Preparation of Natural Rubber Composites with High Silica Contents Using a Wet Mixing Process

Ekaroek Phumnok, Parinya Khongprom, and Sukritthira Ratanawilai

ABSTRACT: A wet mixing process is proposed for filled rubber composites with a high silica loading to overcome the drawbacks of high energy consumption and workplace contamination of the conventional dry mixing process. Ball milling was adopted for preparing the silica dispersion because it has a simple structure, is easy to operate, and is a low-cost process that can be easily scaled up for industrial production. The response surface methodology was used to optimize the making of the silica dispersion. The optimum conditions for a well-dispersed silica suspension with the smallest silica particle size of 4.9 mm were an about 22% silica content and 62 h of ball milling. The effects of dry and wet mixing methods on the properties of silica-filled rubber composites were investigated in a broad range of silica levels from low to high loadings. The mixing method choice had little impact on the properties of rubber composites with low silica loadings. The silica-filled rubber demonstrated in this study, however, shows superior characteristics over the rubber composite prepared with conventional dry mixing, particularly with high silica loadings. When compared to silica-filled natural rubbers prepared by dry mixing (dry silica rubber, DSR), the wet mixing (for WSR) produced smaller silica aggregates with better dispersion. Due to the shorter heat history, the WSR exhibits superior curing characteristics such as a longer scorch time (2.2−3.3 min for WSR and 1.0−2.1 min for DSR) and curing time (4.1−4.5 min for WSR and 2.2−3.1 min for DSR). Additionally, the WSR has superior mechanical properties (hardness, modulus, tensile strength, and especially the elongation at break (420−680% for WSR and 360−620% DSR)) over the DSR. The rolling resistance of WSR is lower than that of DSR. However, the reversed trend on the wet skid resistance is observed.

1. INTRODUCTION

Reinforcing fillers have been developed for rubber composite products to improve their quality characteristics such as the modulus, tensile strength, and abrasion resistance and are critical to practical rubber technology. Nowadays, the amount of the silica (SiO2) filler used as an additive in the tire industry is continuously increasing because silica-reinforced rubber presents a low rolling resistance, low hysteresis, high hardness, and good abrasion resistance, and they are technical advantages over carbon black-filled rubber.1,2 In addition, the improvement of the self-healing capability of the silica-filled rubber composite for extending its long life and safety was studied by several investigators.3−5

The typical way to mix fillers into rubber is by dry mixing, in which the filler particles (commonly carbon black or silica) are directly mixed with the dry rubber in a mechanical mixer before vulcanization. However, the inorganic silica filler is incompatible with certain rubbers, including natural rubber and styrene butadiene rubber. Due to these reasons, silica fillers tend to aggregate, which reduces the filler−rubber interactions. Several methods, such as coupling agents, the addition of a second filler, and the improved interface structure, have been developed to improve the silica distribution in the rubber matrix. Ye et al. investigated the possibility of creating a highly energy-efficient "green tire" by combining BEP and bis-(triethoxysilylpropyl)-tetrasulfide (TESPT) as a coupling agent. The results indicated that BEP significantly improved the silica dispersion, resulting in better static and dynamic mechanical performances.6 Sattayunurak et al. used an organoclay nanofiller and N134 carbon black as secondary fillers in silica-based natural rubber compounds. Organoclay exhibits a significant influence on silica hydrophobation and the silane coupling reaction between silica and elastomers. Thus, organoclay is a preferred secondary filler for silica-filled NR with superior wet traction and rolling resistance.7 Ali et al. investigated a cellulose nanocrystal (CNC)-based hybrid filler to reinforce the natural rubber composite. The simple and efficient coprecipitation methods

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were adopted to decorate the surface of CNCs with silica. The coprecipitation method gives better dispersion, resulting in higher reinforcement. Zhang et al. modified graphene oxide (GO) by using organosilica to improve the mechanical and solvent resistance of silicone rubber (SR). The organosilica-modified GO and SR exhibit good compatibility and interfacial interaction. Sattar and Patnaik modified the interface between silica nanoparticles and solution-polymerized styrene butadiene rubber (SSBR) with the phosphonium ionic liquid (PIL) as an interfacial modifier. The composite with the modified interfacial interaction gives a higher glass transition temperature and better dynamic properties. The detailed molecular mechanisms underlying the improved interface structure can be found in the review article by Sattar. Although these studies successfully developed the methods for well dispersion of silica in a rubber matrix by the conventional dry mixing process. However, the main drawbacks of this method are high energy consumption and being time-consuming because of the high viscosity that makes the processing more difficult. Additionally, some silica is lost as silica dust spreading around the factory during conventional mixing. Thus, a wet mixing process has been developed to overcome these drawbacks. Wet mixing of silica-filled natural rubber is a novel method for improving the silica dispersion in the rubber matrix, thereby achieving excellent mechanical properties of the vulcanizates. The silica powder is dispersed prior to mixing with the latex during the wet mixing process, resulting in a more uniform dispersion of the silica filler, with comparatively low energy consumption.

The two types of wet mixing processes for silica-filled rubber composites are the in situ sol–gel method and the dispersion method. Utrera-Barrios et al. studied the effects of mixing methods (conventional and in situ sol–gel methods) for preparing natural rubber (NR) composites. It was found that the natural rubber composite prepared from the in situ sol–gel method improved the compatibility and superior reinforcement. However, this method has many limitations for industrial applications such as high cost of the raw material and large volume shrinkage and cracking during the drying step. To overcome these issues, the wet dispersion method has been developed to prepare the natural rubber composite. Numerous studies demonstrated that the wet mixing improves mechanical properties of silica-filled rubber. However, these studies were carried out in the range of low silica contents, which limits the scope of applications of those rubber composites. Recently, Ryu et al. prepared a 50 phr nanosilica/rubber composite. The effects of the mixing time in a dry mixer were the main focus of that study. The addition of a second filler was applied in the wet mixing process by Wang et al. who studied a 50 phr silica-filled natural rubber, using nanosilica modified with reduced graphene oxide. The silica-graphene fillers were directly mixed with the latex. The well-dispersed latex solution was then precipitated to produce silica/graphene/natural rubber composites. Sattar et al. prepared a shell-structured silica-filled natural rubber using MgCl₂ as a coagulant and an interfacial modifier by mixing binary colloidal suspensions. The obtained composites reveal the improvement of mechanical and healing properties. However, these studies used commercial nanosilica in the silica dispersion form, so a simple agitator was able to prepare the suspension. However, nanosilica is not preferred for industrial applications because of its high cost. Therefore, precipitated silica, which is widely used in industrial plants, was used in this current study. However, the large particle size of precipitated silica makes it necessary to reduce the particle size and disperse it well in a water suspension. Therefore, an appropriate method is necessary for dispersing the silica prior to mixing with the rubber latex. In the laboratory scale, an agitator bead mill and an ultrasonic dispersion machine are often used to prepare silica dispersions. However, these devices are not suitable for industrial-scale production because of high operating costs and difficulties in scale-up. Ball milling, in contrast, is easily scaled up to industrial size. Due to its simple design, low operating costs, and basic operating principles, ball milling has been widely adopted for the grinding of minerals into fine particles and for the preparation and modification of inorganic solids. Moreover, there has not yet been any prior study on preparing silica dispersions by ball milling for wet mixing of silica as a filler in rubber.

This study utilized the response surface methodology (RSM) for determining nearly optimal dispersion preparation conditions. The physical properties of silica-filled natural rubber, prepared via wet mixing, were compared to those of corresponding vulcanizates prepared via dry mixing.

2. RESULTS AND DISCUSSION

2.1. Optimization of Silica Dispersion Preparation.
Silica powder can be generally ground in a dry or wet ball milling process. However, dry ball milling gives larger silica aggregates because of the interactions between silica particles by H-bonding of silanol groups. In wet ball milling, silica is dispersed in water during the grinding. This gives smaller particle aggregates than in dry silica powder because water forms H-bonds with the silanol groups on silica particles, preventing silica aggregation. Du et al. mentioned hydrolytic weakening due to a double hydrogen atom transfer process, where water molecules spontaneously cause single siloxane bridge breakage. The second molecule acts as a catalyst, assisting in the process of hydrogen migration, which involves the transfer of a hydrogen atom from the first water molecule to the surface. Additionally, other strained Si–O bonds on the silica surfaces may favor the cooperative water dimer reaction. The straining of the structures in a two-membered ring causes the structures to protrude into the surface, allowing water molecules to interact more easily with the Si–O bond and promoting a cooperative reaction. Some researchers have agreed with this explanation in prior reports. Thus, wet ball milling will be used for reducing the silica particle size in this current study.

A silica dispersion with small and uniform particle size distribution is desired for a good and stable silica masterbatch. The two important controlled factors affecting the size distribution are the silica content (X₁) and the milling time (X₂). Analysis of variance (ANOVA) was used to determine the important main interaction effects of factors that influence the silica particle size as shown in Table 6. The predicted values agreed well with the experimental data with a coefficient of determination of $R^2 = 0.943$ and an adjusted coefficient of determination of $R_{adj}^2 = 0.902$. These results imply that 95% of the variations in the silica particle size could be explained by the selected variables. The adjusted $R^2$ ($R_{adj}^2$) is a corrected goodness-of-fit parameter, and it was also close to the coefficient of determination $R^2$, which indicates that the regression predictions accurately approximated the real data points. This model is extremely significant and could be validated by the Fisher value ($F = 23$), which is greater.
than the critical $F$-value at a level of significance $\alpha = 0.95$ ($F_{\text{tabular}} = 3.97$), indicating that the differences in treatment were highly significant. For statistical significance, we expect the absolute value of the $t$-ratio to be >2 or the $P$-value to be less than the significance level ($\alpha = 0.05$). The $P$-values were also used to verify the significance of each coefficient. If the $P$-value is <0.05, then the model terms are significant; thus, the coefficient was more significant when the Student’s $t$-test magnitude was greater and the $P$-values were smaller.  

### Table 1. The Experimental Design for Silica Dispersion Preparation

| case no. | silica (g) | Vultamol | water (g) | ball milling time (h) |
|----------|------------|----------|-----------|-----------------------|
| 1        | 15         | 1        | 84        | 30                    |
| 2        | 7.93       | 1        | 91.07     | 42.73                 |
| 3        | 15         | 1        | 84        | 48                    |
| 4        | 15         | 1        | 84        | 30                    |
| 5        | 5          | 1        | 94        | 30                    |
| 6        | 15         | 1        | 84        | 30                    |
| 7        | 7.93       | 1        | 91.07     | 17.27                 |
| 8        | 15         | 1        | 84        | 30                    |
| 9        | 15         | 1        | 84        | 12                    |
| 10       | 15         | 1        | 84        | 30                    |
| 11       | 22.07      | 1        | 76.93     | 42.73                 |
| 12       | 25         | 1        | 74        | 30                    |
| 13       | 22.07      | 1        | 76.93     | 17.27                 |

### Table 2. Mixing Procedure Used to Prepare the Dry-System 50% Silica Rubber Masterbatch

| time (min) | action                      |
|------------|-----------------------------|
| 0          | ribbed smoked sheet #3 mastication |
| 2          | add 1/2 silica             |
| 4          | add the remaining silica   |
| 6          | dump                       |

### Table 3. The Chemical Formulations Used to Prepare the Wet-System Silica Rubber Masterbatch

| chemicals                        | wet weight (g) |
|----------------------------------|----------------|
| 60% HA concentrated latex        | W20 W35 W50 W65 |
| 22% silica dispersion            | 167 167 167 167 |
| water                            | 91 159 227 296 |
|                                  | 205 137 69     |

### Table 4. The Rubber Compound Formulation of Compound Rubber from the Wet- and Dry-System Silica Masterbatch

| rubber and chemicals | phr | wet system | dry system |
|----------------------|-----|------------|------------|
|                      |     | W20 W35 W50 W65 | D20 D35 D50 D65 |
| RSS#3                |     | 120 130 150 165 | 40 70 100 130 |
| stearic acid         | 1   | 1 1 1 1 | 1 1 1 1 |
| ZnO                  | 5   | 5 5 5 5 | 5 5 5 5 |
| MBTS                 | 1   | 1 1 1 1 | 1 1 1 1 |
| TMTD                 | 0.5 | 0.5 0.5 0.5 | 0.5 0.5 0.5 0.5 |
| DEG                  | 1.2 | 2.1 3.0 3.9 | 1.2 2.1 3.0 3.9 |
| sulfur               | 2.5 | 2.5 2.5 2.5 | 2.5 2.5 2.5 2.5 |

### Table 5. Mixing Procedure Used to Prepare the Rubber Compounds

| time (min) | action                      |
|------------|-----------------------------|
| 0          | rubber masterbatch          |
| 1.5        | add ribbed smoke sheet #3   |
| 4          | add DEG                     |
| 5          | add stearic acid, ZnO, MBTS, and TMTD |
| 6          | dump                       |

### Table 6. Analysis of Variance (ANOVA) for the Fit of Silica Particle Size from Central Composite Design

| source of variation | sum of squares | degree of freedom | adjusted mean square | $F$-value |
|---------------------|---------------|-------------------|----------------------|-----------|
| regression          | 43.3          | 5                 | 8.65                 | 23        |
| residuals           | 2.6           | 7                 | 0.37                 |           |
| total               | 45.9          | 12                |                      |           |

$R^2 = 0.943$. Adj. $R^2 = 0.902$. $F$-value = 23 $\gg$ F0.05 (5.7) tabular = 3.97.

### Table 7. Regression Results from the Data of Central Composite Design Experiments

| coefficient | parameter estimate | standard error | $t$-value | $P$-value |
|-------------|-------------------|----------------|-----------|-----------|
| $a_0$       | 17.5226           | 2.2860         | 7.6651    | 0.000     |
| $a_1$       | -0.3298           | 0.1751         | -1.883    | 0.102     |
| $a_2$       | -0.2888           | 0.1012         | -2.852    | 0.025     |
| $a_{11}$    | 0.0140            | 0.0046         | 3.0       | 0.020     |
| $a_{22}$    | 0.0032            | 0.0014         | 2.3       | 0.061     |
| $a_{12}$    | -0.0047           | 0.0034         | -1.4      | 0.208     |
Y = 17.5226 − 0.3298X_1 − 0.2888X_2 + 0.0140X_1^2 + 0.0032X_2^2 − 0.0047X_1X_2

where Y is the silica particle size (μm), X_1 is the silica content (%), and X_2 is the ball milling time (h).

Notably, to ensure the model’s ability to predict the silica particle size, the following tests listed in Table 8 were used followed by the extrapolation method. As demonstrated, the deviation between experimental and predicted values was less than 10%, indicating the model’s ability to predict the silica particle size at various silica contents and ball milling times. Figure 1 displays the RSM contour plot. The optimum conditions for silica dispersion preparation were calculated to be a 22% silica content and 62 h of ball milling, to get the smallest silica particle size (5.0 μm). However, this long ball milling time needed good engineering management and economic analysis of this process for industrial application. In addition, a dispersing agent should be used to reduce the ball milling time.

Figure 2 shows the particle size distributions of silica before and after milling under the optimum condition. Prior to grinding, the silica particle size distribution was bimodal, with an average particle size of 15 μm and the larger sized population of particles averaging 144 μm in size. However, the silica dispersion could be broken down to aggregate forms with an average size of 4.9 μm after milling under the optimum conditions. In addition, the obtained particle size from the experiment (4.9 μm) and the calculated value (5.0 μm) are almost the same, indicating the excellent prediction of the proposed correlation.

The effects of silica loading on dispersion viscosity are depicted in Figure 3. At a low silica content (5–15%), the viscosity is constant and close to that of water. Silica particles are in a flocculated state in this dilute regime. Additionally, a low silica content results in increased milling difficulty. Therefore, the silica particle size increases with a decreasing silica content, as shown in Figure 1. For silica loadings exceeding 15%, the viscosity exponentially increases with the loading. This trend has also been observed for silica nanoparticle dispersions.35 Due to the fact that the silica particles are well-dispersed in the solution, this condition is ideal for the manufacture of a high-silica content masterbatch. Additionally, this silica content is excellent for grinding, resulting in a fine particle size. However, at a silica loading of 25%, it was observed that the silica was in a gel form due to its high degree of hydroxylation, resulting in a three-dimensional network of polymerization by Si(OH)₂−O−Si(OH)₂−OH.36 The viscosity is too high in that condition, making it not suitable for preparing a silica masterbatch.

### 2.2. Morphology of Silica-Filled Rubbers

The silica-filled rubbers prepared by wet mixing (wet silica rubber, WSR) and by dry mixing (DSR) were investigated. The morphologies of silica-filled rubbers with various silica contents from wet and dry processes are shown in Figure 4. At a low silica content (20 or 35 phr), the choice of the silica preparation method only insignificantly affected the silica distribution in the silica-filled rubber: excellent distributions were obtained. Praserttsri and Rattanasom reported that when the silica loading is 20 phr, the morphology of silica dispersed in silica-filled natural rubber does not significantly differ.37 At silica contents of >50 phr, the silica particle size in WSR was smaller than that in DSR. This is because in the compounding step of the dry process, the shear forces did not suffice to break down silica agglomerates, leaving large agglomerates in the compound.18,32

### 2.3. Curing Characteristics

The scorch time is a critical curing characteristic that can be defined as the amount of time required at a given temperature before the rubber compound begins to vulcanize, which involves a significant amount of accelerator chemistry.37 The scorch time (tₘ) was observed in this study. The effects of the silica content on the scorch time are shown in Figure 5. As the amount of silica increased, the scorch time decreased because of the high heat generation of the filler attrition during compounding that enhanced the rate of vulcanization. In this work, diethylene glycol (DEG) was used to prevent the acidic nature of the silica and the interaction of basic accelerators onto the silica surface.38 The ratio of DEG to silica was kept constant for all silica loadings as shown in Table 4. Thus, a shorter curing time was obtained with the increase in the silica loading due to higher heat transfer from silica to the rubber matrix. The WSR exhibits a longer scorch time than the DSR. In the WSR preparation involving water, the silanol groups on the silica surface might be moisture-treated and would consequently enhance the curing rate.39 However, in the wet mixing process, heat was generated mainly in the compounding step, while in the dry mixing process, heat was generated both in masterbatch preparation and compounding steps. Thus, enormous heat generated in the dry mixing process would accelerate the curing rate. Thus, the scorch time of DSR is shorter than that of WSR. It indicated that the heat generation has a greater influence on the scorch time than the absorption of the curing

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Table 8. Comparison of the Results of Extrapolation Prediction and Additional Experiments

| N  | silica content (%) | ball milling time (h) | predicted value | actual value | absolute relative error (%) |
|----|-------------------|----------------------|----------------|-------------|-----------------------------|
| 1  | 28                | 56                   | 5.4            | 6.2         | 6.45                        |
| 2  | 25                | 58                   | 5.2            | 5.5         | 5.45                        |
| 3  | 22                | 62                   | 5.0            | 4.9         | 2.04                        |
| 4  | 19                | 65                   | 5.3            | 5.6         | 5.56                        |
| 5  | 16                | 69                   | 5.9            | 5.5         | 7.27                        |

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Figure 1. Effects of the silica content (%) and the ball milling time (h) on the silica particle size (mm).
agent. The results in Figure 6 show that the silica content and the choice of silica preparation impact the overall curing time ($t_{90}$). Curing time trends are similar to the trends in the scorch time. The curing time decreased with silica loading. Due to the absence of heat history, the WSR cures more slowly than the DSR.

Huabcharoen et al. reported that as the silica content increased, the scorch and curing times decreased. Additionally, the choice of the method of silica preparation had a significant effect on the scorch and curing times. In a wet system, the silica aggregates in a rubber compound were more broken down and better dispersed than in the dry system. The more finely dispersed microsilica in the rubber phase provided a greater surface area for absorbing the accelerator. As a result, the scorch and curing times for the WSR were longer than those for the DSR.40

### 2.4. Mechanical Properties

The effect of the silica content on the hardness of the composite is illustrated in Figure 7. Generally, the hardness increases with the silica content, as observed by previous researchers.41,42 However, the silica content had a different variable effect on the hardness. At a low silica content (<50 phr), the hardness increased marginally with silica loading. The method of silica preparation had a negligible effect on the hardness of the silica-filled rubber vulcanizates in this regime. In the high-silica content regime (>50 phr), the silica content has a significant effect on the hardness of the silica-filled rubber vulcanizates, as the distance between silica aggregates becomes small enough from strong mutual interactions, resulting in the formation of a mechanically coupled filler–filler network. At a high silica loading, the filler–filler network should significantly increase the hardness. At a 65 phr loading, WSR was harder than DSR. This could be a result of the more uniform filler particle size distribution and particle dispersion generated by the use of the wet mixing (see Figure 4c,h).
The stress at 300% deformation is a measure of a material’s relative stiffness. The stress at 300% deformation of silica-filled rubber is shown in Figure 8 under various silica contents. This parameter correlates very well with the hardness. However, the stress at 300% deformation exhibits an almost constant with the silica content in the low-silica loading (<50 phr) regime. The effect of the silica loading is less pronounced at a high percentage of deformation. Thus, a constant trend was observed at the low-silica loading regime as reported by Julie Chandra et al. In the silica-filled rubber vulcanizates with a high silica content (>50 phr), the silica content has a significant effect on the stress at 300% deformation. With increasing of the silica content, the stress at 300% deformation dramatically increases as those observed in the hardness (see Figure 7), indicating that the rubber composites became harder and stiffer due to the silica–rubber interactions reducing the mobility of rubber chains, making the compound more rigid, and the elasticity of the rubber chains decreased, resulting in the increase in the stiffness. Additionally, the stress at 300% deformation of wet- and dry-process silica-filled rubbers was nearly identical across the silica content range tested in this study.

Figure 9 illustrates the tensile strength of silica-filled rubber vulcanizates prepared using wet or dry methods with varying silica loadings. The tensile strength increased slightly with the silica content up to 50 phr and then increased significantly. The explanation is that the dispersion of silica within the elastomer matrix improved as illustrated in Figure 4 with more restriction of segmental elastomer chain motion. Kim and Song observed a similar trend when working with zinc-free processing aids on silica-reinforced tread compounds for green tires.

The tensile strength of WSR increases as the silica content increases for all silica loadings used in this study. The silica
particles are small with a narrow particle size distribution in the wet mixing system, resulting in a uniform distribution in the rubber matrix, as illustrated in Figure 4. Thus, the rubber phase had less defects, acting as stress concentrations or fault initiators, than in the DSR. Additionally, during the wet mixing, the natural rubber in the latex form contains high concentrations of phospholipids and proteins, and they can interact with the silica.\textsuperscript{46,47} Therefore, the tensile strength of WSR was higher than that of the DSR. Kim and Song also observed the same tendency. They explained that the increase in the silica loading results in the increase in reinforcement due to the large surface area of silica in contact with the elastomer matrix.\textsuperscript{45} Additionally, the WSR rubber was less masticated in the internal mixer than the DSR rubber, resulting in less rubber molecule scissions. As a result, the WSR will be able to stretch further.

### 2.5. Dynamic Properties

Figure 11a–c illustrates the changes in the storage modulus ($E'$), the loss modulus ($E''$), and the damping factor (tan $\delta$) with the silica loading or the choice of the mixing method, as functions of temperature. In the low-temperature regime where the rubber composites are frozen, the silica loading and mixing method have no significant influences on the storage modulus. Above the glass transition temperature ($T_g$), the storage modulus increased with the silica loading because of the filler restricting the mobility of rubber chains.\textsuperscript{15,48–50} At a low silica loading (20 phr), the silica preparation method insignificantly affected the storage modulus. However, the storage modulus of the
WSR was higher than that of the DSR in the high-silica loading regime because of the smaller silica aggregates and good filler dispersion.18 These results indicated that the proposed silica preparation is advantageous for the storage modulus at a high silica loading.

The loss modulus ($E''$) indicates conversion of energy from mechanical deformations to heat, by internal friction. The results show that loss modulus increased with the silica content, as more energy was dissipated by the breakdown of filler–filler networks and by the trapped rubber chains interacting with the filler network.15,48–50 The loss modulus ($E''$) at 0 °C is an indicator of the wet grip performance of a tire. Figure 11b indicates that the loss modulus at 0 °C of the 50 phr WSR is significantly higher than that of the 50 phr DSR indicating the better wet grip performance. However, the 20 phr WSR and the 20 phr DSR display identical values. The damping factor (tan $\delta$) is the ratio of the loss modulus to the storage modulus ($E''/E'$). The tan $\delta–T$ curve shows a maximum peak at the glass transition temperature ($T_g$) of the SiO$_2$/NR vulcanizate.17,51 The 20 phr silica-filled rubber exhibited a relatively high $T_g$ ($\approx -36$ °C) compared to that of the 50 phr case ($-39.58$ to $-41.25$ °C) due to good dispersion of silica at a low silica loading. Although the better silica distribution in the WSR can be seen in Figure 4, the mixing method only insignificantly affected $T_g$. However, Wang et al. revealed that the $T_g$ of silica-filled rubber based on wet mixing was higher than that of dry mixing. This might be due to the effects of the interfacial binding reagent used in their study.17 The tan $\delta$ peak height corresponds to the weakness of the filler–filler network. For a given mixing method, the peak height increases with a decreasing silica content.52 The improved dispersion of silica in a lower-silica content/NR composite weakened the filler–filler network and decreased the amount of NR molecular entanglement with the filler–filler network, owing to the increased participation of rubber chains in chain segment relaxation.53 For a low silica loading (20 phr), the tan $\delta$ peak height of the composite prepared from the wet mixing process is higher than that of the dry mixing process due to silica dispersion. However, the inverse trend was observed for a high silica loading (50 phr).

Figure 7. Effect of the silica content on the hardness of the wet- and dry-process silica-filled NR.

Figure 8. Effect of the silica content on the stress at 300% deformation of the wet- and dry-process silica-filled NR.
because the protein molecule at the surface of the natural rubber latex particle generates H-bonding with the silanol group of the silica filler resulting in stronger rubber–filler interaction.20,21 Thus, the peak height of the 50 phr DSR is higher than that of the 50 phr WSR. Additionally, the rolling resistance and wet skid resistance of natural rubber compounds can be interpreted from the tan δ−T curve. The rolling resistance of a tire is also referred to the rolling loss, and it is primarily caused by the hysteresis loss in the tire material as it travels down the road. To be precise, a tire’s rolling loss is the heat conversion loss of mechanical energy as the tire travels a unit distance. A small tan δ indicates that the tire has a low rolling resistance that is good for energy consumption. Due to the hysteresis-based heat generation during rolling, the surface and interior temperatures of tires are typically higher than room temperature. As a result, the rolling resistance is estimated from tan δ at 60 °C. This tan δ increases with the silica content (see Figure 11c), indicating that the rolling resistance tends to increase.15 The stiffness of the silica-filled rubber composite increases with the silica loading as shown in Figure 11b resulting in an increase in the rolling resistance with the silica loading.54 When considering the effects of the preparation method, the tan δ of WSR was lower than that of DSR because of the improvement of filler dispersion, indicating a low rolling resistance.55 Wet skid resistance is another important safety property. When a car applies its brakes on a wet road, the braking effect depends on wet friction between the rubber and the road surface, which allows the accumulated heat to be dissipated over time due to the presence of water. Hence, it is assumed that wet skidding occurs at or below room temperature. Among others, the resistance to wet skidding is represented by tan δ at 0 °C: a high tan δ suggests that the wet skid resistance is high, which is preferred for car safety during the braking on a wet road. The tan δ decreased with the increase in the silica content. In addition, the preparation method choice had a significant effect on tan δ, where the WSR tan δ was lower than that for DSR, indicating a low wet skid resistance. This trend was also observed by Wang et al. The lower tan δ of WSR indicated high filler–filler interaction with low filler–rubber
However, the filler–rubber interaction can be improved by using an interfacial modifier.\textsuperscript{5,10}

3. CONCLUSIONS

The optimum parameters for silica dispersion preparation were determined by using the RSM technique, for a high silica loading-filled rubber vulcanizate. A ball mill was adopted for silica dispersion because of its simple structure, easy operation, and low cost, along with the easy scale-up for industrial production. The optimum condition minimizing the silica particle size to 4.9 $\mu$m was an about 22% silica content with 62 h of ball milling. However, this long milling time needed good engineering management and economic analysis for industrial application. The wet and dry mixing methods for making a silica-filled rubber composite in low- and high-silica content regimes were investigated. The silica-filled rubber prepared with wet mixing (WSR) exhibited the better silica distribution with less silica agglomerates in the compound as compared with conventional dry mixing (DSR). The WSR exhibited superior properties over DSR, especially at high silica loadings. WSR has longer scorch and curing times than DSR, which is advantageous in controlling the process. The mechanical properties of the WSR (hardness, modulus, tensile strength, and especially the elongation at break) were superior to those of the DSR. In addition, the WSR exhibited the low rolling resistance that is suitable for green tire production.

4. EXPERIMENTAL SECTION

4.1. Materials. High-ammonia concentrated natural latex (NR latex) with a total solid content of 61.5% was purchased from Chana Latex Industry, Songkhla, Thailand. Ribbed smoke sheet #3 (RSS 3) was obtained from Barokat Rubber, Songkhla, Thailand. Silica (Ultrasil VN3) was obtained from Evonik Industries AG, Nordrhein-Westfalen, Germany. It had a specific surface area of 189 m$^2$/g, a pour density of 280 g/L, and a silica content of $\geq$ 97%. A naphthalene sulfonic acid condensate (Vultamol) was obtained from BASF Co., Ltd., Mannheim, Germany. Stearic acid was supplied by Siam Oil & Fat Co., Ltd., Samutsakhon, Thailand. Potassium hydroxide was supplied by Merck Schuchardt OHG, Hohenbrunn, Germany. Zinc oxide (ZnO) was obtained from Thai Poly Chemicals Co., Ltd., Samutsakhon, Thailand. Diethylene glycol (DEG) was produced by Merck Schuchardt OHG, Hohenbrunn, Germany. Sulfur was obtained from Utids Enterprise Co., Ltd., Bangkok, Thailand.

4.2. Preparation and Optimization of the Silica Dispersion. A laboratory ball mill, provided by Lim Karn Chang Ltd. (Songkhla, Thailand), was used to prepare the silica dispersions. The naphthalene sulfonic acid condensate (Vultamol) was used as a dispersing agent. The Vultamol is an anionic dispersant. The hydrophobic tails of Vultamol were laid down to the silica particle surface, and its hydrophilic head was attracted to water molecules.\textsuperscript{25} The silica powder, Vultamol, and water were mixed in various ratios and then ground in a ball mill for a controlled time to obtain silica dispersions. The pH of dispersions was adjusted to 9.5–10 by using 10% potassium hydroxide.

The desired silica dispersion for high-silica masterbatch preparation would have a high silica concentration but with a small particle size. Thus, the silica concentration and ball milling time were the critical parameters in the preparation of silica dispersions. These parameters were optimized in this study utilizing the response surface methodology (RSM) with a central composite design (CCD) of experiments for two factors: the silica content ($X_1$) and the ball milling time ($X_2$). In this study, the silica content was varied between 5 and 25%, and the ball milling time was varied between 12 and 48 h.
experimental design for silica dispersion preparation is shown in Table 1.

4.3. Preparation of the Silica Masterbatch. 4.3.1. Dry System. The dry masterbatch was prepared by the conventional method. The ribbed smoke sheet and silica (Ultrasil VN3) were compounded by using a Haake rheocord RC 500p (Thermo Electron GmbH, Karlsruhe, Germany) for a 50% silica/rubber masterbatch. The initial mixing temperature was 70 °C, the rotor speed was 80 rpm, and the mixing steps are shown in Table 2.

4.3.2. Wet System. In the wet system, the silica dispersion prepared under the optimum conditions (22% silica content and 62 h of ball milling) was used for the masterbatch preparation. The wet process for masterbatch preparation was run as follows. The wet weights of the silica dispersion, natural latex, and water are shown in Table 3, and they were mixed in a mixing tank (Lim Karn Chang Ltd., Songkla, Thailand) with an impeller speed of 250 rpm and a mixing time of 5 min. After good mixing was achieved, the silica and natural latex mixture was coagulated by adding 10% w/w acetic acid. The coagulum was sheeted and leached with tap water at a flow rate of 1 L/min for 10 min. Finally, the silica masterbatch sheet was dried at 70 °C for 24 h in an oven.

4.4. Preparation of the Rubber Compound and Vulcanized Rubber. The rubber was compounded with the silica masterbatch with the additives using a Haake rheocord RC 500p. The compound formulations and compounding steps are shown in Tables 4 and 5, respectively. The mixing temperature was initially 70 °C. The rotor speed was 80 rpm. The compounded rubber was kept cool, and then, sulfur was mixed into the rubber on a laboratory two-roll mill for 2 min.

The rubber vulcanizates were prepared from a rubber compound by vulcanization at 150 °C using a compression molding machine (Hong Yaw Thai Co., Ltd., Samutsakhon, Thailand). The obtained rubber test sheets were stored at room temperature for at least 24 h prior to characterization.

4.5. Characterizations. A Brookfield viscometer model DV-II (Brookfield Engineering Laboratories, Inc., Massachusetts, USA) was used to determine the viscosity of silica dispersions. A laser particle size analyzer (Mastersizer 2000; Malvern Instruments Ltd., Worcestershire, UK) was used to determine the particle size distributions.

The curing characteristics of the rubber compound were determined using an oscillating disk rheometer model A-ODR (Presto Stantest Pvt. Ltd., Haryana, India) in accordance with ASTM D2084.26

The hardness of the vulcanizates at the optimum curing time (t90) was measured following ISO 48-2,27 using a Bareiss Digi Test II hardness tester (Bareiss Prüfgerätebau GmbH, Oberdischingen, Germany). Tensile properties were analyzed by using a Gotech universal tensile strength tester model KT-7010 (Gotech Testing Machine, Inc., Taichung, Taiwan) in accordance with ISO 37. Dumbbell specimens for tensile tests were cut using die C from rubber-vulcanized sheets with a thickness of approximately 2 mm. The specimens were tested with a 1 kN load cell and a 500 mm/min crosshead speed.28 In addition, the morphologies of silica-filled natural rubber were investigated using a JSM-6700F scanning electron microscope (JEOL Ltd., Tokyo, Japan). Untested dumbbell samples were immersed in liquid nitrogen for 4 min to create cryogenic fracture surfaces. After that, the samples were shattered in liquid nitrogen (~196 °C), sputtered with gold, and imaged. Dynamic mechanical thermal analysis (DMTA) was performed on a DMTA instrument (Rheometric Scientific DMTA V, Rheometric, Inc., USA). The samples were tested using the tension mode. The tests were performed from −100 to 100 °C, a heating rate of 5 °C/min, and strain control values of 0.001 (~100 to ~30 °C) and 0.01% (~30 to 100 °C).

■ AUTHOR INFORMATION

Corresponding Author
Sukritthira Ratanawilai — Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai 90112 Songkhla, Thailand; orcid.org/0000-0001-5900-0660; Email: sukritthira.r@psu.ac.th

Authors
Ekaroeck Phumnok — Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai 90112 Songkhla, Thailand
Parinya Khongprom — Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai 90112 Songkhla, Thailand; Air Pollution and Health Effect Research Center, Prince of Songkla University, Hat Yai 90112 Songkhla, Thailand

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c05848

Notes
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