typically indicate the resistance of the polymer chain network to fracture [44].

Elongation at break of unfilled and filled MS-NR composites at different loading and particle size (10, 15, 20, 37 and 75 μm) is shown in Figure 6. It is observed that the value decreases with the incorporation of MS into natural rubber (NR) composites. Many researchers [46–48,50–51] reported a decrease in elongation at break with the addition of more filler to the polymer matrix. With increasing MS loading, the stiffness and brittleness of the NR composite increased gradually, with a concomitant decrease in

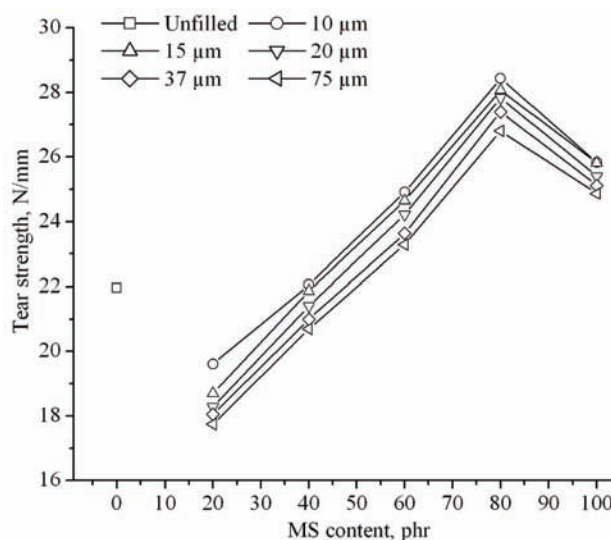


Figure 5. Effect of marble sludge content and micro-size on tear strength of unfilled and filled natural rubber composites.

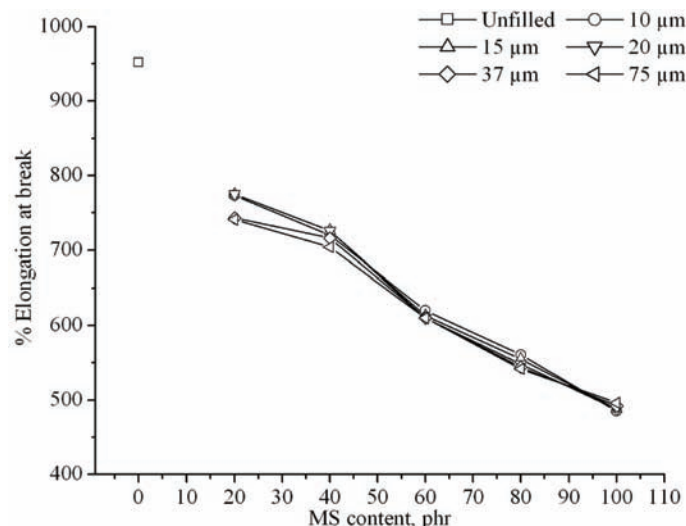


Figure 6. Effect of marble sludge content and micro-size on elongation at break of unfilled and filled natural rubber composites.

the elongation at break. In other words, with the enhancement in rigidity the ductility of composites decreases, consequently the composites break at lower elongation. Incorporation of fillers that have poor adhesion to the polymer matrix seems to cause interruption in the alignment process of the chains. When MS loading is gradually increased, more weak interfacial regions between the filler surface and the rubber matrix are formed. Because cracks travel more easily through the weaker interfacial regions, the composites fracture at a lower degree of elongation with increasing filler content. The better results found when 10, 15, 20, 37 and 75 μm size of MS used with loading of 10 and 30 phr of filler.

Hardness increased with increase in MS content, as shown in Figure 7. This result is expected because, as more MS is incorporated into the NR

matrix, the plasticity and flexibility of the rubber chains are reduced, resulting in more rigid composites [48]. Increase in hardness can also be due to the reinforcement effect of the filler as well as higher extents of crosslinking of the polymeric materials [51]. It is also proven from modulus results that the rubber hardness is correlated with the elastic modulus [52-53]. Higher loading and large micro-sized filler particles cause more rigid compounds. The results also show the effect of micro-size (10, 15, 20, 37 and 75 μm) on hardness. It is observed that the hardness at 90 phr with micro-size 37 and 75 μm is higher as compared to other smaller micro-sized MS filled NR composites.

It is widely known that compression set is another property that can be used to indicate the degree of elasticity. Figure 8 shows the relationship

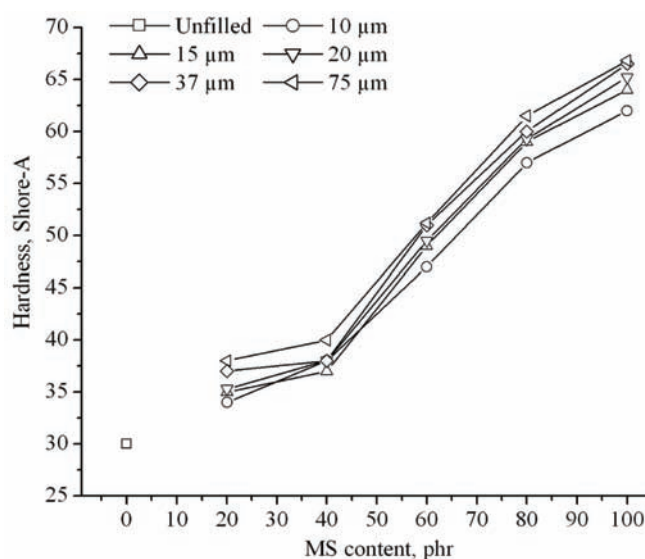


Figure 7. Effect of marble sludge content and micro-size on hardness of unfilled and filled natural rubber composites.

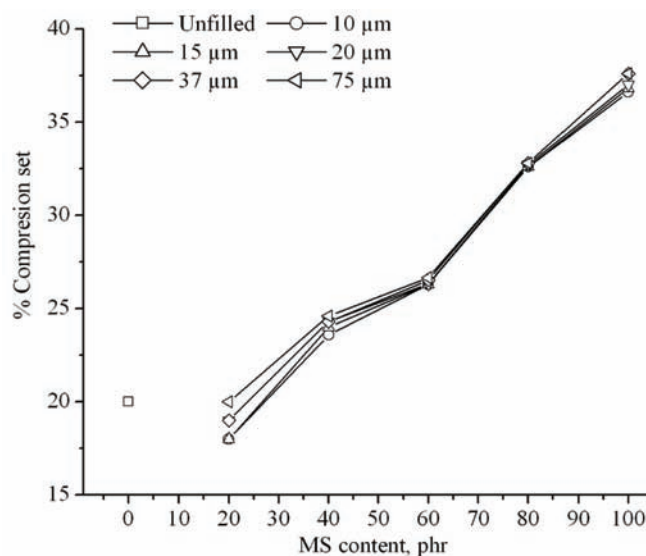


Figure 8. Effect of marble sludge content and micro-size on % compression set of unfilled and filled natural rubber composites.

between MS loading and compression set of NR composites. It can be seen that compression set increased with increasing NR loading. It confirms that the elasticity of cured NR composites has been impaired in the presence of selected micro-sizes of MS particle this increase is explained by the decrease in resilience with addition of MS in NR composite. The reduction in resilience, in turn, means that the elasticity of the compound is reduced [47]. Thus compression set that is proportional to elasticity is reduced with MS loading. The best result for compression set was achieved for the composite of 10 phr loading of filler with 10 μm particle size.

According to Morton [54], resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. Resi-

lience of unfilled and filled MS natural rubber composites at different loading and particle size 10, 15, 20, 37 and 75 μm are shown in Figure 9. The decrease in resilience is explained by the MS particles that introduce a mechanism by which the strain energy diminishes. Since rebound resilience is directly proportional to the degree of elasticity and segment mobility, the presence of MS reduces elasticity and segment mobility of the cured NR composites. Using large amounts of filler results in higher values of hardness and decreases the resilience [54-55]. The mobility of MS particles and slippage of chains attributed to applied stresses on cured composite increases the hysteretic behavior of the cured composite [56]. Therefore, the resilience decreases with increasing MS loading.

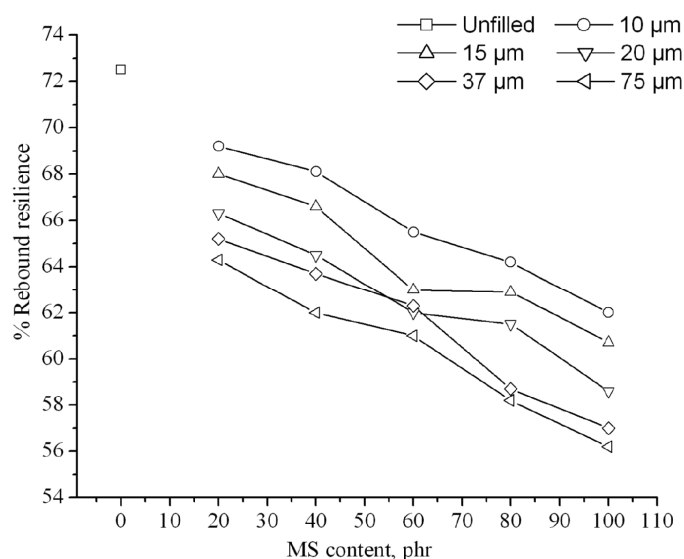


Figure 9. Effect of marble sludge content and micro-size on % rebound resilience of unfilled and filled natural rubber composites.

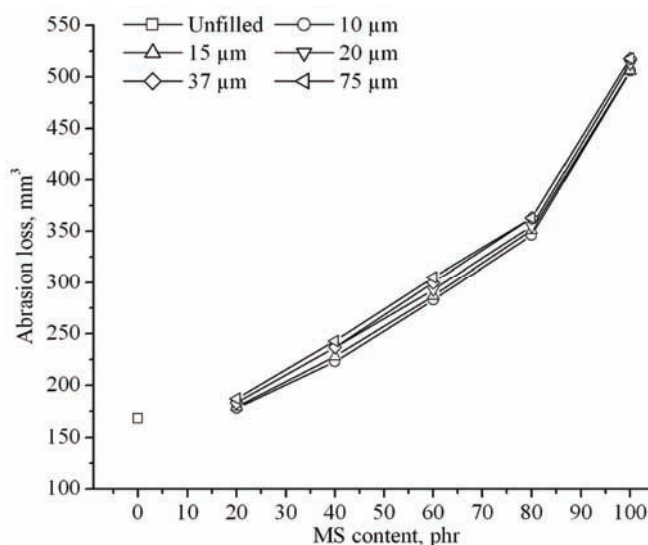


Figure 10. Effect of marble sludge content and micro-size on abrasion loss of unfilled and filled natural rubber composites.

The results of abrasion loss tests are presented in the vertical bar shown in Figure 10. It is clear from the graph that the abrasion loss of NR was influenced by the incorporation of MS. The addition of filler gradually increased abrasion loss until a maximum was attained at 100 phr, as shown in the figure. The lower filler-filler interaction leads to higher abrasion resistance [57]. Therefore, at low 20 phr content MS, the interaction between filler particles is minimized, *i.e.*, the abrasion resistance is maximum.

A swelling test was performed to observe the swelling coefficient filler-rubber matrix interaction. The effects of filler on swelling coefficient are presented in Table 5. The obtained results show a decreasing trend in swelling coefficient after loading the MS. It indicated that the penetration of toluene into MS filled NR composites was reduced by increasing the filler. This means that higher amount of MS loading restricted the penetration of toluene in filled NR composites. The lower swelling coefficient associated with the 10 µm size of MS filled NR composite as compared to 15, 20, 37 and 75 µm filled composites. This is due to better dispersion of smaller particles in NR, thus promoting better filler-rubber matrix interaction.

Equilibrium swelling measurements were performed in order to evaluate the chemical cross-linking density in the unfilled and MS filled NR composite. The values of the crosslink density, calculated by using Flory-Rehner equation, are given in Table 5. A clear linear increase of the apparent crosslink density with the MS content in the NR compound is observed. This indicates the major contribution and strong interaction between the NR and the filler leading to strong physical crosslinks.

After the calculation of crosslink density of unfilled and filled with MS containing varying micro-sized particles, the obtained data showed that the crosslink density increased from 20 to 100 phr filled MS-NR composite. When the MS content increases, the crosslink density also increases but average molecular weight of the polymer between cross-links decreases. This may be due to the increasing amounts of filler in rubber matrix, which imparts reduction in the molecular movement of rubber and make it more difficult for toluene to penetrate through it. Small micro-sized MS particles containing NR composite performed better than larger micro-sized MS containing NR composite. The average molecular weight between crosslinks was inversely proportional to the crosslink density, thus M_c for 100 phr with 75 µm micro-sized MS containing NR composite was much smaller as compared to other MS filled NR composite.

The presented swelling data to some extent supports the observations of the curing characteristics. The maximum torque, minimum torque, the optimum cure time and the scorch time change significantly with the MS content as indicated by the values.

CONCLUSION

The main aim of this study was to investigate the effect of MS filler of the cure characteristics, mechanical and swelling behavior of unfilled and MS filled NR composites. An experimental study of unfilled and MS filled NR composites at different content revealed the following:

1. The torques, which represent the processability of the composites, increase, while the scorch

Table 5. Swelling coefficient, crosslink density (ν), average molecular weight (M_c) and filler-rubber interaction of unfilled and filled MS with selective micro-size in molecular weight between the crosslinks from swelling measurements

Sample	Particle size	Swelling coefficient (α)	Crosslink density $\times 10^{-4}$, g mol/cm ³	Average molecular weight, M_c / g mol ⁻¹	Q_t/Q_g
MS -00	Unfilled	4.95	1.26	7936.5	-
	10	4.02	1.46	6849.3	0.815
	15	4.21	1.37	7299.3	0.851
MS -20	20	4.35	1.29	7752.0	0.870
	37	4.44	1.21	8264.5	0.899
	75	4.52	1.168	8561.6	0.914
	10	3.38	1.823	5485.5	0.684
	15	3.55	1.630	6135.0	0.718
MS -40	20	3.68	1.53	6535.9	0.744
	37	3.89	1.370	7299.3	0.787
	75	3.99	1.288	7764.0	0.806
	10	2.92	2.094	4775.5	0.591
	15	3.02	1.98	5050.5	0.610
MS -60	20	3.17	1.783	5608.5	0.641
	37	3.04	1.92	5208.3	0.660
	75	3.41	1.578	6337.1	0.690
	10	2.39	2.75	3636.4	0.44
	15	2.51	2.37	4219.4	0.507
MS -80	20	2.66	2.25	4444.4	0.537
	37	2.74	2.11	4739.3	0.555
	75	2.87	1.96	5128.2	0.580
	10	2.07	3.17	3154.6	0.419
	15	2.18	2.88	3472.2	0.441
MS -100	20	2.26	2.71	3690.0	0.458
	37	2.41	2.40	4166.7	0.488
	75	2.51	2.25	4444.4	0.508

time and cure time decrease with increasing MS content in NR composites.

2. Tensile strength and tear strength of composites increased to a maximum, attained at 80 phr; further increase led to decrease in both strengths.

3. Modulus, hardness, compression set and abrasion loss increased with increasing MS loading; however, incorporation of MS content reduced the % elongation of break of the composites.

4. The swelling parameter, i.e. the chemical crosslink density increased, while the swelling coefficient, average molecular weight of the polymer between crosslinks and filler-rubber interaction decreased with increasing MS content.

Overall, the results indicate that incorporation of MS in NR elastomeric materials offers a good property set of tensile strength, modulus and hardness.

This work also suggests that MS from marble processing industrial waste could be used as filler for cost savings in NR elastomeric material preparations composite. However, to achieve a better reinforcement,

a smaller micro-size of MS particles should be used.

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NAUČNI RAD

UTICAJ MIKRO MERMERNOG MULJA NA FIZIČKE OSOBINE PRIRODNIH KOMPOZITA GUME

Mermerni otpad u obliku mulja je prikupljan iz industrije mermera u cilju rešavanja ekološkog problema industrijskog otpada. Mulj je osušen, samleven i propušten kroz odgovarajuća sita (10, 15, 20, 37 i 75 μm). Dobijeni prah je okarakterisan pomoću rendgenske fluorescencije i nakon toga inkorporisan u formulaciju NR kompozita sa različitim punjenjem pomoću mikro-čestica veličine 20, 40, 60, 80 i 100 delova po 100 delova gume. Određene su karakteristike očvršćavanja, mehaničke osobine i svojstva bubrenja MS/NR kompozita. Rezultati pokazuju da se minimalni obrtni momenat, maksimalni obrtni momenat, sila istezanja, moduli, sila cepanja, tvrdoća i gustina umrežavanja povećavaju, dok se vreme paljenja, vreme očvršćavanja, brzina očvršćavanja, indeks brzine očvršćavanja, izduženje kod kidanja, kompresija, gubitak abrazije, koeficijent bubrenja, prosečna molekulska masa i interakcija punjača i gume opada smanjuje sa povećanjem MS punjenja.

Ključne reči: prirodna guma, kompoziti, mermerni mulj, punjači, karakteristike očvršćavanja, mehaničke osobine, termalno starenje.