Combining curatives

Combining curatives in sulfur cure systems for tires reduces excessive use of these chemicals and improves the cure efficiency

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Accelerators and activators are indispensable chemicals in the sulfur vulcanization of tires. Accelerators control onset, rate and extent of cross-linking and hence final properties of rubber vulcanizates. Activators are ingredients used to activate accelerators and improve their effectiveness.[1] Sulfenamide accelerators, and zinc oxide (ZnO) and stearic acid activators are used extensively to cure a wide range of industrial articles.[2] For example, in tire belt skim compound, the cure system consists of 5phr sulfur; 0.7phr N,N'-dicyclohexyl-2-benzothiazole sulfenamide (DCBS) accelerator; 2phr hexamethoxy methyl melamine (HMMM) accelerator; 7phr ZnO; and 1phr stearic acid.[3]

ZnO and stearic acid can be harmful to health, safety and the environment. According to the European Directive 2004/73/EC, ZnO is very toxic to aquatic organisms. Stearic acid causes skin and eye irritation and is classified as highly flammable.[4] DCBS and HMMM accelerators may cause eye, skin and respiratory irritation and are harmful to aquatic life.[5,6]

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 1phr.[7] This extended work functionalized ZnO with a sulfenamide accelerator in an organic solvent and examined its effect on the cure properties of natural rubber (NR). The aim was to minimize use of these two chemicals in the cure system and enhance the efficiency of the sulfur vulcanization of the rubber.

Figure 1: Cure traces (torque [dNm] versus time [min]) of the rubber compounds with an increasing loading of the powder. a) compound with 0.63phr powder; b) compound with 2.5phr powder; c) compound with 5.6phr powder
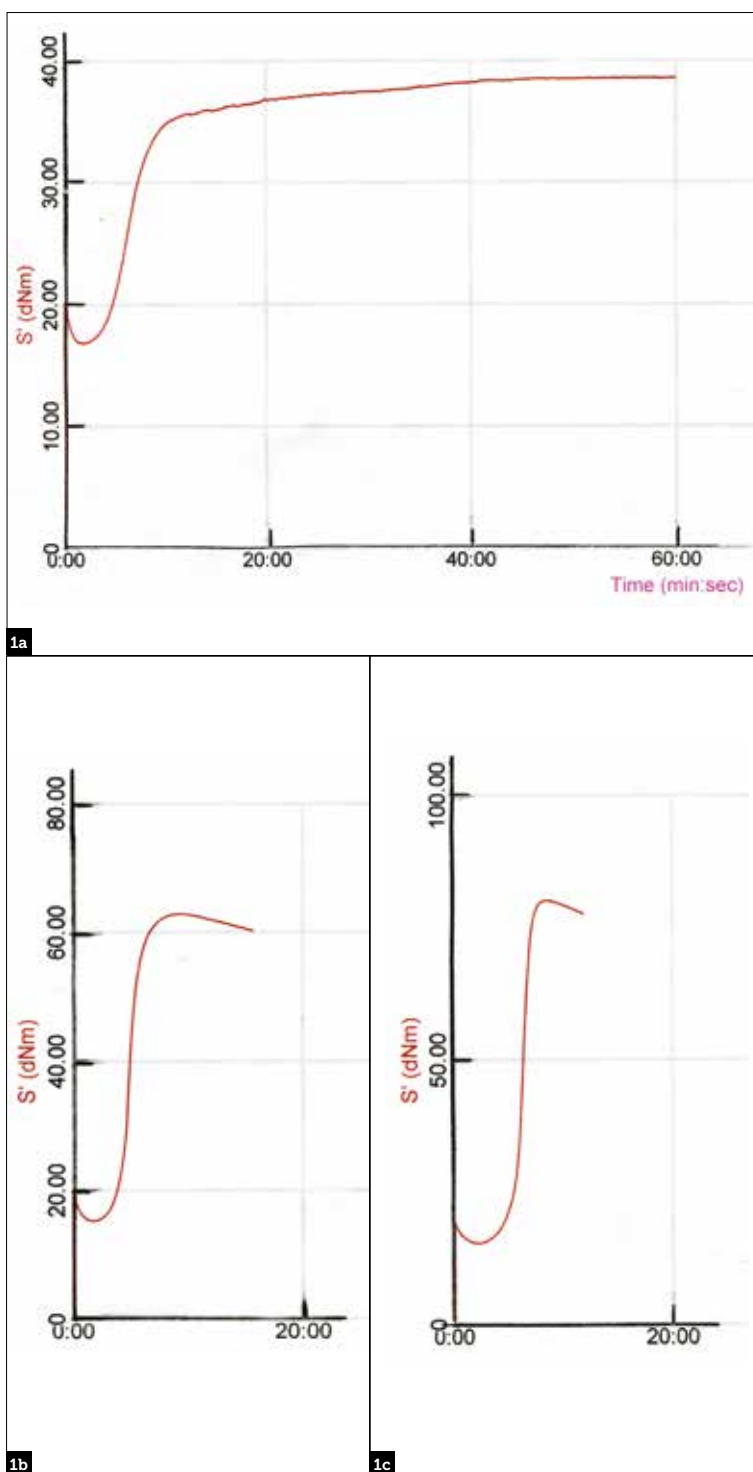
Table 1: Formulations and cure properties of the rubber compounds									
Formulation (phr)	**Compound no**								
	1	2	3	4	5	6	7	8	9
NR	100	100	100	100	100	100	100	100	100
Sulfur	4	4	4	4	4	4	4	4	4
Powder (ZnO+TBBS)	0.63	1.25	1.88	2.5	3.13	3.75	4.38	5	5.63
Curemeter test results at 160°C									
M_L **(dNm)**	17	16	15	15	15	16	17	16	15
M_H **(dNm)**	39	46	56	63	68	75	77	80	80
Δtorque (dNm)	22	30	41	48	53	59	60	64	65
t_{s2} **(min)**	4.3	3.4	3.3	3.3	3.4	3.6	3.7	3.8	4.0
t_{95} **(min)**	30.8	7.7	7.0	6.9	6.8	7.2	7.0	7.1	7.4
CRI (min⁻¹)	3.8	23.2	27.0	27.8	29.4	27.8	30.3	30.3	29.4

phr: parts per hundred rubber by weight. 350mg/g: 350mg of TBBS per 1g of ZnO in the powder

The raw rubber used was standard Malaysian NR grade L (98wt% 1-4 cis content; SMRL) with a viscosity of 89 Mooney units. The other ingredients were sulfur (curing agent; Solvay, Hannover, Germany), N-tert-butyl-2-benzothiazole sulfenamide

Figure 2: Δtorque versus powder loading for the rubber compounds shown in Table 1

(a fast-curing delayed-action accelerator with a melting point of 105°C; Santocure TBBS, Sovereign Chemicals, USA), and ZnO (Harcros Durham Chemicals, Durham, UK).

ZnO was functionalized with TBBS to provide a convenient single

material to use as an additive. The quantity of TBBS required to provide monomolecular coverage of the ZnO was measured. The optimum quantity of TBBS was determined to be 350mg/g. A large batch was then prepared with this ratio from

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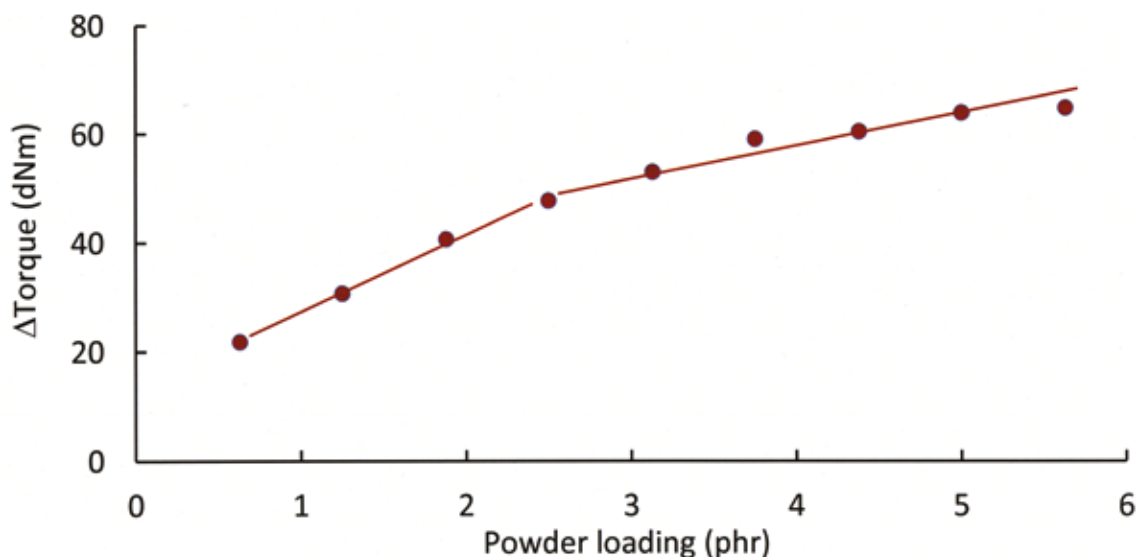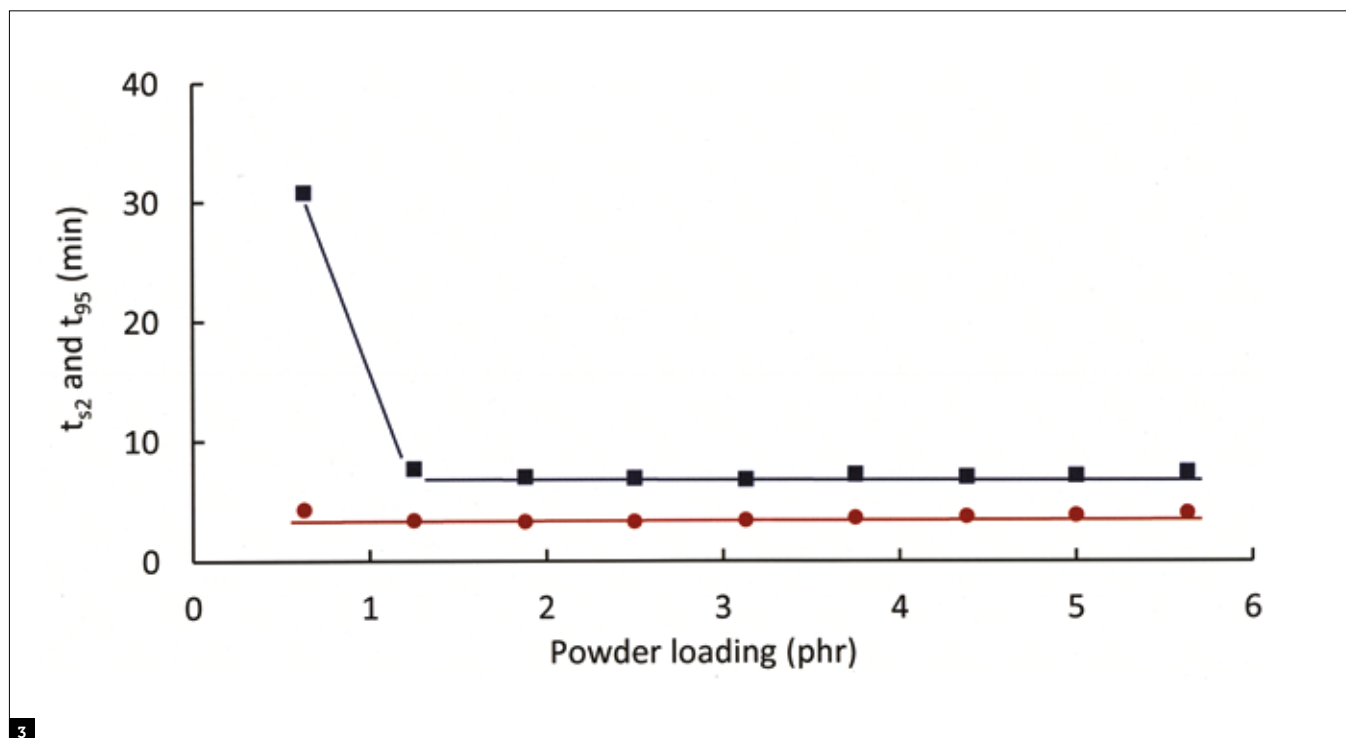
202.0g of ZnO and 70.7g of TBBS, which were mixed in 100ml of ethyl acetate solvent (Sigma Aldrich, UK) in a 500ml beaker. The suspension was stirred magnetically for 15 minutes at room temperature (21.5°C). The mixture was filtered under suction using an electric diaphragm vacuum pump (capable of achieving 50mmHg). The white solid was left to dry overnight and then further dried in a vacuum oven at 50°C. Evaporation of the filtrate on a rotary evaporator indicated the mass lost was 0.110g. The additive will be referred to as 'the powder'.

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 45rpm. The volume of the mixing chamber was 78cm³, and it was 60% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data. To prepare the rubber compounds, the raw rubber was introduced first in the mixer and then after 30 seconds the sulfur and powder were added and mixed for

eight minutes in total. The powder reacted with the sulfur to produce cross-links in the rubber. The loading of the powder in the rubber was increased progressively from 0.63phr to 5.63phr to determine its effect on the cure. The temperature of the rubber compounds during mixing was 59-62°C. In total, nine compounds were made.

The cure properties of the rubber compounds were measured at 160°C (0±2°C) in an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of ±3° and a test frequency of 1.7Hz according to British Standard ISO 3417 2008. From the cure traces (Figures 1a-1c), the 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 British Standard ISO 3417, 2008. Results from these tests are summarized in Table 1.

Δtorque was subsequently plotted against the loading of the powder. Δtorque is the difference between the maximum and minimum torque values on the cure trace of a rubber compound (e.g. Figure 1a)

and is an indication of cross-link density changes in the rubber.

Results and discussion
The minimum torque, M_L, which indicates the uncured rubber viscosity, was about 15-17dNm. The maximum torque, M_H, which shows the extent of cross-links in the rubber, kept rising from 39dNm to 80dNm as the amount of the powder was raised from 0.6phr to 5.6phr (Table 1). Figure 2 shows Δtorque as a function of the powder loading. Δtorque increased from 22dNm to 48dNm when the loading of the powder was raised from 0.6phr to 2.5phr, and it continued rising at a slower rate to 65dNm when the amount of the powder reached 5.6phr. Evidently the addition of 2.5phr of the powder was sufficient to react the sulfur with the rubber to form stable covalent cross-links or chemical bonds between the rubber chains.

As mentioned earlier, the optimum quantity of TBBS in the powder was 350mg/g. Therefore 26wt% of the powder was TBBS and the remaining 74wt% ZnO. On this basis, the 2.5phr powder contained 0.65phr TBBS and 1.85phr ZnO. In most NR-based industrial articles, including tires, the loading of accelerators can get to 4.5phr and

Figure 4: Cure rate index versus powder loading for the rubber compounds shown in Table 1
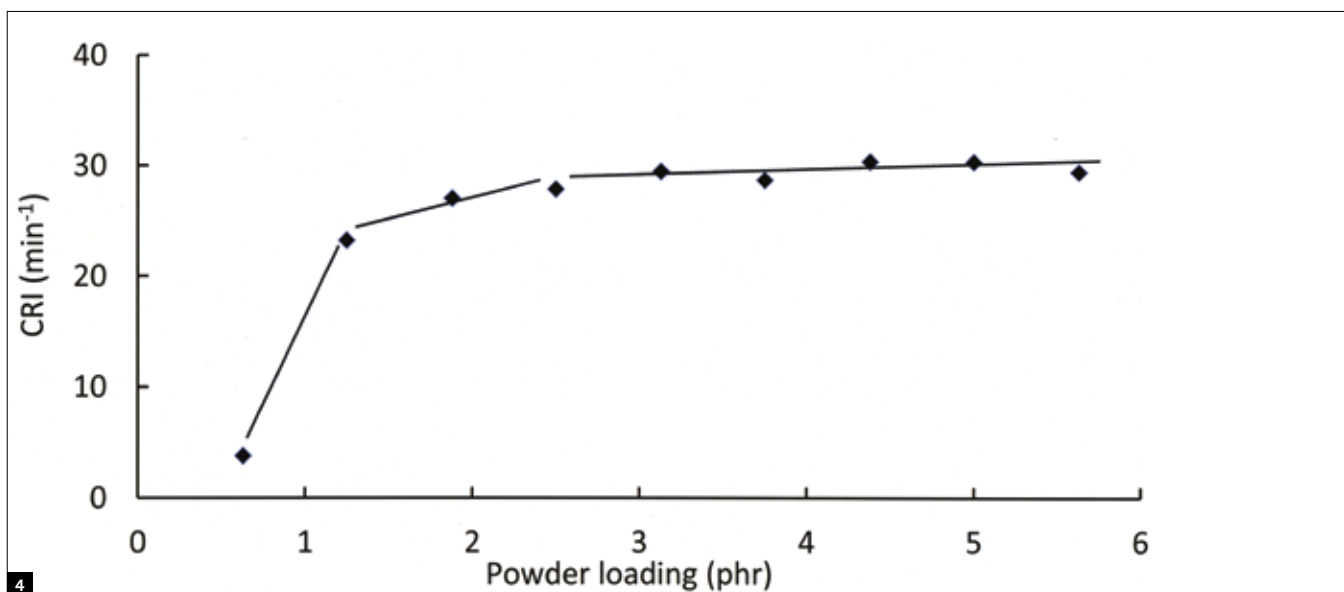
that of ZnO to10phr.[2] Obviously there is scope to reduce the excessive amount of these chemicals in rubber compounds quite substantially.

The scorch time remained unchanged at about 3.3-4.3 minutes when the full amount of the powder was added, though the optimum cure time decreased sharply from 30.8 minutes to 7.7 minutes with 1.25phr of the powder, and was unchanged when the loading of the powder was raised to 5.63phr. 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 1.25phr of the powder was added. The increase was about 510%. Thereafter it continued rising at a much slower rate to 27.8 min^{-1} when the loading of the powder reached 2.5phr. It subsequently plateaued at about 30.3 min^{-1} with the full amount of the powder (Figure 4). Clearly, above 1.25phr of the powder loading, the rate of cure did not rise much, i.e. only 30%.

For a tire belt skim compound, which has 5phr sulfur and 15.7phr chemical curatives, the scorch time (t_{s2}) and optimum cure time (t_{90}) are 2.6 minutes and 9.5 minutes respectively at 160°C.[3] The cure rate index is 15 min^{-1}. It is interesting that with a smaller amount of sulfur, i.e. 4phr, and only 2.5phr of the powder (0.65phr TBBS and 1.85phr ZnO), shorter scorch and optimum cure times and a much faster rate of cure, i.e. CRI up to 27.8 min^{-1}, were recorded for our rubber compounds (compound 4, Table 1). In fact, 20wt% reduction in sulfur and 84wt% less chemical curatives shortened the optimum cure time by 37% (the t_{90} of our compound was about six minutes) and increased the rate of cure by up to 85%. The scorch times were almost the same.

Note also that no stearic acid was used in the cure system. The trend observed here suggests that a much lower consumption of the chemical curatives, i.e. TBBS and ZnO, in sulfur vulcanization yields a significantly shorter cure cycle and therefore a more efficient cure. Other benefits include improvement in health, safety and the environment as well as major cost reduction.

It seems that functionalizing ZnO with TBBS into a single additive is a more efficient method of using these chemicals in rubber vulcanization than the methods are currently in use. This has the added advantage of eliminating secondary accelerators and too much ZnO from the cure system. All the indications are that the sulfur cure systems in tires are basically inefficient, costly and no longer viable – and hence must be improved. Combining the chemical curatives by means of functionalizing them is undoubtedly the most effective way of making green compounds for tires.

Summary

Functionalizing ZnO with TBBS to provide a single additive reduced the excessive use of these chemicals in the sulfur vulcanizations of NR. When the cure properties were compared with those of a typical tire belt skim rubber compound, the optimum cure time was noticeably shorter and the rate of cure significantly faster despite reducing the ZnO and TBBS curatives by over 80wt% in the cure system. It is expected that tire compounds currently in use may suffer from a similar deficiency in their cure systems. **tire**

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