Functionalized Nanosilica for Vulcanization Efficiency and Mechanical Properties of Natural Rubber Composites

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Dear Editor,

Kindly see the manuscript entitled “ **Functionalized nanosilica for vulcanization efficiency and mechanical properties of natural rubber composites**”, for your kind consideration to publish in the Journal of “**silicon** ”. This has not been published elsewhere nor has it been submitted simultaneously for publication elsewhere.

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Yours Sincerely,

Dr. P. Dileep

Functionalized nanosilica for vulcanization efficiency and mechanical properties of natural rubber composites

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Graphical abstract

Highlights

- Sodium isopropyl xanthate (SIPX) is an efficient accelerator for silica modification.
- SIPX- bound nanosilica improves cure time of natural rubber (NR) compounds.
- Improved silica - rubber interaction is achieved by SIPX modification.
- Thermal aging properties of NR composites are improved by SIPX-NS addition.

Abstract

Accelerator functional character was introduced on nanosilica by the chemical reaction of sodium isopropyl xanthate (SIPX) with nanosilica (NS). Functional characteristics of nanosilica were confirmed by the Elemental analysis, thermogravimetric analysis, and infrared spectroscopy. This SIPX functionalized nanosilica (SIPX-NS) incorporated natural rubber (NR) compounds were used to evaluate the dispersion of silica in rubber and also the interaction between rubber and filler. The finely dispersed SIPX-NS particles in the NR matrix are revealed from the morphological analysis. Subtle changes in surface chemistry of silica had a profound influence on the dispersibility in NR matrix. NR 4SIPX-NS composite exhibited improved cure time, tensile strength, flex crack resistance and aging resistance relative to those of NR NS composite. This simple, efficient and cost-effective surface modification of silica improved the vulcanization efficiency and mechanical performance of NR composites and has great potential in the fabrication of high-performance polymer composites.

Keywords: Nanosilica; Surface modification; Sodium isopropyl xanthate; Thermal conductivity; Flex crack resistance

1. Introduction

Nanosilica is an emerging environment-friendly nanofiller used for the reinforcement of elastomers and is not derived from petroleum resources [1][2]. These nanoparticles have high surface energy and a tendency to agglomerate because of the groups like siloxane and silanol

present on silica surface [3]. To overcome this disadvantage, modification of the surface chemistry is necessary to improve its dispersion and compatibility in an organic matrix.

The surface modification of silica particles can be achieved by different chemical procedures such as organoalkoxysilane modification [4][5], polymer grafting [6][7], encapsulation [8][9], *etc.* The modification on the surface of silica through reactions with organosilanes is used in the polymer and rubber industry for the improvement in mechanical properties. The interface between the polymer and filler surface affects the nonlinear viscoelastic behavior, improves mechanical properties and energy efficiency of rubber nanocomposites [10]. Chen *et al.* [11] proposed another method for surface modification of nanofillers with supported rubber additives. Silica-supported vulcanizing accelerator was prepared by grafting 2-benzothiazolethiol [12] onto the surface of silane modified silica to improve the silica-matrix interaction and silica dispersion in SBR. Mathew *et al.* [13] found that plasma treatment of silica could improve the interfacial interaction and mechanical properties of SBR composites. Wang *et al.* [14] developed surface modified silica nanoparticles by combining noncovalent and covalent modification processes in a simple, efficient and cost-effective method. Weng *et al.* [15] developed a new way to promote the dispersion of silica and interfacial strength in rubber/silica composites by grafting with oniums. Liu *et al.* [16] established a simple inhibition-grafting method to prepare silica/polydimethylsiloxane nanocomposites with superior mechanical properties and a low viscosity. Guo *et al.* [17] used sorbic acid to improve the dispersion of silica and mechanical performance of SBR/silica composites.

Natural rubber, an unsaturated elastomer has been widely used due to its excellent elastic property. However, a few drawbacks such as low polarity, poor oil resistance and low air impermeability limit its application in some cases [18]. To overcome these drawbacks, NR is modified appropriately. Xu *et al.* [19] used Epoxidised Natural Rubber (ENR) as an interfacial

modifier to improve the mechanical and dynamical mechanical properties of NR/silica composites. The results indicated the formation of a covalent bond by the ring-opening reaction between the epoxy groups of ENR chains and Si-OH groups on the silica surfaces. Ismail *et al.* [20] selected maleated natural rubber as a coupling agent for paper sludge fiber filled NR composites and found excellent rheological and dynamic properties. According to Gelling [21], NR backbone stereo-regularity disrupted by any type of chemical modifications and hence, reduction in basic strength properties of NR.

In the present work, instead of using the conventional coupling agents, a solid, water-soluble accelerator sodium isopropyl xanthate (SIPX) was adopted as a novel modifier for silica to improve its dispersion in NR matrix and for better interfacial interaction between the matrix and the filler. The modification and its size distribution were characterized by FTIR, TGA, EDX, SEM and dynamic light scattering (DLS). Modification of nanosilica improved curing, mechanical performance, crosslink density and aging resistance of NR.

2. Experimental

2.1. Materials

Rubber Research Institute of India (RRII), Kottayam provided ISNR-5 grade Natural Rubber with 70 ± 2 Mooney viscosity (ML 1+4 @ 100 °C). Nano sized silica particles (520 m²/g. surface area) synthesized in our laboratory [22]. Sodium Isopropyl Xanthate (SIPX) was purchased from Amruta Industries, Mumbai, India. Commercial grades of Tetramethylthiuram disulphide (TMTD), stearic acid, sulphur (S), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), and Zinc oxide (ZnO) were used as received. Merck Specialties Private Limited, India made Toluene and Diethylene glycol (DEG) were purchased and used.

2.2. Methods

2.2.1. Modification of nanosilica with vulcanizing accelerator SIPX

5 g SIPX was dissolved in 50 mL of isopropyl alcohol and to this solution, 10 g of nanosilica (dried at 100 °C for 6 hours) was added. This mixture was heated at 80 °C for 24 hours with continuous stirring. After the reaction, soxhlet extraction of the reaction mixture was carried out using isopropyl alcohol for 8 hours to remove unreacted SIPX. This sample was vacuum dried at 50 °C for 3 hours to obtain SIPX modified nanosilica (SIPX-NS).

2.2.2. Composites Preparation

Thermo Haake Polylab with a rotor speed of 60 rpm maintained at 70 °C was used for compounding as per ASTM D 3184. Table 1 gives the details of the formulation. Initially mastication of NR done for 3 minutes. Stearic acid, zinc oxide and styrenated phenol oil were then added. Then DEG and nanosilica were added and continued the mixing for 3 minutes. TMTD, CBS and S were added and continued the mixing for 2minutes. After this 8 minutes mixing, a laboratory size 6"x12" two roll mill was used to sheeted out the compound for 5 times (5 mm nip gap) and finally sheeted out at a 3 mm nip gap. Before moulding, this compound was allowed to mature for 24 hours at room temperature. A 12"x12" platen size hydraulic press kept at 150 °C & 150 kg/cm² pressure used to vulcanize the compounds to the optimum cure time.

Table 1. Formulation of NR mixes

Ingredients *	Mix Names				
	NR	NR	NR	NR	NR
(phr) ^a	Gum	3NS	3SIPX-NS	4SIPX-NS	5SIPX-NS

ISNR-5	100	100	100	100	100
NS	0	3	0	0	0
SIPX-NS	0	0	3	4	5
DEG	0	0.3	0.3	0.4	0.5

* Zinc oxide 5.0, stearic acid 2.0, styrenated phenol 1.0, Tetramethylthiuram disulphide 0.2, N-cyclohexyl-2-benzothiazole sulphenamide 0.6 and sulphur 2.5 were added in all formulations.

^a parts per hundred of rubber

2.3. Characterization methods

Avatar 370 model Thermo Nicolet FTIR spectrometer was used to conduct Fourier transform IR analysis. JEOL (JED-2300 Model) instrument was used to perform EDX (Energy Dispersive X-ray) analysis. Malvern mastersizer-V3.30 instrument capable of measuring size between 0.1 to 1000 μm and an angular range of 0.032 - 60 degrees used to measure the particle size distribution. The scanning electron microscope of JOEL (Model JSM 8390 LV) was used to analyze tensile fractured surfaces. ASTM D 573 method was used to carry out the thermal aging analysis. TA instruments (model Q-50) Thermogravimetric Analyser was used to perform thermogravimetric analysis. Samples were kept at a nitrogen atmosphere and heated from room temperature to 750 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. Thermal conductivity was measured according to D7340 ASTM Standard using Holmarc's Lee's Disc Apparatus (Model: HOAE-LD18)

RPA 2000 model Rubber Process Analyser from Alpha Technologies, USA kept at an angle of 0.5 degree and 100 cpm frequency was used for rheological characterization according to ASTM D 5289. Universal Testing Machine from Instron, USA was used to analyze the stress-strain properties of samples as per ASTM D 412. Test specimen un-nicked at 90 $^{\circ}$ angle

was used for the tear resistance test according to ASTM D 624. Shore A type Durometer was used to measure the hardness of samples according to ASTM D 2240. Bariess DIN abrader, Germany was used to test abrasion resistance as per ASTM D 5963. According to ASTM D 297 specific gravity was measured using Densimeter. ASTM D 395 standard is used to measure compression set with 9.5 mm spacer thickness. Goodrich flexometer, Dynisco, USA was used to determine the heat build-up analysis as per ASTM D 623. Rebound resilience was measured according to ASTM D 7121 using Wallace Dunlop Tripsometer.

The equation below is used to calculate rebound resilience percentage (RB)

$$RB \% = \frac{1 - \cos(\text{angle of rebound})}{1 - \cos(\text{original angle})} \times 100 \dots\dots\dots 1$$

Demattia flexing machine was used to check flex cracking and crack growth of the samples as per ASTM D 430 and ASTM D 813 respectively.

Following equation was used to determine the tensile retention percentage:

$$\text{Tensile retention \%} = \frac{\text{Tensile strength after aging}}{\text{Tensile strength before aging}} \times 100 \dots\dots\dots 2$$

Swelling of samples in toluene was used to measure the swelling index, mol percentage uptake and crosslink density.

For all samples, equation 3 was used to calculate the percentage solvent uptake ($Q_t\%$)

$$Q_t \text{ mol\%} = \frac{(\text{Mass of solvent sorbed} / \text{Molar mass of solvent})}{\text{Mass of polymer}} \times 100 \dots\dots\dots 3$$

The following equation was used to determine the swelling index.

$$\text{Swelling index} = \frac{(W_s - W_i)}{W_i} \times 100 \dots\dots\dots 4$$

Here, W_s and W_i are the swollen and initial weight of the specimen.

Flory-Rehner equation was used to calculate the crosslink density of samples [23]

$$\text{Crosslink density} = \frac{1}{2M_c} \dots\dots\dots 5$$

M_c mentioned in the above equation is the molar mass of the sample between consecutive crosslinks. M_c is calculated using equation 6.

$$M_c = -\frac{1}{2V_2} \rho_r V_s V_r^{\frac{1}{3}} / (\ln(1 - V_r) + V_r + \chi V_r^2) \dots\dots\dots 6$$

In equation 6, the molar volume of solvent is V_s (for toluene $106.2 \text{ cm}^3/\text{mol}$), rubber density is ρ_r (0.94 g/cm^3), the rubber volume fraction of samples at equilibrium swelling is V_r and the interaction parameter between natural rubber and toluene is χ (0.3787 from the literature [24]). Ellis and Welding equation [25] was used to calculate V_r

$$V_r = (d - fw)^{-1} / (d - fw) \rho_r^{-1} + A_s \rho_s^{-1} \dots\dots\dots 7$$

3. Results and discussion

3.1. Fourier transform infrared analysis

Fig.1. FTIR spectra of NS, SIPX and SIPX-NS

Figure 1 shows curves obtained from FTIR spectroscopy for samples NS, SIPX and SIPX-NS. In NS, the silanol hydroxyl groups stretching vibration and adsorbed moisture together constitute the peak at 3560 cm^{-1} . Si-O-Si linkage symmetric and asymmetric stretching

vibrations generate the absorbance peaks at 807 cm^{-1} and 1107 cm^{-1} respectively [16]. Bending vibrations of -OH groups causes a peak at 1642 cm^{-1} . In SIPX, the $\text{C}=\text{S}$ stretching vibration leads to the absorption band at 1050 cm^{-1} and 1037 cm^{-1} [26]. The symmetric stretching vibration of C-O-C generates a peak at 1191 cm^{-1} [27]. The peaks at 1377 cm^{-1} correspond to symmetric deformation of the C-H bond in CH_3 group in SIPX [28]. The $\text{C}=\text{S}$ vibration peak of SIPX-NS at 1037 cm^{-1} shift towards lower wavenumbers 1002 cm^{-1} and peak at 1050 cm^{-1} shift towards higher wavenumbers 1118 cm^{-1} compared with those of SIPX, due to the coordinated structure of SIPX-NS.

3.2. Elemental analysis

The elemental analysis of the SIPX modified nanosilica shows carbon, sulphur and sodium besides silicon and oxygen. The percentage of elements are tabulated in table 2. This confirms the successful modification of the silica with SIPX.

Table 2. Elemental analysis of SIPX-NS

Materials	Si	Elements (wt%)			
		O	C	Na	S
NS	49.54	50.46	-	-	-
SIPX-NS	38.97	48.95	5.73	4.04	2.31

3.3. Dynamic light scattering analysis (DLS)

The particle size distribution of SIPX-NS was measured using DLS. Figure 2(a) shows an average particle size of 6 nm for NS. The particle size of SIPX-NS is increased to 20 nm, which could be due to the modification and also due to mild agglomeration of NS particles.

Fig. 2. Particle size distribution of (a) NS and (b) SIPX-NS

3.4. Morphological analysis

Fig.3. Scanning electron micrographs of (a) NS and (b) SIPX-NS

Scanning electron micrographs of NS and SIPX-NS are shown in figure 3. SIPX-NS particles show morphological change and higher size compared to NS. The average size of SIPX-NS measured from the micrograph is 20 nm, whereas for NS particle size is 6 nm. This is in agreement with the results of DLS studies. Hydrogen bonds and Van der Waals force among SIPX-NS particles lead to the agglomeration [29].

3.5. Thermogravimetric analysis

Fig.4. TGA of NS and SIPX-NS

Thermograms of NS and SIPX-NS are shown in figure 4. Within the analysis temperature 30-750 °C, two weight loss steps exhibited by nanosilica. The release of adsorbed moisture is the reason for the initial weight loss on heating from 50 to 110 °C [30]. Silanol group's dehydration occurs between temperature 400-600 °C is the reason for second weight loss [31]. Modifying group decomposition on the temperature range between 150-600 °C is the reason for the major weight loss for SIPX-NS. Very low initial weight loss of SIPX-NS between 50-110 °C is due to the increase in the hydrophobic character of silica by the presence of an organic modifying group. Analysis of percentage residue confirmed the presence of 9.3 wt%. of SIPX on silica particles.

3.6. Cure characteristics of NR composites

Fig.5. NR composites cure behavior

Figure 5 illustrates the cure characteristics of natural rubber composites. Table 3 provides the cure parameters. The surface property, concentration and nature of filler influence the cure behavior of composites [32]. Compared to NR SIPX-NS composites, scorch and cure time of NR gum and NR 3NS composites are higher. Silica particles adsorption of curatives leads to an increase in cure time for NR 3NS composite [33]. Lowering of NR SIPX-NS composites optimum cure time (t_{90}) is due to the reduction in surface hydroxyl groups of nanosilica and also the accelerating effect of SIPX present on the modified silica. The scorch time (t_{s2}) of modified nanosilica composites is drastically reduced due to the accelerating efficiency of SIPX. Reduction in scorch time indicates that the NR SIPX-NS composites have lower processability. The torque values are increased with increasing SIPX-NS concentration due to the better crosslink density of composites, as indicated in table 3.

Table 3. NR composites rheological data

Name of sample	ts ₂ (Minutes)	t ₉₀ (Minutes)	M _H -M _L (dNm)
NR gum	3.04	7.31	29.39
NR 3NS	2.65	7.94	29.45
NR 3SIPX-NS	0.89	6.68	29.62
NR 4SIPX-NS	0.85	6.09	29.94
NR 5SIPX-NS	0.93	5.78	31.12

M_H - maximum torque and M_s - minimum torque

3.7. Stress-Strain behaviour of NR composites

Fig.6. Tensile stress-strain curves obtained for NR composites

Figure 6 shows the stress-strain behavior obtained for all NR composites. Higher tensile strength is obtained for NR 4SIPX-NS compared to all other composites. Better rubber and filler interaction is the reason for the higher tensile strength. At a higher concentration of SIPX-NS, aggregation of silica particles causes poor interaction between filler and rubber [34]. NR

3NS composite showed maximum tensile strength [35]. NR 4SIPX-NS shows a 10% and 24% increase in tensile strength compared to NR 3NS composite and NR gum compound respectively.

Elongation at break percentage was found to be decreased with an increase in silica concentration. This is because of the restriction in the movement of polymer chains by the presence of non-deformable silica particles [36]. An increase in modified nanosilica concentration leads to an increase in tear strength and modulus at 300% elongation. This indicates that silica acts as a reinforcing filler. Elongation at break, tensile strength, modulus at 300% elongation and tear strength obtained for natural rubber composites are given in table 4. The concentration of filler, particle size and its dispersion affect the tensile strength and modulus of the composites.

Table 4. Tensile and tear properties of NR composites

Name of sample	Tensile strength (MPa)	Elongation at break (%)	Modulus at 300% elongation (MPa)	Tear strength (N/mm)
NR gum	23.35±0.8	804±15	2.29±0.25	34.90±0.9
NR 3NS	26.20±0.3	751±16	3.64±0.13	43.62±1.2
NR 3SIPX-NS	25.45±0.2	790±8	3.07±0.28	44.71±1.4
NR 4SIPX-NS	28.9±0.33	726±14	3.74±0.03	45.94±1.5
NR 5SIPX-NS	27.52±0.26	732±21	3.72±0.07	46.05±1.8

The tensile properties of the composites are studied after aging at 100 °C for 24 hours, as it is very important to evaluate the performance in practical applications. The percentage retention of the tensile strength is shown in figure 7. NR gum shows lower retention compared to nanosilica filled composites. Luo *et al.* [37] observed a similar result while studying the

effect of silica and antioxidant on NR composites. NR 4SIPX-NS shows excellent tensile retention in comparison with all other natural rubber composites.

Fig.7. Retention of tensile strength of NR composites

3.8. Other technological properties of NR composites

Table 5 includes the tabulated values of other technological properties of NR composites. Composites showed an increase in hardness with the increase of filler loading. This is allied with the modulus increase and crosslink density increase [38] of the composites.

The abrasion resistance of rubber vulcanizates depends on several factors such as filler particle size, structure, surface activity, and filler-rubber interaction [39]. The reduction in abrasion loss for NR SIPX-NS composites attributed to the improvement in service life due to the good interaction between the matrix and filler and better filler dispersion.

The ability of a material to recover from an applied continuous strain is measured in compression set analysis. Percentage of dynamic compression set and compression set values found to be increased with the increase in nanosilica concentration as silica is a non-resilient reinforcing filler [35]. With the increase in modulus of the composite, more restriction in polymer chain mobility occurred even after the applied stress removal. This is confirmed from modulus values which show a linear relationship with the compression set.

In the heat build-up test, the dissipation of energy occurs as heat because of the friction among filler particles and between rubber matrix and filler under cyclic deformation [40]. With the increase in filler loading heat build-up of composites found to be increased. This causes a rise in fatigue failure and leads to inferior mechanical properties of the composites [41]. There is no significant change in heat build-up for NR 4SIPX-NS and NR 3NS samples as the modification improves the filler dispersion in the rubber matrix.

Table 5. Technological properties of NR composites

Sample name	Abrasion loss (cc)	Hardness (Shore A)	Dynamic compression set (%)	Heat build-up (°C)	Compression set (%)	Rebound resilience (%)
NR gum	0.32±0.01	38±1	2.3±0.1	1±0	25.6±0.2	78±3
NR 3NS	0.27±0.02	44±0.5	4.65±0.1	12±1	28.4±0.1	68±2
NR 3SIPX-NS	0.28±0.05	42±0.5	4.75±0.2	11±2	28.5±0.25	68±1
NR 4SIPX-NS	0.23±0.01	44±0.5	7.2±0.2	13±1	34.91±0.17	65±2
NR 5SIPX-NS	0.22±0.01	45±0.5	7.2±0.3	15±2	35.48±0.2	63±1

Table 6 shows the initial flex crack and crack growth of the NR silica composites. Resistance to flex crack and crack growth is the essential dynamic properties required for the rubber products used for dynamic applications. Flex crack resistance of the NR composites mainly depends on the dispersion of filler, nature of crosslink network and concentration and mechanical oxidative aging (antidegradent present) [42][43]. Modified nanosilica filled NR composites showed higher resistance to flex cracking and crack growth compared to unmodified nanosilica filled NR composite. This improved resistance may be due to the presence of long hydrocarbon chains in SIPX-NS, which helped for the better dispersion of nanosilica and improved crosslinking [44]. The lower value for both flex cracking and crack growth resistance for unmodified nanosilica NR composite is due to the agglomerated

nanosilica particles and rigid interaction of nanosilica with NR. The maximum resistance obtained for NR 4SIPX-NS composite as because of the reason that the sulphur-accelerator ratio becomes optimum at this concentration [45].

Tear strength and fatigue life are interconnected as both are related to the breaking energy of the composite [46]. The relationship between crack initiation and tear strength is plotted in figure 8. The plot implies that the factors contributing to improving tear strength may be the same as that are contributing to crack initiation resistance. The crack initiation cycles of NR 5SIPX-NS was lower compared to NR 4SIPX-NS due to the denser crosslink formation [46], as tabulated in table 3.

Table 6. Flex cracking resistance of NR composites

Sample name	Flex crack (kilocycles)	
	Initiation	Crack growth
NR 3NS	45	62
NR 3SIPX-NS	47	66
NR 4SIPX-NS	51	77
NR 5SIPX-NS	50	74

Fig.8. Relationship between tear strength and crack initiation of NR nanocomposites

3.9. Morphology of NR composites

Fig.9. FESEM images of NR 3NS and NR 4SIPX-NS composites

The dispersion of filler in the polymer matrix determines composite samples of ultimate properties. Stress concentration points developed inside the composites due to aggregation of particulate fillers lead to inferior properties while nanoparticles uniform distribution enhances the properties [4]. A little roughness and few agglomerates of silica present on NR 3NS tensile fractured surface (figure 9(a)) indicate that the interfacial interaction between nanosilica and NR is less. NR 4SIPX-NS composite shown in figure 9(b) is rugged with undulations and uniform filler dispersion, indicating that the matrix could transfer the applied stress to the nanosilica during the tensile test.

3.10. Thermal stability of NR nanosilica composites

Figure 10 shows the thermogravimetric curves obtained for the composite samples with nanosilica, modified nanosilica and gum compound. Natural rubber composite samples and gum compound showed a single step degradation pattern. The initiation of this single step degradation occurs by the thermal C-C bond chain scission followed by the hydrogen transfer at the scission site [47]. NR gum showed T_{on} (degradation temperature at 10% wt. loss) at 325 °C. 3 phr nanosilica addition in NR increased T_{on} by 3 °C while 4SIPX-NS had no significant change due to the initial decomposition of adsorbed SIPX on nanosilica particles. The maximum degradation temperature and temperature at 50% degradation (T_{50}) of both NR 4SIPX-NS and NR 3NS samples were the same and were 4 °C higher than the gum compound. The degradation of NR depends upon the nature of the metal ion present, the concentration of xanthate used *etc.* [48]. As the amount of xanthate in SIPX-NS is low, the composite with SIPX-NS has no significant effect on thermal properties. The thermal degradation characteristics are shown in table 7.

Fig.10. TG analysis of NR 4SIPX-NS, NR 3NS and NR gum

Table 7. Data from TG analysis

Name of sample	T_{on} , Onset degradation temperature (°C)	T_{max} , Maximum degradation temperature (°C)	T_{50} , Temperature at 50% degradation (°C)	Residue at 750 °C (%)
NR Gum	325	368	372	4.92
NR 3NS	328	372	375	8.57
NR 4SIPX-NS	326	372	375	8.88

3.11. Thermal conductivity of NR composites

Thermal conductivity data for NR gum, NR 3NS and NR 4SIPX-NS composites are shown in table 8. Thermal conductivity of polymers influenced by the incorporation of fillers [49]. The filler nature, orientation, dispersion in the matrix, volume fraction and thermal conductivity of the filler are the major parameters contributing to the thermal conductivity of composites [50]. Thermal conductivity values of NR nanosilica composites found to slightly higher compared to NR gum as nanosilica has a low value of thermal conductivity [51]. Minor enhancement in thermal conductivity of NR 4SIPX-NS composite compared to NR 3NS composite may be due to the better interaction, which is beneficial for the transmission of a phonon with decreased phonon scattering [52].

Table 8. Thermal conductivity of NR composites

Name of sample	Thermal conductivity (Wm ⁻¹ k ⁻¹)
NR Gum	0.153
NR 3NS	0.172
NR 4SIPX-NS	0.174

3.12. Swelling behaviour and Crosslink density of NR silica composites

Rubber-filler interaction and chemical crosslinks inside the vulcanized composites definitely affect the crosslink density [53]. Solvent molecular size, mobility of polymer chains and free volume inside the composite are the main factors that affect the transport of solvent through rubber matrix. Table 9 shows the tabulated values of the swelling index and crosslink density of composites samples. NR composites showed a decrease in solvent up-take with the increase in silica concentration. Compared to the NR 4SIPX-NS composite NR 3NS sample showed higher toluene up-take. This is due to better silica-rubber interactions and uniform filler dispersion in NR 4SIPX-NS composite. Transportation of solvent molecules through the NR matrix restricted by the uniformly distributed SIPX-NS particles. After vulcanization mobility of the NR chains restricted by filler particles. Maximum crosslink density observed for NR 5SIPX-NS sample and the value was comparable with 4SIPX-NS containing NR composite.

Table 9. Swelling index and crosslink density of NR silica composites

Sample name	Crosslink density (10^{-5} mol/g)	Swelling index (%)
NR gum	7.4±0.1	356±2
NR 3NS	7.93±0.1	337±1
NR 3SIPX-NS	8±0.1	341±1
NR 4SIPX-NS	8.37±0.1	315±2
NR 5SIPX-NS	8.40±0.1	307±1

4. Conclusions

Synergistic effects of the accelerator sodium isopropyl xanthate and nanosilica on thermo-oxidative aging resistance and cure characteristics for natural rubber were studied in this work. A simple and highly efficient modification on the surface of nanosilica was performed using sodium isopropyl xanthate. The modification was confirmed by FTIR, EDX, FESEM, DLS and TGA. Improved rheological, mechanical and aging properties were observed for the modified silica NR composite, which could be credited to the significantly improved rubber-filler interfacial interaction, higher crosslink density and dispersion. Improved interfacial interaction and dispersion of modified silica were revealed by FESEM. NR modified silica composite had high crosslinking density and hence showed high tensile strength retention and flex crack resistance. This indicates the composite has a long service life and can be used for a wide range of applications.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Author contributions

P. Dileep : Conceptualization, Methodology, Visualization, Investigation. Sinto Jacob : Writing- Original draft. C.S. Julie Chandra.: Data Curation, Resources. Midhun Dominic C.D.: Data Curation, Resources. Poornima M P.: Data Curation, Resources. Sunil K. Narayanankutty.: Supervision, Writing, Reviewing and Editing.

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My research didn't generate any data or I reused existing data

Compliance with Ethical Standards

This article does not contain any studies involving animals or human participants performed by any of the authors.

Consent to participate

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Figures

Figure 1

FTIR spectra of NS, SIPX and SIPX-NS

Figure 2

Particle size distribution of (a) NS and (b) SIPX-NS

Figure 3

Scanning electron micrographs of (a) NS and (b) SIPX-NS

Figure 4

TGA of NS and SIPX-NS

Figure 5

NR composites cure behavior

Figure 6

Tensile stress-strain curves obtained for NR composites

Figure 7

Retention of tensile strength of NR composites

Figure 8

Relationship between tear strength and crack initiation of NR nanocomposites

Figure 9

Figure 10

TG analysis of NR 4SIPX-NS, NR 3NS and NR gum

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