THERMALLY INSULATED BIMODAL POLYSTYRENE/MULTI-WALLED CARBON NANOTUBE NANOCOMPOSITE FOAMS

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Abstract

We developed a bimodal polystyrene (PS)/multi-walled carbon nanotube (MWCNT) nanocomposite foam with a thermal conductivity of 30 mW/m-K without using any insulation gas. The MWCNTs were critical to the heat transfer because they decreased radiation significantly through the foams. A theoretical model has been proposed to analyze the thermal conductivity in nanocomposite foams. The proposed model verified the superior heat-blocking characteristics of the bimodal cellular morphology and the MWCNTs as follows: (1) The primary large cells acted to decrease the solid conduction; (2) The secondary small cells induced the Knudsen effect on gas conduction; and (3) The MWCNTs intensively blocked the IR transmission.

Introduction

Numerous countries have invested heavily in developing renewable energy, but these large investments have not proven as profitable as expected [1]. Therefore, it would be more prudent to focus on reducing the energy waste through enhanced insulation. In this context, superthermal insulation materials are urgently required to reduce energy loss and to address the concerns of scarce energy resources. Numbers of studies have been carried out to prepare thermal insulation foams using no insulation gases. Martinez-Diez et al. prepared polyethylene (PE) foams with a thermal conductivity of ~ 37 mW/m-K [2]. Guo et al. [3] and Zhang et al. [4] prepared the polystyrene (PS) foams, and their thermal conductivity was 31.2 mW/m-K.

In fact, the complicated foam morphology of bimodal foam has shown properties superior to those of unimodal foam across a broad range of applications. Because bimodal foams have too much variables, and the heat transfer is more complicated in them than it is in unimodal foams, the models used for unimodal foams are not applicable to bimodal foams. The sophisticated foaming procedure and the intricate foaming mechanism in the scCO₂ foaming method used to produce bimodal foams, means that a specific heat-transfer model is urgently required.

Carbonaceous materials are often added to block thermal radiation. Multi-walled carbon nanotube (MWCNT) as one kind of carbonaceous material can absorb radiation. In the region of near-infrared (NIR) radiation, MWCNTs have been applied in the selective thermal ablation of the tissues [5]. In the region of infrared (IR) radiation, MWCNTs have been used in the application of thermal insulation [6].

In our study, we prepared a bimodal PS/MWCNT foams by scCO₂ foaming. A model was also proposed to reveal the superior thermal insulating property for the bimodal nanocomposite foams. According to our model, the fundamental study of heat transfer in the bimodal PS/MWCNT foams shows that the very low thermal conductivity of 30 mW/ m-K was due to the unique synergy: (1) A large/small cell size ratio of ~ 20 led to a large expansion ratio; (2) Small secondary cells of ~ 5 μm induced the Knudsen effect; (3) MWCNTs led to sufficient radiative absorption.

Materials

Polystyrene, (PS) (Melt flow rate at 200°C/5 kg = 10 g/10 min, density = 1.04 g/cm³) and Multi-walled carbon nanotubes (average outer diameter: 10 nm, average length: 1.5 μm, surface area: 250-300 m²/g, carbon purity 90%) were used to prepare PS/MWCNT nanocomposites. CO₂ (purity > 99%) and pentane (water content < 0.02%) were used as physical blowing agents.

Experimental

Preparation of PS/MWCNTs nanocomposites and foams

PS/MWCNTs 10 wt% was used as masterbatch. The 0.1, 0.25, 0.5, 1, and 2 wt% nanocomposites were prepared via mixing with DSM compounder (Berstorff ZE25, screw length 48D) at 200°C and 100 rpm.

PS and PS/MWCNTs samples were then placed into a high pressure autoclave to dissolve CO₂ and pentane. The samples were saturated at various pressure for 3 days to
absorb sufficient amount of blowing agents. After depressurization, all samples were placed in 100°C boiling water to achieve high expansion ratio.

**Characterizations**

Scanning Electron Microscopy (SEM) was used to observe the foam morphology. The cell density with respect to the solid polymer, \( N_s \), the number average cell diameter, \( \phi_d \), were then calculated. The bulk densities of the samples before and after foaming were measured using the water-displacement method (ASTM D792-00). The cell density with respect to the solid polymer was then calculated by the following:

\[
N_s = \frac{n}{\rho_s A}^{1.5}
\]  

where \( n \) is the number of bubbles in a total area, \( A \), \( \rho_f \) and \( \rho_s \) are the densities of the foam and the solid bulk, respectively.

The thickness of the secondary cell layer surrounding the primary cell (\( \delta_{sec} \)) was calculated as follows:

\[
\delta_{sec} = \frac{d_{pri}}{\sqrt{\phi_{pri} \varepsilon_{VF}}} - d_{pri}
\]  

where \( \phi_{pri} \) and \( d_{pri} \) are the volume ratio and size of primary cells, \( \varepsilon_{VF} \) is the volume fraction of the foams.

Transient Plane Source (TPS) hot disk thermal constants analyzer (Therm Test Inc., TPS 2500, Sweden) was used to measure the thermal conductivity of nanocomposites and foams. The measurement was performed at room temperature using two pieces of sample around 15 mm in diameter. The power output (0.005–0.020 W), test duration (5–20 s) and sensor size (2 or 3 mm in radius) depends on the thermal characteristics of the testing samples.

Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the spectral transmittance of radiation through the foams. The spectral was collected in the spectral range from 4000 to 400 cm\(^{-1}\). To eliminate the effect of sample thickness on IR transmittance, the foams were cut into plate shape with the thickness ranging from 0.2 to 2 mm.

**Heat transfer in bimodal foams**

The total thermal conductivity (\( k_{total} \)) of polymeric foams can be expressed as follows:

\[
k_{total} = k_{con} + k_{rad} = k_{pri} + k_{total} + k_{rad}
\]  

where \( k_{con} \) is the thermal conductivity via conduction including solid conductivity (\( k_{solid} \)) and gas conductivity (\( k_{gas} \)), \( k_{rad} \) is the thermal conductivity by radiation.

**Conduction**

Although bimodal polymeric foams have a non-uniform foam structure, their primary large cells are distributed evenly throughout the whole foam. Therefore, a repeat bubble cluster unit, with a primary large cell surrounded by secondary small cells, can be extracted from the bimodal foam morphology. The repeat unit can be considered as four pieces, and their corresponding thermal resistances are: (1) Secondary cells with a thermal resistance of \( R_{sec1_M1} \) at the top of the repeat unit; (2) Secondary cells with a thermal resistance of \( R_{sec2_M1} \) at the bottom of the repeat unit; (3) Secondary cells with a thermal resistance of \( R_{pri-M1} \) in the repeat unit surrounding the primary cell; and (4) Primary cell with a thermal resistance of \( R_{pri-M1} \) at the center of the repeat unit.

\[
R_{sec1-M1} = \frac{\delta_{sec}}{2k_{pri}\left(d_{pri} + \delta_{sec}\right)^2}
\]  

\[
R_{sec2-M1} = \frac{d_{pri}}{k_{pri}\left(2d_{pri}\delta_{sec} + \delta_{sec}^2\right)}
\]  

\[
R_{pri-M1} = \frac{d_{pri}^2}{k_{pri}\left(d_{pri}^2 + d_{pri}\delta_{sec} + \delta_{sec}^2\right)}
\]

where \( k_{pri} \) is the thermal conductivity of the primary cell region. \( \delta_{sec} \) is the thickness of the secondary cell layer surrounding the primary cell, and \( k_{sec} \) is the secondary cell region’s thermal conductivity.

The thermal conductivity (\( k_{con}^I \)) of the repeat unit is as follows:

\[
k_{con}^I = \frac{\left(2d_{pri}\delta_{sec} + 3d_{pri}\delta_{sec}^2 + \delta_{sec}^3\right)k_{sec} + \left(d_{pri}^2 + d_{pri}\delta_{sec} + \delta_{sec}^2\right)k_{pri}}{\left(d_{pri}^2 + 2d_{pri}\delta_{sec} + 3d_{pri}\delta_{sec} + \delta_{sec}^2\right) + d_{pri}\delta_{sec}^2k_{pri}/k_{sec}}
\]

**Figure 1** Schematic graph (a), and thermal resistance (b) for the model

The equation to calculate the gas conductivity in polymeric foams is summarized below:

\[
k_{gas} = \frac{1}{1 + 2KnB}k_{gas}^{0.314}
\]

where \( \varepsilon_{VF} \) is the void fraction of the foam, \( B \) is the energy transfer between the gas molecules and the cell walls, 1.94, and \( k_{gas}^0 \) is the bulk gas conduction, 26 mW/m.K for air.

The Knudsen number (\( Kn \)) is expressed by: [7]

\[
Kn = \frac{\varepsilon_{mean}}{d}
\]

where \( l_{mean} \) is the mean free path of the gas molecules, 68 nm in an ambient condition and \( d \) is the cell size.

**Radiation**

From macroscopic view point, uniform polymeric foams can be regarded as homogeneous samples. The
spectral extinction coefficient \(K_{\epsilon,\lambda}\) is then independent of foam thickness and the transmittance \(\tau_{n,\lambda}\) can be expressed by:
\[
\tau_{n,\lambda} = ce^{-\int_0^L K_{\epsilon,\lambda} ds}
\]
(10)
where \(L\) is the sample thickness, \(c\) is constant. By linear regression of \(\ln(\tau_{n,\lambda})\) against \(L\), the slope of the straight line is \(K_{\epsilon,\lambda}\). According to the Planck distribution of infrared radiation over wavelength, the Rosseland extinction coefficient \(K_{\epsilon,\lambda}\) is an average of \(K_{\epsilon,\lambda}\) by the local spectral energy.

Using Rosseland extinction coefficient, the radiation through polymeric foams can be expressed by: [8]
\[
k_{rad} = \frac{16n^2\sigma T^3}{3K_{e,R}}
\]
(11)
where \(n\) is the effective index of refraction. Due to the high void fraction in polymeric foams, \(n\) in this study is 1, which is the same value with air.

The radiative absorption efficiency by the MWCNTs is defined as follows:
\[
A_{B} = \frac{k_{rad,PS} - k_{rad,PS/CNT}}{k_{rad,PS}}
\]
(12)
where \(k_{rad,PS}\) and \(k_{rad,PS/CNT}\) represent the radiative thermal conductivity passing through PS foams and PS/MWCNT foams, respectively.

**Results and discussions**

**Cell morphology of PS/MWCNT foams**

Figure 2 shows SEM micrographs of the pristine PS and the PS/MWCNT foams. When less than 30 ml of pentane was added to the foaming chamber to plasticize the PS matrix, all of the samples foamed in this condition had a unimodal foam morphology. At a foaming pressure of 13.8 MPa, the increased amount of pentane increased the expansion ratio from 9- to 19-fold. The foamed samples’ cell density was \(\sim 1 \times 10^{11} \#/cm^3\). Thus, the increased expansion ratio led to an increase in the cell size from 2 μm to 6 μm. When 30 ml of pentane was added to the foaming system, the foaming pressure increased from 13.8 MPa to 20.7 MPa and this increased the cell density to \(\sim 3 \times 10^{11} \#/cm^3\). But it decreased the expansion ratio to \(\sim 15\)-fold and also reduced the cell size. With an increased gas content (that is, a higher gas pressure), the cell density increased, and both the cell size and the expansion ratio decreased.

When the amount of pentane added to the foaming chamber was increased from 30 ml to 60 ml, it not only induced stronger plasticization in the PS matrix, but it also changed the bubble nucleation behavior. The result was a bimodal cellular structure with a large expansion ratio. Two-step depressurization was also applied to prepare bimodal foams with a relatively small expansion ratio. Figure 3 shows the SEM micrographs of the fabricated pristine PS and PS/MWCNT bimodal foams. In our study, the bimodal foams’ primary large cells were 6 ~ 25 times larger in diameter than the secondary small cells. This led to an increased expansion ratio in the PS/MWCNT bimodal foams from 8- to 31-fold. At the same time, the corresponding secondary cells remained similar in size to those of the unimodal foams.

A bimodal cellular structure via scCO\(_2\) foaming can be obtained by inducing bubble nucleation via depressurization control [9] or by using co-blowing agents [10]. The two-step depressurization method adopted in this paper produced bimodal foams by initiating bubble nucleation at two different steps. As for co-blowing agents, adding 60 ml pentane to the scCO\(_2\) foaming system might have induced two phases: a PS-rich phase and a pentane-rich phase. The pentane-rich phase normally has a very low viscosity due to pentane’s strong plasticization effect. Therefore, bubble nucleation in the pentane-rich phase may have been immediately followed by severe cell coalescence. Subsequently, during the second foaming step (that is, heating in 100°C water steam), for either the two-step depressurization method or the co-blowing agents method, the dissolved blowing agents were prone to diffuse into larger cells due to the lower pressure inside them. Thus, compared with the surrounding secondary small cells, the primary large cells grew even greater, and eventually bimodal foams were obtained.
**Thermal conductivity of PS/MWCNT foams**

The proposed model was used to calculate the thermal conductivity of the obtained unimodal and bimodal nanocomposite foams. The thermal conductivity through the gas and solid phases in the PS/MWCNT foams was experimentally obtained by subtracting the radiative thermal conductivity from the measured total thermal conductivity. It is noteworthy that the calculated thermal conductivity via conduction was in good agreement with the experimentally measured data, as Figure 4 shows. This indicated that the modeling of the thermal resistance in both the primary and secondary cell regions adequately describes the actual heat-blocking behavior in the bimodal cellular structure.

The “gas + solid” conductivity for both the unimodal and bimodal nanocomposite foams is mainly influenced by two factors: (i) The gas conductivity in the gas phase and (ii) The solid conductivity through the solid matrix. With respect to gas conduction, the gas confined within the cells of the unimodal and bimodal foams decreased the thermal conductivity by means of the Knudsen effect (see Eq. 8), with a decrease in the cell size. On the other hand, the nanocomposite foams had larger conductivities via conduction with a larger MWCNT concentration, as shown in Figure 4. This was because the bulk solid conductivity of the PS/MWCNT nanocomposites increased with the increased MWCNT concentration. Figure 4 also shows that the foamed sample with a larger expansion ratio had a smaller thermal conductivity than the one with a smaller expansion ratio, due to the decreased volume fraction of the solid matrix.

The advanced bimodal cellular structure more effectively blocked the heat transfer via conduction than the unimodal foam. To maintain small cells and thereby to decrease gas conduction via the Knudsen effect, we obtained a maximum expansion ratio of 18.7-fold in the unimodal foams. The corresponding conductivity via conduction was 30 mW/m·K as Figure 4a shows. The bimodal foams, on the other hand, achieved a much larger expansion ratio up to 31-fold. Meanwhile, the secondary cells in the bimodal foams remained similar in size to those in the unimodal foams. Therefore, the conductivity via conduction in the bimodal foams was successfully decreased to 28 mW/m·K due to the low volume fraction of the foams’ solid matrix and the Knudsen effect in the small secondary cells.

**Figure 4** Thermal conductivity via conduction in (a) unimodal foams and (b) bimodal foams. The curves represent the values calculated by proposed model.

FTIR spectrometry effectively measures radiation by recording the IR-transmitted energy through the foams. The higher the transmittance, the more radiative thermal conductivity there will be. In the foam structure, the short wavelength radiation was easily blocked by the reflection at the cell walls [6]. Thus, the long-wavelength radiation contributed to most of the radiative energy in the PS foam system, which had a large expansion ratio and a weak IR-absorbing polymer matrix. In both the unimodal and bimodal PS foams, the MWCNTs were added to the polymer matrix to effectively absorb the incidental radiation. Figure 5 shows the bimodal PS/MWCNT foams’ spectral transmittance with various MWCNT contents. Adding 0.25 wt% MWCNT decreased the IR transmittance from 84% to 68% at a wavelength of 25 μm (wavenumber = 400 cm⁻¹). When the MWCNT content was further increased to 2.0 wt% in the PS matrix, the IR transmittance was decreased to less than 10%. It was noted that the nanosize MWCNTs’ radiative absorption in the bimodal foams was outstanding.

**Figure 5** Spectral transmittance of bimodal foams (foaming condition: 13.8 MPa with 60 ml pentane added): (1) pristine PS foam 0.64 mm thick, (2) PS/MWCNT 0.25 wt% foam 0.59 mm thick, (3) PS/MWCNT 1.0 wt% foam 0.62 mm thick, and (4) PS/MWCNT 2.0 wt% foam 0.69 mm thick

The effect of MWCNTs on thermal radiation was quantitatively studied using the Rosseland equation (Eq. 11) to calculate the transmitted radiative energy. Figure 6a summary the calculated radiative thermal conductivity...
of both the unimodal and bimodal foams. We note that the radiative thermal conductivity through the PS foam with a large expansion ratio was very high due to the PS matrix’s low IR absorption. Figure 6a shows that the foamed samples’ radiative thermal conductivity increased almost linearly with the expansion ratio’s increase, which ranged from 8- to 30-fold. Therefore, a linear regression \( y = ax + b \) was applied to fit the data shown in Figure 6a. The radiative absorption efficiency (calculated using Eq. 12) is shown in Figure 6b.

Due to their strong IR absorption capacity, the MWCNTs added to the PS matrix helped to block the thermal radiation in the foams, and they enhanced the solid matrix’s radiative absorption efficiency. Their influence on the reduction of IR radiation was especially prominent when the nanocomposite foam had a large expansion ratio. For instance, 1 wt% MWCNTs reduced the radiative thermal conductivity by 8.5 mW/m-K in the bimodal foam with a 28-fold expansion ratio. Consequently, the MWCNTs in a bimodal nanocomposite foam with a larger expansion ratio could absorb more radiative energy than they could in unimodal foam.

The total thermal conductivities of the unimodal and bimodal PS/MWCNT foams are shown in Figure 7, together with the calculated values based on proposed model. Because of their limited expansion ratio, the conduction through the unimodal foams was dominant. And the radiative absorption capacities of the MWCNTs had only a limited effect in reducing the total thermal conductivity. On the other hand, bimodal foams with a large expansion ratio were easily achieved. Therefore, the contribution of the conductivity via conduction to the total thermal conductivity in these foams was decreased. In the bimodal foams, the MWCNTs dramatically absorbed radiation, and the total thermal conductivity was decreased at larger expansion ratios.

By adjusting the expansion ratio and the MWCNT concentration, the lowest thermal conductivity of the unimodal PS/MWCNT foams obtainable in this study was 32.8 mW/m-K. The application of a bimodal cellular structure was effective in further decreasing the total thermal conductivity. This was because the primary large cells present in the bimodal foams induced a larger expansion ratio than they would do in unimodal foams. This expansion reduced the solid conduction while the secondary small cells in the bimodal foams also experienced the Knudsen effect, which reduced gas conduction. Furthermore, the MWCNTs in the bimodal foam with a large expansion ratio absorbed more radiation and contributed to less solid conduction than they did in the unimodal foams. As a result, by tailoring the bimodal cellular structure and the MWCNT concentration, the PS/MWCNT 1.0 wt% bimodal foam achieved a minimum thermal conductivity of 30.2 mW/m-K.

The total thermal conductivity of the foams with a different foam morphology made from various polymers and foaming technologies were summarized and compared in Figure 8. When the polymeric foams had a small expansion ratio below 5-fold, their thermal conductivity was over 50 mW/m-K, regardless of the micro- or nano-cells [11]. This was because the heat transfer in polymeric foams with an expansion ratio of less than 5-fold is dominated by solid conduction. The expansion ratio has to be at least 10-fold to make the polymeric foams’ thermal conductivity below 40 mW/m-K. Therefore, in such a high density foam system, an increase in the expansion ratio will significantly decrease the total thermal conductivity [12]. On the other hand, the total thermal conductivity of the foams with a large expansion ratio became very large as well because of the increased radiative thermal conductivity. For instance, the total thermal conductivity of the low-density expandable PS (i.e., EPS) foams seen in Figure 8 becomes higher than 35 mW/m-K for the expansion ratio over 60-fold [13].

Compared with the unimodal foams, the bimodal nanocomposite foams, consisting of primary large cells, secondary small cells, and carbonaceous additives, had a unique synergy to effectively block the heat transfer through solid conduction, gas conduction, and radiation. Zhang et al. prepared a bimodal PS nanocomposite foam with a 25-fold expansion ratio and over 50 μm secondary cells. The corresponding thermal conductivity was 31.5 mW/m-K [10]. Based on our model, the thermal conductivity can be further decreased by increasing the expansion ratio and decreasing the cell size. We prepared a novel bimodal PS/MWCNT foam with a 28-fold expansion ratio and 5.8 μm secondary cells. This bimodal...
foam structure has an advantage of expansion ratio control while utilizing the Knudsen effect, the MWCNTs then absorb large amount of thermal radiation, and the foam was thus able to achieve a very low thermal conductivity of 30.2 mW/m-K without the use of an insulation gas.

Figure 8 Total thermal conductivity of polymeric foams
* The thermal conductivity of EPS foams were measured at 10°C

Conclusions

In this study, we prepared unimodal and bimodal PS/MWCNT nanocomposite foams using the scCO$_2$ foaming system. Their thermal insulation performances were evaluated experimentally and theoretically. A model based on the thermal resistances in the primary and secondary cell regions was proposed to quantitatively investigate the heat transfer in bimodal nanocomposite foams. Based on the model, we optimized the cellular structure and the MWCNT’s concentration, and then we achieved a minimum total thermal conductivity of 30.2 mW/m-K in the bimodal PS/MWCNT 1.0 wt% foam system with a 28-fold expansion ratio and 5.8 μm secondary cells. In the above bimodal foam, the MWCNTs’ ability to decrease radiative heat transfer by 8.5 mW/m-K was of great importance.

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