

Enhancing the Mechanical Properties of Styrene–Butadiene Rubber by Optimizing the Chemical Bonding Between Silanized Silica Nanofiller and the Rubber

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ABSTRACT: The reinforcing effect of a large amount of synthetic precipitated amorphous white silica nanofiller on the mechanical properties of styrene–butadiene rubber was studied. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl)tetrasulfane (TESPT). TESPT is a bifunctional organosilane that chemically adheres silica to rubber and also prevents silica from interfering with the reaction mechanism of sulfur cure in the rubber. The silica particles were fully dispersed in the rubber and the chemical bonding between the rubber and filler was optimized by the

incorporation of accelerator and activator in the rubber. This study showed that the mechanical properties of the rubber vulcanizate improved substantially when the filler was added. The addition of elemental sulfur affected the rubber properties, although there was no overall advantage, as some properties improved and others deteriorated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 322–332, 2007

Key words: crosslinking; dispersions; elastomers; mechanical properties; silicas

INTRODUCTION

Typical rubber compounds used to manufacture industrial rubber products such as off-road tire treads contain several chemical additives. They include fillers, curing agents, antidegradants, and processing oil.¹ Reinforcing fillers have by far the largest effect on the mechanical properties of rubber vulcanizates. Since the discovery of their reinforcing qualities almost 100 years ago, colloidal carbon blacks have been used extensively in rubber compounds.^{2,3} Other fillers, for example, synthetic silicas, have also proved to be beneficial to the properties of rubber compounds.

The surfaces of silicas possess siloxane and silanol groups⁴ [Scheme 1(a)], which make the filler acidic⁵ and moisture adsorbing.⁶ This causes unacceptably long cure times and slow cure rates⁴ and also a loss of

crosslink density⁷ in sulfur-cured rubbers. Bifunctional organosilanes such as bis(3-triethoxysilylpropyl)tetrasulfane [TESPT; Scheme 1(b)] can be used as primers for treating silica surfaces (Scheme 2) to improve the reinforcing capability of the filler and also form an integral part of curing systems to enhance crosslinking network properties.⁴ This silane possesses tetrasulfane and ethoxy reactive groups.

The tetrasulfane groups are rubber reactive and react in the presence of accelerators at elevated temperatures, with or without the presence of elemental sulfur, to form crosslinks in unsaturated rubbers, for instance, styrene–butadiene rubber (SBR). The ethoxy groups react with the silanol groups on the surfaces of these fillers during compounding, and this leads to the formation of stable covalent filler–TESPT bonds. In addition, the TESPT reaction with silanol groups reduces their numbers, and the remaining groups become less accessible to the rubber chains because of steric hindrance. The fewer, less accessible silanol groups that remain weaken the strong interactions between silica particles.⁴

These changes help to reduce the viscosity of rubber compounds and also improve cure characteristics by preventing acidic silicas from interfering with the reaction mechanism of sulfur-cured rubbers.^{4,8}

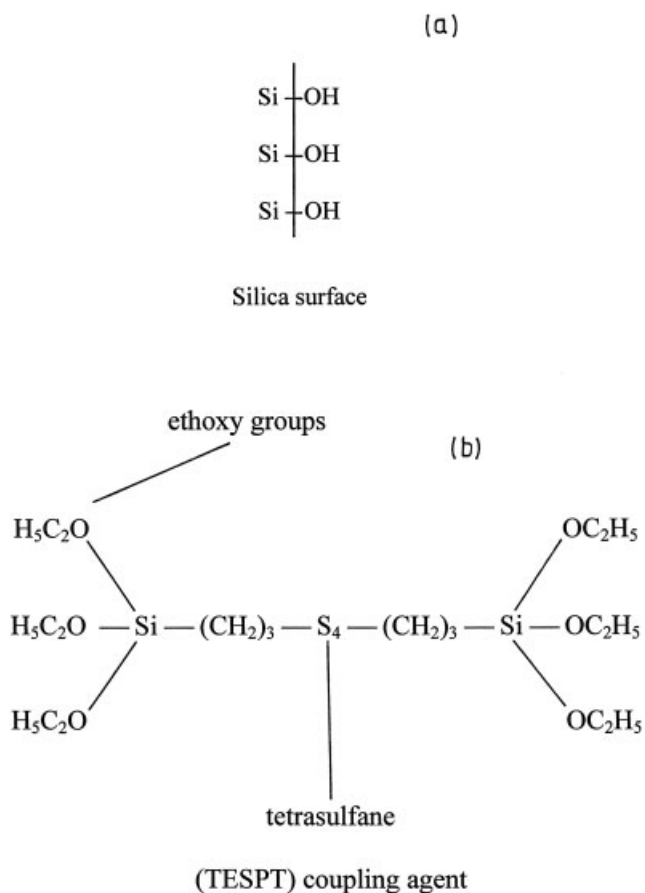
The reinforcement of elastomers by particulate solids has been the subject of numerous studies, and it is generally acknowledged that reinforcement is, to a large degree, due to filler–elastomer adhesion and

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Scheme 1 (a) Silica surface with hydroxyl groups. (b) Chemical structure of TESPT.

filler–filler interaction.⁹ The quality of filler dispersion and types and density of crosslinks also influence the properties of rubber vulcanizates. When fillers are well dispersed in the rubber, the properties, for example, tensile strength and tear strength, improve.¹⁰ Attributes such as resilience, tensile strength, and energy at break are noticeably enhanced in some sulfur-cured rubbers as crosslink density increases.¹¹

Rubber–filler interaction plays a major role in rubber reinforcement. The measurement of bound rubber is a practical means of evaluating the extent of rubber–filler adhesion. The formation of bound rubber increases with factors such as temperature, time, and surface activity of the filler.² Bound rubber is the rubber portion that cannot be separated from the filler when the rubber compound is extracted with a solvent (often toluene) in which the rubber is readily soluble. This is called a coherent gel and includes solvent, the solid filler, and (bound) higher molecular chains. The measurement of bound rubber is usually carried out at ambient temperature and over many days. Wolff⁷ compared the bound-rubber content of some silica-filled SBR vulcanizates in an ammonia atmosphere and showed that this property decreased by approximately 85%. This was due to the splitting of the adsorptive bonds between the rubber and silica

in ammonia. Dannenberg³ discovered that the bound-rubber content in some SBR vulcanizates with 60 parts per hundred rubber by weight (phr) precipitated silica rose by approximately 46% when 1.2 phr of a thiosilane coupling agent was added. This was attributed to an improvement in filler–elastomer adhesion by the silane. Other properties, such as tensile strength and 300% modulus, were also enhanced, but elongation at break and hardness deteriorated as a result of the use of silane.

The aim of this study was to use 60 phr precipitated amorphous white silica nanofiller pretreated with TESPT to reinforce the mechanical properties of SBR. The degree of dispersion of the filler in the rubber was examined by electron microscopy, and the information was used to select a suitable mixing time for preparing the compounds. The effect of elemental sulfur on the cure behavior and mechanical properties of the rubber was also assessed.

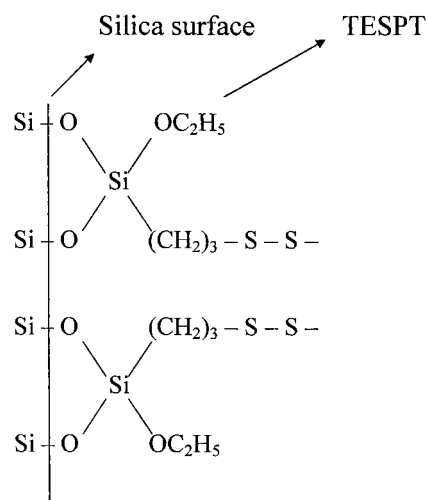
EXPERIMENTAL

Materials: Rubber and filler

The raw elastomer used was SBR (23.5 wt % styrene; Intol 1712, Enichem). The reinforcing filler was Coupsil 8113 (Degussa, Ltd., Frankfurt, Germany). Coupsil 8113 was precipitated amorphous white silica-type Ultrasil VN3, the surfaces of which were pretreated with TESPT. It had 11.3 wt % TESPT, 2.5 wt % sulfur (included in TESPT), a 175-m²/g surface area (as measured by N₂ adsorption), and a 20–54 nm particle size.

Curing chemicals, antidegradants, and processing oil

In addition to the raw elastomer and filler, the other ingredients were *N-t*-butyl-2-benzothiazole sulfenamide (Santocure TBBS, Woluwe, Belgium; a safe-proc-



Scheme 2 TESPT-treated silica surface.

TABLE I
Mixing Conditions for the Rubber and Silica Nanofiller

	Compound						
	1	2	3	4	5	6	7
Formulation (phr)							
SBR	100	100	100	100	100	100	100
Silica	60	60	60	60	60	60	60
Mixing time (min)	4	7	10	13	16	19	22

The rubber compound temperature increased from 50 to 62°C during mixing. The raw elastomer had a viscosity of 54 Mooney units before it was mixed.

essing delayed action accelerator), zinc oxide (activator), sulfur (curing agent), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (Santoflex 13, Brussels, Germany; antidegradant), and heavy paraffinic distillate solvent extract aromatic processing oil (Enerflex 74, Milton Keynes, UK). The oil was added to reduce the rubber viscosity. The cure system consisted of TBBS, zinc oxide, and elemental sulfur. TBBS and zinc oxide were added to optimize the chemical bonding or crosslinks between the rubber and filler. In total, 31 compounds were prepared for this study.

Mixing

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at ambient temperature (~23°C), and the rotor speed was 45 rpm. The volume of the mixing chamber was 78 cm³, and it was half full. Haake Software Version 1.9.1 was used to control the mixing conditions and to store data.

Assessment of the silica dispersion in the rubber

To select a suitable mixing time for incorporating the filler in the rubber, seven compounds were prepared (compounds 1–7; Table I). Before mixing was started, the ram was raised to introduce the filler into the mixing chamber, and then, the raw elastomer was added.

The filler was added when the viscosity of the rubber was still relatively high, which led to improved dispersion.¹² The ram was lowered to keep the rubber in the mixing chamber during mixing. Following the previous findings,¹³ we increased the mixing time from 4 to 22 min to disperse the silica particles fully in the rubber. The temperature of the rubber compounds during mixing was 50–62°C. Twenty-four hours after the mixing ended, the rubbers were examined in a scanning electron microscope to assess the filler dispersion.

Dispersion of the silica particles in the rubber was assessed by a LEO 1530 V P field emission gun scanning electron microscope (Carl Zeiss SMT, Ltd., Cambridge, UK). Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and were then fractured to create two fresh surfaces. The samples, 60 mm² in area and 5 mm thick, were coated with gold and then examined and photographed in the scanning electron microscope. The degree of dispersion of the silica particles in the rubber was subsequently studied from scanning electron microscopy (SEM) photographs. After the SEM photos were examined, a total mixing time of 10 min was considered for the addition of the filler and curing chemicals to the rubber.

Selection of TBBS

To activate the rubber reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the rubber was increased progressively to 9 phr to measure the amount needed to optimize the chemical bonding between the rubber and TESPT and to increase the crosslink density in the rubber. The formation of crosslinks strengthened the rubber–TESPT interaction.⁴ In total, seven compounds were prepared (compounds 8–14; Table II).

Selection of zinc oxide

The loading of zinc oxide in the filled rubber with TBBS was raised to 2.5 phr to determine the amount

TABLE II
Formulations and Mixing Conditions for the Rubbers with Silica and TBBS

	Compound						
	8	9	10	11	12	13	14
Formulation (phr)							
SBR	100	100	100	100	100	100	100
Silica	60	60	60	60	60	60	60
TBBS	0.5	1.5	3.0	4.5	6.0	7.5	9.0
ODR results							
Minimum torque (dN m)	26	27	22	21	18	18	17
Maximum torque (dN m)	34	43	44	46	43	47	43
Atorque (dN m)	8	16	22	25	25	29	26

The compound temperature rose to 56–61°C during mixing.

TABLE III
Formulations and Mixing Conditions for the Rubbers with Silica, TBBS, and Zinc Oxide

	Compound						
	15	16	17	18	19	20	21
Formulation (phr)							
SBR	100	100	100	100	100	100	100
Silica	60	60	60	60	60	60	60
TBBS	3	3	3	3	3	3	3
Zinc oxide	0	0.3	0.5	1.0	1.5	2.0	2.5
ODR results							
Minimum torque (dN m)	22	26	24	22	20	18	19
Maximum torque (dN m)	44	69	81	85	82	80	83
Δ torque (dN m)	22	43	57	63	62	62	64

The compound temperature rose to 56–61°C during mixing.

needed to maximize the efficiency of TBBS and cure. In total, seven compounds were made (compounds 15–21; Table III).

Selection of elemental sulfur for the curing of the filled rubber

To evaluate the effect of elemental sulfur on the cure properties of the filled rubber with TBBS and zinc oxide, six compounds were prepared. The loading of sulfur in the rubber was increased to 2.5 phr (compounds 22–27; Table IV).

After these measurements were completed, four compounds were prepared for further tests (compounds 28–31; Table V). The control compound was made last. The compounds also contained antidegradant (Santoflex 13) and processing oil (Enerflex 74). To prepare compounds 8–31 (Tables II–V), TBBS, zinc oxide, and sulfur were added 4 min after the filler and rubber were mixed together, and mixing continued subsequently for an extra 6 min before the rubber compound was removed from the mixer. The temperature of the rubber compounds during mixing was 56–63°C.

Finally, when the mixing ended, the rubber was recovered from the mixer and milled to a thickness

of about 6 mm for further work. The compounds were kept at ambient temperature (~23°C) for at least 24 h before their viscosity and cure properties were measured.

Curing properties of the rubber compounds

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to British Standard 1673.¹⁴ The viscosity of the rubber filled with silica was also measured at 130°C and plotted against mixing time to assess the effect of prolonged mixing on the rubber viscosity. The 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 from the cure traces generated at $140 \pm 2^\circ\text{C}$ by an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of $\pm 3^\circ$ and a test frequency of 1.7 Hz.¹⁵ The cure rate index, which is a measure of the rate of cure in the rubber, was calculated with the method described in British Standard 903.¹⁶ The rheometer tests ran for up to 2.5 h. The

TABLE IV
Formulations for the Rubbers with TBBS, Zinc Oxide, and Sulfur

	Compound					
	22	23	24	25	26	27
Formulation (phr)						
SBR	100	100	100	100	100	100
Silica	60	60	60	60	60	60
TBBS	3	3	3	3	3	3
Zinc oxide	0.5	0.5	0.5	0.5	0.5	0.5
Elemental sulfur	0	0.2	0.7	1.3	2.0	2.5
ODR results						
Minimum torque (dN m)	24	23	22	23	22	23
Maximum torque (dN m)	81	80	97	106	116	121
Δ torque (dN m)	57	57	75	83	94	98

The compound temperature rose to 57–63°C during mixing.

TABLE V
Formulations, Mooney Viscosity, and Cure Properties of the Rubbers

	Compound			
	28 ^a	29	30	31
Formulation (phr)				
SBR	100	100	100	100
Silanized silica	—	60	60	60
TBBS	3	3	3	3
Zinc oxide	0.5	0.5	0.5	0.5
Elemental sulfur	0.7	0.7	0.2	—
Santoflex 13	1	1	1	1
Processing oil	5	5	5	5
Mooney viscosity				
ML (1+4) at 100°C	32	95	76	71
ODR results				
Minimum torque (dN m)	7	19	19	18
Maximum torque (dN m)	35	80	69	56
Δ torque (dN m)	28	61	50	38
t_{s2} (min)	37	12	13	16
t_{95} (min)	75	38	57	80
Cure rate index (min ⁻¹)	2.6	3.9	2.3	1.6

28^a was the control compound.

cure traces of the compounds that were subsequently used in this study are shown in Figure 1. Results from these experiments are also summarized in Tables II–V.

Test pieces and test procedure

After these measurements were completed, the rubber compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. Pieces of rubber, each approximately 140 g in weight, were cut from the milled sheet. Each piece was placed in the center of the mold to enable it to flow in all directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubber, sheets 23 cm by 23 cm by approximately 2.4 mm thick were used, from which various samples for further tests were cut.

Bound-rubber and crosslink density measurements

The solvent used for the bound-rubber and crosslink density determination was toluene. For the determination, 8 g (control compound) and 10 g (filled compound) of the rubber compounds were cured in a compression mold to produce cylindrical samples 28 mm in diameter and 12 mm in height. The samples were then placed individually in 275 mL of the solvent in labeled bottles and allowed to swell for 16 days at 21°C. The weight of the samples was measured every day until it reached equilibrium. It took approximately 8 days for the control compound and 5 days for the filled compounds to reach equilibrium. The solvent was removed after this time elapsed, and the samples were dried in air for 9 h. The samples

were subsequently dried in an oven at 85°C for 24 h and allowed to stand for an extra 24 h at 23°C before they were reweighed. The bound rubber and crosslink density were then calculated with expressions from refs. 8, 17, and 18 (Table VI).

Hardness

For measuring the hardness of the rubbers, cylindrical samples 12 mm thick and 28 mm in diameter were used. The samples were then placed in a Shore A durometer hardness tester (The Shore Instrument & MFG, Co., New York), and the hardness of the rubber was measured at 20°C over a 15-s interval, after which a reading was taken. This was repeated at three different positions on the sample, and the median of the three readings was calculated¹⁹ (Table VI).

Cyclic fatigue life

The cyclic fatigue life of the rubbers (number of cycles recorded before the samples fractured) was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK), with dumbbell test pieces 75 mm long with a central neck 25 mm long and 3.6 mm wide. 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.²⁰ The test temperature was about 21.5°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 the tests were stopped whenever the fatigue life exceeded 1000 kilocycles (kc). The results are presented in Table VII.

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 halfway along the width and parallel to the length of the strip to form the trouser test pieces for the tear experiments. The tear tests

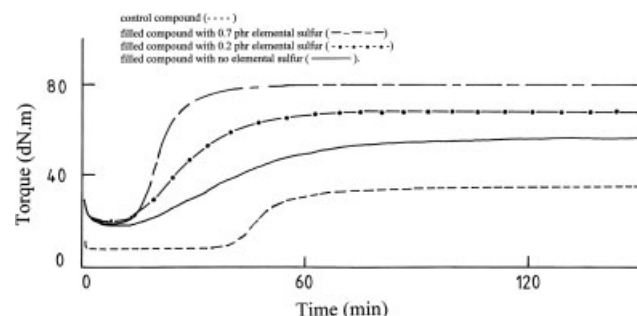


Figure 1 Torque versus time traces by ODR for the rubbers: (---) control compound 28^a, (---) compound 29, (—●—●—) compound 30, and (—) compound 31.

TABLE VI
Crosslink Density, Bound Rubber, and Mechanical Properties of the Rubber Vulcanizates

	Compound			
	28 ^a	29	30	31
Hardness (Shore A)	31	67.5	65	62.5
Tensile strength (MPa)	1.4	25.4	28.3	26.4
Elongation at break (%)	603	945	1060	1308
Stored energy density at break (MJ/m ³)	4	98	132	140
Stored energy density at 100% strain amplitude (MJ/m ³)	0.4	1.7	1.6	1.3
T (kJ/m ²)	2.9	27	37	75
Range of values	2.7–3.1	25–33	34–40	71–89
Bound rubber (%) ⁸	—	65	65	64
Crosslink density $\times 10^{-3}$ (N)	13	32	24	19
Δv (mm ³ /mg)	— ^a	80	110	126
Modulus at different strain amplitudes (MPa)				
Strain amplitude (%)				
100	0.30	1.24	1.37	0.73
200	0.23	1.78	1.70	0.93
300	0.23	2.38	2.15	1.17

N = effective number of chains in a real network or degree of crosslinking.^{17,18} 28^a was the control compound.

^a The rubber was too soft, and the abrasion test could not be performed.

were performed at an angle of 180°, ambient temperature (21°C), and a constant crosshead speed of 50 mm/min²¹ in a Lloyd mechanical testing machine (Hampshire, UK). The tears produced in the rubber after the test pieces were fractured were 16–78 mm in length. In each experiment, the tearing force was recorded to produce traces from which an average force was measured. The first peak corresponded to the onset of crack growth, where the tearing force was still rising, and the last peak corresponded to when the test stopped or the sample broke. These were not considered. The remaining peaks on the trace were used for calculating the average tearing force for the rubber (Fig. 2). In some cases involving the filled rubbers, the test produced only one peak, from which a tearing force was calculated (Fig. 3). For each rubber, five test pieces were used. Details of the tear tests and tear behavior of the rubber are shown in Table VIII. After these measurements were completed and following the procedure described previ-

ously,²² we placed the force values in eq. (1) to calculate the tearing energy (T) for the rubbers:

$$T = 2F/t \quad (1)$$

where F is the force and t is the thickness of the test piece. The median values of T are subsequently noted (Table VI).

Tensile properties

The tensile stress, elongation at break, and stored energy density at break of the rubbers were deter-

TABLE VII
Cyclic Fatigue Life of the Rubber Vulcanizates

Sample	Compound			
	28 ^a	29	30	31
	Cyclic fatigue life (kc)			
1	27.5	75.3	36.1	777.4
2	93.9	121.9	511.3	>1000
3	95.3	438.7	>1000	>1000
4	114.3	445.5	>1000	>1000
5	583.4	470.7	>1000	>1000
6	>1000	989.2	>1000	>1000
7	>1000	>1000	>1000	>1000
8	— ^a	>1000	>1000	>1000

28^a was the control compound.

^a The sample failed at the clamp, and the test was stopped.

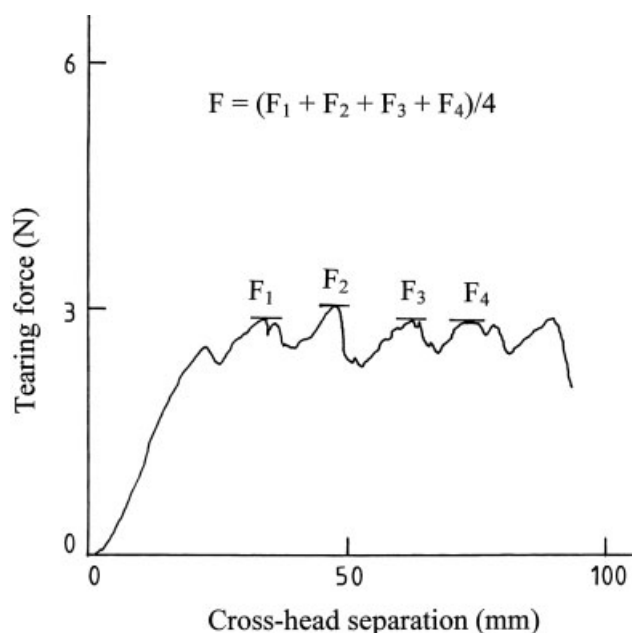


Figure 2 Typical record of the tearing force as a function of crosshead separation. Data for the control compound: $T = 3$ kJ/m².

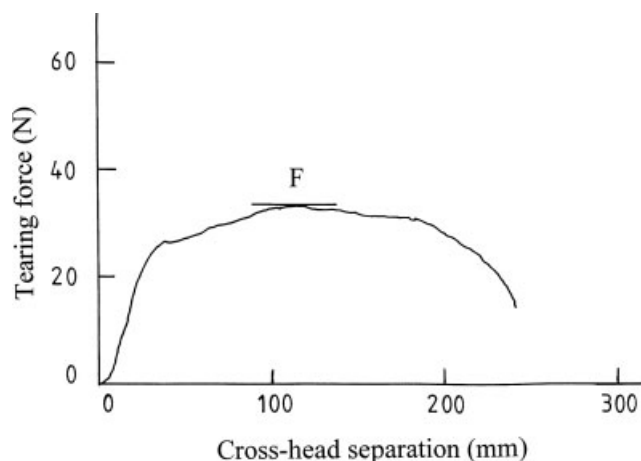


Figure 3 Typical record of the tearing force as a function of crosshead separation. Data for the filled rubber cured with 0.7 phr elemental sulfur: $T \approx 27 \text{ kJ/m}^2$.

mined in uniaxial tension in a Lloyd mechanical testing machine with dumbbell test pieces. The samples were die-stamped from slabs of cured rubber. The tests were performed at 21°C at a crosshead speed of 50 mm/min .²³ Lloyd DAPMAT computer software was used to store and process the data (Table VI).

Abrasion resistance

For determining the abrasion resistance of the rubbers, molded cylindrical test pieces 8 mm thick and 16 mm in diameter were cured. The tests were performed at 23°C in accordance with BS 903: Part A9 : 1995 with method A.1 (Zwick abrasion tester 6102, Croydon, UK and abrasion standard rubber S1).²⁴ For each rubber, three samples were tested to calculate the relative volume loss (Δv ; Table VI).

Loss tangent ($\tan \delta$)

$\tan \delta$ is the ratio between the loss modulus and elastic modulus. The loss modulus represents the viscous component of the modulus and includes all the energy dissipation processes during dynamic strain. $\tan \delta$ was measured in a Rheometric scientific dynamic mechanical thermal analyzer (Surrey, UK) MK II with test pieces 34 mm long, 12 mm wide, and approximately 2.3 mm thick. The tests were performed at 1- and 20-Hz frequencies. The samples were deflected by $256 \mu\text{m}$ (nominal peak to peak displacement) during the test, and the sample temperature was raised from 30 to 100°C at 3°C/min steps.

Modulus at different strain amplitudes

The modulus of the vulcanizates was measured at 100, 200, and 300% strain amplitudes in uniaxial tension with dumbbell test pieces. The tests were

carried out at ambient temperature ($\sim 28^\circ\text{C}$) at a crosshead speed of 50 mm/min in a H T Hounsfield mechanical testing machine (Hounsfield, Surrey, UK). QMAT-DONGLE version 2003 computer software was used to process the data (Table VI).

RESULTS AND DISCUSSION

Filler dispersion and rubber viscosity

To disperse the silica particles fully in the rubber, the mixing time was increased to 22 min. When the SEM photographs were examined [Figs. 4(a,b)], it was evident that 10 min was sufficient to fully disperse the silica particles in the rubber matrix [Fig. 4(b)]. The size of the particles in Figure 4(b) was about 60 nm . It is worth pointing out that the particle size of the filler was $20\text{--}54 \text{ nm}$. However, the viscosity of the rubber compound decreased progressively from 117 to 105 Mooney units as a result of longer mixing times

TABLE VIII
Details of the Tear Tests and Tear Behavior of the Rubber Vulcanizates

Rubber	T (kJ/m^2)	Tear path	Tear length after test piece was fractured (mm)
Compound 28 ^a			
Test piece			
1	2.9	A	23
2	2.7	A	28
3	2.9	A	20
4	3.1	A	24
5	3.0	A	25
Compound 29			
Test piece			
1	25	B	20
2	33	B	16
3	31	B	20
4	26	A	46
5	27	A	78
Compound 30			
Test piece			
1	37	A	40
2	37	A	60
3	34	A	65
4	36	A	70
5	40	A	70
Compound 31			
Test piece			
1	71	A	75
2	80	A	60
3	75	A	60
4	72	A	50
5	89	C	70

Definitions for the tear path: A = crack turned slowly to the edge of the test piece as it propagated; B = crack turned sharply to the edge of the test piece immediately after growth started; C = crack grew linearly parallel to the edges of the test piece all the way. 28^a was the control compound.

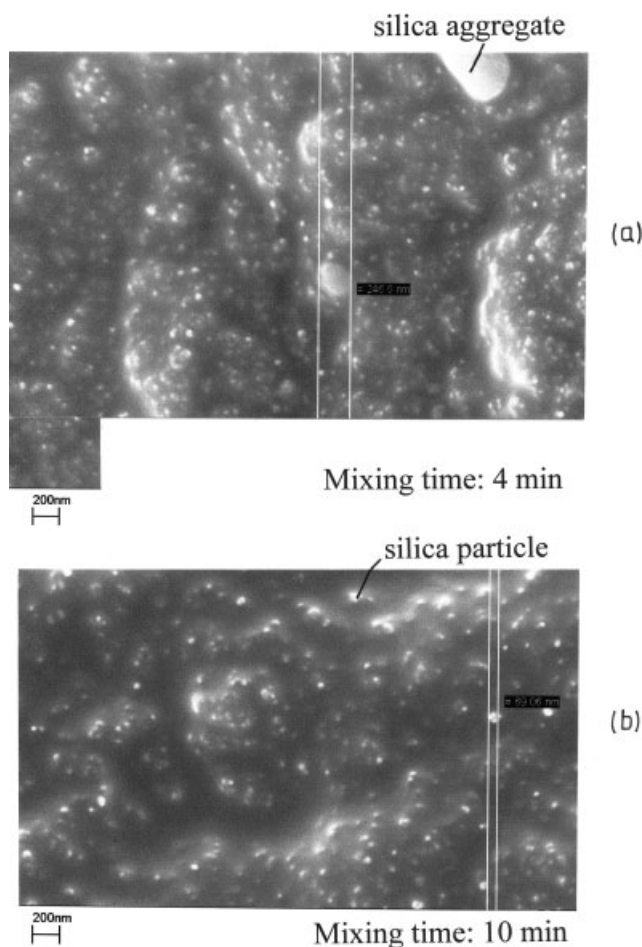


Figure 4 SEM photograph showing the dispersion of the silica particles in the rubber. (a) mixing time = 4 min with poor dispersion and (b) mixing time = 10 min with good dispersion.

(Fig. 5). The rubber broke down during mixing, which caused a reduction in its molecular weight and viscosity.^{12,25} The reduction was due to chain scission,²⁶ or the mechanical rupture of the primary carbon-carbon bonds that were present along the backbone of the rubber chains. This was often compensated by the

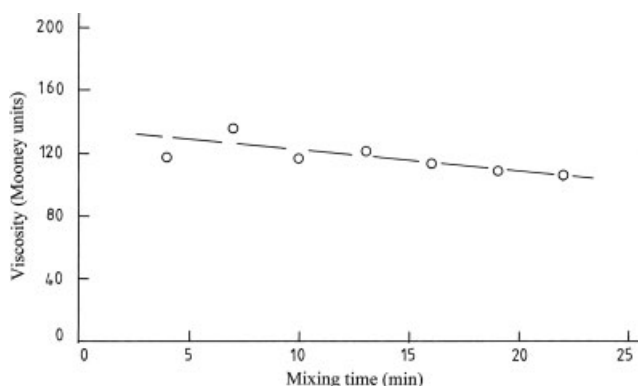


Figure 5 Mooney viscosity versus mixing time for the rubber with silica. Test temperature = 130°C.

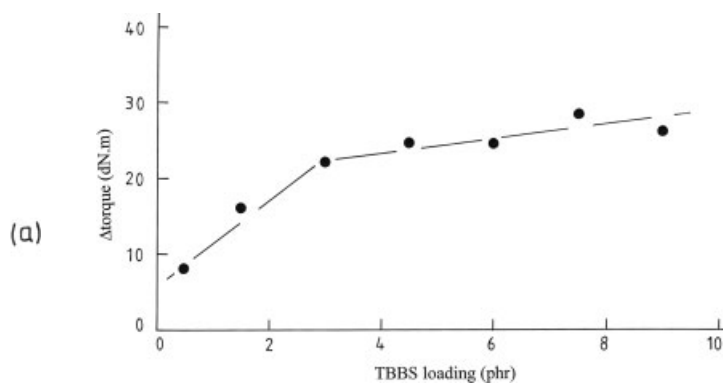


Figure 6 Δtorque versus TBBS loading for the filled rubber.

reinforcing effect of the filler. The viscosity of the rubber increased from 32 to 95 Mooney units after the filler was added (compounds 28 and 29; Table V).

Effect of TBBS, zinc oxide, and elemental sulfur on the crosslink density of the filled rubber

Figure 6 shows the difference between the maximum and minimum torque values on the cure traces of the rubbers tested, and is an indication of crosslink density changes in the rubber (Δ torque) as a function of TBBS loading. Δ torque increased to about 22 dN m as the loading of TBBS was raised to 3 phr. A further increase in the amount of TBBS to 9 phr had little effect on the Δ torque value, which rose to about 26 dN m. Δ torque increased sharply to 56 dN m when 0.5 phr zinc oxide was added to the filled rubber with 3 phr TBBS, and it continued rising at a much slower rate to 64 dN m when the loading of zinc oxide reached 2.5 phr (Fig. 7). Evidently, the addition of 3 phr TBBS and 0.5 phr zinc oxide was sufficient to optimize the chemical bonding between the rubber reactive tetrasulfane groups of TESPT and the rubber.

It was also evident that the addition of elemental sulfur to the cure system influenced Δ torque of the filled rubber with 3 phr TBBS and 0.5 phr zinc oxide.

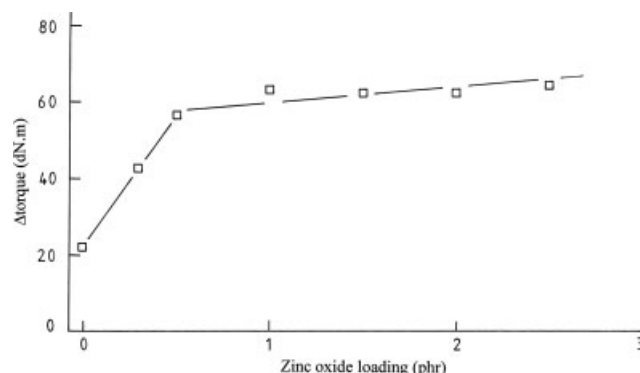


Figure 7 Δtorque versus zinc oxide loading for the filled rubber with 3 phr TBBS.

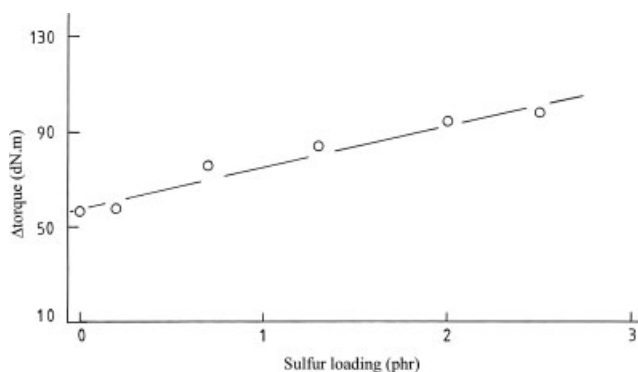


Figure 8 Δtorque versus sulfur loading for the filled rubber with 3 phr TBBS and 0.5 phr zinc oxide.

Δtorque increased from 56 to 98 dN m as a function of sulfur loading (Fig. 8). To prepare the control compound and to evaluate the effect of elemental sulfur on the cure behavior and mechanical properties of the filled rubber with 3 phr TBBS and 0.5 phr zinc oxide, 0.2 and 0.7 phr sulfur were used (Table V). These amounts were selected arbitrarily after we examined Figure 8.

Effect of silanized silica on the curing behavior of the rubber

When silanized silica was incorporated in the rubber (cf. compounds 28 and 29; Table V), the cure time decreased from 75 to 38 min, and the rate of cure sped up, with the cure rate index increasing from 2.6 to 3.9 min⁻¹. Moreover, t_{s2} shortened from 37 to 12 min, and Δtorque rose from 28 to 61 dN m. The TESPT content of the silanized silica was 11.3 wt %. The addition of TESPT improved the cure characteristics of a silica-filled, sulfur-cured natural rubber compound by decreasing the scorch and cure times and increasing the rate of cure.²⁷ This was attributed to the sulfur content of TESPT, which was 2.5 wt %. These results showed a similar trend.

Effect of elemental sulfur on the curing behavior of the filled rubber

The addition of elemental sulfur to the filled rubber affected its cure characteristics (cf. compound 31 with compounds 29 and 30; Table V). t_{s2} and t_{95} shortened from 16 to 12 min and 80 to 38 min, respectively, as a function of sulfur loading. Likewise, the rate of cure and Δtorque increased with the cure rate index increasing from 1.6 to 3.9 min⁻¹, and the latter increased from 38 to 61 dN m, respectively. The effect of the increasing loading of elemental sulfur on the cure behavior of SBR was investigated. The study reported a substantial decrease in the scorch and cure times as well as an increase in the rate of cure for the compounds.²⁸ Our results are similar to these findings.

Effect of silica on the mechanical properties of the rubber

The mechanical properties of the rubber vulcanizate (cf. compounds 28 and 29), as reported in Table VI, were also influenced substantially by the addition of silica. The hardness and tensile strength improved from 31 to 67.5 Shore A and from 1.4 to 25.4 MPa, respectively. A much larger elongation at break of about 945% was recorded for the filled rubber; it was up by almost 56% when compared with the control compound. Similarly, T and stored energy density at break were also up from 3.0 to 27 kJ/m² and from 4 to 98 MJ/m³, respectively. As expected, the rubber became much stiffer after silica was added, with the modulus increasing by a factor of 4 at 100% and 10 at 300% strain amplitudes, respectively. The abrasion resistance improved, but it was not possible to measure the increase more accurately because the control compound was too soft, and the abrasion test had to be stopped shortly after it began.

Effect of elemental sulfur on the mechanical properties of the filled rubber

Interestingly, the mechanical properties of the filled vulcanizate were influenced differently by the added sulfur (cf. compound 31 with compounds 29 and 30; Table VI). The properties that gained the largest benefit were hardness, abrasion resistance, and modulus. The hardness increased from 62.5 to 67.5 Shore A, and the modulus increased by almost 200% at different strain amplitudes when the full loading of sulfur was added to the rubber. Probably the most interesting effect of the sulfur addition was the very substantial improvement in the abrasion resistance of the rubber (compounds 31–29; Table VI). The rubber with 0.7 phr added sulfur had a Δv of 80 mm³/mg, and when the loading of elemental sulfur was reduced to nil, the volume loss increased to 126 mm³/mg. This suggested that elemental sulfur had a very significant influence on this property. Typical sulfur-cured tire tread rubber compounds containing 65 phr reinforcing carbon black (average particle size \approx 30 nm) have a Δv of about 187 mm³/mg.²⁹ The remaining properties were adversely affected by the inclusion of sulfur in the rubber. The elongation at break decreased from 1308 to 945%, the stored energy density at break decreased from 140 to 98 MJ/m³, and T decreased from 75 to 27 kJ/m², respectively. The tensile strength was unchanged at about 26 MPa.

Effect of elemental sulfur on the cyclic fatigue life of the rubber vulcanizate

The cyclic fatigue life of the rubber increased when the filler was added (cf. compounds 28 and 29; Table VII). The shortest minimum fatigue life of about 28 kc

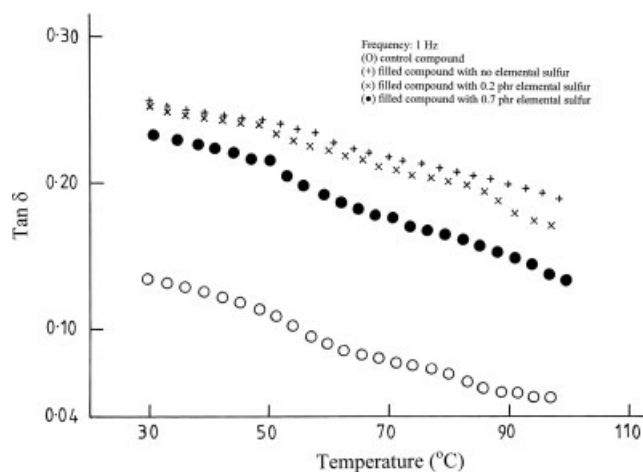


Figure 9 Tan δ versus temperature at 1 Hz: (○) control compound, (+) compound 31, (×) compound 30, and (●) compound 29.

was recorded for the control compound, and the rubber performed better at the upper end, with two samples exceeding 1000 kc. However, the silica filled vulcanizate had a longer minimum fatigue life of about 75 kc, with only two samples exceeding 1000 kc.

Effect of elemental sulfur on the cyclic fatigue life of the filled rubber

The filled rubber with no elemental sulfur (compound 31) had a minimum fatigue life of about 777 kc, with seven samples lasting longer than 1000 kc. The rubber with 0.2 phr added sulfur (compound 30) had a minimum fatigue life of 36 kc, with six samples exceeding 1000 kc. It was interesting to note that the minimum fatigue life decreased from 777.4 to 75 kc with 0.7 phr added sulfur (compound 29), but only two samples lasted longer than 1000 kc. Evidently, the added sulfur was not entirely beneficial to the fatigue life of the filled rubber and adversely affected its performance. The stored energy density (measured from the area under the first stress vs strain trace) at 100% strain, at which the samples were cycled, was 1.3, 1.6, and 1.7 MJ/m³ for compounds 31–29, respectively (Table VI). Fatigue life shortens when stored energy density in the rubber increases.³⁰ Our results, at least for the filled rubbers, seem to confirm this. When the stored energy density in the filled rubber increased from 1.3 to 1.7 MJ/m³, the number of samples failed above 1000 kc decreased, and furthermore, there was a decrease in the minimum number of cycles to failure from 777 to 75 kc (Table VII). Other factors, such as initial flaw size, controlled the fatigue life, too. The number of cycles to failure was inversely proportional to the initial flaw size in the rubber.³¹ It was likely that the samples had flaws of different sizes when they were first cured in the mold, which might have also affected the results.

Effect of elemental sulfur on the loss modulus (tan δ)

Tan δ was influenced by the test frequency, test temperature, and sulfur loading. Tan δ decreased as a function of temperature for the rubbers tested, regardless of the test frequency and rubber formulation. At 1 Hz, when the amount of elemental sulfur in the filled rubber was raised to 0.7 phr, tan δ decreased by 9% at the lowest temperature, that is, 30°C, and by 55% at the highest temperature, that is, 100°C, respectively (Fig. 9). At 20 Hz, a similar trend was also observed with tan δ decreasing by approximately 4% at the lowest and 38% at the highest temperatures, respectively (Fig. 10). The increase in the amount of elemental sulfur reduced the tan δ and energy dissipation processes in the filled rubber. This was more beneficial to the rubber at higher temperatures. Furthermore, tan δ for the unfilled rubber rose noticeably at the higher frequency (cf. Figs. 9 and 10) but remained lower than the values measured for the filled rubbers.

The energy loss in vibration mounts and car tires during dynamic strain affects their service performance, such as heat generation and fatigue life for the former and rolling resistance for the latter.³² Rolling resistance is related to the movement of the whole tire corresponding to deformation at a frequency 10–100 Hz and a temperature ranging from 50 to 80°C. Some tire properties involve frequencies that are too high to be measured; hence, these frequencies are reduced to levels that can be measured more easily in laboratory, for example, 1 and 20 Hz. To meet the requirements of high-performance tires, a low tan δ value at a temperature of 50–80°C to reduce rolling resistance and save energy is often considered.³² The fact that the tan δ of the filled rubber at high temperatures decreased substantially after small amounts of elemental sulfur were added (Figs. 9 and 10) is of significant importance for rubber compounds used in tire tread applications.

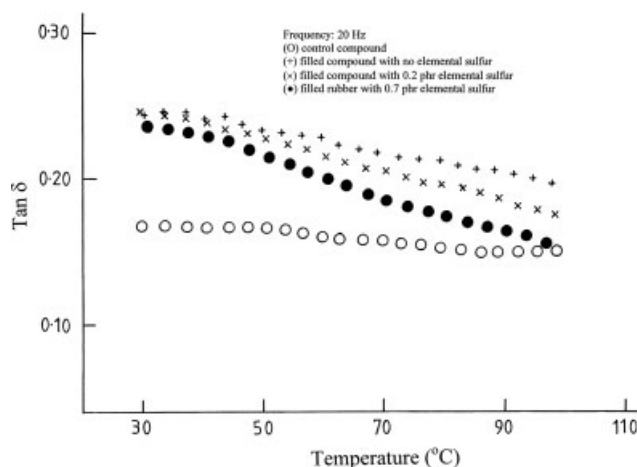


Figure 10 Tan δ versus temperature at 20 Hz: (○) control compound, (+) compound 31, (×) compound 30, and (●) compound 29.

As mentioned earlier,^{7,9,11} filler–rubber adhesion, filler–filler interaction, and crosslink density control, to a large extent, the rubber reinforcement. Because the silica particles were fully dispersed in the rubber [Fig. 4(b)], the filler–filler interaction was negligible. However, the bound-rubber content was 65% (Table VI), which indicated strong filler–rubber adhesion, and the degree of crosslinking of the filled rubber also increased from 19×10^{-3} to 32×10^{-3} N when the full amount of elemental sulfur was added (Table VI). Crosslink density increased as a function of the loading of sulfur.²⁸ Our results are in line with this finding. It was interesting that the inclusion of up to 0.7 phr sulfur had such wide-ranging consequences for the properties of the filled rubber.

CONCLUSIONS

This study showed that precipitated silica pretreated with TESPT is an effective reinforcing filler for SBR. We concluded that

1. The hardness, tensile strength, elongation at break, stored energy density at break, T , minimum cyclic fatigue life, abrasion resistance, modulus, and crosslink density of the rubber vulcanizate increased substantially when the filler was added.
2. For the filled rubber, the improvement in the mechanical properties was mainly due to high level of rubber–filler adhesion, which was produced by the chemical bonding between the rubber and TESPT. This was optimized by the addition of 3 phr TBBS and 0.5 phr zinc oxide to the formulation. The bound-rubber measurements indicated a strong rubber–filler adhesion, too.
3. When up to 0.7 phr elemental sulfur was incorporated in the filled rubber with 3 phr TBBS and 0.5 phr zinc oxide, some properties improved, and others deteriorated. The hardness, abrasion resistance, and modulus were increased, whereas elongation at break, stored energy density at break, T , and cyclic fatigue life decreased. The tensile strength remained unchanged, and there was a large reduction in the energy dissipation processes in the rubber under dynamic strain, particularly at high temperatures.
4. The addition of elemental sulfur to the filled rubber with 3 phr TBBS and 0.5 phr zinc oxide was largely beneficial to the cure properties. t_{52} and t_{95} decreased, and the rate of cure increased noticeably.

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References

1. The Natural Rubber Formulary and Properties Index; Re: EUR053; Archives, Tun Abdul Razak Research Centre, Malaysian Rubber Producers' Research Association. Brickendonbury, Hertford, UK, 1984.
2. Wolff, S.; Wang, M. J.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 163.
3. Dannenberg, E. M. *Rubber Chem Technol* 1975, 48, 410.
4. Wolff, S.; Görl, U.; Wang, M. J.; Wolff, W. *Rubber J* 1994, 16, 16.
5. Hair, M. L.; Hertl, W. *J Phys Chem* 1970, 74, 91.
6. Hockley, J. A.; Pethica, B. A. *Trans Faraday Soc* 1961, 57, 2247.
7. Wolff, S. *Rubber Chem Technol* 1996, 69, 325.
8. Ansarifar, A.; Nijhawan, R.; Nanapoolsin, T.; Song, M. *Rubber Chem Technol* 2003, 76, 1290.
9. Fröhlich, J.; Niedermeier, W.; Luginsland, H. D. *Compos A* 2005, 36, 449.
10. Polmanteer, K. E.; Lentz, C. W. *Rubber Chem Technol* 1975, 48, 795.
11. Nasir, M.; Teh, G. K. *Eur Polym J* 1988, 24, 733.
12. Fries, H.; Pandit, R. P. *Rubber Chem Technol* 1982, 55, 309.
13. Wolff, S. *Rubber Chem Technol* 1982, 55, 967.
14. British Standards Institution, Methods of testing raw rubber and unvulcanized compounded rubber: Methods of physical testing. British Standard 1673: Part 3; London, UK, 1969.
15. British Standards Institution, Methods of test for raw rubber and unvulcanized compounded rubber: Measurement of pre-vulcanizing and curing characteristics by means of curemeter. British Standard 1673: Part 10; London, UK, 1977.
16. British Standards Institution, Methods of test for raw rubber and unvulcanized compounded rubber: Measurement of pre-vulcanizing and curing characteristics by means of curemeter. British Standard 903: Part A60: Section 60.1; London, UK, 1996.
17. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1982.
18. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 521.
19. British Standards Institution, Physical testing of rubber: Method for determination of hardness. British Standard 903: Part A26; London, UK, 1995.
20. British Standards Institution, Methods of testing vulcanized rubber: Determination of resistance to tension fatigue. British Standard 903: Part A51; London, UK, 1986.
21. British Standards Institution, Physical testing of rubber: Method for determination of tear strength trousers, angle and crescent test pieces. British Standard 903: Part A3; London, UK, 1995.
22. Greensmith, H. V.; Thomas, A. G. *J Polym Sci* 1955, 43, 189.
23. British Standards Institution, Physical testing of rubber: Method for determination of tensile stress strain properties. British Standard 903: Part A2; London, UK, 1995.
24. British Standards Institution, Method of testing vulcanized rubber. Determination of resistance to abrasion. British Standard 903: Part A9: Method A.1; London, UK, 1995.
25. Harmon, D. J.; Jacobs, H. L. *J Appl Polym Sci* 1966, 10, 253.
26. Ahagon, A. *Rubber Chem Technol* 1996, 69, 742.
27. Ansarifar, M. A.; Jain, A.; Nanapoolsin, T. *J Rubber Res* 2002, 5, 11.
28. Salgueiro, W.; Marzocca, A.; Somoza, A.; Consolati, G.; Cervený, S. F.; Quasso, F.; Goyanes, S. *Polymer* 2004, 45, 6037.
29. Ansarifar, A.; Azhar, A.; Song, M. J. *Rubber Res* 2003, 6, 129.
30. Bristow, G. M.; Tiller, R. F. *Kautsch Gummi Kunstst* 1970, 23, 55.
31. Lindley, P. B.; Thomas, A. G. *Proceedings of the 4th Rubber Technology Conference*, London; Livesey Ltd., Shrewsbury, UK, 1962; Vol. 1.
32. Wang, M. J. *Rubber Chem Technol* 1998, 71, 520.