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A comparative study of poly(methyl methacrylate) and polystyrene/clay nanocomposites prepared in supercritical carbon dioxide

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Abstract

Poly(methyl methacrylate) and polystyrene/clay nanocomposites have been prepared via pseudo-dispersion polymerizations in the presence of a poly(dimethylsiloxane) surfactant-modified clay (PDMS-clay) in supercritical carbon dioxide. The effects of the PDMS-clay concentration on polymer conversion, molecular weight, and morphology have been investigated. The insoluble dispersion of PDMS-clay is shown to be an effective stabilizer for both MMA and styrene polymerization in $scCO_2$. The nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). While XRD shows featureless patterns for both nanocomposites, the actual distributions of clay are found to be quite different between PMMA and PS nanocomposites, presumably due to the different interaction mechanisms between the polymers and clay. Consequently, the different states of clay in the two nanocomposites play an important role in the mechanical properties of the nanocomposites, and a to a lesser degree in the thermal properties.

Keywords: Nanocomposites; Carbon dioxide; Polymerization

1. Introduction

Polymer/clay nanocomposites in which a small percentage of layered silicates are embedded in a polymer matrix are of interest because they exhibit enhanced material properties compared to the neat polymer [1]. Among various approaches used to prepare nanocomposites, in situ polymerization has proved to be the most successful one, pioneered by researchers from Toyota Motor Company who synthesized the first exfoliated nylon-6/clay hybrid for automotive applications [2]. Since then, several useful vinyl polymer/clay nanocomposites have been prepared via in situ polymerization, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) nanocomposites [3,4]. In order to render clay organophilic and more compatible with organic polymers, the sodium ions of the pristine clay are usually replaced with an alkylammonium surfactant via an ion exchange reaction. By using two different organically modified clays, Wang and coworkers prepared poly(methyl methacrylate)/clay nanocomposites and polystyrene/clay nanocomposites via bulk, solution, suspension and emulsion polymerization [5]. Both exfoliated and intercalated nanocomposites were obtained, depending on the organic treatments of clay as well as the particular preparative method that was used. The exfoliated nanocomposites exhibited superior thermal stabilities and mechanical properties compared to the pure polymers, generally attributed to the uniform dispersion of clay silicate layers in the polymer matrix. However, a drawback of in situ polymerization is that it typically involves large quantities of aqueous/organic solvents which are both environmentally unfriendly and economically prohibitive for an industrial-scale application.

On the other hand, supercritical carbon dioxide ($scCO_2$) has attracted extensive interest as a polymerization and processing medium, primarily driven by the need to replace conventional solvents with more environmentally benign and economically viable systems [6]. One area of interest has been the dispersion polymerization of vinyl monomers, which has been pioneered by DeSimone et al., who reported the first dispersion polymerization of methyl methacrylate in $scCO_2$ [7]. Because the product, poly(methyl methacrylate) is insoluble in $scCO_2$, they used a CO_2-soluble fluorinated homopolymer (poly(dihydroperfluorooctyl acrylate) PFOA) as the stabilizer for the polymerization system. Consequently, the successful dispersion

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polymerization led to a significant improvement in the yield, molecular weight and morphology of the resultant polymer.

Typically, an effective stabilizer for CO_2 polymerizations should have two prerequisites: (1) an anchoring segment which attaches to the monomer/polymer particle either through physical adsorption or chemical grafting; (2) a CO_2-philic (fluorinated- or siloxane-based) segment which projects into the continuous CO_2 phase and provides steric stabilization for the growing polymer particles. Many sophisticated stabilizers ranging from fluorinated and siloxane-based block or graft copolymers [8–10], siloxane-based macromonomers [11], to more recent monofunctional perfluoropolyethers [12] have been utilized.

Recently, Zerda et al. used the in situ polymerization route to prepare highly filled PMMA/clay nanocomposites in $scCO_2$ [13]. In their work, CO_2 was primarily used to lower the viscosity resulting from high loadings (up to 40%) of clay; the clay was modified by conventional hydrocarbon surfactants and resulted in intercalated PMMA/clay nanocomposites. More recently, Dong and coworkers employed a similar in situ polymerization technique to prepare intercalated PS/clay nanocomposites with a more conventional loading (1–10%) of clay in $scCO_2$ [14]. They also modified clay with a hydrocarbon surfactant and found that a longer 'soaking time' during the impregnating process can lead to more exfoliated nanocomposites. Nevertheless, in both studies, no information on the yields or morphologies of the polymers has been mentioned, nor was it clear why in situ polymerization with clay can produce nanocomposites in higher yields while polymerizations in the absence of stabilizer typically result in a non-descriptive, low-yield oligmer in $scCO_2$ [7]. Furthermore, by using hydrocarbon surfactant-modified clay in the two studies, only intercalated nanocomposites have been obtained regardless of the concentration of clay.

We recently reported a route to produce partially exfoliated poly(methyl methacrylate)/clay nanocomposites via in situ polymerization in $scCO_2$, in which we found that the fluorinated surfactant-modified clay can itself serve as a stabilizer and help produce PMMA in high yields in $scCO_2$ [15]. Although the clay is not soluble in CO_2, the stabilization mechanism is similar to that in a conventional dispersion polymerization; FT-IR results indicated hydrogen bond formation between the carbonyl group of the MMA monomer and hydroxyl groups and/or interlayer water of the clay. We referred to this technique as a pseudo-dispersion polymerization. In this paper, we report the use of a different system, a commercially-available surfactant aminopropyl-terminated poly(dimethylsiloxane) (AP-PDMS) modified clay as the stabilizer for the pseudo-dispersion polymerization of methyl methacrylate and styrene in $scCO_2$. This PDMS-based surfactant is known to be CO_2-philic and its longer siloxane chain is expected to provide better steric stabilization compared to the shorter fluorinated chain used previously. Furthermore, we extend our system to polystyrene (PS), which does not have a hydrogen bonding site as PMMA does. Having different interaction mechanisms with clay, PMMA and PS are two model systems that allow us to study the effects of a clay-based stabilizer on both hydrogen-bonding polymers (e.g. PMMA) and non-hydrogen-bonding polymers (e.g. PS). In this paper, the effects of PDMS-clay on the morphologies and properties of PMMA and PS nanocomposites are compared. Two stabilization mechanisms are proposed to account for the different microstructures and mechanical properties between PMMA and PS nanocomposites.

2. Experimental

2.1. Materials

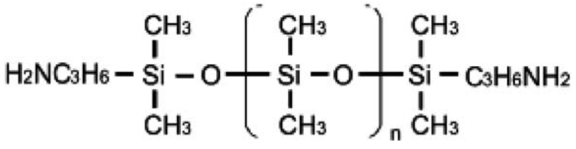
Sodium montmorrillonite (Na-MMT) was obtained from Gelest, Inc and used as received. Dimethyldistearylammonium bromide were supplied by TCI America and used as received. Aminopropyl-terminated poly(dimethylsiloxane) ($M_w = 3500$, structure shown in Fig. 1) was obtained from United Chemical Technologies, Inc. Methyl methacrylate and styrene were purchased from Aldrich Chemical Company and purified by distillation before use. The free radical initiator, 2,2-azobis(isobutyronitrile) (AIBN) was supplied by Polysciences, Inc. PMMA ($M_w = 350$ kDa) and PS ($M_w = 150$ kDa), used as controls, were obtained from Aldrich Chemical Company.

2.2. Modification of clay

Aminopropyl-terminated poly(dimethylsiloxane) was acidified with hydrochloric acid in tetrahydrofuran (acidification ratio = 1/2). The cation exchange procedure was followed using previously described methods [16]. The resultant organoclay was obtained as a yellowish sticky solid, and was denoted 'PDMS-clay'. For comparison, we also modified the clay with a hydrocarbon surfactant dimethyldistearylammonium bromide. The modified clay is comparable to a commercially-used clay (Cloisite 20A from Southern Clay) and was denoted '2C18-clay'. The organic content in PDMS-clay and 2C18-clay was determined to be 65 and 40% respectively, according to thermogravimetric analysis.

2.3. Polymerization

Polymerizations were conducted in CO_2 in a 2.5 ml, high-pressure cell equipped with sapphire windows that allow visual observation of the mixture. In a typical polymerization, the initiator AIBN and PDMS-clay were weighed into the cell containing a magnetic stir bar. The cell was purged with CO_2 via an Isco automatic syringe pump (Model 260D) for a few minutes; then the monomer was injected into the cell. The cell was then filled with CO_2 to 70 bar, and heated to 65 °C. After the desired temperature was reached, the desired pressure was



$$H_2NC_3H_6-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-C_3H_6NH_2$$

Fig. 1. Aminorpropyl-terminated PDMS (AP-PDMS, $n \sim 44$).