Available online at www.sciencedirect.com
ScienceDirect

Polymer 47 (2006) 6303–6310

polymer
www.elsevier.com/locate/polymer

Synthesis and foaming of water expandable polystyrene–clay nanocomposites

Jiong Shen, Xia Cao, L. James Lee*

Department of Chemical and Biomolecular Engineering, The Ohio State University, 125 Koffolt Laboratories,
140 West 19th Avenue, Columbus, OH 43210, United States

Received 26 May 2006; received in revised form 27 June 2006; accepted 28 June 2006
Available online 28 July 2006

Abstract

The typical process used to synthesize water expandable polystyrene (WEPS) was modified and applied to prepare water expandable polystyrene (PS)–clay nanocomposites (WEPSCN). The natural clay can be uniformly dispersed in water due to its hydrophilicity. It can be further carried into the styrene monomer by the formation of water-in-oil inverse emulsion. Via suspension polymerization, spherical PS beads with myriads of water/clay droplets inside were obtained. Upon heating via the hot medium, the PS matrix was expanded to form a cellular structure. Transmission electron microscopy results indicated that nanoclay forms a layer around the cell wall. The presence of nanoclay led to higher water content in the beads and reduced the water loss during storage.

Using CO_2 as the co-blowing agent, foams with a bi-model structure and lower densities were obtained. Furthermore, CO_2 foaming offers an alternative method to utilize dried WEPS/WEPSCN beads. The presence of water cavities significantly enlarges the cell size and leads to a foam product with ultra-low density (~0.03 g/cc) and low thermal conductivity.

Keywords: Water expandable; Polystyrene–clay nanocomposite; CO_2 foaming

1. Introduction

Polymer–clay nanocomposites have been widely investigated because they exhibit superior properties when compared to neat polymers or microparticle-filled composites. Earlier studies have shown that the incorporation of nanoclay into the polymer domain leads to enhanced mechanical properties, higher heat deflection temperature, reduced gas permeability, and improved dimensional stability [1–9]. Recently, considerable efforts have also been devoted to another related research area: polymer–clay nanocomposite foams [10–16]. The presence of nanoclay may enhance cell nucleation, provide foam reinforcement, lower gas escape rate, and result in char formation when foam is under fire. This makes polymer–clay nanocomposite foam an excellent choice for applications requiring high strength, lightweight, and better fire resistance. With an annual consumption of 1.9 billion pounds in 2001, polystyrene (PS) foams (both extruded and expanded) occupy the second largest market share in the US foam portfolio [17]. In this study, expandable PS (EPS) containing nanoclay is our focus.

Morphology control and property enhancement for both nanocomposites and nanocomposite foams depend on good dispersion of nanoclay in the polymer domain. In order to improve the compatibility between the hydrophilic nanoclay and the hydrophobic polymers, the clay surface is usually modified by organic surfactants, often quaternary ammonium compounds. The presence of these low molecular weight hydrocarbons, however, results in negative impacts on the material's fire resistant performance, as evidenced in such industrial fire evaluations as the Oxygen Index Test and the Flame Spread Test. Therefore, it is highly desirable to develop a method to incorporate nanoclay into polymers with uniform

---

* Corresponding author. Tel.: +1 614 292 2408; fax: +1 614 292 3769.
E-mail address: leelj@chbmeng.ohio-state.edu (L. James Lee).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.06.068

clay dispersion, but without the use of fire hazardous surfactants.

EPS is generally prepared via a modified route for styrene suspension polymerization [18]. The route starts with the reaction of styrene monomer dispersed in the water medium containing suitable suspension agents and an organic blowing agent such as pentane. To avoid the use of flammable blowing agents, the concept of WEPS was proposed. Since the solubility of water in PS is very low, the abovementioned route to produce EPS is not feasible for WEPS. Two alternative methods have been reported to date.

The first method to produce WEPS was developed by Crevecoeur et al. [19]. In that method, water was emulsified in a pre-polymerized styrene/PS mixture in the presence of emulsifiers. Subsequently, the inverse emulsion was suspended in a water medium containing suspension agents. Polymerization was continued until a complete conversion. The final products are spherical PS beads with entrapped micrometer-scaled water droplets. The second method was developed by Pallay et al. [20]. Instead of using emulsifiers, starch was used as a water-swellable phase. Pre-polymerization of the styrene/starch mixture was carried out to a conversion of approximately 30%. The viscous reaction phase was subsequently transferred to a water medium containing suitable suspension agents. In the last step, polymerization was completed and water was directly absorbed into the starch inclusions.

To address the demand for surfactant-free expandable PS–clay nanocomposites, the first method (developed by Crevecoeur) was modified and applied in this work. Instead of emulsifying pure water, a mixture of water and a raw clay, sodium montmorillonite (Na^+-MMT), was emulsified in the organic styrene/PS phase. Due to the hydrophilicity of the raw clay surface, a uniform and stable dispersion of clay in water is achieved. Therefore, using water as the carrier, nanoclay can be incorporated into the polymer system.

The selection of emulsifier for water-in-oil (w/o) inverse emulsion is of essential importance to achieve a stable reaction system and uniform water dispersion. Two criteria are used in this study: (1) the hydrophile–lipophile balance (HLB) value falls in the range of 3–6 [21,22], and (2) no reactive group (unsaturated carbon–carbon double bond) in the surfactant molecules. It has been demonstrated that sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is highly efficient to stabilize the water-in-styrene inverse emulsion [19]. According to Hazardous Materials Identification System (HMIS) and National Fire Protection Association (NFPA) ratings, AOT is non-flammable. These aspects match well with our desire to produce fire-hazard-free nanocomposites. Thus, we chose AOT for our system.

2. Experimental

2.1. Materials

The styrene monomer was purchased from Aldrich and used without distillation. The initiators, 2,2′-azobis(isobutyronitrile) (AIBN) and dibenzoyl peroxide (BPO) with a half-life ($t_{1/2}$) at 90 °C of 25 min and 145 min, respectively, were purchased from Aldrich. AOT was supplied by Fluka and used as received. The suspension stabilizers, hydroxyethyl (HEC, $M_w = 250{,}000$) and polyvinyl alcohol (PVA) were supplied by Aldrich and used as received. Nanoclay (Na^+-MMT) was donated by Southern Clay Products.

2.2. Preparation of water/clay mixture

Nanoclay (5 wt% based on emulsified water) was dispersed in emulsified water with the aid of sonication for approximately 2 h. The sonication time was controlled until the formation of a uniform and stable water/clay mixture. Subsequently, 0.5 wt% NaCl (based on emulsified water) was added into the mixture. The salt would facilitate the emulsification of water droplets in the later stage of the process [19]. The concentration and the addition sequence of NaCl need to be taken with care. Details are discussed later.

2.3. Preparation of inverse emulsion

AIBN (0.25 wt% based on styrene), BPO (0.25 wt% based on styrene) and AOT (10 wt% based on emulsified water) were dissolved in styrene. The mixture was heated to 90 °C under the protection of nitrogen and a stirring rate of 350 rpm. The reaction was performed in the bulk phase to a conversion of approximately 60% (determined by offline differential scanning calorimetry (DSC), at which point, the viscosity of the continuous phase is sufficiently high to fixate the water droplets. At a higher stirring rate (700 rpm), water/NaCl or water/NaCl/clay was added into the styrene/PS mixture to form a water-in-oil-in-water (w/o/w) reaction medium. Polymerization was continued for another 10 min. A schematic of the emulsion system is shown in Fig. 1a.

2.4. Suspension polymerization

The viscous inverse emulsion (100 g) was suspended in water (suspension water, 300 g), with the aid of suspension stabilizers HEC (0.6 wt% based on suspension water) and PVA (0.005 wt% based on suspension water). Polymerization was continued under nitrogen atmosphere. The stirring rate and 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. A schematic of the suspension system is shown in Fig. 1b.

2.5. Expansion of compacted beads

The recovered beads were expanded via two different heating media: hot air and oil bath. The heating temperature was set at 135 °C in both cases. After exposure to the hot medium for 1 min, the expanded beads were quenched by either compressed cold air (the hot air method) or an ice–water mixture (the oil bath method).

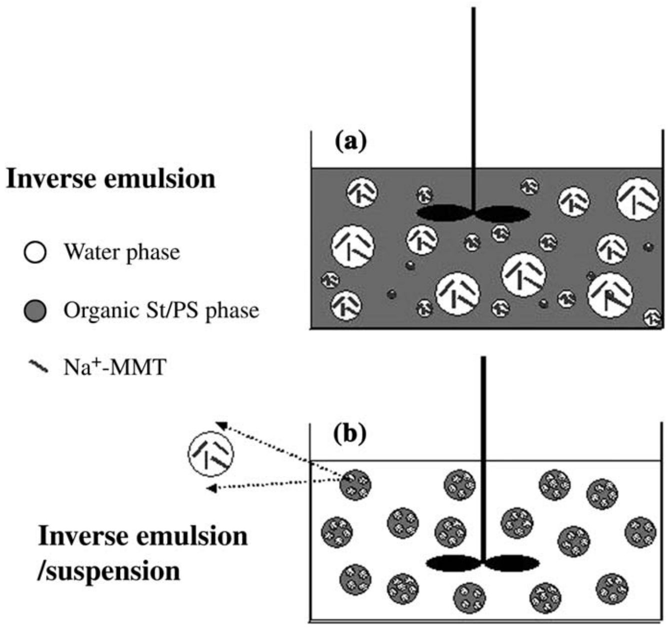

Fig. 1. Schematic representation of the preparation process of WEPSCN (a) emulsification of water/clay mixture in pre-polymerized styrene/PS, and (b) suspension polymerization of styrene/PS droplets containing emulsified water/clay droplets.

2.6. Batch foaming of WEPS/WEPSCN using carbon dioxide (CO_2)

(a) *A two-step batch foaming process*. WEPS/WEPSCN beads were saturated with CO_2 at 25 °C under a pressure of 13.8 MPa. After reaching an equilibrium state, the pressure was quickly released and the beads were taken out of the high-pressure vessel. Subsequently, the beads were immersed into a pre-heated oil bath (135 °C). The total transition time between the end of the pressure release and heating in the oil bath was approximately 1 min. Foaming took place due to the expansion of water droplets and the bubble growth of CO_2 in the PS matrix. The foaming time was set at 1 min, after which the foamed samples were quenched with a mixture of ice and water. (b) *A one-step batch foaming process*. WEPS/WEPSCN were saturated with CO_2 in a high-pressure vessel. The system was allowed to equilibrate at 120 °C and 13.8 MPa for 24 h. At these conditions, CO_2 is in the supercritical state. After equilibrium, the pressure was rapidly released, leading to simultaneous bubble nucleation and growth. The foam structure was fixed by immediate cooling with a mixture of ice and water.

2.7. Continuous foaming of WEPS/WEPSCN using CO_2

A two-stage single screw extruder (Haake Rheomex 252P) was utilized at a screw rotation speed of 20 rpm. A static mixer (Omega, FMX8441S) was attached to the end of the extruder to provide extra distributive mixing. A capillary die with a nozzle of 0.5 mm (diameter) and 10 mm (length) was custom-made to generate a rapid and high-pressure drop during the extrusion. CO_2 was compressed to approximately 1800 psi at 4 °C. The CO_2 pressure and volumetric flow rate were controlled precisely by the pump controller. Upon injection into the barrel, CO_2 was mixed with the polymer melt by the screw rotation. A homogeneous solution of WEPS melt and CO_2 was formed when the mixture flowed through the static mixer. Due to a rapid pressure drop through the narrow capillary die, nucleation occurred and the foamed extrudate flowed out of the nozzle and expanded until vitrified in the ambient air.

2.8. Characterization

The morphology of both compact (before expansion) and expanded beads was examined by a scanning electron microscope (SEM, Hitachi S-4300). Samples were freeze-fractured in liquid nitrogen, and the fracture surface was sputter-coated with gold. The ultimate water content in the beads was determined by thermogravimetric analysis (TGA, Perkin–Elmer TGA 7) operated under a nitrogen atmosphere. The sample was heated from room temperature to 140 °C at 10 °C/min followed by an isothermal heating period of 60 min. The location of nanoclay in expanded beads was examined by a transmission electron microscope (TEM, Phillip CM12), performed using an accelerating voltage of 80 kV. The nanocomposite foams were sectioned into ultra-thin slices (<100 nm) at room temperature using a microtome and then mounted on 200 mesh copper grids. The heat conductivity of foams was measured using a heat flow meter (Fox 200, LaserComp). The temperature difference of the upper and lower plates was set at 40 °C.

3. Results and discussion

The application of EPS is determined by the diameter of the beads and the content of the blowing agent [23]. Foams expanded from large EPS beads (diameter of 800–2000 μm) are generally used for insulation and building panels, while foams expanded from small beads (300–800 μm) are generally used for thin-walled containers. The ultimate bead size is mainly determined during suspension polymerization. It can be controlled by a number of means including mixing speed and the type and content of stabilizers. For WEPS and WEPSCN synthesized in this study, the bead size fell in the range of the large group. The incorporation of 0.5 wt% nanoclay did not exhibit any strong impact on the bead size and size distribution.

In order to achieve foam products with desirable structure and properties, it is important to acquire a uniform distribution of water droplets in the water-in-styrene emulsion. AOT combined with a low concentration of NaCl was reported to be an effective emulsifying system for the preparation of WEPS [19,24]. The basic concept is that the existence of an electrolyte will decrease the repulsion force between ionic head groups of AOT, thus permitting a closer and more compact arrangement of AOT around the water drop. In Crevecoeur's study [19,25,26], 0.9 wt% (based on emulsified water) NaCl

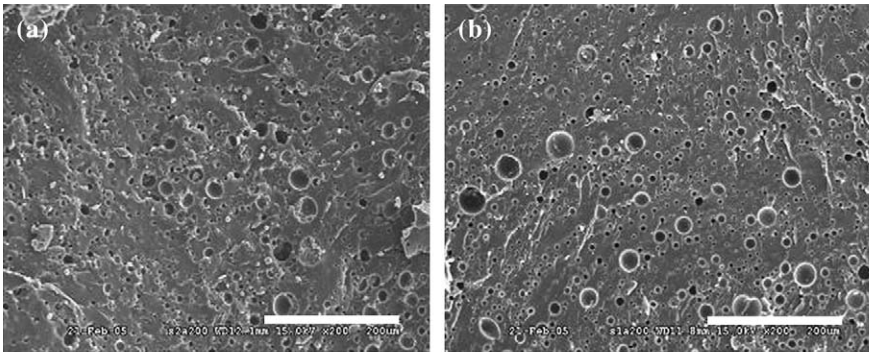

Fig. 2. Dispersion of water droplets in compacted beads, scale bar 200 μm (a) WEPS, designed H_2O 10 wt%, actual H_2O 7.6 wt%, and (b) WEPSCN (0.5 wt% nanoclay), designed H_2O 10 wt%, actual H_2O 9.2 wt%.

was used to improve the stability of the emulsion. In Snijders's study [24], an optimal concentration of NaCl (0.1 wt%) was reported to achieve a homogenous and stable dispersion of water droplets. However, the existence of an electrolyte (e.g. NaCl) can also interfere with the flocculation of clay in water. Thus, the electrolyte should be selected with care [27]. While a low concentration of electrolyte can prevent particle aggregation due to the osmotic repulsion, a high concentration will lead to the compression of double layers at both the planer and edge surfaces. As the concentration of electrolyte increases to the critical flocculation concentration (CFC), all three modes (face-to-face, face-to-edge, edge-to-edge) of clay aggregation will occur. For Na^+-MMT used in this study, the highest NaCl concentration we can use while still maintaining a stable water–clay suspension was 0.5 wt%. We found that the time to add NaCl is another factor that affects the stability of the water–clay suspension. If we added both nanoclay and NaCl into the emulsified water simultaneously (sequence I), the exfoliation of clay became more difficult. However, once the clay has been exfoliated in water, the addition of NaCl (sequence II) merely reduced the stability of this suspension.

The distribution of water droplets in compact beads is illustrated in Fig. 2. With a constant AOT to water (emulsified) ratio (1:10) and the same NaCl concentration, a similar domain size and size distribution of water droplets were obtained for both WEPS and WEPSCN. Most water droplets exhibited a size of 5 μm, with several larger droplets of approximately 20 μm. The ultimate clay content in beads was measured using TGA, and the result is illustrated in Fig. 3. With a designed water content of 10 wt%, the final incorporated water in PS beads was 7.6 wt%, while that in PS containing 0.5 wt% nanoclay was 9.2 wt%. This difference can be attributed to the hydrophilicity of nanoclay, which holds more water into the polymer during synthesis. This hydrophilic property of nanoclay also facilitates the fixation of water within the beads during storage. We measured the water content of beads three months after synthesis. For WEPSCN (the original water content of 9.2 wt%), the residual water was 2.5 wt%, while for WEPS (the original water content of 7.6 wt%), the residual water was only 0.2 wt%.

Two heating media were used to expand compacted beads in this study: hot air and an oil bath. The expansion temperature was 135 °C. The foam structures of WEPS and WEPSCN are illustrated in Fig. 4. Comparing foams expanded by these two methods, it is obvious that a higher expansion ratio (defined by the volume of a bead after expansion divided by that of the same bead before expansion) could be achieved by oil bath (Fig. 4b and d) than by hot air (Fig. 4a and c), as summarized in Table 1. For WEPS, the average expansion ratio was 2.2 when using the air gun, as opposed to 3.0 when using the oil bath. For WEPSCN, the compacted beads expanded nearly 90% more in oil bath (6.1) than by the hot air (3.2). The different performance of these two media can be rationalized as follows. During the expansion, a substantial fraction of water would diffuse out of the beads rather than participating in expansion [26]. If the surrounding medium is hot air, this diffusion would be expedited. However, if the surrounding medium is hot oil, more water can be trapped within the beads and is utilized as the blowing agent. Therefore, a higher expansion ratio can be obtained.

The effect of nanoclay on the expansion, as well as the final foam structures, is illustrated in Fig. 4. Regardless of the heating method applied, compacted beads with nanoclay exhibited much higher expansion ratios, as indicated in Table 1. If heated via hot air, the incorporation of 0.5 wt% nanoclay led to an increase of the expansion ratio from 2.2 to 3.2. If heated via the oil bath, the increase of the expansion ratio due to the presence of nanoclay was more than 100% (3.0 vs. 6.1). While higher water contents may lead to a higher expansion ratio, the

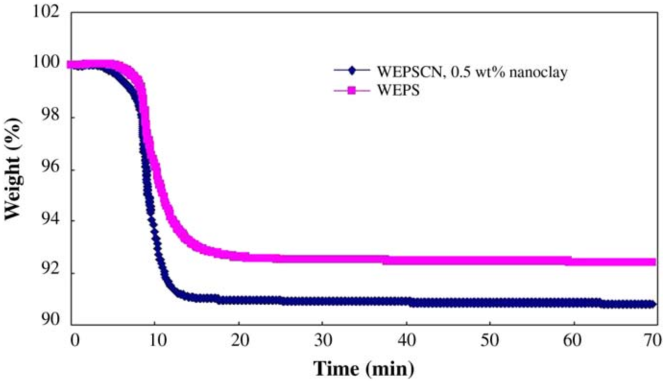

Fig. 3. Water content in beads determined using TGA.

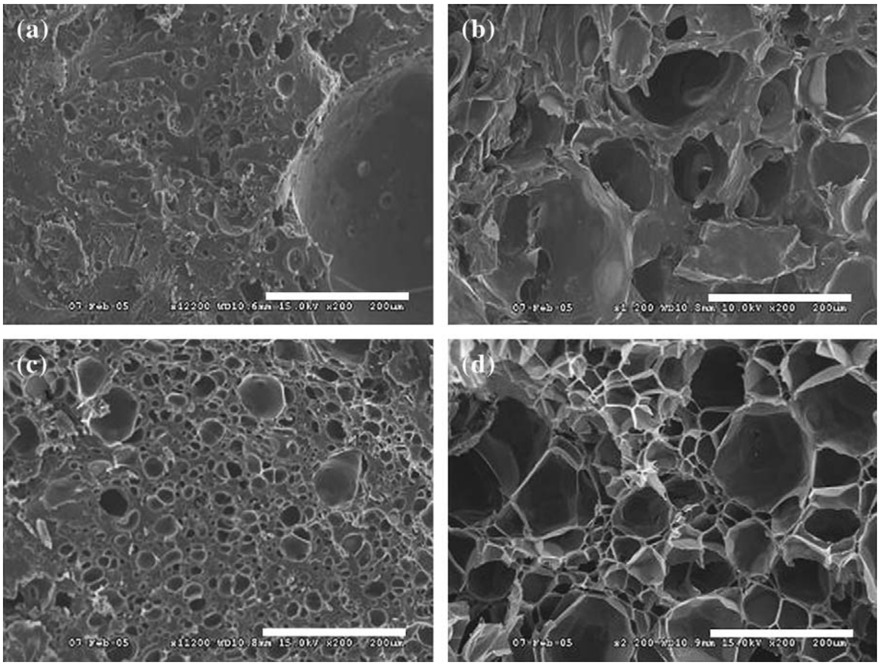

Fig. 4. SEM micrographs of foam morphology of expanded WEPS or WEPSCN beads at 135 °C for 1 min, all beads have designed H_2O 10 wt%, scale bar 200 μm (a) WEPS (7.6 wt% H_2O), air gun (b) WEPS (7.6 wt% H_2O), oil bath (c) WEPSCN (0.5 wt% nanoclay, 9.2 wt% H_2O), air gun, and (d) WEPSCN (0.5 wt% nanoclay, 9.2 wt% H_2O), oil bath.

enhanced barrier property resulting from the nanoclay may also play an important role. Before expansion, nanoclay was dispersed in the water droplets. During expansion, the clay particles were pushed against the cell wall and formed a barrier layer around the cell, as illustrated in Fig. 5. The existence of the clay barrier layer can obviously reduce the loss of water and increase the expansion ratio. Another interesting observation is that a bi-model foam morphology (Fig. 4c and d) was achieved with the addition of nanoclay. Since water is the only blowing agent, this observation suggests a heterogeneous nucleation due to the presence of nanoclay. A reasonable postulation is that those big bubbles were originated from existing water droplets, while those surrounding small bubbles were formed from the nucleation of water vapor on the clay surface.

In an attempt to produce foams with higher expansion ratio and lower density, CO_2 was applied as the co-blowing agent to foam WEPS/WEPSCN beads. In the presence of two blowing agents, water and CO_2, foams with a bi-model structure (also for beads without clay) are expected. To avoid the water loss during the CO_2 saturation, a two-step batch foaming process was applied, as described in Section 2. The water content was measured immediately before the CO_2 co-foaming. WEPS and WEPSCN beads contained 7.7 wt% and 8.6 wt% H_2O, respectively.

Table 1
Expansion ratios of WEPS and WEPSCN (designed water content 10 wt%)

Expansion ratio (α)	WEPS (w/o clay, 7.6 wt% H_2O)	WEPSCN (w/0.5% clay, 9.2 wt% H_2O)
Air gun (135 °C, 1 min)	2.2	3.2
Oil bath (135 °C, 1 min)	3.0	6.1

Our postulation on the cell morphology was verified. As illustrated in Fig. 6, foams exhibited an obvious bi-model cell structure even without nanoclay. A similar cell structure forms for WEPSCN beads. However, instead of possessing a higher expansion ratio, foams prepared using this method showed thick (~0.5 mm) un-foamed skin region, and consequently, a very high bulk density (0.6–0.7 g/cm^3). Various foaming temperatures and foaming times were tried in this study. However, all the foams exhibited similar structures and densities.

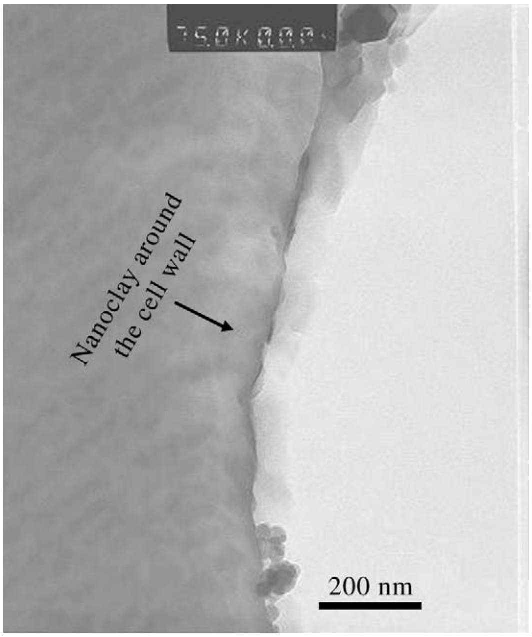

Fig. 5. TEM micrograph showing nanoclay around the cell wall.

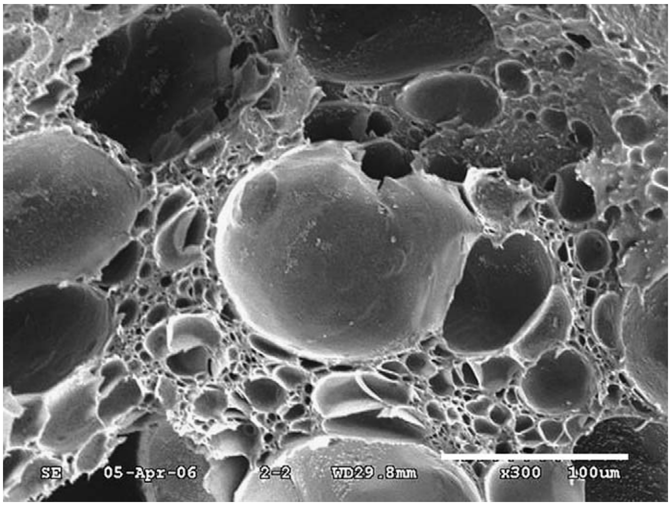

Fig. 6. SEM micrograph of PS foam, WEPS (7.6 wt% H_2O), CO_2 co-blowing, saturation pressure 13.8 MPa, saturation temperature 25 °C, foaming temperature 135 °C (oil bath), foaming time 1 min, scale bar 100 μm.

We believe that the technical barrier for achieving an efficient expansion originates from the lack of a suitable foaming temperature for both water and CO_2. For PS synthesized in this study ($M_w = 237$ kg/mol), a temperature lower than 120 °C appears to be insufficient to generate a high water vapor pressure to expand the viscous PS matrix. On the other hand, a high temperature suitable for water expansion (e.g. 135 °C in this study) may lead to the fast escape of CO_2 out of the beads and ultimately a thick surface skin.

The feasibility of using CO_2 extrusion foaming to expand the WEPS beads was tested using a single screw extruder. Considering the high pressure generated within the extruder and the confinement of the polymer melt by the screw and the extruder barrel, water is expected to be held within the polymer phase during extrusion. This can be verified by the existence of a bi-model foam structure and a higher expansion ratio compared to the foam generated from the neat PS. In order to test the existence of water co-blowing and avoid the interference of nanoclay, only WEPS was tried for the extrusion foaming. Fig. 7a shows the morphology of an extruded PS foam made from the neat PS. In this case, CO_2 was the only blowing agent. Fig. 7b shows the morphology of an extruded PS foam made from WEPS beads containing 7.7 wt% water. In this case, both water and CO_2 served as the dual blowing agent. Comparing these two samples, it is obvious that the existence of water enhances the expansion of PS. The WEPS foam (Fig. 7b) shows much larger cell sizes and a lower cell density than the PS foam (Fig. 7a) under the same foaming conditions, leading to a much lower bulk density (0.17 g/cm^3 vs. 0.5 g/cm^3, foam b vs. foam a). Furthermore, the WEPS foam possesses a bi-model cell morphology due to the existence of two blowing agents, which is demonstrated more clearly in a lower magnification image (Fig. 7c). The extrusion of WEPS beads results in a similar foam structure as the oil bath-based batch foaming of the same material. In addition, no obvious skin region was observed using this foaming route. It is worthwhile to point out that the current extruder was equipped with a capillary die, which is designed to generate a high-pressure drop and facilitate the formation of microcellular suture. In order to produce low-density foams for insulation applications, an extruder with a wide slit die is desirable. Nevertheless, this work demonstrated the feasibility to produce extruded PS foams with a lower bulk density using WEPS beads.

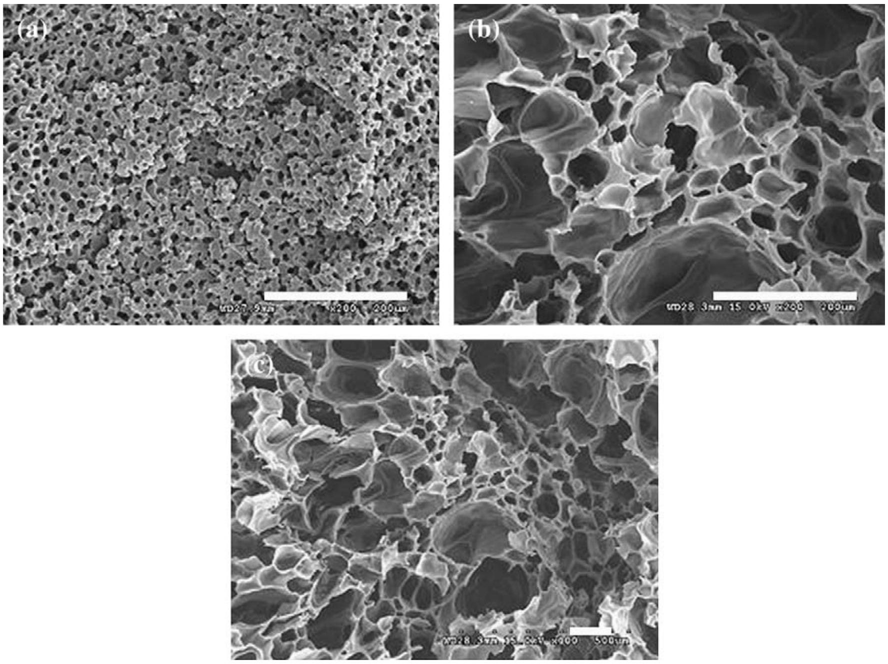

Fig. 7. SEM micrographs of foams prepared using a single screw extruder, CO_2 is the blowing agent (a) foam made from neat PS, scale bar 200 μm, $\rho = 0.50$ g/cc (b) foam made from WEPS beads, water is the co-blowing agent, scale bar 200 μm, $\rho = 0.17$ g/cc (c) lower magnification of foam (b), scale bar 100 μm.

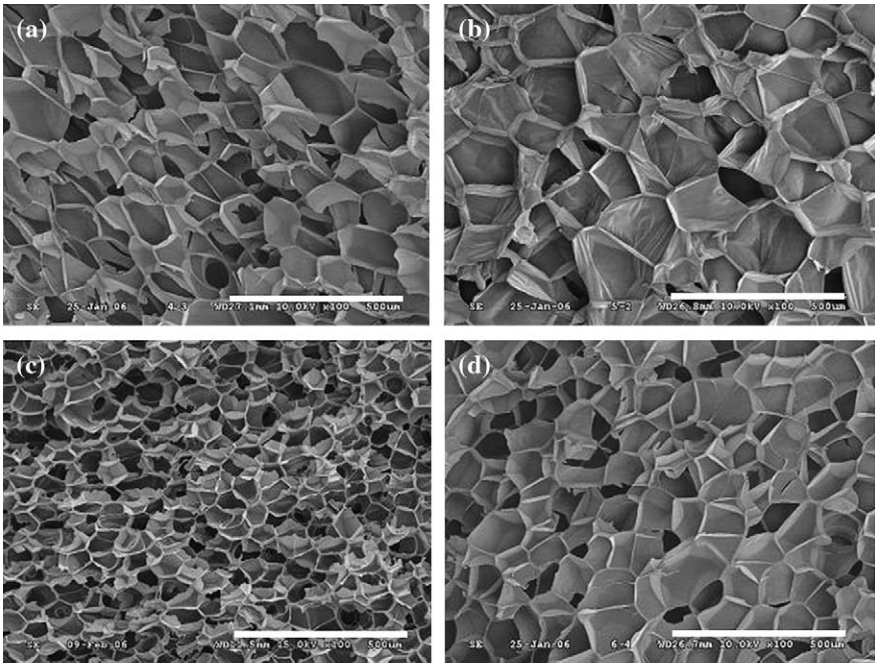

Fig. 8. SEM micrographs of PS foams, batch foaming, CO_2, 13.8 MPa, 120 °C, scale bar 500 μm (a) PS (no cavity), $\rho = 0.07$ g/cc (b) WEPS (7.6 wt% cavity), $\rho = 0.035$ g/cc (c) PS/0.5 wt% nanoclay (no cavity), $\rho = 0.181$ g/cc (d) WEPSCN (0.5 wt% nanoclay, 9.2 wt% cavity), $\rho = 0.032$ g/cc.

All the foams discussed above were expanded using freshly prepared beads, which retained most of the water as synthesized. Since the water loss during storage is inevitable, it is desirable to investigate alternative methods to expand dried beads. WEPS and WEPSCN beads were intentionally dried before foaming. Since styrene/PS has approximately the same density as water, the volume percentage of the cavities in the beads is similar to the weight percentage of water inside the beads. For comparison, we synthesized PS and PS–clay nanocomposite using a similar polymerization procedure, but without entrapping any water droplets, in other words, no cavities. CO_2 foaming via a one-step batch process (introduced in Section 2) was applied here. Four samples were foamed under the same foaming conditions: (a) PS (w/o water cavity) (b) dried WEPS (w/7.6 vol% water cavity), (c) PS (w/0.5 wt% clay, w/o water cavity), (d) dried WEPSCN (w/0.5 wt% clay, w/9.2 vol% water cavity). The resultant foam morphologies are shown in Fig. 8. By comparing Fig. 8a and b, it is clear that the existence of water cavities helps enlarge the cell size and reduce the foam density. With the inclusion of 7.6 vol% cavity, the foam density can be reduced from 0.07 g/cc to 0.035 g/cc.

The addition of nanoclay in the foam formulation has a mixed effect on the foam morphology and the insulation performance. While the barrier resistance and flame retardancy of nanoclay benefit the insulation applications, its nucleation effect often leads to foams with unfavorable morphology (i.e. cell size too small) and density (bulk density too high). However, the nucleation effect of nanoclay can be balanced by the cell enlargement effect caused by the presence of water cavity in WEPSCN. Fig. 8c illustrates PS foams produced from beads containing 0.5 wt% nanoclay. Compared to neat PS foam (Fig. 8a), the nucleation effect of nanoclay significantly reduced the cell size and increased the cell density. Using the same foaming set-up and conditions, this sample could not be expanded to fill the entire mold in batch foaming, leading to a corrugated foam surface. The foam density is 0.181 g/cc, which is too high for insulation applications. However, the presence of 9.2 vol% water cavity (Fig. 8d) enlarged the cell size in a similar manner as in the neat PS case. While more cells were created compared to the neat PS foam (Fig. 8a vs. d), the bubble size remained around 100 μm. The bulk foam density is 0.032 g/cc, which is even lower than its non-clay counterpart (Fig. 8b).

The thermal conductivity of the above mentioned foams was measured at 40 °C and the results are shown in Fig. 9. An extruded PS foam with a bulk density of 0.098 g/cc shows

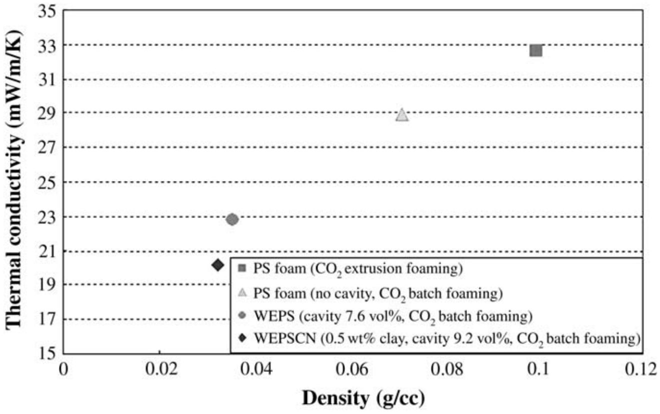

Fig. 9. Thermal conductivity of foams (40 °C).

a thermal conductivity of 32.61 mW/m/K. Batch foaming of WEPSCN produced foams with a very low density (0.032 g/cc) and correspondingly, a very low thermal conductivity (20.18 mW/m/K). For all the samples investigated in this work, the conductivity data shows a monotonic dependence on the bulk density. At the ultra-low density range, the conductivity is very sensitive to the bulk density. Our data indicates that a lower bulk density provides a better thermal insulation value. To achieve ultra-low-density foams (<0.05 g/cc) in traditional manufacturing processes, an expensive vacuum system is often required. Thus, our materials and approach may eliminate the need of this multi-million dollar capital investment in the industrial foam line. Furthermore, using this method, traditional industrial blowing agents such as chlorofluorocarbon and hydrochlorofluorocarbon can be completely replaced with inexpensive and environmentally benign CO_2.

4. Conclusions

Water expandable PS–clay nanocomposites were successfully synthesized via the suspension polymerization of water-in-oil inverse emulsion. Using water as the carrier, surfactant-free nanoclay can be incorporated into the polymer beads. The addition of nanoclay can trap more water in the beads during synthesis and reduce the water loss during storage.

CO_2 foaming of compacted beads offers an alternative method to utilize in-stock WEPS/WEPSCN products with reduced water content. The presence of water cavities significantly enlarges the cell size and leads to foams with ultra-low density and lower thermal conductivity. More significantly, PS–clay nanocomposite foams with considerably large cell size (∼100 μm) and low foam density (<0.05 g/cc) can be produced using this approach.

Future research will be addressed on the following two aspects. First, new formulations (e.g. emulsifiers, suspension agents) will be developed to stabilize the reaction system with higher clay content. The present work demonstrated the feasibility to produce WEPSCN. However, in order to achieve noticeable advantages from nanoclay, such as mechanical enhancement and the char formation, higher clay content is required. Second, CO_2 co-foaming of "wet" WEPS/WEPSCN beads containing water inside will be developed. The key issue is to avoid the water loss during the foaming process. The success of this work may lead to foams with even lower foam density and better insulation performance. With the thinning of the cell wall, it is also possible to achieve an open cell structure. Therefore, by controlling the water content, foams with a wide range of densities and applications (insulation, filtration, sound dampening, etc.) can be produced.

Acknowledgement

The authors would like to thank Owens Corning and Southern Clay for material donations. Dr. Guojun Xu, Dr. Xiangmin Han, and Mr. Bo Yu are greatly acknowledged for providing technical support. The financial supports from the National Science Foundation sponsored Center for Advanced Polymer and Composite Engineering (CAPCE) at The Ohio State University are gratefully appreciated.

References

[1] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, et al. J Mater Res 1993;8(5):1185–9.
[2] Giannelis EP. Adv Mater (Weinheim, Ger) 1996;8(1):29–35.
[3] Giannelis EP. Appl Organomet Chem 1998;12(10/11):675–80.
[4] Gilman JW, Kashiwagi T, Nyden M, Brown JET, Jackson CL, Lomakin S, et al. Chem Technol Polym Addit 1999;249–65.
[5] Alexandre M, Dubois P. Mater Sci Eng R Rep 2000;R28(1–2):1–63.
[6] Beyer G. Plast Addit Compound 2002;4(10):22–8.
[7] Han X, Zeng C, Lee LJ, Koelling KW, Tomasko DL. Polym Eng Sci 2003;43(6):1261–75.
[8] Kim J-K, Hu C, Woo RSC, Sham M-L. Compos Sci Technol 2005;65(5):805–13.
[9] Sorrentino A, Tortora M, Vittoria V. J Polym Sci Part B Polym Phys 2005;44(2):265–74.
[10] Okamoto M, Nam PH, Maiti P, Kotaka T, Nakayama T, Takada M, et al. Nano Lett 2001;1(9):503–5.
[11] Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N, Usuki A. Nano Lett 2001;1(6):295–8.
[12] Nam PH, Maiti P, Okamoto M, Kotaka T, Nakayama T, Takada M, et al. Polym Eng Sci 2002;42(9):1907–18.
[13] Zeng C, Han X, Lee LJ, Koelling KW, Tomasko DL. Adv Mater (Weinheim, Ger) 2003;15(20):1743–7.
[14] Fujimoto Y, Ray SS, Okamoto M, Ogami A, Yamada K, Ueda K. Macromol Rapid Commun 2003;24(7):457–61.
[15] Di Maio E, Iannace S, Di Y, Del Giacomo E, Nicolais L. Plast Rubber Compos 2003;32(7):313–7.
[16] Ray SS, Okamoto M. Macromol Mater Eng 2003;288(12):936–44.
[17] US polymeric foams market tipped to break 8.5 billion pounds by 2006, http://www.azom.com/details.asp?articleID=1557; 2001.
[18] Mark HF, Gaylord NG, Bikales NM. Encyclopedia of polymer science and technology. Plastics, resins, rubbers, fibers. Step-reaction polymerization to thermoforming, vol. 13; 1970. 844 pp.
[19] Crevecoeur JJ, Nelissen L, Lemstra PJ. Polymer 1999;40(13):3685–9.
[20] Pallay J, Kelemen P, Berghmans H, Van Dommelen D. Macromol Mater Eng 2000;275:18–25.
[21] Shinoda K, Friberg S. Emulsions and solubilization. 1986. 174 pp.
[22] Birdi KS, editor. Handbook of surface and colloid chemistry. 2nd ed.; 2003. 765 pp.
[23] Frisch KC. Plastic foams, Part I. New York: Marcel Dekker Inc.; 1972.
[24] Snijders EA. Water expandable polystyrene (WEPS): computational and experimental analysis of bubble growth, Ph.D. Thesis; 2003.
[25] Crevecoeur JJ, Nelissen L, Lemstra PJ. Polymer 1999;40(13):3691–6.
[26] Crevecoeur JJ, Coolegem JF, Nelissen L, Lemstra PJ. Polymer 1999;40(13):3697–702.
[27] Van Olphen H. An introduction to clay colloid chemistry: for clay technologists, geologists, and soil scientists. 1963. p. 301.