

Reinforcement of Silicone Rubber with Precipitated Amorphous White Silica Nanofiller—Effect of Silica Aggregates on the Rubber Properties

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Silicone rubbers often possess poor mechanical properties and must be reinforced with fillers such as synthetic silicas for industrial applications. The effect of up to 60 parts per hundred rubber by weight precipitated amorphous white silica nanofiller on the properties of a peroxide-cured polydimethyl siloxane rubber was studied. The rubber also contained a small amount of vinyl groups. The mechanical properties of the rubber vulcanisate were enhanced noticeably when the filler was added. This was mainly due to a strong filler-filler interaction which produced large silica aggregates in the rubber. The addition of the filler was also beneficial to the crosslink density of the rubber.

Key words: reinforcement; silicone rubber; silica; nanofiller; aggregates; mechanical properties; polydimethyl siloxane; crosslink density

Silicone rubbers are used in a wide range of industrial applications such as seals, electrical, electronics, pharmaceutical, coatings, adhesives, automotives, foams, aerospace, optical and medical. Their useful properties include good resistance to fire, ageing, heat, and weathering. They also have good low temperature flexibility. However, their limited properties in respect of poor resistance to impact and abrasion makes them unsuitable for use in applications where exposure to high stresses may occur. These elastomers, often referred to as polydimethylsiloxane, are produced from diorganosiloxyl units. Methyl (CH_3-) group is the commonest organic group (Scheme 1a), but other grades of silicone elastomers are also prepared by copolymerising small amounts of vinyl ($\text{CH}_2=\text{CH}-$)/methyl siloxyl groups (Scheme 1b) with dimethyl siloxyl

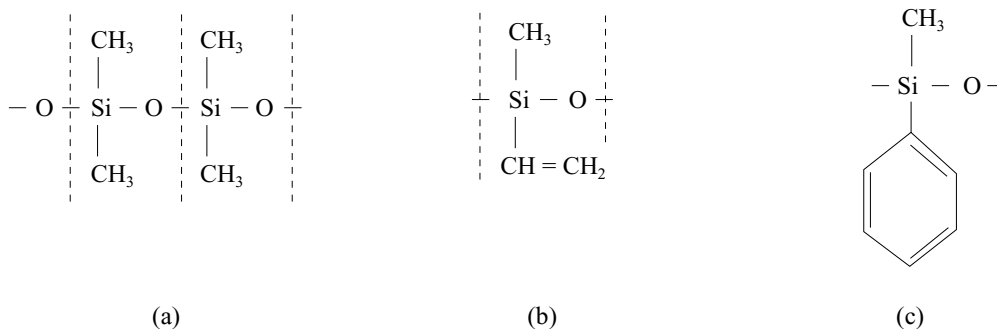
ones, and by terpolymerising phenyl(C_6H_5-)/methyl groups (Scheme 1c) and vinyl/methyl siloxyl groups with dimethyl siloxyl ones. All these grades contain a large quantity of dimethyl siloxyl units. Polmanteer and co-workers¹⁻³ have published some excellent papers on the development and technological progress of silicone elastomers.

As these elastomers often possess weak mechanical properties, they must be reinforced with fillers. Reinforcement of elastomers enhances properties, for example tear strength, tensile strength, hardness, and abrasion resistance⁴. This is brought about by the inclusion of a solid phase such as synthetic silicas, quartz, and metal oxides, which have large surface areas and have been shown to be very effective in improving the rubber

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Scheme 1. (a): Methyl siloxy groups; (b): Vinyl/methyl siloxy group; (c): Phenyl/methyl siloxy group.

properties³. Among these fillers, amorphous silica with surface area ranging from 150 m²/g to 400 m²/g offers the highest reinforcement. Synthetic silicas, for instance precipitated silica, possess siloxane and silanol groups⁵, and the silanol groups (SiOH) are acidic⁶. Moreover, because the surfaces of these fillers are polar and hydrophilic, there is a strong tendency to adsorb moisture⁷. When a large amount of silica is added, the viscosity increases substantially. Increases in compound viscosity due to silica can be attributed to the strong silica-silica interaction⁸.

Rubber reinforcement is mainly due to strong filler-filler interaction⁸ and rubber-filler adhesion⁹. Other factors such as crosslink density¹⁰, filler particle size and dispersion^{11,12}, surface chemistry or activity¹³, and pH of filler¹⁴ also influence the extent by which rubber vulcanisates are reinforced. The measurement of bound rubber is a practical means of evaluating the degree of rubber-filler adhesion. The bound-rubber content for some natural rubber vulcanisates containing 50 p.h.r. precipitated silica was determined and found to be approximately 32% (Tan *et al.*⁸).

This indicated strong rubber-filler adhesion. Processing properties such as viscosity were also increased when silica was added to natural rubber⁸. This was due to strong filler-filler interaction. Improvement in tensile strength, resilience and energy at break has been reported as a function of crosslink density¹⁵.

The aim of this study was to assess the effect of aggregates of precipitated silica nanofiller on the processing, cure and mechanical properties of a peroxide cured silicone rubber. Silicone fluid was also added to the rubber in order to make the silica filler hydrophobic. The fluid is a linear polydimethyl siloxane (PDMS) molecule with a hydroxide group on each end of the chain. The OH on the fluid reacts with OH on the silica surface, *via* a condensation reaction, resulting in coverage of the silica with a PDMS surface. The silica surface thus becomes hydrophobic. The dispersion of silica in the rubber and the fracture surfaces, after the tests were completed, were examined in an electron microscope. The information was subsequently used to understand the failure mechanism of the rubber in different tests.

EXPERIMENTAL

Materials

The raw elastomer used was polydimethyl siloxane Silastic (R) SGM-11. It was a random copolymer in which some of the methyl groups were substituted with vinyl ones producing vinyl/methyl dimethyl silicone rubber. The end groups were dimethyl vinyl siloxane. The vinyl content was 0.065% by weight. The silicone fluid was DC-2737[®], a polysiloxane diol with a total OH content of 5% by weight. Both products were supplied by Dow Corning Limited UK, who also advised on the use of the silicone fluid in the rubber. The curing agent was dicumyl peroxide purchased from Fisher Scientific, UK. The reinforcing nanofiller was precipitated amorphous white silica-type Ultrasil VN3[®] provided by Degussa Limited of Germany. It had a pH of 6.2 (*ISO 787-9*), surface area 175 m²/g (measured by N₂ adsorption) (*ISO 5794-1, Annex D*) and average particle size about 19 nm¹⁶.

Mixing

The compounds were prepared in a Haake Rheocord 90, a small-sized laboratory mixer with counter rotating Banbury rotors. The volume of the mixing chamber was 78 cm³, and a fill factor of 0.77 was used for preparing the compounds. The rotor speed was 30 r.p.m. and the temperature of the mixing chamber was 25°C for making the unfilled rubber, and 160°C for mixing the silicone fluid, filler and rubber. Haake Software Version 1.9.1. was used for controlling the mixing condition and storing data.

Procedure for Preparing the Rubber Compounds

Compounds with an increased loading of peroxide. In order to select a suitable

amount of peroxide for curing the rubber, four compounds were prepared (Compounds 1-4) (*Table 1*). The loading of peroxide was raised from 0.10 p.h.r. to 0.50 p.h.r. and it was mixed with the rubber for 5 min.

Control compound. The control compound was prepared by mixing the rubber with peroxide for 5 min (Compound 5) (*Table 2*).

Compound with 10 p.h.r. of silica. The compound with 10 p.h.r. silica was prepared in three stages (Compound 6) (*Table 2*). In stage 1, the rubber was introduced into the mixer and then the silicone fluid was added. The rotors started and the silica was incorporated into the rubber and mixed for 5 min. The ratio of silica to silicone fluid was 6.4:1. After 5 min had elapsed, the rotors were stopped and the temperature of the mixing chamber was raised to 160°C. In stage 2, the rubber was mixed for 30 min at 160°C after which the rotors stopped and the compound was cooled to below 30°C. In stage 3, peroxide was added to the rubber and mixed for 5 min. Finally, the compound was removed from the mixer and cooled to ambient temperature.

Compound with 60 p.h.r. of silica. The compound with 60 p.h.r. silica was prepared in 5 stages (Compound 7) (*Table 3*). In stage 1, the rubber was introduced in the mixer and then the silicone fluid was added. The rotors started and 20 p.h.r. silica was added and mixed for 5 min. In stages 2 and 3, 20 p.h.r. silica was added and mixed for 5 min, respectively. The ratio of silica to silicone fluid was 6.4:1. After stage 3 had ended, the rotors stopped and the temperature of the mixing chamber was raised to 160°C. In stage 4, the rubber was mixed for 30 min at 160°C, and subsequently the rotors stopped and the compound was cooled to below 30°C before peroxide was added. In stage 5, peroxide was incorporated into the rubber and mixed for 5 min. Finally, the rubber was removed from the mixer and cooled to ambient temperature.

TABLE 1. FORMULATION FOR THE UNFILLED-RUBBER COMPOUND WITH INCREASING LOADING OF PEROXIDE

Formulation (p.h.r.)	Compound number			
	1	2	3	4
Silicone rubber	100	100	100	100
Dicumyl peroxide	0.1	0.2	0.35	0.5
Minimum torque (dN.m)	1.5	2	1.5	2
Maximum torque (dN.m)	24.5	28	28	28
Δ torque (dN.m)	23	26	26.5	26
Scorch time (min)	7	3.5	3	3
Optimum cure time (min)	23	11	9	9
Cure rate index (min^{-1})	6.3	13	17	17

Mixing time: 5 min.

(The compound temperature during mixing was 26°C).

TABLE 2. FORMULATION FOR CONTROL COMPOUND AND COMPOUND WITH 10 P.H.R. SILICA

Formulation (p.h.r.)	Compound 5 ^a
Silicone rubber	100
Dicumyl peroxide	0.2
Mixing time (min)	5
Compound temperature during mixing (°C)	25-28
	<u>Compound 6</u>
	Stage 1 of mixing
Silicone rubber	100
Silicone fluid	1.6
Silica	10
Mixing time (min)	5
Compound temperature during mixing (°C)	25-28
Rotors were stopped and the temperature of the mixing chamber was raised to 160°C	
	Stage 2 of mixing
Mixing time (min)	30
Compound temperature during mixing (°C)	160
Rotors were stopped and the compound was cooled to below 30°C before peroxide was added	
	Stage 3 of mixing
Dicumyl peroxide	0.2
Mixing time (min)	5
Compound temperature during mixing (°C)	27-30
Compound was removed and cooled to ambient temperature	

^aControl compound

TABLE 3. FORMULATION FOR RUBBER COMPOUND WITH 60 P.H.R. SILICA

Formulation (p.h.r.)	Compound 7
	Stage 1 mixing
Silicone rubber	100
Silicone fluid	9.3
Silica	20
Mixing time (min)	5
Compound temperature during mixing (°C)	25-28
	Stage 2 mixing
Silica	20
Mixing time (min)	5
Compound temperature during mixing (°C)	25-28
	Stage 3 mixing
Silica	20
Mixing time (min)	5
Compound temperature during mixing (°C)	25-28
Rotors were stopped and the temperature of the mixing chamber was raised to 160°C	
	Stage 4 mixing
Mixing time (min)	30
Compound temperature during mixing (°C)	160
Rotors were stopped and the rubber compound was cooled to below 30°C before peroxide was added	
	Stage 5 mixing
Dicumyl peroxide	0.2
Mixing time (min)	5
Compound temperature during mixing (°C)	27-30
Rubber compound was removed from the mixer and cooled to ambient temperature	

The reason for adding silicone fluid was that if untreated (hydrophilic) when silica is mixed with PDMS, hydrogen bonds are formed between the oxygen atoms in the polymer backbone and the silanol on the silica surface. If the molecular weight of the PDMS is high enough it only takes a small amount of hydrogen bonding to turn what is initially a high viscosity fluid into a hard brittle material which is extremely crumbly and difficult to process. If the silica OH is completely neutralised, then

obviously the ability of the silica to reinforce the rubber will be greatly reduced. In order to get sufficient interaction with the rubber for reinforcement, the level of hydrophobicity of the silica needs to be controlled. This is done by controlling the silica surface area and the ratio of diol fluid to silica in the elastomer.

After the compounds were made, they were milled to a thickness of about 6.5 mm for further work. The mixing cycles for preparing

the filled rubber compounds were selected to produce silica aggregates in the rubber matrix in order to assess their effects on the rubber properties.

Properties of the Rubber Compounds

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer according to the procedure described previously¹⁷. The scorch time, which is 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 160°C \pm 2°C by an oscillating disc rheometer curemeter (ODR) at an angular displacement of \pm 3° and a test frequency of 1.7 Hz¹⁸. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described in the British Standards¹⁹. Results from these tests are summarised in *Table 4*.

Test Pieces and Test Procedure

After the viscosity and cure properties were measured (*Table 4*), the rubber compounds

were cured in a compression mould at 160°C. Pieces of rubber, each approximately 200 g in weight, were cut from the milled sheets. Each piece was placed in the centre of the mould to enable it to flow in all the directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. The mould was placed in a hydraulic press under 11 MPa pressure during the curing of the rubber. For measuring the mechanical properties of the rubber, slabs of 23 cm by 23 cm by approximately 2.5 mm thick were used, from which various samples for further tests were cut.

Hardness

For determining the hardness of the rubber, cylindrical samples of 12.5 mm thickness and 28 mm in diameter were cured. The samples were then placed in a Shore A Durometer hardness tester, and the hardness of the rubber was measured at 22°C over a 15-s interval after which a reading was taken. This was repeated at three different positions on the sample, and median of the three readings was subsequently determined²⁰ (*Table 5*).

TABLE 4. MOONEY VISCOSITY AND CURE PROPERTIES OF THE RUBBERS

	Compound number		
	5 ^a	6	7
Mooney viscosity [ML(1+4) at 100°C]	4	5	15
	ODR results		
Minimum torque (dN.m)	1.6	2	4
Maximum torque (dN.m)	28	30	66
Δ torque (dN.m)	26.4	28	62
Scorch time (t_{s1} , min)	4	5	4
Optimum cure time (t_{90} , min)	11	16	17
Cure rate index (min^{-1})	14.3	9.1	7.7

^aControl compound

TABLE 5. HARDNESS, TENSILE STRENGTH, STORED ENERGY DENSITY AT BREAK, ELONGATION AT BREAK, TEARING ENERGY, MODULUS, AND CYCLIC FATIGUE LIFE OF THE RUBBERS

Compound number	5 ^a	6	7
	Hardness (Shore A)		
	—	26	54
	Tensile strength (MPa)		
	0.4	0.8	5.5
	Elongation at break (%)		
	130	260	750
	Stored energy density at break (MJ/m ³)		
	0.3	1.1	20
	Stored energy density at 100% strain (MJ/m ³)		
	0.17	0.24	0.45
	Tearing energy (kJ/m ²)		
	0.3	0.7	3.7
Range of values	0.2–0.3	0.5–0.7	3.2–5.5
	Modulus at different strains (MPa)		
Strain amplitude (%)			
50	0.32	0.38	0.70
100	0.21	0.24	0.64
150	—	0.24	0.76
	Cyclic fatigue life (kilo cycles)		
Sample			
1	1	6.7	6.2
2	1	11.5	14.0
3	1	15.8	16.0
4	1	27.3	17.0
5	1	39.0	18.7
6	1	67.4	19.7
7	1	102.6	20.9
8	1	114.6	22.2
9	2	143.4	22.4
10	3	208.2	23.9
11	747	244.5	27.1
Median values	1	67.4	19.7
Standard Deviation	214.4	78.1	5.4

^aControl compound

Tensile Strength

The tensile strength, elongation at break and stored energy density at break of the rubber were determined in uniaxial tension in a Lloyd mechanical testing machine, using dumbbell test pieces of 75 mm long with a central neck of 25 mm long and 3.6 mm wide. The samples were die-stamped from slabs of the cured rubber. The tests were performed at 25°C at a cross-head speed of 50 mm/min²¹. Lloyd DAPMAT computer software was used for storing and processing the data (*Table 5*).

Tear Strength

The tear strength of the rubber was measured using rectangular strips of 100 mm length and 30 mm width which were cut from the cured sheets of rubber. 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 trouser test pieces for the tear experiments. Trouser tear tests were performed at an angle of 180°, at 25°C and at a constant cross-head speed of 50 mm/min²², using a Lloyd mechanical testing machine. The tear produced varied in length from approximately 15 mm to 70 mm. In some cases, tearing produced peaks on the trace where an average force was calculated (*Figure 1*), and sometimes tearing produced a smooth trace from which a force was measured (*Figure 2*). Five test pieces were used for each rubber. Tearing energies were obtained from *Equation 1*²³:

$$T = 2F/t \quad \dots 1$$

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 5* and *6*.

Modulus at Different Strain Amplitudes

The modulus of the rubbers (*Table 5*) was measured at 50%, 100% and 150% strain amplitudes in uniaxial tension, using dumbbell test pieces. The tests were carried out at 22.5°C at a cross-head speed of 50 mm/min in a HT Hounsfield mechanical testing machine. QMAT-DONGLE version 2003 computer software was used to process the data.

Cyclic Fatigue Life

The cyclic fatigue life of the rubber was measured in uniaxial tension in a Hampden dynamic testing machine, using dumbbell test pieces. The test pieces were die-stamped from the sheets of cured rubber. The tests were performed at a maximum constant deflection of 100% (the central neck was stretched to 50 mm), and a test frequency of 1.5 Hz. The test temperature was about 24.5°C, and the strain on each test piece was relaxed to zero at the end of each cycle²⁴. For each rubber compound, 11 test pieces were cycled to failure, and the results were presented in an increasing order of magnitude in *Table 5*.

Silica Dispersion in the Rubber

Dispersion of the silica particles in the rubber was assessed by Stereoscan 360 scanning electron microscope (SEM). Two samples of the unused cured rubber containing the filler were placed in liquid nitrogen for 5 min. The samples were recovered and fractured into two pieces to create fresh surfaces 9 mm² in area. The surfaces were coated with gold, and then examined and photographed in the SEM. The degree of dispersion of the silica in the rubber was subsequently studied from SEM photographs. An Oxford Instruments INCA system was used to determine the composition of the samples. After the cyclic fatigue tests

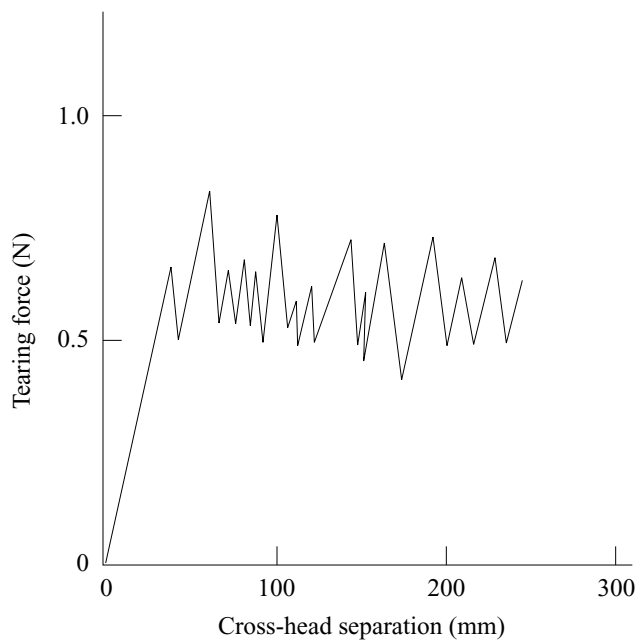


Figure 1. Typical record of tearing force as a function of cross-head separation.
Data for the unfilled rubber ($T \sim 0.7 \text{ kJm}^{-2}$).

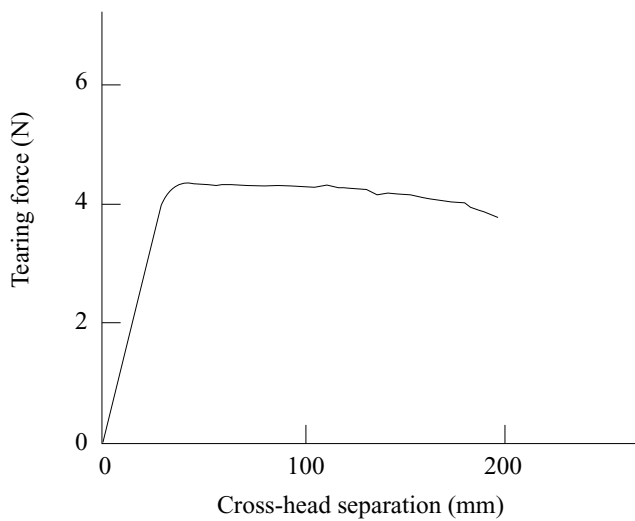


Figure 2. Typical record of tearing force as a function of cross-head separation.
Data for the rubber with 60 p.h.r. silica ($T \sim 3.2 \text{ kJm}^{-2}$).

TABLE 6. DETAILS OF THE TEAR TESTS AND TEAR BEHAVIOUR OF THE VULCANISATES

Vulcanisate	Tearing energy (kJ/m ²)	Tear path	Tear length after test piece was fractured (mm)
Compound 5 ^a	0.2	A	30
	0.2	A	25
	0.3	A	30
	0.3	A	50
	0.3	A	43
Compound 6	0.5	B	64
	0.6	A	57
	0.7	B	66
	0.7	B	65
	0.7	B	37
Compound 7	3.2	B	65
	3.3	A	20
	3.7	B	65
	4.4	A	15
	5.5	B	70

^aControl compound

A = Non-linear: crack turned towards the edges of the test piece during propagation and did not cover the entire length of the test piece.

B = Linear: crack grew along the length of the test piece almost in a straight path, covering the entire length of the test piece.

were completed, the fracture surfaces were examined in the SEM. Some of the samples were subsequently photographed for further examination in order to understand the failure mechanism of the rubber in these tests.

RESULTS AND DISCUSSION

Effect of Peroxide on the Cure of the Rubber

After the compounds were tested by ODR (*Table 4*), the Δ torque which is the difference between the maximum and minimum torque values on the cure traces of the rubbers, was calculated and plotted against the loading of

peroxide (*Figure 3*). The Δ torque is also an indication of crosslink density changes in the rubber¹³. Evidently, 0.2 p.h.r. peroxide was sufficient to optimise the crosslink density of the rubber. Further increase in the loading of peroxide had little or no effect on the Δ torque, which remained essentially unchanged at about 26 dN.m. In the subsequent work, 0.2 p.h.r. peroxide was used to cure all the compounds (*Tables 2 and 3*).

Silica Dispersion in the Rubber after Freeze/Fracture

When the rubber with 10 p.h.r. silica was examined in the SEM (*Figure 4*), large

aggregates of silica approximately 45 μm were seen in the matrix. This was confirmed after their composition was analysed in the SEM (*Figure 5*). There were regions where a high concentration of silica aggregates were present in the rubber (*Figure 6*). Cavities were formed around the silica aggregates due to the filler not wetting the rubber (*Figure 4*). In the sample with 60 p.h.r. silica, the filler dispersion was poor and aggregates about 130 nm in size were seen (*Figure 7*), and in the subsequent work with this rubber, aggregates up to 70 μm were also detected.

Effect of Silica on the Viscosity and Cure

After 10 p.h.r. silica was incorporated in the rubber, the viscosity hardly changed and remained at about 4–5 Mooney units (*Table 4*), but with 60 p.h.r. silica the viscosity rose to 15 Mooney units. The increase in the viscosity was due to strong silica-silica interaction⁸, which produced aggregates in the rubber (*Figure 7*). Probably, the most interesting aspect of the filler loading was the effect it produced on the Δ torque of the rubber vulcanisate. With 10 p.h.r. silica, the Δ torque increased from 26 dN.m to 28 dN.m, and continued rising to 62 dN.m after the full amount of silica was included in the rubber compound. As expected¹³, the silica did not interfere with the reaction of peroxide and formation of crosslinks in the rubber and in fact it was greatly beneficial to it. Also, it has been shown that silica increased the crosslink density to several times that of the unfilled vulcanisate¹¹. The increase in turn improved the properties of the rubber for instance modulus and hardness¹¹. The improvement in the rubber properties (*Table 5*) was due to the presence of silica aggregates and also increase in the crosslink density as indicated by a rise in the Δ torque (*Table 4*). Silica had a detrimental effect on the optimum cure time and rate of cure. The former increased from 11 min to 17 min, and the cure rate index for the

later dropped from 14 min^{-1} to about 8 min^{-1} . The scorch time remained at 4 min – 5 min, irrespective of the loading of the filler.

Mechanical Properties

The mechanical properties as shown in *Table 5* were also influenced by the addition of the filler. The hardness and tensile strength were increased to 54 Shore A and 5.5 MPa, respectively with 60 p.h.r. silica. When the control sample was placed in the hardness tester, no reading appeared because the rubber was too soft. Similarly, the elongation at break and stored energy density at break were also improved from 130% to 750% and 0.3 MJ/m^3 to 20 MJ/m^3 , respectively when the full loading of silica was added to the rubber. The tearing energy rose by almost 10 fold from 0.3 kJ/m^2 to 3.7 kJ/m^2 which indicated a strong filler influence on the tear strength of the rubber. The modulus also increased when silica was incorporated into the rubber. For example, the modulus at 50% strain amplitude rose from approximately 0.3 MPa to 0.7 MPa. A similar trend was also observed at 100% and 150% strain amplitudes. Clearly, the inclusion of silica was beneficial to the rubber stiffness. The cyclic fatigue life lengthened from about 1 kc to 6.7 kc with 10 p.h.r. silica, but shortened to about 6.2 kc when 60 p.h.r. silica was added to the rubber compound (*Table 5*). It was interesting that the minimum fatigue life increased so significantly from 1 kc to 6.7 kc after 10 p.h.r. silica was added, but there was no additional benefit gained from the increase in the amount of the filler to 60 p.h.r. The increase in the loading of silica had a detrimental influence on the maximum fatigue life, which decreased from 244.5 kc to 27 kc. This might have been due to a larger number of voids formed in the rubber during the fatigue tests (comparing *Figures 8* and *9*), which caused the samples to fail sooner.

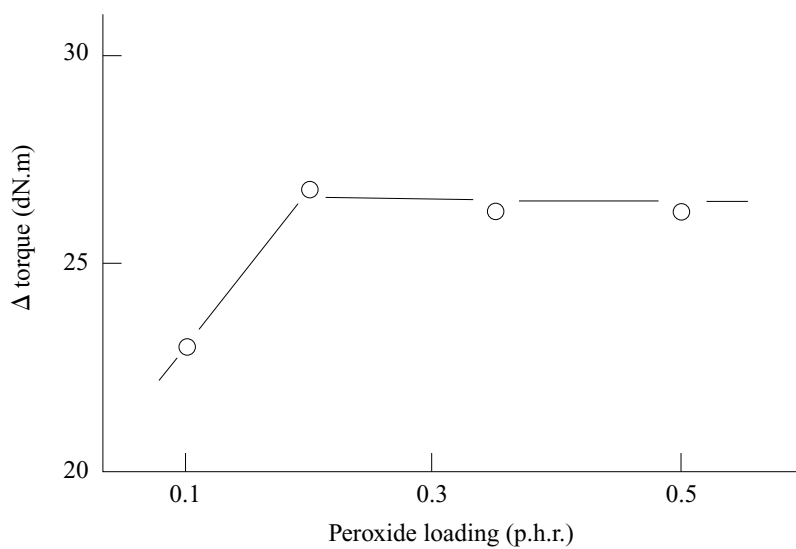


Figure 3. Δ torque as a function of dicumyl peroxide loading for compounds 1-4 shown in Table 1.

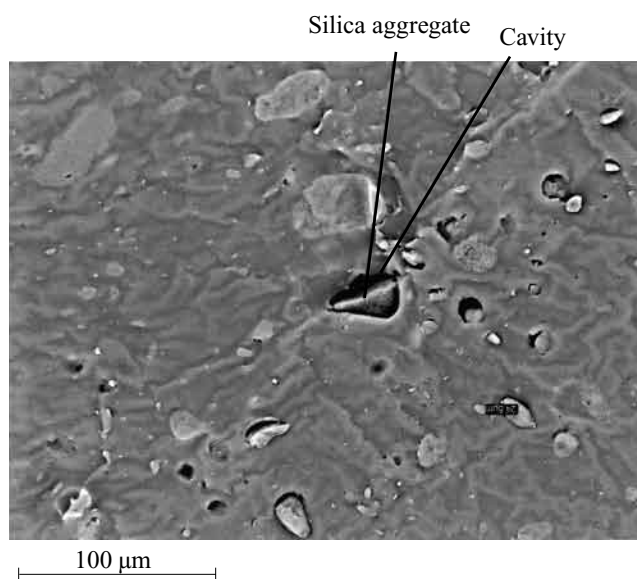


Figure 4. SEM photograph showing silica dispersion in the rubber with 10 p.h.r. silica after freeze/fracture.

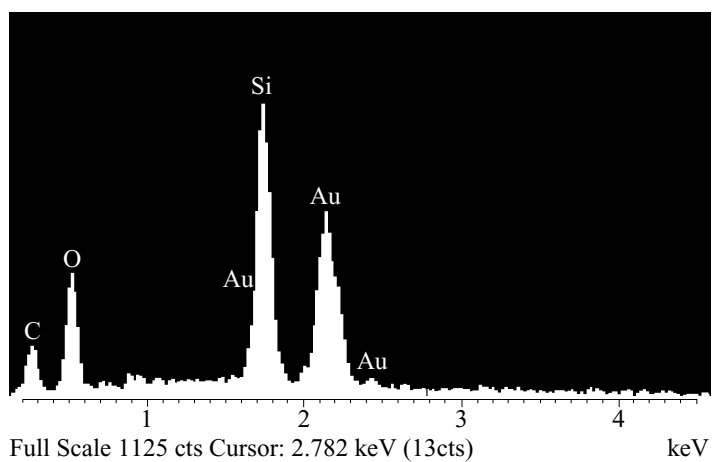


Figure 5. EDX spectrum of the clumps seen as in Figure 4.

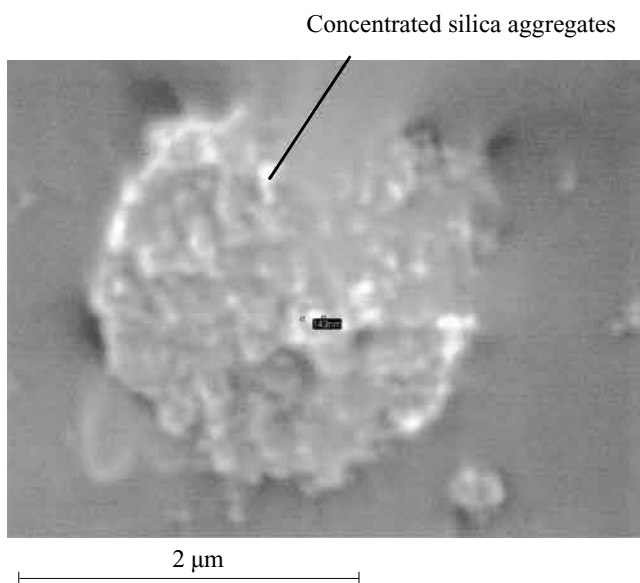


Figure 6. SEM photograph showing large concentration of aggregates in the rubber with 10 p.h.r. silica after freeze/fracture.

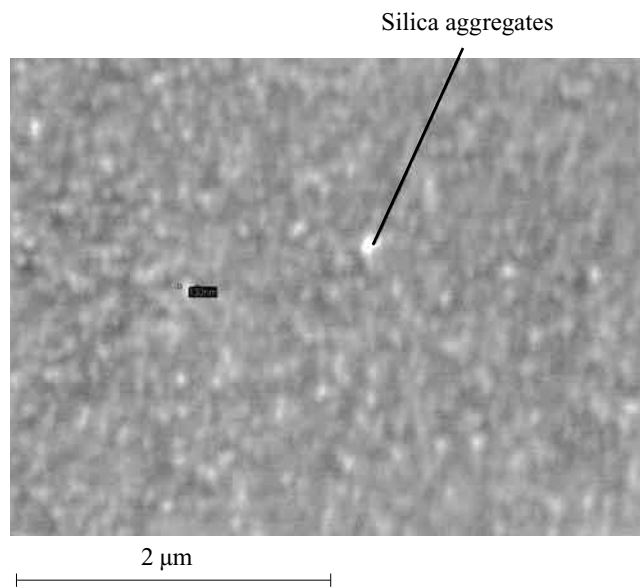


Figure 7. SEM photograph showing silica dispersion in the rubber with 60 p.h.r. silica after freeze/fracture.

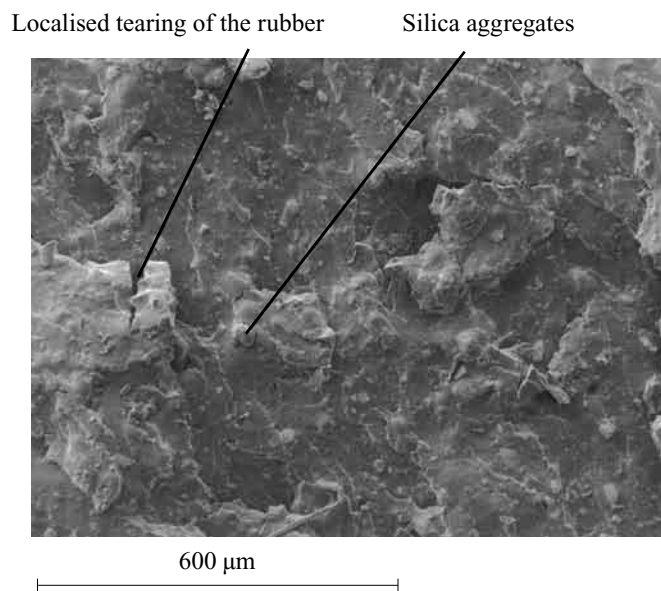


Figure 8. SEM photograph showing typical fracture surface from the fatigue test on the sample with 10 p.h.r. silica.

The stored energy density (measured from the area under the first stress *versus* strain trace) (*Figure 10*) of the unfilled rubber and the rubbers filled with 10 p.h.r. and 60 p.h.r. silica at 100% strain amplitude, which the samples were tested, were 0.17 MJ/m³, 0.24 MJ/m³, and 0.45 MJ/m³, respectively (*Table 5*). Fatigue life shortens when stored energy density in the rubber increases¹⁵. There was no correlation between these two properties, at least for the unfilled and 10 p.h.r. silica-filled rubbers. Other factors such as initial flaw size in the rubber also control the number of cycles to failure²⁵. It is likely that the samples had flaws of different sizes when they were first cured in the mould, which might have also influenced the results.

When the filled rubbers were stretched in the tensile tests, whitening occurred. This was due to voids forming in the rubber when the weak rubber-filler interface failed, this was similar to the ones shown in *Figure 9*. The stress whitening of silicone rubbers was related to the pH and/or residual Na₂O content of the silica¹⁴. It has been suggested that reducing the silica pH could increase the surface energy resulting in an increase in rubber-filler adhesion. This in turn would reduce the amount of voids produced during the stressing of the rubber. Stress whitening was shown to be directly related to silica dispersion, and a silica with a low pH, *i.e.* less than 6 did not stress whiten the rubber upon stressing²⁶. However, the silica used in this study had a pH of 6, and moreover, the silica particles formed aggregates in the rubber matrix. Therefore, the condition was right for the voids to form and the subsequent stress whitening effect to occur in the rubber.

Fatigue Fracture Surfaces

Figure 8 shows typical fracture surface from the fatigue tests performed on the rubber

with 10 p.h.r. silica. The surfaces were rough with evidence of extensive tearing of the rubber. For the rubber with 60 p.h.r. silica (*Figure 9*), two distinct features were observed when the fracture surfaces were examined: the surfaces were uneven; and contained a large number of silica aggregates which were approximately 66 µm in size. In some cases, the silica aggregates were pulled out of the rubber leaving large depressions behind (*Figure 11*). This was evidence of extensive failure at the rubber-filler interface. It seemed that the repeated stressing of the rubber during the cyclic fatigue tests caused failure at the rubber-filler interface and in some cases, created cavities around the aggregates (*Figure 9*).

There are various factors which influence the silica reinforcement of silicone rubbers. There are the interaction of the silanol groups of silica with the oxygen in the siloxane linkage²⁷, the increase in crosslink density due to silica¹¹, aggregation of the filler particles, immobilisation of polymer chains by adhesion to the filler, and trapping of polymer chains in between the network-like aggregates²⁸, and hydrogen bonding between the silica surface silanols and the siloxane backbone²⁹. At 150°C, chemical grafting of the elastomer chains onto the silica surface took place which increased the modulus³⁰. The rubber compounds for this study were prepared at 160°C, and therefore chemical grafting of the elastomer chains onto the silica surface could have taken place, which increased properties such as modulus. However, it was clear from *Figures 4* and *9* that the filler-rubber adhesion was weak. The strong filler-filler interaction which caused large aggregates to form in the rubber contributed to the reinforcement of the vulcanisate. This was attributed to the trapping of the elastomer chains in between the network like aggregates to produce a large effective filler volume²⁸.

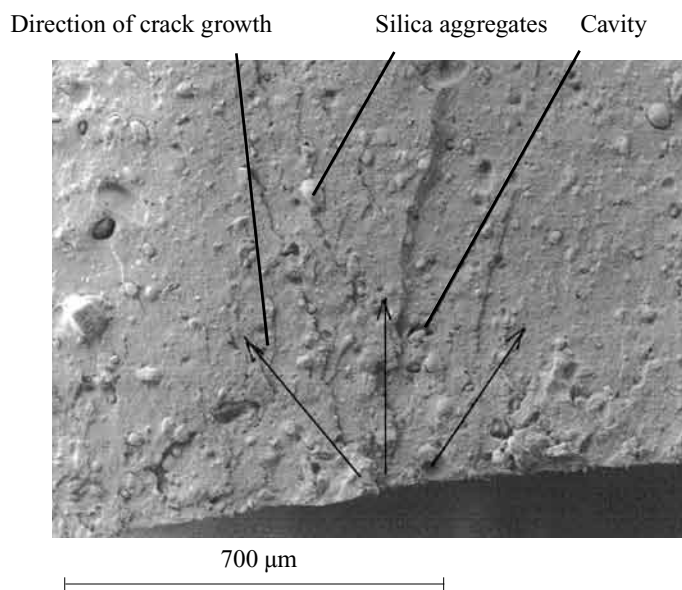


Figure 9. SEM photograph showing typical fracture surface from the fatigue tests performed on the sample with 60 p.h.r. silica. The photo shows the direction of crack growth in the rubber during the fatigue test, silica aggregates, and cavities around the aggregates.

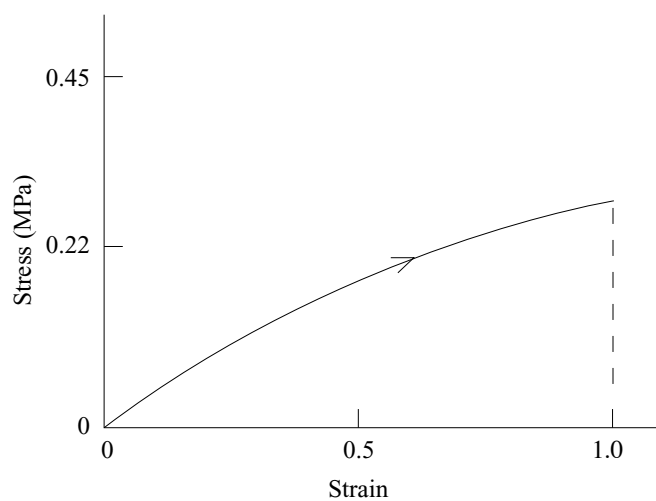


Figure 10. Typical stress versus strain data at 100% strain amplitude. Data for the control rubber (compound 5).

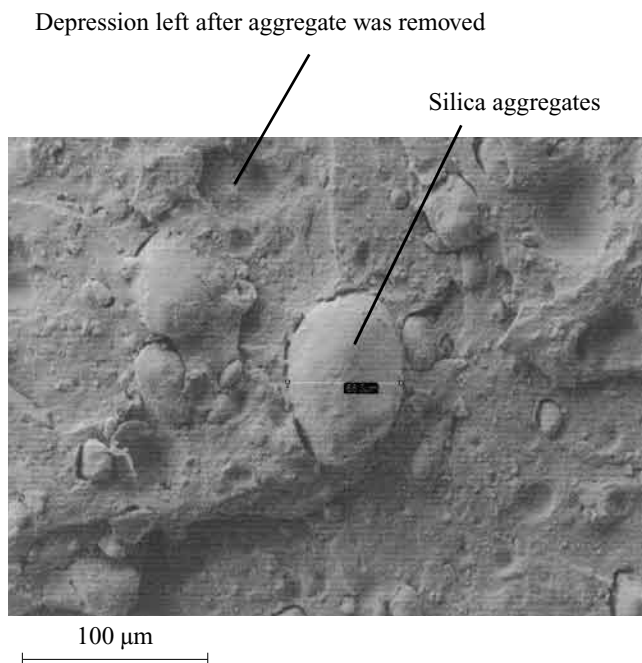


Figure 11. SEM photograph showing typical fracture surface from the fatigue tests performed on the rubber with 60 p.h.r. silica.

CONCLUSIONS

From this study, it was concluded that the hardness, tensile strength, elongation at break, stored energy density at break, and tearing energy of the rubber were improved when up to 60 p.h.r. precipitated amorphous silica was added. The cyclic fatigue life of the vulcanisate was increased with 10 p.h.r. silica, but deteriorated after the full amount of the filler was incorporated into the rubber.

There was evidence that the rubber-filler adhesion was weak. The formation of silica aggregates improved the mechanical properties of the rubber, and the addition of the filler was also beneficial to the crosslink density of the rubber.

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REFERENCES

1. POLMANTEER, K.E. (1988) Silicone Rubber, Its Development and Technological Progress. *Rubb. Chem. Technol.*, **61**, 470–502.

2. POLMANTEER, K.E. (1981) Current Perspectives on Silicone Rubber Technology. *Rubb. Chem. Technol.*, **54**, 1051–1080.
3. WARRICK, E.L., PIERCE, O.R., POLMANTEER, K.E. AND SAAM, J.C. (1979) Silicone Elastomer Developments. *Rubb. Chem. Technol.*, **52**, 437–525.
4. ANDREWS, E.H. (1963) Reinforcement of Rubber by Fillers. *Rubb. Chem. Technol.*, **36**, 325–336.
5. WOLFF, S., GÖRL, U., WANG, M. L. AND WOLFF, W. (1994) Silane Modified Silicas. *Eur. Rubb. J.*, **16**, 16–19.
6. HAIR, M.L. AND HERTL, W. (1970) Acidity of Surface Hydroxyl Groups. *J. Phys. Chem.*, **74**, 91–94.
7. BASSETT, D.R., BOUCHER, E.A. AND ZETTLEMOYER, A.C. (1968) Adsorption Studies on Hydrated and Dehydrated Silicas. *J. Colloidal Inter. Sci.*, **27**, 649–658.
8. TAN, E.H., WOLFF, S., HADDEMAN, M., GREWATTA, H.P. AND WANG, M.J. (1993) Filler-elastomer Interaction. Part IX. Performance of Silicas in Polar Elastomers. *Rubb. Chem. Technol.*, **66**, 594–604.
9. FRÖHLICH, J., NEIDERMEIER, W. AND LUGINSLAND, H.D. (2005) The Effect of Filler-filler and Filler-elastomer Interaction on Rubber Reinforcement. *Composites: Part A*, **36**, 449–460.
10. NASIR, M. AND TEH, G. K. (1988) The Effects of Various Types of Crosslinks on the Physical Properties of Natural Rubber. *Eur. Polym. J.*, **24**(8), 733–736.
11. POLMANTEER, K.E. AND LENTZ, C.W. (1975) Reinforcement Studies – Effect of Silica Structure on Properties and Crosslink Density. *Rubb. Chem. Technol.*, **48**, 795–809.
12. COCHET, PH., BARRUEL, P., BARRIQAND, L., GROBERT, J., BOMAL, Y., PRAT, E. AND RHONE POULENC, E. (1994) Dispersibility Measurement of Precipitated Silicas' Influence of Dispersion on Mechanical Properties. *Rubb. World*, **210**(3), 20–24.
13. WOLFF, S. (1996) Chemical Aspects of Rubber Reinforcement by Fillers. *Rubb. Chem. Technol.*, **69**, 325–346.
14. OKEL, T.A. AND WADDELL, W.H. (1995) Effect of Precipitated Silica Physical Properties on Silicone Rubber Performance. *Rubb. Chem. Technol.*, **68**, 59–76.
15. BRISTOW, G.M. AND TILLER, R.F. (1970) Correlation of Structure and Properties of Natural Rubber Vulcanisates. *Kautsch. Gummi Kunstst.*, **23**(2), 55–59.
16. ANSARIFAR, M.A., CHUGH, J.P. AND HAGHIGHAT, S. (2000) Reinforcing Effects of Precipitated Silicas on Properties of Some Vulcanisates of Styrene-butadiene Rubber. *Iran Polym. J.*, **9**(3), 153–162.
17. *BRITISH STANDARDS* (1969) Methods of Testing Raw Rubber and Unvulcanised Compounded Rubber: Methods of Physical Testing. *BSI 1673: Part 3*.
18. *BRITISH STANDARDS* (1977) Methods of Test for Raw Rubber and Unvulcanised Compounded Rubber: Measurements of Prevulcanising and Curing Characteristics by means of Curemeter. *BSI 1673: Part 10*.
19. *BRITISH STANDARDS* (1996) Methods of Test for Raw Rubber and Unvulcanised Compounded Rubber: Measurement of Prevulcanising and Curing Characteristics by Means of Curemeter. *BSI 903: Part A60: Section 60.1*.
20. *BRITISH STANDARDS* (1995) Physical Testing of Rubber: Method for Determination of Hardness. *BSI 903: Part A26*.
21. *BRITISH STANDARDS* (1995) Physical Testing of Rubber: Method for Determination of Tensile Stress Strain Properties. *BSI 903: Part A2*.

22. *BRITISH STANDARDS* (1995) Physical Testing of Rubber: Method for Determination of Tear Strength Trousers, Angle and Crescent Pieces. *BSI 903: Part A3*.
23. GREENSMITH, H.V. AND THOMAS, A.G. (1955) Rupture of Rubber. III. Determination of Tear Properties. *J. Polm. Sci.*, **43**, 189–200.
24. *BRITISH STANDARDS* (1986) Method of Testing Vulcanised Rubber: Determination of Resistance to Tension Fatigue. *BSI 903: Part A51*.
25. LINDLEY, P.B. AND THOMAS, A.G. (1962) Fundamental Study of the Fatigue of Rubbers. *Proc. Rubb. Technol. Conf., London*, 1–14.
26. BODE, R. AND REISERT, A. (1979) *Kautsch. Gummi Kunstst.*, **32**, 89.
27. BOONSTRA, B.B., COCHRANE, H. AND DANNENBERG E.M. (1975) Reinforcement of Silicone Rubber by Particulate Silica. *Rubb. Chem. Technol.*, **48**, 558–576.
28. THOMAS, D.K. AND MOORE, B.B. (1972) Filler Reinforcement in Silicone Polymers. *Polymer*, **13**, 109–114.
29. COCHRANE, H. AND LIN, C.S. (1993) The Influence of Fumed Silica Properties on the Processing, Curing, and Reinforcement Properties of Silicone Rubber. *Rubb. Chem. Technol.*, **66**, 48–60.
30. ARANGUREN, M., MORA, E., DEGROOT, J. AND MACOSKO, C. (1992) Effect of Reinforcing Fillers on the Rheology of Polymer Melts. *J. Rheol.*, **36**, 1165–1182.