Silica Agglomerate Breakdown in Three-Stage Mix Including a Continuous Ultrasonic Extruder

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Abstract: The dispersive mixing of premixed nano-size untreated and treated silica particles, and compounds in ethylene-propylene-diene terpolymer (EPDM) were studied using an ultrasonic extruder (Ultra) and compared with an internal mixer (Int) processing. The rheological properties and extrudate swell of the compounds were investigated and compared with carbon black filled compounds. The Ultra processing broke down the silica agglomerate sizes effectively, which became smaller than after an Int processing. The silane treated silica exhibited a considerable reduction in the agglomerate sizes compared to the untreated silica in an Int. These results were then compared with carbon black filled compounds. The viscosity of the compounds with untreated and treated silica was higher than the compounds with carbon black. This may be due to the rough surface of the silica particles. The silane treated compounds exhibited a lower viscosity than the untreated compounds. The effect of extrudate swell reduction was minimal on the treated compounds.

Keywords: nano size silica agglomerate; silane coupling agent; internal mixer; ultrasonic extruder; rheological property

1. Introduction

The use of silica to replace of carbon black in rubber compounds has been found to reduce the rolling resistance [1,2]. A good dispersion of silica particle agglomerates improves the performance of tires in terms of the wet traction, snow traction, and low gas mileage. However, silica is known to be more difficult to disperse than carbon black during mixing [3-5]. Silica particles have a polarity while carbon black is non-polar, therefore silica particles result in a strongly combined agglomerate [6].

Various types of continuous mixers and internal rotor mixers have been applied to reduce the size of carbon black or silica agglomerates in rubber matrices [7,8]. Continuous ultrasonic extruders have often been utilized in the study of the breakup of calcite particle agglomerates in a thermoplastic matrix [9]. The high stresses developed during ultrasonic extrusion also allow it to be used in mechanical degradation devulcanization for recycling rubber compounds [10]. This machine breaks chemical bonds including carbon-sulfur (C-S), sulfur-sulfur (S-S), and carbon-carbon (C-C) bonds in vulcanized rubber.

This paper reports on an ultrasonic technique that can disrupt silica agglomerates during mixing. There has been no previous research on breaking up silica particle agglomerates using Ultra. Viscosity measurements were made for each system to compare the processability of the silica aggregate dispersion. A laboratory internal mixer was used for compounding silica and rubber for the first process. The specimen was then processed in a two-roll mill, and finally a laboratory ultrasonic single screw extruder was used for the third process.

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Table 1. Particles and Rubber Used in This Study

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier; product name</th>
<th>Comment BET surface area (m²/g)</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hi-Sil(R)255LD</td>
<td></td>
<td>SA2</td>
</tr>
<tr>
<td></td>
<td>untreated</td>
<td>185 (0.018 μm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silene 732D</td>
<td>35 (0.075 μm)</td>
<td>SA7</td>
</tr>
<tr>
<td></td>
<td>untreated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Black</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cabot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>*Sterling NS-1-N762</td>
<td>29 (0.089 μm)</td>
<td>N762</td>
</tr>
<tr>
<td></td>
<td>*Vulcan 9-N110</td>
<td>143 (0.021 μm)</td>
<td>N110</td>
</tr>
<tr>
<td>Ethylene-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene-</td>
<td>DSM Copolymer;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terpolymer</td>
<td>Keltan EPDM;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EPDM)</td>
<td>2506</td>
<td></td>
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<tr>
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</tr>
</tbody>
</table>

Table 2. Chemical Conformation, Structure, and Names of Silane Used.

<table>
<thead>
<tr>
<th>Type of silane (Code)</th>
<th>Name</th>
<th>Chemical conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane 116 (SN1)³</td>
<td>Hexadecyltrimethoxysilane</td>
<td>(CH₃O)₂Si-C₁₆H₃₂</td>
</tr>
<tr>
<td>Silane 203 (SN2)⁴</td>
<td>Propyltriethoxysilane</td>
<td>(C₃H₇O)₃Si-C₃H₇</td>
</tr>
</tbody>
</table>

1. Hexadecyltrimethoxysilane (Silane-116) OR

RO- Si - OR
(CH₃)₃
CH₃
R=CH₃, n=15

2. Propyltriethoxysilane (Silane-203) OR

RO-Si-OR
(CH₃)₃
CH₃
R=C₃H₇, n=2

2. Experimental

2.1. Materials

The particles used in this study were the silicas of Hi-Sil(R)255LD (SA2) and Silene 732D (SA7), supplied by PPG, and the carbon blacks of N110 and N762, supplied by Cabot.

The EPDM used was a DSM copolymer ethylene-propylene-diene terpolymer (Keltan EPDM 2506) with 56% ethylene and a Mooney viscosity (ML-4) of 28. Information on the particles and rubber is summarized in Table 1.

The silane coupling agents used were Silane-116 and Silane-203 supplied by Degussa. The silica particle SA2 was treated with Silane-116 (SN1) and Silane-203 (SN2) [11]. The coupling between silica SA2, and SN1 and SN2 was followed according to the method of Byers [1]. The names of the silane and chemical structures are summarized in Table 2.

2.2. Mixing

2.2.1. Internal Mixer (Int)

The first stage mixing was carried out using a Brabender PL2000 Plasticorder. A pair of adjustable rotors developed by the authors' [12] was used with a rotor configuration of two long and short flights typical of that used in the tire industry. The mixer chamber had a free volume of 65 cm³ and fill factor of 0.6. The mixing temperature was 100 °C. The rotor speed of 60 rpm was used.

2.2.2. Two Roll Mill (Mill)

The specimen compounded through an Int was then processed by a Mill for 5 to 7 min with a gap distance of 1-2 mm as the second stage of mixing. The diameter of the Mill was 15 cm and the rotation speed was 23 RPM.

2.2.3. Ultrasonic Extruder (Ultra)

The samples prepared in the Mill were fed into an ultrasonic single screw extruder [13,14] as the third stage of mixing. The extruder temperature was set to 100 °C for all three-barrel zones. The material was then introduced and conveyed by the screw to the end of the die with an extruder speed of 30 rpm. The clearance between the die and the ultrasonic horn was fixed at 3 mm. The frequency of the ultrasonic was set to 20 kHz. The break up of silica agglomerate took place in the gap between the die and the ultrasonic horn. The ultrasonic

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where \( \Omega \) is the angular velocity, \( a \) is the cone angle, \( M \) is the torque, and \( R \) is the cone radius.

Their viscosity levels were represented as a function of the shear rate and shear stress.

2.7. Extrusion Characteristics

Every extrudate of the compounds from the capillary die was obtained at a wall shear rate of 1000 (sec\(^{-1}\)). The extrudate diameters of the coupling agent treated and untreated systems, plus 10 v\% and 20 v\% of each system were measured. The extrudate swell ratios relative to the capillary diameter of 1.5 mm were also determined.

3. Results

3.1. SEM observations of Agglomerates

Figure 2 shows typical SEM photographs of SA2, N110, SA2/SN1, and SA2/SN2 processed using an internal mixer. The SA2 particles were compounded into EPDM at 20 v\% in an Int for 7 min. The Image Analyzer analysis revealed the SA2 agglomerate size to be 3.3 \( \mu m \).

SEM photographs of the silica agglomerates in the compounds processed through the Mill (SA2/EPDM) are exhibited in Figure 3. The SA2 agglomerate size was reduced to 0.7 \( \mu m \) after the Mill processing.

The compounds (SA2/EPDM) resulting from the Mill stage were then processed in the Ultra and the agglomerates are shown in Figure 4. The SA2 agglomerate size was further reduced to 0.3 \( \mu m \).

3.2. Shear Viscosity

The shear viscosity of the final compounds was summarized in Figure 5. The viscosities of all the different silica systems, including the treated and the untreated systems, were compared.

3.3. Extrudate Characteristics

Figures 6(a) through (f) show a series of optical photomicrographs of untreated and treated silica compound extrudates with various loading levels at the same die wall shear rate (32\( Q/\pi D^2 = 1000 \text{sec}^{-1} \)).

4. Discussion

4.1. Particle and Agglomerate Characteristics

The size of the ultimate particles can be estimated from the BET surface area, which was cited from supplier. In Figure 7, the number of ultimate particles in an agglomerate was compared as a function of the BET surface area using various techniques. The number of ultimate particles per agglomerate

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Figure 2. SEM photographs of SA2 processed with internal mixer (Int) in EPDM matrix at 20 vol%, 5000 magnification (a) IntSA2, (b) IntN110, and (c) IntSA2/SN1, (d) IntSA2/SN2.

Figure 3. SEM photographs of SA2 processed in two-roll mill (Mill) at (a) 10 vol%, (b) 20 vol% (10000 magnification).

Figure 4. SEM photographs of SA2 processed in ultrasonic extruder (Ultra) at (a) 10 vol%, (b) 20 vol% (10000 magnification).
Figure 5. Viscosity as a function of (a) shear rate, (b) shear stress of ultrasonic extruder (Ultra), internal mixer (Int) with silane treated silica and carbon black system in EPDM matrix at 20 vol%.

Figure 6. Photographs of capillary extrudates from (a) IntSA2, (b) IntSA7, (c) IntSA2/SN1, (d) IntSA2/SN2, (e) IntN110, (f) UltraSA2 in EPDM matrix at extrusion rate of 1000 sec⁻¹.
for IntSA2/SN1, MillSA2, UltraSA2, and IntN110 were roughly 45, 43, 18, and 12, respectively.

The number of aggregates rather than the number of ultimate particles in an agglomerate was also estimated [11]. Based on TEM photographs, the carbon black aggregates had about 7 ultimate particles [18,19] and silica aggregates about 5 particles [5]. This suggests that the IntN110 agglomerates have about 1.7 aggregates. The agglomerate of the untreated SA2 had 25 aggregates, while the treated SA2/SN2 compound had 9.0 aggregates. The Mill processed SA2 (MillSA2) compound had 8.6 aggregates, and the ultrasonic processed SA2 (UltraSA2)

Figure 9. Extrudate swell ratio of silane treated silica, carbon black, and silica with Ultra treated compounds in EPDM matrix as a function of volume loadings at wall shear rate of 1000 (sec\(^{-1}\)) and 100 °C.

had 3.6 aggregates in an agglomerate.

4.2. Comparison to Silane Treated Compounds

The size reduction of the silica agglomerate was plotted as a function of the processing method as seen in Figure 8. The SN1- and SN2-treated SA2 (approximately 20 µm in powder form) exhibited a considerable reduction in the particle agglomerate after an Int processing (IntSA2/SN1, IntSA2/SN2). The IntSA2/SN2 (approximately 0.6 µm) silica agglomerates were smaller than the IntSA2/SN1 (approximately 1.4 µm) after an Int processing. The mechanism for this would appear to be as follows. SN1 has three methoxy functional groups attached to a silicon atom and a hexadecyl hydrocarbon chain. SN2 has three ethoxy functional groups on a silicon atom and a propyl hydrocarbon chain. The ethoxy and methoxy groups in coupling agents react chemically with the hydrogen atom on surface of silica. Ethyl- and methyl-alcohol then evaporate after chemical reaction. After treatment, the surface character of the silica then reduces their polarity, as suggested in Figure 10. Thus, the silane coupling agent then acted as an emulsifying and dispersing material for the silica agglomerates. SN1 seems to bond on silica surface less effectively because the stearic hindrance of SN1 is more significant due to long hydrocarbon chain compared to SN2 this will be discussed further on next manuscript.

The size of the SA2 agglomerate progressively decreased from an Int stage (1st processing) to the Mill stage (2nd processing, Int+1st), then from the Mill
stage to the Ultra stage (3rd processing, Mill+2nd). The SA2 (approximately 100 \(\mu\)m in powder form) exhibited a considerable reduction in the particle agglomerate after an Int processing (IntSA2) (approximately 3.3 \(\mu\)m). IntSA2 exhibited an agglomerate reduction after the Mill processing (MillsA2) (approximately 0.7 \(\mu\)m). MillsA2 also exhibited an agglomerate reduction after the Ultra processing (UltraSA2) (approximately 0.3 \(\mu\)m). The series of Int to Ultra processing created the smallest agglomerate particle size at 0.3 \(\mu\)m.

4.3. Processability

In Figure 5, the shear viscosity of the SA2/EPDM compound processed through Ultra(UltraSA2) and Int(IntSA2) exhibited the highest viscosity at 20 vol\%. The untreated silica SA2-filled system exhibited yield values similar to the Ultra system at 20 vol\%. The silica compounds had a higher shear viscosities than the equivalent carbon black compounds. The UltraSA2 exhibited a higher yield value than the IntSA2 system. The viscosity of the SA2 systems treated with SN1 and SN2 (IntSA2/SN1 and IntSA2/SN2) exhibited a lower viscosity level compared to the untreated system (IntSA2). From SEM and IA, we observed the reduction of the silica agglomerate, which imply higher surface area contacting rubber matrix. It is well known the viscosity increases as particle surface area contacting polymer increases [5,11,15-18]. The implication of viscosity decrease in silane treated system is silane acted as lubricant in the processing. Silane reduced polymer chain friction in this observation. Silane is well known processing agent to lower the viscosity of the compound [20]. The carbon black filled system with N110 (143 m²/g) exhibited the lowest viscosity level compared to the other silica SA2 (150 m²/g)-filled systems including the silica surface modified systems. This represents that the system filled with untreated silica SA2 has a poor processability compared to the carbon black filled system (N110). This may be due to the strong network between silica and the polymer due to the rough surface of the silica.

The capillary extrude swell ratios of each compound are compared in Figure 9. The extruded swell ratio of the Ultra system changed slightly from 10 vol\% to 20 vol\%. The treated SA2/SN1 and SA2/SN2 systems did not change considerably between 10 and 20 vol\%. The untreated SA2 exhibited a significant reduction in the extrude swell. The capillary extrude swell with the carbon black filled system exhibited a significant reduction, which was similar to the SA2 filled system. There were clear differences in the die swell d/D between the untreated and the treated systems. When comparing between the untreated particle and the treated particles, the untreated ones exhibited a significant reduction in the extrude swell.

As the silane coupling agents were added to the silica, the quality of the extrude smoothness improved and the magnitude of the swell d/D decreased, which was highest in the treated SA2/SN2 system, at about 1.4. The fastest decrease was found in the systems with untreated silica and carbon black.

The explanation for the above results is presumed as follows. Silane treated silica is covered with silane on the silica surface, as shown in Figure 10. Untreated silica and carbon black reduce the mobility of the polymer chain, whereas treated silica acts as a lubricant interface between the silica surface and the polymer. Treated silica broadens the molecular weight distribution of the compound, thereby reducing the effect on the extrude swell.

5. Conclusions

1) The particle distribution of silica agglomerates prepared by both Ultra and Mill exhibited well dispersed states, however bigger agglomerates still existed in the Mill system with 10 and 20 vol\% loadings (see Figures 3 and 4).

2) The Ultra and Mill processing produced a substantial reduction in the SA2 agglomerates from an Int processing. The Ultra system would seem to
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contribute to a further break up of the bigger silica agglomerates still existing after the Mill processing.

3) The addition of surface modified silica to the elastomer increased the viscosity level of the compound, however the effect on reducing the swell was minimal.

4) The Ultra processing reduced the size of the silica agglomerates, however it did not reduce the viscosity. The surface modified SA2 systems exhibited a reduction in both the agglomerate size of reduction silica and the viscosity.

5) The best results were obtained after the Ultra processing, which produced a further reduction in the silica agglomerates from an Int processing, as shown in Figure 7. Accordingly, this method facilitates the dispersion of silica agglomerates close to the level of carbon black without using silane coupling agents.

6) As expressed in Figure 8, the Mill processing was found to significantly reduce the SA2 agglomerate sizes.

Acknowledgement

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