



Non-crosslinked thermoplastic reticulated polymer foams from crystallization-induced structural heterogeneities

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ARTICLE INFO

Article history:

Received 25 September 2017
Received in revised form
27 November 2017
Accepted 2 December 2017
Available online 5 December 2017

Keywords:

Foam
Open-cell
Extrusion

ABSTRACT

Reticulated polymer foams are commercially relevant materials suitable for a broad range of applications including impact absorption, environmental protection, biological scaffolds and sacrificial templates for the fabrication of functional materials. However, to the best of our knowledge, scalable fabrication of reticulated polymer foams is limited to crosslinked, thermoset materials which are difficult to process and recycle. We report a facile method to prepare reticulated foams of noncrosslinked, thermoplastic polypropylene (PP) containing a small amount of polytetrafluoroethylene (PTFE) fibers, in a fully-scalable continuous extrusion process. Under the optimum conditions, foams with a mass density of 0.07 g/cm³ and an open-cell content of 97.7% are achieved. The formation of a reticulated foam structure is rarely observed in thermoplastic materials, and is attributed to four effects of the PTFE fibers taking place concomitantly during the foaming process: 1) localized plasticization of the matrix due to the CO₂-philicity of the PTFE fibers which creates weak sites for pore formation, 2) generation of crystalline heterogeneities during extrusion which forms hard segments in a soft matrix, 3) decrease in cell wall thickness, and 4) reinforcement of the cell strut which preserves the cell trace. The method proposed herein may be extended to other thermoplastic materials for fabricating reticulated foams.

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1. Introduction

Reticulated foams are a special class of open-cell foams, devoid of cell membranes between adjacent cells. Instead, a *three-dimensional net* of interconnected solid strands called struts that delineate cavities exist throughout the sample volume. In contrast, open-cell foams also include foams where a substantial portion of the membrane between adjacent cells continues to exist.

The low density (<0.1 g/cm³), [1] large surface area (>10 m²/g), [1] and the unsequestered void architecture in reticulated foams gives rise to unique transport and mechanical properties making them suitable media for environmental protection and remediation [2–5], templates for functional materials [6,7], impact absorbers for cushioning applications, [8] stationary phases in chemical and biochemical reactors [9–12], and scaffolds for tissue engineering [13–15].

In order to produce reticulated polymer foams, a certain size of cell and of shared cell wall must be achieved before the wall can

readily open to create pores and a resulting reticulated structure. However, excessive expansion of the cells can lead to strut breakage causing the cell trace to disappear and the foam structure to collapse. The dimensional limitations pertinent to reticulated foams make the fabrication of reticulated polymer foams both challenging and difficult to scale.

While open-cell foams have been fabricated from thermoplastic materials [16–18], scalable production of reticulated polymer foams is limited to thermoset materials such as polyurethane foams. Unfortunately, the curing reaction required to produce reticulated polymer foams, renders these foams difficult to process and recycle. Given the industrial relevance of reticulated foams due to their broad commercial appeal, thermoset reticulated foams constitute a substantial portion of pre- and post-consumer plastic waste. As a result, any opportunity to replace these nonrecyclable reticulated foams with recyclable, non-crosslinked alternatives is welcome by an industry facing the waste disposal challenge.

In this study, we fabricate reticulated foams of noncrosslinked, thermoplastic, polypropylene (PP) containing polytetrafluoroethylene (PTFE) fibers in an easy-to-scale continuous extrusion process using carbon dioxide (CO₂) as the foam blowing agent. We

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found during the extrusion foaming experiments that controlling the processing temperature can transition the foam structure from closed-cell to open-cell to a reticulated one. Under the optimum temperature conditions, reticulated foams with an open-cell content of 97.7%, mass density of 0.07 g/cm³, and cell diameters ranging from about 10 μm to 100 μm are obtained. The PP/PTFE microfibrillar blend is prepared *in-situ* during blending in a twin-screw extruder and is not chemically modified or crosslinked, thus preserving the processability, and recyclability of the individual components of the blend. The induction of cell-opening which ultimately results in the reticulated foams, is attributed to the concurrent generation of a *structurally heterogeneous melt* [16,18–21] with well dispersed arrays of rigid crystalline segments in a soft molten matrix, PTFE-fiber induced decrease in cell-wall thickness through a several fold increase in expansion ratio and a several orders of magnitude increase in cell density of PP foams, [22] localized plasticization of the soft matrix due to the CO₂-philicity of the PTFE fibers which facilitates pore formation during bubble growth, and the reinforcement of the cell struts by PTFE fibers which helps preserve the cell trace. We anticipate our strategy for generating reticulated foams of PP will act as a guideline for fabricating reticulated foams of other thermoplastic materials with unique properties for advanced applications. For example, the strategy described herein was successfully used in generating reticulated polymer foams of a polypropylene-co-polyethylene random copolymer, which demonstrated superior mechanical performance than the PP-homopolymer counterpart. [23] Our aim is to help make available reticulated foams from a wider material pool to stimulate further development by offering an agenda for the future.

2. Experimental

2.1. Materials

The matrix polymer used in this study is linear isotactic polypropylene (PP) supplied by Japan Polypropylene (Novatec-PP FY4) with MFR = 5. The melting temperature of PP is found using a differential scanning calorimeter (DSC) to be about 438 K. A polytetrafluoroethylene (PTFE) supplied by Mitsubishi Rayon (Metablen™ A-3000) is also used as an additive. The melting temperature of PTFE is 613 K. This PTFE tends to disperse well in PP, deforms into high-aspect ratio fibrils, and shows a strong affinity for CO₂. [22] All materials are used as received. Nitrogen (N₂) and carbon dioxide (CO₂) are purchased from Linde Gas with purity > 99%.

2.2. Blend preparation

Dry blends of PP/PTFE are prepared in proportions of 100/0 (i.e., neat PP is subjected to the same processing as the other samples, to maintain a consistent processing history for accurate comparison), 99.9/0.1, 99.7/0.3, and 97/3 in weight fraction (wt%). The resulting mixtures are fed in the hopper of a co-rotational twin-screw extruder manufactured by Toshiba Machine Co. Ltd. (Trade name: TEM-26SS). The screw diameter is 26 mm and its aspect ratio is 40. The barrel and die of the extruder are maintained at a temperature of 473 K. A cold-water sleeve is utilized to cool the hopper of the extruder. The discharge rate is set at 20 kg/h. Extrudate from the die is shaped into a cylindrical strand, led into a water bath at a temperature of 286 K, and pelletized. The hydrodynamic stresses during blending causes the PTFE domains to extend into high-aspect-ratio fibers (diameter < 500 nm and length > 100 μm, so the aspect ratio is > 200) due to its readiness to undergo plastic deformation and its high ultimate strain properties. The morphology and dispersion of the PTFE in the PP after this

processing are reported in previous publications [22,23]

2.3. Morphology characterization

The growth of the transcrystalline layer or the growth of spherulites during isothermal crystallization, is studied on a model sample with a low PTFE content, PP/PTFE (99.9/0.1 wt%). PP/PTFE (99.9/0.1 wt%) is dilute enough for easy isolation of fibers for visualization of transcrystalline growth on the PTFE fibers or spherulitic growth in the bulk. Thin films of PP/PTFE (99.9/0.1 wt%) are prepared by compression molding to a thickness of 100 μm. The film is placed on a glass slide. The slide is placed on a heat-controlled stage set at a temperature of 483 K for a period of 10 min to erase the thermal history. Then, the stage is cooled to a chosen crystallization temperature and treated isothermally for various time periods. Subsequently, the slide is immersed in liquid nitrogen to quench the morphology and prevent any changes in the crystal structure. The quenched sample is etched using a *permananganate etching* [24] technique before it is coated with a thin layer of platinum using a sputter coater for observation using SEM. The thickness of the transcrystalline layer (defined as the width from one edge to the other) or the diameter of the spherulites is measured from the SEM micrographs.

The morphology of the foams is characterized by dipping the respective sample in liquid nitrogen followed by fracturing the sample to expose the cross-section. The fractured surface is sputter coated with platinum before observation under SEM. The water displacement method described in ASTM-D792 is used to calculate the volume expansion ratio, $\phi = \rho/\rho_f$, of the foam where ρ and ρ_f are the mass densities of samples before foaming and after foaming, respectively. Additionally, the cell density, defined as the number of bubbles per unit volume is estimated from the SEM images of the foams using a method described elsewhere. [25].

2.4. Mass uptake of CO₂

A magnetic suspension balance (MSB) supplied by Rubotherm GmbH is used to determine the mass uptake of CO₂ by PP and PP/PTFE (99.7/0.3 wt%) at a CO₂ pressure of 17.2 MPa, using the method and apparatus described earlier [26,27].

2.5. Open-cell content determination

The open-cell content of the foams is determined using a N₂ gas pycnometer supplied by Quantachrome (Ultrapycnometer 1000) using the protocol explained in ASTM-D6226. The unfoamed skin of the polymer foams is removed using a steel blade to expose the porous structure and allow N₂ permeation. The applied N₂ pressure is set to a low value of 0.07 MPa to minimize collapse of the open-celled structure and the measurements are recorded after 20 min to ensure equilibrium.

2.6. Foam extrusion procedure

A tandem foam extrusion system described in previous investigations is used in this study [22,28]. Pellets of PP/PTFE (100/0 wt%, 99.7/0.3 wt%, or 97/3 wt%) are fed into the first extruder barrel through the hopper. This barrel is maintained at 473 K, a temperature above the melting temperature of PP but below that of PTFE. The PP in the samples melts completely in the first extruder due to the temperature as well as the screw motion which causes shear heating. However, the PTFE continues to remain in solid-state. 10 wt% CO₂ is injected into the first extruder barrel at a constant flow rate using a syringe pump. The dissolution of gas in the polymer melt occurs through convective diffusion in the first

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