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# Kaolin reinforcement of some rubbers with novel sulfur cure systems

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*A large amount of kaolin (China clay) was used to reinforce the hardness, tensile strength, elongation at break, stored energy density at break, tear resistance, and Young's modulus of some sulfur-cured NR, BR and EPDM. The kaolin surface had been pre-treated with 3-mercaptopropyltrimethoxysilane (MPTS) to reduce its polarity and prevent it from adsorbing moisture which could have been detrimental to the cure of the rubbers. For NR, the hardness and Young's modulus improved, tensile strength and tear resistance were unchanged and the remaining properties deteriorated when kaolin was added. The viscosity increased and the scorch and optimum cure times decreased with kaolin. The highest cure rate ever reported for a sulfur-cured NR-based compound was achieved when kaolin was mixed with the rubber. For BR and EPDM, most of the properties including the viscosity gained significantly from the presence of kaolin in the rubbers. It was concluded that kaolin was an extending or non-reinforcing filler for NR, and highly reinforcing for BR and EPDM. Notably, the scorch and optimum cure times and cure rate of BR benefited so much, whereas with the exception of the scorch time, the optimum cure time and cure rate of EPDM were adversely affected by kaolin. The addition of kaolin increased the crosslink density of NR but had a detrimental effect on the crosslink density of BR and EPDM. The early indications are that kaolin is a viable alternative to carbon black and silica/silane systems in rubber reinforcement.*

## 1 Introduction

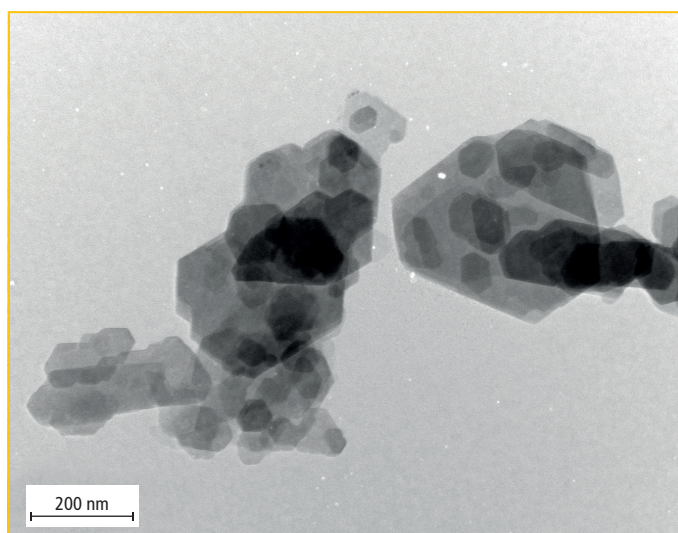
Typical rubber formulations for commercial products such as natural rubber-based conveyor belt covers consist of up to eleven different chemical additives including cure system and reinforcing filler. The cure system is made of sulfur, three accelerators (primary and secondary), and primary and secondary activators (zinc oxide and stearic acid, respectively), adding up to 9.7 parts per hundred rubber (phr) by weight [1]. The reinforcing

filler is carbon black (CB) [1]. In any rubber formulation, chemical curatives and solid fillers are indispensable. The former provides shape stability and the latter, reinforcement of the dynamic and mechanical properties of the cured rubber, which is essential for the performance, durability and life of the final product in service [2, 3].

Excessive use of the chemical curatives is harmful to health, safety, and the environment. According to the European Direc-

tive 67/548/EEC, zinc oxide is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Although the toxicological properties of stearic acid have not been fully investigated, there is enough evidence to suggest that this substance has major potential health hazards. For example, eye irritation, which causes chemical conjunctivitis, and skin irritation that can be harmful if absorbed through the skin. If the latter occurs, it can cause gastrointestinal irritation with nausea and vomiting. Also, inhalation of this substance into the lungs may cause chemical pneumonitis, which may be fatal [4]. Stearic acid is classified as highly flammable [4]. Both of these chemicals are used extensively as activator in sulfur vulcanisation [1, 5]. Besides, CBs could be highly toxic and pose a considerable health risk associated with their use in rubber compounds [6]. There is a need to replace CB with other less harmful solid fillers.

Kaolin (China clay) is a mineral filler with promising potential for use in rubber reinforcement. It has a plate-like structure (**fig. 1**) whereas CB is spherical. The Kaolin surface possesses OH groups (from the  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), which makes it polar and moisture adsorbing. To improve dispersion of the kaolin particles in rubber, the filler surface is often treated with silane [7]. Previous studies where kaolin was used in NR showed promising results. For example, in a study a small amount of kaolin, i.e. 10 phr, was modified with the sodium salt of rubber seed oil (SRSO) and mixed with NR [8].



**Fig. 1:** Transmission electron micrograph showing kaolin particles

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All figures and tables, unless otherwise stated, have been kindly provided by the authors.

The rubber filled with SRSO-modified kaolin cured faster than that of a similar mix containing unmodified kaolin. In addition, the NR vulcanisates containing SRSO-modified kaolin showed considerable increases in tensile modulus, tensile strength, and elongation at break. This indicated kaolin potential as an organo-modified nanofiller. NR nanocomposites reinforced with 20 – 50 phr of saline-modified kaolin showed very impressive mechanical properties and higher thermal stability compared with the pure NR. The hardness and tensile properties improved when the filler loading was raised and an optimum tensile strength was achieved at the highest loading of the modified kaolin [9]. In a recent study, the author and co-worker [10], using kaolin pre-treated with 3-mercaptopropyltrimethoxysilane (MPTS), developed a new method that optimised the reaction between the sulfur in MPTS on the kaolin surface and NR, and the rubber was then cured with additional sulfur and its mechanical properties measured. The hardness

and Young's modulus improved noticeably and the tensile strength rose marginally. Other properties such as the scorch and optimum cure times and rate of cure also benefited from the addition of kaolin to the rubber. All the indications were that kaolin had promising capability for reinforcing rubber properties with major benefits for cure too.

The aim of this preliminary study was to use a high loading of kaolin pre-treated with MPTS to improve the hardness and mechanical properties of some commercially important rubbers. The effect of kaolin on viscosity and cure properties of the rubbers was also investigated. The study used a new method for measuring the exact amount of the chemical curatives required in the sulfur vulcanisation of the rubbers.

## 2 Experimental

### 2.1 Materials

The raw rubbers used were standard Malaysian natural rubber (NR) grade L (98 wt% 1,4-cis content, SMRL), high cis polybutadiene rubber (96 wt% 1,4-cis content, Buna CB24, Bayer, Newbury, UK, not oil extended), ethylene-propylene-diene rubber (EPDM, 48 wt% ethylene content, 9 wt% ethylidene norbornene content, and 13 wt% oil content, Keltan 6251A, Lanxess, The Netherlands). The reinforcing filler was Mercap 100 (Imerys Ceramics, USA). Mercap 100 is kaolin (China clay,  $Al_2Si_2O_5(OH)_4$ ), the surface of which had been pre-treated with 3-mer-

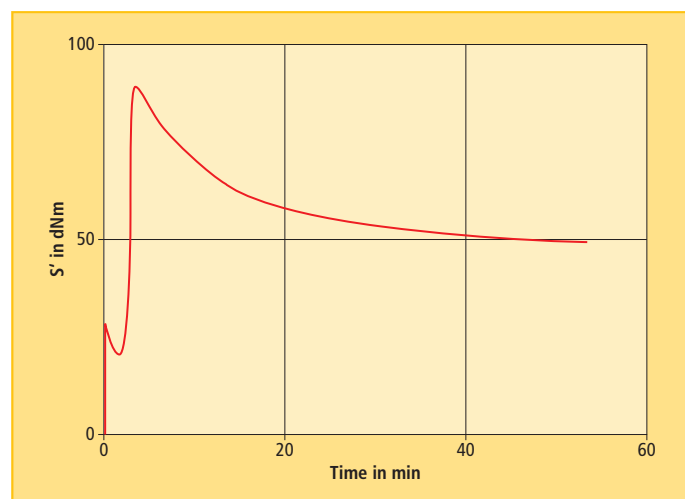
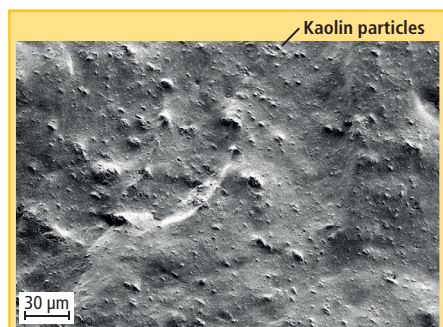
captopropyl-trimethoxysilane (MPTS) to improve dispersion of the filler particles in rubber. MPTS contains less than 2 wt% of sulfur. Mercap 100 has a very fine particle size of about 0.3  $\mu m$  and 25  $m^2/g$  surface area measured by nitrogen adsorption (Imerys Ceramics, USA). It contains approximately 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 °C.

In addition to the raw rubbers and kaolin, the other ingredients were elemental sulfur (curing agent, Solvay, Hanover, Germany), Santocure TBBS (N-tert-butyl-2-benzothiazole sulphenamide, a fast-curing delayed-action accelerator with a melting point of 105 °C, Sovereign Chemicals, USA), zinc oxide (ZnO, an activator, Harcros Durham Chemicals, Durham, UK), stearic acid (an activator, Anchor Chemicals Ltd, UK), and Santoflex 13 (6PPD, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, an antidegradant with a melting point of 45 – 51 °C, Taminco BVBA (Eastman Chemical), Gent, Belgium).

### 2.2 Mixing

The raw rubbers were mixed with the chemical ingredients in a Haake Rheocord 90 (Berlin, Germany), a small 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 condition and storing data. To prepare the unfilled NR, BR and EPDM compounds, the raw rubber was introduced first into the mixer and mixed for 1 min and then sulfur, TBBS, ZnO, stearic acid, and antidegradant were added and mixed for another 12 min. A similar procedure was used for making the kaolin-filled compounds where kaolin was added 3 min after mixing started. A total mixing time of 13 min was sufficient to disperse the kaolin particles fully in the rubber matrix (fig. 2). The temperature of the compounds during mixing was 58 – 62 °C.

**Fig. 2:** Scanning electron micrograph showing the good dispersion of kaolin particles in the rubber matrix – data for the NR compound with 60 phr kaolin after 13 min mixing.



**Fig 3:** Typical torque (vertical axis) versus time cure trace at 160 °C – data for the NR compound with 4 phr sulfur, 3.5 phr TBBS, 0.2 phr ZnO, and 140 phr kaolin

**2.3 Determination of the optimum amount of chemical curatives**

Sulfur is used extensively in the vulcanisation of a wide range of industrial rubber articles. For example, the cure system in a NR-based tyre belt skim compound has 5 phr [11], in a SBR/BR-based compound for footwear 2 phr [12], and in a EPDM-based general gaskets 1 phr of sulfur [13]. In this preliminary study, the NR had 1 phr and 4 phr, BR 0.5 phr and 1 phr, and EPDM 1 phr of sulfur. To react the sulfur with the rubber to form crosslinks, TBBS was added. The loading of TBBS was raised from 0.25 phr to 4.5 phr and 47 compounds were made. Zinc oxide was used as primary activator to improve the effectiveness of TBBS during curing. The loading of ZnO in the rubbers with sulfur and TBBS was increased from 0 to 0.5 phr and 44 compounds were mixed. To evaluate the effect of stearic acid (used as secondary activator with ZnO) on the cure properties of the rubbers with sulfur, TBBS and ZnO, 22 compounds were prepared. The loading of stearic acid was raised from 0 to 2.5 phr to measure the amount needed to improve efficiency of the cure systems.

**2.4 Determination of viscosity, cure properties, hardness and mechanical properties**

The viscosity, cure properties, hardness and mechanical properties of the rubbers were measured according to the procedures described in the British Standards:

- Viscosity: British Standard 1673: Part 3 (1969), using a Mooney viscometer (Wallace Instruments, Surrey, UK) and the results were expressed as Mooney Units (MU).

- Cure properties: British Standard 1673: Part 10 (1977), using an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at  $160 \pm 2$  °C. 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.  $\Delta$ Torque, which is the difference between the maximum and minimum torque values on the cure trace of a compound (fig. 3) and is an indication of crosslink density changes in the rubber was also measured.  $\Delta$ Torque was afterwards plotted against the loading of TBBS, ZnO, and stearic acid.
- Cure rate index (CRI): British Standard 903: Part A60: Section 60.1. (1996). CRI is an indication of the rate of cure in the rubber.
- Hardness: British Standard 903: Part A26 (1995), using cylindrical samples 6 mm thick and 15 mm in diameter, in a Shore A Durometer hardness tester (The Shore Instrument & MFG, Co., New York, USA). The test temperature was 23.5 °C.
- Tensile stress-strain properties (tensile strength, elongation at break, stored energy at break, and Young's modulus): British Standard 903: Part A2 (1995),

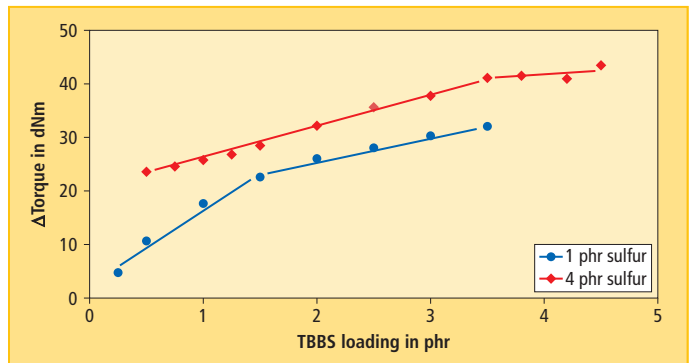
in a LR50K plus materials testing machine (Lloyd Instruments, UK), using standard dumbbell test pieces. Lloyd Nexygen 4.5.1 was used to process and store the data. The test temperature was 22 °C and the crosshead speed was set at 100 mm/min.

- Tear energy: British Standard 903: Part A3 (1995), in a LR50K plus materials testing machine (Lloyd Instruments, UK), using trouser test pieces. The test temperature was at ambient (23 °C), tear angle 180°, and crosshead speed was set at 50 mm/min.

**3 Results and discussion**

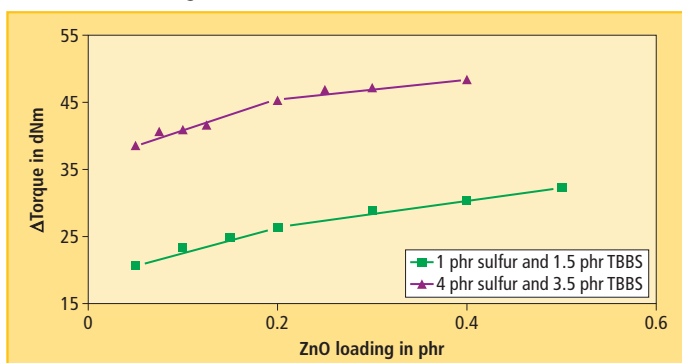
**3.1 Optimum sulfur cure systems for NR, BR and EPDM**

Figure 4 shows  $\Delta$ torque as a function of TBBS loading for the NR rubbers with 1 phr and 4 phr sulfur. For the rubber with 1 phr sulfur,  $\Delta$ torque increased from 5 dNm to 23 dNm as the loading of TBBS was raised to 1.5 phr, and it continued rising at a much slower rate to about 32 dNm when the loading of TBBS reached 3.5 phr. The addition of 1.5 phr TBBS was sufficient to react the

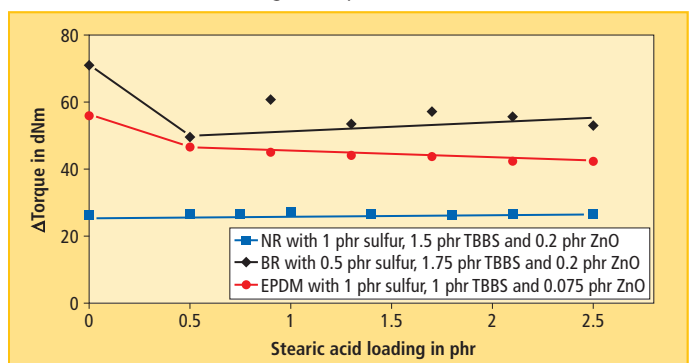


**Fig. 4:**  $\Delta$ Torque versus TBBS loading for NR compounds with different sulfur loadings

**Fig. 5:**  $\Delta$ Torque versus ZnO loading for NR compounds with different sulfur and TBBS loadings



**Fig. 6:**  $\Delta$ Torque versus stearic acid loading for rubber compounds with different sulfur and TBBS loadings in the presence of ZnO



sulfur with the rubber to form crosslinks. For the rubber with 4 phr sulfur,  $\Delta$ torque increased from 24 dNm to 41 dNm as the loading of TBBS was increased from 0.5 phr to 3.5 phr. Subsequently,  $\Delta$ torque rose to 43 dNm when an additional 1 phr TBBS was incorporated in the rubber. Clearly, 3.5 phr TBBS was sufficient to react the sulfur with the rubber.

To enhance the efficiency of cure in the NR with sulfur and TBBS, ZnO was added (fig. 5). The addition of 0.2 phr ZnO to the rubber with 1 phr sulfur and 1.5 phr TBBS was enough to improve the efficiency of TBBS as indicated by an increase in  $\Delta$ torque from 21 dNm to 26 dNm. However, when the loading of ZnO was raised to 0.5 phr,  $\Delta$ torque rose at a much slower rate to about 33 dNm. Similarly,  $\Delta$ torque for the rubber with 4 phr sulfur and 3.5 phr TBBS reached optimum value at 0.2 phr ZnO and thereafter the rise was marginal. Note that a small amount of ZnO, i.e. as low as 0.2 phr, when added as primary activator, improved the performance of TBBS to such a degree during curing as shown by increase in  $\Delta$ torque (fig. 5).

Stearic acid is a fatty acid that is added as co-activator with ZnO in sulfur vulcanisation. It also acts as plasticiser and internal lubricant between polymer chains, and aids dispersion of solid ingredients in the rubber. Zinc stearate is formed when stearic acid reacts with ZnO and is an essential cure activator [14]. The loading of stearic acid in the NR with 1 phr sulfur, 1.5 phr TBBS and 0.2 phr ZnO was raised from 0 to 2.5 phr to increase the dispersion and solubility of ZnO and enhance efficiency of the curing reaction in the rubber. Figure 6 shows  $\Delta$ torque versus stearic acid loading. The inclusion of stearic acid in the cure system had no benefit for  $\Delta$ torque at all, which stayed constant at about 27 dNm. It is abundantly clear that ZnO is a very effective primary activator in improving the performance of TBBS in the absence of secondary activators such as stearic acid.

Figure 7 shows  $\Delta$ torque as a function of TBBS loading for the BR rubbers with 0.5 phr and 1 phr sulfur. For the rubber with 0.5 phr sulfur,  $\Delta$ torque increased from 25 dNm to 45 dNm as the loading of TBBS was raised to 1.75 phr, and then it stopped rising once

the loading of TBBS reached 3 phr. The addition of 1.75 phr TBBS was sufficient to react the sulfur with the rubber to form crosslinks. For the rubber with 1 phr sulfur,  $\Delta$ torque increased from 39 dNm to 61 dNm as the loading of TBBS was raised from 0.5 phr to 3 phr. Subsequently,  $\Delta$ torque remained essentially unchanged when an additional 0.8 phr TBBS was incorporated in the rubber. Clearly, 3 phr TBBS was sufficient to react the sulfur with the rubber.

Zinc oxide was then added to enhance the efficiency of cure in the BR with sulfur and TBBS. For the rubber with 0.5 phr sulfur and 1.75 phr TBBS, the addition of 0.2 phr ZnO was enough to make TBBS more effective as indicated by an increase in  $\Delta$ torque from 62 dNm to 71 dNm. But when the loading of ZnO was raised to 0.35 phr,  $\Delta$ torque showed no increase and remained at about 72 dNm (fig. 8).  $\Delta$ Torque for the rubber with 1 phr sulfur and 3 phr TBBS reached optimum value, i.e. 92 dNm, at 0.2 phr ZnO, and afterwards it rose marginally to about 94 dNm when an extra 0.25 phr ZnO was added. Notably, when 0.5 phr stearic acid was added to the BR with 0.5 phr sulfur, 1.75 phr TBBS and 0.2 phr ZnO,

Fig. 7:  $\Delta$ Torque versus TBBS for BR compounds with different sulfur loadings

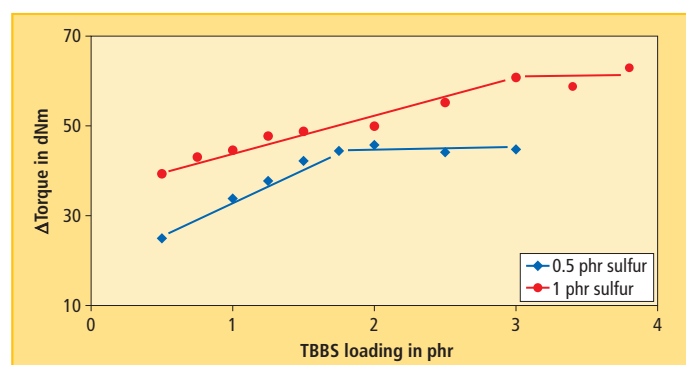


Fig. 8:  $\Delta$ Torque versus ZnO loading for BR compounds with different sulfur and TBBS loadings

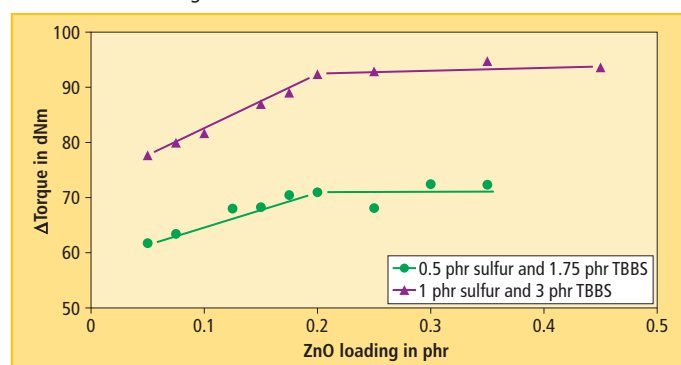


Fig. 9:  $\Delta$ Torque versus TBBS loading for the EPDM with 1 phr sulfur

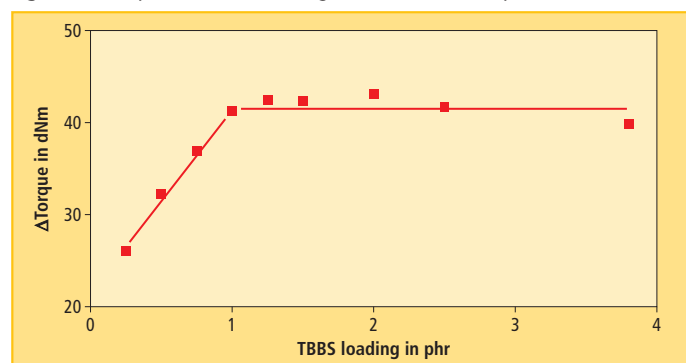
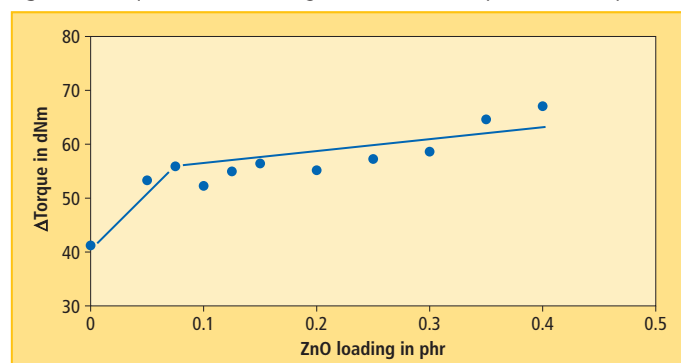


Fig. 10:  $\Delta$ Torque versus ZnO loading for the EPDM with 1 phr sulfur and 1 phr TBBS



$\Delta$ torque first decreased sharply from 71 dNm to 50 dNm and then remained almost steady until the loading of stearic acid reached 2.5 phr. Evidently, small amounts of stearic acid, i.e. up to 0.5 phr, were detrimental to the crosslink density of the rubber as indicated by a drop in  $\Delta$ torque (fig. 6).

Figure 9 demonstrates  $\Delta$ torque versus TBBS loading for the EPDM with 1 phr sulfur.  $\Delta$ Torque increased steeply from 26 dNm to 42 dNm as the loading of TBBS was boosted from 0.25 phr to 1 phr. Subsequently, there was no improvement in  $\Delta$ torque once the amount of TBBS reached 3.8 phr. Apparently, 1 phr TBBS was enough to react the sulfur with the rubber. Zinc oxide was later added to improve the efficiency of TBBS.  $\Delta$ torque rose noticeably from 41 dNm at 0 phr ZnO to 56 dNm at 0.075 phr ZnO and the rate of increase slowed down significantly thereafter.  $\Delta$ Torque then reached to about 67 dNm when the loading of ZnO was raised by an additional 0.325 phr (fig. 10). It is remarkable that a small amount of ZnO, i.e. as low as 0.075 phr, had such a major influence on the performance of TBBS in the cure system as indicated by a significant rise in  $\Delta$ torque. When 0.5 phr stearic acid was mixed with the EPDM with 1 phr sulfur, 1 phr TBBS and 0.075 phr ZnO,  $\Delta$ torque decreased from 56 dNm to 47 dNm and subsequently continued decreasing slowly to about 42 dNm when the amount of stearic acid was raised to 2.5 phr (fig. 6). The crosslink density as shown by  $\Delta$ torque did not benefit from the addition of stearic acid to the rubber.

After these measurements were completed, three cure systems were selected for further work:

- for NR – 4 phr sulfur, 3.5 phr TBBS, and 0.2 phr ZnO
- for BR – 0.5 phr sulfur, 1.75 phr TBBS, and 0.2 phr ZnO
- for EPDM – 1 phr sulfur, 1 phr TBBS, and 0.075 phr ZnO.

To protect the rubbers against environmental ageing, 1 phr antioxidant (6PPD) was also added. Note that there were only three chemicals in the cure systems, i.e. sulfur, TBBS and ZnO, which added up to 7.7 phr in the NR compounds, 2.45 phr in the BR compounds and 2.075 phr in the EPDM compound. This is a significant reduction both in the number and amount of the chemicals in the cure system. In addition to the chemical curatives, the NR compounds had 60 phr and 140 phr kaolin and the BR and EPDM compounds 60 phr kaolin (tab. 1, compounds 1 – 7). These compounds were mixed as described above and their viscosity and cure properties measured. They were then cured at 160 °C and their hardness, tensile properties and tear resistance determined.

### 3.2 Effect of kaolin on the viscosity and cure properties of NR, BR and EPDM

The inclusion of kaolin did not affect the viscosity and cure properties of the rubbers in the same way. The viscosity of NR

Tab. 1: Formulations, Mooney viscosity and cure properties of the rubber compounds

Formulation in phr	Compound number						
	1	2	3	4	5	6	7
NR*	100	100	100	–	–	–	–
BR*	–	–	–	100	100	–	–
EPDM*	–	–	–	–	–	100	100
Sulfur	4	4	4	0.5	0.5	1	1
TBBS	3.5	3.5	3.5	1.75	1.75	1	1
ZnO	0.2	0.2	0.2	0.2	0.2	0.075	0.075
Santoflex 13	1	1	1	1	1	1	1
Kaolin	0	60	140	0	60	0	60
<b>Mooney viscosity</b> ML(1+4'), 100 °C in MU	44	52	85	42	66	70	89
<b>Curemeter data at 160 °C</b>							
$M_L$ in dNm	12	15	20	15	19	16	19.5
$M_H$ in dNm	55	79	89	87	75	71	64
$\Delta M$ in dNm	43	64	69	72	56	55	44.5
$t_{s2}$ in min	4.7	3.2	2.1	11.3	3.5	6.2	2.6
$t_{95}$ in min	8.3	4.8	3.1	47.5	12.5	21.5	40
CRI in min <sup>-1</sup>	27.8	62.5	100	2.8	11.1	6.5	2.7

\*The viscosity of the raw NR, BR and EPDM rubbers were 89, 46, and 88 MU, respectively.

Fig. 11: Mooney viscosity versus kaolin loading for compounds 1–3 (tab. 1).

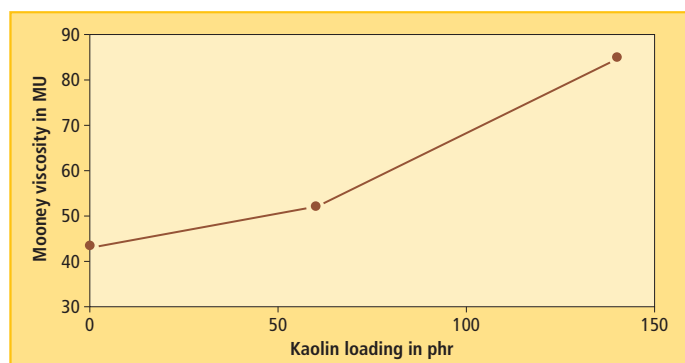
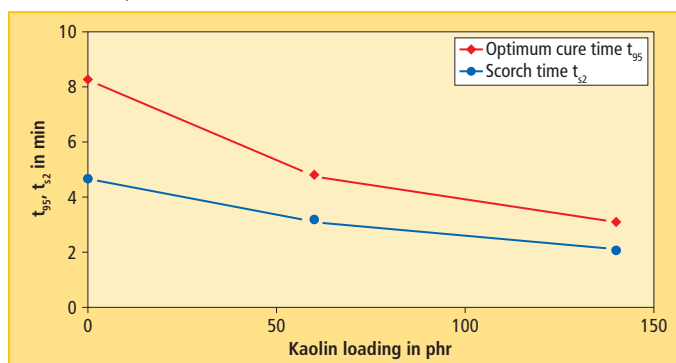


Fig. 12: Optimum cure time  $t_{95}$  and scorch time  $t_{s2}$  versus kaolin loading for compounds 1–3 (tab. 1)



increased from 44 MU to 85 MU when 140 phr kaolin was added (fig. 11). A similar trend was also observed for BR and EPDM where the viscosity rose from 42 MU to 66 MU and from 70 MU to 89 MU, respectively after 60 phr kaolin was mixed with the rubbers (tab. 1). This was expected, since the inclusion of solid particles in raw rubber raises the rubber viscosity [15].

The  $t_{s2}$  and  $t_{95}$  of NR shortened from 4.7 min to 2.1 min and 8.3 min to 3.1 min, respectively with 140 phr kaolin (fig. 12). The rate of cure as indicated by CRI benefited greatly from kaolin and increased from 27.8  $\text{min}^{-1}$  at 0 phr kaolin to 100  $\text{min}^{-1}$  at 140 phr kaolin loading (fig. 13). This was the highest cure rate ever reported for a sulfur-cured NR-based compound (fig. 3). As mentioned above,  $\Delta\text{torque}$  is an indication of crosslink density changes in the rubber.  $\Delta\text{torque}$  for NR increased from 43 dNm to 69 dNm as the loading of kaolin was raised

from 0 phr to 140 phr, which indicated a large rise in the crosslink density of the rubber (fig. 14).

For BR, the addition of kaolin shortened the  $t_{s2}$  and  $t_{95}$  from 11.3 min to 3.5 min and 47.5 min to 12.5 min, respectively. The rate of cure also improved from 2.8  $\text{min}^{-1}$  to 11.1  $\text{min}^{-1}$ . Though, kaolin had a detrimental effect on the crosslink density of the rubber because  $\Delta\text{torque}$  decreased from 72 dNm to 56 dNm (tab. 1).

For EPDM, the  $t_{s2}$  decreased from 6.2 min to 2.6 min but surprisingly, the  $t_{95}$  increased from 21.5 min to 40 min when 60 phr kaolin was added. The rate of cure declined as shown by a large fall in CRI from 6.5  $\text{min}^{-1}$  to 2.7  $\text{min}^{-1}$ . The rubber lost some crosslinks as demonstrated by a reduction in  $\Delta\text{torque}$  from 55 dNm to 44.5 dNm (tab. 1). This revealed the damaging effect of kaolin on the crosslink density of both BR and EPDM.

### 3.3 Effect of kaolin on the hardness and mechanical properties of the NR, BR and EPDM vulcanisates

Table 2 summarises the hardness and mechanical properties of the rubber vulcanisates. These properties benefited to a great extent from the addition and progressive increases in the loading of kaolin. For NR, the hardness increased by 64 % when 60 phr kaolin was added and the trend continued rising by another 28 % when the loading of kaolin reached 140 phr. Similarly, the Young's modulus rose by 170 % with 60 phr kaolin and then by an extra 148 % when the full amount of kaolin, i.e. 140 phr, was reached. This was expected, since when soft rubber is replaced with solid filler, the rubber becomes harder, causing the Young's modulus to increase. The tensile strength and tear resistance were unchanged and the elongation at break and stored energy density at break deteriorated by a total of 65 % and 34 %, respectively when 140 phr kaolin was mixed with the rubber.

Kaolin was very beneficial to the properties of BR and EPDM. For BR, the hardness increased by 23 % and for EPDM, by 34 %, respectively when 60 phr kaolin was incorporated in the rubbers. For BR, the tensile strength, elongation at break and Young's modulus rose by 759 %, 256 % and 114 %, respectively. The effect of kaolin on the properties of EPDM was even more impressive. For this rubber, the tensile strength, elongation at break and Young's modulus improved by 964 %, 332 % and 71 %, respectively. The properties related to fracture were also enhanced very substantially. For BR, the stored energy density at break and tear resistance were increased by 2,442 % and 536 %, respectively and for EPDM, by 3,133 % and 1,479 %, respectively.

Tab. 2: Hardness and mechanical properties of the rubber vulcanisates

Properties	Compound number						
	1	2	3	4	5	6	7
Hardness in Shore A	33	54	69	44	54	41	55
Range of values in Shore A	32–35	51–55	68–70	43–44	54–56	41–42	55–56
Tensile strength in MPa	22	22	20	1.7	14.6	1.4	14.9
Range of values in MPa	21–22	21–22	18–21	1.5–1.8	14.5–15.5	1.3–1.7	14.7–17.5
Elongation at break in %	1,667	997	587	250	889	350	1,512
Range of values in %	1,645–1,669	994–999	577–628	239–283	878–950	333–370	1,492–1,651
Young's modulus in MPa	1.0	2.7	6.7	1.4	3.0	1.4	2.4
Range of values in MPa	1.0–1.1	2.3–3.2	5.8–11.6	1.4–1.7	2.8–3.0	1.3–1.4	1.8–2.7
Stored energy density at break in $\text{MJ/m}^3$	90	90	59	2.4	61	3.0	97
Range of values in $\text{MJ/m}^3$	90–91	86–91	54–65	2.4–3.0	60–70	2.9–3.7	96–121
Tear resistance in $\text{kJ/m}^2$	13	13	14	1.1	7	1.9	30
Range of values in $\text{kJ/m}^2$	11–15	11–20	11–20	0.76–1.7	4.6–11.5	1.3–2.0	26–32

Fig. 13: Cure rate index versus kaolin loading for NR compounds 1–3 (tab. 1)

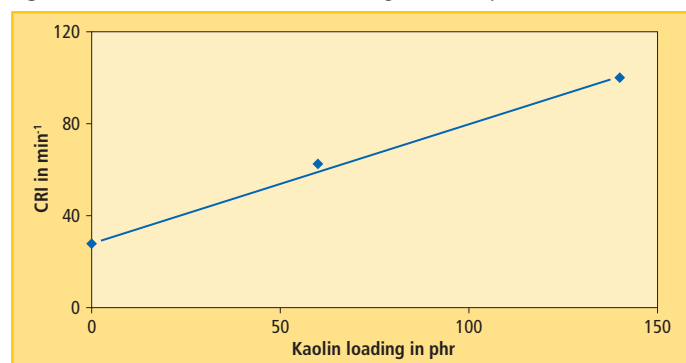
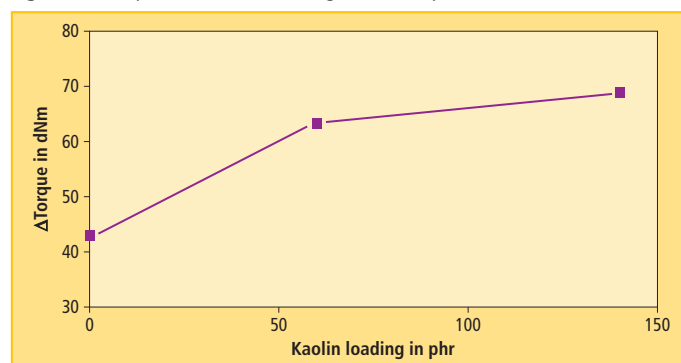


Fig. 14:  $\Delta\text{torque}$  versus kaolin loading for NR compounds 1–3 (tab. 1)



Evidently, kaolin is an extending or non-reinforcing filler for the strain-induced crystallising NR, and highly reinforcing for the non-crystallising BR and EPDM. Since kaolin has a platelet structure (**fig. 1**), it may be assumed that the mechanism by which rubber is reinforced may be different to that by spherical particles such as CB and silica. The results suggest that strain-induced crystallising rubbers such as NR may benefit less from kaolin than the non-crystallising ones, e.g., BR and EPDM. The exact mechanism of reinforcement by kaolin in rubber is under investigation.

## 4 Conclusions

From this study, the following main conclusions can be drawn:

- A new method measured the exact optimum amount of TBBS accelerator and ZnO activator at a given loading of sulfur in the vulcanisation of NR, BR and EPDM and eliminated stearic acid from the cure system entirely. The requirement for ZnO was 0.075–0.2 phr.
- Kaolin was an extending or non-reinforcing filler for the strain-induced crystal-

lising NR and highly reinforcing for the non-crystallising BR and EPDM.

It is anticipated that a reduction in the use of these chemicals will improve health and safety at the work-place, reduce cost, and minimise damage to the environment. The use of MPTS pre-tread kaolin in conjunction with the new method for measuring the exact amount of the curatives in sulfur vulcanisation provides an effective means for designing green compounds for industrial applications. The indications are that kaolin is an ideal replacement for carbon black and silica/silane systems in rubber reinforcement, at least for non-crystallising rubbers.

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