

# *Synthesis, Characterisation and Performance of Nanosilica as Filler in Natural Rubber Compounds*

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*Low particle size silica in the nanometer range was synthesised in an aqueous medium by the sol-gel method using dilute hydrochloric acid and sodium silicate, and characterised using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Infrared Spectroscopy (IR). This synthetic nanosilica had a lower number of hydroxyl groups than commercial silica and hence underwent reduced silica-silica agglomeration. The nanosilica was used as a reinforcing filler in natural rubber compounds, its cure characteristics and mechanical properties were evaluated. Minimum torque, maximum torque, scorch time and cure time were increased with silica loading. Mechanical properties such as tensile strength, Young's modulus, tear strength, abrasion loss, hardness, resilience and compression set were better than those of natural rubber vulcanisates filled with commercial silica. Volume fraction of rubber in a solvent-swollen sample was also higher for the nanosilica compounds.*

**Keywords:** filler; natural rubber; synthetic nanosilica; commercial silica; composite

Polymer materials are used in a wide range of industrial applications such as the food industry, transportation, construction and aerospace. Elastomers comprise about 15-20% of world wide polymer consumption, of which 35% is natural rubber (NR)<sup>1</sup>.

In 2005, the world's NR consumption was 8.76 million tons. IRSG's (International Rubber Study Group) recent forecast for the world's NR consumption was 15.2 million tons in 2020<sup>2</sup>. In the automotive sector, approximately 10% of the total car weight are elastomers<sup>3</sup>. Raw elastomers are reinforced with fillers such as carbon black and

precipitated silica to improve their physical and mechanical properties<sup>4-10</sup>. In recent years, synthetic precipitated silica has been replacing carbon black in rubber products such as tyres, offering significant benefits to some properties. Precipitated silica, which is of mineral origin, reduces rolling resistance in tyres and hence fuel consumption in the transport industry<sup>11</sup>. In green tyres *i.e.*, eco-friendly tyres, silica is used as a filler material for making high-performance tyres with low rolling resistance. Lower rolling resistance results in better fuel economy and hence reduces the impact of tyres on the environment. The fuel saving capacity of such a tyre is 3% to 4% compared to a tyre

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having its tread made from compounds with carbon black, corresponding to a reduction of the rolling resistance of 2%<sup>12</sup>. It is predicted that by 2010, the demand for precipitated silica in tyre applications will be approximately 430 000 metric tons per year<sup>13</sup>.

The reinforcement of rubbers using particulate fillers such as carbon black or precipitated silica has also been studied at length<sup>14-17</sup>. In all these studies, conventional precipitated silica with particle size of the order of microns has been used. The reinforcement effect of the filler is mainly influenced by the filler particle size and surface functionality<sup>18</sup>. The conventional silica filler has a particle size of 3 microns which is significantly larger than the particle size of carbon black. If silica with reduced particle size and hence improved surface area could be prepared, composites with better properties could be obtained. Sufficiently small particle size fillers can give good reinforcement, even when matrix/filler bonding is poor<sup>19,20</sup>.

Polymer nanocomposites containing nanometer sized fillers have received increased attention from both the scientific and industrial communities. The nanocomposites exhibit markedly improved properties when compared with those of the pure polymers or conventional filled composites due to the filler size. These include increased Young's modulus and tensile strength, decreased gas permeability, increased solvent and heat resistance and decreased flammability. A doubling of the tensile modulus and strength has been achieved for nylon-layered silicate nanocomposite with as little as 2 volume % of inorganic content<sup>21-23</sup>. Recently, Tapasikotoky and Dolui, Jerzy Chrusoid and Ludomir Slusaraski<sup>24,25</sup> reported the preparation of silica with particle size in the nanometer range. As lower size particles have higher surface area, nanosilica can be more effective

in improving the mechanical properties of the vulcanisate.

In this study we report the preparation of nanosilica from a cost effective silica source, sodium silicate, by sol-gel method and the properties of the natural rubber compounds containing the nanosilica. The compounds were characterised by X-Ray Diffraction, Scanning Electron Microscopy and Infrared Spectroscopy.

## EXPERIMENTAL

### Materials

Natural rubber used in this study was ISNR-5 obtained from the Rubber Research Institute of India (R.R.I.I), Kottayam, Kerala, India. Zinc oxide, stearic acid, N-(1,3-dimethylbutyl) N'-phenyl-p-phenylenediamine, N-cyclohexyl-2-benzothiazole sulfenamide (CBS), tetramethylthiuramdisulphide (TMTD), sulfur and sodium silicate used were of commercial grades.

### Synthesis of Nanosilica

Nanosilica was synthesised from sodium silicate in an aqueous medium by the sol-gel method using dilute HCl under controlled conditions. Sodium silicate is a cost effective silica source as compared to the more commonly used tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS)<sup>26</sup>. Moreover, by using a purely aqueous medium, the expensive and very often toxic solvent was avoided.

### Characterisation of Nanosilica X-Ray Diffraction (XRD)

The XRD analysis was carried out with a X-Ray Diffractometer, Bruker, D8 Advance

model, employing CuK $\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ) and Ni filter operating at 30 kV and 20 mA.

Rubber Process Analyser (RPA – 2000, Alpha Technologies).

### 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.

### Infra Red Spectroscopy (IR)

The IR spectra of the synthesised silica was recorded with Fourier Transform Infrared Spectroscope, Bruker, Tensor 27 model in ATR mode.

### BET Adsorption

Surface area of the silica was determined by the BET method using nitrogen isotherm on a Micromeritics Tristar 3000, surface area and porosity analyser.

### Preparation of the Composite

The formulation of mixes are given in *Table 1*. Natural rubber - 100 p.h.r., Zinc oxide - 5 p.h.r., stearic acid - 2 p.h.r., N-(1,3-dimethylbutyl)N'-phenyl-p-phenylenediamine) - 1 p.h.r., CBS-0.6 p.h.r., TMTD - 0.2 p.h.r., and sulfur - 2.5 p.h.r. were common to all mixes.

The mixing was done as per *ASTM D-3184* (1989) on a two roll laboratory size mixing mill (150 mm  $\times$  300 mm). After complete mixing, the stock was sheeted out at a fixed nip gap. The samples were kept for 24 h for maturation. The sheets were vulcanised in a hydraulic press at 150°C and 200 kg/cm<sup>2</sup> pressure to their optimum cure time as determined using a

### Measurement of Physical Properties

The tensile properties were measured using a Shimadzu Universal Testing Machine model AG -1, 10 kN according to *ASTM D 412* at a crosshead speed of 500 mm/min. The tear strength was determined according to *ASTM D624* (Die C). The hardness (Shore A) was determined as per *ASTM D2240-86* using Zwick 3114 hardness tester. Abrasion resistance of the sample was measured using DIN 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 *Equation 1*

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

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

## RESULTS AND DISCUSSION

### Characterisation of Synthesised Silica Scanning Electron Microscopy

*Figures 1a* and *1b* show the SEM micrographs of the synthesised silica and commercially available silica, respectively.

TABLE 1. THE FORMULATION OF MIXES

Ingredient (p.h.r.)	Mix No.							
	N <sub>0</sub>	N <sub>3</sub>	N <sub>6</sub>	N <sub>9</sub>	C <sub>0</sub>	C <sub>3</sub>	C <sub>6</sub>	C <sub>9</sub>
Nanosilica	-	3	6	9	-	-	-	-
Commercial silica	-	-	-	-	-	3	6	9

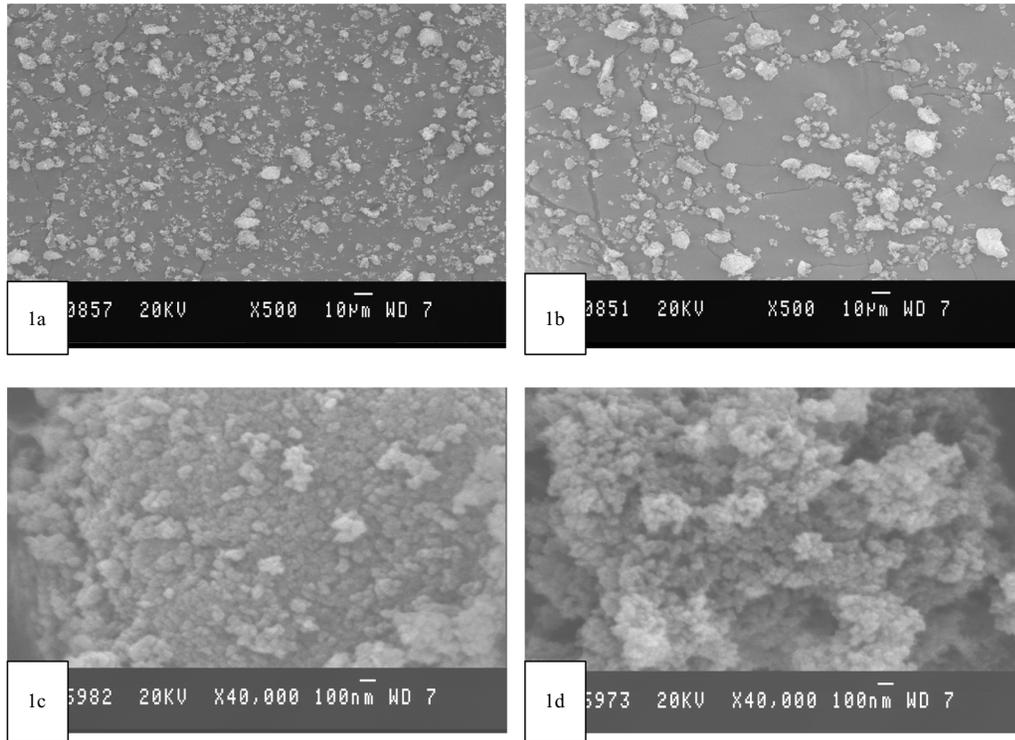


Figure 1. 1a and 1c are SEM micrographs of synthesised nanosilica while 1b and 1d are SEM micrographs of commercial silica.

These micrographs show that the synthesised silica has a lower particle size than that of the commercial silica. The small particle size provides a large external surface area, which would be expected to result in improvement in mechanical properties. Figures 1c and 1d

are the SEM of nanosilica and commercial silica respectively at 40 000 × magnification. It is seen that both the silica are of nanometer size. However, 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  $2\theta=22.08^\circ$  is typical of silica and are seen in both the cases, indicating that both the silicas have a similar structure. The particle size of the synthesised silica was determined from the X-Ray diffraction data using the Debye-Sherrer formula<sup>26,27</sup> as shown in *Equation 2*

$$C_s = 0.9 \lambda / \beta \cos \theta \quad \dots 2$$

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 is 279 nm.

## Infra Red Spectroscopy

*Figures 4* and *5* are the IR spectra of the synthesised silica and commercial silica respectively. The spectra shows that there is an increase in intensity of peak at  $1080 \text{ cm}^{-1}$  (Si-O band) in the case of the synthesised silica and a reduction in intensity of peak at  $3437 \text{ cm}^{-1}$  (of -OH stretching). Less hydroxyl groups in nano silica could explain the lower filler particle agglomeration. This suggests that the synthesised silica will be dispersed better than the commercial silica.

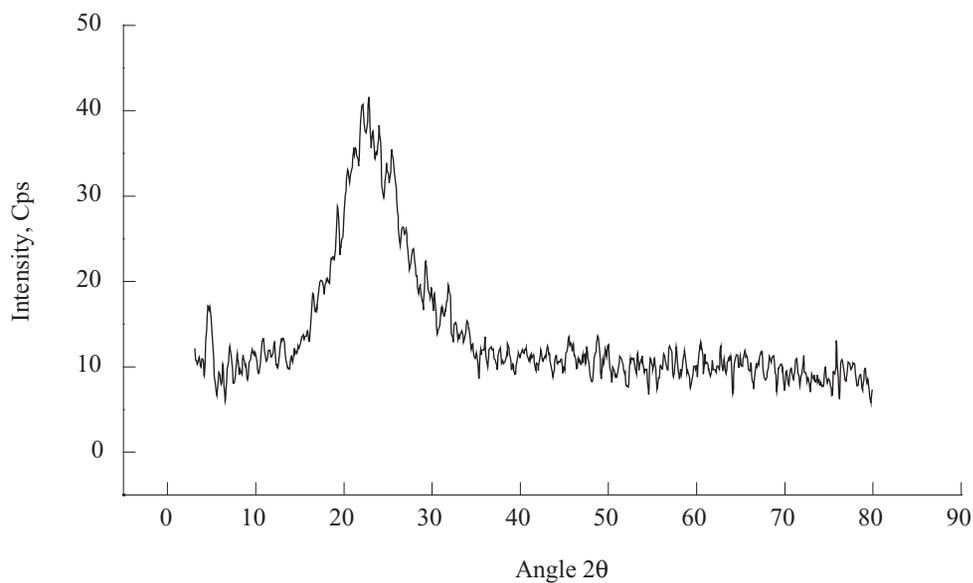
## BET adsorption

By BET adsorption the surface area of the synthesised silica is found to be  $295 \text{ m}^2/\text{g}$  and that of commercial silica is  $178 \text{ m}^2/\text{g}$ . From this it is clear that synthesised silica has higher surface area than that of commercial silica.

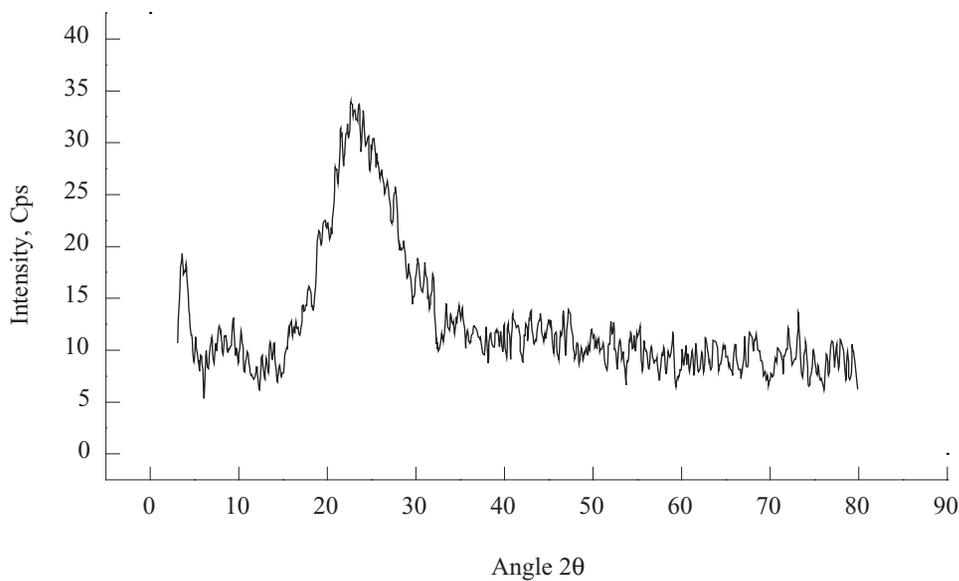
## Cure Characteristics

Variation of minimum torque with silica loading of both sets of composites is shown in *Figure 6*. The minimum torque increases with silica loading in both cases. All N mixes (Nanosilica) show higher values at all silica loadings. The higher viscosity of the synthesised nanosilica composites is most likely due to a better dispersion of the filler particles in the matrix.

*Figure 7* gives the variation of scorch time with silica content. While the scorch time remains more or less constant for commercial silica compounds, it increases linearly for those with the nanosilica. The delayed start of the cure reaction in the case of nanosilica may be attributed to the possible interaction of the silica with the accelerators, making it unavailable for cure reaction. However, the cure time is found to be unaffected by this interaction, as indicated by the almost similar variation of the cure time with silica content in both the cases (*Figure 8*). This indicates that the silica-accelerator interaction is only short term and is reversible at elevated temperatures. *Figure 9* shows the rate of cure reaction with silica loading. The cure rate is higher for the nanocompounds. The differential torque *i.e.*, the difference between the minimum and maximum torque developed during cure is found to be significantly higher for the nanosilica compounds (*Figure 10*). The differential torque is a measure of the extent of the crosslink formation and the filler –matrix interaction. The higher values for the nano silica compounds indicate that it has higher crosslink density. This is evident from the  $V_r$  values of the mixes. *Figure 11* shows that  $V_r$  of the nanosilica-containing mixes is higher at all silica loadings. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix due to its smaller size and hence higher surface area.



*Figure 2. XRD pattern of synthesised nanosilica.*



*Figure 3. XRD pattern of commercial silica.*

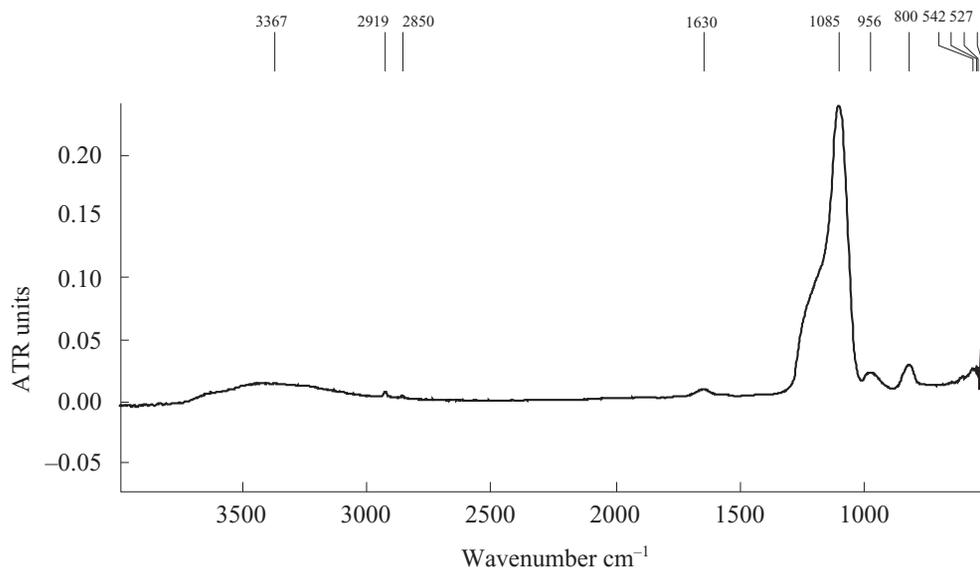


Figure 4. IR spectrum of synthesised silica.

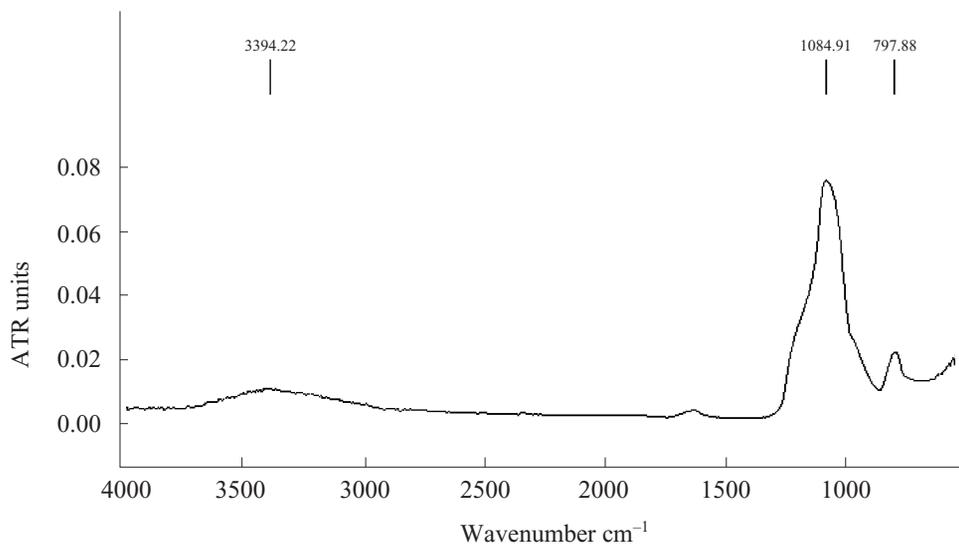


Figure 5. IR spectrum of commercial silica.

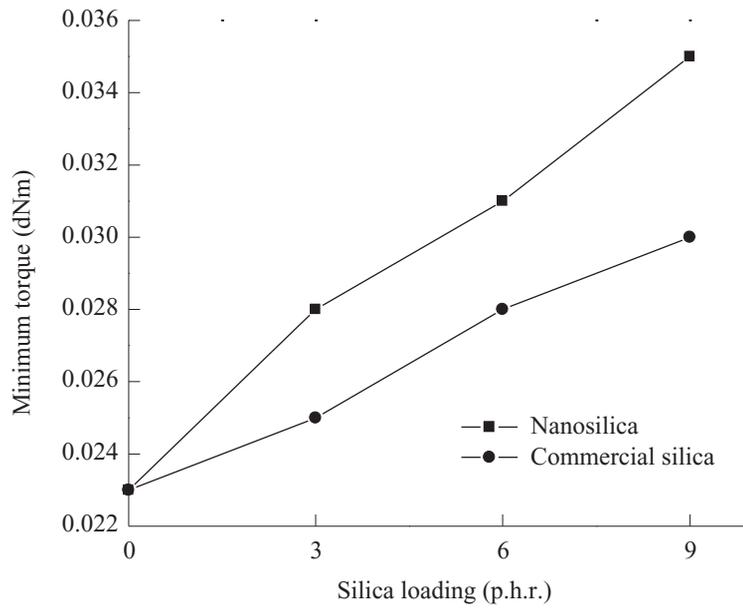


Figure 6. Variation of minimum torque with filler loading.

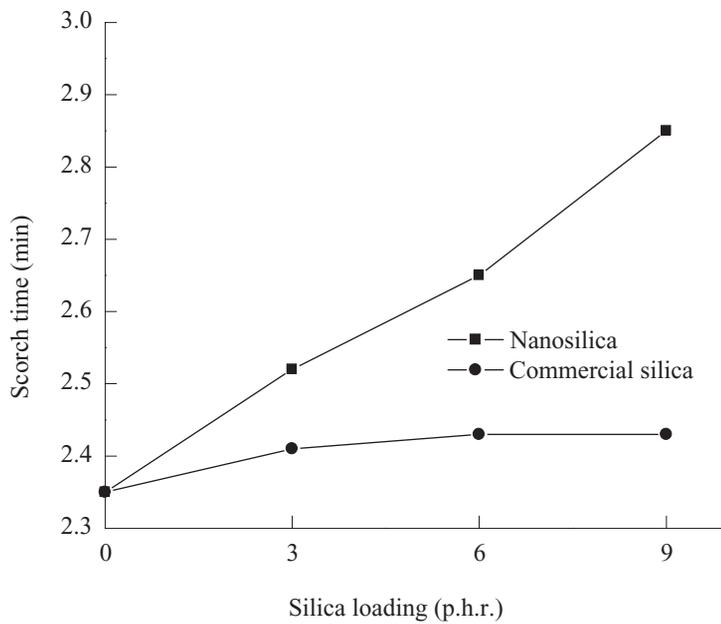


Figure 7. Variation of scorch time with filler loading.

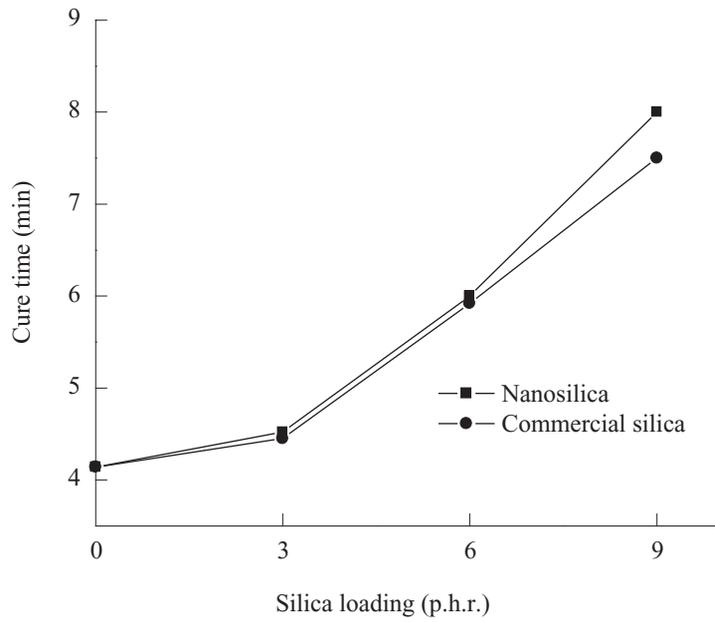


Figure 8. Variation of cure time with silica loading.

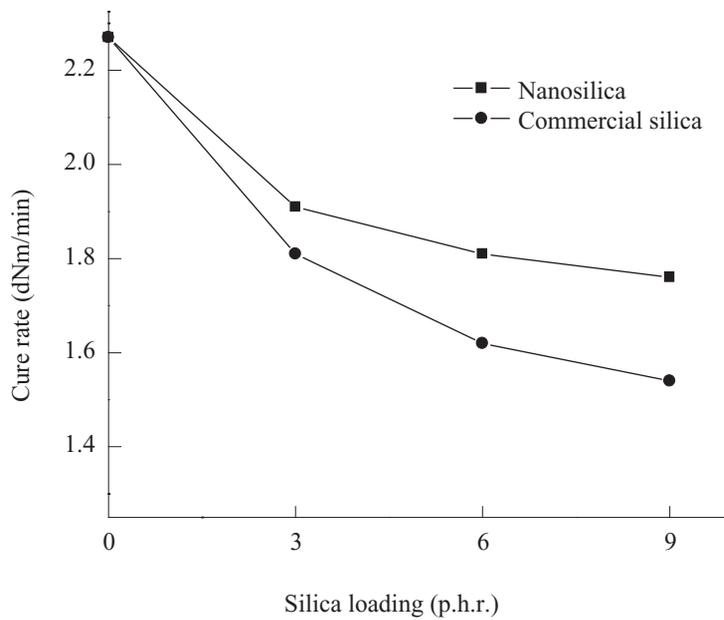


Figure 9. Variation of cure rate with silica loading.

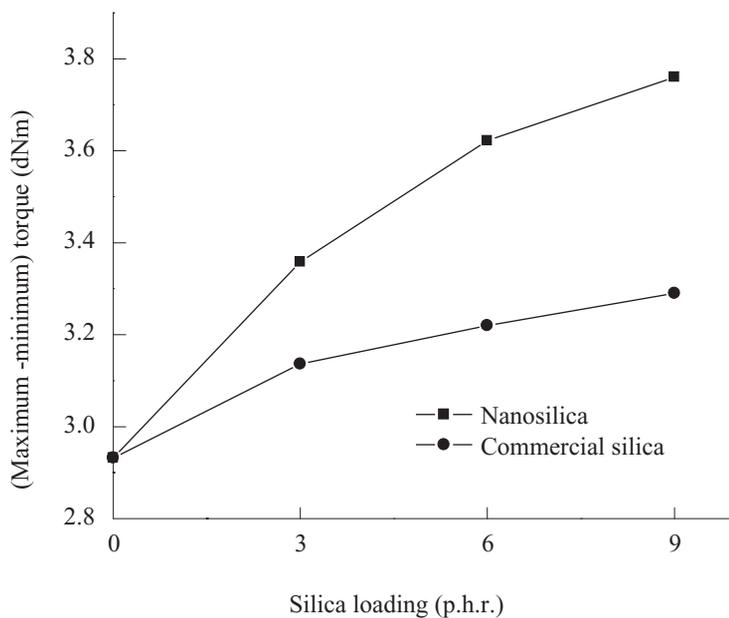


Figure 10. Variation of differential torque with silica loading.

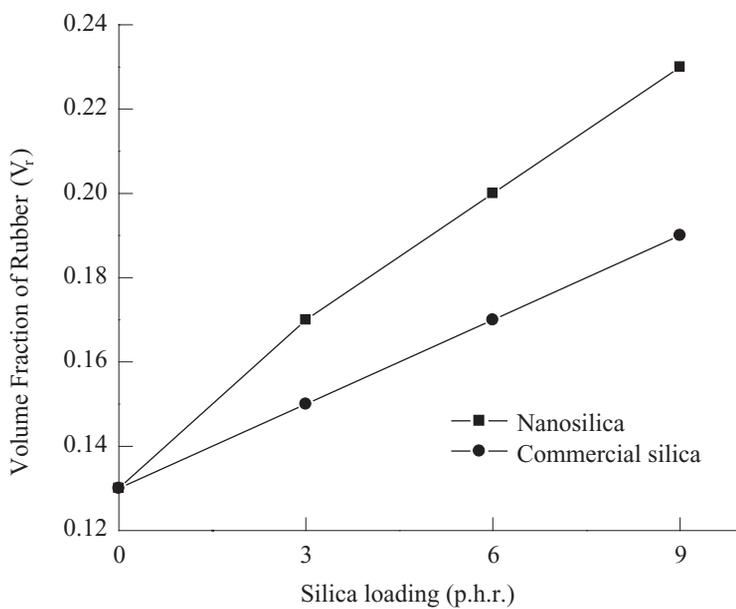


Figure 11. Variation of volume fraction of rubber with silica loading.

## Mechanical Properties

Figure 12 shows the variation of tensile strength with silica loading. As expected, the tensile strength drops at 3 p.h.r. for both the composites and then tends to be regained at higher silica loadings. The initial drop at lower levels of reinforcing fillers is a result of dilution effect in a strain-crystallizing matrix such as natural rubber<sup>28-30</sup>. At 9 p.h.r., the tensile strength is higher than the gum compound in the case of synthesised nanosilica compound whereas it is only half that gum strength in the case of commercial silica containing composite, supporting the better reinforcing efficiency of the nanosilica resulting from higher surface area.

Elongation at break is almost the same for both the composites. It increases with increasing filler loading (Figure 13). The variation of tear strength with silica

loading is almost similar for both the cases. Figure 14 gives variation in tear strength of the composite at filler loadings up to 9 p.h.r. In both the cases, the tear strength drops to a lower value at 3 p.h.r. silica content. Similar to the tensile strength, the tear strength also tends to improve at higher filler loadings. The increase in the case of nanosilica composite is to from 23 kN/m to 48 kN/m whereas for the conventional silica composite, the shift is from 12 kN/m to 30 kN/m. Modulus at 50% strain shows a linear variation with silica loading (Figure 15). At 9 p.h.r. level, the improvement is about 43% for the nanosilica composite whereas it is only 20% for the commercial silica composite. This indicates a more restrained matrix, resulting from better chances of filler-matrix interaction in the case of nanosilica compounds.

Abrasion loss shows a continuous decrease with filler loading (Figure 16). The nanosilica

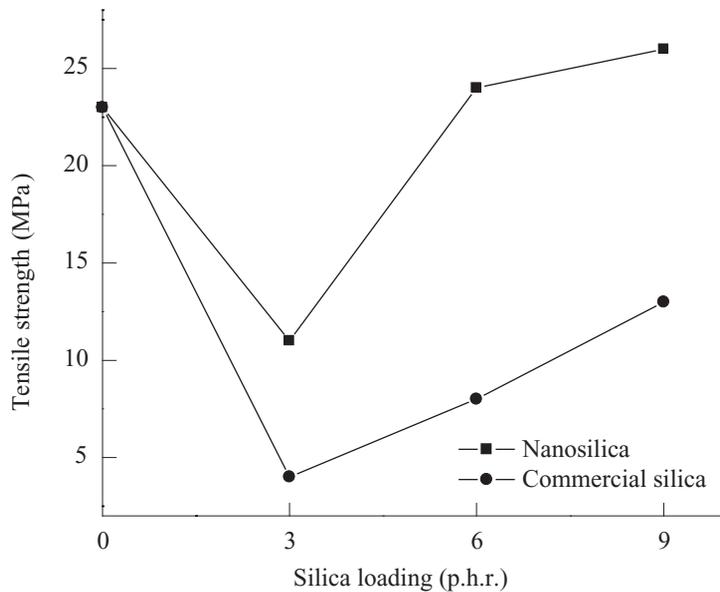


Figure 12. Variation of tensile strength with silica loading.

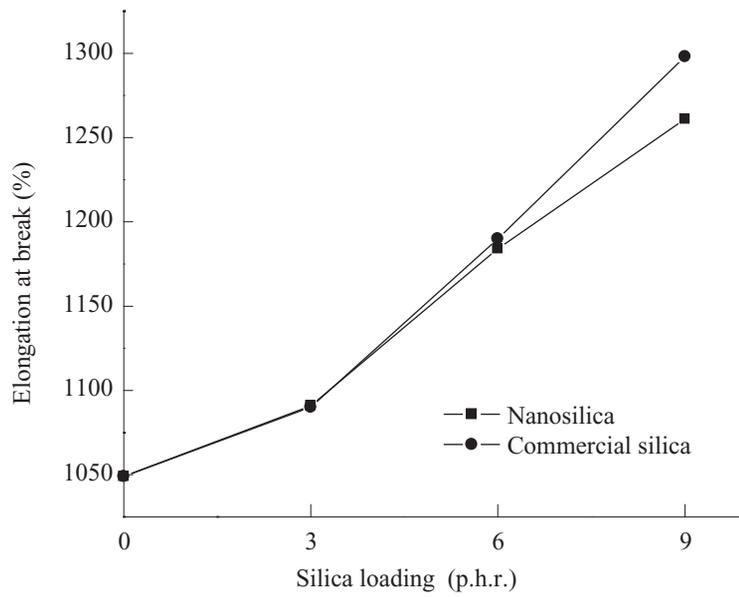


Figure 13. Variation of elongation at break with silica loading.

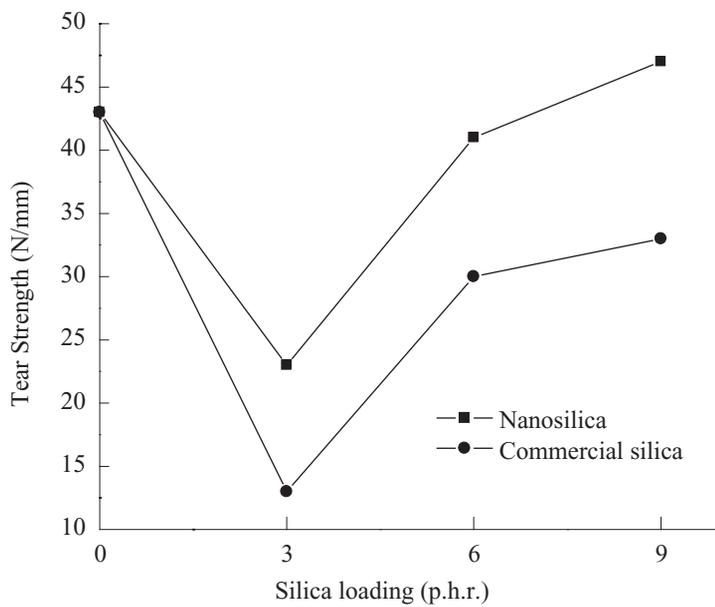


Figure 14. Variation of tear strength with silica loading.

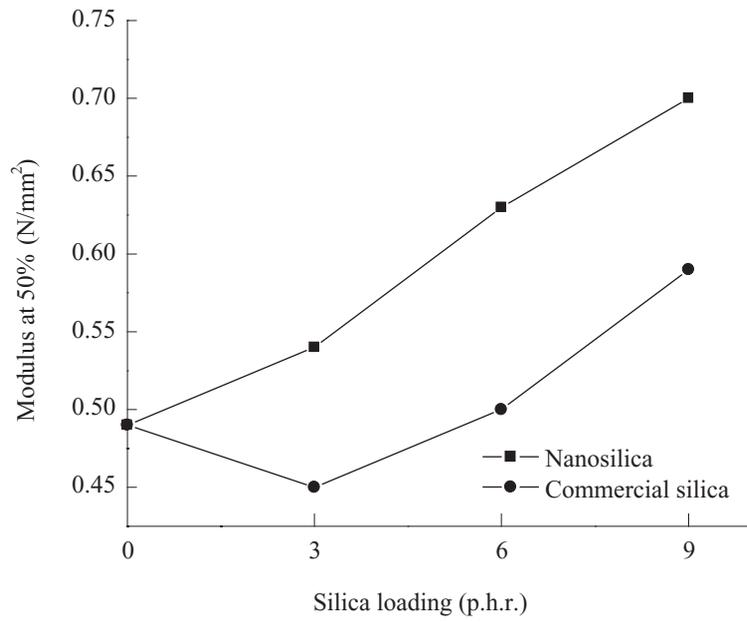


Figure 15. Variation of modulus with silica loading.

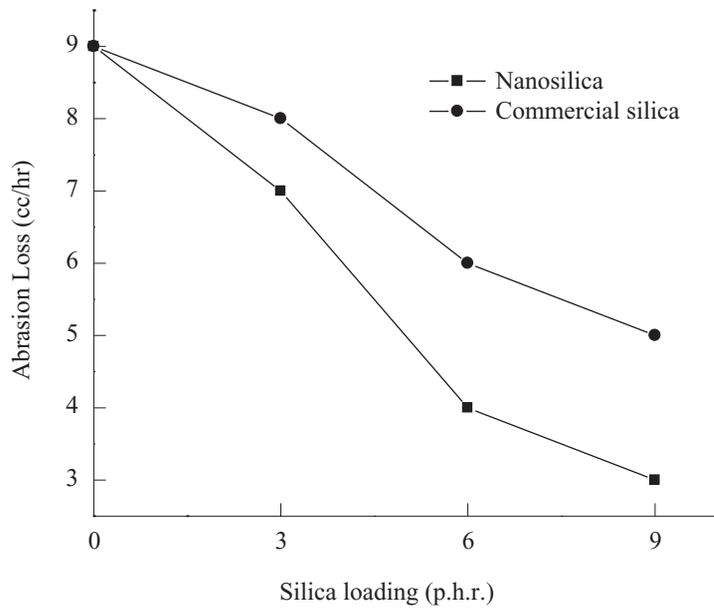


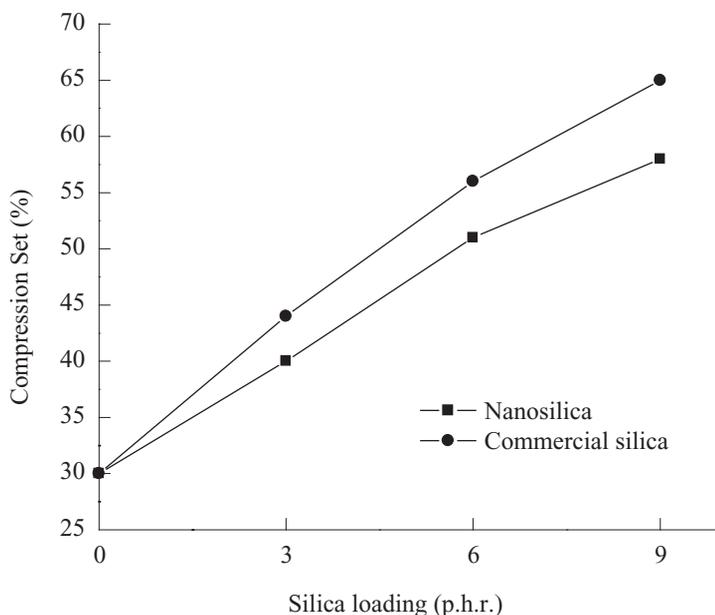
Figure 16. Variation of abrasion loss with silica loading.

composites show significantly lower value for abrasion loss compared to the conventional silica composites. Nanosilica composite shows 67% reduction at 9 p.h.r. loading, compared to 44% in the compound with commercial silica. Compression set, as expected, is higher at higher filler loadings (*Figure 17*). The fillers that are reinforcing in nature will adversely affect the elastic properties, especially at elevated temperatures. This is reflected in the higher compression set of the composites. However, in nanosilica composites, the set is slightly lower compared to the conventional silica compounds, indicating that the extent of agglomeration in nanosilica is lower. The reduced elasticity is also reflected in the resilience values. The resilience is reduced with increasing silica content (*Figure 18*). The synthesised nanosilica shows lower resilience. The inverse relationship between the compression set and

resilience is found to be valid in this case. The hardness increases with filler loading (*Figure 19*), again indicating a better efficiency of the nano filler.

## CONCLUSIONS

Nanosilica prepared by sol-gel method has a particle size lower than that of the commercially available silica. This synthesised nanosilica has a lower number of hydroxyl groups and hence reduced silica-silica agglomeration. The synthesised silica has an average particle size of 13 nm. Minimum torque, maximum torque, scorch time and cure time increased with silica loading. Volume fraction of rubber in a solvent-swollen sample is also higher for the nanosilica compounds. The introduction of nanosilica in the rubber compound improves its tensile



*Figure 17. Variation of compression set with silica loading.*

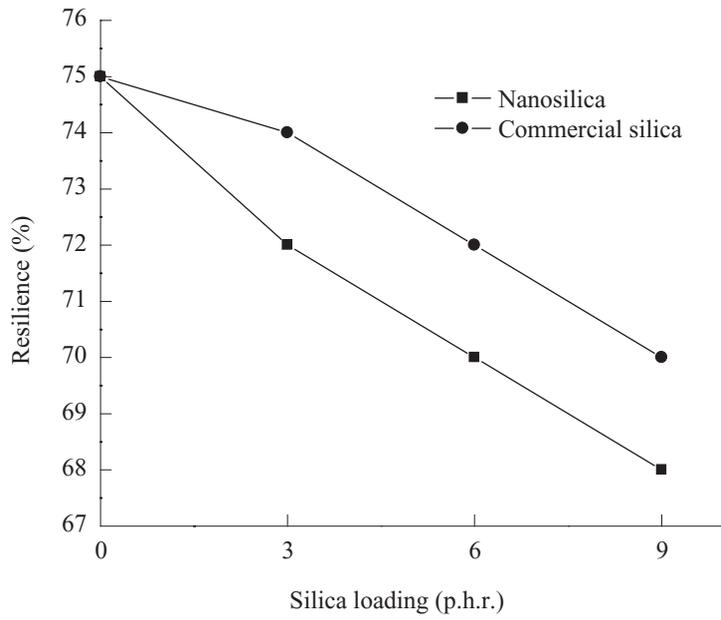


Figure 18. Variation of resilience with silica loading.

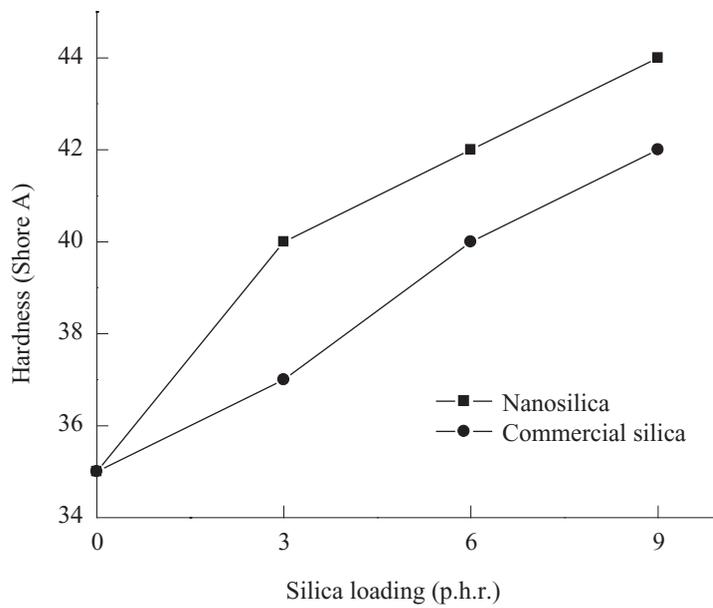


Figure 19. Variation of hardness with silica loading.

strength, modulus and tear strength better than conventional silica. Abrasion loss, hardness and compression set properties are also better for the nanosilica compounds.

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