

Modification of nanosilica particles with hydrophobic modifier bis[3-(triethoxysilyl)propyl]tetrasulfide by using micro-injection in aqueous solutions

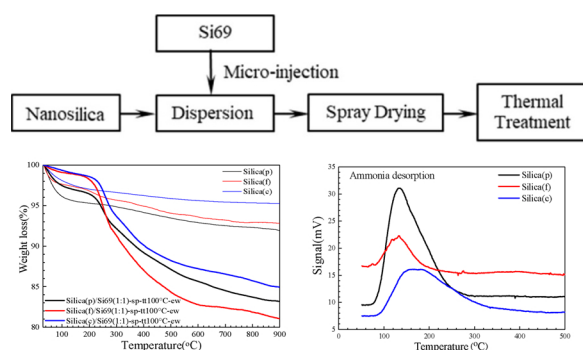


Keyi Yu, Ling Yang, Jingyuan Wang, Zirui Zhu, Ting-Jie Wang*

Department of Chemical Engineering, Tsinghua University, Beijing, 100084, China

GRAPHICAL ABSTRACT

The hydrophobic Si69 was successfully modified on precipitated, fumed and colloidal silica particle surfaces at high grafting density in aqueous solutions by combining micro-injection with aqueous mixing, spray drying, and thermal treatment. The colloidal silica particles achieve the highest grafting density due to its highest activity of silanol.



ARTICLE INFO

Keywords:
Nanosilica
Modification
Dispersion
Filler
Colloidal silica

ABSTRACT

Effective modification of nanosilica particles in aqueous solution with the hydrophobic modifier bis[3-(triethoxysilyl)propyl]-tetrasulfide (Si69) was developed. The modification was carried out through the route of aqueous mixing, spray drying, and thermal treatment. The Si69 hydrolysate was maintained at a low concentration by using micro-injection and well mixed with the nanosilica particles to increase the hydrolysate grafting density on the particle surfaces. Precipitated, fumed, and colloidal silica particles were modified up to a high grafting density of 2.96 nm^{-2} , 3.07 nm^{-2} and 3.25 nm^{-2} , respectively. The dispersibilities of the Si69-modified nanosilica particles were improved significantly. The modification performances of the three kinds of nanosilica particles are different, which result from the silanol characteristics and the Brønsted/Lewis acid sites present on the particle surfaces.

1. Introduction

Nanosilica particles, such as precipitated silica, fumed silica and

colloidal silica, have been widely used in the fields of composites, catalysis, adsorption, biomedicine, etc. [1–8] However, unmodified nanosilica particles exhibit a strong polarity due to the abundance of

* Corresponding author.

E-mail address: wangtj@tsinghua.edu.cn (T.-J. Wang).

<https://doi.org/10.1016/j.colsurfa.2020.124852>

Received 7 February 2020; Received in revised form 7 April 2020; Accepted 9 April 2020

Available online 29 April 2020

0927-7757/ © 2020 Elsevier B.V. All rights reserved.

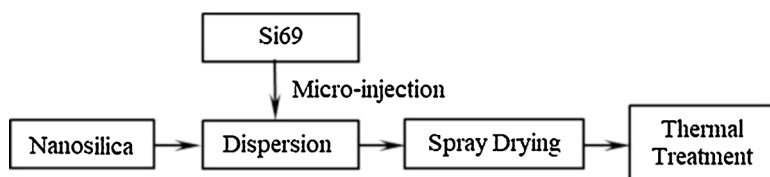


Fig. 1. Modification route with micro-injection involving Si69.

silanol on the surface, which results in easy agglomeration and poor dispersion in polymer matrix. To obtain highly dispersed nanosilica particles, surface modification is necessary. In addition, nanosilica particles are employed in many functional applications, thus modification of the particle surface is also needed. Nanosilica is usually added to rubber, resin, and other materials as a filler to produce composites [1,2,9–11]. The nanosilica with a high dispersion is an ideal filler, because it can not only effectively improve the performance of a composite, but also increase the content of the filler in the composite by up to 40–60 %, which greatly reduces the cost of the product.

Silane coupling agents are often used as modifiers to improve the dispersion and affinity of nanosilica particles in organic matrix. The most commonly used coupling agent in vulcanized rubber is polysulfide silane [12,13], which includes bis[3-(triethoxysilyl)propyl] tetrasulfide (Si69), bis[3-(triethoxysilyl)propyl]disulfide, and γ -mercaptopropyltrimethoxysilane. The sulfur atom in polysulfide silane can participate in the cross-linking reaction of the vulcanization process with polymer chains [14,15]. Si69 is one of the most widely used silane coupling agents, which acts as a bridge between the filler and the matrix. The silanol on the hydrolysate of Si69 dehydrates and condenses with the silanol present on the particle surface, while sulfur atom crosslinks with the polymer chains to form a network structure.

It has been reported in the literatures that in-situ synthesis of nanosilica particles in organic matrix by using sol-gel method results in a high dispersion of particles and a narrow particle size distribution in the matrix [16–18]. In this method, tetraethyl orthosilicate or other silanes are used as raw materials for the preparation of nanosilica and a large amount of organic solvents are needed, which results in high costs and causes pollution during industrialization. In a practical production process, the filler, coupling agent, and raw rubber are usually mixed together at the same time [19–21]. The grafting amount of silica is unknown and unguaranteed in the process. The improvement in particle dispersion and affinity with organic matrix through subsequent blending is very limited [1,22]. Therefore, pre-modification of the nanosilica particles is necessary to guarantee dispersion and affinity in the composite.

The modification of hydrophobic modifiers, as reported in the literatures, is usually carried out in organic solvents, ethanol solution, or latex systems [23–27]. Although a hydrophobic modifier can be well dispersed in organic solvents, the hydrophilic nanosilica particles seriously agglomerate. It is difficult to achieve a high dispersion, adsorption, and grafting between the modifier molecules and particle surface, which leads to a relatively low grafting density that varies from 0.5 to 2.5 nm⁻² maximum [28–33]. Further, this process results in environmental and safety issues, as well as high costs, which limit its practical application. There are few reports on aqueous modification in the literature, because most of the coupling agents are hydrophobic and the aqueous phase is not conducive to the dehydration and condensation between agents and silanol on the particle surface. In addition, the limitation of temperature in the case of aqueous solutions also makes it difficult to achieve a high grafting density.

Precipitated silica particles seriously aggregate during the synthesis and subsequent drying process, leading to a poor dispersion in composites, although the production cost is low. Fumed silica shows a better dispersion, but it is only preferably used for special materials

owing to its high cost. Colloidal silica displays a narrow particle size distribution and high dispersion in aqueous solution owing to the good control during the preparation process [34,35]. The colloidal nanosilica particles suspend stably in aqueous solutions owing to the high zeta potential of the surface. The cost of colloidal silica with the same size about 20 nm, is close to that of precipitated silica.

In this work, a novel aqueous modification process is developed, in which hydrolysis of the hydrophobic modifier Si69 was enhanced by micro-injection to produce the water-soluble hydrolysate of Si69 for modifying the nanosilica particle surface via the route of aqueous mixing, spray drying, and thermal treatment [36,37]. High grafting density and high dispersibility were achieved for the Si69-modified nanosilica. The different modification performances of precipitated silica, fumed silica, and colloidal silica are confirmed to result from the silanol characteristics and the Brønsted/Lewis acid sites present on the particle surface. The colloidal silica achieved the highest grafting density due to it has the highest activity of silanol on the surface, which has great industrial application potential.

2. Materials and methods

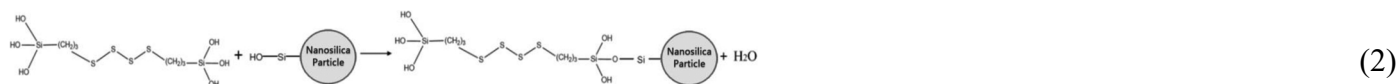
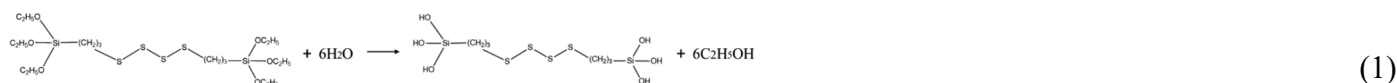
2.1. Materials

Nanosilica particles synthesized by an aqueous precipitation process (abbreviated as “Silica(p)”, Rhodia Silica White Co. Ltd, Qingdao, China) were used as the first kind of nanosilica particles. The BET surface area of the nanosilica particles is 165 m² g⁻¹, which was measured by a surface area analyzer (Autosorb-iQ, Quantachrome Instruments U.S.), and the diameter of the primary particles is about 20 nm. Unmodified fumed nanosilica (abbreviated as “Silica(f)”, AEROSIL 200, Degussa, Germany) was used as the second kind of particles. The BET surface area is 215 m² g⁻¹ and the diameter of the primary particles is about 18 nm. Colloidal silica (abbreviated as “Silica(c)”, Suize Eco-technology Co. Ltd, Guangzhou, China) was used as the third kind of particles. The BET surface area is 151 m² g⁻¹ and the diameter of the primary particles is about 20 nm.

Si69 (Yuanye Biological Technology Co. Ltd, Shanghai, China) with the purity of 98 % was used as the modifier. Anhydrous ethanol (Modern Oriental Technology Development Co. Ltd, Beijing, China) was used as the reagent in ethanol washing. N-hexane (Beijing Chemical Works, Beijing, China) was used as a non-polar dispersion reagent to substitute the organic matrix like rubber.

2.2. Modification process

Si69 is a common silane coupling agent which is insoluble in water, but the hydrolysate of Si69 is water-soluble. Micro-injection is used to facilitate the hydrolysis by increasing the contact area of Si69 in water and is adjustable. The hydrolysate of Si69 contacts and partly grafts on the nanosilica particle surface in water. The Si69 hydrolysate was maintained at a low concentration, which restrains the mutual condensation among the Si69 hydrolysate themselves and enables the hydrolysate to mainly graft on the particle surface. The particle surface was modified via the route of aqueous mixing, spray drying, and thermal treatment. The modification process of Si69 is shown in Fig. 1. The hydrolysis and grafting of Si69 are shown in Eq.s (1) and (2).



The modification process partially refers to our previous work [36,37]. The mass content of the nanosilica particles (SiO_2) was set to 3.6 wt% in the aqueous suspension without any organic solvents. To examine the saturation grafting density, the mass ratio of $\text{SiO}_2/\text{Si69}$ was set to 1:1 by considering the silanol number on the particle surface as $4.5 - 8 \text{ nm}^{-2}$ [38], and Si69 was kept in excess. The Si69 was micro-injected into the suspension at a feed rate of $7 \mu\text{L}/\text{min}$, meanwhile the suspension was stirred at room temperature for 24 h to achieve good mixing. After the aqueous mixing, the suspension was dried in a spray dryer to obtain dried powder, which was sampled and labeled as Silica/Si69(1:1)-sp. The powder was then thermally treated in a sealed steel tube in a muffle furnace at a set temperature. After the thermal treatment, the powder was sampled and sealed, and labeled as Silica/Si69(1:1)-sp-tt for examination. In order to characterize the chemical grafting, the modified powder was washed with anhydrous ethanol for five times to remove any unreacted Si69, and the sample was labeled as Silica/Si69(1:1)-sp-tt-ew. The five-times' washing with anhydrous ethanol ensures that the unreacted Si69 is removed from our previous experiments [36,37].

2.3. Characterization

The BET surface area was measured by a surface area analyzer (Autosorb-iQ, Quantachrome Instruments U.S.). The morphology of the nanosilica particles was observed by using a high-resolution transmission electron microscope (HTEM; JEM-2011, JEOL Co., Tokyo, Japan). The dispersibility of the modified particles was qualitatively examined by HTTEM after ultrasonic treatment in ethanol and n-hexane, respectively. The characteristic groups of Si69 and silanol present on the silica surface were examined by FTIR spectrometry (Nexus 670, Nicolet, USA) by using KBr as the matrix. The contact angles of the samples were measured by using a contact angle analyzer (HARKE-SPCA, Beijing Harke, China). The grafting amounts on the particle surface after washing with ethanol were determined by using a thermogravimetry analyzer (TGA/DSC 1, Mettler Toledo, Swiss). In TG analysis, the heating rate was set at $10 \text{ K}/\text{min}$ in the range $30 - 900 \text{ }^\circ\text{C}$ under a flow of nitrogen gas.

2.4. Measurement of surface acid sites

The relative capacities of the total acid sites on the nanosilica particle surface were determined by temperature-programmed desorption (TPD; ChemBET Pulsar TPR/TPD, Quantachrome Instruments U.S.), using ammonia as the molecular probe. The particle samples were pre-treated in helium atmosphere at $500 \text{ }^\circ\text{C}$ for 60 min, then the ammonia adsorption was conducted at $50 \text{ }^\circ\text{C}$ for 45 min. After the adsorption was completed, the gas was switched to helium for 45 min to remove the physically adsorbed ammonia on the sample surface. Then the desorbed ammonia was recorded in the range $50 - 800 \text{ }^\circ\text{C}$ under a heating rate of $10 \text{ K}/\text{min}$.

The Brønsted and Lewis acid sites were examined by in-situ FTIR spectroscopy, using pyridine as the molecular probe. The samples were pre-treated in vacuum at $350 \text{ }^\circ\text{C}$ and 10^{-5} Pa for 60 min, then the pyridine adsorption was conducted at $50 \text{ }^\circ\text{C}$ for 30 min. The desorption of pyridine was conducted at $150 \text{ }^\circ\text{C}$ and $350 \text{ }^\circ\text{C}$ (10^{-5} Pa , 30 min), respectively, and the infrared spectra of samples after desorption were

recorded, from which the relative capacities of the Brønsted and Lewis acid sites can be calculated.

3. Results and discussions

Three kinds of nanosilica particles, namely precipitated silica (Silica(p)), fumed silica (Silica(f)) and colloidal silica (Silica(c)), were modified via the same procedure under the same condition. The different results obtained for the three kinds of nanosilica particles were analyzed.

3.1. Thermal treatment

After aqueous mixing and spray drying, some of the Si69 hydrolysate is chemically grafted on the particle surface, while the others are physically adsorbed on the particle surface or simply mixed with the particles [36,37,39]. Si69 hydrolysate is uniformly mixed with the nanosilica particles due to its water soluble. A subsequent thermal treatment was performed to promote the conversion from physical adsorption to chemical grafting. Experiments show that the modified nanosilica particles turn to slight yellow at temperature higher than about $160 \text{ }^\circ\text{C}$. It is deduced that S_4 in the Si69 molecules start to oxidize and decompose. Since S_4 takes an important role of a crosslinker during vulcanization with the rubber matrix, the decomposition of S_4 should be avoided during the thermal treatment. Experiments also show that both increasing the temperature and extending the time of the thermal treatment can increase the grafting amount. To avoid the decomposition of Si69 molecules and achieve a high grafting density, as well as to obtain modification results for the three kinds of silica that are comparable, the operating parameters of the thermal treatment process were set at $100 \text{ }^\circ\text{C}$ and 24 h. Experiments showed that the grafting amount on the particle surface under this condition from TG analysis is higher than that at $180 \text{ }^\circ\text{C}$ and 30 min.

3.2. Surface hydrophobicity

Since Si69 has hydrophobic groups, high grafting amount of Si69 on the particle surface brings high hydrophobicity of the particles. The contact angles of the particles were measured to characterize the surface hydrophobicity of the particles, and are listed in Table 1. Table 1 shows that the spray drying and the subsequent thermal treatment increase the hydrophobicity of the three kinds of silica particles significantly. The contact angles of Silica(p) and Silica(f) increase much after thermal treatment. It indicates that Silica(p) and Silica(f) do not reach the saturation grafting amount after spray drying, and the subsequent thermal treatment increases the grafting amount significantly.

Table 1

Contact angles of unmodified and modified nanosilica particles after spray drying and after thermal treatment.

Contact angles	Silica(p)	Silica(f)	Silica(c)
Unmodified / °	22.6	32.2	12.6
After spray drying / °	70.5	54.5	93.9
After thermal treatment / °	90.4	83.4	95.5

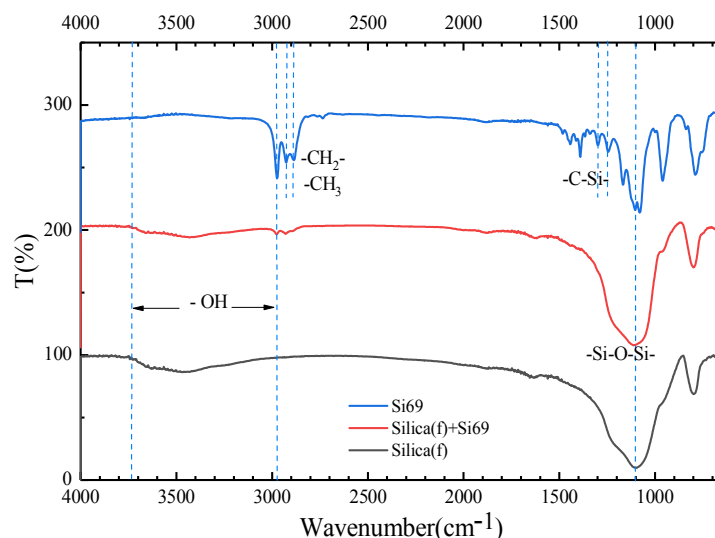


Fig. 2. Infrared spectra of pure Si69, unmodified nanosilica, and Si69-modified nanosilica (Silica(f)).

However, the contact angle of Silica(c) increases much after spray drying, and increases little after the subsequent thermal treatment, indicating that the grafting amount of Silica(c) after spray drying is close to saturation.

3.3. Saturation grafting density

The FTIR spectra of the unmodified and Si69-modified samples were examined. Since Silica(p), Silica(f), and Silica(c) display similar spectra, the spectrum of Silica(f) was taken as the representative, and is shown in Fig. 2. Due to the Si69-modified samples have been washed with ethanol for 5 times, the mixed and physically adsorbed Si69 is completely removed [36,37]. The small peaks at 2974 cm^{-1} and 2880 cm^{-1} are observed from the spectra of the Si69-modified sample, which are assigned to $-\text{CH}_2-$ stretching vibrations, indicating that Si69 is chemically grafted on the particle surface.

By analyzing and comparing the weight losses of the samples before and after modification (ethanol washed and dried), the amounts of Si69 grafted on the particle surface were determined. The TG curves of the particles before and after modification of Silica(p), Silica(f), and Silica(c) are shown in Fig. 3.

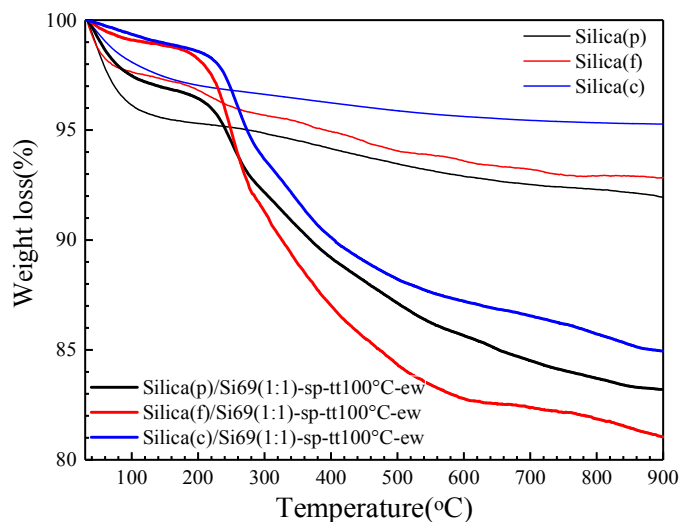


Fig. 3. TG curves of the three kinds of unmodified and Si69-modified nanosilica particles.

In the range $200 - 900\text{ }^\circ\text{C}$, Silica(p/f/c)/Si69-sp-tt100 $^\circ\text{C}$ -ew shows remarkable weight losses, which are attributed to the decomposition of the Si69 grafted on the silica surface. It is known that the bond energies of Si-O, C-Si, C-C, S-C and S-S are 460 kJ/mol , 347 kJ/mol , 332 kJ/mol , 272 kJ/mol , and 268 kJ/mol , respectively [40]. The bond energies of C-C, S-C, and S-S are low, and the C-Si bond ruptures at around $450 - 510\text{ }^\circ\text{C}$ [41]. It indicates that the decomposition and shedding of $-\text{C}_3\text{H}_6-\text{S}_4-\text{C}_3\text{H}_6-$ groups contributes the most to the weight losses observed in the range $200 - 900\text{ }^\circ\text{C}$.

Comparing the TG curves of the three kinds of unmodified and Si69-modified nanosilica particles, the grafting amounts can be calculated from the difference between the curves of the same kinds of particles in the range $200 - 900\text{ }^\circ\text{C}$. Fig. 3 shows that all the three kinds of nanosilica particles display a high chemical grafting amount after modification. From Fig. 3, the number of Si69 molecules chemically grafted on the particle surface per square nanometer, n_{Si69}^s (nm^{-2}), can be calculated.

The mole number of chemisorbed Si69, n_{Si69} (mol), can also be calculated from the weight loss observed in the range $200 - 900\text{ }^\circ\text{C}$:

$$n_{\text{Si69}} = \frac{\Delta W (\%) \times m_{200}}{M_{\text{CSC}}} \quad (3)$$

where the weight loss (%) at $200 - 900\text{ }^\circ\text{C}$ can be calculated as $\Delta W = (m_{200} - m_{900})/m_{200} \times 100\%$, and M_{CSC} (g/mol) is the molecular weight of the $-\text{C}_3\text{H}_6-\text{S}_4-\text{C}_3\text{H}_6-$ group, i.e., 212 g/mol .

The corresponding surface area S (nm^2) of the silica particles is obtained from

$$S = m_{\text{SiO}_2} \times S_{\text{BET-SiO}_2} \times 10^{18} \quad (4)$$

where the mass of SiO_2 in the Si69-modified sample is given by $m_{\text{SiO}_2} = m_{200} - n_{\text{Si69}} \times M_{\text{Si}^*}$. To simplify the calculation, the molar mass of the bidentate group is approximately used as the average molar mass of the grafting group M_{Si^*} (298 g/mol); $S_{\text{BET-SiO}_2}$ (m^2/g) is the specific surface area of the silica particles. Then, the number of Si69 molecules grafted on the particle surface per square nanometer, n_{Si69}^s (nm^{-2}), is

Table 2
Modification results for three kinds of nanosilica particles.

SiO ₂ :Si69 = 1:1	Silica(p)	Silica(f)	Silica(c)
BET / m ² g ⁻¹	165	215	151
Grafting density after thermal treatment / nm ⁻²	2.96	3.07	3.25
Chemical grafting proportion of Si69 / wt%	23.0	30.2	23.9

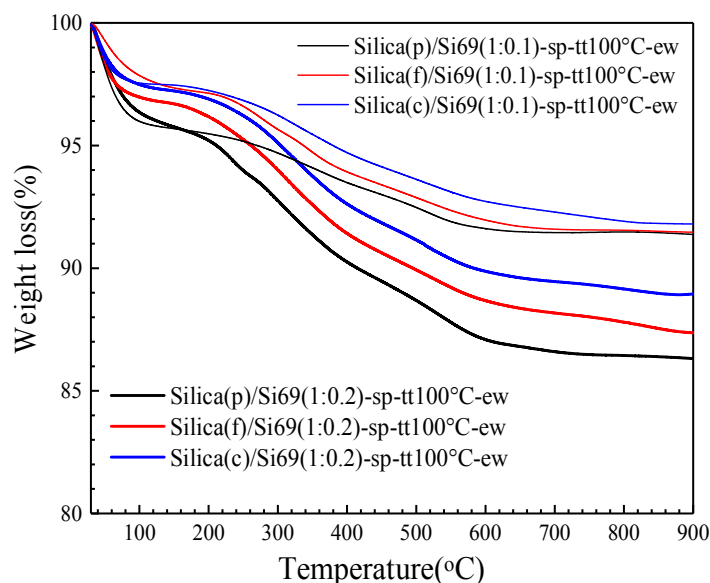


Fig. 4. TG curves of three kinds of Si69-modified nanosilica particles at $\text{SiO}_2:\text{Si69} = 1:0.2$ and $1:0.1$.

calculated as

$$n_{\text{Si69}}^s = \frac{n_{\text{Si69}} \times N_A}{S} = \frac{\frac{\Delta W(\%)}{M_{\text{CSC}}} \times N_A}{\left(1 - \frac{\Delta W(\%)}{M_{\text{CSC}}}\right) \times M_{\text{Si}}^* \times S_{\text{BET-SiO}_2} \times 10^{18}} \quad (5)$$

The calculated results and the related parameters are listed in Table 2.

Table 2 shows that Silica(c) reaches a high grafting density of 3.25 nm^{-2} after thermal treatment. The ratio of $\text{SiO}_2:\text{Si69} = 1:1$ was designed by considering that Si69 is in excess relative to the silanol on the nanosilica surface. From the chemical grafting proportion of the modifier, it is confirmed that Si69 is significantly in excess and that the grafting densities obtained above are the saturation grafting density under these experimental parameters.

3.4. Effects of $\text{SiO}_2:\text{Si69}$ ratio

Considering that the chemical grafting proportions of Si69 are about 20 wt% at the mass ratio of $\text{SiO}_2:\text{Si69} = 1:1$, and the mass ratio of Si69/ SiO_2 in industrial production is only about 10 wt%, the experiments at the ratios of $\text{SiO}_2:\text{Si69} = 1:0.2$ and $1:0.1$ were designed and conducted with the same procedures for comparison. The obtained TG curves are shown in Fig. 4. The grafting density, n_{Si69}^s (nm^{-2}), was calculated according to Eqs. (3)–(5). The grafting densities and chemical grafting proportions of Si69 are listed in Table 3.

For $\text{SiO}_2:\text{Si69} = 1:0.2$, the grafting densities of the three kinds of nanosilica particles are close, being 1.84 nm^{-2} , 1.39 nm^{-2} , and 1.74 nm^{-2} for Silica(p), Silica(f), and Silica(c), respectively. The chemical grafting proportions of Si69 reach about 70 wt%. For $\text{SiO}_2:\text{Si69} = 1:0.1$, the grafting densities of the three kinds of nanosilica particles

Table 3

Modification results of three kinds of nanosilica particles for different $\text{SiO}_2/\text{Si69}$ ratios.

	$\text{SiO}_2:\text{Si69} = 1:0.2$			$\text{SiO}_2:\text{Si69} = 1:0.1$		
	Silica(p)	Silica(f)	Silica(c)	Silica(p)	Silica(f)	Silica(c)
Grafting density / nm^{-2}	1.84	1.39	1.74	0.78	0.84	1.14
Grafting proportion of Si69 / wt%	78.1	77.3	69.8	72.1	92.5	89.4

decrease due to the decrease of Si69 concentration. The chemical grafting proportions of Si69 for Silica(f) and Silica(c) increase obviously, reaching up to 90 wt%.

3.5. Dispersibility of Si69-modified particles

Since the nanosilica particles are easily agglomerate and difficult to be measured in primary size, the average size measured by dynamic light scattering are usually larger than micrometers. In the application process, the nanosilica particles are added and blended into rubber, resin, etc., as a filler to produce composites. High dispersibility will bring a high performance of the composite. Therefore, for reference in applications, the TEM images of the unmodified and Si69-modified particles in ethanol (polar solvent) and n-hexane (non-polar solvent) under the same ultrasonic dispersion procedures were examined to qualitatively compare the dispersibility of the particles, as shown in Fig. 5. It is seen that the unmodified particles agglomerated severely, while all the dispersibilities of the Si69-modified particles were overall improved, which the number of the primary particles in the Si69-modified agglomerates decreased significantly. High dispersion of the modified nano-silica particles indicates that they are easier to be dispersed. Furthermore, the Si69 grafting on the particle surface will increase the primary particle size slightly due to the size of Si69 molecules, but which is too little to be observed by TEM.

Si69 modified particles were examined by FTIR and TG after unreacted Si69 was removed by washing with anhydrous ethanol for five times. The grafting density of Si69 on the particle surface was determined. Moreover, the contact angles and the dispersibility of modified nanosilica particles were also changed significantly. It is confirmed that the hydrophobic Si69 was successfully modified on the nanosilica particles by microinjection.

3.6. Effects of surface silanol

The TG curves of the Si69-modified particles (ethanol washed) after spray drying and after thermal treatment are shown in Fig. 6. From Fig. 6, the grafting densities of the Si69-modified particles were calculated, as listed in Table 4.

Table 4 shows that the grafting densities of Silica(p) and Silica(f) increase much after thermal treatment, indicating that the hydrolysate of Si69 has a uniform mixing with the nanosilica particles and more hydrolysates graft on the particle surface at high temperature. The

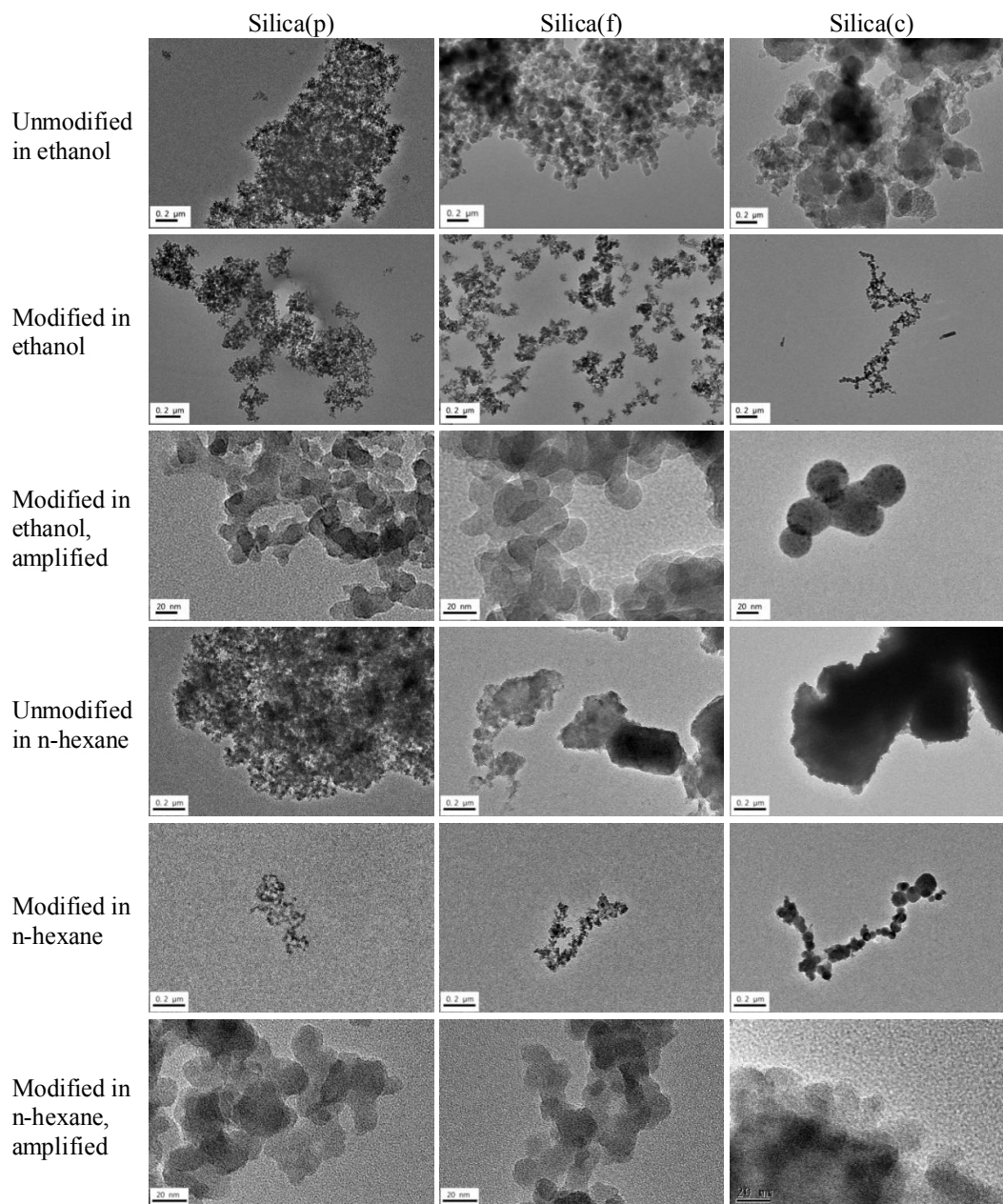


Fig. 5. TEM images of Si69-modified particles after ultrasonic dispersion in ethanol and n-hexane.

thermal treatment increases the grafting density much for Silica(f) and only a little for Silica(c). This indicates that the different activities of the surface silanol affect the surface modification, rather than the densities of silanol. The grafting densities of Silica(c) after spray drying and after thermal treatment are the highest, being 3.13 nm^{-2} and 3.25 nm^{-2} , respectively. The close grafting densities shows that Silica(c) is easily grafted with the hydrolysate even without the thermal treatment and has the highest activity of surface silanol among the three kinds of particles.

Fig. 7 shows the infrared spectra of silanol on unmodified nanosilica particles, which include isolated silanol, geminal silanol, and hydrogen-bonded silanol. The peak at $3200 - 3800 \text{ cm}^{-1}$ is assigned to the stretching vibration of silanol [42,43]. The peak at 3442 cm^{-1} and a shoulder peak at 3637 cm^{-1} for Silica(c) are assigned to the hydrogen-bonded and isolated silanol, respectively, and are observed at lower wavenumbers than the values reported in the literature, namely 3520 cm^{-1} and 3720 cm^{-1} [44]. It is difficult to distinguish isolated

silanol and geminal silanol in the infrared spectra, as their properties are probably similar [45]. The highest intensity of the shoulder peak of Silica(c) at 3637 cm^{-1} corresponds to the most isolated silanol on the particle surface and the highest average activity of silanol. The higher the average activity, the greater is the grafting density during aqueous mixing and spray drying. Therefore, the grafting density of Silica(c) during aqueous mixing and spray drying is the highest and the increase during the subsequent thermal treatment is not obvious, compared to the cases of Silica(p) and Silica(f).

3.7. Effects of surface acid sites

The surface of nanosilica particles contains abundant silanol, which has the properties of a Brønsted acid that provides protons and/or a Lewis acid that accepts electron pairs. The condensation between the silanol of the particle surface and the hydrolysate of a silane coupling agent occurs under the condition that the silanol on the particle surface

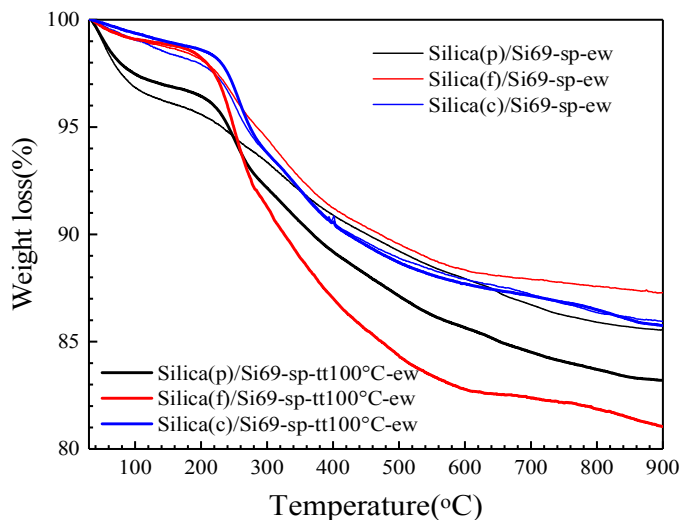


Fig. 6. TG curves of Si69-modified nanosilica particles after spray drying and after thermal treatment.

Table 4

Comparison of grafting densities after spray drying and after thermal treatment.

SiO ₂ :Si69 = 1:1	After spray drying			After thermal treatment		
	Silica(p)	Silica(f)	Silica(c)	Silica(p)	Silica(f)	Silica(c)
Silanol density / nm ⁻²	10.1	5.7	7.8	10.1	5.7	7.8
Grafting density / nm ⁻²	2.28	1.79	3.13	2.96	3.07	3.25
Silanol grafting ratio / %	22.6	31.4	40.1	29.3	53.9	41.7

provides a proton, that is, the surface has a Brønsted acid site [46,47]. A high capacity of Brønsted acid sites means a high activity of silanol on the particle surface.

The relative capacity of the total acid sites of the nanosilica particles was examined by TPD, using ammonia as the molecular probe. Ammonia molecules combine with the acid sites present on the particle surface at set temperature and gradually desorb as the temperature increases. The amount of ammonia desorbed indicates the capacity of the total acid sites. A stronger acid results in firmer bonding of

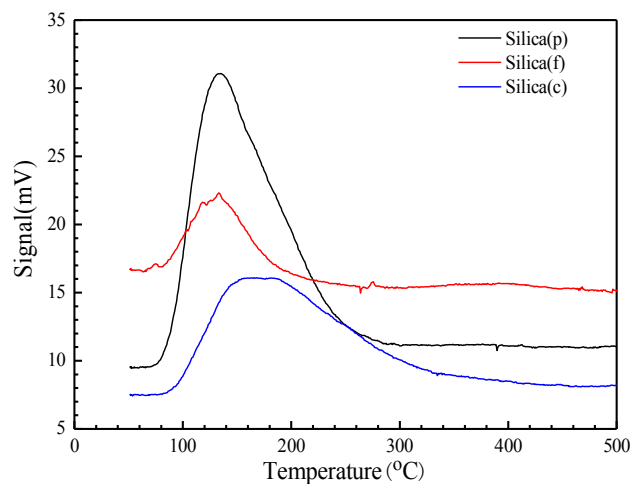


Fig. 8. Ammonia desorption curves of three kinds of unmodified nanosilica particles.

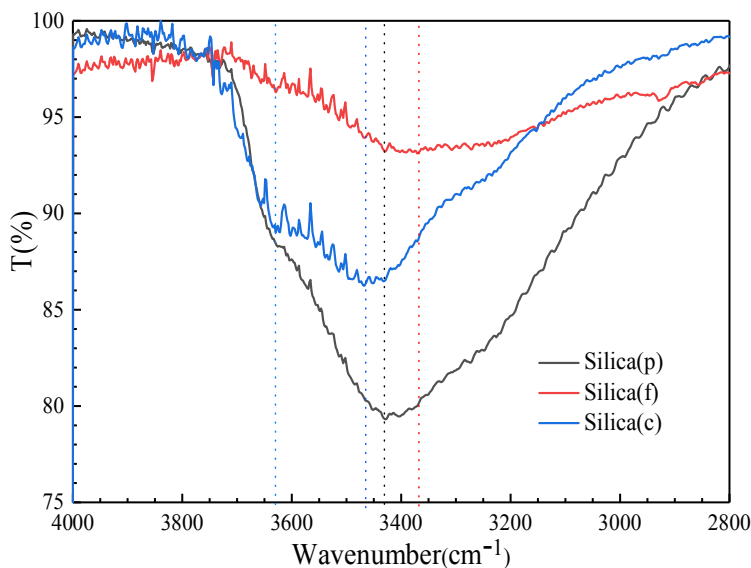


Fig. 7. Infrared spectra of silanol on three kinds of unmodified nanosilica particles.

Table 5
Desorption properties of three kinds of unmodified nanosilica particles.

Particles	Silica(p)	Silica(f)	Silica(c)
Temperature of desorption peak / °C	134.8	126.5	180.6
Temperature of desorption completed / °C	300	230	400
Relative capacity of the total acid sites per unit area	7.1	1.0	3.2

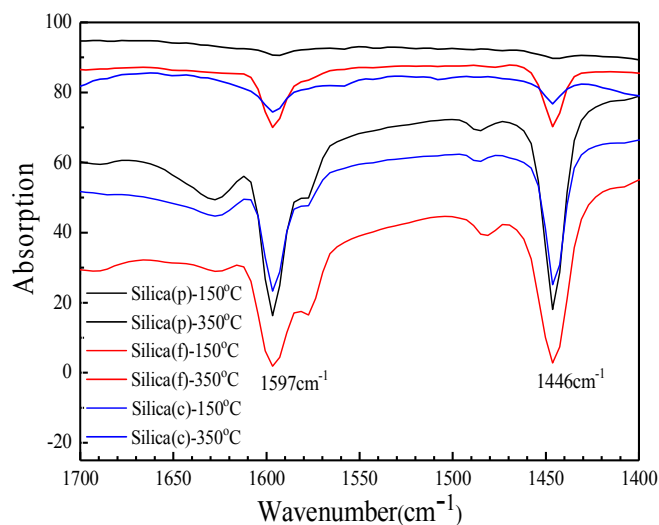


Fig. 9. Infrared spectra of the three kinds of unmodified nanosilica particles with pyridine adsorbed.

Table 6
Relative capacities of Brønsted/Lewis acid sites of three kinds of unmodified nanosilica particles.

Relative capacity per unit area		Silica(p)	Silica(f)	Silica(c)
Total acid	Brønsted	3.55	0.50	1.60
	Lewis	3.55	0.50	1.60
Medium-strong acid	Brønsted	0	0.18	0.46
	Lewis	0	0.18	0.46

ammonia molecules to the surface, which is reflected at the higher desorption temperature. The ammonia desorption curves for the unmodified particles are shown in Fig. 8. From Fig. 8, the temperature of the desorption peak and the approximate temperature at which desorption is completed were determined for the three kinds of particles. The area of the desorption peak of the sample was integrated, and the relative capacity of the total acid sites per unit area of the sample was calculated, as shown in Table 5. Table 5 shows that Silica(c) has the highest desorption temperature, indicating the surface acids are strong. Silica(p) and Silica(f) have weaker acids, and Silica(f) has the lowest capacity of the total acid sites.

The Brønsted and Lewis acid sites were examined by in-situ FTIR spectroscopy, using pyridine as the molecular probe. The absorption peak at 1540 cm^{-1} or 1630 cm^{-1} is assigned to a Brønsted acid, whereas the peak at 1450 cm^{-1} is assigned to a Lewis acid. By comparing the positions and intensities of the infrared absorption peaks of the sample after desorption at 150 °C and 350 °C , the relative capacities of the Brønsted/Lewis acid on different silica surfaces were obtained. The infrared spectra of the three kinds of unmodified nanosilica particles with pyridine adsorbed are shown in Fig. 9. It shows that the absorption peaks of the Brønsted acid are observed at 1597 cm^{-1} , and that of the Lewis acid at 1446 cm^{-1} . Comparing the two absorption peaks in Fig. 9, it is seen that the relative capacities of the Brønsted and Lewis acid sites for the same sample are almost equal, being about half

of the total acid sites. The absorption peak of the sample after desorption at 150 °C represents the capacity of the total acid sites, including weak, medium, and strong acids, whereas that at 350 °C represents the capacity of a medium-strong acid. From Fig. 9 and with the relative capacities of the total acid sites from TPD, the relative capacities of Brønsted/Lewis acid sites of the three kinds of unmodified nanosilica particles are calculated, as shown in Table 6.

From Table 6, it is seen that Silica(p) has the highest capacity of total acid sites, but no medium-strong Brønsted acid sites. Silica(f) has the lowest capacity of total acid sites, and a certain proportion of medium-strong Brønsted acid sites. Silica(c) has the highest capacity of medium-strong Brønsted acid sites, indicating a high activity of silanol. This enables the modification of Silica(c) to achieve the highest grafting density during the aqueous mixing and spray drying stages, and the highest final grafting density among the three kinds of silica.

4. Conclusions

The hydrophobic modifier Si69 was successfully modified on nanosilica particle surfaces at a high grafting density in aqueous solution by employing micro-injection in combination with the route of aqueous mixing, spray drying, and thermal treatment. Precipitated, fumed, and colloidal silica particles were modified up to a high grafting density of 2.96 nm^{-2} , 3.07 nm^{-2} and 3.25 nm^{-2} , respectively. The dispersibility of the Si69-modified nanosilica particles is improved significantly. For colloidal silica, the chemical grafting proportion of Si69 reaches about 90 wt% at the mass ratio of $\text{SiO}_2\text{:Si69} = 1\text{:}0.1$. Because of the existence of sufficient isolated silanol as well as the highest capacity of medium-strong Brønsted acid sites, the colloidal silica surface has the highest activity of silanol, achieving the highest grafting density among the three kinds of silica.

CRedit author statement

Author 1: Keyi Yu: Conceived and designed the experiments, Performed the experiments, Collected the data, Performed the analysis, Wrote the paper, Contributed reagents/materials/analysis tools

Other contribution: Performed the revision

Author 2: Ling Yang: Conceived and designed the experiments, Performed the experiments, Performed the analysis, Contributed reagents/materials/analysis tools

Other contribution: Performed the revision

Author 3: Jingyuan Wang: Performed the experiments, Performed the analysis

Other contribution: Performed the revision

Author 4: Zirui Zhu: Performed the experiments, Contributed reagents/materials/analysis tools

Author 5: Ting-Jie Wang: Conceived and designed the experiments, Performed the analysis, Wrote the paper, Contributed reagents/materials/analysis tools

Other contribution: Performed the revision

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors wish to express their appreciation for the financial support of this study by the National Key R&D Program of China (2017YED0200704) and the National Natural Science Foundation of China (NSFC No.21176134).

References

- [1] Y. Li, B. Han, L. Liu, F. Zhang, L. Zhang, S. Wen, Y. Lu, H. Yang, J. Shen, Surface modification of silica by two-step method and properties of solution styrene butadiene rubber (SBR) nanocomposites filled with modified silica, *Compos. Sci. Technol.* 88 (2013) 69–75.
- [2] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites—a review, *Prog. Polym. Sci.* 38 (2013) 1232–1261.
- [3] S.Y. Chen, C.Y. Huang, T. Yokoi, C.Y. Tang, S.J. Huang, J.J. Lee, J.C.C. Chan, T. Tatsumi, S. Cheng, Synthesis and catalytic activity of amino-functionalized SBA-15 materials with controllable channel lengths and amino loadings, *J. Mater. Chem.* 22 (2012) 2233–2243.
- [4] X. Wang, K.S.K. Lin, J.C.C. Chan, S. Cheng, Direct synthesis and catalytic applications of ordered large pore aminopropyl-functionalized SBA-15 mesoporous materials, *J. Phys. Chem. B* 109 (2005) 1763–1769.
- [5] B. Elisabeth, H. Vincent, L. Jessem, P. Sarunas, P. Claire-Marie, K. Bengt, S. Sofia, Chemical modifications of Au/SiO₂ template substrates for patterned biofunctional surfaces, *Langmuir* 27 (2011) 678.
- [6] J. Kim, J. Cho, P.M. Seidler, N.E. Kurland, V.K. Yadavalli, Investigations of chemical modifications of amino-terminated organic films on silicon substrates and controlled protein immobilization, *Langmuir* 26 (2010) 2599–2608.
- [7] M. Muresanu, A. Reiss, I. Stefanescu, E. David, V. Parvulescu, G. Renard, V. Hulea, Modified SBA-15 mesoporous silica for heavy metal ions remediation, *Chemosphere* 73 (2008) 1499–1504.
- [8] T. Yokoi, T. Tatsumi, H. Yoshitake, Fe³⁺ coordinated to amino-functionalized MCM-41: an adsorbent for toxic oxyanions with high capacity, resistibility to inhibiting anions, and reusability after a simple treatment, *J. Colloid Interface Sci.* 274 (2004) 451–457.
- [9] P. Chu, H. Zhang, J. Zhao, F. Gao, Y. Guo, B. Dang, Z. Zhang, On the volume resistivity of silica nanoparticle filled epoxy with different surface modifications, *Compos. Part A Appl. Sci.* 99 (2017) 139–148.
- [10] J. Lin, X. Wu, C. Zheng, P. Zhang, B. Huang, N. Guo, L. Jin, Synthesis and properties of epoxy-polyurethane/silica nanocomposites by a novel sol method and in-situ solution polymerization route, *Appl. Surf. Sci.* 303 (2014) 67–75.
- [11] Y. Xie, C.A.S. Hill, Z. Xiao, H. Miltz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: a review, *Compos. Part A Appl. Sci.* 41 (2010) 806–819.
- [12] J.W.T. Brinke, S.C. Debnath, L.A.E.M. Reuvekamp, J.W.M. Noordermeer, Mechanistic aspects of the role of coupling agents in silica–rubber composites, *Compos. Sci. Technol.* 63 (2003) 1165–1174.
- [13] N. Suzuki, M. Ito, F. Yatsuyanagi, Effects of rubber/filler interactions on deformation behavior of silica filled SBR systems, *Polymer* 46 (2005) 193–201.
- [14] G. Seo, S.M. Park, K. Ha, K.T. Choi, C.K. Hong, S. Kaang, Effectively reinforcing roles of the networked silica prepared using 3,3'-bis(triethoxysilylpropyl)tetrasulfide in the physical properties of SBR compounds, *J. Mater. Sci.* 45 (2010) 1897–1903.
- [15] H. Peng, L. Liu, Y. Luo, X. Wang, D. Jia, Effect of 3-propionylthio-1-propyl-trimethoxysilane on structure, mechanical, and dynamic mechanical properties of NR/Silica composites, *Polym. Compos.* 30 (2010) 955–961.
- [16] V. Tangpasuthadol, A. Intasiri, D. Nuntivanich, N. Niyompanich, S. Kiatkamjornwong, Silica-reinforced natural rubber prepared by the sol–gel process of ethoxysilanes in rubber latex, *J. Appl. Polym. Sci.* 109 (2010) 424–433.
- [17] B.P. Kappate, C. Das, A. Das, D. Basu, S. Wiessner, U. Reuter, G. Heinrich, Reinforced chloroprene rubber by in situ generated silica particles: evidence of bound rubber on the silica surface, *J. Appl. Polym. Sci.* 133 (2016) 43717.
- [18] B. Chaichua, P. Prasassarakich, S. Poompradub, In situ silica reinforcement of natural rubber by sol–gel process via rubber solution, *J. Sol-Gel Sci. Technol.* 52 (2009) 219–227.
- [19] S. Thongsang, N. Sombatsompom, A. Ansarifard, Effect of fly ash silica and precipitated silica fillers on the viscosity, cure, and viscoelastic properties of natural rubber, *Polym. Adv. Technol.* 19 (2010) 1296–1304.
- [20] S. Prasertsri, N. Rattanasom, Mechanical and damping properties of silica/natural rubber composites prepared from latex system, *Polym. Test.* 30 (2011) 515–526.
- [21] A. Ansarifard, A. Azhar, N. Ibrahim, S.F. Shiah, J.M.D. Lawton, The use of a silanised silica filler to reinforce and crosslink natural rubber, *Int. J. Adhes. Adhes.* 25 (2005) 77–86.
- [22] M. Castellano, L. Conzatti, G. Costa, L. Falqui, A. Turturro, B. Valenti, F. Negroni, Surface modification of silica: 1. Thermodynamic aspects and effect on elastomer reinforcement, *Polymer* 46 (2005) 695–703.
- [23] J.H. Lee, B.S. Kim, J.O. Lee, S. Imaoka, K. Yoshinaga, Cross-linking of grafted copolymer on colloidal silica and introduction of surface amino group, *Polym. J.* 39 (2007) 1018–1024.
- [24] K. K. Yoshinaga, H. Karakawa Sueishi, Preparation of monodispersed polymer-modified colloidal silica particles of less than 50 nm diameter, *Polym. Adv. Technol.* 7 (1996) 53–56.
- [25] Y.K. oshinaga, Y. Tani, Y. Tanaka, Surface modification of fine colloidal silica with copolymer silane-coupling agents composed of maleic anhydride, *Colloid Polym. Sci.* 280 (2002) 85–89.
- [26] C. Zhao, Z. Li, H. Hu, Y. Yang, Y. Huang, J. Yang, In-situ preparation of surface-functionalized SiO₂ nanoparticles with controllable sizes, *J. Nanosci. Nanotechnol.* 17 (2017) 729–734.
- [27] S. Kohjiya, Y. Ikeda, In situ formation of particulate silica in natural rubber matrix by the sol-gel reaction, *J. Sol-Gel Sci. Technol.* 26 (2003) 495–498.
- [28] S.H. Ahn, S.H. Kim, S.G. Lee, Surface-modified silica nanoparticle-reinforced poly(ethylene 2,6-naphthalate), *J. Appl. Polym. Sci.* 94 (2010) 812–818.
- [29] V.M. Gun'ko, M.S. Vedamuthu, G.L. Henderson, J.P. Blitz, Mechanism and kinetics of hexamethyldisilazane reaction with a fumed silica surface, *J. Colloid Interface Sci.* 228 (2000) 157–170.
- [30] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, Aminosilane as a coupling agent for cyclopentadienyl ligands on silica, *J. Organomet. Chem.* 587 (1999) 38–45.
- [31] G.C. Ossenkamp, T. Kemmitt, J.H. Johnston, New approaches to surface alkoxyated silica with increased hydrolytic stability, *Chem. Mater.* 13 (2001) 3975–3980.
- [32] K.C. Vrancken, K. Possemiers, P.V.D. Voort, E.F. Vansant, Surface modification of silica gels with aminoorganosilanes, *Colloids Surf. A: Physicochem. Eng. Aspects* 98 (1995) 235–241.
- [33] M. Zaboriski, A. Vidal, G. Ligner, H. Balard, E. Papirer, A. Burneau, Comparative study of the surface hydroxyl groups of fumed and precipitated silicas. I. Grafting and chemical characterization, *Langmuir* 5 (1989) 447–451.
- [34] H.E. Bergna, W.O. Roberts, *Colloidal Silica: Fundamentals and Applications*, CRC Press, Boca Raton, 1994.
- [35] H.E. Bergna, The colloid chemistry of silica, *Adv. Chem. Ser.* 234 (1994) 1–47.
- [36] B. Qiao, Y. Liang, T.J. Wang, Y. Jiang, Surface modification to produce hydrophobic nano-silica particles using sodium dodecyl sulfate as a modifier, *Appl. Surf. Sci.* 364 (2016) 103–109.
- [37] B. Qiao, T.J. Wang, H. Gao, Y. Jin, High density silanization of nano-silica particles using γ -aminopropyltriethoxysilane (APTES), *Appl. Surf. Sci.* 351 (2015) 646–654.
- [38] D.F. Cadogan, D.T. Sawyer, Gas-solid chromatography using various thermally activated and chemically modified silicas, *Anal. Chem.* 42 (1970) 190–195.
- [39] J. Zheng, D. Han, X. Ye, X. Wu, Y. Wu, Y. Wang, L. Zhang, Chemical and physical interaction between silane coupling agent with long arms and silica and its effect on silica/natural rubber composites, *Polymer* 135 (2018) 200–210.
- [40] R.A. Howald, Book and media review—chemical bonds and bond energy (Sanderson, R.T.), *J. Chem. Educ.* 48 (1971) 561.
- [41] V. Dugas, Y. Chevalier, Chemical reactions in dense monolayers: in situ thermal cleavage of grafted esters for preparation of solid surfaces functionalized with carboxylic acids, *Langmuir* 27 (2011) 14188–14200.
- [42] G. Ghiotti, E. Garrone, C. Morterra, F. Boccuzzi, Infrared study of low temperature adsorption. 1. CO on aerosil, an interpretation of the hydrated silica spectrum, *J. Phys. Chem.* 83 (1979) 2863–2869.
- [43] P. Hoffmann, E. Knözinger, Novel aspects of mid and far IR Fourier spectroscopy applied to surface and adsorption studies on SiO₂, *Surf. Sci.* 188 (1987) 181–198.
- [44] B.A. Morrow, A.J. McFarlan, Infrared and gravimetric study of an aerosil and a precipitated silica using chemical and H/D exchange probes, *Langmuir* 7 (1991) 1695–1701.
- [45] A. Burneau, O. Barres, J.P. Gallas, J.C. Lavalley, Comparative study of the surface hydroxyl groups of fumed and precipitated silicas. 2. Characterization by infrared spectroscopy of the interactions with water, *Langmuir* 6 (1990) 1364–1372.
- [46] T. Bezrodna, G. Puchkovska, V. Shimanovska, I. Chashechnikova, T. Khalyavka, J. Baran, Pyridine-TiO₂ surface interaction as a probe for surface active centers analysis, *Appl. Surf. Sci.* 214 (2003) 222–231.
- [47] B. Bonelli, M. Cozzolino, R. Tesser, M.D. Serio, M. Piumetti, E. Garrone, E. Santacesaria, Study of the surface acidity of TiO₂/SiO₂ catalysts by means of FTIR measurements of CO and NH₃ adsorption, *J. Catal.* 246 (2007) 293–300.