Properties of Rice Husk Ash Silica Filled Natural Rubber and Acrylonitrile-butadiene Rubber Blends

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ABSTRACT

Purpose: Rice husk is burnt and discarded without effective use; however, it is a reliable resource that can be used to extract silica from its ash (RHAS) and can be incorporated in rubber blends as filler. The effect of Natural rubber (NR) and Acrylonitrile-butadiene rubber (NBR) ratio of NR/NBR blends filled with RHAS on physico-mechanical, and swelling percentage in specific oils (brake oil, hydraulic oil, engine oil) and toluene were studied since these blends have potential applications like fluid sealing.

Methodology: RHAS was extracted via sol-gel method and characterized using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopic (FTIR), and Scanning Electron Microscopic (SEM) analyses. NR/NBR blends with different NR to NBR ratios (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) were prepared by incorporating 25 parts per hundred parts of rubber and curing characteristics, physico-mechanical and swelling properties were evaluated.

Findings: The XRD, FTIR, and SEM analyses confirmed that the RHAS contains silica with a combination of nanoparticles and large agglomerates. The blends showed preferable curing characteristics while the hardness, compression set, and tear strength of blends ranged from 60-70 International Rubber Hardness Degrees, 0.5-6%, and 10-20 N/mm, respectively. Although the tensile properties (before ageing) were low, the retention of tensile strength after ageing was better in NR/NBR blends. Blends with high NBR proportion showed tolerable swelling against toluene, hydraulic oil, and engine oil while blends with low NBR proportion showed better swelling resistance to brake oil.

Limitations: Time was limited to evaluate the properties of blends with different loading levels of RHAS.

Value: There is a potential to use these NR/NBR blends in applications like fluid seals which require oil resistance and toluene resistance, where 0.5-6% and about 60-100% swellings are tolerable, respectively, compromising the physico-mechanical properties meanwhile replacing carbon black in respective applications.

Keywords: Acrylonitrile-butadiene rubber (NBR), Equilibrium swelling percentage, Natural rubber (NR), NR/NBR blends, Physico-mechanical properties, Silica extracted from rice husk ash (RHAS)

INTRODUCTION

Rice is a primary source of food for billions of people in the World, and over 90% of the total global rice requirement is produced in the Asian region (Arjmandi *et al.*, 2015). Globally, approximately 760 million tons of rice has been produced in 2019 (Food and Agriculture Organization of the United States, 2020). On average, 20% of the rice is husk (Juliano & Tũaño, 2019), thus it gives an annual total

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production of 152 million tons of husk. While the Global rice production indicates such a large volume of rice production, Sri Lanka has produced approximately 4.6 million tons of rice in 2019 during both 'Yala' and 'Maha' seasons (Central Bank of Sri Lanka, 2020). Therefore, on average, about 0.92 million tons of rice husk (RH) is generated annually in Sri Lanka.

The RH is a valuable resource that is usually used as a fuel for electrical and thermal energy generation (Pode, 2016). Also, it is a reliable and renewable resource for the extraction of silica from its ash (Premaratne *et al.*, 2014). Further, the use of rice husk ash to derive silica is vital and environmentally friendly because it is widely available in paddy cultivating countries around the world, but in most cases; it is discarded as a waste material without effective use (Da Costa *et al.*, 2004). When considering the composition of rice husk ash (RHA), Silica (80%-90%), Alumina (1%-2.5%), and oxides of Calcium, Ferrous, Magnesium, Sodium, and Potassium can be identified (Majumder *et al.*, 2014). This composition of RHA, especially the high content of silica, implies the use of it as an additive in cement and concrete fabrication (Pode, 2016).

Also, silica can be extracted from rice husk ash using different techniques such as sol-gel method which is generally practiced; Indian Institute of Science Precipitated Silica Technology (IPSIT), and chemical pre-treatment with acid or base combined with pyrolysis, thermal treatment, and biological treatment with enzymes, that can be used as green filler in rubber composites (Todkar *et al.*, 2016; Dominic *et al.*, 2020). Ramasamy *et al.*, (2012) have used powdered RH and RHA in Natural Rubber (NR) compounds as fillers and have reported that they have not reinforced the rubber compounds. However, according to Chuayjuljit *et al.*, (2001), the NR compounds filled with silica extracted from RHA have shown better mechanical properties due to their reinforcing ability as carbon black. Further, a significant improvement in thermal, oil, and ozone resistance in silica-filled NR compounds with better mechanical properties have been reported by Arayaprane and Rempel, (2013).

However, mixing of two or more different rubbers into one rubber compound which is called 'rubber

blending' is practiced in the industry to couple the inherent properties of such rubbers into single rubber material, and such rubber blends are used in different applications i.e. tyres, bearings, seals, and other engineering products (Visakh *et al.*, 2013). NR latex which is extracted from *Hevea brasiliensis* (Karunaratne *et al.*, 2005), is converted to raw NR types which are Ribbed Smoked Sheet (RSS), Crepe Rubber, Technically Specified Rubber (TSR), and Centrifuged Latex and these raw NR types are used to make various rubber products (Subramaniam, 2002). Since NR shows better physical properties due to its high molecular weight, strain-induced crystallization, and substantial viscoelastic properties in rubber products, it is widely used in the industry as one of the general-purpose rubbers (De and White, 2001). Usually, NR is blended with specialty rubbers such as acrylonitrile-butadiene rubber (NBR), and polychloroprene rubber (CR), etc. where oil and chemical resistance, and better physico-mechanical properties are required in relevant rubber products i.e. seals and rings, etc (De and White, 2001).

NR/NBR blends are important since they couple specialty properties of NBR with good physico-mechanical properties of NR, and they could be used in special applications where oil and chemical resistance are required (De and White, 2001). According to literature, Ismail *et al.*, (1999) and Yuniari *et al.*, (2017) have found better swelling resistance and hardness in NR/NBR blends having a high content of recycled NBR. El-Nashar and Turkey, (2003) have found better physico-mechanical properties, blend morphology, and improved aging properties of NR/NBR blends. However, according to Inted *et al.*, (2013) the tensile strength and elongation at break of NR/NBR blends have shown lower values though the abrasion resistance is better. According to these studies, the NR and NBR ratio in their blends as well as the incompatibility between NR and NBR phases in such blends can be identified as the reasons for these variations of properties (Salih *et al.*, 2018). As per Kapgate *et al.*, (2015), silica has been used in polar rubber (i.e. NBR) and non-polar rubber (i.e. NR) blends to make them compatible and to overcome the phase separation that occurs due to polarities differences in such rubbers. Therefore, there is a

potential to use rice husk ash silica in NR/NBR blends to improve their properties.

Silica is an inorganic material; hence, it can be incompatible with rubbers that are chemically in organic nature, and therefore, compatibilizers have to be added to improve the compatibility of rubber and silica fillers (Ciesielski, 1999). For example, silane compounds like bis-(triethoxysilylpropyl) tetrasulfide have been used as a compatibilizer in silica-filled NR compounds and better physico-mechanical and dynamic mechanical properties have been observed (Ciesielski, 1999; Saramolee *et al.*, 2016).

The use of this silica filler in NR/NBR blends is more interesting because it could provide better physico-mechanical properties in rubber products, and it may eliminate disadvantageous impacts of using carbon black which is the widely used reinforcing filler in rubber compounds on the environment as well as it could be able to compatibilize the NR and NBR components in their blends (Kapgate *et al.*, 2015; Sattayanurak *et al.*, 2019). Therefore, there is a possibility to use silica in rubber compounds as reinforcement according to the literature. Da Costa *et al.*, (2004) and Carrieri *et al.*, (2020) have mentioned that the replacement of carbon black filler of rubber compounds with silica extracted from RHA is important since the extraction is cost-effective and its use in rubber reinforcement is environmentally friendly than carbon black.

Therefore, it was interesting to investigate the effect of the NR to NBR ratio of NR/NBR blends filled with silica extracted from rice husk ash (RHAS) on their physico-mechanical properties. Especially, the equilibrium swelling percentage of NR/NBR blends in brake oil, hydraulic oil, engine oil, and toluene was interested to study to evaluate the potential of using these blends in such oils and solvent sealing applications respectively, while estimating the possibilities of replacing carbon black using RHAS.

MATERIALS AND METHODS

Materials

Natural rubber, in the form of Ribbed Smoked Sheet (RSS1), NBR (medium acrylonitrile

content), and commercial grade chemicals were used in the composite formulation. All these materials were purchased from Glorchem Enterprise, Colombo, Sri Lanka. Rice husk ash was collected from a clay-brick factory located in Badulla, Sri Lanka.

Extraction of Silica from Rice Husk Ash (RHAS)

The extraction procedure of RHAS was obtained from Premaratne *et al.*, (2014). Firstly, the rice husk ash (RHA) collected from a clay-brick factory was washed with distilled water and maintained at 105 °C temperature in an air circulating oven until obtained a constant weight. Then, dried RHA was burnt at 850 °C for 6 hours in Hobersol Muffle Furnace and cooled overnight to reach room temperature (25 °C). After that, the RHA sample was digested by boiling in 3.0 M NaOH solution for three (03) hours in a round bottom flask keeping the ratio of RHA to NaOH at 1:8 followed by cooling the mixture to room temperature. Then the pH of the mixture was reduced up to pH 2 using 2.5 M H₂SO₄ acid followed by the addition of ammonia to precipitate silica at pH 8.5 at room temperature. Then the mixture was filtered and dried at 120 °C for 12 hours in an air circulating oven. The sample was refluxed with 6.0 M HCl for 4 hours and washed using deionized water repeatedly until the mixture became acid-free. After that, the purified silica was centrifuged at 8000 rpm for 30 minutes and dried at 105 °C for 2 hours. Finally, RHAS was powdered using a mechanical disintegrator.

Characterization of RHAS

X-ray diffraction (XRD) analysis was done using the X-ray diffractometer (RIGAKU, Japan) to confirm the crystallographic nature of RHAS. The RHAS samples were scanned in continuous mode by varying the scanning angle (two theta (2θ)), from 0.50 to 90.0 degrees at a scanning speed of 3 degrees per minute. The Rigaku Data Analysis Software (PDXL Version 2) was used to analyze diffraction data in comparison to the ICDD (International Centre for Diffraction

Data) database embedded in the same software. Further, Scanning Electron Microscopic (SEM) analysis was done using ZEISS GeminiSEM 460 SEM instrument. A Field Emission Scanning Electron Microscopic (FE-SEM) analysis at 10kV was conducted to confirm the crystal sizes of the chemically derived RHAS. Fourier Transform Infrared Spectrophotometer (Bruker, Alpha-T, German) interfaced with OPUS (Version 7.5) software was used for the analysis of RHAS at attenuated total reflectance (ATR) mode at ambient temperature. FTIR spectra of RHAS were collected in frequency from 4000 cm^{-1} to 400 cm^{-1} wavenumbers at the resolution of 4 cm^{-1} wavenumber. All spectra were rationed against the background of the air spectrum.

Preparation of NR/NBR Blends

The formulation for preparing NR/NBR blend compounds was derived referring to the standard

ASTM formulation for oil seals reported in Edirisinghe, (1999). According to the derived formulation, NR was blended with NBR at different ratios followed by compounding with other general compounding ingredients. Table 01 shows the standard ASTM formulation for oil seals (the Control) filled with carbon black, 60 parts per hundred parts of rubber (phr) by weight (Edirisinghe, 1999) and NR/NBR blend compounds with different NR to NBR ratios, and filled with 25 phr of RHAS (treatment). 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 is high (Sattayanurak *et al.*, 2019; Salimi *et al.*, 2009). Therefore, the RHAS loading of NR/NBR blend compounds prepared in this study was kept at 25 phr and the properties of these compounds were compared with the control.

Table 01: Formulation of NR/NBR blend compounds

Ingredient	Activity	Amount (phr)	
		* Control	NR/NBR blend compounds
NBR	Synthetic rubber	100	-
NR:NBR ratio	Synthetic and Natural rubber blend	-	(100:0, 80:20, 60:40, 40:60, 20:80, 0:100)
ZnO	Activator	5	5
Stearic acid	Activator/softener	0.5	0.5
Flectol H	Antioxidant	2	-
Carbon black (CB)(N539)	Reinforcing filler	60	-
TMTD	Primary accelerator	2	2
TBBS	Secondary accelerator	1	1
Sulfur (Insoluble)	Vulcanizing agent	0.5	0.5
DOP	Plasticizer	5	2.5
WSP	Antioxidant	-	2
White oil (Paraffinic)	Plasticizer	-	2.5
RHAS	Silica filler	-	25
TESPT	Coupling agent	-	5
CTP	Vulcanization retarder	-	0.5
DEG	Additive with silica filler	-	1

Note - *Standard ASTM formulation for oil seals (Control) in Edirisinghe and Freakley (1999), Zinc oxide-(ZnO), 1,2-Dihydro-2,2,4-trimethylquinoline-(Flectol H), Tetramethylthiuram disulfide-(TMTD), N-tetrabutyl-2-benzothiazylsulfonamide-(TBBS), Dioctylphthalate-(DOP), 2,2'-Methylenebis[6-(1-methylcycloheyl)-p-cresol]- (WSP), Bis (tetraethoxysilylpropyl) tetrasulfide-(TESPT), N-cyclohexylthiophthalimide-(CTP), Diethylene glycol-(DEG)

The mixing cycle of RHAS containing NR/NBR blend compounds is demonstrated in Table 02(a). To prepare the blends, an open two-roll mill (CT, Thailand) having a 152.4 mm roller diameter was used. When mixing the silane coupling agent (TESPT) with rubber, the temperature of the mill was adjusted to 135 °C followed by cooling down the temperature of the mill up to 70°C when other ingredients were incorporated into the first stage compound. After maturing the first stage compound at room temperature (25 °C) for 24 hours, sulfur and accelerators were mixed using the same two-roll mill, maintaining the mixing temperature below 100 °C. The control

compound was prepared separately as mentioned in Table 02(b).

Properties of NR/NBR Blends

Cure characteristics of blends: Rheographs of NR/NBR blend compounds were obtained using a Moving Die Rheometer (MDR2000 M/S Alpha Technologies, USA) at 150 °C following the ISO 3417:2008 procedure. The scorch time (T_{s_2}), cure time ($T_{c_{90}}$), minimum torque (ML), and maximum torque (MH) of compounds were derived from the rheographs.

Table 02 (a): Mixing cycle of NR/NBR blend compound preparation

Stage of mixing compound	Ingredient	Time (seconds ± 20)	Temperature of mixing (°C)
First stage	NR	0 th	70 $\pm$ 5
	NBR	60 th	
	TESPT	180 th	
	ZnO, Stearic acid, WSP	240 th	70 $\pm$ 5
	DEG	300 th	
	RHAS, White oil, DOP	360 th	
	CTP	450 th	
Second stage	Dump	540 th	<100
	NR/NBR blend	0 th	
	TBBS and TMTD	60 th	
	Sulfur	120 th	
	Dump	180 th	

Table 02 (b): Mixing cycle of control compound preparation

Stage of mixing compound	Ingredient	Time (seconds ± 20)	Temperature of mixing (°C)
First stage	NBR	0 th	70 $\pm$ 5
	ZnO, Stearic acid, Flectol H	120 th	
	DOP	300 th	
	Carbon Black	360 th	
	Dump	540 th	
Second stage	TBBS and TMTD	60 th	<100
	Sulfur	120 th	
	Dump	180 th	

Physico-mechanical properties: The test samples of NR/NBR blend compounds were prepared using the hydraulic hot press machine (CT, Thailand) keeping the temperature and pressure at 150 °C and 20 MPa respectively. The time values of optimum cure ($T_{c_{90}}$) of each compound obtained from the rheographs were considered as the compression time of the test samples. After curing, the test samples were immediately cooled using water to prevent further curing and the samples were conditioned at room temperature for 48 hours before carrying out the physico-mechanical tests. The tensile properties of NR/NBR blend compounds were determined by the tensile testing machine (Instron 3300 Series, USA) at a cross-head speed of 500 mm/min as per ISO 37:2017 procedure using dumb-bell shaped specimens. The aged tensile properties were determined by the ISO 188:2011 test procedure after the aging of test pieces at 100 °C for 24 hours (accelerated aging). The tear strength of compounds was determined by the same tensile testing machine at a cross-head speed of 500 mm/min using angular test pieces according to ISO 34-1:2015 procedure. A manual thickness gauge was used to measure the thickness of the tensile test pieces. The hardness of compounds was determined using Elastocon Digital Hardness Tester (Sweden) following the ISO 48-2:2018 test procedure. The compression set of the blend compounds was measured according to the ISO 815-1:2019 test method.

Equilibrium swelling percentage: The equilibrium swelling percentage of compounds was measured according to the ASTM D-471 test method. The swelling test was performed by immersing the specimens in toluene, engine oil, hydraulic oil, and brake oil (Glycol-based). The swelling property of samples was expressed as the percentage of the original mass of the sample (Ramesan *et al.*, 2005).

Statistical analysis: General Linear Model (GLM) with Tukey's all pairwise comparison tests at 95% confidence interval in Minitab 18 statistical software was used for the data analysis.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

Figure 01 shows the X-ray diffractograms of RHAS (before and after purification). The characteristic narrow two theta (2θ) peak for silica at 21.6 degrees proved that the RHAS sample contained crystalline silica (SiO_2) structures. Almost the same result for rice husk silica has been observed by Rivas *et al.*, (2016). According to their study, such crystallinity could occur in rice husk silica once it is heated in the muffle furnace at high temperatures beyond around 800 °C for a longer time. The powder diffraction analysis was conducted using PDXL (Version-2) software fitted the RHAS samples with the ICDD (International Centre for Diffraction Data) database card 01-077-1317 with the figure of merit (FOM) of 0.695 designating that the low-Cristobalite synthetic structures of silica were available in RHAS. The other peaks in the RHAS samples were due to Thenardite, the Na_2SO_4 according to ICDD database card 01-074-2036. The resulting Thenardite in RHAS samples can be attributed to the existence of residual sodium sulfate crystals formed from the reaction between sodium silicate and sulphuric acid. Premaratne *et al.*, (2014) have reported that multiple peaks are due to the remaining Na_2SO_4 crystals and due to some other forms of silica. The space group and crystallinity of the low-Cristobalite synthetic structure of SiO_2 in RHAS were P41212 and 99.1% according to the analysis, respectively. Also, Singh *et al.*, (2008) have found the same diffraction pattern for silica and have reported that the 2θ peak which occurs around 22 degrees is due to silica compounds.

Figure 01: X-ray diffractogram of RHAS (before and after purification)

Table 03 demonstrates the 2θ values, Miller indices (h, k, l), and lattice parameters of the low-Cristobalite synthetic structure of SiO_2 in RHAS. Almost the same finding as the obtained results of this study has been observed by Saceda *et al.*, (2011). According to their study, sharp peaks for RHAS at 2θ values of 20.9, 21.9, 26.6, 31.4 and 36.0 degrees have been attributed to crystalline forms of silica. However, the average crystalline grain size calculated for RHAS using the Scherrer formula was 20 nm.

According to Gutiérrez-Castorena and Effland, (2010), the low-Cristobalite is a tetrahedral three-layer structure of SiO_2 produced at high temperatures, and it can be attributed to the application of high heat at 800 °C temperature for 6 hours on RHA using the muffle furnace. Therefore, it can be proved that the low-Cristobalite synthetic structure of SiO_2 with a particle size of 20 nm has been extracted from RHA successfully.

Table 03: Two theta values, Miller indices and lattice parameters of RHAS

Bragg's angle (2θ , in degrees)	Miller indices (h, k, l)	Lattice parameters	
		Lattice vectors	Angle between lattice vectors
21.6	1,0,1	a, b and c are 5.0078, 5.0078 and 6.9961 Å respectively and satisfies $a=b \neq c$	α , β and γ are 90.0, 90.0 and 90.0 degrees respectively and satisfies $\alpha=\beta=\gamma$
28.1	1,1,1		
31.2	1,0,2		
35.9	2,0,0		
42.3	2,1,1		

Note: These data were obtained from ICDD, database card 01-077-1317

Scanning Electron Microscopic (SEM) Analysis

SEM images were taken at 10 kV to comprehend the morphology and the particle size of RHAS and they elucidate an agglomeration of RHAS particles due to the inherent surface activity as shown in Figure 02 (a), (b), (c), and (d). Hence, they have not shown clear boundaries as per their agglomerated and amorphous

structure (Premaratne *et al.*, 2014). However, at a magnification of 50 kX, Figure 02 (e) shows some RHAS particles ranging in size from 82.0 nm to 103.9 nm, implying that the RHAS contains particles ranging in size from 82.0 nm to 103.9 nm on average and they are almost homogeneous in size, with some agglomerated particles having larger sizes.

Figure 02: Scanning electron microscopic images of RHAS at different magnifications, (a) at 5.0kX, (b) at 15.0kX, (c) at 20 kX (d) at 25 kX, and (e) at 50 kX magnifications

Fourier Transform Infrared Spectroscopy (FTIR) Cure Characteristics

The FTIR spectrum of RHAS is shown in Figure 03. Broadband in the range around 3800–3000 cm^{-1} wavenumbers can be observed and that is due to the stretching and vibration modes of hydroxyl (-OH) groups of silanol groups and adsorbed water molecules present on the silica surface (Somaratne *et al.*, 2014; Premaratne *et al.*, 2014). The peak at 1639 cm^{-1} wavenumber is due to the bending vibration mode of hydroxyl bonds in the adsorbed water molecules (Zhou *et al.*, 2002; Somaratne *et al.*, 2014; Premaratne *et al.*, 2014). These features have indicated the hydrophilic nature of RHAS. Also, the peaks at 1085 cm^{-1} and 795 cm^{-1} wavenumbers can be attributed to the asymmetric and symmetric stretching vibration modes of the Si-O-Si bonds, respectively, while the peaks at 494 cm^{-1} and 465 cm^{-1} wavenumbers demonstrate the bending vibration of the Si-O-Si bonds (Guo *et al.*, 2008; Somaratne *et al.*, 2014). The stretching vibration mode of the Si-OH bond is represented by the wavenumber of 958 cm^{-1} . Accordingly, it could be reported that silica has been extracted from RHA successfully.

The cure characteristics of the NR/NBR blends are represented in Table 04. The lowest torque (ML) values are considerably lower in NR/NBR blends. The ML values are an indication of stock viscosity and hence, the processability of compounds has slightly increased when the proportion of NBR is increased in the blends. The highest torque (MH) value which is an indication of the state of crosslinking has increased with the increase of NBR proportion in blends. The delta torque (MH-ML), which is an indicator of the crosslink density of rubber vulcanizates has increased with the increase of NBR content in blends. Therefore, it is understandable that the stock viscosity, state of crosslinking, and cross-link density have increased when the NBR percentage in NR/NBR blends is increased (El-Sabbagh and Yehia, 2007). Further, the polar nature of silica and NBR could improve the compatibility between them compared to that of non-polar NR and silica. Also, this behavior can be attributed to the increase in the torque properties of the vulcanization process (Yuniari *et al.*, 2017).

Figure 03: Fourier transform infrared spectrum of RHAS

Table 04: Cure characteristics of NR/NBR blend compounds

NR:NBR ratio	Lowest torque (ML) dNm	Highest torque (MH) dNm	Delta cure (MH-ML) dNm	Ts ₂ (s)	Tc ₉₀ (s)	Cure rate index (s ⁻¹)
*Control	1.8	25.1	23.3	117	395	0.4
100:0	0.1	10.0	9.8	60	228	0.6
80:20	0.2	10.6	10.3	55	225	0.6
60:40	0.3	11.0	10.6	59	225	0.6
40:60	0.3	14.3	14.0	63	375	0.3
20:80	0.5	13.1	12.5	69	331	0.4
0:100	0.8	16.8	15.9	62	300	0.4

*Note: Control is purely an NBR compound filled with 60 phr of carbon black

The scorch time (Ts₂) which indicates the processing safety is around 60 seconds in all the blend compounds. The control sample, which has carbon black (60 phr) as the reinforcing filler, has shown the highest scorch time (117 seconds) compared to that of all the blends. The addition of silica into NR/NBR blends has shown a significant reduction in scorch time. This phenomenon has been attributed to reactions between silica and vulcanization accelerators in the compounds (Chuayjuljit *et al.*, 2001). Similarly, a reduction of cure time (Tc₉₀) can be observed in blends compared to the control (395 seconds). However, the Tc₉₀ values are sufficient for the vulcanization of blends. Also, when the NBR percentage is increased, the Tc₉₀ of blends has increased due to the degree of unsaturation of NBR that is lesser than NR (Ivanoska *et al.*, 2017). The cure rate index of NR/NBR blends is reduced when the NBR proportion is increased and according to the literature, this is due to faster vulcanization of NR than NBR where the degree of unsaturation of NR is higher than NBR which contains different proportions of acrylonitrile (Ivanoska *et al.*, 2017).

Physico-mechanical Properties

Hardness: Figure 04 shows the hardness of NR/NBR blends filled with 25 phr of RHAS.

According to Figure 04, the highest hardness is shown by the control (73 IRHD), while all the NR/NBR blends show slightly less hardness compared to the control. The hardness of NR/NBR blends ranges from 57 IRHD to 67 IRHD. It is observed that the hardness has reduced slightly from 62 IRHD (NR: NBR 100:0) to 57 IRHD (NR: NBR 60:40) when the NR content of blends is reduced by 40 phr. Thereafter, the hardness has increased with the decrement of NR content in the blends. This hardness variation can be attributed to the change of continuous phase of blends from NR to NBR after the NR:NBR 60:40 blend (Edirisinghe, 1999). The increase in hardness from NR:NBR 40:60 blends to NR:NBR 0:100 can be attributed to the high stiffness of NBR (Edirisinghe & Freakley, 2010). Also, this trend is in accordance with the MH values obtained in the rheographs (Table 04). Edirisinghe & Freakley, (2010) have reported that the polarity due to -CN groups in NBR and the formation of the network between fillers and other polar compounds in the mixture could increase the hardness of NBR containing blends. Further, Omran *et al.*, (2010) have observed hardness around 60 IRHD for NR/NBR blends used for oil-resistant articles. Also, George *et al.*, (2006) have investigated the hardness of NR/NBR blends and have received hardness values of around 70 Shore A due to the use of epoxidized natural rubber in compounds. According to the results and literature, these

blends have the potential to be used in products requiring average hardness values of 55 IRHD and 70 IRHD.

Compression Set: The compression set is related to the viscous nature of rubber vulcanizates. The higher compression set values denote higher deformation under prolonged strains and vice versa. Figure 05 represents the compression set of NR/NBR blends. As expected, the compression set is reduced when the proportion of NBR in

blends is increased. The control sample has shown a compression set of 4% and it is not significantly different from the blends having NR:NBR ratio at 40:60, 20:80, and 0:100. The lower compression set values are preferred in seals varying between 1-3% in NBR/poly (chloroprene) rubber blends (Omran *et al.*, 2010). Also, this behavior can be observed due to the higher stiffness of NBR and the presence of polar cyanide ($-\text{CN}$) groups in NBR (Edirisinghe & Freakley, 2010).

Figure 04: Variation of hardness of NR/NBR blends

Figure 05: Variation of compression set of NR/NBR blends

Tensile properties: To study the extensional properties of NR/NBR blends, the tensile strength and elongation at break were measured. The tensile strength of NR/NBR blends (before and after aging) is shown in Figure 06 (a). Lower tensile strengths have been achieved in all the blends compared to that of control. A similar observation has been found by Inted *et al.*, (2013) due to weak interaction between the phases of the blends.

Compared to the control, the addition of 25 phr of RHAS to the NR/NBR blends has significantly affected the tensile strength. The particle agglomeration can be attributed to this inferior reinforcement and comparatively lower tensile properties (Kapgate *et al.*, 2015). After the accelerated aging of rubber vulcanizates (Figure 06 (b)), the tensile strength of blends has approximately been reduced by 10% and it can be accepted in rubber compounds as a good aging property.

Figure 06 (c) shows the elongation at break (before and after aging) of NR/NBR blends. The control sample has shown about 180% and 160% elongation at break for before aging and after aging respectively, and those are the maximum values in the sample series. The NR:NBR 60:40 sample has shown elongation at break around 170% and 140% for before and after aging respectively, while the minimum elongation at break belongs to the NR:NBR 100:0 sample (< 100% for both before and after aging). However, NR:NBR 40:60, NR:NBR 20:80, and NR:NBR 0:100 have indicated around 100% elongation at break in both conditions without a significant variation. Overall, the elongation at break of the NR/NBR blends has shown comparatively low values and this could be attributed to less reinforcement of blends by RHAS due to particle agglomeration (Kapgate *et al.*, 2015; Inted *et al.*, 2013).

Figure 06: Tensile strength (a), retention of tensile strength after aging (b), elongation at break (c) of NR/NBR blends

Tear strength: The resistance to initiate and to propagate a crack is measured by the tear strength. Figure 07 shows the variation of the tear strength of NR/NBR blends. The control sample has shown the highest tear strength (42 N/mm) and that of NR/NBR blends range from 10-23 N/mm. The increase of NBR content in the blends has affected the reduction of tear strength compared to the NR:NBR 100:0 blend according to the results. Therefore, the reduction of the NR proportion in blends which provides strength

properties, and the weak interfacial crosslinks existing between NR and NBR proportion of blends could be the reason for this behavior (Edirisinghe and Freakley, 2010).

Swelling Properties

Figure 08 shows the equilibrium swelling (%) of NR/NBR blends in toluene, engine oil, hydraulic oil, and brake oil (glycol based), respectively.

Figure 07: Variation of tear strength of NR/NBR blends

Figure 08: Variation of equilibrium swelling (%) of NR/NBR blends

Figure 08: Variation of equilibrium swelling (%) of NR/NBR blends

Equilibrium swelling (%) of NR/NBR blends in toluene: Toluene was used as a representative organic solvent to study the swelling behavior of NR/NBR blends in low molecular weight organic solvents. The control has shown around 64% of equilibrium swelling (%) in toluene while the blend of NR:NBR 100:0 and NR:NBR 80:20 shows the highest values of around 94% without a significant difference of equilibrium swelling (%). The blends with NBR proportion of 80 and 100 have shown equilibrium swelling (%) around 70% and 65% being the least values respectively. However, the equilibrium swelling (%) in toluene has reduced dramatically when the proportion of NBR in the blends is increased and this can be attributed to the swelling resistance of NBR in toluene like non-polar organic solvents (Omran *et al.*, 2010).

Equilibrium swelling (%) of NR/NBR blends in engine oil and hydraulic oil: Engine oil and hydraulic oil have shown a less equilibrium swelling of all the blends compared to that in toluene. The equilibrium swelling (%) in engine oil and hydraulic oil varied between 1-10% and 0.5-16% respectively. The blends with an NBR ratio of 0 to 40 have shown the variation of equilibrium swelling (%) in engine oil between 8-10% and they are not significantly different from each other. The NR:NBR 20:80 and NR:NBR 0:100 have shown the least equilibrium swelling (%) in engine oil, which is not significantly different from that of the control (2%). Therefore, it can be reported that the

RHAS filled NR:NBR blends which have high NBR content can withstand engine oil which has a broad molecular weight distribution in terms of swelling resistance (Omran *et al.*, 2010). The highest equilibrium swelling (%) in hydraulic oil (around 16%) is shown by NR:NBR 100:0 and NR:NBR 80:20 blends. Similar to engine oil, a dramatic decline of equilibrium swelling (%) can be observed with the increase of NBR ratio in the blends. The blends having an NBR proportion of 80 and 100 have shown the minimum equilibrium swelling (%) in hydraulic oil (1.3% and 0.3% respectively), while the control shows 0.6% equilibrium swelling (%). The resistance to swelling of NBR in non-polar liquid can be attributed to this behavior (Edirisinghe & Freakley, 2010; Omran *et al.*, 2010).

Equilibrium swelling (%) of NR/NBR blends in brake oil: In the glycol-based brake oil, the blends have shown an increasing trend for equilibrium swelling (%). This can be attributed to the change of the matrix from hydrophobic to hydrophilic by the RHAS, where the swelling is encouraged by hydrophilic liquids such as glycols (Senthilathiban *et al.*, 2016). Equilibrium swelling (%) ranges from 1.2-7.2% in blends from NR:NBR 100:0 to NR:NBR 0:100. The blends with high NBR proportion have shown high equilibrium swelling (%) in brake oil (glycol based), while the control shows the highest (8.5%). The polarity of glycol-based oil could be one reason for the higher swelling of NBR-rich

blends and also the polar nature of RHAS in the blends could affect this behavior (Easton, n.d.).

blends, and the effect of different loading levels of surface modified RHAS in NR/NBR blends on the properties have to be studied.

CONCLUSIONS

The rubber ratio of NR/NBR blends has affected the physico-mechanical properties and swelling properties within acceptable ranges. Also, there is a possibility to use rice husk ash silica (RHAS) in NR/NBR blends for reinforcement, when considering the properties such as hardness, compression set, elongation at break, tear strength and equilibrium swelling percentage. Overall, these blends can be used in applications such as non-marking and non-dynamic rubber articles requiring oil resistance (in engine oil, hydraulic oil and brake oil) and toluene resistance, where the 0.5-6% and 60-100% swells are tolerable respectively, while maintaining the physico-mechanical properties.

As a limitation to be addressed in future works, it can be mentioned that the surface modification of RHAS before incorporating it into NR/NBR

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Conflicts of Interest

The authors declare that there is no conflict of interest for this study.

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