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Experimental validation of the Knudsen effect in nanocellular polymeric foams

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ABSTRACT

This paper is focused on demonstrating that it is possible to reduce the thermal conductivity of polymeric foams by reducing the average cell size below the micron. For this purpose, a wide set of samples with cell sizes from 90 nm to 100 μm and relative densities from 0.12 to 0.6 has been produced and analyzed. In addition, a characterization procedure that allows identifying independently some of the heat transfer mechanisms in polymeric foams has been developed. As a result, it has been demonstrated that Knudsen effect takes place in nanocellular polymeric foams, being this effect very positive to reduce the overall heat transfer.

Through the understanding of the underlying mechanisms it has possible to model the thermal conductivity behavior of these materials in the entire range of cell sizes, and overall porosities. It has been proved that the reduction of the cell size has an effect on the thermal conductivity through the solid phase, this contribution is reduced due to an increment of the tortuosity of the cellular structure and/or a confinement effect in the polymeric matrix.

1. Introduction

Households represent about a 25% of the total energy consumption of the occidental countries, being the space heating more than 50% of this energy (from 60 to 80% in European countries in 2010 [*Energy Efficiency Trends in Buildings in the EU, September 2012*, project co-funded by the European Union)]). Then, by increasing the efficiency of the households heating, and therefore decreasing this energy consumption, it would be possible to obtain both significant economic savings and reductions of the CO_2 emissions. In fact, new dwellings built in 2009 consumed 30%–60% less than dwellings built in 1990 due to the thermal regulations developed in this period.

One of the main strategies to increase the efficiency of the households heating is to improve the thermal insulation of the dwellings, being cellular polymers widely used with this purpose. Their main advantage of these materials is that the thermal conductivity of the polymer matrix, usually not so high, is reduced by the addition of a gaseous phase with a much lower conductivity. For this reason, the analysis of the thermal conductivity of cellular materials from their two component phases and their structure is an interesting topic that has been extensively studied by different authors [1–8].

In a cellular material, it is assumed that the total thermal conductivity (λ_t) can be described by four different contributions (Eq. (1)):

$$\lambda_t = \lambda_g + \lambda_s + \lambda_c + \lambda_r \quad (1)$$

where λ_g is the conduction across the gas phase, λ_s is the conduction along the cell walls and struts of the solid material, λ_c represents the convection within the cells, and λ_r is the thermal radiation term.

In order to reduce the thermal conductivity, there are different approaches. Conduction across the solid phase (λ_s) can be decreased through the development of low density foams in which the contribution of the solid matrix is reduced. The addition of micro-particles and nanoparticles (such as carbon black, carbon nanotubes, etc.) to the polymer matrix allows reducing the radiative term (λ_r) due to an increment of the mean extinction coefficient [9,10].

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On the other hand, it is widely accepted that convection plays a minor role in closed cell materials with cell sizes below 4 mm [11] and also in open cell materials with cell sizes lower than 2 mm [12]. Then, the convection term (λ_c) can be suppressed by developing cellular polymers with cell sizes below 2 mm.

And finally, conduction through the gas (λ_g) phase can be reduced by using two different strategies:

The first one aims at substituting the gas inside the cells, usually air ($\lambda_{air} = 0.026$ W/m K at room temperature), by gases with lower thermal conductivity. But this approach presents two disadvantages: first of all, the gas should be retained inside the foam (which is actually very difficult in the long-term); and secondly, the typical gases with good performance are not very convenient from the environmental point of view. Thus, this method although it is still very common in commercial products is not an optimum solution.

The second approach involves reducing the cell size to the nanometer range, because it is expected that these nanocellular materials present the well-known Knudsen effect [10,13].

This effect implies that when cell size is comparable or smaller than the mean free path of the liquid or gas, the molecules of the latter collide more often with the molecules forming the surrounding solid part than among them. Therefore, the energy transfer through the gas molecules is reduced.

Then, in gas-filled cellular structures, the effective gaseous thermal conductivity (λ'_g) can be described by the Knudsen equation [10]:

$$\lambda'_g = \frac{\lambda'_{go}}{(1+\beta Kn)} \tag{2}$$

where λ'_{go} is the thermal conductivity of the gas (usually air, $\lambda_{air} = 0.026$ W/m K at room temperature and pressure), β is a parameter that takes into account the energy transfer between gas molecules and the limiting solid structure (about 2 for air), and Kn is the Knudsen number that is obtained by dividing the mean free path of the gas molecules ($l_g \approx 70$ nm for air at room temperature) between the average pore diameter (Φ):

$$Kn = \frac{l_g}{\Phi} \tag{3}$$

Combining Eqs. (2) and (3) is obtained that λ'_g decreases significantly when the cell size decreases below the micron. Thus for cellular materials with cells sizes in the nanometer range a reduction of the thermal conductivity of the gaseous phase should be expected. This strategy has the additional advantage of being time independent, so the thermal conductivity is effectively reduced in long-term.

This phenomena was studied by L.W. Hrubesh and co-workers [9] who analyzed how to reduce the thermal conductivity of air-filled aerogels through the analysis of the three major components of thermal transport (conduction through the solid and gas phases, as well as radiation). They found, among others mechanisms, that a reduction of the pore size resulted in a significant reduction of the thermal conductivity of the gaseous phase. This reduction of the thermal conductivity was justified by the Knudsen effect.

Meanwhile, X. Lu et al. [10] studied the correlation between the structure of resorcinol-formaldehyde (RF-) aerogel monoliths and their thermal conductivity. They observed that pore size clearly influenced the conductivity through the gas phase due to the Knudsen effect, obtaining extremely low thermal conductivity values.

Polyisocyanurate aerogels were synthesized by O.J. Lee et al. [14], and their thermal conductivity was determined from vacuum to ambient pressure in order to determine their average pore size. They found that thermal conductivity data can be used to estimate the average pore size using Knudsen equations.

Zirconia ceramics with pore volume fractions from 45 to 75% and pore sizes below 100 nm were prepared and their thermal conductivity was characterized by B. Nait-Ali and co-workers [15]. They concluded that for obtaining a thermally insulating material, the microstructure should exhibit a high volume fraction of pores, which should be as small as possible in order to reduce the thermal conductivity through the gas phase, as Knudsen effect predicts.

Therefore, Knudsen effect has been previously experimentally demonstrated in aerogels or porous ceramics [9,10,14–17], and also in dynamic fluids [18,19]. However, as far as we know, there are not experimental results showing this effect in polymeric foams (i.e. polymeric porous materials obtained by a foaming process); probably due to the technical difficulties associated to the production of nanocellular polymeric foams with appropriate density, cell sizes and external dimensions to characterize their properties as thermal insulating materials.

Nevertheless, there are some theoretical works [20,21] in which the thermal conductivity behavior of microcellular and nanocellular polymeric foams have been studied. C. Forest and co-workers [20] studied the different heat transfer mechanisms of a polystyrene foam with cell sizes both in the micro and nanometer range. First of all, they showed how thermal conductivity of the gaseous phase decreases as cell size decreases due to the Knudsen effect. In addition, they carried out a comparative study between the Ashby model and a model developed for aerogels [9] for the conduction through the solid phase, obtaining that the model developed for aerogels underestimates the contribution of the solid matrix.

The effect of cell size on the thermal conductivity of polymer foams was also analyzed by S.S. Sundarram et al. [21] using finite element analysis and molecular dynamics simulation methods. They observed a significant reduction of the thermal conductivity when cell is reduced from the micrometer to the nanometer range. They stated that this decrease of the thermal conductivity is mainly due to the phonon scattering effect in the solid polymer matrix, being the Knudsen effect less important. Likewise, for a constant relative density, a reduction of the gas phase contribution is predicted when cell size is reduced from 500 μm to 10 μm. However, this unexpected behavior, according to the Knudsen equations, is not found in the present work: foams with cell sizes around 10 μm and foams with cell sizes around 1000 μm present the same gaseous thermal conductivity.

Nanocellular materials and, in particular, nanocellular polymeric foams are promising materials in the cellular materials field due to the expected improvement in some of their physical properties in comparison with conventional or microcellular foams [13,22]. It is expected that these materials will have better mechanical properties than those of conventional cellular materials or microcellular materials [23]. In addition, it is expected that if amorphous transparent polymers are foamed obtaining materials with cell sizes below 50 nm, the cellular material could keep the transparent character of the former solid [24]. Therefore, using these novel materials it would be possible to generate products that cannot be manufactured nowadays.

The most promising technique used to produce nanocellular polymeric foams is the gas dissolution foaming process and in particular the high-pressure or supercritical CO_2 gas dissolution foaming, where CO_2 is used as a physical blowing agent [25–28]. Also, CO_2 presents several advantages for this process due to its excellent characteristics of diffusion in the supercritical state, and the relatively mild conditions to reach this state (31 °C and 7.3 MPa). Likewise, carbon dioxide is a *green* solvent that can be