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ORIGINAL ARTICLE

Fabrication of core/shell hybrid organic–inorganic polymer microspheres via Pickering emulsion polymerization using laponite nanoparticles

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Abstract Oil-in-water (o/w) emulsions of styrene, as monomer oil in water, were achieved successfully via Pickering emulsification with laponite nanoparticles as the sole inorganic stabilizers. The formed emulsions showed excellent stability not only against droplets coalescence (before polymerization) but also against microparticles coagulation (after polymerization). Generally, the number of composite polystyrene microparticles (PS) increased and their sizes decreased with the content of solid nanoparticles used in stabilizing the precursor o/w emulsions. This is consistent with the formation of rigid layer(s) of the inorganic nanoparticles around the PS microparticles thus a better stability was achieved. The composite microparticles were characterized using various techniques such as surface charge, stability, transmission electron microscope (TEM), scanning electron microscope (SEM) and Fourier transform infra-red (FT-IR). Coating films of the prepared latexes were applied to flat glass surfaces and showed reasonable adhesion compared to PS latex particles prepared with conventional surfactants. The effect of employed conditions on the features of the resulting emulsions in terms of stability and particle size has been discussed.

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1. Introduction

The synthesis of structured organic/inorganic hybrid materials is an actual topic of research because they have many potential applications such as delivery systems, photonic crystals, optics, smart microelectronics, smart membranes, separation devises and functional materials (Fang et al., 2009). Hybrid organic–inorganic materials are not simply physical mixtures but they can be broadly defined as molecular or nanocomposites with organic and inorganic components, intimately mixed where at least one of the component domains has a dimension ranging from a few Å to several nanometers. Therefore, they present a combination of the advantageous properties of inorganic nanoparticles and organic or bioorganic materials. Organic/inorganic nanocomposites can be prepared by many methods such as micro-emulsion polymerization, soap-free emulsion polymerization, seeded emulsion polymerization and blending (Palkovits et al., 2005; Lee et al., 2007; Wang et al., 2006; Hwang et al., 2005). It is known that the presence of finely divided solids in processes involving contact of oil and water often results in the formation of solid stabilized emulsions (often referred to as Pickering emulsion). The fine solid powders situated at the surface of droplets form a spherical shell and impede coalescence when two droplets approach each other (Pickering, 1907; Binks and Lumsdon, 2000a; Sullivan and Kilpatrick, 2002; Kahn et al., 2002; Binks, 2002). As the characteristics of Pickering emulsions, the Pickering emulsion polymerization is a feasible way for the preparation of organic (core)/inorganic (shell) hybrid particles or inorganic hollow particles followed by the removal of the template core. It is recognized that the ordinary emulsion route needs relatively large amount of surfactants serving as emulsifiers and recycling the surfactants after polymerization is rather tedious. Pickering emulsion polymerization possesses many advantages including the reduction of foaming problem, lower toxicity and lower cost because of surfactant-free, and so has been extensively studied (Pickering, 1907; Binks and Lumsdon, 2000b,c, 2001; Binks et al., 2002, 2003, 2005, 2010; Binks and Fletcher, 2001; Zhang et al., 2009; Dyab, 2004).

There are several articles that discussed Pickering polymerization using many solid particles such as, nano-SiO_2, TiO_2, Fe_3O_4, $CaCO_3$, laponite, ZnO and clay. Chen et al. (2008) prepared ZnO/polystyrene composite particles using ZnO nanoparticles as a surfactant and different initiators such as the water-soluble potassium persulfate (KPS) and the oil-soluble 2,2-Azobis(isobutyronitrile) (AIBN) initiator. They also reported that, due to the difference of degree of hydrophilicity, AIBN-initiated system resulted in ZnO-shell and PS-core composite particles while KPS-initiated systems resulted in pure PS particles and composite particles with ZnO on the surface or ZnO embedded inside. Another finding was that the ZnO/PS composite particles showed a good pH adjusting ability and can serve as a potential pH buffering material. Luo et al. (2008) synthesized TiO_2/PS core-shell nanospheres by a novel combination of sol-gel and microwave-assisted emulsion polymerization method. They stated that, the obtained nanoparticles have smooth surfaces and the diameter and its distribution of the nanospheres are related to the concentration of the styrene monomer in the emulsion solution.

Bon et al. (2007) described a simple and effective method for the fabrication of organic–inorganic hybrid hollow spheres by a Pickering emulsion polymerization method, and the use of TiO_2 nanoparticles to form colloidosomes that may be used as the polymerization vessels. This type of hybrid hollow sphere can be used in the fields of drug release systems and photocatalytic applications. For example, a drug or any beneficial agent could be added into the formulation in combination with a monomer or reactive oligomer prior to the scaffolding polymerization process. Zhang et al. (2009) used Pickering emulsion polymerization to prepare PS/nano-SiO_2 composite microspheres by using organically modified nano-SiO_2 particles as stabilizer, the PS/nano-SiO_2 composites with core-shell structure and bare PS spheres were obtained at different synthetic conditions. They found that the particle concentration, particle wettability and pH value of particle dispersion have great effects on the morphologies of PS/nano-SiO_2 composites. The relatively low particle concentration or strong particle hydrophilicity or alkaline particle dispersion favored the formation of nano-sized bare PS spheres. A possible mechanism for the formation of the different morphologic composites was also proposed.

Wang et al. (2009) fabricated nanocomposite microspheres with (PS) cores and shells of Fe_3O_4 nanoparticles by Pickering suspension polymerization of styrene stabilized by Fe_3O_4 nanoparticles which acted as effective stabilizers during polymerization and as building blocks for creating the organic–inorganic hybrid nanocomposite after polymerization. The morphologies of magnetic PS microspheres were tunable and could be controlled via the method(s) by which the original Pickering emulsions were prepared due to their high stabilization during the suspension polymerization procedure.

Interestingly, Chen et al. (2010) synthesized polystyrene/zinc oxide (ZnO) hybrid microcapsules having polystyrene as inner shell and ZnO nanoparticles as outer shell by Pickering emulsion polymerization method. They observed the hollow structure and different morphologies obtained under different conditions by field emission scanning electron microscope. In addition, the photoluminescence property of PS/ZnO hybrid could be maintained without any noticeable variation by comparing to pure ZnO particles.

In this work, we employed laponite as solid inorganic nanoparticles as the sole stabilizing system for a polymerizable oil such as styrene followed by polymerization of the stabilized monomer emulsions to produce a type that may be considered as a fortified emulsion.

2. Experimental

2.1. Materials

Styrene, (C_8H_8), from Alpha Chemika (India), was purified and/or deinhibited by washing three times with NaOH (10%) aqueous solution with vigorous shaking, carefully removing NaOH solution using separation funnel then the obtained styrene was dried over anhydrous sodium sulfate (Na_2SO_4). Potassium persulfate (KPS), ($K_2S_2O_8$), from Cambrian chemicals, (purity = 97%). Laponite (RD) was provided by Southern Clay Products Texas, USA. According to the manufacturer, Laponite RD is a fully synthetic clay similar in structure and composition to natural hectorite of the smec-