Effects of Silica on the Cure Properties of Some Compounds of Styrene-butadiene Rubber

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ABSTRACT

The cure properties of some conventional accelerator/sulphur compounds of styrene-butadiene rubber (SBR) with a sulphur to accelerator ratio of ~1.8, containing no filler, and 10, 30, or 50 pphr rubber by weight precipitated amorphous white silica filler type VN3 were studied at 160°C by an oscillating disc rheometer curemeter. The optimum cure time, \( t_{95} \), of the compounds was lengthened substantially from 20 to 280 min when silica loading was raised to 50 pphr. The rate of cure calculated from the cure rate index, decreased sharply from 8.3 to 0.37 min\(^{-1}\) when the amount of silica in the mixes reached 50 pphr. Interestingly, the scorch time, \( t_{92} \), of the compounds was not affected by the addition and increases in the amount of silica, and remained at about 8 min, although, there was some evidence that silica had interfered with the reaction mechanism of sulphur cure and reduced the extent of cure in the rubbers. Our results indicated that the compounds were fully cured when sufficient time i.e., up to 300 min for the mix with 50 pphr filler, was allowed for the reaction in the compounds at elevated temperature to complete.

Key Words: silica, styrene-butadiene rubber, accelerator/sulphur cure compounds, cure properties

INTRODUCTION

In recent years, synthetic silicas such as precipitated amorphous white silica have been replacing carbon blacks, to some extent, in applications such as shoe soles, tyres, and engine mounts. These fillers are being used increasingly as reinforcement in rubber products, that is to say they are added to rubber formulations to improve physical and mechanical properties such as hardness and tear strength, and therefore it is essential to examine their effects on the viscosity and cure properties of rubber compounds beforehand. It has been known for some time that use of silicas in rubber compounds is problematic mainly due to the presence of siloxane and silanols groups on the surface of the filler [1]. The silanol or hydroxyl groups are acidic [2] and interact with basic accelerator or causing detrimental effects, i.e. unacceptably long

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cure times and slow cure rates, on the curing reactions in rubber compounds [1]. In addition, because the surface of the filler is polar and hydrophilic, there is a strong tendency to adsorb moisture [3, 4].

Studies with some sulphur cure system based SBR compounds containing precipitated silica have shown that presence of surface hydration on the filler influences the scorch and cure times of these mixes, i.e. longer cure times occur at the lower levels of adsorbed moisture [5].

Dunnom [6] studied effects of this filler on the cure properties of some compounds of SBR with a sulphur to accelerator ratio of 2, and showed that long scorch times were recorded. His results also revealed that silica retarded the rate of cure in the mixes considerably. Similar findings were reported likewise by Ozanemu and Georget [7] when they measured the scorch and cure times of some sulphur cure system based SBR compounds with a sulphur to accelerator ratio of about 1.7 filled with precipitated silica.

The aim of this preliminary study was to assess effects of precipitated silica on the viscosity and cure attributes of some conventional accelerator/sulphur compounds of SBR with a sulphur to accelerator ratio of about 1.8, which will be utilized in a future work to measure reinforcing effects of different amounts of this filler on the hardness and tear strength of the vulcanizates of these compounds.

In our work, we progressively increased the loading of silica in the mixes to 50 pphr with a view to learn about effects on viscosity and to examine cure properties at different levels of the filler loading. It has been claimed [1] that there is no sulphur cure system at present, which yields satisfactory cure properties in combination with silica unless the chemical groups on the surfaces of the filler are modified by additives such as bifunctional organosilanes. This work also examined this claim with respect to the compounds loaded with silica.

**EXPERIMENTAL**

**Materials**

The raw elastomer used for these studies was styrene-butadiene rubber (styrene 23.5 wt %) (SBR, Intol 1500-Enichem) containing no filler, and 10, 30, or 50 parts per hundred rubber by weight (pphr) of precipitated amorphous white silica filler type Ultrasil VN3 supplied by Degussa AG, Germany. The silica was stored at 18 °C at an ambient relative humidity of 76% for four weeks prior to use. In addition to the elastomer and filler, some other ingredients were also added and are listed in Table 1.

**Mixing Procedure**

Mixing was carried out in two stages on a Farrel Bridge 6" x 12" a two-roll open swing side laboratory mill. A front roll speed of 2 ft/min and a friction ratio of 2 were maintained during mixing. Before mixing commenced, the temperature of the rolls was raised to 70 °C, and the raw elastomer was placed in an oven at 40 °C for 30 min to soften prior to mastication on the mill. The rubber was then recovered and placed on the mill, and masticated for up to 8 min before adding the ingredients. In the first stage of mixing, zinc oxide, stearic acid, processing oil, Santoflex 13 (antidegradant), and white silica were added to the raw elastomer and mixed. The mixing time of the compounds with higher loading of silica increased progressively, because it took longer times to add the larger amounts of the filler to the elastomer on the mill (Table 1). After mixing ended, the compound was removed from the mill and its temperature measured with a thermocouple (Table 1).

The compound was subsequently left at ambient temperature (~23 °C) to cool down to approximately 30–35 °C, before it was re-introduced on the mill and the accelerator and sulphur were added. We allowed up to 7 min extra mixing time for incorporating these two additives (Table 1). Finally, the compound was removed from the mill and its temperature recorded (Table 1). After mixing ended, the compounds were stored in a freezer for 24 h before their cure properties were determined.

**Test Procedure**

The moisture content of the silica was determined by weighing ~4.94 g of the material, and placing it in a vacuum oven at 110 °C under a pressure of 0.04 bar
Table 1. Recipe and mixing conditions for the compounds.

<table>
<thead>
<tr>
<th>Compound number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formulation (pphr)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roll temperature (°C)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
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<tr>
<td>Raw elastomer temperature (°C)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Styrene-butadiene polymer (SBR-Intol 1500)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Processing oil (Ener Flex 74)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Santoflex 13</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Precipitated silica (VN3)</td>
<td>0</td>
<td>10</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Mixing time (min)</td>
<td>21</td>
<td>41</td>
<td>54</td>
<td>57</td>
</tr>
<tr>
<td>Compound temperature (°C), after mixing ended</td>
<td>64</td>
<td>63</td>
<td>65</td>
<td>67.5</td>
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<tr>
<td><strong>Stage 2 mixing</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Roll temperature (°C)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Compound temperature (°C), before mixing started</td>
<td>32</td>
<td>34</td>
<td>33</td>
<td>35</td>
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<tr>
<td>Santocure (CBS)</td>
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<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
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<tr>
<td>Sulphur</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Mixing time (min)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Compound temperature (°C), after mixing ended</td>
<td>62</td>
<td>59</td>
<td>66</td>
<td>64</td>
</tr>
<tr>
<td>Total mixing time (min)</td>
<td>26</td>
<td>46</td>
<td>59</td>
<td>64</td>
</tr>
</tbody>
</table>

| **Silica properties**        |     |     |     |     |
| Moisture content (% by weight) | -5.7 |     |     |     |
| pH                           | 5.9 |     |     |     |

The pH of silica was measured at 20 °C using a WPA CD 720 pH meter, after it was calibrated with pH 4 and 7 buffers. Silica (5 g) was dispersed in 100 mL of de-ionized water, and stirred for 1 min. The pH of the filler was further monitored for 5 min until it stabilized, and finally a reading was recorded.

The Mooney viscosity of the compounds, ML (1+4), was measured at 100 °C in a single-speed rotational Mooney viscometer according to the procedure described in ref. 8. The results are presented in Table 2. The scorch time, \( t_s \): time to 2 units of torque increase above minimum torque (Figure 1), and optimum cure time, \( t_9 \): time to 95% of maximum torque development calculated from the following expression:

\[
T_{new} = 0.95 \left( T_{max} - T_{min} \right) + T_{min}
\]

Where, \( T_{max} \) is maximum torque, and \( T_{new} \) a new torque reading corresponding to 95% cure in the rubber (Figure 1), were determined from the cure traces shown in Figures 1-4 generated at 160±2 °C by oscillating disc rheometer curemeter at an angular displacement of ±3° and a frequency of 1.7 Hertz [9].
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Table 2. The Mooney viscosities, and results from the ODR tests.

<table>
<thead>
<tr>
<th>Compound number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML (1+4), temp. 100 °C (Mooney units)</td>
<td>30</td>
<td>36</td>
<td>59</td>
<td>156</td>
</tr>
<tr>
<td>Monsanto Rheometer 160 °C</td>
<td>18</td>
<td>24</td>
<td>31</td>
<td>40</td>
</tr>
<tr>
<td>Minimum viscosity (dN.m)</td>
<td>63</td>
<td>63</td>
<td>70</td>
<td>88</td>
</tr>
<tr>
<td>Maximum viscosity (dN.m)</td>
<td>8</td>
<td>10</td>
<td>6.5</td>
<td>8</td>
</tr>
<tr>
<td>Scorch time t₀₂ (min)</td>
<td>20</td>
<td>25</td>
<td>78</td>
<td>280</td>
</tr>
<tr>
<td>Optimum cure time t₀₅ (min)</td>
<td>8.3</td>
<td>6.7</td>
<td>1.4</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The cure rate index, which is proportional to the average slope of the cure rate in the steep region of the cure curve, was also calculated using the following expression [10]:

\[ \frac{100}{(t_{05} - t_{02})} \] (2)

RESULTS AND DISCUSSION

The Mooney viscosity, Monsanto rheometer minimum and maximum viscosities, scorch time, optimum cure time, and cure rate index of the compounds are listed in Table 2. These results are also presented in a graphical form in Figures 5–8.

Figure 5 shows Mooney viscosity, ML (1+4), as a function of silica content. The viscosity of the compounds increased steadily from 30 to 59 units of the Mooney when the filler loading was raised to 30 pphr. It is worth noting that the mixing time of the compound containing 30 pphr silica was 13 min longer than the time considered for the mix with 10 pphr of the filler (Table 1). When the amount of silica was increased further by an extra 20 pphr, the rise in the viscosity was even more substantial to 159 units. This occurred in spite of masticating the rubber for a longer time of 64 min (Table 1). Increases in compound viscosity when filler is added, are attributed mainly to filler loading, filler/filler and filler/elastomer interactions [11-13].

In the case of silicas, however, strong filler/filler interactions resulting from polar surface functional groups such as siloxane [1] are believed to be primarily responsible for the increases recorded. It is interesting that Wolff and co-workers [14] measured the Mooney viscosities of some silica filled rubber compounds, and likewise observed large increases,

Figure 1. Torque versus time by ODR at 160 °C for the compound with no silica.

Figure 2. Torque versus time by ODR at 160 °C for the compound with 10 pphr silica.
particularly at high loading of the filler, with some of their results. These workers ascribed the increases to strong filler/filler interaction of silica.

Figures 6 and 7 show scorch time, \( t_{95} \), and optimum cure time, \( t_{55} \), as a function of silica loading, respectively. Evidently, the addition of silica of up to 50 pphr had little or no effect on the time to scorch of these compounds. It is interesting that increase in the acidity of the compound when the loading of silica was raised to 50 pphr; the subject silica had a pH of 5.9, had no obvious detrimental effect on the kinetics of onset of vulcanization or cross-link formation in the rubbers. The time taken for the compounds to scorch was approximately 8 min and it was essentially independent of silica loading (Figure 6). In contrast, the optimum cure time presented on a logarithmic scale for convenience, lengthened substantially from 20 to 280 min when silica was added and then increased progressively to its full loading. The largest increases were recorded when silica loading was boosted by an extra 40 pphr to 50 pphr (Figure 7).

The cure rate index which is a measure of the rate of cure in the rubber, presented also on a logarithmic scale, decreased sharply from 8.3 to 0.37 min\(^{-1}\) (Figure 8) suggesting that silica had retarded the rate of curing reaction in the compounds significantly. Dunnom [6] also observed a similar behaviour when he examined the effects of 50 pphr silica on the cure properties of some accelerator/sulphur compounds of SBR with sulphur to accelerator ratio of 2.

In this study, we allowed the Monsanto rheometer curemeter tests to run for up to 500 min before the curing reaction in the compounds at elevated temperatures was completed. This helped produce full cure traces for the compounds (Figures 1–4), whereas
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Dunnom [6] allowed similar experiments to run for only about 120 min before the measurements were completed. It was evident from his work that this duration was not sufficient to determine whether the compounds could be fully cured eventually.

As expected, the introduction and progressive increases in the amount of silica in the compounds prolonged the cure time, and retarded the rate of cure significantly. The subject silica possessed a moisture content of ~5.7% by weight. This corresponded to a surface hydroxyl concentration somewhere in the range of 9.2 and 15.8 per 100 Å² [3]. As mentioned earlier on, the acidic hydroxyl groups interact with basic accelerator and adversely affect the reaction mechanism of sulphur cure systems. Moreover, the amount of water adsorbed on the surface of the filler, controls the ionization of the hydroxyl groups [15] resulting also in detrimental effects on the cure properties of the rubbers, as we discovered in this study.

The long cure times and slow cure rates recorded for these compounds are unacceptable in industrial applications. Hence, to promote a wider use of silicas in rubber products, it is essential to remedy these processing problems. Bifunctional organosilanes [1, 16, 17] designed for use in sulphur cure systems and polyethylene glycol or diethylene glycol can help normalize cure [1], that is to say to prevent acidic silica from adversely affecting the cure reactions in rubber compounds and producing much shorter cure times and faster cure rates.

It has been known that silica interferes with the reaction mechanism of sulphur cure systems [1]. This can be investigated by examining correlations between $\Delta_{\text{torque}} (T_{\text{max}}-T_{\text{min}})$ and filler loading for different concentrations of sulphur [18]. It has been argued that if the correlations were linear with positive gradients and their extensions intersected the abscissa in one common point, then the reaction mechanism of sulphur cure was not affected by the presence of filler. Wolff [18] observed the correlations for some accelerator/sulphur compounds of SBR containing up to 40 pphr silica, and found no linear relationships between $\Delta_{\text{torque}}$ and silica loading satisfying the above requirement. He concluded that silica had interfered with the reaction mechanism of sulphur cure, reducing the cross-link yield or extent of cure in the mixes.

We carried out a similar study by utilizing the Monsanto rheometer minimum and maximum viscosities (Table 2), and likewise found no linear correlation between $\Delta_{\text{torque}} (T_{\text{max}}-T_{\text{min}})$ and silica loading intersecting the abscissa (Figure 9). The line in Figure 9 appears to have a zero gradient. This suggested that
silica had interfered with the cross-link yield or extent of cure, but evidently not with the attainment of full cure in the compounds (Figures 1–4). It was also interesting to note that our results were almost identical to the ones reported for the silica filled SBR mixes with a sulphur to accelerator ratio of 1 [18].

CONCLUSION

Contrary to what is claimed [1], this study has revealed that conventional accelerator/sulphur compounds of SBR with a sulphur to accelerator ratio of about 1.8, containing up to 50 pphr precipitated silica can be fully cured when sufficient time is permitted for the curing reactions in the rubbers to complete at elevated curing temperature. This is in spite of silica interfering with the reaction mechanism of sulphur cure, and reducing the cross-link yield or extent of cure in the rubbers.

The introduction and progressive increases in the loading of silica prolong the cure time and decrease the rate of cure of these compounds significantly. Interestingly, silica has little or no effect on the scorch time of the compounds, which remains essentially independent of the filler loading.

The long cure times and the slow curing rates of these compounds are unacceptable, and these processing problems have to be remedied if further industrial exploitation of these compounds is to be contemplated.

The Mooney viscosities of the compounds increase when silica is added, notably, these increases are much larger at the highest loading of the filler.

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REFERENCES