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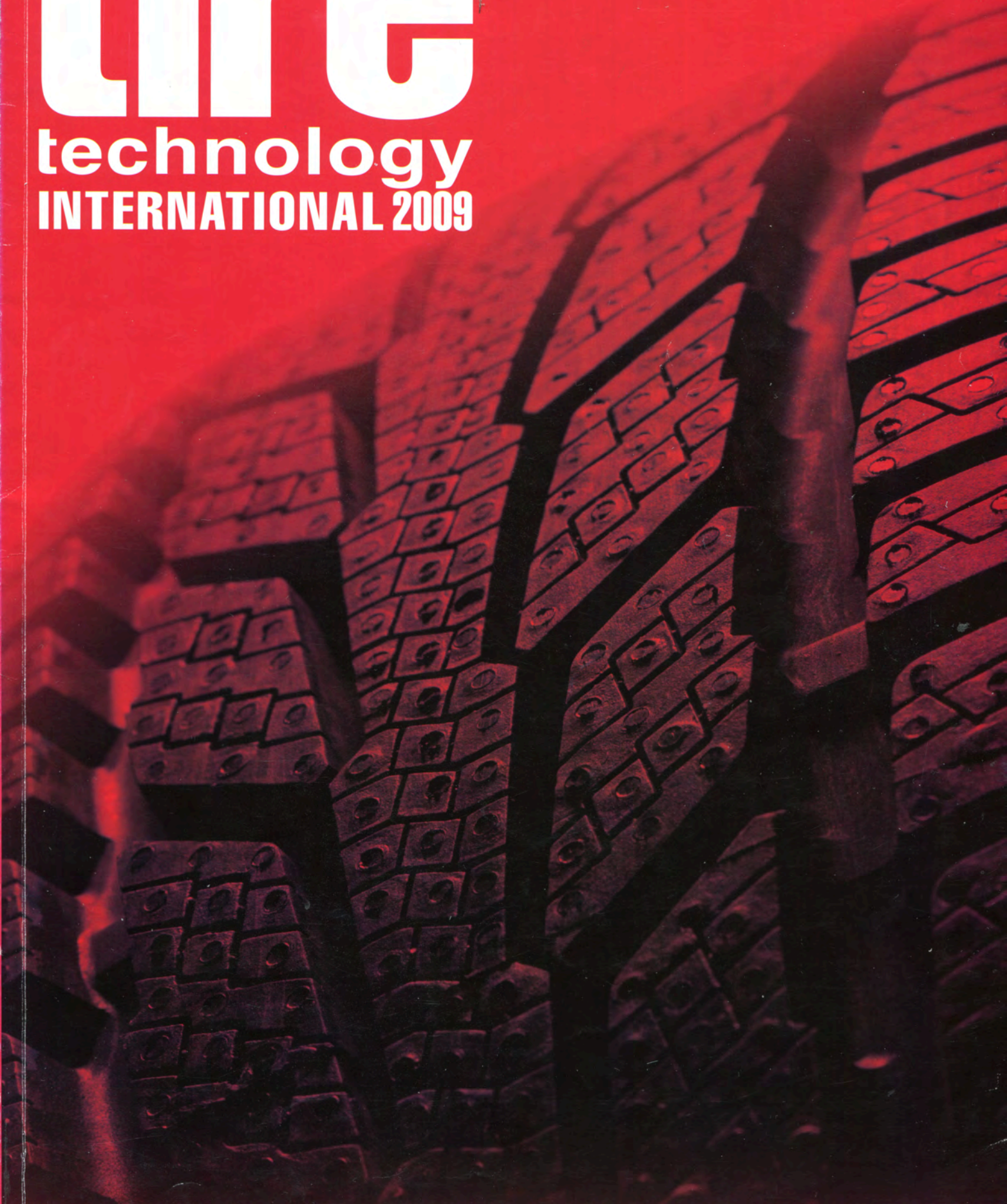
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Curing rubber compounds

efficiently and cost-effectively

Rubber compounders and tire manufacturers could benefit from reducing or eliminating harmful and expensive chemicals from the curing process

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The implementation of the European Union Regulation REACH, and a need to use materials and resources more efficiently to reduce waste and pollution, have imposed a considerable burden on rubber compounders and tire manufacturers.

The methods which are widely used to cure silica-filled rubber compounds with sulfur for green tire applications, do not take into account the exact requirements for the curing chemicals and are therefore inefficient, too expensive, and harmful to health and to the environment.

Rubber compounds used to manufacture tires contain several ingredients. They include fillers, curing agents, antidegradants and processing aids¹. Traditionally, fillers and curing chemicals have performed two distinct functions in rubber compounds.

Reinforcing fillers for example colloidal carbon blacks and synthetic silicas with large surface areas ranging from 150 to 400m²/g, are very effective in improving the mechanical properties of rubber such as hardness, tensile modulus and abrasion resistance².

Table 1: Recipe and ODR test results for the SBR, BR, NR and IR rubber compounds

Ingredients	Compound no.			
	1	2	3	4
SBR	100	-	-	-
High cis BR	-	100	-	-
NR	-	-	100	-
IR	-	-	-	100
Silanised silica	60	60	60	60
TBBS	3	7.5	6	7
ZnO	0.5	0	0.3	1
Santoflex 13	1	1	1	1
Processing oil	5	0	0	0
Cure system	3.5	7.5	6.3	8
ODR results				
Minimum torque (dN m)	18	37.5	26	26
Maximum torque (dN m)	56	129	107	137
Δtorque (dN m)	38	91.5	81	111
Scorch time, t ₅₂ (min)	16	8	9	8
Optimum cure time, t ₉₅ (min)	80	83	27	34
Cure rate index (min ⁻¹)	1.6	1.3	5.6	3.9

Curing agents, for instance sulfur, in combination with accelerators and activators, produce stable chemical crosslinks between the rubber chains in unsaturated elastomers. The cure systems in tire-tread rubber compounds often consist of primary and secondary accelerators, primary and secondary activators and elemental sulfur, which add up to 11 parts per hundred rubber by weight (phr)³. Reducing the use of these harmful and expensive chemicals, or eliminating them altogether, will be greatly beneficial to rubber compounders and tire manufacturers.

Styrene-butadiene rubber (SBR) (23.5 wt % styrene, Intol 1712, Polimeri Europa UK Ltd, Hythe, UK), high cis polybutadiene rubber (BR) (Buna CB 24, Bayer; not oil-extended, Newbury, UK) with a minimum 96 wt % cis 1-4 content, natural rubber (NR) (standard Malaysian natural rubber grade L) with 98 wt % cis 1-4 content, and synthetic polyisoprene (IR) with a minimum 96 wt % cis-1-4 content (Kraton IR-307, Kraton Polymers) were used in this study.

These elastomers are used in the manufacture of passenger car and truck tires. The reinforcing filler was Coupsil 8113 (Evonik Industries AG of Germany),

which is a precipitated amorphous white silica-type Ultrasil VN3 – the surfaces of which had been pre-treated with bis (3-triethoxysilylpropyl)tetrakisulphane (TESPT)⁴. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), 175m²/g surface area (measured by N₂ adsorption), and a 20-54 nm particle size. This filler is known as a 'crosslinking filler'.

The chemical bonding between the tetrasulphane groups of TESPT and the rubbers was maximized by adding N-t-butyl-2-benzothiazole sulphenamide (Santocure TBBS; a safe-processing delayed-action accelerator), ZnO (activator) and stearic acid (activator).

A heavy paraffinic distillate solvent extract aromatic-processing oil (Enerflex 74) was added to the SBR compound to reduce its viscosity. To protect the rubbers against environmental ageing, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (Santoflex 13, antidegradant) was also included in the rubber compounds.

Four rubber compounds each having 60phr of Coupsil 8113 were prepared in a Haake Rheocord 90, a small-size laboratory mixer with counter-rotating Banbury rotors. The rotors and mixing chamber were maintained at 23°C for making the SBR, BR and IR compounds and 48°C for making the NR compound. The rotor speed was 45rpm. The volume of the mixing chamber was 78cm³, and it was 55% full during mixing. The filler particles were dispersed well in the rubbers by increasing the mixing time to 17 minutes. Full details of the mixing

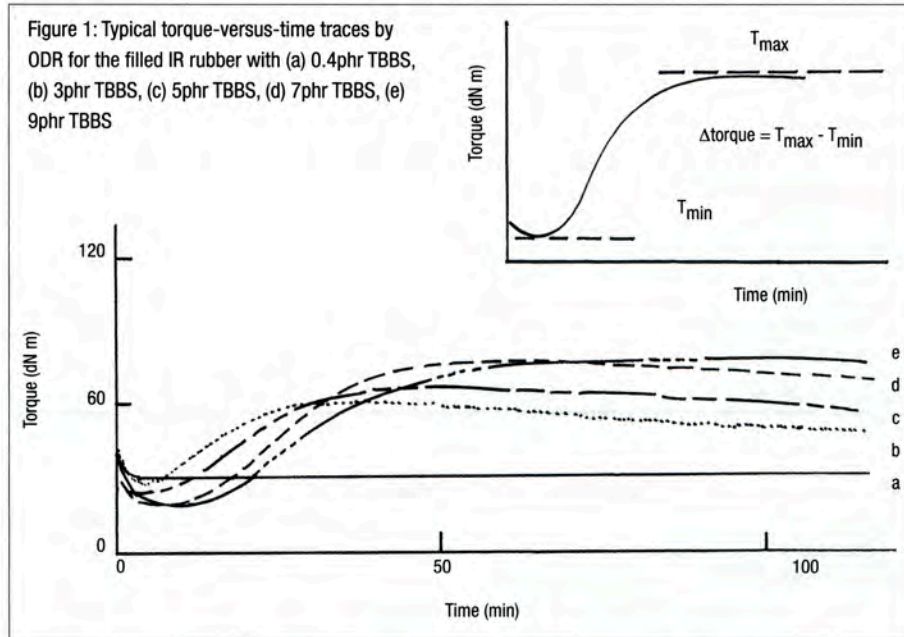


Figure 2: Δtorque versus TBBS loading for the filled SBR, BR and NR rubbers

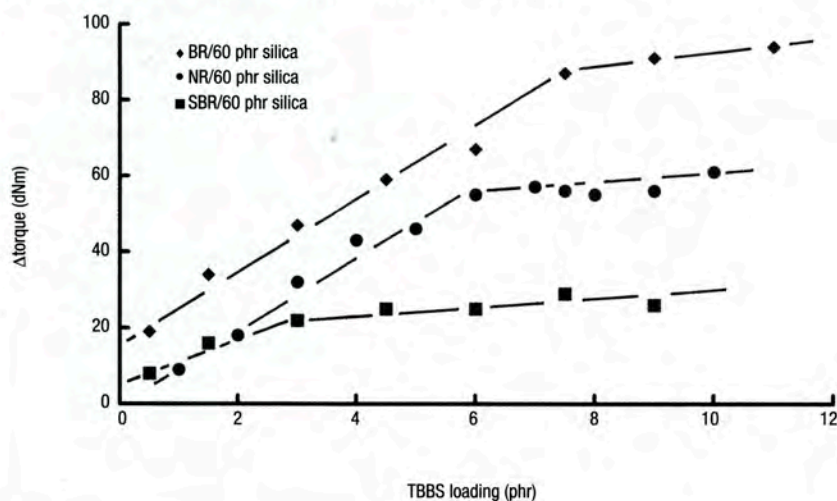


Table 2: Mechanical properties of the SBR, BR, NR and IR rubber vulcanisates

	Compound no.			
	1	2	3	4
Hardness (Shore A)	62.5	72	75	80
Tensile strength (MPa)	26	17	37	17
Elongation at break (%)	1308	606	837	404
Stored energy density at Break (mJ/m ³)	140	49	137	33
T (kJ/m ²)	75	30	58	17
Range of values	71-89	10-103	46-95	10-23
Relative volume loss in the abrasion tests, Δv (mm ³ /mg)	126	15.5	-	-
Modulus (MPa) at 100% strain amplitude	0.73	2.2	2.2	3.0
Modulus (MPa) at 200% strain amplitude	0.93	2.2	3.2	3.7
Modulus (MPa) at 300% strain amplitude	1.17	2.6	4.2	4.3
Cyclic fatigue life (kc)	777->1000	40->1000	34-99	16-39

conditions of these compounds were reported previously⁵⁻⁷.

The rubber compounds were subsequently tested by an oscillating disc rheometer curemeter (ODR) at 140°C to produce cure traces from which Δ torque was calculated⁸. Δ torque is the difference between the maximum and minimum torque values on the cure traces of the rubbers and is an indication of crosslink-density changes (Figure 1). Δ torque was subsequently plotted against the loading of TBBS, ZnO and stearic acid.

Optimizing the chemical bonding between the filler and rubber via the

tetrasulphane groups of TESPT is a very efficient method for crosslinking and reinforcing rubber compounds.

Figure 2 shows Δ torque versus TBBS loading for the filled NR, BR and SBR rubbers. For the SBR, Δ torque increased from 8 to 22 dN m when 3phr TBBS was added. Thereafter, Δ torque increased at a much slower rate to 26 dN m as the loading of TBBS was raised to 9phr. It seemed that 3phr TBBS was sufficient to start the reaction between the tetrasulphane groups of TESPT and the rubber. Similarly, for the BR, Δ torque increased to 87 dN m when the loading

of TBBS was raised to 7.5phr. Further increases in the amount of TBBS had little effect on Δ torque, which remained at about 90 dN m. For the NR, Δ torque increased sharply from 9 to 55 dN m as the loading of TBBS was raised to 6phr, and it continued rising at a much slower rate to about 61 dN m when the loading of TBBS reached 10 phr. For the IR, Δ torque increased to about 60 dN m as the loading of TBBS reached 7phr and remained at this level thereafter, when the amount of TBBS was raised to 10phr. The TBBS requirement for this rubber was slightly higher than that of the NR (Figure 3).

The filled SBR, NR, BR and IR rubbers needed 3, 6, 7.5 and 7phr TBBS, respectively, to fully react the tetrasulphane groups of TESPT with the rubber chains.

ZnO was incorporated into the rubbers to increase the efficiency of TBBS. For the SBR with 3phr TBBS, Δ torque increased from 22 to 57 dN m as the loading of ZnO was raised to 0.5phr. The rate of increase of Δ torque slowed down considerably with Δ torque rising from 57 to 64 dN m as the amount of ZnO reached 2.5phr. For the BR with 7.5phr TBBS, Δ torque increased to 131 dN m when 0.5phr ZnO was added and showed no further improvement thereafter when an extra 1phr ZnO was incorporated into the rubber. For the NR with 6phr TBBS, Δ torque increased sharply to 91 dN m when 0.3phr ZnO was included, and it continued rising at a much slower rate to 112 dN m when the loading of ZnO reached 2phr (Figure 4). The IR with 7phr TBBS needed 1phr ZnO to increase the efficiency of cure. For this rubber, Δ torque increased from 60 to 109 dN m as the loading of ZnO was raised to 1phr. Δ torque subsequently rose to 125 dN m when the amount of ZnO reached 2.0phr. It was interesting that the IR, which is the synthetic analog of NR and is chemically and structurally similar to it, needed an extra 1phr TBBS and 0.7phr ZnO to fully cure compared with the NR (Figure 5).

The filled SBR rubber with 3phr TBBS, filled NR rubber with 6phr TBBS, filled BR rubber with 7.5phr TBBS, and filled IR with 7phr TBBS required 0.5, 0.3, 0.5, and 1phr ZnO, respectively, to optimize the chemical bonding between the rubber and filler and produce a fully efficient cure.

Stearic acid is a fatty acid that is added

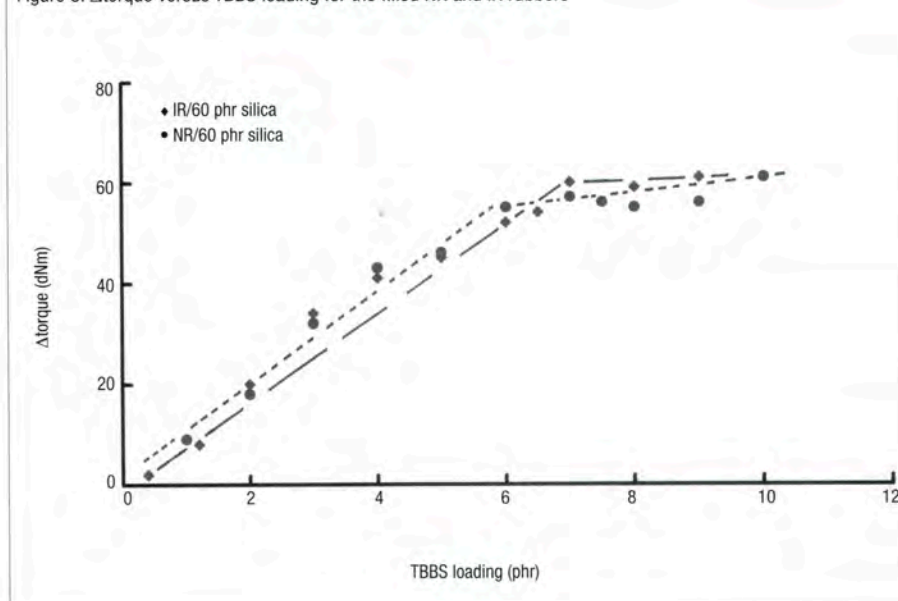
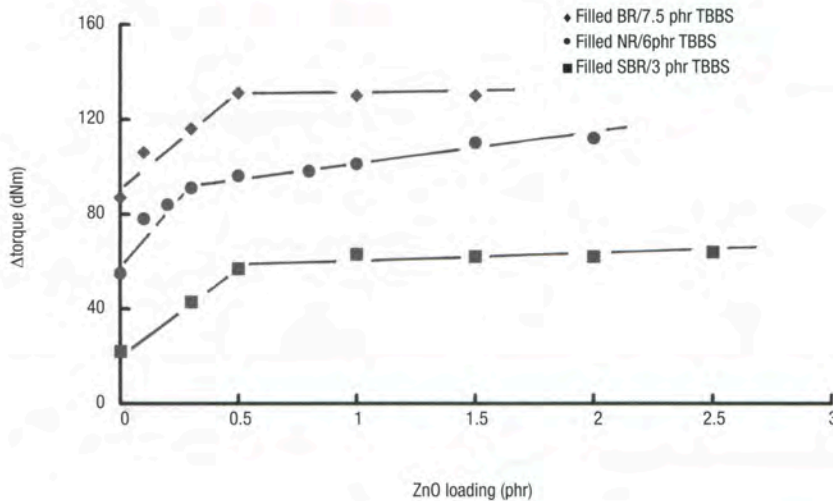
Figure 3: Δ torque versus TBBS loading for the filled NR and IR rubbers

Figure 4: Δ torque versus zinc oxide loading for the filled SBR with 3phr TBBS, filled BR with 7.5phr TBBS and filled NR with 6phr TBBS



to improve the solubility of ZnO in rubber. The loading of stearic acid in the rubbers with TBBS and ZnO was increased to 2.5phr to measure the amount needed to optimize the efficiency of TBBS and cure. For the SBR with 3phr TBBS and 0.5phr ZnO, Δ torque decreased from 57 to 46 dN m as the loading of stearic acid reached 2.5phr. For the BR with 7.5phr TBBS and 0.5phr ZnO, initially Δ torque increased from 131 to 134 dN m with up to 1phr stearic acid, and then it dropped to approximately 113 dN m as the loading of stearic acid was increased progressively to 2.5 phr. However, the BR was fully cured with 7.5 phr TBBS and required no ZnO. For the NR with 6 phr TBBS and 0.3 phr ZnO, Δ torque decreased from 91 to about 83 dN m when up to 2 phr stearic acid was added (Figure 6). However, for the IR with 7phr TBBS and 1 phr ZnO, Δ torque increased from 109 to 121 dN m when 1phr stearic acid was incorporated in the rubber and then, it returned to its original value when the loading of stearic acid was increased to 2phr. Notably, the Δ torque values measured for the NR were noticeably lower than those calculated for the IR (Figure 7).

Stearic acid had no beneficial effect on the chemical bonding between the filler and rubber and in fact, it was detrimental to Δ torque and therefore to the crosslink density and cure of the rubbers.

After the TBBS, ZnO and stearic acid requirements were measured for the rubbers, four formulations were produced

(Table 1). The rubber compounds were cured at 140°C in a compression mold to produce sheets approximately 2.4mm thick and cylindrical samples 15.6mm in diameter and 9.5mm in height for further work. The hardness, tensile strength, elongation at break, stored energy at break, tensile modulus, tearing energy, and abrasion resistance of the rubber vulcanisates were determined using the procedures described in the British Standards 9039-12 (Table 2). The cyclic fatigue life of the rubbers (number of cycles recorded when the samples fractured) was measured in uniaxial tension with dumbbell test pieces at a constant maximum deflection of 100% and a test frequency of 1.42Hz¹³.

The test temperature was 22°C and the strain on each test piece was relaxed to zero at the end of each cycle. For each rubber, eight test pieces were cycled to failure and tests were stopped whenever the fatigue life exceeded 1,000kc.

Good mechanical properties are essential for the performance, durability and life of tire compounds in service. As the results in Table 2 show, the rubber vulcanisates possessed good properties in spite of substantially reducing the curing

Figure 5: Δ torque versus ZnO loading for the filled NR with 6 phr TBBS and filled IR with 7phr TBBS

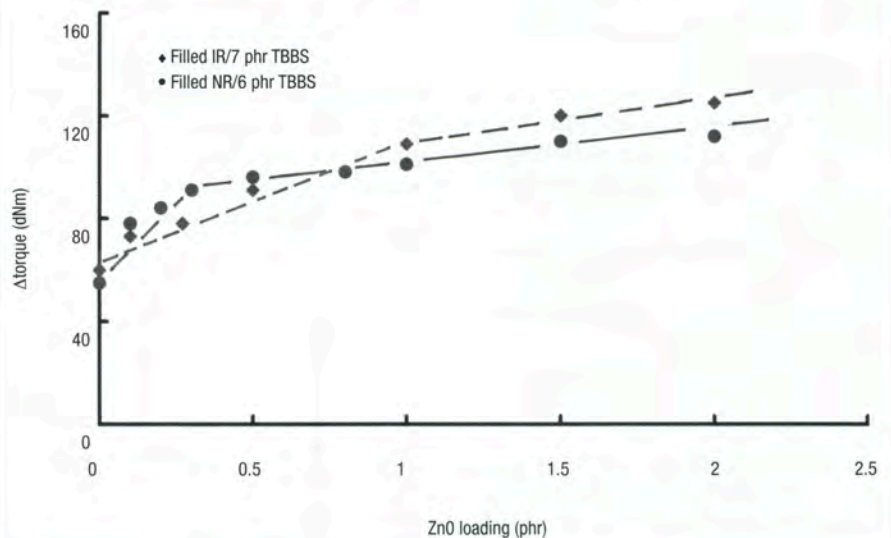
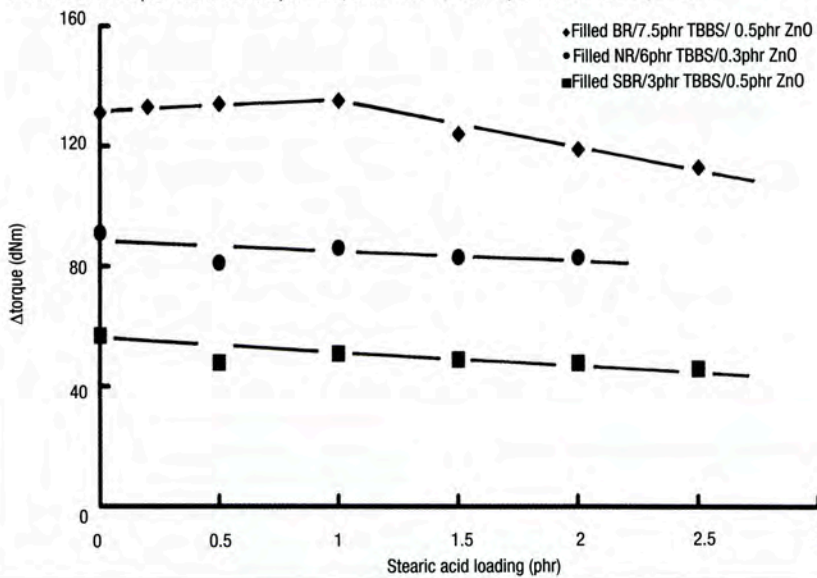


Table 3: Sulfur (in TESPT), TBBS and ZnO requirements based on the actual weights of the chemicals measured in the filled SBR, BR, NR and IR rubber compounds (see Table 1)

Compound	S/TBBS (g/g)	ratio	S/TBBS/ZnO (g/g/g)	ratio
SBR	-	-	0.45/0.9/0.15	3/6/1
BR	0.45/2.25	1/5	-	-
NR	-	-	0.45/1.8/0.09	5/20/1
IR	-	-	0.45/2.1/0.3	1.5/7/1

Figure 6: Δ torque versus stearic acid loading for the filled SBR with 3phr TBBS and 0.5phr ZnO, filled BR with 7.5phr TBBS and 0.5phr ZnO, and filled NR with 6phr TBBS and 0.3phr ZnO



chemicals. The hardness was somewhere between 62.5 and 80 Shore A, and the tensile modulus between 0.73-4.3MPa at strain amplitudes from 100-300%.

The properties related to fracture were also impressive. For example, the tensile strength was 17-37MPa, elongation at break 404-1308% and stored energy density at break 33-140mj/m³.

The tearing energy, which is of a major importance to the impact behavior of tires in service, was in the region of 17-75kJ/m². It is worth noting that the relative volume loss in the abrasion tests, was very low for the BR and below the average for the SBR.

The shortest and longest cyclic fatigue lives were recorded for the IR and SBR, respectively. For the SBR and BR, seven and four test pieces, respectively, lasted longer than 1,000kc. The IR had the shortest fatigue life, followed by the NR.

The mechanical properties of the rubber vulcanisates were impressive in spite of reducing the curing chemicals substantially in the rubbers.

As mentioned earlier, Coupsil 8113 has 2.5% by weight sulfur included in TESPT. The actual weights of sulfur, TBBS and ZnO in the rubber compounds are calculated and summarized in Table 3. As the results show, at a given loading of sulfur, to optimize the chemical bonding between the rubber and filler and to achieve the most efficient cure, the requirements for TBBS and ZnO were totally different. This was because of the dissimilar composition of the rubbers.

The formation of stable covalent filler-TESPT bonds is essential in rubber

reinforcement¹⁴, and a large improvement in the rubber properties was seen, as indicated in Table 2. Interestingly, stearic acid was not at all essential to cure the rubbers.

The methods used at present to cure silica-filled tire compounds with sulfur, TBBS and ZnO do not take into account these different requirements and hence cannot be efficient. It is likely that a similar problem exists with the use of these curing chemicals in rubber compounds filled with carbon black.

In conclusion, a proper use of sulfur, TBBS and ZnO for curing SBR, BR, NR and IR rubber compounds for tire applications must take into account the composition of rubber at a given loading of sulfur. This will increase the efficiency

of sulfur-curing without compromising the good mechanical properties of the rubber vulcanisates. Other benefits include improvement in health and safety, less damage to the environment and cheaper tires. **tire**

Acknowledgement

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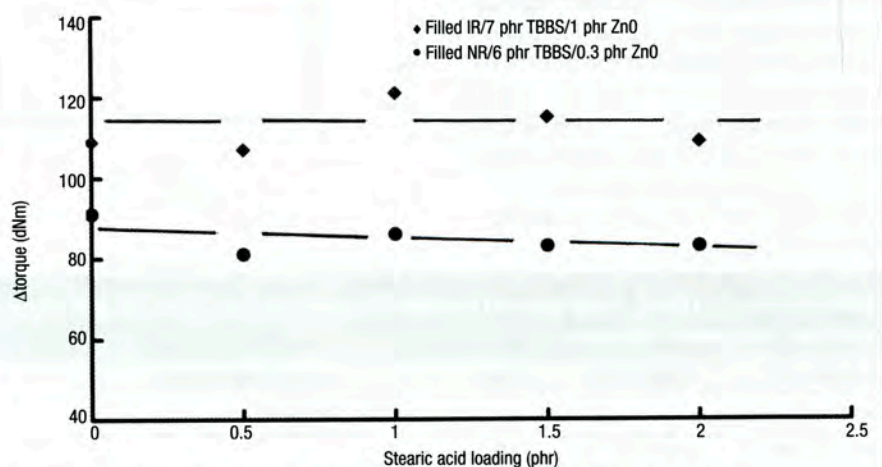


Figure 7: Δ torque versus stearic acid loading for the filled NR with 6phr TBBS and 0.3phr ZnO, and filled IR with 7phr TBBS and 1phr ZnO