Suspension Polymerization of Inverse Emulsion of Water Expandable Polystyrene/Clay Nanocomposites

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Introduction

Recently, considerable efforts have been spent on the research of polymer/clay nanocomposite foams [1-7]. As compared to the conventional foams, nanoclay-reinforced polymeric foams offer great potential for the enhancement of both mechanical and physical properties. In order to improve the compatibility between the hydrophilic nanoclay and the hydrophobic polymers, the clay surface is often modified by surfactants, usually quaternary ammonium compounds, to render the clay surface hydrophobic. The quaternary ammonium, however, is considered fire hazards based on industry fire tests, such as oxygen index and flame surface spread rates Therefore, it is highly desirable to achieve uniform clay dispersion in the polymer matrix while avoiding the use of fire hazardous surfactants.

In this work, the typical process used to synthesize water expandable polystyrene (WEPS) [8-10] was modified and applied to prepare polystyrene/clay nanocomposites. A raw nanoclay, sodium montmorillonite (Na^+-MMT), was dispersed in water and a uniform clay dispersion can be achieved due to the hydrophilicity of the natural clay surface. The water/clay mixture was then emulsified in the pre-polymerized styrene/PS mixture to form water-in-oil (w/o) inverse emulsion, with the aid of an amphiphillic and non-flammable surfactant. Subsequently, the viscous inverse emulsion was suspended in water in the presence of suspension stabilizers that can be removed after the completion of polymerization. The polymer products were spherical PS beads with myriads of water/clay droplets inside. Upon heating via the hot medium, the PS matrix was expanded by the vapor pressure of water and the foam products were obtained.

The blowing agent (water) is environmentally benign and non-flammable. In addition, according to HMIS (Hazardous Materials Identification System) and NFPA (National Fire Protection Association) ratings, the surfactant (AOT) used in this process is also non-flammable. Thus the ultimate polymer/clay nanocomposite foams overcome the fire-hazard of the nanocomposites through traditional approaches and meet the stringent requirements for industrial fir resistance applications.

Experimental

Materials. The styrene monomer was purchased from Aldrich and used as received. 2,2'-azobis (isobutyronitrile) (AIBN) and dibenzoyl peroxide (BPO), which have half time (t1/2) at 90°C of 25 mins and 145 mins, respectively, from Aldrich were used as initiators. The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was supplied by Fluka and used as received. The suspension stabilizer hydroexyethyl (HEC) and polyvinyl alcohol (PVA) were supplied by Aldrich and used as received. Nanoclay (Na+-MMT) was donated by Southern Clay Products.

Preparation of water/clay mixture. Nanoclay (5wt% or 10wt% based on water) was dispersed in emulsified water. Uniform and stable water/clay mixture was formed with the aid of sonication. After that, 0.5wt% NaCl was added in the mixture to facilitate the emulsification of water droplets in the organic phase in the later stage.

Preparation of inverse emulsion. AIBN, BPO and surfactant AOT (10wt% related to the emulsified water) were dissolved in styrene and the reaction mixture was stirred (350 rpm) at 90°C under the protection of nitrogen. Reaction was performed in the bulk for certain time up to the conversion of approximately 60% (determined by offline DSC). Subsequently, water/clay/NaCl mixture prepared in the first stage was added into the prepolymerized (styrene/PS) system and emulsified by stirring at 700 rpm for another 10 mins. Schematic of the suspension system is shown in Fig. 1a.

Suspension polymerization of styrene/PS containing emulsified water/clay droplets. The viscous inverse emulsion (100g) was suspended in water (suspension water, 300g), with the aid of suspension stabilizers HEC and PVA. Polymerization was continued under nitrogen atmosphere. The stirring rate and the temperature were kept at 350 rpm and 90°C, respectively. Finally, the suspension was cooled to room temperature and the spherical products were recovered by filtration. Schematic of suspension system is shown in Fig. 1b.

Expansion of WEPS and water expandable PS/Clay nanocomposites (WEPSCN). Expandable beads were expanded by two different heating mediums: hot air and oil bath. The heating temperature was 135°C for both cases. After exposure to hot medium for 1 minute, expanded beads were quenched by compressed cold air (the hot air method) or ice-water mixture (the oil bath method).

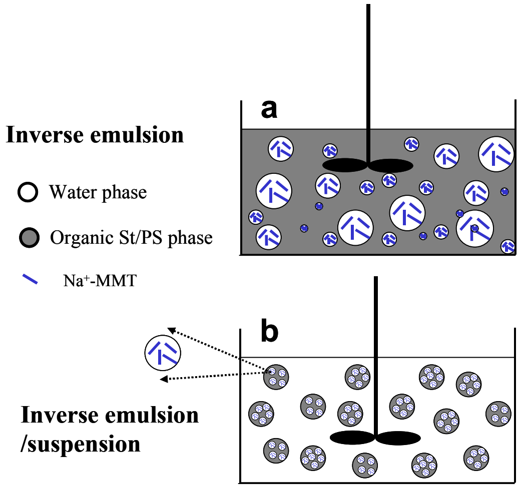

Figure 1. Schematic representation of the preparation process of WEPS: (a) emulsification of water (blowing agent) in a styrene/PS mixture, and (b) suspension polymerization of styrene/PS droplets containing emulsified water.

Scanning Electron Microscopy (SEM). The morphology of both compact (before expansion) and expanded beads was examined by a scanning electron microscope (SEM, HITATCHI S-4300), operated at 15 KV. Samples were freeze-fractured in liquid nitrogen and the fracture surface was sputter-coated with gold.

Results and Discussions

In order to achieve the foam products with good structure and comprehensive properties, it is desirable to acquire uniform water droplets distribution in the inverse emulsion stage. AOT combined with a low concentration of NaCl (0.9%) was reported to be an effective emulsifying system for the preparation of WEPS [8]. An even lower NaCl content (0.5%) was used in this study considering the effect of ionic groups on the stability of the dispersion of nanoclay. The distribution of water in compact beads is illustration in Fig. 2. Due to the constant AOT/emulsified water ratio (1:10) for both WEPS and WEPSCN, similar domain size and size distribution are obtained. Most water droplets exhibit a size of 5 μm, with several larger droplets of approximately 10μm. With the incorporation of nanoclay, the shape of emulsified water is more regular compared to those without nanoclay.

The foam structures of WEPS and WEPSCN are illustrated in Fig. 3. Comparing foams prepared by heating over the air gun (Fig. 3 a&c) and the oil bath (Fig. 3 b&d), it is obvious that a higher expansion ratio can be achieved in the latter case, as summarized in Table 1. For WEPS, the average expansion ratio is 2.2 if using the air gun, as opposed to 2.95 while using the oil bath. For WEPSCN, the difference is more apparent. Compacted beads expanded nearly 90% more by the oil bath (6.1) than by the hot air (3.2). The reason of this observation can be the different diffusion rate of water in air and in oil. Once exposed to a hot medium (air/oil), a large concentration difference of water inside and outside the beads leads to the diffusion of water out of the beads, rather than expansion. However, the diffusion rate of water is much slower in the oil. Therefore, more water can be trapped inside the beads and cause expansion during the oil heating.

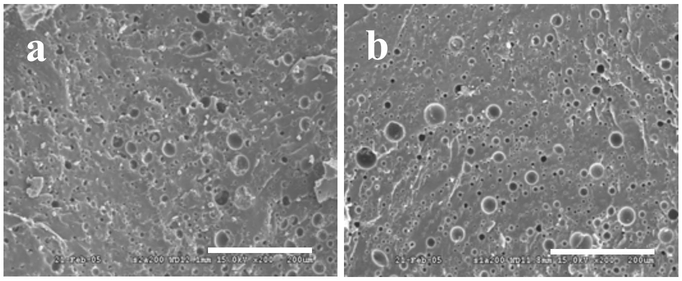

Figure 2. SEM micrograph of compacted beads (a) WEPS (10% H_2O) (b) WEPSCN (0.5wt% nanoclay, 10% H_2O), scale bar 200 μm

The effect of nanoclay on the expansion and thus the final foam structures are also illustrated in Fig. 3. No matter which heating method was applied, compacted beads with nanoclay exhibit much higher expansion ratios, as indicated in Table 1. If heated via the hot air, the incorporation of 0.5% nanoclay leads to an increase of expansion ratio from 2.2 to 3.2. If heated via the oil bath, the increase of expansion ratio associated with the nanoclay is more than 100% (2.95 vs. 6.1). This phenomenon can be attributed to the barrier properties of the nanoclay. Before expansion, most of the clay exists in the emulsified water phase. During expansion, the clay particles can be pushed against the cell wall, forming a barrier layer around the cell, which obviously can diminish the loss of water through the diffusion. Therefore, a higher expansion ratio can be achieved. A very interesting observation is that, with the addition of clay, bi-model foam morphology is achieved (Fig. 3d), with the small cells of 10μm and the larger cells of

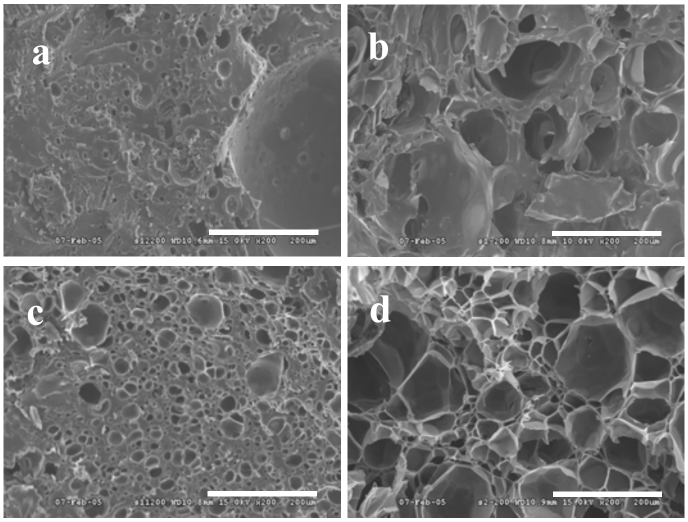

Figure 3. SEM micrograph of foam morphology of expanded WEPS/WEPSCN beads (a) WEPS (10% H_2O), air gun (135°C, 1min) (b) WEPS (10% H_2O), oil bath (135°C, 1min) (c) WEPSCN (0.5wt% nanoclay, 10% H_2O), air gun (135°C, 1min) (d) WEPSCN (0.5wt% nanoclay, 10% H_2O), oil bath (135°C, 1min), scale bar 200 μm

100μm. One possible reason is the co-nucleation of bubbles on the clay surface. Future research will be addressed on this topic.

Table 1. Expansion ratios of WEPS and WEPSCN

Expansion ratio (α)	**WEPS** **W/O clay** **10% H_2O**	**WEPSCN** **W/ 0.5% clay** **10% H_2O**
Air gun (135°C, 1min)	2.2	3.2
Oil Bath (135°C, 1min)	2.95	6.1

Conclusions

Fire hazard-free and water expandable PS/clay nanocomposites were successfully synthesized via the inverse emulsion/suspension polymerizations. In the polymer (PS) domain, a uniform dispersion of tiny water droplets containing nanoclay was achieved. Oil bath was demonstrated to be a better heating media to achieve a high expansion, as compared to the hot air. With the incorporation of very small amount of nanoclay, the expansion ratio can be substantially increased and the final foam structures exhibited the bi-model cell morphology. The distribution and dispersion of nanoclay in compacted beads and how it affects the nucleation and expansion of the cells during the foaming process are challenge research topics and are currently under investigation.

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