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New rubber compound

Ethylene-propylene-diene rubber cured with a new single chemical additive and reinforced with mineral kaolin is a suitable compound for possible use in tires

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

Ethylene-propylene-diene (EPDM) rubber is a highly versatile polymer with outstanding properties. The saturated ethylene-propylene backbone gives it very good resistance to environmental aging by oxygen and ozone. EPDM rubber also possesses excellent weather, water and heat resistance and can be reinforced with solid fillers, for example CB and silica, to produce vulcanizates with good mechanical and dynamic properties.¹⁻³ EPDM rubber can be cured with sulfur because of the presence of unsaturated monomers such as dicyclopentadiene, ethylidene norbornene and trans-1,4 hexadiene in its molecular structure. Sulfur vulcanization imparts shape stability and good mechanical properties on the final product, but further reinforcement is required by solid fillers.

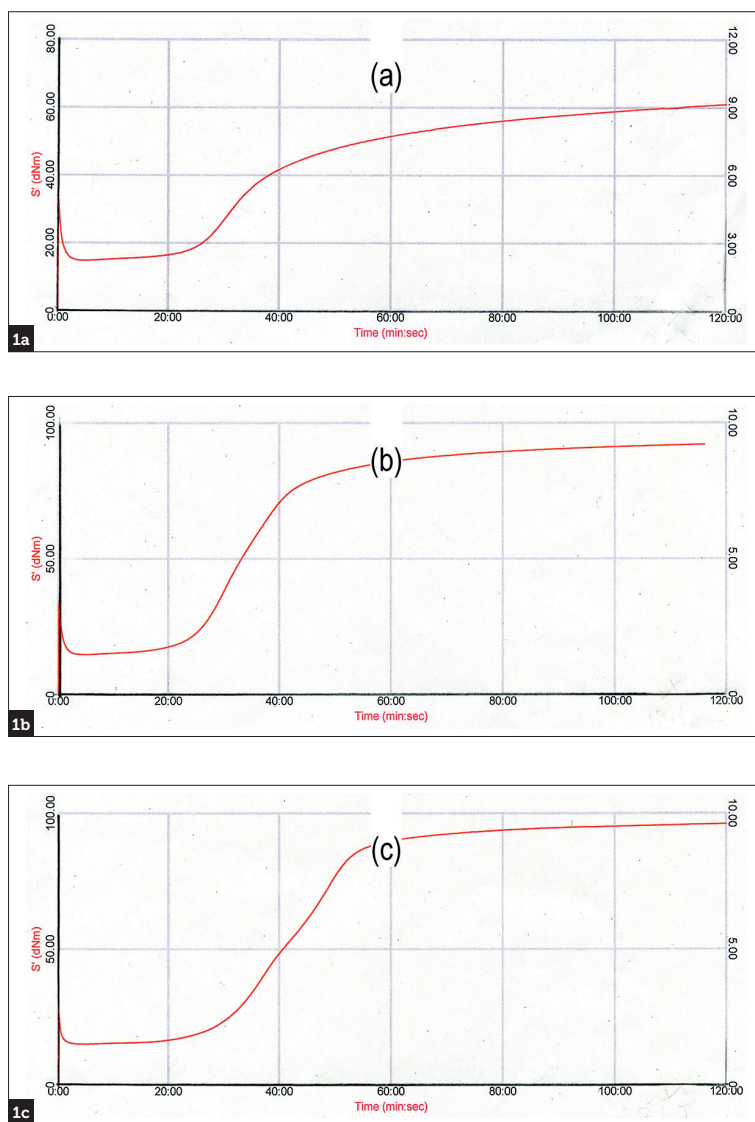
Carbon black-reinforced EPDM rubber is used in a wide range of automotive applications such as hoses, window gaskets and weather strips.⁴ However, EPDM rubber is not used in tire applications, where crystallizing natural rubber is the preferred polymer because of its superior mechanical properties.⁵

In this preliminary study, EPDM rubber was reinforced with mineral kaolin (China clay) and cured with a new single chemical additive. The viscosity, cure properties, hardness and mechanical properties of the rubber compound were then measured and compared with those of the unfilled rubber compound. Results indicate that kaolin is a very effective filler for reinforcing the hardness and mechanical properties of the rubber and that using a single chemical additive to cure the rubber reduces the use of curatives.

The method

The raw rubber used was EPDM rubber (48wt% ethylene, 9wt% ethylidene norbornene and 13wt% oil, Keltan 6251A, Lanxess,

Figure 1: Cure traces (torque [dNm] versus time [min]) from ODR tests. Data for the unfilled rubber compound with 0.75phr powder (1a), with 3.2phr powder (1b) and with 5.5phr powder (1c). All the compounds had 1phr sulfur



Netherlands). The reinforcing filler was Mercap100 (Imerys Ceramics, USA). Mercap 100 is kaolin (China clay; $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), the surface of which had been pre-treated with 3-mercaptopropyl- trimethoxysilane (MPTS) to reduce its polarity and prevent it from adsorbing moisture. MPTS contains less than 2wt% of sulfur. Mercap 100 has a very fine particle size of about $0.3\mu\text{m}$ and $25\text{m}^2/\text{g}$ surface area measured by nitrogen adsorption. It contains approximately 90 parts per million

(ppm) of sulfur, which primarily comes from trace secondary minerals, mainly pyrite (FeS_2) with a melting point of $1,100^\circ\text{C}$ ($2,012^\circ\text{F}$).

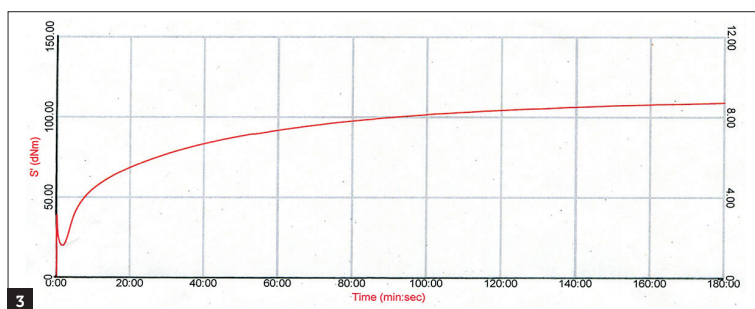
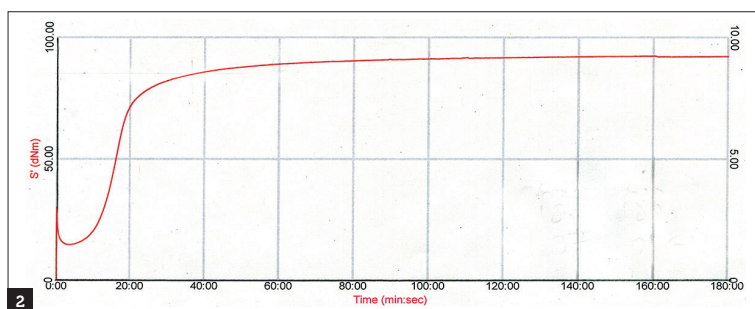
The powder was placed in an oven at 80°C (176°F) for at least 48 hours to remove any moisture, before mixing it with the rubber. In addition to the raw rubber, the other ingredients were elemental sulfur (curing agent, Solvay, Hannover, Germany), N-tert-butyl-2-benzothiazole sulfenamide (a fast-curing delayed action accelerator

with a melting point of 105°C (221°F) (Santocure TBBS, Sovereign Chemicals, USA), zinc oxide (ZnO, an activator, Harcros Durham Chemicals, Durham, UK), and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD, an antidegradant with a melting point of 45°C (113°F), Santoflex 13, Brussels, Belgium).

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 35mg/g based on the approximate surface areas of the TBBS molecule ($6 \times 10^{-19} \text{m}^2$) and the ZnO ($50 \text{m}^2/\text{g}$) used. Gradually the amount of TBBS to coat the zinc oxide was increased from 100mg/g to 350mg/g to find a material with optimum properties. The material with 35mg/g TBBS led to a very slow cure, but material with 350mg/g gave a good cure, comparable to much higher loadings of TBBS, which is as high as 3phr by weight in some compounds. The optimum quantity of TBBS in the powder was 350mg/g. A large batch of the surface-modified zinc oxide was then prepared with this ratio from 100g of ZnO and 35g of TBBS, which was mixed in 150ml 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 325mbar and further dried at 50°C (122°F) at 100mbar for two hours to leave a free-flowing white solid. The obtained white solid showed a mass loss of 0.47g, indicating the bulk of the TBBS was absorbed onto the ZnO. The surface modified additive will be referred to as the 'powder'. In a different

Figure 2: Cure trace (torque [dNm] versus time (min)) from ODR test. Data for the rubber compound with 0phr kaolin, 1phr sulfur, 3.2phr powder, 1phr 6PPD

Figure 3: Cure trace (torque [dNm] versus time (min)) from ODR test. Data for the rubber compound with 60phr kaolin, 1phr sulfur, 3.2phr powder, 1phr 6PPD



experiment, the loading of the powder with 350mg/g of TBBS was increased progressively to determine its effect on the cure properties of the sulfur-filled EPDM rubber.

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°F) 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 to control the mixing conditions and store data. To prepare the unfilled rubber compound, the raw rubber was introduced first into the mixer and mixed for one minute and then sulfur, the powder and 6PPD were added and mixed for another 12 minutes. A similar procedure was used for making the kaolin-filled rubber compound where kaolin was added three minutes after mixing started. For both rubber compounds,

the total mixing time was 13 minutes. The loading of the powder was raised progressively from 0.75phr to 5.5phr to determine its effect on the cure. The temperature of the rubber compounds after mixing ended was 60-68°C (140-154.4°F). In total, 11 different rubber compounds were prepared and each of their cure properties measured.

The viscosity, ML (1+4), of the rubber compounds was measured at 100°C (212°F) in a single-speed rotational Mooney Viscometer (British Standard 1673: Part 3, 1969). The cure properties of the rubber compounds were measured at 160±2°C in an oscillating disk rheometer curemeter (ODR, Monsanto, Swindon, UK) (British Standard 1673: Part 10, 1977). The ODR tests ran for two hours to measure the effect of an increasing loading of the powder on the cure properties of the unfilled rubber (Figures 1a, b and c), and for three hours until the cure for both the unfilled and kaolin-filled rubber compounds reached equilibrium. From the cure traces (Figures 1, 2

and 3), 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.

To ensure that the unfilled and kaolin-filled rubber vulcanizates had the same cross-link density to show the effect of the filler more precisely, the maximum torque on the marching cure trace was chosen to produce the same Δ torque, i.e. arbitrarily selected at 74dNm, for both compounds (Figures 2 and 3). This subsequently gave 37 minutes and 41 minutes cure time for the unfilled and kaolin-filled rubber compounds respectively. Note that Δ torque is the difference between the maximum and minimum torque values on the cure trace of a rubber compound and is an indirect indication of cross-link density changes in the rubber. In calculating the Δ torque for the filled rubber, the minimum torque of the unfilled rubber was used to eliminate contribution from the filler to the higher initial viscosity of the filled compound, which could have adversely affected calculations for the Δ torque. The cure rate index (CRI), which measures the rate of cure in the rubber, was also calculated (British Standard 903: Part A60: Section 60.1, 1996). Δ Torque, t_{s2} , t_{95} and CRI were subsequently plotted against the loading of the powder to

Figure 4: Scorch time, t_{s2} , versus powder loading (●), optimum cure time, t_{95} , versus powder loading (■) for the unfilled rubber compound (Table 1)

Figure 5: Cure rate index versus powder loading for the unfilled rubber compound

Figure 6: Δ Torque versus powder loading for the unfilled rubber compound

Table 1: Mooney viscosity, hardness, cure properties and mechanical properties of the rubber compounds

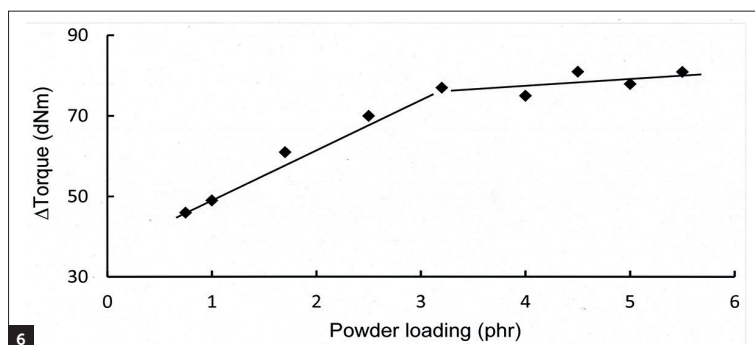
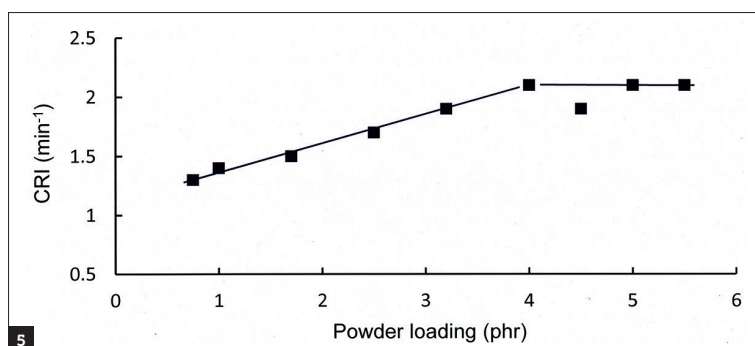
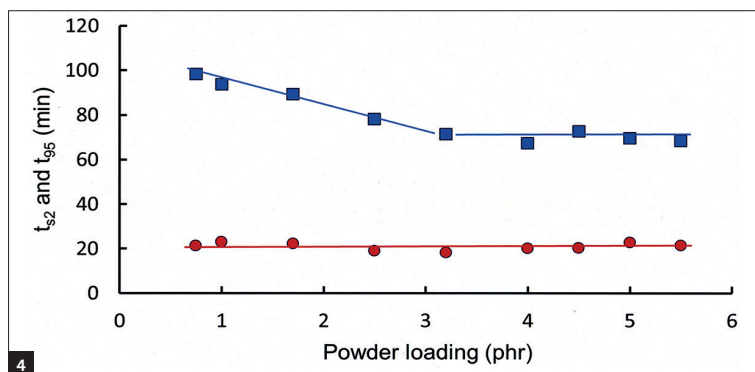
Table 1: Mooney viscosity, hardness, cure properties and mechanical properties of the rubber compounds

Compound	Unfilled	Filled
Mooney viscosity ML (1+4)	72	88
ML (dNm)	15	15
MH (dNm)	89	89
Δ Torque (dNm)	74	74
t_{s2} (min)	7.5	2.5
t_{95} (min)	37	41
CRI (min^{-1})	3.4	2.6
Hardness (Shore M)	36	54
Tensile strength (MPa)	1.5	15.5
Elongation at break (%)	390	1,120
Stored energy density at break (MJ/m^3)	4.5	104
Tear energy (kJ/m^2)	2.5	16

Formulations:

Unfilled rubber compound: EPDM: 100phr; kaolin: 0phr; sulfur: 1phr; powder: 3.2phr; Santoflex 13: 1phr

Filled rubber compound: EPDM: 100phr; kaolin: 60phr; sulfur: 1phr; powder: 3.2phr; Santoflex 13: 1phr



determine the effect of the powder on these properties. The hardness (British Standard 903: Part A26, 1995), tensile stress-strain properties (British Standard 903: Part A2, 1995), and tear energy (British Standard: 903: Part A3, 1995) were also measured and the results summarized (Table 1).

Results and discussion

Figure 4 shows t_{s2} and t_{95} as a function of powder loading for the unfilled rubber compound tested. The scorch time was essentially unchanged, showing no clear trend, and remained at about 18.1–23.0 minutes as the loading of the powder was raised progressively from 0.75phr to 5.5phr. However, the optimum cure time decreased sharply from 98.2 minutes at 0.75phr to 71.4 minutes at 3.2phr of the powder. Thereafter it remained

at a steady value of 67.3–72.7 minutes when the loading of the powder reached 5.5phr. The rate of cure as indicated by the CRI rose steeply from 1.3min^{-1} at 0.75phr to 2.1min^{-1} at 4phr of the powder. It subsequently plateaued at about $1.9\text{--}2.1\text{min}^{-1}$ when the full amount of the powder was incorporated in the rubber (Figure 5). The CRI result of 1.9min^{-1} at 4.5phr of the powder could be an anomaly.

Figure 6 shows Δ torque versus powder loading for the unfilled rubber compound tested. Δ Torque increased from 46dNm to 77dNm when the loading of the powder was raised from 0.75phr to 3.2phr. Δ Torque thereafter continued rising at a much slower rate to about 81dNm when the loading of the powder reached 5.5phr. Evidently the addition of 3.2phr of the powder was enough to react with sulfur to

form stable covalent cross-links between the rubber chains. Notably, when the loading of the powder exceeded 4phr, the rubber was brittle and weak. 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% was ZnO. On this basis, 3.2phr of the powder contained 0.83phr TBBS and 2.37phr ZnO. After these measurements were completed, 1phr sulfur and 3.2phr of the powder were used to cure the unfilled and filled rubbers. To reinforce and protect the rubber against environmental aging, 60phr kaolin and 1phr 6PPD were added to the rubber. The addition of kaolin had a major effect on the mechanical properties of the rubber vulcanizate. The hardness increased by 50%, tensile strength by 993%, elongation at break by 187%, stored energy density at break by 2,211% and tear energy by 540% (Table 1). This showed the highly reinforcing properties of kaolin in the rubber.

In the carbon black-filled natural rubber-based tire belt skim (TBS)

compound, the cure system consists of 2.7phr accelerators (primary and secondary) and 8phr activators (primary and secondary), adding up to 10.7phr and 5phr sulfur.⁶ Clearly, using the powder in place of the accelerators and activators and adding a smaller amount of sulfur, i.e. as low as 1phr, will significantly reduce the use of these harmful chemicals in the cure system and at the same time maintain the good mechanical properties that are essential for long service life.

Furthermore the TBS has 55phr carbon black that can be replaced with an equivalent amount of the silane pre-treated kaolin, since kaolin is a highly reinforcing filler for rubber. For instance, the tensile strength of TBS is 21.5MPa and its elongation at break 370%,³ whereas the tensile strength of the kaolin-filled EPDM rubber vulcanizate is 15.5MPa and its elongation at break is 1,120% (Table 1). In addition to these benefits, the use of the powder to cure and the kaolin to reinforce the EPDM rubber will provide an environmentally

friendly, cost-effective and safer compound for possible use in tires, for example in belt skim compounds for tires. **tire**

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