Research Article

Tianhao Chang, Huiguang Bian*, Yao Xiao, Junxiu Xue, and Chuansheng Wang

Investigation on *in situ* silica dispersed in natural rubber latex matrix combined with spray sputtering technology

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Abstract: In this study, different processes are performed for the preparation of natural rubber latex (NRL)/silica composites. A novel approach is to use spray sputtering technology combined with *in situ* method to improve the dispersion of silica in rubber latex matrix and further improve the properties of vulcanizates. Results show that *in situ* silica in rubber matrix prepared from NH_4Cl and Na_2SiO_3 has better Payen effect than other processes. Meanwhile, when the *in situ* silica reached 10 phr in the rubber matrix, the dosage can suitably match the dispersion capacity of the spray sputtering process with superior comprehensive mechanical properties. Compared with the traditional precipitation method, the tensile strength and tear strength of the silica/NR composites prepared by spray sputtering technology combined with *in situ* method were increased by 34.7% and 19.7%.

Keywords: *in situ* method, wet mixing, silica/NR composites, physical properties, dispersion

1 Introduction

As an important reinforcing agent for rubber, silica has advantages in improving the wet-skid resistance of tires

and reduce the rolling resistance of semi-steel radial tires (1–3). Silica mixed with rubber-carbon black systems is widely used in tread rubber, especially in all rigid radial tires. Actually, filler dispersion has become a trending topic for researchers from the whole world. However, the traditional dry mixing process (4–6), which mixed rubber and fillers in a mixer with strong shear action, consumes a lot of energy (more than 50% of the consumption in the whole processing) (7). The quality between different batches of rubber is uneven in the ordinary dry mixing process, which not only decreases the quality control of the subsequent process, but also causes dust pollution (8). Therefore, in recent years, the wet mixing process of rubber (9–14) has been developed, which can improve the dispersion of inorganic fillers in rubber and reduce dust pollution. During wet mixing, the fillers are added into latex, and the compounded rubber will be obtained when the filler is evenly mixed, but the filler is difficult to coprecipitate completely (15–18). Others add the precursor of inorganic fillers to the latex to generate inorganic fillers *in situ* (19–22) by a chemical reaction, thus making latex solidified to prepare compounded rubber (23,24).

Sodium silicate or solution of water glass is added into latex to obtain the mixture for the preparation of silica *in situ*. When the mixture is well mixed, the acid solution is added into the latex to produce silica *in situ* and solidify the latex, which can improve the dispersion of silica-filled. However, the partial acid concentration can be strong if the silica *in situ* reaction speed performs fast in the process of adding acid, which can influence the dispersion of fillers in suspension. Especially, the particle size is not easy to control in the case of higher filling degrees and the agglomeration of silica cannot be avoided (25).

The reinforcing effect of silica in the NRL matrix is mainly related to the dispersion state of silica and the interfacial interaction between them. The spray sputtering technology combined with *in situ* method is very efficient in increasing the dispersion and mechanical

* Corresponding author: Huiguang Bian, College of Mechanical and Electrical Engineering, Qingdao University of Science and Technology, Qingdao 266061, China; Shandong Provincial Key Laboratory of Polymer Material Advanced Manufacturing Technology, Qingdao University of Science and Technology, Qingdao 266061, China, e-mail: bianhuiguang@163.com

Tianhao Chang, Yao Xiao, Junxiu Xue, Chuansheng Wang: College of Mechanical and Electrical Engineering, Qingdao University of Science and Technology, Qingdao 266061, China; Shandong Provincial Key Laboratory of Polymer Material Advanced Manufacturing Technology, Qingdao University of Science and Technology, Qingdao 266061, China

properties of NR/silica composites. Tang *et al.* studied the properties of spherical natural rubber/silica composite powders via spray drying (26). Xing *et al.* combined *in situ* organic modification of montmorillonite and the latex compounding method in SBR latex (27). The *in situ* silica formation has a small particle size while spraying and sputtering processes can lead to a uniform distribution, which both increase the contact area between the rubber hydrocarbon and the silica particles (28–31). Besides, there is the velocity difference between the material liquid column and the compressed air at the nozzle during high-pressure spraying. Meanwhile, the material liquid column is splitting and broken due to the disturbance of the compressed air, making the mixed liquid atomized (31–35). Under the high pressure, the SiO_2 agglomerates will be fully dispersed, and the protective film on the surface of the latex particles will be destroyed by the gas vibration waves and the friction from gas, so that the filler will be mixed with the rubber hydrocarbon into the rubber for crushing, dispersing, and mixing, thus avoiding a series of problems caused by traditional acid flocculation and improving the dispersion of fillers in rubber matrix (36–39). Therefore, silica can reinforce the rubber well and improve the physical properties of the compound. Figure 1 shows the schematic of the preparation of silica/NR composites by spray sputtering technology combined with *in situ* method. In summary, spray

sputtering technology can instantly dehydrate and prevent secondary agglomeration of *in situ* silica after stirring. Once dry and agglomerate, the mechanical mixing in the following process can hardly disperse evenly. The participation of the spray sputtering method greatly enhances the dispersion effect of *in situ* silica.

In this study, an attempt was made to prepare NRL/silica composites by *in situ* combined with the spray sputtering method. Na_2SiO_3 is first introduced into the NRL matrix. After that, HCl or NH_4Cl solution with Si_{69} suspension is titrated for the preparation of silica *in situ*. Compared with wet mixing with commercial silica-filled, some interesting results in mechanical properties are achieved. In addition, micromorphology and Payne effect are investigated among three methods with different amounts of silica loading.

2 Experimental

2.1 Materials

Natural rubber latex (NRL) (60 wt% solids) was imported from Thailand. Silica was purchased from Qingdao Croatia Ltd Co. (China). Na_2SiO_3 was provided by Tianjin Hengxing

Figure 1: Schematic of preparation of silica/NR composite by spray sputtering combined with *in situ* method.

Chemical Reagent Manufacturing Ltd Co. (China). HCl (analytical purity) was obtained from Jinan Shenghe Chemical Ltd Co. (China). NH_4Cl was purchased from Tianjin Beichen-Fangzheng Reagent Factory. Zinc oxide, stearic acid, accelerator D (diphenyl guanidine), accelerator DM (2,2'-dibenzothiazole disulfide), and sulfur were all commercially available industrial-grade products. All investigated silica/NR compounds were based on basic formulation according to Table 1.

2.2 Preparation of NRL/silica slurry in three different ways

2.2.1 *In situ* method from HCl

HCl solution with a mass fraction of 0.05 was prepared. The dissolved Na_2SiO_3 was added to the flask with three necks filled with NRL. Then, the HCl solution (0.05 wt%) was titrated slowly into the latex solution until the pH of the solution reached about 7. The process was then carried out under the condition of stirring by a paddle mixer (Shanghai Yikong Company, China) at 1,500 rpm and 25°C for 30 min. At the same time, suspension of SiO_2 could be obtained *in situ* and Na_2SiO_3 was completely converted to SiO_2 . Deionized water was added to the cased nozzle clogging when spraying. Finally, NRL/silica slurry by *in situ* method from HCl was obtained for spray drying.

2.2.2 *In situ* method from NH_4Cl

NH_4Cl solution with the mass fraction of 0.2 was prepared. The dissolved Na_2SiO_3 was added to the flask with NRL. Then the NH_4Cl solution (0.2 wt%) was titrated slowly into the solution under the same condition until the pH of the solution reached about 6–7. At this time, SiO_2

could be generated suspending in the slurry. Deionized water was added and mixed with slurry vigorously stirring. Finally, NRL/silica slurry by *in situ* method from NH_4Cl was obtained for spray drying.

2.2.3 Traditional latex precipitation method

Silica from Qingdao Croatia Ltd Co. (China) was added into NRL suspension at the same processing of other two methods to obtain NRL/silica suspension for traditional wet mixing by precipitation drying.

2.3 Preparation of NRL/silica masterbatches by spray sputtering method

The amount of silica varied from 5 to 15 to replace carbon black in the rubber matrix, as shown in Table 2. For every 5 phr of silica increased, carbon black decreased by 5 phr and Si_{69} increase by 1 phr.

The NRL/silica slurry was poured into a container tank. The mixture was atomized by a gas-assisted spray gun under the pressure of 0.5–1.5 MPa. The mixture was sprayed onto a self-designed high-temperature mill roller at 150°C with a scraper. Then, the mixture was atomized into small droplets. After contacting the Teflon coating on a high-temperature mill roll, the moisture contained in droplets rapidly evaporated to produce dry masterbatches. At the same time, the masterbatches with a certain thickness could be scraped and placed aside for further processing.

2.4 Preparation of NRL/silica composites

The obtained masterbatches were refined in an internal mixer (Qingdao University of Science and Technology,

Table 1: Formulation of silica/NR composites

Component	Contents (phr) ^a	Component	Contents (phr) ^a
NR	100.0	Carbon black N660	Variable from 23.5 to 38.5
Silica	Variable from 0–15.0	Si_{69}	2.0
Accelerator D ^b	0.5	Zinc oxide	3.0
Accelerator DM ^c	1.5	Stearic acid	2.0
Sulfur	Variable from 0–3.0		

^a Parts per hundred rubbers. ^b Diphenyl guanidine. ^c Dibenzothiazole disulfide.

Table 2: Silica/NR composites experimental program

Experiment number	Amount of the silica (phr)	Type of the silica
1	0	No
2	5	Precipitated silica from commercial available
3	5	Preparation by HCl with <i>in situ</i> method
4	5	Preparation by NH ₄ Cl with <i>in situ</i> method
5	10	Precipitated silica from commercial availability
6	10	Preparation by HCl with <i>in situ</i> method
7	10	Preparation by NH ₄ Cl with <i>in situ</i> method
8	15	Precipitated silica from commercial availability
9	15	Preparation by HCl with <i>in situ</i> method
10	15	Preparation by NH ₄ Cl with <i>in situ</i> method

China). The process parameters of the mixer were set as follows: filling coefficient 0.7, initial temperature 80°C, rotor speed 80 rpm, and mixing time 6 min. The masterbatches, N660, zinc oxide, stearic acid, accelerator D, and accelerator DM were added to the internal mixer, respectively. The mixing cycle time was 5 min. Sulfur was finally added into rubber masterbatches via an open mill (SK-168 from Shanghai Double Wing Rubber Machinery Factory). The process parameters of the open mill were set as follows: roller spacing 3 mm and roll temperature 50°C. And the shear ratio of front and rear rolls was: 1:4. At last, the rubber compound was vulcanized by a QLB-400X2 flat vulcanizing machine (Qingdao Yadong Rubber Machinery Factory) after resting for 16 h.

2.5 Characterization

- (1) Vulcanization characteristics were carried out according to GB/T16584-1996. The conditions of vulcanization were at 150°C/10 MPa × T₉₀ (min).
- (2) The Payne effect was tested by the RPA2000 Rubber Dynamic Processing Analyzer (Alpha Technologies Co of USA) with a strain of 0.28–50% and a frequency of 60 rpm.
- (3) The vulcanizate samples were subjected to brittle fracture in liquid nitrogen and subjected to gold-spray treatment and then analyzed by scanning electron microscopy (JEOL, Japan).
- (4) The dynamic mechanical properties were characterized by the Dynamic Mechanical Analyzer (GABO Company of Germany). The samples were measured in the fixed frequency mode, at an operating frequency of 10 Hz and a heating rate of 2°C per min. The samples were evaluated in the temperature range from –65°C to 65°C.

- (5) The tensile strength and tear strength were tested by TS2005b type Tensile Testing Machine from U-CAN Technology Co. (China) according to GB/T528-1999.
- (6) For tensile tests, the sample was dumb-bell-shaped according to GB/T528-2009 Type 1, and for tear tests, GB/T 529-2008 Type B. Shore A hardness was carried out according to GB/T531-1999.

3 Results and discussion

3.1 Mechanical properties

The mechanical properties amount of silica for NR/silica composites with different processes is shown in Figure 2. From the experiment of variable dosage, the tensile strength and tear strength of the vulcanized rubber prepared by *in situ* method increase first and then decrease with the increase of the dosage which is different from that of the traditional wet mixing method. The threshold value of *in situ* preparation of silica appears at 10 phr, while the threshold value of the wet mixing method does not appear in the whole range of variables curve. The reason might be that the silica generated by the *in situ* method has a smaller particle size of filler agglomeration and is dispersed well with appropriate interaction fillers and rubber matrix via spray sputtering method when 10 phr loading. Thus, the interfacial interaction in silica/NRL composites is improved which forming a regular filler network than wet mixing without *in situ* silica at 10 phr. Especially, the tensile strength and tear strength of NH₄Cl treated vulcanizates are 34.7% and 19.8% higher than those of ordinary silica vulcanizates, respectively. When the dosage exceeds 10 phr, the properties of the vulcanized composites prepared by the *in situ*

Figure 2: The mechanical properties amount of silica for NR/silica composites with different processes: (a) shore A hardness, (b) percentage of breaking elongation, (c) tear strength, and (d) tensile strength.

method combined with spray sputtering method are decreased because of the enhancement of the filler network effect (Payne effect) formed among nanoparticles and the reduction of reinforcement effect. This phenomenon will be verified in Section 3.2 with further efforts.

It can be concluded from Figure 2 that the tensile strength and tear strength of the vulcanizates obtained by *in situ* method are significantly higher than those of the wet mixing with commercial silica-filled, while the hardness and elongation at break have no obvious change. In addition, the mechanical properties of vulcanized composites treated by the NH_4Cl method are the most ideal among them. Above all, within a certain range, the

mechanical properties of vulcanizates increase as the dosage of silica increases. When silica exceeds a certain amount, the mechanical properties of vulcanizate composites prepared by spray sputtering technology combined with *in situ* method decrease with the increase of silica content, which reduces the reinforcing effect of fillers on the compound. The reason might be that the silica particles produced *in situ* have a smaller size of aggregates and uniform distribution, which increases the contact area between rubber hydrocarbons and silica particles. The good adsorption and bonding effect between fillers and rubber composites make the silica-filled *in situ* combined with spray sputtering method reinforce rubber

well and improve the mechanical properties of rubber composites. However, with the increase of silica production, the interaction between filler and filler is greater than that between rubber and filler, and agglomeration occurs to a certain extent which affects the dispersion of silica, thus decreasing the physical and mechanical properties of NRL/silica composites.

3.2 Payne effect of NR/silica composites with different silica dosages

Payne effect (40,41) is a phenomenon in which the shear storage modulus G' of the rubber nonlinear decrease with the increase of strain. Within a certain range, the elastic modulus decreases rapidly with the increase of strain, and the viscoelasticity reaches its maximum value in the region where the elastic modulus decreases. The dynamic modulus of filled rubber decreases sharply with the increase of strain due to the failure of the interaction force between fillers. Therefore, the value of $\Delta G' = G'_0 - G'_\infty$ can indicate the interaction between filler-filler and filler-rubber matrix to some extent. In this section, controlling the same condition via spray sputtering technology combined with the *in situ* method with NH_4Cl treated, Figure 3 shows the data of 0 phr ($\Delta G' = 8.04$), 5 phr ($\Delta G' = 10.15$), 10 phr ($\Delta G' = 15.66$), and 15 phr ($\Delta G' = 22.6$) by rubber process analyzer (RPA) test.

Regularly, the lower the Payne effect is, the better the dispersion of the filler in the rubber matrix and the weaker the network structure of the filler will be. As can be seen from Figure 3, the value of $\Delta G'$ is low with 0 and 5 phr silica which means the interaction force

between filler aggregates is not serious, and a less large-scale filler network has been formed. The $\Delta G'$ increased obviously beyond 15 phr silica loaded. As the dosage of silica increases, the distance between fillers and fillers decreases, and the interaction between silica and rubber matrix increases. Therefore, a greater external force is needed to overcome the interaction between silica in the dynamic strain process. However, the degree of filler network is excessive and the reinforcing between rubber and fillers is declined, leading to a lower mechanical property of composites. That might be because the specific surface area of *in situ* silica is larger, which is more liable to agglomeration. In addition, the interaction between silica and the natural rubber matrix is inherently weak and the developed three-dimensional filler network structure will be decreased under giant dynamic strain. When the filler agglomeration is serious, the filler network has a stronger tendency to collapse under the action of strain, resulting in a larger value of $\Delta G'$. The comprehensive mechanical properties of the compound reach the best with 10 phr silica loaded mainly because 10 phr loading of silica is more compatible with the dispersion capability of this process. Meanwhile, the interfacial interaction between rubber-filler and filler-filler can be beneficial for reinforcing comprehensive properties appropriately.

3.3 Microscopic appearance

Scanning electron microscopes (SEM) tests were conducted on JSM-7500F from JEOL (Japan) with surface gold-spray treatment. In order to compare the particle size of silica generated by different preparation methods and its dispersion in composites, we selected rubber composites filled with different preparation methods under 10 phr dosage for scanning electron microscope observation. When 10 phr of silica is added, the SEM images of rubber composites are shown in Figure 4.

It can be concluded from Figure 4a that silica unevenly disperses in vulcanizates obtained by preparation of silica commercially and the local agglomeration is obvious, which decreases the reinforcing effect of rubber. In Figure 4b and c, silica disperses better than the conventional wet mixing method and the aggregate size of fillers is relatively smaller, which verifies the advancement of reinforcement for rubber composites by *in situ* combined with a spray sputtering method. In case of traditional drying, it is possible for well-dispersed silica to again flocculate which leads to agglomerates. During *in situ* combined with spray sputtering method, the droplets enfolded *in situ* silica with

Figure 3: The effect of different amounts of silica on Payne effect of NH_4Cl process.

appropriate spraying pressure hit the high-temperature roller and then sputter into smaller-grade droplets onto the surface of the roller with instantaneous evaporation of water, which can efficiently improve the dispersion and further enhance the interfacial bonding strength of *in situ* silica for rubber matrix. However, some aggregates of silica can also be observed by *in situ* methods from HCl in Figure 4b. That might be because the HCl solution belongs to strong acid and reacts more intensely with Na_2SiO_3 than NH_4Cl with aggregates generation, which leads to worse mechanical properties than *in situ* preparation from NH_4Cl by spray sputtering process.

3.4 Dynamic mechanical performance analysis

Dynamic mechanics analyzer (DMA) can measure the response of vibration deformation and temperature function of a given material under the action of cyclic stress-strain. Controlling 10 phr silica loading in NR-carbon black matrix, Figure 5 shows the results of loss factor-temperature of NR/silica composites with different processes from

–65°C to 65°C. To some degree, the loss factor-temperature curve can reflect filler dispersion, the strength of filler network, wet traction, and rolling resistance of composites with fillers.

In the tire industry, it is difficult to coordinate the relationship among rolling resistance, wet-skid resistance, and wear resistance of traditional tires. These three indexes have become important indexes to evaluate the performance of automobile tires in the modern tire industry. Especially, the loss factor ($\tan \delta$) values at two important temperatures of 0°C and 60°C can measure the wet slip resistance and rolling resistance of tires to a certain extent. The value of $\tan \delta$ near 0°C is used to indicate the anti-skid performance of the tread compound. The larger the $\tan \delta$ value is, the stronger the holding ability of the tread compound is. The rolling resistance of tread rubber is characterized by the value of $\tan \delta$ between 40°C and 60°C; the lower value of $\tan \delta$ indicates the lower rolling resistance and the less heat generated by the friction of the tire on the road surface.

In the glass transition zone, the internal friction of the material mainly comes from the internal friction among the rubber macromolecular chains. The conventional silica-filled method has the lowest peak value

Figure 4: SEM images of composite preparation by spray sputtering method with a different type of silica: (a) silica commercially available, (b) *in situ* preparation from HCl solution, and (c) *in situ* preparation from NH_4Cl solution.

Figure 5: Loss factor-temperature of NR/silica composites with different processes (subfigures (b–d) are partially enlarged drawings of subfigure (a)).

which indicates that more rubber molecular chains are trapped in the filler network structure. As a result, a small number of rubber molecular chains participate in the chain segment relaxation process. In other words, the dispersion of fillers in the rubber matrix and the interaction between filler and rubber interface will affect the value of the loss factor $\tan \delta$. The peak value of loss factor ($\tan \delta$) of *in situ* silica from the NH_4Cl method is the largest among them because the silica produced by the *in situ* method has a large contact area and good compatibility with rubber latex. Thus, the agglomerate effect is difficult to achieve, and the strength of the network of composite fillers is weak. There are relatively few rubber molecules retained in the filler network structure, which

means that more rubber molecules are involved in the chain segment movement to increase $\tan \delta$.

With the increase in temperature, the activity of the rubber molecular chain is enhanced. When the temperature reaches about 60 $^\circ\text{C}$, the breaking and reconstruction of the filler network structure in the process of dynamic mechanics is the main reason for the energy loss of the rubber system. The uniform dispersion of silica and the strong adhesion between filler and natural rubber matrix can restrict the movement of rubber molecular chains. Therefore, the energy consumption of breaking and rebuilding the filler network structure is reduced, which leads to the low value of loss factor and nice rolling resistance.

4 Conclusion

Different processes are performed in this work to disperse silica into NRL-carbon black matrix. When a load of silica reached 10 phr, the capacity of filler dispersion can be suitably matched with spray sputtering technology combined with an *in situ* process. In this case, NR/silica composites obtained from the NH_4Cl solution can reach better mechanical behavior. Meanwhile, the microscopic appearance shows that the NR/silica composites prepared by *in situ* silica from the NH_4Cl method combined with spray sputtering technology at 10 phr have better dispersion compared with other processes. Moreover, the NR/silica composites prepared by *in situ* silica from the NH_4Cl method combined with spray sputtering technology perform well in dynamic mechanical properties.

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