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Silane-silica Reinforcement of Some Natural Rubber Vulcanisates

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The hardness, cyclic fatigue life, cohesive tear strength, tensile strength, elongation at break and stored energy at rupture of some conventional accelerator/sulphur compounds of natural rubber with a sulphur to accelerator ratio of 2.5, containing 10 parts per hundred rubber by weight (p.p.h.r.) precipitated amorphous white silica were measured. The compounds also contained no silane, and 2.5, 5, 7.5 and 10 p.p.h.r. bis[3-triethoxysilylpropyl-)tetrasulphane bifunctional organosilane to prevent the silica from interfering with the reaction mechanism of sulphur cure system in the rubber. This study showed that the cyclic fatigue life and stored energy were optimised to 176 kc and 134 MJ/m^3 respectively, when 7.5 p.p.h.r. silane was added to the rubber. The hardness and tensile strength improved to 45 Shore A and 31.5 MN/m^2, respectively, after 10 p.p.h.r. silane was introduced into the compound. Interestingly, the inclusion of silane had a detrimental effect on the cohesive tear strength and elongation at break of the vulcanisate.

Key words: silane; silica; reinforcement; NR vulcanisate; sulphur cured; physical properties; mechanical properties

Reinforcing fillers like colloidal carbon blacks have been utilised for many years to enhance physical and mechanical properties of rubber products such as engine mountings, car tyres and shoe soles. These materials, when added to the formulation, help to enhance attributes such as hardness, rupture energy, cut and tear strength considerably, making rubber compounds suitable for industrial uses. Synthetic silicas like precipitated amorphous white silica have been replacing carbon blacks, to some extent, in many applications, offering similar benefits. It has been suggested that by 2005, 85 percent of car tyres will contain silica, and truck tyres will use about 15% by weight of this material[1]. Increase in the use of silica in rubber products is likely to continue strongly.

Precipitated silicas are prepared from chemical reaction between a sodium silicate solution and sulphuric acid[2], and also by precipitation from water-soluble silicates[3]. The surfaces of these fillers possess siloxane and silanol functional groups[4], and the silanol or hydroxyl groups are acidic[5]. Acidic silicas interact with basic accelerator, causing detrimental effects on the cure properties of rubber compounds such as unacceptably long cure times and slow

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cure rates[4], and also loss of crosslink yield[6] in sulphur cure systems. Moreover, silicas adsorb moisture[7,8] because the surfaces of these fillers are polar and hydrophilic. The amount of water adsorbed on the surface of the filler controls the ionisation of the hydroxyl groups[9], and this also has an adverse influence on the cure attributes of rubber compounds. When a large amount of silica is added, the viscosity increases significantly[10], resulting in undesirable consequences to the processibility of rubber compounds, and also excessive wear and tear of the processing equipment. Increases of compound viscosity through incorporation of a large amount of silica could be attributed primarily to the strong silica-silica interaction[10]. To normalise cure, that is to say to prevent acidic silica from adversely affecting the cure reaction in rubber compounds and to reduce viscosity by weakening or destroying silica-silica interactions[4], bifunctional organosilanes such as bis[3-triethoxysilylpropyl-)tetrasulphane (TESPT) are utilised with the filler in rubber mixes[4].

Effects of TESPT silane on the Mooney viscosity and cure properties of some sulphur cure system-based natural rubber compounds containing different amounts of precipitated silica were studied by the author and co-workers[11,12]. It emerged that different properties were not affected in the same way. For example, 2.5 p.p.h.r. silane was needed to shorten the scorch time in a mix with 60 p.p.h.r. silica, whereas 7 p.p.h.r. silane helped to reduce the viscosity and shorten the optimum cure time of the same compound. In a recent investigation[13], we discovered that the cyclic fatigue life and cohesive tear strength of this rubber were maximised after adding 7 p.p.h.r. silane to the formulation. Other studies have also revealed promising results. Wolff and co-workers[4] showed that when black was replaced with TESPT-modified precipitated silica in passenger and truck tread compounds, a marked reduction in rolling resistance was recorded and the tread-wear index was decreased by approximately 7 percent.

It has been acknowledged that rubber-to-filler interaction plays a major role in enhancing physical and mechanical properties of rubber vulcanisates. The measurement of bound rubber is a practical means of evaluating the degree of rubber-filler interaction[14]. Wolff and co-workers[15] measured the bound-rubber content for some natural rubber vulcanisates, containing 50 p.p.h.r. precipitated silica, and reported a 31.8 % bound-rubber. This indicated a strong filler-elastomer interaction for silica. In a new study, Wolff[16] compared the bound-rubber content of some silica filled SBR vulcanisates in an ammonia atmosphere, and showed that this property decreased by approximately 80%. This was due to a split between the adsorptive bonds between the rubber and silica in ammonia. Dannenberg[14] discovered that the bound-rubber content in some SBR vulcanisates with 60 p.p.h.r. precipitated silica rose by roughly 40%, when 1.2 p.p.h.r. of a silane coupling agent was added. This was attributed to an improvement in filler-elastomer interaction by the silane. Other properties like tensile strength and modulus were also enhanced noticeably. Interestingly, elongation at break and hardness deteriorated as a result of the use of silane[14].

Mechanical and physical properties of elastomers are determined to a large extent by the density of crosslinks in them. Silicas influence the formation of crosslinks in rubbers during the curing process[16]. Polmanteer and co-worker[17] examined effects of crosslink density or network chain density as it was termed, on tensile strength and modulus of some silicone rubbers. They found that these properties increased significantly as a function of chain density. For instance, the tensile strength improved very rapidly with increase in chain density and reached a maximum. Thereafter, it decreased with increase in chain density. The modulus, however, rose progressively as the chain density reached a maximum. Since the modulus was dependent primarily on the network chain density, this result was expected. A similar study for silica/silane filled sulphur cured rubber vulcanisates will be of an interest.

The aim of this work was to examine how a progressively increasing amount of TESPT silane influenced the hardness, cohesive tear strength, cyclic fatigue life, tensile strength, elongation at break, and stored energy density at rupture of a sulphur-cured natural rubber vulcanisate containing 10 p.p.h.r. precipitated silica. We aimed mainly at optimising the silane in these compounds, and maximising the benefits of this additive to various properties. The idea was to improve the design of such mixes and control the costs of materials and processing.

THEORETICAL ASPECTS

Fracture mechanics started with the original work of Griffith[18], who proposed that a pre-existing crack of length c in a body under tension, having linear stress-strain relationships, extends if:

$$-de/dA > \gamma \qquad \ldots 1$$

where $-de/dA$ is the energy release rate and γ is the surface free energy.

Rivlin and Thomas[19] utilised the original theory of Griffith and proposed the energy balance criterion known as the fracture mechanics approach, for studying the tearing behaviour of highly elastic and non-linear rubbers.

The tearing energy T can be defined by the following expression:

$$T = -(\delta U/\delta A) \qquad \ldots 2$$

where U is the total elastic energy stored in the specimen, A is the area of one fracture surface of the crack, and the partial derivative indicates that the specimen is held at constant length, l, so that the external forces do not work. The tearing energy, T, can be calculated in terms of applied forces or deformation for various test-piece geometries. The tearing energy of a rubber is a measure of its tear strength, and is independent of the test piece geometry and hence can be considered to be an intrinsic property of the vulcanisate studied[19].

For trousers test-piece (*Figure 1*) the tearing energy is given by relation[20]:

$$T = 2F\lambda/\tau - wW \qquad \ldots 3$$

where F is the force applied to each leg, this is calculated from the tearing force *versus* cross-head separation trace and is the average force on the graph (*Figure 2*), t and w are the

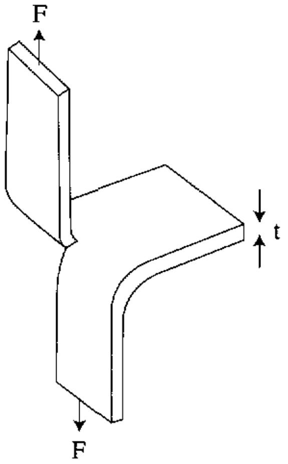

Figure 1. Trousers tear test piece.

test-piece thickness and width, respectively, W is the strain energy density in the legs and λ is the extension ratio ($\lambda = 1+ e$, where e is the maximum strain in the legs). When extension in the legs is ignored, *Equation 3* simplifies, since $\lambda \rightarrow 1$ and $W \rightarrow 0$, to:

$$T = 2F/t \qquad \dots 4$$

EXPERIMENTAL

Material

There were six conventional accelerator/sulphur compounds with a sulphur to accelerator ratio of 2.5 tested (*Table 1*). *Mix 1* had no silica and silane. Compounds 2–6, each contained 10 parts per hundred rubber by weight (p.p.h.r.) precipitated amorphous white silica-type Ultrasil VN3®, and also no silane, and 2.5, 5, 7.5, and 10 p.p.h.r. bis[3-triethoxysilylpropyl-]tetrasulphane (TESPT), respectively. This silane, also known as Si69® coupling agent, is a sulphur containing material and is suitable for use in sulphur cure system-based rubber compounds[4]. The silica was stored at 18°C and an ambient relative humidity of 76% for four weeks prior to use, and possessed a moisture content of ~ 5.7% by weight, a pH of 5.9, and an average particle size of about 19 nm. The rubber used was a Standard Malaysian Rubber grade 5L. In addition to the elastomer, silica and silane, some other ingredients were also added. These are listed in *Table1*.

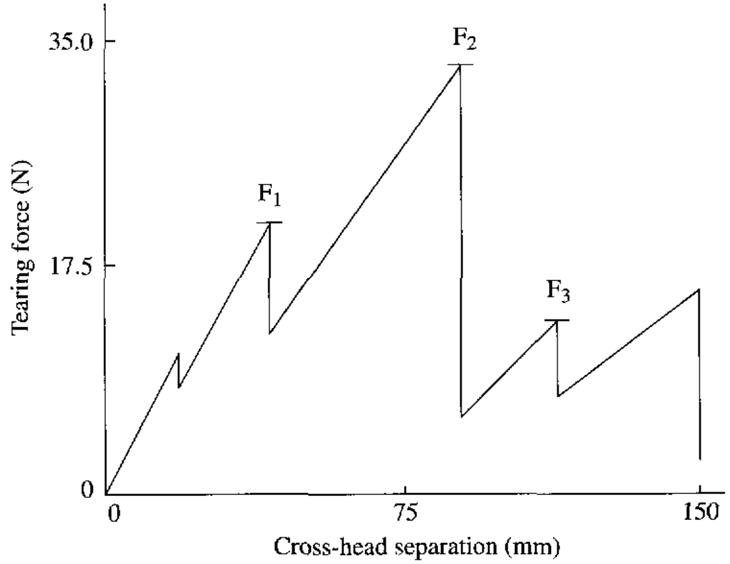

Figure 2. Typical record of tearing force as a function of cross-head separation. Data for the control compound; T=16 kJ/m2 and tear rate 0.67 mm/s.

TABLE 1. RECIPE AND MIXING CONDITIONS FOR THE COMPOUNDS

Formulation (p.p.h.r.)	Compound number					
	1[a]	2	3	4	5	6
	Stage one mixing					
Roll temperature, °C (Before mixing started)	41	51	46	42	38	41
Mastication time of the raw elastomer, (min) (Before the ingredients were added)	8	8	10	9	12	9
Natural rubber (SMR L)	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2
Santoflex 13® (Antidegradant)[b]	1	1	1	1	1	1
Silane (TESPT)[c]	0	0	2.5	5	7.5	10
Silica (Ultrasil-Type VN3®)[d]	0	10	10	10	10	10
Mixing time, (min)	14	24	31	35	16	20
Compound temperature, °C (After mixing ended)	68	66	56	58	66	69
Roll temperature, °C (After mixing ended)	65	68	51	49	67	72
	Stage two mixing					
Roll temperature (Before mixing re-started) °C	53	57	45	47	43	51
Compound temperature (°C) (Before mixing re-started)	32	34	32	36	32	31
Santocure® (CBS)[e]	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
Zinc oxide	5	5	5	5	5	5
Mixing time, (min)	12	12	18	9	12	9
Total mixing time, (min) (Stage 1 & 2)	26	36	49	44	28	29
Compound temperature, °C (After mixing ended)	60	66	61	56	60	66
Roll temperature, °C (After mixing ended)	62	64	54	56	62	67
Machine 1						
Friction ratio	1.8	1.8	1.8			
Front roll speed (Feet/min)	29.6	29.6	29.6			
Machine 2						
Friction ratio, (%)				1.5	1.5	1.5
Front roll speed				–	–	–

[a] Control compound

[b] N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

[c] bis[3-triethoxysilylpropyl-]tetrasulphane

[c,d] Supplied by Degussa AG, Germany

[e] N-cyclohexyl-2-benzothiazole sulphenamide

Mixing

Mixing was carried out in two stages on two Farrel Bridge 6" x 12". two-roll open swing side laboratory mills. This was, because the first mill broke down after the third compound was prepared. and a second mill had to be used to complete our preparations. Before mixing commenced. the raw elastomer was placed in an oven at 50°C for 20 min, to soften it prior to mastication on the mill. The rubber was then recovered and placed on the mill and masticated for up to 12 min before adding the ingredients.

In the first stage of mixing, stearic acid, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (Santoflex 13®) (antidegradant), and silane treated silica were added to the raw elastomer and mixed. It has been suggested[14] that an efficient method of using the silane is by pre-mixing with the filler before addition to the raw elastomer. Following this advice and before silica was added to the raw elastomer on the mill, it was mixed with the silane for approximately 6 min at ambient temperature (~ 23°C) in an electric blender. After mixing ended, the compound was removed from the mill, and its temperature measured with a thermocouple. The compound was subsequently left at ambient temperature to cool down to approximately 30°C–36°C, then the accelerator, sulphur and, lastly, zinc oxide were added. The accelerator was N-cyclohexyl-2-benzothiazole sulphenamide (Santocure CBS®). We allowed up to 12 min extra mixing time for incorporating these three additives. Finally, the compound was removed from the mill, and its temperature recorded. After mixing ended, the compounds were stored at 23°C for 48 h, before their cure properties were determined. and then cured to produce slabs for further work. Full details of the mixing procedure are given in *Table 1*.

Test-procedure

Properties of the uncured compounds. The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer according to the procedure described in a *British Standard*[21]. The scorch and optimum cure times were determined from the cure traces (*Figure 3*) generated at 160°C ± 2°C by oscillating disc rheometer curemeter (ODR) at an angular displacement of ±3°, and a frequency of 1.7 Hertz[22]. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using a method defined in a *British Standard*[23].

After these measurements were completed (*Table 2*), the compounds were cured at 160°C in a pressure and temperature controlled hydraulic press to form sheets, 9" x 9" in dimensions and approximately 2.8 mm thick, from which various samples for further tests were prepared.

Properties of the vulcanisates. For determining the hardness of the vulcanisates, cylindrical samples of rubber about 12 mm thick and 1" in diameter were prepared. The samples were then placed in a Shore A tester, and the hardness of the rubber was measured at ambient temperature (~ 23°C) over a 30-second interval after which a reading was taken[24]. This was repeated at three separate locations on the sample, and median of three readings was subsequently indicated[24] (*Table 3*). Results are also plotted in *Figure 4*.

The cyclic fatigue life of the rubbers was measured in uniaxial tension in a Hampden dynamic testing machine, using dumb-bell test pieces (*Figure 5*). These test pieces were die-stamped from the sheets of vulcanised rubber. The tests were performed at a constant maximum deflection of 100%, and a test frequency of 1.42 Hz. The test temperature was about 23°C, and the strain on each

TABLE 2. RESULTS FROM THE MOONEY VISCOSITY MEASUREMENTS, AND THE ODR TESTS CARRIED OUT AT 160°C

Compound numbers	1[a]	2	3	4	5	6
Mooney viscosity, ML(1+4) at 100°C	37	60	35	34	35	37
ODR Results						
Minimum torque (dN.m)	11	17	9	9	9	9
Maximum torque (dN.m)	68	72	69	68	62	61
Scorch time, t_{s2} (min)	5.4	6.1	5.2	4.3	4.4	4.2
Optimum cure time, t_{95} (min)	10.6	12.7	10.6	10.3	10.4	10.5
Cure rate index (min^{-1})	19.2	15.2	18.5	17	17	15.9

[a] Control compound

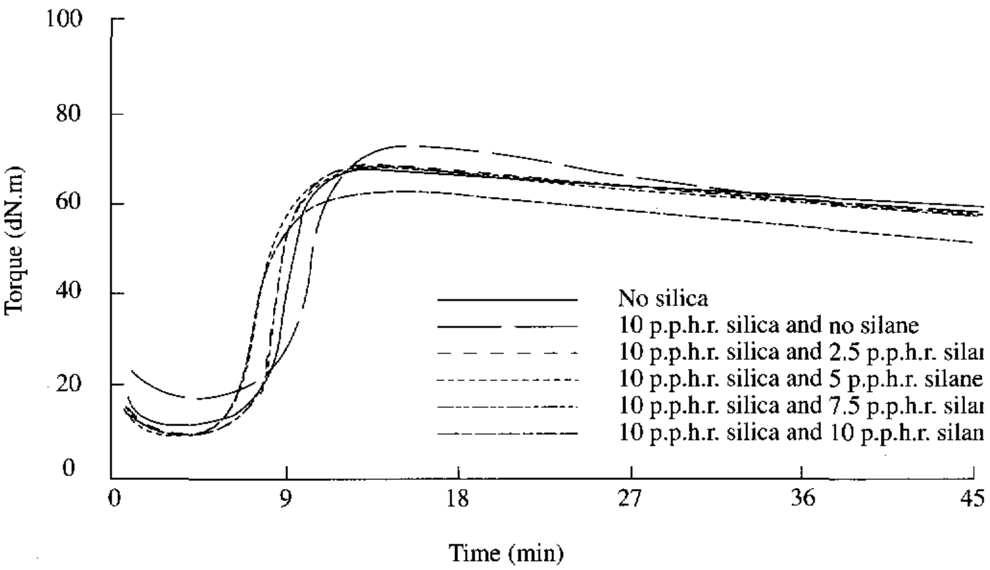

Figure 3. Torque versus *time traces by ODR at 160°C for the six compounds tested.*

TABLE 3 HARDNESS VALUES OF THE VULCANISATES TESTED

Compound numbers	1[a]	2	3	4	5	6
	Hardness (Shore A)					
Reading						
1	38 0	34 5	33 5	40 5	43 5	43 5
2	38 5	35 0	34 5	41 0	44 0	45 0
3	39 5	36 0	35 0	41 5	44 5	46 5
Median values	38 5	35 0	34 5	41 0	44 0	45 0

[a] Control compound

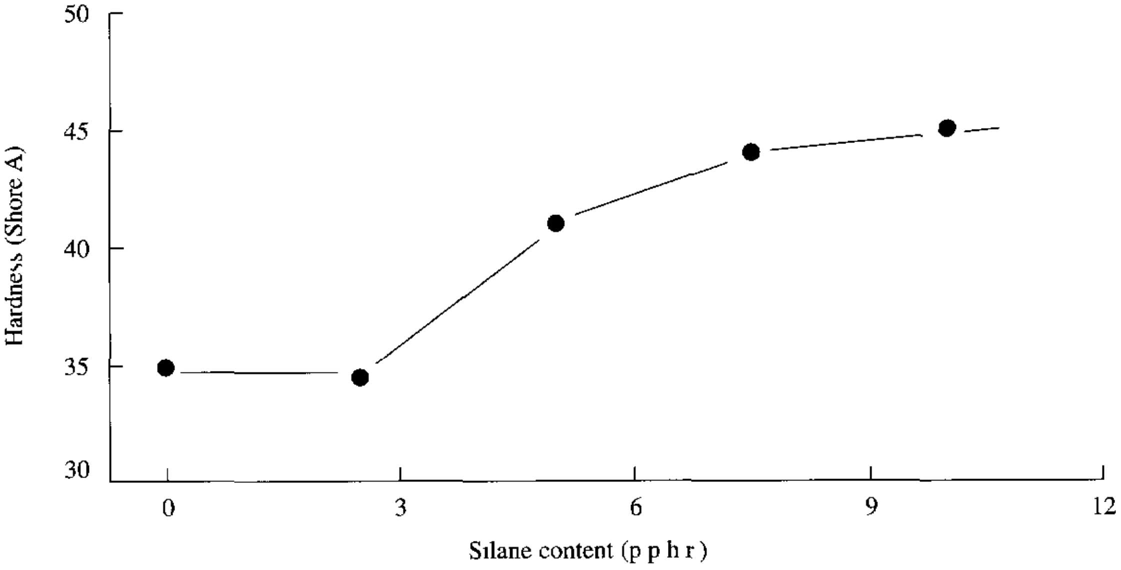

Figure 4 Hardness (Shore A) as a function of silance content

test piece was relaxed to zero at the end of each cycle. For each rubber, 12 test pieces were cycled to failure and median of the twelve readings was determined (*Table 4*). Results are likewise shown in *Figure 6*.

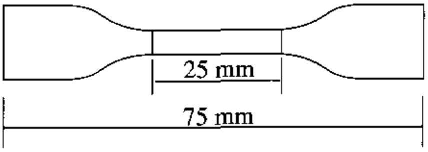

Figure 5. Dumb-bell test piece for cyclic fatigue life tests.

Rectangular strips, 100 mm long and 30 mm wide, were cut from the vulcanised sheets 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 1*, 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 in a Lloyd mechanical testing machine. In these experiments, the minimum and maximum cross-head speeds of the machine at 2 and 1000 mm/min, equivalent to about 0.017 and 8.33 mm/s, respectively, were utilised for tearing the rubber. The tear rate was measured from one half of the cross-head speed of the testing machine. For example, a cross-head speed of 120 mm/min was equivalent to 120/60 or 2 mm/s. This number was divided by 2, since a trousers test piece has two legs (*Figure 1*), to calculate a nominal tear rate of 1 mm/s. The tear produced in the rubber after

TABLE 4. CYCLIC FATIGUE LIFE TEST RESULTS

Compound numbers	1[a]	2	3	4	5	6
Sample number			Cyclic fatigue life (kc)			
1	79.4	105.9	88.0	74.0	91.7	109.4
2	112.9	107.7	106.1	82.1	114.1	117.0
3	113.0	116.5	113.8	82.6	125.9	120.3
4	118.8	125.6	117.0	87.5	135.7	122.4
5	128.5	136.4	120.1	92.0	173.7	125.8
6	131.6	151.6	128.4	99.2	174.9	144.9
7	138.8	154.8	137.6	105.4	177.3	149.4
8	139.7	170.8	138.3	107.0	186.2	152.8
9	154.0	183.8	156.6	111.7	200.8	180.9
10	154.6	194.9	176.6	118.8	221.7	189.8
11	157.6	232.6	184.6	130.1	248.0	217.8
12	192.2	337.0	207.7	132.0	309.7	226.7
Median values	135.2	153.2	133.0	102.3	176.1	147.2
Standard deviation	27.3	62.7	33.9	18.2	58.3	38.5

[a] Control compound

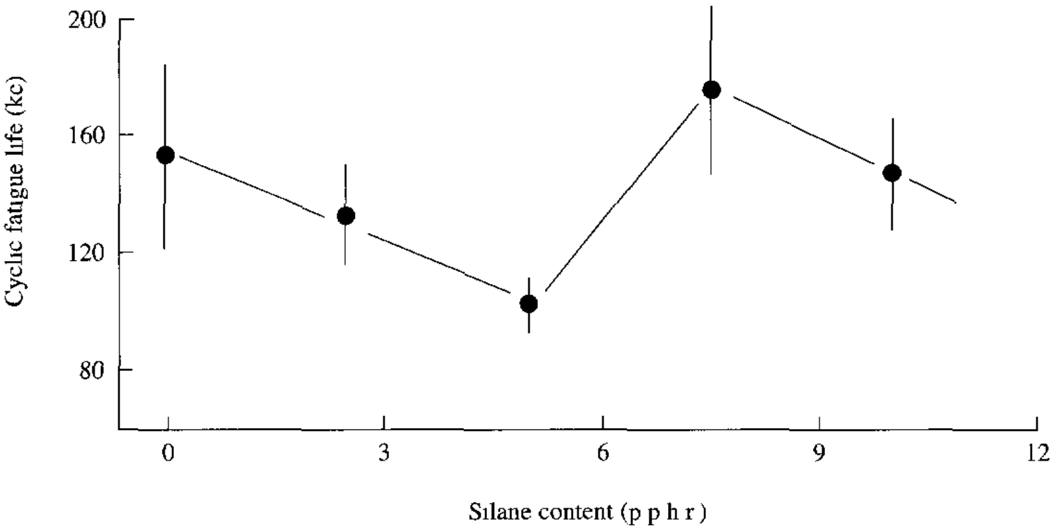

Figure 6 Cyclic fatigue life as a function of silane content (The vertical bars indicate standard deviations)

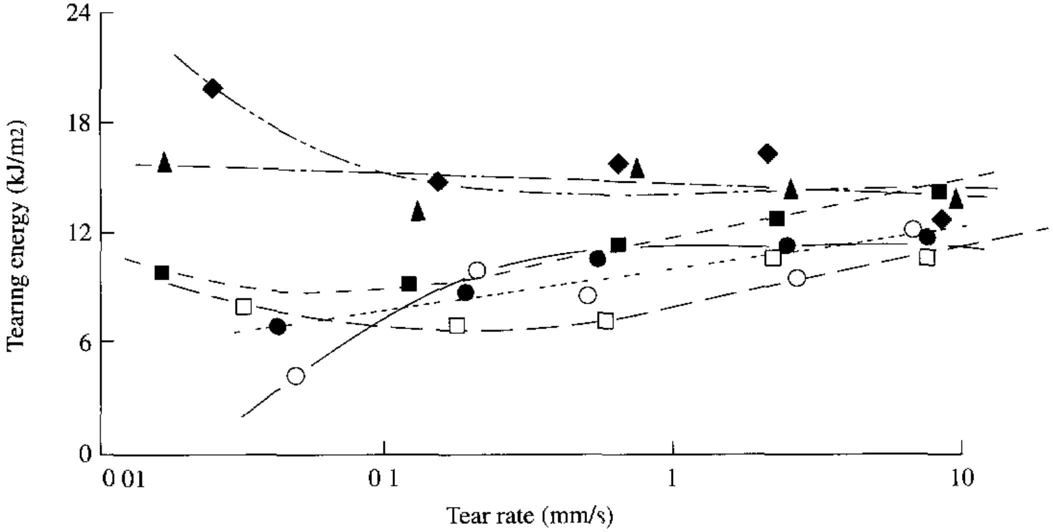

Figure 7 Tearing energy versus *tear rate. (▲) Control compound Rubber with 10 p p h r silica (◆) No silane, (■) 2.5 p p h r silane, (□) 5 p.p h r silane, (●) 7 p p h r silane, (○) 10 p p h r silane*

TABLE 5. DETAILS OF THE TEAR TESTS AND TEAR BEHAVIOUR OF THE VULCANISATES TESTED

Vulcanisate	Tear rate (mm/s)	Tearing energy (kJ/m^2)	Tear path	Tear length (mm) after test piece was fractured
Control compound	0.017	16	Non-linear	25
	0.13	13	Linear	50
	0.67	16	Linear	55
	2.5	15	Non-linear	30
	8.3	14	Linear	48
Compound 2	0.025	20	Non-linear	32
	0.15	15	Non-linear	30
	0.63	16	Non-linear	35
	2.08	17	Non-linear	50
	8.3	13	Linear	35
Compound 3	0.017	10	Non-linear	25
	0.12	9	Non-linear	45
	0.64	11.5	Non-linear	40
	2.25	13	Linear	75
	8.08	14.5	Non-linear	40
Compound 3	0.033	8	Non-linear	48
	0.18	7	Linear	60
	0.58	7	Non-linear	25
	2.25	11	Linear	60
	7.5	11	Linear	60
Compound 4	0.042	7	Non-linear	25
	0.19	9	Non-linear	20
	0.54	11	Non-linear	25
	2.4	11	Non-linear	45
	7.08	12	Linear	75
Compound 5	0.05	4	Non-linear	20
	0.21	10	Non-linear	15
	0.5	9	Non-linear	25
	2.67	10	Linear	65
	6.67	12	Non-linear	20

Definitions:

Linear: Crack grew along the lenght of the test piece

Non-linear: Crack turned towards the edges of the test piece during propagation.

TABLE 6. TENSILE STRENGTH, ELONGATION AT BREAK AND STORED ENERGY DENSITY AT RUPTURE OF THE VULCANISATES

Compound numbers	1[a]	2	3	4	5	6
	Tensile Strength (MPa)					
Sample number						
1	27.2	21.1	23.9	24.3	27.1	26.7
2	28.5	22.7	28.7	25.8	28.7	31.4
3	29.8	24.5	30.5	25.9	30.4	31.4
Median values	28.5	22.7	28.7	25.8	28.7	31.4
	Elongation at break (%)					
Sample number						
1	1530	1346	1275	1173	1302	1231
2	1598	1391	1286	1243	1315	1288
3	1677	1429	1399	1373	1404	1303
Median values	1598	1391	1286	1243	1315	1288
	Stored energy density at rupture (MJ/m^3)					
Sample number						
1	128	95	110	107	114	106
2	130	100	120	108	134	126
3	143	112	132	126	134	132
Median values	130	100	120	108	134	126

[a]Control compound

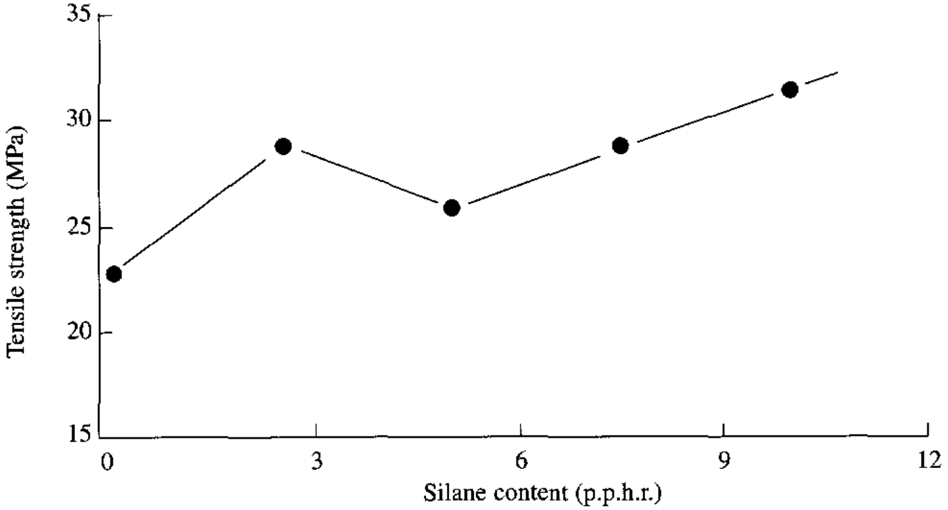

Figure 8. Tensile strength as a function of silane content.

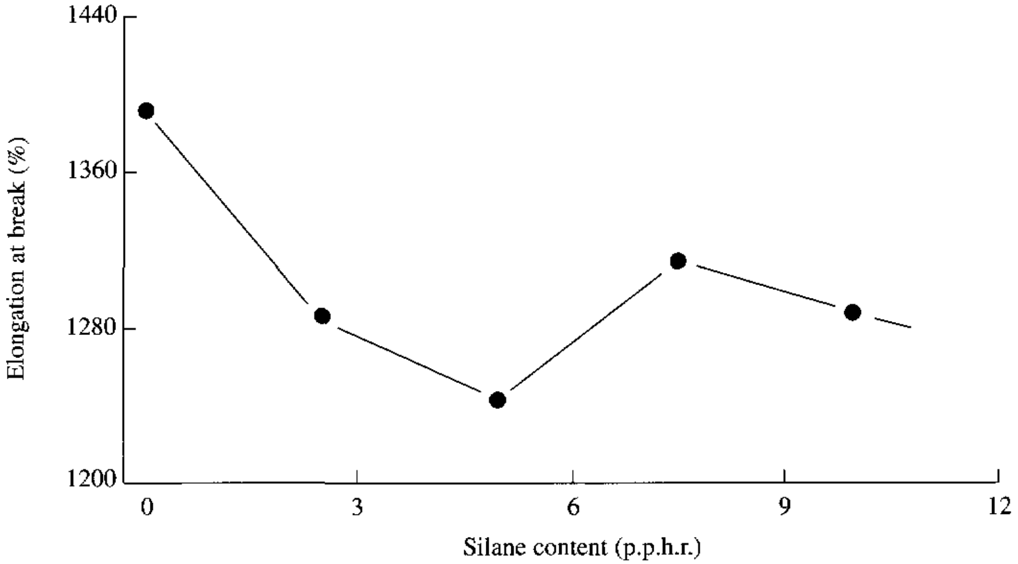

Figure 9. Elongation at break as a function of silane content.

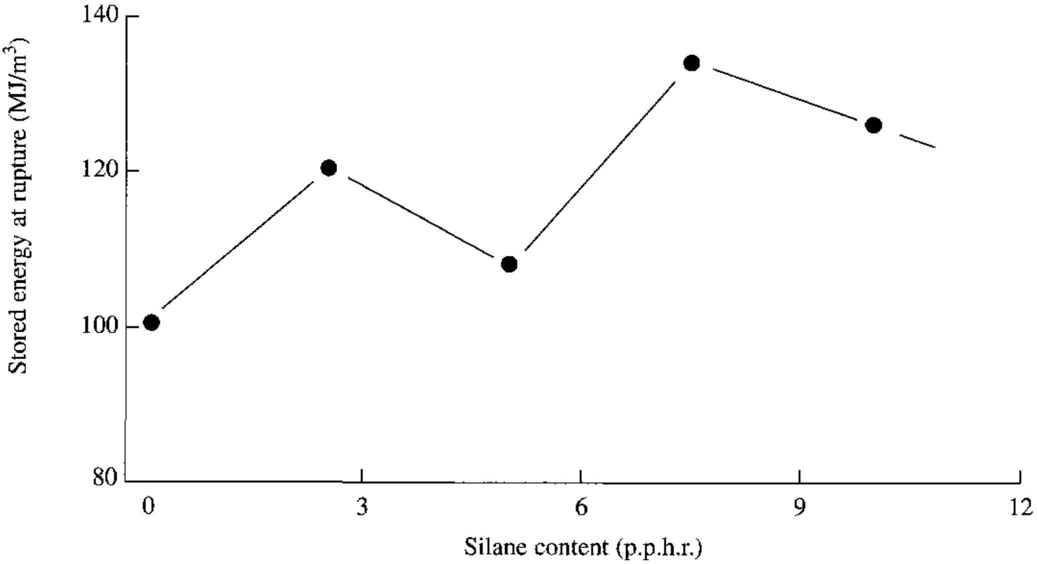

Figure 10. Stored energy at rupture as a function of silane content.

the test pieces were fractured varied from approximately 15 mm to 75 mm (*Table 5*). In each experiment, the tearing force was recorded on a chart on a linear-linear axis to produce a trace from which an average force was measured (*Figure 2*). The first peaks corresponding to the onset of crack-growth, where the tearing force was still rising, and the last peak corresponding to when test stopped or leg break occurred, were ignored. The remaining peaks on the trace were utilised for calculating an average tearing force for the rubber (*Figure 2*). After these measurements were completed, and following the procedure described previously[18], extension in the legs of trousers test pieces was ignored and force values were placed in *Equation 4* to calculate tearing energies for the vucanisates. Two test pieces were fractured at each cross-head speed to calculate a tearing force for the rubber. The tearing energies were subsequently plotted against nominal tear rate on logarithmic scales to produce energy *versus* tear rate profile (*Figure 7*). Full details of the tear tests are given in *Table 5*.

The tensile stress, elongation at break, and stored energy density at rupture of the vulcanisates were determined in uniaxial tension, likewise in a Lloyd mechanical testing machine, using dumb-bell test-pieces (*Figure 5*). 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[25]. A Lloyd DAPMAT computer software was utilised for storing and processing the data (*Table 6*). Results are also presented in a graphical form in *Figures 8–10*.

RESULTS AND DISCUSSION

Figure 4 shows hardness (Shore A) as a function of silane content. The hardness of the rubber with 10 p.p.h.r. silica and no silane is 35 Shore A. The addition of 2.5 p.p.h.r. silane offers no benefit to this property, which remains essentially unchanged at about 35 Shore A. However, the hardness increases progressively from 35 to 45 Shore A, when the loading of silane is raised by an extra 7.5 p.p.h.r. to 10 p.p.h.r. Notably, the inclusion of silane helps the hardness to improve.

Results from the cyclic fatigue life tests as a function of silane content are shown in *Figure 6*. The fatigue life of the vulcanisate shows a substantial decrease from ~153 kc to about 102 kc, when the loading of silane is increased to 5 p.p.h.r. Mixing 7 p.p.h.r. TESPT, helps to lengthen the life to ~ 176 kc, an increase of about 74 kc. This trend reverses when the amount of silane is raised by an extra 3 p.p.h.r. to 10 p.p.h.r. The life shortens noticeably to about 147 kc as a result of this change in the loading of silane.

The tearing energy *versus* tear rate result is presented on logarithmic scales in *Figure 7*. The tear strength of the rubber with no silane and silica deteriorates slightly as a function of tear rate, and the tearing energy decreases from 16 at 0.017 kJ/m^2 to 14 kJ/m^2 at 8.3 mm/s. Similarly, the tearing energy of the vulcanisate with 10 p.p.h.r. silica and no silane reduces from 20 kJ/m^2 to about 13 kJ/m^2 as the tear rate increases from 0.025 mm/s to 8.3 mm/s, respectively. Evidently, the incorporation of 10 p.p.h.r. silica helps to enhance the tear strength of the rubber only at the lowest tear rate, 0.025 mm/s, and no further improvement is observed as the rate increases to its highest, 8.3 mm/s. The tear strength of the rubber with silica is lowered when 2.5 p.p.h.r. silane is introduced, and the tearing energy drops to 10 kJ/m2 at 0.017 mm/s. However, this property improves to about 14.5 kJ/m^2 when the tear rate extends to ~ 8 mm/s. When the loading of silane is raised by an extra 7.5 p.p.h.r. to 10 p.p.h.r., there is no additional benefit and the tear strength remains essentially unchanged For example, the tearing energies measured for the vulcanisates with 5, 7 5 and 10 p p h r silane enhance from ~7 kJ/m^2 to 12 kJ/m^2 as the tear rate increases from 0 033 mm/s to 7 5 mm/s It is noteworthy that the tearing energy of the rubber with 10 p p h r silane is about 4 kJ/m^2 at 0 05 mm/s This is the lowest energy measured in these tests

Figures 8–10 show tensile strength, elongation at break and stored energy at rupture as a function of silane content, respectively The tensile strength improves from ~ 23 MPa to 29 MPa when 2 5 p p h r silane is included in the rubber (*Figure 8*) However, when the loading of silane is raised to 5 p p h r, this property reduces to about 26 MPa It is interesting that as the amount of silane is boosted to 10 p p h r, tensile strength improves gradually to reach 31 MPa Elongation at break decreases from 1391% to 1243% when up to 5 p p h r silane is present in the vulcanisate (*Figure 9*) Though, this property enhances to about 1315% after the loading of silane is raised to 7 5 p p h r, but deteriorates thereafter to 1288% as silane increases to 10 p p h r Likewise, stored energy improves from 100 MJ/m^3 to 120 MJ/m^3 and subsequently diminishes to 108 MJ/m^3 when 2 5 p p h r and 5 p p h r silane is added, respectively (*Figure 10*) Further increases in silane to 7 5 p p h r helps to maximise the stored energy to 134 MJ/m^3 however this property deteriorates to about 126 MJ/m^3 when 10 p p h r silane is included in the rubber

To the best of the authors' knowledge, there is little or no work done to measure the bound rubber content and crosslink density of sulphur-cured natural rubber vulcanisates with silica and silane, like the ones used in this study We will measure the bound-rubber content and crosslink density of our samples The idea is to examine how the properties reported in this study may depend on these two measurements This will help to shed light on some of the mechanisms of reinforcement by silica and silane in these rubbers and the interpretation of our results These results will be reported in due course

CONCLUSIONS

This study has shown that when up to 10 p p h r TESPT silane is added to a conventional accelerator/sulphur compound of natural rubber with a sulphur to accelerator ratio of 2 5, containing 10 p p h r precipitated amorphous white silica type Ultrasil VN3®, the physical and mechanical properties of the vulcanisate are not affected in the same way We have learnt that

- The Hardness of the rubber improves from about 35 to 45 Shore A with 10 p p h r TESPT silane per 10 p p h r silica
- The cyclic fatigue life and stored energy at rupture optimise to ~176 kc and 134 MJ/m^3 from ~153 and 100 respectively, after 7 5 p p h r TESPT silane per 10 p p h r silica is added However, there is a large scatter in the cyclic fatigue test results
- The tensile strength increases from ~ 23 to 31 5 MN/m^2 when 10 p p h r TESPT silane per 10 p p h r silica is incorporated in the rubber
- The cohesive tear strength and elongation at break of the vulcanisate deteriorate as a result of introducing the silane into the formulation

In summary, we may optimise some properties of the vulcanisate by adding 7 5 p p h r and 10 p p h r TEPST silane per 10 p p h r silica This helps to control the costs of raw materials and processing, and will also enhance the design of such rubbers However it must be mentioned that some attributes may deteriorate as a result of mixing the silane in the rubber

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