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Radiation-induced admicellar polymerization of isoprene on silica: Effects of surfactant's chain length

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ABSTRACT

This research compared radiation-induced admicellar polymerization with the traditional thermal process and studied the influence of the hydrocarbon chain length of different surfactants on film formation. Three types of surfactants were used in this study: dodecyl trimethyl ammonium bromide (DTAB), tetradecyl trimethyl ammonium bromide (TTAB) and cetyl trimethyl ammonium bromide (CTAB). Isoprene was used as a monomer for the formation of thin film inside the surfactant bilayers, called admicelle, adsorbed on silica surface. The results showed that an optimum dose can lead to a better film formation on silica, compared with the thermal method. However, when the dose was over the optimum value, the formation of polyisoprene film was diminished. The formation of polyisoprene film was found to depend not only on the hydrocarbon chain length of the surfactant, but also on the density of adsorbed surfactant on silica surface.

1. Introduction

Admicellar polymerization is a well-known technique used to improve the surface of materials by coating the surface with nanoscale polymer thin film. The thin film is formed by a polymerization of monomers inside the admicelles. This technique was first introduced by Wu et al. [1]. Admicellar polymerization consists of a four-step process: admicelle formation on the surface, monomer adsolubilization, polymerization of the monomer dissolved in admicelles, and surfactant removal to expose the surface of polymer film. Fig. 1 illustrates the process to modify the silica surface by radiation-induced admicellar polymerization.

The adsorption of the surfactant on the silica surface is a critical step. Different surfactants have dissimilar adsorptivity. Using surfactants with similar chemical structure but varying hydrocarbon chain length not only affects the adsorption on silica, but also influences the monomer adsolubilization in the admicelles. Previously, a research group investigated the influence of the surfactant tail length of these three surfactants on the adsolubilization of naphthalene and α-naphthol in the surfactant bilayers adsorbed on the silica surface [2]. They found that critical micelle concentration (CMC) increased with decreasing tail length. However, the plateau adsorption and area per molecule did not increase with decreasing tail length. Another research group reported the study of the influence of chain length and electrolyte on the adsorption equilibrium and kinetics of alkyl trimethyl ammonium surfactants at the silica–aqueous solution interface [3]. There was also another interesting report on the adsorption of alkyl trimethyl ammonium bromides on negatively charged alumina at pH 10 described by a four-region model of adsorption isotherm study [4].

The surface modification of silica has received a great deal of attention as a reinforcing filler for polymers and rubbers. The natural surface of silica is composed of siloxane $[SiOR_2]_n$ and silanol $[R_3SiOH]$ groups, both of which are acidic and polar, resulting in a very poor compatibility with polymer matrixes or rubbers. The modification of silica surface by admicellar polymerization is one of the methods that have been employed by several researchers. This method has been applied to different polymers varying from homopolymer, such as polystyrene, to copolymer, for examples styrene–butadiene copolymer and styrene–isoprene copolymer [5–9]. Nevertheless, the majority of these previous works on admicellar polymerization often utilized thermal process and chemical initiators to induce the formation of polymer film. Each initiator offered distinct film formation efficiency and had dissimilar effect on the ratio between the monomer to the initiator, which was difficult to control. Unreacted initiators could become an environmentally destructive contamination.

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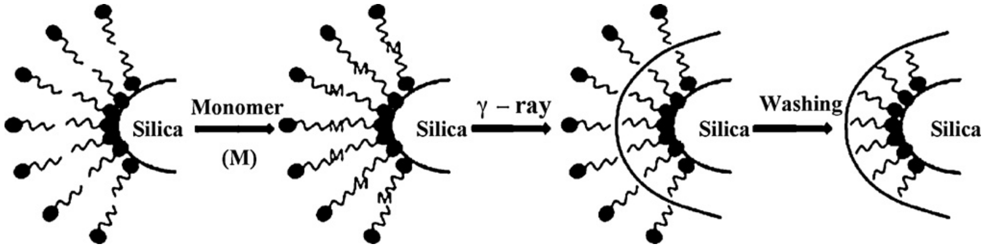


Fig. 1. A schematic of radiation-induced admicellar polymerization for the modification of silica surface.

Unlike the traditional thermal reaction, radiation can initiate reaction without any catalysts or initiators. As a result, the use of radiation-induced polymerization as an alternative for thermal polymerization will leave no contamination, making it safe for end users allergic to chemicals. This non-toxic aspect can greatly broaden the applications of natural rubber products. The initiation process of the radiation-induced polymerization can take place at ambient temperature, thus saving energy as well as reducing production cost. In addition, radiation processing requires no heat control, since the formation of polymeric free radicals does not depend on temperature, but rather on radiation absorption of the polymer matrix. When compared with other chemical process, radiation process provides better control over the reaction, by simply adjusting the total dose. Radiation processes can be applied to samples in all states: solid, liquid and gas. The utilization of radiation in admicellar polymerization offers smooth dispersion of polymer on the silica surface, since gamma radiation has extremely high penetration depth. From previous works, radiation polymerization has been applied to different types of polymers such as poly(diethyl fumarate) [10], polyisoprene [11], poly(vinyl chloride) [12], poly(beta-pinene) [13], poly(methyl methacrylate) and poly(butyl methacrylate) [14].

Radiation-induced admicellar polymerization was applied to this work for the purpose of silica surface modification. The modification was done by the polymerization of isoprene monomer on the silica surface to enhance compatibility between the polar inorganic silica surface and the nonpolar hydrocarbon elastomer as well as to improve mechanical properties of natural rubber products that use silica as a filler.

Results from our previous work [15] demonstrated that radiation-induced admicellar polymerization improved the film formation and mechanical properties of the natural rubbers more effectively than the thermal technique. This research expands the previous synthetic method to include the influence of the hydrocarbon chain length of different surfactants: DTAB, TTAB, and CTAB on film formation. In this work, thermal process was also applied, along with the radiation process, in order to study and compare the influence of both processes on the film formation.

2. Experimental

2.1. Materials and instruments

Silica Hi-Sil®233 (Siam Silica Co., Ltd., Thailand), dodecyltrimethylammonium bromide ($[CH_3(CH_2)_{11}N(CH_3)_3]Br$, or DTAB) (98.0%, Fluka, Switzerland), tetradecyltrimethylammonium bromide ($[CH_3(CH_2)_{13}N(CH_3)_3]Br$ or TTAB) (99%, Acros, Belgium), Cetyltrimethylammonium bromide ($[CH_3(CH_2)_{15}N(CH_3)_3]Br$ or CTAB) (98%, Fluka, Switzerland), isoprene (98%, Fluka, Switzerland), potassium persulfate ($K_2S_2O_8$, Fluka, Switzerland), and tetrahydrofuran (Fisher Scientific, USA) were used as received. Gamma irradiator used was a Gammacell 220 Excel from MDS, Nordion, Canada.

2.2. Thermal admicellar polymerization

The surfactant was dissolved in 100 ml of distilled water. The amounts of surfactants used were 2.5, 1.5 and 1 mmole for DTAB, TTAB and CTAB, respectively, according to the adsorption study of previous work [2]. The solution was adjusted to pH 8 by sodium hydroxide [5]. Then 2.5 g of silica was added into the mixture. The mixture was continuously stirred for 24 h. Ethanol, potassium persulfate and isoprene were afterward added. The molar ratio of the surfactant to ethanol was 1:43, while that of the monomer to potassium persulfate was 10:1. The molar ratio of the surfactant to the monomer was varied (1:2, 1:4, 1:6, 1:8, 1:10, 1:12 and 1:14) to determine the optimum condition. The mixture was then gradually stirred and heated to 80 °C, where the temperature was held for 3 h to induce the polymerization. The silica samples were subsequently filtered and washed many times with distilled water until the redundant surfactant and the upper layers of admicelle formed on silica surface were completely removed. After the washing steps have been thoroughly done, the washing water was analyzed by UV to see whether there is some remaining outer-layered surfactant. We further confirmed the removal of the outer-layered surfactant by floating test. Once the outer-layered surfactant has been removed, the surface will be hydrophobic and therefore the samples will be floating on the water surface. On contrary, if there is some remaining outer-layered surfactant, the surface will still be hydrophilic and the samples will be sinking down at the bottom. The silica samples were later dried in an oven at 40 °C for 3 days, before the characterization.

2.3. Radiation-induced admicellar polymerization

The experiment was mostly done the same way as in the thermal process, except that there was no addition of potassium persulfate and gamma radiation was used instead of heat. The amounts of surfactants used were 2.5, 1.5 and 2.5 mmole for DTAB, TTAB and CTAB, correspondingly. The molar ratio of the surfactant to ethanol was 1:43, whereas that of the surfactant to the monomer was 1:6. To determine the optimum dose, the mixture was irradiated at the total doses of 5, 6, 7, 8, 9, 10, 11, 12 and 13 kGy, at the dose rate of 0.17 kGy/min. The washing and drying processes were done precisely the same way.

2.4. Film formation analysis

The polymeric film content coated on silica was thermal gravimetrically determined by burning the modified silica in a furnace at 600 °C for 1 h. The film formation was calculated using the following equation:

$$\%\text{Film formation} = \frac{\text{Weight of modified silica} - \text{weight of initial silica}}{\text{Weight of initial silica}} \times 100$$

According to the equation, the film formation is gravimetrically calculated from the added-on weight after the polyisoprene film was coated on the silica. The weight of the initial silica is the weight of the unmodified silica.

2.5. Characterization

A thermal gravimetric analyzer (TGA) from Netzsch, Model STA 409C, was used for thermogravimetric analysis. A heating rate of 10 °C/min from ambient temperature to 600 °C was used for all experiments. The infrared spectra were taken on a Fourier transform infrared spectrometer (FTIR) Spectrum 2000 by Perkin Elmer. The silica samples were pressed into KBr pellets. The spectrum of polyisoprene was taken by dissolving the polymer in chloroform and casting the solution between two KBr plates. Scanning electron microscope (SEM) by JEOL (Model JSM-5410LV) was used to study surface morphology and elemental analysis. The silica sample was put on carbon tape attached to a brass plate. The distribution and size of the silica particles were analyzed by a transmission electron microscope (TEM) from JEOL, Model AJEM-200CX. The samples were added into ethanol, dropped on a copper plate and left undisturbed for 24 h.

3. Results and discussion

3.1. The optimum ratio of the surfactant to isoprene for thermal admicellar polymerization

The silica samples modified by thermal admicellar polymerization were burned to quantify the polymeric film content coated on the silica surface. The results are displayed in Fig. 2. Initially, the film content increased with the monomer. At high monomer content, the film formation started to stabilize, with the molar ratio of the surfactant to the monomer being 1:6, 1:4 and 1:8 for DTAB, TTAB and CTAB, in that order. The molar ratio of monomer to initiator is 10:1. The reaction temperature was 80 °C, while the reaction time was 3 h. These conditions indicated that the film formation was saturated. Therefore, they will be used as an optimum condition for each corresponding surfactant.

From the TGA thermograms and their derivative profiles, in Figs. 3 and 4, it can be seen that the thermal degradation range of polyisoprene using natural rubber is between 350 and 500 °C, with the maximum rate of weight loss centered at 400 °C. Throughout the entire experiment the untreated silica lost less than 10% of its original weight which was mostly due to moisture. In contrast, the modified silica had similar degradation pattern to that of the polyisoprene. The TGA thermograms and the dTGA profiles of the silica samples modified by three surfactants with different chain lengths showed that the sample modified by CTAB had the highest degradation rate, followed by those modified with DTAB and TTAB. This result agrees quite well with the result of the film content. The TGA thermograms of these three samples indicated that the weight loss due to the degradation of the polyisoprene film was approximately 6, 4 and 5% for CTAB, TTAB and DTAB, respectively.

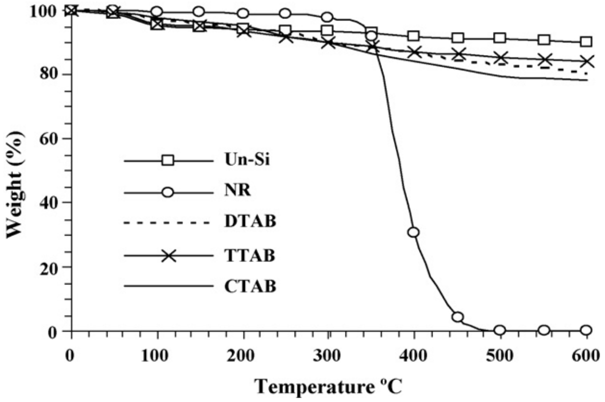


Fig. 3. TGA thermograms of unmodified silica (Un-Si), natural rubber (NR) and silica samples modified by DTAB, TTAB and CTAB via thermal admicellar polymerization.

3.2. The effects of gamma radiation on the polymeric film formation

The optimum ratio of the surfactant to the monomer obtained from the thermal admicellar polymerization was applied to the radiation admicellar polymerization in order to find the optimum dose. The derived optimum dose was then used to identify the optimum ratio of the surfactant to the monomer for the radiation-induced admicellar polymerization. The controlled ratios used were 1:6, 1:4 and 1:8 for DTAB, TTAB and CTAB, respectively. The effects of total dose on the film formation were investigated and the results are shown in Fig. 5.

Fig. 5 illustrates that for the silica modified by radiation-induced admicellar polymerization, the film formation increased with total dose, up until 8 kGy, after which it started to level off. At high dose, the formation of free radicals of monomer, hydrogen and hydroxyl groups are redundant. These radicals can form the chain-transfer reaction to reduce the film formation [15].

Figs. 6 and 7 present the TGA thermograms and the dTGA profiles of unmodified silica, polyisoprene (using natural rubber) and the silica samples modified by radiation-induced admicellar polymerization with the three surfactants at the total dose of 8 kGy. The

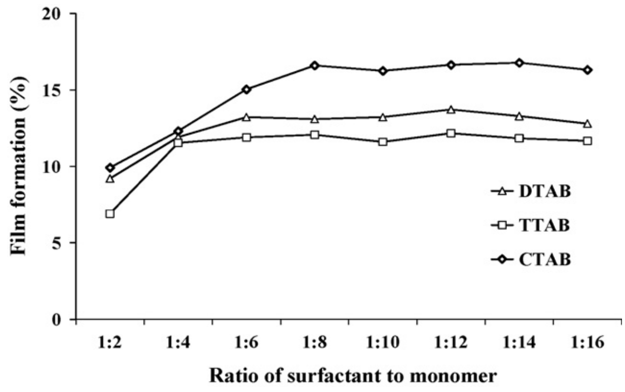


Fig. 2. Effects of the ratios of the surfactant to isoprene on the film formation induced by thermal admicellar polymerization.

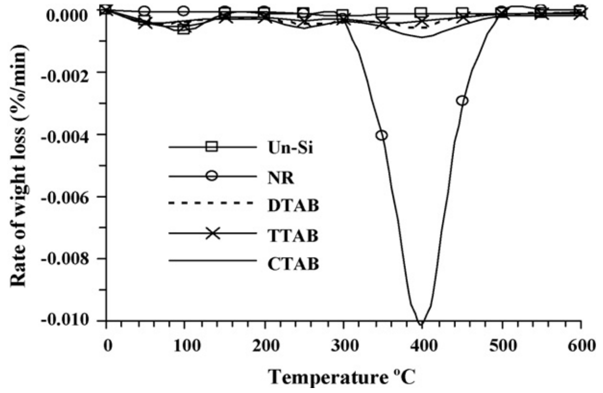


Fig. 4. dTGA profiles of unmodified silica (Un-Si), natural rubber (NR) and silica samples modified by DTAB, TTAB and CTAB via thermal admicellar polymerization.

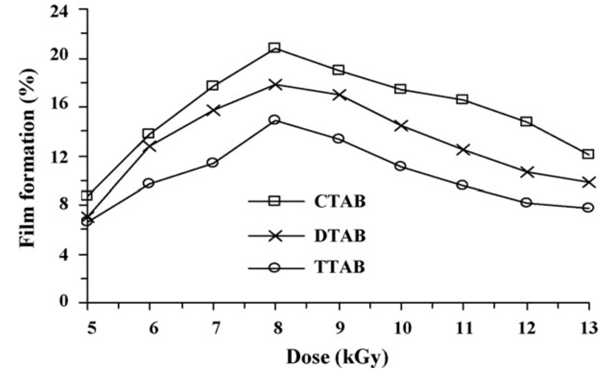


Fig. 5. The effects of total dose on the film formation of radiation-induced admicellar polymerization.

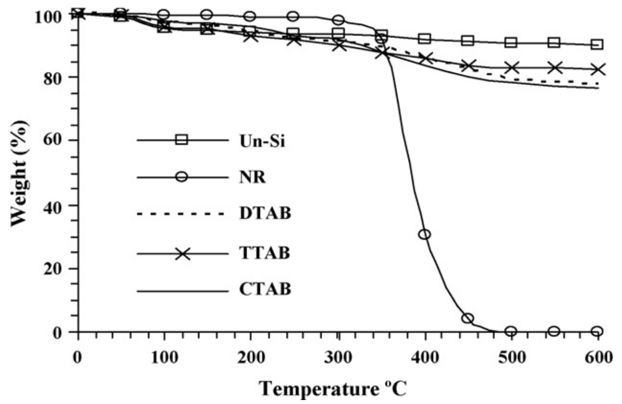


Fig. 6. TGA thermograms of unmodified silica (Un-Si), natural rubber (NR) and the silica samples modified by DTAB, TTAB and CTAB via radiation-induced admicellar polymerization.

major degradation step of the modified silica samples falls in the same range as that of polyisoprene, with CTAB having the highest rate of degradation among the three surfactants. The weight loss between 350 and 500 °C, due to the polyisoprene degradation, of the samples with CTAB, TTAB and DTAB as the surfactant was about 8, 6 and 7%, respectively. Afterward, the optimum total dose, 8 kGy, was applied to determine the optimum molar ratio of the surfactant to the monomer for the admicellar polymerization induced by radiation (Fig. 8).

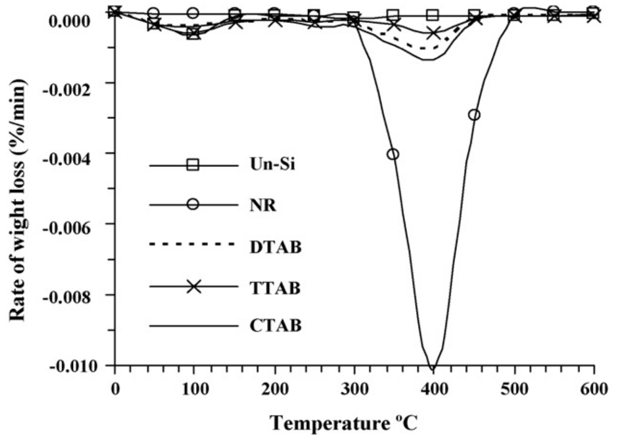


Fig. 7. dTGA profiles of unmodified silica (Un-Si), natural rubber (NR) and the silica samples modified by DTAB, TTAB and CTAB via radiation-induced admicellar polymerization.

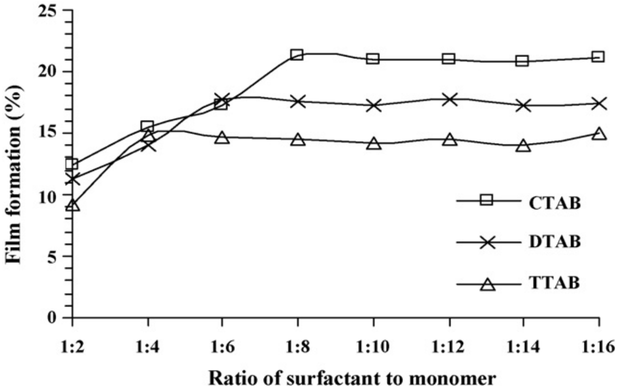


Fig. 8. The effects of the molar ratio of the surfactant to isoprene on the film formation polymerized at the total dose of 8 kGy.

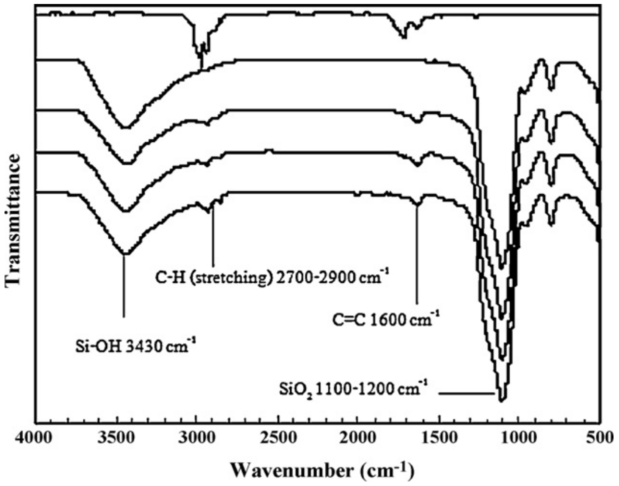


Fig. 9. FTIR spectra of, from top to bottom, polyisoprene, unmodified silica, and silica samples modified by thermal admicellar polymerization using DTAB, TTAB and CTAB, respectively.

The film formation escalated with the molar ratio of the surfactant to the monomer before reaching its saturation point at 1:8, 1:6 and 1:4 for CTAB, DTAB and TTAB, respectively. These ratios are subsequently used as an optimum condition for each corresponding surfactant.

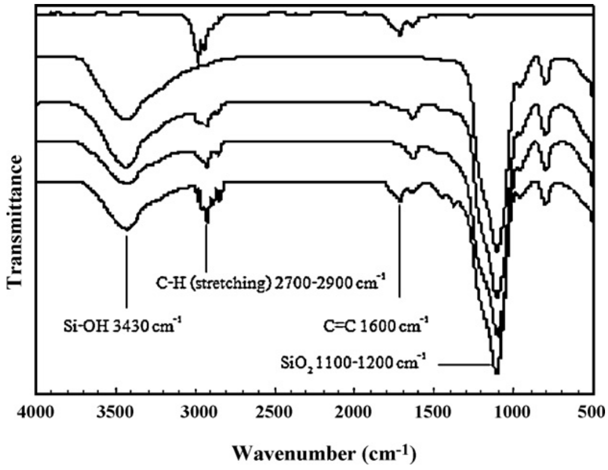
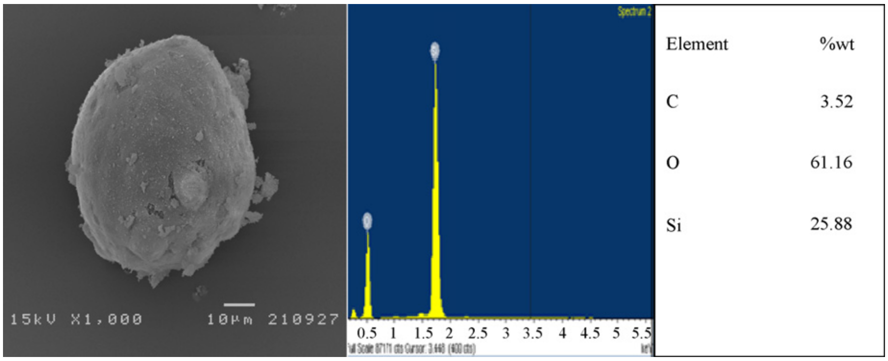


Fig. 10. FTIR spectra of, from top to bottom, polyisoprene, unmodified silica, and silica samples modified by radiation-induced admicellar polymerization using DTAB, TTAB and CTAB, respectively.



Element	%wt
C	3.52
O	61.16
Si	25.88

Fig. 11. SEM images and elemental analysis of the unmodified silica.

3.3. *FTIR characterization of polyisoprene*

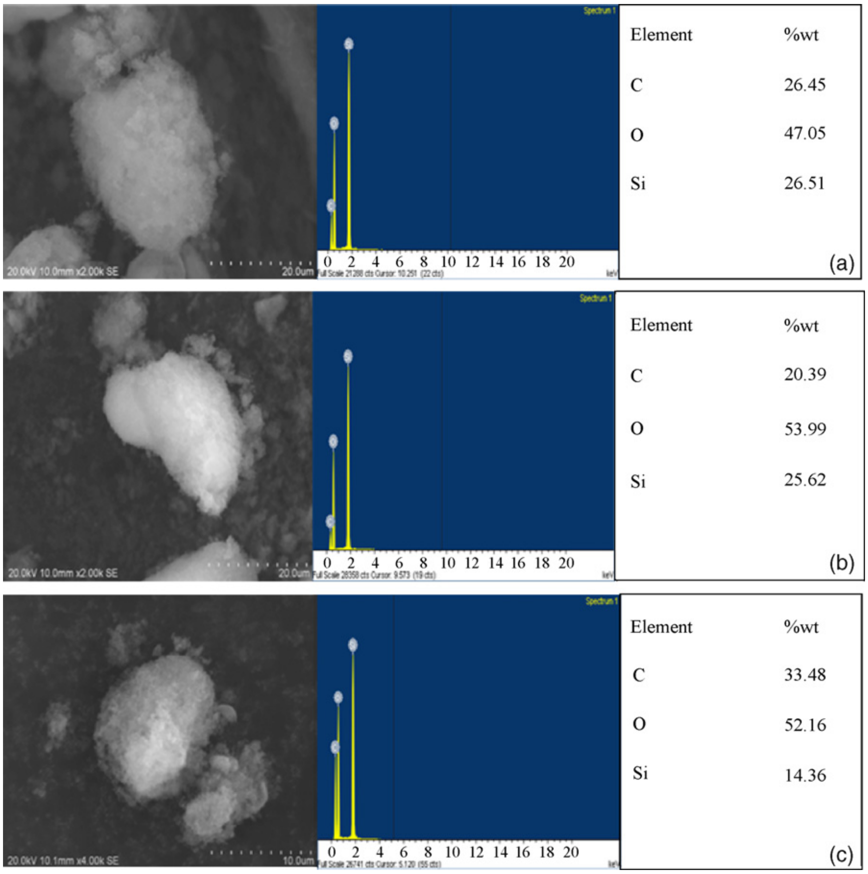
FTIR was employed to verify the existence of the polyisoprene film coated on the modified silica surface. The FTIR spectra of the silica samples modified via the thermal admicellar polymerization are demonstrated in Fig. 9, whereas those of the radiation-induced admicellar polymerization are shown in Fig. 10. For comparison's sake, the FTIR spectra of pure polyisoprene and unmodified silica are presented in both figures as well.

The FTIR spectrum of polyisoprene shows two characteristic peaks at approximately 1610 and 2953 cm^{-1} which represent the C=C stretching vibration and C–H stretching modes of –CH$_3$ group in aliphatic compounds, respectively. As for the unmodified silica, a broad band between 3000 and 3600 cm^{-1} is assigned to the O–H stretching vibration of the silanol groups, while a strong band centered at about 1090 cm^{-1} corresponds to the Si–O–Si antisymmetric stretching vibration of the siloxane groups. From both Figs. 9 and 10, it is obvious that in addition to the two distinctive peaks of the silanol and siloxane groups, the FTIR spectra of all the silica samples modified by both thermal and radiation methods also show two characteristic bands of polyisoprene. These results clearly confirm the presence of the polyisoprene film on the modified silica surface and also prove the capability of radiation process as an effective technique to induce admicellar polymerization.

3.4. *Surface morphology*

3.4.1. *Surface morphology and elemental analysis by SEM*

SEM was used to compare the surface morphology and the elemental analysis of the unmodified silica and the silica samples modified via both thermal and radiation processes. Fig. 11 shows relatively smooth surface of the unmodified silica. However,



(a)

Element	%wt
C	26.45
O	47.05
Si	26.51

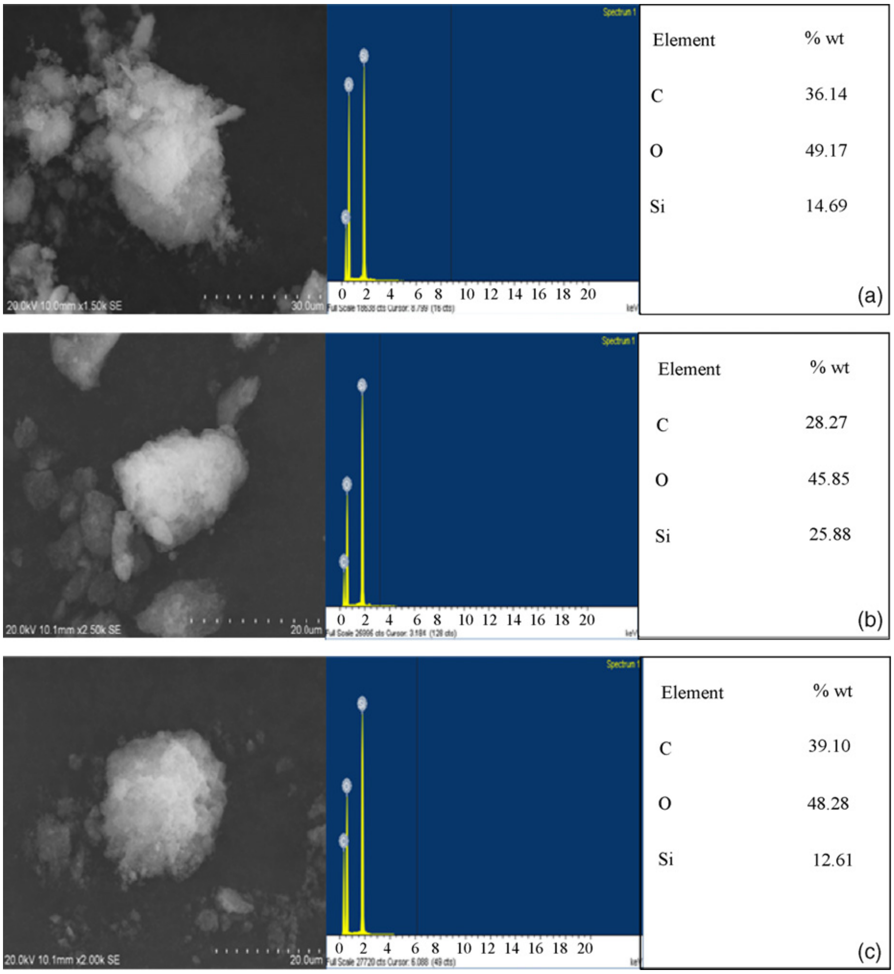
(b)

Element	%wt
C	20.39
O	53.99
Si	25.62

(c)

Element	%wt
C	33.48
O	52.16
Si	14.36

Fig. 12. SEM images and elemental analysis of the silica samples modified with thermal admicellar polymerization using (a) DTAB, (b) TTAB, and (c) CTAB.



Element	% wt
C	36.14
O	49.17
Si	14.69

(a)

Element	% wt
C	28.27
O	45.85
Si	25.88

(b)

Element	% wt
C	39.10
O	48.28
Si	12.61

(c)

Fig. 13. SEM images and elemental analysis of the silica samples modified with radiation-induced admicellar polymerization using (a) DTAB, (b) TTAB, and (c) CTAB.

these particles tend to congregate into clusters. On the contrary, Figs. 12 and 13 expose a comparatively rough surface and dispersed particles of the silica modified by both thermal and radiation methods. A better dispersion of the modified silica is a result of the polyisoprene film formation of the silica surface.

The elemental analysis reveals that the carbon content of the unmodified silica is approximately 4%, while that of the silica samples modified via both methods is much higher, varying from 20 to 40%. The increase of the carbon content stems from the fact that carbon is one of the major components of polyisoprene film coated on the silica surface. At the same surfactant, the carbon content of the silica surface modified by radiation technique is higher than that of the one modified by thermal approach. However, within the same polymerization method, the silica samples modified with CTAB has higher carbon content than those modified with DTAB and TTAB. Since TTAB molecules appear to pack in a more efficient manner than both the CTAB and DTAB molecules [2].

3.4.2. *TEM morphology*

Figs. 14–16 display the distribution and size of the unmodified silica, silica modified by thermal treatment and the silica modified by radiation method, in that order. Apparently, the unmodified silica particles accumulate into big groups. When blended with the natural rubber, these aggregated particles therefore result in a poor dispersion, whereas all of the modified silica samples have a much better dispersion than the unmodified sample. The reason that the modified samples showed less agglomerates than the unmodified ones is due to the functionality on the surface of the samples. The surface of the unmodified silica is full of silanol and siloxane groups. These two hydrophilic groups tend to have strong interactions, thus resulting in agglomerates. On contrary, the surface of the modified samples is covered with the polyisoprene film. These hydrocarbon chains have no interactions with each other, and therefore causing no agglomerates.

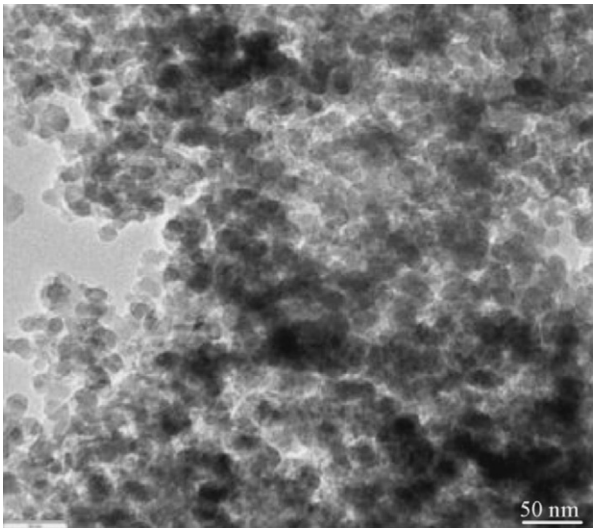


Fig. 14. TEM image of the distribution and size of the unmodified silica.

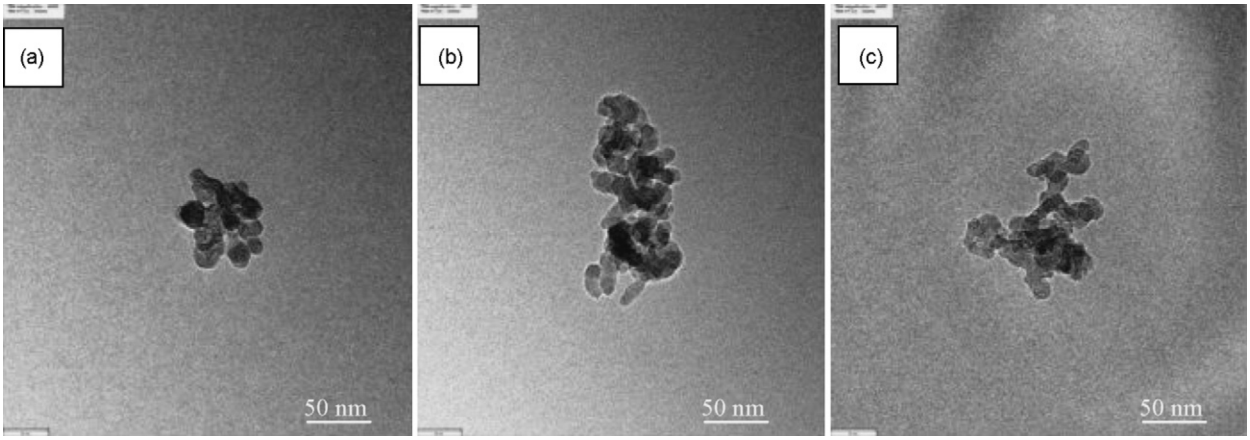


Fig. 15. TEM images of the distribution and size of the silica samples modified with thermal admicellar polymerization using (a) DTAB, (b) TTAB, and (c) CTAB.

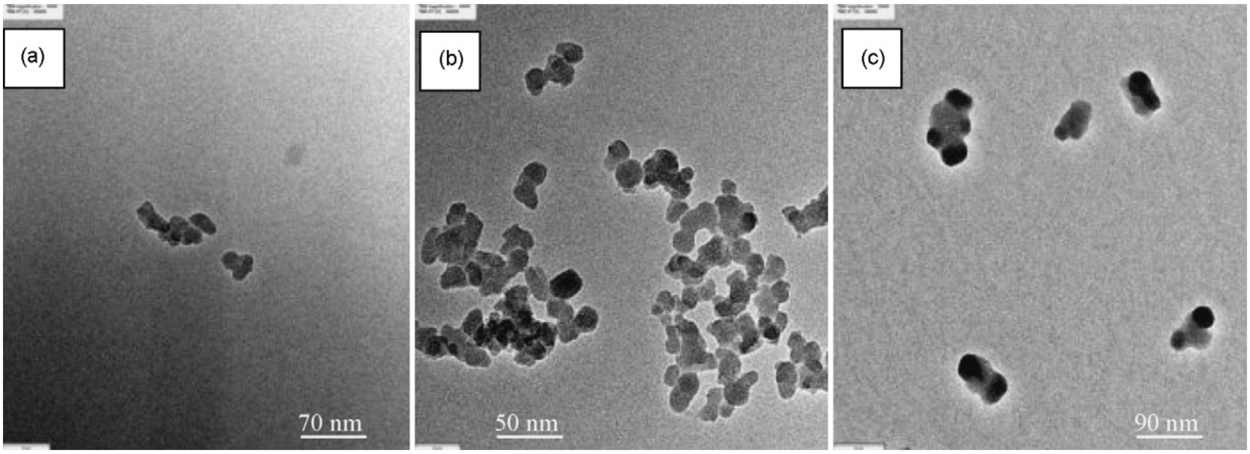


Fig. 16. TEM images of the distribution and size of the silica samples modified with radiation-induced admicellar polymerization using (a) DTAB, (b) TTAB, and (c) CTAB.

4. Conclusion

At an optimum total dose the radiation-induced admicellar polymerization provides a better film formation on the silica surface when compared with the traditional thermal process. Among the three surfactants used in this study, CTAB is shown to be the most effective surfactant for modifying the silica surface with admicellar polymerization.

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