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Mixed surfactants for silica surface modification by admicellar polymerization using a continuous stirred tank reactor

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Abstract

The objective of the present study was to investigate the use of mixed surfactants of centyltrimethyl ammonium bromide (CTAB) and polyoxyethylene octyl phenol ether ($OPEO_{10}$ or Triton X-100) for admicellar polymerization using a continuous stirred tank reactor to modify the silica surface for rubber compounding application. The effects of the molar ratio of CTAB to $OPEO_{10}$ and the surfactant adsorption structure were investigated to relate them to the mechanical properties of the rubber compound. For any given structure of surfactant adsorption (monolayer or bi-layer coverage), a mixed surfactant system having any molar ratio of CTAB to $OPEO_{10}$ gave better mechanical properties of the rubber compound than those of the pure surfactant system of CTAB or $OPEO_{10}$. From the rubber testing results, the best mechanical properties of the rubber compound were achieved at a 1:3 molar ratio of CTAB to $OPEO_{10}$ with the monolayer coverage structure of surfactant adsorption. The use of the mixed surfactants was found to provide better physical properties of the rubber compound as well as to reduce the significant amount of surfactants required as compared to the pure CTAB system.

Keywords: Admicellar polymerization; Silica; Surfactant; Rubber compounding

1. Introduction

Fillers are usually added to rubber to improve physical properties such as tensile strength, abrasion, modulus and tear resistance. Carbon blacks are the most common and efficient fillers for the preparation of high quality rubber products such as tires because they offer excellent reinforcement at a relatively low cost. However, carbon black can only be used in products with a black color. A search for alternative fillers, which permit the production of highly durable colored products, has led to silica.

Silica has the potential to be used as an alternative filler because it provides natural color, lower hysteresis loss, and a lower rolling resistance, leading to fuel savings as compared to the case of carbon black for tire applications. However, the silica surface requires a modification of its surface properties because untreated silica cannot form chemical bonds with rubber due to the poor compatibility of hydrophilic silica with hydrophobic rubber [1–4]. Several methods, such as bifunctional organosilanes, grafting, and in situ polymerization are available for the modification [5–15]. Although the compatibility can be enhanced with bifunctional organosilanes, the organosilane agents are expensive [7].

The modification of the silica surface by in situ polymerization, however, beneficially reduces compound curing times and improves the specific rubber compound performance in both the chemical and physical properties [9,10,14,15]. Admicellar polymerization starts with surfactant adsorption on the surface of solid particles to form admicelles, and continues with adsolubilization of monomers into the admicelles, and polymerization of the monomers inside the admicelles, and then completes with the washing of the outer layer of the surfactant to allow for the exposure of the polymer film [5–7]. The admicellar polymerization has been used as a novel technique in a number of surface modification applications: poly(methyl methacrylate) on polyester fabric [16]; poly(styrene-co-divinyl benzene)

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on alumina particles [17]; poly(vinyl pyrrolidone) on sand [18]; poly(styrene–isoprene) on glass fiber [19]; polystyrene on cotton [20]; poly(methyl methacrylate on silica [21]; poly(2,2,2-triflorethyl acrylate) on alumina alloys [22]; polyaniline on zirconia [23]; and poly(styrene–isoprene) on clay [24]. The technique was first successfully performed in batch systems for the surface modification of silia [6,7]. Recently, our group developed a continuous admicellar polymerization for the surface modification of silica for rubber compounding. Possibilities of using a continuous mode operation have been investigated and show great potential for producing a large amount of modified silica with consistent properties [15]. However, the method requires the use of a cationic surfactant, which may prevent further development to a commercial scale because of the high cost and non-biodegradability of the cationic surfactant. A mixture of a cationic surfactant and a nonionic surfactant is an alternative for the silica surface modification by in situ polymerization to reduce the amount of the cationic surfactant.

The objective of the present research focused on the use of a mixture of a cationic surfactant and a nonionic surfactant in the admicellar polymerization on precipitated silica, Hi-Sil®255, by a continuous stirred tank reactor (CSTR). The adsorption isotherms of various molar ratios of the cationic to nonionic surfactant were studied. Then, the admicellar polymerization step, both in monolayer and bi-layer structures of surfactant adsorption on the silica surface, was carried out in the CSTR. The effects of the surfactant adsorption structure and the molar ratio of the surfactants on the properties of the modified silica and on rubber compound using different modified silica samples were assessed.

2. Experimental

2.1. Materials

Hi-Sil®255, precipitated silica with a specific surface area of $170 \pm 15\,\mathrm{m}^2/\mathrm{g}$, was obtained from PPG-Siam Silica Co., Ltd. (Bangkok, Thailand). Cetyl trimethylammonium bromide (CTAB) with 98% purity, styrene with 99% purity, and isoprene with 98% purity were purchased from Fluka (Buchs, Switzerland). Polyoxyethylene otyl phenyl ether (OPEO_{10} or Triton X-100) with 100% purity was supplied by Fluka (Buchs, Switzerland). 2,2′-Azobisisobutyronitrile (AIBN), a water insoluble initiator, with 98% purity, was obtained from Aldrich Chemicals Company (Milwaukee, USA). Sodium hydroxide pellets with 99% purity were obtained from BDH Laboratory Supplies (Philipsburg, USA). Ethyl alcohol, absolute anhydrous, was purchased from ITALMAR Co., Ltd. (Bangkok, Thailand). All chemicals were used as received without further purification.

2.2. Adsorption experiment

The adsorption experiments of surfactants on silica were conducted in a series of 24 ml capped vials. A 2 g silica sample was mixed well with 20 ml surfactant solutions having different concentrations and molar ratios of CTAB to OPEO_{10} at a constant pH 8. The samples were allowed to equilibrate at 30 °C for 24 h and were centrifuged at 2000 rpm for 10 min. Afterwards, the supernatant was taken for CTAB and OPEO_{10} concentration analysis. A total organic carbon analyzer (Shimadzu, TOC-500A) and a UV–vis spectrophotometer (Perkin-Elmer, Lamda 10) were used for the qualitative analysis of CTAB and OPEO_{10}, respectively. The amount of surfactants adsorbed on the silica surface was calculated using the concentration difference method. The data plotted were the amount of surfactants adsorbed against the equilibrium surfactant concentration to obtain the surfactant adsorption isotherm for different molar ratios of CTAB to OPEO_{10}. The charges of surfactant-adsorbed silica at different conditions were measured using a zeta meter (ZETA-METER, 3+) to localize the point of the monolayer coverage of the surfactant, when the negatively-charged silica was neutralized by the positively-charged CTAB.

2.3. Surface modification procedure

The amorphous precipitated silica was modified using styrene and isoprene as co-monomers at a 1:3 molar ratio. The amount of co-monomers fed into the feed tank was 5 g/kg of silica and the polymerization time was 30 min [15]. The surface modification procedure was performed as follows: (1) adding 1 kg of silica into the feed tank, (2) adding different amounts of surfactants with different CTAB to OPEO_{10} molar ratios were added to 12.5 l of deionized water and stirring until the surfactants are completely dissolved, (3) adjusting the pH of the surfactant solution to 8 by adding a sodium hydroxide solution, (4) adding the silica to the surfactant solution in the feed tank, (5) dissolving azobisisobutyronitrile (AIBN) and 1:3 molar monomers into absolute anhydrous ethanol at a ratio of 30 ml per 0.5 g of AIBN and then slowly adding this mixture to the feed tank, and (6) allowing the system to equilibrate with constant stirring for 24 h, to obtain the feed stock solution.

The same CSTR system successfully used previously was employed here in Ref. [15]. The reactor was heated to 70 °C in a water bath with a circulating heater to initiate the polymerization reaction. A constant flow rate of the feed solution to the reactor was achieved by using a peristaltic pump. The optimum residence time of the reaction was controlled at 30 min [15]. The effluent, collected in the product tank, was allowed to settle and the supernatant was decanted. To remove all remaining chemicals, the modified silica was further washed by deionized water for 5 d with daily stirring until the wash water did not foam on agitation. The silica was then dried at 110 °C for 24 h and reground into a powder through a 120-mesh sieve. These samples of modified silica at different operating conditions were used as fillers for rubber compounding experiments.

2.4. Characterization and testing procedure

Nitrogen BET surface areas and mean agglomerate particle sizes of silica before and after the modification, were determined using a surface area analyzer (Quantachrome, Autosorb-1) and a particle analyzer (Malvern Mastersizer, X Version 2.15), respectively. The surface morphology of the modified and unmodified silica samples was examined by a scanning electron microscope (JEOL, JSM-5200). Thermogravimetric Analyzer (TGA, Du Pont Instrument TGA 2950) was used to confirm the polymer formation on the modified silica samples.

The rubber compound formula used in this study was given in our previous work in Ref. [15]. The compound is a primary rubber formulation modified by eliminating poly(ethylene gycol), which is used to complex with the silanol groups on the surface of the silica to prevent them from reacting with the activator. The formulation was designed specifically for physical properties testing [7].

One kilogram of each silica sample was used for the rubber compounding. The rubber, filler and other ingredients (except the vulcanizing agent) were first 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 a time corresponding to T_{90} as determined on the moving die rheometer. The determination of compound and vulcanized properties was obtained with standard test procedures: cure time (ASTM D 2084–93), tensile properties (ASTM D 412–92), tear strength (ASTM D 2262–83), abrasion loss (ISO 4649), flex cracking (ISO 132), compression set (ASTM D 395–89), resilience (ISO 4662), hardness (shore A) (ASTM D 2240). At least three testings were performed for each testing parameters. The average values were then obtained with most standard deviation of all testing parameters was less than 10%.

3. Results and discussion

3.1. Surfactant adsorption

Fig. 1 shows the typical S-shaped curves of the adsorption isotherms on silica at different CTAB:OPEO$_{10}$ molar ratios, pH 8 and 30 °C. For a molar ratio of CTAB:OPEO$_{10}$, the surfactant adsorption increased with increasing equilibrium surfactant concentration and then leveled off at high equilibrium surfactant concentrations. Interestingly, the pure CTAB system was found to have the highest value of the maximum surfactant adsorption (600 μmol/g silica) while the pure OPEO$_{10}$ system established the lowest (350 μmol/g silica). For the case of mixed surfactants, an increase in the fraction of OPEO$_{10}$ decreased the maximum surfactant adsorption. The results can be explained in that the columbic forces between the positively-charged head groups of CTAB and the negatively-charged surface of silica is much stronger and provides higher adsorption than the steric interaction between the head groups of OPEO$_{10}$ and the silica surface. Table 1 shows the maximum surfactant adsorptions on silica at different molar ratios of CTAB to OPEO$_{10}$. These values of the maximum surfactant adsorptions and the corresponding values of the equilibrium surfactant concentrations were used to calculate the total amounts of surfactants required for preparing the feed solutions for the admicellar polymerization step. The maximum surfactant adsorption or complete adsorption of surfactants on the silica surface, which is named here as the bi-layer coverage, was prepared at the equilibrium surfactant concentration equal to the CMC.

Table 1
Surfactant adsorption onto silica at different molar ratios of CTAB to OPEO$_{10}$, pH 8 and 30 °C

Molar ratio of CTAB:OPEO$_{10}$	Maximum asorption[a] (μmol/g silica)	Adsorption at monolayer (μmol/g silica)
0:1	350	–
1:3	390	230
1:1	530	200
3:1	580	160
1:0	600	200

[a] To be used as the bi-layer coverage structure of surfactant adsorption.

Fig. 2 shows the plots between the total amount of surfactants adsorbed and the molar ratios of the adsorbed surfactants on the silica surface at different molar ratios of CTAB:OPEO$_{10}$ in the feed solution. Interestingly, the results reveal that for any given

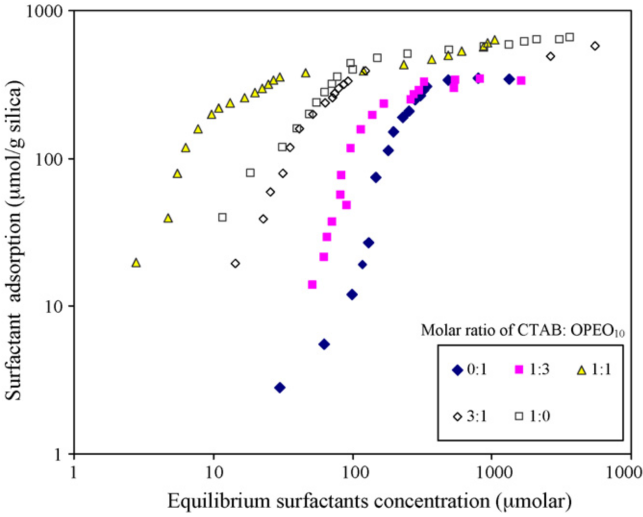

Fig. 1. Adsorption isotherms of surfactants onto silica at pH 8 and 30 °C with various CTAB:OPEO$_{10}$ molar ratios.

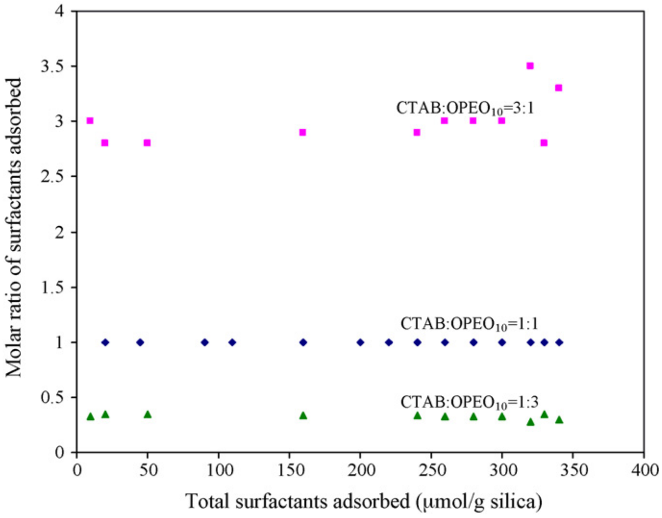

Fig. 2. Molar ratio of surfactants adsorbed onto silica at different feed CTAB:OPEO$_{10}$ molar ratios.

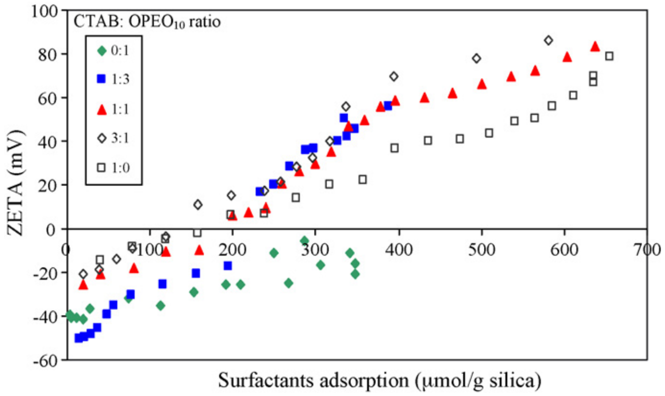

Fig. 3. Charge on silica surface as a function of surfactant adsorption in different surfactant concentrations with various CTAB:OPEO$_{10}$ molar ratios.

feed molar ratio of CTAB to OPEO$_{10}$, the CTAB to OPEO$_{10}$ molar ratio of the adsorbed surfactants (admicelles) was the same as that in the feed solution.

As mentioned earlier in the objective of the present work, the use of mixed surfactants was to minimize the amount of CTAB required for the admicelle formation prior to the admicellar polymerization step. In addition, the condition at the monolayer coverage structure of surfactant adsorption in the admicelle formation was considered in order to reduce the quantity of surfactants. In this study, the monolayer coverage structure of surfactant adsorption is defined at the point where the charge on the silica surface becomes neutral. Fig. 3 shows the zeta potential on the silica surface as a function of the surfactant adsorption at different molar ratios of CTAB to OPEO$_{10}$. Due to the negatively-charged silica surface, the adsorption of the positive head groups of CTAB on the silica surface results in the depression of the negative charges of silica. Therefore, the neutral surface is obtained when CTAB completely covers the surface of silica, which is named here as the monolayer coverage structure. The adsorption concentration of surfactant at 200 µmol/g of silica was obtained with pure CTAB. An increase in the molar ratio of CTAB to OPEO$_{10}$ resulted in the increase in the surfactant concentration to form the monolayer coverage structure on the silica. For 1:3, 1:1, 3:1 and 1:0 molar ratios of CTAB to OPEO$_{10}$, the monolayer structure of surfactant absorbed on the surface of silica was found to be at 240, 200, 160 and 200 µmol/g of silica, respectively. However, in the case of the OPEO$_{10}$ alone, the monolayer structure was not able to be determined by the zeta potential measurement because the negative surface of silica was observed in the studied range of the adsorption concentration. This is because the nonionic structure of OPEO$_{10}$ cannot neutralize the negatively-charged silica surface as confirmed experimentally in Fig. 3. Table 1 summarizes the amounts of surfactants adsorbed with the monolayer and bilayer coverage structures of surfactant adsorption to be used for the admicle formation in the admicellar polymerization step.

3.2. Characterization of modified silica

For a given controlled condition used in the admicellar polymerization step, the silica BET surface area is reduced substantially after the surface modification, as shown in Fig. 4. For any given molar ratio of CTAB to OPEO$_{10}$, the modified silica surface with the bi-layer coverage structure had a slightly lower surface area than that with the monolayer coverage structure. The CTAB to OPEO$_{10}$ ratio did not show any significant effect on the surface area after the surface modification.

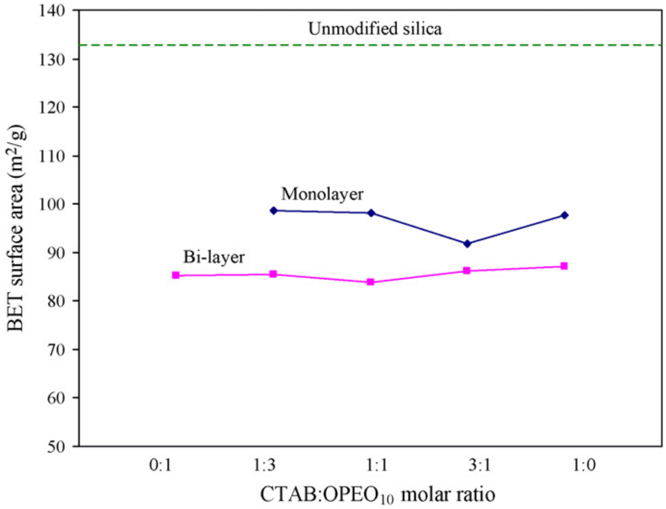

Fig. 4. BET surface area of modified silica at different CTAB:OPEO$_{10}$ molar ratios with monolayer and bi-layer surfactant adsorption compared to the unmodified silica.

Fig. 4 shows the effect of the feed molar ratio of CTAB to OPEO$_{10}$ on the mean agglomerate particle size of the modified silica with the two structures of monolayer and bi-layer surfactant adsorption. An increase in the mean agglomerate particle size of all modified silica samples is due to the formation of the polymer film coating on the silica particles and the development of polymer bridges between silica particles. For a given molar ratio of CTAB to OPEO$_{10}$, the mean agglomerate particle size of the modified silica with the bi-layer coverage structure was larger than that with the monolayer coverage structure, as shown in Fig. 5. It is also worth mentioning that using only CTAB in the

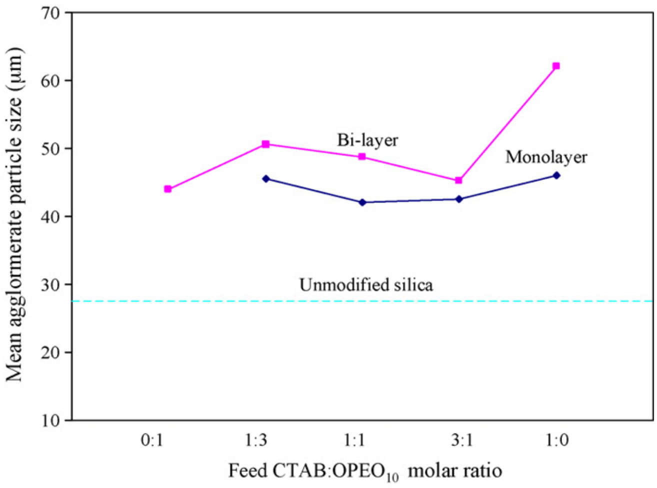

Fig. 5. Mean agglomerate particle size of modified silicas prepared at different CTAB:OPEO$_{10}$ molar ratios with monolayer and bi-layer surfactant adsorption structures.

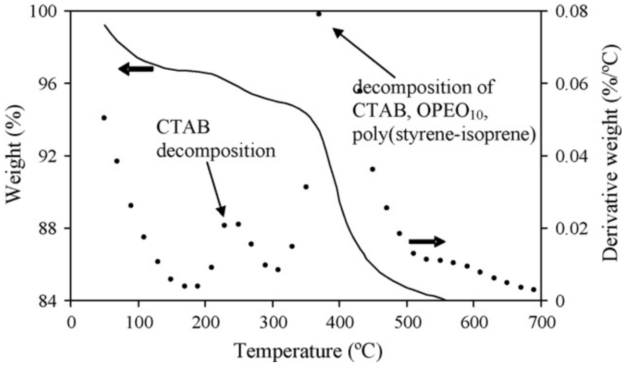

Fig. 6. TGA results of the modified silica surface at 1:3 CTAB:OPEO$_{10}$ molar ratio and the bi-layer adsorption.

surface modification resulted in the highest mean agglomerate particle size in both monolayer and bi-layer structures. This is because the admicelles of the pure CTAB system provide the highest solubilization capacity for the monomers than the other systems.

In addition, the existence of the polymer layer coating on the silica particles is also verified by using the TGA technique, as shown in Fig. 6. The figure clearly shows the decomposition of CTAB taking place between 200 and 280 °C, and 300 and 450 °C while the polymer started from 280 to 400 °C [25].

The scanning electron micrographs (SEM) of the unmodified and modified silica samples using 1:1 CTAB:OPEO$_{10}$ molar ratio with monolayer and bi-layer coverage structures are shown in Fig. 7. The modified silica micrographs show an increase in particle size compared to that of the unmodified one. The smooth surface was obtained after the surface modification. This might possibly be due to the agglomeration of particles during the surface modification process. This also confirms the polymer formation onto the surface of all modified silica samples.

3.3. Rubber compound physical properties

The effects of the molar ratio of CTAB to OPEO$_{10}$ as well as the surfactant adsorption structure on rubber compound physical properties were studied. The rubber compound physical properties, using different modified silica samples compared with the unmodified silica, are summarized in Table 2. As shown in the table, the adsorption structure of the mixed surfactants has no significant effect on the cure time. The monolayer and bi-layer coverage structures of various molar ratios of CTAB to OPEO$_{10}$ from 1:3 to 3:1 resulted in the significant reduction of the cure time in the range of 4.82–7.12 min as compared with 18.63 min for the unmodified silica. In addition, the results showed that for various ratios of CTAB to OPEO$_{10}$, the modified silica samples provided significant improvement in the resilience of the rubber compound. The type of surfactant adsorption structures on the silica surface also affected the physical properties of the rubber compound. For example, the bi-layer coverage structure yielded both better compression set and abrasion than those derived from the monolayer coverage structure. On the other hand, the hardness of the rubber compound using the modified silica with the monolayer coverage structure for any molar ratio of CTAB to OPEO$_{10}$ was better than that with the bi-layer structure.

To determine the overall properties of the rubber compounds using different modified silica samples, the results were compared qualitatively and summarized by ranking the result from low to high quality of each physical property using a number “1” (low) to “9” (high) in order to determine the optimum condition of the silica modification system. The qualitative summary of rubber physical properties using different modified silica samples is shown in Table 3. The best overall mechanical properties of the rubber compound was obtained from the use of the modified silica produced from a 1:3 molar ratio of CTAB:OPEO$_{10}$ with the monolayer coverage structure of surfactant adsorption. Interestingly, the improvement of the overall mechanical

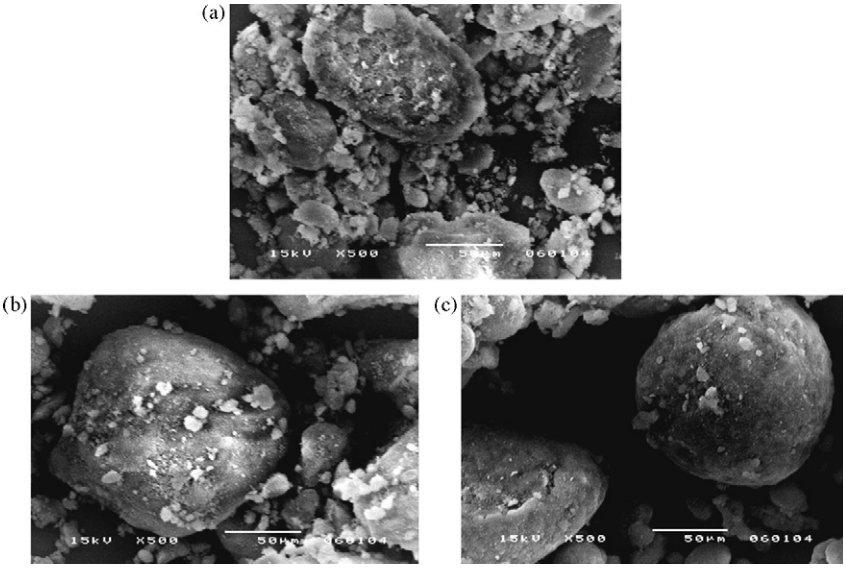

Fig. 7. Scanning electron micrograph of the unmodified silica (a) and modified silica using 1:1 CTAB:OPEO$_{10}$ molar ratio with monolayer structure (b) and bi-layer structure (c).

Table 2
Rubber compound physical properties using different modified silicas compared to the unmodified silica

Property	Unmodified silica	B01	M13	B13	M11	B11	M31	B31	M10	B10
Cure time (min)	18.63	6.81	5.28	5.55	5.49	4.87	5.58	5.00	4.82	7.19
100% modulus @ before aging (MPa)	0.77	1.15	1.57	1.52	1.15	1.29	1.54	1.67	1.22	1.66
200% modulus @ before aging (MPa)	1.57	1.92	2.72	2.55	2.02	2.24	2.62	2.77	2.10	2.75
300% modulus @ before aging (MPa)	2.84	2.93	4.27	3.96	3.22	3.45	4.13	4.28	3.40	4.16
Tensile strength @ before aging (MPa)	19.84	29.12	29.88	30.59	29.91	29.27	29.35	30.63	30.69	29.49
Tear strength @ before aging (N/mm)	30.27	69.85	69.82	68.8	64.74	49.81	75.38	50.62	65.60	52.80
Abrasion (ml/kcycle)	0.96	0.40	0.44	0.41	0.44	0.43	0.42	0.35	0.46	0.44
Resilience (%)	56.7	65.00	65.37	66.5	67.03	65.53	63.43	64.53	69.20	75.30
Compression set (%)	83.11	49.63	54.48	42.67	58.80	46.30	53.98	46.17	57.59	58.13

01,13,11,31,10: different CTAB:$OPEO_{10}$ molar ratio; M, B: type of adsorption structure, monolayer, bi-layer, respectively.

Table 3
Qualitative summary of rubber physical properties using different modified silicas

Property	B01	M13	B13	M11	B11	M31	B31	M10	B10
100% modulus @ before aging (MPa)	2	7	5	1	4	6	9	3	8
100% modulus @ after aging (MPa)	9	8	5.5	3	4	7	5.5	2	1
200% modulus @ before aging (MPa)	1	7	5	2	4	6	9	3	8
200% modulus @ after aging (MPa)	7	9	5	2	6	8	3	4	1
300% modulus @ before aging (MPa)	1	8	5	2	4	6	9	3	7
300% modulus @ after aging (MPa)	7	9	3	5	6	8	2	4	1
Tensile strength @ before aging (MPa)	1	5	7	6	2	3	8	9	4
Tensile strength @ after aging (MPa)	8	9	3	5	6	4	1.5	1.5	7
Tear strength @ before aging (N/mm)	8	7	6	4	1	9	2	5	3
Tear strength @ after aging (N/mm)	2	9	3	6	5	7	1	8	4
Abrasion (ml/kcycle)	8	3	7	3	5	6	9	1	3
Resilience (%)	7	6	5	3	4	9	8	2	1
Compression set (%)	6	4	9	1	7	5	8	3	2
Hardness @ before aging (shore A)	2	9	4	3	1	8	5	7	6.5
Hardness @ after aging (shore A)	5	8	3	7	1	9	4	6	2
Total	74	108	75.5	53	60	97	84	61.5	58.5

01,13,11,31,10: different CTAB:$OPEO_{10}$ molar ratio; M, B: type of adsorption structure, monolayer, bi-layer, respectively.

properties of the rubber compound using the modified silica obtained from the admicellar polymerization with the monolayer coverage structure of surfactant adsorption was found to be better than that with the bi-layer coverage structure. This might be due to the smaller size of the former giving a better dispersion in the rubber. Thus, a conclusion can be drawn that the mechanical properties of the rubber compound is enhanced by the increase in the affinity between rubber and silica. The use of the mixed surfactants at a 1:3 molar ratio of CTAB to $OPEO_{10}$ can reduce the amount of total surfactants to only 38% and the amount of CTAB to about 13% of that for the pure CTAB system.

4. Conclusions

Mixed surfactants of CTAB to $OPEO_{10}$ for admicellar polymerization using a continuous stirred tank reactor was successfully used to modify the silica surface for the reinforced fillers capable of improving the mechanical properties in rubber compounding**.** Both the molar ratio of the surfactants and the surfactant adsorption structure play significant roles to the physical properties of modified silica and rubber compound. The formation of the polystyrene–isoprene results in the decrease in the specific surface area and increase in the mean agglomerate particle size of the silica particles. The best mechanical properties of the rubber compound were achieved at a 1:3 molar ratio of CTAB to $OPEO_{10}$ with the monolayer coverage structure of surfactant adsorption. The use of the mixed surfactants provides better physical properties of the rubber compound as well as to reduce the significant amount of surfactants required as compared to the pure CTAB system.

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