Revisiting the sulfur vulcanisation of rubber

This item was submitted to Loughborough University’s Institutional Repository by the/an author.

Citation: SHEIKH, S.H. ... et al., 2018. Revisiting the sulfur vulcanisation of rubber. Rubber Fibres Plastics International, 13(3), pp. 216-220.

Additional Information:

- This paper is produced with kind permission of the publisher.

Metadata Record: https://dspace.lboro.ac.uk/2134/34180

Version: Published

Publisher: Dr Heinz B. P. Gupta

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
The Drop That Makes The Difference

Hansen & Rosenthal KG
E-Mail: export.sales@hur.com
www.hur.com

Hansen & Rosenthal is the Producer of Anti Ozone Waxes and Plasticizers
Revisiting the sulfur vulcanisation of rubber

S. H. Sheikh, A. Ansarifar, J. Dushyanthan, G. W. Weaver, K. G. U. Wijayantha

Sulfenamide accelerators in combination with zinc oxide activator are used extensively in the sulfur cure systems of a wide range of industrial rubber articles. However, the excessive use of these chemicals has raised major concerns regarding their adverse effect on marine life and human health as well as the environment. Zinc oxide was functionalised with a sulfenamide accelerator in an organic solvent to provide a convenient single material to use as an additive. The effect of the additive on the cure properties of natural rubber was then measured. The aim was to minimize the use of these two chemicals in the cure system and enhance the efficiency of the sulfur vulcanisation of the rubber. Functionalising zinc oxide with the accelerator reduced the excessive use of these chemicals in the cure system. When the cure properties were compared with those of a sulfur cure-based natural rubber compound used to make tyres, the optimum cure time was noticeably shorter and the rate of cure significantly faster despite reducing the use of these two curatives by almost 77%. All the indications are that the cure efficiency improves considerably when the chemicals in the cure system are reduced.

1 Introduction

When the Hevea brasiliensis tree is tapped, latex exudes, which has a solid rubber content between 25% and 40% by weight. The solid rubber or cis-1,4-polyprene (NR) is extracted from the latex. The useful properties of NR are high tear strength, high abrasion resistance, long flex life and high resilience [1]. Natural rubber is used in many industrial applications for instance, tyres, antivibration mountings, and belting because of its excellent properties [2]. However, for shape retention, rubber must be cured. Rubber formulations have come a long way since Charles Goodyear discovered that heating raw rubber with sulfur modified the rubber to retain its shape. This was subsequently termed vulcanisation. To enhance the efficiency of vulcanisation in rubber, there has been an increasing trend to use more chemical curatives. The availability of new classes of chemicals known as accelerators and activators has sped up this process in recent years [3].

Sulfenamide accelerators, and zinc oxide (ZnO) and stearic acid activators are used extensively to cure a wide range of industrial articles. For example, in NR-based tyre belt compound systems [4], the cure system consists of sulfur (5 phr), N,N′-dicyclohexyl-2-benzothiazole sulfenamide accelerator (DCBS, 0.7 phr), hexamethoxy methyl melamine accelerator (HMMM, 2 phr), ZnO (7 phr), and stearic acid (1 phr). Zinc oxide and stearic acid can potentially be harmful to health, safety and the environment. According to the European Directive 2004/73/EC, zinc oxide is very toxic to aquatic organisms. Stearic acid causes skin and eye irritation and is classified as highly flammable [5]. DCBS and HMMM accelerators may cause eye, skin and respiratory irritation and are harmful to aquatic life [6, 7].

Previously, we reported a new method for measuring the chemical curatives in sulfur cure systems for rubber, which eliminated stearic acid entirely and reduced the ZnO requirement to less than 1 phr [8, 9]. Although it cannot be denied that sulfur vulcanisation is a much more efficient process today than it was at the time of Charles Goodyear, nevertheless serious health and safety issues related to its excessive use in rubber have emerged. Additionally, the chemical curatives are damaging to aquatic life and the environment. Consequently, the use of these chemicals is restricted by the new European chemicals policy, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and various legislations for environment, health and safety. It is worth mentioning that the exact amount of the chemical curatives in the sulfur vulcanisation of rubber has never been measured accurately and moreover, there is no reason why so many and so much of these chemicals need to be used in rubber compounds today. In this work ZnO is functionalised with a sulfenamide accelerator in an organic solvent and the effect on the cure properties of natural rubber is examined. The aim was to minimize use of these two chemicals in the cure system and enhance the efficiency of the sulfur vulcanisation of the rubber.

2 Experimental

2.1 Materials and mixing

The raw rubber used was standard Malaysian natural rubber (NR) grade L (98 wt% 1,4-cis content; SMRL) with a viscosity of 89 Mooney units. The other ingredients were sulfur (curing agent; Solvay Barium Strontium, Hanover, Germany), N-tert-butyl-2-benzothiazole sulfenamide (a fast-curing delayed action accelerator with a melting point of 105 °C; Santocure TBB5, Sovereign Chemicals, USA), and zinc oxide (activator; ZnO, Harcros Durham Chemicals, Durham, UK).
Zinc oxide was functionalised with TBBS to study the minimum amount of TBBS needed to satisfactorily crosslink the rubber. Adsorbing the TBBS onto the ZnO provided a convenient single material component to use as an additive. The quantity of TBBS required to provide monomolecular coverage of the zinc oxide was determined to be 35 mg/g based on the approximate surface areas of the TBBS molecule (6 \times 10^{-19} \text{ m}^2/\text{g}) and the ZnO (50 m$^2$/g) used. Gradually, the amount of TBBS to coat the zinc oxide was increased from 100 mg/g to 350 mg/g to find a material with optimum properties. The material with 35 mg/g TBBS led to a very slow cure, but material with 350 mg/g gave a good cure comparable to much higher loadings of TBBS.

A large batch was then prepared with this ratio from 202.0 g of ZnO and 70.7 g of TBBS which was mixed in 100 ml of ethyl acetate solvent (Sigma Aldrich, UK) in a 500 ml beaker. The suspension stirred magnetically for 15 min at room temperature (21.5 °C). The volume of the mixing chamber was 78 cm$^3$, and the rotor speed was set at 45 rpm. The initial set at ambient temperature (23 °C) progressively to determine its effect on the cure properties of the rubber. The raw rubber was mixed with the chemical ingredients in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter-rotating rotors to produce compounds. The Banbury rotors and the mixing chamber were initially set at ambient temperature (23 °C) and the rotor speed was set at 45 rpm. The volume of the mixing chamber was 78 cm$^3$, and it was 60 % full during mixing. Polylab monitor 4.17 software was used for controlling the mixing conditions and storing data. To prepare the rubber compounds, the raw rubber was introduced first in the mixer and then after 30 s, the sulfur and powder were added and mixed for 8 min in total. The powder reacts with the sulfur to produce crosslinks in the rubber. The temperature of the rubber compounds during mixing was 52 – 62 °C. In total, nineteen rubber compounds were prepared.

### 2.2 Testing of the rubber compounds

The cure properties of the rubber compounds were measured at 160±2 °C in an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of ±3° and a test frequency of 1.7 Hz according to the British Standard ISO 3417:2008. The tests ran for up to an hour. From the cure traces scorch time, $t_{s2}$, which is the time for the onset of cure, and the optimum cure time, $t_{95}$, which is the time for the completion of cure, were determined. The cure rate index, which measures the rate of cure in the rubber, was calculated using the method described in the same British Standard. Results from these tests are summarised in tables 1 and 2. $\Delta$Torque was subsequently plotted against the loading of the powder. $\Delta$Torque is the difference between the maximum and minimum torque values on the cure trace of a rubber compound and is an indication of crosslink density changes in the rubber.

### 3 Results and discussion

#### 3.1 Effect of an increasing loading of TBBS in the powder on the cure properties of the rubber

As mentioned earlier, in one experiment the loading of TBBS in the powder was raised from 100 mg/g to 350 mg/g equivalent to an increase of 0.135 phr to 0.383 phr in the formulation, (tab. 1), to measure the optimum amount required to cure the rubber. When the cure traces of the rubber compounds are examined, it can be observed that the curve for Compound 1 (0.135 phr TBBS) rises over a period of 60 min and no plateau is reached (fig. 1a). The curve for Compound 6 (0.351 phr TBBS) reaches a plateau (fig. 1b). The torque remains at this level for Com-

---

**Tab. 1:** Formulations and cure properties of the rubber compounds with increasing amounts of TBBS in the powder (amount of powder is the same for all formulations)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR in phr</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur in phr</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>TBBS in phr</td>
<td>0.135</td>
<td>0.192</td>
<td>0.247</td>
<td>0.296</td>
<td>0.342</td>
<td>0.351</td>
<td>0.358</td>
<td>0.367</td>
<td>0.376</td>
<td>0.383</td>
</tr>
</tbody>
</table>

**Curemeter test results at 160 °C**

| M$\text{M}$ in dNm | 17 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| M$\text{s}$ in dNm | 32 | 32 | 32 | 31 | 31 | 38 | 46 | 45 | 51 | 50 |
| $\Delta$Torque in dNm | 15 | 17 | 16 | 16 | 23 | 30 | 29 | 35 | 35 | 36 |
| $t_{s2}$ in min | 10.7 | 8.5 | 10.4 | 9.1 | 4.4 | 3.2 | 3.2 | 3.6 | 3.5 | 3.6 |
| $t_{95}$ in min | 55.4 | 54.5 | 55.5 | 54.8 | 41.4 | 9.9 | 10.7 | 8.4 | 8.1 | 8.9 |
| CRI in min$^{-1}$ | 2.2 | 2.2 | 2.2 | 2.2 | 2.7 | 14.9 | 13.3 | 20.8 | 21.7 | 18.9 |

**Tab. 2:** Formulations and cure properties of the rubber compounds with increasing amounts of the powder (constant amount of TBBS in powder 350 mg/g)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR in phr</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur in phr</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Powder in phr</td>
<td>0.63</td>
<td>1.25</td>
<td>1.88</td>
<td>2.5</td>
<td>3.13</td>
<td>3.75</td>
<td>4.38</td>
<td>5</td>
<td>5.63</td>
</tr>
</tbody>
</table>

**Curemeter test results at 160 °C**

| M$\text{M}$ in dNm | 17 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| M$\text{s}$ in dNm | 39 | 46 | 56 | 63 | 68 | 75 | 77 | 80 | 80 |
| $\Delta$Torque in dNm | 22 | 30 | 41 | 48 | 53 | 59 | 60 | 64 | 65 |
| $t_{s2}$ in min | 4.3 | 3.4 | 3.3 | 3.3 | 3.4 | 3.6 | 3.7 | 3.8 | 4.0 |
| $t_{95}$ in min | 30.8 | 7.7 | 7.0 | 6.9 | 6.8 | 7.2 | 7.0 | 7.1 | 7.4 |
| CRI in min$^{-1}$ | 3.8 | 23.2 | 27.0 | 27.8 | 29.4 | 27.8 | 30.3 | 30.3 | 29.4 |
compound 7 (0.358 phr TBBS). Afterwards, a reversion of the vulcanisation is observed if the amount of TBBS is further increased to 0.383 phr (Compound 10, **fig. 1c**). It is clear that a larger amount of TBBS in the powder shortens the cure cycle very substantially. Besides, it was interesting that the cure behaviour was so sensitive to small changes in the amount of TBBS in the powder. As **figure 1** shows, the cure curve rises first, then reaches an equilibrium and finally undergoes reversion as the loading of TBBS in the powder is increased from 100 mg/g to 350 mg/g.

The increase in the loading of TBBS in the powder has a major influence on the crosslink density and cure rate of the rubber as indicated by big rises in the value of $\Delta$torque and cure rate index (CRI), respectively. $\Delta$Torque was almost constant at about 15 dNm to 17 dNm with up to 0.296 phr TBBS in the powder. It then rose sharply to 36 dNm when the TBBS loading in the powder reached 0.383 phr (**fig. 2**). The cure rate index was unaffected by increase in the TBBS loading in the powder up to 0.296 phr but rose sharply to about 21.7 min$^{-1}$ when the TBBS loading in the powder reached 0.376 phr and then decreased to 18.9 min$^{-1}$ at 0.383 phr TBBS loading in the powder (**fig. 3**). The scorch time was somewhere between 10.7 and 9.1 min with up to 0.296 phr TBBS in the powder and then decreased to 4.4 min at 0.342 phr TBBS in the powder. It subsequently reached a plateau around 3.2 – 3.6 min when the TBBS loading in the powder was raised to 0.383 phr (**fig. 4**).

The increase in the loading of TBBS in the powder for up to 0.296 phr had little or no effect on the optimum cure time which remained essentially unchanged at about 54.5 min to 55.5 min. However, this was followed by a sharp decrease to 41.4 min at 0.342 phr and then to 10.7 min at 0.358 phr TBBS loading in the powder. The optimum cure time attained a constant value at around 8.1 min to 8.9 min when the loading of TBBS in the powder was increased to 0.383 phr. It is clear that increase in the amount of TBBS in the power to above 0.342 phr was greatly beneficial to the cure cycle of the rubber by significantly reducing the optimum cure time (**fig. 4**). The cure rate benefited significantly at above 0.342 phr TBBS in the powder with the highest rate, 21.7 min$^{-1}$, recorded at 0.376 phr TBBS in the powder. But the cure rate index decreased to 18.9 min$^{-1}$ when the TBBS loading in the powder was raised further to 0.383 phr. The powder with 350 mg/g TBBS (equivalent to 0.383 phr in the formulation) was selected for further work because the rubber compound cured with this powder had the largest $\Delta$torque value, and very short scorch and optimum cure times. For this rubber compound, the cure rate index was 18.9 min$^{-1}$ (**tab. 1**).

### 3.2 Effect of an increasing loading of the powder on the cure properties of the rubber

In this experiment, the amount of TBBS in the powder was kept constant at 350 mg/g. The loading of the powder in the rubber was subsequently raised from 0.63 phr to 5.63 phr (**tab. 2**). When the cure traces were examined,
for the rubber compound with 0.63 phr powder the cure reached equilibrium after 40 min (fig. 5a). Though, when the loading of the powder was raised to above 0.63 phr, the cure underwent reversion soon after 8 min and the cure cycle was a lot shorter. The cure reversion accelerated when the loading of the powder in the rubber kept rising to its highest level, i.e., 5.63 phr (fig. 5b and c).

The minimum torque, $M_m$, which indicates the uncured rubber viscosity, was not affected by increase in the loading of the powder in the rubber and remained at around 15 dNm to 17 dNm. The maximum torque, $M_h$, which shows extent of crosslinks in the rubber, kept rising from 39 dNm to 80 dNm as the loading of the powder was raised from 0.63 to 5.63 phr (tab. 2). Figure 6 shows $\Delta$Torque as a function of the powder loading. $\Delta$Torque increased from 22 dNm to 48 dNm when the loading of the powder was raised from 0.63 phr to 2.5 phr, and it continued rising at a much slower rate to about 65 dNm when the loading of the powder reached 5.63 phr. Evidently, the addition of 2.5 phr powder was sufficient to react the sulfur with the rubber to form stable covalent crosslinks or chemical bonds between the rubber chains. As mentioned earlier, the optimum loading of TBBS in the powder was 350 mg/g. Therefore, 26 wt% of the powder was TBBS and the remaining 74 wt% ZnO. On this basis, the 2.5 phr powder contained 0.65 phr TBBS and 1.85 phr ZnO. In some NR-based industrial articles such as rubber thread and tyre bead filler/apex rubber compound, the loading of accelerators can reach 4.5 phr [10] and that of ZnO to10 phr [11], respectively. Obviously, there is scope to reduce the excessive amount of these chemicals in rubber compounds quite substantially.

The scorch time was fairly constant about 3.3 min to 4.3 min when the full loading of the powder was added. The optimum cure time decreased sharply from 30.8 min to 7.7 min with 1.25 phr powder and afterwards, it showed no obvious trend and remained somewhere between 6.8 min and 7.4 min when the loading of the powder was raised to 5.63 phr (fig. 7). The rate of cure as indicated by the cure rate index (CRI), benefited significantly from the addition and progressive increase in the amount of the powder. It rose sharply to 23.2 min$^{-1}$ when 1.25 phr powder were added. The increase was about 510 %. Afterwards, it continued rising at a much slower rate to 27.8 min$^{-1}$ when the loading of the powder reached 2.5 phr. It subsequently plateaued at about 27.8 min$^{-1}$ to 30.3 min$^{-1}$ with the full loading of the powder (fig. 8). Clearly, above 1.25 phr powder loading, the rate of cure gained not as much, i.e., only by 30 %.

For a tyre belt skim compound, which has 5 phr sulfur and 10.7 phr chemical curatives.
the scorch time ($t_{s2}$) and optimum cure time ($t_{90}$) are 2.6 min and 9.5 min at 160 °C, respectively. The cure rate index is 14.5 min$^{-1}$. It is interesting that with a smaller amount of sulfur, i.e. 4 phr, and only 2.5 phr of the powder (0.65 phr TBBS and 1.85 phr ZnO), shorter scorch and optimum cure times and a much faster rate of cure, i.e. CRI of 27.8 min$^{-1}$, were recorded for our rubber compound (Compound 4, tab. 2). In fact, 20 wt% reduction in sulfur and 77 wt% less chemical curatives shortened the optimum cure time by 34 % (the $t_{90}$ of our rubber compound was 6.3 min) and increased the cure rate by 130 %. But the scorch time ($t_{s2}$) of our rubber compound (Compound 4) was 27 % longer than that of the tyre belt skim compound. Note also that no stearic acid was used in the cure system. The trend observed here suggests that a much lesser consumption of the chemical curatives, i.e., TBBS and ZnO, in sulfur vulcanisation, yields significantly shorter cure cycle and hence a more efficient cure. Other benefits include improvement in health, safety and the environment as well as major cost reduction. It seems that functionalising ZnO with TBBS into a single additive is a more efficient method of using these chemicals in rubber vulcanisation than the methods which are currently in use. This has the added advantage of eliminating secondary accelerators and too much ZnO from the cure system. All the signs are that the sulfur cure systems currently in use in industrial rubber compounds such as tyres are basically inefficient, too costly and no longer viable and hence must be improved. Combining the chemical curatives by means of functionalising them undoubtedly is the most effective way in making green compounds for industrial rubber articles.

4 Summary

Functionalising ZnO with TBBS to provide a single additive component reduced the excessive use of these chemicals in the sulfur vulcanisations of NR. Some powders were tested and the following conclusions drawn:

- When the loading of TBBS in the powder was raised progressively to 0.383 phr, the scorch time and optimum cure time of the rubber decreased at 0.351 phr TBBS. The rate of cure as indicated by the cure rate index increased at 0.351 phr TBBS in the powder. The crosslink density as shown by $\Delta$torque rose, reaching a high value at 0.383 phr TBBS loading in the powder.
- When the loading of the powder in the rubber was raised increasingly to 5.63 phr, the scorch time was unchanged and the optimum cure time reduced at 1.25 phr powder. The rate of cure as shown by the cure rate index accelerated at 1.25 phr powder. The crosslink density as indicated by $\Delta$torque rose, reaching its maximum value at 5.63 phr powder.

5 References

Reference to common names, trade names, names of goods, etc., does not warrant the assumption that such names are unrestricted and may therefore be used by anyone. Legally protected registered trademarks are often involved, even if these are not expressly shown as such.

Subscriptions, terms of receipt and delivery:
Annual subscription fee EUR 120 (4 issues per year, incl. delivery costs). Single issue EUR 35 (domestic fees are understood as inclusive of the appropriately valid value added tax). Orders are accepted by the publisher and all national and international book shops. Taking up of a new subscription applies initially for the current calendar year. The subscription is automatically renewed if it is not cancelled in writing six weeks before the end of the calendar year. The subscription fees are invoiced each year in advance and, when participating in direct debit payment, they will be debited automatically. Should the magazine not be delivered due to reasons that are outside our control, there is no right to claim later delivery or reimbursement of subscription fees already paid in advance. The legal domicile for trading is Ratingen, which also applies for all other purposes, insofar as claims for payment are to be enforced.

Copyright and publisher's rights:
Articles signed with the author's name or signature do not necessarily represent the editor's opinion. Unrequested manuscripts will only be returned if return postage is provided. The publisher requires that the author possesses copyright and rights for use of all constituents of the material submitted, namely also for pictures and tables, etc which are also submitted. With acceptance of the manuscript, the right to publication, translation, reprints, electronic storage in databanks, additional printing, photocopying and microfiche copying is transferred to the publisher. The magazine and all its contributions and pictures are protected by copyright. All use beyond the limits established by the law on the author's copyright is not permitted without approval of the publisher.