Polar Copolymer–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 onto the surface, (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 modified using copolymers of isoprene or 1,3-butadiene with vinyl acetate, acrylonitrile, 4-methoxystyrene, 4-chlorostyrene, and methyl methacrylate on the silica surface. 4-Methoxystyrene/butadiene modification afforded the most promising candidate based on evaluation in a silica-filled, natural/styrene–butadiene rubber shoe sole compound that also has been used as a model tire 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 has been shown to be a flexible process capable of producing unique materials useful in improving rubber cure properties and the cured compound physical properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The surface modification of substrates by admicellar polymerization (polymerization of monomer solubilized in adsorbed surfactant bilayers) has been investigated for approximately a decade. Early systems included polystyrene on alumina,[1] polytetrafluoroethylene on alumina,[2] polystyrene on titanium dioxide,[3] and polystyrene on silica.[4,5] Recently, we reported on the synthesis and rubber testing results of silicas modified by styrene, 1,3-butadiene, isoprene, and their copolymers.[6] The use of modified silicas were shown to improve important elastomer composite properties, such as tear strength, cut growth resistance, and cure rate.

This study expands the synthetic method to include the copolymerization of polar monomers with 1,3-butadiene and isoprene by utilizing redox initiation of polymerization at both 5°C and ambient conditions and thermal initiation of reaction at 70°C. The research presented further demonstrates

the generality of this method in tailoring the surface and composite properties of substrates using a variety of monomer structures and polymerization techniques. It also demonstrates the ability to form copolymers utilizing monomers which are more water soluble than either styrene or isoprene.

ULTRATHIN FILM FORMATION

The method utilized for the modification of inorganic powders by admicellar polymerization can be considered to occur in four basic steps (Fig. 1). Step one consists of admicelle (adsorbed micelle) formation by the adsorption of a suitable surfactant bilayer onto the surface of the substrate. The choice of surfactant is influenced by the chemical and electrostatic nature of the substrate as well as by the initiator system selected. An analysis of the point of zero charge for the substrate provides guidelines as to the pH ranges in which either cationic or anionic surfactants might be utilized. The reaction or dissolution of the substrate or reaction components
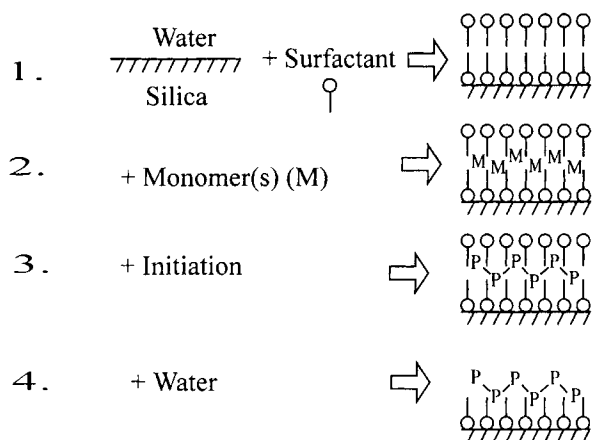

Figure 1 Schematic of the four-step process for ultra-thin film formations: (1) adsorption; (2) adsolubilization; (3) polymerizations; (4) washing.

in certain pH ranges may further define or limit the operating conditions.

Step two in the process involves the solubilization of monomers into the admicelle, called adsolubilization. Many organic monomers are nearly insoluble in water, thus, when introduced into the system, they preferentially partition into the organic interior of the admicelle. However, even relatively soluble monomers, e.g., vinyl acetate and acrylonitrile, can be utilized in this procedure. Adsolubilization can be accomplished either after the formation of the admicelles or simultaneously along with adsorption of the surfactants.

Step three is the *in situ* polymerization of the monomer. For free-radical polymerization, this is accomplished through the generation of radicals capable of initiating polymerization. Once the polymerization reaction has been initiated and the monomer is being consumed in the admicelle, the monomer in the bulk solution can begin to reequilibrate by diffusing into the admicelle. If the reaction is continued for a sufficient time period, essentially all of the monomer can be converted into polymer.

Step four is the washing of the treated powder to remove excess surfactant in order to expose the polymer-modified surface. The need for this step is optional, depending upon the application.

EXPERIMENTAL

Materials and Equipment

All materials were obtained commercially and used as received. Hexadecyl trimethylammonium bromide (CTAB) was obtained from Sigma Chemical

Co. (St. Louis, MO) at a purity of 99%. Ethanol was purchased from EM Science (Gibbstown, NJ) with an analysis of 95% ethanol and 5% methanol. *tert*-Butyl hydroperoxide (TBH), 70%; 4-chlorostyrene, 97%; vinyl acetate, 99+%; acrylonitrile, 99+%; ferrous sulfate, 98+%; ethylenediamine tetraacetic acid tetrasodium salt (EDTA), 98%; methoxychlor, 95%; and 1,3-butadiene, 99+%, were purchased from Aldrich Chemical Co. (Milwaukee, WI). Sodium formaldehyde sulfoxylate (SFS), 100%; 4-methoxystyrene, 98%; and 2,2'-azobis-2-methypropionitrile (AIBN), 98%, were obtained from Pfaltz & Bauer (Waterbury, CT) at 100% purity. Methyl methacrylate, 99%, was obtained from Johnson Matthey Electronics (Ward Hill, MA), and 4-chlorostyrene, 99%, from Polysciences (Warrington, PA). MACOL® OP 10 SP (MACOL) and Hi-Sil® 233 were obtained from PPG Industries, Inc. (Pittsburgh, PA).

Methods

All isoprene-containing samples were prepared using AIBN as the initiator with CTAB selected as the surfactant. A representative sample mixture consisted of 160 g of silica, 15 g of CTAB, 1.15 g of AIBN, 100 mL of ethanol, and 6 g total of monomers in a 1 : 1 mol ratio. The CTAB was dissolved in 1 L of deionized water that had been adjusted to pH 8 using sodium hydroxide. The AIBN was dissolved in the ethanol, and the monomers were then added. The ethanol/AIBN/monomer solution was slowly added to the CTAB solution, and the total volume brought up to 2 L using pH 8 water. The samples were placed in a sealed 2 L vessel, allowed to equilibrate at room temperature for 1 day, and then immersed in a 70°C water bath for 4 h. Polymerizations were carried out on both stirred and unstirred systems. The reaction was quenched by placing the reaction vessels in an ice bath.

1,3-Butadiene-containing samples were prepared using both a redox initiation scheme and AIBN for the thermal initiation of reaction. AIBN-initiated samples were prepared as described above for the isoprene mixtures, with the following changes: After equilibration, the closed reaction vessel was chilled to near 0°C by placing it in an ice bath and the vessel was then opened to add liquid butadiene (cooled to −10°C in a freezer) with the excess allowed to vent to obtain the desired weight of 1,3-butadiene for the reaction. A representative redox sample mixture consisted of 160 g of silica, 9.95 g of MACOL, 2 g of TBH, 2.8 g of EDTA, 1.2 g of SFS, and 6 g total of monomers in a 1 : 1 mol ratio.

Table I   Silica Test Methods

Property	Method	Instrument
BET N_2 Surface Area (single point)	ASTM D 3037-92	Micrometrics ASAP 2400
Dibutyl phthalate absorption	ASTM D 2414-92	Brabender plastigraph
Mean agglomerate particle size	ASTM F 662-86	Coulter multisizer II
Mercury porosimetry (total pore surface area, mean pore diameter, mean pore volume)	ASTM D 4284-83	Quantachrome Autoscan 33
% Carbon	ASTM E 350-90	Leco 521 analyzer

The surfactant, TBH, EDTA, SFS, and liquid monomer were dissolved in deionized water for a total volume of 2 L. The feed solution was contacted with the silica and allowed to equilibrate for 12 h and then chilled to near 0°C in an ice bath. The vessel was opened and liquid butadiene was added to excess, allowed to vent to the proper weight, and then sealed. The chilled vessel was allowed to equilibrate for 4 h. The vessel was then opened briefly to add 0.02 g of ferrous sulfate and then resealed. The vessel was then allowed to react for 2 or more h. The reaction was quenched by opening the reaction vessel and adding methoxychlor dissolved in ethanol.

After polymerization, the silica was allowed to settle and the supernatant decanted and disposed. The treated silicas were washed in a countercurrent bath consisting of filtered water flowing upward through a table-top buchner funnel equipped with a porous filter plate. The material was washed until the wash water no longer foamed upon agitation. The modified silica was then filtered and dried in an oven at 70°C for 12 h to remove water and/or unpolymerized monomer.

Testing Procedures

Properties of the surface-modified silicas were determined using the methods and instrumentation listed in Table I. The rubber compound physical properties of the surface-modified silicas were evaluated using a Converse[7] high-performance compression shoe sole formulation that was modified to also be representative of a tire compound as previously described; methods and instruments are listed in Table II.

RESULTS AND DISCUSSION

Table III shows the effect of the polymer modification on the nitrogen BET (single-point determination) surface area, median particle size, total pore surface area, and average pore diameter of the precipitated silicas. Data show that the polymer-modification process reduces nitrogen and total Hg pore surface areas and increases median Hg pore diameter, which is consistent with previous findings in the styrene, isoprene, and 1,3-butadiene homo- and copolymer systems.[6] The changes in surface and pore properties are probably the result of the blocking of some of the micropores in the precipitated silica by the polymer formed.

A comparison of the percent carbon in each of the modified silicas show an overall higher percentage carbon in the copolymers formed with isoprene than those formed with 1,3-butadiene. This may in part be due to process differences since isoprene is added as a liquid with the quantity easily determined and controlled, whereas there were problems in ob-

Table II   Rubber Compound Test Methods

Property	Method	Instrument
Cure (maximum torque, dNm; T_{90}, min)	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 at 36 kc)	ASTM D 813-87	DeMattia flex fatigue tester
Dynamic (G' and G'' moduli at 2% strain at 30°C, MPa)	ASTM D 2231-87	Rheometrics RDAII (rotational concentric shear mode)

Table III   Effect of Polymer Modification on the Surface Properties of the Control Silica

Silica	Surface Area (m²/g)	Particle Size (μm)	Total Hg Pore Surface Area, m²	Hg Pore Diameter (angstroms)	% Carbon
Hi-Sil® 233	141	15.1	166	316	0
VA-I	102	19.85	153	311	4.2
4MS-I	103	17.26	147	317	4.0
4CS-I	103	19.87	144	340	3.8
A-I	106	18.65	149	340	3.5
MMA-I	106	25.52	144	357	4.2
VA-B	130	18.20	164	315	< 1
4MS-B	117	18.86	159	316	2.3
4CS-B	110	18.07	151	337	3.1
A-B	118	22.66	154	324	1.7
MMA-B	116	21.69	162	314	2.2

VA = vinyl acetate, I = isoprene, 4MS = 4-methoxystyrene, 4CS = 4-chlorostyrene, A = acrylonitrile, MMA = methyl methacrylate, and B = 1,3-butadiene.

taining consistent amounts of gaseous butadiene in the glass reaction vessels. Another possible cause of lower percent carbons in the butadiene systems is the mass transfer resistance that must be overcome during polymerization with butadiene. Most of the isoprene is in the admicelle or in the bulk aqueous phase, with only a small portion in the vapor phase. Therefore, as isoprene in the admicelle is consumed during polymerization, equilibrium can be reestablished by isoprene diffusing from the aqueous phase into the interior of the admicelle. However, for the butadiene reactions, a considerable portion is in the vapor phase above the water, and for an equilibrium concentration of butadiene to be reestablished in the admicelle, it must first dissolve into the aqueous phase and then diffuse into the admicelle interior. Adsolubilization studies have shown that this

transfer takes a significant amount of time for butadiene, up to 4 h, for equilibrium to be achieved in a system of similar dimensions.[8]

The results of the rubber compound physical testing of the polymer-modified silicas are shown in Table IV for copolymers made using isoprene and in Table V for copolymers prepared with 1,3-butadiene. The results for certain tests are also shown graphically in Figures 2–6. Each rubber property in the figures is plotted vs. the measured nitrogen surface area of the modified silica. The solid line represents the regression curve and the shaded lines represent the 95% confidence limits of the > 600 untreated silicas in the compound database.[9] As with the homo- and copolymers of styrene, isoprene, and 1,3-butadiene, the data show that the use of a precipitated silica modified by the admicellar polymer-

Table IV   Isoprene Copolymer Rubber Compound Physical Properties

Property	Control	VA-I	4MS-I	4CS-I	A-I	MMA-I
T_{90} cure time	4.4	1.8	1.7	1.9	2.0	1.9
Maximum torque	23.0	16.5	17.3	18.2	18.1	16.5
Break strength	20.6	19.0	18.4	18.4	18.5	17.8
Elongation to break	657	605	598	584	596	602
20% modulus	0.63	0.59	0.59	0.60	0.59	0.64
100% modulus	1.41	1.56	1.62	1.66	1.59	1.60
300% modulus	3.85	4.29	4.47	4.50	4.34	4.30
Ratio, M300/M100	2.7	2.8	2.8	2.7	2.7	2.7
Tear energy	11.5	12.1	12.3	11.4	11.2	10.6
Cut growth	17.0	Failed	Failed	Failed	Failed	Failed
G' at 2% strain	3.66	1.89	1.83	1.81	1.99	2.36
G'' at 2% strain	0.382	0.145	0.132	0.133	0.155	0.200

VA = vinyl acetate, I = isoprene, 4MS = 4-methoxystyrene, 4CS = 4-chlorostyrene, A = acrylonitrile, MMA = methyl methacrylate, and B = 1,3-butadiene.

Table V   1,3-Butadiene Copolymer Rubber Compound Physical Properties

Property	Control	VA-B	4MS-B	4CS-B	A-B	MMA-B
T_{90} cure time	4.4	4	3.8	3.2	3.7	3.1
Maximum torque	23.0	27.7	27.0	26.1	27.9	26.8
Break strength	20.6	21.6	21.9	22.6	22.0	22.3
Elongation to break	657	689	671	611	599	653
20% modulus	0.63	0.72	0.70	0.73	0.78	0.74
100% modulus	1.41	1.38	1.43	1.47	1.39	1.44
300% modulus	3.85	3.47	3.61	3.90	3.39	3.77
Ratio, M300/M100	2.7	2.5	2.5	2.7	2.4	2.6
Tear energy	11.5	15.2	17.1	14.6	14.0	15.9
Cut growth	17.0	13.1	15.4	17.6	12.8	17.9
G' at 2% strain	3.66	3.27	3.66	3.29	3.56	3.83
G'' at 2% strain	0.382	0.278	0.289	0.253	0.280	0.291

VA = vinyl acetate, I = isoprene, 4MS = 4-methoxystyrene, 4CS = 4-chlorostyrene, A = acrylonitrile, MMA = methyl methacrylate, and B = 1,3-butadiene.

ization of any of the polar monomers copolymerized with isoprene or 1,3-butadiene generally decreases compound cure time (see Fig. 2). This may be partially due to the blocking of portions of the silica surface, inhibiting the ability of the silica surface silanol groups to interact with the chemical additives used for rubber vulcanization. Differences in the effectiveness of using the isoprene copolymers vs. the 1,3-butadiene copolymers for elastomer reinforcement are evident upon examination of the cured rubber compound physical properties. Data show that all five copolymers with 1,3-butadiene increased the maximum torque values by approximately 10%

compared to the control (Table V), while all five copolymers made with isoprene showed decreases in the maximum torque values (> 15%) compared to the control silica (see Fig. 3 and Table IV).

Modulus values at 20% elongation (20% modulus) and tear strength data also show differences between the copolymers with isoprene and those with 1,3-butadiene. All five butadiene copolymers showed significant increases in 20% modulus values, whereas all five isoprene copolymers were within experimental reproducibility of the control (see Fig. 4). The tear strength values of the rubber compounds was increased for all five copolymers with
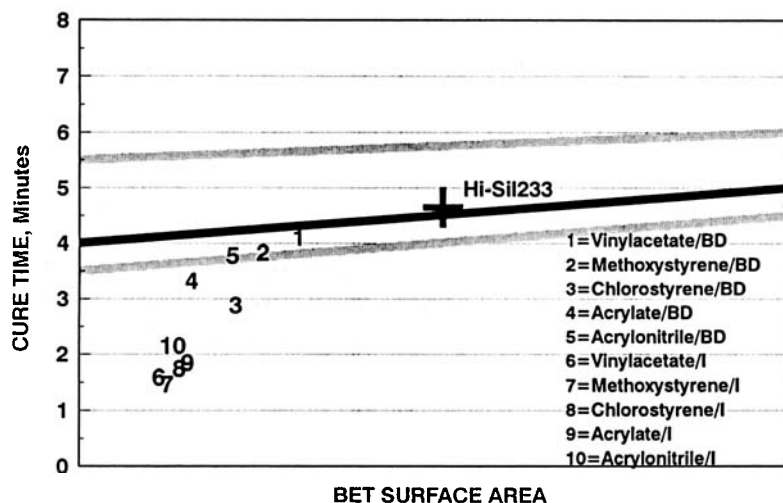
TIME TO 90 % CURE
vs SILICA SURFACE AREA

Figure 2   Time to reach 90% of compound cure vs. BET N_2 single-point surface area.

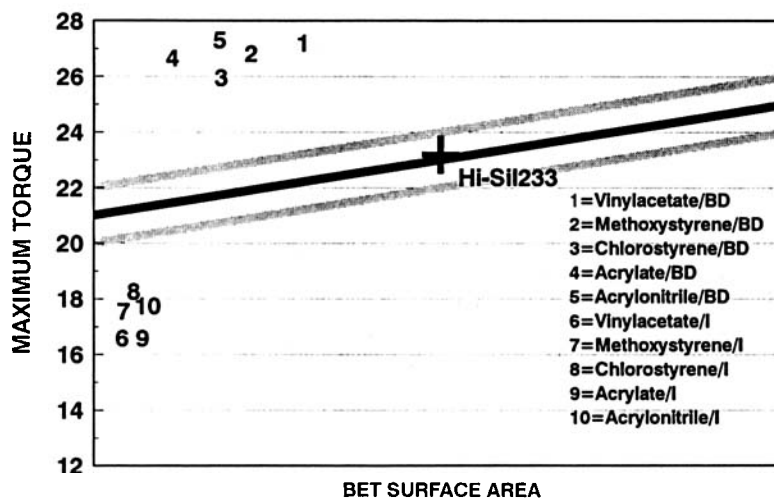# MAXIMUM RHEOMETER TORQUE
vs SILICA SURFACE AREA

Figure 3 Maximum torque measured on the Monsanto MDR2000 vs. BET N_2 single-point surface area.

butadiene, while those compounds prepared using the isoprene copolymers were unchanged when compared to use of the unmodified control silica (see Fig. 5).

There are also significant differences between the isoprene and butadiene copolymers in the results of the cut-growth resistance measured using the DeMattia Flex Fatigue test. All five butadiene co-polymer-treated silicas showed equal or improved cut growth resistance (see Fig. 6 and Table V). Rubber compounds prepared using the silicas modified by the five copolymers containing isoprene all failed in the test (Table IV), indicating that the cut propagated completely across the 25 mm sample strip before reaching 36,000-cycle flexing milestone used for standard evaluation of cut growth.

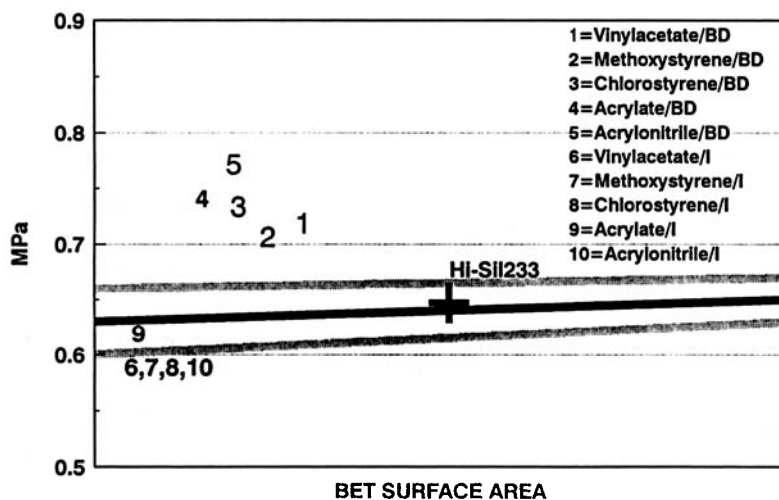# MODULUS @ 20% ELONGATION
vs SILICA SURFACE AREA

Figure 4 Modulus at 20% elongation vs. BET N_2 single-point surface area.
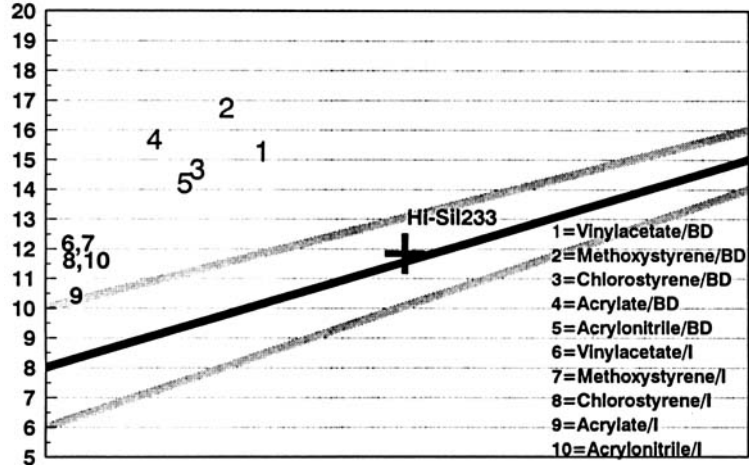
TEAR STRENGTH
vs SILICA SURFACE AREA

Figure 5   Tear strength vs. BET N_2 single-point surface area.

Comparison of the methoxystyrene/butadiene copolymer-modified silica data to the results previously obtained for the homo- and nonpolar copolymers of styrene, isoprene, and butadiene[6] shows that one of the common ingredients in the most successful systems is butadiene (see Table VI). The results are shown qualitatively in Table VII, in which a "+" indicates greater than 10% improvement in the property over the control, a "−" indicates a greater than 10% negative impact on the property, and an "=" indicates no significant effect. A "+" is given a value of 1; an "=," a value of 0; and a "−," a value of −1 for qualitative totaling of the columns. Use of any of these three modifications affords improvements in the cure rate and tear strength of their respective compounds. The butadiene homo-

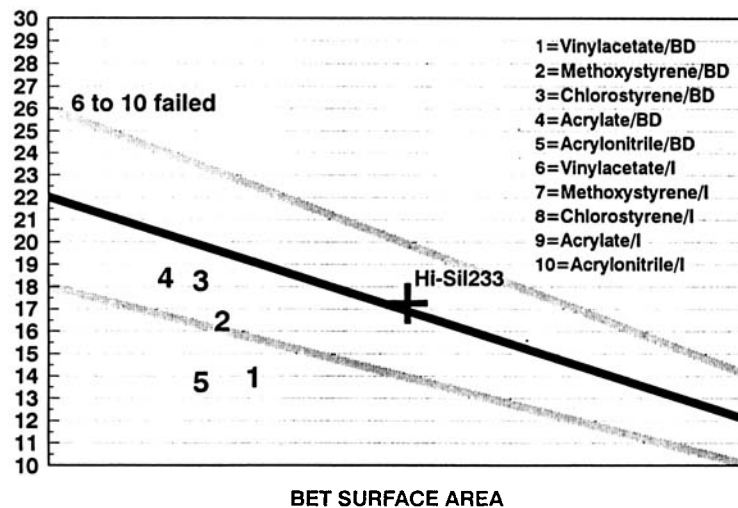# DEMATTIA FLEX FATIGUE
vs SILICA SURFACE AREA

BET SURFACE AREA

Figure 6   Cut length after 36,000 cycles on the Demattia flex fatigue test vs. BET N_2 single-point surface area.

polymer showed additional improvements in cut growth and the dynamic property G'' and a negative effect on the dynamic property of G'. G' is used as indirect evidence of polymer reinforcement, while G'' is related to the hysteresis or heat buildup of the rubber under stress. Thus, a system which improves the reinforcement while decreasing the heat buildup is desirable. The styrene/butadiene copolymer modification also improved the ratio of the modulus values measured at 300 and 100% elongations (M300/M100 ratio) as well as the cut-growth resistance, while showing a negative effect on G'. The 4-methoxystyrene/butadiene copolymer modification showed improvements in maximum torque, 20% modulus, and G'', without adverse effects on the other properties tested. As can be seen, the 4-methoxystyrene/butadiene-modified silica affords the greatest overall improvement of the rubber compound physical properties, with no detrimental affects on any of the properties tested.

SUMMARY

The results of this study further demonstrate that surface modification of precipitated silicas by admicellar polymerization produces a new class of reinforcing fillers capable of improving the rubber cure and the cured compound's physical properties. Admicellar polymerization modifies the silica surface, which serves to beneficially reduce compound curing times and improve specific rubber compound performance properties. The present data again show that the type of polymer modification can sig-

nificantly affect the rubber compound properties. The results of this work using copolymers prepared with a nonpolar and polar monomer show that it should be possible to custom design surface-modified fillers/reinforcers for use in a wide variety of applications. It has been shown that the process of admicellar polymerization is successful even with monomers having a relatively high solubility in water. The partitioning of these more water-soluble monomers between the aqueous phase and the admicelle, as well as the interactions between monomers during adsolubilization, are areas for future studies.

One perplexing observation that has come from this study is the difference in the rubber compound

Table VII   Qualitative Summary of Changes in Polymer-modified Silica Rubber Physical Properties

Property	PB-3	SBR-1	4MS-B
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' at 2% strain	−	−	=
G'' at 2% strain	+	=	+
Total	+3	+4	+5

Table VI   Selected Butadiene Homo- and Copolymer Rubber Compound Physical Properties

Property	Control	PB-3	SBR-1	4MS-B
T_{90} cure time	4.4	2.0	2.1	3.8
Maximum torque	23.0	22.1	23.4	27.0
Break strength	20.6	21.9	21.4	21.9
Elongation to break	657	622	723	671
20% modulus	0.63	0.67	0.64	0.70
100% modulus	1.41	1.48	1.39	1.43
300% modulus	3.85	3.95	4.17	3.61
Ratio, M300/M100	2.7	2.5	3.0	2.5
Tear energy	11.5	19.1	15.4	17.1
Cut growth	17.0	15.1	10.3	15.4
G' at 2% strain	3.66	3.16	3.14	3.66
G'' at 2% strain	0.382	0.327	0.344	0.289

PB-3 = polybutadiene sample #3,[6] SBR-1 = styrene/butadiene sample #1,[6] 4MS-B = 4-methoxystyrene/butadiene.

behavior between copolymers of isoprene and copolymers of 1,3-butadiene. It is somewhat surprising that the addition of a methyl group to butadiene causes so much difference in the rubber compound properties of the modified silicas. One possible explanation is that because butadiene is slightly smaller it is able to penetrate more deeply into the pores of the silica, giving more entanglement of the polymer strands with the silica. It is thought that when these entangled strands participate in the rubber vulcanization process that they form anchors for reinforcement to the silica particles. Another possible explanation is because the butadiene is a gas there may be pore condensation of butadiene in the smallest pores. When this liquid butadiene is polymerized, it would form firm anchors for polymer strands coming out from these "plugs." Pore condensation calculations make this possibility unlikely, but since the interfacial tension between the water and butadiene as well as the contact angle are unknown, this explanation cannot be ruled out. A third possible explanation is that the presence of the methyl group sterically inhibits the crosslinking of polyisoprene copolymers during the vulcanization process when compared to butadiene. Therefore, with the same amount of polymer present on the modified silicas, the butadiene-modified silica would have more "anchors" attaching it to the bulk rubber compound.

The results demonstrate that admicellar polymerization is a flexible process, allowing for a relatively easy transfer of procedures from the emulsion polymerization literature. The results reemphasize the need to further explore this new area of polymer and surface chemistry. Similarities and differences between existing technologies such as silane coupling agents or emulsion polymerization and admicellar polymerization are also areas for future studies.

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