

Novel Technique for Crosslinking and Reinforcing High-Cis Polybutadiene Rubber Using a Silanized Silica Nanofiller

A. Ansarifar,¹ L. Wang,¹ R. J. Ellis,² Y. Haile-Meskel³

¹*Institute of Polymer Technology and Materials Engineering, Loughborough University, Leicestershire, LE11 3TU, United Kingdom*

²*Avon Vibration Management Systems, Limited, Bumpers Way, Chippenham, Wiltshire, SN14 6NF, United Kingdom*

³*Avon Automotive, Bumpers Farm Industrial Estate, Chippenham, Wiltshire, SN14 6NF, United Kingdom*

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ABSTRACT: A large amount of a precipitated amorphous white silica nanofiller was mixed with a high-cis polybutadiene rubber. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl)tetrasulfide (TESPT). TESPT is a sulfur-containing bifunctional organosilane that chemically adheres silica to rubber. The rubber was cured primarily with sulfur in TESPT, and the cure was optimized by the addition of a sulfenamide accelerator, which helped to form sulfur chemical bonds between the rubber and the filler. The hardness, tensile properties, tear strength, abrasion resistance, modulus, and cyclic fatigue life of the

cured rubber improved substantially when the filler was added. Interestingly, this new technique produced a rubber with good mechanical properties, and only one accelerator was needed to optimize the chemical bonding between the rubber and the filler and fully cure the rubber. As a result, a substantial reduction in the use of the curing chemicals was achieved. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1135–1145, 2007

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

INTRODUCTION

Rubber compounds used to manufacture industrial rubber articles such as tires, hoses, and conveyor belts contain up to eight classes of rubber chemicals. They include curing systems (elemental sulfur, accelerators, and activators), processing aids, antidegradants, flame retardants, and coloring pigments. For example, the curing system in an all-season tire tread rubber compound, which is a blend of high-cis polybutadiene, styrene-butadiene rubber, and natural rubber and is filled with a highly reinforcing carbon black nanofiller, consists of up to five different chemicals, which add up to 9.4 parts per hundred rubber by weight (phr).¹ Rubber chemicals are harmful to health, safety, and the environment, and their use is restricted by legislation.

The selection of raw materials and manufacturing processes that do not harm the environment is of great importance to the rubber industry.² Raw rub-

bers such as polybutadiene rubber often possess weak mechanical properties and must be reinforced with fillers. The reinforcement of rubbers enhances their properties, such as the tear strength, tensile strength, hardness, and abrasion resistance.³ This is brought about by the inclusion of solid phases such as synthetic silicas, quartz, and metal oxides, which have large surface areas and have been shown to be very effective in improving rubber properties.⁴ Among these fillers, amorphous white silicas with surface areas ranging from 150 to 400 m²/g offer the highest level of reinforcement.

The surfaces of silicas possess siloxane and silanol groups (SiOH),⁵ which make the filler acidic⁶ and moisture-adsorbing.⁷ This causes detrimental effects such as unacceptably long cure times and slow cure rates⁵ and also a loss of the crosslink density⁸ in sulfur-cured rubbers. Bifunctional organosilanes such as bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), known also as the Si69 coupling agent, are used to remedy the deficiencies of the filler mentioned previously.⁵ These materials can be used as primers for treating silica surfaces to make the filler more suitable for use in rubber. TESPT is used to improve the reinforcing capability of precipitated silicas and also forms an integral part of curing systems to improve crosslinking network properties.⁵

This silane possesses tetrasulfane and ethoxy reactive groups. The tetrasulfane groups are rubber-reactive⁵ and react in the presence of accelerators at ele-

Correspondence to: A. Ansarifar (m.a.ansarifar@lboro.ac.uk).

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vated temperatures, that is, 140–260°C, without elemental sulfur being present, to form crosslinks in unsaturated rubbers, such as polybutadiene rubber. 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 rubber–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 interaction between the silica particles.⁵ These changes help to reduce the viscosity of rubber compounds and also improve the cure characteristics by preventing acidic silicas from interfering with the reaction mechanism of sulfur-cured rubbers.^{5,9}

The aim of this study was to use a precipitated silica nanofiller pretreated with TESPT to crosslink a polybutadiene rubber and reinforce its mechanical properties. This was achieved by the optimization of the chemical bonding between the rubber and the filler. The bound rubber and crosslink density of the rubber were also measured to assess the extent of rubber–filler adhesion and chemical bonding between the rubber and the filler, respectively.

EXPERIMENTAL

Materials: Rubber, filler, and rubber chemicals

The raw rubber used was high-cis polybutadiene (Buna CB 24, Bayer; not oil-extended) containing 98% 1,4-cis. The reinforcing nanofiller was Coupsil 8113, which was supplied by Degussa, Ltd. (Hanau, Germany). Coupsil 8113 is a precipitated amorphous white silica (type Ultrasil VN3), the surfaces of which were pretreated with TESPT. It has 11.3 wt % silane, 2.5 wt % sulfur (included in TESPT), a 175 m²/g surface area (measured by N₂ adsorption), and a 20–54-nm particle size.

In addition to the raw rubber and filler, the other additives were *N-t*-butyl-2-benzothiazole sulfenamide (TBBS; a safe-processing delayed-action accelerator from Santocure), zinc oxide (an activator), stearic acid (an activator), elemental sulfur (a curing agent), and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine

(Santoflex 13; an antidegradant). TBBS, zinc oxide, and stearic acid were added to optimize the chemical bonding or crosslinks between the rubber and filler. In all, 37 rubber compounds were prepared for this study.

Mixing

The compounds were prepared in a Haake Rheocord (Berlin, Germany) 90, a small laboratory mixer with counter-rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at the ambient temperature (~23°C), and the rotor speed was 45 rpm. The volume of the mixing chamber was 78 cm³, and it was 52% full during the mixing. Haake software (version 1.9.1) was used for controlling the mixing conditions and storing data. The torque values were also recorded during mixing and subsequently plotted against the mixing time to study the effect of prolonged mixing on the viscosity of the rubber compounds.

Evaluation of the dispersion of silica particles in the rubber

To select a suitable mixing time for incorporating the filler into the rubber, seven compounds were prepared (compounds 1–7; Table I). The filler was introduced into the mixing chamber first, and then the raw rubber was added before the mixing started. The mixing time was increased to 22 min to disperse the silica particles fully in the rubber. Twenty-four hours after the mixing ended, the rubbers were examined in a scanning electron microscope to assess the filler dispersion.

The dispersion of the silica particles in the rubber was assessed with a Leo 1530 VP field emission gun scanning electron microscope (Cambridge, UK). Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 60 mm² in area and 5 mm thick, were coated with gold and then were 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.

TABLE I
Recipes and Mixing Times for the Rubber and the Filler

	Compound						
	1	2	3	4	5	6	7
Mixing time (min)	4	7	10	13	16	19	22
Compound temperature after the end of mixing (°C)	50	51	52	50	50	54	55

Formulation: 100 phr polybutadiene rubber and 60 phr silica.

TABLE II
Formulations and ODR Test Results for the Rubbers with an Increasing Loading of TBBS

	Compound							
	8	9	10	11	12	13	14	15
TBBS (phr)	0.5	1.5	3	4.5	6	7.5	9	11
Minimum torque (dN m)	61	58	54	50	46	50	41	41
Maximum torque (dN m)	80	92	101	109	113	137	132	135
Δ torque (dN m)	19	34	47	59	67	87	91	94

Formulation: 100 phr polybutadiene rubber and 60 phr silica.

Addition of TBBS to crosslink the filled rubber

Accelerators are ingredients used to control the onset and rate of cure and the crosslink density in rubber. To activate the rubber-reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the rubber was increased progressively to 11 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.⁵ In all, eight rubber compounds were prepared (compounds 8–15; Table II).

Addition of zinc oxide to improve the cure of the filled rubber with TBBS

Activators are chemicals used to enhance the effectiveness of the accelerators during the curing reaction in rubber. The loading of zinc oxide in the filled rubber with TBBS was raised to 1.5 phr to measure the amount needed to maximize the efficiency of TBBS and the cure. In all, six compounds were made (compounds 16–21; Table III).

Addition of stearic acid to improve the cure of the filled rubbers with TBBS and with TBBS and zinc oxide

Stearic acid is a fatty acid that is added to improve the solubility of zinc oxide in rubber. The loading of stearic acid in the filled rubber with TBBS and zinc

oxide was increased to 2.5 phr to measure the amount needed to optimize the efficiency of the accelerator and cure. Similar measurements were also made for the filled rubber with TBBS to examine the effect of stearic acid on the cure. In all, 14 compounds were mixed (compounds 22–35; Tables IV and V).

After these measurements were completed, two compounds were prepared for further tests (compounds 36 and 37; Table VI). The control compound (compound 36) was made through the addition of 1.5 phr elemental sulfur, 7.5 phr TBBS, and 1 phr anti-degradant to the rubber. The amount of elemental sulfur in the control compound was the same as the 2.5 wt % sulfur concentration in TESPT. TBBS, elemental sulfur, and the antidegradant were added together 10 min after the mixing started, and the mixing continued subsequently for an extra 6 min before the rubber was removed from the mixer. A similar procedure was used for preparing the filled compound, and before the mixing started, the filler was placed in the mixing chamber, and then the raw rubber was added. The filler was added when the viscosity of the rubber was still relatively high, and this led to an improved dispersion.¹⁰ For the filled rubber (compound 37), TBBS and the antidegradant were added at the same time.

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 the ambient temperature ($\sim 23^\circ\text{C}$) for at least 24 h before their cure properties were measured.

TABLE III
Formulations and ODR Test Results for the Rubbers with an Increasing Loading of Zinc Oxide

	Compound					
	16	17	18	19	20	21
Zinc oxide (phr)	0	0.1	0.3	0.5	1	1.5
Minimum torque (dN m)	50	44	44	46	44	42
Maximum torque (dN m)	137	150	160	177	174	172
Δ torque (dN m)	87	106	116	131	130	130

Formulation: 100 phr polybutadiene rubber, 60 phr silica, and 7.5 phr TBBS.

TABLE IV
Formulations and ODR Test Results for the Rubbers with an Increasing Loading of Stearic Acid

	Compound						
	22	23	24	25	26	27	28
Stearic acid (phr)	0	0.2	0.5	1	1.5	2	2.5
Minimum torque (dN m)	46	46	46	46	43	41	40
Maximum torque (dN m)	177	179	180	181	167	160	153
Δ torque (dN m)	131	133	134	135	124	119	113

Formulation: 100 phr polybutadiene rubber, 60 phr silica, 7.5 phr TBBS, and 0.5 phr zinc oxide.

Viscosity and cure properties of the rubber compounds

The effect of the silica addition on the viscosity of the rubber was determined through the plotting of the torque values recorded during mixing against the mixing time. The scorch time, which is the time for the onset of cure, and the optimum cure time, 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 cure meter (ODR) at an angular displacement of $\pm 3^\circ$ and a test frequency of 1.7 Hz.¹¹ The cure rate index, which is a measure of the rate of cure in rubber, was calculated with the method described previously.¹² The rheometer tests ran for up to 2 h. The results from these tests are summarized in Tables II–VI.

Test pieces and test procedure

After these measurements were completed, the compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. For measuring the mechanical properties of the rubbers, sheets that were 23 cm \times 23 cm and approximately 2.7 mm thick were used, from which various samples for further tests were cut.

Bound rubber and crosslink density of the rubbers

The solvent used for the bound rubber and crosslink density determination was toluene. For the determination, 8 (control compound) or 10 g (filled compound) of the rubber compound was cured in a com-

pression mold to produce cylindrical samples 28 mm in diameter and 12 mm high. The samples were then placed individually in 280 mL of the solvent in labeled bottles and allowed to swell for up to 5 months at 21°C . The weight of the samples was measured every 3–4 days until it reached equilibrium. It took approximately 1 month and 13 days for the control compound and 4 months and 23 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 the expressions in refs. 13 and 14, respectively (Table VI).

Hardness

For determining the hardness of the rubber, cylindrical samples that were 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 rubbers was determined at 26.5°C after a 15-s interval. This was repeated at three different positions on each sample, and the medium of the three readings was subsequently indicated¹⁵ (Table VI).

Tensile properties

The tensile stress, strain at break, and stored energy density at break for the cured rubbers were deter-

TABLE V
Formulations and ODR Test Results for the Rubbers with an Increasing Loading of Stearic Acid

	Compound						
	29	30	31	32	33	34	35
Stearic acid (phr)	0	0.2	0.5	1	1.5	2	2.5
Minimum torque (dN m)	50	44	42	41	41	39	38
Maximum torque (dN m)	137	110	111	107	107	105	103
Δ torque (dN m)	87	66	69	66	66	66	65

Formulation: 100 phr polybutadiene rubber, 60 phr silica, and 7.5 phr TBBS.

TABLE VI
Recipes for the Rubber Compounds, ODR Test Results at 140°C, Mechanical Properties, Bound Rubber, and Crosslink Densities of the Cured Rubbers

		Compound	
		36	37
Formulation (phr)	High-cis polybutadiene	100	100
	Silanized silica	0	60
	Elemental sulfur	1.5	—
	TBBS	7.5	7.5
	Santoflex 13	1	1
ODR results	Minimum torque (dN m)	13.5	37.5
	Maximum torque (dN m)	105	129
	Δ torque (dN m)	91.5	91.5
	Scorch time (min)	30	8
	Optimum cure time (min)	167	83
	Cure rate index (min ⁻¹)	0.73	1.3
Mechanical properties	Hardness (Shore A)	45	72
	Tensile strength (MPa)	1.1	16.7
	Elongation at break (%)	232	606
	Stored energy density at break (MJ/m ³)	1.8	49
	Stored energy density at 100% strain amplitude (MJ/m ³)	0.45	1.5
	Tearing energy (kJ/m ²)	1.2	30
	Range of values (kJ/m ²)	1.2–3.8	10–103
	Relative volume loss in abrasion tests (mm ³ /mg)	819	15.5
	Modulus at 50% strain amplitude (MPa)	0.60	2.8
	Modulus at 100% strain amplitude (MPa)	0.38	2.2
	Modulus at 200% strain amplitude (MPa)	0.18	2.2
	Modulus at 400% strain amplitude (MPa)	— ^c	2.6
Modulus at 500% strain amplitude (MPa)	— ^c	2.8	
Bound rubber (%) ^a	—	93	
Crosslink density (mol/m ³) ^b	155	141	

^a From ref. 13.

^b From ref. 14.

^c No data were available because the samples fractured at strains below 300%.

mined in uniaxial tension in a Lloyd mechanical testing machine (Hampshire, UK) with dumbbell test pieces 3.6 mm wide with a central neck 25 mm long. These samples were die-stamped from sheets of the cured rubber. The tests were performed at 21°C and at a constant crosshead speed of 50 mm/min.¹⁶ Lloyd DAPMAT computer software was used for storing and processing the data (Table VI).

The modulus of the rubbers at 50–500% strain amplitudes were measured from the tensile stress versus tensile strain data, using a QMAT-DONGLE version software.

Tear strength

The tear strength of the rubber was measured with rectangular strips, 100 long and 30 mm wide, which were cut from the cured sheets of rubber. A sharp crack, approximately 30 mm long, was introduced into the strips half-way along the width and parallel to the length of the strips to form the trouser test pieces for the tear experiments. Trouser tear tests were performed at an angle of 180°, at 21°C, and at a

constant crosshead speed of 50 mm/min¹⁷ with a Lloyd mechanical testing machine. The tear that was produced varied in length from approximately 13 to 77 mm. In some cases, tearing produced peaks on the trace from which an average force was calculated (Fig. 1), and sometimes tearing produced a single peak from which the force was measured (Fig. 2). Five test pieces were used for each rubber. The tearing energy (T) values were obtained as follows:¹⁸

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

where F is the force and t is the thickness of the test piece. The results and full details of the tear tests are given in Tables VI and VII.

Cyclic fatigue life

The cyclic fatigue life of the rubbers was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK) with dumbbell test pieces. The test pieces were die-stamped from the sheets of cured rubber. The tests were carried out at a

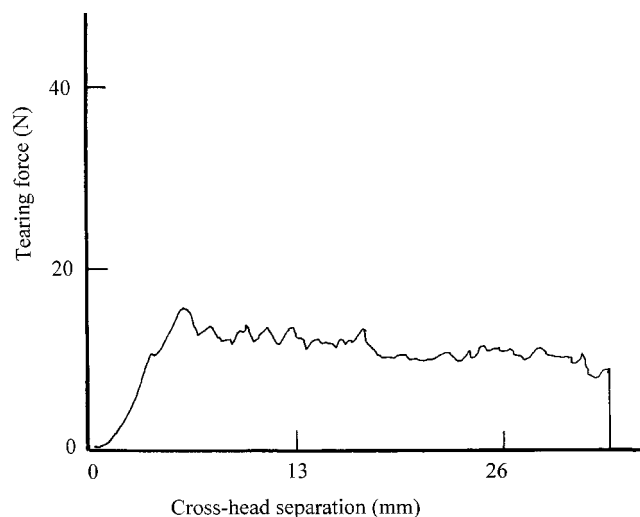


Figure 1 Typical record of the tearing force as a function of the crosshead separation (tearing energy for the filled rubber = 12.5 kJ/m²; see also Table VII).

constant maximum strain amplitude of 100% (the central neck was stretched to 50 mm) and a test frequency of 1.4 Hz. The test temperature was 21°C, and the strain on each test piece was relaxed to zero at the end of each cycle. For each rubber, eight samples were used, and the tests were stopped whenever the fatigue life exceeded 1000 kilocycles (kc). Some samples exceeded 1000 kc and did not fail, and some failed below this number. For the latter, the median

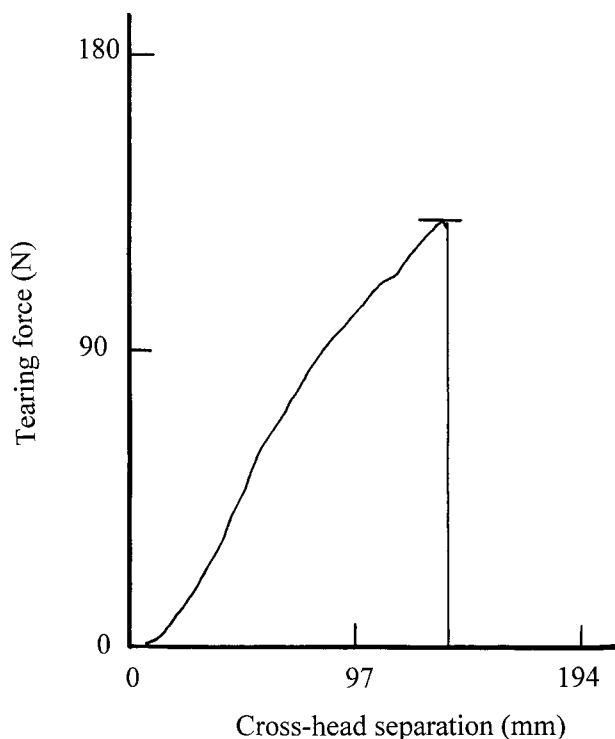


Figure 2 Typical record of the tearing force as a function of the crosshead separation (tearing energy for the filled rubber = 103 kJ/m²; see also Table VII).

TABLE VII
Details of the Trouser Tear Tests and Tear Behavior of the Rubbers Fractured at 50 mm/min

Rubber test piece	Tearing energy (kJ/m ²)	Tear path	Tear length after the test pieces were fractured (mm)
Compound 36			
1	1.2	Nonlinear	56
2	1.2	Nonlinear	50
3	1.2	Nonlinear	47
4	1.3	Linear	77
5	3.8	Nonlinear	59
Compound 37			
1	10	Nonlinear	45
2	12.5	Nonlinear	73
3	30	— ^a	13
4	47	— ^a	13
5	103	Knotty tearing	29

In knotty tearing, the crack turned in a semicircular path as soon as crack growth started. In nonlinear tearing, the crack turned toward the edge of the test piece almost immediately after the tearing began.

^a The crack turned by 90° toward the edge of the test piece almost immediately after the tearing began.

values of the results were noted.¹⁹ The results are presented in Table VIII.

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 British Standard 903, Part A9, Method A.1 (a Zwick 6102 abrasion tester and S1 abrasion standard rubber, Croydon, UK).²⁰ For each rubber, three samples were tested to calculate the relative volume loss (Table VI).

RESULTS AND DISCUSSION

Filler dispersion in the rubber

When the SEM photographs were examined, it was evident that increasing the mixing time improved the dispersion of the silica particles in the rubber matrix.

TABLE VIII
Cyclic Fatigue Life of the Cured Rubbers

Sample	Cyclic fatigue life (kc)	
	Compound 36	Compound 37
1	0.004	40
2	0.039	117.1
3	0.208	260.4
4	0.316	630
5	1.09	>1000
6	3.01	>1000
7	>1000	>1000
8	>1000	>1000

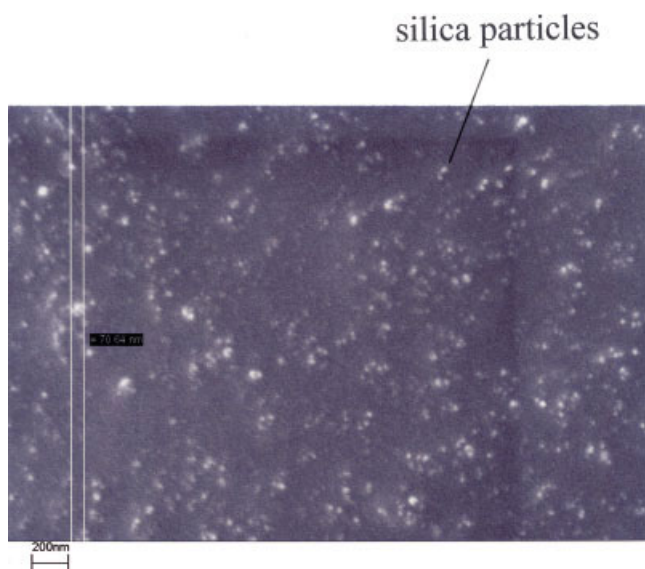


Figure 3 SEM photograph showing the full dispersion of the silica particles in the rubber (mixing time = 16 min).

Sixteen minutes of mixing was sufficient to fully disperse the filler particles in the rubber (Fig. 3). The size of the particles in Figure 3 was approximately 70 nm, which was fairly similar to the actual particle size of the filler (20–54 nm). Shorter mixing times produced poor dispersion, and silica aggregates up to 240 nm in size were observed in the rubber (Fig. 4).

Effect of silica on the viscosity and cure properties of the rubber

The minimum torque in the ODR tests was proportional to the viscosity of the uncured rubber com-

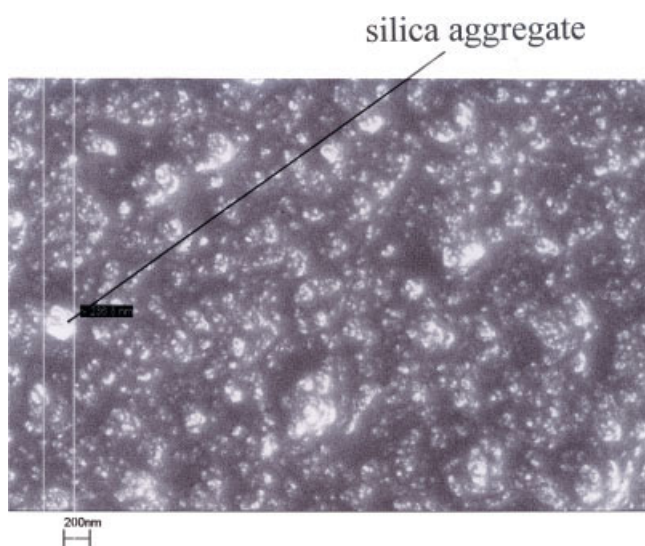


Figure 4 SEM photograph showing the poor dispersion of the silica particles in the rubber (mixing time = 7 min). (From A. Ansarifard et al., Proceedings of the 5th International RubberChem Conference, Munich, Germany, 2006, Paper 5, pp 1–12. Reproduced with the kind permission of Rapra Technology, Ltd. www.rapra.net).

pound. The minimum torque increased from 13.5 to 37.5 dN m when the filler was added. A similar trend can also be seen in Figure 5. The torque values measured during the mixing cycles were initially higher for the filled rubber at 37 N m than those for the control compound at about 28 N m (Fig. 5).

The torque was proportional to the viscosity of the rubber during mixing. However, as the mixing time was increased to 4 min, the torque decreased to about 16.5 N m and remained at this level for both compounds after the mixing time was increased to 16 min. Clearly, prolonged mixing reduced the viscosity of the rubber compounds. Rubber breaks down during mixing, and this causes a reduction in its molecular weight and viscosity.^{10,21} The reduction is due to chain scission, or the mechanical rupture of the rubber chains. This is often compensated by the reinforcing effect of the filler.

Normally, silica-filled rubber has a much higher viscosity than an unfilled or control compound. However, it is evident from Figure 5 that the torque measured during mixing did not differentiate between the two compounds as the mixing time was increased to 16 min. Therefore, it was concluded that this technique was not suitable for assessing the effect of the filler on the viscosity of the rubber at long mixing times.

The cure properties of the filled rubber were noticeably better than those of the control compound. The scorch and optimum cure times were 30 and 8 min and 167 and 83 min for the control compound and the filled rubber, respectively. The cure rate index, which is a measure of the rate of cure in rubber, was 0.73/min and 1.3/min, respectively, for the rubbers. The large improvement observed in the cure properties of the filled rubber was due to the faster cure kinetics of the sulfur in TESPT versus that of elemental sulfur. Some studies have shown that TESPT shortens the scorch and optimum cure times and increases the rate of cure in silica-filled rubber compounds.^{22,23}

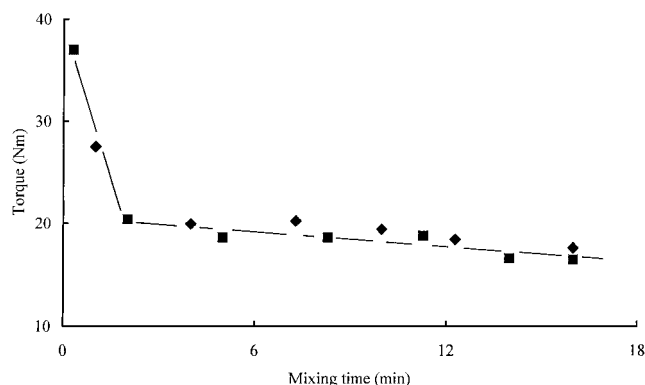


Figure 5 Torque versus the mixing time from the mixing cycles for the control and filled compounds in Table VI: (◆) control compound and (■), filled rubber.

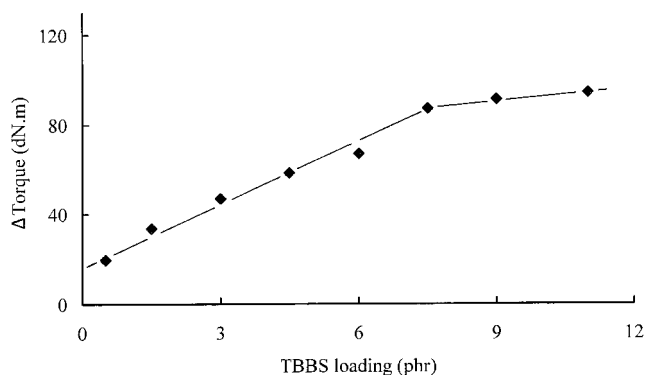


Figure 6 Δ torque versus the TBBS loading for the filled compound.

Δ torque, which is an indication of crosslink density changes in rubber, remained unchanged for both compounds at 91.5 dN m. The crosslink densities of the control and filled rubbers measured in the swelling tests were 155 and 141 mol/m³, respectively (Table VI), and they were noticeably different despite the same Δ torque values. In the control compound, the ratio of elemental sulfur (1.5 phr) to TBBS (7.5 phr) was less than unity, and this made the cure system an efficient vulcanization (EV) system. EV cure systems produce a high level of monosulfidic crosslinks,²⁴ whereas the sulfur in TESPT forms mainly disulfidic crosslinks in rubber.⁵ Previous studies have shown that crosslink density measurements are affected by the various types of crosslinks in rubber.²⁵ Although for the two rubbers with the same concentration of sulfur the Δ torque values were the same, the crosslink density measurements were affected by the different types of crosslinks in the rubbers (Table VI).

Effect of TBBS on the formation of chemical bonding between the rubber and filler

Figure 6 shows Δ torque as a function of the TBBS loading. Δ torque increased to 87 dN m when the

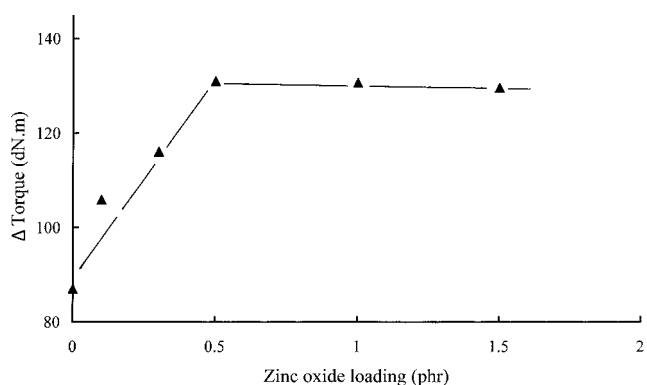


Figure 7 Δ torque versus the zinc oxide loading for the filled rubber with 7.5 phr TBBS.

loading of TBBS was raised to 7.5 phr. Further increases in the amount of TBBS had little effect on Δ torque, which remained at about 90 dN m. The crosslink densities of the filled rubbers containing 1.5 or 7.5 phr TBBS, measured in the swelling tests, were 115 and 141 mol/m³, respectively, showing a large increase as a function of the TBBS loading. This was similar to the trend shown in Figure 6. Moreover, the bound rubber was 84 and 94% at 1.5 and 7.5 phr TBBS loadings, respectively. Evidently, the increase in the amount of TBBS was beneficial to the chemical bonding between the rubber and the filler and the rubber–filler adhesion.

It was evident that the addition of 7.5 phr TBBS was sufficient to optimize the chemical bonding between the rubber-reactive tetrasulfane groups of TESPT and the rubber. The formation of chemical bonding or crosslinks strengthened the rubber–filler interaction.⁵

Effect of zinc oxide and stearic acid on the efficiency of TBBS and the cure of the filled rubber

The inclusion of zinc oxide enhanced the crosslink density of the rubber even more significantly (Fig. 7). Δ torque for the filled rubber with 7.5 phr TBBS increased to 131 dN m when 0.5 phr zinc oxide was added and showed no further improvement thereafter when an extra 1 phr zinc oxide was incorporated into the rubber.

Figure 8 shows the effect of stearic acid on the cure behavior of the filled rubber with 7.5 phr TBBS. The addition of stearic acid to the rubber offered no benefit to the crosslink density and in fact had a detrimental effect on the torque values. Δ torque decreased from 87 to 66 dN m when 0.2 phr stearic acid was added and remained at this level until the loading of stearic acid reached 2.5 phr.

Interestingly, when stearic acid was added to the filled rubber with 7.5 phr TBBS and 0.5 phr zinc oxide (Fig. 9), initially Δ torque increased from 131 to 134

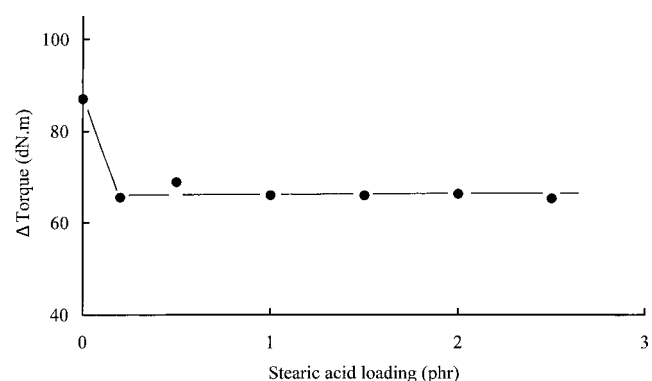


Figure 8 Δ torque versus the stearic acid loading for the filled rubber with 7.5 phr TBBS.

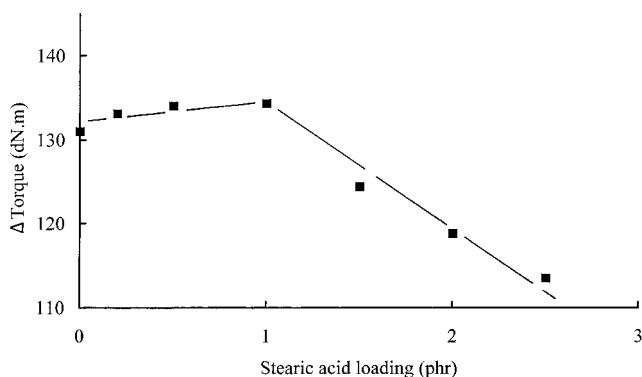


Figure 9 Δ torque versus the stearic acid loading for the filled rubber with 7.5 phr TBBS and 0.5 phr zinc oxide.

dN m with up to 1 phr stearic acid, and then it dropped to approximately 113 dN m as the loading of stearic acid was increased progressively to 2.5 phr. The cure gained little benefit from the inclusion of stearic acid in the rubber.

It is evident from Figure 7 that the addition of zinc oxide increased Δ torque or the crosslink density. The crosslink density, to a large extent, controls the mechanical properties of cured rubber.^{24,25} The filled rubber with 7.5 phr TBBS was too brittle when zinc oxide was added and was not used in this study. As Figures 8 and 9 indicate, stearic acid offered the crosslink density little or no improvement and in fact was detrimental to the cure of the filled rubber with 7.5 phr TBBS. When Δ torque reached 120 dN m, the rubber became too brittle and lost its elasticity because of excessive crosslinks.

Effect of silica on the mechanical properties of the cured rubber

The inclusion of the filler improved the mechanical properties of the cured rubber noticeably (compounds 36 and 37; Table VI). The Shore A hardness increased from 45 to 72, the tensile strength increased from 1.1 to 16.7 MPa, the elongation at break increased from 232 to 606%, and the stored energy density at break increased from 1.8 to 49 MJ/m³. Probably the most interesting results were recorded for the tear strength and abrasion resistance of the rubber. The tearing energy rose from 1.2 to 30 kJ/m², and the relative volume loss in the abrasion tests decreased from 819 to 15.5 mm³/mg. The latter indicated a substantial increase in the abrasion resistance of the rubber filled with silica. The modulus at different strains also gained a benefit from the addition of the filler to the rubber. For example, at 50% strain, the modulus rose from 0.6 to 2.8 MPa, and this trend continued as the strain on the rubber was increased to 200%. The increase in the strain amplitude also affected the modulus of the rubbers. The modulus of the control

compound decreased from 0.60 to 0.18 MPa as a function of the strain up to 200%. A similar behavior was observed for the filled rubber, for which the modulus decreased from 2.8 to 2.2 MPa for up to 200% strain, and then it increased to its original value when the strain reached 500%.

Effect of silica on the cyclic fatigue life of the rubber

The cyclic fatigue life of the rubber increased when silica was added (Table VIII). A minimum fatigue life of 0.004 kc was recorded for the control compound, and then it increased to 40 kc when silica was incorporated into the rubber. The filled rubber also performed better at the upper end, with four samples exceeding 1000 kc, whereas for the control compound, only two samples exceeded 1000 kc.

The stored energy density (measured from the area under the first stress versus the strain trace) at 100% strain, at which the samples were cycled, was 0.45 and 1.5 MJ/m³ for the control and filled rubbers, respectively (Table VI). The fatigue life decreases as a function of the stored energy density in the rubber.²⁴ However, our results showed the filler to be beneficial to the fatigue life of the rubber. Factors such as the initial flaw size in the rubber also control the fatigue life. The number of cycles to failure is inversely proportional to the initial flaw size in the rubber.²⁶ It is likely that the samples had flaws of different sizes when they were first cured in the mold, which might have affected the results. The fatigue test results should therefore be treated with some caution.

Rubber reinforcement is mainly due to strong filler–filler interactions²⁷ and rubber–filler adhesion.²⁸ Other factors such as the crosslink density,²⁹ filler particle size and dispersion,^{30,31} surface chemistry or activity,⁸ and filler pH³² also influence the extent to which cured rubbers are reinforced. The 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 the ambient temperature and over many days and is a practical means of evaluating the degree of rubber–filler adhesion. The formation of bound rubber increases with factors such as the temperature and time as well as the surface activity of the filler.¹³ The bound rubber content for some cured natural rubber containing 50 phr precipitated silica was determined and found to be approximately 32%.¹³ This indicated strong rubber–filler adhesion. Processing properties such as the viscosity were also increased when silica was added to natural rubber.²⁷ This was attributed to the filler load-

ing and filler–polymer and filler–filler interactions. Improvements in the tensile strength, resilience, and energy at break have been reported as a function of the crosslink density.²⁴

Because the silica particles were fully dispersed in the rubber matrix (Fig. 3), the filler–filler interaction made no contribution to the rubber reinforcement. However, the full dispersion of the silica particles and the filler loading contributed to the improved mechanical properties of the rubber.

The bound rubber content in the filled rubber was 93% (Table VI), which indicated very strong filler–rubber adhesion. Moreover, the crosslink density of the filled rubber was 141 mol/m³, which corresponded to a Δ torque value of 91.5 dN m (Table VI). This also confirmed contribution from the crosslinks or chemical bonding between the rubber and the filler via TESPT to the rubber reinforcement.

The pretreatment of the silica surfaces with TESPT destroyed most or all of the OH groups⁵ and introduced sulfur-containing TESPT onto the surfaces of silica, which formed covalent bonds between the rubber and filler at the elevated curing temperature. It was therefore concluded that the improvement in the mechanical properties of the cured rubber was mainly due to a high level of rubber–filler adhesion and strong sulfur chemical bonding between TESPT and the rubber.

As mentioned earlier,¹ the cure systems in industrial rubber compounds often consist of up to five different rubber chemicals, including accelerators, activators, and curing agents. For these compounds, a tensile strength of 22 MPa, an elongation at break of 490%, a modulus of 2.7 MPa (at 100% strain), and a tear strength of 6 kJ/m² have been reported.³³ It was interesting that when the silanized silica nanofiller was used in the rubber, only one accelerator was needed to optimize the chemical bonding between the rubber and the filler and to produce a cured rubber with good mechanical properties (Table VI). This new approach resulted in a substantial reduction in the use of the curing chemicals without compromising the important properties of the cured rubber, which are essential for maintaining long life and good performance in service.

This also helped to improve health and safety in the workplace and minimize harm to the environment. Furthermore, a significant cost saving was also achieved by the reduction of the number and amounts of the curing chemicals in the rubber.

CONCLUSIONS

From this study, it can be concluded that

1. To optimize the chemical bonding between the rubber and filler, 7.5 phr TBBS was needed.

When zinc oxide was added to the filled rubber with 7.5 phr TBBS, the rubber was too brittle. The addition of stearic acid to the filled rubbers with TBBS and with TBBS and zinc oxide offered no benefit to the crosslink density of the rubber.

2. The hardness, tensile properties, tear strength, abrasion resistance, modulus, and cyclic fatigue life improved substantially when the filler was incorporated into the rubber. The bound rubber and crosslink density measurements indicated strong rubber–filler adhesion and chemical bonding between the rubber and filler, respectively, which were essential for the reinforcement of the rubber properties.

In summary, this novel technique for crosslinking and reinforcing high-cis polybutadiene rubber with a silanized silica nanofiller has numerous advantages over sulfur-cured carbon black filled rubber compounds.

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