J. Rubb. Res., **6(3)**, 129–152

A New Design Concept for Natural Rubber Compounds Using Silanised Precipitated Silica

A. ANSARIFAR[*#], A. AZHAR[*,**] AND M. SONG[*]

The reinforcing effect of 30 p.h.r. silanised precipitated amorphous white silica filler on the technical properties of a sulphur cured natural rubber compound, with a sulphur to accelerator ratio of about 0.046, was studied. The surfaces of the silica were pre-treated with bis[3-triethoxysilylpropyl-)tetrasulphane (TESPT), a bifunctional organosilane, to prevent the silica from interfering with the reaction mechanism of the sulphur cure system in the rubber This study showed that hardness, tensile strength, abrasion resistance, stored energy density at rupture, and cohesive tear strength of the rubber were enhanced substantially, but elongation at break and cyclic fatigue life deteriorated after the filler was added to the rubber Interestingly, the technical properties of the rubber improved even more significantly without the added sulphur, and by optimising the reaction between the rubber reactive tetrasulphane groups of TESPT and the rubber compound. The improved properties were due to the fine dispersion of the filler in the rubber matrix, and also the strong rubber/TESPT interaction. The latter was produced by the addition of 4.4 p h.r of a sulphenamide type accelerator to the rubber compound.

Key words: silanised precipitated silica; dispersion; natural rubber; sulphur cure; technical properties; electron microscopy; fillers

Natural rubber (NR) is a versatile elastomer and is used widely to manufacture a wide range of industrial rubber products for example engine mountings, tyres, and isolation bearings. Raw elastomers such as NR can not be used for industrial applications unless they are reinforced with additives such as carbon black or/and synthetic silica. There are numerous other ingredients such as accelerators, activators, and processing aids, which are added to and mixed with raw elastomers, often in internal mixers, to make them suitable for use in service.

Reinforcing fillers are by far the most important group of additives used for enhancing physical and mechanical properties of rubber compounds. Since the discovery of their reinforcing qualities in 1904, colloidal carbon blacks have been used extensively to enhance technical properties of rubbers. The term reinforcement with respect to elastomers is defined as the increase in properties such as tensile strength, tear resistance, hardness, abrasion resistance and stiffness[1]. This is brought about by the inclusion of a second solid phase such as carbon black.

---

[*] Institute of Polymer Technology and Materials Engineering, Loughborough University, Leicestershire LE11 3TU, United Kingdom

[**] Rubber Research Institute of Malaysia, Malaysian Rubber Board, PO Box 10150, 50908 Kuala Lumpur, Malaysia

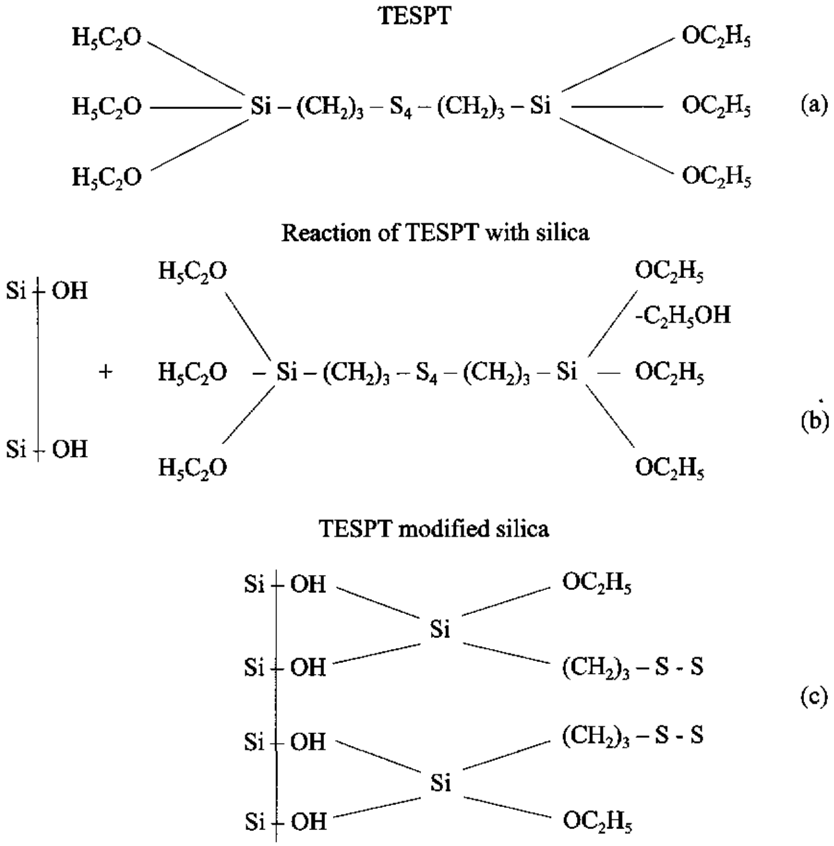
[#] Corresponding author (e-mail. m.a.ansarifar@lboro ac uk)

In recent years, because of higher prices of carbon black, the rubber industry has been forced to concentrate more on silica fillers as an alternative to carbon black Synthetic silica has been replacing carbon black in some applications, offering major benefits to properties. Silicas differ significantly from carbons both in their methods of manufacture and chemical composition These fillers are prepared by a variety of techniques such as precipitation from water-soluble silicates[2], and also from chemical reaction between a sodium silicate solution and sulphuric acid[3] The surfaces of silicas possess siloxane and silanol functional groups[4], and the silanol groups are acidic[5] The acidic silanol groups interact with the basic accelerators, causing detrimental effects such as unacceptably long cure times and slow cure rate[4], and also loss of crosslink density[6] in sulphur-cured systems. Moreover, because the surfaces of these fillers are polar and hydrophilic, there is a strong tendency to adsorb moisture[7,8] , which adversely influences curing reaction in these systems and hence properties of the cured rubber The amount of water adsorbed on the surfaces of these fillers controls the ionisation of the silanol groups[9], resulting also in detrimental effects on the cure-attributes of rubber compounds similar to the ones described above[4] When a large amount of silica is added, the viscosity increases substantially[10], causing undesirable effects on the processibility of rubber compounds, and also excessive wear and tear of the processing equipment. For these reasons, use of silica in rubber products was hampered until bifunctional organosilanes such as TESPT were available

TESPT (*Scheme 1a*) is used to improve the reinforcing capability of fillers with silanol groups on their surfaces such as precipitated silicas, and also as an integral part of curing systems to enhance crosslinking network properties[4]. This silane possesses tetrasulphane and ethoxy reactive groups The tetrasulphane groups are rubber reactive and react in the presence of accelerators at elevated temperatures, *i e* 140°C–240°C, with or without elemental sulphur being present, to form crosslinks in rubbers containing chemically active double bonds such as NR[4] (*Scheme 2*) The ethoxy groups react with the silanol groups on the surfaces of these fillers during compounding (*Scheme 1b*), and this leads to the formation of stable filler/TESPT bonds (*Scheme 1c*) In addition, TESPT reaction with silanol groups reduces their numbers, and the remaining groups become less accessible to the rubber chains because of the TESPT layer[4] The fewer, less accessible silanol groups that remain weaken the strong silica-silica interaction and thus prevent the formation of silica network[4] These changes help reduce the viscosity of rubber compounds[4,11], and also improve cure characteristics by preventing acidic silicas from interfering with the reaction mechanism of sulphur-cured systems[4,11]. As a result of these improvements, silica and silane are being used increasingly in rubber products, and this is likely to continue

The silanisation reaction of silica surfaces takes place in two different ways Firstly, silica and silane are mixed together in the required ratio and homogenised in an additional, preliminary mixing stage The modification reaction is carried out at the optimum temperature and reaction time[12], or, silanisation is carried out *in situ*[13] This is usually done in an internal mixer in the first stage of mixing, where the silane is added together with, or after the addition and dispersion of the silica This process is carried out within the specified limits of temperature increases in the mixer and strict mixing times[13]

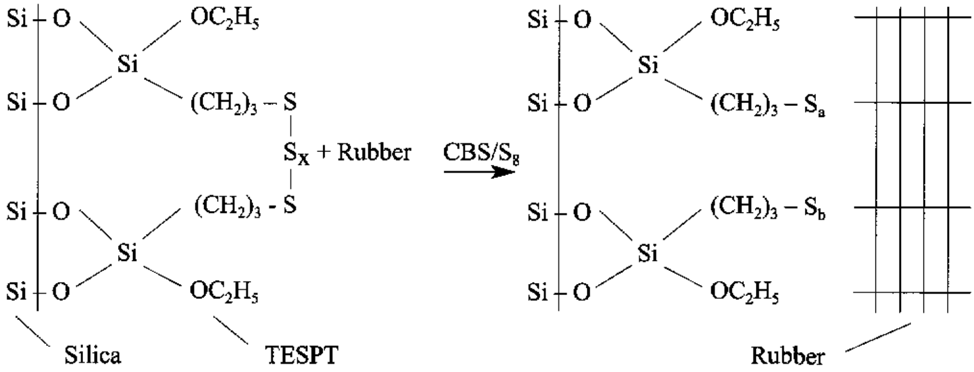
Effect of up to 10 p h r TESPT on the technical properties of some sulphur cured



Chemical structure of TESPT (a), Reaction of TEPT with silica (b), TESPT modified silica (c).

Scheme 1

natural rubber compounds containing 10 p.h.r. precipitated silica were studied by the author and co-workers[14]. The silanisation of the silica surfaces was carried out *in situ*. The silica was sprayed with TESPT in a glass flask at ambient temperature (~ 23°C) and was shaken manually for about 20 min to facilitate the wetting out of the filler surfaces by TESPT before it was added into the mixer. The study revealed that properties such as cohesive tear strength and tensile strength were improved slightly after the filler and TESPT were added to the rubber. In a recent study[15], the degree of dispersion of the silica in some natural rubber compounds was assessed by electron microscopy. The silica was sprayed with TESPT before it was added to the rubber compound. It emerged that the silica particles were poorly dispersed in the rubber and probably had not been properly silanised. This had adversely affected the ability of the filler to optimise the rubber properties.



The accelerated crosslinking reaction of TESPT modified silica with rubber in the presence of elemental sulphur.

Scheme 2

Stumpe[16] reported that undispersed fillers weakened the rubber by creating structural flaws and were damaging to the properties of rubber compounds. Polmanteer and Lentz[17] examined effects of silica dispersion on the physical properties of some sulphur-cured synthetic rubbers, and discovered that some properties (tensile strength, tear strength and 300% modulus) were improved as the quality of the filler dispersion increased. The silica fillers and rubber compounds which were tested[17] were different from the ones used in this study, but the findings were of significant interest to the present work. Interestingly, Pal and De[18] observed a similar behaviour when they examined effect of silica dispersion on the properties of a cured rubber such as tensile strength. They also found that the silica dispersed better as the loading of TESPT in the mix was raised.

The density of crosslinks in elastomers determines their mechanical and physical properties. Silica and silane influence the formation of crosslinks and crosslink density in rubbers during the curing process[4]. Pal and De[18] examined the effect of reinforcing silica on the vulcanisation, and technical properties of a sulphur-cured natural rubber compound in the presence of TESPT coupling agent. The loading of the silica and silane in the rubber increased progressively from 0 p.h.r. to 40 p.h.r. and 0 p.h.r. to 2 p.h.r., respectively. Properties such as tensile strength, 300% modulus, and tear strength of the rubbers containing TESPT were noticeably higher than rubbers without any coupling agent, but compression set, rebound resilience, and hardness were adversely affected by the addition of silane to the rubber compounds.

Rheometer tests have been used extensively to assess effect of concentration of curing agents on the properties of rubber compounds. Wolff[12] discovered that different accelerator or sulphur concentrations in the curing system yielded different crosslink densities in some TESPT/silica filled rubber compounds. Changes in crosslink density were studied by measuring Δ torque, where Δ torque was the difference between the maximum and minimum torque values on the cure traces of the rubbers tested.

The aim of this study was to evaluate the reinforcing effect of 30 p.h.r. silanised precipitated amorphous white silica on the technical properties of some sulphur-cured natural rubber compounds. The degree of dispersion of the silica in the rubber was examined by electron microscopy, and the information was utilised to select a suitable mixing time for incorporating the filler into the rubber. Rheometer tests were also used to assist with the selection of curing agents in the rubber compounds. The properties tested were cohesive tear strength, elongation at break, cyclic fatigue life, tensile strength, hardness, stored energy density at rupture, and abrasion resistance. It emerged that the presence of the filler had a profound influence on some of the properties of the rubber.

EXPERIMENTAL

Materials

The raw elastomer used in this study was standard Malaysian natural rubber grade L (SMR L). The reinforcing filler was Coupsil 8113® supplied by Degussa AG, Germany. Coupsil 8113® is silanised precipitated amorphous white silica-type Ultrasil VN3®. The surfaces of the filler were pre-treated with bis[3-triethoxysilylpropyl-]tetrasulphane (TESPT), a bifunctional organosilane, to prevent the silica from interfering with the reaction mechanism of sulphur cure in the rubber. TEPST is also known as Si69 coupling agent, and is a sulphur containing material (*Scheme 1*) that is suitable for use in sulphur cured rubber compounds such as NR. Properties of Coupsil 8113® are shown in *Table 1*. The filler was kept in a sealed plastic container for four weeks before use. In addition to the rubber and filler, the other additives were zinc oxide, sulphur, *N*-cyclohexyl-2-benzothiazole sulphenamide (Santocure CBS®), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (Santoflex 13®). In total, twenty nine compounds were prepared for this study.

Mixing the Rubber Compounds

Control compound. Mixing was carried out in two stages on a two-roll open swing side laboratory mill. Before mixing commenced, the raw elastomer was placed in an oven at 60°C for 1 h, to soften it prior to mastication on the mill. The rubber was then placed immediately on the mill and masticated for up to 12 min before adding the ingredients. The compound temperature was about 61°C.

In the first stage of mixing, the zinc oxide, CBS and antioxidant were added to the raw elastomer and mixed for 8 min. The compound temperature was 60°C. In the second stage, sulphur was added to the elastomer and mixed for 6 min. The compound temperature was about 61°C. Finally, the compound was removed from the mill, and stored at 23°C for 48 h, before its viscosity and cure properties were determined.

Filled compounds. The compounds containing the filler were prepared in a HAAKE RHEOCORD 90, a small sized laboratory mixer with counter rotating type rotors. In these experiments, the rotors and the mixing chamber were maintained at 50°C, and the rotor speed was 45 r.p.m. HAAKE Software Version 1.9.1. was utilised for controlling the mixing condition and storing data.

TABLE 1. PROPERTIES OF COUPSIL 8113®

Item	Properties
Silica	Ultrasil VN3®
N_2 surface area (m^2/g)	175
Silane	Bis-(3-triethoxysilylpropyl)-tertrasulphane (Si69® coupling agent)
Silane content (%)	11.3
Appearance	*White to slightly yellow powder*
Solubility	Insoluble in all common organic and inorganic solvents
Range of particle size[a] (μm)	0.020 – 0.054

[a] Measured by transmission electron microscope

TABLE 2. RECIPE AND MIXING CONDITIONS FOR THE RUBBER AND FILLER

Formulation (p.h.r.)	Compound number					
	1	2	3	4	5	6
Natural rubber	100	100	100	100	100	100
Coupsil 8113®	14	14	14	14	14	14
Mixing time (min)	1	2	3	5	8	11
Compound temperature (°C) (After mixing ended)	61	72	72	81	78	77

Properties of the Rubber Compounds

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer according to the *British Standards* procedure[19]. The scorch and optimum cure times were determined at 140°C ± 2°C by an oscillating disc rheometer at an angular displacement of ±3° and a test frequency of 1.7 Hz[20]. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated following the *British Standards* method[21]. The rheometer tests ran for up to 3 h.

Procedure for Designing the Filled Compounds

Filler dispersion. Filler-batch mixing time is an effective way to disperse fillers in rubber compounds[13]. In order to select a suitable mixing time for incorporating the filler in the rubber, six compounds were prepared (*Table 2*). The mixing time was increased from 1 min to 11 min. Twenty four hours after mixing ended, samples of rubber approximately 2 mm wide, 50 mm long, and 2 mm thick, were placed on top of a flat glass top, and a source of ordinary white light was positioned underneath them in

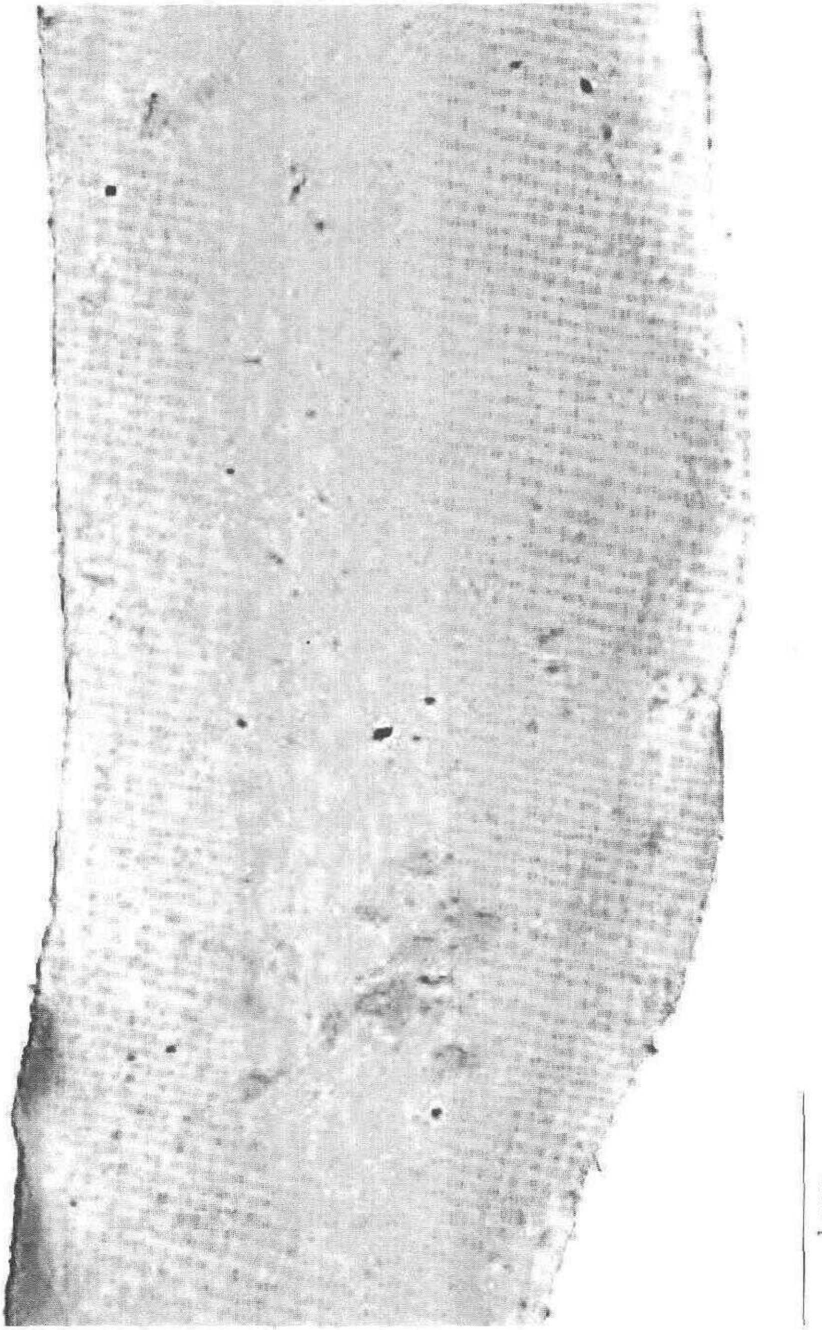


Figure 1. Sample of rubber compound containing 14 p.h.r. silanised silica. Mixing time 8 min.

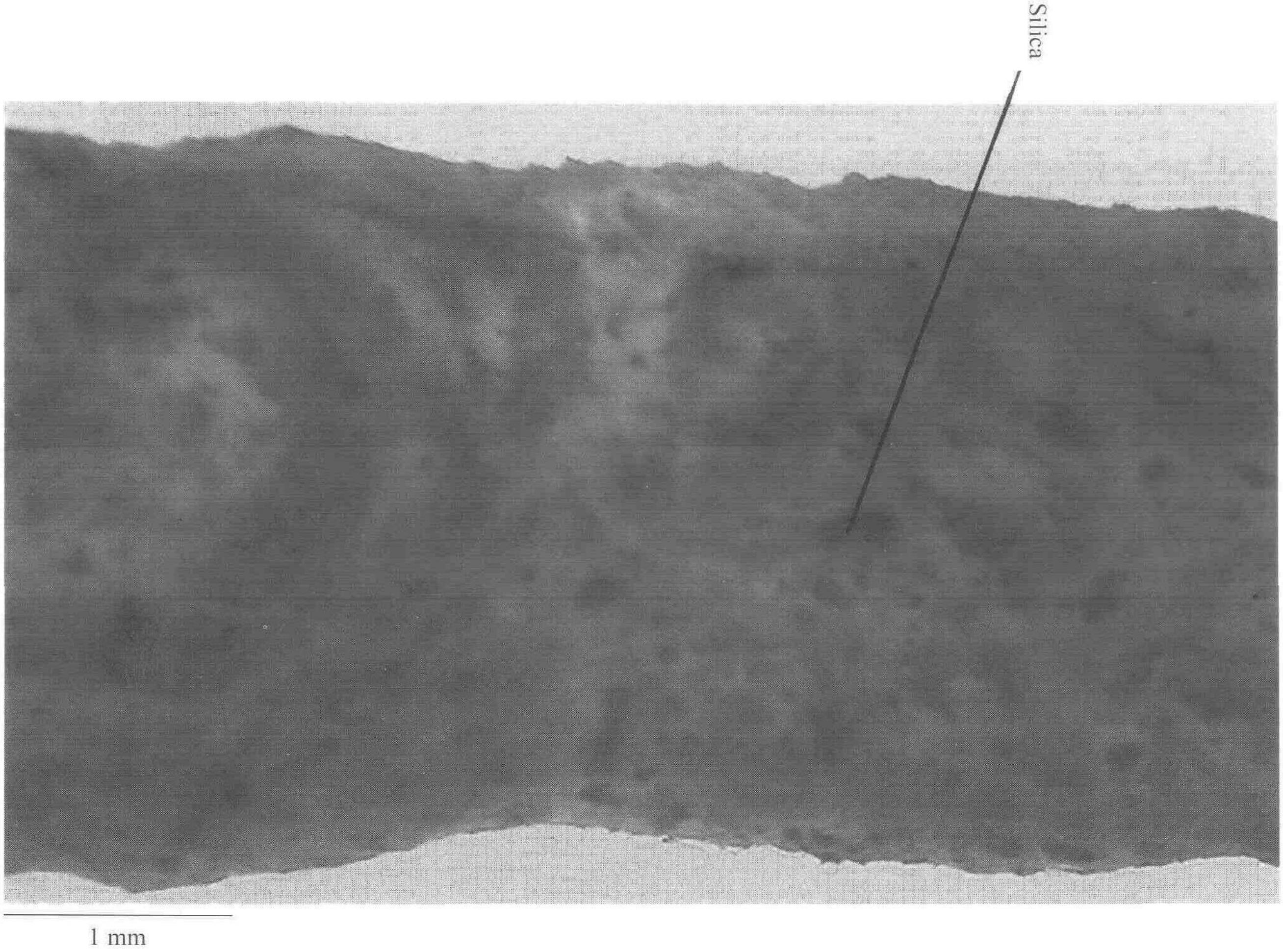


Figure 2. Sample of rubber compound containing 14 p.h.r. silanised silica showing agglomerates. Mixing time 3 min.

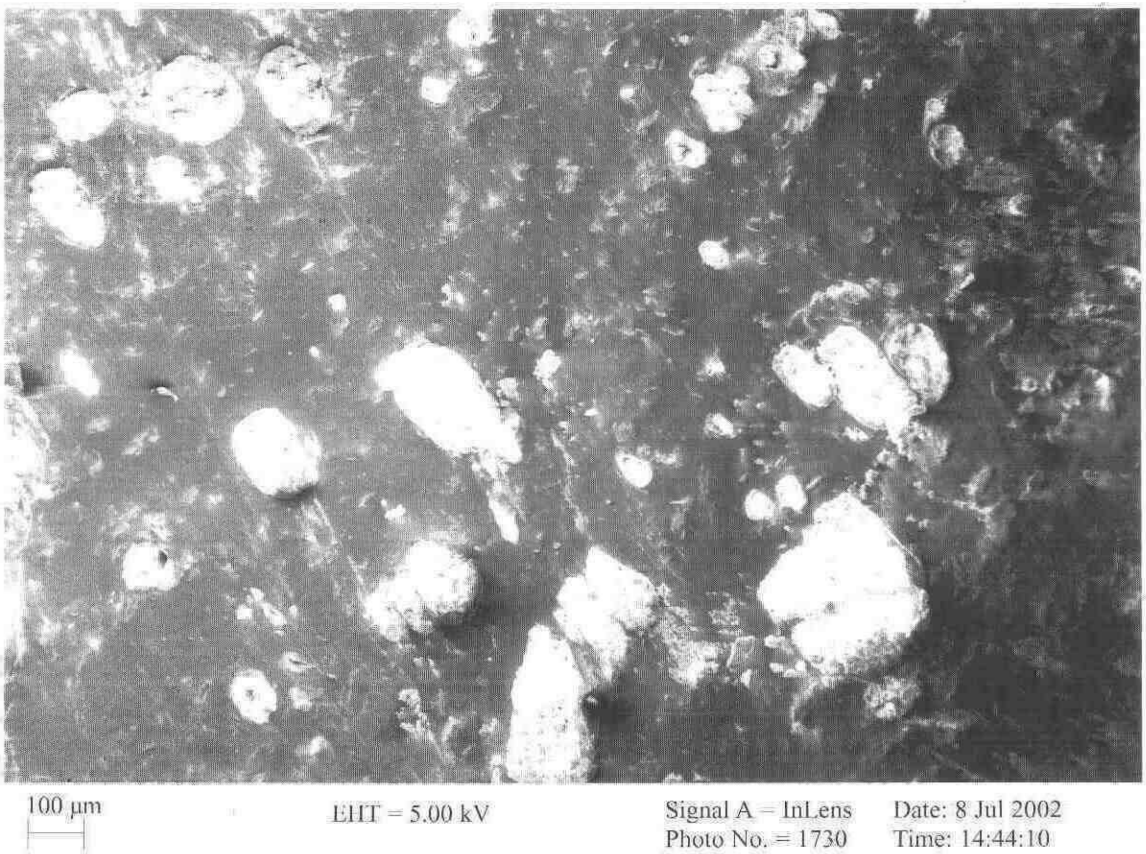


Figure 3. SEM micrograph showing silica dispersion in the rubber. Mixing time 3 min.

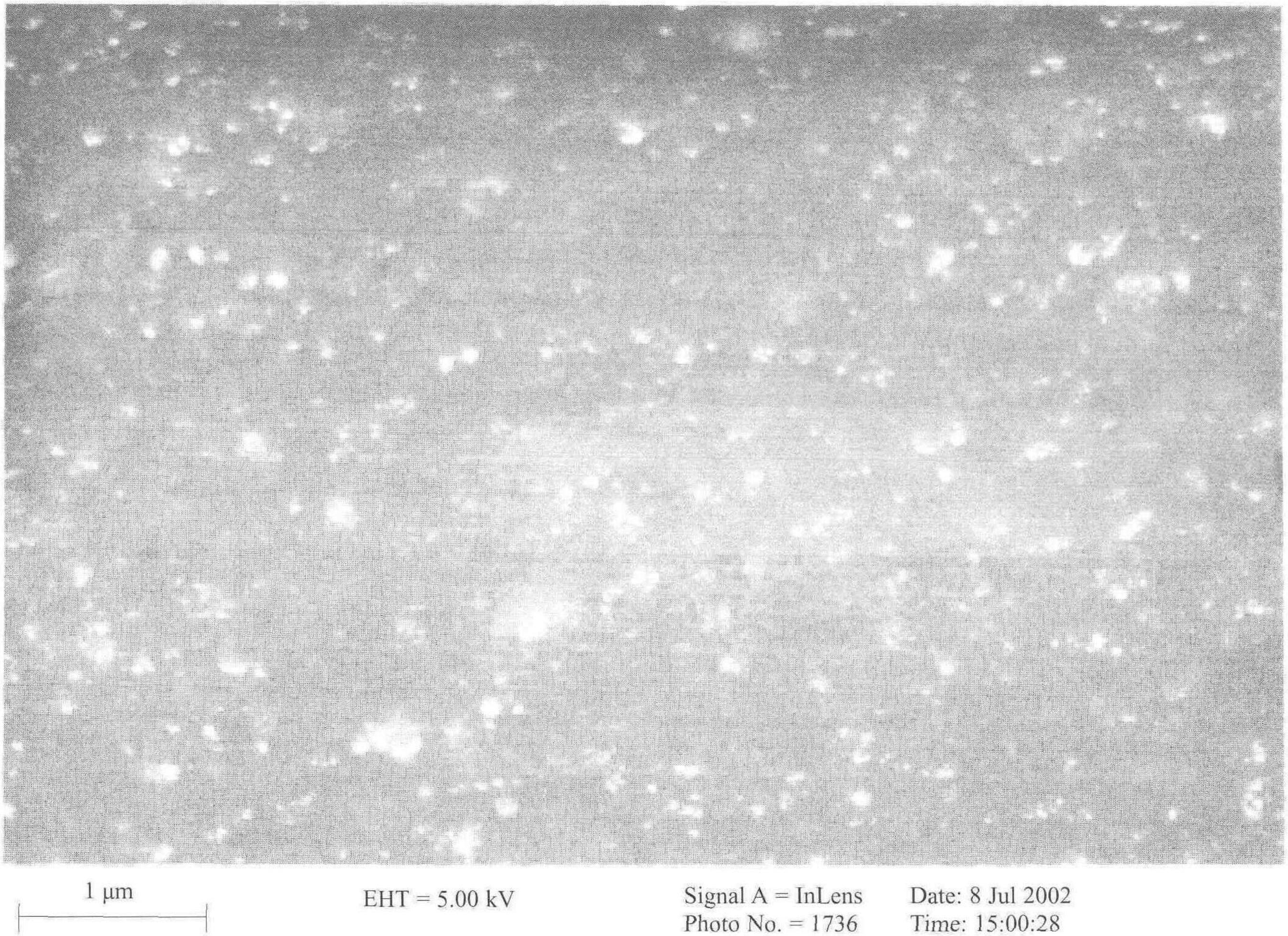


Figure 4. SEM micrograph showing silica dispersion in the rubber. Mixing time 8 min.

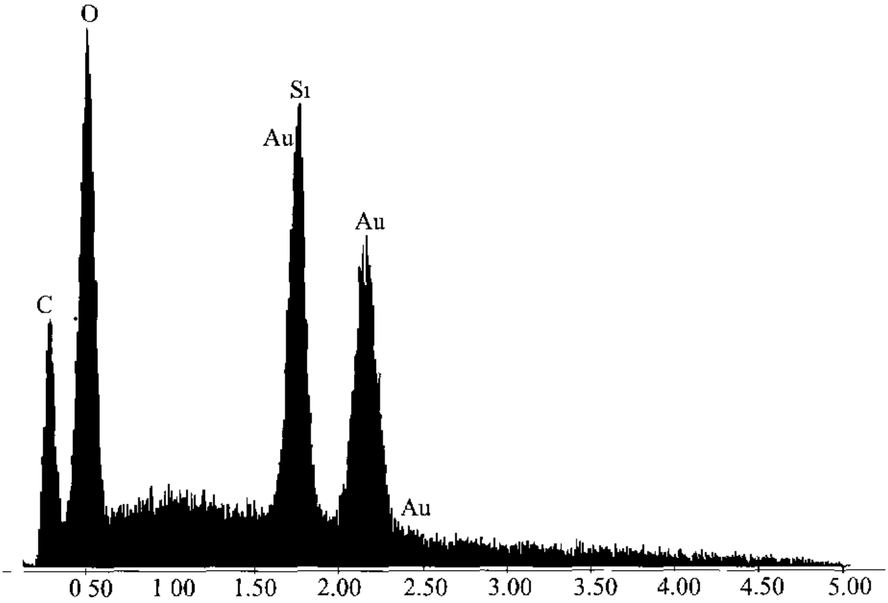


Figure 5. Composition of the agglomerates seen in Figure 3.

order to shine light through the rubber and visually observe the dispersion of the filler. A digital camera was also used to photograph the samples. The photographs were subsequently printed out for further analysis. Some samples were completely transparent (*Figure 1*), and a few were impenetrable by light (*Figure 2*). In fact in the latter case, large agglomerates of the filler were also seen. To investigate this further, dispersion of the filler in the rubber was assessed by a LEO 1530 VP Field emission gun scanning electron microscope (SEM). Samples of the uncured rubber, 12 mm^2 in area, and 5 mm thick were coated with gold, examined and then photographed in the SEM. The degree of dispersion of the filler was subsequently studied from two SEM photographs shown in *Figures 3* and *4* . In the opaque sample (*Figure 2*) agglomerates up to 300 μm in size were measured (*Figure 3*). However, in the transparent sample (*Figure 1*) the size was reduced to about 0.04 μm (*Figure 4*). The particle size of the filler was about 0.020 μm – 0.054 μm (*Table 1*). Energy Dispersive X-ray Microanalyser EDAX Phoenix was used to determine the composition of the agglomerates (*Figure 5*). This confirmed that the filler was poorly dispersed in the opaque samples, but was finely dispersed in the transparent one. It was concluded that the rubber transparency was a good indication of the quality of the filler dispersion in the rubber. In the subsequent work with the rubbers containing 30 p.h.r. filler, we selected a filler-rubber batch mixing time of 10 min to produce transparent rubber compounds before the other ingredients were added into the mixer.

Selection of accelerator. Fifteen compounds were prepared and tested in the rheometer at 140°C to measure Δ torque. The loading of the accelerator (CBS) in the rubber was increased

TABLE 3. RECIPE AND MIXING CONDITIONS FOR THE FILLED RUBBER AND ACCELERATOR

Formulation (p.h.r.)	Compound number														
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	Stage one mixing														
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Coupsil 8113®	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Mixing time (min)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Compound temperature °C	78	78	79	78	78	79	79	77	79	79	80	79	80	78	77
	The rotors were stopped and the compound was cooled down to 50°C before mixing restarted														
	Stage two mixing														
Santocure® (CBS)	0	0.3	0.6	0.9	1.3	1.8	2.2	2.6	3.0	3.4	3.8	4.4	4.8	5.5	5.9
Mixing time (min)	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Compound temperature (°C) (After mixing ended)	–	72	72	72	72	72	72	72	72	72	72	71	72	71	71

Santocure®: N-Cyclohexyl-2-benzothiazole sulphenamide (CBS)

TABLE 4. RECIPE AND MIXING CONDITIONS FOR THE FILLED RUBBER WITH ACCELERATOR AND ACTIVATOR

Formulation (p.h.r.)	Compound number				
	22	23	24	25	26
	Stage one mixing				
Natural rubber	100	100	100	100	100
Coupsil 8113®	30	30	30	30	30
Mixing time (min)	10	10	10	10	10
Compound temperature (°C)	79	79	78	79	79
	The rotors were stopped and the compound was cooled down to 50°C before mixing restarted.				
	Stage two mixing				
Santocure® (CBS)	4.4	4.4	4.4	4.4	4.4
Zinc oxide	0	1	2.5	4	5.5
Mixing time (min)	3	3	3	3	3
Compound temperature (°C) (After mixing ended)	71	72	72	70	72

TABLE 5 RECIPE AND MIXING CONDITIONS FOR THE COMPOUNDS

Formulation (p.h.r.)	Compound number		
	27[a]	28	29
	Stage four mixing		
Natural Rubber (SMR L)	100	100	100
Silanised silica (Coupsil 8113)®	0	30	30
Mixing time (min)	–	10	10
Compound temperature (°C)	–	80	79
	The rotors were stopped and the compound was cooled down to 50°C before mixing restarted		
	Stage four mixing		
Santocure® (CBS)	4.4	4.4	4.4
Mixing time (min)	–	1	1
Compound temperature (°C)	–	70	68
	The rotors were stopped and the compound was cooled down to 50°C before mixing restarted		
	Stage four mixing		
Zinc oxide	2.5	2.5	2.5
Mixing time (min)	–	1	1
Compound temperature (°C)		69	65
	The rotors were stopped and the compound was cooled down to 50°C before mixing restarted		
	Stage four mixing		
Santoflex 13® (Antidegradant)[b]	1	1	1
Sulphur	0.2	0.2	0
Mixing time (min)	–	3	3
Compound temperature (°C) (After mixing ended)	–	72	70

[a] Control compound (mixing condition described in the text)

[b] Santoflex 13® N-(1,3-dimethylbutyl)-N′ -phenyl-p-phenylenediamine

TABLE 6. RESULTS FROM THE VISCOSITY MEASUREMENTS AND THE ODR TESTS CARRIED OUT AT 140°C

Compound numbers	27[a]	28	29
Mooney viscosity, ML (1 + 4) at 100°C	25	71	71
		ODR results	
Minimum torque (dN.m)	7	22	21
Maximum torque (dN.m)	40	89	79
Δ torque ($D_{max} - D_{min}$)	33	67	58
Scorch time, t_{s2} (min)	84	20	18
Optimum cure time, t_{95} (min)	140	46	57
Cure rate index (min^{-1})	1.79	3.85	2.56

[a] Control compound

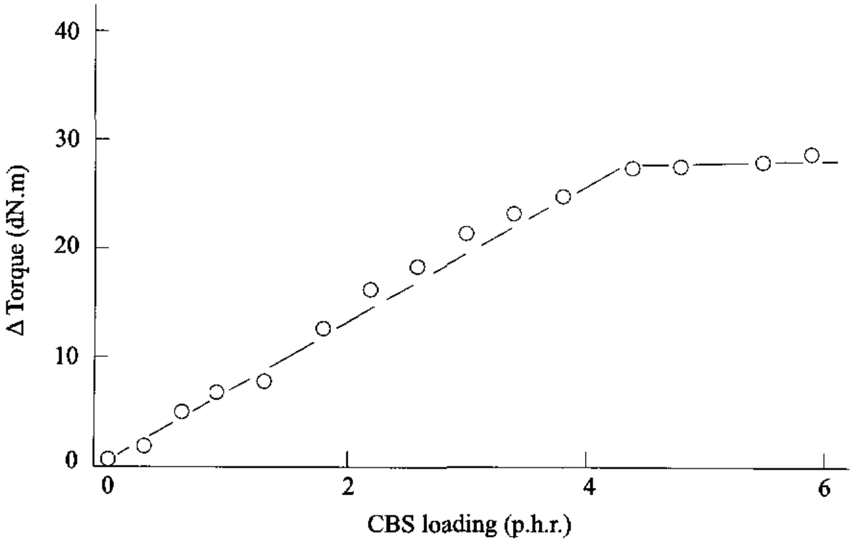


Figure 6. Torque versus CBS loading for the rubber containing 30 p.h.r. silanised silica.

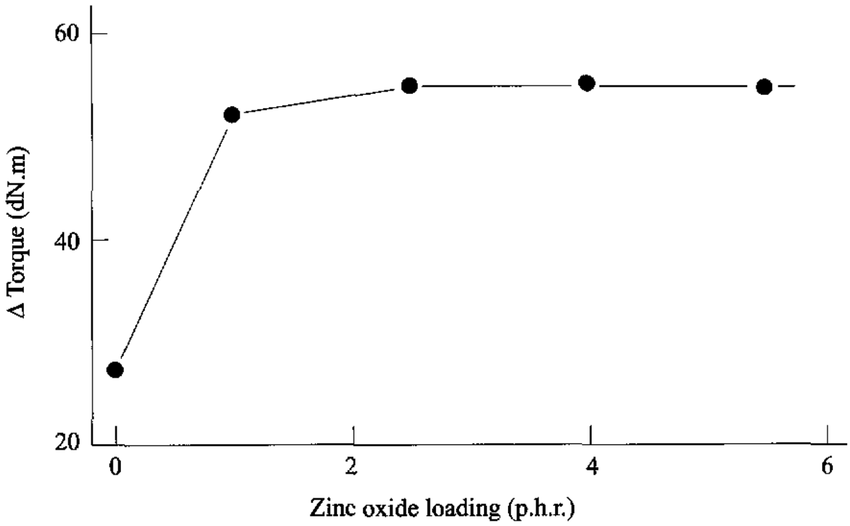


Figure 7. Torque versus *zinc oxide loading for the rubber containing 30 p.h.r. silanised silica.*

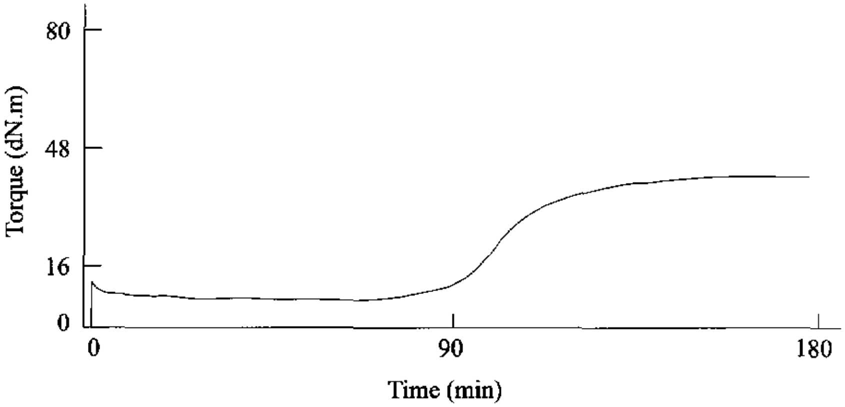


Figure 8. Torque versus *time by ODR at 140°C for the control compound.*

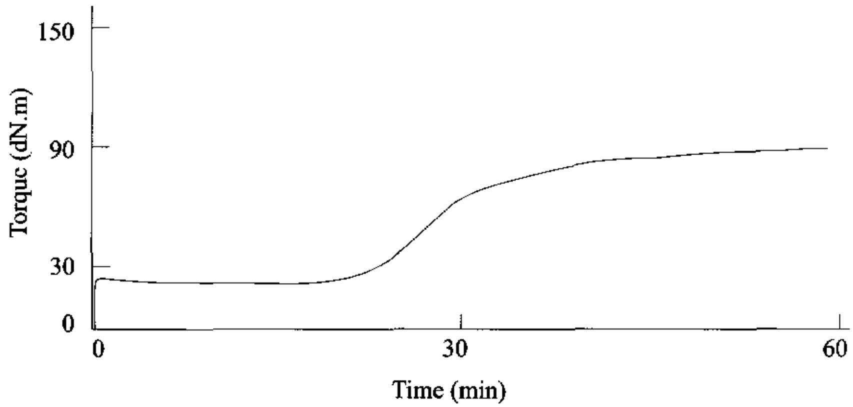


Figure 9. Torque versus *time by ODR at 140°C for the filled compound with 0.2 p.h.r. sulphur.*

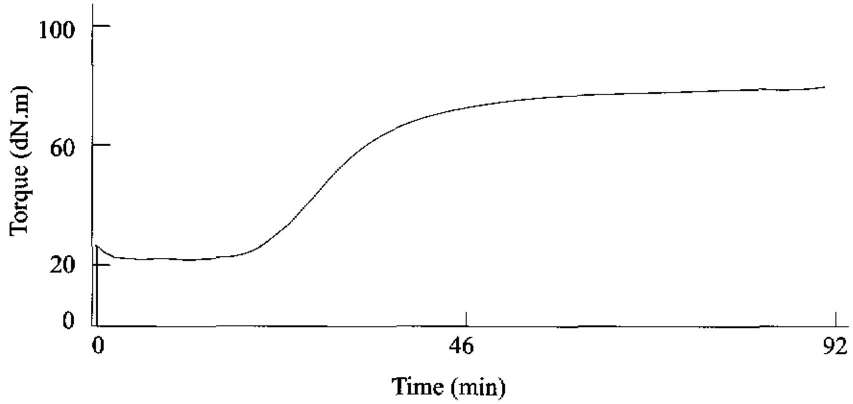


Figure 10. Torque versus *time by ODR at 140°C for the filled compound with no added sulphur.*

from 0 p.h.r. to 5.9 p.h.r. (*Table 3*) in order to maximise the reaction between the rubber reactive tetrasulphane groups of TESPT and the rubber compound. This in turn strengthened the rubber/TESPT interaction. Full details of the mixing conditions are given in *Table 3*. *Figure 6* shows Δ torque *versus* CBS loading. Evidently, 4.4 p.h.r. CBS optimised the crosslink density of the rubber.

Selection of activator. Five compounds were prepared and tested in the rheometer at 140°C to measure Δ torque. The loading of zinc oxide in the rubber was increased from 0 p.h.r. to 5.5 p.h.r. (*Table 4*) in order to optimise the efficiency of the accelerator by way of selecting a suitable loading of the zinc oxide. Full details of the mixing condition are given in *Table 4*. *Figure 7* shows Δ torque *versus* zinc oxide loading. Apparently, 2.5 p.h.r. of this additive optimised the effectiveness of the accelerator.

After these measurements were completed, two filled compounds were selected for further work (*Table 5*). The compounds also contained antidegradant to protect them against environmental ageing. One of the filled compounds contained 0.2 p.h.r. sulphur in order to assess effect of sulphur on the properties of the rubber. The control compound was prepared lastly (*Table 5*). The compounds were kept at ambient temperature (23°C) for at least 24 h before their viscosity[19] and cure properties[20,21] were measured (*Table 6*). The cure properties were determined from some cure traces shown in *Figures 8–10*. The compounds were subsequently cured in a compression mould at 140°C in a hydraulic press to form test pieces for measuring the technical properties of the rubber.

Test Pieces and Test Procedure

Hardness. For determining the hardness of the rubbers, cylindrical samples 12.5 mm thick and 28 mm in diameter, were cured. The samples were then placed in a Shore A Durometer hardness tester, and the hardness of the rubber was measured at ambient temperature (23°C) over a 15-second interval after which a reading was taken. This was repeated at three different positions on the sample, and median of the three readings calculated[22] (*Table 7*).

Abrasion resistance. For determining the DIN abrasion resistance index value of the rubbers, moulded cylindrical test pieces, 8 mm thick and 16 mm in diameter were cured. The tests were performed at 23°C in accordance with *BS ISO 4649:2002*[23] using method B (rotating test piece) (*Table 7*) by Rubber Consultants (Tun Abdul Razak Research Centre, Brickendonbury, Hertford, U.K.)

Cyclic fatigue life. The cyclic fatigue life of the rubbers was measured in uniaxial tension in a Hampden dynamic testing machine, using dumbbell test pieces 3.6 mm wide (*Figure 11*). The test pieces were die-stamped from the sheets of cured rubber. The tests were performed at a constant maximum deflection of 100% (the central neck was stretched to 50 mm), and a test frequency of 1.42 Hz[24]. The test temperature was about 23°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 median of the eight readings was determined. The results were presented in an increasing order of magnitude in *Table 8*.

Cohesive tear strength. Rectangular strips, 100 mm long and 30 mm wide, were cut from the cured sheets of rubber and a sharp crack, approximately 30 mm in length, was introduced into the strips half way along the width and parallel to the length of the strips, to form the trousers test pieces shown in *Figure 12*, for the tear experiments. Trousers tear tests were performed at an angle of 180°, at ambient temperature (~23°C) and at a constant cross-head speed of 100 mm/min[25] in a Lloyd mechanical testing machine. The tears produced in the rubber after the test pieces were fractured were 22 mm to 70 mm in length. In each experiment, the tearing force was recorded to produce a trace from which an average force was measured (*Figure 13*). The first peak corresponding to the onset of crack-growth, where the tearing force was still rising, and the last peak corresponding to when test stopped or the sample broke were not considered. The remaining peaks on the trace were utilised for calculating an average tearing force for the rubber (*Figure 13*). For each

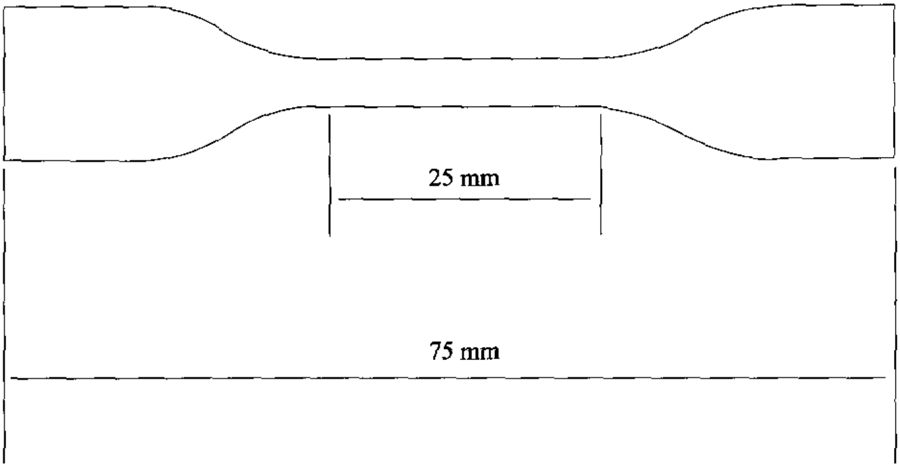


Figure 11. Dumbbell test piece for cyclic fatigue life tests.

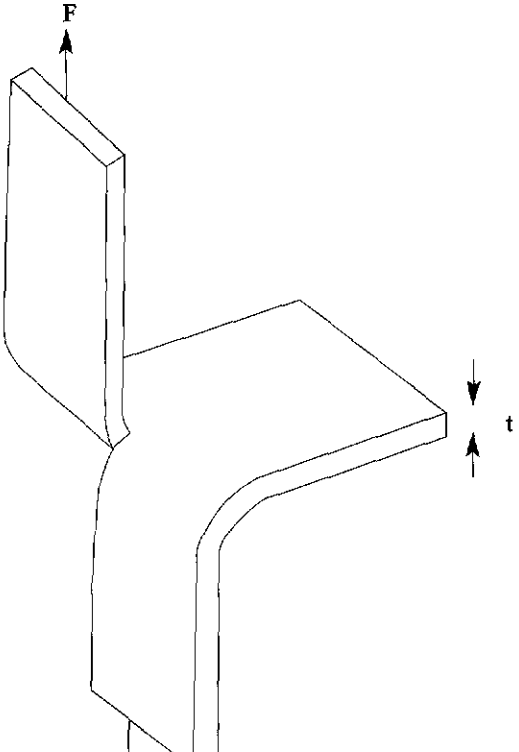


Figure 12. Trousers tear test piece.

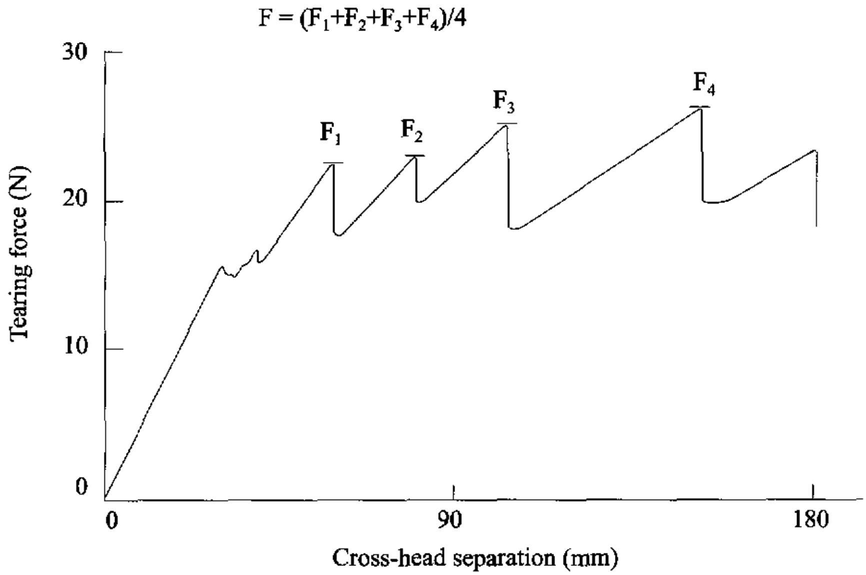


Figure 13. Typical record of tearing force as a function of cross-head separation. Data for the control compound: T = *17 kJ/m*^{2}.

TABLE 7. HARDNESS AND DIN ABRASION RESISTANCE INDEX VALUES OF THE RUBBERS

Compound numbers	27[a]	28	29
Reading	Hardness (Shore A)		
1	24.5	53	52
2	25.0	53	52
3	26.5	54	52
Median values	25.0	53	52
	DIN Abrasion resistance index value (%)		
	–	107	69

[a] Control compound

TABLE 8. CYCLIC FATIGUE LIFE TEST RESULTS

Compound numbers	27[a]	28	29
	Cyclic fatigue life (kc)		
Sample number			
1	79.9	45.8	58.8
2	118.7	45.9	60.8
3	122.4	50.6	63.7
4	134.4	55.5	63.8
5	137.4	57.0	65.4
6	148.6	60.8	69.6
7	164.0	63.9	70.9
8	164.6	75.4	77.7
Median values	135.9	56.3	64.6
Standard deviation	25.9	9.3	5.7

[a] Control compound

TABLE 9. TEARING ENERGIES OF THE VULCANISATES

Compound numbers	27[a]	28	29
	Tearing energy (kJ/m^2)		
Sample number			
1	16.5	35.6	41.7
2	17.1	36.6	44.7
3	17.3	37.7	47.8
4	20.5	37.9	48.0
5	–	41.7	48.9
Median values	17.2	37.7	47.8
Range of values	3.9	6.1	7.2

[a] Control compound

TABLE 10. TENSILE STRENGTH, ELONGATION AT BREAK AND STORED ENERGY DENSITY AT RUPTURE

Compound numbers	27[a]	28	29
	Tensile strength (MPa)		
Sample number			
1	19.2	35.0	37.7
2	19.4	35.8	38.4
3	22.1	37.2	38.5
Median values	19.4	35.8	38.4
	Elongation at break (%)		
Sample number			
1	1621	934	1038
2	1647	950	1075
3	1671	996	1084
Median values	1647	950	1075
	Stored energy density at rupture (MJ/m^3)		
Sample number			
1	78.8	127.6	142.6
2	83.4	134.6	149.0
3	91.8	141.0	153.6
Median values	83.4	134.6	149.0

[a] Control compound

compound, five test pieces were used. After these measurements were completed, and following the procedure described previously[25], extension in the legs of the test pieces was ignored and the force values were placed[26] in *Equation 2*:

$$T = 2F/t \qquad \dots 2$$

where F is the force, and t is the thickness of the test piece, to calculate tearing energies for the rubbers. The median values of the tearing energies were subsequently noted (*Table 9*).

Tensile properties. The tensile stress, elongation at break, and stored energy density at rupture of the rubbers were determined in uniaxial tension in a Lloyd mechanical testing machine, using dumbbell test pieces (*Figure 11*). These samples were die-stamped from slabs of cured rubber. The tests were performed at ambient temperature (*ca* ~ 23°C) and at a cross-head speed of 500 mm/min[27]. Lloyd DAPMAT computer software was utilised for storing and processing the data (*Table 10*).

RESULTS AND DISCUSSION

Properties of the rubber, as reported in *Tables 7–10*, were influenced differently by the filler The tensile strength and stored energy density at rupture were increased from about 19 MPa to 36 MPa and 83 MJ/m^3 to 135 MJ/m^3 respectively, when the filler was added to the rubber (*Table 10*) Similarly, the cohesive tear strength (*Table 9*) and hardness (*Table 7*) were also improved from about 17 kJ m^2 to 38 kJ/m^2 and 25 to 53 Shore A respectively, as a result of adding the filler to the rubber Probably the most interesting effect of the filler addition was the very substantial increase in the DIN abrasion resistance index value of the rubber The filled rubber with 0 2 p h r added sulphur had an index value of about 107% (*Table 7*) Typical tyre tread rubber compounds containing 65 p h r reinforcing carbon black (average particle size about 0 03 μm) have index values of 95%[28] Notably the inclusion of the filler had a detrimental effect on the elongation at break and cyclic fatigue life of the rubber The elongation at break dropped from about 1650% to 950% (Table 10), and the fatigue life shortened from approximately 136 kc to 56 kc (*Table 8*) It was interesting that the filled rubber with no added sulphur possessed even better properties For example, the tensile strength and stored energy density at rupture were increased to about 38 MPa and 149 MJ m (*Table 10*), respectively The elongation at break recovered to 1070% (*Table 10*), but the hardness remained unchanged at 52 Shore A (*Table 7*) The abrasion resistance index value decreased significantly to 69% (*Table 7*), and was noticeably lower than the values reported for typical tyre tread compounds[28] Moreover, the cohesive tear strength and cyclic fatigue life were also enhanced to about 49 kJ/m^2 (*Table 9*) and 65 kc (*Table 8*) respectively, for the filled rubber with no added sulphur (*Table 5*)

As mentioned earlier[4], the tetrasulphane groups of TESPT are rubber reactive and react in the presence of accelerators at elevated temperatures, with or without elemental sulphur being present, to form crosslinks in unsaturated rubbers The reaction between these groups and the rubber compound was maximised with 4 4 p h r CBS (*Figure 6*) This helped to eliminate the need for extra added elemental sulphur to control the technical properties of the rubber In fact, it was evident from the results (*Tables 7–10*) that adding sulphur to the compound had a detrimental effect on the technical properties of the filled rubber This work confirmed that the silanised precipitated silica was truly a multifunctional filler and performed at least two functions in the rubber It greatly reinforced some physical and mechanical properties of the cured rubber, and at the same time, the tertasulphane groups of TESPT crosslinked with the rubber compound, removing the need to add elemental sulphur This was achieved by finely dispersing the filler in the rubber matrix by means of selecting a suitable filler-rubber batch mixing time, and also by optimising the reaction between the tetrasulphane groups of TESPT and the rubber compound by way of adding the right amounts of CBS and zinc oxide

CONCLUSIONS

This study has shown that when 30 p h r silanised precipitated amorphous white silica was added to a sulphur cured natural rubber compound, with a sulphur to accelerator ratio of about 0 046, the technical properties of the rubber were profoundly affected

It emerged that:

- The tensile strength, stored energy density at rupture, hardness, abrasion resistance, and cohesive tear strength of the filled rubber were substantially higher than the control compound. However, the elongation at break and cyclic fatigue life were adversely affected when the filler was incorporated in the rubber compound.
- The properties aforementioned (not including the hardness and abrasion resistance) were improved far greater without the added sulphur, and by optimising the reaction between the rubber reactive tetrasulphane groups of TESPT and the rubber compound. The improved properties were due to the fine dispersion of the filler in the rubber matrix, and also the use of the right amounts of CBS and zinc oxide in the rubber compound. The latter helped to strengthen the rubber/TESPT interaction.

ACKNOWLEDGEMENT

We wish to express our gratitude to the Malaysian Rubber Board for their invaluable support of this project. *Schemes 1* and *2* in this article were reprinted from *Reference 15* (Copyright 2003), with permission from Elsevier Science Limited, UK. We are also grateful to Degussa AG, Germany for supplying us with the technical information about the filler. The SEM and TEM studies of the samples were carried out at Loughborough Materials Characterisation Centre, UK.

Date of receipt: February 2003
Date of acceptance: August 2003

REFERENCES

1. ANDREWS, E.H. (1963) Reinforcement of Rubber by Fillers *Rub. Chem Technol.*, **36**, 325–336.
2. WAGNER, M.P. (1981) Precipitated Silicas — Compounding Alternative with Impending Oil Shortages. *Elastomerics*, 40–44.
3. GLASSVEN (1999) Precipitated Silicas for Tire Reinforcement. *Tire Technol Inter.*, 36–37.
4. WOLFF, S., GÖRL, U, WANG, M.J. AND WOLFF, W. (1994) Silane Modified Silicas. *Eur Rub J.*, **16**, 16–19.
5. HAIR, M.L. AND HERTL, W. (1970) Acidity of Surface Hydroxyl Groups. *J Phys Chem.*, **74**, 91–94.
6. WOLFF, S. (1996) Chemical Aspects of Rubber Reinforcement by Fillers. *Rub Chem Technol.* **69**, 325–346
7. BASSETT, D.R.E., BOUCHER, A. AND ZETTLEMOYER, A.C. (1968) Adsorption Studies on Hydrated and Dehydrated Silicas. *J. Colloidal Interface Sci.*, **27**, 649–658.
8. HOCKLEY J.A. AND PETHICA, B.A. (1961) Surafce Hydration of Silicas. *Trans. Faraday Soc.* **57**, 2247–2622.
9. WAGNER, M.P. (1976) Reinforcing Silicas and Silicates. *Rub. Chem Technol.*, **49**, 703–774
10. TAN, E.H., WOLFF, S., HADDEMAN, S.M., GREWATTA, H.P. AND WANG, M.J. (1993) Filler-Elastomer Interaction IX. Performance of Silicas in Polar Elastomers. *Rub. Chem.Technol.*, **66**, 594–604.
11. ANSARIFAR, M.A., AND NIJHAWAN, R. (2000) Effects of Silane on Properties of

Silica Filled Natural Rubber Compounds *J Rubb Res*, **3(3)** 169–184

12 WOLFF, S (1996) Chemical Aspects of Rubber Reinforcement by Fillers *Rubb Chem Technol*, **69**, 325 345

13 WOLFF, S (1982) Optimisation of Silane-Silica OTR Compounds 1 Variations of Mixing Temperature and Time During the Modification of Silica with Bis-(3-triethoxysilylpropyl)-tetrasulfide *Rub Chem Technol*, **55**, 967–989

14 ANSARIFAR, M A JAIN A AND NANAPOOLSIN, T (2002) Silane-Silica Reinforcement of Some Natural Rubber Vulcanisates *J Rubb Res* **5(1)** 11–27

15 ANSARIFAR M A, CHONG, L K, ZHANG, J, BELL, A AND ELLIS, R J (2003) Effect of Bifunctional Organosilane on the Joint Strength of some Silica Filled Natural Rubber Compounds to Nylon 6,6 *Inter J Adhes*, **23**, 177–188

16 STUMPE, N A AND RAILSBACK, H E (1964) Carbon Black Dispersion — Photographic Technique and Rating System *Rubb World*, **151** 41–43

17 POLMANTEER K E AND LENTZ, C W (1975) Reinforcement Studies — Effects of Silica Structure on Properties and Crosslink Density *Rub Chem Technol*, **48** 795–809

18 PAL PK AND DE SK (1982) Effect of Reinforcing Silica on Vulcanisation, Network Structure, and Technical Properties of Natural Rubber *Rubb Chem Technol*, **55**, 1370–1388

19 *BRITISH STANDARD 1673 Part 3* (1969) Methods of Testing Raw Rubber and Unvulcanised Compounded Rubber Methods of Physical Testing

20 *BRITISH STANDARD 1673 Part 10* (1977) Methods of Test for Raw Rubber and Unvulcanised Compounded Rubber Measurement of prevulcanising and Curing Characteristics by Means of Curemeter

21 *BRITISH STANDARD 903 Part A60 Section 60 1* (1996) Methods of Test for Raw Rubber and Unvulcanised Compounded Rubber Measurement of Prevulcanising and Curing Characteristics by Means of Curemeter

22 *BRITISH STANDARD 903 Part A26* (1995) Physical Testing of Rubber Method for Determination of Hardness

23 *BRITISH STANDARD BS ISO 4649* (Method B) (2002) Methods of Testing Vulcanised Rubber Determination of Resistance to Abrasion

24 *BRITISH STANDARD 903 Part A51 (1986)* Methods of Testing Vulcanised Rubber Determination of Resistance to Tension Fatigue

25 *BRITISH STANDARD 903 Part A3* (1995) Physical Testing of Rubber Method for Determination of Tear Strength Trousers, Angle and Crescent Test Pieces

26 GREENSMITH, H V AND THOMAS, A G (1955) Rupture of Rubber III Determination of Tear Properties *J Polym Sci* **43**, 189–200

27 *BRITISH STANDARD 903 Part A2* (1995) Physical Testing of Rubber Method for Determination of Tensile Stress Strain Properties

28 Archives, Tun Abdul Razak Research Centre MRPRA, Brickendonbury, Hertford SG13 8NL, UK The Natural Rubber Formulary and Properties Index Re EUR053