

Low density thermoplastic nanofoams nucleated by nanoparticles

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ABSTRACT

We report the successful production of thick, homogeneous nanocellular foams with high pore volume by carbon dioxide foaming of thermoplastic polymers. The addition of nanoscale additives, either silica nanoparticles or POSS, was shown to enhance cell nucleation density for polymethacrylate and styrene–acrylonitrile copolymers by three orders of magnitude.

This approach is especially effective using acrylic copolymers with improved CO₂ affinity such as poly(methyl methacrylate-co-ethyl acrylate) or poly(methyl methacrylate-co-ethyl methacrylate), for which nanoscale additive levels below 0.5 wt% contributed to the production of nanofoams with 100 nm average cell size, relative density of 0.15 (85% porosity) and cell densities exceeding 10¹⁶ cells/cm³.

Well-dispersed additives with size of 7 nm or less gave the finest cell morphologies. Designed experiments also showed that foaming at higher pressures (above 30 MPa) and lower temperatures (40 °C and below) increased cell density and reduced cell size, and that porosity could be maximized by adjusting post-foaming annealing temperature.

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1. Introduction

Nanoporous structures have found numerous applications, from catalysis to filtration and electronic materials. The methods used to produce these structures with polymeric materials have typically involved an organic solvent, and relied on either a phase separation (membranes) or a gelation (aerogels and xerogels), followed by removal of the solvent, a difficult step given the capillary forces generated during circulation in narrow channels, especially for samples thicker than a few millimeters.

Yet, applications such as effective thermal insulation require thicker cellular materials, at least a few millimeters thick. Organic and inorganic aerogels are the finest nano-structured insulation materials used to-date and have illustrated the benefit of having a nanoporous structure to exploit the Knudsen effect. Thermal conductivities as low as 10 mW/m K were obtained for organic aerogels with pore size in the range of 10–50 nm, *i.e.* smaller than the mean free path of air molecules at ambient temperature and pressure (*ca.* 75 nm), combined with a low density (high void fraction or porosity close to 85–90%) which reduces the contributions on heat conduction via phonon transport through the solid [1].

Gas foaming remains the most attractive method to produce porous materials at relatively low cost. Microcellular foams can be produced relatively easily in batch process, and a significant effort was devoted to the development of continuous processes [2]. Such foams have cell densities of about 10¹² cm⁻³, cell density being defined, as proposed by Kumar and Suh [3], as the final number of cells in a foam volume corresponding to 1 cm³ of the polymer prior to foaming. Yet the benefit for insulation is rather insignificant when cells remain larger than a micron. As shown in Fig. 1, the theoretical gas contribution to thermal conductivity, k_{gas} , of a foam is reduced about by half when the cell size approaches 200 nm, and cells need to be about 100 nm to see a three-fold reduction.

Generating and stabilizing a large number of cells at the nanoscale (*ca.* 100 nm) by a gas foaming process are a major challenge and are getting increased consideration in academia and industry. A major step was a very thorough study by Krause et al. [4], which showed how CO₂ foaming could be used with high glass transition temperature polymers to produce 100 μm thick membranes with very fine cells (100–300 nm). However, cells were only observed in the core of the samples, while a significant portion of the material close to the free surfaces was essentially unfoamed. As a result, the overall relative density was close to 1.

Handa and Zhang [5] proposed to improve upon processes to make microcellular poly(methyl methacrylate) (PMMA) using high pressure CO₂ by making use of the retrograde vitrification behavior of PMMA, an approach also followed by Nawaby et al. [6] using ABS copolymers. These materials appear to develop a second, low glass

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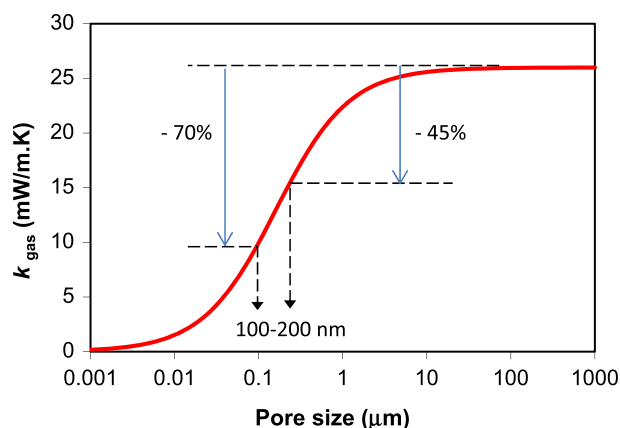


Fig. 1. Predicted reduction of gas thermal conductivity due to the Knudsen effect.

transition temperature, below which the material becomes rubbery. The CO₂ soaking conditions are set in this narrow region, right above the liquid–gas line of CO₂, at about 0 °C and 3.4 MPa. Nuclei are formed upon depressurization without visible expansion. Foaming is then produced by immersing the material in a heated water bath to produce ultra-microcellular foams with cell size around 0.5 microns and cell densities close to 10¹³ cells/cm³.

A comparison by Ruckdäschel et al. [7] of cell densities and cell sizes achieved in work reported in the published literature before 2010 reveals that few submicron foams have been produced with relative densities (ratio of foam density to polymer density) below 0.5, or with cell densities above 10¹⁴ cm⁻³. Miller et al. [8] produced poly(ester imide) foams with cell density of the order of 10¹⁴ cm⁻³ and relative densities reaching 0.47. More recently, Reglero-Ruiz et al. showed how addition of a triblock acrylic copolymer could decrease cell size in PMMA foams, and they reported structures with 300 nm cells and relative density of 0.7 [9]. The process was further improved to yield foams with cell densities reaching 4 × 10¹⁴ cm⁻³.

Yet, despite this recent progress in the field, producing thick¹ foams with smaller cells (ca. 100 nm) and higher cell densities (ca. 10¹⁶ cm⁻³ or more) expected to be required to achieve the low foam densities needed for super insulation materials remains tremendously challenging. Additionally, the presence of micron-size pores in these foams could be detrimental to thermal performance, as was explained by Ohshima [10]. Thus homogeneous cell size distributions are preferred.

In the following, a method to increase cell density while decreasing relative density is proposed. The proper choice of polymer, nucleating additive and foaming conditions made it possible to produce unique CO₂-blown nanoporous materials with homogeneous cell size around 100–200 nm [11]. The approach proved successful not only in drastically improving upon the cell densities reported to-date by two orders of magnitude, but also in allowing controlled cell growth resulting in high porosities corresponding to relative density as low as 0.15. Such nanofoams could be good candidates for high performance insulation.

2. Experimental

2.1. Materials

“PMMA” is a homopolymer powder of methyl methacrylate (MMA) commercialized by Sigma–Aldrich as 120 kg/mol. “PMMA-

co-EA” is a random copolymer of MMA with 9 wt% ethyl acrylate (VM100 from Arkema). “PMMA-co-EMA” is a random copolymer of MMA with 50 wt% ethyl methacrylate (360 kg/mol, $T_g = 96$ °C) obtained from Scientific Polymer Products (Ontario, NY). “SAN” is a styrene copolymer with 31 wt% acrylonitrile (Dow Chemical Tyril™125).

Molecular weight distributions were determined by GPC analysis using an Agilent 1100 series liquid chromatograph equipped with two Polymer Laboratories PLgel 5 μm Mixed-C columns connected in series, and an Agilent G1362A refractive index detector. Tetrahydrofuran was used as the eluant with a flow rate of 1 mL/min at 35 °C. Molecular weights listed in Table 1 are reported as apparent molecular weights with respect to a set of PMMA standards.

Glass transition temperatures, T_g , were determined by differential scanning calorimetry (Q100 DSC, TA Instruments), on the second heating curve of a temperature cycle between 0 and 200 °C. Heating rate was 10 °C/min, and T_g is detected at the half-height of the transition of the heat flow curve.

“POSS” is a methacryl-substituted polyhedral oligomeric silsesquioxane (Sigma–Aldrich).

“SiO₂” describes colloidal silica particles prepared by reaction of tetraethoxysilane with ethanol and water (37/37/26 vol%) at 23 °C and pH = 2 (adjusted with 0.5 M HCl). Gelation of the primary particles is obtained by adding NaOH to pH = 6.5. The average particle size was estimated to be 4 nm by small angle X-ray scattering (SAXS). Additional colloidal silica suspensions (Ludox, Sigma–Aldrich) with various average particle sizes (according to the supplier) were also used: SM30 (~7 nm), HS30 (~15 nm), TM (~32 nm). Unless specified, the 4 nm colloidal SiO₂ in wet gel form was used.

Viscosity of the pure polymers was obtained by small amplitude oscillatory shear with Rheometrics RDS-II rheometer with a force rebalance transducer and equipped with 25 mm parallel plates. The strain amplitude was adjusted to keep the torque values measured within a reasonable level without exceeding the linear viscoelasticity region. Frequency sweeps were obtained at 180 °C in the range 100–0.1 radians/s, with 5 points per decade of frequency. Shear viscosity of polymers laden with CO₂ was obtained using a high pressure sliding plate rheometer (McGill University, Montreal, Canada). Measurements at 35–105 °C and 20–40 MPa were used to build a mastercurve at 35 °C and 30 MPa as previously described by Park and Dealy [12].

2.2. Specimen preparation

Composites of PMMA and PMMA-co-EA with SiO₂ were obtained by adding the silica gel or suspension directly to the polymer powder, and melt-blended at 180 °C for 10 min in an open Haake Rheomix to allow evaporation of residual water. POSS was first diluted to a 3 wt% solution in ethanol, added to either SAN or PMMA-co-EMA, and melt-blended at 180 °C. A nitrogen blanket was used to minimize ethanol vapors during compounding. All samples were pressed into 3 mm thick plaques by compression molding at 180 °C.

Nanoparticle dispersion was examined by small angle X-ray scattering (SAXS) experiments performed at the Advanced Photon

Table 1
Characteristics of polymers used to produce nanofoams.

Polymer	M_n (kg/mol)	M_w (kg/mol)	T_g (°C)
PMMA	59.3	96.0	118
P(MMA-co-EA)	61.5	94.3	98
P(MMA-co-EMA)	159.8	459.5	96
SAN	45.1	96.1	107

¹ Defined as having thickness of several millimeters.

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