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Short Communication

Preparation and Studies of Nitrile Rubber Nanocomposites with Silane Modified Silica Nanoparticles

Das Chayan and Kapgate Bharat P.
Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur, INDIA

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Abstract

Rubber silica nanocomposites are prepared by mixing nitrile rubber (NBR) with surface modified silica nano particles. Silica nano particles are synthesized by sol-gel method that involves hydrolysis followed by condensation of tetraethyl orthosilicate (TEOS). Surface modification of silica particles is done with the treatment of silane coupling agent viz. 3-mercaptopropyltrimethoxysilane. Presence of silane coupling agent in silica is revealed by IR studies. Thermogravimetric analysis is done to find out silica content in the composites and to study the thermal properties. Stress strain studies are found to be useful to assess the improvement of the mechanical properties of the composites.

Keywords: sol-gel, surface modification, rubber - silica nanocomposite.

Introduction

Synthesis of nano silica has gained much attention due to its superior properties and most widely being used as filler in rubber, paint, adhesive, functional fibre, plastic etc[1-4]. Stober and co-workers reported a simple synthesis process of spherical and monodispersed silica nanoparticles via sol-gel method[5]. The synthesis takes place in two steps viz. hydrolysis and condensation of silicon alkoxides in a mixture of alcohol and water[6]. Ammonia is used as a catalyst.
Hydrolysis: $Si–(OR)_4 + H_2O \rightarrow Si–(OH)_4 + 4R–OH$, Condensation: $2Si–(OH)_4 \rightarrow 2(Si–O–Si) + 4H_2O$

One of the important application of silica is it’s use as a filler in rubber matrix for reinforcement. Nano silica has more prominent reinforcing effect over commercial micro silica owing to it’s better dispersion capability in rubber matrix. However, they have tendency to form agglomerate due to high surface energy and ability to form inter particle hydrogen bonding via the hydroxyl (silanol) groups present on the surface[7-8]. This results in strong filler-filler interactions which is not favorable for effective reinforcement.

This problem can be overcome via surface modification of the silica particles. Silane coupling agents are the most used type of modifier agents[9-11]. Organo-modification of nanosilica surface with organosilanes can efficiently improve its compatibility with organic matrix and also increase the degree of dispersion. As a result, thermal and mechanical properties of the composite are improved.

In this work, the effect of surface modified silica on the thermal and mechanical properties of the nitrile rubber (NBR) has been studied. Silica nano particles are synthesized by sol-gel method followed by surface modification with the treatment of *γ*–mercptopropyltrimethoxysilane (γ-MPS). Silica rubber composites are then prepared by mixing the surface modified silica with nitrile rubber (NBR) along with other additives followed by vulcanization. Amount of γ-MPS is varied in composites 2 and 3 as 2% and 3% respectively. Composite 1 is prepared with unmodified silica particles i.e. γ-MPS is not used in this case. Thermogravimetric analysis and stress-strain studies are carried out for all three composites. Thermal and mechanical properties of composites 2 and 3 are compared with composite 1 to see the effect of surface modification of silica particles on the properties of the rubber composites.

Material and Methods

Acrylonitrile rubber (NBR) KNB-35L was used as a raw rubber. Tetraethyl orthosilicate (TEOS) 98% was purchased from Acros Organics. γ-MPS (*γ*–mercpto propyltri methoxysilane) 99% was purchased from Aldrich.THF and Ammonia were purchased from Merck. Toulene and Ethanol were purchased from Fischer Scientific. Sulfur, Zinc oxide (ZnO), Stearic acid, Mercaptobenzothiazoledisulfide (MBTS), and polyethylene glycol (PEG) were purchased from Sara Polymer Pvt. Ltd.

Preparation of silica nanoparticles by sol-gel method: Silica nanoparticles were synthesized by sol gel process by the reaction of ethanol (8 mole), water (3 mole) and TEOS (0.5 mole) as reported in literature[12]. 25% ammonia (0.08 mole) was used as catalyst. A thermal treatment at 150°C for 2 h was given to the silica particles to remove physisorbed water. Surface modification of the silica particles were carried out following a reported procedure by refluxing silica and *γ*–mercptopropyltrimethoxysilane (γ-MPS) in toluene at 110°C for 3h followed by washing and drying[13].

Preparation of rubber composite: On a two roll open mixing mill, silica and cross linking ingredients were mixed with rubber (Compounding formulation is given in table 1). Then vulcanization was done by heat pressing at 140°C for 10 min. in a mold to obtain rubber composites in the form of a thin sheet of thickness *ca.* 1 mm.

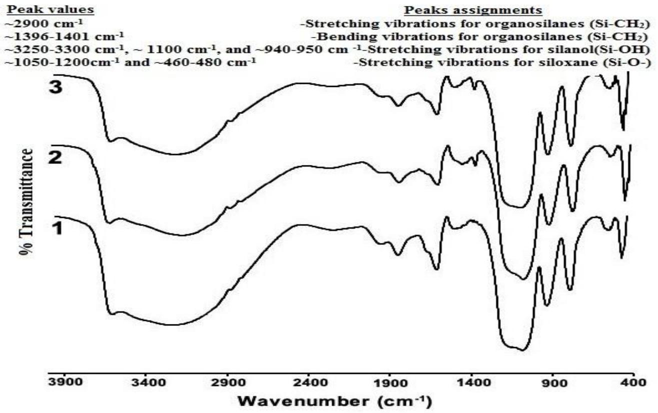
Table - 1
Compounding formula of rubber vulcanizates

Ingredients (phr)^a	**1**	**2**	**3**
NBR	100	100	100
Nanosilica	6	5	5
Silane coupling agent^b	0	2%	3%
Zinc oxide	4	4	4
Stearic acid	1	1	1
MBTS^c	1	1	1
Sulphur	1.5	1.5	1.5
Polyethylene glycol	0.5	0.5	0.5

Characterizations: FT-IR spectra of the silica nanoparticles were obtained using a Perkin- Elmer FT-IR spectrophotometer. Thermogravimetric analyses (TGA) were done using a Perkin Elmer Thermal Analyzer. The sample was placed in a alumina pan and heated in the temperature range 30-800^{0}C under air and the heating rate was 10^0 C/min. Tensile tests of cured samples were carried out using Zwick1456 (model 1456, Z010, Ulm Germany) with crosshead speed 200 mm/min (ISO 527).

Results and Discussion

FTIR: FTIR spectra of the silica nanoparticles are shown in figure - 1. Presence of silane coupling agent, γ-MPS is evident from the vibrational peaks around ~2900 cm^{-1} and 1400 cm^{-1}. These are the characteristic peaks for organosilanes that corresponds to the Si-CH$_2$ stretching and bending mode respectively[13]. The rest of the peaks are assigned to the silanol (~3450 cm^{-1}, ~ 1100 cm^{-1}, and ~950 cm $^{-1}$) and siloxane groups (~1200 cm^{-1} to 1100 cm^{-1} and ~467 cm^{-1}).



Peak values	**Peaks assignments**
~2900 cm^{-1}	-Stretching vibrations for organosilanes (Si-CH$_2$)
~1396-1401 cm^{-1}	-Bending vibrations for organosilanes (Si-CH$_2$)
~3250-3300 cm^{-1}, ~ 1100 cm^{-1}, and ~940-950 cm $^{-1}$	-Stretching vibrations for silanol(Si-OH)
~1050-1200cm^{-1} and ~460-480 cm^{-1}	-Stretching vibrations for siloxane (Si-O-)

Figure - 1
FT-IR Spectra of silica nanoparticles

Thermogravimetry: The results of thermogravimetric analysis of the rubber composites are given in Table- 2 and figure - 2. The amounts of combined silica in the composites are determined from residual weight percentage. Nature of the curve is similar for all the composites **1-3.** First weight loss observed at the temperature range 350^{0}C to 490^{0}C is due to degradation of the rubber component. The next weight loss at the temperature range 520^{0}C to 640^{0}C is due to the decomposition of carbonaceous residue[14]. The onset temperature of composites **2** and **3** containing surface modified silica increases little compared to that of **1**. The temperature at maximum weight loss (T$_{max}$) is determined from the peaks obtained in Derivative Thermogravimetry (DTG)[15]. It is observed that the value is higher for the composites containing surface modified silica particles indicating greater thermal stability for them over that of composite containing unmodified silica. The value of T$_{max}$ is highest for composite **2**.

Table - 2
Thermogravimetric analysis

Sample	**Silica content (phr)^a**	**Onset temp. (^{0}C)**	**Temp. at Max. Wt. loss. (^{0}C)**
1	**6**	**406**	**423**
2	**5**	**411**	**457**
3	**5**	**410**	**432**

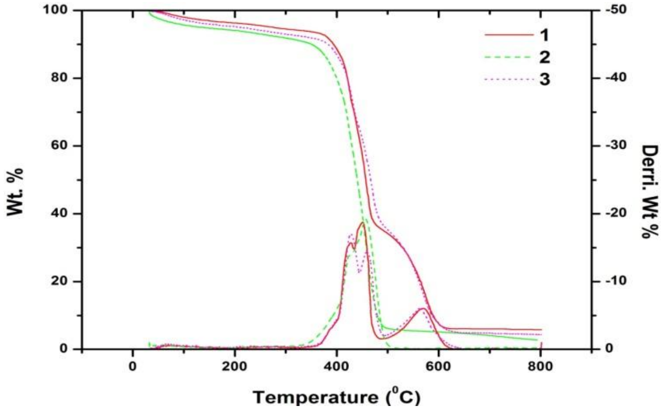


Figure - 2
Thermogravimetric analysis of rubber composites

Mechanical Properties: Mechanical properties of the composites 1-3 are tabulated in table 3. Hardness values are found to be around 45 and that is less for rubber composites containing modified silica. Stress-train studies shows that 50%, 100%, 200% and 300% modulus are comparable for both type of composites containing unmodified (1) and modified silica nano particles (2 and 3). But tensile strength values are higher for the surface modified silica rubber nano composites compared to that of unmodified silica rubber nano composite. Also, it is increased significantly from 2 to 3 with increase in silane coupling agent, γ-MPS. Elongation at break is also increased for composites 2 and 3 compared to that for 1. The value is more for composite 2 that contains lesser γ-MPS this time. This result is in accordance with the observation in the previous section where higher thermal stability of the composite **2** in comparison to the others was noted. These results suggest that better silica reinforcement in the rubber matrix has been achieved due to surface modification of silica nano particles with silane coupling agent, γ-MPS[16].

Table - 3
Mechanical properties of rubber composites

Mechanical Properties	**1**	**2**	**3**
$\sigma_{50\%}$ (MPa)	0.62	0.64	0.61
$\sigma_{100\%}$ (MPa)	0.81	0.78	0.79
$\sigma_{200\%}$ (MPa)	1.00	0.91	0.96
$\sigma_{300\%}$ (MPa)	1.17	1.04	1.12
Tensile Strength (MPa)	2.68	3.46	4.58
Elongation at break (%)	567	765	683
Hardness (Shore A)	46.0	41.0	43.9

Conclusion

Nitrile rubber - silica nanocomposites are prepared with surface modified silica nanoparticles and their thermal and mechanical properties are studied. Presence of silane coupling agents in silica nano particles is detected from FTIR studies. Improvement in mechanical properties is observed from Stress-strain studies. It shows higher tensile strength and elongation at break for the rubber composites containing surface modified silica particles compared to that containing silica particle without surface modification. This is in accordance with the thermogravimetric analysis where similar improvement in thermal stability is also observed. Hence, better reinforcement in the rubber matrix by using surface modified silica nanoparticles can be concluded. Further studies in this area are underway where some modification in synthetic technique will be taken care of and comparison of properties, including dynamic mechanical analysis, will be done with unfilled rubber composite.

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