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The Effect of Chemical Treatment on Rice Husk Ash Silica-Filled Natural Rubber Vulcanisates

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Rice husk ash (RHA) is a silica-rich waste product of the rice industry. Chemical treatment of RHA was developed to obtain high purity and reactive silica, via a simple method consisting of alkaline extraction and acid precipitation. The effects of the chemical treatment on the particle size and surface area were measured. 20 parts per hundred rubber (phr) of precipitated silica was then incorporated into natural rubber (NR), using a laboratory-sized two-roll mill. For comparison, commercial silica was used as a control. The cure characteristics and mechanical properties of the vulcanisates were evaluated. The chemical treatment of the RHA resulted in a significant decrease in its particle size and an increase in its specific surface area. The precipitation of RHA with hydrochloric acid (HCl) and nitric acid (HNO_3) resulted in smaller particle sizes with reductions of 55% and 49%, respectively from the initial size before precipitation. Both acid precipitation increases the specific surface area by 53%. These changes involved the removal of organic and metal components from RHA, confirmed by Fourier transform infrared (FTIR) spectroscopy and Energy-dispersive X-ray (EDX) analysis. However, the mechanical properties of the vulcanisates produced from the treated RHA were lower than those of the commercial silica. This biomass-derived filler has the potential to be further developed as an alternative to commercial silica sourced from mining.

Keywords: Natural rubber; rice husk ash; mechanical properties; curing characteristics; silica

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Silica, a crucial raw material, is utilized in various industries including ceramics, rubber, plastics, micro-electronics, food production, pharmaceuticals, personal care products, as well as structural and adsorptive materials. Traditionally, silica is produced from quartz sand or quartz rock, which is sourced from mining. The traditional way to produce silica involves high energy consumption and high levels of pollution, which limits its large-scale commercial applications with much concern on mineral resources and sustainable development [1]. Thus, there is a need to find an abundant and cheap material with comparable performance to silica as a viable alternative.

Rice husk (RH) is a by-product of rice milling and an agricultural waste material. Many efforts have been made to utilize the rice husk. One of the common ways is by using it as a fuel, simply by burning the rice husk. The burned rice husk produces ash, i.e. consists of > 90% silica with some metallic impurities, which can also be used in various ways [1-3]. Failure to utilize this rice husk ash (RHA) would lead to significant waste, environmental pollution, and energy depletion [4]. Hence, assessing the utility of RHA is crucial. RHA presents itself as a cost-effective and economical raw material for the production of silica. Silica from RHA is green and renewable compared with that from quartz sand, and it can be claimed as bio-silica [1].

A simple method for silica ash removal is the treatment of the husks with sodium hydroxide (NaOH) solutions [5, 6]. The alkali treatment may result in further changes to the husks that require investigation. Metallic impurities can adversely affect the properties of silica from RHA and its application, so it is important to purify silica to improve its characteristics. Many researchers utilize acid leaching as a successful approach to diminish the presence of metallic impurities in RHA. Acids include mineral acids such as hydrochloric acid (HCl), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and nitric acid (HNO_3), and organic acids such as acetic, citric, and oxalic acid [7-9]. There have been several reports on the chemical treatment of the RHA, before and after combustion [10-12]. Most techniques successfully obtained amorphous silica of high purity, small particle size and high surface area [13].

In addition to silica, RHA also contains carbon black, which are residues resulting from incomplete combustion [14, 15]. Both silica and carbon black have long been recognized as the main reinforcing fillers used in the rubber industry to enhance certain properties of rubber vulcanisates, such as modulus and tensile strength. Many attempts have been made to use the RHA as filler, for natural and synthetic rubbers. An early investigation by Haxo and Mehta [16] proved that ground RHA, which was obtained via a special burning process, acts as a moderately reinforcing filler

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for rubbers, such as styrene-butadiene rubber (SBR), ethylene propylene diene methylene rubber (EPDM), and natural rubber (NR) [17]. The influence of the RHA incorporation on the mechanical properties and fatigue behaviour of epoxidised natural rubber (ENR) was also investigated [18]. However, the RHA was compounded in rubber without undergoing any chemical treatment. To date, only a limited number of studies have been published on the utilisation of chemically treated RHA in rubber materials [10, 15, 19].

The objective of this research is to substitute the commercial silica commonly employed as a reinforcing filler in the natural rubber industry with silica derived from RHA. Chemical treatment was applied to the RHA, and its effects on particle size and surface area were examined. Subsequently, mechanical properties such as tensile properties and hardness were investigated for rubber products filled with RHA silica and compared with those reinforced with commercial silica. In addition to enhancing the value of rice husk ash, the aim is to promote the utilisation of natural rubber by reducing its raw material costs.

EXPERIMENTAL

Materials

The raw elastomer used in this study was the standard Malaysian NR (grade SMR20). The RHA was obtained from Maero Tech Sdn. Bhd. In addition to the raw elastomer and RHA, the other additives used were sulphur, zinc oxide, stearic acid and n-cyclohexyl benzothiazole sulfenamide (CBS).

To obtain silica, the initial step involved extracting silica from the RHA as sodium silicate, utilizing aqueous NaOH. NaOH is preferred over sodium carbonate (Na_2CO_3) as the alkaline treatment method for producing silica from RHA. This preference arises because Na_2CO_3 generates a significant amount of CO_2 during the extraction process, rendering it environmentally unsustainable [20]. Alkaline pretreatment using NaOH is commonly preferred for its lower cost, higher effectiveness, and shorter reaction times, reducing the energy intensity of the pretreatment process compared to other options [21].

The RHA was digested in a 15% NaOH solution for approximately 60 minutes under pressure (15 psi). The use of 5% NaOH has been previously reported [19]. Following filtration of the reacted slurry, a viscous, transparent, colourless sodium silicate solution was obtained. The residue was then filtered, washed several times with distilled water, and dried at 100 °C for 24 h. The digested RHA was labelled as 15% D.

After alkaline treatment, the sodium silicate was divided into two samples: one treated with 1 M nitric acid (HNO_3) and the other with 1 M hydrochloric acid (HCl) to precipitate the silica for approximately 4 h. Subsequently, the wet precipitated silica samples were dried in an oven for 24 h at 100 °C. The precipitated samples were labelled as 15% D HNO_3 and 15% D HCl.

Mixing

The compounds were prepared using a laboratory-sized two-roll mill. For comparison, commercial silica (Tokusil® 255G, Tokuyama Co., Tokyo, Japan) was also used as a control. In total, three compounds were prepared for this study based on the formulation provided in Table 1. One with commercial silica and two with silica derived from RHA (15%D HCl and 15% D HNO_3). The filler loading used in this work was fixed at 20 per hundred rubbers (phr). According to the literature, good properties of silica-filled rubber compounds have been achieved when using 20 to 30 phr of silica in NR containing compounds since the surface area and surface activity of silica are high [22]. Nip gap, roll mill speed ratio, time of mixing and sequence of the addition of the ingredients, were kept the same for all the compounds. After mixing ended, the compounds were kept at an ambient temperature (23 °C) for at least 24 h before vulcanisation.

Table 1. Rubber formulations.

Ingredients	Parts per hundred of rubber (phr)
SMR 20	100
Zinc oxide	3
Stearic acid	2
Antioxidant	1
Filler*	20
CBS	1.4
Sulphur	1.5

*Commercial (control)/precipitated silica (15% D HCl and 15% D HNO_3)

The respective scorch time (t_2), cure time (t_{90}) and cure rate index (CRI) of the vulcanisates were determined using a rotorless rheometer at 160 °C. The Mooney viscosity (ML_{1+4}) at 100 °C was determined using a Mooney viscometer.

Characterisation

Particle size distributions of the RHA and silica samples were measured using a particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd., Malvern, UK). Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) analyses were carried out using Hitachi TM3030Plus Table-top to ascertain morphology and the elemental composition of samples respectively. Fourier transform infrared spectroscopy (FTIR) data were obtained from the Perkin Elmer Spectrum One FTIR spectrometer.

Compression moulding was performed on the vulcanisates at 160 °C, according to the respective t_{90} values using a laboratory hydraulic press. Stress-strain data were determined according to ASTM D 412, using a universal testing machine (5569, Instron, Canton, MA) at a crosshead speed of 500 mm/min with C-type dumbbell specimens. Tensile strength, tensile modulus and elongation at break were obtained from the tests. To ensure the uniformity of the rubber vulcanisates, five test pieces were selected from different parts of the same moulded sheet for each composition. The hardness test used in this study was conducted according to ISO 48, using a dead load hardness tester (H14, Wallace Instrument Ltd., Surrey, England) with the results being read directly in the International Rubber Hardness Degrees (IRHD).

RESULTS AND DISCUSSION

Effects of Chemical Treatment on the Particle Size

The results of the particle size and surface area analyses are summarized in Table 2 and Figure 1. It is evident that the digestion of RHA using a 15% NaOH solution significantly reduces its initial size (prior to digestion) by 32% and increases its specific surface area by 150%. The precipitation of RHA with HCl and HNO_3 further reduces its particle size and increases its specific surface area. HCl results in smaller particle sizes compared to HNO_3, with reductions of 55% and 49%, respectively, from the initial size before precipitation. This outcome is in line with previous observations by Chakraverty et al. [23] who investigated the impact of different acid treatments on the removal of metallic components and found that leaching with 1N HCl is particularly efficient. Both HCl and HNO_3 precipitation methods increase the specific surface area by 53%. HCl is generally considered stronger than HNO_3 in terms of its acidic strength. The strength of an acid is determined by its ability to donate protons (H^+ ions) in a solution. In addition, nitrate is a weaker nucleophile than chloride, which can influence the leaching process in hydrolysis.

Acid leaching has a significant impact on the surface area of silica. The increase in surface area of acid-leached silica is primarily attributed to the hydrolysis of hemicellulose and cellulose into smaller compounds [9]. Pre-treatments with hydrochloric acid and nitric acid can eliminate metallic impurities such as iron (Fe), manganese (Mn), calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg), which influence the purity and colour of silica [11, 12]. In general alkaline treatment is primarily aimed at removing organic impurities and increasing the reactivity of RHA [6], while acid treatment focuses on removing metallic impurities and further enhancing its purity and suitability for specific applications [24]. Obtaining high-purity silica is crucial, as impurities diminish its effectiveness as a filler in composites. The production mode significantly influences the impurity level of silica [12].

Table 2. Particle size and surface area of all the samples.

Sample	RHA	15% D	Tokusil 255G	15% D HCl	15% D HNO_3
Average particle size [µm]	289.40	194.85	181.04	88.09	99.02
Specific surface area [m^2/g]	0.06	0.15	0.14	0.23	0.23

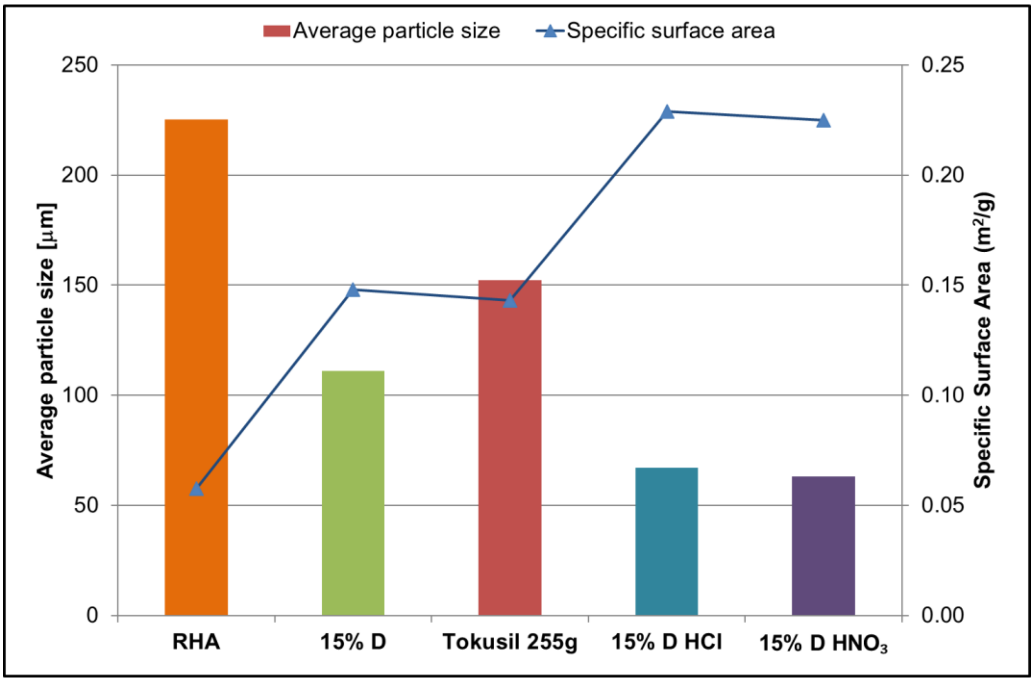


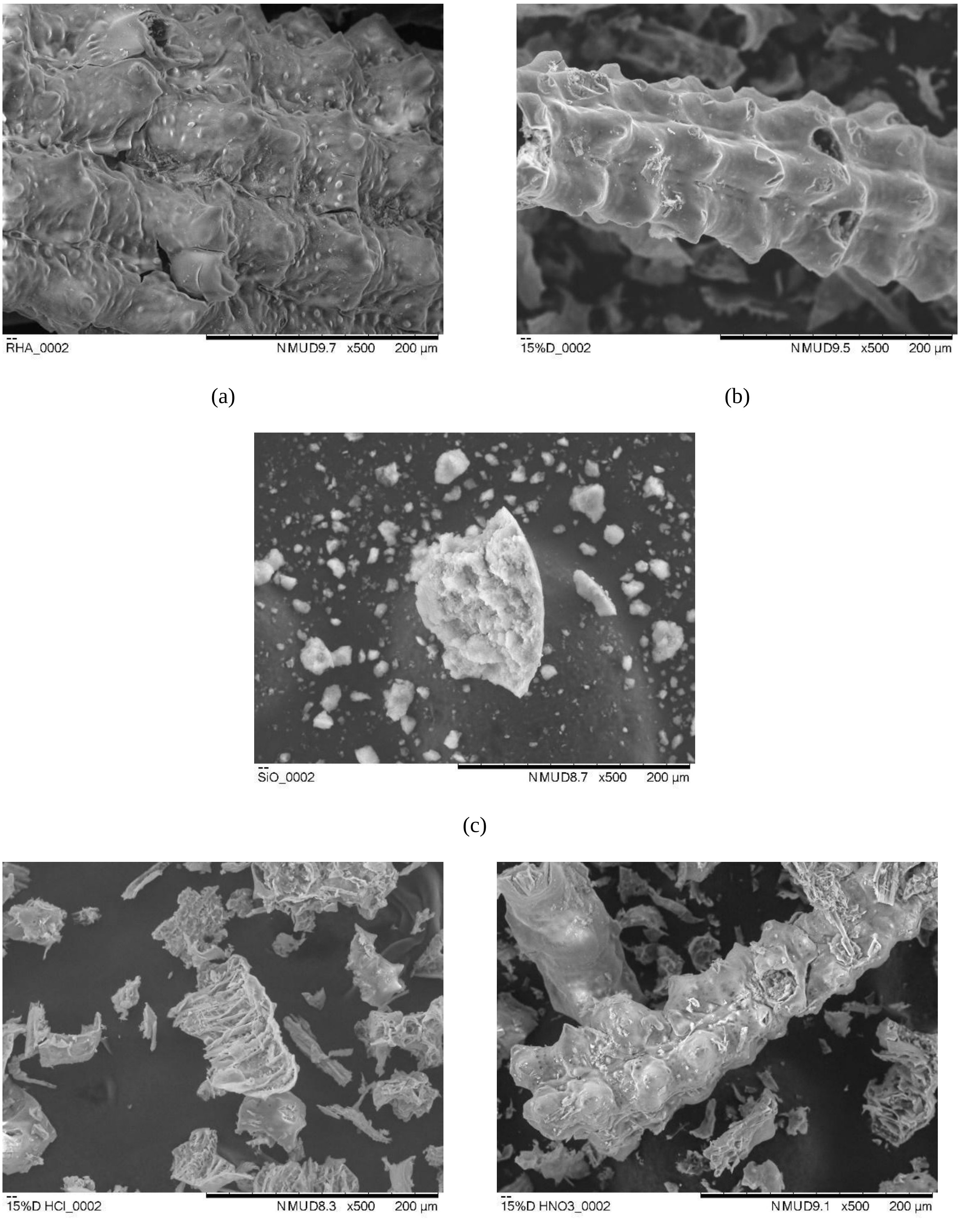
Figure 1. Particle size and surface area of all the samples.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) Analysis

SEM micrographs of RHA, commercial silica and precipitated silica are shown in Figure 2. RHA particles were irregular in shape. The average size of precipitated silica, 15% D HCl was relatively smaller, compared to 15% D HNO_3. Both precipitated silica have irregular shapes, whereas conventional silica is more spherical. Irregularities in the morphology of silica observed under SEM could be attributed to both crystalline and amorphous regions within the silica itself. In crystalline structures, impurities are the main contributors to irregularities, while amorphous irregularities arise from the nature of the silica lattices. Agglomeration of both conventional silica and precipitated silica was due to hydrogen bonding between silanol groups on the surface of silica [4].

Table 3 presents the chemical composition of RHA, commercial silica and both precipitated silicas. According to EDX chemical analysis data, 15% D depicts the most efficient inorganic/metal ion removal, followed by 15% HCL and 15% HNO_3. However, alkali treatment recorded high chloride (Cl) and titanium (Ti) might be due to the complex Cl and Ti which is insoluble in aqueous alkali. Acid treatment shows greater removal. The content of silica and oxygen which represent the formation of SiO_2 shows a fluctuation in results. Using EDX, as the surface technique, detected X-Ray was dominantly from the surface. The application into silica which content of pores contributed to its limitation. This is similar to oxygen, which EDX effectively identifies in heavier elements such as metal ions.

Acid treatments were efficient in the removal of magnesium, potassium, calcium and manganese from RHA [13]. Thus, the pretreatment of RHA can reduce the content of metal ions like K^+ and obtain a higher content of SiO_2. The content of silicon in the 15% D HNO_3 is slightly higher than that of the 15% D HCl, respectively.



(a) (b)

(c)

(d) (e)

Figure 2. SEM micrograph of (a) RHA, (b) 15% D, (c) Tokusil 255g (d) 15% D HCl, and (e) 15% D HNO_3.

Table 3: EDX analysis of all the samples.

Element	Weight percentage (%)				
	RHA	**15% D**	**Tokusil 255G**	**15% D HCl**	**15% D HNO_3**
O	51.19	49.72	52.39	41.6	47.92
Si	30.37	34.83	19.11	13.82	23.19
C	17.28	14.6	28.5	41.14	27.92
Al	0.51	0	0	1.49	0.3
K	0.23	0	0	0.05	0.1
Cl	0.15	0.49	0	0.11	0.27
Ti	0.08	0.35	0	0	0
Fe	0.08	0	0	0.02	0.06
Mg	0.06	0	0	0.09	0.22
P	0.05	0	0	0.09	0
Mn	0.01	0	0	0	0
Cl	0	0	0	1.59	0

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of RHA, commercial silica and both precipitated silicas are shown in Figure 3. Most functional groups found on both 15% D HCl and 15% D HNO_3 are the same as those found on commercial silica (Tokusil 255G). The vibration peaks around 1068 and 795 cm^{-1} were typical of Si–O–Si bands attributed to asymmetric stretching and symmetric stretching, respectively [25, 26]. These peaks were the main indices of the silica materials. Absorption in the broadband range of approximately 3800–3000 cm^{-1} wavenumbers was very weak, which may indicate interference or noise from the instrument. The FTIR analysis achieved here in this experiment is similar to those reported by other workers who carried out similar studies [27]. Accordingly, it could be reported that silica has been extracted from RHA successfully.

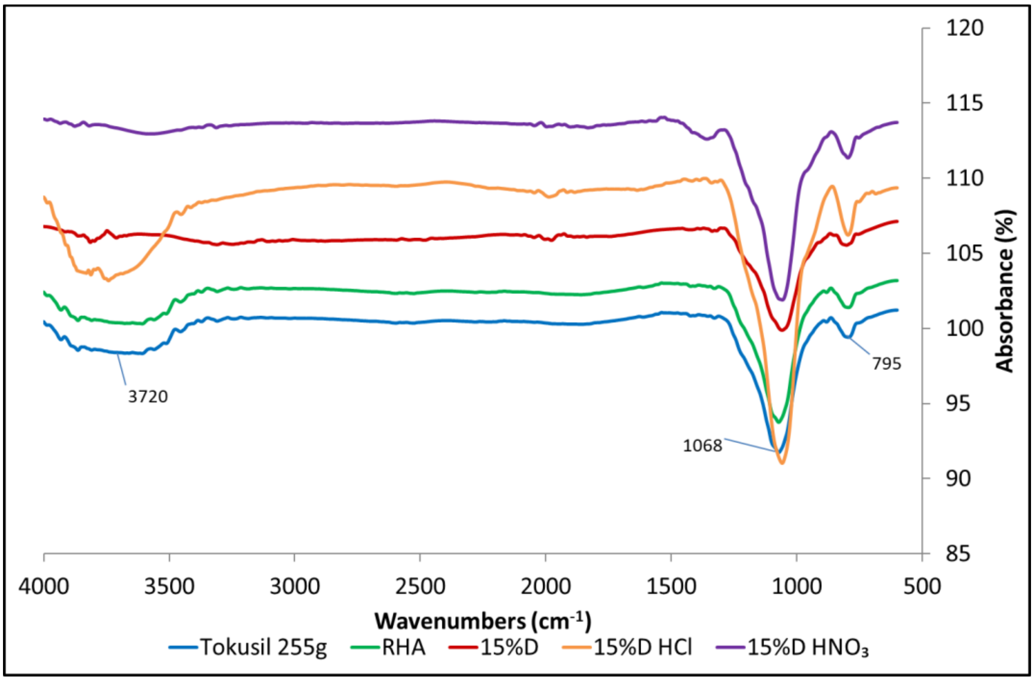


Figure 3. FTIR spectra of all the samples.

Table 4. Curing characteristics and Mooney viscosity of the NR vulcanisates.

Cure characteristics	Tokusil 255G	15% D HCl	15% D HNO_3
Scorch time, t_{S2} [min]	1.6	1.6	1.6
Cure time, t_{90} [min]	3.5	5.1	5.1
Minimum torque, M_L [dN.m]	0.2	0.1	0.2
Maximum torque, M_H [dN.m]	1.7	1.8	1.7
Cure rate index, CRI [min^{-1}]	46.3	32.8	36.1
Mooney viscosity [ML $_{1+4}$ at 100˚C]	43	35	36

Curing Characteristics and Mooney Viscosity of the NR Vulcanisates.

Table 4 shows the curing characteristics and Mooney viscosity of the NR vulcanisates. Both the precipitated silica samples obtained higher cure time and lower cure rate, compared to the controlled silica. The different trends in the cure characteristics may be attributed to the difference in the filler properties, due to different types of acid treatment used. In general, a faster cure rate can be obtained with fillers which have lower surface area, but with higher moisture and metal oxide contents [28]. This was in agreement with our findings, where among the types of silica being investigated, Tokusil 255G has the lowest surface area and therefore, shorter t_{90} values. It was found that the Mooney viscosities of both the precipitated silica samples were lower than the controlled silica. This indicates that there was a lower restriction for the molecular motion of the macromolecules, probably due to the lower interaction between the silica and the rubber matrix [19]. The higher Mooney viscosity for the controlled silica indicates that there was a higher restriction for the molecular motion of the macro-molecules, probably due to the greater interaction between the commercial filler and the rubber matrix. This seems to be the opposite for the particle size of the fillers.

Tensile Properties

The tensile strength of both precipitated silica samples was lower compared to the controlled silica, as indicated in Figure 4. The reduction in strength may be caused by the agglomeration of the filler particles to form domains, which act as foreign particles, or simply may be due to the physical contact between the aggregates [19]. In the case of a highly polar filler, such as silica, that is incompatible with hydrocarbon rubbers, filler agglomerates may take place primarily by contact between aggregates [29, 30]. Figure 5 shows the effects of the chemical treatment on the tensile modulus (M100, M300 and M500, respectively) of the NR vulcanisates. It can be seen that the tensile modulus for sample 15% D HNO_3 is comparable with the controlled silica.

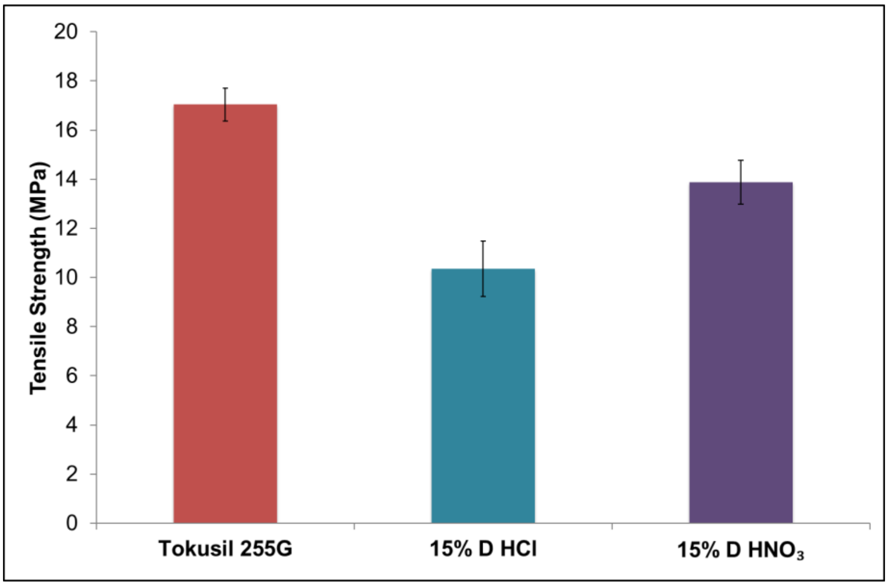


Figure 4. Effect of the chemical treatment on the tensile strength of the NR vulcanisates.

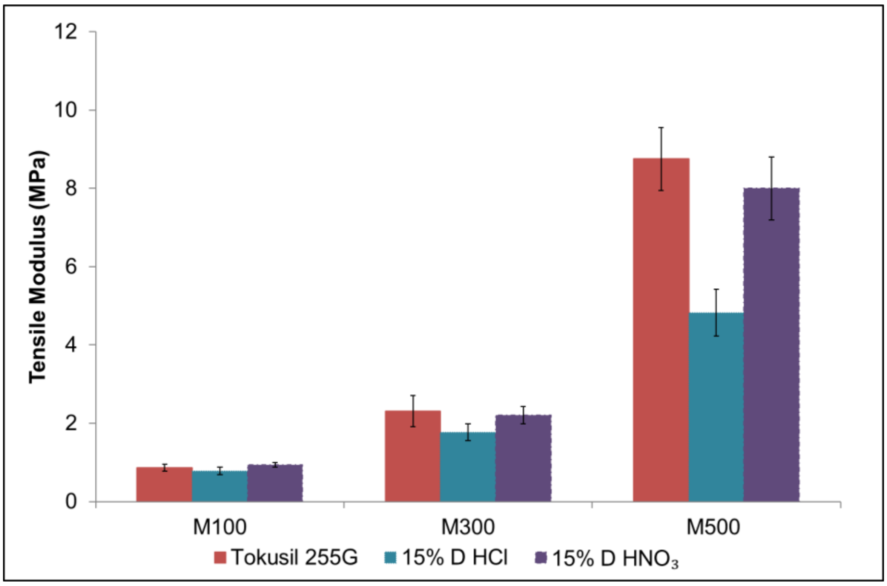


Figure 5. Effect of the chemical treatment on the tensile modulus of the NR vulcanisates.

The reinforcement of elastomers by particulate fillers has been thoroughly investigated in numerous studies. It is generally accepted that this phenomenon is largely dependent on the polymer and filler properties, and their processing methods. Generally, the primary factors of the filler that influenced the reinforcement of the elastomer were: (i) the particle size, which determined the surface area per unit weight and thus, the solid elastomer interface per cm^3 of the composite; (ii) specific surface activity per cm^2 of the surface area; (iii) shape and structure, as determined by the void volume under standard packing conditions; and (iv) particle porosity, commonly referred to as pores, in a very small size [31].

Hardness

Figure 6 shows the effects of the chemical treatment on the hardness of the NR vulcanisates. Both the 15% D HCl and 15% D HNO_3 have higher hardness values compared to the controlled silica. Measured hardness values can also serve to verify the impact of particle size on the resulting properties of the vulcanisates. Here, the hardness value increases as the particle size decreases, indicating a greater number of cross-links. This behavior resembles the hardening of the blend by a vulcanisation system [32]. Furthermore, it was observed that hardness correlates with the surface area and particle size of the fillers.

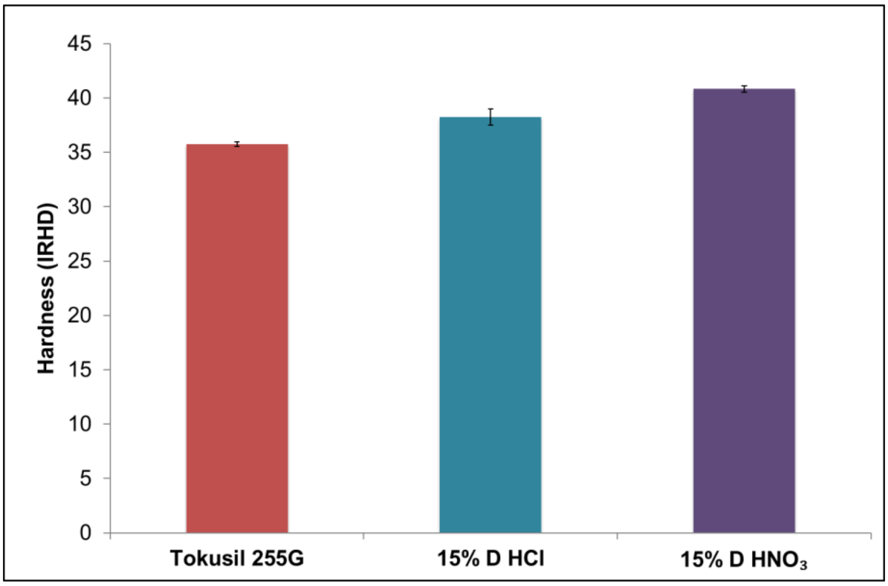


Figure 6. Effect of the chemical treatment on the hardness of the NR vulcanisates.

Composites reinforced with higher surface area and smaller particle sizes demonstrated higher hardness values. This increase in hardness for fillers with higher surface area is attributed to improved filler dispersion, increased interfacial area promoting high interfacial interaction, and enhanced stress transfer from strained polymer chains to filler particles [33, 34].

CONCLUSIONS

The effects of the chemical treatment performed on the RHA on its particle size, curing characteristics and mechanical properties were investigated. The results indicated that treating the RHA with chemicals (digestion and precipitation) significantly decreases its particle size and increases its specific surface area. The cure times (t_{90}) were found to be longer, while the hardness was higher for both the precipitated silica samples, as compared to the commercial silica. The NR vulcanisates with 20 phr of the precipitated silica showed mechanical properties not much inferior to the commercial silica-filled NR composite. Therefore, silica obtained under these conditions has a potential to be used as filler in rubber vulcanisates, due to its extremely low cost, as it can be easily obtained from the by-product of the rice industry.

The challenge in this study lies in selecting a method that produces high-purity silica, as impurities diminish its efficiency as a filler in composites. The impurity level of silica is greatly influenced by the production mode. Enhancing vulcanisate performance can be achieved by modifying the physical and chemical nature of precipitated silica. However, the extent of improvement depends on the ability to control various relevant characteristics of silica. A systematic study from the perspective of filler-polymer interactions is expected to provide a better understanding of significant and relevant parameters.

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