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Surface functionalization of rubber latex nanoparticles with sulfidosilane moieties

Mahnaz Shahzamani, Rouhollah Bagheri, Mahmood Masoomi
Chemical Engineering Department, Isfahan University of Technology, Isfahan, Iran
Correspondence to: R. Bagheri (E-mail: Bagheri@cc.iut.ac.ir)

ABSTRACT: Polybutadiene latex particles were functionalized with bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT) in the presence of zinc oxide as an activator and ethanol as a co-solvent. The success of this reaction was confirmed both by the peaks attributed to Si-O groups at 1085 and 1110 cm^{-1} and C-S bond at 630 cm^{-1} which appeared after reaction in Attenuated Fourier Transform Infrared (ATR-FTIR) Spectra and also by increasing in the particle size diameter of latex particles (from 95 to 127 nm) in Dynamic Light Scattering analysis. X-ray Diffraction results also showed changes in crystalline structure of the modified particles (as a strong decrease in the intensity of peak at $2\theta=19.54$). The effect of reactant concentration in a constant amount of TESPT (by varying the water and ethanol content), reaction time, activator size (micro and nanoparticles), and pH (≈ 7, 8.5) were investigated on degree of grafting (obtained from thermogravimetric analysis and ATR-FTIR spectra), particle size diameter, cross-link density, and swelling ratio of the samples. The amounts of silane grafting and cross-link density of polymer particles were increased by an increase in the reaction time. The highest grafting degree was observed at low concentration of TESPT. Silane functionalization was also improved in a slight basic condition (pH=8.5) rather than neutral pH. The grafting reaction took place such as sulfur pre-vulcanization and the possible mechanism of this reaction was discussed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43268.

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INTRODUCTION

The modification of polymer latex particles with functional groups has received much attention in colloidal polymer science because of their potential to produce novel functional materials and applications in different industrial fields including coatings, adhesives and so forth. The interesting properties of these polymer latexes are dependent on the presence of surface chemical groups. These chemical groups can be so various including amino, hydroxyl, carboxyl, silane, etc.[1–4]

Modification of rubber materials with different functional monomers has also gained significant interest to use in *in situ* sol-gel hybrid nanocomposites[5–8] over the last years. This treatment improves the interaction between rubber and inorganic materials specially silica. It was found that grafting of SBR and natural rubber (NR) by vinyl[9] and methyl methacrylate monomers,[10]resulted in better dispersion of silica in rubber. Moreover, silica in epoxidized NR grafted by 3-aminopropyltriethoxysilane[11] was chemically bound to rubber network. Rubber fuctionalization can be carried out in latex, solution, or solid phase, but in spite of a large number of researches in this area, there are a few studies on silane functionalization of rubber latex in aqueous media.[5,7,8]

Similar surface properties of silane functionalized latexes with silica particles make them convenient to use in organic-inorganic hybrid materials.[2–4,12] Silane modification of polymer latex particles can be done in two ways, one by direct polymerization or copolymerization of functional co-monomer and the other by postpolymerization modification. Organotrialkoxysilanes have been used to modify the polymer latexes in emulsion polymerization. The incorporation of silanol groups on polystyrene latex particles[3,13,14] to synthesize core-shell hybrid materials[1,2,12,13, 15–17] and silica hollow microspheres have been reported in literature. Moreover, Silane functionalization of rubber latexes has also been carried out by graft polymerization.[5,7,8] It has been reported that silane modified particles would improve the mechanical properties in an organic-inorganic hybrid nanocomposite compare with original latex, because of the strong covalent bonding.[5,7,8]

Polybutadienes rather than other polymers are more suitable for postpolymerization reaction because of the terminal and

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internal double bond of each repeat unit. Combination of various microstructures including 1,4 cis, 1,4 trans, and 1,2 vinyl in this material caused to appear different crystalline behavior and thermal properties.[18] The most industrially chemical modification of preformed latex particle is sulfur prevulcanization that is commonly used for NR latex.[19,20] It can also be applied for other types of synthetic diene rubber latex. In this process, it is possible to vulcanize individual latex particles by heating with sulfur and organic vulcanization accelerators without decreasing the stability of the polymer colloid.[21]

In the current work, it is interested in silane-functionalized polybutadiene for using it in nanostructured organic-inorganic composites, such as aerogels. Aerogels are highly porous nanostructured materials with high surface area. These extremely light materials are good candidate for thermal and acoustic insulators, heat storage devices, catalyst supports, and adsorbent for environmental clean-up. However, the three-dimensional network of silica aerogels indicated very low compression strength.[22,23] Organic components are generally used to enhance their mechanical properties.[1] Modified polybutadiene nanoparticles can be covalently attached to the porous structure of silica aerogel during the synthesis, enhancing properties.

In the present study, the modification of polybutadiene latex (PBL) particles with sulfidosilane moieties in a process like sulfur pre-vulcanization of rubber latexes is described. To the best of our knowledge, for the first time Evans *et al.* patented this method for modification of unsaturated rubbers especially for Styrene-butadiene rubber.[24] Here, in this novel approach triethoxysilyl groups incorporated on the surface of PBL particles through sulfur bond attachment. In the following, Bis[3-(triethoxysilyl) propy] tetrasulfide (TESPT) used as a functional material covalently bonds to polymer chain and zinc oxide as an activator helps to carry out this reaction. This chemical reaction was confirmed by ATR-FTIR spectroscopy, elemental analysis, and X-ray diffraction (XRD) method. Then, the effect of medium composition (water and ethanol content), reaction time, activator particle size and its content on chemical grafting was studied.

EXPERIMENTAL

Materials

PBL used in this work (~40 wt % solid cont., particle size: 90 nm, pH=8.5) was supplied from a Petrochemical Company, Iran. Silane coupling agent namely, bis[3-(triethoxysilyl) propy] tetrasulfide (TESPT, Si69) was received as a gift from Evonik Degussa Company, Belgium. Micronized Zinc oxide (ZnO) and stearic acid both were of commercial grade. Nano zinc oxide (99%, 10–30 nm) was provided from US research nanomaterials, USA. Deionized water and absolute ethanol were used in this work.

Synthesis of Silane Functionalized Particles

PBL particles having triethoxysilane moieties were prepared using 0.11 molar ratio of silane groups per total amount of double bonds [$(2\times[\text{TESPT}]/[\text{C=C}])=0.11$]. Table I shows the formulation of ingredients used for this modification and the preparation conditions are presented in Table II. First series of experiments (from 1 to 6 in table II) were carried out in 3 different concentrations of TESPT in Ethanol (50, 33, and 20 wt %) at two concentrations of polymer in water (18.2 and 11.2 wt %) using constant amount of TESPT and microparticles of zinc oxide (5 phr). Second series of experiments (7–9) were took place in various amounts of nano zinc oxide (1, 2, 3 phr) to evaluate the effect of this activator on the reaction. In all of the above experiments, the reaction carried out at the pH of 8.5. To show the effect of pH, one sample (10 in Table II) was prepared at pH=7 in the same condition. The pH of the mixture was adjusted to 7 by adding equivalent quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate (0.2 g of each per 100 g of water).

Table I. The Basic formulation Used for Chemical Modification of Polybutadiene Latex Particle

Ingredients	Dry content (Phr)
Polybutadiene	100
TESPT	54.1
ZnO microparticle (or nanoparticle)	5 (or 1,2,3)
Stearic acid	1
Water	variable
Ethanol	variable

The following procedure was used to prepare the samples. PBL and TESPT were diluted with various amounts of deionized water and ethanol, respectively (according to table II). Zinc oxide particles (micro and nano) were emulsified in aqueous alcoholic media to obtain 50 wt % concentration in water–ethanol mixture as follows: polyethyleneglycol (Mw=20,000 g/mol) as a dispersing agent was first added to water (0.1 g per 100 g water), then ethanol was added to get water to ethanol ratio of 3:1. After 10 min stirring, zinc oxide particles gradually were dispersed in it. Mixing was continued until the mixture was fully homogenized. The dispersed nanoparticles of zinc oxide were also sonicated by Hielscher sonicator (UP400S model) for 20 min followed by 30 min more stirring before addition to the latex mixture. Then, PBL, zinc oxide dispersion, and stearic acid were charged into a 250 mL 3-necked round bottom flask equipped with a reflux container and a magnetic stirrer. The mixture was stirred under nitrogen, and it was heated up to reaction temperature at 80°C for 15 min. Then, TESPT solution was fed into the system by starved-feed addition method within 30 min. The reaction proceeded at the adjusted pH for 8 h.

All latex samples were coagulated and dried then, were subjected to soxhlet extraction with ethanol for 24 h under nitrogen to extract the unreacted silane coupling agents. The samples were dried in an oven at 40°C for 24 h.

Characterization

The modified solid samples were characterized with ATR-FTIR on Bruker Tensor27. The elemental analysis (CHNSO) together with energy dispersive X-ray spectroscopy was used to investigate the presence of sulfur(S) and silicon (Si) in the modified particles. The Dynamic light scattering technique was also used

Table II. Preparation Conditions of Modified Polybutadiene Particles

	Modified latex particles	PB Conc. in H_2O (wt %)	TESPT Conc. in EthOH (wt %)	ZnO (phr) (microsize)	ZnO (phr) (nanosize)	pH
Effect of reactant concentration	1	18.2	**50.0**	5	–	8.5
	2	18.2	**33.3**	5	–	8.5
	3	18.2	**20.0**	5	–	8.5
	4	11.8	**50.0**	5	–	8.5
	5	11.8	**33.3**	5	–	8.5
	6	11.8	**20.0**	5	–	8.5
Effect of activator size and content	7	18.2	20	–	**1**	8.5
	8	18.2	20	–	**2**	8.5
	9	18.2	20	–	**3**	8.5
Effect of pH	10	18.2	20	5	–	**7**

on Malvern 100HSa for particle size analysis using diluted modified latex samples (0.25 g/L). pH of the samples was determined by pHmeter model pH462. XRD technique was used to evaluate the crystalline structure of the particles. XRD analysis was carried out using a Philips X'pert model at a wavelength of 1.54 Cu Kα radiations scanning over angle ranging 10–90°. The silica content was measured via thermogravimetric analysis using Perkin Elmer STA6000 at the heating rate of 20°C/min in Argon atmosphere. The residual weight at 600°C represents the weight of the total inorganic content in the sample. The relative amounts of grafted silane were calculated by the following formula:

$$\text{Degree of grafting (wt \%)} = \frac{\text{Residual weight}}{\text{Initial Weight}} \times 100 \tag{1}$$

In another way, the relative degree of silane grafting (R) was also determined here by ATR-FTIR spectra, as the area under Si-O absorption peaks at 1085–1110 cm^{-1} region divided by that of CH_2 absorption peak (at 1445 cm^{-1}) that remained unchanged during modification, used as a measure of silane functionalization.

$$R = A_{1085-1110}/A_{1445} \tag{2}$$

The cross-link densities of modified particles were determined according to ASTM D6814-02. The samples were immersed in toluene at room temperature to ensure swelling equilibrium. The Flory-Rehner equation was used for calculation of cross-link density:

$$\upsilon_e = -\left[\left(\ln(1-V_r) + V_r + \chi_1 V_r^{\,2}\right] / \left[V_1\left(V_r^{\,1/3} - V_r/2\right)\right] \tag{3}$$

where υ_e is the network chain density (mol/cm^3), V_r is a volume fraction of rubber in a swollen network, V_1 is the molar volume of toluene (106.3 cm^3/mol) and χ_1 is the Flory–Huggins interaction parameter between toluene and polybutadiene (0.47)[25]:

$$V_r = [W_d/\rho_d]/[(W_d/\rho_d) + (W_s/\rho_s)] \tag{4}$$

where W_d and W_s are the weight of dry rubber and the weight of solvent adsorbed by the sample, respectively. ρ_d is the density of the rubber compound (0.915 g/cm^3), and ρ_s is the density of toluene (0.87 g/cm^3). The swelling ratio was calculated based on the following formula:

$$\text{Swelling Ratio} = \frac{W_d + W_s}{W_d} \tag{5}$$

RESULTS AND DISCUSSION

Chemical Modification of PBL Particles

Qualitative evidence of TESPT grafting on polybutadiene particles were provided by ATR-FTIR spectroscopy. ATR-FTIR spectra of polymer particles before and after modification are shown in Figure 1. As can be seen in this figure, after reaction two peaks appeared at 630 and 1249 cm^{-1} which can be assigned to C-S and CH_2-S bonds, respectively. Moreover, the absorbing peaks around 800 and 1050–1110 cm^{-1} are attributed to a combination of Si-O-C and Si-O-Si groups. The weak bands at 1326 and 1370 cm^{-1} can be because of the unhydrolyzed ester groups (Si-O-CH_2CH3).[26,27] This indicated that PBL particles functionalized with silane groups through carbon–sulfur attachment.

Figure 2 shows the XRD patterns of pure and modified polybutadiene. The diffraction peak at 2θ of 19.54° following by a

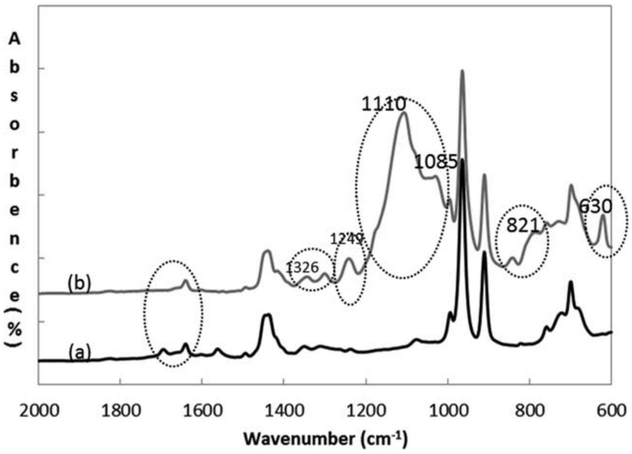

Figure 1. ATR-FTIR spectra of (a) pure and (b) modified polybutadiene (sample no.3).

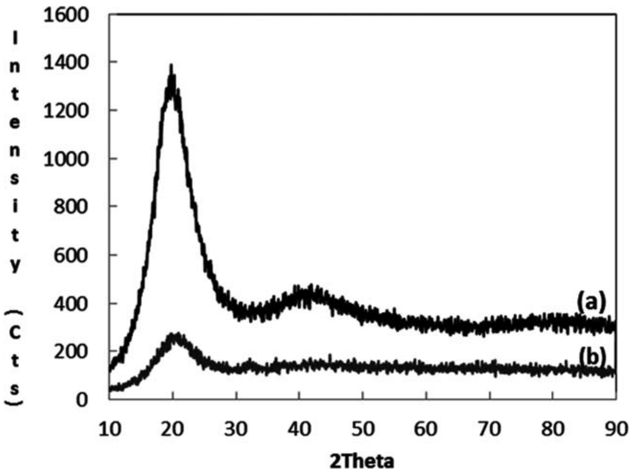

Figure 2. XRD patterns of (a) pure polybutadiene and (b) modified polybutadiene (sample no. 3).

broad peak at 40.9° can be attributed to the crystalline nature of trans-1,4 units in pure polybutadiene[28,29] which decrease highly after modification. This difference can be because of the sulfidosilane moieties which prevent regular packing of chain segments. The cross-links can also decrease crystallinity by reduction in the mobility of chain segments. It is also reported in literature[30,31] that rubber vulcanization and specially sulfur combined in the form of side groups could also effectively retard crystallization. Furthermore, structural changes (cis–trans conversions) that take place during silane functionalization of rubber particles can also reduce considerably the tendency of polybutadiene to crystallize.[30,31] As can be seen in ATR-FTIR Spectra (Figure 1), variations at 1600–1700 cm^{-1} region may be attributed to these structural changes that occurred in polymer after modification.

Figure 3 represents particle size distribution of PBL before and after reaction. As seen in this figure, the average particle size increases a little after treatment.

Increasing the particle size diameter of polymer latex is generally because of the coagulation phenomenon. When the particles increase considerably, the colloidal stability of latex particles would decrease.[13,18] On the other hand, a type of thickening is also observed during modification or slight pre-vulcanization of the latex that the stability in which case may not be affected.[32]

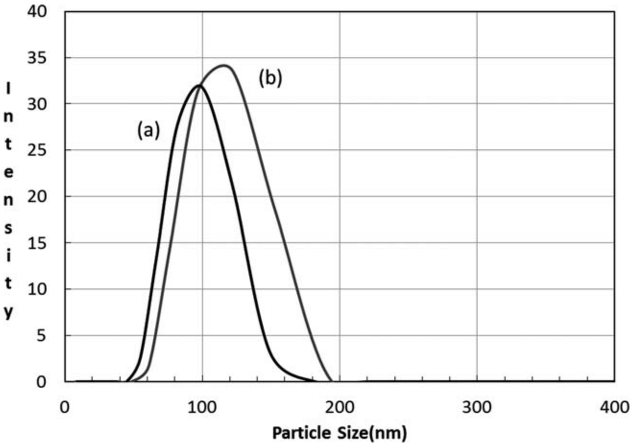

Figure 3. Particle size distribution of (a) pure and (b) modified polybutadiene (sample no. 3).

In this research, the aggregation was interpreted as silane modification of latex particles while inter-particle cross-linking occurred through hydrolysis and subsequent condensation of ethoxysilane groups. It is believed that an increase in modified latex particle size diameter (from 95 to 127 nm) does not disturb the latex stability. However it is known that the colloidal stability of functionalized latex particles decreases as the particles show a significant increase in size. Thus, controlling the particle size of latex by regulating the conditions to avoid the hydrolysis and condensation reactions is of great importance.

The presence of sulfur and silane in modified polymer after reaction was also confirmed by elemental analysis of sulfur and energy dispersive X-Ray spectroscopy (EDX), respectively. The obtained data are given in Tables S1 and S2 (in supporting information). Thermogravimetric analysis of the pure and modified particles were compared in Figure S1 (given in supporting information) also proved silane modification of polybutadiene particles.

Effect of Reaction Conditions

Effect of Reactant Concentration. First series of experiments was carried out at slight basic condition (pH=8.5, Table II) in three different concentrations of TESPT in Ethanol (20, 33.3, and 50 wt %) and two concentrations of polymer in water (18.2 and 11.2 wt %) in two series of experiments. Grafting degree calculating from TGA and FTIR results, cross-link density, swelling ratio, and latex particle size diameter of these samples were reported in Table III. Relative amounts of grafting and cross-link density evolution as a function of TESPT concentration in ethanol at two different water contents were plotted in Figure 4(a,b). It should be noted that TESPT content in two series of experiments is constant and by decreasing the amount of ethanol its concentration increased. As it is seen in Figure 4(a) (high polymer latex content in water, 18.2 wt %) the degree of silane grafting increases as TESPT concentration decreases, while the cross-link density increases at high TESPT concentration. This behavior in low polymer latex content (11.8 wt %) [Figure 4(b)] is less considerable. It can be seen that the grafting degrees obtained from FTIR results are in agreement with those obtained from TGA. It can be concluded that increasing the amount of ethanol as a co-solvent facilitated transfer of TESPT to the polymer particles. It leads to improve silane degree of grafting through enhancing the collision between particles. So the degree of silane grafting reaction would reduce with decreasing the amount of ethanol. However, the effect of ethanol was weakened by diluting the media with addition of water.

The particle size of latex was not affected strongly at different concentrations as evidenced by DLS data in Table III. The particle size diameter varied between 95 and 127 nm. It can be seen that the highest diameter (127 nm) belongs to the latex at low concentration of TESPT with low water content. The increase in particle size with an increase in the amount of ethanol was

Table III. Particle Size Diameter, Grafting Degree, Cross-Link Density, and Swelling Ratio of Modified Latex Samples

Entry	Particle size (nm)	Degree of grafting TGA	Degree of grafting FTIR	Cross-link density ($\times10^{-5}$) (mol/cm^3)	Swelling ratio
1	99.5	9.21	3.892	4.875	5.925
2	98	8.41	3.681	2.952	7.344
3	127.9	10.95	7.424	3.140	7.051
4	92.7	6.41	3.149	4.598	6.061
5	102.8	7.53	2.412	3.688	6.611
6	99.4	8.59	3.461	3.253	6.951
7	136.2	10.287	8.318	6.134	5.422
8	115.4	6.844	-	16.223	2.794
9	114.3	9.034	-	9.833	3.543
10	177.5	6.765	4.597	3.781	5.591

consistent with the fact that the lower concentration of TESPT showed the higher silane grafting, although the latex stability was slightly diminished.

Effect of Reaction Time. The modification of PBL particles was studied at various reaction times (0, 2, 4, 6, 8, 10 h) for sample no.3. The intensities of the peaks at 1050–1110 cm^{-1} assigned to silane bands in FTIR spectra were increased as the reaction time increased from 2 to 10 h. The degrees of grafting were calculated from the area under ATR-FTIR spectra and their cross-link densities were plotted in Figure 5. As expected, the cross-link density and grafting degree gradually increased with increasing reaction time. The rate of grafting reaction decreased after 8 h, but the cross-linking continued without decreasing. The grafting sites on the surface of polymer particles decreased during the time, leading to decrease in the reaction rate.

Effect of Activator Particle Size. The influence of the particle size of zinc oxide as an activator on this reaction was examined. For this purpose, a series of functional PBL using two size scale (micro and nano) and different amounts of zinc oxide nanoparticles (1, 2, 3 phr) were prepared in the same condition. The grafting degree, latex particle size, and cross-link density of the modified latexes were summarized in Table III. The grafting degrees of the samples were also calculated from ATR-FTIR spectra and thermogravimetric analysis.

It was observed that grafting degree of TESPT in the presence of 1 phr zinc oxide nanoparticles corresponds to 5 phr of those microparticles. As expected, zinc oxide nanoparticles because of their high surface area would provide more grafting sites on the latex particles. However, the TGA results indicated that increasing the amount of ZnO nanoparticle to 3 phr had an inverse effect on grafting efficiency of TESPT. It might be interpreted as the adsorption ability of ZnO nanoparticles, disrupting ionic

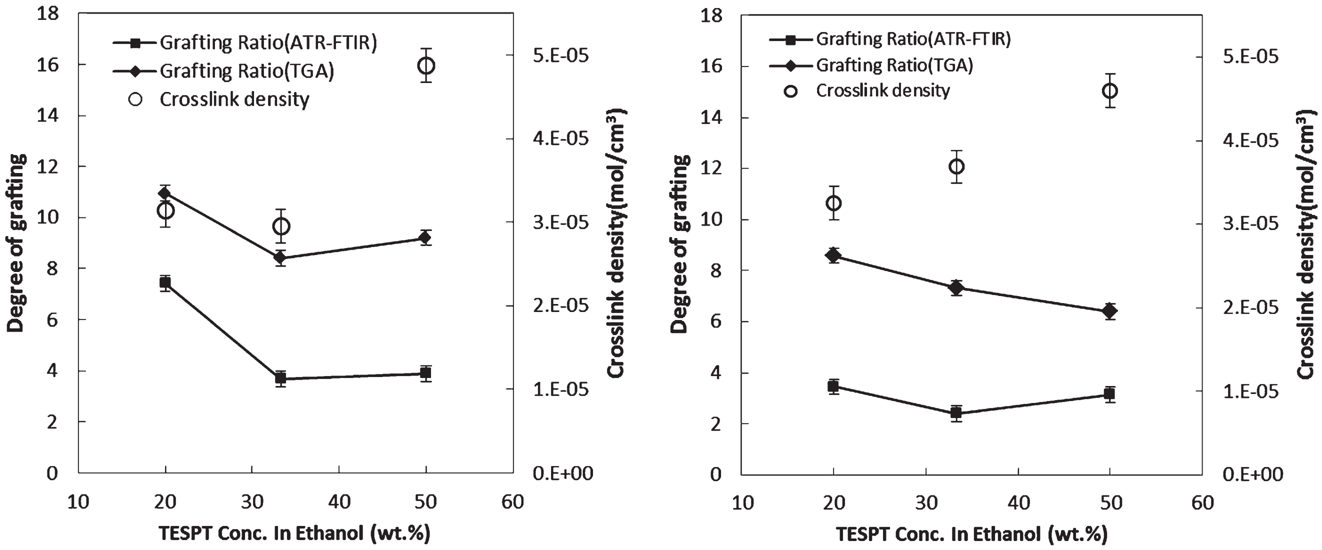

Figure 4. Effect of TESPT concentration on cross-link density (○) and grafting degree obtained from FTIR (■) and TGA (◆) results when mixed with (a) polymer latex containing 18.2 wt % solid content; (b) polymer latex containing 11.8 wt %.

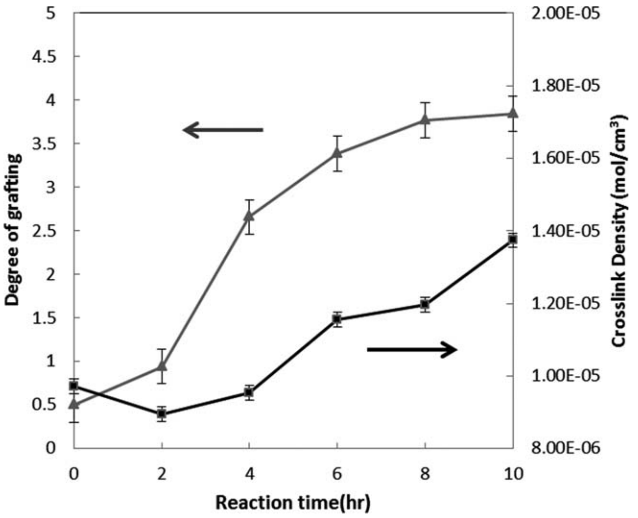

Figure 5. Effect of reaction time on grafting degree and cross-link density of modified polybutadiene latex (sample no. 3).

balance of media to hinder the reaction. On the other hand, ZnO nanoparticles (1 phr) led to higher cross-link density in polybutadiene particles compared with microparticles (5 phr). This would be because of more diffusion of zinc oxide nanoparticles into rubber particles providing higher activating functions rather than ZnO microparticles. As indicated in Table III, the latex particle size increases at 1 phr of ZnO nanoparticle after modification resulting in the decrease of colloidal stability of latex by ZnO nanoparticles.

Effects of pH. In this work, to consider the effect of pH, two experiments were designed at two different pH values: neutral pH (pH=7) and pH of PBL (pH=8.5) [samples no. 3 and 10 according to Table II).

TESPT as a coupling agent can be incorporated onto the polybutadiene particles by reaction of sulfide groups with unsaturated bonds of polybutadiene. Furthermore, its alkoxysilane groups may hydrolyze into Si-OH groups and then condensation reaction occurs.[2] These reactions are affected by pH of the aqueous media. It has been reported that hydrolysis of a silane coupling agent is catalyzed by both acid and alkali, the relative rate of the hydrolysis in acidic, basic, and neutral medium being of the order of 100:10:1.[3,13,33] So the hydrolysis and condensation of ethoxysilane groups can be avoided by buffering the latex at neutral pH.[3,13]

In this study, it was found that the silane grafting degree at pH=8.5 was higher than that at pH=7 (Table III). Better reaction of TESPT via sulfur attachment could be because of the fact that the rate of vulcanization reactions in polymer latex enhanced under basic condition.[32]

The pH of latex also affects the colloidal stability of latex. As seen in Table III, the average particle size of modified polybutadiene under normal condition (pH=7), was larger than that in basic media. The influence of pH should be considered either for the effects on the surfactant and its adsorption ability on the particles surface, or for influences on the hydrolysis/condensation rates.[13] The former improves physicochemical coagulation of the latex and the latter causes to inter-particle cross-linking. Since the rates of hydrolysis/condensation kept down at neutral pH, the increase in particle size is probably because of the influence of pH on the surfactant adsorption. Moreover, it should be noted that performing this reaction in acidic condition turned the system into the gel.

The Proposed Mechanism

Figure 6 illustrates the silane functionalization of PBL particle with TESPT. The reaction carried out without sulfur in the presence of zinc oxide as an activator and stearic acid. It is known that TESPT before being considered as a coupling agent has been introduced as a sulfur donating accelerator.[34,35]

In the present work, the transport of TESPT across the aqueous phase was facilitated by dissolving it in ethanol. As it was confirmed before in Effect of Reactant Concentration section, the grafting degree was increased as ethanol increased in the system. TESPT, as an accelerator, in the presence of Zinc oxide formed

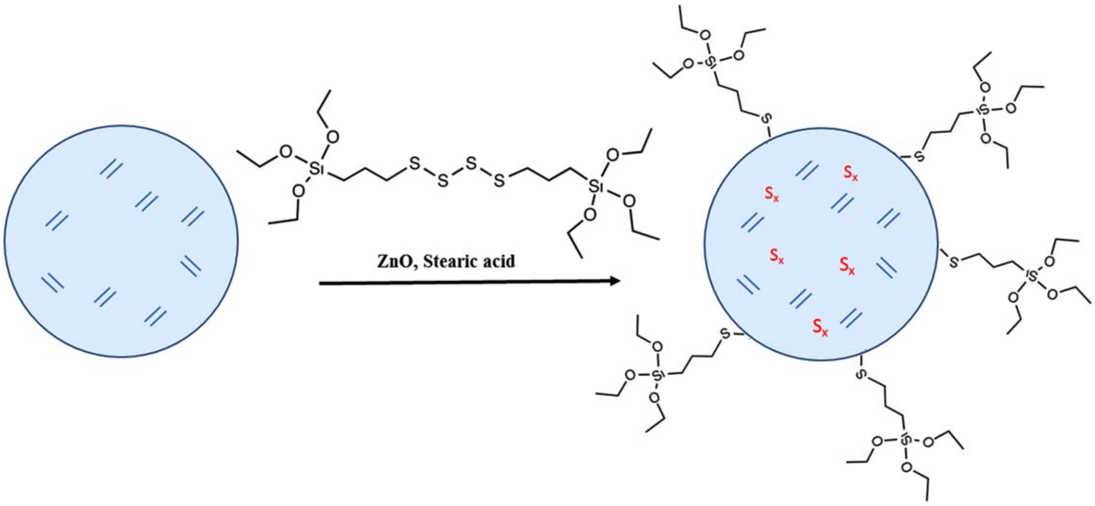

Figure 6. Schematic representation of the silane-fuctionalized surface of polybutadiene latex particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

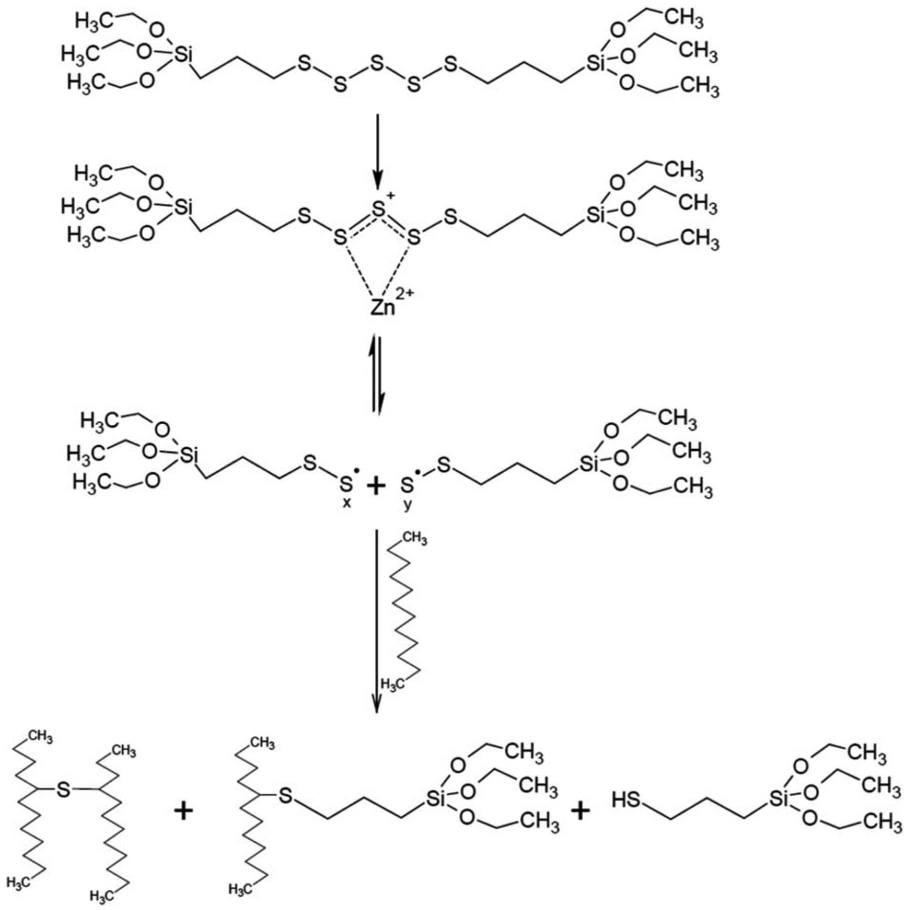

Figure 7. The possible reactions in modification of rubber latex particles with TESPT.

an active sulfurating agent before migrating to the surface of polymer particles.[34] When these reactive agents reach the surface of rubber particles, there are two possibilities: (1) Diffusion into the particles and (2) reaction with the molecules. It is known that TESPT as a coupling agent contains two types of functional groups, tetrasulfide group that can react with unsaturated bonds of polybutadiene and the alkoxy groups that tend to be in ethanolic aqueous media. As there are less tendencies to diffuse into the rubber particles, the reaction can occur on the surface. During the reaction time, desulfuration and rearrangement of sulfur–sulfur bonds can occur and lead to a stable network containing mono and disulphide cross-links.

The cross-linking and network formation could be because of three reasons: (1) inter-particle cross-linking as a result of hydrolysis and condensation of alkoxy silane groups in TESPT; (2) intra-particle cross-linking because of sulfur vulcanization; and (3) cross-linking reactions on the particles which are a combination of two former reactions. As considered before (in Chemical Modification of PBL Particles section), the inter-particle cross-linking can cause to slight increase in the particle size diameter. Zinc oxide nanoparticles because of their low particle size diameter and high surface area collide further with all the latex ingredients and lead to higher cross-link density compared with zinc oxide microparticles.

In spite of significant progress in understanding the principal features of sulfur pre-vulcanization over the years, there is not a specified chemistry for this reaction.[21,36] It was reported[21,36,37] that the mechanism of vulcanization in dry rubber and latex pre-vulcanization is of the same nature. However, pre-vulcanization of latex in aqueous media proceeds much more rapidly at the same temperature and the same vulcanizing ingredients. In the present work, according to the results in Effects of pH section, it was observed that silane degree of grafting increased in basic media rather than neutral pH. So it can be concluded that the silane functionalization took place on the surface of polymer particles in a process similar to sulfur pre-vulcanization of rubber latexes.[19,21,36] It is believed that an ionic mechanism is dominant in this ethanolic aqueous media which can be illustrated in Figure 7.

CONCLUSION

In this work, PBL particles were modified by TESPT using Zinc oxide as an activator which surrounded by ethanol and water as media. The reaction was evidenced by peaks assigned to Si-O and C-S groups in ATR-FTIR spectroscopy and also confirmed by DLS. The reduction in crystalline properties of the particles after modification was studied by XRD. It was observed that cross-link density and swelling ratios of silanized latex particles were nearly correlated with degree of silane grafting. Degree of grafting was calculated from TGA and ATR-FTIR spectra. As the time of reaction increased, cross-link density and degree of grafting were also increased. Increasing in the amount of ethanol as a co-solvent caused to an increase in the grafting degree, whereas the cross-link density decreased. Functionalization of latex in basic media led to higher grafted amounts rather than neutral pH. It was found that zinc oxide nanoparticles as an activator resulted in more cross-link density and grafting degree rather than zinc oxide microparticles. The conditions should be adjusted to avoid premature hydrolysis and condensation, although the observation results in adequate stability of the latex.

In this work, the reaction mechanism of incorporating the sulfidosilane groups onto polymer latex particles is different from other silane modification reported in previous works, which were carried out by graft polymerization. Because of the presence of sulfur groups in TESPT as a functional material, the silane modification can occur as well as sulfur pre-vulcanization in rubber latex and the ionic mechanism was dominant in the media.

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