



Nanocellular polymer foams nucleated by core-shell nanoparticles



Shanqiu Liu^a, Bram Zoetebier^a, Lars Hulsman^a, Yuanyuan Zhang^a, Joost Duvigneau^{a, b, *}, G. Julius Vancso^{a, **}

^a Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

^b Aerotech Development BV, Drienerlolaan 5, 7522 NB, Enschede, The Netherlands

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ABSTRACT

The synthesis of low surface energy polymer grafted silica nanoparticles is reported for the utilization as highly efficient cell nucleation agents to obtain nanocellular, CO₂ blown polystyrene (PS) and poly(methyl methacrylate) (PMMA) films in a batch process. For nanoparticle surface functionalization hydroxyl-terminated perfluoropolyether and poly(dimethylsiloxane) (PDMS) were used. Their successful grafting to silica nanoparticles was confirmed by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). Following melt blending of the modified silica nanoparticles with PS or PMMA their dispersions were evaluated by scanning electron microscopy (SEM) analyses. We demonstrate that proper selection of the polymer grafts results in nucleation efficiencies of up to approximately 0.5 (*i.e.* 1 foam cell per 2 particles on average), which is the highest value reported so far for nanofillers as nucleation agents. This number was confirmed by the presence of only 2 to 4 nanoparticles per cell in nanocellular PS and PMMA foams containing SiO₂ nanoparticles with a PDMS shell as was observed in cross sectional SEM images. The lowest density foam we obtained ($\sim 0.32 \text{ g cm}^{-3}$) had a nanocellular morphology with a cell size and cell density of $\sim 440 \text{ nm}$ and $1.85 \times 10^{13} \text{ cells cm}^{-3}$, respectively. It is shown that the use of a low surface energy thin shell around silica nanoparticles is beneficial for cell nucleation compared to untreated particles.

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1. Introduction

Low density polymer foams with cell sizes of several hundreds of nanometers or smaller comprise a relatively new class of materials that is considered to be of interest for numerous applications, *e.g.* in lightweight structural supports [1], catalysis [2], thermal insulation [3], sound insulation [4], electromagnetic shielding [5,6] and tissue engineering [7]. For instance, Miller and coworkers [8] reported that the confinement of polymer chains in cell walls of nanocellular polyetherimide (PEI) foams leads to a significant increase of toughness and strain at break compared to the microporous material. This enables utilization as lightweight structural support. In addition, when cell diameters are close to, or smaller

than, the collision mean free path of gas molecules making up air between successive impacts ($\sim 70 \text{ nm}$ at standard conditions) [9], the gas phase thermal conduction is minimized. This so called Knudsen effect renders nanocellular polymer foams very promising candidates as high performance thermal insulation materials [10,11]. For instance, Sundarram and coworkers reported a value of $15 \text{ mW m}^{-1} \text{ K}^{-1}$ for the thermal conductivity of a nanocellular polyetherimide foam with a cell size and porosity of 86 nm and 80% , respectively. Despite the rather high polyetherimide foam density the thermal conductivity value for the nanocellular foam reported was significantly lower compared to that of conventional polyurethane based foams ($20\text{--}22 \text{ mW m}^{-1} \text{ K}^{-1}$) [12].

For the applications mentioned, control over the foam bulk density is as important as having a nanocellular morphology [13]. Among the possible foaming strategies usually employed, CO₂ assisted batch foaming is frequently used for the preparation of nanoporous foams [14–19]. This is mainly ascribed to CO₂ being considered as a green alternative to other blowing agents. A further advantage is the easy adaptation of batch foaming conditions over a wide pressure and temperature range [20]. Unfortunately, due to

* Corresponding author. Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands.

** Corresponding author.

E-mail addresses: j.duvigneau@utwente.nl (J. Duvigneau), g.j.vancso@utwente.nl (G.J. Vancso).

size limitations, batch foaming still remains a laboratory scale process [21]. It is foreseen that in the near future novel foaming concepts will be developed that will allow the upscaling of nanocellular foam production to technologically relevant levels.

The majority of the batch foamed nanocellular materials reported in the open literature had foam thicknesses restricted to below a millimeter. In addition, the foams typically had relatively low porosities, *i.e.* below 80%. It was only recently that Costeux and coworkers [13] reported the batch foaming of PMMA copolymers with thicknesses exceeding a few millimeters and a maximum porosity of 85%. However, the production of low density nanocellular polymer foams remains a challenge due to *i*) low cell nucleation numbers, *ii*) fast diffusion of CO₂ out of the foaming polymer and *iii*) coalescence of cells during foaming.

In order to enhance cell nucleation to levels exceeding 10¹⁴ cells cm⁻³, the introduction of nanostructured phases to polymers prior to foaming is considered a promising approach. According to the classical nucleation theory (CNT) [22,23] heterogeneous nucleation is preferred over homogeneous nucleation once the interfacial energy and domain size of the heterogeneous phase are properly selected. For instance, foaming of block copolymer blends [24–27] and nanocomposites [13,17,28–36] have been reported.

Nano-clay and silica nanoparticles are among the most widely used heterogeneous nucleation agents [33,34,37]. For example, He and coworkers [33] reported that the addition of nanosilica to polycarbonate prior to batch foaming significantly decreases the foam cell size and increases the cell density compared to neat polycarbonate foams. Ozisik and coworkers [34] described that fluorinated silane modified silica nanoparticles reduced the nucleation free energy barrier and increased the cell density of PMMA foams compared to foams containing pristine silica nanoparticles.

Despite effectively increasing the cell density of polymer foams upon the addition of (modified) nanoparticles, a closer examination of their nucleation efficiency shows that nanoparticles are still often poor nucleation agents. The nucleation efficiency is defined as the ratio of the number of cells per cm³ of unfoamed material to the number of nanoparticles per cm³ unfoamed material [29]. This definition, as it is obvious, incorporates cell coalescence and cell collapse. Table 1 shows for a number of selected polymer nanoparticle systems the calculated nucleation efficiencies. Obviously the nucleation efficiency is often orders of magnitude below unity. In the best case the nucleation efficiency was 0.1, meaning that for every 10 particles added 1 cell was nucleated.

In order to enhance the nucleation efficiency of silica nanoparticles Yang and coworkers [38] reported on the grafting of highly

CO₂-philic poly(ionic liquid) from silica nanoparticles as nucleation agents for the foaming of microcellular polystyrene foams. Surface initiated atom-transfer radical polymerization (SI-ATRP) was used to graft poly[2-(methacryloyloxy)ethyl]trimethylammonium tetrafluoroborate (P[MATMA][BF₄]) from silica nanoparticle surfaces. Grafted layers with thicknesses of several tens of nanometer were achieved. The authors demonstrated that the CO₂ solubility was slightly enhanced due to the presence of the surface confined P[MATMA][BF₄] phase. Compared to microcellular polystyrene foams prepared with bare silica nanoparticles the cell density increased (factor ~5) and the cell size decreased (factor ~2). However, the overall nucleation efficiency of these polymer decorated nanoparticles remained poor (<1.7 × 10⁻³).

In this work, we employed a simple “grafting to” approach of low molar mass CO₂-philic and low surface energy polymers on silica nanoparticles in order to have a thin, low surface energy shell around the silica nanoparticles. We explored the nucleation efficiency and foam morphology of the resulting materials. PDMS (19.8 mJ m⁻²) and Fluorolink E10, *i.e.* a hydroxyl-terminated perfluoropolyether, (18.0 mJ m⁻²) were selected as the matrix polymers due to their known low surface energy and good wetting property with CO₂ [34,40,41]. For comparison, PS grafted nanoparticles were also synthesized. The core-shell nanoparticles obtained were used as highly efficient heterogeneous nucleation agents for the CO₂ batch foaming of PS and PMMA. We report on substantial enhancement of heterogeneous nucleation efficiency values of up to 0.5.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS) ≥ 99.0%, (3-aminopropyl)-trimethoxysilane (APTMS) 97%, 2-propanol 99.5%, copper(I) bromide 98% and polystyrene (M_w = 230,000 g mol⁻¹, ρ = 1.05 g cm⁻³) were purchased from Aldrich (Milwaukee, WI, USA). Ammonium hydroxide solution 28–30%, triethylamine (TEA) 99.5%, copper(II) bromide 99%, α-bromoisobutryl bromide ≥ 99%, hydrochloric acid 37%, aluminum oxide (for chromatography), nonafluorobutyl methyl ether ≥ 99%, hydrofluoric acid (48%) and poly(-dimethylsiloxane) monoglycidyl ether terminated (PDMS-G) (M_w = 1000 g mol⁻¹) were purchased from Sigma-Aldrich (St. Louis, MO, USA). PMMA was a gift from Arkema (VM100, *i.e.* a PMMA-co-EA polymer, ρ = 1.18 g cm⁻³) (La Garenne-Colombes, France). Absolute *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Biosolve (Valkenswaard, the Netherlands). Ethanol absolute for analysis was purchased from Merck (Darmstadt, Germany). Hydroxyl-terminated perfluoropolyether (Fluorolink E10, M_w = 1700 g mol⁻¹) was a gift from Solvay Solexis (Milan, Italy). *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA) 98% was purchased from Acros Organics (Geel, Belgium). Styrene was passed through an aluminum oxide column prior to polymerization to remove the inhibitor used. Copper(I) bromide was purified by stirring appropriate amounts in water free acetic acid for 24 h, followed by filtration, washing with ethanol for three times and subsequent vacuum drying for at least 12 h. Milli-Q water was produced by a Millipore Synergy system (Billerica, MA, USA). Unless otherwise mentioned all other chemicals were used as received.

2.2. Methods

2.2.1. Silica nanoparticle preparation by the Stöber method, hydrolysis and APTMS functionalization

Stöber-type silica nanoparticles: to prepare Stöber silica

Table 1

Overview of the (calculated) nucleation efficiency of different polymer/nanofiller systems selected from the literature.

Nanocomposites	Nucleation efficiency
Polypropylene/nanoclay [28]	<1.0 × 10 ⁻⁴
PMMA/nanoclay [17]	<1.0 × 10 ⁻⁴
PS/nanoclay [17]	<1.0 × 10 ⁻⁴
PS/nanoclay [35]	7.4 × 10 ⁻⁴
PMMA-co-EA/SiO ₂ [13]	0.1
PMMA/SiO ₂ [13]	4.8 × 10 ⁻³
PMMA/SiO ₂ [31]	2.8 × 10 ⁻⁴
PMMA/fluorinated silane modified SiO ₂ [34]	1.5 × 10 ⁻⁴
PMMA/hydroxyl-terminated SiO ₂ [35]	8.6 × 10 ⁻⁶
Polycarbonate/SiO ₂ [33]	1.8 × 10 ⁻²
PS/carbon nanofibers [29]	2.0 × 10 ⁻²
PS/carbon nanotubes [29]	9.1 × 10 ⁻⁵
PS/amino-terminated SiO ₂ [38]	<3 × 10 ⁻⁴
PS/SiO ₂ with poly(ionic liquid) grafts [38]	<1.7 × 10 ⁻³
PS/SiO ₂ with PS grafts [39]	<2.0 × 10 ⁻²

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