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The perfect cure

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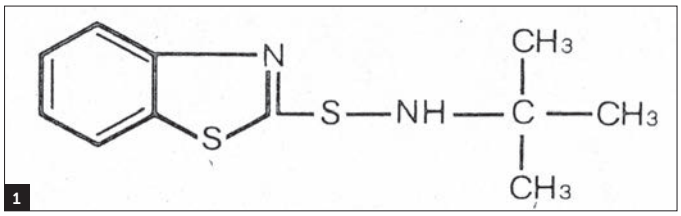
The perfect cure

Two new additives were prepared for curing natural rubber with sulfur and the measured cure properties showed a high level of efficiency for curing tire compounds

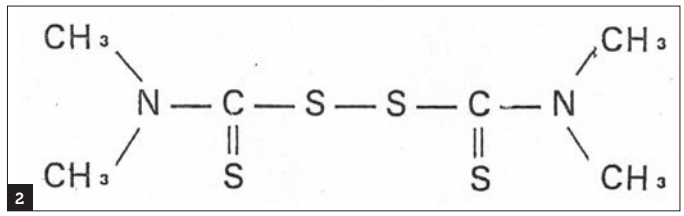
by Ali Ansarifar, Kornkanok Noulta, Saad H Sheikh and Xujin Bao (Department of Materials) and George W Weaver and K G Upul Wijayantha (Department of Chemistry), Loughborough University, UK

In the processing of raw rubber, sulfur is added for shape retention. To enhance the efficiency of curing and the vulcanization process, chemical curatives known as accelerators and activators are frequently used. However, excessive use of chemical curatives has raised major concerns about their adverse impact on human and animal health as well as on the environment. In most tire compounds, sulfenamide accelerators and zinc oxide are used in combination with sulfur to achieve efficient vulcanization. Since these chemicals are essential to improve the curing process, it is likely that their use in tire compounds will continue for some time. Therefore, their use must be lowered without compromising the cure properties and adversely affecting the cure cycle of tire compounds.

In this study, zinc oxide was treated separately with two organic accelerators (one of which was a sulfur-donor chemical) to produce two convenient single material components to use as additives. The effect of each additive on the cure properties of natural rubber containing 4phr by weight of elemental sulfur was subsequently measured. The loading of sulfur was selected arbitrarily. Natural rubber is used extensively in tire applications and sulfur is the most widely used curing agent in tire compounds. The aim of this work was to minimize use of these chemicals in cure systems and improve efficiency of the sulfur vulcanization process with a view to reducing cost and harmful effects while shortening the cure cycle.



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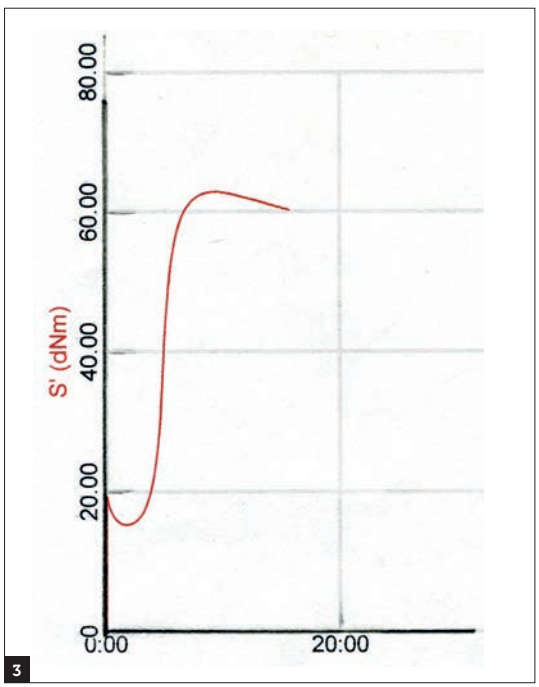


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The method

The raw rubber used was standard Malaysian natural rubber grade L (98wt% 1, 4-cis content; SMRL) with a viscosity of 89 Mooney units. The other ingredients were sulfur (curing agent: Solvay Barium Strontium, Germany); N-tert-butyl-2-benzothiazole sulfenamide [Figure 1] (a fast-curing delayed action accelerator with a melting point of 105°C/221°F), Santocure TBBS, Sovereign Chemicals, USA; Tetramethylthiuram disulfide [Figure 2] (a fast-curing, sulfur-donor accelerator with ~13% of the sulfur available to react with rubber and a melting point of 156°C/313°F), TMTD, Sigma-Aldrich, UK; and zinc oxide (ZnO; an activator, Harcros Durham Chemicals, UK). The TMTD accelerator proved to be a highly effective sulfur donor in the curing of rubber blends for tires.

Zinc oxide was treated with each accelerator by evaporation of a suspension of ZnO in a solution of TBBS or TMTD in dichloromethane (Fisher Scientific, UK) to provide convenient single-material components to use as additives. The quantity of TBBS required to provide monomolecular coverage of the ZnO was determined to be 35mg/g based on the approximate surface areas of the TBBS molecule ($6x10^{-19}m^2$) and the ZnO ($50m^2/g$) used. Similarly, the quantity of TMTD required to provide monomolecular coverage of the zinc oxide was determined to be 24mg/g based on the approximate surface areas of the TMTD molecule ($7.9x10^{-19}m^2$) and the ZnO ($50m^2/g$) used.



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Figure 1: The chemical structure of the TBBS accelerator

Figure 2: The chemical structure of the TMTD accelerator

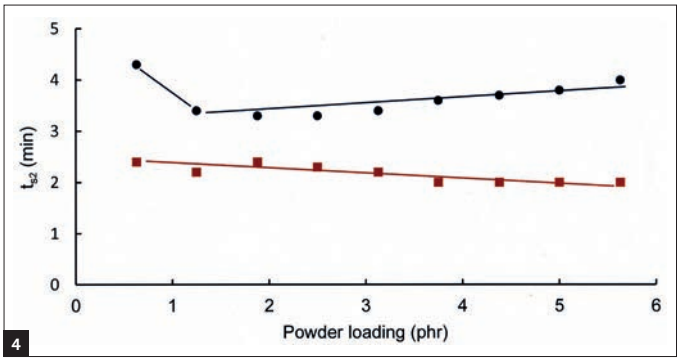
Figure 3: Typical torque (dNm) versus time (min) trace from ODR test. Data for rubber compound with 4phr sulfur and 2.5phr of ZnO/TBBS powder

The amount of TBBS or TMTD used to coat the zinc oxide was gradually increased from 100mg/g to 350mg/g to find a material with optimum properties. The material with 35mg/g TBBS or TMTD led to a very slow cure but material with 350mg/g gave a good cure, comparable to much higher loadings of TBBS or TMTD, which is 3phr in some compounds. The optimum quantity of TBBS or TMTD in the powder was 350mg/g. This meant that 26wt% of the powder was TBBS or TMTD and the remaining 74wt% ZnO. On this basis, the 2.5phr powder contains 0.65phr TBBS or TMTD and the remaining 1.85phr is ZnO. In some articles, for example NR-based aircraft tire tread, the chemical curatives (accelerators and activators) in the cure system can add up to 8.3phr.

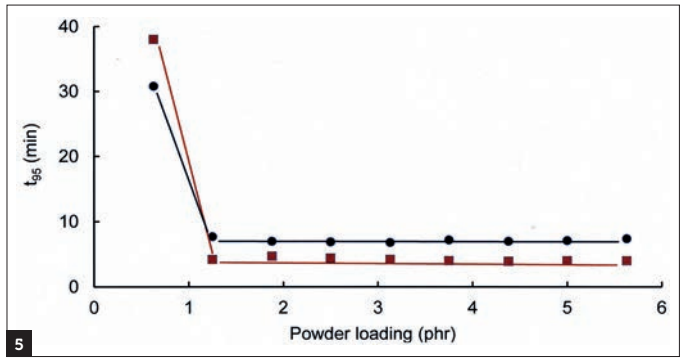
A large batch of the surface-modified ZnO was then prepared with this ratio from 100.0g of ZnO and 35.0g of TBBS or 24.0g of TMTD, which was mixed in 200ml of the solvent in a 500ml round-bottomed flask. The suspension was stirred magnetically for 15 minutes at room temperature (21.5°C/70.7°F) to ensure uniform coating. The mixture was evaporated on a rotary evaporator at 100mbar and further dried at 50°C at 20mbar for two hours to leave a free-flowing white solid. The obtained white solid showed a mass loss of 0.213g, indicating the bulk of the TBBS was absorbed onto the ZnO. The surface modified additives will be referred to as the 'powder'. In a different experiment, the loading of the powders with 350mg/g of TBBS or TMTD was increased progressively to determine the effect on the cure properties of the rubber.

The raw rubber was mixed with the chemical reagents in a Haake Rheocord 90 (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°F) and the rotor speed was set at 45rpm. The volume of the mixing chamber was $78cm^3$ and it was 60% full during mixing. Polylab monitor 4.17 software was used to control the mixing condition and to store data.

To prepare the rubber compounds, the raw rubber was introduced into the mixer and then, after 30 seconds, the sulfur and the new powder were added and mixed for eight minutes. The loading of the powders was raised progressively from 0.63phr to 5.63phr to determine the effect on the cure. The temperature of the rubber compounds was 52-62°C (125-144°F). In total, 18 rubber compounds were made.



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The cure properties of the rubber compounds were measured at 160°C (±2C°) in an oscillating disc rheometer curemeter (ODR, UK – British Standard ISO 3417). From the cure traces, scorch time, t_{s2} (the time for the onset of cure), and the optimum cure time, t_{95} (the time for the completion of cure), were determined. The cure rate index (CRI), which measures the rate of cure in the rubber, was also calculated using the same British Standard as above. ΔTorque, t_{s2}, t_{95} and CRI were subsequently plotted against the loading of the powders. ΔTorque is the difference between the maximum and minimum torque values on the cure trace of a rubber compound (Figure 3) and is an indication of crosslink density changes in the rubber.

Results and discussion

The powders had different effects on the cure properties of the rubber. The compound that was cured with the ZnO/TBBS powder had a longer scorch time of 4.3 min at 0.63phr of the powder. However, as the loading of the powder was raised to 5.63phr, the scorch time shortened slightly to 4 min. The compound that was cured with the ZnO/TMTD powder had a scorch time of 2.4 min at 0.63phr of the powder, which decreased to 2 min when the full amount of the powder was incorporated into the rubber (Figure 4).

The optimum cure time of the compound cured with the ZnO/TBBS powder was 30.8 min at 0.63phr of the powder, which reduced very sharply to about 7.4 min at 5.63phr of the powder. Interestingly, the compound that was cured with the ZnO/TMTD powder had a much higher optimum cure time of 38 min at 0.63phr of the powder and decreased abruptly to 4 min at 5.63phr of the powder (Figure 5). For the compound cured with the ZnO/TBBS powder, the rate of cure as indicated by the cure rate index rose sharply from 3.8 min^{-1} at 0.63phr to 23.2 min^{-1} at 1.25phr of the powder and then attained a higher value of 29.4 min^{-1} at 5.63phr of the powder (Figure 6). The rubber compound cured with the ZnO/TMTD powder had a much faster cure rate.

Figure 4: Scorch time, t_{s2} versus powder loading, (■) ZnO/TMTD powder, (●) ZnO/TBBS powder

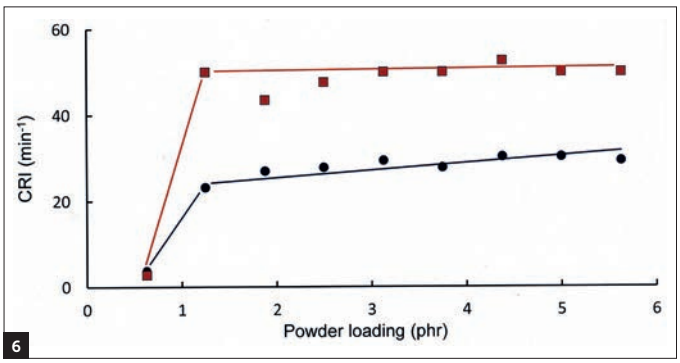
Figure 5: Optimum cure time, t_{95}, versus powder loading, (■) ZnO/TMTD powder, (●) ZnO/TBBS powder

Figure 6: Cure rate index versus powder loading, (■) ZnO/TMTD powder, (●) ZnO/TBBS powder

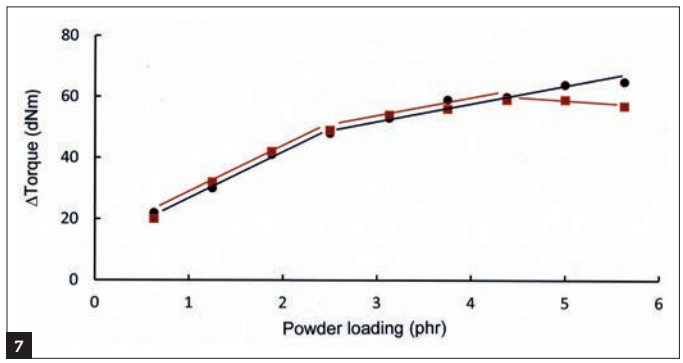
Figure 7: ΔTorque versus TBBS and TMTD loading for the compounds with 4phr sulfur. (■) ZnO/TMTD powder, (●) ZnO/TBBS powder

Interestingly the powders had a very similar effect on the crosslink density changes in the rubber as shown by the ΔTorque values. For the compound cured with the ZnO/TBBS powder, the ΔTorque rose sharply from 22dNm at 0.63phr to 48dNm at 2.5phr of the powder and continued rising at a much slower rate to about 65dNm at 5.63phr of the powder. Similarly, for the compound cured with the ZnO/TMTD powder, ΔTorque rose from 20dNm at 0.63phr to 49dNm at 2.5phr of the powder. Subsequently ΔTorque continued increasing at a much slower rate to about 59dNm at 4.38phr of the powder and finally reached a slightly lower value of 57dNm when the full amount of the powder was added to the rubber (Figure 7).

It appears that optimum cure can be achieved with 2.5phr of either powder, but the indications are that the ZnO/TMTD powder offers a more efficient cure cycle because of the shorter scorch and optimum cure times and a much faster rate of cure of the compounds tested. It's possible the ZnO/TMTD powder in combination with elemental sulfur can replace the current sulfur cure systems in tire compounds. Moreover, a significant reduction in the excessive use of these chemicals helps to minimize adverse impact on human and animal health as well as on the environment. **tire**



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