การหุ่อหุ้มอนุภาคระดับนาโนของซิลิกาด้วยพอลิสไตรีนผ่านการเกิดพอลิเมอร์แบบดิฟเฟอเรนเชียลไมโครอิมัลชัน

Encapsulation of silica nanoparticles by polystyrene Via differential microemulsion polymerization

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บทคัดย่อ

อนุภาคระดับนาโนของซิลิกาถูกห่อหุ้มด้วยพอลิสไตรีนผ่านกระบวนการเกิดพอลิเมอร์แบบดิฟเฟอเรนเชียลไมโครอิมัลชัน โดยใช้โซเดียมโดเดซิลซัลเฟต และ 2,2' เอโซบิสไอโซบิวทิโรไนไตร์ลเป็นสารลดแรงตึงผิวชนิดแอนไอออนิก และสารเริ่มปฏิกิริยาแบบละลายในน้ำมัน ตามลำดับ ผลการทดลองพบว่า อัตราส่วนโดยน้ำหนักของสารลดแรงตึงผิว/สไตรีนมอนอเมอร์ที่ใช้มีค่าต่ำถึง 0.20 และมีร้อยละผลได้ของพอลิสไตรีนเท่ากับ 64 ในการเตรียมอนุภาคนาโนคอมพอสิตได้ถูกนำไปตรวจสอบหาขนาดอนุภาคและสัณฐานวิทยา พบว่า อนุภาคซิลิกา/พอลิสไตรีนนาโนคอมพอสิต มีขนาดอนุภาคเฉลี่ยประมาณ 43 นาโนเมตร

Abstract

Nanosized silica was encapsulated by polystyrene via *in situ* differential microemulsion polymerization. In this process, 2-2'-azoisobutyronitrile and sodium dodecyl sulfate were used as oil soluble initiator and anionic surfactant, respectively. The weight ratio of surfactant/styrene monomer in this study was as low as 0.20. The yield of polystyrene was about 64%. The prepared hybrid particles were investigated for their particle size and morphology. It is found that the particle size of the obtained nanocomposites was about 43 nm.

คำสำคัญ: การเกิดพอลิเมอร์แบบดิฟเฟอเรนเชียลไมโครอิมัลชัน นาโนคอมพอสิต ซิลิกา พอลิสไตรีน
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1. Introduction

Polymer/inorganic composite nanoparticles are of great interest in a wide range of applications, in particular, in the field of polymer-based nanocomposite materials. The preparation of composite nanoparticles is one of the most important topics in nanotechnology. Such composite nanoparticles can mainly be prepared by encapsulation or grafting of polymers onto the surface of inorganic nanoparticles (Yang, Khong, Kan and Sun, 1997; Erdem, David, Victoria, Dimonie and El-Aasser, 2000; Erdem, David, Victoria, Dimonie and El-Aasser, 2000; Yu, Yu, Guo and Gao, 2001).

In recent years, there has been increasing interest in the synthesis of colloidal polymer encapsulation. Most of the work done in that field has been described in many literatures (Yang et al., 1999; Erdem et al., 2000; Erdem et al., 2000; Yu et al., 2001). However, there have no literatures which can prepare encapsulated silica nanoparticles lower than 50 nm. Ding et al. prepared the monodisperse PS/SiO_2 composite particles (PSCPs) by in situ emulsion polymerization. Nanosized silica was modified with the oleic acid. Styrene monomer, added to fully dispersed silica particles modified by oleic acid used as seeds. Particle size of the encapsulated particle was around 180-250 nm (Ding, Zhao, Lui, Zhang and Wang, 2004). Zeng et al. reported the synthesis of carboxyl-functionalized polystyrene/silica (PS/SiO_2) composite nanoparticles by post-addition of methacrylic acid (MAA) via emulsion polymerization using the MPTMS as silane coupling agent. The obtained composite nanoparticles were about 60 nm (Zeng, Yu and Guo, 2004). Chen et al. prepared PS/SiO2 core-shell hybrid colloids via surfactant-free emulsion polymerization by using azodiisobutyrami-dinedihydrochloride (AIBA) (cationic) as initiator. The resulted core shell particle size was about 200 nm (Chen et al, 2005). From the literature survey in above, the resultant particle size of the encapsulated particle was quite different from the raw silica nanoparticles. In addition, although the emulsion polymerization with the high amount of surfactant was used but the particle size could not decrease to enclose with the beginning of the silica nanoparticles. The thick layer of the polymer on the silica nanoparticle was not appreciated since the interfacial behavior of the coated polymer is not dependent on the thickness of the coated polymer. In addition, the large size reduced the specific surface areas of the encapsulated particle.

A differential microemulsion polymerization was proposed (He, Pan and Rempel, 2003), which the nanoparticle sized could be controlled and a less amounts of surfactant was used in the system. He and Pan have synthesized PS nanoparticles using sodium dodecyl sulfate (SDS) as the surfactant and APS as the initiator by a differential microemulsion polymerization method. The resulted particle size, at a low amount of SDS (SDS/styrene weight ratio of 0.26), was 23.3 nm (He and Pan, 2004). Narakarnkorn et al. reported the synthesize of nanosized poly(methyl methacrylate) initiated by 2,20-azoisobutyronitrile via differential microemulsion polymerization using sodium dodecyl sulfate (SDS) as the surfactant and AIBN as the oil-soluble initiator. The resulted particle size, at a low amount of SDS (SDS/styrene weight ratio of 1/130), was 20 nm. So the differential microemulsion polymeri- zation was possibly an efficient process to produce the polystyrene encapsulated silica nanoparticles with the particle size was not quite different from the raw silica nanoparticles.

The present work, the silica nanoparticles encapsulated by polystyrene latex nanoparticles via *in situ* differential microemulsion polymerization by using sodium dodecyl sulfate (SDS) as the surfactant and AIBN as the oil-soluble initiator. The effects of the amounts of initiator and SDS on the particle size and the percentage of conversion of polystyrene were investigated. Moreover, the effect of the silane pre-treatment on the particle size, the percentages of conversion, and morphology of polystyrene encapsulated silica nanoparticles were also studied.

2. Experimental

2.1. Materials and apparatus

styrene with 0.005 % of inhibitor (AR grade, Sigma-Aldrich Chemie Gmbh), sodium dodecyl sulfate (SDS) powder (97% purity, Cognis, Bangkok, Thailand), 2,20-azoisobutyronitrile (AIBN) (AR grade, Siam chemical industry Co.,LTD., Samutprakarn, Thailand), methanol (practical grade), Silicon dioxide, nanopowder, 15 nm, (Sigma-Aldrich, Missouri, USA) Z-6030 Silane (Dow Corning, Michigan, USA) were used as received. Distilled water was used as obtained from the Department of Materials Science at Chulalongkorn University, Bangkok, Thailand. A 500 cc Pyrex glass reactor (Aldrich, Canada), which was equipped with a double jacket condenser, a dropping funnel for monomer feeding, a magnetic stirrer with a stirring/temperature controlled digital hotplate.

2.2. Preparation of polystyrene latex nanoparticles

Polystyrene latex nanoparticles were prepared by differential microemulsion polymerization. The reaction operational procedures were as follows. SDS and AIBN were placed in a certain amount of distilled water in the reactor and heated under constant agitation (150 rpm) with a constant nitrogen feed through a gas inlet tube. After rising the temperature to 70 °C a styrene was added in a differential manner (continuously in very small drops) by a dropping funnel for about one and half hours. Afterwards, the reaction system was kept at 70 °C for an additional hour in order to receive a higher conversion of the microemulsion polymer before cooling.

2.3. Separation of polymer samples for charac terization

The resultant polymer was precipitated using an excess of methanol and was separated by a vacuum filtration technique. The surfactant and initiator were washed with a sufficient amount of warm distilled water and methanol.

2.4. Preparation of polystyrene encapsulated silica nanoparticles.

2.4.1. Preparation of Pre-treated silica nanoparticles with MPTMS

MPTMS, a silane coupling agent applied to silica nanoparticle surfaces as a dilute aqueous solution (0.5% silane concentration). Aqueous solutions were prepared by adjusting the pH of the water 4.5 with acetic acid and then adding the silane while stirring. After adding the silane to the acidified water, it was necessary to stir the mixture for a minimum of 30 minutes before it hydrolyses and forms a clear homogeneous solution. The silica nanoparticles were treated by mixing with the silane at very high shear without any additional solvent. Afterward silica nanoparticle surfaces were dried briefly at 120 °C.

2.4.2. Synthesis of polystyrene encapsulated silica nanoparticles

Polystyrene encapsulated silica nanoparticles were prepared by *in situ* differential microemulsion polymerization. The reaction operational procedures were as follows, the pre-treated silica nanoparticles were placed with SDS, AIBN in the reactor. Then a certain amount of distilled water was added. The next step followed like 3.2 and 3.3.

2.5. Characterization of Nanosized polystyrene and polystyrene encapsulated silica nanoparticles

Particle size and Particle size distribution

After the polymerization was completed, the number-average diameter (Dn) of the polymer particles was measured using a dynamic light scattering technique (DLS, National Metal and Materials Technology Center, Bangkok, Thailand).

Polymerization conversion

The resultant solid content of the PS polymer and conversion of the monomer were investigated by a gravimetric method and calculated from the ratio of the weight of the styrene converted to PS and the weight of the total styrene added.

Molecular weight and its distribution

Average molecular weights (Mn and Mw) and the molecular weight distribution were determined by gel permeation chromatography (GPC, National Metal and Materials Technology Center, Bangkok, Thailand) equipped with an RI detector (Water 150-CV refractive index detector) in tetrahydrofuran at 30 ^{o}C. A column set was employed consisting of columns filled with a PL gel 10 μm mixed B 2 columns.

Morphology

Morphology of both polystyrene latex nanoparticles and polystyrene encapsulated silica nanoparticles were investigated by transmission electron microscope (TEM)

3. Result and discussion

Figure 1 shows the effect of AIBN amount with 0.08-0.3 g at two SDS concentrations on the conversion of the resultant PS. The highest conversion, 64% obtained when using the lowest AIBN amount at 0.08 g. When the amount of AIBN reached to 0.12 g, the conversion decreased to 50%. Then, when the amount of AIBN was 0.18 g, the conversion was increased to 59%. The conversion of PS was standing about 60%, with an increasing amount of AIBN to 0.24 and 0.3 g. The reason for this was probably that the micelles are the important nuclei for styrene to polymerize in the differential microemulsion polymerization system which using oil-soluble initiator (He et al., 2003). Therefore, at the lower amount of AIBN, the system had a little of the nuclei which contain the free radical of AIBN so the dispersion of styrene monomer enhancing to convert to more PS and hence the conversion was higher. While the conversion become higher, with the increase in amount of AIBN. As a result of the nuclei which contain the free radical of AIBN was higher, the dispersion of styrene monomer in each nuclei decreased so the conversion decreased. When increasing the more amount of AIBN, the conversion increased due to the styrene monomer dispersion reduced in each nuclei, it could give the small size and stable of polystyrene nanoparticles (He et al., 2003). The excess amount of AIBN could give the standing conversion because polystyrene nanoparticles had stability enough to stop the chain propagation. However, a slightly different SDS concentration which was used higher than CMC in these two systems may offset the difference in the amount of micelle, which may be the reason that there was no significant difference in the conversion between the two systems (He et al., 2003).

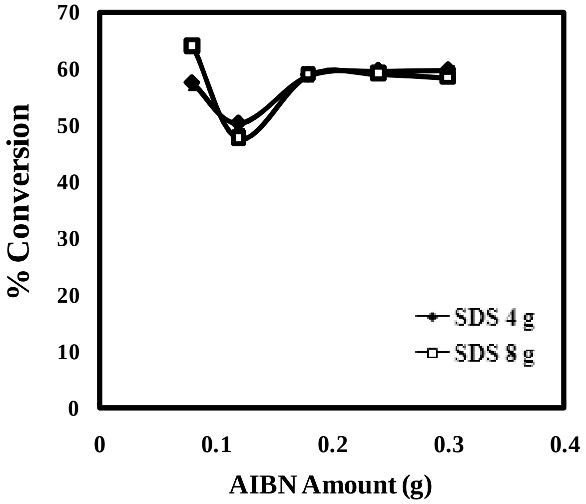

Figure 1. Effect of AIBN amount on the conversion of polystyrene

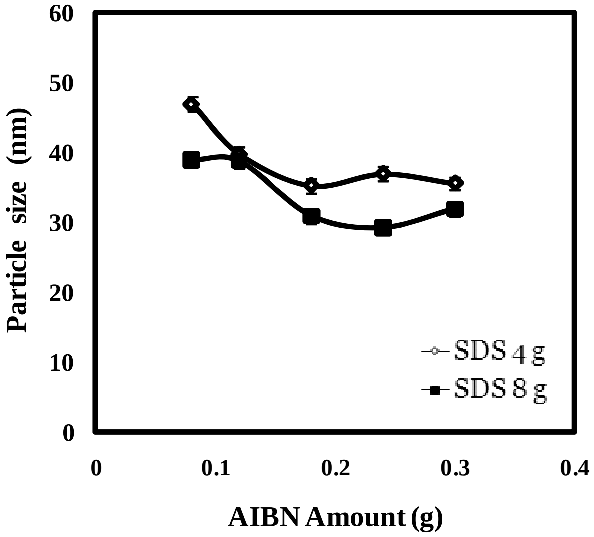

Figure 2. Effect of AIBN amount on the particle size of polystyrene

The results with respect to the effect of AIBN amount on the particle size are shown in Figure 2. It was indicated in Figure 2 that, with an increase in the AIBN amount, the particle size decreased. The particle size (Dz) of PS was 47 nm with an AIBN amount of 0.08 g. However, when the amount of AIBN was 0.12 g the particle size of PS become smaller (39.67 nm). The particle size of PS was standing about 36 nm, with an increasing amount of AIBN (0.18, 0.24 and 0.3 g). It is therefore believed that the styrene monomer dispersion reduced in each nucleus which contains the free radical of AIBN, it could give the small size and stable of polystyrene nanoparticles (He et al., 2003). However, a slightly different SDS concentration which was used higher than CMC in these two systems may offset the difference in the amount of micelle, which may be the reason that there was no significant difference in the particle size between the two systems (He et al., 2003).

A series of encapsulation experiments was carried out in the in situ differential microemulsion polymerization. Table 1 shows the particle size and PDI of polystyrene and polystyrene encapsulated silica nanoparticles. It indicated that the polymerization of styrene monomer which encapsulated the pre-treatment of silica nanoparticle with MPTMS was similar to the polymerization of styrene monomer which encapsulated the un-treatment of silica nanoparticle. The reason for this was probably that polystyrene encapsulated silica nanoparticles were slightly larger than PS nanoparticles. Beside the PDI was not different. The silica nanoparticles in micelle could provide the nuclei for styrene to polymerize.

Table 1 Particle size and PDI of polystyrene and polystyrene encapsulated silica nanoparticles

Sample	Particle size (nm)	Particle Dispersion Index (PDI)
PS	38	0.148
Treated	43	0.136
Untreated	44	0.128

4. Conclusion

Synthesis of polystyrene and polystyrene encapsulated silica nanoparticles was investigated. The differential microemulsion polymerization method is more effective not only decreasing the particle size of polystyrene and polystyrene encapsulated silica nanoparticles but also decreasing the amount of surfactant required.

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