

Effect of Silane Integrated Sol-Gel Derived *In Situ* Silica on the Properties of Nitrile Rubber

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ABSTRACT: Nitrile rubber/silica composites are prepared by a sol-gel process using tetraethoxysilane as precursor in the presence of γ -mercaptopropyltrimethoxysilane as a silane coupling agent. Here, we follow a novel processing route where the silica particles are generated inside the rubber matrix before compounding with vulcanizing ingredients. The effect of *in situ* generated silanized silica on the properties of the rubber composite has been evaluated by studying curing characteristics, morphology, mechanical and dynamic mechanical properties. Enhanced rubber-filler interaction of these composites is revealed from stress-strain studies and dynamic mechanical analysis. Excessive use of silane shows an adverse effect on mechanical properties of the composites. Due to finer dispersed state of the *in situ* silica and enhanced rubber-filler interaction, the mechanical properties and thermal stability of the composites are improved compared to corresponding *ex situ* processed composite. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40531.

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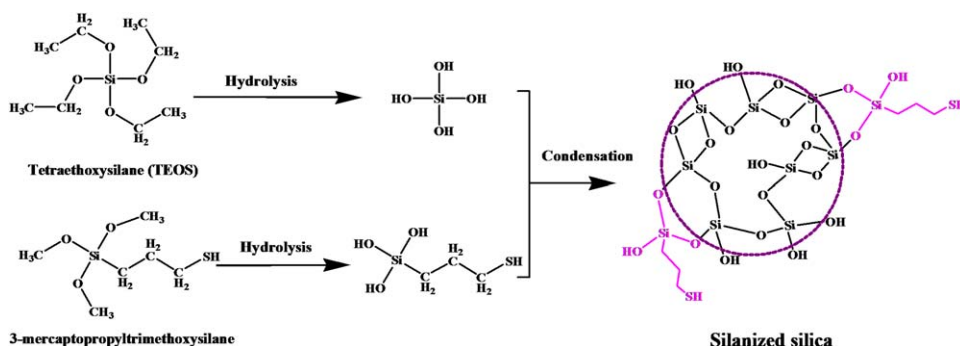
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INTRODUCTION

This work originates from our interest on studies of the reinforcement effect of *in situ* generated silica in elastomers. Silica as reinforcing filler with suitable coupling agents has a potential to provide better tear strength, resistance to cut, chip and chunking properties, low rolling resistance, and low heat buildup as compared to carbon black.^{1–3} But, the large number of polar hydroxyl groups on the silica surface tend to form strong interparticle hydrogen bonding that leads to the formation of silica aggregates in the rubber matrix. This causes difficulties in processability and hampers a significant reinforcement effect.^{4–6} There have been several efforts to overcome this problem among which modification of silica surface by silane treatment is an important one.^{7–11} Also, *in situ* generation of silica into rubber matrix by sol-gel process has attracted attention in recent past in order to achieve better filler dispersion and improved composite properties. A sol-gel process that involves hydrolysis followed by condensation of precursors like tetraethoxysilane (TEOS) can be carried out by soaking and solution methods.¹² In the soaking type, unvulcanized or vulcanized sheets of rubber allowed to swell in TEOS, followed by immersion in basic or acidic aqueous solution of catalyst. In the solution method, dissolution of rubber in a proper solvent, followed by the addition of TEOS, water, and catalyst to the rubber solution is carried out.¹²

Several reports are available in the literature on the *in situ* generation of silica in the different rubber matrices such as natural rubber (NR),^{13–19} isoprene rubber (IR),^{20–22} styrene butadiene rubber (SBR),^{23–26} polydimethylsiloxane (PDMS),^{27,28} ethylene propylene diene monomer rubber (EPDM),^{29–31} butadiene rubber (BR),¹¹ acrylic rubber (ACM),³² and chloroprene rubber (CR).³³ However, research on nitrile rubber (NBR) filled with *in situ* silica is very limited. Ikeda and coworkers studied *in situ* silica filled NBR composites where silica was generated by sol-gel method.^{34,35} These studies showed low degree of swelling of NBR in TEOS due to its polar nature and, hence, low amount of silica generation. The affinity of silica particles grown *in situ* by sol-gel process toward NR phase in NR/NBR blend system was revealed by one of our previous studies.³⁶ There are also some reports available in the literature on *in situ* silica generation into NBR latex and carboxylated nitrile rubber (XNBR) by sol-gel reaction.^{26,37} Nevertheless, *in situ* silica generation in NBR matrix before crosslinking has not been reported till now where simultaneously silane coupling agent is used.

Our recent studies on nitrile rubber silica composites showed that γ -mercaptopropyltrimethoxysilane (γ -MPS) acts for such rubber systems as an effective silane coupling agent in modifying the silica surface and in improving the ultimate properties of the composites.³⁸ Surface modification of silica by



Scheme 1. *In situ* generation of silanized silica by sol-gel method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

organosilane can efficiently improve its compatibility with organic rubber matrix and increases the degree of dispersion owing to its different functionality at two ends.^{8–10} In general, surface modification of silica by organosilane is done by either pretreatment of silica before mixing with rubber or during physical mixing of silica with rubber. In the present work, organosilane has been used in the reactive sol-gel system to investigate the effect of silane treatment during generation of silica *in situ* into rubber matrix. The amount of organosilane has been varied to assess its influence on the properties of the composites. Similar approaches of *in situ* silica generation along with different organosilanes in NR latex^{14,39–41} and aminopropylsilane in epoxidized SBR solution were reported.⁴² Properties of all the synthesized composites were evaluated in terms of curing characteristics, morphology, mechanical and dynamic mechanical properties. Amount of 1 phr silane is found to be optimum in bringing maximum improvement in mechanical properties as well as in processability with accelerated cure rate. Properties of *in situ* silica filled composite are compared with unfilled composite as well as with externally added silica filled composite of similar composition. Morphological studies reveal more uniform filler dispersion within the rubber matrix in case of *in situ* generated silica compared to silica added externally. This uniform filler morphology is in accordance with improved mechanical properties and rubber-filler interaction observed in the former case.

EXPERIMENTAL

Materials

Nitrile rubber (NBR) KNB-35L (acrylonitrile content 34 mol %) and precipitated silica (VN3) were provided by Heritage Rubber (Nagpur, India). TEOS 98% and *n*-butylamine were purchased from Acros Organics (NJ). MPS 99% was purchased from Aldrich (USA). Tetrahydrofuran (THF) and toluene were purchased from Fischer Scientific (India). Soluble rhombic sulfur (99.8), zinc oxide (manufactured by American process zinc oxide 98.5% min.; sulfur 0.2% max.; moisture and other volatile matter 0.5% max.; total impurities including moisture 1.5% max. and coarse particles 0.25% max.), stearic acid, and mercaptobenzothiazole disulfide (MBTS) were collected from Sara Polymer Pvt. Ltd (Nagpur, India).

Generation of Silica into Nitrile Rubber by Sol-Gel Process

Generation of *in situ* silica into NBR matrix and its concurrent modification with organosilane (γ -MPS) was carried out by

sol-gel process (Scheme 1). Nitrile rubber was dissolved in THF and γ -MPS added to the solution in varying amount for different compositions (Table I) and set to stirring for homogeneous mixing. After that, 30 wt % TEOS, water (TEOS : water mole ratio = 1 : 2) and *n*-butylamine (0.096 mol) as a catalyst were added to the solution and was continuously stirred for 3 h. The resultant solution was kept for gelling at room temperature for 5 days, followed by vacuum drying at 50°C till constant weight of the sheet was obtained. THF being a polar solvent allows preventing the phase separation between hydrophilic water and hydrophobic rubber and TEOS. This process was used only for *in situ* silica filled composites 2–5.

Compounding of Rubber Vulcanizates

The compounding of rubber was carried out on a two roll mill with friction ratio 1 : 1.2 at ambient temperature fitted with water cooling arrangement. The formulations of the NBR compounds prepared for present study are given in Table I. The compounding process was carried out by masticating the *in situ* silica filled NBR on a two roll mill for 5 min followed by compounding with crosslinking ingredients on a two roll mill further for 10 min, minimum distance between roll was adjusted to 1.5 mm. This process was followed for all *in situ* silica filled composites 2–5. Composite 6 was prepared by externally mixing NBR with precipitated silica along with silane for 15 min followed by mixing of crosslinking ingredients on a two roll mill for further 10 min with minimum distance between roll was adjusted to 1.5 mm. Similarly, sample 1 was prepared without

Table I. Formulations of Rubber Compounds

Ingredients ^a	1	2	3	4	5	6
NBR	100	100	100	100	100	100
γ -MPS	0	0	1	2	3	1
<i>In situ</i> silica ^b	–	2	5	5	6	–
Ppt. silica (VN3)	–	–	–	–	–	5
Zinc Oxide	4	4	4	4	4	4
Stearic acid	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5

^a phr: parts by weight per hundred parts of rubber

^b *In situ* silica content determined by thermogravimetric analysis

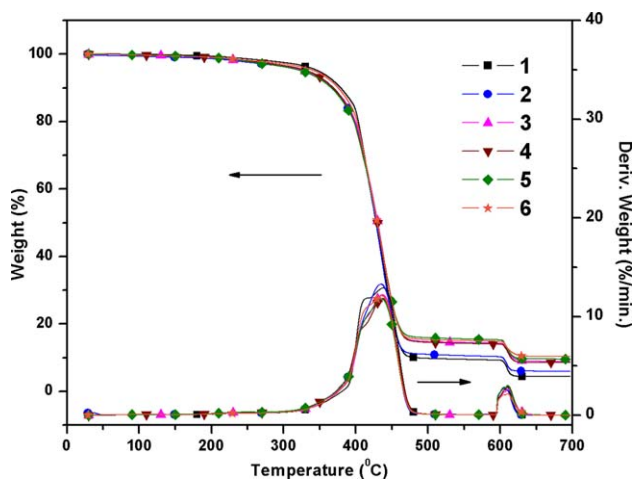


Figure 1. TGA of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

any filler on two roll mill. The resultant compounds were then cured using compression molding press at 160°C temperature and at 10 ton pressure with respect to their corresponding cure time (t_{90}) to get a vulcanized rubber sheet of 1 mm thickness.

Characterization

Curing Studies. Curing studies of rubber compound were carried out by using moving die rheometer (MDR:SIS-V50 Scaraeus) with an amplitude of $\pm 0.5^\circ$ and a frequency of 1.67 Hz for all the samples at 160°C for 60 min.

Transmission Electron Microscopy. Morphology of composites was studied by transmission electron microscopy (TEM). Ultrathin sections of the samples were cut by ultramicrotome EM UC6/FC6 (Leica) at about -150°C and images were obtained using a TEM Libra 200 (Carl-Zeiss) with an acceleration voltage of 200 kV.

Thermogravimetric Analysis. Thermal stability and *in situ* silica content of the rubber vulcanizates were determined by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) using a TGA Q5000 of TA instruments. The sample was placed in an alumina pan and heated in the temperature range 30–700°C under air at the heating rate of 10 °C/min.

Stress–Strain Studies. Tensile tests of cured samples were carried out using Zwick 1456 (Model 1456, Z010, Ulm Germany) with crosshead speed 200 mm/min (ISO 527). In addition, hardness of the composites was measured on Shore A scale by using a durometer.

Dynamic Mechanical Analysis. Dynamic mechanical analysis was performed with an Eplexor 2000N dynamic measurement system (Gabo Qualimeter, Ahlden, Germany) using a constant frequency of 10 Hz in the temperature range from -100°C to $+140^\circ\text{C}$. Samples were analyzed in the tension mode. For the measurement of the complex modulus, E^* , a static load of 1% pre-strain was applied, and then the samples were oscillated to

a dynamic load of 0.5% strain. Measurements were done with a heating rate of 2 °C/min under liquid nitrogen flow.

Swelling Studies. Swelling measurements were carried out by soaking the cured samples in toluene for 7 days at room temperature. After each 24 h the solvent was changed with fresh toluene. Seven days later sheets were removed and solvent on the surface were blotted with blotting paper and immediately weighed on analytical balance. Crosslinking density ν , defined by the number of elastically active chains per unit volume, was measured by Flory–Rehner equation [eq. (1)]⁴³:

$$\nu = V_s \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{\left(V_r^{1/3} - \frac{V_r}{2}\right)} \quad (1)$$

where, V_s is the molar volume of toluene (106.2), V_r is the volume fraction of rubber in swollen gel, and χ is the Flory–Huggins (NBR–toluene) interaction parameter which is 0.472 for NBR–toluene system.⁴⁴

RESULTS AND DISCUSSION

Thermogravimetric Analysis

TGA of all the compounds 1–6 was carried out to assess their thermal stability. The thermal decomposition of rubber is a single step process, which is due to the thermal scissions of C–C bonds, accompanying a transfer of hydrogen at the site of chain scission.⁴⁵ The results are illustrated in Figure 1 and Table II. Silica content of the composites was determined from residual weight percentage (Table II). It is interesting to note that presence of silane coupling agent increased the amount of *in situ* silica generation into NBR matrix. Role of silane in enhancing the sol–gel reaction and increasing silica generation is reported in the literature.³⁵ The degradation in the temperature range 350°C to 490°C is resulted due to degradation of rubber. The next weight loss at temperature range 560°C to 640°C is due to the decomposition of carbonaceous residue. Although onset temperature values of the composites are comparable but there is significant increase in T_{max} (temp. at max. wt. loss) for all the *in situ* silica filled composites 2–5 compared to those of unfilled composite 1 and externally added silica filled composite 6. Among the *in situ* silica filled composites the highest thermal stability is shown by composite 3. This is attributed to the uniform distribution of silanized silica into rubber matrix that leads to improved rubber–filler interaction which in turn binds with a rubber chain more tightly and restricts its movement. This inhibition in chain movement and slow diffusion of

Table II. Thermogravimetric Analysis of NBR Composites

Sample	1	2	3	4	5	6
Onset temp (°C)	260	258	267	260	260	256
Temp. at max. wt. loss (°C)	418	435	437	437	436	418
<i>In situ</i> silica (phr)	-	2	5	5	6	-

1, unfilled; 2, *in situ* silica filled; 3, *in situ* silica filled with 1 phr silane; 4, *in situ* silica filled with 2 phr silane; 5, *in situ* silica filled with 3 phr silane; 6, precipitated silica filled with 1 phr silane.

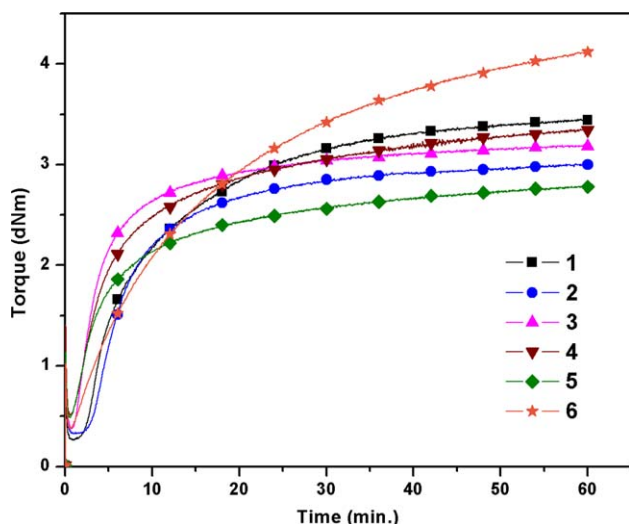


Figure 2. Curing behavior of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decomposed products from the bulk rubber matrix results in delayed decomposition temperature for composite 3. This composite also shows best mechanical properties which will be discussed in subsequent section.

Curing Characteristics

Curing behavior of unfilled, *in situ* silica filled and precipitated silica (VN3) filled nitrile rubber is illustrated in Figure 2, Figure 3 and Table III. It is observed here that incorporation of silica into rubber resulted in increase in minimum torque due to increased viscosity. On the other hand, Δ torque for silica filled compounds are found to decrease compared to that of unfilled one which may be due to adsorption of cure accelerator on surface silanol groups of silica, which prevents the crosslinking reaction.² However, for compound 3 and 4 where organosilane is used as surface modifier, increase in torque and Δ torque were observed compared to untreated *in situ* silica filled composite 2 although silica content in former compounds are higher. It is believed that bifunctionality of silane plays significant roles. It reacts with surface silanol groups of silica via hydrolyzable methoxy group and prevents the adsorption of cure accelerator on silica surface.⁷ In addition, it contributes to crosslinking by sulfur linkage with rubber chain through its thiol group. Notably, there is steep increase in torque in the early stages of vulcanization for silane modified *in situ* silica filled composites 3–5 which is due to some partial curing before actual vulcanization starts owing to presence of thiol group on organosilane.⁴⁰ It is also noticed that for composite 5 where amount of silane used is highest there is a fall in torque. This is attributed to the plasticizing effect of polysiloxane cluster, which might be formed due to self-condensation of hydrolyzed methoxy groups of silane to a long chain polysiloxane cluster, which can act as a plasticizer.^{9–11} Among the surface modified *in situ* silica filled composites 3–5, shortest cure and scorch time and highest cure

rate index is observed for the composite 3 where silane used is minimum (1 phr). With increase in silane concentration prolonged effect on cure and scorch time with lower cure rate index for composites 4 and 5 may be again due to plasticizing effect that interferes in crosslinking reaction. Composite 6, prepared for comparative study, with same loading of precipitated silica and organosilane as composite 3, shows somewhat higher minimum torque indicating increased compound viscosity due to aggregation tendency of precipitated silica into rubber matrix. Also, worst cure and scorch time and lowest cure rate index is found for compound 6 compared to that composite 3 shows the effect of silane in modifying the surface silanol group of silica.

Morphology of NBR/Silica Vulcanizates

TEM images of all the *in situ* silica filled composites 2–5 are shown in Figure 4. TEM images show black colored silica particles dispersed over grayish colored rubber matrix. A homogeneous dispersion of silica particles of different shape and size into the rubber matrix is observed. Higher silica content for composites 3–5, where organosilane is used as modifier, compared to composite 2 is evident from greater density of silica particles in the former cases. This observation is in accordance with results obtained in thermogravimetric study and is attributed to the presence of organosilane in the reactive sol-gel reaction generating silica *in situ* into rubber matrix.³⁵

At higher magnification some long chain clusters were observed for composites 4 and 5 where greater amount of silane is used (Figure 5). These clusters are believed to be polysiloxane long chains formed by self-condensation of organosilane and act as plasticizing agent as discussed earlier in curing behavior section.

TEM images of composite 6 (Figure 6) with similar composition of composite 3 but containing externally added silica shows the presence of large number of aggregates. This is due to strong interparticle interaction of silica. So, it can be concluded

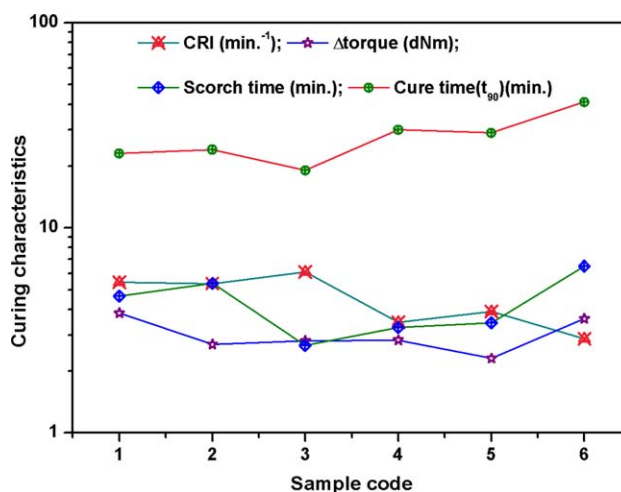


Figure 3. Curing characteristics of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Curing Characteristics of NBR Composites

Curing characteristics	1	2	3	4	5	6
Torque (min.dNm)	0.29	0.32	0.37	0.51	0.48	0.6
Torque (max.dNm)	4.13	3.02	3.20	3.36	2.80	4.21
Delta torque (dNm)	3.84	2.7	2.82	2.84	2.31	3.61
Cure time (t_{90}) (min)	23	24	19	30	29	41
Scorch time (min) ts1	4.65	5.37	2.67	3.27	3.45	6.51
Scorch time (min) ts2	6.6	11.49	6.42	10.47	22.35	15.21
Cure rate index (min^{-1})	5.45	5.36	6.12	3.47	3.91	2.89

1, unfilled; 2, *in situ* silica filled; 3, *in situ* silica filled with 1 phr silane; 4, *in situ* silica filled with 2 phr silane; 5, *in situ* silica filled with 3 phr silane; 6, precipitated silica filled with 1 phr silane.

that *in situ* silica in the presence of organosilane shows better filler dispersion compared to conventional mixing of silica with organosilane into rubber matrix. This observation supports the results obtained in cure study.

Mechanical Analysis

Stress–strain studies of all the composites are given in Table IV and Figure 7. It can be seen here that tensile moduli at $\sigma_{50\%}$, $\sigma_{100\%}$, $\sigma_{200\%}$, and $\sigma_{300\%}$ increases for the filled composites

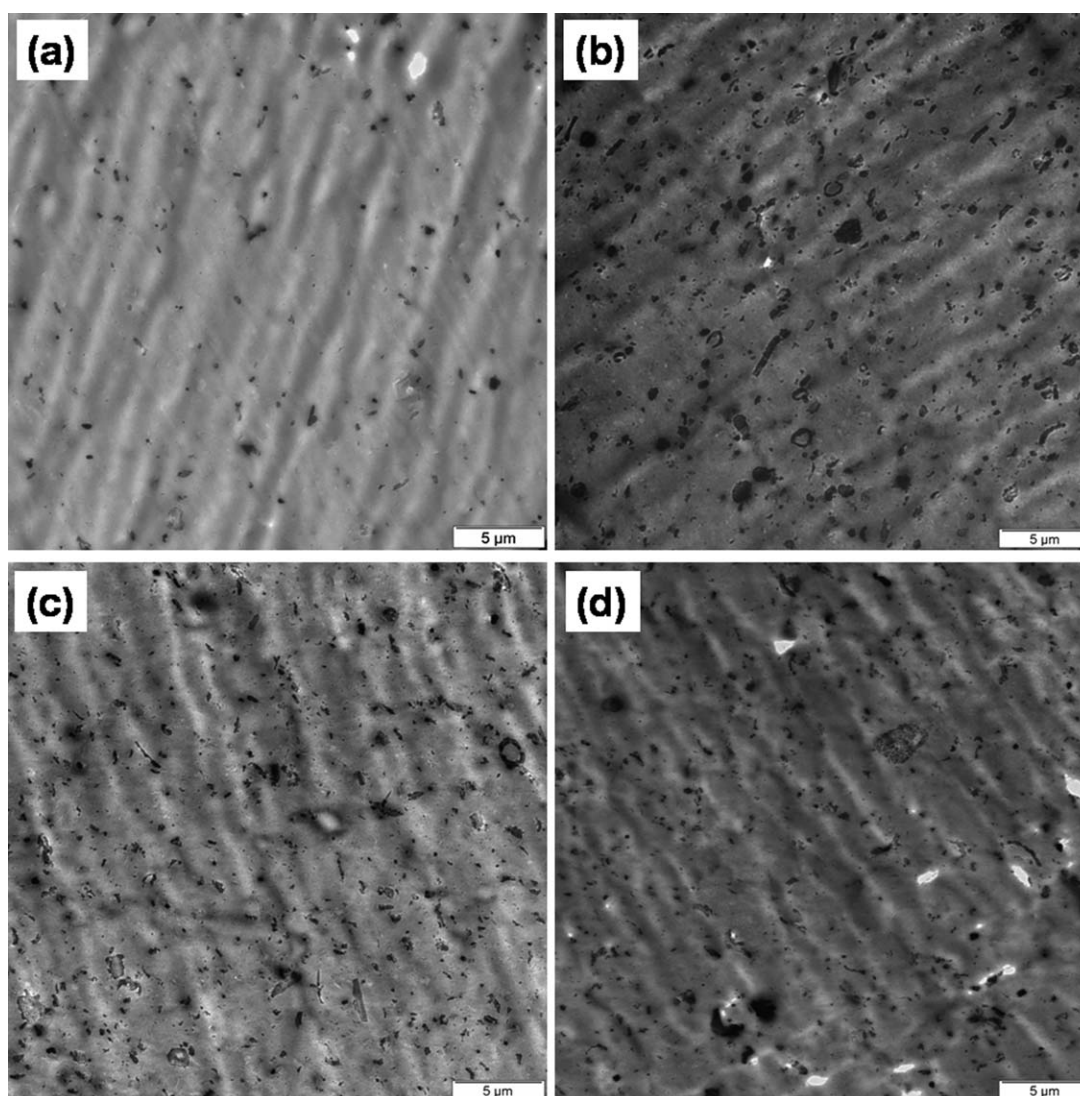


Figure 4. TEM images of NBR composites filled with (a) *in situ* silica (2); (b) *in situ* silica with 1 phr silane (3); (c) *in situ* silica with 2 phr silane (4); (d) *in situ* silica with 3 phr silane (5).

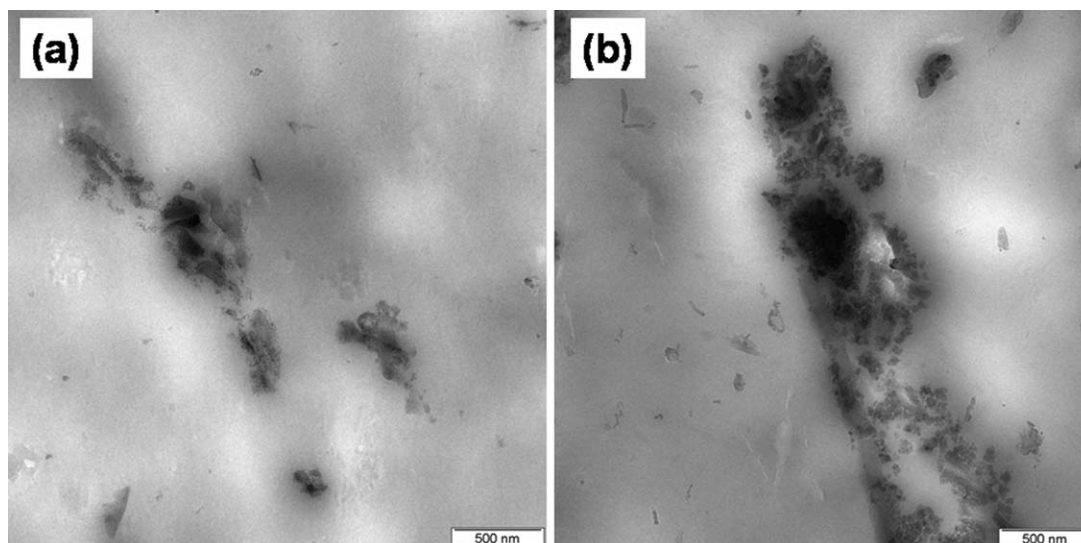


Figure 5. TEM images of composites 4 and 5 showing long chain polysiloxane clusters, (a) *in situ* silica filled with 2 phr silane (4); (b) *in situ* silica filled with 3 phr silane (5).

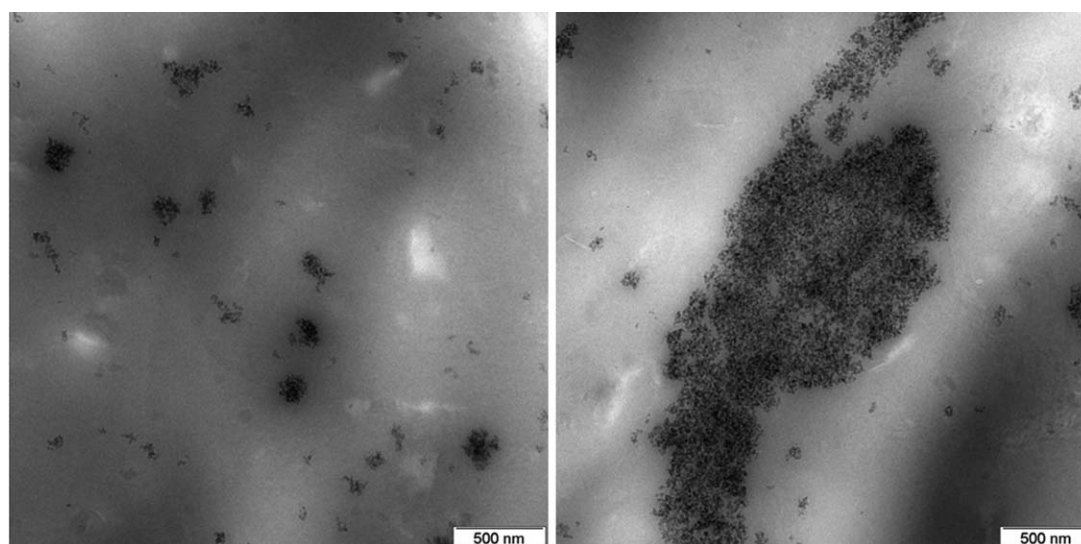


Figure 6. TEM images of composite 6 filled with precipitated silica with 1 phr silane.

Table IV. Mechanical Properties of NBR Composites

Mechanical properties	1	2	3	4	5	6
$\sigma_{50\%}$ (MPa)	0.56	0.63	0.75	0.76	0.76	0.76
$\sigma_{100\%}$ (MPa)	0.72	0.75	0.86	0.95	0.92	0.98
$\sigma_{200\%}$ (MPa)	0.89	0.84	1.07	1.22	1.16	1.32
$\sigma_{300\%}$ (MPa)	1.08	0.92	1.31	1.6	1.52	1.72
Tensile strength (MPa)	2.81	2.84	5.35	4.89	3.83	4.26
Elongation at break (%)	705	779	801	612	590	566
Crosslinking density ($\nu \times 10^5$)	6.902	3.099	4.944	4.769	3.314	4.654
Hardness (Shore A)	40	42	44	46	46	47

1, unfilled; 2, *in situ* silica filled; 3, *in situ* silica filled with 1 phr silane; 4, *in situ* silica filled with 2 phr silane; 5, *in situ* silica filled with 3 phr silane; 6, precipitated silica filled with 1 phr silane.

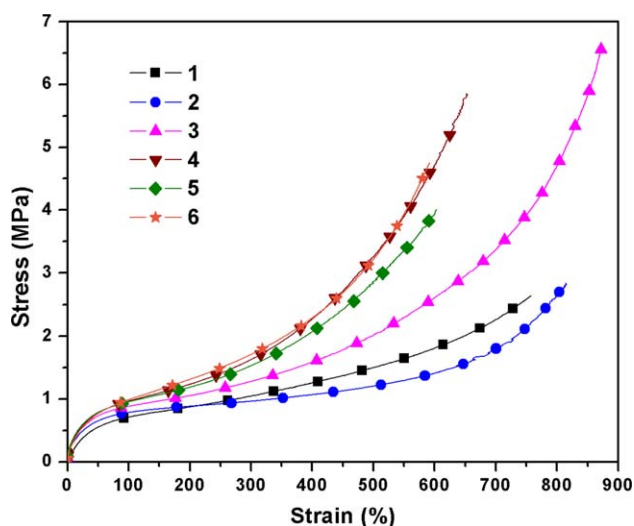


Figure 7. Stress–strain curves of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared to unfilled one and it increases further for composites modified with silane. This result indicates the reinforcing nature of silica as strong phase interaction between rubber and inorganic silica is resulted in the presence surface modifier.

An interesting point to note here is that highest tensile strength is observed for the composite 3 where silane used is 1 phr. However, there is fall in tensile strength for composite 4 and 5 as silane concentration increases. As per our previous discussion, here also, it can be explained in terms of formation of long chain polysiloxane by self-condensation of organosilane

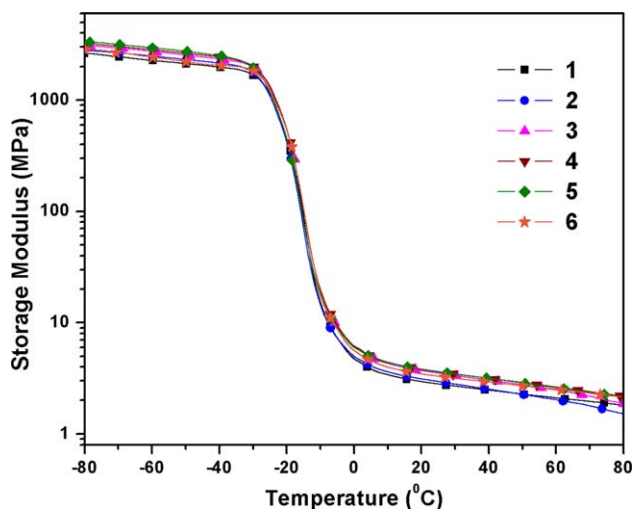


Figure 8. Storage modulus versus temperature of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when present at higher concentration that acts as a plasticizer.^{9–11} This result agrees with crosslinking density determined by Flory–Rehner equation [eq. (1) and Table IV] where expected trend is followed for these composites.

Another important observation is made for composite 2, filled with unmodified *in situ* silica, where moduli up to 200% strain is higher than composite 1 (unfilled) but it becomes lower above 200% strain. This result indicates that untreated *in situ* silica shows no significant reinforcement effect above 200% elongation due to the lack of phase interaction between silica and rubber matrix in the absence of surface modifier.¹¹ This is supported by the crosslinking density value which is lower for this composite 2.

When we compare between composite 6 filled with precipitated silica and composite 3 filled with *in situ* silica with same filler loading and silane content, higher values of tensile moduli ($\sigma_{50\%}$, $\sigma_{100\%}$, $\sigma_{200\%}$ and $\sigma_{300\%}$) for composite 6 is noticed. However, tensile strength and elongation at break of composite 6 becomes lower than composite 3. This might be due to the presence of large size silica aggregates formed by filler–filler interaction as revealed by TEM images (Figure 6). It is reported in literature that such filler structure becomes dominant at small deformations but breaks at larger deformations.^{46–48}

It is well known fact that the hardness values of the composites are closely related to the modulus at low strain. The hardness value for the composites progressively increase and is maximum for externally filled composite 6 where agglomerated filler structure exists due to strong interaction between the silica particles.

Dynamic Mechanical Analysis

Rubber–filler interaction and glass transition temperature of all the composites were studied by dynamic mechanical analysis. Temperature dependence of storage modulus and $\tan \delta$ are shown in Figures 8 and 9. Figure 8 shows that storage modulus

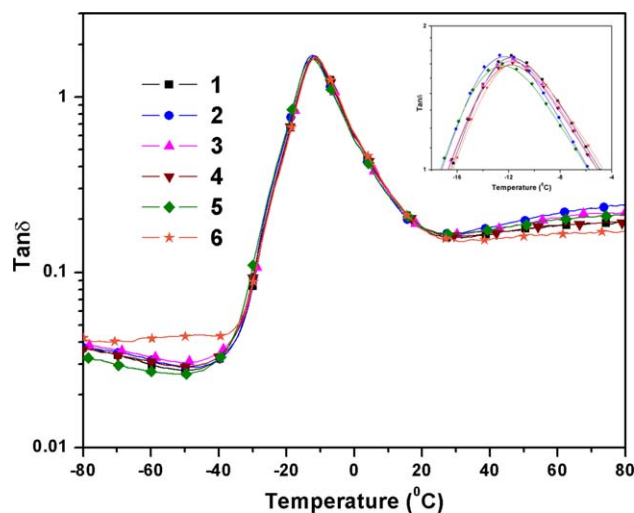


Figure 9. $\tan \delta$ versus temperature of NBR composites: unfilled (1); *in situ* silica filled (2); *in situ* silica filled with 1 phr silane (3); *in situ* silica filled with 2 phr silane (4); *in situ* silica filled with 3 phr silane (5); precipitated silica filled with 1 phr silane (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values of all the silanized *in situ* silica filled composites, above glass transition temperature, are higher compared to unfilled composite. Thus stronger filler–rubber interaction in the former composites can be concluded which is brought about by silane treatment of uniformly dispersed silica generated *in situ* into rubber matrix by sol–gel process. Presence of silane in the reactive sol–gel system favors phase interaction between silica and rubber matrix through its mercapto group and form a sulfur linkage with rubber chains. This in turn restricts the movement of rubber chains and eventually results in better rubber–filler interaction.

Further, higher storage modulus values of *in situ* silica filled composite **3** over precipitated silica filled composite **6** is also noticed. Since organosilane used in both the cases is same, it can be concluded that surface modification by organosilane and hence rubber–filler interaction are more effectively achieved in case of silica generated *in situ* into rubber matrix.

Temperature versus $\tan \delta$ plot gives a peak corresponding to the glass transition temperature of the composites. Glass transition temperatures of all the composites are found to be comparable in Figure 7(b). However, a slight negative shift of $\tan \delta$ peak for composite **4** and **5** compared to that of **3** observed from a close view (inset) can be attributed to the plasticizing effect of polysiloxane. Also, negative shift of $\tan \delta$ peak of **2** over that of **1** indicates less interfacial bonding between silica and rubber matrix in **2**. Thus strongest rubber–filler interaction in **3** is revealed by this study which is in good agreement with the other results discussed before.

CONCLUSIONS

Sol–gel silica was grown in nitrile rubber in the presence of varying amount of silane coupling agent viz. γ -MPS before the vulcanization process. The rubber filled with sol–gel silica was compounded with other rubber additive in conventional way and processed further. Morphological studies revealed more uniform dispersion of the silica which was generated *in situ* by sol–gel method compared to silica added externally. Stress–strain studies showed improvement in mechanical properties for all the silica filled composites over unfilled one and the effect was more pronounced for silane treated silica filled composites. Highest tensile strength, better state of cure with improved processability, and maximum thermal stability were observed for composite **3** filled with *in situ* silica silanized with 1 phr silane. Further increase in silane dosage resulted in adverse effect in curing processability and mechanical properties. Improved rubber–filler interaction was also supported from dynamic mechanical analysis. Thus, *in situ* generation of silica in the presence of organosilane appeared to be an efficient approach of filler incorporation into nitrile rubber to achieve better filler dispersion and improved mechanical and thermal properties. Thereby, silane dosage plays an important role to optimize the final compound properties. The effect of silane concentration at higher filler content and the application of such an approach to other rubber systems will be of great interest for future studies.

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