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Advanced bimodal polystyrene/multi-walled carbon nanotube nanocomposite foams for thermal insulation

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ABSTRACT

We developed an advanced bimodal polystyrene (PS)/multi-walled carbon nanotube (MWCNT) nanocomposite foam with a very low thermal conductivity of 30 mW/m-K without using any insulation gas. The MWCNTs significantly decreased the radiative thermal conductivity of the foams with the high infrared (IR) absorption capability and increased the optimal expansion ratio of the foams to minimize the total thermal conductivity. The radiative blocking effect of MWCNTs was quantitatively modeled by calculating the IR absorption index of the unfoamed nanocomposites and calculating the IR extinction coefficient of the foamed nanocomposites. In addition, a theoretical model to analyze the optimal expansion ratio in synergistic bimodal nanocomposite foam was developed for the first time. The calculated values were in good agreement with the experimental data to verify the superior heat-blocking characteristics of the MWCNTs in the bimodal cellular morphology.

1. Introduction

There is a strong global demand for innovative materials with superthermal insulation properties to help save energy. Numerous countries have invested heavily in developing renewable energy to replace conventional energy, but these large investments have not proven as profitable as expected [1]. For example, there was very little contribution, less than 0.2%, of the wind, tidal, and solar energy to the total produced energy in Canada during 2010–2014 [2]. Therefore, it would be more prudent to focus on reducing the energy waste through enhanced insulation as well. In fact, industrial and residential buildings typically consume more than 60% of the total energy produced [2], and it will be desirable to decrease the waste energy from the heating and cooling system with improved insulation. To this end, the European Commission introduced the Energy Saving 2020 to increase the energy efficiency 20% by 2020 [3]. In this context, superthermal insulation materials are urgently required to reduce energy loss and to address the concerns of scarce energy resources.

Polymeric foam is one type of insulation materials with a low thermal conductivity [4]. An environmentally hazardous insulation gas is often used in these foams to enhance their thermal insulation performance. Fluorocarbons, for example, are one type of insulation gas. Their thermal conductivity of ~12 mW/m-K is much lower than that of air at 26 mW/m-K [5]. But the 1996 Montreal Protocol called for an international ban on the ozone-depletion potential (ODP) posed by chlorofluorocarbon (CFC)-based blowing agents [6]. At that time, the foam industry had been using low ODP hydrochlorofluorocarbon (HCFC)-based blowing agents, such as HCFC-22, HCFC-141b and HCFC-142b, during its transition away from CFCs. However, the HCFC-based foams were phased out in January 2002 from Europe and in January 2010 from North America. Some companies then started to use hydrofluorocarbons (HFCs), but their high global warming potential (GWP) limited the usage. With these insulation gases, the polymeric foams' initial

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thermal conductivity is typically around 28 mW/m-K [7]. Along with the insulation gases' escape over time, the thermal conductivity of foams may become higher than 30 mW/m-K in a few years [7]. It should also be noted that an increased expansion ratio with higher insulation-gas dependency may increase the overall conductivity, because of a significant increase in radiation [8,9]. So there is an optimal expansion ratio to minimize the overall thermal conductivity, and the value of the optimal expansion ratio is relatively low for most polymers with a zero or low IR absorption index. But as demonstrated in the later section of this paper, the optimal expansion ratio can be increased by adding carbonaceous materials to block heat transfer.

Efforts have been made to avoid the environmentally dangerous insulation gas while maintaining a low thermal conductivity of the insulation material. Vacuum panels are an outstanding choice because they offer better insulation properties (below 10 mW/m-K), but they can be easily damaged during installation or during their usage (e.g., by nails in the walls), or by an inevitable and gradual vacuum loss over time. Glassfiber-based insulation products typically have 40 mW/m-K, and they have a moisture absorption potential which can increase both their thermal conductivity and the generation of fungus. Loose-fill cellulose has a thermal conductivity similar to glassfiber, i.e., 40 mW/m-K, but the small particles contained in cellulose can cause house dust. Expanded vermiculite mineral in the form of loose particles, on the other hand, has a relatively large thermal conductivity of 70 mW/m-K due to its low porosity. Researchers have also tried to reduce the cell size to nano-scale to decrease the gas-conduction contribution using the Knudsen Effect. But the overall conductivity of the nanocellular foams increased, ranging 80–110 mW/m-K [10,11], because of the increased polymer-conduction contribution through a lower expansion ratio from the severe cell rupture. In a nutshell, it has been found extremely difficult to further decrease the thermal conductivity to below 31 mW/m-K without using the environmentally problematic insulation gas [12–14]. The low expansion ratio of the foams with small cells can be increased by introducing large cells into the foams, i.e., by forming a bimodal cellular structure [15]. But the increased expansion ratio will increase the radiative heat transfer and, therefore, an effective radiation blocking mechanism is desperately needed for the use of foams with a large expansion ratio for insulation.

Uniquely structured nanocomposite foams that use carbonaceous materials as additives would be of great value in achieving low conductivity without using any insulation gas. Carbonaceous materials are, in fact, often added to these foams to act as a black body and to block heat radiation. The black body effectively absorbs the electromagnetic radiation for all of the frequencies and all of the incident angles [16]. Multi-walled carbon nanotube (MWCNT) is one kind of carbonaceous material that can be brought to an excited electronic state after absorbing radiation in an electromagnetic field. The absorbed radiative energy is finally converted into thermal energy after the rapid relaxation from an excited electronic state to a ground state [17,18]. In the near-infrared (NIR) radiation region, MWCNTs have been applied in the selective thermal ablation of tissues [19]. In the infrared (IR) radiation region, MWCNTs have been used in thermal insulation applications [20]. In addition, MWCNTs with a high aspect ratio [18,21] have acted as effective heterogeneous cell-nucleating agents in the supercritical CO_2 ($scCO_2$) foaming process. This has increased the cell density, reduced the cell size, and altered the cellular morphology [22–24]. When a nanocomposite foam with a complicated cellular morphology has a strong IR absorption index, a largely expanded and small-size cell structure effectively blocks both radiation and conduction, and thus lowers the overall thermal conductivity [20]. Polystyrene (PS) has strong non-bond interactions with MWCNTs that ensure a good dispersion of the MWCNTs [25,26]. The PS/MWCNT's foam morphology is easily tailored by controlling the foaming pressure and temperature [27–29]. Therefore, PS/MWCNT was selected as a case example in the preparation of nanocomposite foams for the insulation purpose.

In our study, we prepared novel bimodal PS/MWCNT nanocomposite foams by the $scCO_2$ foaming process. By adding MWCNTs, the IR absorption index of the nanocomposite foams increased from 0.004 to 0.02 at 1 wt% concentration, and their expansion ratios could be increased up to 31-fold with this bimodal structure. Consequently, these foams had an extremely low thermal conductivity of 30 mW/m-K, without the use of any insulation gas. The model we developed showed that the bimodal MWCNT nanocomposite foams' superior thermal insulating property had accurately predicted the system's thermal conductivity. Further, based on this model, the fundamental study of heat transfer in bimodal PS/MWCNT foams showed that the exceedingly low thermal conductivity had been due to this foams' unique synergy: (1) The MWCNTs decreased the thermal conductivity by radiation because of their ability to absorb it and, thereby, to increase the optimal expansion ratio that minimizes the total thermal conductivity; (2) The bimodal cellular structure decreased the thermal conductivity via conduction by increasing the expansion ratio.

2. Theoretical fundamentals of heat transfer in bimodal polymeric foams

When the polymeric foams have cells of less than 3 mm in diameter, the convection in foam is negligible [30], and the total thermal conductivity (k_{total}) of polymeric foams can be expressed as follows:

$$k_{total} = k_{rad} + k_{con} \tag{1}$$

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

2.1. Radiation

Radiation can easily pass through the high-porosity polymeric foams. Due to the very low radiative absorption of low-density polymeric foams, radiation can contribute up to 40% of the total thermal conductivity [31]. Therefore, blocking radiation is essential to reduce the total thermal conductivity. When radiation passes through polymeric foams, it can be attenuated either by reflection on the cell wall surfaces or by absorption via the dense polymer thin films (cell walls). Because radiation is multi-reflected inside the foam, the surrounding cell walls will ultimately absorb it. Consequently, we can apply the diffusion-approximated Rosseland Equation to the foam structure [8,32]. The detailed calculation can be found in the supporting information.

2.2. Conduction

The thermal conductivity of a material with repeat units can be represented by the thermal conductivity of a single unit. In case of bimodal polymeric foams, although they have a non-uniform foam structure, their primary large cells are normally distributed evenly throughout the whole foam due to the uniformly distributed cell-nucleation agent in the polymer matrix. Therefore, a repeat bubble cluster unit, with a primary large cell surrounded by secondary small cells, can be extracted from the bimodal foam morphology, as Fig. 1a and b shows. The heat flow in the single bubble cluster is sufficient to represent the heat transfer in the whole foam