Wet Mixing with Organic Solvent for Synthesized cis-1,4-Polyisoprene-Based Rubber Composites

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ABSTRACT: In this work, well-dispersed fumed SiO₂/cis-1,4-polyisoprene rubber (IR) masterbatch was first obtained through an effective wet mixing method, and the properties of the corresponding vulcanizate were studied. Before curing with activator and sulfur, IR solution was blended and co-coagulated with SiO₂ suspension modified by bis(3-trimethoxysilylypropyl) tetrasulfide in n-hexane. The modification of TESPT imparted evenly distributed SiO₂ particles in IR and improved interfacial binding among SiO₂ and IR. Hence, the prepared compound presented better processability and the corresponding vulcanizate presented higher physical performance, including higher tensile strength, lower heat buildup, and better fatigue resistance than that prepared in the dry mixing method. Additionally, higher wet skid resistance and lower rolling resistance could be observed in fabricated SiO₂/IR vulcanizate. The employed wet mixing method is economical and efficient, which is promising in preparing rubber composites with comprehensive performance.

1. INTRODUCTION

Recently, it is well recognized that the nanoscale fillers with high specific surface area are very effective for tires both from eco-friendly aspect and high performance, and the effectiveness depends greatly on the dispersion of the filler particles in a polymer matrix. In tire industry, silica (SiO₂) is a kind of nanoscale fillers secondary only to carbon black that could significantly improve the low rolling and wet skid resistance of tires. However, the existence of the siloxane and silanol groups in SiO₂ molecules results in its high surface energy and agglomeration, leading to weaker interfacial binding force between SiO₂ and rubber matrix and poorer processing performance, which limits the real applications of SiO₂. To increase the interfacial binding force, numerous methods including rubber's molecule functionalization and SiO₂ surface modification are proposed, and the later one is demonstrated as simple and cost-effective. Amongst, bis(3-trimethoxysilylypropyl) tetrasulfide (TESPT) is one of the mostly used coupling agents since Wolf's pioneering research, which could not only modify the hydroxyl groups on the surface of nano-SiO₂ with nonpolar alkyl chain to enhance its dispersion in rubber but also participate in the vulcanization process through releasing sulfur-containing chemicals at high temperature.

Although TESPT-modified SiO₂ could provide rubber with much better properties, the method integrating modified SiO₂ with a rubber matrix still be taken into serious consideration. In the traditional dry mixing method, the TESPT, SiO₂, rubber matrix, and other ingredients are simultaneously mixed during two-roll milling and internal mixing processes. The molecules of coupling agent react with the hydroxyl groups on the surface of nano-SiO₂ in situ under heat and shear force. However, high energy consumption and severe dust pollution are annoying problems that are still could not be resolved so far, despite being simple and commonly used. More importantly, high viscosity of the compound and relatively weaker shearing force lead to the low coupling efficiency, which inevitably results in agglomerations of SiO₂ and the inhibition of the intrinsic properties of nanoscale materials. Especially, it is extremely hard to process rubber compounds with fumed SiO₂, which possesses much smaller size, higher specific surface area, lower density, and more desirable reinforcement properties compared with precipitated SiO₂. More eco-friendly wet mixing is thus developed for natural rubber (NR) and solution polymerized styrene butadiene rubber (SSBR) due to its relatively lower energy consumption, higher modification efficiency, and significantly improved dispersion of SiO₂ in...
Scheme 1. Fabrication Route of SiO2/IR Vulcanizate through Wet Mixing Method

method is only applicable for the NR latex, while the IR could not be solved in water to form the water-born emulsion.

In view of this, an efficient wet mixing method was specifically designed for IR-based synthetic rubber, which involved the modification of SiO2 with TESPT in n-hexane and subsequent mixing with n-hexane solution of IR, followed by flocculation in poor solvent. n-hexane is the most used solvent of IR with the relative lower boiling point and similar solubility parameters, which could evaporate more easily and benefit to the following drying procedure. Modification of SiO2 with TESPT in hexane and mixing with IR directly was more time-saving and easier to realize better mixing with IR solution in hexane, which avoids the tedious steps including washing, drying, grinding, and re-dispersing, which always consume several days and more energy. It was shown that this wet mixing method significantly improved the dispersion of fumed SiO2 in IR with the correspondingly elevated bound rubber content (BRC) as well as the lowered Payne effects.

Accordingly, the fabricated SiO2/IR vulcanizate exhibited enhanced mechanical property, higher wet skid resistance, and lower rolling resistance than that obtained in the dry mixing method. The wet mixing method proposed in this study was effective, time-saving, and applicable for other synthetic rubbers, which provides the researchers and experts in this field with a new pathway to unfold the properties of synthetic rubber composites.

2. EXPERIMENTAL SECTION

2.1. Materials. Fumed SiO2 particles (~12 nm; Cabot Corp., USA) with BET specific surface area of 206 m²/g, were dried at 150 °C for 2 h to remove the absorbed moisture. Bis-(3-trimethoxysilylpropyl) tetrasulfide (TESPT) was obtained from Shandong Yanggu Huatai Chemical Co., Ltd. Cis-1,4-polysoprene rubber (IR, SKI-5 PM) with Mw of 272,100 was purchased from JSC Kauchuk Co. in Russia. Other ingredients, such as curing agent (sulfur), accelerators (N-tert-butyl-2-benzothiazolesulfenamide (TBBS)), activator (zinc oxide (ZnO)), stearic acid (SA), and anti-aging agent (2,6-diter-buty-4-methylphenol (BHT)) were all commercially available products and used as received.
2.2. Preparation of SiO₂/IR Masterbatch. The fabrication of SiO₂/IR wetting masterbatch is illustrated in Scheme 1. Typically, 30 g SiO₂ and 3 g TESPT were mixed into 1 L n-hexane and stirred at 50 °C for 3 min under a rate of 20,000 rpm (Scheme 1a,b). After that, the obtained SiO₂ suspension modified with TESPT was poured into the 2 kg IR solution (5 wt %) and mixed at 50 °C for 30 min (Scheme 1c) under a rate of 300 rpm. Subsequently, the masterbatch of SiO₂/IR was coagulated in 6 L prepared ethanol and stirred for 1 min at a rate of 300 rpm during which a part of unreacted TESPT was removed using ethanol (Scheme 1d). Also, the flocculate was dried thoroughly in a 45 °C vacuum oven until a constant weight was reached after extruded by a micro extruder.

2.3. Fabrication of SiO₂/IR Vulcanizate. The SiO₂/IR vulcanizate was obtained in the following steps. In detail, the calculated ZnO, SA, BHT, TBBS, and sulfur were uniformly blended into the compounds by the two-roll mill at 70 °C for 5 min, and the sheets with an approximate thickness of 2.5 mm were obtained (Scheme 1d-e). As a comparison, gum IR and SiO₂/IR dry compound were also fabricated as the following: The calculated IR, SiO₂, TESPT, ZnO, SA, and BHT were uniformly blended in a Banbury mixer. Then, TBBS and sulfur were uniformly blended into the compounds by the two-roll mill, and the sheets with an approximate thickness of 2.5 mm were obtained. The vulcanizates were cured at 145 °C under 15 MPa for 60 min in a press vulcanizer and named as G-IR, W-SIR, and D-SIR, which corresponded to gum IR, SiO₂/IR prepared in wet mixing and dry mixing, respectively. The formulations of samples are listed in Table 1.

Table 1. Formulation of SiO₂/IR Compounds

| materials | GIR  | D-SIR | W-SIR |
|-----------|------|-------|-------|
| rubber    | 100  | 100   | 100   |
| ZnO       | 5    | 5     | 5     |
| SA        | 2    | 2     | 2     |
| BHT       | 2    | 2     | 2     |
| TBBS      | 1    | 1     | 1     |
| SiO₂      | 0    | 30    | 30    |
| TESPT     | 0    | 3     | 3     |
| sulfur    | 1.5  | 1.5   | 1.5   |

2.4. Characterization. The modification of SiO₂ was confirmed with Vertex 70 Fourier transform infrared spectrometer (FTIR, Bruker, Germany) over the wavenumber range of 400−4000 cm⁻¹, X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) using Al Kα radiation, and thermogravimetric analysis (TGA, Perkin Elmer, USA) at a heating rate of 10 °C/min from room temperature to 650 °C in a nitrogen stream. Before tests, the silica suspension was dried first at room temperature in a fume hood and extracted in ethanol in a Soxhlet extractor for 48 h to remove the residual TESPT and then dried completely in a vacuum oven.

The morphologies of samples were characterized using field emission scanning electron microscopy (SEM, XL-30) under an accelerated voltage of 15 kV and JEM 1011 transmission electron microscopy (TEM, JEOL, Japan) with an acceleration voltage of 100 kV.

The bound rubber content (BRC) was determined by extracting the uncured compound according to the literature. In detail, 0.5 g uncured rubber compound was cut into small pieces and transferred into a copper net cage with 300 mesh size, which were then soaked with toluene for 72 h at room temperature, and the solvent was renewed every 24 h. Finally, the residual compound was dried at 60 °C in a vacuum oven to a constant weight. The weight of the samples before and after extraction was weighed and the BRC was calculated according to the following equation

\[
\text{BRC} = \frac{w_2 - w_m (m_i + m_2)}{w_m (m_i + m_2)} \times 100\% \tag{1}
\]

where \( w_2 \) is the weight of sample after drying and \( w_1 \) is the weight of the sample before swelling. \( m_i \) and \( m_2 \) are the fraction of filler and rubber in the compound, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Modification of SiO₂. The used fumed SiO₂ had an average size of 12 nm, which was obtained by collecting more than 300 particles in TEM images, as shown in Figure 1a. Different from the traditional reaction in water or in situ during drying mixing, the silanol groups on the SiO₂ surface could be successfully reacted with ethoxy groups maybe through a strong shear force in n-hexane within several minutes (Scheme 1a,b), which could be demonstrated in Figure 1b–d. For the wet mixing method, silanization could be carried out at a rate of 20,000 rpm stirring. Although the stirring time was extremely short than traditional procedure, the shearing force was far larger than that suffered in the internal mixer. In our work, the modification was carried out at 50 °C for 3 min under a 20,000 rpm stirring. Although the stirring time was extremely short than traditional procedure, the shearing force was far larger than that suffered in the internal mixer. The shear stress was absorbed in the chamber of high-speed stirring homogenizer and knocked against violently the chamber wall and with molecules including TESPT and silica itself. It might be the huge instantaneous energy that break down the Si−O bond of TESPT and facilitate the condensation of it and the hydroxyl groups on silica (Scheme 1a,b). To confirm this, silica suspension with a certain volume was first dried at room temperature in a fume hood and then extracted in ethanol in a Soxhlet extractor for 48 h to remove the residual TESPT.6
After drying again, the resulted powder was characterized using FT-IR, XPS, and TGA, and the results are shown in Figure 1.

After modification, two obvious peaks in FT-IR spectra at 2970 and 2927 cm\(^{-1}\) emerged, which were ascribed to the stretching vibration of \(-\text{CH}_2-\) groups in the TESPT backbone (Figure 1b).\(^{12}\) To further confirm the modification of TESPT on SiO\(_2\), the XPS spectra were obtained (Figure 1c). Evidently, there were an increased C 1s peak at 284.5 eV and a weak S 2p peak at 163.4 eV in SiO\(_2\)-TESPT, which could be seen in magnification inserted. The C 1s peak in SiO\(_2\) may be derived

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**Figure 1.** (a) Size distribution, (b) FT-IR spectra, (c) XPS spectra, and (d) TGA curves of pure and modified SiO\(_2\) in \(n\)-hexane.

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**Figure 2.** Bar graphs of (a) BRC and (b) \(G'-\varepsilon\) curves of compounds with different mixing methods.
from the conductive adhesive, which was used to fix sample. Additionally, the TGA curves of SiO2 before and after modification were displayed in Figure 1d. For pure SiO2, there was about 0.5% weight loss at 650 °C, which might be the evaporation of the absorbed water while apparent degradation in several steps appeared in SiO2-TESPT, and the weight loss was 7.3%, which indicated a grafting ratio of about 6.8 wt %. Obviously, the developed method to modify SiO2 using TESPT was efficiently and time-saving in comparison with the traditional ones, which always took longer time in the range between several hours to a few days.12−14

### 3.2. Dynamic Rheological Properties of SiO2/IR Compounds

In the filler-reinforced rubber, bound rubber content (BRC) is an important parameter measuring the interaction between filler and rubber, which is defined as the content of rubber molecules that are closely adsorbed on the surface of filler particles and can hardly be extracted by good solvent.29 It is the result of the strong interaction between filler and rubber, including physical and chemical adsorption, mechanical riveting and etc. To obtain the exact BRC of as-prepared rubber compounds, the samples of G-IR, D-SIR, and W-SIR were placed in the oven at 45 °C before testing to avoid the interference of the storage conditions.

Usually, the BRC increases when the interaction between filler and rubber is enhanced. Figure 2a showed the BRC of G-IR, D-SIR, and W-SIR. Apparently, W-SIR displayed the highest BRC. In detail, the BRC of W-SIR was about 3.35 times of that of D-SIR, which was 33.2 ± 2.4% and 9.9 ± 2.5%, respectively. In fact, it was ready to aggregate for SiO2 with limited modification in D-SIR due to hydrogen interactions among abundant silanol groups.12 Thus, the BET surface area of SiO2 that could absorb IR molecules was relatively low, and the affinity between polar SiO2 and non-polar IR is difficult to be improved for large difference of surface energy between SiO2 and IR. As a consequence, the BRC of D-SIR was much lower. Whereas, the existence of TESPT with amphiphilicity could not only reduce the difference of surface energy to enhance the affinity between SiO2 and IR but also benefit to well dispersion of SiO2 with less silanol groups and more effective BET area.8,12 Hence, the BRC of W-SIR was much higher than that of D-SIR.

The dynamic rheological properties of G-IR, D-SIR, and W-SIR were tested by RPA, and the curves of storage modulus in rubber without aggregates. In addition, the difference of surface energy between SiO2 and IR in the dry mixing method for limited modification with TESPT in situ. Hence, severe agglomerations happened through strong hydrogen bonding among SiO2 particles. For W-SIR, the fumed SiO2 could couple with TESPT more sufficiently, which served as a protector to avoid the interaction among SiO2 and did favor to disperse uniformly in rubber without aggregates. In addition, the difference between the maximum and minimum torque value \(M_L - M_H\) reflects the crosslinking degree of vulcanize. According to the data listed in Table 2, W-SIR possessed the highest \(M_L - M_H\) value (15.3 dN·m) compared to D-SIR and G-IR whose \(M_H - M_L\) value was 12.3 dN·m and 5.3 dN·m, respectively. The well-dispersed SiO2 particles provided much more crosslinking

### 3.3. Vulcanization Performance of SiO2/IR Compounds

Generally speaking, vulcanization characteristics of rubber compounds should be assessed to optimize the processing parameter in industries. The vulcanization curves and the corresponding characteristics of rubber with SiO2 in different mixing methods are displayed in Figure 3 and Table 2.

![Figure 3. Vulcanization curves of G-IR, D-SIR, and W-SIR compounds.](https://doi.org/10.1021/acsomega.0c03957)

| sample  | \(M_L\) (dN·m) | \(M_H\) (dN·m) | \(M_L\) (dN·m) | \(t_2\) (min) | \(t_0\) (min) | CRI (min⁻¹) |
|---------|----------------|----------------|----------------|---------------|---------------|---------------|
| G-IR    | 1.2            | 6.5            | 5.3            | 33.8          | 41.0          | 13.9          |
| D-SIR   | 3.5            | 15.8           | 12.3           | 7.7           | 59.3          | 1.9           |
| W-SIR   | 2.7            | 18.0           | 15.3           | 5.9           | 33.7          | 3.6           |

*CRI was obtained by the equation: \(\text{CRI} = 100/(t_0 - t_2)\)*

2. As we all know, the minimum torque \(M_L\) value relates to the compounds viscosity and the aggregate degree of filler.33−36 It can be seen that W-SIR possessed the medium torque \(M_L\) value (2.7 dN·m), which was lower than that of D-SIR (3.5 dN·m) but much higher than that of G-IR (1.2 dN·m) without SiO2. Typically, the aggregate degree of rigid SiO2 contributed to the increase of viscosity of compounds with an increased \(M_L\) value.35 Thus, the higher \(M_L\) value of D-SIR implied poorly distribution of SiO2 in the dry mixing method for limited modification with TESPT in situ. Hence, severe agglomerations happened through strong hydrogen bonding among SiO2 particles. For W-SIR, the fumed SiO2 could couple with TESPT more sufficiently, which served as a protector to avoid the interaction among SiO2 and did favor to disperse uniformly in rubber without aggregates. In addition, the difference between the maximum and minimum torque value \(M_L - M_H\) reflects the crosslinking degree of vulcanize. According to the data listed in Table 2, W-SIR possessed the highest \(M_L - M_H\) value (15.3 dN·m) compared to D-SIR and G-IR whose \(M_H - M_L\) value was 12.3 dN·m and 5.3 dN·m, respectively. The well-dispersed SiO2 particles provided much more crosslinking
points tightly chemical bonding with IR chains through TESPT, which resulted in the rapid growth of the torque value of W-SIR.

Furthermore, there was variation in the scorch time ($t_{s2}$), cure time ($t_{90}$), and curing rate index (CRI) of G-IR, D-SIR, and W-SIR. Amongst, the scorch time $t_{s2}$ determines the scorch performance and processing safety.\(^2\) Obviously, W-SIR
possessed the shortest $t_{1/2}$ (5.9 min) and $t_{90}$ (33.7 min) in comparison with D-SIR and G-IR whose $t_{1/2}$ and $t_{90}$ was 7.7 min, 33.8 min and 59.3 min, 41.0 min, respectively, while the CRI of D-SIR was the lowest (1.9 min$^{-1}$), which was much smaller than that of W-SIR (3.6 min$^{-1}$) and G-IR (13.9 min$^{-1}$). The lower $t_{1/2}$ implied more evenly as well as heavily restriction of SiO$_2$ particles on the movements of IR molecule chains. Rigid fillers will hinder the movement of rubber molecules, resulting in the increase of molecular cohesiveness energy and heat buildup. Therefore, the scorch time is shorter than that of pure rubber without SiO$_2$.\textsuperscript{37} In addition, rubbers filled particles with a higher structure and a larger specific surface area are more likely to be scorch. For W-SIR, SiO$_2$ presented better distribution with a much higher specific surface area compared with it in D-SIR, which could be demonstrated in the following TEM images. The more evenly distribution of SiO$_2$ exerted more absorbed more rubber molecules and resulted in higher BRC, indicating that more IR molecules are absorbed on the surface of SiO$_2$ and exhibited in the glass state with little movement. SiO$_2$ and absorbed rubber could serve as rigid filler, leading to poorer movement of rubber chain and less $t_{1/2}$. Hence, it is easier to understand that W-SIR presented the lowest $t_{1/2}$ for the most uniformly dispersed SiO$_2$ and most rightly interaction with IR chains, which could be demonstrated from the highest BRC.

The lower CRI was ascribed to the existence of silanol groups on the SiO$_2$ surface, which could absorb curing agents and react with the activator as well as the accelerator.\textsuperscript{12} For D-SIR, the modification of SiO$_2$ with TESPT was pretty limited. As a result, more curing agents were absorbed and more activator as well as accelerator was consumed owing to more silanol groups existed in D-SIR, leading to the most retarded curing process. In comparison, there were less silanol groups on the SiO$_2$ surface due to relatively sufficient modification of TESPT in $\alpha$-hexane. Correspondingly, less curing agents were absorbed and less activator as well as accelerator was reacted, which resulted in relatively lower $t_{1/2}$, $t_{90}$, and CRI than D-SIR. Taken together, W-SIR exhibited the highest processing efficiency with enough processing safety.

### 3.4. Morphology of SiO$_2$/IR Vulcanizates.

The morphologies of samples prepared in wet and dry mixing methods are shown in Figure 4. There were invisible aggregates of SiO$_2$ in D-SIR, which were circled in red line in Figure 4a. In addition, the size of distributed white dots in Figure 4a was larger than 12 nm, indicating poorly dispersion of SiO$_2$ through the in situ dry mixing method. Under-silica, the size of distributed white dots in Figure 4b was larger than 12 nm, indicating relatively uniform distribution of SiO$_2$ in IR matrix through the wet mixing method.\textsuperscript{38}

As a result, stress concentration was easy to occur in D-SIR when characterized using TEM (Figure 4a2). By contrast, even no particles could be observed in the SEM image of W-SIR (Figure 4b1) and SiO$_2$ dispersed quite uniformly without aggregates in W-SIR (Figure 4b2), which suggested that the wet mixing method is an effective way to obtain composite with well-dispersed SiO$_2$.\textsuperscript{90}

### 3.5. Mechanical Properties of SiO$_2$/IR Vulcanizates.

The mechanical properties are of great significance for actual applications. The mechanical properties of G-IR, D-SIR, and W-SIR are shown in Figure 5 and Table 3. As shown, the fumed SiO$_2$ could improve the tensile strength of IR in both dry and wet method from 21.2 to 23.5 and 29.8 MPa, respectively. Also, the tensile stress at 300% elongation of W-SIR was 10% higher than that of D-SIR. When compounding with SiO$_2$ in the dry and wet method, the elongation at break decreased from 1200 to 725 and 800%, respectively. Compared with D-SIR, W-SIR presented higher BRC, which inferred that the interaction between SiO$_2$ and IR molecules was stronger. The well-dispersed SiO$_2$ particles could transfer the stress more evenly to the connected IR chains. Hence, the tensile stress and elongation at break were much higher. However, stress concentration was readily happened in D-SIR due to lots of SiO$_2$ aggregates and poor interfacial binding between SiO$_2$ and IR, which caused lower tensile stress.\textsuperscript{16,17} Except that, it could be found that the results errors of W-SIR were much smaller than that of D-SIR, which could also imply better dispersion of SiO$_2$ in IR matrix through the wet mixing method.\textsuperscript{38}

The compression heat buildup could reflect the durability of a tire.\textsuperscript{12,39} The higher the temperature rises, the more likely the mechanical properties of the tire trade are deteriorated. The effect of different mixing method on the heat buildup of SiO$_2$ filled in IR through is exhibited in Figure 5c. As shown, the rising temperature of SiO$_2$ filled IR composites in both the dry and wet method was much higher than that of G-IR. As for D-SIR, the friction between SiO$_2$ aggregates with limited modification of TESPT was much larger than that in W-SIR well-dispersed SiO$_2$. Thus, more heat was produced when rubber deformed. Whereas, SiO$_2$ modified more sufficiently with TESPT uniformly distributed in IR and acted as a crosslinking agent through chemical bonding with IR chains. When deformation happened, little friction among SiO$_2$ particles and the slippage of IR chains were much lower, resulting in relatively lower heat buildup.

Furthermore, the flexion fatigue times are also an important parameter concerned to the lifetime of rubber products. As displayed in Figure 5d, the flexion fatigue times increased with addition of SiO$_2$ and W-SIR possessed much more fatigue times than that of D-SIR with the same content of SiO$_2$. The phenomenon may be caused by the following two reasons. On the one hand, stress concentration was easy to occur in D-SIR for tremendous SiO$_2$ aggregates in IR, and on the other hand, the much higher heat buildup did harm to the performance of IR.

### 3.6. Dynamic Properties of SiO$_2$/IR Vulcanizates.

Figure 6 demonstrates the temperature-dependent loss factor ($\tan \delta$) of SiO$_2$/IR in different mixing methods by DMA, in which $\tan \delta$ was the ratio of loss modulus and storage modulus ($E''/E'$). The glass transition temperature ($T_g$) of SiO$_2$/IR vulcanizates could be determined by the maximum peaks of $\tan \delta$-T curves.\textsuperscript{40} As can be seen in Figure 6, W-SIR showed the relative higher $T_g$ (−44.8 °C) than that of D-SIR (−48.8 °C), which was attributed to the well dispersion of SiO$_2$ with sufficient modification. The higher $\tan \delta$ peak corresponds to a weaker filler—filler network.\textsuperscript{12} The better dispersion of silica in...
the IR weakened the filler–filler network structure and reduced the amount of IR molecular chains trapped in the filler–filler network with more rubber chains participating in chain segment relaxation.\textsuperscript{41} In addition, the well-dispersed fumed SiO\textsubscript{2} served as crosslinking points in W-SIR, restricting the movement of IR chains. Hence, IR chains moved harder in W-SIR with much higher crosslinking degree than that in D-SIR. Correspondingly, the $T_g$ was much higher for W-SIR than that of D-SIR with poor dispersion and interfacial binding force.

In addition, the wet skid resistance and rolling resistance of tires could also be evaluated by the curve of $\tan\delta$-$T$. The rolling resistance of a tire is also called rolling loss, which mainly comes from the hysteresis loss of the tire material when moving on the road. To be exact, the rolling loss of a tire is the heat energy converted by mechanical energy when the tire moves for a unit distance on the way.\textsuperscript{42} According to the classical literature ref 42, the smaller the $\tan\delta$ value is the lower rolling resistance the tire has when the other structural parameters remain unchanged. The surface and interior temperatures of tire are usually higher than room temperature due to the hysteresis of heat generation during rolling on the road. Therefore, $\tan\delta$ at 60 °C higher than room temperature is used to characterize the rolling resistance.\textsuperscript{42}

The wet skid resistance is another important property related to the safety. When the tire brakes on the wet road, it depends on the wet friction between the rubber and the road surface where the accumulated heat could be diffused in time owing to the existence of water.\textsuperscript{43} Hence, it is assumed that the wet skidding happens at or even lower than room temperature.\textsuperscript{44} Amongst, wet skid resistance was represented by $\tan\delta$ at 0 °C, where the $\tan\delta$ at 0 °C was higher and the wet skid resistance was higher, which is now the most used parameter to characterize wet skid resistance.\textsuperscript{45,46} As can be seen, the $\tan\delta$ values of W-SIR were relatively higher at 0 °C and much higher at 60 °C than that of D-SIR (magnified in curves inserted as shown in Figure 6), which suggested that W-SIR exhibited higher wet skid resistance and lower rolling resistance simultaneously.

4. CONCLUSIONS

The fumed SiO\textsubscript{2}/IR compound was manufactured for the first time through one-step wet mixing method, and the properties of the corresponding vulcanizate (W-SIR) were investigated. The SiO\textsubscript{2} particles could be modified efficiently with TESPT in $n$-hexane and disperse more uniformly in the IR matrix. The filler–filler aggregates structure was weakened and the filler–rubber interaction was strengthened efficiently in that the silanol groups on SiO\textsubscript{2} were successfully shielded by modification with TESPT, which was demonstrated through TEM, BRC, and lower Payne effect. Thus, W-SIR possessed better vulcanization processability containing suitable $t_2$ and higher vulcanization rate than that prepared in the traditional dry mixing method. Furthermore, W-SIR vulcanizate presented much better physical properties containing lower heat buildup, better fatigue resistance, and tensile strength. In addition, the obtained vulcanizate displayed higher wet skid resistance and lower rolling resistance in dynamic performance. Thus, it can be seen that the developed wet mixing method shows great perspective in obtaining fumed SiO\textsubscript{2} filled rubber composites with low-cost, time-saving, and comprehensive performance.

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