

Effect of Silane modification on the Mechanical Properties of Coconut Shell Powder Reinforced Styrene Butadiene Rubber Composites

M.P.Sreejith, Aparna K Balan, V. Shaniba, E.Purushothaman*

Department of Chemistry, University of Calicut, Kerala, 673635, India

*Corresponding author: E-Mail: epurushot@yahoo.com

ABSTRACT

Natural fiber reinforced polymer composites provide the customers with more alternatives in the material market due to their unique advantages. Natural fibers are rich in cellulose and they are cheap, easily renewable source of fibers with the potential for polymer reinforcement. This article focuses on the use of coconut shell powder (CSP) as reinforcing filler in Styrene Butadiene Rubber (SBR) matrix. Silane modified and unmodified CSP-SBR composites were prepared by an open mill mixing technique. The processing characteristics and the curing behavior of the composites were determined by Monsanto Rheometer. The mechanical properties like tensile strength, Young's modulus and hardness were also measured. Filler reinforcement ability of modified CSP is more when compared with unmodified CSP; there for, silane modified CSP-SBR composites shows better physicomachanical properties.

KEY WORDS: SBR, silane modified coconut shell powder, Tensile strength.

1. INTRODUCTION

Synthetic rubbers in its vulcanized form are used to produce various rubber products such as soles, hoses, belt, mats, tyres, seals etc. Carbon black and silica are the main fillers added in the vulcanization of the rubber. Even though they impart strength and better properties, but they are relatively expensive. In recent years there is increasing interest in the development and use of natural fillers as the reinforcing material in polymer composites. Many researchers have reported the processing advantages and improvement in the mechanical properties of natural fiber reinforced rubber composites (O'Connor, 1977; Coran, 1974; Boustany and Arnoldshort, 1976). The development of cellulosic materials as a rubber reinforcing filler has drawn increasing interest because of its low cost/high volume applications. It has several advantages compared with inorganic fillers, lower density, greater deformability, less abrasiveness to equipments, moreover, lignocellulose based fillers are derived from renewable resources.

The most serious concern with natural cellulosic material is its hydrophilic nature due to the presence of strongly polarized hydroxyl groups, and hence they are inherently incompatible with hydrophobic materials. This may lead to poor interfacial adhesion between the polar filler and the nonpolar matrix. This incompatibility may cause problems in the composite processing and material properties. The formation of hydrogen bond between hydrophilic centers lead to agglomeration of filler particles and unevenly distribute throughout the nonpolar polymer matrix during compounding and processing (Raj, 1989; Kazayawoko, 1999). When two materials are incompatible, introduction of a third material that has properties intermediate between those of the other two by forming a weak bonding layers can make them relatively compatible.

In order to improve interfacial bonding, modification of the filler surface is essential (John, 2005; Hristov, 2004; Tserki, 2005). The treatments to improve the fiber matrix adhesion in composites include chemical modification of filler (using anhydrides, isocyanates, acetylation, benzylation, alkalization etc) grafting of polymers in to lignocellulosic and use of compatibilizers and coupling agents (Abdul Khalil and Ismail, 2001). A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix. Silane coupling agents have been used in the rubber industry for the last three decades to improve the performance of fillers in rubber compounds. They are recognized as efficient coupling agents extensively used in composites and adhesive formulations (Rider and Arnott, 2000). A silane coupling agent contains functional group that can react with the rubber and the filler. In this way, the rubber filler adhesion is increased and consequently the reinforcing effect of the filler is enhanced.

In this work coconut shell powder (CSP) is used as an alternative filler for SBR. The coconut shell powder shows similarity with hard wood powder in chemical composition and exhibits some excellent properties compared to mineral filler (eg; silica, kaolin, mica, talc etc.) such as low cost, renewable, high specific strength-to-weight ratio, low density and environment friendly (Yanjun Xie, 2010; John and Anandjiwala, 2009; Fornko and Gozalez, 2005; Park, 2008). The aim of this work is to investigate the feasibility of using unmodified coconut shell powder (UCSP) and silane modified coconut shell powder (SCSP) as a reinforcing filler in SBR matrix and evaluation of their cure characteristics and mechanical properties.

2. MATERIALS AND METHODS

SBR-1502 (Synaprene) with 75% butadiene content was purchased from synthetic and chemicals limited, Bareilly, UP, India. Coconut shell powder was purchased from Sip India Exports (Erode, Tamil Nadu, India) and dried in hot air oven at 60°C and the powder was sieved in to 53-90 micron size. NaOH (Merck) and tri ethoxy vinyl silane (Sigma Aldrich) were used as received. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, 2, 2, 4-Trimethyl-1, 2-dihydroquinoline (TDQ), N-Cyclohexyl-2-benzothiazylsulphenamide (CBS) were of commercial grade and were obtained from local rubber suppliers.

Table.1. Chemical composition of coconut shell powder

Composition	Wt (%)
Lignin	29.4
Pentosans	27.7
Cellulose	26.6
Moisture	8
Ash	0.6
Solvent extractives	4.2
Uronic anhydrides	3.5

2.1. Silane modification of CSP: The dried CSP was treated with 10% NaOH for 5h with continuous stirring using a mechanical stirrer and was kept for 24h. Washed with water until the water become neutral. The powder was filtered out and dried in hot air oven at 70 °C for 24h and subjected to silane treatment. Dissolved 1% silane (tri ethoxy vinyl silane) in 90/10 methanol in water mixture and adjust the pH of the solution to 3.5- 4 using acetic acid with continuous stirring for 10 min. 0.5% DCP (dicumyl peroxide) was added to the solution. Immersed the alkalinized CSP in the solution and left it for agitation for 1h. Washed the powder with distilled water and dried.

2.2. X-ray Diffraction and FT-IR Spectroscopy: X-ray spectra of unmodified and silane modified samples were recorded with Bruker AXS D X-ray diffractometer using CuK_α radiation ($\lambda=1.5406 \text{ \AA}$) running at an accelerating voltage of 30 kV. The diffractogram was recorded in terms of 2θ in the range 5-90°. The crystallinity index (CI) was calculated using the following equation

$$CI (\%) = [(I_{002}-I_{101})/I_{002}] \times 100$$

where I_{002} is the maximum intensity of the I_{002} lattice reflection and I_{101} is the maximum intensity of X-ray scattering broad band, due to amorphous region of the sample (Segal, 1959) The IR spectrum of the samples were recorded using JASCO (Model 4100) Fourier transform spectrometer in the region of 4000-400 cm^{-1} .

2.3. Preparation of the composite: The formulation shown in Table 2 was employed except for the amounts of CSP which varied from 5 to 20 parts per hundred (phr). Total mixing time has been kept to a minimum to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that the mill roll temperature was not too high to avoid the cross linking during mixing. This has been achieved by cooling with water. The samples were named as UCSP for unmodified CSP and SCSP for silane treated CSP.

Table.2. Mixing formulation

Ingredient	Phr
SBR	100
Zinc oxide	5
Stearic acid	2
TDQ	1
Processing oil	1/20 th of filler
CSP	0, 5, 10, 15, 20
CBS	1.8
Sulfur	2.4

2.4. Curing and testing of rubber vulcanizates: Optimum cure time (t_{90}) for each compound was determined by using Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D 2084-93, operating at 160°C. After getting the cure time the compounds were vulcanized in a hydraulic press to optimum cure time at the temperature along the mill grain direction under a pressure of 6.7 MPa. (mold dimension 150 x 150 x 2 mm^3). To study the stress strain behavior, Universal Testing Machine INSTRON-3365 (Series IX Automated Materials Testing System 1.38, model-441, Instron Corporation, United States) was used. Tensile properties of the composites were examined according to ASTM D 412-1998. Shore-A-Durometer was used to measure the hardness of the prepared SBR-CSP composites according to ASTM D 2240-2004.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectra: The alkali treatment changes the native cellulose by a process known as alkalization (Mercerization)



The FTIR spectra of unmodified coconut shell powder (UCSP) and silane modified coconut shell powder (SCSP) which are shown in Figure 1. From the spectrum, in unmodified CSP a broad peak in the region 3315-3516 cm⁻¹ which is characteristic of the cellulosic -OH group was obtained. The intensity of this group is reduced in alkali treated CSP due to the removal of -OH groups by -ONa. Peaks were found at 1603, 962, 1167 and 1057 cm⁻¹ may be attributed to the presence of C=C, Si-OEt, Si-O-Si, indicating the presence of polysiloxanes deposited on the fiber and the occurrence of a condensation reaction between the silane coupling agent and the filler.

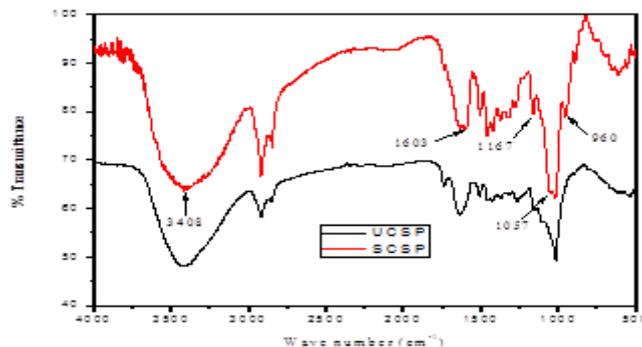
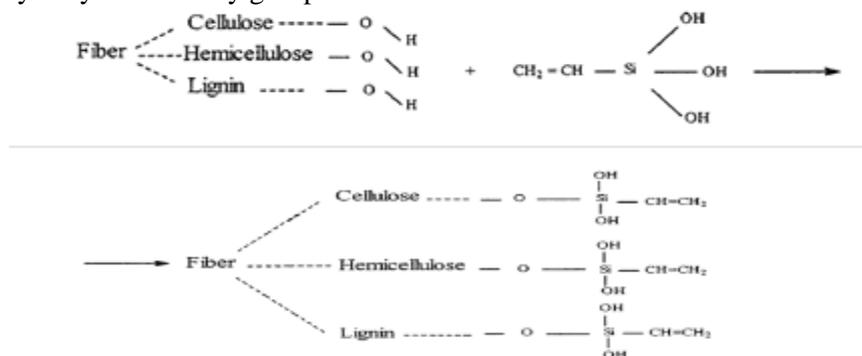


Figure.1.FTIR Spectra of unmodified, silane modified CSP

The alkali treatment results the partial removal of lignin and other alkali soluble components from the filler surface and increases the adsorption of silane coupling agent. Silanes were found to be effective in improving interface properties (Fernanda et al., 1997; Gonzalez et al., 1997; Ghatge and Khisti, 1989) In the presence of water, hydrolysable alkoxy group leads to the formation of silanols.



Scheme.1.Reaction of silane with -OH groups of natural fiber (Sreekala, 2000)

3.2. XRD analysis: X-ray diffraction studies (Figure 2) of unmodified and silane modified filler were carried out to investigate the crystalline behaviour of CSP. XRD analysis showed two main peaks representing the planes 101 and 002 at 2θ around 16° and 22° respectively.

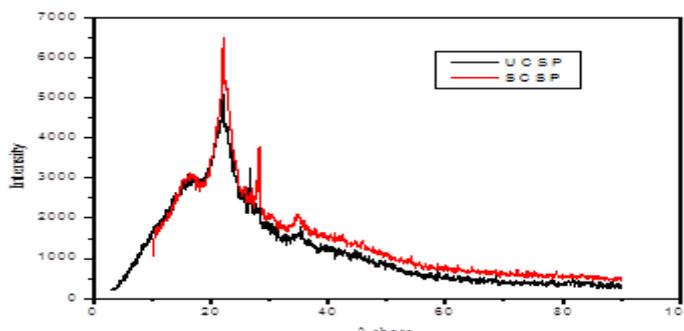


Figure.2.XRD Spectra of unmodified, silane modified CSP

The calculated crystallinity index (CI%) was found 39.19% in the case of unmodified CSP whereas it was 52.06% for silane modified CSP. The higher CI of silane modified CSP than unmodified one due to the removal of residual lignin, increased the exposure of the cellulose, resulting in the crystalline index. X-ray pattern shows that the silane modified CSP peaks were more intense than unmodified CSP. The CI% for the raw fiber increased of about 32.8%. i.e. chemical treatments were able to remove part of the amorphous materials like hemicellulose, lignin, and some other non cellulosic materials

3.3. Cure characteristics: Table 3 represents the optimum cure time, minimum torque, maximum torque and scorch time of CSP modified SBR composites. Both scorch time and optimum cure time were found to decrease consistently with increase with filler loading.

Table.3.Cure characteristics of SBR-CSP composites

Samples	Loading (phr)	Maximum Torque (Nm)	Minimum torque (Nm)	Scorch time (min ⁻¹)	Cure time (min ⁻¹)
SBR		10.13	0.51	5.13	12.1
UCSP	5	10.78	0.58	4.59	10.41
	10	11.36	0.60	3.47	10.26
	15	11.87	0.72	3.34	10.21
	20	12.85	0.73	3.25	10.18
SCSP	5	10.91	0.57	4.33	11.29
	10	11.03	0.62	3.35	9.59
	15	11.67	0.67	3.30	9.40
	20	12.36	0.73	3.22	9.39

This clearly indicates that filler increases the rate of curing of SBR-CSP composites. It was reported that as the filler loading increases, the incorporation time of filler in to rubber matrix also increases and consequently generates more heat due to additional friction (Herrera-Franco and Valadez-Gonzalez, 2005). It was also observed that (Table 3) at a given loading both scorch time and optimum cure time are shorter for silane treated CSP which indicates the enhanced interaction between the filler and matrix.

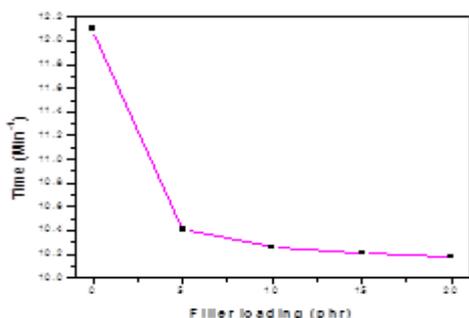


Figure 3 Effect of filler loading on cure time of rubber vulcanizate with UCSP

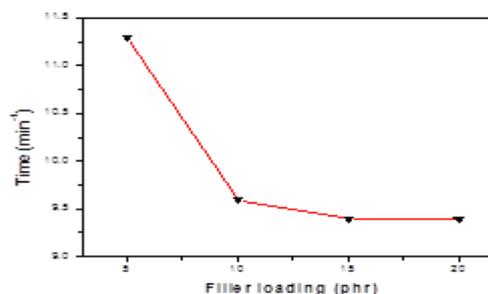


Figure 4 Effect of filler loading on cure time of rubber vulcanizate with SCSP

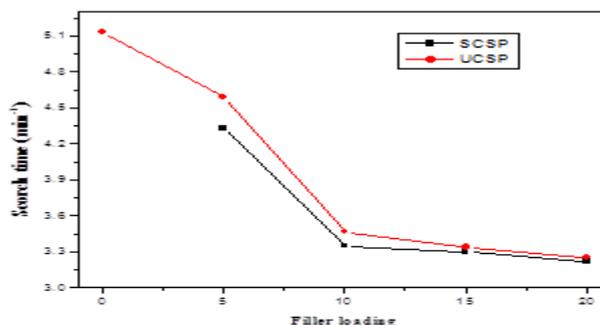


Figure.5.Effect of filler loading on scorch time of rubber vulcanizate

3.4. Mechanical Properties

3.4.1. Tensile strength: The tensile strength of SBR-CSP composites is shown in the figure 6 and 7. It is clear that the tensile strength of the composites were improved by the addition of CSP in to the SBR matrix. The stronger rubber-filler interaction would increase the effectiveness of the stress transferred from the rubber matrix to filler particles dispersed in the rubber matrix and consequently enhance the tensile strength. (Ismail and Chung, 1998)

The silane modified composite showed higher tensile strength than that of the unmodified composites. The hydrophobic structure of silane effectively prevents the gathering as well as the regular packing of filler particles and enhances compatibility with the matrix. The composite having 20 phr filler loading showed maximum tensile strength (figure 8).

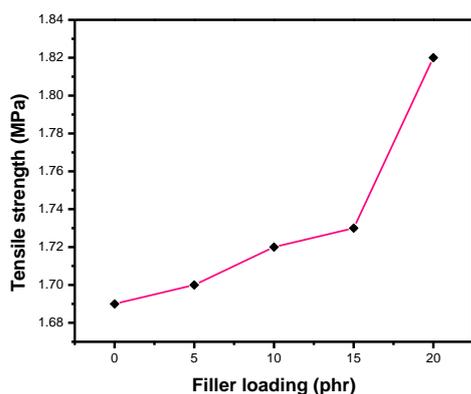


Figure 6 Effect of filler loading on tensile strength of rubber vulcanizate with UCSP

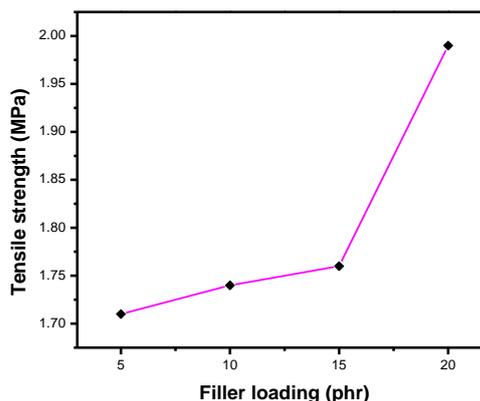


Figure 7 Effect of filler loading on tensile strength of rubber vulcanizate with SCSP

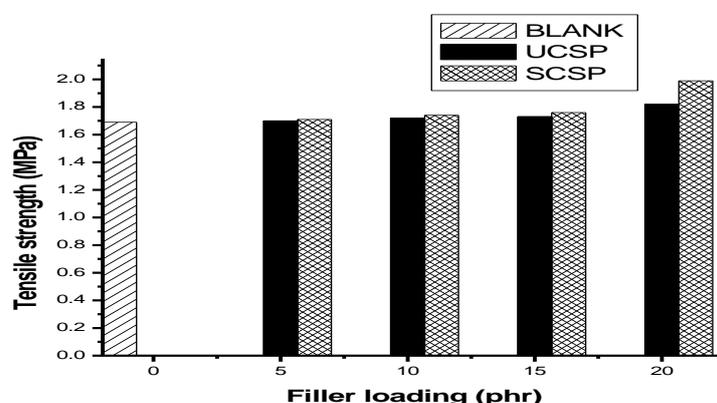


Figure 8 Comparison of Tensile strength of SBR with UCSP and SCSP composites

3.4.2. Young's modulus: The Young's modulus of the composites continued to increase with increase in filler content. (Figures 9 and 10). This is an indication of the material stiffness for SBR composites containing fillers. Fillers are known to increase the modulus, provided that the modulus of the filler is higher than that of the polymer matrix.

3.4.3. Hardness: The results reveal that the hardness of the filled vulcanizates increases consistently with increasing filler loading (figure 11). This is due to the fact that the addition of more rigid filler in to a rubber matrix reduces the elasticity of the rubber chains and leads to an increase in rigidity. According to Jacques (Jaques, 1971) more reinforcing filler would result in harder vulcanizates. This is evident from the results that the silane modified composites showed higher hardness than the unmodified composites.

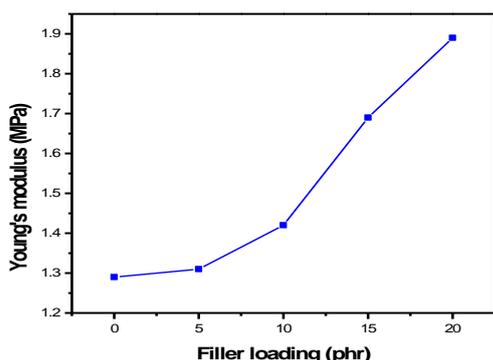


Figure 9 Effect of filler loading on Young's modulus of rubber vulcanizate with UCSP

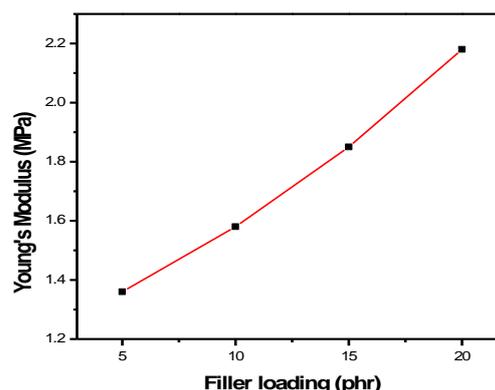


Figure 10 Effect of filler loading on Young's modulus of rubber vulcanizate with SCSP

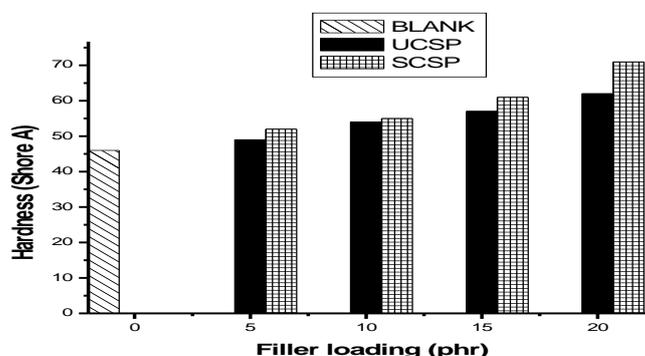


Figure 11 Comparison of Hardness of SBR with UCSP and SCSP composites

4. CONCLUSIONS

It can be concluded from the above discussion that CSP can be used as a reinforcing filler in SBR vulcanizates. Cure characteristics such as cure time and scorch time of the SBR compounds decrease with increase in filler loading. The silane modified composites showed better cure characteristics than the unmodified composites. Mechanical properties such as tensile strength, Young's modulus and hardness show an increasing trend with increase in filler loading. The results showed that the vulcanizates containing 20 phr filler loading exhibit better properties. The SCSP composites exhibit relatively higher tensile strength and hardness than the UCSP reinforced composites

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