

Admicellar polymerization modified silica via a continuous stirred-tank reactor system: Comparative properties of rubber compounding

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Abstract

Fillers such as silica are often added to rubber to improve performance in commercial applications. The use of silica in rubber compounds improves important compound properties such as tensile strength and cut growth resistance. A difficulty with using silica as a filler is the high energy of mixing due to both poor rubber–filler and strong filler–filler interactions. Improved compatibility between the silica and rubber can be achieved using admicellar polymerization to modify the silica surface. Previously, this process had been performed only in batch reactors, which are usually not appropriate for industrial applications, especially for providing a consistent product. In this work, a continuous stirred-tank reactor (CSTR) for admicellar polymerization was developed. The feed was comprised of precipitated silica, cetyltrimethylammonium bromide (CTAB) cationic surfactant, styrene and isoprene comonomers, and 2,2'-azobisisobutyronitrile initiator. The results showed that the modified silica reduced T_{90} cure times and improved modulus, abrasion resistance, and compression set. The optimum conditions for surface modification of silica by the admicellar polymerization process were 5 g comonomer loading per kg silica and a 30-min reaction time. In comparison with the modified silica using a batch process, the modified silica obtained from the CSTR process was found to be superior in the performance of rubber compound.

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1. Introduction

Fillers are often added to rubber to improve performance in commercial applications. There are several fillers used in the rubber industry. Carbon black is the most widely used reinforcing filler for rubber, providing excellent reinforcement at a relatively low cost. Reinforcing silica is generally more expensive than carbon black but provides reinforcement with a neutral color. Silica can also provide additional property benefits and compounding flexibility that is not obtainable with carbon black. However, unmodified precipitated silica lacks the ability to make strong silica–rubber bonds [2–5]. Additionally, the difference in nature between the two materials, mineral versus organic, and the strong filler–filler in-

teractions necessitate high mixing energies and can lead to poor dispersion of the silica. For this reason, methods to improve the compatibility between hydrocarbon elastomers and precipitated silica by modification of the silica surface are of considerable interest.

Several methods such as bifunctional organosilanes, grafting, and in situ polymerization are available for the modification [6–16]. Silica modified by the in situ polymerization of organic monomers significantly increases rebound resilience and can produce greater overall improvements in rubber compound performance than that modified by more expensive silane coupling agents [7,8].

Admicellar polymerization consists of four main steps: surfactant adsorption onto the surface of solid particles, adsolubilization of monomers into admicelles, polymerization, and washing of the outside layer of surfactant [6–8]. Previously, admicellar polymerization had been successfully

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performed only in batch systems, which usually cannot provide the consistent products needed for industrial applications [7,8]. The objective of the present research was to develop a continuous stirred-tank reactor system to produce modified silica by in situ polymerization (admicellar polymerization) of organic monomers in the surfactant layer adsorbed onto the surface of precipitated silica in order to enhance silica/elastomer interactions leading to improving rubber product performance. Additionally, a systematic study of the effects of comonomer loading and reaction time on the properties of rubber compounding samples with modified silica was examined.

2. Experimental

2.1. Materials

Hi-Sil[®]255, precipitated silica with specific surface area of $170 \pm 15 \text{ m}^2/\text{g}$, was obtained from PPG-Siam Silica Co., Ltd. Hexadecyltrimethylammonium bromide (CTAB) 98%, styrene 99% and isoprene 98% were purchased from Fluka (Buchs, Switzerland). 2,2'-Azobisisobutyronitrile (AIBN) with 98% purity, a water insoluble initiator, was obtained from Aldrich Chemicals Company (Milwaukee, WI, USA). Sodium hydroxide pellets with 99% purity were obtained from J.T. Baker Inc. (Philipsburg, USA). Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences (Bangkok, Thailand). Ethanol, absolute anhydrous, was obtained from J.T. Baker Inc. (Edo. De Mex, Mexico). All materials were used without further purification.

2.2. Adsorption experiment

Adsorption experiments of CTAB onto silica were conducted in a series of 24 ml vials with screw lids. Two-gram samples of silica were mixed with 20 ml of surfactant solutions containing different CTAB concentrations at a constant pH of 8. The mixture in each vial was then equilibrated at 30°C for 24 h and centrifuged at 2000 rpm for 10 min afterwards. The supernatants were analyzed for CTAB concentration by a TOC-500A Shimadzu total organic analyzer. The amount of CTAB adsorbed onto silica was calculated by the concentration difference method. Then, the CTAB adsorbed data were plotted against the equilibrium CTAB concentration to obtain the CTAB adsorption isotherm. From the adsorption isotherm, an equilibrium CTAB concentration corresponding to the bilayer coverage region was selected to avoid the formation of micelles.

2.3. Experimental set-up of a continuous admicellar polymerization system

A reactor system used in this study consisted of a stirred feed tank and a reactor and an unstirred product tank. The 17 l feed stainless steel feed tank had a sealable lid and inter-

rior baffles to promote good mixing. The feed tank was well mixed by a mechanical stirrer penetrating a seal on the vessel lid. The reactor vessel was a 1-l-borosilicate glass bottle with a screw cap. The product tank was a 17 l stainless steel tank. The liquid in the reactor was mixed well using a magnetic stirrer with a magnetic bar. To start the polymerization, reactor temperature was maintained at $70 \pm 2^\circ\text{C}$ using a circulating heater and water jacket. The flow rate of the feed solution was controlled using a peristaltic pump (Masterflex Digital console drive with easy-load model 7518-60 head) to obtain different hydraulic retention times. The stirring speed was not examined and was kept constant at a rate capable of keeping the slurry well mixed and suspended.

2.4. Surface modification procedure

The amorphous precipitated silica was modified using styrene and isoprene comonomers at a 1:3 molar ratio. The total comonomer loadings were 5, 20 and 30 g/kg silica. The polymerization times were controlled at 30, 45 and 60 min, which are denoted by S, M and L, respectively.

The preparation procedure of the feed solution consisted of: (1) adding 200 g CTAB to 12.5 l deionized water and stirring until the surfactant was completely dissolved, (2) adjusting the pH of the surfactant solution to 8 using a dilute sodium hydroxide solution, (3) adding 1 kg silica to the surfactant solution in the feed tank, (4) dissolving 1.65 g AIBN and 5 g of 1:3 molar ratio of styrene to isoprene in 99.7% ethanol at the ratio of 30 ml per 0.5 g AIBN and then adding this mixture to the feed tank, and (5) allowing the system to equilibrate at room temperature with constant stirring for 24 h.

The mixture in the feed tank was then fed into the reactor continuously using the peristaltic pump at the three different flow rates. The reactor was heated to 70°C to initiate the polymerization reaction. The reaction effluent was collected in the product tank and the supernatant was decanted. The modified silica was washed by counter-current washing for 5 days with daily stirring or until the wash water no longer foamed on agitation. The silica was then dried at 110°C for 24 h and reground gently into powder through a 120-mesh sieve. The experimental matrix is shown in Table 1.

2.5. Analysis and testing procedures

All nitrogen BET surface areas and mean agglomerate particle sizes of silica samples before and after the modification step were investigated using a surface area analyzer

Table 1
Experimental matrix and sample designations used in this study

Comonomers per kg silica	Polymerization time (min)		
	30 (short)	45 (medium)	60 (long)
5	5S	5M	5L
20	20S	20M	20L
30	30S	30M	30L

Table 2
Rubber compound formulation used in this study

Ingredient	Parts per hundred rubber (PHR)
Natural rubber (STR 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
Sulphur	2

(Autosorb-1 Quantachrome) and a particle size analyzer (Malvern Mastersizer X Ver. 2.15), respectively.

The rubber compound formulation used for physical evaluation is given in Table 2 and was designed specifically for physical properties testing [8]. The formula was slightly modified by eliminating polyethylene glycol, which is sometimes used to form complexes with the silanol groups on the surface to prevent them from reacting with the activator.

A two-stage mixing procedure was employed to prepare all compounds. An amount of 1 kg of different silica samples prepared was used for each batch of rubber compounding. In the first stage, the rubber, filler and other ingredients (except vulcanizing agent) were mixed in a Dispersion Kneader Machine for 13 min. The vulcanizing agent was added to the master batch in the second mixing step using a two-roll mill for 3 min. All compounds were cured at 150 °C to T_{90} as determined on the moving die rheometer. Standard test procedures as prescribed by ISO or ASTM were used for the determination of compound and vulcanizate properties

(Table 3). For each testing parameter, an average value was calculated from at least three testings. Most standard deviation of all testing parameters were less than 10%.

3. Results and discussion

3.1. Adsorption isotherm of CTAB

From the plot between CTAB concentration and surface tension, the critical micelle concentration (CMC) of CTAB is approximately 900 μM close to the reported value of 920 μM [14]. To minimize the loss of comonomer used in the adsorption and polymerization steps, it is necessary to have the equilibrium CTAB concentration below its CMC in order to avoid the formation of micelles in the system. Hence, 12.5 l CTAB solution of 48,900 μM and 1 kg silica were used in this study which corresponds to the bilayer coverage region of the CTAB adsorption isotherm.

3.2. Surface characterization

Admicellar polymerization has been shown to affect a variety of physical characteristics of silica, including BET surface area and mean agglomerate particle size. As expected, all modified silica samples had BET surface areas less than that of the unmodified silica, some by as much as 30% (see Table 4). For each level of the comonomer loading, the modified silica with 30-min reaction time (S) had the lowest surface area, while the highest surface area was obtained with 45-min reaction time (M). Though the reason for this is not completely clear, recent studies have shown that

Table 3
Rubber compound test methods

Property	Method	Instrument
Cure time (min)	ASTM D 2084-93	Monsanto MDR 2000
Tensile properties (Max. stress, MPa; elongation to break, %; modulus, MPa)	ASTM D 412-92	Instron Model 1011
Tear strength (N/mm)	ASTM D 2262-83	Lloyd Instruments LS 500
Abrasion loss (vol. loss/kilocycles)	ISO 4649	Akron Abrasion Tester
Flex cracking (kilocycles)	ISO 132	DeMattia Flex Cracking
Compression set (%)	ASTM D 395-89	Compression Set tester, MILANO/ITALIA
Resilience (%)	ISO 4662	Wallace Dunlop Tripsometer
Hardness (shore A)	ASTM D 2240	Lever Loader Model 716

Table 4
Physical properties of modified silica samples produced under different conditions

Modified silica	Surface area (m^2/g)	% Reduction in surface area	Mean agglomerate particle size (μm)	% Increase in particle size
Hi-Sil [®] 255	171	–	50.85	–
5S	119	30	92.76	82
5M	141	17	98.32	93
5L	124	27	102.68	102
20S	129	24	78.94	55
20M	143	16	81.17	60
20L	135	21	69.72	37
30S	139	18	85.15	67
30M	157	8	80.23	58
30L	153	10	70.25	38

at low comonomer loadings, small polymer aggregates are formed primarily in the pores of the silica, blocking access to these areas and causing a decrease in the surface area. At higher monomer loadings, much of the formed polymer may be found in droplets which are primarily on the silica surface. Therefore, during processing (washing and sieving), many of these surface aggregates may be removed, exposing the silica surface and pores [17].

Table 4 also shows the data on changes in the mean agglomerate particle size. As seen from the table, the mean agglomerate particle size of all modified silica samples increased, some by as much as 100%. At the lowest comonomer loading of 5 g for any given residence time (5S, 5M, or 5L), the highest degree of agglomeration was found. The results indicate that the degree of agglomeration strongly depends on the comonomer loading. It has been reported that the increase in the mean agglomerate particle size resulted from the formation of polymer bridges between silica particles [15]. The observed trends may be due to the change in the distribution of monomers within the admicelle at different comonomer loadings. At low monomer loadings, the monomers are evenly distributed, making the joining of contacting particles likely [5]. At intermediate and high monomer loadings, the monomers form droplets on the surface which do not serve to join the particles and which, as stated above, can be removed during processing and the washing step. Additionally, as stated in previous studies, some of the reason for changes in aggregate size may be due to the processing of the silica, specifically, that grinding it back to powder by forcing it through a sieve will not restore it to its previous form [7].

In order to verify the existence of poly(styrene-isoprene) on the silica surface, after the polymerization step, tetrahydrofuran (THF) was used to extract the polymer from the modified silica. From the FTIR spectra, Fig. 1, it confirms the formation of poly(styrene-isoprene). The thermogravimetric analysis (TGA) was also employed to determine the amounts of poly(styrene-isoprene) of all modified silica samples. The results of the polymer amounts at different conditions were

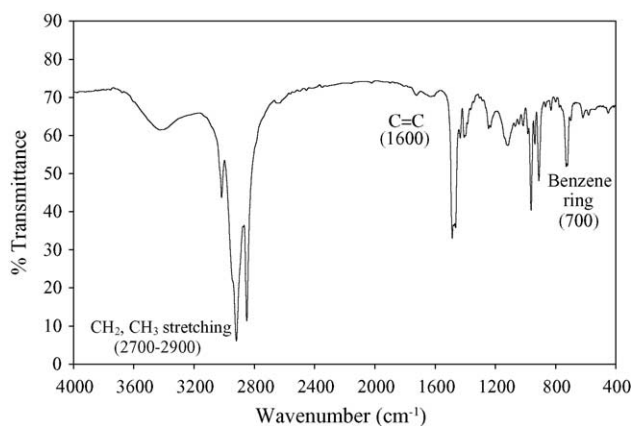


Fig. 1. FT-IR spectrum of the extracted material from modified silica using the following conditions: 70 °C, 30 comonomers loading per kg silica and 30-min residence time.

Table 5
Rubber compound physical properties using different modified silica samples obtained from the present study compared to the modified silica of the previous batch systems (1:3 molar ratio of styrene to isoprene)

Property	Hi-Sil [®] 255 ^a	Batch ^a	(5) ^b	5S	5M	5L	(20) ^b	20S	20M	20L	(30) ^b	30S	30M	30L
T ₉₀ cure (min)	18.63	5.98	13.28	4.86	4.50	4.89	8.78	4.97	4.77	4.71	12.78	4.89	4.80	4.77
100% modulus @ 25 °C (MPa)	0.77	1.33	2.01	1.92	2.34	2.22	2.39	2.51	1.91	1.88	2.32	1.65	1.96	2.08
300% modulus @ 25 °C (MPa)	2.84	4.19	3.61	5.55	5.82	5.53	4.30	6.32	5.13	4.78	3.99	4.56	5.01	5.22
Tensile strength @ 25 °C (MPa)	19.84	26.43	21.83	27.54	27.44	27.51	25.20	26.98	26.86	28.00	21.05	27.10	26.99	25.62
Tear strength @ 25 °C (N/mm)	30.27	75.37	57.97	58.94	56.12	56.55	67.91	56.95	59.96	58.35	45.94	59.09	55.45	53.31
Hardness @ 25 °C (shore A)	51.40	55.30	53.67	57.67	57.30	56.77	52.61	58.73	57.23	56.63	55.47	55.94	58.13	59.10
Flex cracking (kilocycle)	113.10	35.84	55.41	60.44	70.25	72.16	50.54	30.77	37.76	32.37	58.28	35.50	21.16	19.60
Abrasion (ml/kilocycle)	0.96	0.66	0.77	0.48	0.48	0.53	0.57	0.51	0.49	0.52	0.69	0.56	0.53	0.57
Resilience (%)	56.7	73.60	49.33	74.20	74.70	65.40	54.26	76.70	72.20	75.00	44.45	77.50	79.90	75.90
Compression set (%)	83.1	76.02	72.16	69.06	66.90	69.92	67.69	71.71	66.28	63.52	77.20	63.69	67.04	68.17

5, 20, 30: styrene-isoprene loading, g/kg silica; S, M, L: the reaction time of polymerization, min (30, 45, and 60 min).

^a Results from Thammathadanukul et al. [8].

^b Results from Chinpan [7] (with the residence time of 4 h).

Table 6

Qualitative comparison of improvement in rubber physical properties using modified silica obtained from this work (CSTR) and some previous studies (BATCH) based on using unmodified silica

Modified silica	5S	5M	5L	20S	20M	20L	30S	30M	30L
The present study	+6	+6	+6	+6	+6	+6	+5	+6	+6
Thammathadanukul	+4	+4	+4	+2	+2	+2	+1	+1	+1
Chinpan 5	+5	+7	+7	+5	+4	+3	+2	+4	+5
Chinpan 20	+3	+4	+3	+3	+1	+1	−1	+1	+1
Chinpan 30	+4	+6	+7	+5	+3	+3	+3	+3	+3

found to correspond to the changes in the surface area and the mean agglomerate particle size [15,18].

3.3. Physical properties of rubber compounds

Rubber compound testing results of the continuous admicellar polymerization process are summarized in Table 5 which includes the results for batch-modified silica from Chinpan [7] and Thammathadanukul et al. [8]. As mentioned before, the CSTR system was employed to modify the silica surface at three different levels of comonomer loadings, 5, 20, 30 g/kg silica and three residence times of 30, 45, and 60 min. As can be seen from Table 5, all modified silica obtained from both the previous works using batch processes and the present study using a continuous process gave significant improvement of rubber properties with respect to the testing parameters as compared to the unmodified silica. The results confirm that the admicellar polymerization can improve the compatibility between silica and natural rubber resulting in better mixing of silica and better rubber properties. The effects of the different surface-modified silica on various rubber physical properties are summarized qualitatively in Table 6. The scores in Table 6 were determined by assigning a “+1” value if the rubber compound testing resulted in a 10% or greater improvement in the tested property, a “+0” if the change in the property was between a 10% decline and a 10% improvement in the property, and a “−1” if the change was a decline of 10% or more in the property compared to those of the unmodified silica, and then added the scores for the ten properties evaluated. Thus, scores could range from −10 to +10. The equal weight thus given to all variables does not imply that they are all equally important, but rather gives a simple method of qualitatively analyzing overall improvement. The results show that the CSTR-modified silica exhibits overall improvements in rubber compound testing, as did the batch-system admicellar polymerization modified silica. The results in Table 6 show that the CSTR-modified silica gives significant improvement in compound performance over most of the batch-modified silica, with equal or better performance in all but one comparison. The results from previous batch studies showed that certain monomer loadings were better than others, while the CSTR-modified silica were consistently better at all monomer loadings. Thus, the continuous system appears to provide greater improvement in rubber compound performance than most batch-produced silica. This can be explained that a CSTR system can produce

more uniform polymer layer coating on the silica surface than a batch process. According to the results of compound testing, the optimum conditions for the modification were 5 g comonomer loading per kg silica and 30-min retention time. It should be noted that all the reaction times did well and produced consistent results.

4. Conclusions

In this study, a continuous stirred-tank reactor was demonstrated successfully to modify amorphous silica via admicellar polymerization for rubber application. After modification, all the treated silica was found to have lower BET surface areas and larger mean agglomerate particle sizes as compared to the unmodified silica. Comparison of the rubber compound properties with the unmodified silica and those modified in batch polymerization systems shows that the continuous system can produce modified silica that are equal or superior in performance in rubber compounds as compared to those produced from batch processes because the CSTR-modified silica has more consistent properties. Low monomer loading and a 30 min residence time produce excellent results, which is advantageous in that it lowers the cost of materials and equipment size needed for commercialization. This finding is a significant step toward the commercialization of the admicellar polymerization for surface modification of silica.

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