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ORIGINAL PAPER

Rice husk fibers and their extracted silica as promising bio-based fillers for EPDM/NBR rubber blend vulcanizates

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Abstract
Bio-based natural wastes could be considered eco-friendly alternatives to conventional fillers for enhancing the properties and reducing the cost of final rubber products. Thus, in the present research, EPDM/NBR rubber blend composites filled with kaolin and mixed with rice husk fibers (RHFs) were prepared. Homogeneity of the EPDM/NBR blends was improved by the incorporation of maleic anhydride (MAH) as a compatibilizing agent (1 phr), as evidenced by scanning electron microscopy (SEM). Of all EPDM/NBR blend ratios investigated, the 25/75 blend revealed good mechanical properties, thermal stability, and the least weight swell at equilibrium (Q%) in motor oil and brake fluid. EPDM/NBR/kaolin (25/75/30) blend vulcanizates containing RHFs at various loadings demonstrated a significant improvement in swelling resistance, primarily in motor oil and brake fluid, accompanied by a slight reduction in the mechanical properties at high RHFs content. That was complemented by the enhancement of thermal stability of the rubber blends, as demonstrated by TGA analysis. Among the filler types investigated (RHFs, silica ash (SA), rice husk silica (RHS), and kaolin), RHFs exhibited the best swelling resistance of the composite vulcanizates in motor oil and brake fluid. In addition, RHS could be used successfully as a supporting filler for carbon black-reinforced EPDM/NBR composite vulcanizates because it enhanced their thermal stability and swelling resistance in the motor oil.

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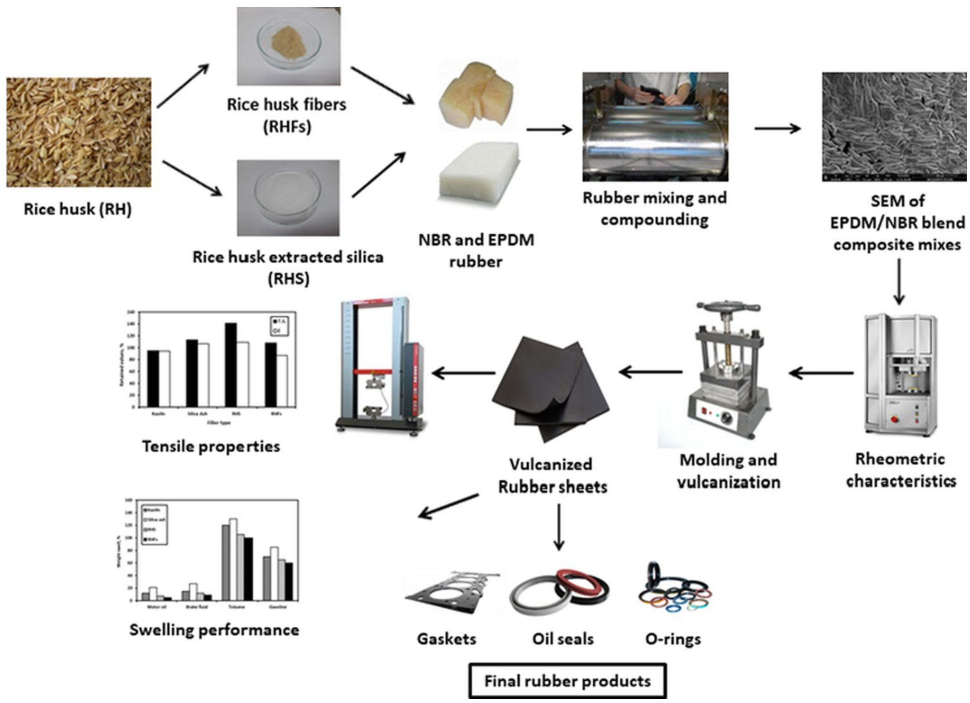
Graphical Abstract



Keywords EPDM/NBR rubber blend · Rice husk · Swelling resistance · Thermal stability · Mechanical properties

Introduction

In rubber applications, it is necessary to blend two polymer types in order to get the desired physico-mechanical properties and good swelling behavior that meet certain product specifications. Nitrile rubber (NBR) has excellent oil resistance but it is subjected to degradation at high temperatures. A more practical useful approach to improve NBR aging resistance is its blending with ethylene propylene diene monomer rubber (EPDM) which has good melt processability, thermal stability, and excellent ozone-resistant properties (Antunes et al. 2009). Therefore, EPDM/NBR blend vulcanizates have shown good mechanical properties with improved thermal stability as well as good oil resistance. Generally, EPDM and NBR are incompatible on the microstructure scale. Various compatibilizing agents have been examined to improve their compatibility (Mayasari and Setyadewi 2018; Soares et al. 2002; Mayasari et al. 2020). Maleic anhydride (MAH) has been frequently used as a compatibilizer for both types of rubber due to its high reactivity with thermoplastic elastomers upon mixing at room temperature. From our previous work, EPDM grafted with MAH, acrylic acid, and acrylic esters have successfully been used as compatibilizers for NBR/EPDM rubber blends (Botros and Tawfic 2006; Botros and Moustafa 2002, 2003; Botros et al. 2009). Recently, the physico-mechanical properties and swelling performance of EPDM/NBR rubber blends compatibilized with MAH have been improved significantly upon addition and increasing the content of halloysite nanotubes (HNTs) in the blends (Paran et al. 2023).

Nowadays, bio-based natural wastes could be regarded as green alternatives to replace conventional and relatively expensive fillers for improving the properties and lowering the cost of the rubber product since they meet the standards of environmental protection and sustainable development. Natural fibers derived from agricultural waste are finding their way into the polymer industry due to numerous benefits such as light weight, low cost, and environmental friendliness (Islam et al. 2015). Among the natural wastes that cause environmental pollution upon burning are rice husk fibers (RHFs). Due to their high cellulosic and silica content, RHFs have attracted the attention of researchers for their use as an alternative or supporting filler in the rubber industry (Khalaf and Ward 2010). In order to accomplish a desired combination of properties and cost reduction, the main task is the partial replacement of conventional reinforcing fillers (carbon black and silica), used in the rubber industry, with readily available and inexpensive agricultural waste materials like RHFs. Due to its high silica content (≈ 83%), rice husk ash (RHA) is considered a natural source for the production of silica. EPDM/NBR blends reinforced with various types of nanofiller have been investigated, including nanoclay (Ghassemieh 2009), organoclays (Ersali et al. 2012), and nanosilica (Jovanovic et al. 2013).

Rice husk ash (RHA) has also been successfully used as a new alternative filler for natural rubber (NR)/EPDM blends to improve the compression set and hardness properties of the rubber products (Rahmaniar 2019). Although RHA has poorer reinforcing ability than silica, it has provided better mechanical properties than $CaCO_3$. Therefore, RHA could be used as a nonreinforcing filler to replace $CaCO_3$ in rubber blends for economic and ecological reasons (Arayapranee and Rempel 2008). Improvements in the tensile properties and thermal stability of NR composites containing RHS have been observed. Further improvement was recorded by surface modification of RHS with bis(triethoxysilyl propyl) tetrasulfide and/or NaOH and liquid epoxidized natural rubber (LENR), which increased the interaction between RHS and the NR matrix (Salim et al.; 2019; Syafri et al. 2011). NR composites reinforced with marble sludge (MS)/RHS mixed filler have exhibited good mechanical and swelling properties at a low cost and could be used instead of general-purpose fillers like china clay, calcium carbonate, and talc (Ahmed et al. 2014). NBR reinforced with cement waste and RHS has shown improvement in modulus of elasticity with a decrease in elongation (Al-Mosawi et al. 2017). Additionally, NBR-RHA composite material with good thermal stability, low electrical conductivity, and high dielectric properties has been prepared. That composite could be used as a semiconducting material (Mohamed et al. 2009). Silica-rich red brick waste (RBW) powder/NBR eco-friendly composites have been used for insulation and antistatic applications (Shafik et al 2022). Silica extracted from RHFs has also been used as a combined filler with carbon black for NBR rubber (Bandara et al. 2020). Recently, EPDM composites reinforced with nano-size rice husk powder (nRHP) have possessed improved mechanical and dielectric properties and could be used in electrical insulation applications (Amin et al. 2018).

The aim of the present research is to utilize rice husk fibers (RHFs) and rice husk silica (RHS) agro-waste materials as supporting fillers in rubber blend composite vulcanizates, as well as evaluate their physico-mechanical properties and swelling behavior in automotive oils and solvents, for environmental protection against pollution resulting from the burning of agro-waste materials. For this purpose, EPDM/NBR blend formulations were designed using RHFs and RHS as supporting fillers for application in automotive rubber products (e.g., oil seals, gaskets, hoses, automobile spare parts, and O-rings). The compatibility of EPDM with NBR using various MAH loadings as a compatibilizer was investigated. The effects of different EPDM/NBR blend ratios, RHFs loadings, and filler types on the curing characteristics, physico-mechanical properties, as well as swelling performance in motor oil, brake fluid, toluene, and gasoline were also studied. Moreover, the influence of RHS as supporting filler for carbon black-reinforced EPDM/NBR blend vulcanizates was examined.

Experimental

Materials

Ethylene propylene diene monomer rubber (EPDM–Buna EPT 9650) of 53% ethylene and 6.5% ethylidene norbornene (ENB) contents, and 63 Mooney viscosity (ML 1 + 4125°C). It is a product of LANXESS Buna, Germany. Butadiene acrylonitrile rubber (NBR-Krynac 3345) of 33% acrylonitrile content and 45 Mooney viscosity (ML 1 + 4100°C) is a product of BAYER Chemical Company, Germany. The maleic anhydride (MAH) compatibilizer is from SISCO Research Laboratories PVT Ltd, India. Rice husk was collected from farms in Alexandria. High abrasion furnace (HAF) carbon black N330 (CB) was a product of Hangzhou Epsilon Chemical Co., Ltd., China. Kaolin of commercial grade was supplied from Transport and Engineering Co., Alexandria, Egypt. The curing of rubber composites was carried out using sulfur (S) and N-cyclohexyl-2-benzothiazole sulfenamide (CBS) curing system. The other compounding rubber ingredients are of commercial grades used in the rubber industry, such as zinc oxide (ZnO) and stearic acid activators, and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) antioxidant, which are supplied from Transport and Engineering Co., Alexandria, Egypt. The motor oil (Mobil Super 15W-50 XHP) is a product of ExxonMobil, and the brake fluid (Bendix DOT 3) is a product of Al-Manar Company under the license of Garret Transportation I Incorporation, USA. All other chemicals are of pure grade and were used as received.

Preparation of the rice husk raw material

The rice husk raw material was collected, washed several times with distilled water to remove its associated impurities, dried, and then subjected to mechanical grinding and sieved to the smallest mesh size of 300 (≈ 44 microns) to get the rice husk fibers (RHFs) in powder form.

Extraction and isolation of silica from the rice husk raw material:

The rice husk raw material was burned in a muffle at 600 °C for 3 h. Then, the resulting silica ash (SA) was treated with HCl to remove the insoluble inorganic salts, followed by refluxing with NaOH solution to dissolve the silica as sodium silicate. The filtrate was then neutralized with HCl to pH = 10.5 to form silica gel, and left for 72 h to complete precipitation and isolation of silica (El-Sakhawy et al. 2020; Ahmed et al. 2020).

Mixing, rheological properties and vulcanization of EPDM/NBR rubber blends

EPDM and NBR rubbers were mixed with other compounding ingredients and curatives onto an open two-roll mill of 170-mm diameter, 300-mm working distance, and 24 rpm speed of slow roll at a 1:1.25 gear ratio according to ASTM D3182-21a. The base recipe for all rubber formulations in this study contains: ZnO 5 phr, stearic acid 2 phr, antioxidant (TMQ) 1 phr, CBS 1 phr, and S 2 phr (parts per 100 parts of rubber). In the first stage, EPDM was masticated onto the two-roll mill for 2 min, then MAH and NBR were successively added to the EPDM, and mixing was continued for 3 min. ZnO, stearic acid, and TMQ antioxidant were subsequently added and mixed for 2 min. for each component. Then, the fillers under investigation were incorporated into the rubber blend and mixed for 5 min. Finally, the curative ingredients (CBS and S) were subsequently added to the rubber mixes and mixed for 2 min. for each component. Rheological characteristics of the rubber mixes were assessed by using moving die rheometer MDR–one rheometer (TA Instrument), at 152 ± 1 °C according to ASTM D2084-19a. The following parameters were determined: maximum torque (M_H), minimum torque (M_L), scorch time (ts_2), optimum cure time (tc_{90}), and cure rate index (CRI). Then, the rubber blend mixes were vulcanized at their optimum cure times (tc_{90}) by the aid of a hydraulic press in a clean polished mold (15 cm × 15 cm × 0.2 cm) under a pressure of 4 MPa at 152 ± 1 °C. The cure rate index was calculated according to the following equation:

$$CRI = \frac{100}{tc_{90} - ts_2}$$

Table 1 Rice husk and rice husk ash composition by XRF analysis

Main constituents	Rice husk (RHFs)	Rice husk ash (RHA)
SiO_2	15.43	82.93
TiO_2	–	0.02
Al_2O_3	0.1	0.34
MnO	0.02	0.06
Fe_2O_3	0.07	0.14
MgO	0.07	0.52
CaO	0.29	1.04
Na_2O	0.04	0.27
K2O	0.54	2.21
P_2O_5	0.10	0.57
SO_3	0.19	0.33
Cl	0.08	0.22
Loss on ignition (LOI)	83.08	11.36

Characterization

Gravimetric analysis

Chemical composition of the rice husk fibers (RHFs) was determined using chemical treatment and gravimetric analysis for determination of its main constituents.

X-ray fluorescence (XRF)

Silica content in the rice husk ash (RHA) was determined using X-ray fluorescence (XRF) analyzer (Type: Axios Advanced, Sequential WD-XRF spectrometer, PANalytical 2005, Netherlands).

FTIR spectroscopy

Chemical structure and main functional groups of the rubbers (EPDM and NBR), RHFs and their extracted silica (RHS) were investigated using FTIR spectroscopy. The spectra were recorded at a wavenumber range of 4000–400 cm^{-1} with JASCO FTIR-6100E, Japan.

Scanning electron microscopy (SEM)

Homogeneity of the rubber blend mixes was examined by scanning electron microscope, Model JXA-840A (JEOL Technics Co. Ltd., Tokyo, Japan) at a magnification M = 1000×. The surface of the samples was coated with gold using the sputtering technique prior to SEM observations.

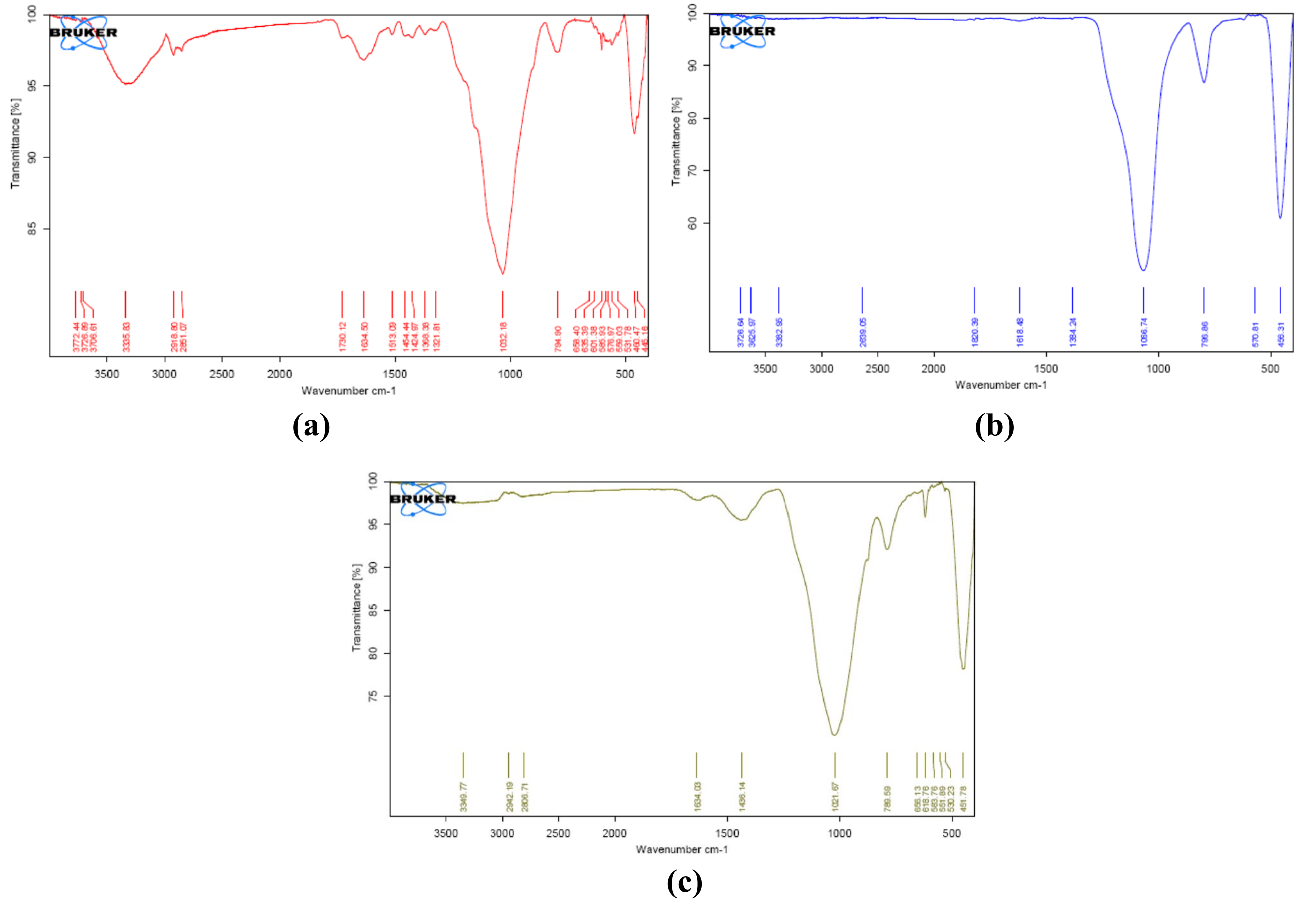


Fig. 1 FTIR spectra and of **a** rice husk fibers, **b** rice husk silica, and **c** commercial silica

Thermal gravimetric analysis (TGA)

Thermal stability of the rubber composites was evaluated using thermogravimetric analysis (TGA, TA instrument 2910 series). The samples (≈10 mg) were placed in a corundum dish, and the measurements were conducted at a heating rate of 10 °C/min in nitrogen atmosphere from ambient temperature up to 700 °C.

Physico-mechanical properties of EPDM/NBR blend composite vulcanizates

Sheets of the EPDM/NBR rubber blend composite vulcanizates were cut into dumbbell-shaped specimens (5 cm long and 0.4 cm wide), using an ASTM cutter. The thickness of each specimen was measured using a standard thickness gauge. Physico-mechanical properties (tensile strength, MPa, and elongation at break, %) of the rubber blend composite vulcanizates were determined, after and before accelerated thermal aging, utilizing a Zwick/Roell Z010 tensile tester machine with load cell (Type: Xforce P and Nominal force: 10 KN), according to ASTM D412-16 (2021). The physico-mechanical data were measured in five replicates for the average. Accelerated thermal aging was carried out in an air-circulated oven at 90 °C, for 7 days according to ASTM D573-04 (2019). The retained values of tensile strength (TS) and elongation at break (E %), after thermal aging, are calculated according to the following equations:

$$\text{Retained Tensile strength } (\%) = \frac{\text{TS (after aging)}}{\text{TS (before aging)}} \times 100$$

$$\text{Retained Elongation at break } (\%) = \frac{E\,\%\ \text{(after aging)}}{E\,\%\ \text{(before aging)}} \times 100$$

Swelling tests and crosslink density

Swelling behavior of the rubber blend composite vulcanizates was assessed by measuring their weight swell at equilibrium (Q%) in the automotive oils (motor oil and brake fluid), gasoline, and toluene. The swelling test in toluene

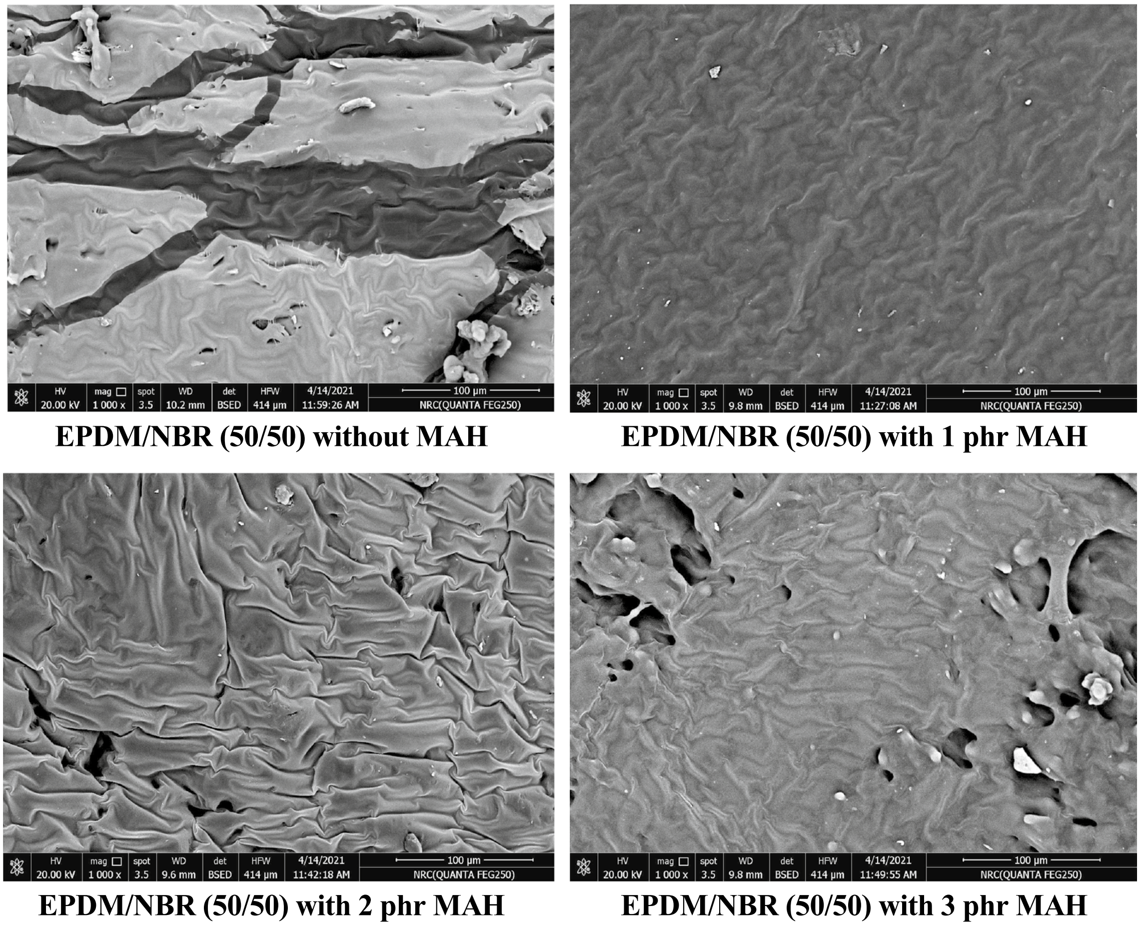


Fig. 2 SEM of EPDM/NBR (50/50) blend mixes in the presence and absence of different MAH loadings. Magnification = 1000×

and gasoline was conducted at 25 °C for 48 h, according to ASTM D471-97. On the other hand, weight swell at equilibrium (Q %) of the vulcanizates in motor oil and brake fluid was conducted at 100 °C for 7 days. It was measured and calculated according to the following equation:

$$Q\% = \frac{W_s - W_d}{W_d} \times 100$$

where W_s is the weight of the specimen after swelling, and W_d is the weight of the dry specimen. The average of five replicates was considered.

The equilibrium swelling in toluene was used to determine the crosslink density of the rubber vulcanizates and was calculated using the Flory–Rehner equation as follows:

$$M_c = -\frac{\rho V_s V_r^{\frac{1}{3}}}{\left[\ln\left(1 - V_r\right) + V_r + XV_r^2\right]}$$

where M_c is the molecular weight between two successive crosslinks (g/mol), ρ is the rubber density (mol/m^3), X is the polymer–solvent interaction parameter, V_s is the molar volume of the solvent (m^3/mol), and V_r is the volume fraction of polymer in swollen state obtained from masses and densities of rubber and solvent. The rubber-solvent interaction parameter (X) is 0.39 for NBR and 0.49 for EPDM. The crosslink density (v) is calculated from the following equation:

$$v = \frac{1}{2M_c}$$

Results and discussion

Characterization of the rice husk fibers (RHFs)

The chemical composition of rice husk fibers (RHFs) was determined using gravimetric chemical analysis. The results showed that RHFs' main constituents are as follows: Cellulose 36.2, Hemicellulose 21.2, Lignin 25.3, Ash 15.4,

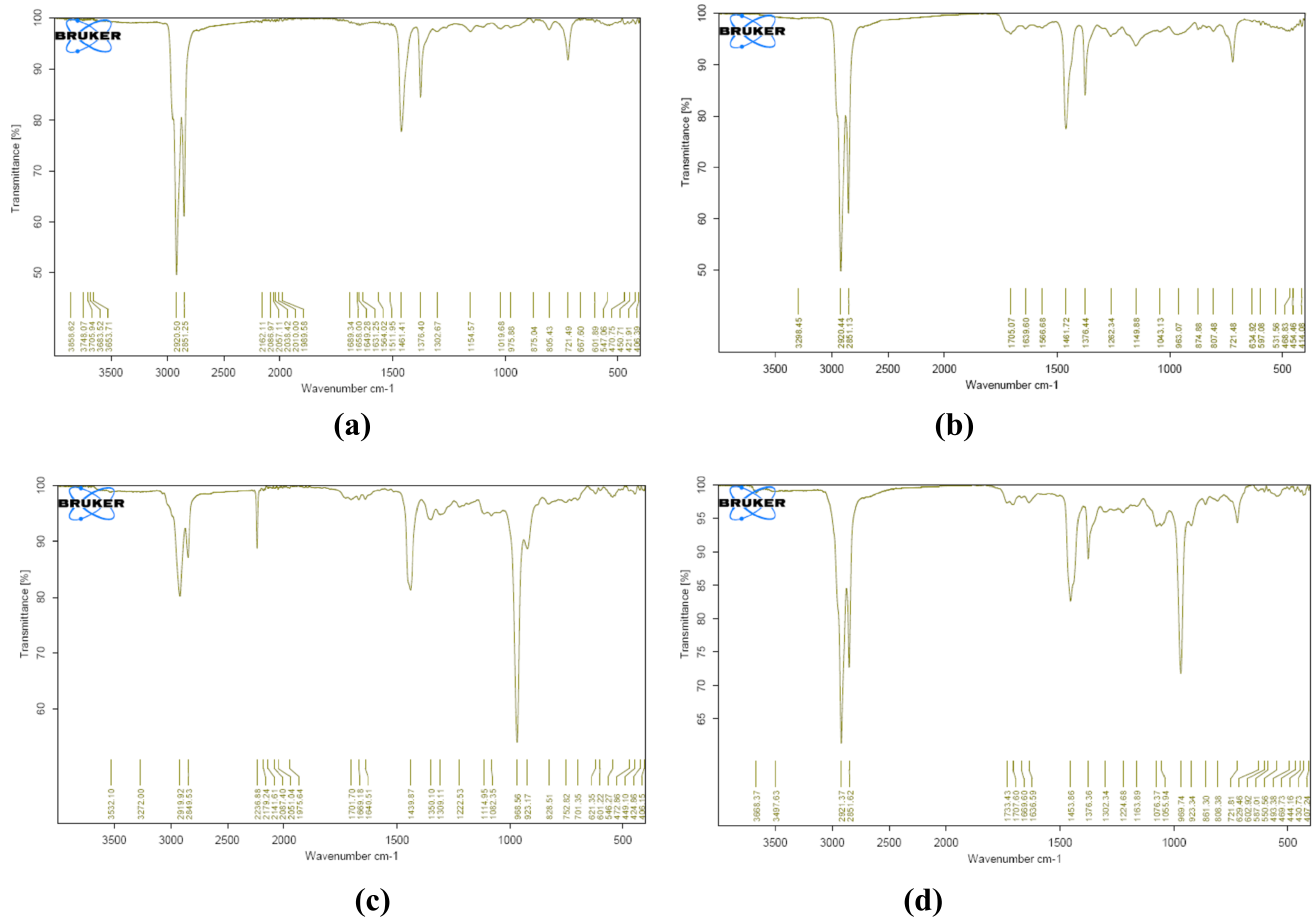


Fig. 3 FTIR spectra of **a** EPDM, **b** EPDM-g-MAH, **c** NBR, and **d** EPDM-g-MAH/NBR blend

Table 2 Formulations, rheometric characteristics, and physico-mechanical properties of EPDM/NBR/kaolin/RHFs (50/50/30/15) rubber composites containing different MAH amounts

	Sample code			
Ingredients, phr	S0	S1	S2	S3
EPDM	50	50	50	50
NBR	50	50	50	50
MAH	–	1	2	3
Kaolin	30	30	30	30
RHFs	15	15	15	15
Rheometric characteristics at 152 °C				
M_L, dNm	1.4	1.4	1.2	1.4
M_H, dNm	23.1	25.8	22.8	25.8
ts_2, min	2.5	3.5	3.6	3.1
tc_{90}, min	23	24.1	26.6	26.8
CRI, $min.^{-1}$	4.9	4.8	4.3	4.2
Physico-mechanical properties				
Tensile strength, MPa	9.0	8.7	8.6	8.7
Elongation at break, %	540	510	480	500
Crosslink density (v), mol/m^3	5.6×10^{-4}	6.9×10^{-4}	7.1×10^{-4}	7.2×10^{-4}

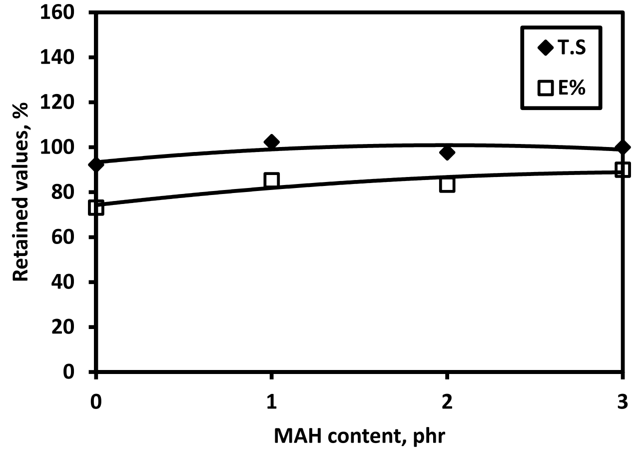


Fig. 4 Retained values (%) of tensile strength and elongation at break (%) of EPDM/NBR/kaolin/RHFs (50/50/30/15) blend composite vulcanizates, after thermal aging at 90 °C for 7 days, versus MAH contents

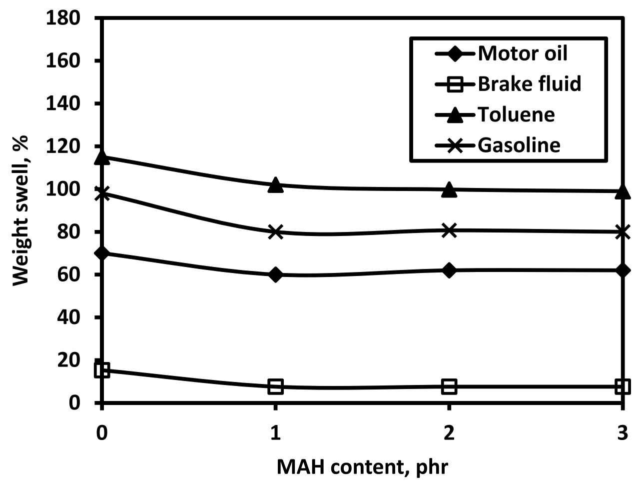


Fig. 5 Weight swell (Q %) of EPDM/NBR/kaolin/RHFs (50/50/30/15) blend composite vulcanizates in motor oil, brake fluid, toluene, and gasoline, versus MAH contents

and extractives 1.9 wt. %. On the other hand, X-ray fluorescence (XRF) analysis of RHFs (Table 1) revealed high silica content (82.93%) in the rice husk ash (RHA), which could be a main renewable source of silica that is widely used in various industries. FTIR spectroscopy was carried out to examine the functional groups characteristics of the RHFs, rice husk silica (RHS), and commercial silica (CS). FTIR spectra (Fig. 1) showed the chemical functionality (cellulosic hydroxyl groups (–OH)) of RHFs which appeared at 3335 cm^{-1}. In addition, FTIR spectrum of RHS showed characteristic peaks of the siloxane bonds (Si–O) at 1066.7 cm^{-1}, 796.8 cm^{-1}, and 458 cm^{-1}, which are similar to the characteristic peaks of CS (Dhaneswara et al. 2020).

Preparation and characterization of EPDM/NBR/kaolin (50/50/30) rubber blends in presence of RHFs

Effect of maleic anhydride (MAH) loading on the homogeneity of EPDM/NBR (50/50) rubber blend

EPDM and NBR (50/50) were mixed with various amounts of MAH (0, 1, 2, and 3 phr) onto two-roll mill to be tested as a compatibilizer utilizing scanning electron microscopy (SEM).

The SEM micrographs (Fig. 2) showed phase separation between EPDM and NBR rubbers, i.e., two discrete phases were observed in the absence of MAH. However, no phase separation was observed upon incorporation of different MAH loadings (1, 2, and 3 phr), indicating the homogeneity improvement of EPDM/NBR rubber blend. Therefore, 1 phr MAH is quite enough to get homogenous blend.

The FTIR spectra of EPDM, EPDM-g-MAH, NBR, and EPDM-g-MAH/NBR blend are shown in Fig. 3.

As shown in Fig. 3a, the characteristic peaks of EPDM at 2920 cm^{-1} and 2851 cm^{-1} are assigned to the stretching vibration of CH_2–, the band at 1640 cm^{-1} is due to the characteristic absorption of C = C, the peaks at 1461 cm^{-1} and 1376 cm^{-1} are assigned to the in-plane bending vibration of CH–, and the peak at 721 cm^{-1} is due to the out-of-plane bending of C-H bond. Upon mixing MAH with EPDM, the characteristic carbonyl group (C = O) of MAH appeared in the spectrum of EPDM-g-MAH at 1705 cm^{-1}, which proves the successful grafting of MAH onto EPDM upon mixing (Fig. 3b). On the other hand, the FTIR spectrum of NBR (Fig. 3c) shows the CH_2– stretching vibrations at 2919.9 cm^{-1} and 2849.5 cm^{-1}, CH_2 bending vibration at 1439.8 cm^{-1}, the characteristic C≡N vibration at 2236.8 cm^{-1} and the C–H out-of-plane bending vibration at 965.5 cm^{-1}. Also, it is interesting to note that the C≡N characteristic peak of NBR at 2236.8 cm^{-1} disappeared upon its mixing with EPDM-g-MAH, confirming the reactive mixing and formation of EPDM/NBR homogeneous blends (Fig. 3d), as evidenced by SEM micrographs.

Effect of MAH different loadings on the physico-mechanical properties of EPDM/NBR/kaolin/RHFs blend composite vulcanizates

Various MAH loadings (0, 1, 2, and 3 phr) were incorporated into EPDM/NBR/kaolin/RHFs (50/50/30/15) blend mixes. Formulations, rheometric characteristics of the mixes, and physico-mechanical properties of the composite vulcanizates are listed in Table 2. It is clear that increasing the MAH loadings led to a slight increase in the optimum cure time (tc_{90}) and consequently a slight decrease in the cure rate index (CRI) of the rubber blend mixes. On the other hand,

Table 3 Formulations, rheometric characteristics, and physico-mechanical properties of EPDM/NBR/kaolin/RHFs blend composites with different EPDM/NBR blend ratios

	Sample code				
Ingredients	S4	S5	S1	S6	S7
EPDM	100	75	50	25	0
NBR	0	25	50	75	100
MAH	1	1	1	1	1
Kaolin	30	30	30	30	30
RHFs	15	15	15	15	15
Rheometric characteristics at 152 °C					
M_L, dNm	1.7	1.5	1.4	0.7	0.6
M_H, dNm	26.8	29.4	25.8	20.9	15.1
ts_2, min	5.1	3.5	3.5	3.9	4.0
tc_{90}, min	30.9	23.0	24.1	25.5	26.6
CRI, $min.^{-1}$	3.9	5.1	4.8	4.6	4.4
Physico-mechanical properties					
Tensile strength, MPa	4.5	8.4	8.7	8.9	13.2
Elongation at break, %	200	380	510	620	800
Crosslink density (v), mol/m^3	4.4×10^{-4}	5.5×10^{-4}	6.9×10^{-4}	8.1×10^{-4}	12.4×10^{-4}

the mechanical properties of the rubber composite vulcanizates were almost unchanged. The retained values (%) of tensile strength and elongation at break % of the composites, after thermal aging at 90 °C for 7 days, were improved upon addition of 1 phr MAH, indicating improvement of thermal stability of the rubber composite vulcanizates. In addition, the retained values % remained unchanged by increasing the MAH loading up to 3 phr, i.e., 1 phr MAH was an adequate amount to get improved thermal stability of the composites under investigation, as shown in Fig. 4. Therefore, MAH (1 phr) was selected as the optimum loading due to the improvement of EPDM/NBR blend homogeneity and the enhancement of thermal stability of the EPDM/NBR/kaolin/RHFs (50/50/30/15) composite vulcanizates.

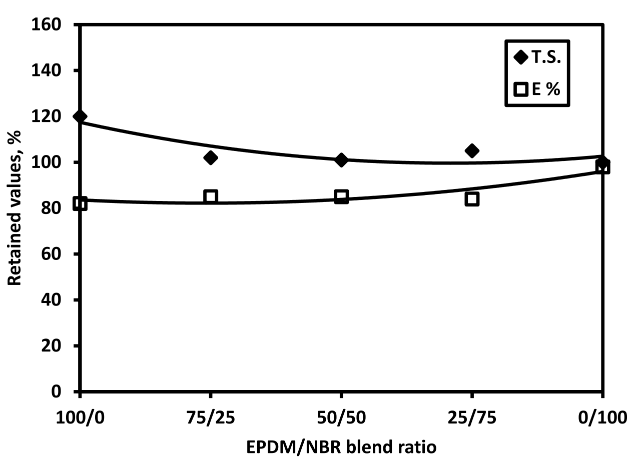


Fig. 6 Retained values (%) of tensile strength and elongation at break (%) of EPDM/NBR/kaolin/RHFs (EPDM/NBR/30/15) blend composite vulcanizates, after thermal aging at 90 °C for 7 days, versus rubber blend ratios

On the other hand, the incorporation of MAH (1 phr) into EPDM/NBR/kaolin/RHFs (50/50/30/15) blend composites reduced slightly the weight swell (Q %) in automotive oils, toluene, and gasoline. However, the Q % was almost unchanged by further increasing MAH loading in the composites. Conversely, the crosslink density increased slightly upon addition of MAH (1 phr) to the blend composite, while it was almost unchanged by further increasing MAH loading in the composites (Table 2). Generally, the composite vulcanizates exhibited low swelling resistance in toluene, gasoline, and motor oil, while swelling resistance in the brake fluid was superior, as shown in Fig. 5. Therefore, 1 phr MAH was quite enough loading to produce EPDM/NBR/kaolin/RHFs (50/50/30/15) blend composite vulcanizate possessing excellent swelling resistance in the brake fluid. Based on the above findings (morphology study, thermal stability, and swelling behavior of the rubber blend composites), 1 phr MAH was selected as the optimum loading for further investigation.

Effect of EPDM/NBR blend ratio on properties of the EPDM/NBR/kaolin/RHFs composite vulcanizates

EPDM/NBR/kaolin/RHFs blend composite vulcanizates of different EPDM/NBR blend ratios (75/25, 50/50, and 25/75), containing RHFs (15 phr), were prepared in the presence of the optimum MAH loading (1 phr). Formulations, rheometric characteristics of the mixes, and physico-mechanical properties of the rubber blend composite vulcanizates are illustrated in Table 3. It is clear that blending EPDM with NBR led to a decrease in the optimum cure time (tc_{90}) and

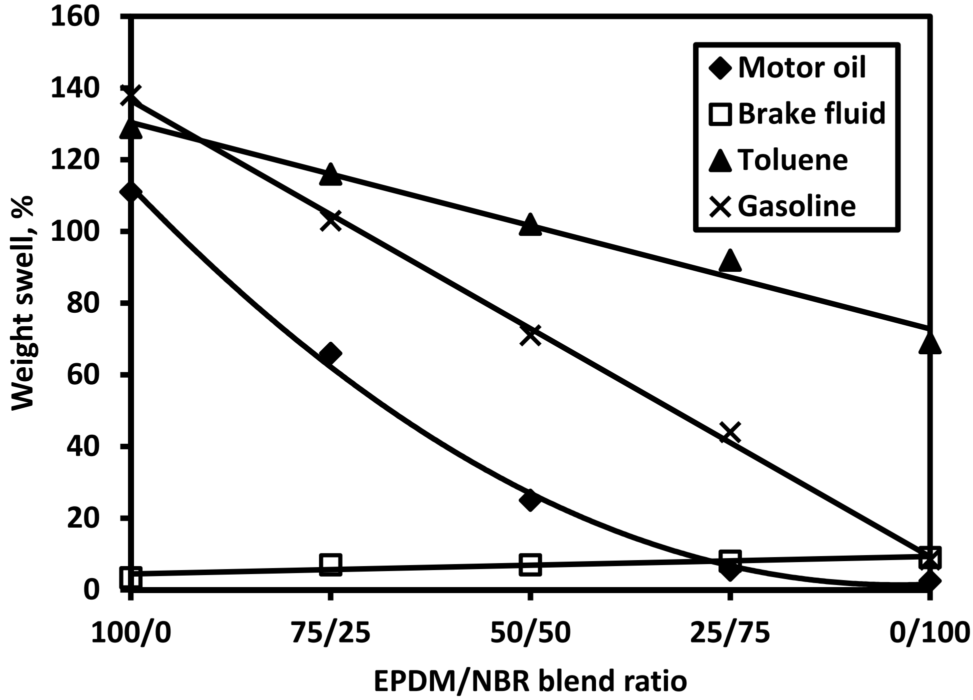


Fig. 7 Weight swell (Q %) of EPDM/NBR/kaolin/RHFs (EPDM/NBR/30/15) blend composite vulcanizates of different rubber blend ratios in motor oil, brake fluid, toluene, and gasoline

Table 4 Formulations, rheometric characteristics, and physico-mechanical properties of EPDM/NBR/kaolin (25/75/30) rubber blend composites containing various RHFs contents

	Sample code				
Ingredients	S8	S9	S6	S10	S11
EPDM	25	25	25	25	25
NBR	75	75	75	75	75
MAH	1	1	1	1	1
Kaolin	30	30	30	30	30
RHFs	–	10	15	20	30
Rheometric characteristics at 152 °C					
M_L, dNm	0.5	0.7	0.7	0.7	0.5
M_H, dNm	15.7	18.5	20.9	22.7	25.0
ts_2, min	5.2	4.3	3.9	3.4	2.8
tc_{90}, min	29.4	26.4	25.5	26	24.3
CRI, $min.^{-1}$	4.2	4.6	4.6	4.4	4.5
Physico-mechanical properties					
Tensile strength, MPa	11.8	9	8.9	8.4	7.6
Elongation, %	915	705	620	600	510
Crosslink density (v), mol/m^3	6.5×10^{-4}	7.2×10^{-4}	8.1×10^{-4}	8.2×10^{-4}	9.5×10^{-4}

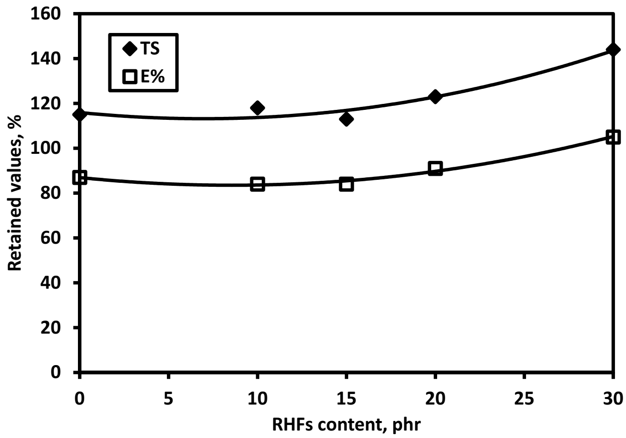


Fig. 8 Retained values (%) of tensile strength and elongation at break (%) of EPDM/NBR/kaolin/RHFs (25/75/30/RHFs) blend composite vulcanizates, after thermal aging at 90 °C for 7 days, versus RHFs contents

consequently an increase in the cure rate index (CRI) of the rubber blend composite vulcanizates, as compared to the parent rubbers. Also, it is obvious that the entire EPDM/NBR/kaolin/RHFs composite vulcanizates of different EPDM/NBR rubber blend ratios possessed moderate tensile strength values compared to those of the parent rubbers. However, elongation at break % of the vulcanizates increased with increasing NBR content in the blends. Upon thermal aging, those rubber blend composite vulcanizates possessed equivalent retained tensile strength (≈ 100%) as well as equivalent retained elongation at break (≈ 85%), indicating excellent thermal stability of the composites (Fig. 6). On the other hand, the weight swell (Q %) of the composite vulcanizates in motor oil, toluene, and gasoline decreased remarkably due to increasing the NBR content in the blend. In addition, as shown in Table 3, the crosslink density of the vulcanizates increased with NBR content, which explains the remarkable reduction of weight swell (Q %) in motor oil, toluene, and gasoline, besides the polar nature of NBR. However, Q% increased faintly in the brake fluid (but still at very low values) with NBR content in the blends, which could be attributed to the polar nature of brake fluid (Fig. 7). Furthermore, it is interesting to note that the NBR/kaolin/RHFs (100/30/15) rubber composite vulcanizate exhibited superior swelling resistance in gasoline due to the hydrophilic nature of both NBR and RHFs. As a result, of the entire rubber blend ratios investigated, EPDM/NBR/kaolin/RHFs (25/75/30/15) composite vulcanizate possessed excellent swelling resistance in both motor oil and brake fluid, along with good thermal stability. Therefore, the EPDM/NBR (25/75) blend ratio was selected for further investigation.

Effect of RHFs loading on the properties of EPDM/NBR/kaolin (25/75/30) blend composite vulcanizates

EPDM/NBR/kaolin (25/75/30) blends loaded with different amounts of RHFs (0, 10, 15, 20, and 30 phr) were prepared in the presence of MAH optimum loading (1 phr). Formulations, rheometric characteristics of the mixes, and physico-mechanical properties of the composite vulcanizates are listed in Table 4. It is obvious that the maximum torque (M_H) of the rubber blend mixes increased by increasing the RHFs in the blend. This may be attributed to the improved interfacial interaction between the RHFs and the rubber matrix. On the other hand, a slight decrease in the optimum cure time (tc_{90}), and a slight increase in the cure rate index (CRI) were observed. Also, it is clear that tensile strength and elongation at break % of the composite vulcanizates decreased slightly with increasing RHFs content in the composites. Upon thermal aging, the retained values (%) of the composites' mechanical properties increased as RHFs content increased up to 30 phr, indicating thermal stability improvement of the composite vulcanizates (Fig. 8).

According to the thermal gravimetric analysis (DTA/DTG) shown in Fig. 9 and the data in Table 5, the maximum decomposition temperature of the EPDM/NBR/kaolin/RHFs (25/75/30/RHFs) blend loaded with different amounts of RHFs (0, 10, 15, 20, and 30 phr) shifted from 458°C (for the blend without RHFs) to 468 °C (for the blend loaded with 30 phr RHFs), supporting the notion that adding more RHFs to the rubber blend improves the thermal stability of rubber vulcanizates. In addition, the maximum weight loss decreased by increasing RHFs content in the blend. However, the improvement in thermal stability did not alter the general pathway of thermal degradation below 500 °C. This may be attributed to the homogenous distribution and the good interaction between the RHFs and the rubber matrix.

On the other hand, as shown in Fig. 10, the weight swell (Q%) of EPDM/NBR/kaolin/RHFs (25/75/30/RHFs) composites in motor oil, brake fluid, toluene, and gasoline decreased with increasing RHFs content in the composites. This may be attributed to increasing the interfacial interaction between the RHFs and the rubber matrix upon increasing the RHFs content, which enhances the crosslink density of the composites (Table 4). Generally, the swelling resistance of the composite vulcanizates could be ranked in the following descending order: swelling resistance in motor oil > brake fluid > gasoline > toluene. More interestingly, EPDM/NBR/kaolin/RHFs (25/75/30/30) composite vulcanizate possessed superior swelling resistance in both motor oil and brake fluid, besides excellent thermal stability.

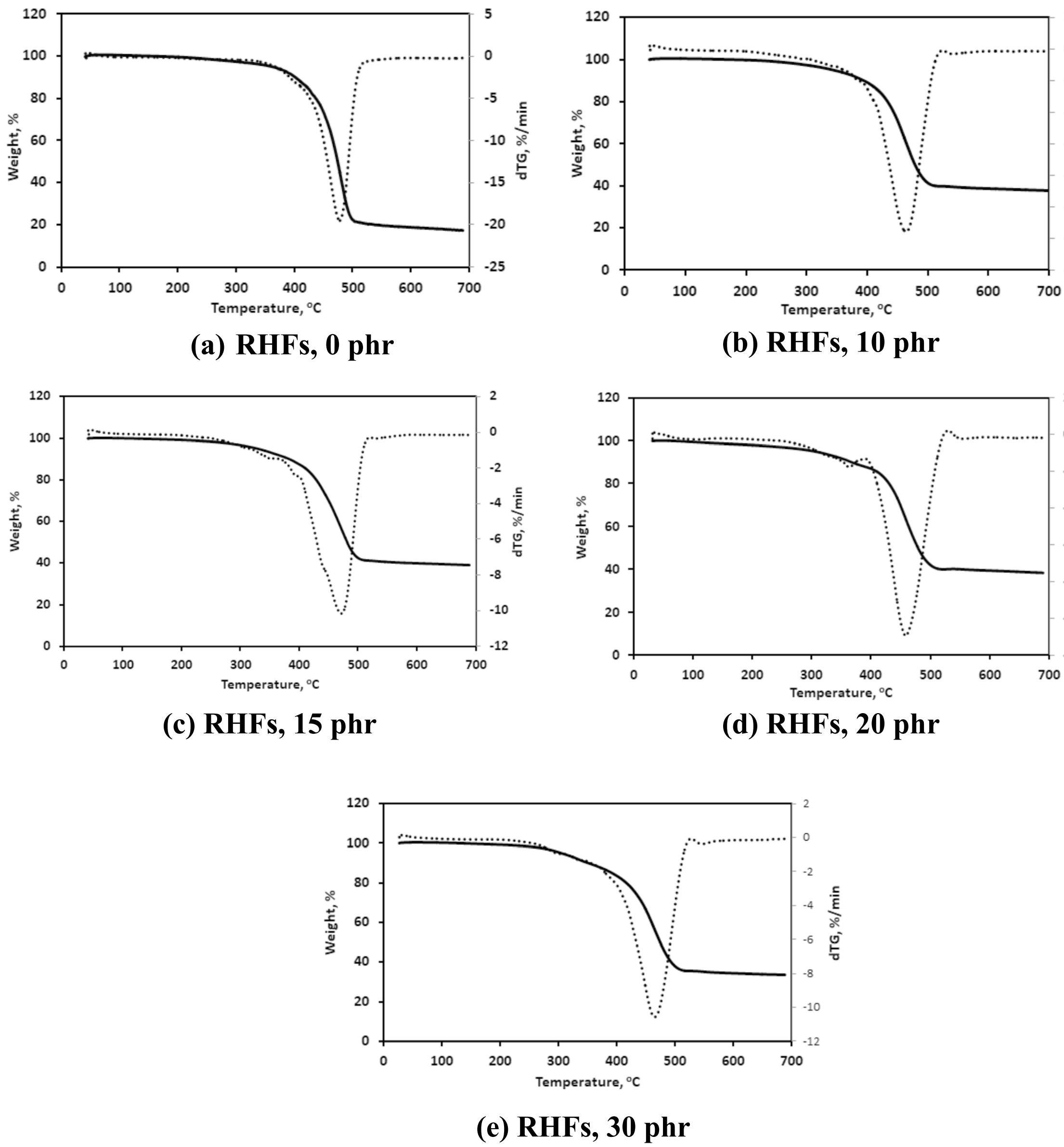


Fig. 9 TGA and DTA thermograms of EPDM/NBR/kaolin/RHFS (25/75/30/RHFs) blend vulcanizates containing various RHFs loadings: (**a**) 0 phr, (**b**) 10 phr, (**c**) 15 phr, (**d**) 20 phr, and (**e**) 30 phr

Table 5 TGA results of EPDM/NBR/kaolin/RHFs (25/75/30/RHFs) blend loaded with various RHFs contents

RHFs content in the blend, phr	Temperature at 5% weight loss, °C	Temperature at maximum decomposition rate, °C	Maximum weight loss, %
0	305	458	82.5
10	310	460	66.1
15	330	463	62.2
20	343	465	61.3
30	361	468	60.7

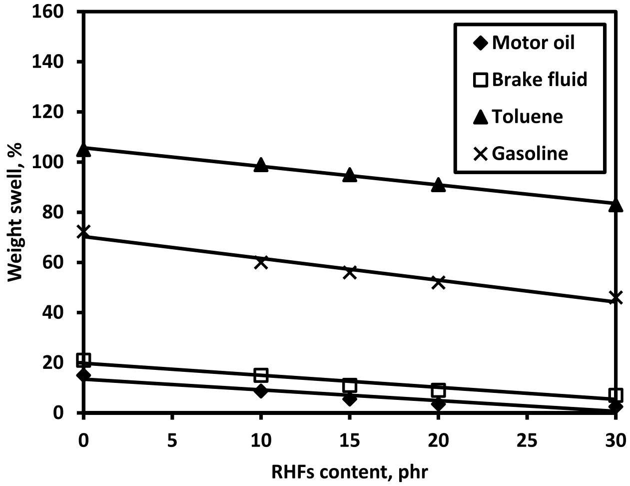


Fig. 10 Weight swell (Q %) of EPDM/NBR/kaolin/RHFS (25/75/30/RHFs) blend composite vulcanizates in motor oil, brake fluid, toluene, and gasoline versus RHFs contents

Effect of filler type on the properties of EPDM/NBR (25/75) blend vulcanizates

EPDM/NBR (25/75) blends were mixed with different types of fillers (30 phr), namely kaolin, RHFs, silica extracted from rice husk (RHS), and silica ash (SA), onto a two-roll mill. Formulations, rheometric characteristics of the mixes, and physico-mechanical properties of the composite vulcanizates are illustrated in Table 6. It is clear that the EPDM/NBR rubber (25/75) blend mixes loaded with RHS possessed the shortest optimum cure time (t_{C90}) and consequently the highest cure rate index (CRI), compared to the other fillers investigated. Also, it is obvious that the tensile strength and elongation at break (%) of the composite vulcanizates could be ranked, according to the filler type, in the following descending order: Kaolin > SA > RHS > RHFs. The physico-mechanical properties were measured after thermal aging at 90°C for 7 days. The retained values (%) of tensile strength and elongation at break (%) were calculated and are expressed in Fig. 11. It is noticeable that vulcanizates containing the entire fillers under investigation showed high retained values (%), demonstrating thermal stability of the composites.

On the other hand, those composite vulcanizates possessed low weight swell (Q %) values in both motor oil and brake fluid, illustrating excellent swelling resistance (Fig. 12). More specifically, the composites loaded with RHFs and RHS revealed the least weight swell (Q %) in motor oil and brake fluid, confirming superior swelling resistance in the automotive oils. Also, it is interesting to note that those rubber composites possessed the greatest crosslink density (Table 6), which is in good agreement with the swelling test results, as expected.

Table 6 Formulations, rheometric characteristics, and physico-mechanical properties of EPDM/NBR (25/75) blends loaded with different filler types

	Sample code			
Ingredients, phr	S12	S13	S14	S15
EPDM	25	25	25	25
NBR	75	75	75	75
MAH	1	1	1	1
Kaolin	30			
RHFs		30		
RHS			30	
SA				30
Rheometric characteristics at 152 °C				
M_L, dNm	0.7	3.4	0.7	0.7
M_H, dNm	9.5	19.5	9.7	9.5
ts_2, min	5.3	5.9	3.0	2.7
tc_{90}, min	11.5	22.0	7.0	9.8
CRI, $min.^{-1}$	16.2	6.2	24.8	14.0
Physico-mechanical properties				
Tensile strength, MPa	7.9	3.5	4.5	5.0
Elongation at break, %	1065	290	560	880
Crosslink density (v), mol/m^3	5.2×10^{-4}	7.1×10^{-4}	6.5×10^{-4}	4.6×10^{-4}

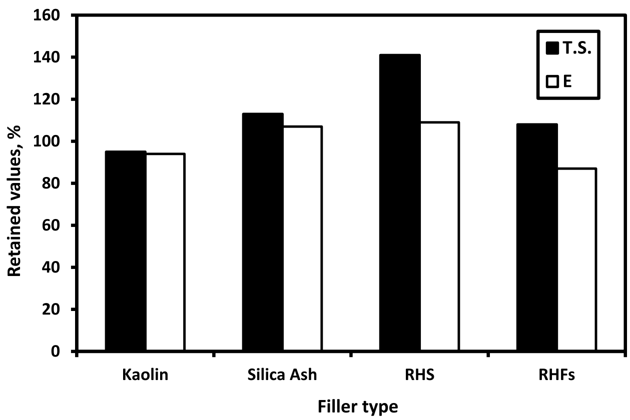


Fig. 11 Retained values (%) of tensile strength and elongation at break (%) of EPDM/NBR (25/75) blend composite vulcanizates, after thermal aging at 90 °C for 7 days, versus filler types (30 phr)

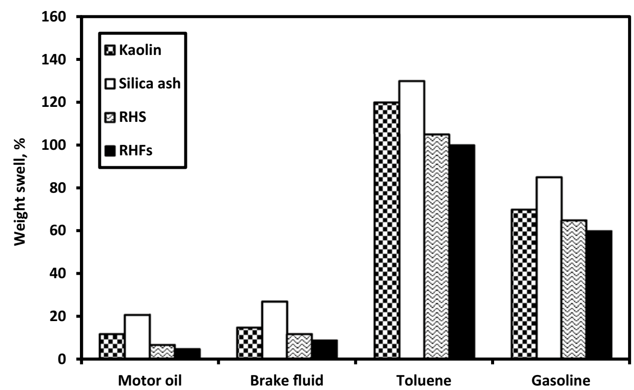


Fig. 12 Weight swell (Q %) of EPDM/NBR (25/75) blend composite vulcanizates in motor oil, brake fluid, toluene, and gasoline, versus filler types (30 phr)

Table 7 Formulations, rheometric characteristics, and physico-mechanical properties of EPDM/NBR/CB (25/75/40) blend composites containing RHS different loadings

	Sample code					
Ingredients, phr	S16	S17	S18	S19	S20	S21
EPDM	25	25	25	25	25	25
NBR	75	75	75	75	75	75
MAH	1	1	1	1	1	1
CB	40	40	40	40	40	40
RHS	–	5	10	15	20	25
Rheometric characteristics at 152 °C						
M_L, dNm	2.3	2.9	3.0	3.1	3.4	3.7
M_H, dNm	27.3	27.0	30.1	32.9	34.0	35.1
ts_2, min	3.4	3.7	3.4	3.1	2.9	2.8
tc_{90}, min	28.9	28	25.8	24.3	22.7	24.4
CRI, $min.^{-1}$	3.9	4.1	4.5	4.7	5.0	4.6
Physico-mechanical properties						
Tensile strength, MPa	19.7	15.9	13.3	12.6	12.8	11.3
Elongation at break, %	625	530	450	410	420	400
Crosslink density (v), mol/m^3	9.3×10^{-4}	9.8×10^{-4}	10.7×10^{-4}	11.1×10^{-4}	11.8×10^{-4}	12.3×10^{-4}

Effect of rice husk silica (RHS) as a supporting filler on the properties of carbon black-reinforced EPDM/NBR blend composite vulcanizates

EPDM/NBR (25/75) blends reinforced with carbon black (40 phr) in combination with different amounts of RHS (0, 5, 10, 15, 20, and 25 phr) were prepared. Formulations, rheometric characteristics of the mixes, and physico-mechanical properties of EPDM/NBR/CB (25/75/40) composite vulcanizates loaded with various amounts of RHS are represented in Table 7. It is obvious that incorporation of RHS into the rubber blend mixes led to slightly reducing the optimum cure time (tc_{90}) and consequently increasing the cure rate index (CRI). Also, tensile strength and elongation at break (%) of the composite vulcanizates decreased with increasing RHS content up to 10 phr, and thereafter the mechanical properties remained almost unchanged. Upon thermal aging, the retention of mechanical properties is acceptable since the entire EPDM/NBR/CB (25/75/40) vulcanizates containing various amounts of RHS retained 100% of their tensile strength and 80% of their elongation at break, indicative of excellent thermal stability (Fig. 13). On the other hand, the entire composite vulcanizates possessed superior swelling resistance in the motor oil at all RHS contents (Fig. 14). Also, it should be noted here that the crosslink density of the composites increased with increasing RHS loading (Table 7). Therefore, RHS could be used successfully in combination with

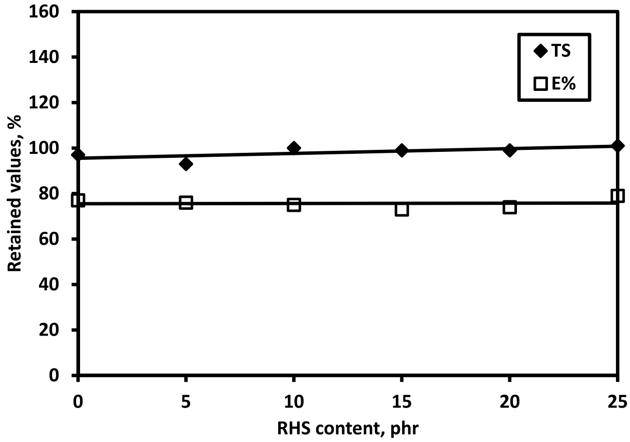


Fig. 13 Retained values (%) of tensile strength and elongation at break (%) of EPDM/NBR/CB/RHS (25/75/40/RHS) blend composite vulcanizates, after thermal aging at 90 °C for 7 days, versus RHS content

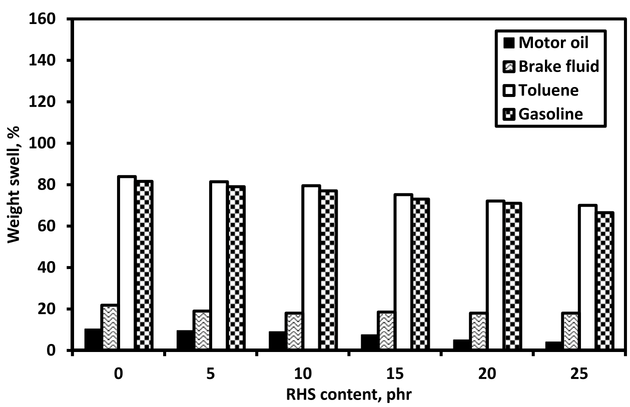


Fig. 14 Weight swell (Q %) of EPDM/NBR/CB/RHS (25/75/40/RHS) blend composite vulcanizates in motor oil, brake fluid, toluene, and gasoline, versus RHS content

CB to enhance the thermal stability and swelling resistance of the composite vulcanizates, mainly in the motor oil, besides reducing the rubber product cost.

Conclusions

Rice husk fibers (RHFs) and their extracted silica (RHS) agro-waste materials were efficiently utilized as supporting fillers in EPDM/NBR rubber blend composite vulcanizates. The promising results of the present research are concluded as follows:

- Maleic anhydride (MAH, 1 phr) was sufficient to obtain EPDM/NBR homogeneous blends.
- EPDM/NBR/kaolin/RHFs (50/50/30/15) composite vulcanizate possessed good mechanical properties and thermal stability, along with superior swelling resistance in both motor oil and brake fluid. However, NBR/kaolin/RHFs (100/30/15) rubber composite vulcanizate exhibited superior thermal stability and swelling resistance in gasoline.
- Different RHFs loadings (0–30 phr) reduced slightly the mechanical properties of EPDM/NBR/kaolin/RHFs (25/75/30/RHFs) composite vulcanizates, but the retained values of the mechanical properties after thermal aging revealed good thermal stability of the vulcanizates, as confirmed by TGA analysis. Also, the composite containing 30 phr RHFs demonstrated superior swelling resistance in both motor oil and brake fluid at a low cost. This may be attributed to increasing the interfacial interaction between the RHFs and the rubber matrix upon increasing the RHFs content, which enhances the crosslink density of the rubber composites.
- Among all filler types investigated, RHS (30 phr) remarkably reduced the curing time and increased the cure rate index of the EPDM/NBR (25/75) rubber blend mixes. Also, the rubber composites loaded with RHFs and RHS revealed superior swelling resistance in both motor oil and brake fluid, which is in good agreement with the crosslink density measurements.
- EPDM/NBR/CB/RHS (25/75/40/RHS) composites loaded with various RHS contents possessed good mechanical properties and retained 100% of their tensile strength and 80% of their elongation at break upon thermal aging. Therefore, RHS could be used successfully in conjunction with CB as a supporting filler to enhance the thermal stability and swelling resistance of the EPDM/NBR blend vulcanizates, primarily in motor oil, besides lowering the final product cost.
- Therefore, since they meet the standards of environmental protection and sustainable development, RHFs and RHS agro-waste could be successfully proposed as green supporting fillers for the production of automotive rubber products resistant to automotive oils with desirable mechanical properties and good thermal stability at low cost (e.g., oil seals, gaskets, hoses, automobile spare parts, and O-rings).

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Author contributions Prof. Dr. Samir H. Botros and Associate Prof. Mohamed M. Eissa suggested the plan of the work, wrote and edited the main manuscript text, prepared figures, designed the rubber formulations, and measured the physico-mechanical properties of the vulcanizates. Dr. Mohamed Diab provided the rice husk fibers and prepared the rice husk silica. Dr. Emad measured the rheometric characteristics of the rubber mixes and prepared their vulcanizates. Prof. Dr. Nehad Rozik measured the swelling performance of the rubber vulcanizates in automotive oils and solvents. All authors reviewed the manuscript.

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Data availability Enquiries about data availability should be directed to the authors.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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