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Heat transfer in microcellular polystyrene/multi-walled carbon nanotube nanocomposite foams

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ABSTRACT

We report the heat-transfer characteristics of polystyrene (PS)/multi-walled carbon nanotube (MWCNT) nanocomposite foams with a large expansion ratio (18-fold) and a microcellular cell size (5 μm) that have never been achieved before. These PS/MWCNT foams exhibited excellent thermal insulation performance even without insulation gas. The 5 μm-sized cells in these PS/MWCNT foams are small enough to induce Knudsen effect, and also lead to a distinct radiation behavior that has never been reported; that is, because of the unique synergy of the small cells and the MWCNTs, the short wavelength radiation below the cell size is 100% blocked while the long wavelength radiation over the cell size is strongly attenuated. We made an in-depth analysis of the heat transfer through the PS/MWCNT foams using models. Adding 2 wt% MWCNTs into the PS matrix, 86% of the radiative thermal conductivity was effectively blocked, and the radiative contribution was reduced to 3.5% of the total thermal conductivity. However, the MWCNTs increased the solid conductivity of the PS/MWCNT foams due to their inherently high thermal conductivity. So, a compromised content of 1 wt% MWCNTs was added to optimize solid conduction and radiation, and thereby to minimize the total thermal conductivity to 32.8 mW/m K.

1. Introduction

Polymeric foams with thermal insulation are expected to make great contribution to addressing urgent economic and environmental concerns by preserving energy resources, reducing greenhouse gas emissions, and helping to alleviate climate change. For example, thermal-insulation polymer foams with low thermal conductivity are widely used to save energy in the heating and cooling of buildings and factories.

Numerous studies have been carried out on the thermal conduction (i.e., heat transfer) properties of polymeric foams. It is considered that gas conduction, solid conduction and radiation jointly influence the heat-transfer properties of polymeric foams [1]. The heat-transfer properties can be effectively decreased by using an insulation gas to decrease gas conduction [2], by applying a large expansion ratio to decrease solid conduction [3], and/or by mixing with carbonaceous materials to decrease radiation [4]. The thermal

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conductivity of an insulation gas, such as fluorocarbons, is on the order of ~12 mW/m K, which is much lower than that of air (i.e., 26 mW/m K), but the insulation gas either imposes environmental problems or is cost-prohibitive to the manufacturers [2]. The insulation gas would also diffuse out of the foams and deteriorate the long-term thermal insulation performance.

Another efficient method to lower the gas conductivity is to make use of the Knudsen effect via small cells [5]. Aerogel, a nanoporous material, has superior thermal insulation performance due to the Knudsen effect (low gas conductivity) and large porosity (low solid conductivity) [6]. Unfortunately, because of the time-consuming processing method, the large amount of an organic solvent involved in the fabrication, and the low cost-efficiency, the aerogel usage is still limited in industry. Supercritical CO_2 ($scCO_2$) foaming is a promising method to produce eco-friendly thermal insulation materials with smaller cells compared to the conventional foams. Especially nanocells have been developed successfully [7]. Although the smallest cell size using $scCO_2$ foaming is 10–40 nm, the expansion ratio that has been achieved so far is less than 1.5 [8–10]. As a consequence, the thermal conductivity of nanofoam with 1.5-fold expansion is typically 80 mW/m K at least [5], which is much higher than the required thermal conductivity of an insulation material. Recently, Costeux et al. modified the foaming process and produced 5-fold expanded nanocellular foams (cell size < 80 nm) [11]. Our analysis to be shown below predicts that the thermal conductivity of these materials should be at least 45 mW/m K. To achieve superthermal insulation, both a small cell size and a large expansion ratio are the prerequisites, but it is extremely difficult to produce nanocellular foams with a large expansion ratio of over 10 with the current state-of-the-art foam technology due to the high chance of cell opening through the thin cell walls [7,9,11,12]. Once cell opening is active, the gas contained within the cells can easily escape to the environment, and therefore, the available gas to foam expansion becomes limited, resulting in a small expansion ratio. If cell opening occurs at the last minute of expansion, we may be able to maintain the large expansion ratio that was achieved, by quickly freezing the foam structure [13]. But if cell opening occurs before major expansion takes place because of too thin a wall thickness between nano cells, then there will be less amount of gas available for expansion, and thereby, expansion will be suppressed. So until the limiting factors of these existing technologies are overcome, we will not be able to fabricate nanocellular foams with low thermal conductivity.

Herein, we prepared the polystyrene (PS)/multi-walled carbon nanotube (MWCNT) foams by $scCO_2$ foaming for thermal insulation and studied the fundamentals of heat transfer in PS/MWCNT foams. To the best of our knowledge, these PS/MWCNT foams have the smallest cell size of 5–6 μm at such a high expansion ratio of 18-fold. Although the cell size was increased, compared to the nanofoams, to achieve large expansion, the Knudsen effect in the 5 μm cells still attributes to decrease the gas conductivity significantly by 1.2 mW/m K. In addition, we discovered for the first time that the radiation with wavelength less than the cell size was intensively attenuated by reflection at the interfaces between cell walls and air, while the radiation with wavelength larger than the cell size was strongly attenuated by absorption via MWCNTs. The radiative thermal conductivity contributes up to 22% of the total thermal conductivity in PS foam. Dispersed MWCNTs in PS foams are quite efficient to block the long wavelength radiation. In order to understand the specific effects of MWCNTs on the heat transfer in PS/MWCNT foams, we made an in-depth study using the gas conduction model, the Glicksman model, and the Rosseland model. According to those models, we found that MWCNTs decrease the radiative thermal conductivity but increase the solid conductivity. The minimal thermal conductivity was 32.8 mW/m K without using any insulation gas when a 1 wt% of MWCNTs were added to the PS foam with 18-fold expansion. In the future, if an improved $scCO_2$ foaming technology enables us to fabricate 18-fold PS/MWCNT foam with a reduced cell size on the order of 100 nm or smaller, the thermal conductivity will go below 16.4 mW/m K according to our models because the Knudsen effect will decrease the gas conductivity to 7.1 mW/m K. The superthermal insulation PS/MWCNT foams will then greatly help to save energy.

2. Theoretical fundamentals of heat transfer in MWCNT nanocomposite foams

Since their discovery by Iijima in 1991, carbon nanotubes (CNTs) with unique thermal, electrical, and mechanical properties have been widely studied [14–17]. The superior properties of CNTs makes them potential design candidates for novel materials [18,19]. In this work, CNTs were used to reduce thermal conductivity of foams. Thus, a clear understanding of how and to what degree the addition of CNTs relates to the thermal conductivity of polymer/CNT foams needs to be explored. To understand the fundamentals of heat transfer in CNT nanocomposite foams, one must first review the heat transfer mode in polymeric foams. When there is a temperature difference between two sides of the foam, heat transfers from a higher temperature to a lower one through 3 modes: (1) convection via the exchange of molecules or atoms in fluids; (2) conduction via the movement of free electrons or lattice vibrations of the atoms and molecules; (3) radiation via the photons. In polymeric foams with a cell size of less than 3 mm, the convection term is negligible, because the density difference in these small cells cannot induce an exchange of air molecules [20]. To be conducted, heat flux must pass through either the polymer phase or the gas phase in polymeric foams. Hence, the total thermal conductivity (λ_{total}) of a polymeric foam must include the gas conductivity (λ_{gas}), the solid conductivity (λ_{solid}) and the radiative thermal conductivity (λ_{rad}) [1]. It can be expressed as follows:

$$\lambda_{total} = \lambda_{gas} + \lambda_{solid} + \lambda_{rad} \quad (1)$$

2.1. Gas conductivity (λ_{gas})

When the confined space is much smaller, collisions among the gas molecules become insufficient, and gas conduction is affected by the energy transfer between the gas molecules and cell walls. To determine the degree to which gas