

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF RICE HUSK NANOSILICA IN NATURAL RUBBER

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Abstract: Rice husks are the hard protecting coverings of grains of rice. Several million tons of rice husks, which can be considered as an agricultural waste, are obtained every year. Precipitated silica is commonly used reinforcing filler in rubber industry. The objective of the present work is to replace commercial silica commonly used in natural rubber industries with high purity rice husk- nanosilica (RHNS). Nanosilica was obtained from rice husk through a simple sol gel method. The synthesized RHNS was characterized by FTIR, XRD, SEM, BET, TEM etc. From BET analysis the surface area of RHNS was found to be 252m²/g which is greater than that of commercial silica (CS). The particle size of RHNS was found to be 10-15 nm. The mechanical properties of natural rubber incorporated with RHNS shows better results than commercial silica.

Keywords: rice husk, nanosilica, surface area.

Introduction

Rice husk, which is considered as an agricultural waste, is a major source of amorphous silica [1]. The main components of rice husk are cellulose (25 to 35%), hemicelluloses (18 to 21%), lignin (26 to 31%), silica (15 to 17 %), soluble (2 to 5%), and moisture ca. 7.5% [2]. In the present study we mainly focus on the synthesis of silica from rice husk due to its high silica content, greater availability and low cost. Rice husk silica can provide aesthetic color to the composite and the proper utilization of rice husk may reduce green house effect and environmental pollution. Burning of rice husk below 700⁰ C results in the formation of amorphous rice husk ash. The rice husk ash so formed may contain several metallic impurities like Fe, Mn, Na, K, Ca etc. can decrease its surface area and purity. Several attempts are made to synthesize pure rice husk silica by eliminating these metallic impurities. The major treatments are acid or alkaline leaching of rice husk followed by calcination at higher temperature [3-5]. Silica with high degree of purity was synthesized from potassium

permanganate treated rice husk. Silica with 99.9% percent purity was obtained by treating rice husk with Aquaregia followed by piranha solution.

Composite materials are used in a variety of applications ranging from household appliances to aeronautics. The strength and stiffness of the composite is mainly determined by the reinforcement. Composite reinforcement may be in the form of fibers, particles, or whiskers. There is significant enhancement in the mechanical properties of plastics can be obtained by the use of fillers such as clay, silica, fly ash, wood floor, glass flakes, ligno cellulosic residues etc. The principal purpose for adding fillers is most often to reduce the cost of the overall material. Fillers can also be added to impart special properties to the plastic part such as flame retardance, color and opacity (no light transmission). Fillers are usually mixed into the liquid or molten plastic material. The reinforcement efficiency of fillers was greatly influenced by their topography, surface area, purity, particle size etc.

Silica is often used as filler in rubber and plastics. The hydrophilic nature of silica is mainly due to the presence of surface silanol groups. The –OH groups on the surface of silica cause silica particles to agglomerate and reagglomerate. Smaller particles have higher specific surface area which provides better matrix-filler interaction. Most polymers, being hydrophobic in nature do not wet the filler surface effectively. This results in inferior mechanical properties of the composite. Usually silane coupling agents were used to improve the adhesion between silica and hydrophobic matrix like rubber. In the present study we were able to synthesize high purity rice husk nanosilica, can be used as reinforcing filler in natural rubber. Enhancement in the mechanical properties of RHNS – NR composite was found to be superior to CS-NR composite.

Characterization of rice husk nanosilica (RHNS)

Fourier Transform Spectroscopy

FTIR spectra of RHNS were recorded on a Thermo Nicolet FTIR Spectrometer Model Avatar 370. Samples in the form of thin films, <1mm thickness, were employed.

X-ray diffraction

Samples for X-ray powder diffractometer were first finely ground and then mounted on a glass slide. The sample was analyzed in a Bruker AXS D8 Advance X-Ray powder diffractometer.

BET Method

Surface area of nano particles was measured using BET method. Surface area analysis was done using Smart Sorb 93, Surface Analyzer. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature

COMPOUNDING FORMULATION OF MIXES

Table 1

Ingredients (phr)	Mix A	Mix B
Natural rubber	100	100
ZnO	5	5
Stearic acid	2	2
RHNS	2	-
Commercial silica(CS)	-	2
TQ	1	1
MOR	0.6	0.6
TMTD	0.15	0.15
Sulphur	2.5	2.5

Compounding formulations of mixes

Compounding

The mixing was done as per ASTM D-3185(1989) on two roll laboratory size mixing mill (150mm* 300mm). Once a smooth band was formed on the roll, the ingredients were added in the following order: Activator ZnO, Coactivator stearic acid, TQ then accelerators TMTD and MOR then cross linking agent sulphur. After complete mixing. The stock was finely sheeted out through a tight nip gap.

Cure characteristics

Cure characteristics of the mixes were determined as per ASTM D 2084-1995 using Rubber Process Analyser (RPA 2000-Alpha technologies).It uses two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The sample of approximately 5g was placed in the lower die that is oscillating through a small deformation angle (0-2⁰) at a frequency of 50 cpm. The torque transducer on the upper die senses the forces being transmitted through the rubber. The torque is plotted as a function of time and the curve is called a cure graph. The important data that could be taken

from the torque-time curve are minimum torque, maximum torque, Scorch time (T'10) optimum cure time (T'90) and cure rate index.

Moulding

Vulcanization of various test samples was carried out in an electrically heated hydraulic press having 45cm ×45cm platen at 150⁰c at a pressure of 200 kg /cm² on the mould up to optimum cure time. Moulded samples were conditioned for 24 hours, before testing.

Modulus, tensile strength and elongation at break (stress-strain properties)

These tests were carried out according to ASTM D 412-1988, using dumbbell specimens. Test specimens were punched out from the molded sheets using the C-type die, along the mill grain direction. The measurements were carried out at a cross head speed of 500 mm/ min on a Shimadzu Model AGI Universal Testing Machine according to ASTM standards, D 412-68 and D 624-54 respectively.

Tear strength

Tear resistance of the sample was tested as per ASTM D 624-1998, using un-nicked 90° angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The measurements were carried out at a crosshead speed of 500 nm per minute on a Shimadzu Model AGI Universal Testing according to ASTM standards, D 412-68 and D 624-54 respectively. The tear strength was reported in N/mm.

Hardness

The testing was done as per ASTM D 2240-1997 using shore A type Dorometer. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

Abrasion resistance

The abrasion resistance of the samples was studied with a DIN Abrader (DIN 53516). Molded samples of 6±0.2mm diameter and 12mm thickness were prepared as per ASTM D 5963-04. Abrasion loss was calculated using the equation.

Abrasion loss = (loss of wt. / specific gravity)

Rebound resilience

Rebound resilience was determined by vertical rebound method according to ASTM D2 832-88. In this method plunger suspended from a given height (400±1mm) above the specimen was released and the rebound height was measured. The resilience scale was marked in 100 equally spaced divisions and hence the rebound height was equal to the resilience.

Synthesis of rice husk nanosilica (RHNS)

Rice husk (RH) was collected from a local mill in Thrissur. It was thoroughly cleaned with tap water to remove adhering soil and dirt. 100g of the cleaned RH was refluxed with 1L, (1N) HCl at 90°C for one hour to remove metallic impurities. After the reaction, the acid was completely removed from the RH by washing with distilled water. It was then dried overnight in an oven at 110°C. The treated RH was calcined in a muffle furnace at 650°C for 6 hours. Silica with high degree of purity was obtained in the form of white ash (WRHA). 10g of WRHA is refluxed with 2.5N NaOH solution for 4 hours. The resulting solution is continuously stirred and filtered to obtain clear sodium silicate solution. Silica gel was produced by adding conc. HCl drop wise to sodium silicate solution with constant stirring until P^H equal to 9. The gel obtained was aged for 24 h and washed with double distilled water, dried in an oven at 80°C for 24 h. The obtained silica particles were well ground to obtain nanosilica (RHNS).

RESULTS AND DISCUSSION

FTIR of RHNS

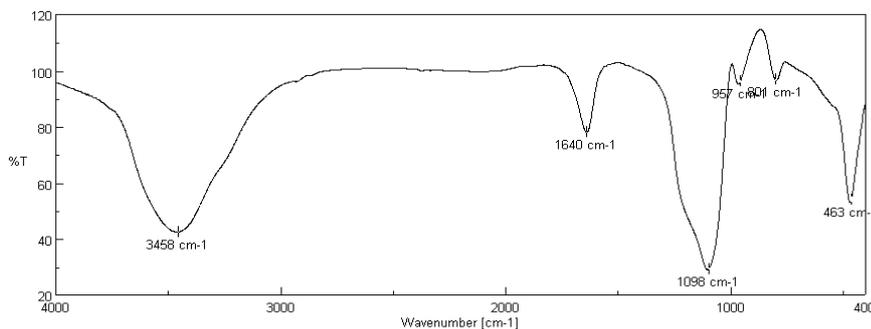


Fig1: FTIR of RHNS

The bands from 465 cm^{-1} to 485 cm^{-1} belongs to bending vibration of O-Si-O. Also the bands from 1090 cm^{-1} to 1100 cm^{-1} and from 790 cm^{-1} to 815 cm^{-1} belongs to Si-O-Si stretching modes. Band at 1640 cm^{-1} corresponds to -OH bending vibrations. Bands from 3450 cm^{-1} to 3640 cm^{-1} are due to the chemically absorbed water and also due to the surface hydroxyl groups.

BET ADSORPTION

Surface area of RHNS is found to be 252 m^2/g , which is higher than that of commercial silica (178 m^2/g). Higher the surface area lower will be the particle size and higher will be the reinforcing efficiency of the filler. From BET analysis it is clear that RHNS has higher surface area than CS.

XRD pattern of RHNS

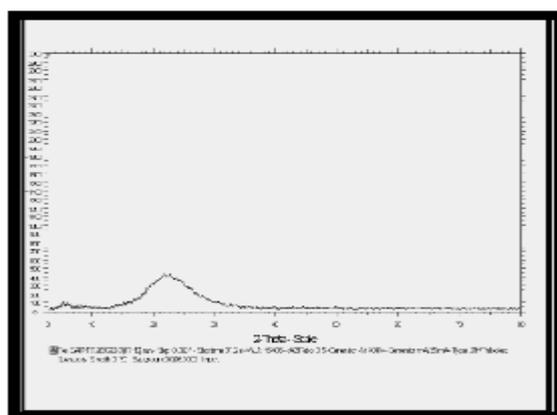


Fig 2: XRD of synthesized RHNS

XRD pattern of RHNS shows a broad peak at $2\theta=22^{\circ}$ which confirms the amorphous nature of RHNS.

SEM image of RHNS

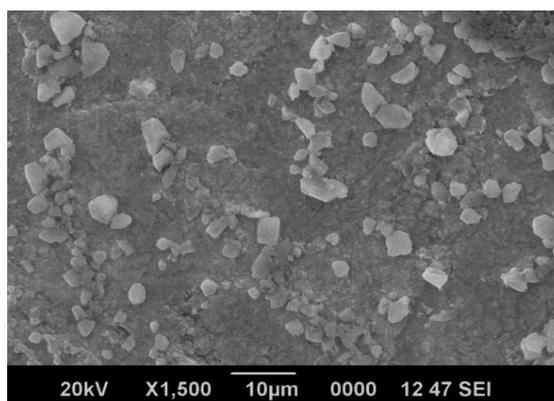


Fig 3: SEM image of RHNS

From fig 3: it was found that particles of RHNS were highly agglomerated. This agglomeration was due to the hydrogen bonding between silanol groups on the surface of RHNS.

EDX of RHNS

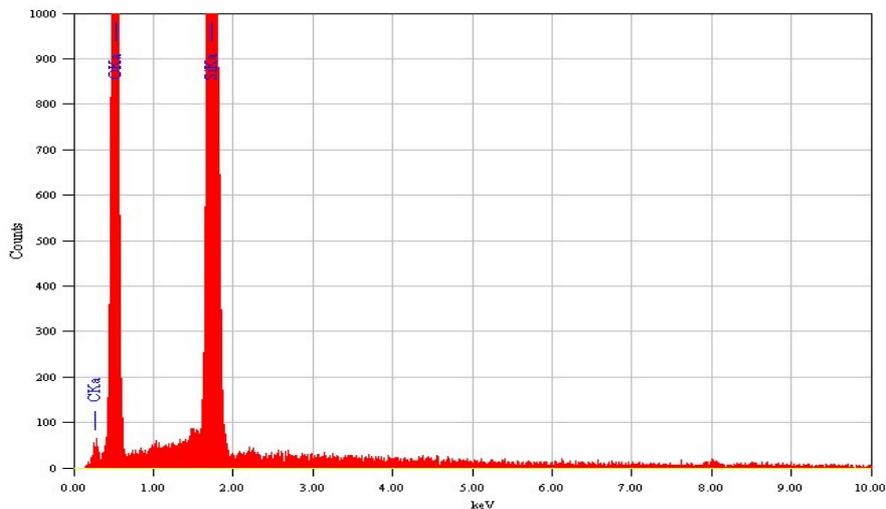


Fig 4: EDX of RHNS

The above EDX profile of RHNS contained predominantly the elements Si , O, C. Both Si and Oxygen peaks correspond to the silica. The small peak corresponding to C may be due to the unburnt carbon.

TEM image of RHNS

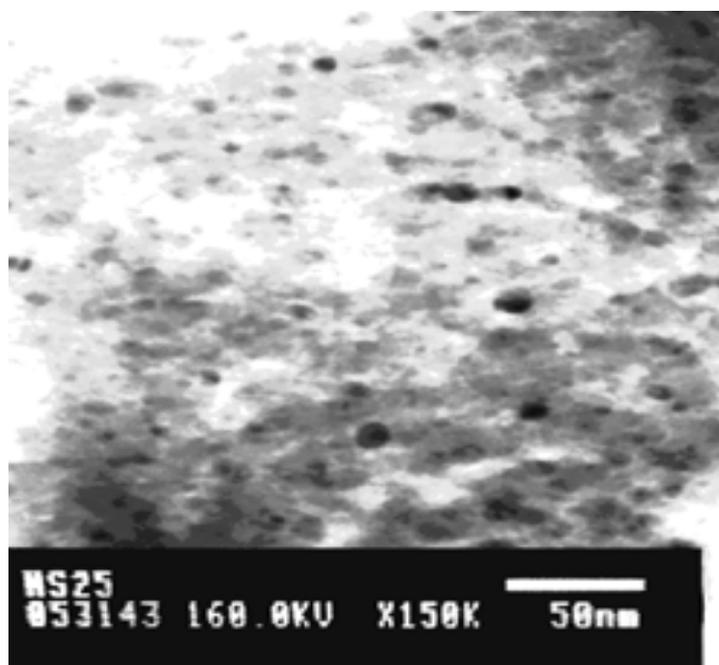


Fig 5: Tem image of RHNS

The above figure shows that the particles are spherical in shape, agglomerated and the size of RHNS was found to be 10nm.

Composite	Differential Torque(dNm)	Cure time(min)	Scorch time(min)
NR-RHNS(2phr)	2.65	6.00	3.25
NR-CS(2phr)	2.30	5.30	2.50

Table 2: Variation of torque, cure time and scorch time of the composite.

From the table it is clear that NR-RHNS composite shows a higher differential torque. The Differential torque is a measure of crosslink density and stiffness in the rubber. This increase in torque is due to the presence of silica rubber crosslink that imparts more restriction to deformation. Scorch time is higher for NR-RHNS composite than NR-CS composite. The delayed start of cure reaction in the case of RH nanosilica may be attributed to the possible interaction of the silica with the accelerators making it unavailable for cure reaction.

COPOSITE	TENSILE STRENGTH (Nmm ²)	TEAR STRENGTH (Nmm)	HARDNESS	ABRSAION LOSS (cc/hr)	RESILIENCE (%)
NR-RHNS(2phr)	24.0	38.0	37.5	0.6	50.0
NR-CS(2phr)	22.5	36.0	37.0	1.0	45.0

Table 3: Variation of mechanical properties of the composite

NR-RHNS composite shows higher tensile strength than NR-CS composite. It shows better reinforcing efficiency of the RHNS resulting from the higher surface area and better interaction of nanosilica with the matrix. The higher tear strength value of NR-RHNS composite is due to the better interaction of nanosilica with the matrix. The smaller particle size of the nanosilica helps it better arrest or deviate the tear cracks, resulting in higher tear resistance. The NR-RHNS composite shows significantly lower value for abrasion loss compared to the commercial silica composites, again indicating a better efficiency of RHNS. Resilience which is an indication of material elasticity is higher for NR-RHNS system.

Reason for the overall improvement in the mechanical properties of the composite

The high purity of RHNS, as opposed to commercial silica, may be an important reason that overall mechanical properties are superior. Theoretically, mechanical properties would be improved upon increasing of the amount of silica. As the same amount of filler was added, RHNS contained more silica than commercial silica thus improving the mechanical

properties of the products. The particle size of the filler also affect the mechanical properties of rubber products .Generally, the reinforcing power is greater when the particle size of the filler is smaller. As a consequence, with finer particle size, RHNS offers more reinforcing effects to the products. Surface area also plays an important role in reinforcing rubber. In our case, RH nanosilica has higher surface area thus giving better mechanical properties to the products.

Conclusion

Low particle size silica can be successfully prepared from rice husk under controlled conditions. The particle size of the synthesized RHNS was found to be 10 nm. The surface area of RHNS was also higher than that of commercial silica. Maximum torque, scorch time, differential torque, cure time, tensile strength, tear strength, abrasion resistance, and rebound resilience were increased by the addition of RH nanosilica. Thus rice husk nanosilica can be used as“green filler” in natural rubber compounding.

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