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# Rubber products prepared from silica modified by radiation-induced admicellar polymerization

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## ABSTRACT

Unmodified silica, silica modified with Si69, silica modified by thermal admicellar polymerization and silica modified by radiation-induced admicellar polymerization were applied as rubber reinforcement. Mechanical properties of these different rubber formulae were subsequently tested. The results revealed that the mechanical properties of rubber reinforced with silica modified by admicellar polymerization were superior to those reinforced with unmodified silica or silica modified with Si69. As for the silica modified by admicellar polymerization, cetyltrimethyl ammonium bromide (CTAB) proved to be the most effective surfactant, compared to dodecyltrimethyl ammonium bromide (DTAB) and tetradecyltrimethyl ammonium bromide (TTAB).

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## 1. Introduction

Applications of natural rubber as everyday products are continuously increasing. Fillers are normally added to rubber to achieve desired properties suitable for specific applications. Silica is well-known as one of the most common fillers in the rubber industry. Nevertheless, adhesion between the surfaces of silica and rubber is rather poor, since the silica surface is hydrophilic, while the rubber surface is hydrophobic. This weak adhesion can result in detachment of silica particles from the rubber matrix. A number of research groups modified the silica surface by a technique called admicellar polymerization to form a thin polymeric film on the silica surface, in order to enhance the adhesion between the surfaces of silica and rubber (Kitiyanan et al., 1996; Nontasorn et al., 2005; Thammathanukul et al., 1996; Wu et al., 1987). Admicellar polymerization was initially introduced by Wu et al. (1987). The technique comprises of a 4-step process: admicelle formation on the surface, monomer adsorption, polymerization of monomers dissolved in admicelles and surfactant removal to expose the formed polymer film. A number of researches have applied admicellar polymerization to modify the silica surface and analyzed the mechanical properties of rubber reinforced with the modified silicas. Thammathanukul et al. (1996) compared rubber reinforcement

using two silicas differing in surface area using either a bifunctional organosilane coupling agent or the in situ polymerization of styrene–butadiene and styrene–isoprene copolymers. The results showed that both surface modification processes dramatically increased the compound cure rate and improved tensile properties, tear strength, abrasion resistance and compression set of the cured compound. Nontasorn et al. (2005) developed a continuous stirred tank reactor (CSTR) for modifying amorphous silica via admicellar polymerization for rubber application. The comparison showed that the continuous system can produce modified silica with superior performance in the rubber compounds compared to those produced from batch processes, since CSTR-modified silica has more consistent properties.

The third step of the admicellar polymerization, which is the induction of the polymerization reaction in the admicelle, is traditionally induced by the thermal process and the chemical initiators. As an alternative to the thermal process, radiation has been successfully applied by different researchers to induce polymerization for various polymers, ranging from poly(diethyl fumarate) to poly(methyl methacrylate) (Alkassiri, 2005; Cataldo et al., 2008a, 2008b; Hayakawa et al., 1965; Yaodong et al., 2005). For the polymer industry, radiation technology offers a large number of benefits and is hence preferred over some other conventional methods (Bhattacharya, 2000). The radiation process requires no catalyst or additive to initiate the reaction, thus the purity of the products can be maintained. While chemical initiation is limited by the concentration and purity of the initiators, radiation dose can be varied widely, resulting in a better controlled reaction. Moreover, radiation-induced process is

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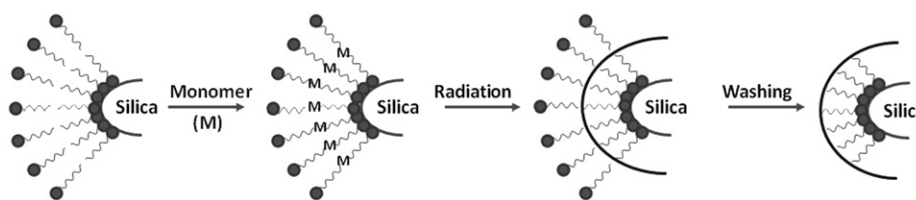


Fig. 1. Surface modification of silica by radiation-induced admicellar polymerization.

contamination-free, temperature independent and a good sterilizing technique. Recently, Nummeechai et al. (2008) investigated the possibility of using gamma radiation as an alternative method to induce polymerization of isoprene on silica surface by admicellar polymerization. The results showed that gamma irradiation can indeed be successfully applied to induce admicellar polymerization of isoprene to form an ultrathin film of polyisoprene on silica surface. Fig. 1 illustrates the process of the surface modification of silica by radiation-induced admicellar polymerization.

Yooprasert et al. (2010) compared radiation-induced admicellar polymerization of isoprene on silica surface with the traditional thermal process. The results showed that radiation-induced admicellar polymerization at an optimum dose can lead to a better film formation on silica, compared with the thermal method. This research further expands these studies by applying silicas modified by radiation-induced admicellar polymerization as fillers for natural rubber and investigating the mechanical properties of the reinforced natural rubber. The effects of silica modified by radiation-induced admicellar polymerization on the mechanical properties of the reinforced rubber were compared with those of the unmodified silica and silica treated with Si69.

## 2. Experimental

### 2.1. Materials and instruments

Natural rubber (STR 5L) and silane coupling agent (Si69) were obtained from Bangkok Rubber Co., Ltd. (Bangkok, Thailand). Silica (Hi-Sil<sup>®</sup>233) was supplied by Siam Silica Co. Ltd. (Bangkok, Thailand). Three types of surfactants used for this study were dodecyltrimethyl ammonium bromide [ $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$  or DTAB (98.0%, Fluka, Switzerland)], tetradecyltrimethyl ammonium bromide [ $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br}$  or TTAB (99%, Acros, Belgium)] and cetyltrimethylammonium bromide [ $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$  or CTAB (98%, Fluka, Switzerland)]. All chemical were used as received.

### 2.2. Admicellar polymerization

#### 2.2.1. Thermal admicellar polymerization

The surfactant was dissolved in 100 ml of distilled water. The amount of surfactants used was 0.0025, 0.0015 and 0.0010 mol for DTAB, TTAB and CTAB, respectively. The solution was adjusted to pH 8 by sodium hydroxide. 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 later 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 ratios of the surfactant to the monomer were 1:6, 1:4 and 1:8 for DTAB, TTAB and CTAB, respectively. The molar ratio used was an optimum value determined by the effects of the ratios on the film formation induced by thermal admicellar polymerization. The details of the film formation study are available from our previous work (Yooprasert et al., 2010) and hence will not be repeated

here. 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 unnecessary surfactant was completely removed. The silica samples were later dried in an oven at 40 °C for 3 days, before the characterization.

#### 2.2.2. 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 surfactant used were 0.0025, 0.0015 and 0.0025 mol for DTAB, TTAB and CTAB, respectively. The molar ratio of the surfactant to ethanol was 1:43, whereas that of the surfactant to the monomer was 1:6. The mixture was irradiated for the total dose of 8 kGy, at the dose rate of 0.17 kGy/min. The optimum dose used was determined by the effects of gamma radiation on the film formation. The details of the film formation study to verify the optimum dose are available from our previous work (Yooprasert et al., 2010) and therefore will not be duplicated here. The washing and drying processes were done precisely the same way.

### 2.3. Rubber mastication, compounding and vulcanization

Rubber (STR 5L, 600 g) was masticated in an Internal Mixer (Lab Tech Engineering Co., Ltd., Bangkok, Thailand) at 60 °C. After masticating the rubber for 3 min to reduce its viscosity, the ingredients according to the formulation of the rubber compound, shown in Table 1, were added, gradually and respectively. The first two compounds added were activators (zinc oxide and stearic acid, respectively.) and the mixture was masticated for 2 min. Next, the filler (unmodified or modified silica) was put in and the mastication continued for another 2 min. After that, processing aids (PEG 400, Shellflex oil and wax) were correspondingly added. Then, antioxidation reagent (22CP46) was added and the mixture was thoroughly masticated. Subsequently, accelerators (mercapto benzothiazole (MBT), mercapto benzothiazyl disulfide (MBTS) and tetramethylthiuram monosulfide (TMTM), respectively) were added and the mastication was maintained for another 2 min. Finally, sulfur was added as a vulcanizing agent. The rubber compound was thoroughly masticated to ensure that all ingredients were fully mixed. After mastication, a Rheometer (EK 100H, EEKON) was used to determine cure time. The rubber compound was compression molded with a Compression Mold (DAH TYAN Industrial Co., Ltd.) at 160 kg/cm<sup>2</sup> at a 160 °C cure temperature. The vulcanized rubber was left intact for 24 h, before it was subjected to mechanical tests.

### 2.4. Properties testing

Sample thicknesses were determined using a gauge from Teclock Corporation. Sample preparations were done using a Cutting Board and Machine from CEAST. Abrasion tests were performed using an Abrasion Tester from FRANK. The universal

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