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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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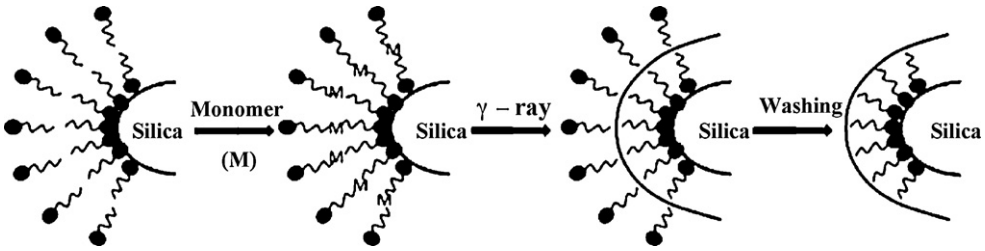

Fig. 1. A schematic of radiation-induced admicellar polymerization for the modification of silica surface.

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:

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