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# Synthesis of polybutadiene-silica nanoparticles via differential microemulsion polymerization and their hydrogenated nanoparticles by diimide reduction

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ABSTRACT

Polybutadiene (PB)–$SiO_2$ nanoparticles were successfully synthesized via differential microemulsion polymerization. The core-shell structured PB-$SiO_2$ nanoparticles were designed to achieve a monodispersion with reduced nanosilica aggregation. A high monomer conversion (81.5%), grafting efficiency (78.5%) and small particle size (27 nm) with narrow size distribution was obtained under optimum reaction conditions when using an extremely low surfactant concentration, 5 wt% based on monomer. The PB-$SiO_2$ latex could be hydrogenated by diimide reduction in the presence of hydrazine and hydrogen peroxide to provide hydrogenated polybutadiene (HPB)–$SiO_2$. A high hydrogenation degree of 98.6% was achieved at a ratio of hydrazine to hydrogen peroxide of 0.75:1, and showed a maximum degradation temperature of 469.6 °C resulting in excellent thermal stability. A new nanocomposite of PB-$SiO_2$ and HPB-$SiO_2$ could be used as a novel nanofiller in natural rubber. Especially, NR/HPB-$SiO_2$ composites had improved mechanical and thermal properties, and exhibited good resistance toward ozone exposure.

## 1. Introduction

Polymer nanocomposite materials (polymer/filler) have increasing potential for future applications due to the advantageous properties of the organic polymer species such as elasticity, processibility with inorganic fillers providing high thermal stability and reinforcement [1,2]. One of the most common inorganic systems is nanosilica that has many functional properties and effective reinforcement. It has been widely used in colloidal products, paints, catalysis, chromatographic separation, rubber and plastic reinforcement due to silica is chemically inert and optically transparent [3]. Many previous studies have reported on improved properties of rubber filled with nanosilica. The chlorosilane-modified silica grafted with 2-mercaptobenzimidazole]. (MB) was prepared as a novel antioxidant in styrene-butadiene rubber [4]. The hydrogenated acrylonitrile butadiene rubber (HNBR) composites filled with fumed silica was prepared to improve their ablation performance and thermal stability [5]. However, the difficulties as an access to well dispersed silica in rubber matrix are due to the large quantity of hydroxyl groups on the surface of the nanosilica and the high surface energy and polarity, resulting in inferior compatibility and less stability between the rubber matrix and nanosilica; thus severe agglomeration and weak rubber-filler interaction occurred [6]. The great advantage provided by nanosilica can only be achieved if the particles are finely dispersed in the polymer matrix.

Encapsulation is regarded as being of major importance since it offers interesting potential applications in different fields. Thus, encapsulation of nanosilica with polymer can improve the compatibility of nanosilica in the rubber matrix resulting in an improvement of filler dispersion and performance of the rubber composite [7,8]. Polyisoprene (PIP)–$SiO_2$ nanoparticles, produced with a size of 20–60 nm with a narrow size distribution via differential microemulsion polymerization (DMP) resulted in reduced nano-$SiO_2$ aggregation in the PIP matrix and have been used as an effective nano-filler in NR latex. The NR filled with PIP-$SiO_2$ clearly presented an improvement in the storage modulus, tensile strength, modulus at 300% strain and anti-aging properties

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[9]. In addition, poly(methyl-methacrylate) (PMMA)/$SiO_2$ nanocomposite particles could be prepared by grafting polymerization of MMA onto the $SiO_2$ surface, which could be well-dispersed in the NR matrix and exhibited good interfacial adhesion with the NR phase [10]. Hybrid nanoparticles of polystyrene (PS)-encapsulated silica were also prepared by DMP and the resulting particles were used as a filler in the NR latex resulting in improved tensile strength, modulus at 300% strain and flammability of NR at low PS-encapsulated silica loading of 3–9 parts per hundred rubber (phr) [11].

However, rubbers such as polybutadiene (PB) and polyisoprene (PIP) suffer from a drawback in their thermal and ozone stability due to the C=C in their polymer backbones. The C=C of the rubber are sensitive to oxygen, ozone and heat resulting in rubber degradation and the reduction of mechanical and thermal properties. Hydrogenation of diene-based rubbers is an important process to obtain hydrogenated rubber and improve their thermal properties and oxidative stability while maintaining their elastomeric properties [12]. NR latex was hydrogenated by diimide reduction, using hydrazine and hydrogen peroxide with copper sulfate as catalyst. A high hydrogenation degree of 65% was achieved at a ratio of hydrogen peroxide to hydrazine of 1.3:1 [13]. Moreover, hydrogenated polyisoprene (HPIP)–$SiO_2$ nanocomposites were synthesized via DMP followed by diimide hydrogenation with boric acid as promoter, providing a hydrogenation degree of 98% at a ratio of hydrogen peroxide to hydrazine of 1.5:1 [14]. HPIP-$SiO_2$ composites were used as a nanofiller in natural rubber leading to improvement of mechanical properties, retention of tensile strength after thermal aging and ozone resistance.

In the present study, we propose to synthesize monodispersed PB-$SiO_2$ nanocomposites via differential microemulsion polymerization and hydrogenated polybutadiene (HPB)–$SiO_2$ nanocomposites by diimide reduction. For DMP, the effect of silica loading, surfactant concentration, monomer to water ratio and initiator concentration on monomer conversion, grafting efficiency, silica encapsulation efficiency and particle size were studied. For diimide reduction as a green process of hydrogenation, the influence of hydrazine hydrate and hydrogen peroxide concentration on the hydrogenation degree and particle size were also investigated. For rubber application, the mechanical properties of tensile strength, modulus and elongation at break, the thermal properties of glass transition temperature and decomposition temperature, and ozone resistance of NR/PB-$SiO_2$ and NR/HPB-$SiO_2$ composites were studied.

## 2. Experimental

### 2.1. Materials

Nano-$SiO_2$ (Aerosil 200, hydrophilic fumed silica, 12 nm) was supplied by Degussa. Vinyl trimethoxysilane (VTS, ≥98%, Sigma Aldrich) as a coupling agent and ammonia solution (25 wt% $NH_4OH$, Fisher Scientific) as a catalyst were used for surface modification of nano-silica. 1,3-butadiene (BD, ≥99.5%, Air Liquid), potassium persulfate (KPS, ≥99%, Sigma Aldrich), sodium dodecyl sulfate (SDS, ≥99%, Fisher Scientific), sodium bicarbonate ($NaHCO_3$, ≥99%, EMD) were used without further purification for synthesis of polybutadiene (PB)–$SiO_2$ nanoparticles. Deionized water was used in all polymerization. Methyl ethyl ketone (MEK, ≥95%, Fisher Scientific) was used to precipitate the PB-$SiO_2$ nanoparticle. Hydrazine hydrate ($N_2H_4$, ≥99%, Sigma Aldrich), hydrogen peroxide solution (30 wt% $H_2O_2$, Sigma Aldrich) and boric acid as promotor ($H_3BO_3$, ≥99.5%, EMD) were used as received for diimide reduction. Natural rubber (NR) latex with approximately 60 wt% dry rubber content (DRC), sulfur as vulcanizing agent, zinc oxide (ZnO) and zincdiethyl dithiocarbamate (ZDEC) as vulcanization accelerators were purchased from the Rubber Research Institute of Thailand for NR/PB-$SiO_2$ composite preparation.

### 2.2. Surface modification of nano-$SiO_2$

Modified nano-$SiO_2$ was prepared according to our previous reported procedure [15]. Firstly, 5 g of nano-$SiO_2$ was dispersed in 150 mL of deionized water with sonication in an ultrasonic bath for 1 h after that the dispersed solution was stirred at 550 rpm for 30 min. Then, 0.15 g of VTS was added dropwise into the dispersed solution and 25 wt% $NH_4OH$ was fed to adjust the pH of the solution to around 10. The solution was stirred for 30 min at room temperature, and then heated up to the reaction temperature at 90 °C, while stirring was maintained at 550 rpm. The reaction was allowed to proceed for an additional 24 h. After that the suspension was dried at 110 °C until constant weight to obtain the modified nano-$SiO_2$. Then, the modified nano-$SiO_2$ was extracted with acetone for 24 h to remove the free VTS. Finally, VTS-$SiO_2$ was dried in an oven at 55 °C until constant weight was reached.

### 2.3. Synthesis of polybutadiene-$SiO_2$ nanoparticles

A differential microemulsion polymerization technique was used for synthesizing PB-$SiO_2$ nanoparticles. The reactions were carried out in a 300 mL Parr stainless steel reactor equipped with a feeding tube, a thermocouple and an impeller stirrer. Typically, VTS-$SiO_2$ was dispersed in deionized water with sonication in an ultrasonic bath for 1 h. Afterwards, different amounts of VTS-$SiO_2$, SDS, KPS, $NaHCO_3$ and deionized water were charged into the reactor. The solution was stirred at 350 rpm for 45 min under a nitrogen atmosphere at room temperature and then the system was heated up to 50 °C and the pressure was increased to 100 psig using nitrogen gas. The feeding tube was filled with BD (liquid under 22 psig at room temperature) and then, the tube was connected with the reactor. The condensed BD monomer was continuously fed dropwise into the reactor at a given rate of 0.3 mL/min as controlled by a needle valve. After the addition of the BD monomer was completed, the reaction system was maintained at 50 °C at a constant stirring rate and left to proceed for a given time to reach a desired conversion.

After the polymerization was stopped, the PB-$SiO_2$ latex was precipitated using excess methyl ethyl ketone to produce the coagulated rubber. The coagulated rubber composite was dried in a vacuum oven at room temperature until constant weight was reached and was then extracted with cyclohexane using a soxhlet apparatus to remove free PB. The monomer conversion and grafting efficiency (GE) were determined by a gravimetric method and calculated from Eqs. (1) and (2), respectively:

$$\text{Monomer conversion (\%)} = \frac{\text{Weight of monomer reacted}}{\text{Weight of monomer charged}} \times 100 \tag{1}$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of monomer grafted}}{\text{Weight of monomer polymerized}} \times 100 \tag{2}$$

An acid etching method was used to determine the silica encapsulation efficiency [15,16]. The composite latex was slowly added to an excess HF solution. The resulting dispersion was dried and the weight percent of the residue was determined gravimetrically. The silica encapsulation efficiency was calculated using Eq. (3):