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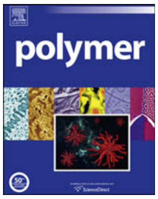

Synthesis and foaming of water expandable polystyrene-activated carbon (WEPSAC)

Jintao Yang [a], Shu-Kai Yeh [a], Nan-Rong Chiou [b], Zhihua Guo [a], Thomas Daniel [b], L. James Lee [a,*]

[a] *Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, USA*
[b] *Nanomaterial Innovation Ltd., Columbus, OH 43212, USA*

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ABSTRACT

In this study, water acts as a co-blowing agent to support carbon dioxide (CO_2) in the extrusion foaming process of polystyrene (PS) to produce foams with very low density for thermal insulation applications. Herein, we report a simple suspension polymerization method to prepare water expandable polystyrene (WEPS) based on a PS/water containing activated carbon (AC) composite. AC pre-saturated with water was introduced into the styrene monomer to form a water-in-oil inverse emulsion without emulsifiers. Via suspension polymerization, water expandable PS/AC (WEPSAC) beads could be subsequently obtained. Low density PS foams (~0.03 g/cc) were successfully produced in the CO_2 extrusion foaming process using WEPSAC. Because of lower foam density and better IR absorption due to the presence of water containing AC, WEPSAC foams provided a lower thermal conductivity than conventional talc reinforced PS foams.

1. Introduction

Polymeric foams are widely used in applications such as insulation, cushions, absorbents, and scaffolds for cell attachment and growth [1–3]. Polystyrene (PS) is one of the major foam materials in the market [4,5]. Currently, hydrogen-containing chlorofluorocarbons (HCFCs) and fluorocarbons (HFCs) are the main blowing agents for PS foaming. However, HCFCs and HFCs have to be replaced soon due to the ozone-depletion and global warming problems. Among various alternative blowing agents, carbon dioxide (CO_2) is the most promising material because it is nonflammable, inexpensive, environmentally benign and has relatively high solubility than other inert gases in many polymers [6,7]. However, the low solubility and high diffusivity of CO_2 in polymers make it difficult to produce low density foams necessary for thermal insulation applications.

Water has been used as a co-blowing agent in the batch polymer foaming process for many years. Water expandable polystyrene (WEPS) is a good example [8–10]. WEPS is generally synthesized by preparing a water-in-oil mixture for styrene suspension polymerization. The first method to produce WEPS was developed by Crevecoeur et al. [8]. 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 complete conversion. The final products are spherical PS beads with entrapped micrometer-scaled water droplets. The second method was developed by Pallay et al. [11]. 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.

We recently reported a modified route of suspension polymerization to prepare water expandable polystyrene/clay nanocomposites (WEPSCN) [12]. The presence of nanoclay in the water-in-oil emulsion reduced the amount of emulsifiers used and enhanced the water stability in the PS beads. Although low density (~0.03 g/cc) foams were obtained by using WEPSCN in the CO_2 batch foaming process, it is difficult to use WEPS or WEPSCN in the extrusion foaming process because water tends to evaporate away in the early portion of the extruder when the WEPS or WEPSCN pellets are crushed and melted by the rotating screw in the heated barrel. A better water carrying material or process is needed to solve this problem in the extrusion foaming process.

Activated carbon (AC) has an exceptionally high surface area which makes it an excellent water-absorbent material. Previously, our group has studied the effect of moisture content in the

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* Corresponding author. Tel.: +1 614 292 2408; fax: +1 614 292 3769.
E-mail address: lee.31@osu.edu (L.J. Lee).

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extrusion foaming process by adding activated carbon particles containing different amounts of water together with PS into a twin-screw extruder. However, most of the water was evaporated by the heat generated from the extruder and only a slight decrease in foam density was observed [13]. In this study, AC pre-saturated with water was introduced into a styrene/PS solution. The viscous mixture was subsequently transferred to a water medium containing suspension agents. Via the suspension polymerization, PS beads containing AC/water droplets were obtained. Applying these beads into the extrusion foaming process with CO_2 as a blowing agent, more water could be trapped. This technology can be easily scaled up for industry applications because both suspension polymerization and extrusion foaming are well-established industrial processes. The extruded foams were characterized for cell morphology, IR transmission and thermal conductivity.

2. Experimental

2.1. Materials

PS (CX5197; $M_n = 86{,}000$) from Total Petrochemicals (formerly Nova) was used as received. Foaming agent CO_2 (>99.9%) was provided by Praxair. Wood based activated carbon (AC) particles with diameters of 38 μm were provided by MeadWestvaco Corp. Styrene was purchased from Aldrich and distilled before use. The initiators, 2,2′-azobis(isobutyronitrile) (AIBN) and dibenzoyl peroxide (BPO) with a half-life ($t_{1/2}$) at 90 °C of 25 and 145 min, respectively, were purchased from Aldrich. The suspension stabilizer, hydroxyethyl (HEC, $M_w = 250{,}000$) and polyvinyl alcohol (PVA) were supplied by Aldrich and used as received.

2.2. Suspension polymerization

53 g PS, 0.25 g AIBN, 0.15 g BPO and 3 g AC absorbed 7.5 g water were mixed with 47 g styrene and the mixture was kept overnight at room temperature. Adding some PS into styrene monomer can increase the mixture viscosity. This makes the drop suspension more stable. The increased viscosity also prevents the AC particles from aggregation. Approximately 100 g of viscous solution was suspended in 300 g of water with the aid of suspension stabilizers HEC (0.6 wt% based on the suspension water) and PVA (0.005 wt% based on suspension water) at 80 °C and a high stirring rate of 800 rpm. During the polymerization, the stirring rate and temperature were kept at 600 rpm and 90 °C, respectively. After about 5 h, the suspension was transferred to an autoclave and post-cured at 120 °C and 0.69 MPa (100 psi) in a nitrogen atmosphere for 12 h to achieve complete conversion. Finally, the suspension was cooled to room temperature and the final products, WEPSAC pellets, were collected by filtration.

2.3. Expansion of WEPSAC beads

After the suspension polymerization, the moisture content of the beads was determined by drying them in an oven. The average water content was found to be around 13.0%. To control the water content, the beads were dried at 70 °C in a vacuum oven for a specific duration of time. The beads with different moisture contents were immersed in an oil bath at 135 °C for 30 s. After that, the expanded beads were quenched by an ice-water mixture.

2.4. Batch foaming of WEPSAC by CO_2

In this study, a two-step batch foaming process was employed. The beads were first saturated with CO_2 at 25 °C under a pressure of 13.8 MPa (2000 psi) for 24 h to reach the equilibrium. After that, the pressure was quickly released and the beads were removed from the high-pressure chamber. The beads were subsequently immersed into an oil bath at a temperature of 135 °C for 15 s. The expanded beads were quenched in an ice-water mixture.

2.5. Extrusion foaming

Extrusion foaming was carried out by pumping the blowing agent (CO_2) into a twin-screw extruder (Leistritz ZSE-27; $L/D = 40$; $D = 27$ mm) using a gas/liquid injection port. For the PS/3.0 wt% AC sample without water, PS containing 5.0 wt% AC was pre-compounded with pure PS to dilute the AC content to 3.0 wt% via extrusion. For WEPSAC samples, the pre-dried PS beads (water content is around 8.0 wt%) were directly fed into the hopper by a volumetric feeder. The extruder is outfitted with a slit die, a shaping die, and rollers for foam uptake. During the extrusion foaming process, the screw speeds of the feeder and extruder were both kept at 50 rpm. The pressure of CO_2 was kept at 7.58–8.27 MPa (1100–1200 psi). The die temperature was kept at 120 °C and the die pressure was in the range of 8.62–9.31 MPa (1250–1350 psi) depending on different samples. The openings of the slit die and shaping die were kept as a constant. Foam samples were cut and removed before entering the rollers to maintain the cell morphology.

2.6. Foam characterization

The specimens for characterization were prepared by cutting segments out of extruded foams and then sanded on a sandpaper to achieve a thickness about 6.5 mm. During this process the skin of the foam was removed. After sanding, compressed air was blown on the foams to remove residual powders. The morphology of the foam was observed by a scanning electron microscope (SEM, Phillips XL30). Samples were cryo-fractured in liquid nitrogen, and the fracture surface was sputter-coated with gold. The Scion Image software was used to determine the cell size. For non-circular cells, an equivalent diameter was calculated by assuming that the cells are in circular shape.

Infrared (IR) transmission of each sample was measured using an in-house IR transmission tester to provide a property relevant for thermal insulation applications. This test provided data at a localized point, so the test was performed at several locations on the specimens and the resulting values were averaged. IR transmission is the ratio of power exiting to that entering the sample. The input power was 0.5 W for all samples measured. The distance between the optical fiber output of the laser diode and the power meter was about 5 cm.

The thermal conductivity was measured using a heat flow meter (FOX 200, Laser Comp). The temperature difference between the top and bottom plate was set at 40 °C.

3. Results and discussion

For the water expandable PS beads, the uniform distribution of water in PS plays a key role in achieving the foam product with desirable structure and properties. To realize this goal, surfactants such as sodium bis(2-ethylhexyl)sulfosuccinate (AOT) or water-swellable materials, for example starch, were introduced to facilitate the dispersion of water. However, the existence of surfactants and starch will deteriorate the fire resistance property and mechanical strength of the foam. In our case, AC was used as a water carrier and reinforcement material to avoid the use of surfactants and the loss of mechanical strength. Due to their exceptionally high surface area, almost three times the amount of water can be trapped by AC.

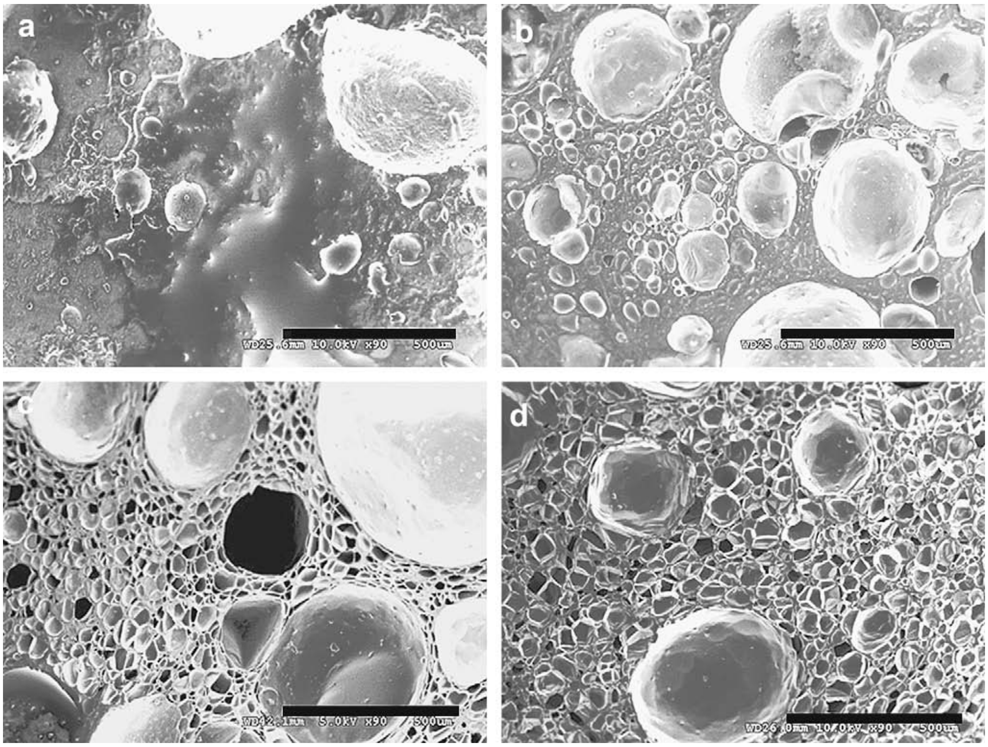

Fig. 1. SEM micrographs of foam morphology of water expandable PS/3.0% AC foams with different water contents in oil bath at 135 °C for 15 s, (a) dried beads, (b) 5.2 wt% water, (c) 10.1 wt% water, and (d) 12.3 wt% water. The scale bar is 500 μm.

The structures of foamed PS beads in the oil bath at 135 °C with different moisture contents are shown in Fig. 1. In the SEM micrographs, the large cavities and the smaller bubbles were formed during the suspension polymerization and the batch foaming process, respectively. It is obvious that the expansion ratio and the cell density increased with increasing water content. For the dried beads, only large cavities were observed, while the smaller bubbles were formed from the nucleation and growth of water vapor. The

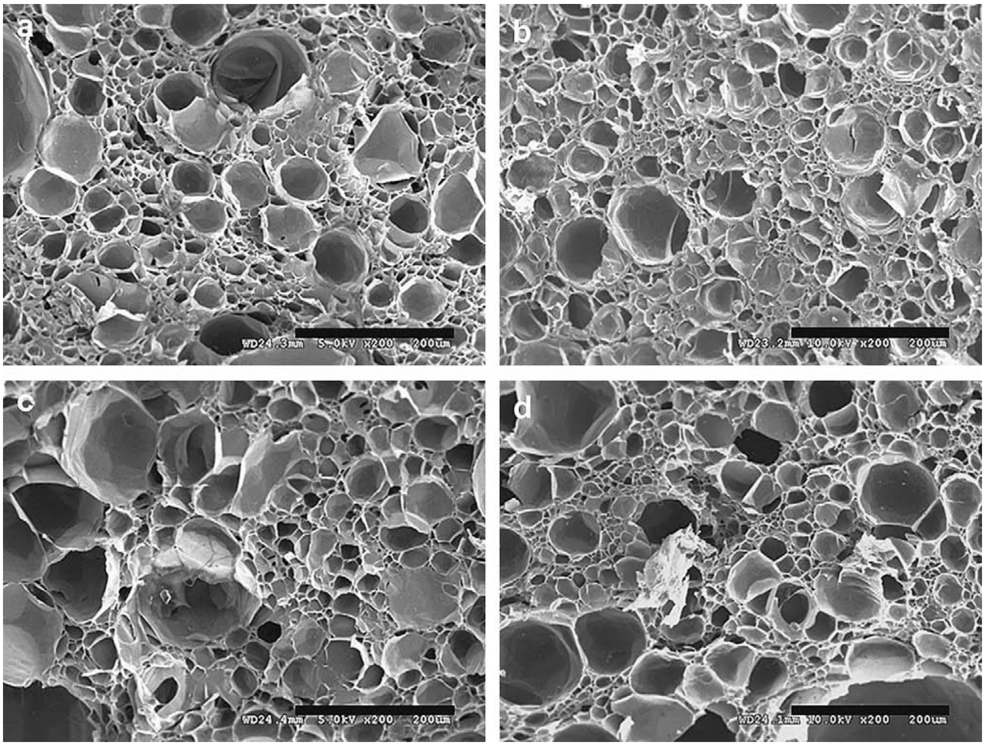

Fig. 2. Foam morphologies of water expandable PS/3.0% AC foams with different water contents expanded by using the combination of water and CO_2 as blowing agents in oil bath at 135 °C for 15 s, (a) dried beads, (b) 5.2 wt% water, (c) 10.1 wt% water, and (d) 12.3 wt% water. The scale bar is 200 μm.

Table 1
Bulk density of PS/1.0% talc, PS/3.0% AC and water expandable PS/3.0% AC foams.

	PS/1.0% talc	PS/3.0% AC	Water expandable PS/3.0% AC
Bulk density (g/cm^3)	0.043	0.043	0.032

WEPSAC beads saturated with CO_2 at 25 °C were also foamed in the same oil bath in an attempt to enhance the expansion ratio and to lower the foam density. It was found that the expansion ratio greatly increased due to the combination of two blowing agents, i.e. CO_2 and water. The cell morphologies are presented in Fig. 2. Although not well-defined, a bi-model foam structure was observed even in the foam made from dried beads. Since CO_2 was the sole blowing agent in dried beads, the large bubbles originated from the cavities shown in Fig. 1(a).

The feasibility of using WEPSAC in CO_2 in the extrusion foaming process was tested in the twin-screw extruder. Table 1 shows the bulk densities of different foams produced under the same operating conditions. It is clear that the dry AC did not change the foam density while the WEPSAC foam showed a much lower density (0.032 vs. 0.043 g/cc). This observation demonstrates that some water in WEPSAC was able to survive the harsh environment in the extruder and could serve as a co-blowing agent in foam extrusion. Since both water and CO_2 served as blowing agents, they produced a foam with a higher expansion ratio and hence a lower bulk density.

The morphology of extruded foam samples obtained by SEM is shown in Fig. 3. As shown in the images, the PS/3.0 wt% AC foam has the smallest cell size, indicating that AC can act as a nucleating agent. Comparing Fig. 2(b) and (c), the WEPSAC foam shows a larger cell size, which demonstrates that the existence of water helps to enlarge the cell size and reduces the foam density. Cell distribution is analyzed by Scion Image software and a minimum number of 100 cells are counted. The analyzed results are also shown in Fig. 3. It can be seen that the WEPSAC foam has a broader cell distribution and an increased portion of larger cells (>200 μm). The large cells are probably created by water.

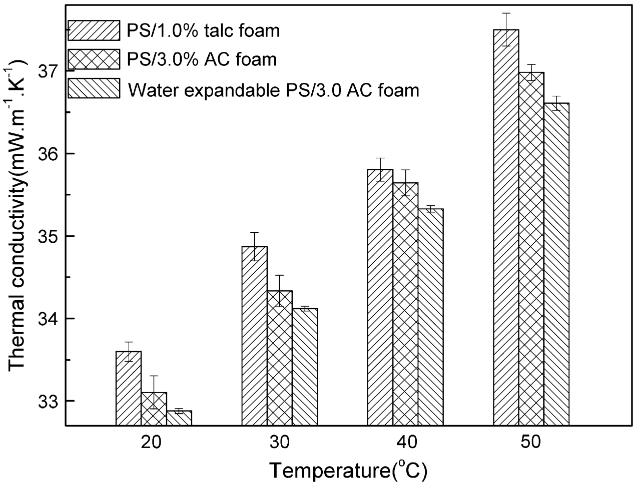

Fig. 4. The thermal conductivity of different foams.

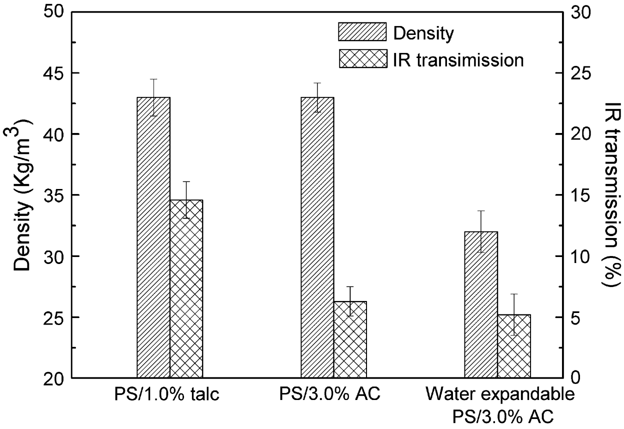

Fig. 5. IR absorption at 5 s exposure and bulk density of different foam samples.

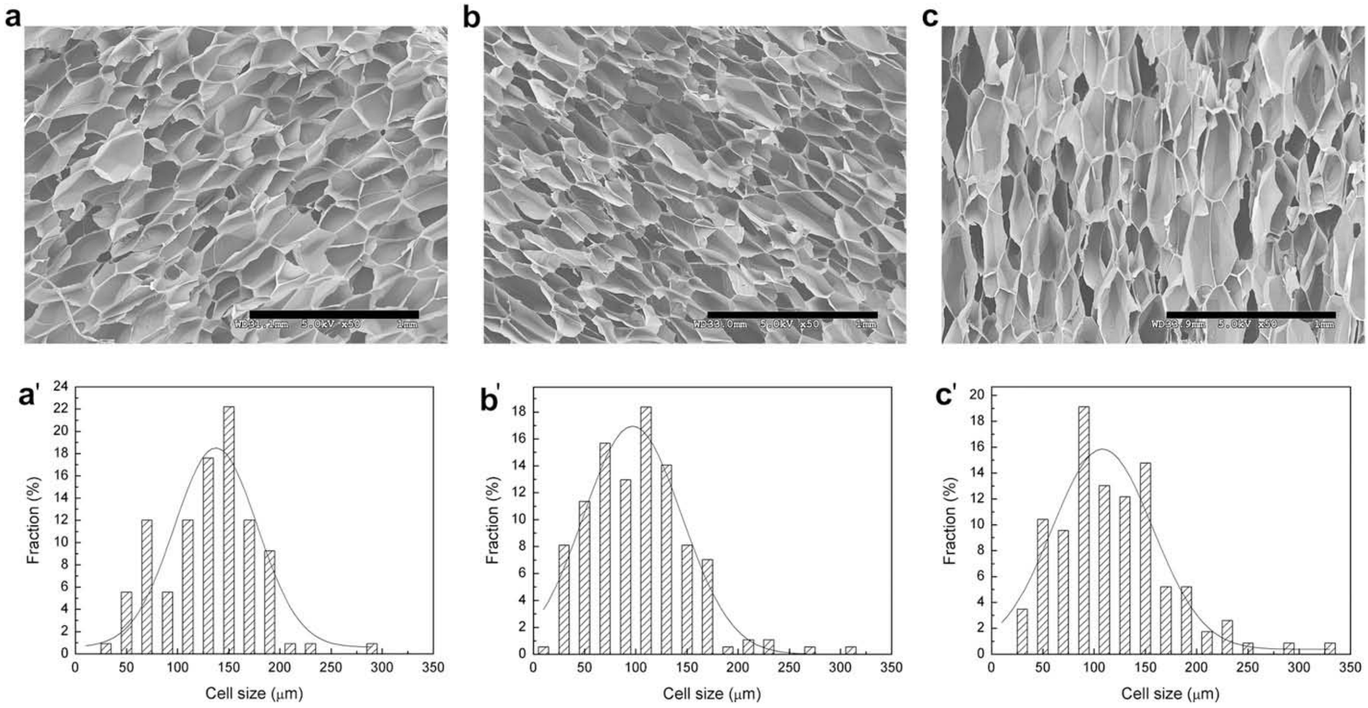

Fig. 3. Foam morphology and cell size distribution of (a) PS/1.0% talc, (b) PS/3.0% AC, (c) water expandable PS/3.0% AC foams. The scale bar is 1 mm.

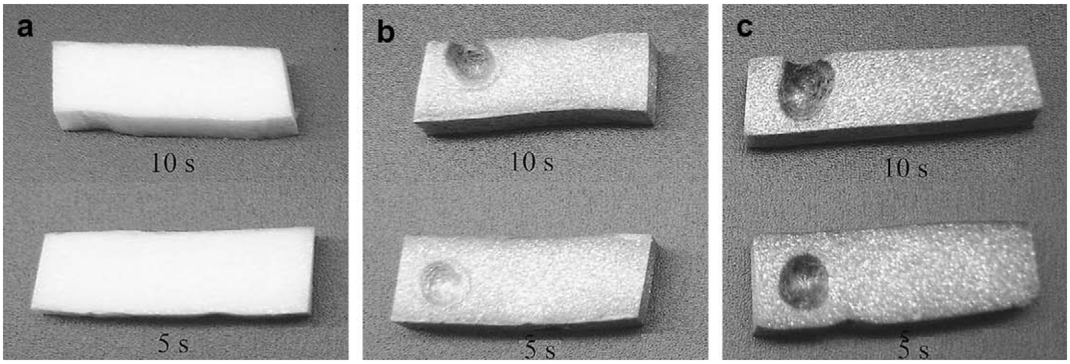

Fig. 6. (a) PS/1.0% talc, (b) PS/3.0% AC and (c) water expandable PS/3.0% AC foams samples after IR absorption with different exposure times (5 and 10 s).

The thermal conductivity of foams was measured at various temperatures and the results are presented in Fig. 4. For each sample, the thermal conductivity increases linearly with temperature within the temperature range investigated in this study. Heat conduction is caused by the collision of gas and/or solid molecules. At a higher temperature, these molecules have a higher mobility causing a higher collision probability. So the sample has a higher thermal conductivity at a higher temperature. This is well known in gases and amorphous solids. It is clear that the addition of AC decreased the thermal conductivity of PS foams and the WEPSAC foam possessed the lowest value. The overall thermal conductivity (λ) of a closed-cell foam comprises three components, conduction through the gas phase (λ_g), conduction through the cell wall and the solid struts (λ_s), and thermal radiation (λ_r) [14]. Since AC has a higher thermal conductivity than PS, the addition of AC will slightly increase λ_s. However, the presence of AC can greatly decrease λ_r through strong IR absorption. For the PS/1.0% talc and PS/3.0% AC, the contribution of λ_g is approximately the same due to the same bulk density. Therefore, the overall thermal conductivity is mainly determined by the combination of λ_s and λ_r. Since the change of λ_r is more significant in the presence of AC, the PS/3.0% AC has a lower thermal conductivity than PS/1.0% talc. As for the WEPSAC, the lower foam density will increase the contribution of λ_g, in addition to the changes occurred in λ_s and λ_r. This leads to the lowest thermal conductivity of the WEPSAC foam sample.

It is well known that carbon is a good IR absorber. Fig. 5 shows the IR transmission of different foams. The foam density is also presented for comparison. The transmission values decreased from 14.6% for pure PS foam to about 6.3% for PS with 3.0 wt% of AC and about 5% for WEPSAC with 3.0 wt% of AC. The difference of IR absorption is further demonstrated in Fig. 6. During the IR measurement, the temperature of samples increases due to IR absorption. When the temperature was higher than glass transition temperature, the foam would collapse and form a cavity. Fig. 6 shows that the cavity size, corresponding to the heat produced by the IR absorption, increased with the exposed time. Therefore, the cavity size can qualitatively reflect the IR absorption. Comparing the three images, the existence of cavity on the PS/AC foams verifies the higher IR absorption caused by AC. Furthermore, the cavity on the surface of WEPSAC sample is much larger than that of PS/AC even though the time of the IR exposure and AC loading of both samples were the same. Since IR absorption is related to the specific surface area of the dispersed AC particles, the larger cavities on the WEPSAC foam samples imply a better AC dispersion than that in the PS/AC foam. Our SEM study supports this observation.

4. Conclusions

In summary, water expandable PS/AC beads were successfully synthesized via a modified suspension polymerization process. Using AC as the carrier, water was introduced into the beads without emulsifiers. The synthesized WEPSAC beads trapped more water than just adding water containing AC in the PS extrusion foaming process. Water acted as a co-blowing agent, which enlarged the cell size and decreased the foam density in the CO_2 extrusion foaming process. With the addition of water containing AC, IR transmission through the foam decreased substantially. Together, the WEPSAC foam showed the lowest thermal conductivity in this study. This new material is useful for replacing the ozone-depleting blowing agents in thermal insulation foam applications.

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