การเตรียมอนุภาคระดับนาโนของซิลิกา/พอลิเมทิลเมทาคริเลตคอมพอสิต ผ่านการเกิดพอลิเมอร์แบบดิฟเฟอเรนเชียลไมโครอิมัลชัน

Preparation of silica/poly(methyl methacrylate) composite nanoparticles via differential microemulsion polymerization

Presented in The 2nd Progress in Advanced Materials: Micro/Nano Meterials and Applications

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บทคัดย่อ

จุดประสงค์ของงานวิจัยนี้ คือ การเตรียมอนุภาคระดับนาโนของซิลิกา/พอลิเมทิลเมทาคริเลตคอมพอสิต ผ่านการเกิดพอลิเมอร์แบบดิฟเฟอเรน-เชียลไมโครอิมัลชัน โดยใช้โซเดียมโดเดซิลซัลเฟต และ 2,2' เอโซบิสไอโซบิวทิโรไนไตร์ลเป็นสารลดแรงตึงผิวชนิดแอนไอออนิก และสารเริ่มปฏิกิริยาแบบละลายในน้ำมัน ตามลำดับ ด้วยการป้อนเมทิลเมทาคริเลตมอนอเมอร์ทีละหยดเข้าไปในเครื่องปฏิกรณ์โดยใช้ช่วงระหว่างการหยดสั้นมาก โดยอนุภาคของนาโนซิลิกาได้ถูกเตรียมผิวด้วยสารคู่ควบประเภท 3-เมทาคริลอกซีโพรพิลไตรเมทอกซีซิเลนเพื่อปรับปรุงการยึดเกาะระหว่างผิวของอนุภาคซิลิกาและพอลิเมทิลเมทาคริเลต อนุภาคของนาโนคอมพอสิตที่เตรียมได้ถูกนำไปตรวจสอบหาขนาดอนุภาค เปอร์เซ็นต์ผลได้ และสัณฐานวิทยา ผลการทดลอง พบว่า อนุภาคระดับนาโนของซิลิกา/พอลิเมทิลเมทาคริเลตคอมพอสิตมีขนาดอนุภาคเฉลี่ยประมาณ 40 นาโนเมตร และร้อยละผลได้มีค่าประมาณ 82

Abstract

This research aimed to prepare silica (SiO_2)/poly(methyl methacrylate) (PMMA) composite nanoparticles via *in situ* differential microemulsion polymerization process. Sodium dodecyl sulfate (SDS) and 2,2' azobis(isobutyronitrile) (AIBN) were used as an anionic surfactant and oil soluble initiatior, respectively. The methyl methacrylate monomer feed into the reactor was provided in very small drops and the time interval between drops was very short. Nano-SiO_2 particles were first treated with 3-methacryloxypropyl trimethoxysilane (MPTMS) coupling agent to improve the particle-PMMA interfacial adhesion. The obtained composite nanoparticles were investigated for their particle size, %yield and morphology. The results showed that the nanocomposite particles had an average particle size about 40 nm. the yield of SiO_2/PMMA composite nanoparticles was as high as 82%.

คำสำคัญ: นาโนซิลิกา พอลิเมทิลเมทาคริเลต การเกิดพอลิเมอร์แบบดิฟเฟอเรนเชียลไมโครอิมัลชัน
Keywords : nanosilica, poly(methyl methacrylate), differential microemulsion, polymerization

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1. Introduction

In recent years, the nanomaterials are a major driving force for innovative nanotechnology. Many of the applications of nanotechnology are materials-related, such as biomedical, semiconductor, catalysis, and coating. Researches onto inorganic/organic composite nanoparticles have increased significantly for their superior properties. (Min, Bo, Shuxue and Limin, 2006; Zhang, Zheng, Zhang, Chen and Yang, 2006; Xu, Wang, Tong, Du and Zhong, 2006). They can be offer wide applications in various fields such as catalysis, semiconductors, coatings and composites. Several methods have been reported for the preparation of inorganic/organic composite particles.

Hergeth et al. first applied an emulsion polymerization process to encapsulate inorganic particles by a polymer layer, so-called core-shell particles, where the *in-situ* polymerization of the monomer occurred mainly at the surface of unmodified particles due to the adsorption of monomer on the surface, followed by polymerization in the adsorp layer. Min et al. reported the preparation of the poly(methyl methacrylate)/silica (PMMA/SiO_2) composite nanoparticles via a free radical copolymerization of methyl methacrylate (MMA) with 1-vinylimidazole in the presence of ultrafine aqueous silica sols. The average particle sizes and the silica contents of the nanocomposite particles were in the ranges of 120-330 nm and 15-20%, respectively. Zhang et al. reported the preparation of 131-225 nm silica-poly(methyl methacrylate) core shell nanospheres (CSNs) with 51-195 nm cores by an emulsion polymerization. The thicknesses of PMMA shells were found to be dependent on the amount of monomer and grafted silica nanoparticles, the concentration of surfactant and the sizes of grafted silica nanoparticles, and the morphologies of CSNs were affected by the kind of monomer. They investigated the formation of hollow polymer nanospheres. However, the concentration of surfactant was an important parameter on the size of CSNs and the thickness of the coated PMMA. Xu et al. reported the preparation of the 57 nm in diameter of the PMMA/SiO_2 composite nanoparticles through microemulsion polymerization by using the silica particles coated with 3-(trimethoxysilyl) propyl methacrylate (MSMA) in both acidic and alkaline conditions. However, the microemulsion method requires a much higher amount of surfactant compared with conventional emulsion polymerization. The surfactant is expensive and has significantly negative impact on the properties of the polymers. Moreover, it takes cost to remove the surfactant after polymerization. A differential microemulsion polymerization is a new technique to produce the polymers with particle sizes of less than 50 nm, in which the monomer feed was provided in very small drops and the time interval between drops was very short. It was indicated that a lower amount of surfactant was needed in this system. This method provided PMMA with particle size of about 20 nm. The surfactant amount required could be as low as 1/130 of the monomer amount in weight (Narakankorn, Pan, Rempel and Kiatkamjornwong, 2007). So the differential microemulsion polymerization of PMMA via an oil-soluble initiator was expected to produce the PMMA/SiO_2 composite nanoparticles with particle sizes of less than 50 nm.

This research aimed to prepare SiO_2/PMMA composite nanoparticles via in situ differential microemulsion polymerization process. The obtained composite nanoparticles were investigated for their partcle size, % conversion and morphology.

2. Experimental

2.1 Materials

Methyl methacrylate monomer (MMA) (commertial grade, TMMA Co.,Ltd.), Sodium dodecyl sulfate (SDS) powder (97% purity, Industrial Cognis, Bangkok Thailandgrade), 2,2'-azoisobutyronitrile (AIBN) (Siam Chemical Industry Incorporation, Samutprakarn Thailand), methanol (practical grade), silicon dioxide (silica) nanopowder (15 nm, Sigma-Aidrich, Missouri, USA), distilled water and γ-Methacryloxypropyltrimethoxysilane (Z-6030 silane, Dow Corning, Michigan, USA). All reagents were used as received without further purification.

2.2. Preparation of SiO_2/PMMA composite nanoparticles

The silica nanoparticles were first treated with γ-Methacryloxypropyltrimethoxysilane in acidic condition. SiO_2/PMMA composite nanoparticles were prepared through differential microemulsion polymerization. The recipes used in this work are given in Table 1. AIBN and SDS were used as initiator and surfactant, respectively. The initiator, surfactant, nanosilica and distilled water were mixed in 500 cc Pyrex glass reactor, equipped with a stirrer, a condenser, a dropping funnel for monomer feeding and N_2 gas inlet. After the temperature was raised to 70 °C under constant agitation (200 rpm) using a magnetic stirrer with constant nitrogen feed through a gas inlet tube, the PMMA monomer was added in a differential manner (continuously addition in very small drops) for about 1.5 h. Afterwards, the reaction temperature was kept at 70 °C for an additional hour before a cooling operation was applied. The SiO_2/PMMA composite nanoparticles were separated from the obtained latex for characterization by precipitating with an excess methanol, washing with distilled water and drying under vacuum at 60 °C for 12 h.

Table 1 Recipe used in the present work.

Pretreated silica (g)	AIBN (g)	SDS (g)	MMA (ml)
0.394	0.15	1.4	22.5

2.3. Characterization

Particle Size

Particle size of SiO_2/PMMA composite nanoparticles was measured using a dynamic light scattering technique (DLS).

% Yield

% Yield of SiO_2/PMMA composite nanoparticles was measured using a gravimetric method.

Morphology

Morphology of SiO_2/PMMA composite nanoparticles was investigated using transmission electron microscopic (TEM) technique.

3. Results and discussion

Table 2 presents the particle size and particle size distribution (PDI) of the SiO_2/PMMA composite nanoparticles prepared by differential microemulsion polymerization.

Table 2 Particle size and particle size distribution (PDI) of SiO_2/PMMA composite nanoparticles.

Samples	Particle Size (nm)	PDI
Pretreated silica/PMMA	40.35	0.450
Untreated silica/PMMA	31.67	0.476

It can be seen that the particles of pretreated silica/PMMA are larger than that of untreated silica/PMMA due to the effect of silane coupling agent. It indicated that the PMMA shell of pretreated silica/

PMMA composite nanoparticles is thicker than the untreated one. Moreover, the particle size distributions of both pretreated and untreated silica/PMMA composite nanoparticles are slightly different.

% Yield of SiO_2/PMMA composite nanoparticles as measured by the gravimetric method was about 82%.

Figure 1 shows the TEM micrograph of SiO_2/PMMA composite nanoparticles. It indicated that PMMA has coated over the surface of the silica nanoparticles.

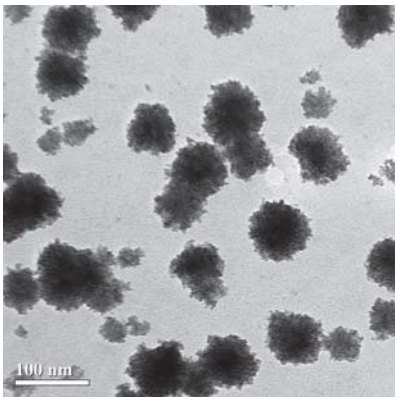

Figure 1. TEM micrograph of SiO_2/PMMA composite nanoparticles.

4. Conclusion

Silica/PMMA composite nanoparticles of less than 50 nm could be prepared through differential microemulsion polymerization. The SiO_2 nanoparticles were encapsulated by PMMA shell. In addition, the yield of SiO_2/PMMA composite nanoparticles was as high as 82%.

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