SURFACE MODIFICATION OF MONTMORILLONITE AND APPLICATION TO THE PREPARATION OF PMMA/MONTMORILLONITE NANOCOMPOSITES IN SUPERCRITICAL CARBON DIOXIDE

Md. Daloar Hossain, Ha Soo Hwang, Min Young Lee, and Kwon Taek Lim*

Division of Image and Information Engineering, Pukyong National University, Busan 608-739, Korea
E-mail: ktlim@pknu.ac.kr
Fax: +82-51-625-2229

ABSTRACT

Partially exfoliated poly (methyl methacrylate) (PMMA) / montmorillonite clay nanocomposite was synthesized via the free radical polymerization of MMA in the presence of alkyl ammonium substituted polysilsesquioxane surfactant-modified clay and AIBN initiator in supercritical CO2. MMT clay was initially cation exchanged with the surfactant to enhance its hydrophobicity and to expand the interlamellar spaces of silicate platelets. The 3-D structured surfactant reduces surface energy of the clay dramatically which promotes miscibility of polymer/clay nanocomposite. The intercalation and dispersion of clay were quantified by both X-ray diffraction and transmission electron microscopy. The reaction was also conducted in aqueous ethanol solvents in order to compare the morphologies of nanocomposites obtained from different solvents.

INTRODUCTION

Layered silicate based nanocomposites have received considerable attention in recent years as an effective method of enhancing polymer properties, e.g. increased stiffness and strength, improved gas barrier resistance, superior thermal and fire stabilities. Montmorillonite, the most preferred and widely used smectic clay is of particular interest because it offers a high aspect ratio (10-1000) and a high surface area. Due to an isomorphic substitution within the layers, the clay layer is negatively charged, which is counterbalanced by cations in the interlayer space.

The natural montmorillonite is hydrophilic and is generally considered unsuitable for hosting non-polar organic molecules without prior treatment. Interlayer cations can be exchanged with organic cations to obtain organophilic montmorillonite producing an ‘organoclay’, which has an expanded interlayer spacing and more readily produces a polymer–clay nanocomposite. Employing suitable surfactants with simple ion-exchange reactions could achieve different natures of morphologies: intercalated, intercalated and flocculated and exfoliated. Although the exfoliated structures are usually claimed to have the most significant property improvements, there are in reality very few unequivocal
examples because the strong electrostatic force between clay layers tends to hold them together and underlies the preferred face-to-face stacking geometry in agglomerated clay tactoids. On the other hand, partially exfoliated nanocomposites are more readily produced having silicate layers exfoliated into secondary particles which contain several stacked, coplanar layers. Moreover, such mixtures of partially exfoliated/intercalated structures exhibit enhanced properties, i.e., high modulus and impact strength, etc, especially when these secondary particles are uniformly dispersed in the polymer matrix. The change in surface energy shows the variation of wetting characteristics of the clay surface with polymers or monomers which ultimately affect the composites properties. In general, most of the traditional surfactants are linear forms; even though the interlayer d-spacing can be increased, they still retain the intercalated features of nanocomposites. Theoretically incorporating a 3-D structure into a layered silicate should have a significant influence on the intercalated technique. Singh and Balazs had studied the effect of polymer architecture in polymer/clay nanocomposites by using linear and branching units. At the same molecular weight, a linear structure tends to be intercalated by increasing the extent of branching units. Consequently the free energy of interaction between surfactants and MMT is decreased resulting exfoliation of layered silicates. Ru-Jong Jeng and coworkers showed montmorillonite-intercalated behavior of 3-D structured dendritic surfactants. Herein they achieved large d-spacings of intercalation or direct exfoliation by different 3-D structures and hydrophobicity of dendritic surfactants.

The surfactant-modified clay is used in many polymer/clay nanocomposites prepared via in situ polymerization. However, a drawback of this method is that it usually involves large quantities of aqueous/organic solvents as the polymerization medium, which is both environmentally unfriendly and economically prohibitive for an industrial-scale application. Supercritical carbon dioxide (scCO₂), on the other hand, 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 procedures. 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 scCO₂. Because the product, poly(methyl methacrylate) is insoluble in scCO₂, they used a CO₂-soluble fluorinated homopolymer (poly(dihydroperfluoroctyl acrylate) PFOA) as the stabilizer for the polymerization system. Consequently, the successful dispersion polymerization led to a significant improvement in the yield, molecular weight and morphology of the resultant polymer. Many sophisticated stabilizers ranging from fluorinated and siloxane-based block or graft copolymers, siloxane-based macromonomers, to more recent monofunctional perfluoropolyethers have been utilized. In this manuscript, we report the polymerization of MMA in presence of synthesized alkyl ammonium substituted polysilsesquioxane (QPSSQ) surfactant-modified clay.
EXPERIMENTAL

Alkyl ammonium substituted polysilsesquioxane (QPSSQ) surfactant (Fig. 1) was synthesized according to the synthetic route described elsewhere. Organophilic clay was prepared by the ion exchange reaction. Na⁺-MMT (5 g) was dispersed in 500 ml deionized water and the dispersion was stirred vigorously overnight. 5 g of QPSSQ was dissolved in 200 ml deionized water. The QPSSQ solution was slowly added into the clay suspension, the mixture was stirred for 24 h at room temperature. The ion-exchanged clay was filtered, thoroughly washed with deionized water several times and dried at 50º C in a vacuum oven. This organically modified MMT is denoted as OMMT. Polymerizations were conducted in scCO2 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 QPSSQ-clay were weighed into the cell containing a magnetic stir bar. The cell was purged with CO2 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 CO2 to 70 bars, and heated to 65º C. After the desired temperature was reached, the desired pressure was achieved by the addition of more CO2. The reaction was allowed to proceed with stirring for a specific time, and then the cell was cooled and the CO2 was slowly vented. Unless specified, the final product was taken out and dried at room temperature in a vacuum oven overnight. Nanocomposites were also synthesized by bulk polymerization and dispersion polymerization in ethanol (95%)/water to compare with that obtained in scCO2 at same clay loading.

RESULT AND DISCUSSION

Exfoliation of the pristine montmorillonite is impeded by electrostatic attraction between the negatively charged clay layer and the cations, such as Na⁺ and Ca²⁺ in the gallery. Therefore a pretreatment is usually necessary for the preparation of exfoliated MMT composites. In this work alkyl ammonium substituted polysilsesquioxane (QPSSQ) is used as a modifier for the clay. This 3-D structured surfactant has cubic silsesquioxane moiety on both terminal positions of the molecule. When treated with this surfactant, the surface of the original inorganic MMT become organophilic and the interlayer galleries are also enlarged. At the same time larger size clay bundles split to small

Fig. 1. Chemical structure of alkyl ammonium substituted polysilsesquioxane (QPSSQ).
tactoids. Small MMA monomers can easily enter into the galleries due to long alkyl chain of 3-D structured surfactant and highly dispersive scCO\textsubscript{2} solvent. Although scCO\textsubscript{2} is not suitable for the dispersion of clay, the QPSSQ-modified clay formed a milk-like suspension under magnetic stirring. As the reaction proceeded, the suspension appeared to thicken, and precipitated powder accumulated on the windows. During the polymerization in the galleries, the small MMA molecules grow to form PMMA macromolecules together with releasing a large quantity of heat. The size of the PMMA macromolecule chains is much larger than the gallery space of the clay. According to the intercalative polymerization mechanism, the interlayer spacing of MMT should be enlarged and exfoliated by the growing PMMA macromolecule chains and uniformly dispersed in the PMMA matrix. The process is schematically shown in Fig. 2. The evidence of the proposed mechanism is provided by XRD and TEM results in Fig. 3 and 4.

By using the Bragg equation, the d (001) spacing values of the samples were calculated and shown besides each peak. After the cation exchange with QPSSQ, the d-spacing was expanded from 12.0 Å (A) to 20.97 Å (B). As is seen from curve D and E, the d-spacing of PMMA/MMT nanocomposites prepared in ethanol/H\textsubscript{2}O and in scCO\textsubscript{2} are found to be two different values which indicate the intercalation and subsequent polymerization of MMA inside inter-gallery spaces. A significant portion of clay platelets were exfoliated along with intercalated which was confirmed by TEM analysis in Fig. 4. The ratio of PMMA intercalated part in the case of scCO\textsubscript{2} is greater than that of ethanol/H\textsubscript{2}O as evidenced by XRD. This proves more dispersive property of scCO\textsubscript{2} compared to ethanol/H\textsubscript{2}O solvent. On the other hand, 5 % water is responsible for decreasing surface energy of clay platelets leading to weaker forces between the layers, which might facilitate exfoliation.\textsuperscript{16} In the bulk polymerization (curve C in Fig. 3 and image b in Fig. 4) there is no significant intercalation of MMA monomer into the inter-gallery spaces.

Fig. 2. Scheme of the formation of PMMA/MMT nanocomposite particles in scCO\textsubscript{2} and in ethanol/water solvent.
Fig. 3. XRD pattern of (A) Na⁺-MMT; (B) OMMT; (C) PMMA/MMT prepared in bulk polymerization (D) PMMA/MMT prepared in ethanol/water; (E) PMMA/MMT prepared in scCO₂

Fig. 4. TEM images of (a) Organically modified MMT (b) PMMA/MMT nanocomposites prepared in bulk polymerization (c) PMMA/MMT nanocomposites prepared in scCO₂ (d) PMMA/MMT nanocomposites prepared in ethanol/H₂O.
CONCLUSION

PMMA/clay nanocomposites have been synthesized via a novel polymerization technique in scCO₂. It has been found that the polymerization media greatly affects the dispersion of organically modified clay resulting different distributions of clay that seems to play an important role in mechanical properties of the nanocomposites. Although in scCO₂ organically modified clay was not dispersed well, MMA could easily be dispersed through interlayer spaces of the clay due to having available space for 3-D surfactant and high dispersive scCO₂ solvent for MMA. On the other hand, in ethanol/water solvent, clay dispersed very well which resulted in exfoliated and intercalated PMMA/MMT nanocomposite mixture. However, our experimental results revealed that better intercalated PMMA/MMT nanocomposites could be obtained by the polymerization of MMA in scCO₂.

REFERENCES