



Novel synthesis with an atomized microemulsion technique and characterization of nano-calcium carbonate (CaCO₃)/poly(methyl methacrylate) core-shell nanoparticles

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ABSTRACT

The synthesis of hard-core/soft-shell calcium carbonate (CaCO₃)/poly(methyl methacrylate) (PMMA) hybrid structured nanoparticles (<100 nm) by an atomized microemulsion polymerization process is reported. The polymer chains were anchored onto the surface of nano-CaCO₃ through use of a coupling agent, triethoxyvinyl silane (TEVS). Ammonium persulfate (APS), sodium dodecyl sulfate (SDS) and n-pentanol were used as the initiator, surfactant and cosurfactant, respectively. The polymerization mechanism of the core-shell latex particles is discussed. The encapsulation of nano-CaCO₃ by PMMA was confirmed using a transmission electron microscope (TEM). The grafting percentage of the core-shell particles was investigated by thermogravimetric analysis (TGA). The nano-CaCO₃/PMMA core-shell particles were characterized by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The FTIR results revealed the existence of a strong interaction at the interface of the nano-CaCO₃ particle and the PMMA, which implies that the polymer chains were successfully grafted onto the surface of the nano-CaCO₃ particles through the link of the coupling agent. In addition, the TGA and DSC results indicated an enhancement of the thermal stability of the core-shell materials compared with that of the pure nano-PMMA. The nano-CaCO₃/PMMA particles were blended into a polypropylene (PP) matrix by melt processing. It can also be observed using scanning electron microscopy (SEM) that the PMMA chains grafted onto the CaCO₃ nanoparticles interfere with the aggregation of CaCO₃ in the polymer matrix (PP matrix) and thus improve the compatibility of the CaCO₃ nanoparticles with the PP matrix.

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1. Introduction

In recent years, considerable effort has been expended on the elaboration of core-shell nanoparticles (CSNPs). Microemulsion polymerization is a unique process for producing CSNPs of nanosize scale (Aguilar, Gonzalez-Villegas, Rabelero, Mendizábal, & Puig, 1999). CSNP core/shell composite materials consist of a core structural domain covered by a shell domain (Fleming, Mandal, & Walt, 2001), which may be composed of a variety of materials including polymers, inorganic solids, and metals (Wang, Liu, Ohnuma, Kainuma, & Ishida, 2002; Wang et al., 2007). Such materials have been widely used in some fields, such as paints (Li, Jones, Dunlap, Hua, & Zhao, 2006; Nishizawa, Nishimura,

Saitoh, Fujiki, & Tsubokawa, 2005), cosmetics (Chen, Rajh, Wang, & Thurnauer, 1997; Hong, Li, & Pan, 2007; Ringward & Pemberton, 2000), coatings (Nishizawa et al., 2005; Rajh, Tiede, & Thurnauer, 1996), adhesives (Dong et al., 2008), industrial electronic materials (Bawden & Turner, 1988), reinforcement of rubber/plastics (Kato, Uchida, Kang, Uyama, & Zkada, 2003) and biochemistry (Galperin & Margel, 2007), because the integrated properties of such materials are better than those of their single component counterparts (Hall, Davis, & Mann, 2000). The method generally used to synthesize core-shell particles is stepwise emulsion polymerization (Chen, Qian, & Zhang, 2008; Erdem, Sudol, Dimonie, & El-Aasser, 2000; Liu, Ye, Lin, & Zhou, 2008; Liu, 2006; Yang & Lu, 2005), in which latex core particles are produced in the first step, and the shell polymer is produced in the second step. In this method, the core particles act as “seed particles”, on the surface of which the shell polymers are supposed to be dispersed. During emulsion polymerization, the surfactant plays a major role by stabilizing

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the dispersion medium. In the conventional emulsion polymerization process (Ni et al., 2005; Zhu, Shi, Cai, Zhao, & Liao, 2008), the in situ emulsion polymerization process (Chen, Liu, Zhang, & Wang, 2007; Ding et al., 2004; Li et al., 2007; Liu et al., 2008), and the miniemulsion process (Antonietti & Landfester, 2002; Asua, 2002; Crespy & Landfester, 2009; Erdem et al., 2000; Rabelero et al., 2005; Topfer & Schmidt-Naake, 2007; Zyl, de Wet-Roos, Sanderson, & Klumperman, 2004), the percentage of surfactant is low, resulting in an insufficient number of micelles to provide sufficient protection for single inorganic particles. Thus, during polymerization, there is a high possibility of agglomeration of and instability in the dispersion, resulting in less encapsulation of the inorganic particles by the polymer matrix.

Recently, we have synthesized polystyrene nanoparticles (nPS) and poly(methyl methacrylate) (nPMMA) particles by a modified microemulsion polymerization process (Mishra & Chatterjee, 2011a) as well as a novel atomized microemulsion process (Mishra & Chatterjee, 2011b), and the isolated nPS and nPMMA particles were blended with polypropylene (PP) (Chatterjee & Mishra, 2012; Mishra & Chatterjee, 2011b) and linear low-density polyethylene (LLDPE) (Mishra, Chatterjee, & Rana, 2011) to study their rheological, thermal and mechanical properties. In our previous work (Mishra, Chatterjee, & Singh, 2011), we have successfully prepared nano-CaCO₃/PS core-shell particles, with CaCO₃ as a core and PS as a shell, by an atomized polymerization technique, and the isolated CSNPs were incorporated in a PP matrix.

This present work is an extension of our previous work to develop an efficient process for the production of nano-CaCO₃/PMMA core-shell nanoparticles by the atomized microemulsion process. Furthermore, we have also focused on improving the performance of the (nano-CaCO₃/PMMA)/PP nanocomposites by enhancing the interfacial adhesion by adding a small amount (1 wt.%) of encapsulated nano-CaCO₃. Thus, this approach will improve the compatibility of the nano-CaCO₃ with the polymer matrix through the lipophilic polymer layer (PMMA

layer) grafted onto the surface of the nano-CaCO₃. The polymer shell coatings not only prevent the aggregation of nanoparticles but also produce excellent compatibility between the filler particles and the polymer matrix (Shen, Lin, Li, & Nan, 2007).

2. Experimental

2.1. Materials

Nano-CaCO₃ particles with diameters in the range of 10–50 nm were synthesized by the solution spray process reported elsewhere (Kulkarni, Patil, Ghosh, & Mishra, 2009; Mishra, Kulkarni, Patil, & Ghosh, 2009). The nanoparticles were modified by the silane coupling agent, triethoxyvinyl silane (TEVS). The monomer, methyl methacrylate (MMA); the initiator, ammonium persulfate (APS); the surfactant, sodium dodecyl sulfate (SDS); and the cosurfactant, n-pentanol, were purchased from S.D. Fine Chemicals Ltd., Mumbai, India. MMA was treated with a 5% NaOH aqueous solution to remove the inhibitor and was distilled under reduced pressure in a nitrogen atmosphere prior to polymerization. All other materials were of analytical grade and were used without further purification. Water was double distilled and deionized.

2.2. Surface modification of the nano-CaCO₃

TEVS was used for the modification of the nano-CaCO₃ particles. First, the desired amount of silane coupling agent, i.e., TEVS (5 phr with respect to weight of CaCO₃) was dissolved in acetone, and 20 g of nano-CaCO₃ particles was dispersed in the silane-acetone mixture under mechanical stirring at 500 rpm. The mixture was then sonicated for 1 h and stirred at 500 rpm at room temperature for 2 h. The TEVS and CaCO₃ reacted in the dispersion overnight. Afterwards, the surface modified nano-CaCO₃ particles were collected by filtration and rinsed four times with acetone, and the filter cake was dried at 100 °C under low vacuum for 12 h.

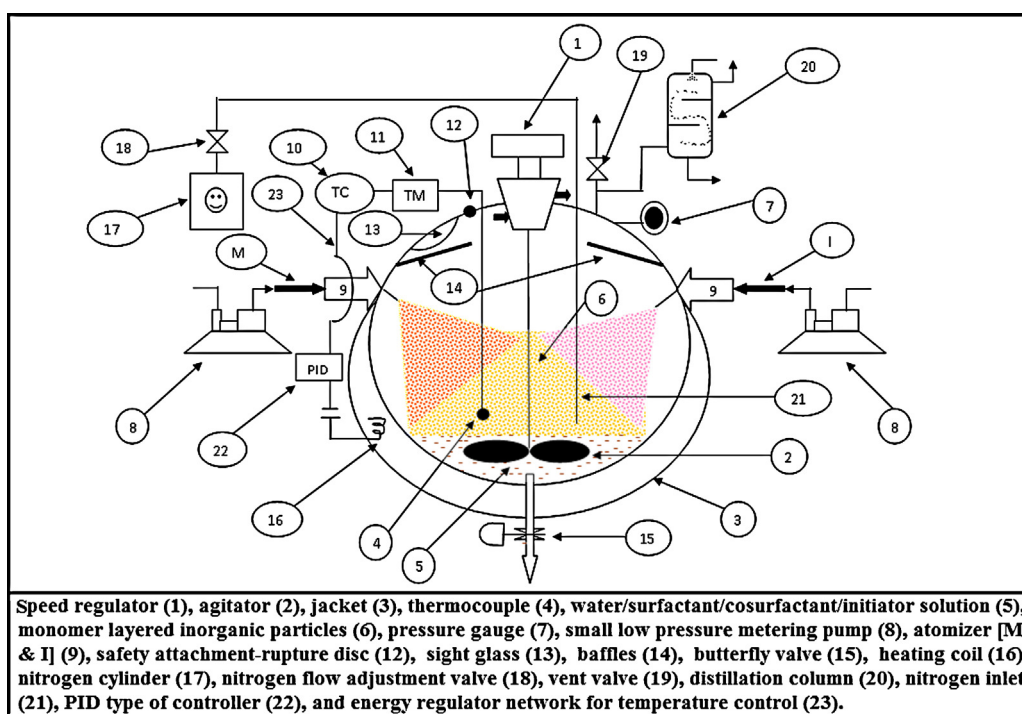


Fig. 1. Atomized reaction vessel for synthesis of nano-CaCO₃/PMMA core-shell particles via the atomized microemulsion technique.

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