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Rubber composites based on silane-treated stöber silica and nitrile rubber: Interaction of treated silica with rubber matrix

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Abstract

Role of silane-treated stöber silica as reinforcing filler for nitrile rubber (NBR) has been studied. Stöber silica is synthesized by sol–gel method, and the surface of silica is modified with the treatment of silane-coupling agent viz. γ -mercaptopropyltrimethoxysilane (γ -MPS) in varying proportions. Average particle size of stöber silica of spherical shape in the range of 200 to 400 nm is evident from scanning electron microscopy (SEM). Surface modification of silica particle with silane-coupling agents decreases surface energy and reduces agglomeration of silica particles in rubber matrix. Stress–strain study and dynamic mechanical analysis of silica-filled composites are compared with the unfilled ones. Analysis of cross-linking density, mechanical properties, and storage moduli indicates a strong rubber–filler interaction in the silane-treated, silica-filled NBR composites. Silane treatment is found to be effective in uniform dispersion of silica in rubber matrix and in improving the mechanical properties of rubber composite. Different functionalities of organosilane at its both end improve the compatibility of silica with rubber matrix and offer better rubber–filler interaction.

Keywords

Stöber silica, surface modification, rubber–filler interaction, rubber composite, reinforcement

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Introduction

Nitrile rubber (NBR) is an emulsion copolymer of acrylonitrile and butadiene. The polar acrylonitrile group present in NBR imparts excellent fuel and oil resistance, and hence it is widely used in many important industrial applications like fuel and oil supply hoses, rollers, drive belts, seals, and so on. NBR is a random copolymer having stereo-irregular molecular structure that results in the deficiency of stress-induced crystallization behavior that does not contribute to significant mechanical properties. So, addition of reinforcing fillers is required for the necessary improvement in the properties of NBR.^{1–3} Silica is one of the widely used reinforcing fillers for the rubber composites due to its capability of providing very good dynamic properties of passenger car tires, good tear strength, resistance to cut, chip, and chunking. It also improves thermal conductivity and decreases heat build-up of rubber composites.^{4–7} However, the drawbacks of silica as a filler is its tendency to agglomerate into rubber matrix due to the presence of surface silanol groups that form interparticle hydrogen bonding.^{8,9} This results in poor dispersion of silica into rubber matrix. Also, there is an increase in compound viscosity that leads to difficulty in processability and retardation in curing.^{10–12} One of the ways to overcome this problem is surface modification of silica particles by reactive mixing of silica in the presence of some surface modifier.^{13,14} Different organosilanes are used in this purpose for modification of silica surface. They generally have hydrolysable alkoxy groups at one end that can interact with silanol groups present on the silica surface. On the other end of this organosilane, there is some hydrophobic group that can bridge with rubber chain. Thus, organosilanes can efficiently improve the compatibility of organo-modified silica with rubber matrix and increase the degree of dispersion (Figure 1). As a result, thermal and mechanical properties of the composites are improved compared to that of the composites with unmodified silica.

A numerous research has been carried out using precipitated silica and surface-modified precipitated silica with different types of rubber to evaluate their effect on dispersion, physical properties, bound rubber content, and rubber–filler interaction.^{15–20} In this work, we have studied the role of surface-modified stöber silica synthesized by sol–gel process, as reinforcing filler for NBR. Polymer stöber silica composites has been extensively studied for various important applications, whereas studies on stöber silica as reinforcing filler for rubber composites is limited as compared to amorphous precipitated silica.^{13,21} A few studies on stöber silica rubber composites report that stöber silica is more homogeneously dispersed compared to precipitated silica.^{22–24} Our preliminary studies on NBR silica composites using γ -mercaptopropyltrimethoxysilane (γ -MPS) as modifier showed improvement in mechanical properties of the composites.²⁵ Here, we report the results obtained from more thorough and detailed studies on the morphology and mechanical properties of the NBR composites containing silane-treated stöber silica. Synthesis of silica particles are carried out by sol–gel method followed by surface modification with the treatment of γ -MPS. Silica-rubber composites are then prepared by mixing the surface modified silica with NBR along with other additives followed by vulcanization. Amount of γ -MPS has been varied in the surface treatment of stöber silica to see its effect on the properties of rubber composites. Fourier-transform infrared (FTIR) analysis of silane-treated silica confirms the presence of γ -MPS on silica particles. Mechanical properties of composites with

Figure 1. Schematic diagram of bridging of rubber and silica produced by organosilane.

surface-modified silica are compared with those of unfilled rubber composite to see the effect of surface modification of silica on the ultimate properties of the rubber composites.

Experimental

Materials

Tetraethoxysilane, 98% (TEOS) and γ -MPS 99% were purchased from Acros Organics and Aldrich, respectively. Toluene and ethanol were purchased from Fischer Scientific. Ammonia was purchased from Merck. NBR, KNB-35L, was used as a raw rubber

Table 1. Formulations of rubber compounds.

Ingredients ^a	1	2	3	4
NBR	100	100	100	100
Silica ^b	—	7	7	7
Zinc oxide	4	4	4	4
Stearic acid	1	1	1	1
MBTS	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5

NBR: nitrile rubber; MBTS : mercaptobenzothiazole disulfide.

^aphr: parts by weight per hundred parts of rubber.

^bCompounds **2**, **3**, and **4** contains silica treated with 1%, 2%, and 3% γ -mercaptopropyltrimethoxysilane with respect to the weight percentage of silica, respectively.

procured from Heritage rubber, Nagpur, India. Sulfur, zinc oxide (ZnO), stearic acid, and mercaptobenzothiazole disulfide (MBTS) were collected from Sara Polymer Pvt. Ltd. Nagpur, India.

Synthesis of stöber silica particles by sol-gel process

Silica particles were synthesized by Stöber method.²⁶ Ethanol (466 ml, 8 mole), water (54 ml, 3 mole), and TEOS (141 ml, 0.6 mole) were mixed and stirred for 5 min on magnetic stirrer. Then 28 ml ammonia (25%) was added to it and continuously stirred for 24 h. The colloidal solution thus obtained was centrifuged and dried at 100°C for 3 hours.

Postmodification of silica particles by γ -MPS

Silica particles (6 gm) were dispersed in toluene (120 ml) by mechanical stirring. To this, γ -MPS solution (0.06 gm in 10 ml toluene) was mixed so that the amount of γ -MPS is 1% with respect to the weight percentage of silica. The resultant mixture was refluxed for 3 h at 110° with continuous stirring. The solution was then centrifuged to precipitate out modified silica and washed several times with toluene and acetone in order to remove any unreacted silane and finally dried at 150°C for 2 h. The modified silica thus obtained is considered as 1% silane-treated silica and this terminology is subsequently used in this article. This 1% silane-treated silica is used for the preparation of compound **2**. The same procedure was followed to obtain silica treated with 2% and 3% of γ -MPS (by weight percentage of silica), by adding appropriate amount of γ -MPS and used for the preparation compound **3** and compound **4**, respectively.

Compounding of rubber

The masticated NBR was compounded with synthesized silica and other cross-linking ingredients on a two-roll mill for approximately 10 min (formulation is given in Table 1). The compounded rubber was then subjected to vulcanization using compression molding at 160°C for corresponding cure time (t_{90}) to obtain vulcanized rubber sheet of 1 mm thickness.

Characterization

FTIR spectra of the silica particles were determined using a Shimadzu IR-Affinity spectrophotometer. Curing studies of rubber compounds were carried out using rubber process analyzer, Scarabaeus SIS V50, Germany, in an isothermal time sweep mode for all the samples at 160°C for 60 min. Scanning electron microscopy (SEM) images of modified and unmodified silica particles were taken using scanning electron microscope (Ultra Plus; Carl Zeiss SMT, Germany) at an acceleration voltage of 3 kV and the samples were sputter coated with 3 nm platinum. Morphology of the fractured surface of silica-filled composites was studied by SEM (JEOL JSM-6380A, Japan). Thermogravimetric analysis (TGA) of the composites was carried out by a Perkin Elmer Thermal Analyzer. The sample was placed in a alumina pan and heated in the temperature range of 30–700°C under air and the heating rate was 20°C/min. Stress–strain studies of cured samples were carried out using Zwick tensile tester (model 1456, Z010; Ulm Germany) with a crosshead speed of 200 mm/min (ISO 527). Dynamic mechanical analysis was performed with an Eplexor 2000N dynamic measurement system (Gabo Qualimeter, Ahlden, Germany) using a constant frequency of 10 Hz in a temperature range from –100°C to +140°C. Samples were analyzed in the tension mode. For the measurement of the complex modulus (E^*) a static load of 1% prestrain 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 K/min under liquid nitrogen flow. Swelling measurements were carried out by soaking the samples in toluene for 7 days at room temperature. Cross-linking density ν , defined by the number of elastically active chains per unit volume, was measured by Flory–Rehner equation shown below.

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

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

Results and discussion

FTIR spectroscopy

Figure 2 shows FTIR spectra of both modified (Figure 2(b)–(d)) and unmodified (Figure 2(a)) stöber silica. In all these spectra, the broad peak at 3,450 cm^{-1} is assigned to stretching vibration of silanol (O–H group) along with adsorbed water. The peaks at 950 cm^{-1} and 800 cm^{-1} are due to Si–O stretching and the deformation of Si–OH, respectively, in silanol. The peaks at 1,100 cm^{-1} and 470 cm^{-1} are due to asymmetric and symmetric stretching of Si–O–Si in siloxane group, respectively. Further inspection of these spectra reveals the presence of two small peaks of around 2,930 cm^{-1} and 2,840 cm^{-1} and one peak of around 1,450 cm^{-1} for all the spectra of the silane-treated silica (Figure 2(b)–(d)) in addition to the absorption bands corresponding to the vibration of specific functional group

Figure 2. FTIR spectra of (a) untreated silica, (b) 1% silane-treated silica, (c) 2% silane-treated silica, (d) 3% silane-treated silica, and (e) pure silane (γ -MPS). FTIR: Fourier-transform infrared; γ -MPS: γ -mercaptopropyltrimethoxysilane.

present in spectrum of unmodified silica (Figure 2(a)). These small peaks of around $2,930\text{ cm}^{-1}$ and $2,840\text{ cm}^{-1}$ are characteristic bands of organosilane corresponding to symmetric and antisymmetric stretching of $-\text{CH}_2$ group, respectively, while the peak at $1,450\text{ cm}^{-1}$ corresponds to $\text{Si}-\text{CH}_2$ bending vibration present in organosilane.^{27–30} All these peaks are clearly observed in the spectra of organosilane viz. γ -MPS shown in Figure 2(e). Presence of these additional characteristic bands of organosilane in the spectra of modified silica thus indicates grafting of organosilane on the silica surface. This is also supported by the presence of a weak band at $2,550\text{ cm}^{-1}$, which is a characteristic band of $-\text{SH}$ group, in the spectra of modified silica.³⁰ Notably, the intensity of this weak band decreases as the amount of organosilane on silica surface decreases.

Curing characteristics

Curing characteristics of the NBR composites with modified silica and without silica are compared and demonstrated in Figure 3 and Table 2. As the silane-treated silica is

Figure 3. Curing characteristics of (a) unfilled composite (1), (b) 1% silane-treated silica-filled composite (2), (c) 2% silane-treated silica-filled composite (3), (d) 3% silane-treated silica-filled composite (4).

Table 2. Curing characteristics of rubber compounds.

Curing characteristics	1	2	3	4
Torque, min.dNm	0.26	0.92	1.1	1.39
Torque, max.dNm	3.45	3.61	3.39	3.76
Delta torque	3.19	2.69	2.29	2.39
Cure time(t_{90}), min	29	29	32	30
Scorch time (t_{s1}), min	4.41	2.22	4.29	3.45
Cure rate index (CRI), min^{-1}	4.06	3.73	3.60	3.76

feasibly compatible with the rubber matrix, henceforth, the physical properties of the composites have eventually improved. The reinforcing nature of the silane-treated silica attributes to this enhanced torque values. It is seen from Figure 3 that the torque value for 1% and 3% silane-treated, silica-filled composites have increased compared to the unfilled composite (1). For 2% silane-treated silica-filled composite (3), the initial torque is observed to be greater, up to almost 30 min, than the unfilled composite. However, the torque value of 1 takes over that of the 3 by a slight margin later on. Composite 4 with 3% silane treatment show the highest torque, which is with fine accord with the cross-linking density value (Table 3). As far as cure kinetics is concerned, prolonged effect on scorch and cure time indicates some interference caused by filler on the curing. One

Table 3. Mechanical properties of nitrile rubber (NBR)/silica composites.

Compounds	1	2	3	4
$\sigma_{100\%}$, MPa	0.72	0.76	0.86	0.92
$\sigma_{200\%}$, MPa	0.89	0.91	1.07	1.27
Tensile strength, MPa	2.81	3.10	3.55	3.60
Elongation at break, %	731	706	627	517
Hardness, Shore A	40	41	42	45
Cross-link density, $\nu \times 10^5$	7.002	7.039	7.282	9.582

Figure 4. Scanning electron microscopy (SEM) images of (a) untreated silica particles and (b) modified silica particles (3% silane treated).

reason may be the surface silanol groups on silica surface could adsorb accelerators and affects the curing process.⁶ Also, steric hindrance offered by the bulky trimethoxy group on the silane-coupling agent may affect cross-linking.^{31,32} Cure kinetics can be interpreted in terms of cure rate index ($CRI = 100/t_{90} - t_{s1}$). Lower CRI values for the filled composites indicate prolonged effect on curing process and the effect is found to be the most pronounced for the composite 3 (with 2% silane-treated silica), though not much by margin with the rest of the composites. Same could be the reason for lowering of torque after 30 min for this composite 3 compared to unfilled composite as discussed before.

Morphology

SEM micrographs in Figure 4(a) and (b) show the morphology of unmodified and surface-modified stöber silica particles, respectively. Figure 4(a) shows relatively high aggregation of untreated silica due to the initial aggregation of silica particles during sol–gel process to form stable particles. Whereas silane-modified silica particles are found to be relatively well dispersed with low aggregation and with average particle size in the

Figure 5. Scanning electron microscopy (SEM) images of nitrile rubber (NBR) composite filled with (a) untreated silica, (b) 1% silane-treated silica (**2**), (c) 2% silane-treated silica (**3**), and (d) 3% silane-treated silica (**4**).

range of 300 to 200 nm. This is attributed to the surface treatment of silica by organosilane that decreases the surface energy of silica and lowers its aggregation and thus eventually leads to homogeneous dispersion of the silica particles.¹³ In both the figures, some particles in the nanometric range, with a diameter of less than 100 nm, are also noted.

SEM images of all the silane-treated, silica-filled NBR composites **2–4** are shown in Figure 5 along with the composite filled with untreated silica at the same filler loading. Figure 5(a) shows the silica morphology in NBR matrix (this mix is not shown in the table) where the NBR was filled with untreated stöber silica, that is, no silane treatment is done for this silica. A large cluster of silica aggregates is observed here that shows agglomerated nature of stöber silica in rubber matrix in the absence of a surface modifier. On the other hand, uniform dispersion of spherical silica into rubber matrix is evident in all the surface-modified silica composites **2–4** (Figure 5(b)–(d)). This is attributed to the surface modification of silica by grafting of silane-coupling agent viz. γ -MPS at its surface. This bifunctional silane-coupling agent bridges silica and rubber and hence increases their compatibility at the interface (Figure 1), leading to better filler dispersion in the rubber matrix.

Thermogravimetry

TGA of all the rubber composites (**1–4**) are shown in Figure 6. Silica content of all the filled composites are calculated (7 phr) from the residual weight percentage. The weight

Figure 6. Thermogravimetric analysis of (a) unfilled composite (1); (b) 1% silane-treated silica-filled composite (2); (c) 2% silane-treated silica-filled composite (3); (d) 3% silane-treated silica-filled composite (4).

loss appears at the temperature range of 350°C to 490°C, which is due to the degradation of the rubber. The next weight loss at the temperature range 560°C to 640°C is due to the decomposition of carbonaceous residue. Temperature at maximum weight loss ($T_{\max}$) is given by the peak in DTG curve. All the filled and unfilled composites show similar thermal behavior as onset temperature and $T_{\max}$ is found to be around 265°C and 445°C, respectively, for all the composites.

Mechanical properties

Stress-strain studies show that the moduli $\sigma_{100\%}$ and $\sigma_{200\%}$ are more for silane-treated, stöber silica composites (2-4) compared to that of unfilled composite (1) (Table 3 and Figure 7). Moreover, the values increase progressively with increase in silane content for the filled composites. Similar trend in tensile strength is also observed for treated composites.^{17,18} This is attributed to the increase in cross-linking density calculated by Flory-Rehner equation (Eqn. 1) that matches nicely with the above trend. This is in agreement with the better dispersion of silica in rubber matrix due to silane treatment of silica as discussed in the morphology section. However, elongation at break decreases for silane-treated silica composites as compared to unfilled composite. Hardness values of composites are found to increase with increase in silane proportion in the filled composites, which is in agreement with the stress-strain behavior discussed above.³³

Figure 7. Stress–strain curves of (a) unfilled composite (1), (b) 1% silane-treated silica-filled composite (2), (c) 2% silane treated silica-filled composite (3), (d) 3% silane-treated silica-filled composite (4).

Dynamic mechanical analysis

Dynamic mechanical analysis of rubber composites provides very significant information about rubber–filler interaction. In general, the movement of rubber chains increases with the increase in temperature. When the loss tangent ($\tan \delta$) of such process is plotted against temperature, a peak appears at a particular temperature that is commonly known as glass transition temperature (T_g). Figure 8(i) shows that $\tan \delta$ peaks of unfilled and all the silica-filled composites are comparable. However, a close view (in inset) reveals a small reduction in the peak height (T_g) for filled composites that may be due to the presence of reinforcing filler particles. A slight progressive positive shift of T_g is also noticed here for the filled composites as silane content in the composites increases. It is a well known fact that a strong rubber–filler interaction can restrict the movement of rubber chain that is reflected via the reduction in $\tan \delta$ peak and a shifting of the T_g toward the positive temperature. This observation is in accordance with the increase in cross-linking density and improved mechanical properties as discussed earlier.^{34–36} The higher storage modulus for silane-treated silica composites are observed when compared to unfilled composite (Figure 8(ii)). This also supports strong rubber–filler interactions in the filled composites. It is reported in literature that a joint shell network can be formed between rubber and filler in which rubber molecules are adsorbed or chemically linked on the filler surface. Moreover, stronger the interfacial interaction between polymer and filler

Figure 8. Temperature dependence of (i) $\tan \delta$ and (ii) storage modulus of (a) unfilled composite (1), (b) 1% silane-treated silica-filled composite (2), (c) 2% silane-treated silica-filled composite (3), and (d) 3% silane-treated silica-filled composite (4).

greater will be the reduction in the mobility of rubber chains.^{33,37} This contributes to higher values for storage modulus. In fact, this is what is observed for the composites with treated silica in the present study.

Conclusion

Stöber silica, modified with γ -MPS, is used as reinforcing filler for NBR to see its effect on the cure characteristics, morphology, thermal degradation, stress-strain behavior, and dynamical mechanical properties of the composite. Morphology study shows more uniform filler dispersion in all the composites filled with silane-treated silica. Stress-strain studies indicate improvement in mechanical properties for the silane-treated composites compared to the unfilled one. Further, for the silane-treated composites, there is increase in moduli and tensile strength with increase in silane content in the rubber composites. Better reinforcement for the silane-treated silica composites is attributed to improved rubber-filler interaction in these composites caused by surface modification of silica by silane treatment. This is also supported by the results obtained from the dynamic mechanical analysis studies. Present study shows that mercaptosilane can play a significant role in modifying the surface of stöber silica and hence increase its capability as reinforcing filler for NBR. At present, we are studying its effect on the in situ silica generation in the NBR.

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