

# Comparison of Rubber Reinforcement Using Various Surface-Modified Precipitated Silicas

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## SYNOPSIS

The reinforcement of a natural rubber compound by various surface-modified precipitated silicas was compared. Compound physical properties were determined for two silicas differing in surface area and were used as controls to evaluate these silicas after surface modification by using either a bifunctional organosilane coupling agent ( $\gamma$ -mercaptopropyl-trimethoxy-silane) or a new surface modification process. This new process is based on the *in situ* polymerization of organic monomers solubilized inside surfactant bilayers that are adsorbed onto the silica surface to afford silicas modified with styrene-butadiene and styrene-isoprene copolymers. Both surface modification processes afford materials that dramatically increase the compound cure rate, thereby significantly reducing  $T_{90}$  cure times, while also improving tensile properties, tear strength, abrasion resistance, and compression set of the cured compound. The silane-modified silica gives a higher flex-cracking resistance than do the silicas modified by the *in situ* polymerization of organic monomers, whereas these latter silicas significantly increase rebound resilience and offer greater overall improvements in rubber compound performance. The rubber compound physical properties obtained using the modified, higher surface area Hi-Sil<sup>®</sup> 255 silica are generally improved relative to those obtained using the modified Hi-Sil<sup>®</sup> 233 silica. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The reinforcement of elastomers by particulate fillers has been the subject of numerous investigations. The filler properties that primarily influence elastomer reinforcement are surface area, particle size, structure, and surface activity. Currently, the surface area, mean agglomerate particle size, and structure of the filler are analyzed during filler production in routine tests for quality control such as BET adsorption of nitrogen, particle sizing, and oil absorption. However, the role of filler surface chemistry in reinforcing elastomers is much less understood.<sup>1-4</sup>

There are many types of fillers used in the rubber industry. Carbon blacks are the most widely

used reinforcing fillers since they provide excellent reinforcement of general-purpose rubbers at a relatively low cost. Unfortunately, the only color of a rubber product available is black. Reinforcing precipitated silicas of equivalent particle size to carbon blacks are used to produce highly reinforced compounds with a neutral color,<sup>5</sup> but are generally more expensive. Use of silica can also provide additional physical property benefits and compounding flexibility that are not obtainable with carbon black. Due to its nonpolar nature, the surface of carbon black appears well suited to reinforce the nonpolar hydrocarbon elastomers. This suggests that if the surfaces of nonblack fillers, such as precipitated silica, can be modified to reduce its polarity so as to make it more compatible with elastomers "rubber-ready fillers" with improved reinforcing capabilities can be prepared.

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One successful example that improved the reinforcing effect of precipitated silica in hydrocarbon elastomers is the use of bifunctional organosilane coupling agents which effectively promotes polymer-filler interactions via formation of covalent chemical linkages.<sup>6-9</sup> This serves to increase the wettability and compatibility of silica with hydrocarbon elastomers. However, organosilanes are expensive and significantly increase the cost of a rubber product.

Espiard et al.<sup>10</sup> studied the use of silica as a nucleation site for emulsion polymerization. Their results demonstrated that silica particles can be encapsulated by poly(ethyl acrylate). Espiard, et al.<sup>11</sup> also developed a method for synthesizing organophilic, 20–70 nm-size silica particles containing surface vinyl groups. The use of these particles in rubber reinforcement has not, however, been investigated.

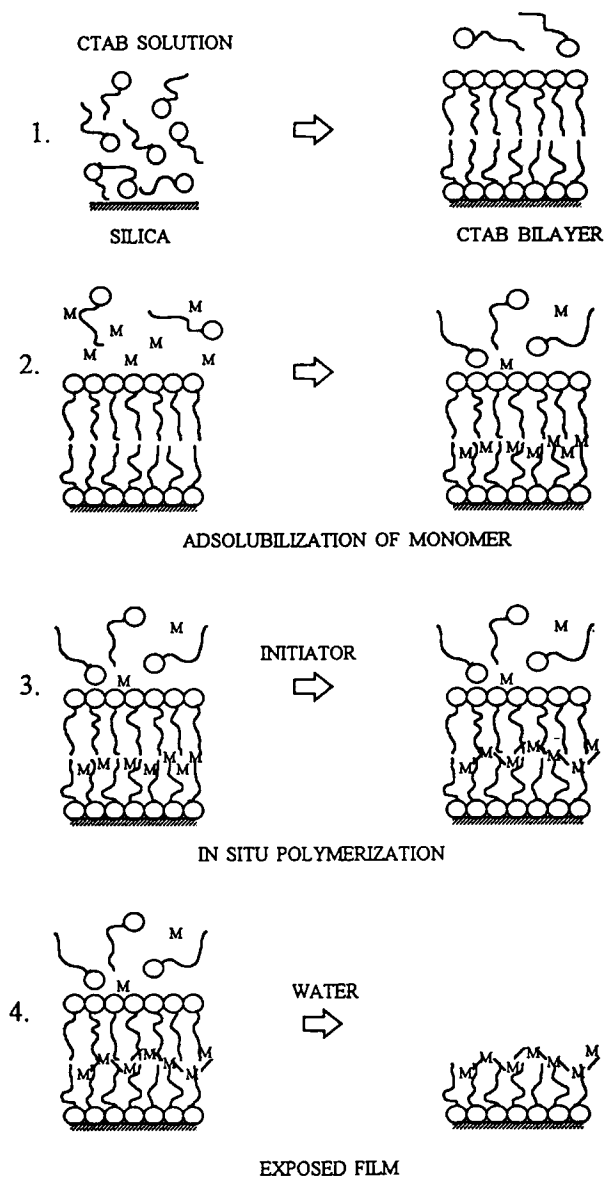
A new surface-modification process which is based on the in situ polymerization of organic monomer(s) in surfactant layers adsorbed from aqueous solution onto the surface of precipitated silica has recently proven successful in improving rubber compound cure and cured physical properties.<sup>12,13</sup> The method used for the modification of inorganic powders by the formation of ultrathin polymer films in adsorbed surfactant bilayers, called admicelles, was first reported in 1987.<sup>14,15</sup> This novel process has been studied on a variety of inorganic substrates using varying types of surfactants and initiators and has been applied to a variety of industrially important substrates. The process consists of four basic steps: (1) adsorption of the surfactant, (2) adsolubilization of the monomer(s), (3) polymerization of the monomer(s), and (4) washing to remove the surfactant (Fig. 1). Detailed studies of the process are available for the formation of polystyrene on alumina,<sup>14</sup> polytetrafluoroethylene on alumina,<sup>16</sup> polystyrene on titanium dioxide,<sup>17</sup> and polystyrene on precipitated silica.<sup>18,19</sup>

The present study is a comparison of various organic-polymer, surface-modified precipitated silicas and their effect on the cure properties and the cured physical properties of a natural rubber compound. Comparisons to two commercial precipitated silicas having different surface areas and pore-size distributions and to a commercial organofunctional silane-coupled silica are presented.

## EXPERIMENTAL

### Materials

Two amorphous precipitated silicas manufactured by PPG Industries (Pittsburgh, PA) were used in



**Figure 1** Ultrathin film forming process.

this study: Hi-Sil® 255 silica, a control silica denoted as C-1, having a specific surface area of 165 m<sup>2</sup>/g and Hi-Sil® 233 silica, C-2, having a specific surface area of 131 m<sup>2</sup>/g. Ciptane® 255LD silica, PPG Industries, is the trade name of Hi-Sil 255 silica that is modified by reacting with 3% by weight of  $\gamma$ -mercaptopropyltrimethoxysilane (A-189) which was obtained from OSi Industries (Tarrytown, NY). All materials used for surface modification by the in situ polymerization process were obtained commercially and were used as received. Hexadecyltrimethylammonium bromide (CTAB), 99%; styrene, 99%; isoprene, 99%; and ethanol, 95%, were purchased from Aldrich Chemical Co. (Milwaukee,

WI). 1,3-Butadiene, 99%, was obtained from Scott Specialty Gases (Plumsteadville, PA). Sodium hydroxide, 97%, was obtained from EM Science (Gibbstown, NJ). The VA-044 (2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride) water-soluble initiator was obtained from Wako Pure Chemical Industries (Richmond, VA). The 2,2'-azobis-2-methylpropionitrile (AIBN) water-insoluble initiator was obtained from Pfaltz & Bauer (Waterbury, CT).

### Surface-modification Procedure

Both the Hi-Sil 255 and Hi-Sil 233 precipitated silicas were modified by using combinations of styrene and butadiene and of styrene and isoprene as the comonomers. Samples denoted SI-1 and SI-2 represent styrene-isoprene (SI)-modified Hi-Sil 255 silica and Hi-Sil 233 silica, respectively. Experimental runs were performed as follows:

1. The weighed control silica was placed in a screw-capped plastic bottle in a ratio of 80 g of solids per liter of feed solution.
2. Styrene and isoprene comonomers in a 25 : 75 mol % ratio and AIBN were added to the alcohol, the vessel capped, and the mixture stirred until the AIBN was totally dissolved.
3. CTAB was weighed, added to deionized water which was adjusted to pH 8 by using sodium hydroxide, and stirred until dissolved.
4. The AIBN/comonomers solution was mixed with the surfactant solution, deionized water was added to adjust this solution to the desired total volume, and the mixtures added to the bottle containing a control silica.
5. The reaction mixture was allowed to equilibrate for 12 h, then placed in a 70°C water bath to initiate polymerization and allowed to react for 4 additional hours.
6. After polymerization, the silica in the bottle was allowed to settle and the supernatant decanted. The silica slurry was placed in a Buchner funnel and allowed to countercurrent wash for 5 days with daily stirring or until the wash water had no persistent foaming upon agitation.
7. The silica was then dried at 70°C for 72 h and reground into a powder through a 120 mesh sieve.

Samples SB-1 and SB-2 represent styrene-butadiene (SB)-modified Hi-Sil 255 silica and Hi-Sil 233 silica, respectively. A stainless-steel tank con-

taining silica, surfactant, VA-044 initiator, styrene, and 30 L of deionized water adjusted to pH 8 was sealed and evacuated to 1 psia. The system was then pressurized with 1,3-butadiene to an equilibrium pressure of 34 psia. The tank, containing styrene and butadiene comonomers in approximately a 15 : 85 mol % ratio, was heated in a water bath to initiate polymerization. After polymerization, the vapors in the tank were forced out by air and vented into a hood. The slurry was then washed and dried and the dried powder ground.

### Testing Procedures

The properties listed in Table I were determined for the control silicas and all treated silicas. Extracted polymer was analyzed by Fourier transform infrared (FTIR) spectroscopy. Extraction was performed by boiling 5 g of the treated silica in refluxing tetrahydrofuran for 4 h. The slurry was cooled to room temperature, filtered, and rinsed with hot tetrahydrofuran and the polymer precipitated by addition of the filtrate to water. Observations on the silica aggregate were performed by transmission electron microscopy (TEM).

The rubber compound formula used for all evaluations is given in Table II. The compound is a basic rubber formulation designed specifically for physical properties testing,<sup>20,21</sup> modified by using natural rubber and by eliminating poly(ethylene glycol), which is sometimes used to complex with the silanol groups on the surface of the silica to prevent them from reacting with the activator.

Standard test procedures as prescribed by ISO or ASTM were used for the determination of compound and vulcanizate properties and are listed in Table III. A two-stage mixing procedure was employed to prepare all compounds. In the first stage, the rubber,

**Table I Silica Properties Testing**

| Measurement   | Instrument                                    |
|---|---|
| BET N <sub>2</sub> surface area (multipoint), pore volume | Micromeritics FlowSorb II 2300                |
| Mean agglomerate particle size                            | Malvern Mastersizer                           |
| % Carbon  | Elements analyzer Perkin-Elmer-2400 Series II |
| Transmission electron microscope (TEM)                    | JEOL JEM-200 CX                               |
| Fourier transform infrared spectroscopy (FTIR)            | Perkin-Elmer System 2000                      |

**Table II Rubber Compound Formula**

| Ingredient                    | Parts per Hundred<br>(phr) Rubber |
|-------------------------------|-----------------------------------|
| Natural rubber (TTR 5L)       | 100                               |
| Silica                        | 40                                |
| Zinc oxide                    | 5                                 |
| Stearic acid                  | 2                                 |
| Paraffinic oil                | 5                                 |
| Antioxidant (6PPD)            | 1                                 |
| Benzothiazyl disulfide (MBTS) | 1.8                               |
| Diphenyl guanidine (DPG)      | 0.25                              |
| Sulfur                        | 3                                 |

filler, and other ingredients (except accelerator and vulcanizing agent) were mixed in a Banbury internal mixer with a batch size adjusted to a fill factor of 0.7. The vulcanizing agent and accelerators were added to the masterbatch in a second mixing step using a two-roll mill. All compounds were cured at 150°C to a time corresponding to  $T_{98}$  as determined on the moving die rheometer.

## RESULTS AND DISCUSSION

### Silica Surface Characterization and Polymer Analysis

The data in Table IV show that each surface modification affected a variety of the physical characteristics of silica, including mean agglomerate particle size, surface area, and pore volume. In general, modification of precipitated silica by the in situ polymerization of organic monomer(s) reduces the BET nitrogen surface area by up to approximately 50% and pore volume by up to approximately 20% and increases the mean agglomerate particle size by up to approximately 50%. Ciptane 255LD silane-modified silica showed no appreciable changes in mean agglomerate particle size and pore volume and only about a 10% decrease in surface area compared to Hi-Sil 255 silica. Both silicas modified by forming an SB copolymer contained over 10% carbon by weight, while those modified by forming an SI copolymer contained approximately 5% carbon by weight. The silane-treated Ciptane silica contained only 0.8% carbon by weight. Figures 2–5 are transmission electron micrographs of the modified silicas studied based on the Hi-Sil 255 silica. They are the C-1 control, Ciptane silane-modified, SB-modified, and SI-modified Hi-Sil 255 silicas, respectively. These micrographs qualitatively indicate that the treated silicas developed a higher degree of agglom-

eration of aggregated particles than did the unmodified C-1 control. This is particularly true for the polymer-modified silicas. The TEM analyses also show that there is no significant increase in the size of the primary (also called the ultimate) silica particle.

The increase in the mean agglomerate particle size measured by using the Malvern Mastersizer is consistent with the higher degree of agglomeration observed by TEM measurements. This size increase may simply be attributed to the subsequent reprocessing of the modified silicas such as washing, drying, and regrinding steps, but could possibly be a result of the organic polymer-forming process by affording increased aggregate–aggregate interactions. As expected, the silica surface areas and pore volumes are significantly decreased as the polymer formed in situ and any remaining surfactant cover part of the surface of the silica filling a portion of the pores. This is consistent with atomic force micrographs of precipitated silica and styrene-modified silica which show that the organic polymer emanates from one pore and leads into another pore.<sup>12</sup>

The percent carbon content analysis supports the idea that essentially all the monomers react to form a polymer and that this polymer as well as some of the surfactant remains on the silica surface, even after the washing step. The predicted data shown in Table V are based upon the assumption that all of the monomer and one-half of the adsorbed surfactant remain after washing. Comparison of present results with the percent carbon content found by Waddell et al.<sup>12</sup> shows that the SI-modified silica prepared by using the same surfactant, namely, the cationic surfactant CTAB, gave approximately the same percent carbon content: approximately 5.5%. The SB-modified silicas, which were previously prepared by using Triton X-100 and sodium dodecyl sulfate as the surfactant types, gave 3.9% and only 0.3% carbon, respectively.<sup>12</sup> In the present study, approximately 11% carbon by weight of the SB copolymer is formed on the silica using CTAB as the surfactant. One explanation for the higher percent carbon obtained in the present experiments is in the method of preparation. Samples were previously produced in glass vessels with the butadiene added as a chilled liquid and the butadiene allowed to vent to the proper weight.<sup>12</sup> The glass vessels limited the highest pressure of butadiene that could safely be added. The present samples were produced in a stainless-steel vessel which had no pressure limitations and a relatively large head space compared to the glass vessel. Higher amounts of butadiene could be added to the reaction vessel and therefore

**Table III Rubber Compound Test Methods**

| Property   | Method         | Instrument                              |
|--|----------------|---|
| Cure time ( $T_{90}$ , min : s)  | ASTM D 2084-93 | Monsanto MDR 2000                       |
| Tensile (maximum stress (MPa);<br>elongation at break (%);<br>modulus at elongation (MPa)) | ASTM D 412-92  | Lloyd Instruments LR 5K                 |
| Tear strength (N/mm)   | ASTM D 2262-83 | Lloyd Instruments LS 500                |
| Abrasion loss (mg/kilocycles)  | ISO 4649       | Akron abrasion tester                   |
| Flex cracking (kilocycles)   | ISO 132        | DeMattia flex cracking                  |
| Compression set (%)  | ASTM D 395-89  | Compression set tester<br>MILANO/ITALIA |
| Rebound resilience   | ISO 4662       | Wallace Dunlop tripsometer              |
| Hardness, Shore A  | ASTM D 2240    | Lever Loader Model 716                  |

more would be available for consumption during the polymerization reaction.

To qualitatively determine how firmly the SB copolymer was attached to the silica surface, SB-modified 255 silica was refluxed in tetrahydrofuran in order to extract the polymer. The extracted material was analyzed using FTIR and the spectrum compared to standard reference spectra and diagnostic absorption bands of the polymers.<sup>22</sup> The extracted polymer showed the characteristic peaks of SB rubber standards and not of styrene only or butadiene only (see Figs. 6 and 7). A mass balance on the system again showed that it was not possible to extract all of the polymer on the surface, with approximately 20% of the polymer being extractable. This result is consistent with that previously obtained where 25% of the polymer was extractable.<sup>19</sup> The inability to fully extract the polymer using refluxing tetrahydrofuran again demonstrates that the polymer is quite firmly embedded in the silica pores.

### Rubber Compound Testing

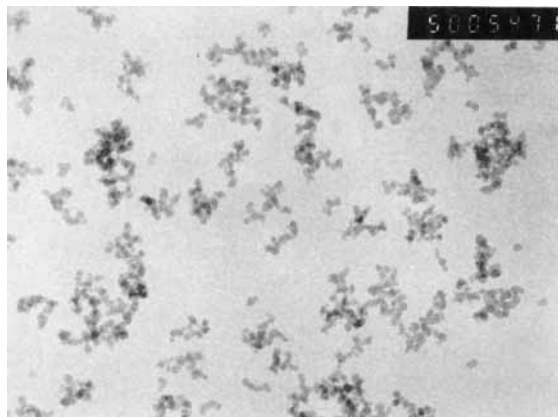
The effects of the various surface modifications on the rubber compound cure and cured physical prop-

erties were investigated. The complete performance data of all silicas studied in the rubber compound formulation (Table II) are summarized in Table VI. The data show that while the use of amorphous precipitated silica modified by a silane coupling agent decreased the compound cure time those of compounds containing silicas modified by the admicellar polymerization of comonomers are even more dramatically reduced, particularly for silica modified with SB. This decrease in cure time for the copolymer-modified silicas is again consistent with the formation of copolymer within the silica pores, covering some of the surface silanol groups, thereby reducing their reactivity toward the polar chemical additives used in rubber vulcanization, namely, the accelerators and zinc oxide activator. The greater decrease in  $T_{90}$  cure times for the compounds containing the SB-modified silicas than those of the SI-modified silicas may simply be due to the higher amount of the SB copolymer formed on the silica surface as indicated by the higher percent carbon values.

A comparative study of the cured rubber compound physical properties shows that all polymer-modified silicas significantly improve the modulus,

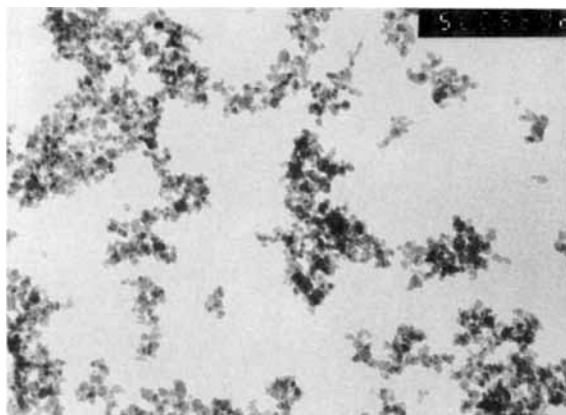
**Table IV Silica Physical Properties**

| Silica               | Mean Agglomerate Particle Size ( $\mu\text{m}$ ) | Surface Area ( $\text{m}^2/\text{g}$ ) | Pore Volume ( $\text{cm}^3/\text{g}$ ) | % Carbon |
|----------------------|--|--|--|----------|
| Hi-Sil 255 silica    | 18.96  | 165                                    | 0.1502                                 | 0.41     |
| Ciptane 255LD silica | 18.36  | 150                                    | 0.1511                                 | 0.81     |
| SBR 255              | 28.82  | 78                                     | 0.1191                                 | 11.27    |
| SIR 255              | 23.27  | 100                                    | 0.1360                                 | 5.31     |
| Hi-Sil 233 silica    | 16.87  | 131                                    | 0.1497                                 | 0.40     |
| SBR 233              | 17.67  | 82                                     | 0.1225                                 | 11.48    |
| SIR 233              | 20.83  | 86                                     | 0.1309                                 | 5.91     |

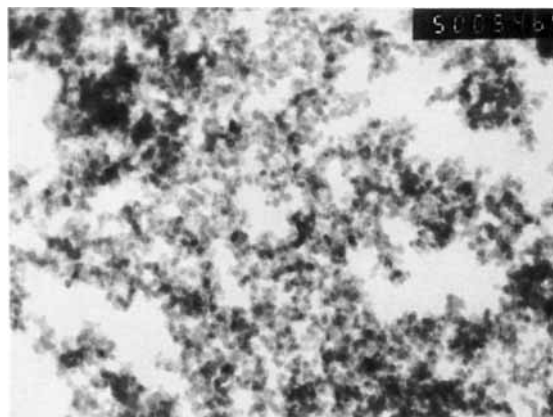


**Figure 2** Transmission electron micrograph of Hi-Sil 255LD control silica (C-1) at 75,000 magnification.

tensile, tear strength, abrasion resistance, and compression set values. The resilience values of the cured rubber compounds were increased upon using the in situ polymerization of comonomers, especially those of the SB-modified silica, while the compound using the silane-treated silica was relatively unchanged when compared to that of the control Hi-Sil 255 precipitated silica. There are also significant compound performance differences in the flex cracking resistance between using the silane-treated silica-filled and the in situ polymer-modified silicas. All copolymer-modified silicas adversely reduced the number of flexing cycles required to reach the same grade of cracking. This result is in contrast with previous results obtained by Waddell et al.<sup>12</sup> who found that SB copolymer-modified silica at about a 4% modification showed much lower cut propagation upon flexing. Additional studies are required to clarify this discrepancy since the degree of filler dispersion affects fatigue properties.



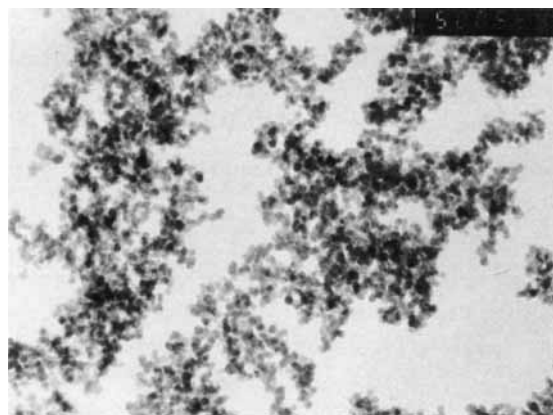
**Figure 3** Transmission electron micrograph of Ciptane 255LD silica at 75,000 magnification.



**Figure 4** Transmission electron micrograph of SB-modified Hi-Sil 255LD silica (SB-1) at 75,000 magnification.

The effects of the different surface-modified silicas on various rubber physical properties are qualitatively summarized in Table VII, where a “+” designation means an improvement in the property by greater than approximately 10% compared to the control, a “-” designation means an undesirable effect on the property by greater than about 10% compared to the control, and an “=” designation means no significant difference. A “+” is assigned a value of 1, a “-” is given a value of -1, and an “=” is given a 0 value for qualitative calculation of overall improvement relative to the respective control silicas. Table VIII shows the percent improvement/degradation of treated-silicas on the rubber compound physical properties compared to the controls.

As can be seen from the tables, use of either the silane-treated silica or silicas modified by the



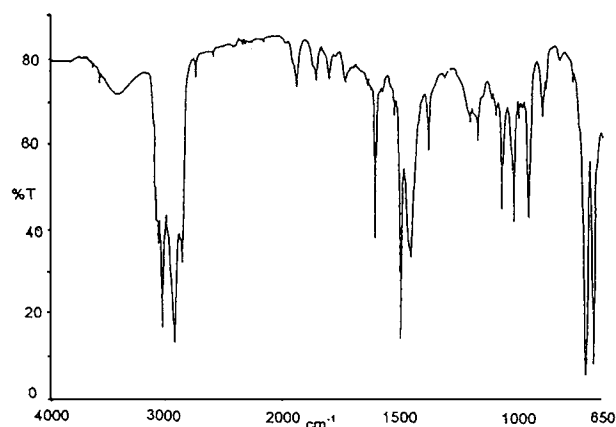
**Figure 5** Transmission electron micrograph of SI-modified Hi-Sil 255LD silica (SI-1) at 75,000 magnification.

**Table V Measure % Carbon Compared to the Predicted % Carbon**

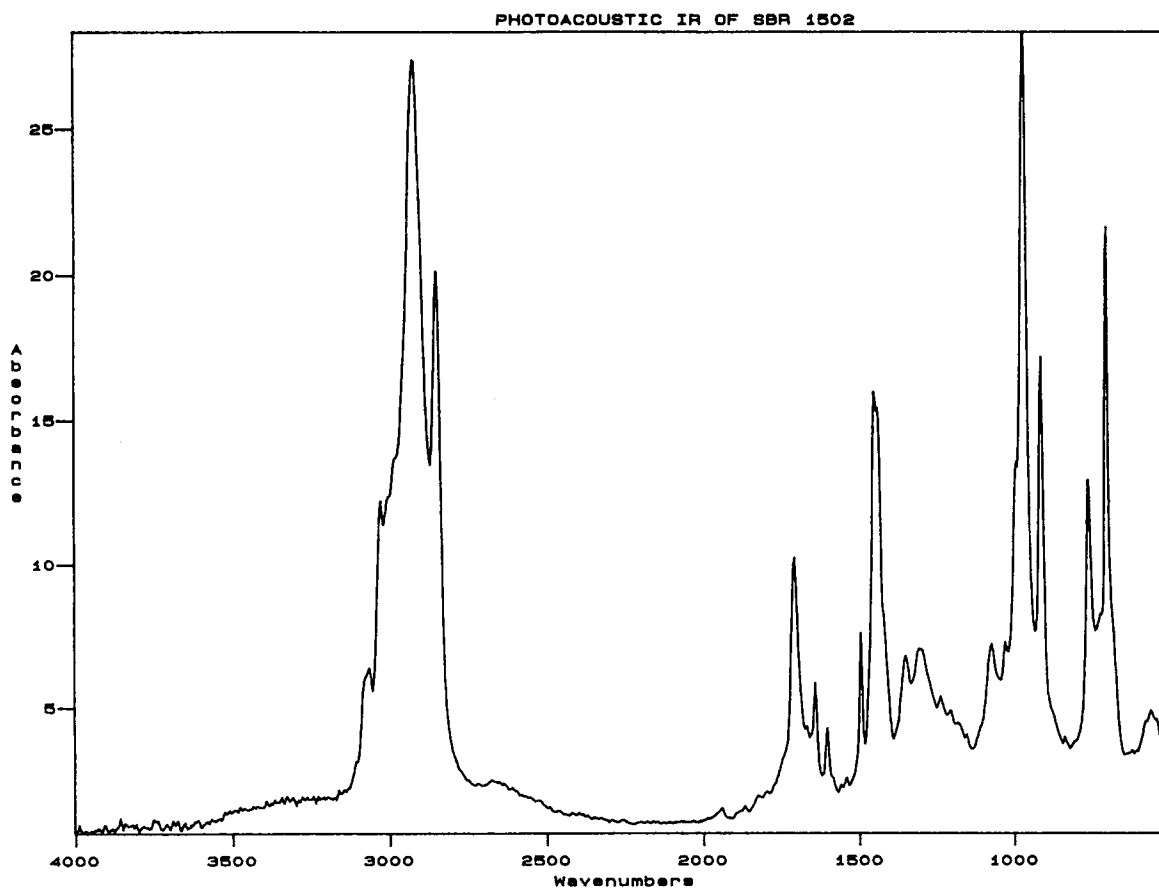
| Silica          | Measured % Carbon | Predicted % Carbon |
|-----------------|-------------------|--------------------|
| SB-modified 255 | 11.27             | 10.32              |
| SI-modified 255 | 5.31              | 5.59               |
| SB-modified 233 | 11.48             | 10.32              |
| SI-modified 233 | 5.91              | 5.59               |

in situ polymerization in an adsorbed surfactant bilayer affords improvements in the cure rate, modulus, tensile, tear strength, abrasion resistance, and compression set at ambient temperature. The SB- and SI-modified silicas also improved the rebound resilience, but in the present studies showed a negative effect on the flex cracking resistance.

A comparison can also be made of the copolymer-treated silicas to the silane-coupled silica, Ciptane 255LD. All copolymer-treated silicas afford greater improvements in rubber performance than do the silane-modified silica. Modified silicas SB-1, SI-1,

**Figure 7** Transmission Fourier transform infrared spectrum of the tetrahydrofuran-extracted polymer from the SB-modified Hi-Sil 255LD silica (SB-1).

and SI-2 outperform SB-2. Modified silica, SB-1, the SB-modified Hi-Sil 255 silica affords the greatest overall improvement of the rubber compound physical properties compared to the corresponding Ciptane 255LD silica. Use of SB-1 showed significant

**Figure 6** Photoacoustic Fourier transform infrared spectrum of SB rubber (SBR 1502).

**Table VI Rubber Compound Physical Properties**

| Property                                    | C-1   | Ciptane | SB-1  | SI-1  | C-2   | SB-2  | SI-2  |
|---|-------|---------|-------|-------|-------|-------|-------|
| $T_{90}$ at 150°C (min:s)                   | 18:38 | 13:47   | 4:53  | 5:59  | 13:51 | 3:57  | 6:38  |
| Maximum stress,<br>(MPa)                    | 19.84 | 21.97   | 26.74 | 26.43 | 19.79 | 23.01 | 25.02 |
| Elongation at break<br>(%)                  | 749.5 | 648.3   | 650.0 | 695.2 | 688.5 | 558.8 | 648.4 |
| Modulus at 100%<br>(MPa)                    | 0.77  | 1.09    | 1.42  | 1.33  | 0.99  | 1.55  | 1.36  |
| Modulus at 200%<br>(MPa)                    | 1.57  | 2.50    | 2.68  | 2.54  | 2.01  | 2.90  | 2.66  |
| Modulus at 300%<br>(MPa)                    | 2.84  | 4.83    | 4.31  | 4.19  | 3.44  | 4.67  | 4.52  |
| Tear strength<br>(N/mm)                     | 30.3  | 62.1    | 57.8  | 75.4  | 30.1  | 45.8  | 59.2  |
| Abrasion loss<br>(mg/kilocycles)            | 0.96  | 0.76    | 0.52  | 0.66  | 0.99  | 0.66  | 0.53  |
| Flex cracking<br>resistance<br>(kilocycles) | 113.1 | 127.1   | 31.6  | 35.8  | 77.6  | 32.1  | 41.2  |
| Compression set (%)                         |       |         |       |       |       |       |       |
| 70 h at 25°C                                | 16.5  | 9.9     | 5.0   | 7.0   | 15.6  | 12.4  | 7.4   |
| 70 h at 100°C                               | 83.1  | 56.9    | 75.8  | 76.0  | 73.6  | 74.9  | 71.5  |
| Resilience                                  |       |         |       |       |       |       |       |
| at 25°C                                     | 56.7  | 62.5    | 84.4  | 73.6  | 59.0  | 86.1  | 77.4  |
| at 100°C                                    | 55.2  | 59.9    | 82.9  | 73.7  | 58.2  | 87.1  | 78.9  |
| Hardness, Shore A                           |       |         |       |       |       |       |       |
| at 25°C                                     | 51.4  | 52.3    | 53.2  | 53.1  | 51.4  | 52.4  | 53.6  |
| at 100°C                                    | 52.8  | 53.4    | 55.3  | 55.7  | 55.0  | 56.4  | 57.5  |

C-1 = control 1, Hi-Sil 255 silica; C-2 = control 2, Hi-Sil 233 silica.

improvements in cure rate, modulus at 100% elongation, abrasion loss, compression set at 25°C, and resilience.

Previously,<sup>12,13</sup> SB modification at about a 4% level afforded the most promising candidate based on evaluation in a silica-filled compound having a natural rubber/SB rubber blend (70/30) when compared to homopolymer-modified and SI copolymer-modified silicas of similar carbon content. In this study, however, the SB-modified silica with greater than 11% carbon content is not significantly different in performance compared to the SI-modified silicas, which have less than 6% carbon content. Thus, the differences in performance of the modified silicas may simply be due to the differences in their polymer contents. The decreasing performances in elongation at break, tear strength, flex-cracking resistance, and compression set of SB-2 may be due to the greater loss of the silica surface area that accompanied this higher polymer content, since many rubber physical properties are directly related to the surface area of the silica.<sup>23</sup> These results suggest that the SB-mod-

ified silica might have an optimum modification level in which to improve performance. A lower percent carbon than 11% in the final product appears directionally beneficial. Further studies examining the percent polymer content in the modified silica are needed to maximize the performance of these silicas in rubber formulations. It is also probable that different percent polymer contents may be required for formulations based on different polymers or the percent of a particular elastomer in a blend.

In the present study, the SI-modified silicas afforded greater improvement in the compound's physical properties. Since their percent carbon contents are similar, this may be related to structural similarities between the SI modification and the natural rubber (*cis*-1,4-polyisoprene) compound used in this study, compared to the natural rubber/SB rubber compound previously used.<sup>12</sup> This may emphasize one of the strengths of the present surface-modification process: the ability to custom modify the silica surface with a variety of in situ polymers of known composition.



**Table VII Qualitative Summary of Surface-modified Silica Rubber Physical Properties Compared to the Control Silicas**

| Property                 | Ciptane | SB-1 | SI-1 | SB-2 | SI-2 |
|--------------------------|---------|------|------|------|------|
| $T_{90}$ at 150°C        | +       | +    | +    | +    | +    |
| Maximum stress           | +       | +    | +    | +    | +    |
| Elongation at break      | -       | -    | =    | -    | =    |
| Modulus at 100%          | +       | +    | +    | +    | +    |
| Modulus at 200%          | +       | +    | +    | +    | +    |
| Modulus at 300%          | +       | +    | +    | +    | +    |
| Tear strength            | +       | +    | +    | +    | +    |
| Abrasion loss            | +       | +    | +    | +    | +    |
| Flex cracking resistance | +       | -    | -    | -    | -    |
| Compression set          |         |      |      |      |      |
| 70 h at 25°C             | +       | +    | +    | +    | +    |
| 70 h at 100°C            | +       | =    | =    | =    | =    |
| Resilience               |         |      |      |      |      |
| at 25°C                  | =       | +    | +    | +    | +    |
| at 100°C                 | =       | +    | +    | +    | +    |
| Hardness, Shore A        |         |      |      |      |      |
| at 25°C                  | =       | =    | =    | =    | =    |
| at 100°C                 | =       | =    | =    | =    | =    |
|                          | +9      | +8   | +9   | +8   | +9   |

Therefore, the improvement of filler- elastomer interaction by the in situ polymerization process depends not only on the amount of polymer formed, but also appears to depend upon the structure of the in situ polymer. The compounds prepared using modified-Hi-Sil 255 silica show greater improvements in physical properties than do those prepared

using Hi-Sil 233 silica. This may only be due to the higher surface area of the Hi-Sil 255 precipitated silica since the modification procedures used were the same for the two silicas. Another area for future study is in the variation of surface-modification process conditions in order to determine if the amount of surfactant and the percent of in situ

**Table VIII Percent Improvement of Surface-modified Silica Rubber Physical Properties Compared to the Control Silicas**

| Property                 | Ciptane (%) | SB-1 (%) | SI-1 (%) | SB-2 (%) | SI-2 (%) |
|--------------------------|-------------|----------|----------|----------|----------|
| $T_{90}$ at 150°C        | 26          | 74       | 68       | 71       | 52       |
| Maximum stress           | 11          | 35       | 33       | 16       | 26       |
| Elongation at break      | -14         | -13      | -7       | -19      | -6       |
| Modulus at 100%          | 42          | 84       | 73       | 57       | 37       |
| Modulus at 200%          | 59          | 71       | 62       | 44       | 32       |
| Modulus at 300%          | 70          | 52       | 48       | 64       | 59       |
| Tear strength            | 105         | 91       | 149      | 52       | 96       |
| Abrasion loss            | 21          | 46       | 31       | 33       | 46       |
| Flex cracking resistance | 12          | -72      | -68      | -59      | -47      |
| Compression set          |             |          |          |          |          |
| 70 h at 25°C             | 40          | 70       | 58       | 20       | 52       |
| 70 h at 100°C            | 32          | 9        | 9        | -2       | 3        |
| Resilience               |             |          |          |          |          |
| at 25°C                  | 10          | 49       | 30       | 46       | 31       |
| at 100°C                 | 9           | 50       | 34       | 50       | 36       |
| Hardness, Shore A        |             |          |          |          |          |
| at 25°C                  | 2           | 4        | 3        | 2        | 4        |
| at 100°C                 | 1           | 5        | 5        | 3        | 5        |

polymer formed are important material variables since the conditions under which these silicas were modified were designed to give maximum surface coverage with the polymer coating without producing thick surface films.

## SUMMARY

A detailed characterization of surface-modified-precipitated silicas, both by the in situ polymerization of organic comonomers and by silane coupling agents, has been accomplished. The results show that the organic copolymer treatment increases the mean agglomerate particle size and decreases the N<sub>2</sub> BET surface area and pore volume. Only 20% of the polymer is extractable. The surface characteristics of the silica thus appear to be permanently modified.

The comparison of silicas modified by this new technique with those modified by a silane coupling agent shows that both techniques increase the cure rate and improve certain properties of the natural rubber compound. Except for flex-cracking resistance, in situ polymer-modified silicas afford greater overall improvement of natural rubber compound performance. The greatest percentage improvements relative to use of the silane coupling agent are maximum stress (SB-1 and SI-1), modulus at 100% elongation (SB-1 and SB-2), tear strength (SI-1), abrasion loss (SB-1 and SI-2), compression set at 25°C (SB-1 and SI-1), and resilience (SB-1 and SB-2). In comparison to an earlier study,<sup>12</sup> the present data also suggest that the type and the amount of polymer modification can significantly affect the rubber compound properties. In situ polymer-modified Hi-Sil 255 silica gave greater rubber compound physical property improvements than did a similarly modified Hi-Sil 233 silica, which is a lower surface area silica. The net greatest improvement relative to Ciptane 255LD silica was demonstrated by the SB-modified Hi-Sil 255 silica.

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