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A novel method for the optimization of sulfur cure systems for rubber using software

A. Ansarifar, K. Noulta, G. W. Weaver, K. G. U. Wijayantha, S. Kahagala Gamage

The goal of this study was to find a software approach that would make the optimization of the vulcanization system more efficient. For this purpose, a natural rubber (NR) was mixed with different amounts of elemental sulfur at ambient temperature to produce rubber compounds. Zinc oxide was treated with an organic accelerator to produce a convenient single material component to use as additive. The effect of an increasing loading of the surface modified zinc oxide on the cure properties of the sulfur-filled rubber compounds was subsequently measured at a high temperature in a curemeter. Using a JavaScript program, the cure test results were processed to develop a highly efficient method for optimizing sulfur cure systems for rubber. All the essential information such as scorch and optimum cure times, rate of cure, crosslink density changes in the rubber, and chemical curatives requirement at a given loading of sulfur were subsequently provided for the user. This method removes the need to mix and test the raw rubber with chemical curatives repeatedly to find a compound with ideal cure properties for industrial applications.

1 Introduction

There have been two major technological developments over the years, which have enabled the rubber industry to manufacture a wide range of industrial articles such as tires, conveyor belts, hoses and seals. Sulfur curing, or sulfur vulcanization, is an important first stage in the processing of raw rubber into useable industrial articles. This is then followed by the addition of solid fillers for example carbon black [1], silica [2] and kaolin or China clay [3], to reinforce or improve mechanical and dynamic properties of rubber.

Sulfur is the most widely used curing agent and sulfur vulcanization provides shape retention for the rubber by forming stable chemical covalent crosslinks between the rubber chains. However, reaction of sulfur with rubber even at elevated temperature is slow and inefficient, and thus additional chemical curatives known as accelerators and activators are frequently added to complete the vulcanization process [4]. To achieve a high level of efficiency in sulfur vulcanization, organic accelerators such as sulfenamide accelerators, which are often used in combination with zinc oxide as primary activator, and stearic acid as secondary activator, are added with sulfur [5]. These chemicals are essential for improving the curing process, but their excessive use must be lowered without compromising the cure properties or adversely affecting the cure cycle of rubber compounds.

To produce a rubber compound, raw rubber is mixed with chemical curatives as well as other chemical additives, such as solid fillers and antidegradants, and then tested in a curemeter to determine its cure properties, such as scorch time, optimum cure time and crosslink density changes. This procedure may have to be repeated several times by changing the chemical curatives if the rubber compound does not possess the desired cure characteristics for industrial applications and is often expensive and highly inefficient. The goal was therefore to find a software approach that would make the optimization of the vulcanization system more efficient.

In this study, natural rubber (NR) was mixed with different amounts of elemental sulfur at ambient temperature to produce rubber compounds. Zinc oxide was treated

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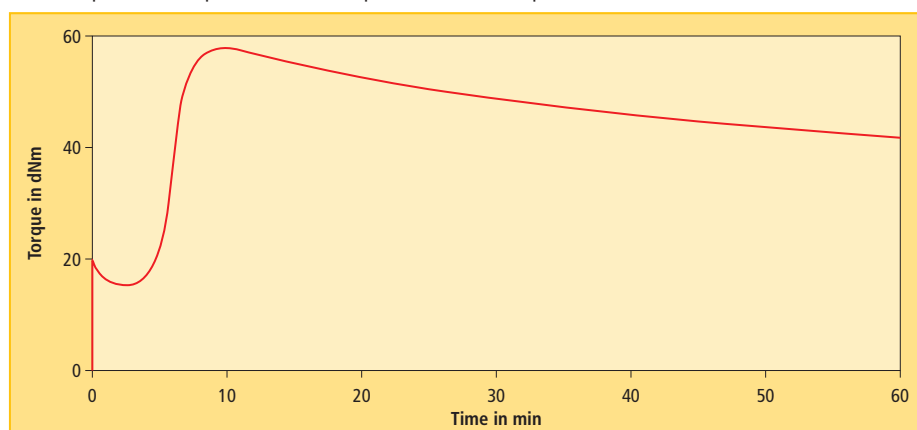
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All figures and tables, unless otherwise stated,
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Fig. 1: Typical cure trace of a rubber compound produced at 160 °C in curemeter. Data for the rubber compound with 3 phr sulfur and 1.88 phr of the TBBS/ZnO powder.



with an organic accelerator to produce a convenient single material component to use as additive [6]. The effect of an increasing loading of the surface modified zinc oxide on the cure properties of the sulfur-filled rubber compounds was subsequently measured at a high temperature in a curemeter. Using a JavaScript program, the cure test results were processed to develop a highly efficient method for optimizing sulfur cure systems for rubber. All the essential information such as scorch and optimum cure times, rate of cure, crosslink density changes in the rubber, and chemical curatives requirement at a given loading of sulfur were subsequently provided for the user. This method removes the need to mix and test the raw rubber with chemical curatives repeatedly to find a compound with ideal cure properties for industrial applications. It provides a rapid and efficient way of optimizing the sulfur cure system. It is anticipated that excessive use of these chemicals in the curing of rubber and rubber waste will be reduced significantly and moreover, the compounding stage of rubber processing will be shorter using this novel method.

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 TBBS, Sovereign Chemicals, USA), and zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK).

Zinc oxide was treated with the TBBS accelerator by evaporation of a suspension of ZnO in a solution of TBBS in dichloromethane (Fisher Scientific, UK) to provide a convenient single material component to use as 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 ($6 \cdot 10^{-19} \text{ m}^2$) and the ZnO ($50 \text{ m}^2/\text{g}$) 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 the material with 350 mg/g gave a good cure, comparable to much higher loadings of TBBS, which is as high as 3 phr in some compounds [7]. The optimum quantity of TBBS in the TBBS/ZnO powder was 350 mg/g. A large batch of the surface-modified zinc oxide was then prepared with this ratio from 100.0 g of ZnO and 35.0 g of TBBS, which was mixed in 200 ml of the solvent in a 500 ml round-bottomed flask. The suspension was stirred magnetically for 15 min at room temperature (21.5 °C/70.7 °F) to ensure uniform coating. The mixture was evaporated on a rotary evaporator at 100 mbar and further dried at 50 °C at 20 mbar for 2 h to leave a free-flowing white solid. The obtained white solid showed a mass loss of 0.213 g, indicating the bulk of the TBBS was absorbed onto the ZnO. The surface modified additive will be referred to as the 'TBBS/ZnO powder'.

The raw rubber was mixed with the chemical reagents 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/73.4 °F) and the rotor speed was set at 45 min⁻¹. The volume of the mixing chamber was 78 cm³, and it was 60 % full during mixing. PolyLab monitor 4.17 software was used to control 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 the TBBS/ZnO powder were added and mixed for 8 min in total. The loading of sulfur in the rubber was increased progressively from 1 phr to 5.5 phr and that of the TBBS/ZnO powder from 0.50 phr to 5.63 phr to determine its effect on the cure. The sulfur powder reacted with the unsaturated carbon-carbon double bonds of the NR in the presence of TBBS/ZnO powder to produce chemical crosslinks in the rubber. The temperature of rubber compounds during mixing was 52 °C to 62 °C (131 °F to 144 °F). In total, 63 rubber compounds were made.

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 $\pm 3^\circ$ and a test frequency of 1.7 Hz according to the British Standard ISO 3417. From the cure traces (**fig. 1**), 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 (CRI), which measures the rate of cure in the rubber, was calculated using the method described in British Standard ISO 3417, 2008. Results from these tests are summarized in **table 1**. ΔTorque was subsequently plotted against the loading of the TBBS/ZnO powder to measure the amount of the powder required for the optimum cure of the rubber compounds. ΔTorque is the difference

Tab. 1: Formulations and cure properties of the rubber compounds at optimum loading of TBBS/ZnO powder (TBBS/ZnO: 26 wt%/74 wt%)

Compound	1	2	3	4	5	6
NR in phr	100	100	100	100	100	100
Sulfur in phr	1	2	3	4	5	5.5
TBBS/ZnO powder in phr	1	1.4	1.88	2.5	3.13	5
TBBS/ZnO ratio in phr	0.26/0.74	0.36/1.04	0.49/1.39	0.65/1.85	0.81/2.32	1.3/3.7
Curemeter test results at 160 °C						
M_i in dNm	16	15	15	15	14	14
M_h in dNm	33	47	58	63	74	95
ΔTorque in dNm	17	32	43	48	60	81
t_{s2} in min	7.2	5.1	4.2	3.3	3.8	4.2
t_{95} min	12.2	9.2	7.9	6.9	7.2	7.7
CRI in min ⁻¹	20	24.4	27.0	27.8	29.4	28.6

between the maximum and minimum torque values on the cure trace of a rubber compound (**fig. 1**) and is an indication of cross-link density changes in the cured rubber.

2.3 Development of software for optimizing the sulfur cure system

The following steps were taken in a chronological order to store and process cure test results from **table 1**, and to develop a new method for selecting the sulfur cure system.

- The data from **table 1** was copied to a digital spreadsheet.
- The relationship between the sulfur loading, TBBS/ZnO powder loading, t_{s2} , t_{95} , CRI, and Δ torque were examined and then modelled using a developed algorithm. The developed algorithm processed the sulfur loading and outputted the value of the aforementioned properties and then created a function, which took any numeric input from the sulfur trendline and produced the subsequent numerical value on the existing trendline.
- The method was then replicated for each of the properties provided in **table 1**. Individual algorithms for converting numeri-

cal sulfur loading inputs into different outputs for each property were created, i. e. one algorithm for each property.

- A webpage was created using the information in the spreadsheet from **table 1** and the algorithms for each property were written in JavaScript. The digital data spreadsheet was written into the webpage, displaying information in a table for user (**fig. 2a**).
- A program for a Radar chart was subsequently created and produced on the webpage with spokes for each of the following properties: t_{s2} , t_{95} , CRI, minimum torque M_L , maximum torque M_H , Δ torque, TBBS/ZnO powder loading, and sulfur loading (**fig. 2b**).
- Both a numerical input text box and a slider were used to input continuous data for sulfur loading between reasonable values, for example between 1 phr and 2 phr.

In summary, the program was written in HTML. Initial prototypes of the program were developed on Excel. Using the data from **table 1**, a function was created that converted the discrete data points provided into continuous extrapolated data points between the points provided to a resolution of 1 dp.

Functions were created for each set of the provided points. For example, one function for extrapolating between 1 phr and 2 phr of the sulfur loading, another function for extrapolating between 2 phr and 3 phr of the sulfur loading. This was repeated for the remaining sulfur loadings and was performed individually for all the variables. These functions were used to create algorithms that received sulfur loading inputs in phr to produce discrete extrapolated outputs for all the variables. These algorithms were written in JavaScript and the outputs of these functions were displayed on a generated Output Box Radar chart.

3 Results and discussion

3.1 Effect of an increasing loading of TBBS/ZnO powder on the crosslink density changes in the rubber with different amounts of sulfur

Figures 3 to 8 show Δ torque as a function of TBBS/ZnO powder loading for the rubber compounds tested. For the compound with 1 phr sulfur (**fig. 3**), Δ torque increased from 8 dNm to 17 dNm when the

Fig. 2: Typical webpage, displaying information for user (a) and typical Radar chart created on the webpage with spokes for each of the properties (b)

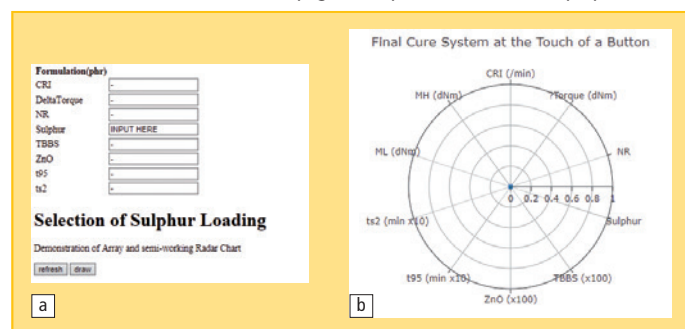


Fig. 3: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 1 phr sulfur

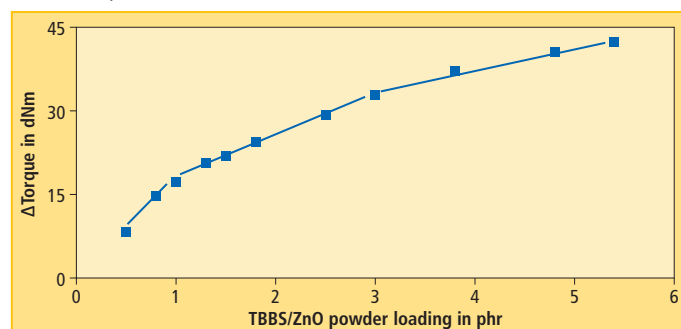


Fig. 4: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 2 phr sulfur

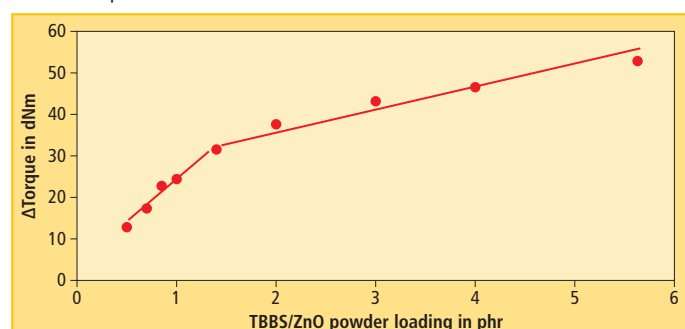
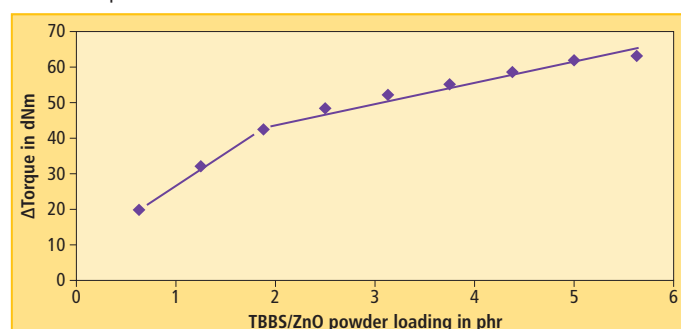


Fig. 5: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 3 phr sulfur



loading of the TBBS/ZnO powder was raised from 0.5 phr to 1 phr. It continued rising at a much slower rate to about 33 dNm at 3 phr and subsequently reached 42 dNm at 5.4 phr of TBBS/ZnO powder. Evidently, the addition of 1 phr of the TBBS/ZnO powder was enough to cause the sulfur to react with the rubber to form stable covalent crosslinks (chemical bonds) between the rubber chains. As mentioned earlier, the optimum quantity of TBBS in the TBBS/ZnO powder was 350 mg/g. Therefore, 26 wt% of the TBBS/ZnO powder was TBBS and the remaining 74 wt% was ZnO. On this basis, the 1 phr TBBS/ZnO powder contained 0.26 phr TBBS and 0.74 phr ZnO.

For the rubber with 2 phr sulfur (**fig. 4**), Δ torque increased sharply from 13 dNm to 32 dNm when the loading of the TBBS/ZnO powder was raised to 1.4 phr. Thereafter, Δ torque attained a value of 53 dNm when the full amount of the TBBS/ZnO powder, i.e. 5.63 phr, was added to the rubber. A similar trend was also observed for the rubber with 3 phr sulfur (**fig. 5**). For this rubber, Δ torque rose from 20 dNm to 42 dNm with 1.88 phr of the TBBS/ZnO powder and then continued increasing to about 63 dNm when the

full amount of the TBBS/ZnO powder was incorporated in the rubber. As expected, Δ torque showed noticeable improvement as the loading of sulfur was raised further to 4 phr (**fig. 6**). For the rubber with 4 phr sulfur, Δ torque rose from 22 dNm to 48 dNm when the loading of the TBBS/ZnO powder reached 2.5 phr and it continued rising to 65 dNm at the optimum loading of the TBBS/ZnO powder.

Similarly, for the rubber with 5 phr sulfur (**fig. 7**), Δ torque rose from 27 dNm at 0.63 phr to 60 dNm at 3.13 phr of the TBBS/ZnO powder. Subsequently, Δ torque continued rising at a slower rate to about 83 dNm when the loading of the TBBS/ZnO powder reached 5.63 phr. Finally, the Δ torque for the rubber with 5.5 phr sulfur (**fig. 8**), showed a major improvement from 31 dNm to 81 dNm as the loading of the TBBS/ZnO powder was raised progressively from 0.63 phr to 5 phr. But the rate of increase in Δ torque slowed down, reaching about 112 dNm, when the amount of the TBBS/ZnO powder was raised to 10.4 phr.

It is interesting that for curing the rubber fully, the optimum loading of TBBS/ZnO

powder increased linearly as a function of sulfur loading for up to 5 phr and thereafter, it rose sharply (**fig. 9**). In NR-based industrial rubber formulations, the loading of sulfur does not exceed 3 phr [7] and hence the correlation between the optimum loading of the TBBS/ZnO powder and sulfur content as shown in **figure 9** can be valid for industrial rubber formulations which use TBBS and ZnO curatives. After these measurements were completed, the results were processed to develop a software for selecting sulfur cure systems for the rubber.

3.2 Software-based method for optimizing the sulfur cure system

As mentioned earlier, the digital data spreadsheet was written into the webpage, displaying information in a table for user (**fig. 2a**) and a program for a Radar chart was subsequently created and produced on the webpage with spokes for each of the properties (**fig. 2b**). Each algorithm processed the inputted sulfur loading for each reading and outputted a value for each property. For instance, a sulfur loading of 1.5 phr outputted values of TBBS: 0.31; ZnO: 0.89; Δ torque: 24.5; t_{s2} : 6.7; t_{95} : 10.7 and CRI: 22.2.

Fig. 6: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 4 phr sulfur

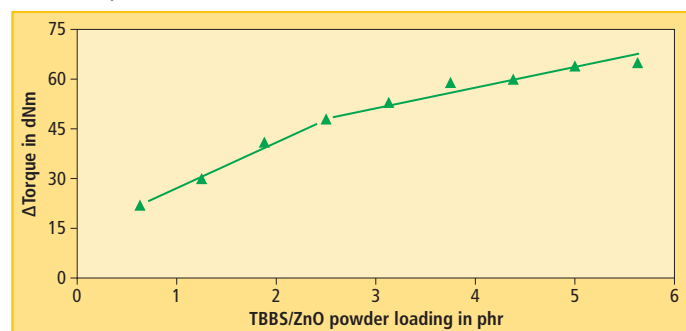


Fig. 7: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 5 phr sulfur

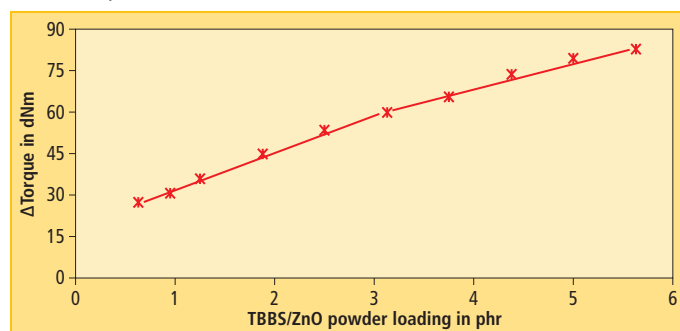


Fig. 8: Δ Torque vs TBBS/ZnO powder loading for the rubber compound with 5.5 phr sulfur

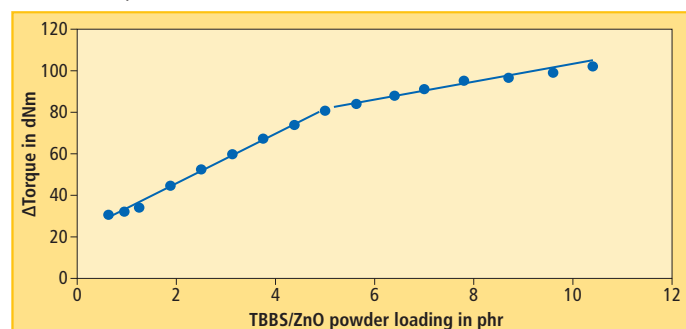
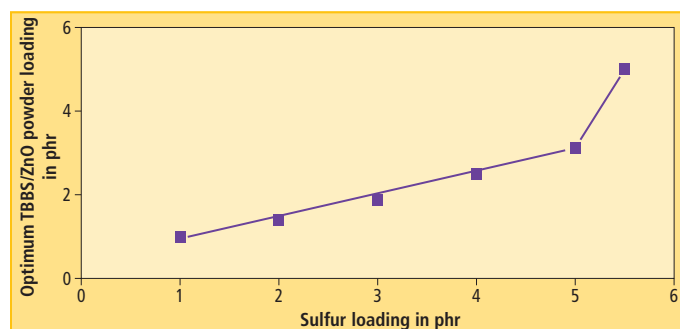


Fig. 9: Optimum TBBS/ZnO powder loading vs sulfur loading



These values were subsequently displayed in a table after the program had been executed (**fig. 10a**) and on a Radar chart for a more visual interface (**fig. 10b**). For a sulfur loading of 4.5 phr, outputted values of TBBS: 0.73; ZnO: 2.085; Δ torque: 54; t_{s2} : 3.55; t_{95} : 7.05 and CRI: 28.6 were produced. The results were subsequently displayed in a table (**fig. 11a**) and on a Radar chart (**fig. 11b**).

Note that the numbers for TBBS and ZnO loading in the table (**fig.10a**) were divided by a factor of 100, and for those of t_{s2} and t_{95} , by a factor of 10 when the Radar chart was constructed (**fig. 10b**). For the sake of clarity of presentation, the original TBBS and ZnO, and t_{s2} and t_{95} values from **table 1**, were multiplied by factors 100 and 10, respectively. For the 4.5 phr sulfur loading, the TBBS and ZnO numbers from the table (**fig. 11a**) were divided by factors 100 and 10, respectively, and those of t_{s2} and t_{95} , by a factor of 10 as indicated in the Radar chart (**fig. 11b**).

As **figure 10** and **figure 11** show, the software provides an efficient method for optimizing sulfur cure systems for rubber. This is achieved by inserting a value for the sulfur loading into the program and then performing the tasks described above. For example, when the information in the table (**fig. 10a**) is judged to be unsuitable, i.e. t_{95} may be too long or too short, then another value for sulfur loading may be inserted into the program

and the task is performed again. This can be repeated several times until a sulfur loading is found at which cure properties, i.e. t_{95} , may be desirable for user. Once this method is fully implemented into the compounding process, major reduction in processing time may be achieved.

4 Summary

Natural rubber containing different amounts of elemental sulfur was cured at elevated temperature with a single surface modified TBBS/ZnO powder. The optimum loading of the TBBS/ZnO powder required to fully cure the rubber at 1 phr, 2 phr, 3 phr, 4 phr, 5 phr, and 5.5 phr elemental sulfur was determined. Using a JavaScript program, the cure test results were stored and processed to develop a highly efficient method for optimizing the sulfur cure system for the rubber. This method offers significant advantages over the traditional way of selecting the sulfur cure system for rubber. It provides useful information on the scorch and optimum cure times, rate of cure, crosslink density changes in the rubber, and chemical curatives requirement at a given loading of sulfur and by doing so, it removes the need to mix and test raw rubber with chemical curatives repeatedly to find a compound with ideal cure properties for industrial applications. Furthermore, using the TBBS/ZnO

power helps to reduce excessive use of the chemical curatives in the sulfur vulcanization of rubber, offering significant reduction in cost, major improvement in health and safety at work place, and less adverse impact of chemical curatives on the environment. All the indications are that a semi or fully automated software-based tool for optimizing cure systems for rubber based on the loading of sulfur is a very efficient way forward and can potentially reduce the time in the compounding stage of rubber processing.

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Fig. 10: Webpage, displaying information for the rubber at 1.5 phr sulfur loading after the program was executed (a) and Radar chart created with spokes for each of the properties (b)

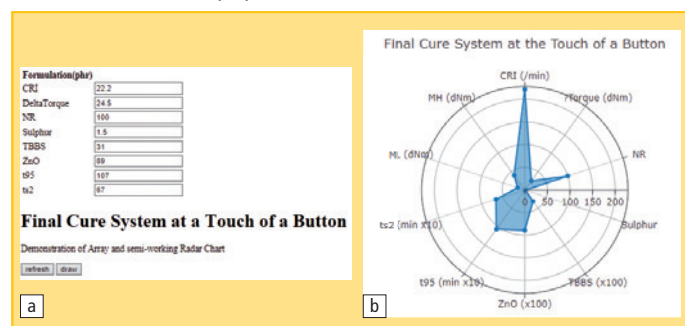
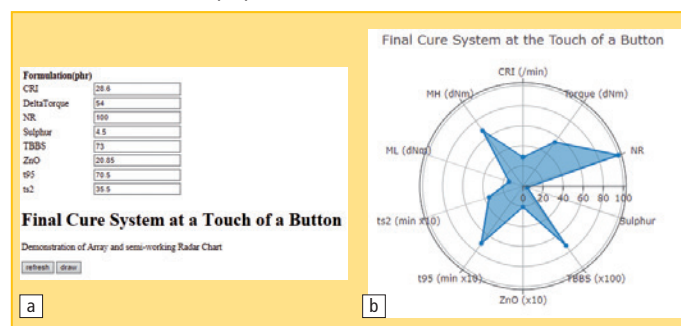


Fig. 11: Webpage, displaying information for the rubber at 4.5 phr sulfur loading after the program was executed (a) and Radar chart created with spokes for each of the properties (b)



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