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Natural Rubber Composites Reinforced with Green Silica from Rice Husk: Effect of Filler Loading on Mechanical Properties

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Abstract: Natural rubber (NR) composites filled with silica are typically used for tire tread applications owing to their low energy consumption and low rolling resistance. Tire tread properties vary broadly depending on the compound formulation and curing conditions. Silica loading is recognized as a critical factor influencing the mechanical properties of the composites. In this work, we aim to investigate the effect of silica loading (10–50 phr) on the mechanical properties of NR composites. Silica was prepared from rice husk waste via chemical treatment and subsequent calcination at 600 °C. Prior to the compound mixing process, silica was modified by a silane coupling agent to improve compatibility with the NR matrix. The NR compounds reinforced with silane-modified silica from rice husk were prepared using a two-roll mill machine. The scorch and cure times increased as the silica loading increased. The mechanical properties of the NR composites, including tensile strength, elongation at break, modulus, hardness, and abrasion loss, were examined as a function of silica loading. Tensile strength increased and reached the maximum value at 20 phr but decreased at high loading owing to the agglomeration of silica in the NR matrix. With increasing silica loading, hardness and modulus increased, whereas elongation at break and abrasion resistance decreased slightly. These results indicate that NR composites filled with silica are stiffer and harder at a higher silica loading due to the strong interaction between silica and the NR matrix, inhibiting the segmental mobility of rubber chains. We anticipate that the compound formulation presented in this work could potentially be adapted to tire tread applications.

Keywords: natural rubber; rice husk; silica; composites; compounds; mechanical properties

1. Introduction

The tire industry has grown continuously worldwide, with increased global demand every year [1]. Tire tread is one of the most important parts of tires and determines the performance of vehicles since it directly contacts the pavement surface for a long operation time under a heavy load [2,3]. Therefore, tire tread is easily worn out and damaged compared to other parts. Moreover, tire tread–pavement interaction creates a frictional force called skid resistance, which is an important factor that limits vehicle speed and the design of pavement geometry for driving safety [4–7]. To meet industrial requirements and ensure durability based on safety standards, further significant development of tire tread with a low rolling resistance coefficient, high traction, and good wear resistance is necessary [8–10].

In general, natural rubber (NR) is used as the major constituent in tread compounds owing to its low heat build-up level and good mechanical strength [11,12]. Tire tread

compounds consist of several components depending on the formulation, in which reinforcement filler is an essential component that helps to improve their mechanical properties [13–15]. The primary reinforcing fillers in the rubber industry are carbon black (CB) and silica (SiO_2) [16–18]. Each filler possesses its own advantages. CB provides a greater modulus and hardness, improving the rubber's resistance to tearing, abrasion, and flexing fatigue, than silica. However, its rolling resistance and wet traction are constrained. Besides, manufacturing CB by incomplete combustion of heavy petroleum products produces toxic gases and hazardous waste, causing long-term negative effects to human health and environmental problems [19,20]. Silica, with a similar specific surface area and loading to CB, provides less reinforcing power than CB because of its weaker polymer–filler interaction. Mixing silica and rubber compounds without compatibilizers could result in poor dispersion and agglomeration since silica (polar and hydrophilic surface) is incompatible with non-polar rubber [21]. Nonetheless, silica improves the processability of rubber and yields lower rolling resistance, resulting in reduced fuel consumption and low carbon emissions. Moreover, it can be derived from renewable bioresources, such as rice straw [22], rice husk [23], corn cob [24], sugarcane bagasse [25], and bamboo leaf [26]. Therefore, silica could be used as a partial or complete replacement for CB fillers. Replacing CB fillers entirely with silica is enchanting; silica is attractive since silica is an eco-friendly renewable feedstock that can be used to produce fuel-saving tires [27,28]. Nonetheless, surface modification of silica before mixing is required to enhance the compatibility between silica and the rubber matrix. Silane coupling agents are usually used to achieve this aim [29,30]. Despite significant progress in silica-reinforced NR composites, the optimal silica loading to achieve the desired mechanical properties varies broadly depending on the silica properties, mixing procedure, and formulation [31–35].

In this work, silica was extracted from rice husk via a chemical treatment and subsequent calcination process. Rice husk was chosen herein as a bio-resource of silica due to the vast amount of rice husk waste in Thailand. Furthermore, among several bioresources, rice husk contains the greatest silica content [36,37]. Prior to mixing with NR to make a composite, silica derived from rice husk was modified by a silane coupling agent to enhance its compatibility with NR. Silica loading in the composites varied from 10 to 50 phr, while the other components were fixed. The effect of silica loading on the mechanical properties of the NR composites is investigated and discussed in this study.

2. Experimental

2.1. Materials and Chemicals

Rice husk was obtained from a rice mill in Singburi province, Thailand. Concentrated hydrochloric acid (37%, HCl) and ethanol (CH_3OH , purity > 99.5%) were purchased from RCI Labscan Ltd. (Bangkok, Thailand). Potassium bromide (KBr) was purchased from PIKE technologies. Bis [3-(triethoxysilyl) propyl] tetrasulfide ($\text{C}_{18}\text{H}_{42}\text{O}_6\text{S}_4\text{Si}_2$, Si69, purity > 90%) as a silane coupling agent was purchased from Sigma Aldrich. Natural rubber (STR20L grade) was purchased from Thai Hua Rubber Company. Deionized (DI) water was employed throughout all experiments.

2.2. Preparation of Silica from Rice Husk

Rice husks were first washed twice with tap water and dried in an oven at 105 °C for 24 h. The dried rice husks were treated with a 1 M HCl solution at 80 °C for 1 h and then washed with DI water until the washed water was neutral. The HCl-treated rice husks were dried in an oven at 105 °C for 24 h. After that, they were loaded in a ceramic tray, calcined in a CWF 11/13 Carbolite chamber furnace at 600 °C for 1 h with a heating rate of 5 °C min^{-1} , and naturally cooled to room temperature under an air atmosphere. The white product after calcination was obtained and is denoted as RHS. The RHS was thoroughly ground with an agate and mortar and then sieved through a 100- μm mesh sieve. The preparation process of silica from rice husk is schematically depicted in Figure 1a.

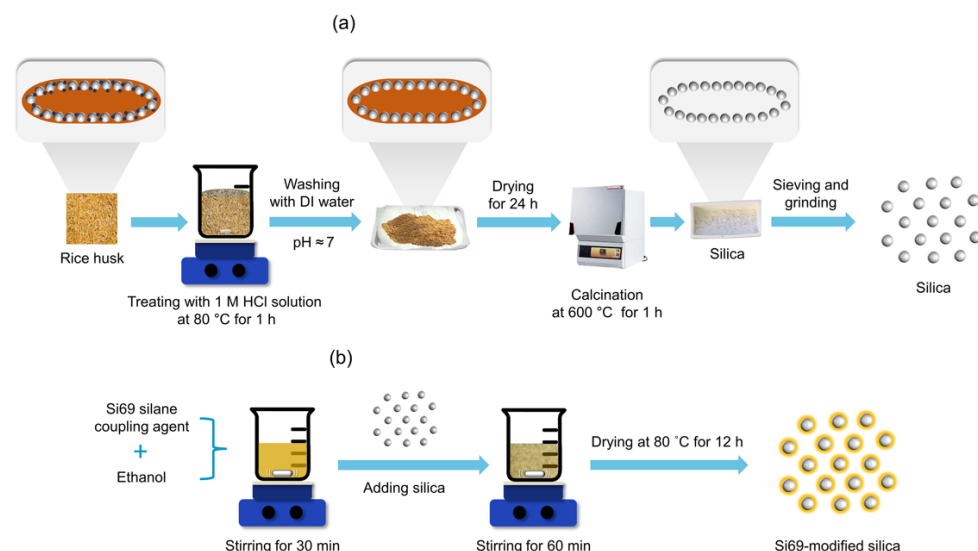


Figure 1. Schematic illustration showing the preparation processes of (a) silica from rice husk and (b) silane-modified silica.

2.3. Preparation of Silane-Modified Silica

A certain amount of Si69 (5.45 mL) was mixed with ethanol (800 mL) and stirred for 30 min to obtain a homogeneous solution. The RHS powders (100 g) were soaked in the ethanol mixture containing Si69 and stirred for 60 min. The ethanol was then evaporated at 80 °C for 12 h in an oven, resulting in the Si69-modified RHS (Si69-RHS) with a light yellow color. The overall preparation process of silane-modified silica is schematically shown in Figure 1b. The Si69-RHS was further used as reinforcement fillers in the NR composites.

2.4. Characterization of RHS and Si69-RHS

The morphology was investigated using a Hitachi SU3500 scanning electron microscope at an acceleration voltage of 10 kV. The energy-dispersive spectroscopy (EDS) analysis was undertaken with an Oxford Instruments Aztec One spectrometer equipped with a scanning electron microscope. The samples were coated with a thin gold film by sputtering before the investigation. Fourier transform infrared (FTIR) spectra were acquired on a Bruker Alpha-E spectrophotometer in the wavenumber range of 500–4000 cm^{-1} . The samples were mixed with KBr and pressed into a pellet form for measurement. Thermogravimetric analysis (TGA) was conducted using a TGA 2 Mettler Toledo Mettler in the temperature range of 50–900 °C at a heating rate of 10 °C min^{-1} under nitrogen flow. The specific surface area was measured on a Micromeritics 3Flex surface characterization analyzer at liquid N₂ temperature (−196 °C). Before the measurement, silica was heated at 100 °C for 6 h under a vacuum. The specific surface area was calculated from the adsorption isotherm in the relative pressure range of 0.05–0.30 using the Brunauer–Emmett–Teller (BET) theory.

2.5. Preparation of NR Compounds Filled with Silica

The formulations of NR compounds filled with Si69-RHS are shown in Table 1. The NR compound formulae are designated as C-*x*, where *x* represents the Si69-RHS loading. The mixing process was performed using a conventional laboratory two-roll mill (YFTR 8"). The obtained NR compounds were stored at 25 °C for 24 h in a closed container prior to curing assessment using an M-2000 moving die rheometer (MDR). The testing procedure was carried out according to the method described in the American Society for Testing and Materials (ASTM) D5289. The respective scorch time (*t*₂) and cure time (*t*_{c90}) were obtained from an MDR at 150 °C.

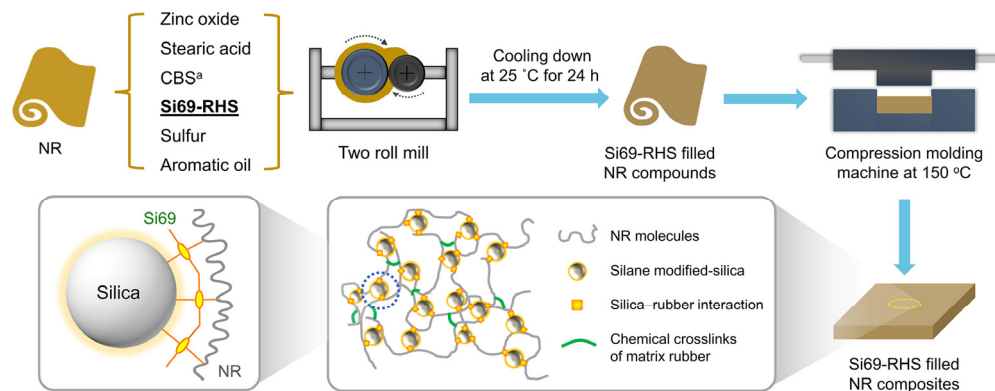
Table 1. Formulations of the NR compounds filled with Si69-RHS.

Materials	Part Per Hundred (phr)					
	C-0	C-10	C-20	C-30	C-40	C-50
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
CBS ^a	1	1	1	1	1	1
Si69-RHS	0	10	20	30	40	50
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
Aromatic oil	10	10	10	10	10	10

^a *N*-Cyclohexyl-2-benzothiazolesulfenamide.

2.6. Preparation of the NR Composites and Testing

The NR compounds were compressed using a compression-molding machine (Yong-Fong Machinery, Ltd., Model YFY HM-100, Samut Sakorn, Thailand) at 150 °C according to their respective cure times to obtain vulcanized NR composites (Figure 2). The fractured surfaces of the vulcanized NR compounds were investigated by a scanning electron microscope at an acceleration voltage of 10 kV. The dispersion of Si69-RHS in the NR matrix was examined by EDS mapping analysis. The NR composites were cut into a specific shape according to the ASTM for each mechanical test as follows: The stress–strain curves of the composites were measured on a Hounsfield H50KS testing machine according to ASTM D412 at a crosshead speed of 500 mm min^{−1}; hardness was measured using a Shore type A durometer according to ASTM D2240; and abrasion resistance was tested using a QC-615A AKRON abrasion test machine according to ASTM D2228. All mechanical values were obtained from the average of 5 samples.

**Figure 2.** Schematic illustration showing the preparation of silica-filled NR composites. ^a *N*-Cyclohexyl-2-benzothiazolesulfenamide.

3. Results and Discussion

3.1. Characterization of RHS and Si69-RHS

Figure 3a,c displays the SEM images of RHS and Si69-RHS, respectively. These images reveal irregular-shaped particles broken into a micron scale of less than 100 µm. No significant morphological change is observed between RHS and Si69-RHS, indicating no effect of surface modification on the RHS morphology. The EDS analysis was conducted to confirm the presence of Si69 on RHS by measuring the elemental composition in the sample. From the EDS spectra (Figure 3b,d), only silicon (Si K) and oxygen (O K) signals were detected for the RHS, while an additional small signal of sulfur (S K) was found for Si69-RHS. This result confirms the presence of Si69 on RHS.

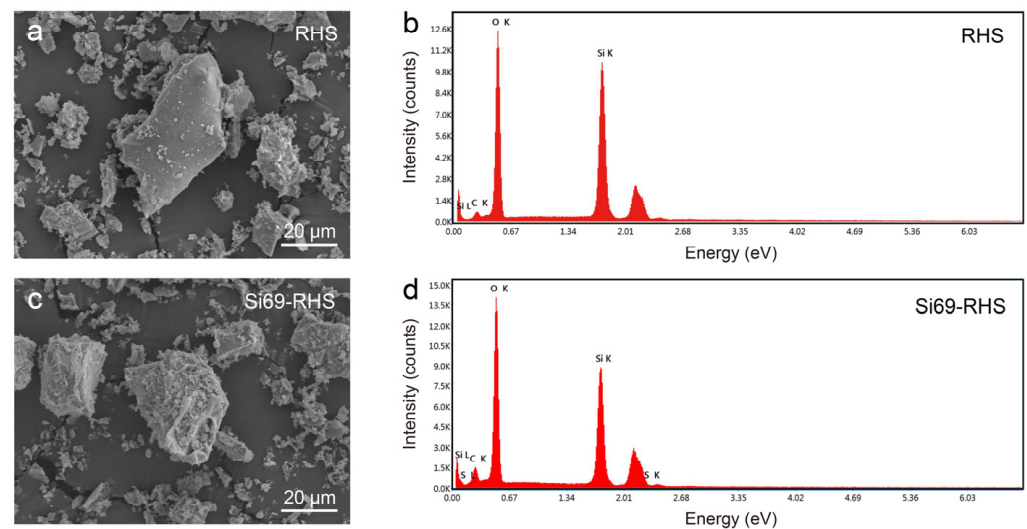


Figure 3. SEM images and the corresponding EDS spectra of RHS (a,b) and Si69-RHS (c,d). Note: The peak at 2.12 keV corresponds to the Au K signal from the sputtered gold films.

The FTIR spectra of RHS and Si69-RHS shown in Figure 4 reveal similar absorption features. A broad peak covering approximately $3200\text{--}3600\text{ cm}^{-1}$ and the peak at 1650 cm^{-1} are attributed to O–H stretching and O–H bending, respectively, indicating the presence of water molecules. The absorption at 1096 and 810 cm^{-1} can be assigned to the Si–O–Si stretching bond, which is the characteristic peak of silica [38]. However, the O–H stretching and bending peaks of Si69-RHS became weaker, while a very small peak of the C–H stretching bond from Si69 appeared at 2995 cm^{-1} (shown in the inset) [39–41]. The suppression of the O–H peak and the emergence of the C–H peak of Si69-RHS indicate its greater hydrophobicity and reduced water absorption [40].

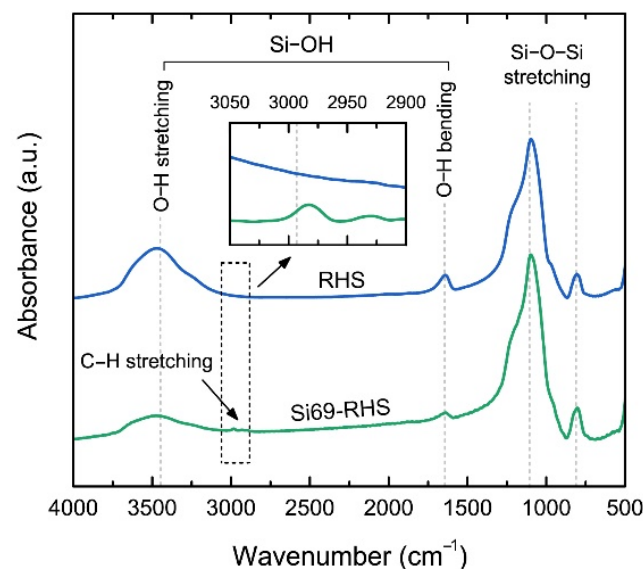


Figure 4. Comparative FTIR spectra of RHS and Si69-RHS.

To further confirm the presence of Si69 on RHS, TGA thermograms were recorded and are depicted in Figure 5. For the first stage ($50\text{--}150\text{ }^{\circ}\text{C}$), the RHS exhibited a significant weight loss of approximately 7%, while a weight loss of less than 2% was observed for Si69-RHS. The lower weight loss of Si69-RHS compared to RHS was due to less water absorption on Si69-RHS caused by its hydrophobic surface, as discussed in the FTIR analysis [40]. With an increase in temperature, the weight of RHS slightly decreased from 92.8% at $150\text{ }^{\circ}\text{C}$ to 91.4% at $900\text{ }^{\circ}\text{C}$. This small weight loss of RHS was due to the

almost complete decomposition of organic compounds during the calcination process. In contrast, a noticeable weight loss of approximately 4.2% was observed for Si69-RHS with a temperature range of 150–700 °C, which was attributed to the decomposition of Si69 [42,43]. According to the EDS, FTIR, and TGA analyses, the results are in good agreement to confirm that RHS was successfully modified by Si69.

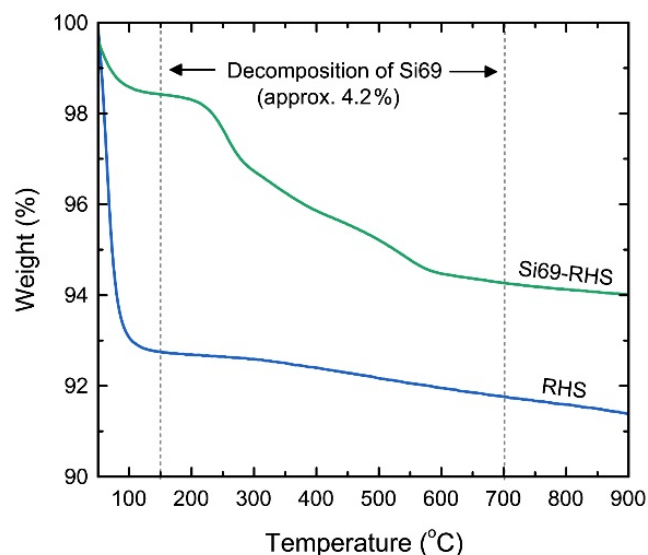


Figure 5. Comparative TGA curves of RHS and Si69-RHS under N₂ flow.

3.2. Characterization of Si69-RHS/NR Composites

The scorch and cure times of the NR compounds filled with various Si69-RHS loadings are shown in Figure 6. Both scorch and cure times tended to be longer with an increase in the Si69-RHS loading. This increasing trend was in agreement with several previous reports in the literature [44–46]. The high specific surface area ($\sim 280 \text{ m}^2 \text{ g}^{-1}$) of Si69-RHS could result in an increase in interaction with other components in compounds causing a disturbance in the vulcanization process and, thus, delaying scorch and cure times [47].

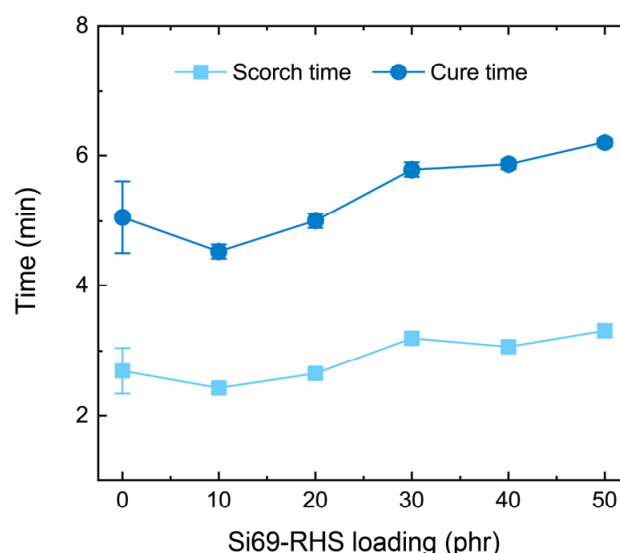


Figure 6. Scorch and cure times of the NR compounds filled with various Si69-RHS loadings.

Figure 7 presents the SEM images taken from the fractured surface of the NR composites. The NR composites without Si69-RHS had a relatively smooth surface (Figure 7a). The fractured surface had no obvious formation of voids and became rougher as the Si69-RHS loading increased (Figure 7b–f). However, it is difficult to identify and evaluate the

dispersion of Si69-RHS in the NR matrix from the SEM images. To solve this issue, EDS mapping analysis was conducted by measuring the dispersion of the Si element (blue) along with C (yellow) and O (green) elements, as shown in Figure 8. The Si element revealed uniform dispersion without agglomeration in the NR matrix at the Si69-RHS loadings of 10 and 20 phr. Good dispersion of the Si69-RHS in the NR matrix with good compatibility could help improve the mechanical properties of the composites. However, agglomeration began to be observed when the Si69-RHS loading reached 30 phr and became larger at higher loadings (i.e., 40 and 50 phr).

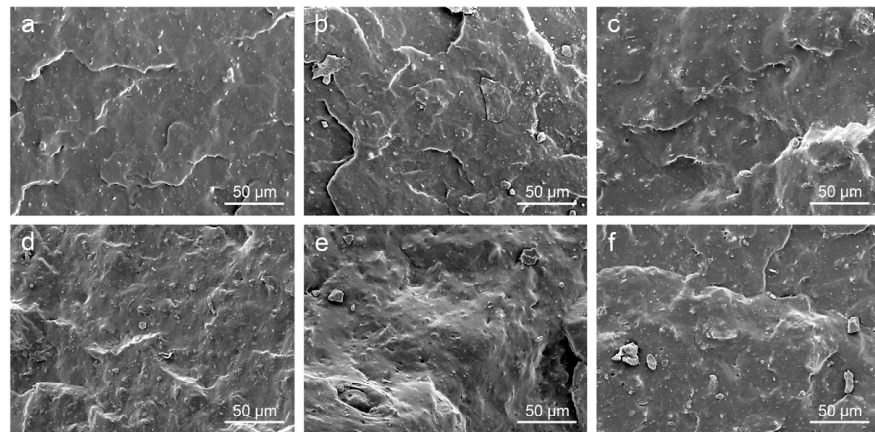


Figure 7. SEM images of the NR composites filled with various Si69-RHS loadings: (a) 0 phr, (b) 10 phr, (c) 20 phr, (d) 30 phr, (e) 40 phr, and (f) 50 phr.

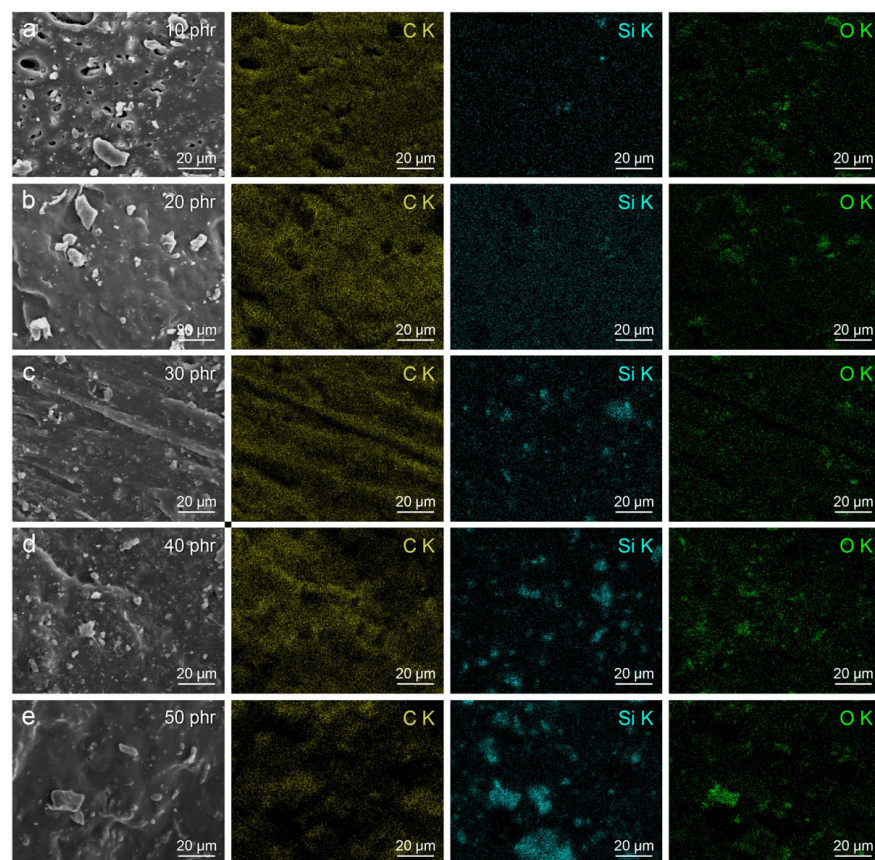


Figure 8. SEM-EDS mapping analysis of the NR composites filled with various Si69-RHS loadings: (a) 10 phr, (b) 20 phr, (c) 30 phr, (d) 40 phr, and (e) 50 phr. The yellow, blue, and green represent the carbon (C K signal), silicon (Si K signal), and oxygen (O K signal) elements, respectively.

The mechanical properties of the NR composites filled with Si69-RHS were examined. Tensile strength, modulus, and elongation at break can be determined from the stress–strain curves, as shown in Figure 9a. From Figure 9b, tensile strength increased with increasing Si69-RHS loading until reaching a maximum value of 20.9 ± 1.8 MPa at 20 phr, which was an approximately 26% improvement from that of NR (16.6 ± 1.5 MPa). The increase in tensile strength was attributed to good dispersion of Si69-RHS in the NR matrix and good interfacial interaction between the matrix and fillers, which can facilitate a more efficient energy-transfer process [44,48]. However, a further increase in Si69-RHS loading greater than 20 phr had an adverse effect on the tensile strength of the NR composites. The decrease in tensile strength is caused by the agglomeration of fillers in the NR matrix (>20 phr), as shown in the EDS mapping analysis (Figure 8). The change in tensile strength in this study is similar to the findings of Prasertsri and Rattanasom [44] and da Costa et al. [49]. With an increase in Si69-RHS loading from 0 to 50 phr, the elongation at break gradually decreased from 734% to 599%, as shown in Figure 9c. In contrast, the opposite trend was observed for the modulus at 100% of elongation (100% modulus). The 100% modulus increased from 1.04 ± 0.11 MPa at 0 phr to 1.38 ± 0.08 MPa at 40 phr but slightly dropped to 1.30 ± 0.06 MPa at 50 phr (Figure 9d).

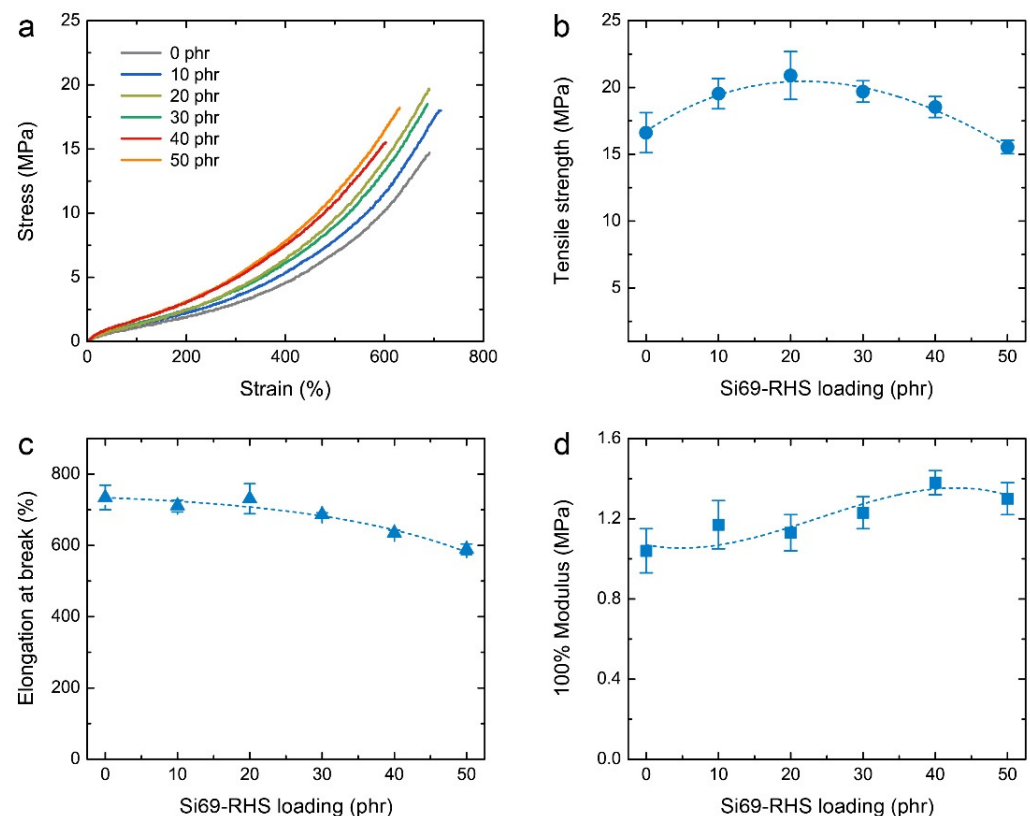


Figure 9. Mechanical properties of the NR composites filled with various Si69-RHS loadings (10–50 phr): (a) stress–strain curves, (b) tensile strength, (c) elongation at break, and (d) 100% modulus.

As shown in Figure 10a, the hardness (shore A) of the composites showed a similar trend with the 100% modulus, which continuously increased from 33.2 ± 0.8 to 44.9 ± 0.1 with increased Si69-RHS loading. According to the reports by Jacques et al. [50] and da Costa et al. [49,51], the hardness and modulus of vulcanized NR composites normally increase with the use of particulate fillers. From our results, it is clear that the NR composites became stiffer and harder when reinforcing with the Si69-RHS fillers since the interaction between NR and Si69-RHS could restrict the segmental mobility and movement of rubber chains, which decreased the elasticity of the rubber composites [45,52].

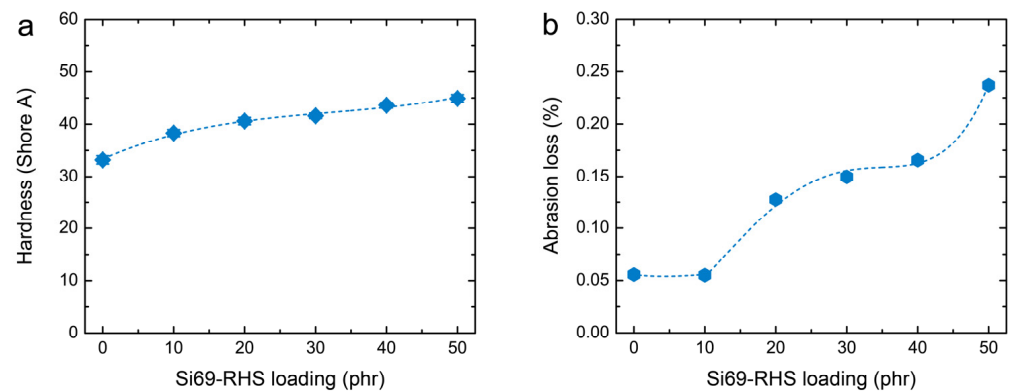


Figure 10. (a) Hardness (Shore A) and (b) abrasion loss of the NR composites filled with various Si69-RHS loadings.

Abrasion resistance is another important property for practical applications of rubber tires since it reflects a tire's ability to resist the progressive removal of material at the surface from mechanical rubbing and scraping [53]. It was found that a high Si69-RHS loading reduced abrasion resistance, as reflected by the higher value of abrasion loss (Figure 10b). The abrasion loss of the NR composites filled with Si69-RHS loading of 50 phr was $0.24 \pm 0.02\%$, which was about five-times greater than without Si69-RHS ($0.06 \pm 0.01\%$). Although the abrasion loss of the NR composites filled with Si69-RHS increased significantly, it showed satisfactory results for practical use. The mechanical properties of the NR composites discussed above are summarized in Table 2.

Table 2. Mechanical properties of the NR composites filled with various Si69-RHS loadings.

Si69-RHS Loading (phr)	Tensile Strength (MPa)	Young Modulus (MPa)	Elongation at Break (%)	Hardness (Shore A)	Abrasion Loss (%)
0	16.6 ± 1.5	1.04 ± 0.11	734 ± 35	33.2 ± 0.8	0.06 ± 0.01
10	19.5 ± 1.5	1.17 ± 0.12	711 ± 17	38.3 ± 0.7	0.06 ± 0.01
20	20.9 ± 1.8	1.13 ± 0.09	731 ± 42	40.6 ± 0.7	0.13 ± 0.01
30	19.7 ± 0.8	1.23 ± 0.08	686 ± 5	41.6 ± 0.5	0.15 ± 0.02
40	18.5 ± 0.8	1.38 ± 0.06	635 ± 8	43.6 ± 0.5	0.17 ± 0.02
50	15.5 ± 0.5	1.30 ± 0.08	589 ± 15	44.9 ± 0.1	0.24 ± 0.02

4. Conclusions

NR composites were successfully prepared at different Si69-RHS loadings from 0 to 50 phr. High Si69-RHS loadings could disturb the NR vulcanization process, thus, prolonging both the scorch and cure times. The Si69-RHS fillers were uniformly dispersed in the NR matrix with good compatibility at low loading (i.e., 10 and 20 phr); however, agglomeration began to be observed at 30 phr. For the mechanical properties of the NR composites, tensile strength reached the maximum value at a Si69-RHS loading of 20 phr and decreased at high loadings (>20 phr) owing to the agglomeration of fillers in the NR composites. With increasing Si69-RHS loading, hardness and 100% modulus tended to increase, whereas the opposite trend was observed for elongation at break and abrasion resistance. These results indicate that the addition of Si69-RHS could inhibit the mobility of the rubber chain, making the composites stiffer and harder. The results presented in this work could be helpful in further optimizing and developing a suitable formula for the NR composites for tire tread applications.

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