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Isothermal crystallization of lightly sulfonated syndiotactic polystyrene/montmorillonite clay nanocomposites

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ABSTRACT

Lightly sulfonated syndiotactic polystyrene (sPS) nanocomposites were prepared using a solution intercalation technique, and the effect of montmorillonite clay on the crystallization kinetics of sulfonated sPS ionomer nanocomposites was systematically studied. Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to evaluate the dispersion of clay platelets within sPS and sulfonated sPS ionomer (SsPS) matrices. Experimental results obtained from WAXD and TEM revealed a predominately exfoliated morphology within the SsPS ionomer containing 5 wt.% of organically-modified clay. The corresponding non-sulfonated sPS control exhibited a mixed morphological structure consisting of intercalated platelets and many platelets that were present as micron-sized agglomerates. Using differential scanning calorimetry (DSC), the Avrami approach was used to elucidate information related to nucleation and growth within the sPS and SsPS systems during the isothermal crystallization process. Pristine and organically-modified clays significantly increased the overall crystallization rate of the SsPS ionomer, while the nanoclays slightly decreased the crystallization rate of the non-ionic sPS. The mechanistic origins of increased crystallization rates within the SsPS ionomer clay nanocomposites were attributed to multiple phenomena including disruption of the ionomer electrostatic network and a nucleating effect due to the presence of well-separated, homogeneously dispersed clay platelets.

1. Introduction

Polymer/clay nanocomposites are very important materials from an industrial perspective due to the potential material property enhancements that can be realized with only a small addition of properly dispersed nanoscale clay platelets [1,2]. Therefore, a significant amount of research has been focused on the preparation of polymer/clay nanocomposites using industrially important semicrystalline polymers such as polypropylene [3,4], polyethylene [5,6], polyesters [7–10], polyamides [11,12], and syndiotactic polystyrene [13–23]. However, the organophillic character of many industrially important semicrystalline polymers prevents sufficient interaction between the polymer and clay resulting in poor dispersion of the naturally polar aluminosilicate clay within the hydrophobic polymer matrix.

Ion-containing polymers (specifically, ionomers containing less than ca. 10 mol% ionic functionality along the chains) have been investigated as the host matrix for the preparation of polymer/clay nanocomposites [24,25] and as compatibilizers between a host matrix and clay platelets as well [26–28]. The advantage of utilizing ionomers as matrices and compatibilizers in polymer/clay nanocomposites originates from strong specific interactions that can occur between the ionic groups of the ionomer and the highly charged, polar clay surface. The improved interaction between the ion-containing polymer and polar clay through favorable electrostatic interactions may facilitate the development of intercalated and exfoliated morphologies. The resultant intercalated and exfoliated morphologies reveal and expose the high clay surface area necessary to realize enhanced mechanical, thermal, and barrier properties [24,25].

Initial demonstration of the effectiveness of ionomers as host matrices for the preparation of polymer nanocomposites was provided by Chisholm et al. [24]. This study revealed that incorporation of as little as 1.0 mol% $-SO_3Na$ groups onto poly(butylene terepthalate) (PBT) resulted in the formation of an exfoliated morphology of organically-modified montmorillonite clay platelets that were well-dispersed throughout the PBT ionomer matrix. Polyester ionomer clay nanocomposites have also been prepared using poly(ethylene terepthalate) (PET) containing up to 5.8 mol% sodium sulfonate ionic groups [25]. Barber et al. have shown that

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incorporation of low levels of sodium sulfonate groups into PET along with the utilization of organically-modified montmorillonite clay results in the formation of highly intercalated and exfoliated ionomer clay structures. This study using PET ionomers, supported the previous work completed by Chisholm and coworkers using PBT ionomers and further demonstrated that ionomers may be used as matrices to create intercalated and exfoliated polymer nanocomposites.

Since the initial work of Chisholm et al., further research has been conducted using ionomers as host matrices for the development of polymer nanocomposites. Nanocomposites have been prepared using ionomers based on polypropylene, polyethylene [29], and polystyrene [30]. Important aspects of ionomer nanocomposite preparation have been investigated such as the effects of ionic functionality on clay platelet dispersion [25], the effects of melt processing on the degree of exfoliation [31], and the effect of surfactant structure [32] on the ionomer nanocomposite morphology. However, in order for semicrystalline ionomer nanocomposites to be effectively used in industrial and commercial applications, a detailed understanding of the effect of clay on the crystallization behavior of the ionomer matrix is of fundamental importance.

Our initial ionomer nanocomposite studies [24,25] provided information on the effect of tactoid, intercalated, and exfoliated morphological clay arrangements on the crystallization behavior of polyester ionomers. However, conflicting information was obtained from the study of the polyester based ionomer nanocomposites systems based upon poly(ethylene terepthalate) and poly(butylene terepthalate). It was found that the crystallization half-time (the time required for the material to reach 50% crystallinity during isothermal crystallization) slightly increased for PBT ionomer nanocomposites. The increase in crystallization half-time suggested the overall rate of bulk crystallization is decreased and clay did not act as a nucleating agent within the PBT ionomer matrix. Moreover, isothermal crystallization data of PBT ionomer nanocomposites revealed the crystallization half-time was not dependent upon the morphological state of the dispersed clay particles. In contrast, Barber et al. [25] found the crystallization behavior of PET ionomer nanocomposites to be dependent upon the degree of clay exfoliation within the ionomer matrix. The crystallization half-time of PET ionomer nanocomposites increased with increasing degree of clay exfoliation indicating the exfoliated nanoscale platelets are less effective nucleants relative to micron-sized clay tactoids.

Due to the contrasting effect of clay on the crystallization kinetics and behavior of semicrystalline PBT and PET ionomers, it necessary to further study the effect of clay on the crystallization behavior and kinetics of a *model* semicrystalline ionomer. Sulfonated syndiotactic polystyrene (SsPS) has been utilized as a model semicrystalline ionomer in fundamental investigations studying the link between ionic aggregation and crystallization behavior of ionomers [33–36]. Since the ionic species of SsPS are incorporated through a post-polymerization sulfonation reaction and not through copolymerization (as with previous studies), varying the ionic content does not significantly disrupt the microstructure and molecular weight distribution of the resulting SsPS copolymer. Additionally, a significant advantage of utilizing SsPS as a model semicrystalline ionomer results from the high stereoregularity of sPS, which allows it to crystallize rapidly from the melt. The wealth of fundamental information on the crystallization behavior of sulfonated sPS provided by these studies renders it a prime candidate for a detailed study of the effect of clay on the crystallization behavior and kinetics of semicrystalline ionomers in general.

In a previous study, the preparation and characterization of SsPS nanocomposite morphology has been reported as a function of ionic content and neutralizing counterion [37]. It was shown that the degree of clay exfoliation increased with increasing ionic content and with increasing size of the neutralizing counterion. This study provided initial qualitative observations on the non-isothermal crystallization behavior of SsPS nanocomposites by monitoring the peak crystallization temperature on cooling from the melt. However, a more detailed quantitative study of the effect of clay on the crystallization behavior and kinetics of SsPS is needed to gain further insight into the possible mechanism of crystallization of the SsPS ionomer in the presence of montmorillonite clay. Thus, the purpose of this study is to determine the effect of pristine and organically-modified clay on the morphology, crystallization behavior, and isothermal crystallization kinetics of SsPS, a model semicrystalline ion-containing polymer.

2. Experimental

2.1. Materials

Syndiotactic polystyrene (Questra 102) MW of 310,000 g/mol was donated by the Dow Chemical Company. Reagent grade chloroform, 1,1,2-trichlorobenzene (TCB), methanol, sulfuric acid, and potassium monopthalate were obtained from Fisher Scientific. Hexanoic anhydride and cesium hydroxide were received from Sigma Aldrich. Cloisite® Na^+ and Cloisite® 10A were donated by Southern Clay Products. The clays were used in the received state without additional drying. The cation exchange capacities for Cloisite® Na^+ and Cloisite® 10A are 92.6 and 125 and milliequivalents/100 g, respectively. The organic modification agent for Cloisite® 10A is a quaternary amine salt consisting of a dimethylbenzyl, hydrogenated tallow. The hydrogenated tallow is made up of ~65% C18, ~30% C16, and ~5% C14 chains. Cloisite®10A has been shown to produce intercalated and exfoliated nanostructures in many styrenated polymer matrices [13,38–41] and is thus a proper choice for enhancing polymer clay interactions in the sPS matrix. Cloisite® Na^+ and Cloisite® 10A will be identified as Na^+MMT and OMMT respectively. The clay organic modification agent, Arquad DMHTB-80E was donated by Akzo Nobel Surface Chemistry, LLC.

2.2. Sulfonation of syndiotactic polystyrene

Previous differential scanning calorimetry (DSC) investigations of SsPS ionomers have identified the effect of the degree of sulfonation on the crystallization behavior of SsPS [34]. It has been demonstrated that incorporating greater than 2.0 mol% of ionic content within sPS drastically inhibits the ability of sPS to crystallize. Therefore, we have chosen to lightly sulfonate sPS to yield an ion-containing polymer with 1 mol% sulfonation. By introducing 1 mol% sulfonate groups, the crystallization kinetics of SsPS occurs on a readily observable timescale at crystallization temperatures similar to that of the sPS homopolymer. Thus, direct comparisons between the behavior of the SsPS ionomer and the sPS homopolymer can be made.

The sulfonation agent was prepared according to previously published procedures [34] using chloroform as the solvent. Chloroform (25 mL) was added to a 50 mL volumetric flask containing 0.03 mol of hexanoic anhydride. The chloroform/hexanoic anhydride solution was cooled in an ice bath for 1 h, and then 1 mL of concentrated sulfuric acid was added to the chilled solution and shaken vigorously. Additional chloroform was added to the volumetric flask to the 50 mL mark.

sPS was dissolved in chloroform at 100 °C for 1.5 h in a PARR pressure reactor to yield a 2.5% w/v solution. After 1.5 h, the solution was cooled to 70 °C and then transferred to a three-neck round bottom flask. Additional chloroform was added to yield a 1% w/v sPS solution. The sPS solution was allowed to equilibrate at 70 °C