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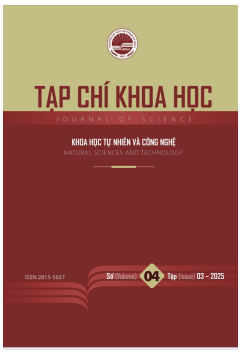

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Study on content of hydrophilic silica from rice husk in reinforced deproteinized natural rubber materials

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Abstract

The environment is an area of global concern that the whole world is concerned about, especially issues such as global warming and the depletion of natural resources. Scientists have made efforts to overcome these negative impacts. Not out of this trend, the polymer material science is one of the major fields that emits a lot of greenhouse gases. In this study, we focus on improving the mechanical properties, include: Hardness, tensile strength, elongation.... There are two components: first, the matrix part is made from rubber. The disadvantage of synthetic rubber is that it is difficult to biodegrade, but natural rubber is available. In addition, the filler mainly used is carbon black, a product derived from petroleum. This filler is mainly derived from petroleum, it is not a finite resource to be used sustainably, so an alternative filler is needed. In this study, we use deproteinized natural rubber (DPNR) instead of synthetic rubber for the purpose of being environmentally friendly and increasing the service life and silica filler, which is thermally inert and derived from the ash after combustion of rice husk. The current research is called hydrophilic silica from rice husk (Hi-Silica). The Hi-Silica ratio was examined from about 0 to 70 parts per hundred rubber (phr). The results showed that Hi-Silica at 40 phr of rubber gave the best durability through mechanical property tests and has stability at high temperatures.

Keywords: Hydrophilic silica, rice husk, deproteinized natural rubber, reinforced materials, fillers, polymer

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1. Introduction

Natural rubber has been widely used for a long time around the world with advantages such as elasticity, abrasion resistance, biodegradability, and environmental friendliness. Its chemical composition includes rubber polymer, nitrogen-containing compounds, acetone extracts, ash (inorganic substances), and moisture. Rubber polymer is mainly poly-1,4-isoprene and about 2% of poly-3,4-isoprene. Nitrogen-containing compounds are mainly proteins and amino acids that play a role in increasing the swelling of rubber in water and increasing the insulating ability. Acetone extracts are fatty acids, fatty acid esters, phospholipids...[1]. Ash components are inorganic compounds and salts that catalyze rubber oxidation reactions [2].

Because of its natural origin, natural rubber contains many protein components and many publications have shown that proteins such as immunoglobulin E1–3 cause allergies to humans when in contact with the skin and mucous membranes [3]. Therefore, the deproteinization step must be carried out before the product is applied, especially in the medical field. In addition, removing protein from natural rubber can reduce the aging phenomenon of the product and increase the usage time. Common methods of removing protein from natural rubber include: Chemical [4], [5], biological [6], [7]. In which the process using urea and the surfactant sodium dodecyl sulfate (SDS) can reduce the nitrogen content in rubber to 0 µg/l [8]. This process allows the production of protein-free natural rubber from high ammonium natural rubber (HANR), in addition to DPNR with protein residues suitable for the intended use. When comparing the maximum strain, rubber samples with different protein contents all had similar maximum strains, but the maximum stress of deproteinized natural rubber was up to 6 times higher than that of completely protein-free natural rubber, and these values tended to decrease in direct proportion to the protein content in natural rubber due to the decrease in cross-link density [9], [10].

Due to the increasing demand for durability and resistance, the reinforcement of deproteinized natural rubber is necessary to meet the needs of life while meeting the criteria of durability, usage time, efficiency, user-friendliness, and environmental friendliness. Reinforcement materials are widely used in the construction, aerospace, automotive, and biomedical industries... This is a combination of core materials and matrix materials to increase durability and resistance compared to the original material. In which, core materials have a reinforcing role and are often in the form of: Granules, fibers, and panels. The matrix material is the dispersion medium of the reinforcing material to create the homogeneity and continuity of the reinforcing material [11]. There are many methods to classify reinforcing materials mainly based on the characteristics of the reinforcement and the matrix.

Besides rubber trees, Vietnam is one of the world's leading rice-exporting countries, along with Thailand and India [12]. Rice husks are a by-product in the process of rice production and processing. This is a type of by-product that needs to be reused to save costs and protect the environment because it is derived from plants. In rice husk, the maximum ash content is about 22.15% and the silica in the ash is about 93% [13]. Up to now, there have been many published studies on the use of silica from rice husk in the production of tire treads [14], [15]. Some results are given as follows: Tensile strength reaches its maximum value at 20 mass parts of silica. Hardness (Shore A) is investigated along with changes in silica content, and the results show that hardness is proportional to silica content. Although the hardening temperature is improved but the elasticity of the material is reduced. This has been concluded previously when natural rubber materials use granular fillers. Next, the abrasion resistance is 50 times higher than that of materials without fillers [16], [17].

2. Experimental

2.1. Chemicals and experimental equipment

HANR 62.25% dry rubber content (DRC) was received from Dong Nai Rubber Corporation. Urea (CAS number: 57-13-6) was obtained from Sigma Aldrich. SDS (CAS number: 151-21-3) was obtained from Sigma Aldrich. Zin Oxide (ZnO CAS number: 1314-13-2) was sourced from VWR Chemical. Stearic Acid (SA CAS number: 57-11-4) was obtained from Sigma Aldrich. 2,2,4-Trimethyl-1,2-dihydroquinoline polymer (RD CAS number: 105-60-2) was received from Sinopec. Treated Distillate Aromatic Extract (TDAE oil) was sourced from HJ oil. N-tert-butyl-2-benzothiazolesulfenamide (TBBS CAS number: 14324-55-1) was provided by Heinan GO Biotech. Sulfur (S_8 CAS: 7704-34-9) was obtained from Sigma Aldrich. Hydrophilic silica (Hi-Silica CAS: 112926-00-8) from rice husk was sourced from Biosilico.

The protein content in natural rubber was determined by the Kjeldahl method according to the Vietnam national standard TCVN 10791:2015. The samples were prepared in solid form and chopped. Then the samples were mineralized with a mixture of concentrated H_2SO_4 and catalysts such as $CuSO_4$, K_2SO_4 and Se under an alcohol lamp flame for 1 hour. The mixture after mineralization was diluted and neutralized with NaOH to convert NH_4^+ ion gas into NH_3. NH_3 gas was bubbled into water and titrated with H_3BO_3 with methyl red indicator.

The structure of HANR and DPNR is characterized by the JEOL ECA-400 FT-NMR device. 1.6 mg of samples were prepared by cutting and soaking in chloroform D solvent for two days. Measurements were carried out at 400MHz frequency with 128 scans and 17.6 ppm dynamic range.

The bonds on the Hi-Silica surface using the Jasco 6300 FTIR instrument. Hi-Silica samples were prepared in powder form, then mixed with KBr and compressed into a film before measurement. The measurement was adjusted at 20 scans, wavelength in the range of 4000 – 400 cm^{-1}, and the resolution was 4 cm^{-1}.

The curing curve was determined by the Rotorless Rheometer Model RLR-4 according to ISO 6502/JIS K6300-2 standards to characterize the curing process. Unvulcanized rubber samples weighing approximately 10 grams were prepared and placed between two rotating disks of the apparatus. The test was carried out at a constant temperature of 150°C, with an oscillation arc of 0.5° and a frequency of 100 cycles per minute (1.66 Hz) for 60 minutes. The torque function was continuously recorded against time and the resulting rheographs were analyzed to determine the vulcanization properties. The t_{90} value, which represents the time required to reach 90% of the maximum torque (M_H), was obtained from these rheographs.

The tensile strength measurement method uses A Toyoseiki Strograph VG5E according to JIS K6251 standard to investigate the stress-strain curve. The measuring sample is cut into a paddle shape according to No.7 of JIS K6251 standard to ensure the accuracy and reliability of the measurement process. The sample clamping speed during the measurement is set to 200 mm/min.

The hardness measurement method according to the Shore A scale is used by Teclock GS-709N (A) rubber hardness tester according to the Vietnam national standard TCVN 1597-1:2007 to determine hardness. The sample is rectangular. The size of the sample allows measurement at three points. The perpendicular distance from the measuring point to the edge of the sample is not less than 13 mm. Measurement procedure: Wipe the surface of the sample clean. Place the sample on a horizontal plane. Use your hand to press the measuring device firmly onto the sample. The sample is rectangular and must

allow measurement at five points. Read and record the hardness index displayed on the device 3 seconds after applying pressure to the sample.

The abrasion measurement method uses GTFO12D of Japan according to the Vietnam national standard TCVN 5363:2006 to determine abrasion resistance. Conical cylindrical sample according to the cutting machine model. Abrasion of material on sandpaper roller with size 450 x 450 (mm x mm) under 2 kg pressure in 100 revolutions. Test sample thickness is not less than 2 mm. Perform at least 3 tests, and average the results of each measurement.

The measuring cross-link density through the swelling test according to the Vietnam national standard TCVN 2752:2013. The vulcanized rubber samples were cut into 2 x 2 (cm x cm) dimensions and weighed to measure the mass. The samples were then soaked in toluene at room temperature and protected from light for six days. After the soaking period, the samples were weighed and analyzed. The cross-link density was calculated using the Flory-Rehner equation.

The mass change and mass velocity are determined by using Labsys TG/DSC1600, TMA. Samples were prepared in an aluminium oxide crucible. Starting from room temperature to 900 °C with a maximum heating rate of 10°C/min in an atmosphere

2.2. Preparing deproteinized natural rubber (DPNR)

A mixture of HANR 30% DRC (Diluting from HANR 62.25% DRC) containing 1% SDS and 0.1% urea was prepared and incubated at room temperature and stirred for 1 hour. After 1 hour, the mixture was centrifuged at 10000 rpm for 30 minutes. The serum was then removed and the cream was obtained, which was dried at 50°C for two days to obtain DPNR. The entire protein separation process is summarized in Figure 1.

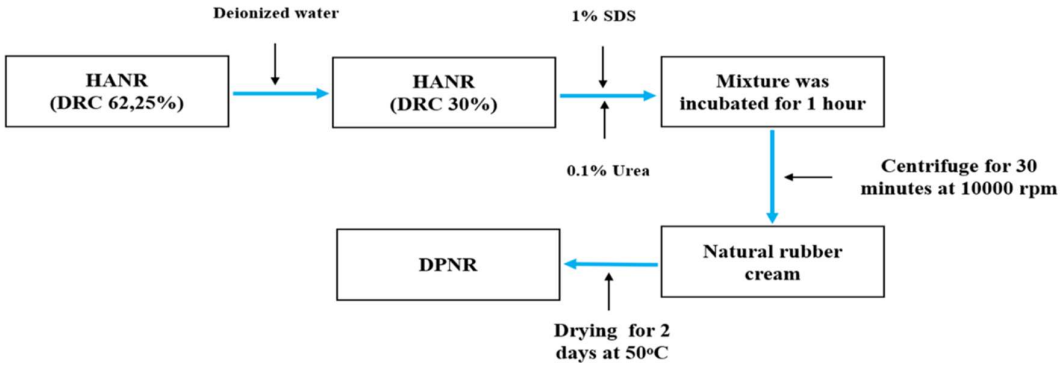

Figure 1. Prepare deproteinized natural rubber process

Table 1. Chemical compounds.

No.	Chemical	Content (phr)
1	DPNR	100
2	ZnO	5
3	SA	3
4	RD	1
5	Hi-Silica	0 → 70
6	TDAE oil	5
7	TBBS	3.5
8	S_8	2

2.3. Preparing samples

The vulcanization composition is presented in Table 1. The mixing process is as follows Figure 2. First, the rubber is pre-kneaded in the TOYOSEIKI Labo Plasstomill 4M150 closed mixer at 60°C for 10 minutes, then the chemicals are added to the mixing process in order from top to bottom as shown in Table 1. Each chemical is added 2 minutes apart. When the mixing process is finished, the mixture is cooled for 12 hours for vulcanization. The samples will be named according to the Hi-Silica content, including 8 samples: 0 phr, 10 phr, 20 phr, 30 phr, 40 phr, 50 phr, 60 phr, 70 phr. The samples are vulcanized at 150°C under a pressure of 10MPa with an optimal vulcanization time.

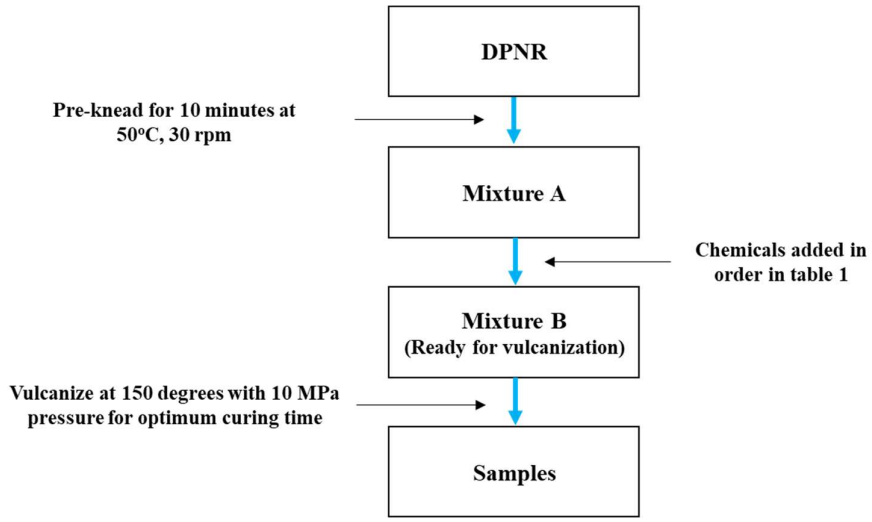

Figure 2. Preparing samples process.

3. Results and Discussion

Through the preparation process, the samples are summarized in Figure 3.

3.1. The protein content and structure of HANR and DPNR

The protein content before and after the urea and SDS removal process was determined by the Kjeldahl method. The dry natural rubber samples before and after the incubation and single centrifugation were investigated. The results showed that the dry natural rubber sample without protein removal had a nitrogen content of 0.27% and a protein content of 1.68%. The dry natural rubber samples that had undergone the incubation and single centrifugation process had a nitrogen content of 0.084% and a protein content of 0.525%, similar to the published results [14].

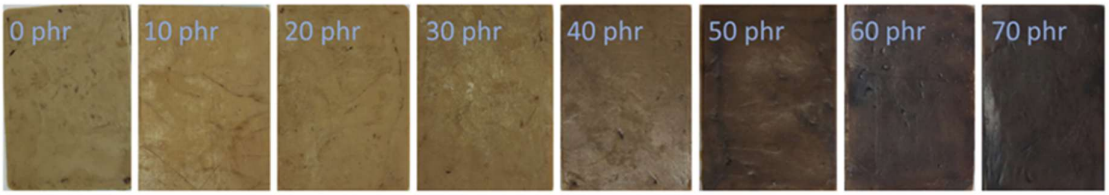

Figure 3. Samples from 0 phr to 70 phr.

The ^{1}H NMR spectra of HANR and DPNR are shown in Figure 4. In the spectra, three major signals appeared in both HANR and DPNR samples at 1.6, 2.0 and 5.1 ppm, which were assigned to methyl, methylene and unsaturated methine protons of cis-1,4-isoprene units [18], [19]. The small signals appearing at 0.86 ppm of the HANR sample are due to the presence of fatty acids and this signal is strongly reduced in intensity in the DPNR sample. In addition, some signals of methyl, methylene and unsaturated methine protons tend to increase in intensity possibly due to the removal of proteins which increases the solubility of rubber in non-polar solvents [20].

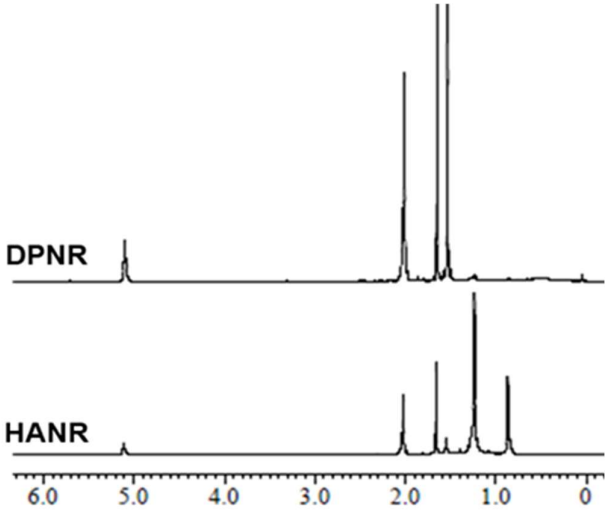

Figure 4. ^{1}H NMR spectra of HANR and DPNR.

3.2. The bonds on the Hi-Silica surface

The results of the absorption peak appearing on the Hi-Silica particle surface were examined by infrared spectroscopy in Figure 5. The predominant absorbance peak at 1079 cm^{-1} is attributed to the Si–O–Si asymmetric stretching vibration. The bands located at 802 cm^{-1} and 472 cm^{-1} are ascribed to the Si–O symmetry stretching vibration and bending vibration [21]. The presence of O-H bonds shows the hydrophilicity of the Hi-Silica particle surface, respectively. The bands centered at 3649 cm^{-1} and 959 cm^{-1} are assigned to the SiO–H asymmetric stretching vibration and bending vibration [22], respectively. The band at 1863 cm^{-1} belonged to H–O–H bending vibration [23].

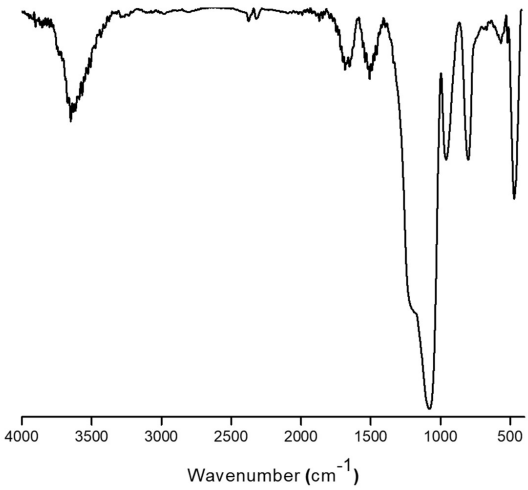

Figure 5. FT-IR spectrum of Hi-Silica

3.3. The curing parameters of samples from 0 phr to 70 phr

The curing curve of 8 samples is shown in Figure 6 and the parameters of the samples are shown in Table 2. There is a general trend shown, with the increase in Hi-Silica content, the curing time increases, the curing time of the samples is extended, the curing speed decreases, the maximum torque and the minimum torque increase, this can be explained by two hypotheses. The first hypothesis is that due to the adsorption capacity of Hi-Silica, the accelerators, and sulfur are absorbed onto the Hi-Silica surface and the free content in the unvulcanized rubber mixture is reduced. The second hypothesis is that Hi-Silica containing mildly acidic Si-OH silanol groups may interact with TBBS to reduce the promoter activity [24]. However, there is a difference between the 50 phr and 60 phr samples, the cure time and the optimal cure time decrease with increasing Hi-Silica content. The time from the start of cure to the optimal cure of the 50 phr sample is 12.46 minutes, for the 60 phr sample it is 13.44 minutes, which is completely reasonable when the cure rate decreases. In addition, when the Hi-Silica content of the 60 phr sample is larger than the 50 phr sample, when subjected to pressure during the cure process, it will cause greater internal friction, leading to more heat generation from the internal friction phenomenon [25], which may cause desorption phenomenon for physical adsorption with some chemical components, causing a slight decrease in the cure time.

3.4. The tensile strength of samples from 0 phr to 70 phr

For rubber materials, elongation and tensile strength are important factors that must be clarified. Stress-strain tests were conducted on samples from 0 to 70 phr in Figure 7. A clear trend can be observed. With the 0 phr sample, the lowest stress with a value of 17.16 MPa and the largest elongation of up to 839% is achieved because there is no reinforcing phase. The tensile strength increases with increasing Hi-Silica content from 10 to 40 phr, then begins to decrease with further increase in silica content. At this level, the relatively well-dispersed Hi-Silica particles achieve optimal reinforcement, helping to improve tensile strength thereby creating a physical network with the rubber, limiting the movement of the rubber chain when external forces are applied, leading to increased modulus and durability. When the Hi-Silica content increases from 50 to 70 phr, at this content the silica particles begin to agglomerate due to the interaction between the silanol groups on the surface, forming secondary particles with larger sizes than the original. Furthermore, there is no chemical bond between natural rubber and the Hi-Silica, increasing

the Hi-Silica content leads to difficulty in forming crosslinks in the rubber network and forming a rubber network with a discontinuous structure in the latter network. As a result, samples with Hi-Silica content greater than 40 phr have reduced mechanical properties. This phenomenon has also appeared in previous studies with the wet mixing method [26], [24].

Table 2. Curing parameters of samples from 0 phr to 70 phr.

No.	Sample	Scoring time (min)	Optimum curing time (min)	Curing rate (min^{-1})	Maximum torque(M_H) (dN.m)	Minimum torque(M_L) (dN.m)
1	0 phr	4.84	7.05	45.45	12.88	0.84
2	10 phr	7.13	9.59	40.65	15.08	1.60
3	20 phr	9.36	13.00	27.47	16.75	2.22
4	30 phr	9.85	14.45	21.74	18.24	2.84
5	40 phr	10.24	16.77	15.29	26.96	7.3
6	50 phr	8.90	21.36	8.03	34.87	11.8
7	60 phr	6.9	20.34	7.44	40.22	13.51
8	70 phr	6.91	26.42	5.13	37.58	16.99

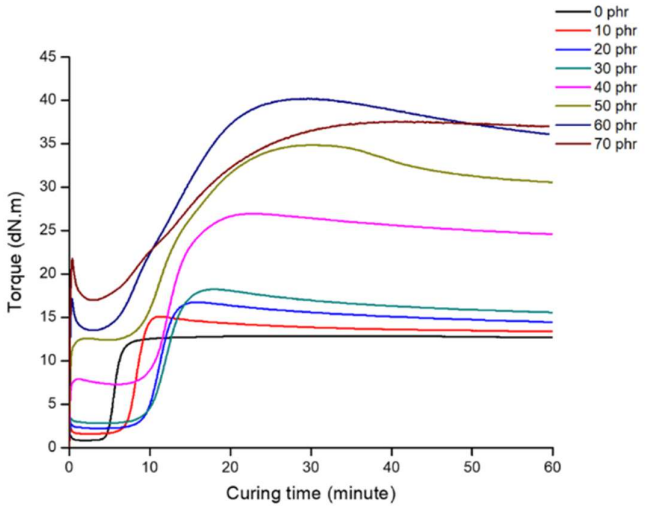

Figure 6. Vulcanization cure of samples from 0 phr to 70 phr.

3.5. The cross-link density of samples from 0 phr to 70 phr.

To evaluate the effect of silica on the vulcanization process. The cross-link density was calculated experimentally and the results are presented in Table 3. The cross-link density value for the sample without Hi-Silica reached 1,95.10-4 mol/cm3, which is consistent with previous studies. A general trend was observed when the Hi-Silica content increased, leading to a decrease in cross-link density, which affects all mechanical properties of the material such as hardness, abrasion resistance, elongation, and stress. An exception was the 10 phr sample, which had a higher cross-link density than the 0 phr sample without silica. The reason for this phenomenon is due to the hydrophilic nature of this material. The hydrophilic of Hi-Silica limited the contact of rubber with toluene, and the amount of absorbed toluene decreased, leading to an inhibition of the swelling phenomenon of rubber. At this point, the mechanical properties of the material are no longer determined by the rubber but by the filler, also known as the network confinement effect [27].

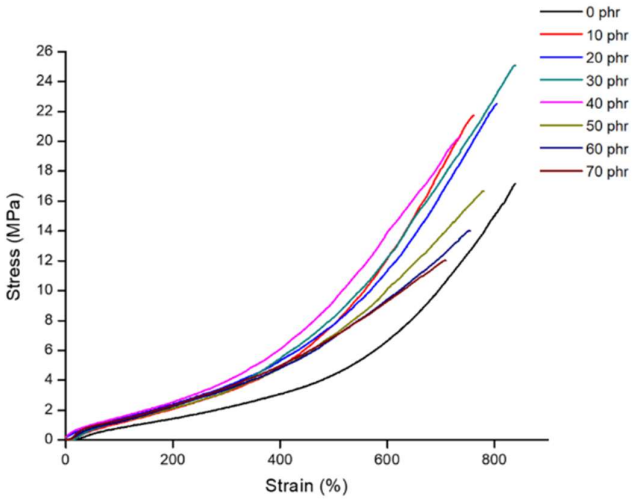

Figure 7. Stress-Strain curve of samples from 0 phr to 70 phr.

Table 3. Crosslink density of samples.

No.	Sample	Crosslink density (10^{-4} mol/cm^3)
1	0 phr	1,95
2	10 phr	2,39
3	20 phr	1,84
4	30 phr	1,64
5	40 phr	1,41
6	50 phr	1,24
7	60 phr	1,18
8	70 phr	1,12

3.6. The hardness and abrasion of samples from 0 phr to 70 phr

The results of Shore A hardness and wear mass loss are shown in Figure 8. The hardness values increase proportionally to the Hi-Silica content. As the silica content increases, the physical adsorption between rubber and Hi-Silica increases, which hinders the movement of the polymer chain. In addition, the hardness increases significantly from the 50 phr sample due to the strong aggregation of Hi-Silica forming a semi-continuous structure (percolation) that enhances the ability to transmit stress. As a result, the local hardness increases [25].

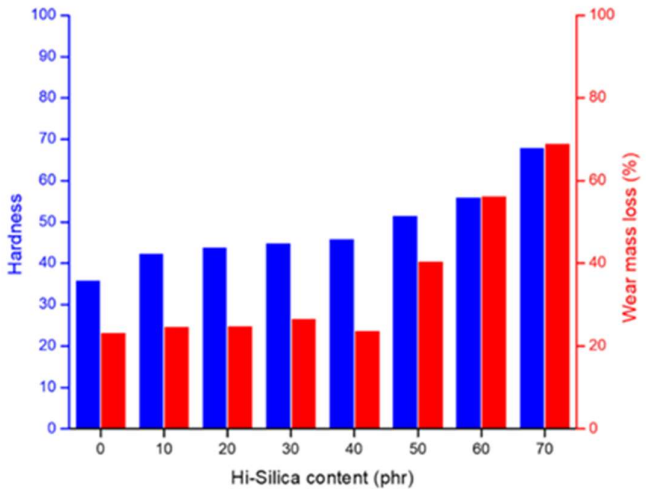

Figure 8. The hardness and wear mass loss of samples from 0 phr to 70 phr.

Wear mass loss is an important factor for reinforced materials. It can be clearly seen that the more Hi-Silica, especially for models from 0 to 30 phr [24], the more wear mass loss. The reason for this trend is that this type of hydrophilic precipitated silica cannot form chemical bonds with the polymer chain in rubber during the cross-linking process. Therefore, the more Hi-Silica is added the lower the bonding density, leading to increased wear mass loss or reduced wear resistance. At the Hi-Silica content threshold of 40 phr this can be considered the optimal content of this Hi-Silica filler.

3.7. The thermal properties of 40 phr samples

Thermal properties studies play an important role in assessing the durability and temperature variation of rubber materials. TGA-DTG techniques were used to study the 40 phr sample and their results are shown in Figure 9. First, in the period from room temperature to 136°C, no mass loss was observed and the mass loss rate was negligible. Next, in the period from 136°C to about 290°C, a mass loss trend appeared from 0% to 5.6% mass, the maximum mass loss rate during this period reached 1.41%/°C. This period is believed to be the desorption of moisture adsorbed on the Hi-Silica surface [28]. The stage from 290°C to about 688°C, this is the stage where the mass loss rate reaches its maximum value during the entire material decomposition process, the rate reaches 8.21%/°C at 380°C, which is decomposition temperature or T_d. Here, the sulfur cross-links will be broken first due to the weakest bond energy, then the C–C bonds in the polyisoprene chain will begin to break, leading to strong polymer decomposition [29]. This process ends with the remaining mass of the sample being 25.14%. This stage is the over-combustion in the atmosphere of the organic components in the sample, mainly rubber and additives. The remaining components include ash, ZnO and Hi-Silica.

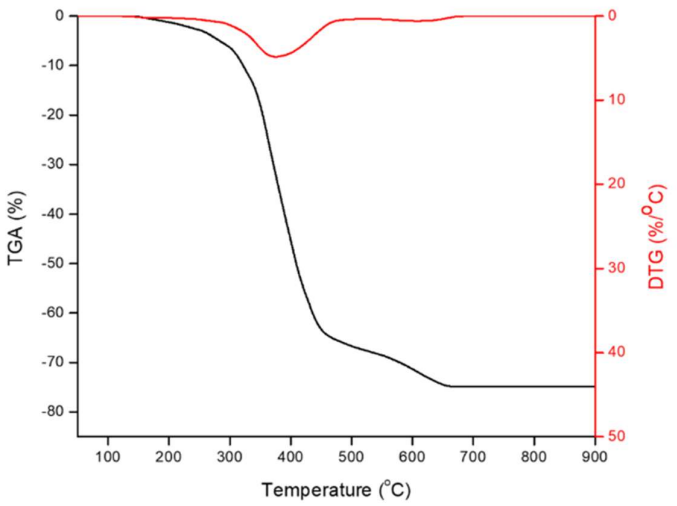

Figure 9. TGA-DTG curve of 40 phr sample.

4. Conclusion

Based on the experimental results for the preparation of deproteinized natural rubber reinforced with Hi-Silica from rice husk.

First, the change in protein content after incubation and Kjeldahl centrifugation was demonstrated. DPNR was determined to have better solubility in non-polar solvents than HANR through the 1H NMR spectrum. Second, FT-IR spectroscopy identified the bonds present on the Hi-Silica surface. It was confirmed to have a hydrophilic surface.

Second, the vulcanization time of the samples is prolonged, the vulcanization speed decreases, the maximum torsional moment and the minimum torque increase. Tensile strength increases with increasing Hi-Silica content from 10 to 40 phr, then begins to decrease with further increases in Hi-Silica content. As the Hi-Silica content increases from 50 to 70 phr there is a deterioration in mechanical properties. A general trend was observed as increasing Hi-Silica content resulted in decreasing cross-link density. Hardness values increase proportionally to Hi-Silica content. The more silica, the more mass is lost due to abrasion, especially in the range 0-30, at the Hi-Silica content threshold of 40 phr this can be considered the optimal content of this Hi-Silica filler.

Finally, from room temperature to 136^{o}C, no mass loss was recorded and the mass loss rate was negligible. Next, the period from 136^{o}C to about 290^{o}C showed a trend of mass loss from 0% to 5.6% of mass. The period from 290^{o}C to about 688 ^{o}C, at the end of this process, the mass of the remaining sample was 25.14%.

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