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Article

Silica Modified by Using Alcohol Polyoxyethylene Ether and Silane Coupling Agent together to Achieve High Performance Rubber Composites Using Latex Compounding Method

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Abstract: Nowadays, the study of preparing silica/rubber composites, which can be used in "green tire", in energy saving method is fast-growing. In our work, silica modified by using alcohol polyoxyethylene ether (AEO) and 3-Mercaptopropyltriethoxysilane (K-MEPTS) together were investigated. Thermal gravimetric analyzer (TGA) result indicated that both AEO and K-MEPTS could be grafted on the silica surface. Raman spectroscopy confirmed that the AEO could generate a certain steric hindrance for the mercaptopropyl group on K-MEPTS. Silica modified by using AEO and K-MEPTS together can be completely co-coagulated with the rubber in preparing silica/natural rubber (NR) composites by latex compounding method. AEO can form a physical interface between silica and rubber; meanwhile, K-MEPTS can form a chemical interface between silica and rubber. The effects of chemical and physical interface between silica and rubber on dynamic and mechanical performances of silica/NR composites were also given in this research. A proper combination of physical and chemical interface between silica and NR can improve performances of silica/NR composites.

Keywords: chemical and physical interface; surface modification of silica; latex compounding method; silica/NR composite

1. Introduction

Silica is a non-carbon filler that serves as an extremely important reinforcing filler in the rubber industry [1]. Previous researchers have confirmed that silica could provide a combination of good mechanical performances [2], high wet grip resistance [3], and low rolling resistance [4] for silica/rubber composites. At present, silica/rubber composites are commonly used in producing the tread of "green tire" [5,6].

As an inorganic particle, silica has huge amounts of hydroxyl groups (–OH) on its surface [7], leading to the nature of the silica particle [8-10]. Therefore, silica particle is less compatible with a hydrophobic polymer, such as rubber [11]. However, the silica surface is modifiable because of the numerous reactive hydroxyl groups [12,13]. Silica modification is an effective way to improve the compatibility between silica and rubber. Treatment with reactive silane coupling agent (SCA) is one of the major methods in silica modification [14,15]. In principle, SCA possesses readily hydrolyzable alkoxy group that can react with hydroxyl groups on the silica surface to form a stable siloxane linkage [16]. Surface active agent (SAA) is another modifier that is commonly used in silica

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modification. SAA can absorb on the silica surface, resulting in covering silica surface and reducing the amount of hydroxyl groups exposed.

NR, which contains 93%–95% cis-1,4-polyisoprene, is an essential biosynthesized polymer [17]. It is naturally in the form of a colloidal system known as NR latex, in which rubber particles are dispersed in an aqueous medium [18,19]. Therefore, the latex compounding method can be applied in preparing silica/NR composites to solve the problems of low efficiency and high pollution in the outdated mechanical blending method [20,21].

The key to the latex compounding method is to make sure that the silica can be completely co-coagulated with the rubber. What's more, the performance of silica/rubber composites is determined by the silica dispersion and the interface between silica and rubber. Thus, preparing a modified silica with an ideal organic surface is important for preparing high performance silica/rubber composites by latex compounding method.

In previous research, silica/rubber masterbatches had been prepared by latex compounding method [21-24]. Various sulfide containing SCAs had been used for silica modification in these preparations. The dispersion of silica in aqueous phase was improved by the help of sulfide-containing SCA. Moreover, the sulfide-containing SCA could form "coupling bridge" [25], which was a typical chemical interface between silica and rubber, resulting in improving the dynamic performances of silica/rubber composites [26]. The essence of silica modified by SCA in the aqueous phase is that the hydroxyl groups on the silica react with the hydroxyl groups of hydrolysates of SCA [27]. The polycondensation also occurs among the hydroxyl groups of hydrolysates of SCA, producing the polycondensates of SCA, which results in the aggregation of several SCA molecules [28]. Therefore, using SCA only in silica modification is not efficient enough to improve the dispersion of silica. Meanwhile, only chemical interface existing between silica and rubber is detrimental to the stretching of rubber molecular chain under external force [29-31]. Moreover, the reaction between rubber and sulfide-containing SCA ("scorchy" behavior) is inevitable during the process [32], even though the mixing time and temperature are precisely controlled. Therefore, utilizing sulfide-containing SCA only in silica modification for preparing silica/rubber composites is not the ideal method.

SAA could modify silica directly in the aqueous phase without polycondensation, and most of SAA had no react with rubber under any conditions. Therefore, only physical interface between silica and rubber can be formed by the help of SAA [33-35]. However, dynamic performance of silica/rubber composites is very poor in the absence of chemical interface between silica and rubber [8,29]. Meanwhile, in our previous research, silica modified by SAA can not be completely co-coagulated with the rubber in preparing silica rubber masterbatches by latex compounding method.

In this research, the silica/NR masterbatches, which was a floc containing silica and rubber, were prepared by latex compounding method. Alcohol polyoxyethylene ether (AEO) [36] (as presented in Fig. 1), which was a widely used nonionic SAA, and 3-Mercaptopropyltriethoxysilane (K-MEPTS) [37] (as presented in Fig. 1), which had been commercially developed and widely used in the rubber industry, were selected as modifiers to use together in silica modification in aqueous phase. This method was rarely mentioned by previous researchers. The magnitude of chemical and physical interface between silica and rubber could be varied by adjusting the amount of AEO and K-MEPTS used in silica modification. The performances of silica/NR composites, which contained different ratios of AEO and K-MEPTS, were compared. The effects of chemical and physical interface between silica and rubber on different performance of silica/NR composites were also shown in this comparison. Furthermore, the interaction between AEO and K-MEPTS also played an important role in the preparation of silica/NR composites. The effect of this interaction on silica modification and preparation of silica masterbatches and composites was introduced in this research.

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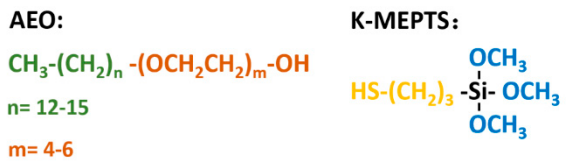

Fig. 1 Chemical structure of AEO and K-MEPTS

2. Experimental

2.1. Materials

High-ammonia NR latex with 60% total solid content was purchased from Hainan Rubber Industry Group Co., Ltd. (China). Precipitated silica water slurry of K-160 (nanoparticle size: 20–30 nm, BET specific surface: 160.06 m^2/g) was produced by Wilmar China (Jiamusi, China). AEO (average molecular weight: 421) was provided by Usolf. K-MEPTS (molecular weight: 196) was obtained from Nanjing Capatue Chemical Co., Ltd. (China). The rest of the required materials were commercially available.

2.2. Preparation of modified silica

Water was added into the precipitated silica slurry, and the solid content of silica slurry was measured to dilute to the 10% concentration. The silica water slurry was conducted under high-speed stirring for 30 min to obtain a stable suspension. Five beakers, numbered 1–5, were prepared, and 1000 g of silica slurry was transferred to each beaker. The temperatures of all silica water slurry were heated to 70 °C under stirring. K-MEPTS (6, 6, 4, and 2 g) was added into beakers 1–4, and AEO (4, 6, 8, and 8 g) was added into beakers 2–5, respectively. The slurry was stirred for 0.5 h, and the modified silica slurry was then obtained. According to the amount of AEO and K-MEPTS added in silica modification, we named the modified silica in beakers 1–5 as A0K6-MS, A4K6-MS, A6K4-MS, A8K2-MS, and A8K0-MS, respectively. The amounts of KH590 and AEO used in different modified silica are listed in Table 1.

Table 1 Formulation of modified silica and its name

Materials	A0K6-MS	A4K6-MS	A6K4-MS	A8K2-MS	A8K0-MS
Silica (dry weight) /g	100	100	100	100	100
K-MEPTS /g	6	6	4	2	0
AEO /g	0	4	6	8	8

2.3. Preparation of masterbatches

The modified silica slurry was cooled to room temperature and blended with the NR latex. The solid content of the NR latex was confirmed in advance, and the weight ratio of silica to NR was 50:100 (e.g., 50 g of silica nanoparticles for every 100 g solid content of NR). Then, mixture of silica and NR latex was stirred for 0.5 h and coagulated with 3% formic acid solution. Finally, the flocs were washed with water six times and then dehydrated in a drying oven at 60 °C for 36 h to obtain silica/NR masterbatches. The masterbatches compounded with A0K6-MS, A4K6-MS, A6K4-MS, A8K2-MS, and A8K0-MS in preparation was named A0K6-MB, A4K6-MB, A6K4-MB, A8K2-MB, and A8K0-MB, respectively.

2.4. Preparation of silica/NR composites

The formulation of silica/NR compounds is demonstrated in Table 2. Silica/NR compounds were obtained by three stages of mixing. First, the masterbatches were masticated in an internal mixer

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equipped with an oil circulating system to keep the processing temperature at 55 °C. Then, zinc oxide, stearic acid, and *N*-1,3-dimethylbutyl-*N*'-phenyl-*p*-phenylenediaminewere added to the masterbatches successively. Second, compounds were kneaded for 5 min in the same internal mixer at 150 °C and then naturally cooled down to room temperature. Finally, *N*-cyclohexyl-2-benzothiazole-sulfenamide, diphenyl guanidine, and sulfur were uniformly blended in sequence with the cooled compound on a 6-inch mill (Shanghai Rubber Machinery Works No. 1, China) under room temperature. The total mixing time was kept not more than 15 min. The silica/NR compounds that contain A4K6-MB, A6K4-MB, and A8K2-MB are denoted as A4K6-C, A6K4-C, and A8K2-C, respectively.

Table 2 Formulation of silica/NR compounds

Materials	Amount (phr[a])
Masterbatches	155
Stearic acid	2.0
Zinc oxide	5.0
N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine	2.0
N-Cyclohexyl-2-beozothiazole sulfenamide	2.0
1,3-Diphenylguanidine	1.0
Sulfur	2.0

[a] parts per hundred of rubber.

The scorch time (T_{10}) and optimum cure time (T_{90}) of the compound were measured using disc vulkameter. The compounds were vulcanized at 143 °C according to their optimum cure time (T_{90}) in a standard mold to produce the silica/NR vulcanizates, which were stored at room temperature for at least 24 h before determining the performances.

2.5. Characterizations

The groups on pure and modified silica was characterized by Fourier transform infrared spectroscopy (FT-IR; Bruker Optik GmbH Co, Tensor 27, Germany), using the absorption mode under a wave number ranging from 4,000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.The samples were pressed into pellets together with potassium bromide.

Raman measurements were obtained using a Renishaw in Via Confocal Raman spectrometer (Gloucestershire, UK) coupled to a DMLM Leica microscope. The laser excitation wavelength is 514 nm. The power of 514 nm argon ion excitation laser at the source is approximately 50 mW, and 20 mW (highest power) at the surface of the sample. The Raman spectra of the samples were obtained from pressed solid samples in a sealed capillary tube.

Weight losses measurements of pure and modified silica and the masterbatches were performed on a thermal gravimetric analyzer (TGA) STARe system (Mettler–Toledo Co., Switzerland) under nitrogen atmosphere. Samples for TGA tests were heated at a heating rate of 10 °C/min. The residual weight of masterbatches, NR, silica, K-MEPTS and AEO were recorded as R_m, R_r, R_s, R_5 and R_A, respectively.

The filler dispersion in silica/NR masterbatches and silica/NR composites were observed under a Tecnai G2 20 transmission electron microscope (TEM FEI Co., USA) with an accelerating voltage of 200 kV. Thin sections for TEM observations were cut by a microtome at −100 °C and collected on copper grids.

The dynamic rheological performances of silica/NR compounds and silica/NR composites were analyzed using RPA2000 (Alpha Technologies Co., USA) at 60 °C. For the rubber compounds, the strain varied from 0.1% to 400% at the test frequency of 1 Hz. For the rubber vulcanizates, the strain varied from 0.1% to 40% at the test frequency of 1 Hz. The test of each specimen was repeated 3 times.

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The vulcanization characteristics of silica/NR compounds were measured at 143°C by a P3555B2 disc vulkameter (Beijing Huanfeng Chemical Machinery Trial Plant, China). The test of each specimen was repeated 3 times.

The mechanical performances of the silica/NR composites were investigated according to ASTM D638 specifications using a CMT4104 electrical tensile tester (Shenzhen SANS Test Machine Co., China) with across head speed of 500 mm/min. The test of each specimen was repeated 5 times.

3. Results and discussion

3.1. Characterization of silica modified by AEO and K-MEPTS

3.1.1 FT-IR of pure and modified silica

As shown in Fig. 2, compared with the FT-IR spectra of the pure silica, all curves of the modified silica have absorption peaks at 2930 cm^{-1}, 2970 cm^{-1} and 2870 cm^{-1}, which is attributed to vibrations of $–CH_2–$ and $–CH_3$ bonds [38]. The appearance of organic groups, such as $–CH_2–$ and $–CH_3$, on the modified silica surface shows that K-MEPTS and AEO exist on the silica surface.

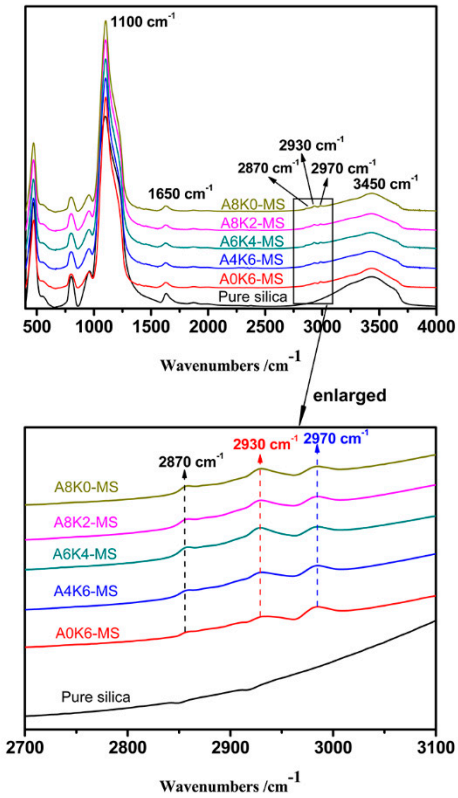

Fig. 2 FT-IR spectra of pure silica and all modified silica

The absorption peaks at 3450 cm^{-1} and 1650 cm^{-1} correspond to the stretching and deforming vibration modes of the –O–H bonds [39], respectively. The relative intensity (RI) of the peak at 3400 cm^{-1} is determined by the number of –O–H bonds; therefore, a high RI means a large amount of hydroxyl groups on the silica surface. RI can be calculated by using the normalized FT-IR data, and the RI of all samples are listed in Table 3. The total weight of modifier used in the silica modification is equal for A4K6-MS, A6K4-MS and A8K2-MS, but the RI decreases sequentially. Therefore, AEO is a more effective modifier than K-MEPTS in changing the hydrophilicity of silica. This result could be attributed to the structure of AEO molecule, which was likely to cover multiple hydroxyl groups on the silica surface. In contrast, a K-MEPTS molecule could react with up to one hydroxyl group on the silica surface. The decrease in the hydrophilic nature of silica generally means that the dispersion of

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silica in aqueous phase is improved. Therefore, silica modified by using AEO and K-MEPTS together is an effective method in improving silica dispersion in aqueous phase, which is one of the key for preparing high performance silica/NR composites by latex compounding method.

Table 3 RI of the peak at 3400 cm^{-1} for pure silica and all modified silica

Samples	Pure silica	A0K6-MS	A4K6-MS	A6K4-MS	A8K2-MS	A8K0-MS
RI	0.318	0.211	0.189	0.184	0.178	0.196

3.1.2 Raman spectroscopy of pure and modified silica

Fig. 3 shows no peak on the curve of pure silica; therefore, no organic groups presents on the surface of pure silica. Meanwhile, Fig. 3 shows one peak on the curve of A8KO-MS and two peaks on others curve. The peak at 2930 cm^{-1} corresponds to methylene bonds, demonstrating that the AEO and K-MEPTS were grafted on the silica surface. Another peak is recorded at 2570 cm^{-1}, which corresponds to –S-H bonds, indicating that K-MEPTS was grafted on the silica surface.

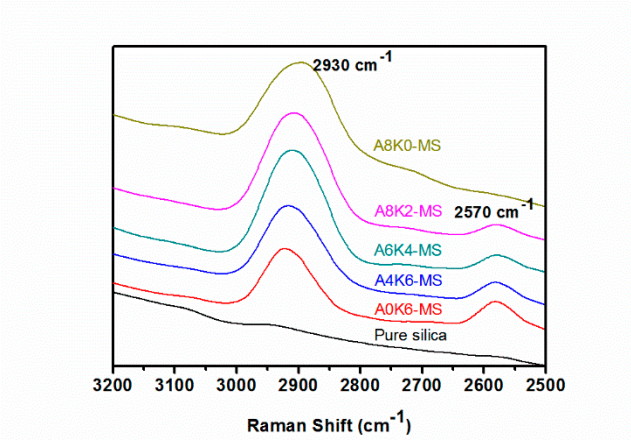

Fig. 3 Raman spectra of pure silica and all modified silica

The peak intensity around 2570 cm^{-1} for A4K6-MS is significantly weaker than that of A0K6-MS. The only difference for A0K6-MS and A4K6-MS wass whether AEO should be utilized in silica modification. The most probable reason for this result was that AEO could generate a certain steric hindrance for the mercaptopropyl group on K-MEPTS.

3.1.3 TGA curves of pure and modified silica

As illustrated in Fig. 4 and Table 4, all the samples exhibit large weight losses in the region between 35°C and 120°C (first region). The weight loss in this region was caused by the removal of the adsorbed water. In a word, the amount of adsorbed water on the silica surface shows the same tendency as the amount of hydroxyl groups on the silica surface.

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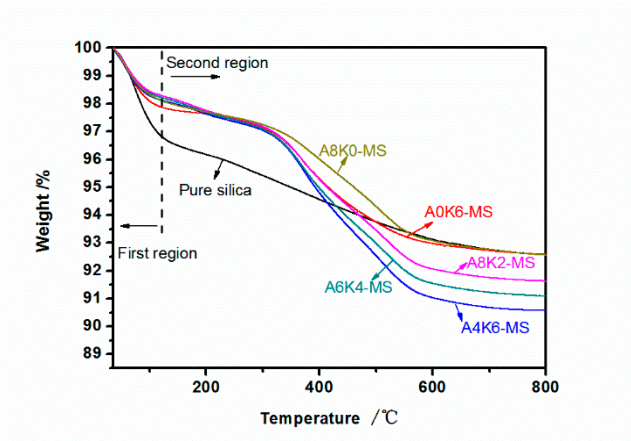

Fig. 4 TGA curves of pure silica and all modified silica

All of modified silica present a large weight loss in the region between 120°C and 800°C (second region). The weight loss of modified silica was due to the degradation of AEO and K-MEPTS, and the weight loss of pure silica was due to the dehydroxylation of hydroxyl groups. All modified silica has a larger weight loss than pure silica in the second region; meanwhile, A4K6-MS also has a larger weight loss than A0K6-MS in the second region. This is a noteworthy evidence, which indicates that both K-MEPTS and AEO were grafted on the silica surface.

Table 4 Weight losses of pure and modified silica in the first and second regions

Samples	Weight loss in the first region (35°C –120°C) /%	Weight loss in the second region (120°C –800°C) /%
Pure silica	3.16	4.27
A0K6-MS	2.13	5.31
A4K6-MS	1.88	7.54
A6K4-MS	1.78	7.13
A8K2-MS	1.71	6.66
A8K0-MS	1.90	5.55

3.1.4 Schematic diagram of modifiers on the silica surface

The interaction between AEO and K-MEPTS is shown in Fig. 5 based on the above results. The activity of the mercaptopropyl on K-MEPTS would be affected by this interaction. Therefore, the chargeability and reactivity of silica modified by using AEO and K-MEPTS together differ from that of silica modified by using K-MEPTS only.

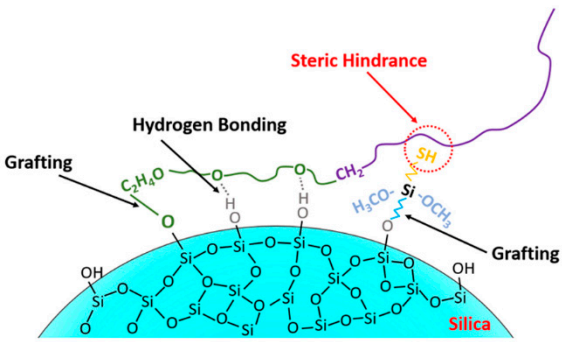

Fig. 5 Schematic diagram of the interaction between AEO and K-MEPTS in silica modification

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3.2 Characterization of silica/NR masterbatches prepared by pure silica and modified silica

3.2.1. Co-coagulation of silica/NR mixture in preparing the masterbatches

The co-coagulation of silica/NR mixture in preparing the masterbatches by use of several modified silica and pure silica (A0K0-MS) are shown in Fig. 6. Images of silica/NR mixtures, which are prepared by adding the NR latex into the silica slurries and stirring for 10 minutes, are shown in Fig. 6 (a). Images of masterbatches, which are prepared by adding the 3% formic acid solution into mixtures, are shown in Fig. 6 (b). A6K4-MS is selected as representative for silica modified by using AEO and K-MEPTS together, because the phenomenon in preparing silica/rubber masterbatches is almost the same for A4K6-MS, A6K4-MS and A8K2-MS.

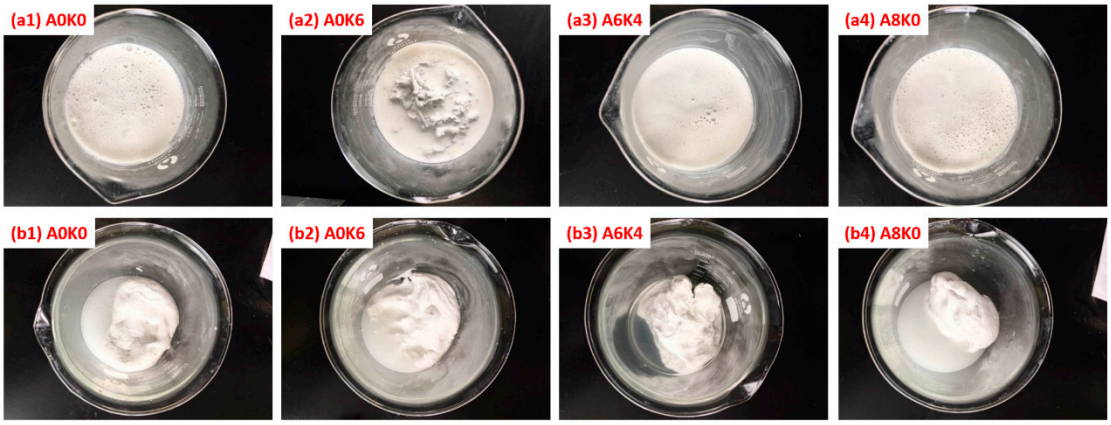

Fig. 6 Preparation process of the masterbatches with pure and modified silica

As presented in Fig. 6 (a2), part of the mixture was coagulated when NR was mixed with A0K6-MS, even if the formic acid solution was not added into this mixture. This phenomenon indicates that K-MEPTS can promote the coagulation of NR latex. As presented in Fig. 6(b), A0K6-MB, A8K0-MB, and pure silica masterbatch are largely clustered, and the residual aqueous phase is white and turbid with abundant silica. Conversely, A6K4-MB is coagulated as complete sediments, and the residual aqueous phase is clear.

The difference in coagulation phenomenon in different masterbatches was caused by electrostatic attractive or repulsive force as presented in Fig. 7. The surface of both silica particle and NR latex particle were negatively charged, causing an electrostatic repulsion in a system, as presented in Fig. 7(a) [40]. Therefore, pure silica/NR masterbatch had a huge amount of silica loss in the aqueous phase. K-MEPTS was positively charged, and its electronegativity contributed to the charge neutralization of silica particles. The changes in the silica surface charge contributed to the adsorption between rubber and silica. However, excessive K-MEPTS could result in significant positive charge on the silica surface. Therefore, a strong attractive forces between silica particles and rubber latex particles would damage the electrical layer stability of the rubber latex particles, which was destroyed in this condition, as shown in Fig. 7(b). Therefore, mixture that consisted of A0K6-MS and NR latex was coagulated in the absence of formic acid solution.

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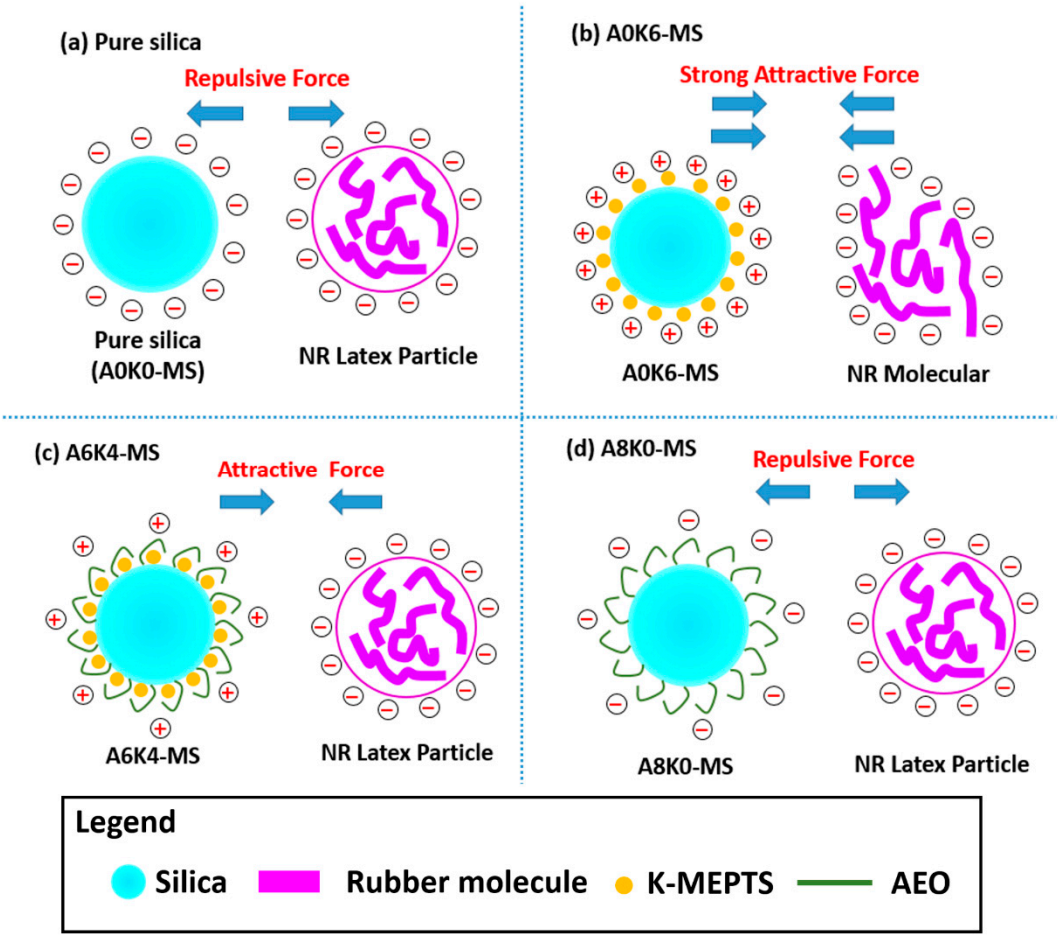

Fig. 7 Schematic diagram of the electrostatic force between pure or modified silica and NR

The positive charge of K-MEPTS, which was grafted on the silica surface, was weakened by the help of steric hindrance generated by AEO. Therefore, the attractive force between the NR latex particles and modified silica was adjusted to the appropriate level. Thus, A6K4-MB was successfully prepared. However, AEO was a nonionic surfactant that had no effect on the electrical performance of the silica surface. Therefore, a repulsive force still existed between A8K0-MS and NR latex particles, as presented in Fig. 7(d). In this condition, the co-coagulation of mixture latex, which consisted of NR latex and A8K0-MS, was unsatisfactory.

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3.2.2 Actual amount of silica in silica/NR masterbatches

Table 5 Weight losses of six kinds of silica/NR masterbatches

Samples	Weight residual /%	Theoretical amount of silica in masterbatches /phr	Actual amount of silica in masterbatches /phr
Pure NR	1.32	-	-
Pure silica	92.57	-	-
KH-590	9.13	-	-
AEO	3.27		
A0K6-MB	26.32	50	38.33
A4K6-MB	30.76	50	49.55
A6K4-MB	30.83	50	49.83
A8K2-MB	30.65	50	49.46
A8K0-MB	23.71	50	33.31
A0K0-MB	22.89	50	30.96

The actual amount of silica in the masterbatches are calculated using the following equation:

$$\text{Silica content (phr)} = \frac{100\times(R_m - R_r)}{R_s + S_A\times R_A + S_5\times R_5 - (1+S_5+S_A)\times R_m} \quad (1)$$

where R_m, R_r, R_s, R_5 and R_A are the 800°C weight (%) of masterbatches, rubber, silica, K-MEPTS and AEO, respectively. S_5 is the weight ratio of K-MEPTS to modified silica and S_A is the weight ratio of AEO to modified silica. The calculated results according to this equation are shown in Table 5. For all masterbatches that contain silica modified by using K-MEPTS and AEO together, the actual amount of silica in the masterbatches is approximately equal to the addition amount of silica (50phr). In contrast, the actual amount of silica in A0K6-MB, A8K0-MB, and A0K0-MB, is obviously lower than the addition amount of silica (50phr). This result further indicates that a huge loss of silica has occurred during coagulation when K-MEPTS or AEO is used individually in silica modification. The results are consistent with the observed macroscopic phenomena in 3.2.1.

Because of the interaction between AEO and K-MEPTS, silica modified by using AEO and K-MEPTS together has appropriate chargeability and can be completely co-coagulated with the rubber, which is another key for preparing high performance silica/NR composites by latex compounding method.

3.2.3 Micromorphology of the silica/NR masterbatches observed by TEM

As shown in Fig. 8, silica can be uniformly dispersed in the matrix without serious aggregation in these masterbatches. The silica dispersion in A6K4-MB is a little bit more homogeneous than in other samples. This composite has fewer silica aggregates than the others. This result demonstrates that the electrostatic attractive force between A6K4-MS and rubber molecule is the most appropriate in these three masterbatches that are successfully prepared.

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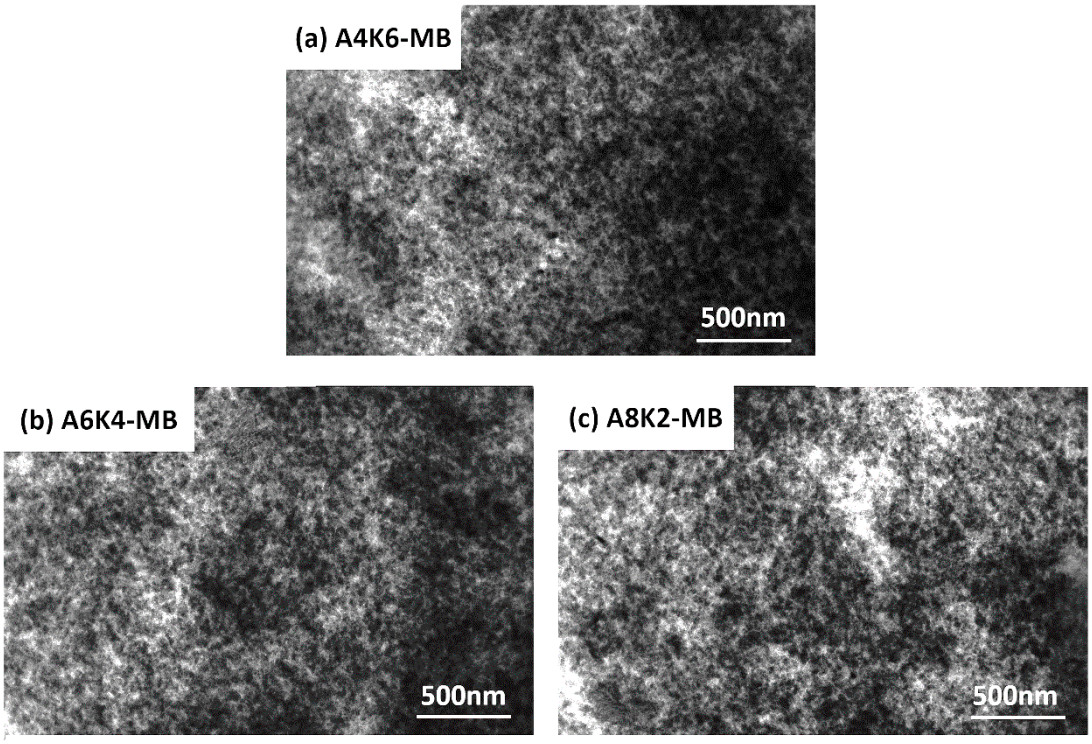

Fig. 8 TEM images of (a) A4K6-MB, (b) A6K4-MB and (c) A8K2-MB

3.3 Characterization of the preparation process of silica/NR composites

The method of preparing A4K6-C, A6K4-C and A8K2-C is described in 2.4. A0K6-C cannot be prepared by use masterbatches because of huge silica loss in preparing A0K6-MB. Therefore, mechanical blending method is used for preparing A0K6-C.

Table 6 Vulcanization characteristics of four kinds of silica/NR compounds

Samples	T_{10} /min:sec	T_{90} /min:sec	ΔM/ dNm
A0K6-C	0:39	3:02	30.39
A4K6-C	2:03	5:17	28.72
A6K4-C	3:15	5:52	26.89
A8K2-C	3:43	7:20	24.95

As shown in Table 6, A0K6-C has the shortest scorch time (T_{10}) in all silica/rubber compounds. The scorch time of A4K6-C, A6K4-C, and A8K2-C is longer than that of A0K6-C and increases in turn. The reactivity of mercaptopropyl group decreases when a certain steric hindrance generated by AEO existing. Therefore, AEO has an effect on slowing the rate of reaction between K-MEPTS and rubber. The "scorchy" problem can be mitigated by using AEO and K-MEPTS together in silica modification. Meanwhile, the △M of A0K6-C is a little bit more than that of A4K6-C. The silica modified by K-MEPTS could function as a "cross-linking point", resulting in improving crosslinking density of silica/rubber composite, which could be reflected by △M. Therefore, AEO has a little effect on preventing the reaction between K-MEPTS and rubber.

3.4 Characterization of silica dispersion in silica/NR composites

3.4.1 Payne effect of silica/NR compounds investigated by RPA

At approximately 1% strain, the G′ decreases rapidly with increasing strain and approaches to 0 kPa with sufficiently large strain as shown in Fig. 9. The Payne effect is indicated by the ΔG′, which

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is the difference between the maximum and the minimum G′ in the curve [41]. This effect can be attributed to deformation-induced changes in the microstructure of the material. The Payne effect is not significant when ΔG′ is small. The low Payne effect indicates high uniformity of the filler dispersion.

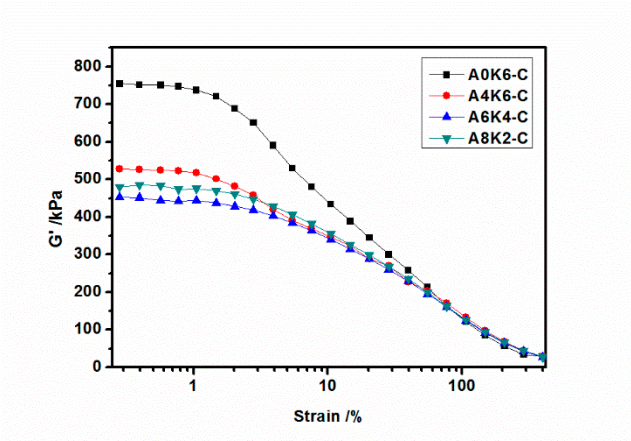

Fig. 9 Strain amplitude dependence of the storage modulus (G′) of four kinds silica/NR compounds

As shown in Fig. 9, A0K6-C exhibits a more obvious Payne effect than other silica/NR compounds. This finding indicates that the dispersion of silica modified by AEO and K-MEPTS together in the NR matrix is more homogeneous than that of silica modified by K-MEPTS only in the same matrix. As indicated in section 3.1.1, AEO could effectively reduce the hydrophilic of silica, resulting in improving silica dispersion in NR matrix. Meanwhile, the Payne effect of the composite decreases with the increase of AEO used in silica modification, and then reaches a minimum value when the weight ratio of AEO to silica is 6:100 and that of K-MEPTS to silica is 4:100 (A6K4-C). This result shows the same tendency as the silica dispersion in silica/NR masterbatches. Therefore, the silica dispersion masterbatches directly affects the dispersion of silica in silica/NR compounds, which further indicates the importance of preparing silica/NR masterbatches with homogeneous silica dispersion.

3.4.2 Micromorphology of the silica/NR composites observed by TEM

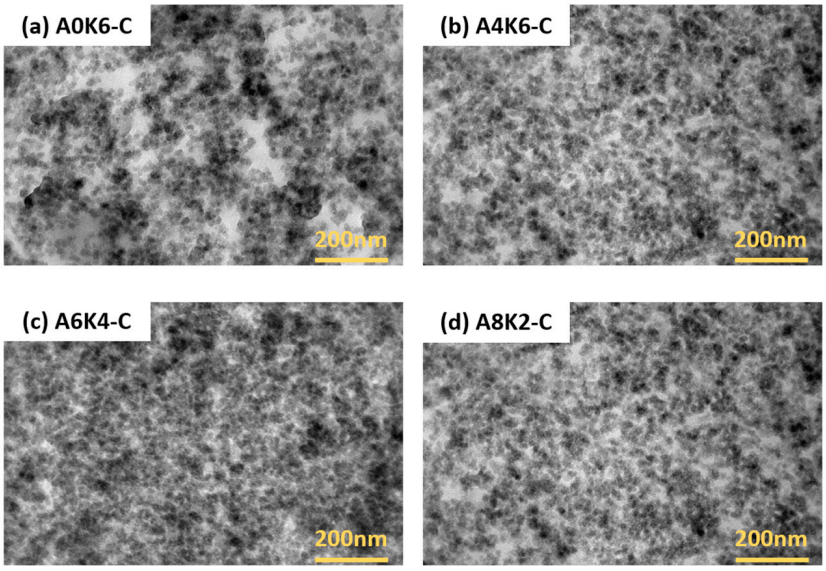

Fig. 10 TEM images of four silica/NR composites

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As shown in Fig. 10, the silica dispersion in vulcanizates of A4K6-C, A6K4-C and A8K2-C is significantly more homogeneous than in vulcanizate of A0K6-C, because the latter contains more silica aggregates. AEO could graft on the silica surface but could not react with rubber, resulting in forming physical interface between silica and rubber. This physical interface played a role in reducing the polarity of silica and improving the compatibility between silica and rubber, thus improving the dispersion of silica in rubber. In contrast, K-MEPTS could graft on the silica surface and react with rubber, resulting in forming chemical interface between silica and rubber. The silica particles could be connected with the rubber molecules by the help of K-MEPTS. Therefore, this chemical interface played a role in preventing the aggregation of primary silica particles. Silica modified by using AEO and K-MEPTS together could make full use of the advantages of chemical and physical interaction between silica and rubber. In this research, the silica/NR composites has the best silica dispersion when the weight ratio of AEO to K-MEPTS is 6:4 in the condition of silica modified by 10% weight modifiers.

3.5 Characterization of silica/NR composites

3.5.1 Mechanical performances of silica/NR composites

As shown in Fig. 11 (a) and (b), A0K6-C vulcanizate exhibits 50% higher modulus and 40% lower elongation at break than A4K6-C vulcanizate; meanwhile, the tensile strength of A0K6-C vulcanizate is 40% lower than that of A4K6-C vulcanizate. The chemical interface formed by K-MEPTS could function as a "coupling bridge" to improve the reinforcing efficiency of silica on rubber, which was reflected by a high modulus. However, excessive chemical interface between silica and rubber could leaded to stress-concentrated regions [31], resulting in a low elongation at break. Because of the physical interface formed by AEO, the most elongated rubber chains could slip along the surface of silica and equalize the high stress [42], resulting in a proper modulus and elongation at break of A4K6-C vulcanizate.

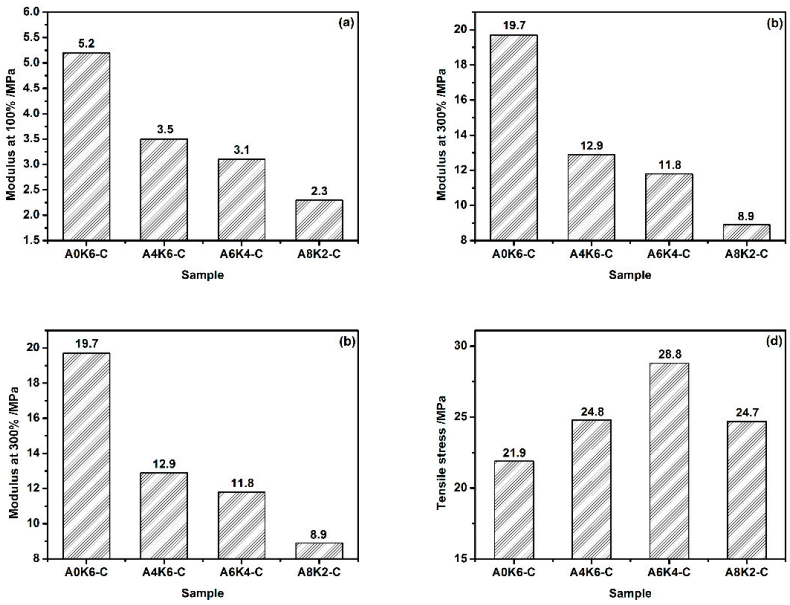

Fig. 11 Mechanical performances of silica/NR composites: (a) modulus at 100%, (b) modulus at 100% elongation, (c) elongation at break and (d) tensile strength

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For vulcanizates of A4K6-C, A6K4-C and A8K2-C, with decreasing K-MEPTS used in silica modification, the modulus decreases but the elongation at break increases. The chemical interface between silica and rubber becomes stronger with the increase of K-MEPTS used in silica modification; meanwhile, the physical interface between silica and rubber becomes stronger with the increase of AEO used in silica modification. As presented in Fig. 11 (d), the tensile strength of the composites has a peak (a value of 28.8 MPa) at the sample of A6K4-C vulcanizate. Tensile strength of silica/NR composite was affected by both the modulus and the elongation at break. Therefore, mechanical performances of silica/NR composites are the best, when a proper combination of physical and chemical interface exists between silica and NR. In this research, the silica/NR composites has the best mechanical performances when the weight ratio of AEO to K-MEPTS is 6:4 in the condition of silica modified by 10% weight modifiers.

3.5.2 Dynamic performances of silica/NR composites

In tire applications, the tan δ values at 60 °C are typically used in predicting rolling resistance.

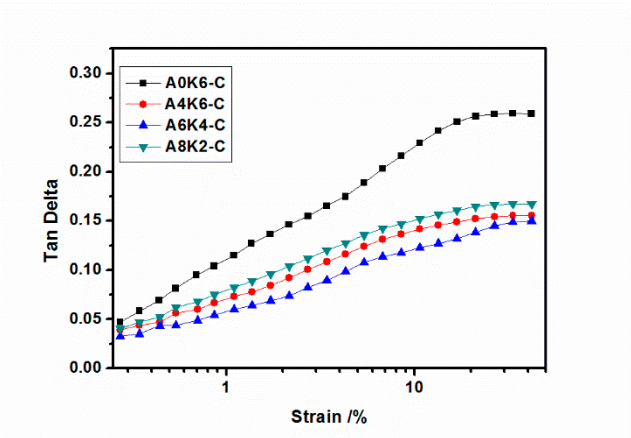

Fig. 12 Strain-tan δ curve of four kinds silica/NR composites (60 °C)

As presented in Fig. 12, the tan δ values at 60 °C in strain from 0.28% to 40% are arranged from high to low in the following order: A0K6-C vulcanizate, A8K2-C vulcanizate, A4K6-C vulcanizate, and A6K4-C vulcanizate. The rolling resistance of the A0K6-C vulcanizate is the highest in these four kinds of silica/NR composite. In theory, the silica fixed with the rubber molecules by chemical interaction ("coupling bridge") could hardly enhance internal friction loss [4,27]. However, many silica aggregates were still present in A0K6-C vulcanizate. The mutual friction between silica particles that were conglutinated tight under cyclic reversed loading was still strong. Therefore, combining a good silica dispersion and a proper chemical interface between silica and rubber were beneficial to improve the dynamic performances of silica/NR composites. The physical interface formed by AEO played a role in improving silica dispersion in rubber matrix. Thus, silica modified by using AEO and K-MEPTS together could be utilized to improve silica dispersion while silica and rubber are fixed together.

The tan δ value of A4K6-C, A6K4-C and A8K2-C vulcanizates is lower than that of A0K6-C vulcanizate, especially under high strain; moreover, the increase amplitude of their tan δ value is low with increasing strain. A6K4-C vulcanizate has the lowest tan δ in all samples, which means that using A6K4-C composite as tire tread, the rolling resistance of tire minimally changes with increasing vehicle load. Therefore, using AEO and K-MEPTS is a novel method for preparing silica/NR composites with excellent dynamic performances. In this research, the silica/NR composites has the best dynamic performances when the weight ratio of AEO to K-MEPTS is 6:4 in the condition of silica modified by 10% weight modifiers.

4. Conclusion

In this research, latex compounding method was used to prepare high-performance silica/NR composites. Silica is well dispersed in the aqueous phase and can be completely coagulated with the rubber, when silica is modified by using AEO and K-MEPTS together. AEO and K-MEPTS can be grafted on the silica surface simultaneously. Meanwhile, AEO is a more effective modifier than K-MEPTS in changing the hydrophilicity of silica.

AEO can generate a certain steric hindrance for the mercaptopropyl group on K-MEPTS, resulting in appropriate chargeability and reactivity for silica modified by using AEO and K-MEPTS together. Therefore, "scorchy" behavior can be solved in this work.

AEO and K-MEPTS can form a physical and a chemical interface between silica and rubber, respectively. AEO and K-MEPTS act synergistically to improve the mechanical and dynamic performances of silica/NR composites. In this research, the silica/NR composites has the best mechanical performances when the weight ratio of AEO to K-MEPTS is 6:4 in the condition of silica modified by 10% weight modifiers.

Through this study, we can further optimize the preparation of masterbatches using latex compounding method and expand the application range of masterbatches. We hope that the preparation of silica/NR masterbatches by latex compounding method can present practical and profound applications in the rubber industry.

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