

Organic Polymer-Surface Modified Precipitated Silica

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SYNOPSIS

To improve the performance of rubber compounds using precipitated silica as a reinforcing filler, the silica surface was directly modified by (1) adsorption of a surfactant, (2) adsolubilization of an organic monomer, (3) *in situ* polymerization of the monomer in the surfactant bilayer, and (4) partial surfactant removal. Silica was thus surface modified with polymerized styrene, isoprene, butadiene, and copolymers. Styrene–butadiene modification afforded the most promising candidate based on evaluation in a silica-filled model tire compound. Compound physical testing showed that cure times were decreased, and break strength, tear energy, elongation to break, and cut growth resistance were increased. Thus, surface modification of silica by the *in situ* polymerization of organic monomers affords unique materials useful in improving rubber cure properties and cured compound physical properties. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The use of precipitated silica in rubber compounds provides beneficial properties, including (i) tear, flex, abrasion and heat resistance; (ii) hardness, stiffness and modulus; (iii) adhesion to adjoining compounds and to wire and fabric reinforcements; (iv) low heat build-up; (v) high resilience; and (vi) neutral color,¹ leading to product applications that include tire treads, wire and fabric coat compounds, conveyor belts, hoses, rubber-covered rolls, engine mounts, bumper strips, and cable jackets. For example, off-the-road tire treads are compounded with silica to reduce heat build-up and to increase resistance to heat aging and to chipping/chunking,^{2–5} and rubber stocks for brass-coated wire use silica as an adhesion promoter in addition to resorcinol-formaldehyde resin^{6–8} and organocobalt^{9–10} adhesives. Carbon black, however, is still the particulate filler of choice, since the inherent reinforcing effect of silica in hydrocarbon elastomers is not comparable. This is primarily due to the nature of the nonbonded interaction¹¹ between the silica and polymer functionalities. The dipole-induced dipole interactions

between the polar groups (siloxane, silanol) on the surface of silica aggregates with the non-polar groups (alkyl, olefin, aryl) of hydrocarbon elastomers are weak compared to the hydrogen-bonding interactions between surface silanol groups in silica agglomerates. In addition, the dispersive forces between a nonpolar molecule and silica are low, while those between a nonpolar molecule and carbon black are high.^{12–15}

For these reasons, methods to improve the compatibility between hydrocarbon elastomers and precipitated silica by modification of the silica surface are of considerable interest. Bifunctional organosilanes such as 3-mercaptopropyltrimethoxysilane^{16–17} and bis-(3-triethoxysilylpropyl-)tetrasulfide^{18–19} afford chemical modifications of the silica surface that significantly increase the interactions between silica and hydrocarbon elastomers.¹⁵ Modification of the silica surface by grafting of alkyl groups has been accomplished by esterification with methanol or hexadecanol.²⁰ Silica has been coated by reaction with styrene-*co*-vinylmethyldiethoxysilane.²¹ The objective of the present research is to develop modified silicas by *in situ* polymerization of organic monomers in surfactant layers adsorbed onto the surface of precipitated silica in order to enhance silica/elastomer interactions and thus improve rubber product performance.

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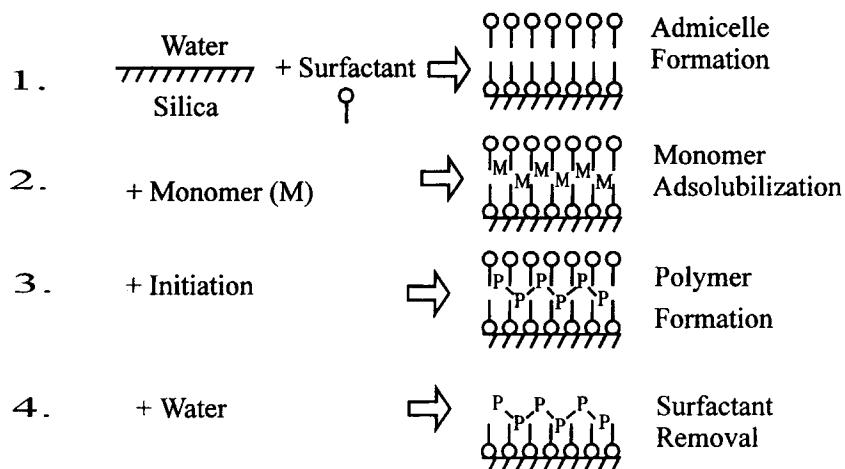


Figure 1 The four-step surface modification process.

The surface modification process utilized for this study can be considered to occur in four steps: (1) adsorption; (2) adsolubilization, (3) polymerization, and (4) washing (Fig. 1). In Step 1 an adsorbed micelle, or admicelle, is formed on the substrate. An admicelle can be viewed as the surface analog of a micelle. The formation of adsorbed surfactant bilayers due to adsorption on surfaces has long been established. In 1955, Iler²² represented the patchy adsorption of quaternary ammonium cationic micelles onto silica surfaces. By adjusting the pH of the feed solution, the surface charge of the silica particles can be adjusted to facilitate the adsorption of cationic surfactant molecules. If the pH of the solution is below the point of zero charge (PZC) of the substrate, the surface will be positively charged; if the pH is above the PZC the surface will be negatively charged. Silica has a PZC of ≈ 3 ²³ and a minimum solubility in water at a pH between 7 and 8. In this study, therefore, a feed pH of 8 was chosen; this maximized the negative charge on the surface while dissolving a negligible amount of the silica.

The feed concentration of the surfactant was chosen so that at equilibrium the bulk concentration of the surfactant was below the surfactant's critical micelle concentration (CMC) in order to avoid emulsion polymerization during Step 3. This combination of conditions produced a maximum level of surfactant adsorption without silica dissolution or formation of micelles.

In Step 2, monomer is solubilized into the admicelle, a process called adsolubilization. In the absence of micelles, the bilayer acts as a two-dimensional solvent to concentrate the monomer near the surface of the substrate. Wu et al.²⁴ reported that a mass balance could be accomplished on the system, showing that the monomer that disappeared from the bulk during this process was later recoverable by extraction as polymer. They also found that further adsolubilization of monomer occurred during the polymerization process as monomer in the bilayer was consumed.

Step 3 involves the polymerization of the monomer. The means by which this is accomplished can

Table I Silica Test Methods

Property	Method	Instrument
BET N ₂ surface area (single point)	ASTM D 3037-92	Leeds and Northrup 4200
Dibutyl phthalate (DBP) absorption	ASTM D 2414-92	Brabender Plastigraph
Median agglomerate particle size	ASTM F 662-86	Coulter Multisizer II
Mercury porosimetry (total pore surface area, median pore diameter, median pore volume)	ASTM D 4284-83	Quantachrome Autoscan 33
% carbon	ASTM E 350-90	Leco 521 Analyzer

Table II Rubber Compound Formulation

Ingredient	Parts Per Hundred Rubber
Natural rubber	70
Styrene-Butadiene rubber	30
Silica	45
Naphthenic oil	17.5
Butylated bisphenol	0.75
Stearic acid	1.5
Zinc oxide	4
Sulfur	2
Benzothiazyl disulfide	2.5
Diphenyl guanidine	0.8

vary; see the Experimental section. The process appears to be amenable to most emulsion polymerization formulations with admicelles replacing micelles. Wu et al.²⁵ determined the kinetic parameters of the polymerization of styrene in sodium dodecyl sulfate (SDS) admicelles on alumina and found them to be comparable to those for emulsion polymerization of styrene in SDS micelles. They also used ellipsometry to show that the admicelle swells during the polymerization process as adsolubilized monomer is consumed and additional monomer from the bulk phase moves into the bilayer.

Step 4 entails washing the treated material to remove the excess surfactant. This is done by repeatedly exposing the substrate to fresh water. Batchwise washing in bottles, followed by settling, decanting, and refilling are effective, but are time consuming for larger batches. Continuous, counter-current washing greatly increases the rate of surfactant removal. Detailed discussions of the process are available for the systems of polystyrene on alumina, polystyrene on titanium dioxide, polytetrafluoroethylene on alumina, and polystyrene on silica.²⁶⁻³⁰

EXPERIMENTAL

Material

All materials were obtained commercially and used as received. Hexadecyl trimethylammonium bromide (CTAB), ethylenediamine tetraacetic acid tetrasodium salt (EDTA), 1,3-butadiene, 1-dodecanethiol, styrene, *tert*-butyl hydroperoxide (TBH), methoxychlor, sodium dodecyl sulfate (SDS) and ferrous sulfate were purchased from Aldrich Chemical Company (Milwaukee, WI). Alcohol was purchased from EM Science (Gibbstown, NJ) with an analysis of 95% ethanol and 5% methanol. Styrene and tetrahydrofuran (THF) were obtained from Fisher Scientific (Fair Lawn, NJ). Sodium formaldehyde sulfoxylate (SFS) and 2,2'-azobis-2-methylpropionitrile (AIBN) were obtained from Pfaltz & Bauer (Waterbury, CT). Hi-Sil[®] 233, an amorphous precipitated silica having a BET N₂ surface area of approximately 150 m²/g and dibutyl phthalate absorption of approximately 190 mL/100 g of silica, and MACOL[®] OP 10 SP (MACOL), a polyethoxylated (\approx 10 EO groups) octyl phenol, were obtained from PPG Industries, Inc. (Pittsburgh, PA). Triton[®] X-100 (TRITON), a polyethoxylated (\approx 10 EO groups) octyl phenol, was obtained from Rohm and Haas (Philadelphia, PA).

Surface Modification Procedure

Experimental runs using the liquid monomers styrene and isoprene, were performed in general as described below:

1. AIBN and the appropriate weight of monomer(s) were added to the alcohol at a ratio of 40 ml of alcohol per gram of AIBN, and stirred until the AIBN was entirely dissolved.
2. CTAB was weighed, added to deionized water

Table III Rubber Compound Test Methods

Property	Method	Instrument
Cure (maximum torque, dNm; T_{90} , minutes)	ASTM D 2084-92	Monsanto MDR2000
Tensile (elongation to break, %; break strength, MPa; modulus, MPa)	ASTM D 412-87	Instron 4204
Molded groove tear (N/mm)	ASTM D 2262-83 (modified)	Instron 4204
Cut growth (mm @ 36 kc)	ASTM D 813-87	DeMattie Flex Fatigue Tester
Dynamic (G' and G'' moduli @ 2% strain @ 30°C, MPa)	ASTM D 2231-87	Rheometrics RDAII (rotational concentric shear mode)

Table IV Polymer-Modified Silica Physical Properties

Modified Silica	Surface Area (m ² /g)	Particle Size (μm)	Total Hg Pore Surface Area (m ² /g)	Hg Pore Diameter (Angstroms)	% Carbon
Control	141	15.1	166	316	—
Polystyrene	124	16.8	155	334	3.6
Polyisoprene-1	116	16.8	156	371	2.0
Polyisoprene-2	101	12.8	153	360	4.8
Polybutadiene-1	128	18.2	162	362	0.9
Polybutadiene-2	130	16.9	156	358	1.6

that had its pH adjusted to 8 using sodium hydroxide, and stirred until it dissolved. If MACOL was used, unmodified deionized water was used.

3. The weighed silica was placed in a glass or plastic screw-capped reaction vessel (bottle) at a ratio of up to 80 grams of solids per liter of feed solution.
4. The AIBN/monomer solution was slowly added to the surfactant solution; that solution was brought to the desired total volume with deionized water and then added to the reaction vessel containing the silica.
5. The reaction vessel was allowed to sit for at least six hours to equilibrate the system.

6. The reaction vessel was immersed in a 70°C water bath for at least two hours to initiate polymerization.

7. The silica in the reaction vessel was allowed to settle, the supernatant was decanted, and the silica washed until the wash water no longer foamed on agitation.
8. The silica was then filtered, dried, and passed through a 250-mesh sieve.

For experimental runs using AIBN and butadiene, the procedure was modified as follows:

- 5a. The reaction vessel containing equilibrated initiator, silica, surfactant, and any liquid

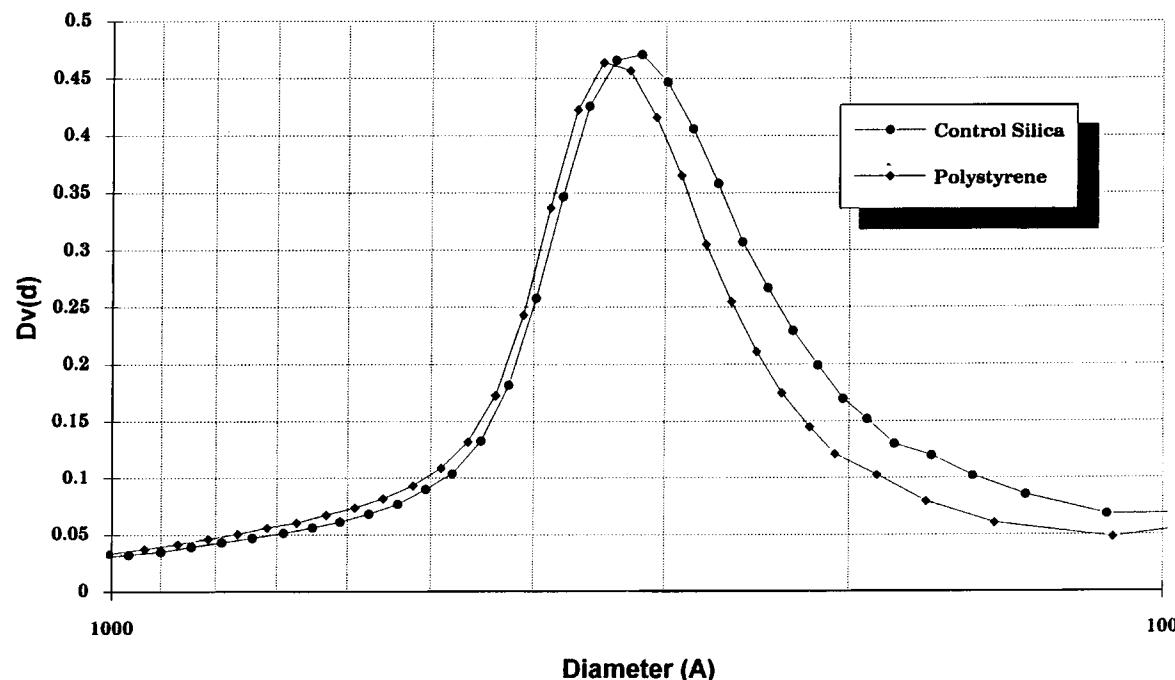


Figure 2 Change in Hg pore volume [Dv(d)] vs. Hg pore diameter for control and polystyrene-modified silicas.

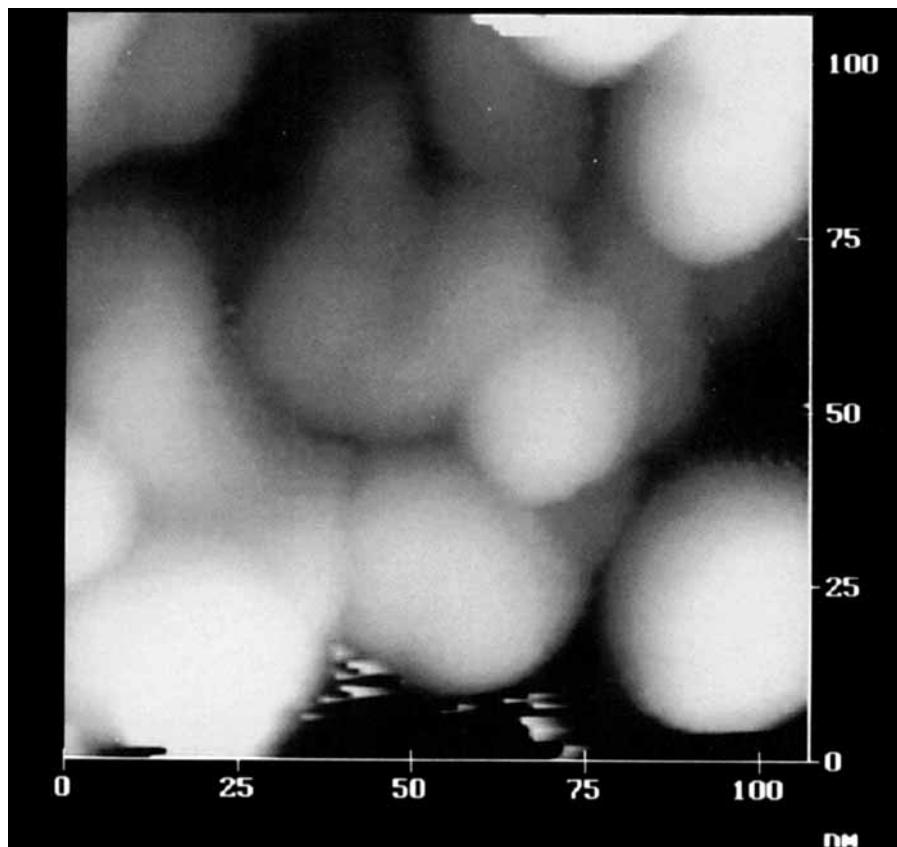


Figure 3 Atomic force micrograph of precipitated silica.

comonomers was chilled to 0°C. Butadiene was then added in excess and allowed to vent to the desired weight and reaction vessel tightly capped. The reaction vessel was then allowed to sit for at least six hours to equilibrate the system before initiating polymerization.

For experimental runs using the oxidation/reduction (REDOX) initiation system, the procedure is as follows, with the washing procedures after polymerization the same as Steps 7 and 8 above.

1. TRITON or MACOL, deionized water, TBH, styrene or isoprene, and EDTA were stirred in a capped container until dissolved.
2. The weighed silica was placed in a glass or plastic reaction vessel at a ratio of up to 80 grams of solids per liter of solution.
3. The feed solution was added to the silica and the reaction vessel was capped, allowed to sit for at least six hours to equilibrate the system, and then chilled to 5°C.

4. Butadiene was added in excess to the system, the system was allowed to vent to the desired weight, and the reaction vessel was recapped and returned to 5°C. The reaction vessel was allowed to sit for at least six hours to re-equilibrate the system.
5. The reaction vessel was then briefly opened in order to add ferrous sulfate and a small amount of butadiene, and then the vessel was recapped. The system was stirred at 5°C for from one to 24 hours to achieve reaction.
6. After the desired reaction time period, the vessel was opened and the polymerization reaction quenched by the addition of methoxy-chlor in alcohol.

For experimental runs using SDS as the surfactant, the procedure was identical to that for CTAB, except that the feed solution was adjusted to a pH of 2.

Testing Procedures

Properties of the surface-modified precipitated silicas were determined by using the methods and instrumentation listed in Table I.

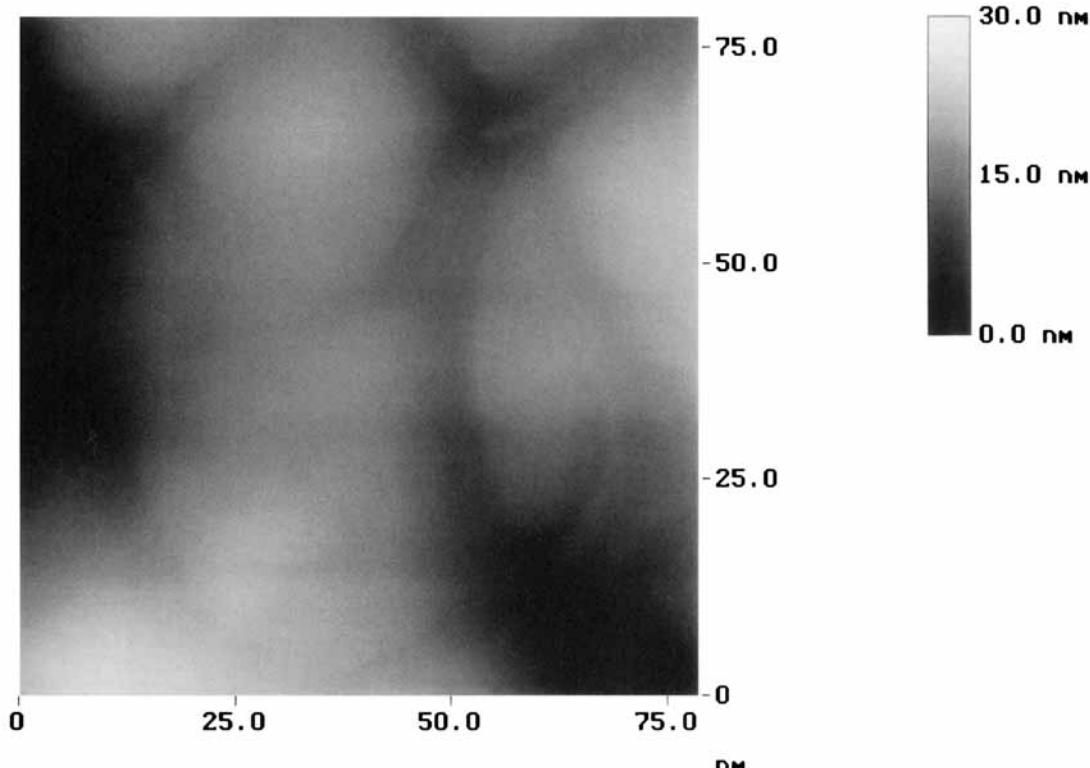


Figure 4 Atomic force micrograph of polystyrene-modified silica.

Rubber compound physical properties of the surface-modified silicas were evaluated using the formulation shown in Table II and the methods and instruments listed in Table III. The compound is a high-performance shoe-sole formulation reported by Converse,³¹ modified by (i) use of appropriate levels of precipitated silica in place of all of the Dixie clay, (ii) inclusion of a naphthenic processing oil, and (iii) elimination of special ingredients such as polyethylene glycol and polyethylene. Since the compound is sulfur vulcanized and consists of a blend of natural and styrene-butadiene rubbers, it is also thought to be an appropriate model for tire compounds.³² Compounds were mixed in a Brabender internal mixer equipped with Banbury-type blades according to ASTM D 3182-87 in the order and in the relative amounts specified in Table II. Sulfur and accelerators were added in a second mixing step. Compounds were cured for 20 minutes at 160°C.

Atomic force microscopy of the styrene-modified and control silica surfaces was performed in non-contact mode with a Nanoscope (III) (Digital Instruments, Santa Barbara, CA). Surface modification of precipitated silica (nitrogen BET surface area of 141 m²/g, DBP absorption of 200 mL/100g silica)

was accomplished using styrene, isoprene, butadiene, and their combinations as described above. Reactions were performed to examine synthetic variables: surfactant type (cationic, anionic and nonionic) and concentration, surfactant/silica ratio, thermal and oxidation-reduction initiations of reaction, and reaction time.

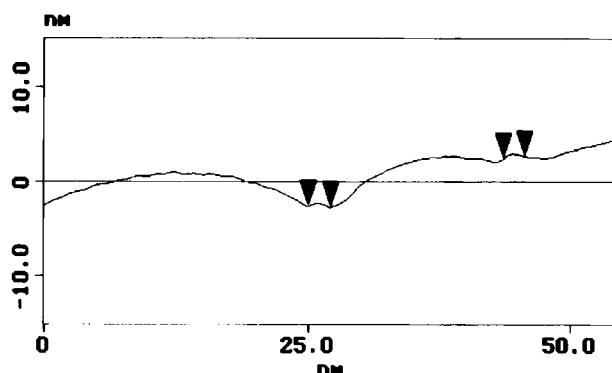


Figure 5 Atomic force micrograph depth profile of polystyrene-modified silica.

Table V Rubber Compound Physical Properties (S = Polystyrene, I = Polyisoprene, B = Polybutadiene)

Property	Control	S	I-1	I-2	B-1	B-2
T_{90} Cure time	4.4	2.3	3.9	3.0	2.1	2.0
Maximum torque	23.0	15.2	17.0	19.1	20.7	22.1
Break strength	20.6	17.0	20.5	21.2	20.1	21.9
Elongation to break	657	600	601	619	653	622
20% modulus	0.63	0.55	0.60	0.65	0.61	0.67
100% modulus	1.41	1.30	1.55	1.56	1.50	1.48
300% modulus	3.85	3.60	4.00	4.07	3.77	3.95
Ratio, M300/M100	2.7	2.8	2.6	2.6	2.5	2.7
Tear energy	11.5	7.0	10.5	12.0	16.3	19.1
Cut growth	17.0	23.5	16.0	15.3	17.6	15.1
G' @ 2% strain	3.66	1.43	1.40	1.64	3.11	3.16
G'' @ 2% strain	0.382	0.133	0.122	0.157	0.303	0.327

RESULTS AND DISCUSSION

Homo-Polymer Surface Modifications

Table IV shows (1) the effect on silica physical properties of modifying the silica by polymerizing styrene, isoprene, or butadiene onto the surface, and (2) the percent of carbon present in these modified silicas.

Data show that the modification of precipitated silica by polymerizing styrene, isoprene, or butadiene onto the surface reduces nitrogen BET and total Hg pore surface areas and increases median Hg pore diameter. The apparent increase in Hg pore diameter probably results from blocking of some of the micropores in the precipitated silica by the organic polymer formed. Data also indicate that reaction time can be an important process variable since the % carbon increases with increasing reaction time using butadiene as the monomer in a REDOX initiated system: polybutadiene 1 was formed upon reaction for three hours and polybutadiene 2 was formed by an identical reaction, but for six hours' duration.

Figure 2 plots the change in Hg pore volume versus the Hg pore diameter and shows that polystyrene modification does not significantly change the silica pore structure. Figures 3 and 4 are atomic force micrographs of precipitated silica and the polystyrene-modified silica, respectively. Obvious differences are revealed as a small band reaching from one pore to another in the modified silica but not significantly filling the pore. Figure 5 shows that these areas on the modified silica consist of nanometer-scale material. The 2.1 nm diameter of these areas are consistent with the thickness of strands of polystyrene. These areas are not present on the untreated silica.

The results of rubber compound physical testing of the homo-polymer-modified silicas are shown in Table V. Data show that use of a silica modified by polymerizing styrenes onto the surface generally affords decreases in compound cure time, break strength, tear strength, cut growth resistance (resistance to crack propagation upon flexing), reinforcement (G') and hysteresis as measured by G'' compared to use of the control silica. The reductions in compound cure time and hysteresis (heat buildup) are desirable; however, the accompanying decreases in other physical properties are not desirable. Thus, use of a polystyrene surface-modified silica does not improve rubber compound physical properties. This result is thought to result from the absence of significant interactions between the thermoplastic polystyrene and the diene of the elastomers used in the evaluation compound, Table II.

Use of a silica modified by polymerizing isoprene onto the surface generally results in decreases in compound cure time, reinforcement, and hysteresis, but does maintain compound tear strength and cut growth resistance compared to use of the control silica. Results of using a silica modified by polymerizing butadiene onto the silica surface show decreases in compound cure time and hysteresis, and an increase in tear strength compared to the control silica. Data also show that an increase in the amount of polybutadiene on the silica surface as determined by the % carbon content results in an increase in the tear energy and cut growth resistance of the rubber compound. The polybutadiene-modified silica thus appears to be the more desirable surface modification for use in the natural rubber/styrene-butadiene rubber compound blend if tear energy and cut growth resistance are important criteria. High-

Table VI Copolymer Modified Silica Physical Properties

Silica	Surface Area (m ² /g)	Particle Size (μm)	Total Hg Pore Surface Area (m ² /g)	Hg Pore Diameter (Angstroms)	% Carbon
Control	141	15.1	166	316	—
SB-1	108	18.5	146	388	3.9
SB-2	140	17.8	169	370	0.3
SI-1	94	14.7	143	359	5.5
SI-2	116	15.9	156	346	3.4
IB	123	18.1	110	301	0.9

strain modulus (300% M) as a measure of polymer-filler interaction¹ remains essentially unchanged, however.

Copolymer Surface Modifications

Surface modification of silica was accomplished using various combinations of styrene, isoprene, and butadiene as the organic co-monomers. Styrene-butadiene (SB)-modified silica 1 was prepared using Triton® X-100 as the surfactant, and SB-modified silica 2 was prepared using SDS as the surfactant. Styrene-isoprene (SI)-modified silica 1 was prepared using CTAB as the surfactant while SI-modified silica 2 was prepared using MACOL as the surfactant. Isoprene-butadiene (IB)-modified silica was prepared using Triton as the surfactant.

Data in Table VI show the effect that these copolymerization reactions have upon the properties of precipitated silica. In general, modification reduces nitrogen BET surface area values. Data also

show that the surfactant can be an important process variable since 3.9% styrene-butadiene is formed on the silica surface when using a nonionic surfactant, but only 0.3% is formed on the silica surface when using an anionic surfactant. Figure 6 is a plot of the change in Hg pore volume versus the Hg pore diameter and shows that SB modification on silica changes the silica pore structure.

Rubber compound test data (Table VII) show that modification of silica by polymerizing a styrene-butadiene, styrene-isoprene, or isoprene-butadiene copolymer onto the silica surface decreases the compound cure time and hysteresis (G''), and increases tear energy and the ratio of the modulus values measured at 300% and 100% elongation compared to the control silica. The increase in the modulus value at 300% elongation and increase in the ratio of the modulus value at 300% elongation to that at 100% elongation are used as indirect evidence for covalent bond formation between silica and diene rubber when using silane modifiers. In

Table VII Copolymer Rubber Compound Physical Properties

Property	Control	SB-1	SB-2	SI-1	SI-2	IB
T ₉₀ Cure time	4.4	2.1	3.2	2.8	3.2	2.2
Maximum torque	23.0	23.4	19.7	24.2	23.6	23.1
Break strength	20.6	21.4	20.2	22.1	21.5	22.2
Elongation to break	657	723	641	633	629	640
20% modulus	0.63	0.64	0.55	0.60	0.58	0.66
100% modulus	1.41	1.39	1.22	1.51	1.46	1.53
300% modulus	3.85	4.17	3.41	4.91	4.43	4.90
Ratio, M300/M100	2.7	3.0	2.8	3.3	3.0	3.2
Tear energy	11.5	15.4	10.9	15.8	14.1	17.8
Cut growth	17.0	10.3	14.8	18.1	22.5	19.2
G' @ 2% strain	3.66	3.14	2.85	3.5	3.41	3.58
G'' @ 2% strain	0.382	0.344	0.256	0.370	0.335	0.325

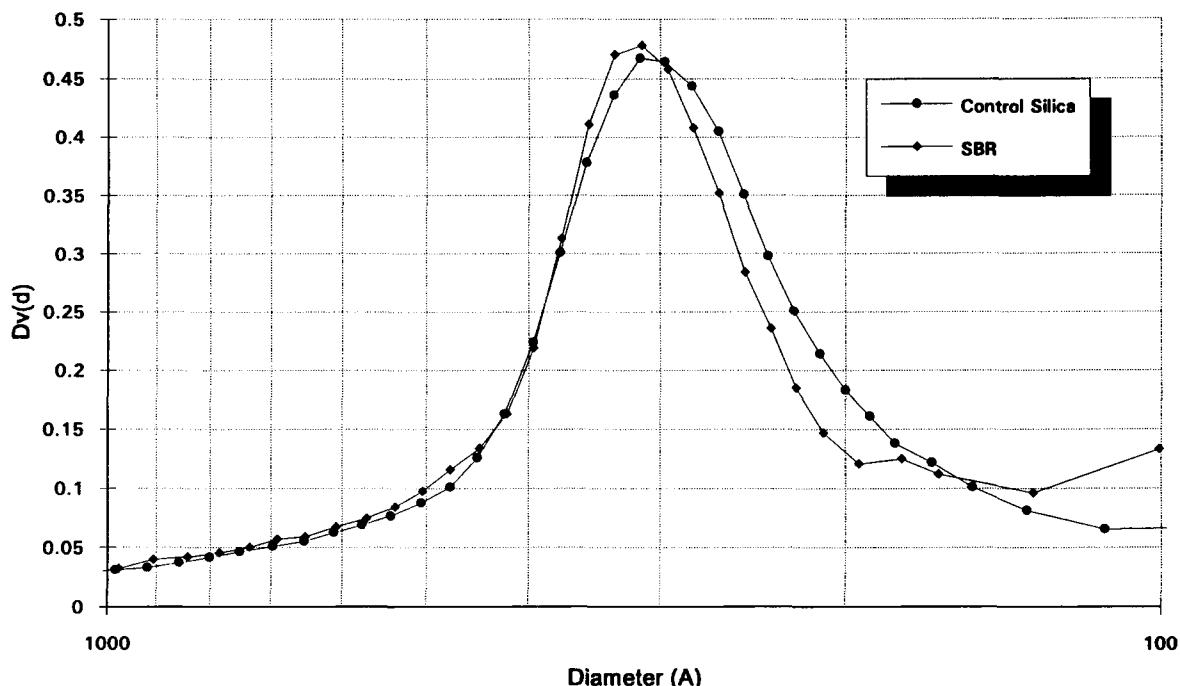


Figure 6 Change of Hg pore volume [$D_v(d)$] vs. Hg pore diameter for control and styrene-butadiene-modified silicas.

addition, cut growth resistance is also increased for the compound with the styrene-butadiene-modified silica prepared using the nonionic surfactant that affords 3.9% carbon. Finally, as was observed for the polybutadiene-modified silica, an increase in the polymer content of styrene-isoprene on the silica surface results in an increase in tear energy and cut growth resistance of the compound.

Figures 7-14 graphically display compound data for each property listed in Tables V and VII for averages of the various synthetic preparations of the polystyrene (S), polyisoprene (I), polybutadiene (B), styrene-isoprene (SI), styrene-butadiene (SB), and isoprene-butadiene (IB) modified silicas. In Figures 7-14 the solid line is the regression curve and the dashed lines represent the 95% confidence limits of the 600+ untreated silicas in the compound database.³² These figures show that all silica surface modifications decrease cure times. Other properties are dependent on the polymer modification.

Table VIII qualitatively summarizes the effects of polymer treatments on the various rubber physical properties, with the + designation meaning improvement of greater than 10%, the - designation meaning a negative or undesirable effect greater than 10% different, and the = meaning no significant effect. The totals were calculated by assigning a +1

value to a +, a -1 value to a -, and a zero value to an = designation. As can be seen, copolymer (in particular styrene-butadiene) modifications appear most promising.

As can be seen from Tables V and VII and Figures 7-14, in most tests polystyrene modification caused a degradation of the rubber compound properties. Polyisoprene and polybutadiene modifications offer improvements over polystyrene, particularly in tear strength and cut growth resistance, perhaps due to their ability to crosslink to the sulfur-vulcanized rubber compound (even though the 300% M is not increased). It is interesting that the styrene-isoprene, isoprene-butadiene, and styrene-butadiene copolymers all offer superior characteristics to the homopolymers. The only exception is the styrene-butadiene copolymer modified silica containing 0.3% carbon that was prepared using the anionic SDS surfactant. Thus, an anionic surfactant is not useful in providing a medium for significant surface modification of precipitated silica. Currently the understanding of exact factors in the modified silicas that affect a given rubber compound property is limited. The inability to completely extract the polymer from the surface of the silica²⁹ makes it difficult to determine correlations between polymer composition or molecular weight and rubber compound properties.

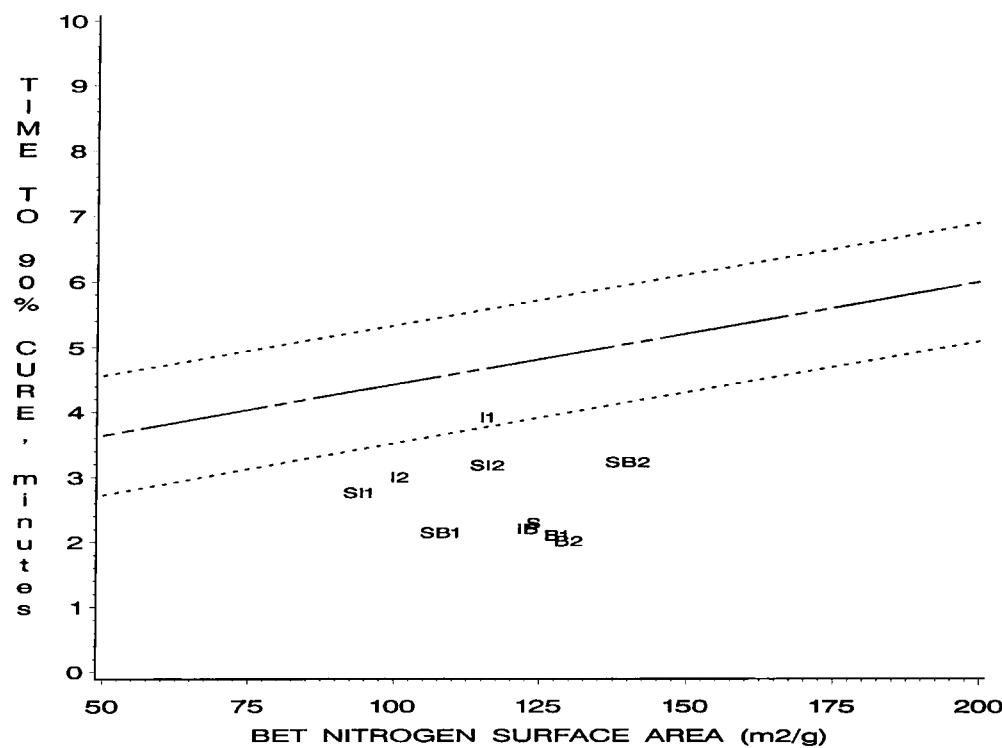


Figure 7 Time to reach 90% cure (minutes) for rubber formulation vs. BET N₂ single-point surface area (m²/g) of modified silicas.

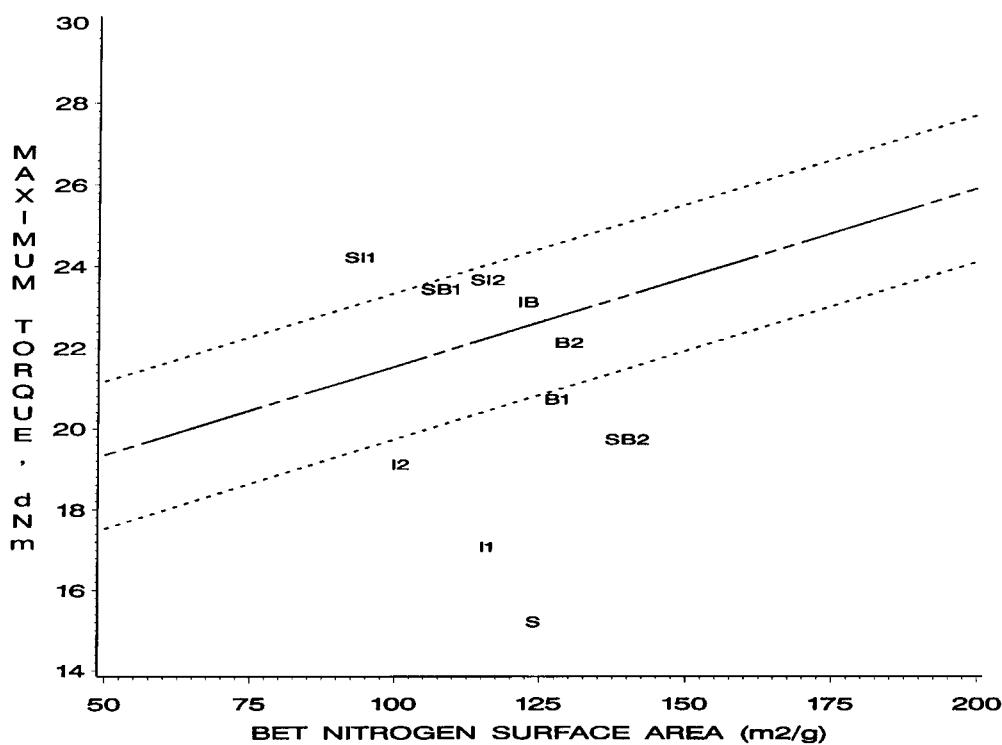


Figure 8 Maximum Torque (dNm) measured on the Monsanto MDR2000 for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

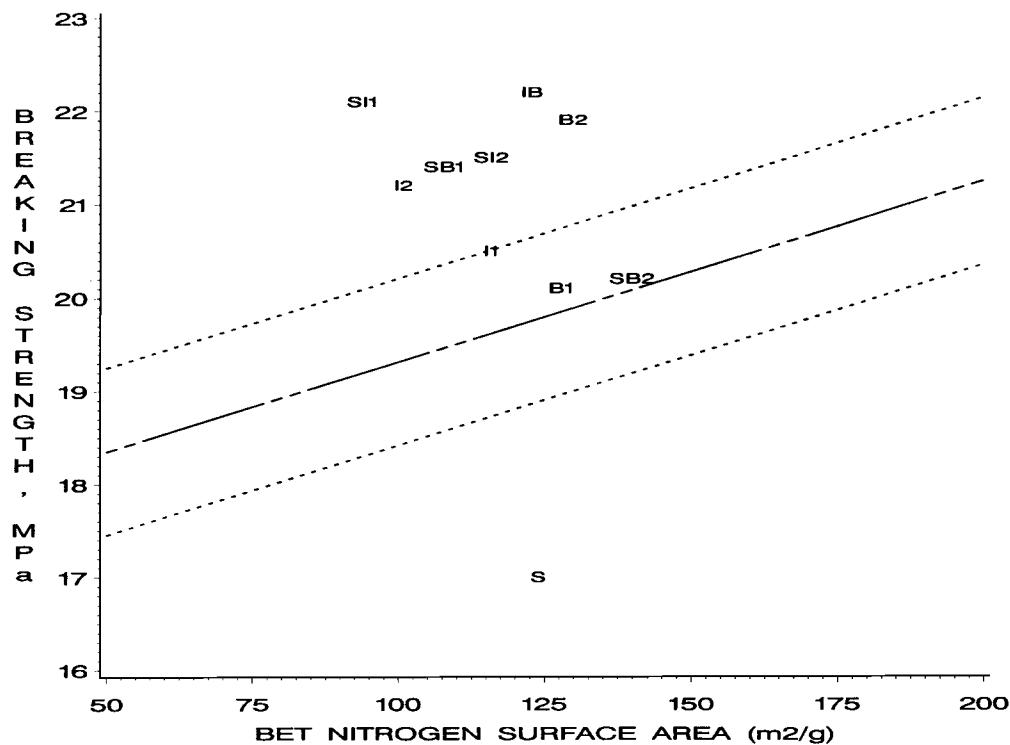


Figure 9 Breaking strength (MPa) for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

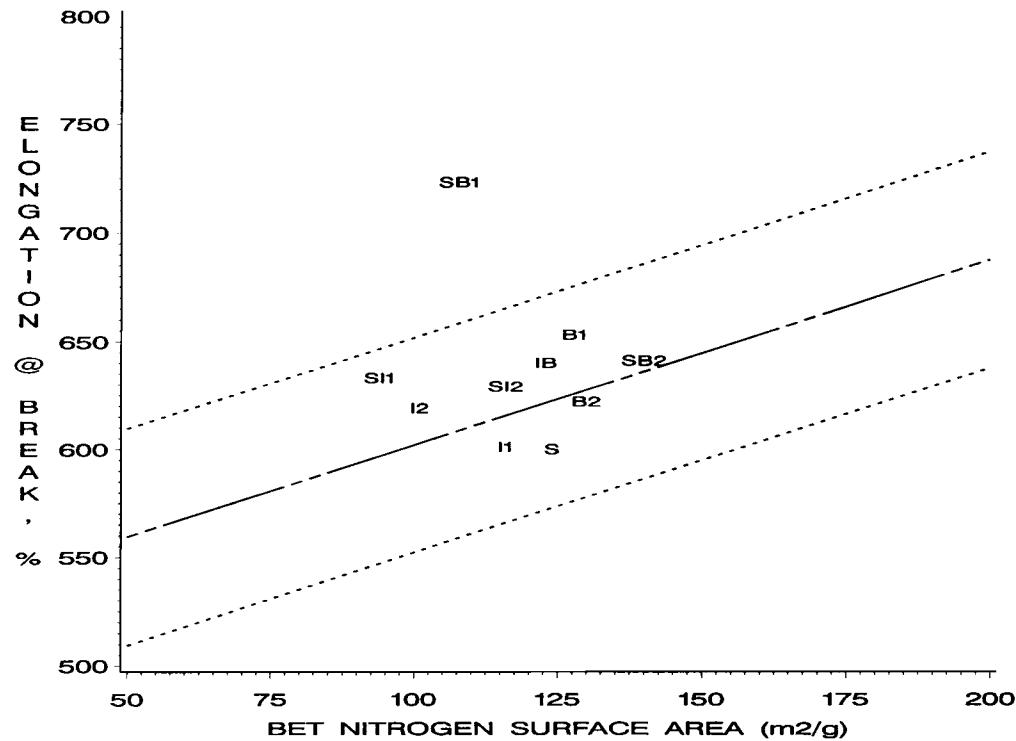


Figure 10 Elongation to break (%) for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

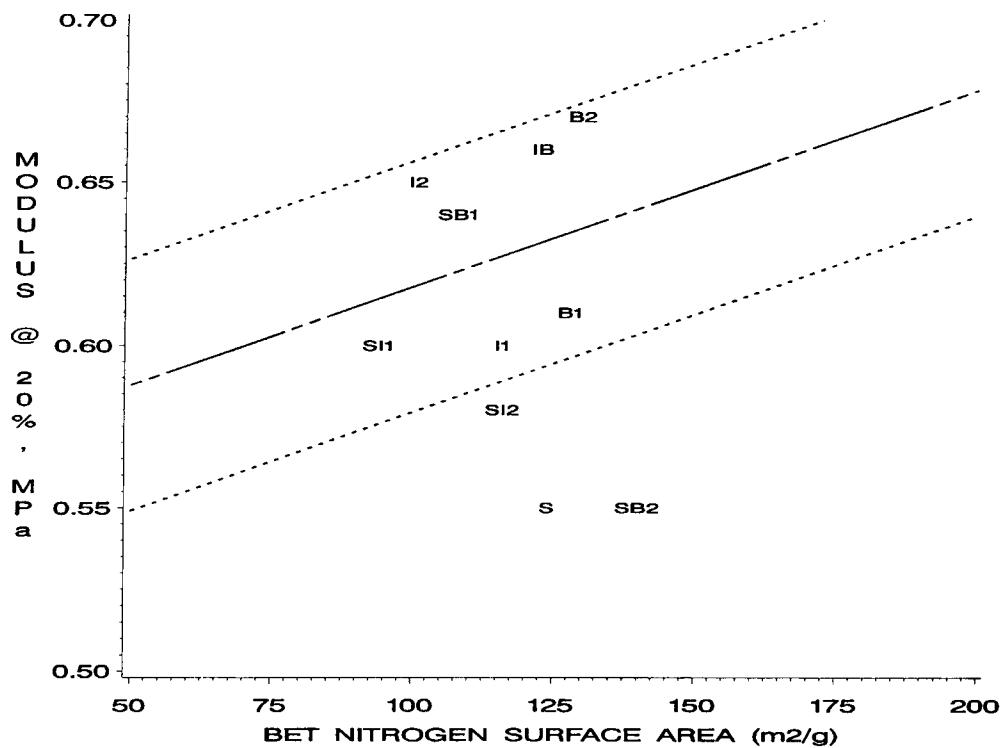


Figure 11 Modulus at 20% elongation (MPa) for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

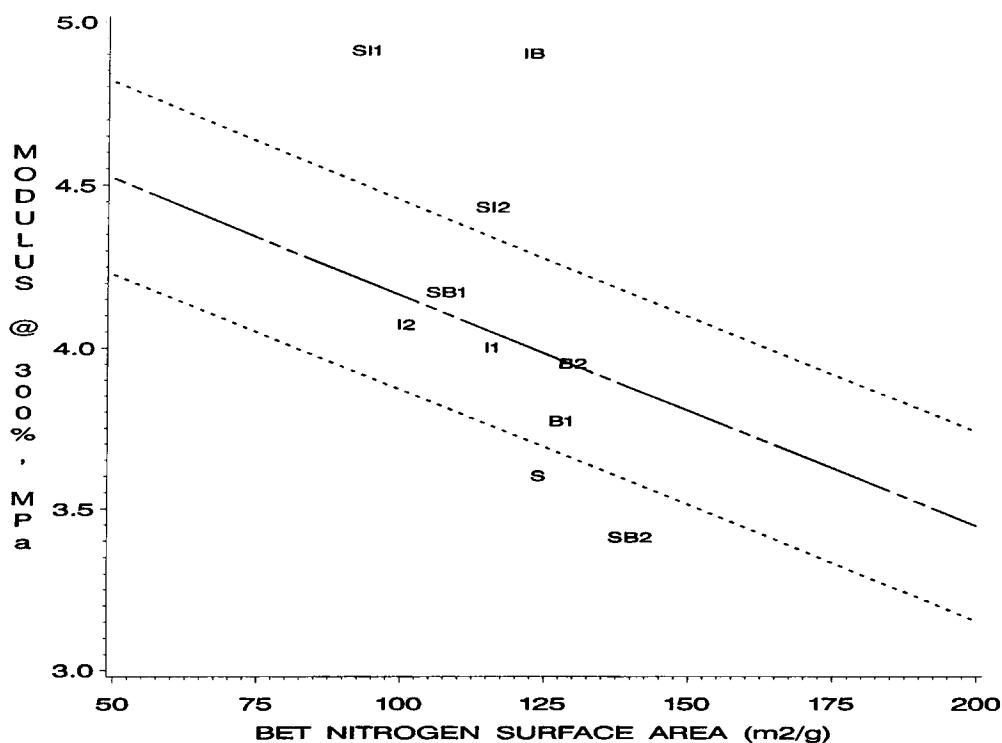


Figure 12 Modulus at 300% elongation (MPa) for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

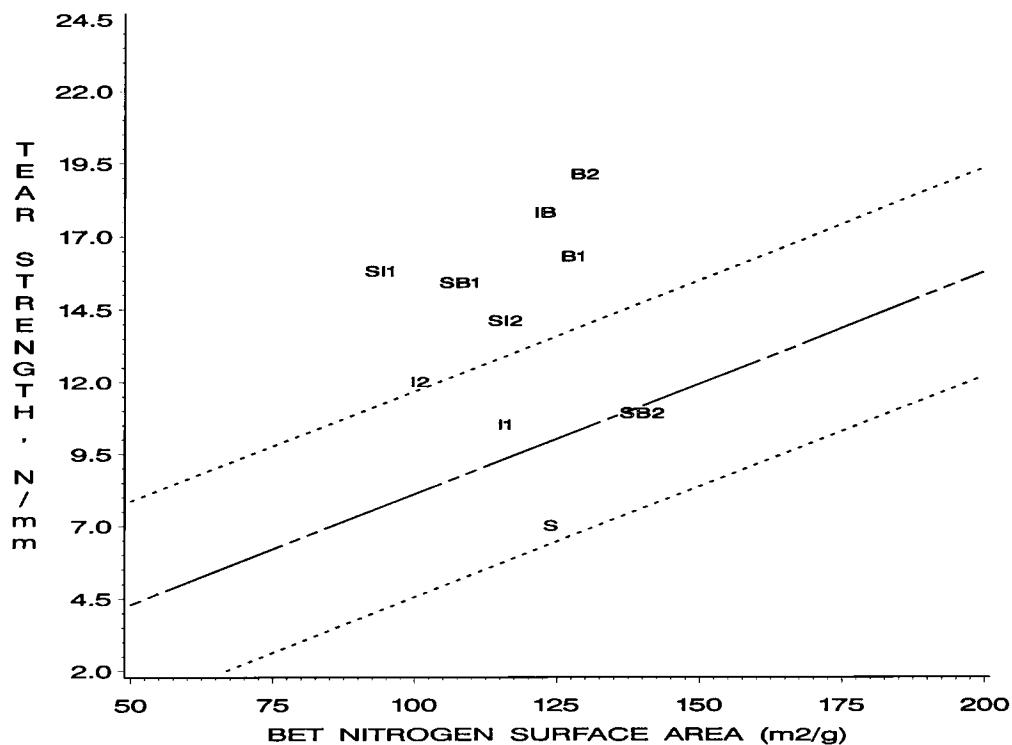


Figure 13 Tear strength (N/mm) for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

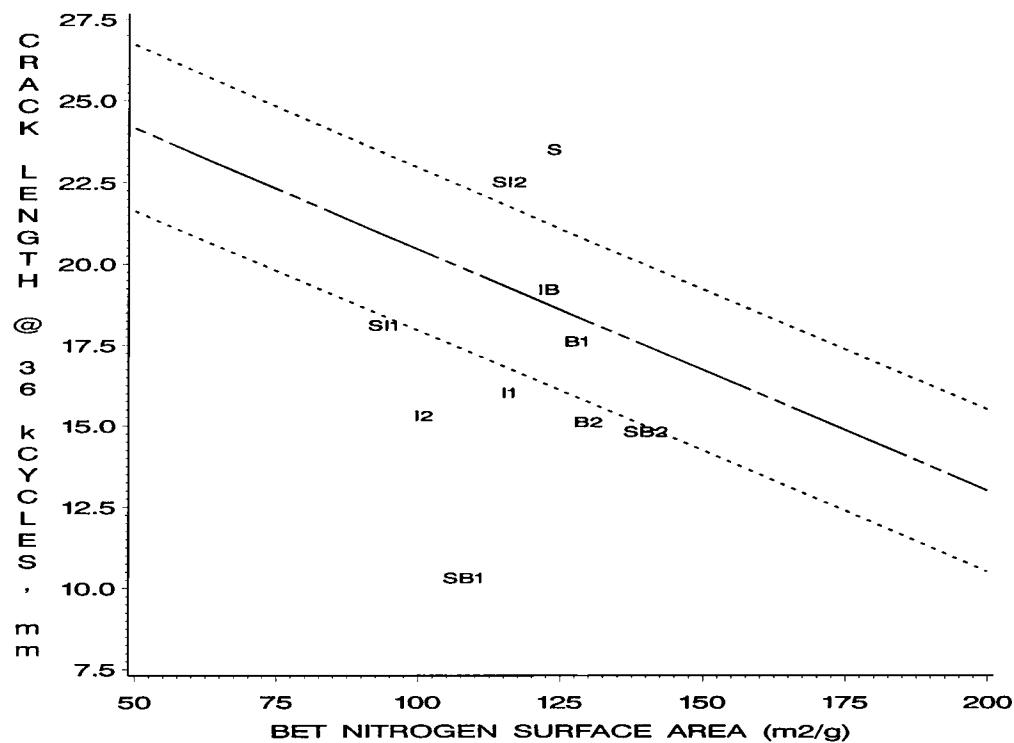


Figure 14 Cut length (mm) after 36,000 cycles on the DeMattia flex fatigue test for rubber formulation vs. BET N₂ single-point surface area of modified silicas.

Table VIII Qualitative Summary of Polymer-Modified Silica Rubber Physical Properties

Property	S	I-1	I-2	B-1	B-2	SB-1	SB-2	SI-1	SI-2	IB
T_{90} Cure time	+	+	+	+	+	+	+	+	+	+
Maximum torque	—	—	—	—	=	=	—	=	=	=
Break strength	—	=	=	=	=	=	=	=	=	=
Elongation to break	=	=	=	=	=	+	=	=	=	=
20% modulus	—	=	=	=	=	=	—	=	=	=
100% modulus	=	+	+	=	=	=	—	=	=	=
300% modulus	=	=	=	=	=	=	—	+	+	+
Ratio, M300/M100	=	=	=	=	=	+	=	+	+	+
Tear energy	—	=	=	+	+	+	=	+	+	+
Cut growth	—	=	+	=	+	+	+	=	—	—
G' @ 2% strain	—	—	—	—	—	—	—	=	=	=
G'' @ 2% strain	+	+	+	+	+	+	+	=	+	+
	-4	+1	+2	+1	+3	+5	-2	+4	+4	+4

The exact effect of different surfactants on the process is still an unknown. Nonionic and cationic surfactants both adsorb well on silica surfaces and can afford comparable levels of organic polymer. Yet with the same polymer treatment, their use affords different rubber compound physical properties. Ways to analyze the modified silica surface are being investigated further in order to examine the extent and location of the polymer modification. Atomic force microscopy has been used to measure attractive forces between (i) a silica glass sphere and an oxidized silicon surface in calcium chloride solution³³; (ii) a spherical silica particle of colloidal dimension and a flat silica surface with adsorbed nonionic surfactants³⁴; and (iii) colloidal silica glass spheres³⁵; and to study natural clay and mica surface morphologies.³⁶⁻⁴⁰ These results and the present images provide confidence that atomic force microscopy may yield additional insights on the mechanics and effects of the organic polymer surface modification process.

Finally, this process introduces a new area to polymer and surface chemistry. Significant changes in elastomer compound properties can be achieved by use of the new materials afforded by this process.

SUMMARY

Surface modification of precipitated silica by *in situ* polymerization of organic monomers produces a new class of materials shown useful in improving rubber cure and compound physical properties. The nature of the monomer, surfactant, polymerization initiator system, and reaction time are important variables

that can be controlled in order to afford specifically modified silicas useful in reinforcing elastomeric compounds by reducing compound cure times and by improving rubber product performance. Modification of the silica surface reduces nitrogen BET and total Hg pore surface areas, and increases the median Hg pore diameter. Atomic force micrographs of precipitated silica and the polystyrene-modified silica show nanometer-scale areas resulting from polymerization that stretch from one pore to another in a silica aggregate, but that do not significantly fill the pore. Copolymer modifications are thought most promising, since compound cure time and hysteresis (G'') decrease, while tear energy, the ratio of the 300% to 100% modulus, and cut growth resistance values all increase compared to the control silica. The process introduces a new area of polymer and surface chemistry that needs to be further explored. The effects of this process have been studied and do indicate areas where additional research is needed to achieve an in-depth understanding of the mechanics involved.

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