

## ***Hybrid NBR/Chitosan/Nano-Silanised Silica Based Green Rubber Products***

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*In the present study hybrid NBR/chitosan/nano-silanised silica blends were prepared by melt blending for utilisation of chitosan (the second most abundant biopolymer) in development of green rubber products. The non-reinforcing nature of chitosan was improved by addition of nano-silanised silica. The effect of nano-silanised silica loading on crosslink density, tensile properties, surface hardness, tear strength, abrasion resistance and morphology of blends was studied. Improvement in both mechanical and morphological properties of NBR-chitosan blends was observed upon addition of nano-silanised silica. FTIR analysis was also carried out to study the interaction between rubber phase and chitosan as a result of compatibilisation by nano-silanised silica.*

**Keywords:** Biopolymer; chitosan; silanised silica; compatibilisation; automotive; green rubber

Biodegradability, abundance and non-immunogenic nature of biopolymers make them attractive for various applications including bio-medical, packaging, agriculture, construction, automotive *etc.*<sup>1</sup>. From all these areas, biopolymers can also act as fillers for elastomers<sup>2</sup>. Chitosan is a linear polysaccharide composed of  $\alpha$  (1 $\rightarrow$ 4)-linked 2-amino-2-deoxy- $\beta$ -D- glucopyranose. It is obtained by N-deacetylation of chitin<sup>3</sup>. Chitin is considered to be the second most abundant biopolymer on earth, first being the cellulose<sup>4</sup>. Crustaceans such as crabs, shrimps and lobsters are abundantly available raw sources of chitin<sup>5</sup>. It is estimated that about  $10^{10}$  -  $10^{11}$  tonnes of chitin is produced per year<sup>6</sup>. Approximately 75% of the total weight of shellfish including crabs, shrimps and krill are rendered as waste and chitin constitutes about 20 - 58% of the

dry weight of this waste<sup>7</sup>. Due to unavailability of a proper waste management system, this huge amount of waste is quite hazardous for the environment as such sea food wastes are usually left away at sea to spoil, or they get burned or landfilled<sup>8</sup>. Such types of waste is major source of surface pollution in coastal areas<sup>9</sup>. In view of the above issues, chitin should be extracted from crustaceans' shells and treated in a proper way to produce value added products, thus minimising the waste by utilising to obtain products with desired properties. Chitosan is considered to be the most important derivative of chitin that is obtained as a result of deacetylation of chitin under alkaline conditions. Various areas of research including membranes, biomedicines, hydrogels, water treatment food packaging are already utilising chitosan as a raw material<sup>10</sup>.

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One of the effective uses of biopolymers would be to utilise them as a bio-fillers in elastomeric products because most biopolymers have a much higher modulus than elastomers<sup>11</sup>. The major issue resulting from incorporation of bio-fillers in elastomers is their incompatibility since biopolymers are hydrophilic while most synthetic elastomers are hydrophobic in nature<sup>12</sup>. Moreover, biopolymers cannot bear high processing temperature and due to their hydrophilic nature they are more prone to absorb moisture which can cause swelling of the filler leading to dimensional instabilities<sup>13</sup>. The chemical structure of chitosan contains a number of hydroxyl groups all of which contribute towards its highly hydrophilic nature. This hydrophilicity will render chitosan useless as a reinforcing filler for most of the elastomers and its addition into an elastomeric product would be considered as conventional non-reinforcing filler<sup>14</sup>. Various studies have been focused on overcoming the issue of incompatibility between elastomers and bio-fillers. Surface treatment of bio-fillers, incorporating hybrid fillers and use of appropriate coupling agents are considered to be the most suitable methods for dealing with incompatibility between bio-fillers and elastomers<sup>15-17</sup>. Coupling agents are used to enhance the adhesion between the filler and the polymer by creating a strong bond between them at their interface. Silane and organotitanates are considered as efficient coupling agents<sup>18</sup>. One of the most effective way of incorporating bio-fillers in elastomers is to modify them with different types of silane. Silanised silica is considered as an alternate reinforcing filler to the carcinogenic carbon black and its utilisation forms the basis of a number of initiatives taken in recent decades for producing green rubber products<sup>19</sup>. The automotive industry utilises a number of rubber products for their parts manufacturing. Nitrile rubber finds wide spread applications in automotive rubber products. Due to oil resistance properties it acts as an excellent sealant. Moreover, it is widely used in making

hydraulic seals, tubing, roll covers and conveyer belts for the automotive industry<sup>20</sup>.

Utilising a hybrid filler of chitosan and silanised silica can be considered a viable route for producing reinforced green rubber products. Such a hybrid filler should utilise large quantities of chitosan that are supported by low weight fractions of silanised silica to develop a viable option for a reinforcing bio-filler. This approach will help to reduce large amount of bio-waste left by unused chitin, as most of it will be used as bio-filler for elastomers. In the present study, a hybrid filler system consisting of chitosan and nano-silanised silica is used to strengthen NBR thus producing green rubber products.

## EXPERIMENTAL

### Materials

Acrylonitrile butadiene rubber (NBR), containing 34% acrylonitrile contents was supplied by Meralastik Rubber and Engineering Products. Chitosan of low molecular weight (50,000 - 190,000 Da) and average size of 30 - 70 microns having a spherical shape and smooth surface was supplied by Sigma-Aldrich, UK. Silane 69 (Evonik, Germany), silica VN3 type, N-tert-butylbenzothiazole-2-sulphenamide (TBBS, Kawaguchi, Japan, a delayed action accelerator) were provided by Meralastik Rubber and Engineering Products. Stearic acid as processing aid, zinc oxide (ZnO) as an activator and N-(1,3-Dimethylbutyl)-N-Phenyl-P Phenylenediamine (6-PPD) as an antidegradent were purchased from the local market.

### Method

Compounds were prepared based on the formulation listed in *Table 1*. Mixing and the compounding procedure was carried out in a Brabender-Plasticorder D-47055 set at 40°C

and 50 rpm. NBR was added in the mixer and masticated for about 30 s. Chitosan was dried at 70°C for 3 h (until constant weight was achieved) in vacuum oven prior to processing. Silica was also pre-treated with silane prior to processing. Silica was heated to 120°C for 4 h to eliminate moisture from its surface. Silane was added to silica in a rotary mill and rotated for about 24 h until silane was coated onto silica particles. The dried chitosan was added and mixing was continued for a further 12 min. All other additives *i.e.* zinc oxide, stearic acid, 6-PPD, TBBS, nano-silanised silica and sulphur were added and mixed for an extra 3 minutes. The resulting random compound obtained from the melt mixer was passed through a two-roll mill to obtain a uniform compound. The compound was then compression molded to sheets based on their respective cure time obtained from a moving die rheometer.

### Characterisation

*Cure properties.* Moving Die Rheometer (MDR) analysis was done to study the cure properties of hybrid NBR/Chitosan/nano-silanised silica blends. 5 - 6 g of uncured specimen was placed in a moving die rheometer at 130°C for 30 min. Maximum and minimum torque values, scorch time, cure time and cure rates were determined by the MDR analysis.

*Fourier transform infrared (FT-IR/ATR) spectroscopy.* FT-IR analysis was carried out using JASCO FT-IR 4100 with 32 scans at 4 cm<sup>-1</sup> resolution and wave number ranging from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. FT-IR finger prints of NBR, NBR-chitosan and hybrid NBR/chitosan/nano-silanised silica blends were obtained from the sample surface through ATR technique. For pure chitosan, dried chitosan powder was mixed with dry potassium

TABLE 1. FORMULATION (PHR) FOR HYBRID NBR/CHITOSAN/NANO-SILANISED SILICA BLENDS

Formulation	NBR	Chitosan	ZnO	Stearic acid	TBBS	6PPD	Sulfur	Silica
C30Si0	100	30	3	1	0.7	1.5	1.5	0
C30Si1	100	30	3	1	0.7	1.5	1.5	1
C30Si3	100	30	3	1	0.7	1.5	1.5	3
C30Si5	100	30	3	1	0.7	1.5	1.5	5
C30Si10	100	30	3	1	0.7	1.5	1.5	10

TABLE 2. MIXING PROCEDURE OF HYBRID NBR/CHITOSAN/NANO-SILANISED SILICA BLENDS

Mixing Procedure	
Stage 1	
0-30''	Rubber mastication
30''-12'	Addition of dried chitosan
12'-15'	Addition of curatives
Stage 2	
0-3'	Compound of stage 1 through 2 roll mill
3'-25'	Compression molding at 140°C based on cure time from MDR

bromide (KBr) and pressed at a pressure of 40 - 60 MPa in pellet making assembly to form a pellet. FT-IR analysis was carried out on this pellet at a wavenumber ranging between 400  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$ .

*Crosslink density.* Crosslink density of chitosan filled rubber vulcanisates was determined by swelling method using the Flory Rehner Equation. Samples were allowed to swell in toluene for about 72 h until constant weights were obtained. Weight of the specimen before and after swelling was determined. Swelled samples were dried in oven until constant weights were obtained. Kraus correction<sup>21</sup> was also applied to overcome the effect of fillers in vulcanisates as discussed by Faridah *et al.*<sup>22</sup>. According to Kraus<sup>21</sup> when vulcanisates containing reinforcing fillers are allowed to swell in a solvent, the layer of rubber in direct contact with the filler particles do not swell as much as the rubber layer away from the filler particles. Hence the swelling becomes normal at a greater distance of rubber layer from the filler particles. Kraus<sup>21</sup> developed an expression to overcome the difficulties associated by adding reinforcing fillers. The Kraus equation can be represented as follows:

$$\frac{v_{ro}}{v_r} = I-m \left( \frac{\phi}{I-\phi} \right) \quad \dots 1$$

where  $\phi$  is the volume fraction of filler,  $v_{ro}$  is the volume fraction of rubber in swollen unfilled vulcanisates and  $v_r$  is the volume fraction of rubber in swollen filled vulcanisates. The volume fraction  $v_r$  was determined by the following formula<sup>23</sup>:

$$v_r = \frac{(D-FH)/\rho_r}{(D-FH)/\rho_r + A_o/\rho_s} \quad \dots 2$$

Here,  $H$  is the weight of specimen under observation,  $D$  is the weight of de-swollen specimen,  $F$  is the weight fraction of insoluble (filler) component,  $A_o$  is the weight of absorbed solvent (Toluene),  $\rho_r$  and  $\rho_s$  are the densities of rubber and toluene respectively.  $v_{ro}$  values obtained by regression were substituted in the Flory Rehner equation mentioned below to calculate chemical crosslink density ( $\text{mol/g}$ )<sup>24</sup>:

$$\nu = \frac{\ln(1-V_{ro}) + V_{ro} + XV_{ro}^2}{2\rho V_s(V_{ro}^{1/3} - 0.5V_{ro})} \quad \dots 3$$

where  $\nu$  is the crosslink density in mole/g,  $X$  is the rubber-solvent interaction parameter (for NBR-Toulene,  $X= 0.48$ )<sup>17</sup>,  $V_s$  is the molar volume of solvent (for toluene,  $V_s= 106.4 \text{ cm}^3/\text{mol}$ )<sup>25</sup>.

*Tensile properties.* Tensile strength, elongation at break and tensile modulus of hybrid NBR/chitosan/nano-silanised silica blends were studied according to *ASTM D-412*<sup>26</sup>, type C at ambient temperature using a universal testing machine TIRA Test 2810 with a crosshead speed set at 50 mm/min.

*Hardness.* Hardness values of crosslinked hybrid NBR/chitosan/nano-silanised silica blends were reported according to *ASTM D 2240*<sup>27</sup> at ambient temperature using a Shore A durometer.

*Tear strength.* Tear strength was determined according to *ASTM D-624*<sup>28</sup> (Type C) to study the extent of reinforcement in hybrid NBR/Chitosan/nano-silanised silica blends.

*Abrasion resistance.* Abrasion resistance of hybrid NBR/chitosan/nano-silanised silica blends was determined using an Akron abrasion tester at 5000 cycles with a 15° angle of inclination. Abrasion resistance was

reported as the reciprocal of volume loss. Morphology of abraded surfaces was studied using an optical microscope.

*Morphological studies.* Scanning electron microscope (SEM) micrographs of hybrid NBR/chitosan/nano-silanised silica blends were taken at 1500 $\times$  and 2500 $\times$  on a JEOL JSM 5910 SEM at 15KV intensity. All specimens were sputtered coated with gold prior to SEM to prevent electrostatic charging during examination.

## RESULTS AND DISCUSSIONS

### Cure Properties

The cure properties obtained from the moving die rheometer experiment are presented in *Table 3*. There were very small changes in  $\Delta$ torque values with different silica loading. The overall  $\Delta$ torque values reflected very low crosslinking in the samples. This could be due to presence of the acidic group (OH) on the surface of chitosan which hindered crosslinking of the chains. Whereas, the cure rate index increased with the increase in loading of silanised silica.

### FTIR/ATR Analysis

FTIR/ATR analysis was carried out to study the interactions between NBR, chitosan and nano-silanised silica in blends. ATR spectra of pure NBR, chitosan, NBR-chitosan (C30Si0)

and nano-silanised silica compatibilised NBR-chitosan blends (C30Si1 and C30Si10) are shown in *Figure 1*. Absorption peaks of chitosan were observed at 3100  $\text{cm}^{-1}$  to 3600  $\text{cm}^{-1}$  which are broad bands indicating the combined overlap of N-H and O-H stretch of hydroxyl and primary amine groups of chitosan. The peak at 2873  $\text{cm}^{-1}$  arises due to C-H stretch of  $\text{CH}_2$ . Peaks at 1663  $\text{cm}^{-1}$  and 1595  $\text{cm}^{-1}$  indicates the overlapping of N-H bend of primary amine and amide group of chitosan. The broad band near 1092  $\text{cm}^{-1}$  is due to vibration of C-O stretch and the peak at 890  $\text{cm}^{-1}$  correspond to saccharide structure *i.e.* C-O-C linkage of chitosan. Absorption peaks of nitrile rubber were observed near 2237  $\text{cm}^{-1}$  indicating the nitrile group and near 969  $\text{cm}^{-1}$  indicating trans-1-4-butadiene. The peak near 1442  $\text{cm}^{-1}$  indicates out of plane C-H wagging. For NBR-chitosan blends, when chitosan was incorporated in NBR, few additional peaks were observed corresponding to the peaks observed in chitosan. This indicates the incorporation of chitosan in NBR. When respective amounts (1, 3, 5, and 10 phr) of nano-silanised silica was added to NBR-chitosan blends an additional peak was observed at 1095  $\text{cm}^{-1}$  which indicates the incorporation of silanised silica in blends. Increase in intensity and broadening of peak (at 1095  $\text{cm}^{-1}$ ) for silanised silica was observed as the loading of silanised silica increases. This indicates interaction between silanised silica and nitrile rubber. Moreover, slight increase in intensity and broadening of peaks (at 3100 - 3600  $\text{cm}^{-1}$ , 1663  $\text{cm}^{-1}$ , 1595  $\text{cm}^{-1}$ ) for chitosan was also observed with

TABLE 3. CURE DATA OF HYBRID NBR/CHITOSAN/NANO-SILANISED SILICA BLENDS

Sample	Max. torque	Min. torque	T <sub>C90</sub>	T <sub>S2</sub>	Cure rate index
C30Si0	10	5.8	16.8	3.3	5.49
C30Si1	8.8	5.5	18.8	3.6	5.71
C30Si3	10.1	6	22.2	5.4	6.17
C30Si5	11	6.8	22.1	6	6.21
C30Si10	11.9	6.8	23.3	6.9	6.29

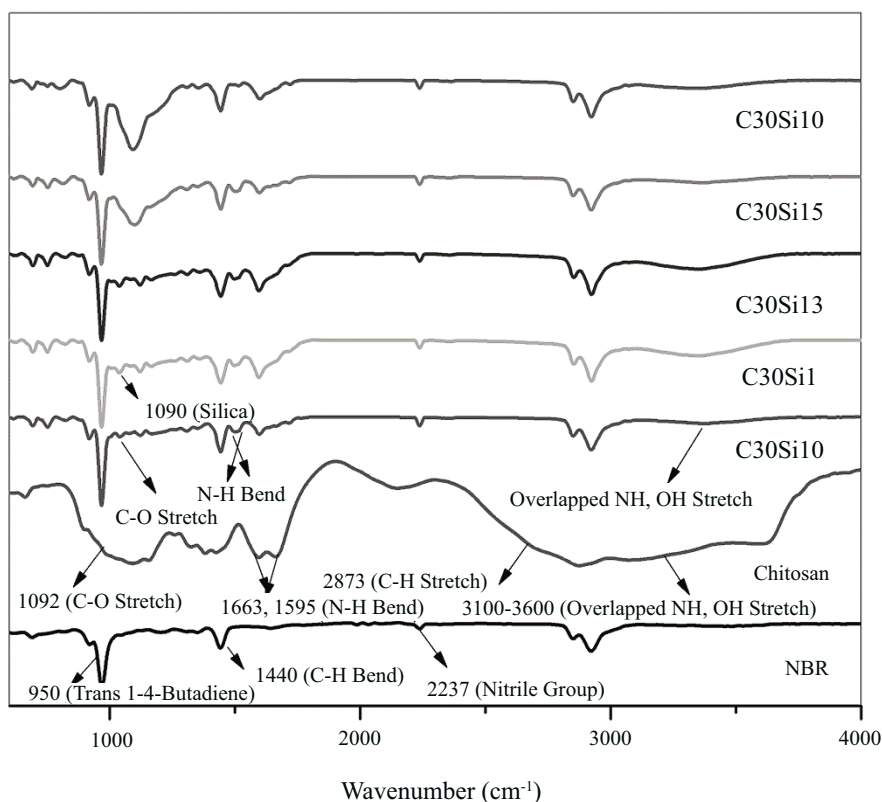


Figure 1. FTIR/ATR Spectra of pure NBR, pure chitosan, NBR-chitosan blend and hybrid NBR/chitosan/nano-silanised silica blends

increased loading of silanised silica which indicates better interaction between nitrile rubber and chitosan. This improvement is due to better networking provided by nano-silanised silica as pre-treatment of nano-silica with silane introduces additional functional groups *i.e.* organo-functional alkoxy silane molecules on the surface of silica. These functionalities can form extra crosslinks with sulphur and networks with chitosan particles as a result of which interaction between NBR and chitosan increased. Hence it is evident that incorporation of a compatibiliser improves the interaction between bio-filler and elastomer leading to a product with improved properties.

### Crosslink Density

The effect of nano-silanised silica on the crosslink density values of NBR/chitosan/nano-silanised silica blends is shown in *Figure 2a*. The crosslinking results obtained from swelling measurements were corrected by applying the Krauss correction term. *Figure 2a* shows that crosslink density of NBR/chitosan/nano-silanised silica blends increases continuously as a result of increase in amount of nano-silanised silica. *Figure 2b* shows the Krauss plot for various fractions of nano-silanised silica added in the blends. According to Kraus<sup>21</sup> the ratio  $v_{ro}/v_r$  linearly decreases

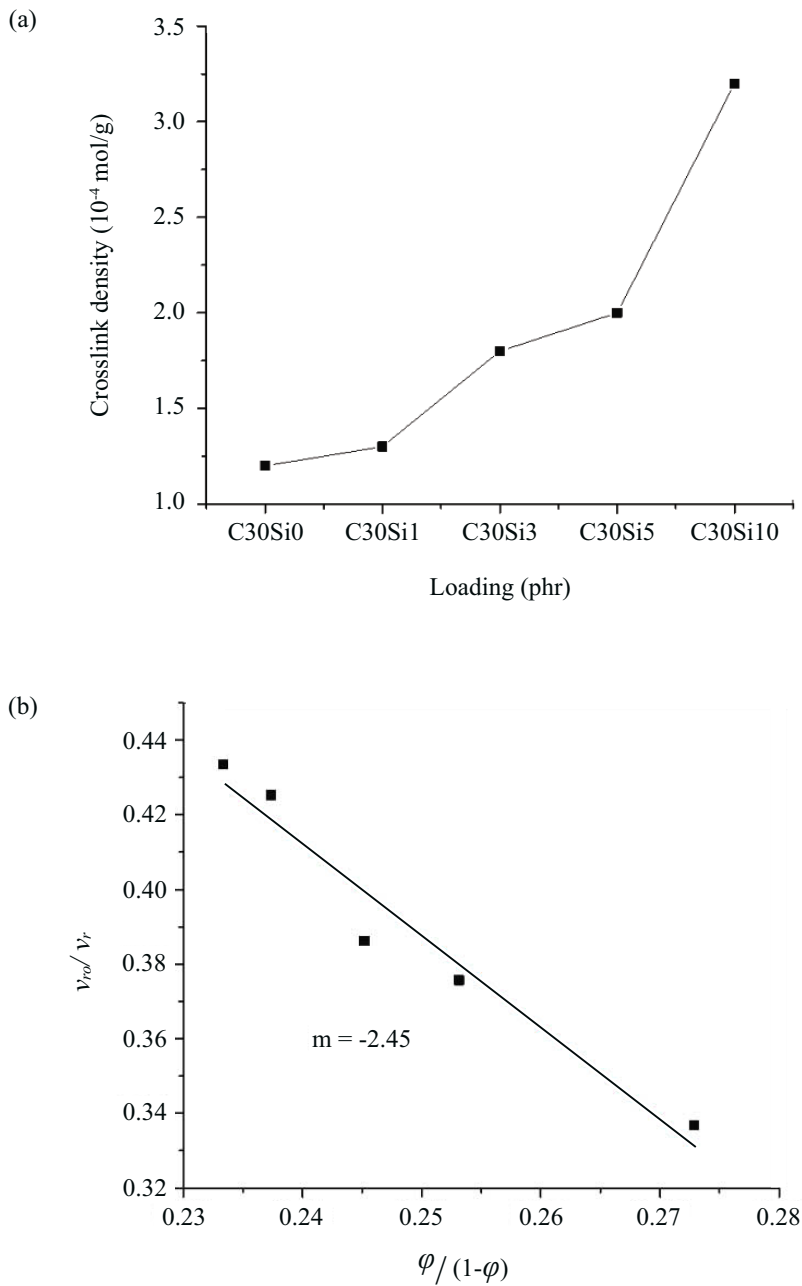
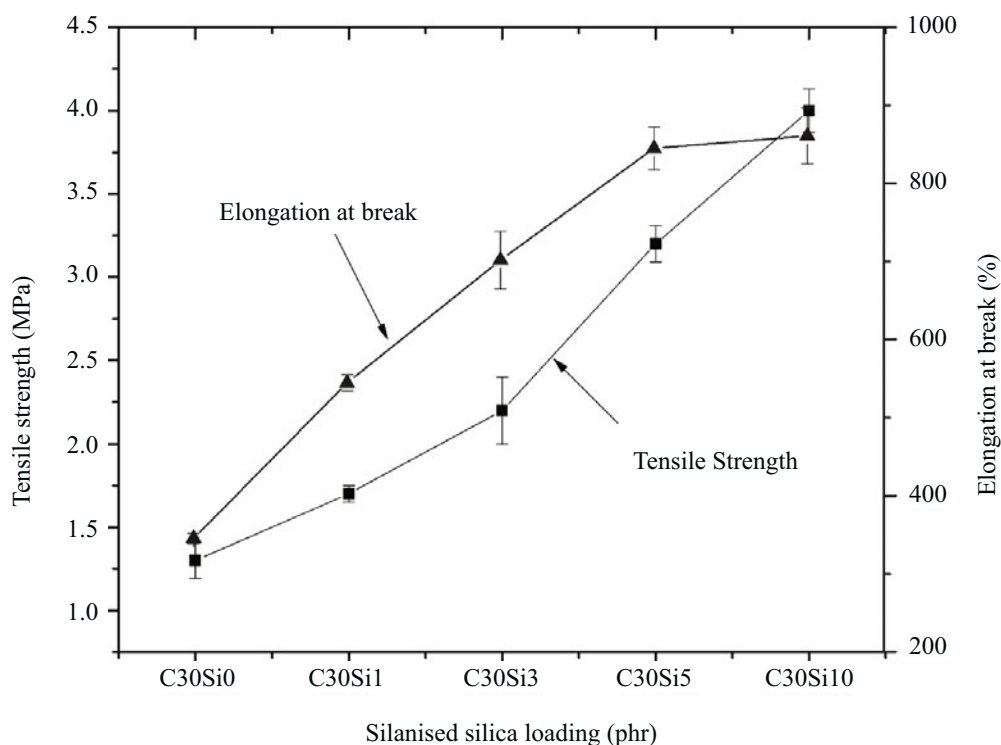


Figure 2. (a)Effect of nano-silicised silica loading on crosslink density of hybrid NBR/chitosan/nano-silicised silica blends, (b) Kraus plot for hybrid NBR/Chitosan/nano-silicised silica blends

with the increase in filler loading. This is due to different swelling ratios as a result of rubber-filler interactions. Hence the slope  $m$  indicates the extent of rubber-filler interaction. The calculated value of  $m$  (2.45) indicates better reinforcement of NBR by adding chitosan and nano-silanised silica hybrid filler. The increase in crosslink density is attributed to better compatibilisation in blends which restricts the penetration of solvent leading to reduced swelling by formation of more crosslinks. When silica was pre-treated with silane, the tetra sulfane group of silane were activated at the surface of silica during vulcanisation. This newly activated group provides extra sulphur for curing, hence more crosslink sites would be generated which results in an increase in crosslink density.

### Tensile Properties

Tensile strength, elongation at break and tensile modulus at 100%, 200% and 300% elongation were studied according to *ASTM D-412*<sup>26</sup> at ambient temperature. It was observed that tensile strength and elongation at break increased continuously as a result of increasing amounts of compatibiliser as shown in *Figure 3*. Increase in tensile strength is attributed to better dispersion and reduction of particle size as compatibiliser *i.e.* nano-silanised silica content increases. This improved dispersion is due to the reduction of particle size with the addition of nano-silanised silica which provides compatibilisation along with reinforcing effects. Due to increase in interaction between chitosan and rubber by



*Figure 3. Effect of nano-silanised silica loading on tensile strength and elongation at break of hybrid NBR/chitosan/nano-silanised silica blends*



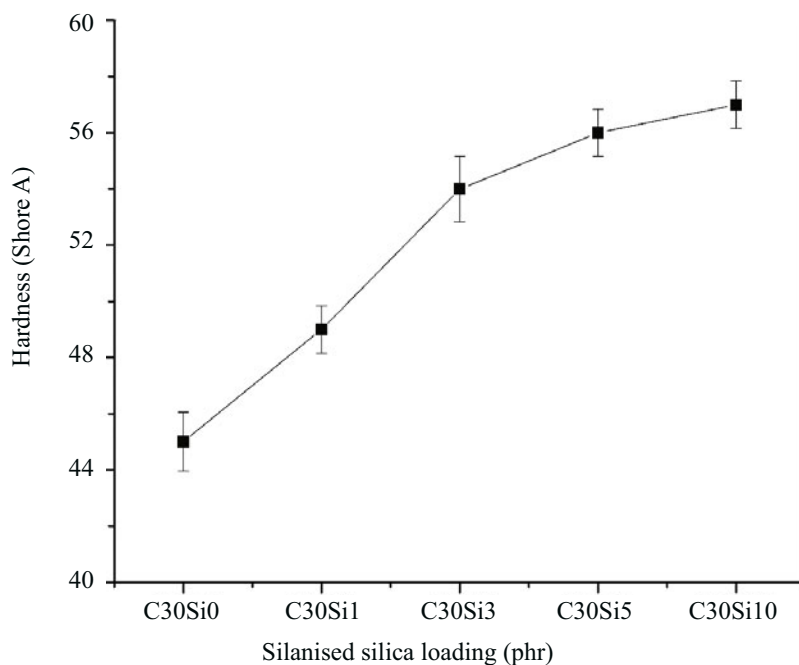
addition of nano-silanised silica, the formation of agglomerates reduces in the compound due to which dispersion improves. Increase in tensile strength can also be due to reactive sites generated at silica that interact with rubber and chitosan leading to formation of an extensive crosslink network which provides strengthening effects. However, the overall low tensile strength was due to the low  $\Delta$ torque values and crosslink density of the samples. It was concluded that chitosan provided hindrance in the crosslinking process and hence the compound showed poor mechanical properties.

A similar trend was observed for elongation at break which increased progressively with increasing compatibiliser. This again may be due to the fact that dispersion of filler *i.e.* chitosan becomes more homogenous by increasing the amount of nano-silanised silica thus improving its strength instead

of making it rigid and stiff. This increase in mechanical properties is in accordance with the results of crosslink density as increase in crosslink density is an indication of improved mechanical properties. No significant effect on tensile modulus was observed by addition of nano-silanised silica which indicates that nano-silanised silica does not impart rigidity to the blends but reinforces them, as evident from the results of tensile strength and elongation.

### Hardness

Hardness values increased progressively as a result of silanised silica loading as shown in *Figure 4*. This increase in hardness may be due to reinforcing effect of chitosan provided by nano-silanised silica. Addition of nano-silanised silica restricts the flexibility of rubber chains making them rigid thus increasing hardness. Increase in hardness was more prominent at lower loadings of compatibiliser

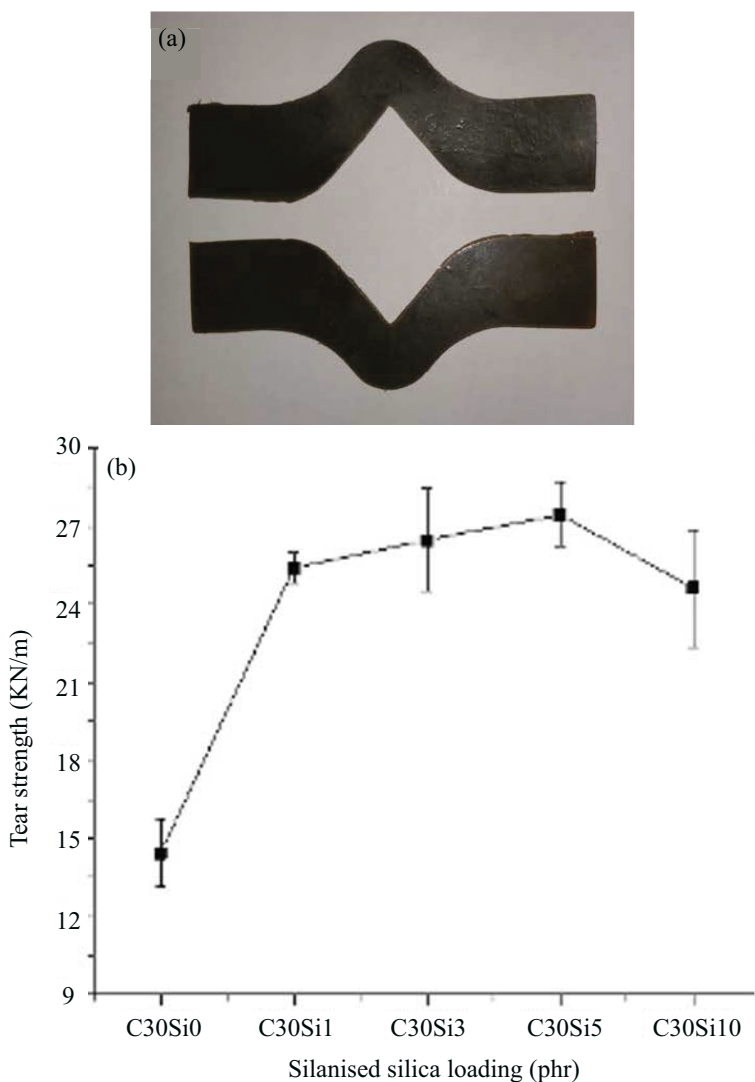


*Figure 4. Effect of nano-silanised silica loading on hardness of hybrid NBR/chitosan/nano-silanised silica blends*

but at higher loadings *i.e.* 5phr and 10phr very slight increase in hardness was observed. This confirms that addition of nano-silanised silica imparts strengthening effects to blends instead of making them more rigid and stiff as evident from the results of tensile strength and elongation. Results are also in accordance with the results of tensile modulus as no significant increase in modulus was observed as a result of increase in amount of nano-silanised silica.

### Tear Strength

Extent of reinforcement was also analysed by a tear test. Specimen of required dimensions were cut from the molded sheets according to *ASTM D 624*<sup>28</sup> (Type C) as shown in *Figure 5a*. An increment in tear strength of hybrid NBR/Chitosan/nano-silanised silica blends was observed by increasing nano-silanised silica content as shown in *Figure 5b*. This



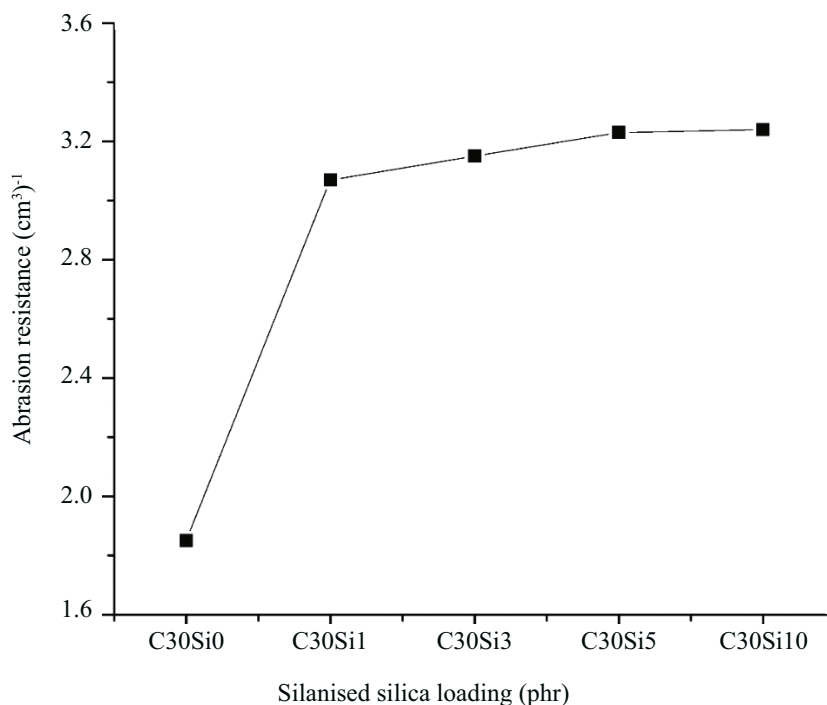
*Figure 5. (a) Specimen for tear testing, (b) Effect of nano-silanised silica loading on tear strength of hybrid NBR/Chitosan/nano-silanised silica blends*

increment is due to the reinforcing behavior of chitosan and nano-silanised silica. Improved interfacial bonding due to reduced particle size led to better reinforcement thus leading to an increment in tear strength. Extent of reinforcement is more prominent at lower loadings however a marginal effect on tear strength is observed at higher loadings. This is due to the fact that addition of nano-silanised silica does not impart too much rigidity as evident from the results of mechanical properties.

### Abrasion Resistance

In an Akron abrader, the rubber test piece is a disk which rolls over an abrasive wheel at a specific slip angle. The selection of a specific slip angle ensures rotation of the rubber disc at a speed which is different from the circumferential velocity of the abrasive wheel. These conditions ensure that the heat buildup

in the specimen is minimised. The Akron abrasion resistance values of filled NBR specimens are shown graphically in *Figure 6*. The results shown in *Figure 6* noticeably demonstrates the superiority of the hybrid filler reinforced NBR over the chitosan filled NBR specimens. As the concentration of nano-silanised silica increases the Akron abrasion index increases due to the enhanced dispersion and distribution of hybrid fillers as well as better compatibilisation between the constituents of the specimens. On an Akron abrader, the abrasion experienced by the specimen is based on microscale tearing and fatigue mechanism during testing. For filled elastomeric systems, the combination of microscale tearing and fatigue experienced during abrasion testing can be an effective tool to study the effect of filler addition on abrasion resistance. The hybrid filler particles are expected to resist the generation of microscale tearing and delay the fatigue experienced during abrasion testing



*Figure 6. Effect of nano-silanised silica loading on abrasion resistance of hybrid NBR/chitosan/nano-silanised silica blends*

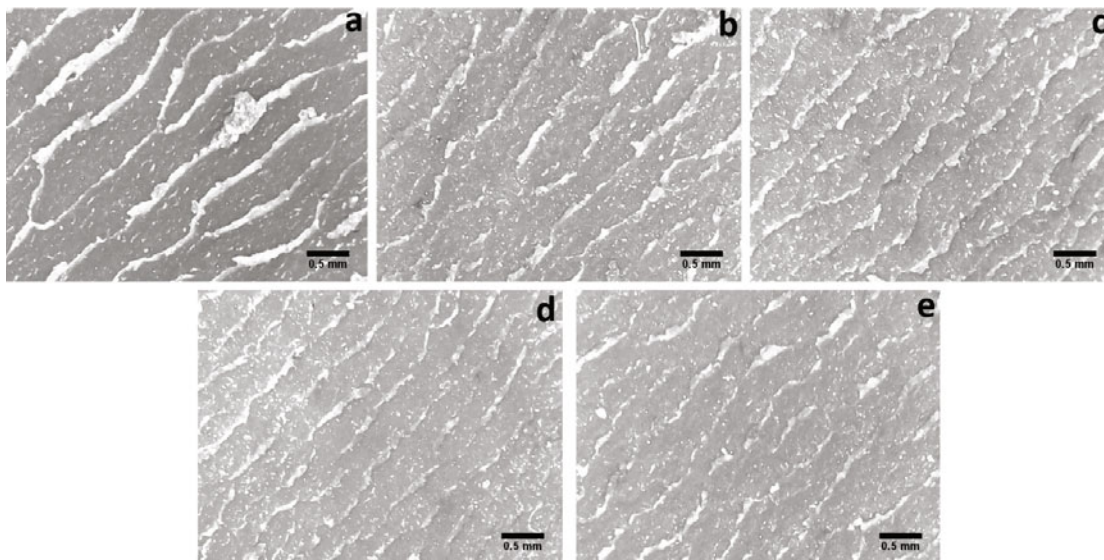
because of their higher modulus and their ability to act as a knot that resists tearing. The enhanced compatibilisation, dispersion and distribution of the hybrid fillers will ensure uniform interface between filler and NBR along with the removal of agglomerates that can generate individual filler particles that can resist abrasion.

In order to better understand the effect of filler addition on abrasion resistance of specimens, OM fractographs of the abraded surfaces were taken at 100X resolutions to locate the type and intensity of degradation produced during abrasion resistance. The OM fractographs of all the specimens are shown in *Figure 7*. OM fractograph for C30Si0 is shown in *Figure 7a* which reveals thick coarse sized ridges twisted around themselves throughout the abraded surface. Formation of these ridges can be attributed to microscale tearing and fatigue phenomena caused by rolling of the Akron abrader. Formation of these parallel ridges may lead to an abrasion failure due to roll formation mechanism thus leading to reduced abrasion resistance. When

respective amounts (1%,3%, 5%, 10%) of nano-silanised silica was added, a prominent change in morphology of fractographs was observed. OM fractographs of hybrid NBR-nano Silanised silica-chitosan blends are shown (C30Si1-*Figure 7b*, C30Si3-*Figure 7c*, C30Si5-*Figure 7d*, C30Si10-*Figure 7e*). From these fractographs it is quite evident that due to addition of nano-silanised silica, finer and smooth abrasion patterns were obtained. Moreover, the region between the ridges was more uniform and debris free compared to the C30Si0 blend. These smooth and fine abrasion patterns indicate less abrasion loss and ultimately high abrasion resistance of the blends.

### Scanning Electron Microscope (SEM)

Field emission scanning electron microscopy of NBR-Chitosan and NBR-Chitosan blends compatibilised by silanised silica was carried out to reveal the morphology of specimens. Liquid nitrogen assisted fractured surfaces of rubber blends were analysed at different levels of magnification.



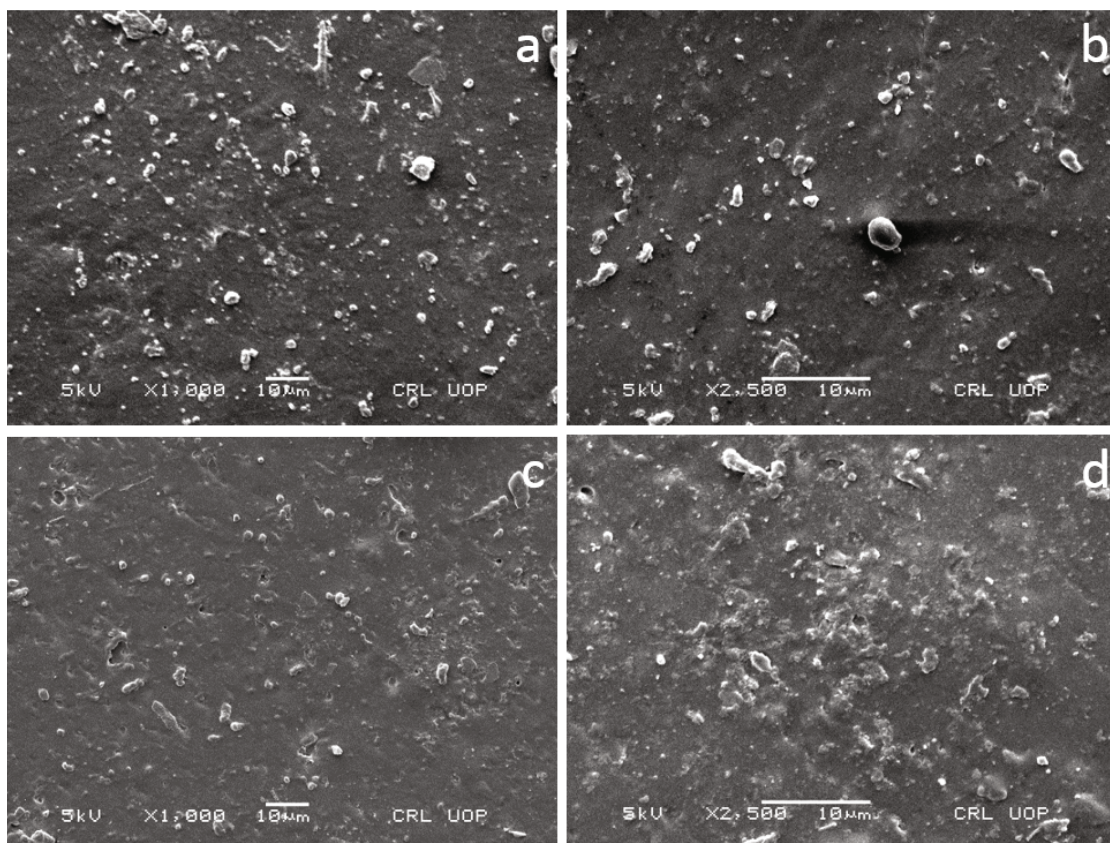
*Figure 7. Optical micrographs of abraded surfaces of (a) C30Si0, (b) C30Si1, (c) C30Si3, (d) C30Si5 and (e) C30Si10 specimens at 100× magnification*

SEM micrographs are shown in *Figure 8*. *Figures 8a* and *b* show the fractured surface micrographs of C30Si0 at 1000 $\times$  and 2500 $\times$  magnifications while fractured surface micrographs of C30Si5 at 1000 $\times$  and 2500 $\times$  magnifications are shown in *Figures 8c* and *d*. These micrographs show NBR as a continuous major phase with micron size chitosan dispersed in NBR. From *Figures 8a* and *b* it is evident that a number of chitosan particles are poorly distributed in the NBR matrix due to inadequate adhesion of filler with the matrix. Moreover, agglomeration of chitosan particles can also be observed which indicate filler-filler interactions instead of matrix-filler interaction which may lead to poor mechanical properties of blends. With the inclusion of 5 wt% of nano-

silanised silica, improvement in morphology can be observed leading to slightly smooth and homogenous surface. From *Figures 8c* and *d*, the role of silanised silica in stabilising the dispersion and adhesion of chitosan in the NBR matrix can be clearly visualised. This improved dispersion and adhesion of chitosan may lead to improvements in mechanical properties of rubber blends.

## CONCLUSIONS

Improvement in mechanical and morphological properties of NBR-chitosan blends was observed by addition of nano-silanised silica. Nano-silanised silica provides



*Figure 8. SEM micrographs at two different magnifications for C30Si0 (a-1000 $\times$ , b-2500 $\times$ ) and C30Si5 (c-1500 $\times$ , d-2500 $\times$ )*

a strengthening effect to the blends instead of making them rigid and stiff as revealed by the results of tensile strength, elongation at break, tensile strength, surface hardness. Increase in crosslink density and abrasion resistance was also observed upon addition of nano-silanised silica. Presence of hydrogen bonding and absence of any covalent network was revealed from the FTIR results. Improvement in morphological properties revealed better dispersion and distribution of chitosan by adding nano-silanised silica as evident from the results of scanning electron microscope. This addition of nano-silanised silica in NBR-chitosan blends suggests the possibility to utilise chitosan as a bio-filler in elastomers thus reducing the surface pollution in coastal areas caused by unused chitin.

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