

# NANOSILICA BASED NYLON 6 CHLOROPRENE SHORT FIBRE COMPOSITES

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Nanosilica was synthesized by acid hydrolysis of sodium silicate using dilute hydrochloric acid. The synthesized silica was characterized by XRD and SEM. The particle size of silica as obtained from XRD analysis was 13 nm. This synthesized nanosilica was used in place of commercial silica in HRH bonding system for chloroprene rubber / nylon 6 short fibre composite and also used as reinforcing filler in the hybrid composite. Cure characteristics and mechanical properties of the hybrid composites were evaluated. Minimum torque and cure time were increased with silica content and varied with fibre loading. Scorch time decreased with silica content. Nanosilica improved the tensile strength, modulus, tear strength, abrasion loss and hardness of the vulcanizates compared to conventional silica.

**Keywords:** Composite, Fibres, Nylon, Rubber, Silica

## INTRODUCTION

Short fibre reinforced elastomers combine the rigidity of fibre with the elasticity of rubber. Short fibre reinforced rubber composites offer a great advantage over traditional composites in manufacturing and processing operations (Foldi *et al.*, 1996). In comparison with particulate filler composites, short fibre reinforced systems possess a high degree of reinforcement even at relatively low fibre content (Saikrasun *et al.*, 1999). Short-fibre-reinforced rubber has been successfully used in the production of V-belts, hoses, tire treads, seals, and complex-shaped mechanical goods (Foldi *et al.*, 1996). The

ultimate properties of the composite depend on fibre concentration, fibre dispersion, fibre-rubber adhesion, fibre orientation, and fibre aspect ratio (Varghese *et al.*, 1997; Sreeja *et al.*, 2002; Sreeja *et al.*, 2002a; Sreeja *et al.*, 2003; Seema *et al.*, 2006; Abdelmouleh *et al.*, 2007). A number of synthetic and natural fibre were used by earlier workers in natural and various synthetic rubbers. The fibre-matrix interfacial bond has a decisive effect on the service properties of composites. The effect of adhesion system on the physico-mechanical and electrical properties of SBR/Polyester short fibre composite was studied by Ismail *et al.* (1999). Atomic force microscopy study of short melamine fibre reinforced EPDM rubber

was reported by Rajeev *et al.* (2001). Wazzan studied physico-mechanical properties of EPDM/ Nylon-6 short fibre composite (Wazzan 2004). Different techniques have been employed to achieve a strong interface or good adhesion between fibres and matrix. Studies on interfacial adhesion with different short fibres and matrices have been reported (Seema *et al.*, 2006; Geethamma *et al.*, 1998; Seema *et al.*, 2005). Geethamma *et al.* (1995) found that the natural rubber-coir fibre interface bond could be improved by the addition of a resorcinol-hexamethylene tetramine-silica dry bonding system. Rajeev *et al.* (2003) studied the effect of a dry-bonding system in improving the interfacial bond in short melamine fibre-acrylonitrile-butadiene rubber (NBR) composite. The effect of a urethane resin on short polyester fibre-polyurethane composites was studied by Suhara *et al.* (1997, 1998). Sreeja *et al.* (2002) reported the effect of a urethane resin based bonding agent for styrene-butadiene rubber-whole tire reclaim-short nylon fibre composites. Effect of an epoxy-based bonding agent on the cure characteristics and mechanical properties of short nylon fibre reinforced NBR composite was studied by Seema *et al.* (2006).

Compared to the coating of adhesive by dipping process, the use of tri-component dry bonding system consisting of hexamethylenetetramine, resorcinol and silica (HRH system) is easier as the constituents can be added to the rubber matrix like any other compounding ingredient and additional processes like dipping and drying can be avoided. In most of the studies reported so far, the silica used in the system was conventional silica with particle size in the micrometer range (Sreeja *et al.*, 2002; Ismail *et al.*, 1999; Rajeev *et al.*, 2001; Wazzan 2004; Geethamma *et al.*, 1998). As the role of silica is to improve the

wettability of the fibre surface, silica with lower particle size and hence higher surface area can be more effective as a component of the HRH system. Recently Tapasikotoky *et al.* (2004) and Chrusoid *et al.* (2003) have reported the preparation of silica with particle size in nanometer range.

In this work we report the effect of nanosilica on the properties of short nylon fibre reinforced chloroprene rubber composites. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler.

## MATERIALS & METHODS

### Materials used

Chloroprene rubber (CR) used in this study was supplied by Toyo Soda Mfg. Co. Ltd., Tokyo. Nylon fibre (N6) obtained from SRF Ltd., Chennai, India, was chopped to approximately 6mm length. Zinc oxide, stearic acid, magnesium oxide, ethylene thiourea, N-(1,3-dimethyl butyl) N'-phenyl-p-phenylene diamine, hexa methylene tetramine (hexa) and resorcinol used were of commercial grade.

### Synthesis of nanosilica

Nanosilica was synthesized by acid hydrolysis of sodium silicate using dilute hydrochloric acid as suggested by Taposikotoky and Dolui (2004). Sodium silicate is a cost effective silica source as compared to the more commonly used tetra ethoxy silane (TEOS) or tetra methoxy silane (TMOS) (Chrusoid *et al.*, 2003). Moreover, by using a purely aqueous medium, the expensive and very often toxic solvent could be avoided.

15 per cent sodium silicate solution was added with stirring to 1 per cent polyvinyl alcohol solution to form a homogenous mixture. Then 0.5 N HCl, was added slowly

with stirring at a temperature of 60 °C. The pH of the mixture was maintained between 1 and 2. The solution was stirred at 60 °C for 30 minute to carry out acid hydrolysis of sodium silicate. The sol-gel mixture was then washed well to remove all the sodium chloride formed. It was dried at 50 °C and then muffled at 600 °C.

### Characterization of nanosilica Scanning Electron Microscopy (SEM)

The prepared silica surfaces were sputter coated with gold and examined under SEM (model No. S 360), Cambridge Instruments, U. K.

### X-Ray Diffraction (XRD)

The XRD analysis was carried out with X-Ray Diffractometer, Bruker, D8 Advanced model, employing CuK $\alpha$  radiation ( $\lambda = 1.54$  Å) and Ni filter operating at 30 kV and 20 mA.

### Preparation of the composites

The formulation of mixes is given in Table 1.

CR-100 phr, Zinc oxide-5 phr, Stearic acid-0.5 phr, N-(1, 3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, Magnesium oxide -4 phr, Ethylene thiourea-0.5 phr were common to all the mixes.

Table 1. Formulations

| Mix No. |                 | Nylon-6 | Ingredients (phr)* |                   | HRH* |
|---------|-----------------|---------|--------------------|-------------------|------|
|         |                 |         | Nanosilica         | Commercial silica |      |
| MixA    | A <sub>0</sub>  | -       | -                  | -                 | -    |
|         | A <sub>10</sub> | 10      | -                  | -                 | 1.67 |
|         | A <sub>20</sub> | 20      | -                  | -                 | 3.33 |
|         | A <sub>30</sub> | 30      | -                  | -                 | 5    |
| MixB    | B <sub>0</sub>  | -       | 3                  | -                 | -    |
|         | B <sub>10</sub> | 10      | 3                  | -                 | 1.67 |
|         | B <sub>20</sub> | 20      | 3                  | -                 | 3.33 |
|         | B <sub>30</sub> | 30      | 3                  | -                 | 5    |
| MixC    | C <sub>0</sub>  | -       | 6                  | -                 | -    |
|         | C <sub>10</sub> | 10      | 6                  | -                 | 1.67 |
|         | C <sub>20</sub> | 20      | 6                  | -                 | 3.33 |
|         | C <sub>30</sub> | 30      | 6                  | -                 | 5    |
| MixD    | D <sub>0</sub>  | -       | 9                  | -                 | -    |
|         | D <sub>10</sub> | 10      | 9                  | -                 | 1.67 |
|         | D <sub>20</sub> | 20      | 9                  | -                 | 3.33 |
|         | D <sub>30</sub> | 30      | 9                  | -                 | 5    |
| MixE    | E <sub>0</sub>  | -       | -                  | 6                 | -    |
|         | E <sub>10</sub> | 10      | -                  | 6                 | 1.67 |
|         | E <sub>20</sub> | 20      | -                  | 6                 | 3.33 |
|         | E <sub>30</sub> | 30      | -                  | 6                 | 5    |

\* phr- parts per hundred rubber.

\* hexamethylenetetramine: resorcinol: silica was in the ratio 2:2:1. Total loading was 16% on fiber content

The mixing was done as per ASTM D-3190 (2001) on a two-roll laboratory size mixing mill (150mm × 300mm). Chopped Nylon 6 fibre was added in small increments in order to obtain uniform dispersion. After complete mixing the stock was finally sheeted out through tight nip so as to orient the fibers in the mill grain direction. The thin sheet obtained was cut in the required dimensions and stacked one above the other to the desired thickness. The sheets were vulcanized in a hydraulic press at 160 °C and at 200 kg cm<sup>-2</sup> pressure, to their respective optimum cure time.

### Cure characteristics

Cure characteristics of the mixes were determined as per ASTM D 2084-1995 using rubber process analyzer (RPA 2000, Alpha Technologies, USA).

### Measurement of mechanical properties

The tensile properties were measured using Shimadzu universal testing machine model AG-1, 10 kN, according to ASTM D 412 at a crosshead speed of 500mm/min. Test specimens were punched out, with fibres oriented along (longitudinal) and across (transverse) the mill direction for measuring mechanical properties. Tear strength was determined according to ASTM D 624 (Die C). Hardness (Shore A) was determined as per ASTM D2240-86 using a Zwick 3114 hardness tester. Abrasion resistance of the samples was measured using an abrader based on DIN 53516. Rebound resilience was determined by the vertical rebound method according to ASTM D 2832-88. Compression set at constant strain was measured according to ASTM D 395-86 method B.

### Volume fraction of rubber, $V_r$

$V_r$  of the samples was determined from

the equilibrium swelling data using the equation (Cassidy *et al.*, 1983)

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0 \rho_s^{-1}}$$

where D is the deswollen weight of the sample, F the weight fraction of the insoluble component, T the initial weight of the sample,  $\rho_r$  the density of the rubber,  $\rho_s$  the density of the solvent and  $A_0$  the weight of solvent absorbed.

## RESULTS AND DISCUSSION

### Characterization of nanosilica

#### Scanning electron microscopy (SEM)

Figures 1a and 1b show the SEM photographs of the synthesized and commercially available silica, respectively. These pictures show that the synthesized silica has lower particle size than the commercial silica. The small particle size provides large surface area, which results in improved mechanical properties. Figures 1c and 1d are the SEM of nanosilica and commercial silica respectively at 40,000X magnification. It is seen that both the silicas are of nanometer size. In the case of commercial silica the particles are agglomerated to a larger extent.

#### X-Ray diffraction studies

X-Ray diffraction patterns of the two types of silica are shown in figures 2 and 3. The peaks at  $2\theta=22.08^\circ$  and  $32.15^\circ$ , typical of silica, are seen in both the cases, indicating that both the silicas have similar structure. The particle size of the synthesized silica was determined from the X-ray diffraction data using Debye-Sherrer formula (Alexander 1968)

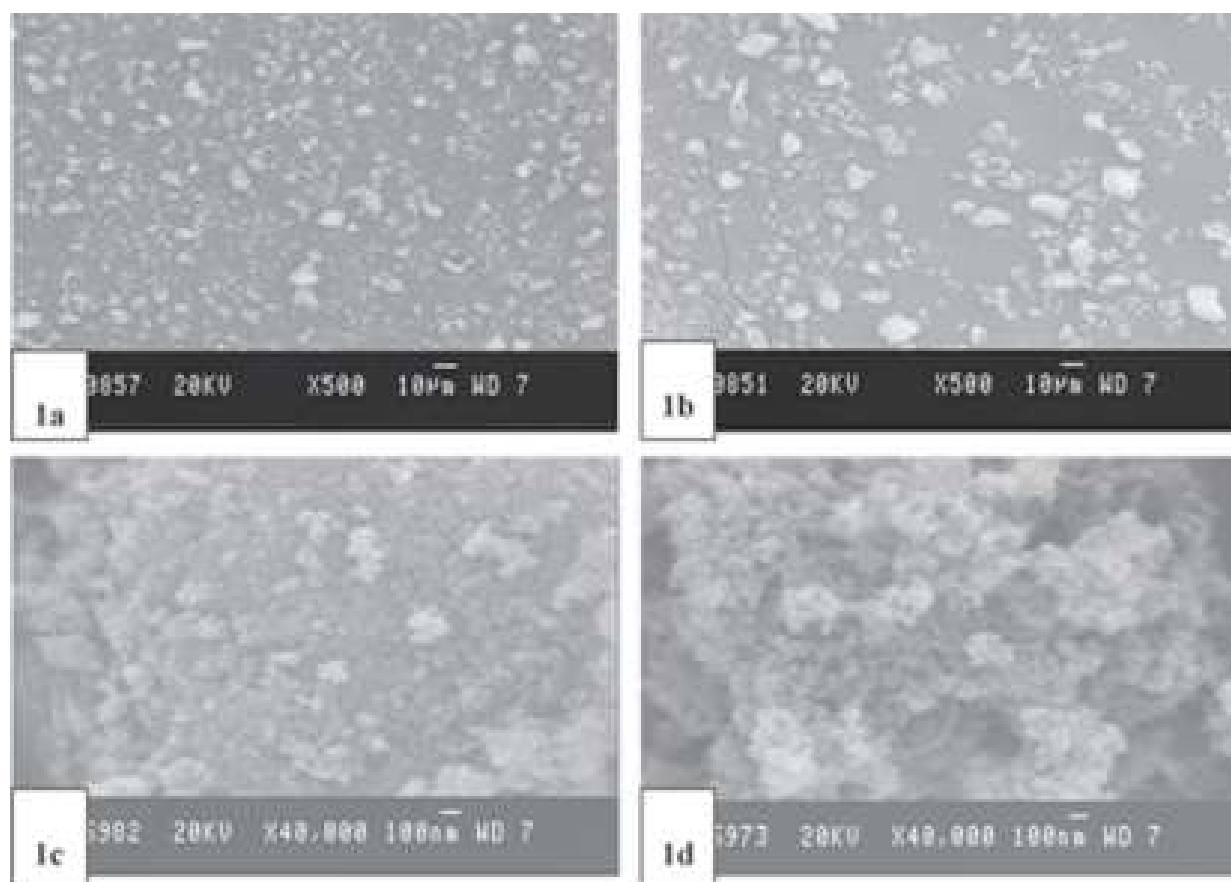


Fig. 1. 1a and 1c SEM picture of synthesized nanosilica, 1b and 1d SEM picture of commercial silica

$$C_s = 0.9\lambda / \beta \cos \theta$$

where,  $C_s$  is the particle size,  $\lambda$  is the wavelength of the incident x-ray beam,  $\beta$  is the full width at half maximum (FWHM) of the X-ray diffraction peaks

and  $\theta$  is half of the angle  $2\theta$  corresponding to the peak. The average particle size,  $C_s$ , of the prepared silica is found to be 13 nm and that of the commercial silica 34 nm.

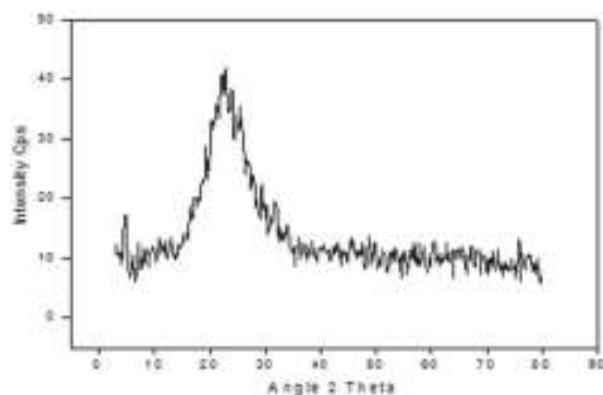


Fig. 2. XRD pattern of synthesized nanosilica

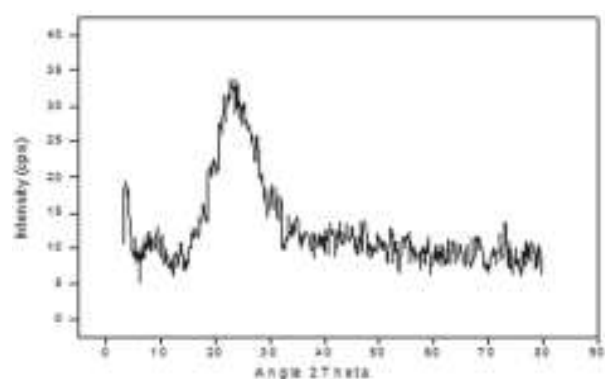


Fig. 3. XRD pattern of commercial silica



### Cure characteristics

Variation of minimum torque with fibre loading at various silica contents are shown in Figure 4. The minimum torque increases with fibre loading up to 20 phr. At 30 phr, however, the values are lower. This may be attributed to probable entanglement of the fibres at higher concentrations. Mixes B, C and D series show viscosity higher than the E series. The higher viscosity of the nanosilica composites may be due to the better interaction between silica and the rubber matrix. Lower particle size silica has higher surface area and hence can have improved interactions. The higher viscosity indicates that the processability of the

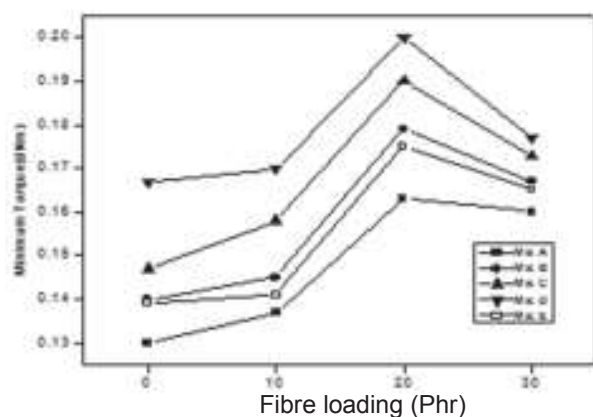


Fig. 4. Variation of minimum torque with fibre loading

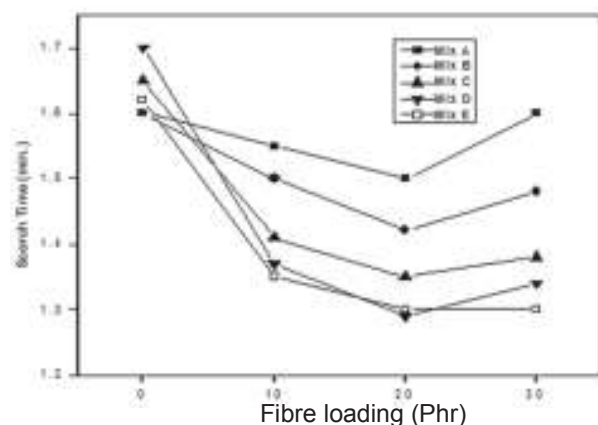


Fig. 5. Variation of scorch time with fibre loading

composite is marginally affected in the presence of fibres. Figure 5 gives the variations of scorch time with silica content and fibre loading. Scorch time decreases with fibre loading up to 20 phr and then slightly increases for all the mixes except Mix E as it contains commercial silica. Scorch time increases from 1.55 to 1.7 minutes by the addition of 9 phr nanosilica. The delayed start of cure reaction in the case of nanosilica composites may be attributed to the possible interaction of the silica with the accelerators, making it unavailable for cure reaction. By the introduction of nylon fibre in the mixes the scorch time decreases. The scorch time is decreased from 1.70 minutes to 1.29 minutes by the addition of 20 phr of nylon fibre to the mix containing 9 phr of nanosilica ie from the mixes  $D_0$  and  $D_{20}$ . This indicates that the nylon fibre has an accelerating effect on cure reaction. Similar results in the case of short nylon fibre reinforced NBR composite using an epoxy-based bonding agent have been reported earlier (Seema *et al.*, 2006). The variation of cure time with filler loading is shown in Figure 6. Cure time shows the same tendency for all the mixes. Cure time increases with fibre content up to 10 phr fibre fibre loading and after wards it decrease up

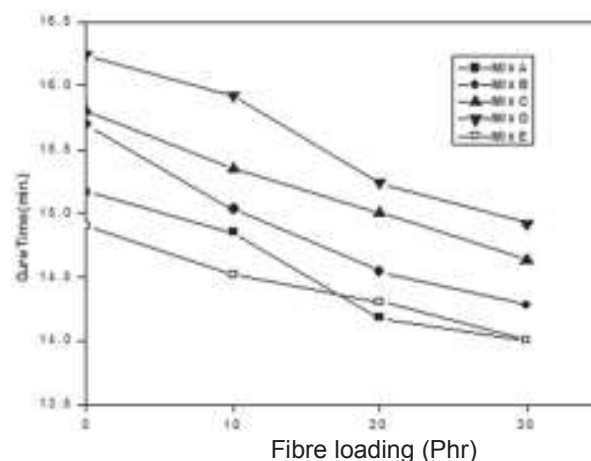


Fig. 6. Variation of cure time with fibre loading

to 20 phr and then remains more or less same. The initial increase of cure time is due to the interaction of silica with the accelerators and cure time is higher for higher silica loading. The decrease in cure time by higher fibre loading is due to the accelerating effect of nylon fibre in the cure reaction. This accelerating effect is more pronounced up to 20 phr fibre loading after that the effect is less. The higher heat generation in the mix during mixing/processing at higher fibre loading has resulted in longer heat history of the compounds and consequent lower scorch/cure times. The differential torque *i.e.*, the difference between the minimum and maximum torques developed during cure is increased with fibre loading and silica content. The differential torque is higher for nanosilica composites (Fig. 7). The differential torque is a measure of the extent of the crosslink formation and the filler-matrix interaction. The higher values for the nanosilica compounds indicate that the matrix is more restrained. This is evident from the  $V_r$  values of the mixes. Figure 8 shows that  $V_r$  of the nanosilica-containing mixes is higher than that of mixes containing commercial silica. This may be arising from

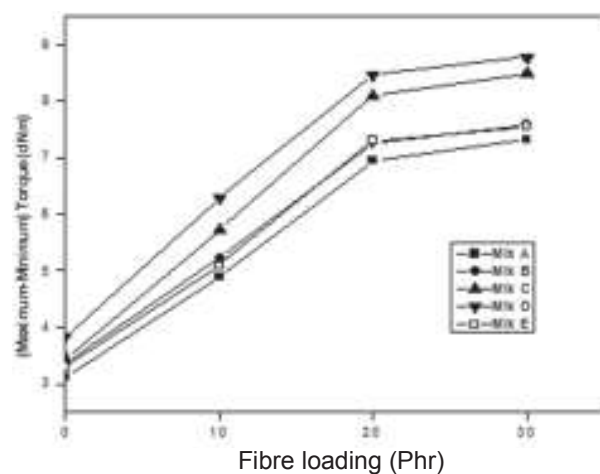


Fig. 7. Variation of differential torque with fibre loading

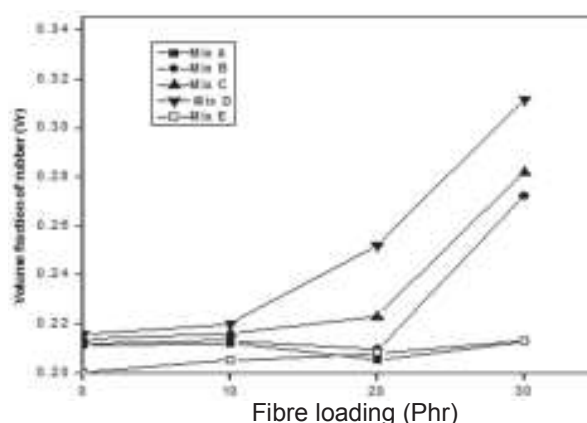


Fig. 8. Variation of volume fraction of rubber with fibre loading

improved silica interaction rubber hydrocarbon. Nanosilica can interact better with the matrix because of their higher surface area.

### Mechanical properties

The tensile strength increases with fibre content with an initial minor drop at 10 phr (Fig. 9). This drop may be due to the dilution effect of the fibres at lower loadings (Murty *et al.*, 1982; Sreeja *et al.*, 2003). At higher fibre loadings, however, the reinforcing effect takes over, resulting in an improved ultimate strength.

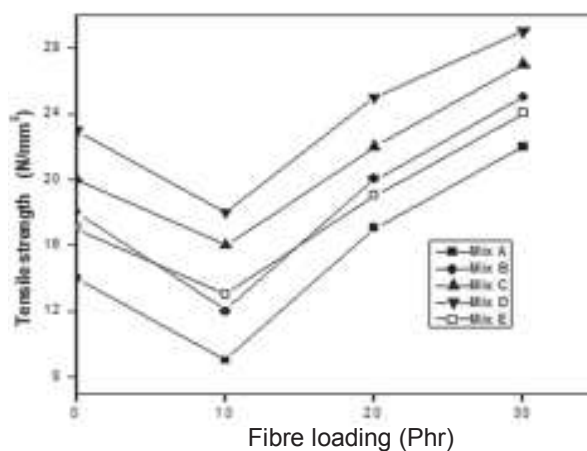


Fig. 9. Variation of tensile strength with fibre loading in longitudinal direction

At any fibre content the tensile strength is higher for the nanosilica filled samples. For the gum compound containing no fibre, the improvement is 43 per cent while for the 30 phr fibre-filled sample, 93 per cent improvement in tensile strength was obtained with 6 phr nanosilica. With the conventional silica the corresponding improvement in the tensile strength are 21 and 71 per cent, respectively. The tensile strength values of the E series mixes containing the conventional silica are close to that of B series mixes which contain only 3 phr nanosilica. The improved efficiency of nanosilica may be attributed to its higher surface area which gives better interaction between the fibre and the matrix.

For the samples with fibres oriented in the transverse direction (fibres oriented perpendicular to the direction of application of force), the variation is shown in Figure 10. In all the cases, the tensile strength drops at 10 phr fibre loading and then recovers marginally. Even at 30 phr fibre loading the tensile strength is lower than that of the corresponding non-fibre composites. The transverse orientation of fibres is not effective in transferring the load. As the crack can propagate easily with the fibres

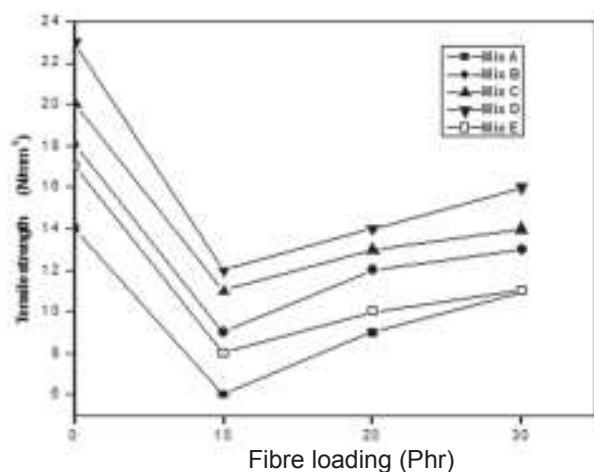


Fig. 10. Variation of tensile strength with fiber loading in transverse direction

oriented parallel to its propagation path, the samples fails easily, resulting in lower tensile strength. With increasing nanosilica content the tensile strength is improved (Series B-D). Tensile strength increases from 11 N/mm<sup>2</sup> to 16 N/mm<sup>2</sup> by the incorporation of 9 phr nanosilica in 30 phr fibre loaded composites. This shows that nanosilica is effective in restricting easy propagation of the crack by possible interaction with matrix. For the 6 phr conventional silica mixes (Series E), the values are lower than that of the Series B containing 3 phr nanosilica.

The variation of tear strength with fiber loading is shown in Figure 11. The tear strength registers a significant increase in the presence of short fibres. Tear strength increases from 27 N/mm to 95 N/mm by the addition of 30 phr fibre in the case of Mix A. With nanosilica, the tear strength is improved consistently for all the mixes.

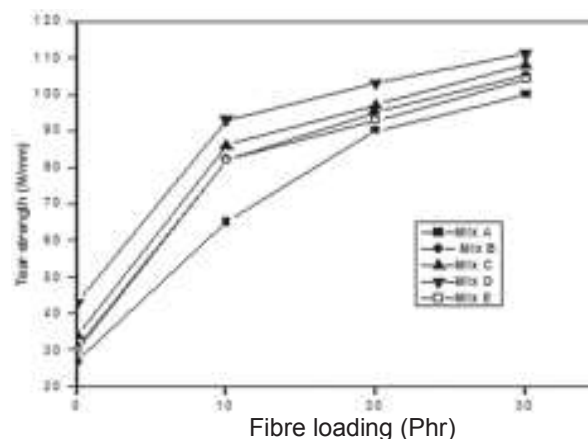


Fig. 11. Variation of tear strength with fibre loading in longitudinal direction

At 9 phr loading the tear strength is improved by 59 per cent for the gum compound ( $A_0$ ) and by 11 per cent for the 30 phr fibre filled sample ( $A_{30}$ ). The smaller particle size of the nanosilica helps in deviating the tear path, resulting in higher tear resistance. For the commercial silica



(Series E), the improvement is only limited and is close to that of Series B.

For transverse orientation of fibres, the variation of tear strength is shown in Figure 12. Here also tear strength increases with fibre loading, (to a limited extent), compared to the mixes where fibres are oriented longitudinally. When the fibres are oriented across the tear path the resistance to tear propagation is more. The non-silica mixes (Series A) shows an improvement of 203 per cent with 30 phr fibre loading which is further improved in the presence of 9 phr

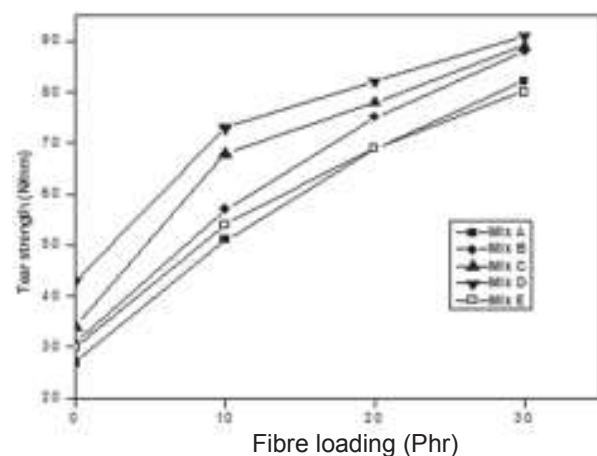


Fig. 12. Variation of tear strength with fibre loading in transverse direction

nanosilica (Mix D<sub>30</sub>). In the case of the gum compound (Mix A<sub>0</sub>) the corresponding improvement with 9 phr nanosilica is 59 per cent. With the conventional silica the improvement is only marginal at all concentrations.

Figure 13 shows the variation of the elongation at break (EB) with fibre loading. There is a sudden drop in the EB at 10 phr fibre loading and then it remains almost constant for all the mixes. With fibres distributed uniformly, the matrix becomes more restrained and hence fracture occurs

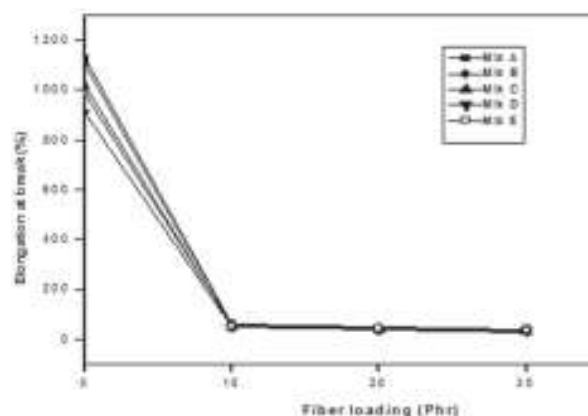


Fig. 13. Variation of elongation at break with fibre loading in longitudinal direction

at lower strains. With fibres oriented in the transverse direction, the EB is reduced beyond 10 phr loading (Fig. 14). The presence of silica does not seem to have a significant effect on the EB of the fibre-filled

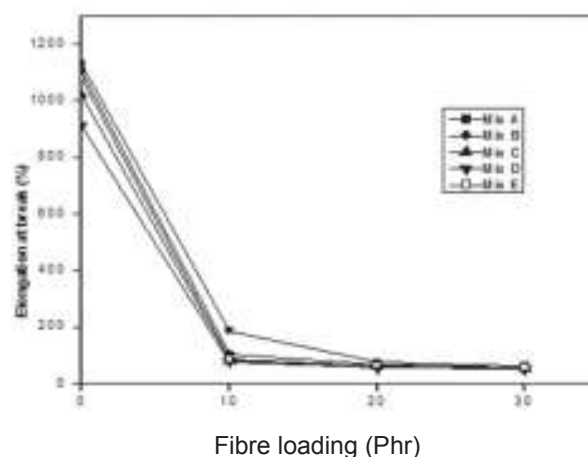


Fig. 14. Variation of elongation at break with fibre loading in transverse direction

samples. In the case of the gum compound (Mix A<sub>0</sub>), the EB is reduced marginally with increasing silica content.

The modulus at 20 per cent elongation increases linearly with fibre content. At all fibre loading, addition of nanosilica further improves the modulus. From the Figure 15, modulus value is found to increase,

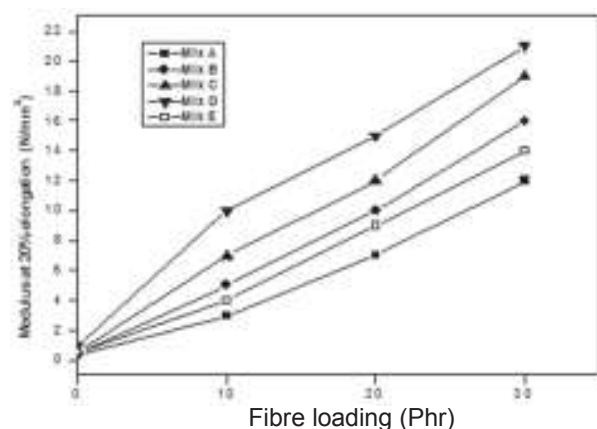


Fig. 15. Variation of modulus with fibre loading in longitudinal direction

resulting almost 1500 per cent improvement. For the commercial silica, the corresponding value is only 160 per cent. This shows that the nanosilica improves the fibre-matrix interaction better than the commercial silica. This may be attributed to relatively higher surface area and the presence of higher concentration of surface OH groups of the nanosilica. The silica is reported to be improving the interaction between the fibre and the rubber matrix through hydrogen bonding (Ismail *et al.*, 1999). With no fibres in the matrix the silica is not effective in improving the modulus, as evident from the

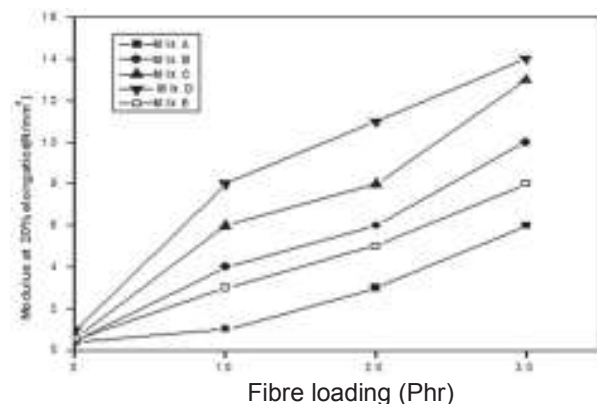


Fig. 16. Variation of modulus with fibre loading in transverse direction

very low modulus of the gum compound. Similar trend is observed in transverse direction also (Fig. 16).

Variation of the abrasion loss of the Series A-E is shown in Figure 17. The abrasion loss decreases with both fibre content and nanosilica loading. The mixes containing commercial silica (Series E) show higher abrasion loss compared to even the non-silica mixes (Series A). This again indicates that the commercial silica is not

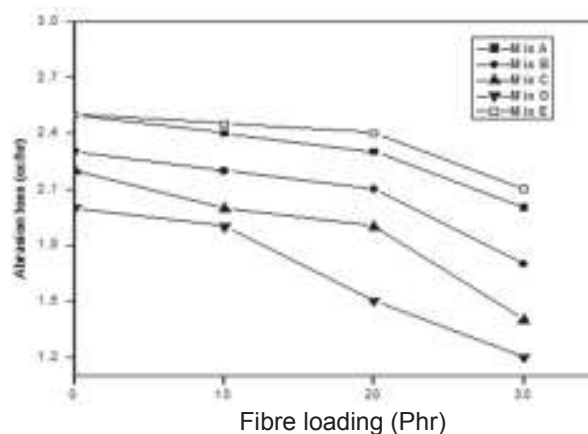


Fig. 17. Variation of abrasion loss with fibre loading

effective in restraining the matrix, like the nanosilica. During an abrasion test the matrix as well as the reinforcing fibre are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In the case of nanosilica hybrid composites a strong interfacial adhesion between the fibre and matrix renders the matrix stiffer resulting in lower abrasion loss.

Figure 18 shows the variation of compression set with fibre loading. Compression set increases with fibre content. The compression set registers a 138 per cent increase at 30 phr fibre loading (Series A). In the presence of reinforcing fillers, the viscoelastic dissipation of energy at the filler-matrix interface is increased. At

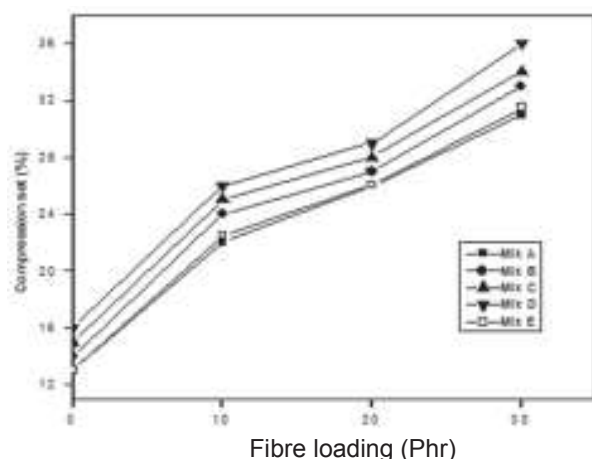


Fig. 18. Variation of compression set with fibre loading

the elevated temperature of compression test, the matrix becomes soft and undergoes irreversible flow resulting in incomplete recovery on removal of the applied stress. This gives rise to higher compression set values in the case of reinforced matrices. In the presence of the nanosilica, the reinforcement is further enhanced and hence the viscoelastic dissipation is also more. This gives rise to higher compression set in the case of nanosilica composites. In the presence of 9 phr of nanosilica, the compression set of the 30 phr fibre loaded

sample (Mix A<sub>30</sub>) is increased by 16 per cent. Since the commercial silica is not effective as a reinforcing filler, the set values are almost equal to that of the Series A composites.

The resilience, an indication of the material elasticity, decreases with fibre content and silica content for all the mixes, as expected (Fig. 19). Resilience shows a reduction from 60 per cent at 0 phr fibre loading to 46 per cent at 30 phr fibre loading (Series A). With increasing silica content, the resilience is further reduced. With 9 phr nanosilica, the resilience of the 30 phr fibre loaded samples is lowered to 41 per cent. The dissipation of energy at the fiber-matrix interface results in lower resilience of the composites. With a lesser reinforcing commercial silica, the reduction in resilience is only marginal.

Hardness, as expected, is higher for the fibre-filled samples (Fig. 20). With nanosilica the hardness is further enhanced. For the gum compound (Mix A<sub>0</sub>), hardness is improved with increasing nanosilica content. With 6 phr commercial silica (Mix E<sub>0</sub>) the hardness is only marginally improved. It is less than that of the Mix with 3 phr nanosilica (Mix B<sub>0</sub>).

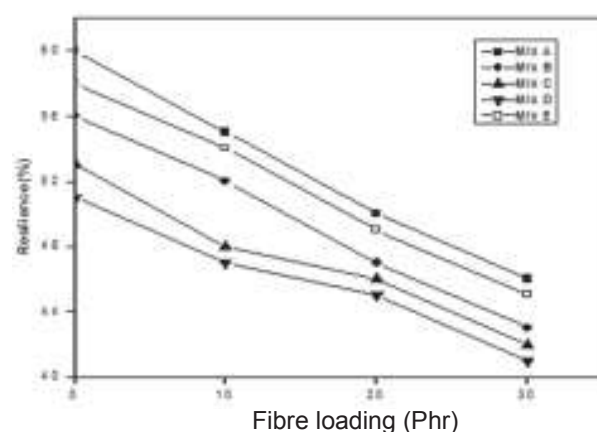


Fig. 19. Variation of resilience with fibre loading

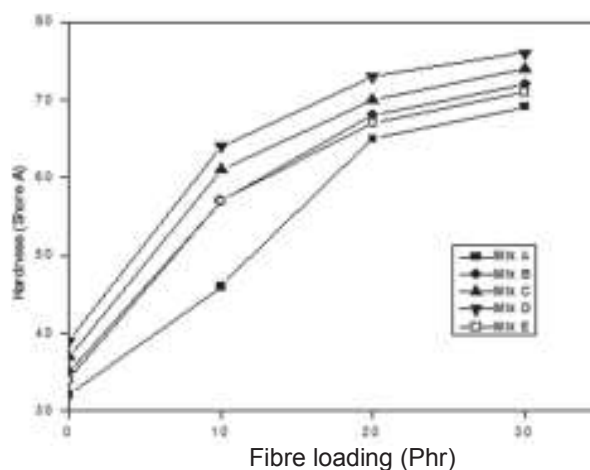


Fig. 20. Variation of hardness with fibre loading

## CONCLUSIONS

Nanosilica could be successfully prepared by acid hydrolysis of sodium silicate. The particle size of the synthesized nanosilica was found to be 13 nm and that of commercial silica was 34 nm. The synthesized silica could be used in composites based on chloroprene rubber and nylon-6 short fibres. Minimum torque is higher for fibre filled samples and it increases with silica content. Scorch time decreases with silica loading. Cure time is lower at higher fibre content. Differential

torque increases with silica content. Volume fraction of rubber, a measure of the crosslink density, increases with nanosilica. The HRH dry bonding system based on nanosilica is more efficient than the one with commercial silica. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. The composites show anisotropy in mechanical properties.

## REFERENCES

- Abdelmouleh, M., Boufi, S., Belgacem, M.N. and Dufreshe, A. (2007). Short natural fibre reinforced polyethylene and natural rubber composite: Effect of silane coupling agents and fiber loading. *Composite Science and Technology*, **67**: 1627-1639.
- Alexander, L.E. (1968). X-ray diffraction methods in Polymer Science, (John Wiley, New York).
- Cassidy, P.E., Aminabhavi, T.M. and Thompson, C.M. (1983). Water permeation through elastomers and plastics. *Rubber Chemistry and Technology*, **56**: 594-619.
- Chrusoid, J. and Slusaraski, L. (2003) Synthesis of nanosilica by the sol-gel method and its activity towards polymers. *Material Science*, **21**: 461-468.
- Foldi, A.P., De, S.K. and White, R., Eds.; (1996). Short fibre polymer composites, Woodhead Publishing Limited: Cambridge, England, Chapter 9.
- Geethamma, V.G., Thomas, M.K., Lakshminarayanan R. and Thomas, S. (1998). Composite of short coir fibre and natural rubber: Effect of chemical modification, loading and orientation of fiber. *Polymer*, **39**: 1483-1491.
- Geethamma, V.G., Joseph, R. and Thomas, S. (1995). Short coir fibre-reinforced natural rubber composite: Effect of fibre length, orientation and alkali. *Journal of Applied Polymer Science*, **55**: 583-595.
- Ismail, M.N. and Ghoneim, A.M. (1999). The effect of adhesion system on the physico-mechanical and electrical properties of SBR/Polyester short fiber composite. *Polymer-Plastics Technology and Engineering*, **38**: 71-86.
- Murty, V.M. and De, S.K. (1982). Short Jute fibre reinforced rubber composite. *Rubber Chemistry and Technology*, **55**: 287-298.
- Rajeev, R.S., De, S.K., Bhowmick, A.K., Kao, G.J.P. and Bandyopadhyay, S. (2001). Atomic force microscopy studies of short melamine fibre reinforced EPDM rubber. *Journal of Material Science*, **36**: 2621-2632.
- Rajeev, R.S., De, S.K., Bhowmick, A.K. and Bandyopadhyay, S. (2003). Short melamine fibre filled nitrile rubber composite. *Journal of Applied Polymer Science*, **90**: 544 -558.
- Saikrasun, S., Amornsakachai, T., Sirisihna, C., Meesiri, W. and Bualek-Limcharoen, S. (1999). Kevlar reinforcement of polyolefin based thermoplastic elastomer. *Polymer*, **40**: 6437-6446.
- Seema, A. and Kutty, S.K.N. (2006). Effect of an epoxy-based bonding agent on the cure characteristics and mechanical properties of short nylon fiber reinforced NBR composite. *Journal of Applied Polymer Science*, **99**: 532-539.
- Seema, A. and Kutty, S.K.N. (2005). Cure characteristics and mechanical properties of short nylon fibre Neoprene rubber composites containing epoxy resin as bonding agent. *Polymer-Plastic Technology and Engineering*, **44**: 1139-1158.

- Sreeja, T.D. and Kutty, S.K.N. (2002). Effect of urethane based bonding agent on the cure characteristics and mechanical properties of NR/WTR-short nylon fiber composite, *Polymer-Plastic Technology and Engineering*, **41**: 77-89.
- Sreeja, T.D. and Kutty, S.K.N. (2002). Studies on NBR-short nylon fiber composites, *Journal of Elastomers and Plastics*, **34**:157-169.
- Sreeja, T.D. and Kutty, S.K.N. (2002). Effect of a urethane resin based bonding agent on the cure characteristics and mechanical properties of styrene-butadiene rubber whole tire reclaim-short nylon fibre composites. *Progress in Rubber Plastics Recycling, Technology*, **18**: 283-295.
- Sreeja, T.D. and Kutty, S.K.N. (2003). Cure characteristics and mechanical properties of short nylon fiber reinforced NR-Reclaimed rubber blends. *Polymer-Plastics Technology and Engineering*, **42**: 239-252.
- Suhara, F., Kutty, S.K.N. and Nando, G.B. (1997). Cure characteristics of short polyester fibre - polyurethane elastomer composite with interfacial bonding agents based on polymeric 4,4/ Diphenyl methane diisocyanate. *International Journal of Polymeric Materials*, **38**: 205-218.
- Suhara, F., Kutty, S.K.N. and Nando, G.B. (1998). Mechanical properties of short polyester fibre-polyurethane elastomer composite with different interfacial bonding agent. *Polymer-Plastics Technology Engineering*, **37**: 241-252.
- Tapasikotoky and Dolui, S.K. (2004). Synthesis and characterization of PVA/Silica hybrid composites derived through the sol-gel method in aqueous medium. *Journal of Sol-Gel Science and Technology*, **20**: 107-114.
- Varghese, S., Kuriakose, B., Thomas, S. and Koshy, A.T. (1997). Mechanical and viscoelastic properties of short fiber reinforced NR composite': Effect of interfacial adhesion, fiber loading and orientation. *Journal of Adhesive Science and Technology*, **8**: 235-246.
- Wazzan, A.A. (2004). Physico-Mechanical properties of EPDM/ nylon-6 short fiber Composite. *International Journal of Polymeric Materials*, **53**: 59-67.