Grafting Hydroxy-Terminated Polybutadiene onto Nanosilica Surface for Styrene Butadiene Rubber Compounds

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ABSTRACT: Hydroxy teminated polybutadiene (HTPB) was grafted onto the surface of nanosilica particles via toluene di-isocyanate (TDI) bridging to reduce filler–filler interactions and improve dispersion of nanosilica in rubber. Also, this prepolymer as modifier contains double bonds which participate in sulfur curing of styrene butadiene rubber (SBR) matrix to enhance filler/polymer interaction and reinforcement effects of silica. The reactions were characterized by titration and Fourier transforms infrared spectroscopy. Thermogravimetric analysis was utilized to evaluate the weight percentage of grafted TDI and HTPB. About 60% of the hydroxyl sites of silica were reacted with excess TDI in the first reaction. In the second reaction, HTPB as desired reactive coating was grafted on the functionalized nanosilica to constitute about 24 wt % of the final modified silica. The sedimentation experiments showed good suspension stability for the modified nanosilica in the organic media. Scanning electron microscopy revealed nanoscale dispersion of modified silica aggregates in the SBR matrix at concentration of about 14 phr. Also, vulcanization characteristics and mechanical properties of compounds demonstrated that HTPB grafting improved dispersion of nanosilica as well as its interaction to the rubber matrix as an efficient reinforcement. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4721–4728, 2012

Key words: surface modification; nanosilica; HTPB; SBR; reinforcement

INTRODUCTION

Application of nanosilica improves performance of rubber compounds.[1–4] This reinforcement requires good dispersion and strong interfacial bonding between two phases.[5–7] Silica particles bond to each other (filler–filler interactions) due to hydrogen bonding of hydroxyl groups on their surface.[8] Surface modification of silica particles improves filler dispersion by decreasing interaction between particles and increasing polymer–filler interactions. Moreover, it prevents adsorption of curatives to filler due to reduction of hydroxyl content of silica surface.[9] These hydroxyl functional groups undergo conventional organic reactions with multi functional molecules as coupling agents, *in situ* polymerization and grafting.[10–14] Grafted polymer chains onto inorganic surface of nanosilica improve steric hindrance and organic affinity of nano particles. Steric hindrance prevents aggregation of modified nano particles, and their organic affinity increases the ability to disperse in organic solvents and polymers.[15]

Many types of polymers have been grafted onto the surface of nanosilica by various techniques.[4,12,16–20] Many parameters affect the dispersion of the grafted silica in the rubber compounds. Among important parameters such as particle size, particle–polymer interactions and the molecular weight of the grafted polymers, polymer grafting density has the major effect. The activity of surface hydroxyl groups or their substituted groups determines the grafting density.[20] There are three types of hydroxyl groups on the surface of silica particles with different activities: isolated, vicinal, and geminal. Isolated hydroxyl groups are more reactive for grafting while hydrogen bonding deactivates two other kinds of hydroxyl groups.[8] These kinds of hydroxyl groups could be substituted by multifunctional active agents such as amino silane, scandium triflate, and organic isocyanate. After surface modification of nanosilica, the remained functional groups are active sites for subsequent polymer grafting.[15,19,21,22] Also, toluene 2,4-di-iso-cyanate (TDI) posses high reactivity with hydroxyls because of its highly unsaturated bonds. TDI has two isocyanate groups with different activities at para and ortho positions. Recently, several papers reported the utilization of TDI as a surface modifier of silica for subsequent grafting.[17,18,20–23]

Dubois et al. studied isocyanate modification effects and subsequent grafting of multi hydroxyl

molecules on fumed silica in polyurethane matrix by polymerization compounding.[17] Hydroxyl sites of nanosilica particles were modified by excess TDI. Then, the retained free isocyanate groups were reacted with either glycerin, bis-phenol-A (BA) or hydroxy-terminated polybutadiene (HTPB). This interfacial condensation process generated a reactive coating with active sites. In such a way, the coating of fumed silica particles was able to participate in the bulk polymerization process and chemically bond to the polyurethane matrix. They reported better bonding between filler and matrix by observing improved dynamic mechanical properties, higher elastic modulus and less moisture uptake with respect to unmodified silica. Che et al. indicated that dispersion properties of modified nano-silica is improved by the surface grafting of polyacetal (PAc) via bridging toluene 2,4-di-iso-cyanate (TDI). The grafting percentage was much higher than direct grafting of PAc.[20] Yang et al. prepared polyamide 6-silica nano composites in a two-step process. At first, acyl caprolactam initiator was formed by addition of ε-caprolactam to isocyanate groups of modified silica. Then, ε-caprolactam was polymerized in the presence of sodium caprolactamate catalyst as in situ ring opening anionic polymerization. Additionally, it was found that polymer-functionalized silica was finely dispersed in the polyamide 6 matrix with aggregate sizes in the range of 20–40 nm. Zhao et al. prepared isocyanate modified silica particles by using hydroxy-terminated poly(ethylene oxide) of various molecular weights. The product was used to manufacture reproducible and reliable substrates for oligo-nucleotide synthesis in DNA micro array-based assays.[21] Also, Zhang and Lee investigated the grafting of polyethylene glycol onto the modified surface of nano-silica. They used toluene as solvent, 1,4-phenylene diisocyanate (PPDI) as reactant, and dibutyltion dilaurate (DBTDL) as catalyst. As a one-step process, PPDI reacted with silica at first. Then, PEG was grafted onto isocyanate modified surface of nanosilica as the second reaction. They studied the effects of reaction time, temperature, and molar ratio of reactant on the grafting process. Also, they obtained optimum grafting of PEG conditions. They determined maximum grafting of PEG and maximum overall grafting as 22.6 and 35%, repectively.[22]

In the current article, HTPB was grafted on the surface of nanosilica via bridging TDI. Oligomers of polybutadiene coat the surface of nanoparticles with a thin film of prepolymers. This coating on the nanosilica particles could participate in rubber vulcanization via double bonds on HTPB backbone. The effect of this surface treatment on improvement of filler dispersion and reinforcement in a SBR compound was investigated. This modification method is prom-

ising in dispersion of fumed nanosilica in rubber compounds.

EXPERIMENTAL

Materials

The hydrophilic fumed silica (Aerosil 200) was purchased from Degussa AG, Germany with an average primary particle size of 12 nm and a specific surface area of 200 ± 25 m^2 g^{-1} (N2, BET). The hydroxyl group concentration was around 4.3 OH/nm^2.[8] The nano particles were dried at 200°C under vacuum for 24 h. Hydroxyl terminated polybutediene prepolymers (HTPB) have been prepared by H$_2$O$_2$ initiated free radical polymerization of 1,3-butadiene in 2-propanol-water solvent system. The synthesized HTPB was characterized with functionality of 2.6, number average molecular weight of 2800 g mol^{-1} and poly dispersity index of 3.1. It was dried before usage at 50°C under vacuum for 48 h.[24] Toluene diisocyanate (TDI, Enichem, Italy) was an 80 : 20 mixture of 2,4 and 2,6 isomers and it was used as received. Toluene (Merck, Germany) was dried with sodium and distillation method. Dibutyltin dilaurate (DBTDL, Merck, Germany) was used as received. Styrene–butadiene rubber (SBR-1502) was obtained from Bandar-Imam Petrochemical Company (BIPC) of Iran. In this study, it is used as a rubber matrix with styrene content of 23.5%, specific gravity of 0.945, and Moony viscosity (ML4) of 84 at 100°C. The chemical structure of butadiene in SBR-1502 co-polymer consists of 55% trans-1,4, 9.5% cis-1,4, and 12% 1,2-butadiene with 176,000 g mol^{-1} as number average molecular weight.

Preparation and characterization

TDI substitution onto nanosilica Surface (SiO$_2$-TDI)

The main step of this study was isocyanate substitution on the surface of nanosilica as an interfacial condensation process. For this purpose, 5 g of dried nanosilica (7.14 mmol of hydroxyl group) was sonicated in 250 cm^3 anhydrous toluene as a solvent for 10 min at room temperature. Then, 12.44 g of TDI (71.4 mmol) was added at 60°C with 100 ppm of DBTDL as a catalyst. TDI was reacted with hydroxyl groups of nanosilica surface in a glass reactor during 12 h at 60°C under the protection of dry nitrogen atmosphere and stirring. The concentration of TDI was calculated so that the NCO/OH ratio is 10. The excess TDI was used to assure reaction of one TDI molecule with only one silica particle. This will promote preferred reactions for the isocyanate groups at para-positions rather than ortho positions due to the steric hindrance. This will prevent agglomeration of

TABLE I
The Values of TDI Modification and HTPB Grafting

No.	Ingredients	Content (wt %)
1	SiO$_2$ (Aerosil 200)	76.5
2	HTPB	10.93
3	TDI	12.57

silica particles by simultaneous reaction of both NCOs (orto and para) with the silica hydroxyl sites of adjacent particles. Also, variation of excess TDI ratio did not affect the amounts of reacted TDI with nanosilica.[20] After the reaction, the excess isocyanate was removed by liquid–liquid extraction via anhydrous toluene and several sequential centrifugation. Each step of centrifugation was performed for 25 min to remove all unreacted and physically adsorbed TDI or DBTDL. The slurry was dried in vacuum at 50°C for 48 h and the final product was marked as SiO$_2$-TDI.

HTPB grafting onto SiO$_2$-TDI

TDI functionalized nanosilica was sonicated in anhydrous toluene for 5 min at concentration of about 20 g L^{-1} under dry nitrogen atmosphere to prevent side reaction with moisture. Ultrasonic oscillations were applied by Hielscher UIP 1000hd (Germany). Subsequently, diluted and dried HTPB with toluene was added in a glass reactor in stochiometric amount. TDI–HTPB grafting reaction was started by addition of 100 ppm DBTDL to reaction mixture and held at 70°C for 12 h. Then, the particles were washed by anhydrous toluene for several times to remove all unreacted and adsorbed DBTDL or HTPB from the surface of the particles. They were separated by centrifugation via Heraeus centrifuge model Varifuge RF (Germany) at 6000 rpm ($\approx$ 8050g) for 30 min. After being dried at 70°C under vacuum for 6 h, HTPB-grafted nanosilica was obtained and marked as SiO$_2$-TDI-HTPB. The results of TDI modification and HTPB grafting values are reported in Table I. Figure 1 shows the basic scheme of the TDI functionalization and HTPB grafting on the surface of nanosilica.

Rubber compounding

The samples were composed of SBR-1502 compounded with neat and HTPB-grafted nanosilica. Also, unfilled compound of similar composition (i.e., without nanosilica) was used as the reference compound. Table II shows the rubber compound formulation used in this study. Ingredients of the rubber compounds were mixed on a Collin two-roll laboratory mill of 150 mm diameter, 350 mm length, speed of 24 rpm, and speed ratio of 1.4 according to ASTM

D 3182. The sheeted compound was conditioned at 25°C ± 2°C for 24 h in a closed container before the determination of the optimum cure time at 150°C. The compounds were compression molded in Collin hot press at 150°C and 30 MPa for t_{90}+4 min (optimum vulcanization time + mold temperature stabilization time) with 2 mm thickness. The dumbbell specimens cut from these sheets and they were used for tensile testing.

Characterization of the modified nanosilica

Determination of isocyanate groups of the reaction system

Isocyanate modification of silica was evaluated by back titration and thermogravimetric analysis (TGA). According to procedure of ASTM D 2572–97, back titration was used to determine the content of isocyanate groups in the product of the TDI-nanosilica reaction.[20] For this purpose, 20 mL of purified SiO$_2$-TDI suspension and 10 mL of 0.1 mol L^{-1} di-n-butylamine in toluene were loaded into a flask. They were mixed at room temperature for 1 h. The unreacted di-n-butylamine was back titrated with 0.1 mol L^{-1} HCl. The end of titration was controlled by bromphenol blue as pH indicator. The content of isocyanate groups was calculated by the following equation:

$$\text{NCO \%} = \frac{[(B - V) \times N \times 0.042]}{W} \times 100 \qquad (1)$$

where B (mL) is volume of 0.1 mol L^{-1} HCl for titration of the blank, V (mL) volume of 0.1 mol L^{-1} HCl for titration of the specimen, N normality of HCl, 0.0420 milli-equivalent weight of the NCO group, and w specimen weight in grams.

Determination of the grafting percentage

The HTPB grafting on silica were characterized by Fourier transform infrared spectroscopy (FTIR) using a Bruker Equinox55 (Germany) at frequency range from 500 to 4000 cm^{-1} with a 0.5 cm^{-1} resolution on a KBr pellet technique. Thermogravimetric analysis (TGA) was performed using a PL Thermal science (UK) PL-STA at scan rates of 10°C min^{-1} and the amount of grafted HTPB-TDI was characterized by the measured weight loss from 25 to 700°C of 5–20 mg of samples in air. Also, these results provide the isocyanate grafted density. The polymer-grafted percentage on silica was calculated according to the following eq. (2)[20]:

$$\text{Grafting(\%)} = \frac{\text{Polymer grafted (g)}}{\text{Silica charged (g)}} \times 100\% \qquad (2)$$
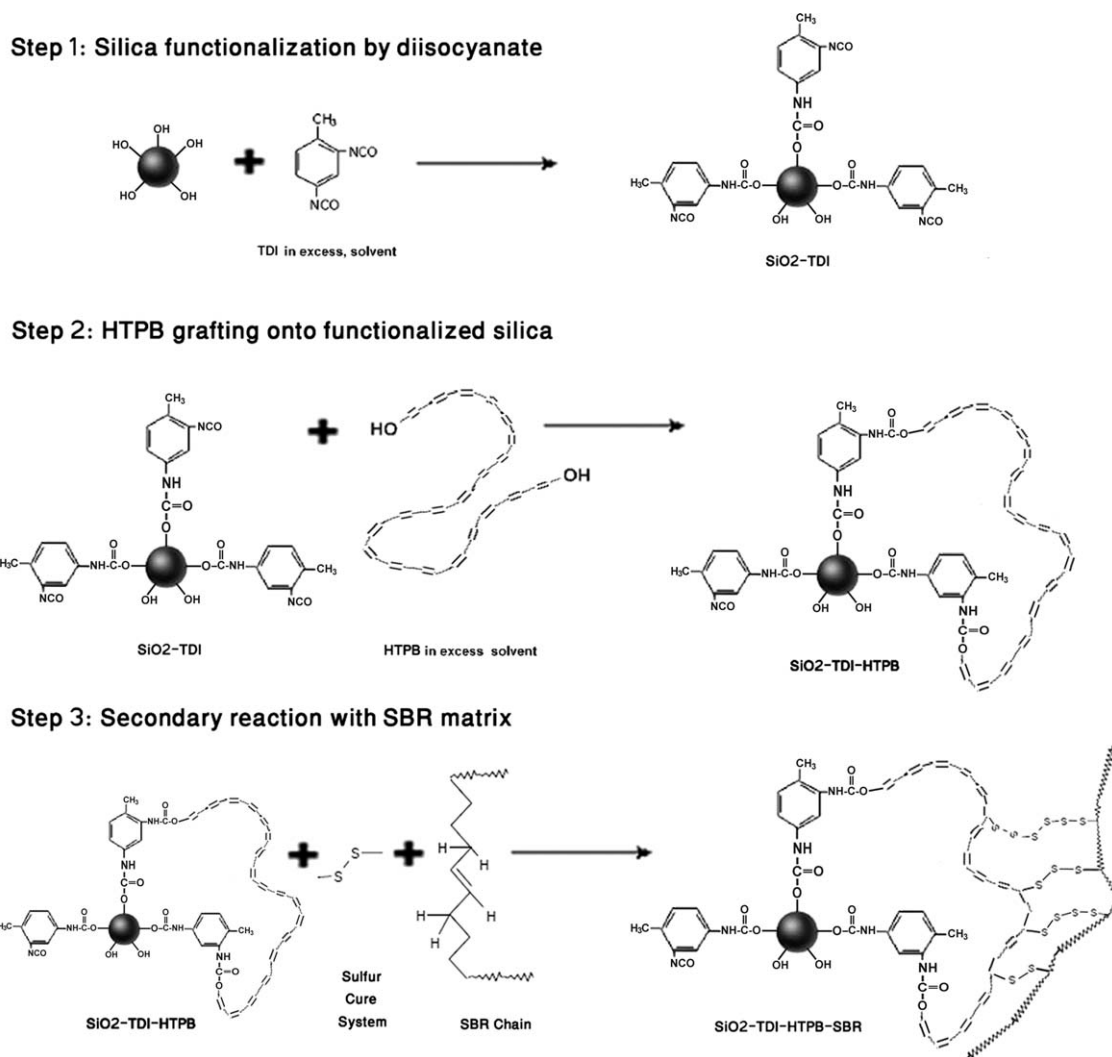
Figure 1 Schematic illustration for TDI modification and HTPB grafting onto nanosilica and sulfur curing of grafted HTPB.

Vulcanization, morphological, and mechanical properties

Vulcanization characteristics were registered at vulcanization temperatures of 150°C in test conditions (1.667 Hz, ±1.5 deg arc strain amplitude) by using Moving Die Rheometer (Hiwa900 MDR). For each Compound, three samples were analyzed.

To characterize dispersion of silica in rubber matrix, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were carried out by using a Philips XL30 electron microscope (Netherlands) operating at an acceleration voltage of 30 kV on fractured surfaces of SBR cured compounds.

Stress–strain properties of all samples were evaluated by a universal testing machine (Hiwa200). Tensile tests of the samples were carried out with a crosshead speed of 500 mm min^{-1} at 20°C according to ASTM D638. Three samples were tested for each compound and values of time, force, crosshead position and extension were saved each 0.03 s in all tests.

RESULTS AND DISCUSSIONS

Characterization of reactions by FTIR

The FTIR spectrums of pristine nanosilica, TDI modified nanosilica, and HTPB-grafted nanosilica

TABLE II
SBR Compound Formulation

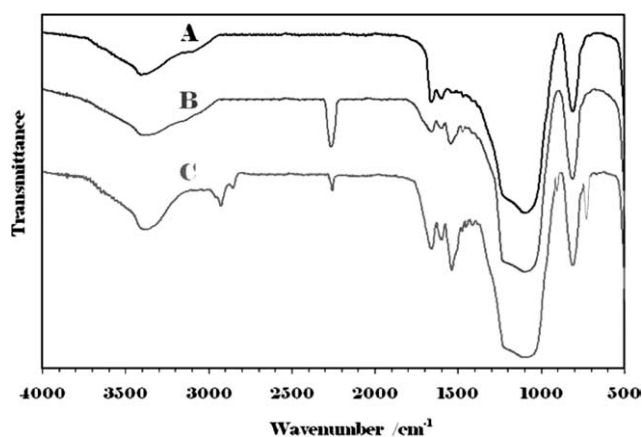| No.	Ingredients (phr)	Typical formulation	Neat nanosilica formulation	HTPB grafted nanosilica formulation
1	SBR 1502	100	100	100
2	Zinc oxide	3	3	3
3	Stearic acid	1	1	1
4	Sulfur	1.8	1.8	1.8
5	TBBS	1.2	1.2	1.2
6	TMTD	0.1	0.1	0.1
7	Aerosil 200	0	14	14
8	TDI	0	0	2.3
9	HTPB	0	0	2

Figure 2 FTIR spectra of: (A) nano silica, (B) TDI modified nanosilica, and (C) HTPB grafted nanosilica.

are shown in Figure 2. In this figure, Spectrum A represents unmodified nanosilica.[20] Significant absorbance of Si—O—Si stretch can be observed at 1099 cm^{-1}, and the absorbencies at 1550–1650 and 3434 cm^{-1} can be attributed to the surface hydroxyl groups of silica. The spectrum of SiO_2-TDI presents some new peaks because of isocyanate functionalities on the surface of the silica. The clear and strong absorption at 2278 cm^{-1} was related to asymmetric stretching of the active terminal isocyanate functionalities at the FTIR spectrum B. Additionally, the aromatic C—C stretch was observed for the backbone of benzene at 1614 and 1455 cm^{-1}. The absorptions at 1646 and 1555 cm^{-1} can be assigned to the C=O and C—N stretches of the generated carbamate linkages between the reacted isocyanate groups and hydroxyl groups of nanosilica. These evidences confirmed that a fraction of isocyanate groups reacted with some hydroxyls on the surface of nanosilica and other parts of the isocyanate groups were remained active. For SiO_2-TDI-HTPB, the stretching vibrations of the C=O and C—N stretches for more
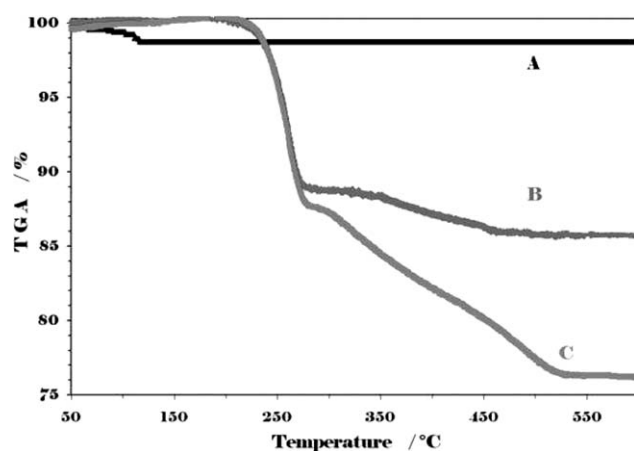
generated carbamate linkages at 1646 and 1555 cm^{-1} were enhanced by reaction between the remained isocyanate groups and hydroxyl groups of HTPB. Meanwhile, the absorption at 2278 cm^{-1} decreased due to the reaction of reserved isocyanate groups with hydroxyl groups of HTPB. However, it was not disappeared completely, since some isocyanate groups are remained because of HTPB coverage. Also, C=C double bond of HTPB backbone was intensified absorption at 1640–1680 cm^{-1} which will participate in sulfur vulcanization system. The above results verified that the surface of nanosilica was grafted with HTPB via TDI.

Characterization of modified silica by TGA

Thermogravimetry analysis (TGA) was used to evaluate weight percentage of substituted TDI and grafted HTPB on nanosilica. Figure 3 shows TGA curves for the analysis of neat nanosilica, TDI functionalized nanosilica, and HTPB-grafted nanosilica at a temperature rate of 10°C min^{-1}, respectively. The pristine nanosilica indicates a gradual weight loss around 100°C about 2.5 wt % due to loss of the adsorbed water, and hardly any weight loss can be observed in the temperature 100–600°C.

SiO_2-TDI depicts two stages of weight loss, a distinct mass loss at region 230–310°C and a second gradual step at 310–440°C. The total weight loss was about 16% based on the weight retention of the residue at 600°C as the reference. Therefore, the isocyanate grafted density was equal to 0.84 mmol per gram neat silica, and it did not change with the TDI/nanosilica mass ratio. Also, the back titration experiment supported the observed TGA results for SiO_2-TDI by the measured functional groups around 0.86 mmol per gram neat silica. The TGA curve of SiO_2-TDI-HTPB also had two stages of weight loss about 12.5 wt % at 230–290°C and about 11 wt % at

Figure 3 Thermogravimetric analysis data for: (A) Nanosilica, (B) SiO_2-TDI, (C) SiO_2-TDI-HTPB at a ramp of 10°C min^{-1}.
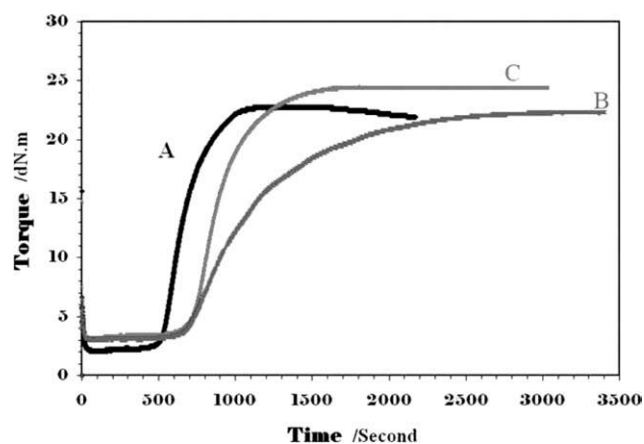

Figure 4 Vulcanization characteristic curves at 150°C for: (A) gum reference compound, (B) 7 phr neat nanosilica, and C) 7 phr HTPB grafted nanosilica.

No.	Filler (phr)	Minimum torque (dN m^{-1})	Maximum torque (dN m^{-1})	Scorch time ts_2 (s)	Optimum cure time t_{90} (s)	Cure rate index (90%TI, 2 dN m^{-1})
A	No filler	2.069	22.761	539.162	883.750	17.891
B	Neat nanosilica (14 phr)	3.062	22.141	713.005	1977.744	17.575
C	HTPB grafted nanosilica (14 phr)	3.235	24.555	719.654	1217.172	5.332

the second step 290–530°C. The total weight loss was 23.5 wt %. However, the weight loss of the first stage was larger than that of SiO$_2$-TDI, and it can be attributed to the simultaneous decomposition of HTPB and TDI. HTPB has a long flexible chain and both of its ends can easily attach on the substituted TDI molecules on nanosilica particles. A previously grafted HTPB chain prevents other HTPB chains from grafting to free remained isocyanate sites around nanosilica particles. This TGA result is in good agreement with related FTIR analysis showing coverage of nano-silica by HTPB molecules.
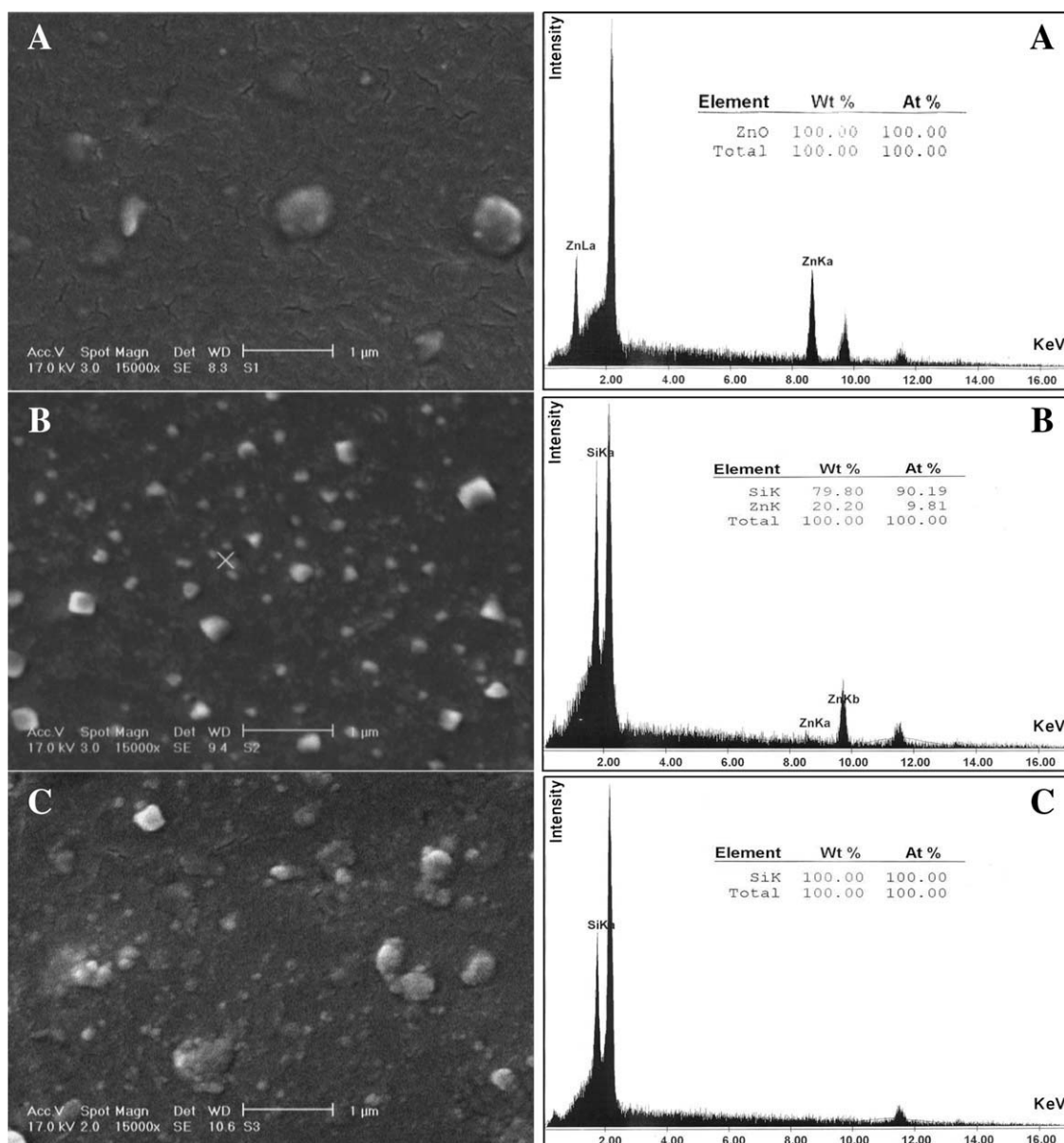

Figure 5 SEM and EDX of cryogenically fractured vulcanizates (A) S1: gum vulcanizate, (B) S2: 14 phr neat nanosilica and (C) S3: 14 phr HTPB-grafted nanosilica.
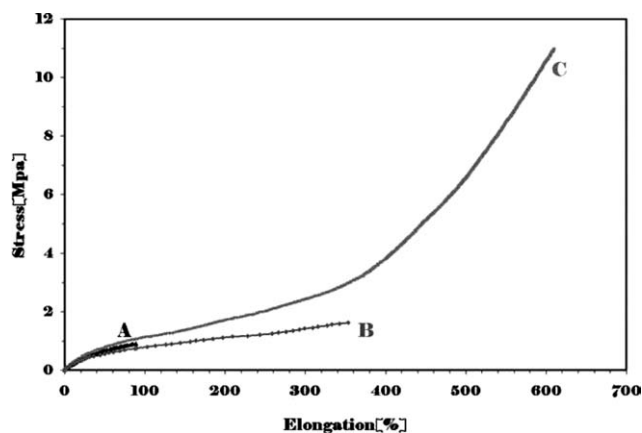
Figure 6 Mechanical properties for SBR compounds (A) gum reference vulcanizate, (B) 14 phr neat nanosilica, and (C) 14 phr HTPB grafted nano silica.

Visual observation of suspensions

A transparent strong gel was formed when 25 g L^{-1} neat nanosilica was dispersed in toluene and sonicated for 5 min by ultrasonic homogenizer. Disperse ability seems good, and transparency shows the formation of nanosize agglomerates of silica assigned to no diffraction by structures smaller than 380 nm (the wave length of visible light). Nevertheless, the small agglomerates sediment completely after 30 min, leading to disappearance of transparency. Stability of dispersion for TDI-modified and HTPB-grafted nanosilica was greatly enhanced in toluene, and no considerable sedimentation was found after 2 weeks.

On the other hand, the viscosity of neat nanosilica suspension was decreased significantly from a viscous gel to a liquid solution after TDI modification and HTPB grafting. This can be explained by less particle–particle interactions as a result of surface modification. The grafted HTPB chains would cause a stable hindrance layer between nanosilica particles. Also, it prevents from agglomeration of grafted silica in organic media such as toluene and possibly polymeric matrix.

Vulcanization characteristics

Vulcanization characteristics are shown in Figure 4 for SBR compounds with no silica, unmodified, and modified nanosilica. Minimum torque (M_l) increased by addition of silica fillers for both Compounds B and C as expected. Maximum torque (M_h) for HTPB-grafted nanosilica is larger than unmodified one. It may be related to strong bonds between SBR matrix and HTPB surface modifier during their covulcanization.

It is important to note considerable decrease in vulcanization rate of the compound containing unmodified silica (B). This has been attributed to

acidity of unmodified silica surface as a result of presence of hydroxyl groups. They absorb accelerators and reduce vulcanization rate.[25] In the presence of HTPB-grafted nanosilica, vulcanization rate is similar to that of gum rubber compound as shown in Figure 4 and Table III. Therefore, the adverse effect of silica was eliminated by HTPB grafting. $M_h - M_l$ is a measure of hydrodynamic effect of filler as well as crosslink density of rubber. The value of $M_h - M_l$ for the compound containing unmodified silica (B) is less than that of gum rubber compound (A). It might be due to lower crosslink density of compound B as a result of adverse effect of silica on vulcanization. On the other hand, the value of $M_h - M_l$ for the compound containing HTPB-grafted nanosilica (C) is more than that of Compounds (A) and (B). Hence, cross-link density of rubber compound was increased due to surface modification of silica.

SEM and EDX study of fractured surfaces of vulcanized samples

SEM and EDX analysis were obtained to investigate the effect of HTPB grafting on the dispersion of nanosilica. Figure 5(a) shows SEM image of the reference gum vulcanizate in which dispersion of large zinc oxide particles of size 150–700 nm in vulcanized gum SBR is clear. Figure 5(a) is the local EDX analysis which confirms large particles as zinc oxide. Figure 5(b) demonstrates dispersion of zinc oxide and unmodified nanosilica. The decrease in size of zinc oxide particles might be due to increase in compound viscosity by the application of higher filler content in comparison to the gum SBR. Figure 5(b) is the overall EDX analysis of the second sample. Figure 5(c) demonstrates the dispersion of the HTPB-grafted nanosilica and zinc oxide particles in vulcanized SBR compounds. It displays that HTPB-grafted nanosilica aggregates have smaller size (<150 nm) than unmodified nanosilica (130–450 nm) in the second sample. All of the large aggregates observed on the micrographs were detected as zinc oxide by several local EDX analyses such as shown in Figure 5(a). Several local EDX analyses were also carried out on the smaller size fillers, and they were confirmed to be nanosilica, as shown in Figure 5(c). Consequently, the HTPB-grafted nanosilica aggregates have been homogeneously distributed and dispersed with no reagglomeration.

Mechanical properties in uniaxial tension

Mechanical properties of SBR compounds are presented in Figure 6 and Table IV. The elongation at break improved from 88.76% for the reference gum compound to 353.59% by the application of the unmodified nanosilica. There is no considerable

TABLE IV
Tensile Mechanical Properties of SBR Compound

No.	Ingredients (phr)	Typical formulation	Neat nanosilica formulation	HTPB grafted nanosilica formulation
1	Tensile strength (Mpa)	0.91 [0.05]	1.63 [0.09]	10.98 [1.03]
2	Maximum force (N)	12.53 [0.70]	22.47 [1.28]	132.26 [12.33]
3	Elongation at TS (%)	88.76 [6.69]	353.59 [38.11]	609.95 [32.39]
4	Stress at 100% (Mpa)	0.00 [0.00]	0.79 [0.01]	1.13 [0.01]
5	Stress at 300% (Mpa)	0.00 [0.00]	1.42 [0.11]	2.44 [0.13]
6	Strain energy (mJ mm^{-3})	0.51 [0.03]	3.60 [0.26]	21.91 [1.35]

The values in the brackets represent standard deviation from average.

enhancement in tensile strength. HTPB-grafted nanosilica increased elongation at break from 88.76 to 609.95% and tensile strength from 0.91 to 10.98 MPa. According to Table IV, energy at break for SBR compound containing HTPB-grafted nanosilica was intensified about 42.96 times higher than SBR gum. This is an important criterion for reinforcement. Also, the breaking energy for the vulcanizate containing HTPB-grafted nanosilica was amplified about seven times more than the one with unmodified nanosilica. Furthermore, strong hardening effect appears in the sample with HTPB-grafted nanosilica. This is an indication of large amount of occluded rubber as a result of proper bonding of rubber to silica aggregates.[26]

CONCLUSIONS

A two-step process was successfully performed to modify fumed nanosilica surface by TDI-HTPB grafting as a reactive coating, and reactions were characterized by different techniques. With application of excess TDI in the first step, some isocyanate groups reacted with the hydroxyls on the nanosilica surface and unreacted isocyanate groups were reserved to react with HTPB in the second step. The active isocyanate groups of the substituted TDI work as bridges for interfacial condensation reactions with HTPB. Occurrence of reactions and presence of reaction products were confirmed by FTIR, back titration, and TGA methods. This modified nanosilica showed better dispersion when incorporated into SBR matrix compared than unmodified one. The dispersion is improved by the elimination of hydroxyl groups and reduction of filler–filler interactions. The enhancement in filler–rubber interactions by using HTPB-grafted nanosilica led to drastic increase in mechanical strength of SBR compounds. This is possible due to participation of HTPB double bonds in sulfur vulcanization of SBR matrix and formation of chemical linkages.

In addition, surface modification eliminated the negative effect of silica acidity in reducing the vulcanization rate of rubber compounds. This modification technique seems promising in reducing the size of fumed silica aggregates to nanometric scales and improving rubber compound dynamic properties, which will be discussed in future works.

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