

Effects of Saturation Pressure of CO₂ on Nanofoams nucleated from Block Copolymer Nanodomains

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Supercritical (sc) carbon dioxide (CO₂) is environmentally friendly blowing agent to produce macro- or micro-foams into polymeric materials. Block copolymers self-assemble themselves into periodically ordered nanostructures. We utilize the nanodomains of block copolymers as templates for the fabrication of nanofoams in polymeric media. A block copolymer with a CO₂-philic minor block forms spherical CO₂-philic nanodomains in neat bulk. Such CO₂-philic spherical nanodomains work as nuclei for cells of nanofoams. We successfully control the size of cells by varying the saturation pressure of CO₂.

Key words: supercritical carbon dioxide, template, block copolymer, nanocellular

1. INTRODUCTION

Carbon dioxide has been used for an environmentally friendly blowing agent for making macrofoams or microfoams. The typical size of such cells (foams) are no less than an order of micron. In general, we cannot introduce cells using blowing agent with the size smaller than the minimum nucleus size of cells. Extremely small nuclei have to pay a thermodynamic penalty associated with the surface energy of the cell times the total area created by the nucleation. Therefore, it is very difficult to achieve the typical cell size smaller than a micron. The cell size also rapidly increase by coalescence in polymeric media swollen by blowing agent. For the last few decades, a number of methods are invented to control the cell (foam) size in polymeric materials using supercritical carbon dioxide (scCO₂) by varying pressure, depressurizing rate, temperature, polymer blends and many others.[1-7] Expansion of cells is easily controlled by tuning the process; however, the nucleation cannot be fully controlled. Controlling nuclei of cells is the key for fabricating smaller cells in polymeric materials.

Block copolymers self-assemble themselves into well-ordered periodic nanodomain structures. Such self-assembled nanodomains are ideal templates to create nanoscopic patterns combined with a variety of techniques.[8-12] We have developed a novel method to make cellular structures with 10 to 30 nm in diameter using a block copolymer templates and carbon dioxide as a blowing agent.[13-14] A block copolymer with CO₂-philic block forms spherical nanodomains, which are expected to localize CO₂ in the domains. Therefore, we are able to initiate "foaming" from nuclei with a size of ca. 10 nm. By carefully choosing the temperature and saturation pressure, densely packed cells of 10 – 30 nm in diameter are fabricated. In this paper, we present a novel method of introducing nanocellular structures in polymeric materials.

2. EXPERIMENTS

2.1 Polymer Synthesis and Sample preparation:

Poly[styrene-block-perfluorooctylethyl methacrylate] (PS-PFMA) was synthesized by sequential anionic polymerization of styrene and perfluorooctylethyl

methacrylate in THF at –78° C. The detail of the synthesis and characterization has been described.[15] A part of the PS block was removed prior to the addition of perfluorooctylethyl methacrylate to determine the molecular weight of PS block using size exclusion chromatography. The molecular weight of PFMA block was determined by ¹H nuclear magnetic resonance measurement. The molecular weights of PS and PFMA blocks are 20,000 and 13,000, respectively. The PS-PFMA copolymer was dissolved in a mixture of 80 wt % of toluene (Wako Pure Chemical Industries, Ltd.) and 20 wt % of 1,1,1,3,3,3-hexafluoro-2-propanol (Wako Pure Chemical Industries, Ltd.). Films were cast from the solution and vacuum dried at room temperature for 12 hours. The specimens for ellipsometry measurements were prepared by spin-coating of the solution on silicon wafer as obtained.

2.2 CO₂ Processing

A stainless steel high-pressure vessel for CO₂ processing was connected to a high-pressure liquid chromatography pump (JASCO PU-2086 plus) with a cooling head, and to a backpressure regulator (JASCO SCF-Bpg). Films of PS-PFMA were placed in the high-pressure vessel and annealed at 60° C for 1 hour with a constant pressure controlled using the pressure regulator. The vessel was placed in an ice bath to quench the films to 0° C while maintaining the pressure using the pump and the regulator. Depressurization rate was controlled at 0.5 MPa/min.

2.3 Scanning Electron Microscopy (SEM)

Specimens are cryo-fractured in liquid nitrogen to expose the internal cellular structures to the surface for SEM observation. An environmental scanning electron microscope (ESEM) (Philips XL20 ESEM-FEG) equipped with a field emission gun was employed without conductive coating at an approximate pressure of 0.8 Pa of water vapor to prevent charge-build-up. 5 to 6 keV of electron beam was used for the observation with working distance of less than 10 mm to obtain secondary electron images. The PS-PFMA block copolymer microdomains in as-cast films were not identified by the secondary electron image under the above

experimental condition; therefore, the images obtained are topographic images of the fractured surfaces.

2.4 Spectroscopic Ellipsometry

The refractive indices of the original and nanocellular thin films were determined using a spectroscopic ellipsometer (JASCO M-200). Analytical ellipsometric measurements were performed in the range of wavelength (400 – 800 nm) at an incident angle of 60° relative to the surface normal. The refractive indices of nanocellular films were computed assuming constant refractive indices throughout the films.

3. RESULTS AND DISCUSSION

3.1 Nanofoams

PS-PFMA block copolymer monoliths were processed using the scCO₂ protocol described in the experimental section. The cryo-fractured surfaces of such monoliths are observed using SEM. A typical example of SEM images is shown in Figure 1. Since PFMA is CO₂-philic, CO₂ localizes itself in PFMA spherical domains of an order of 10 nm. Nanodomain structures of the PS-PFMA block copolymer work as templates and provide nuclei for cellular formation. The original PFMA domains in as-cast specimens appeared to be spherical[14] and did not change much even after long thermal annealing well above the glass transition temperature.[16,17] The SAXS profile showed a single peak, which indicate a poor long range order.[14] The observed spherical domains may not be equilibrium structure due to the strong segregation of PFMA and PS and resulting reduced mobility.[18]

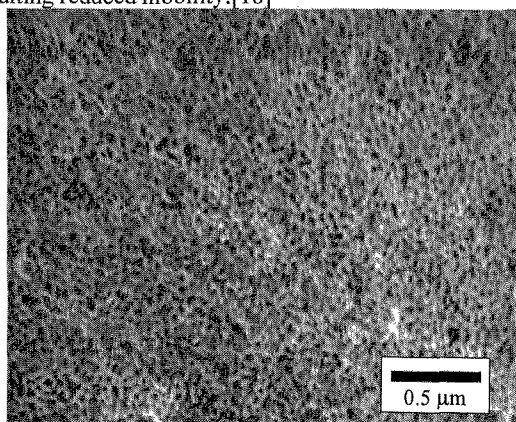


Figure 1. An SEM image of cryo-fractured surface of a nanocellular monolith using a PS-PFMA block copolymer template and the scCO₂ process, in which the monolith was immersed in 10MPa of CO₂ at 60 degree C and quickly quenched to 0 degree C isobarically.

By changing the saturation pressure of CO₂, the cell size is successfully controlled. The diameters of the cells processed with various saturation pressures are measured and their distributions are shown in Figure 2. It is clearly observed that the average size increases with pressure up to 20 MPa and then decrease with pressure. This strange behavior is related to the dependence of the glass transition temperature (T_g) of PS, which is a component of continuous domain, swollen by CO₂ on the CO₂ pressure. The T_g of PS decrease with CO₂ pressure up to 20 MPa due to absorption but the static pressure (above 20 MPa) finally increase the T_g of PS.[19] The size distribution also increases with pressure.

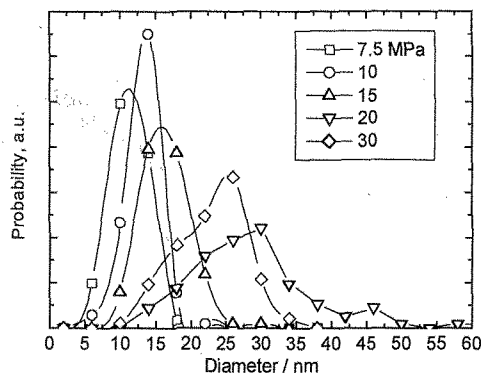


Figure 2. Size distributions of nanocells depending on the saturation pressure of CO₂ (7.5 – 30 MPa). The average size grows with increasing saturation pressure of CO₂.

3.2 Shape of cells

The shape of cells is not perfect spherical shape, but rather elongated. It is clearly observed by plotting the diameter in the long (D_L) and short (D_S) axes versus the saturation pressure of CO₂. At low saturation pressures, D_S is fairly uniform and significantly smaller D_L . This trend is suggesting that the shape of the cells is rather short cylinder with various length but with the same diameter. Since the PS-PFMA block copolymer has fairly high PFMA fraction, roughly 29 % in volume, with which cylindrical structures may be favored in theory, the spherical domain structures we observed before the process may not be the equilibrium structure but metastable one influenced by the sample preparation method and suppressed chain mobility due to the strong segregation of the blocks[18]. It is known that, in strong segregation, domain shape and size tend to be frozen once domains are formed. Absorbed CO₂ may increase the effective volume of PFMA domains even more, weaken the effective interaction, enhance the chain mobility and allow the morphology change to cylindrical structures. In a separate paper, we will report that, in the case of lower fraction of PFMA, more regular, monodisperse spherical cells are observed.

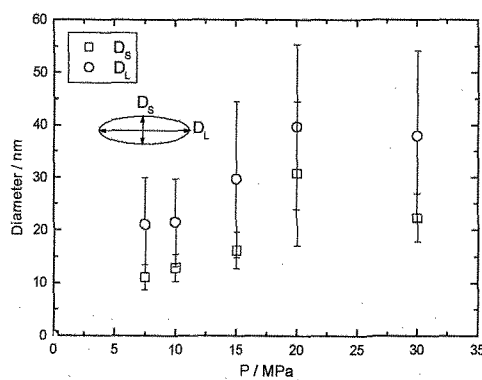


Figure 3. Diameters in short (D_S) and long axis (D_L) as a function of saturation pressure, P . The error bars indicate the standard deviation of the size and hence are symmetric around the average values (symbols).

With increasing saturation pressure, the difference

between D_L and D_S becomes smaller, which indicates that the cells are more spherical. We speculate that inverse micelles, in which block copolymers are surrounding a droplet of CO_2 , may be formed rather than the PFMA domains accommodate CO_2 since the larger amount of CO_2 is trapped in the polymer specimens during the process. By controlling the saturation pressure alone with the other parameter constant, the size was successfully controlled from 10 to 30 nm in diameter. The control of cell shape and size with a number of parameters such as block fractions, expansion temperature, confinement in thin films will be reported in separate papers.

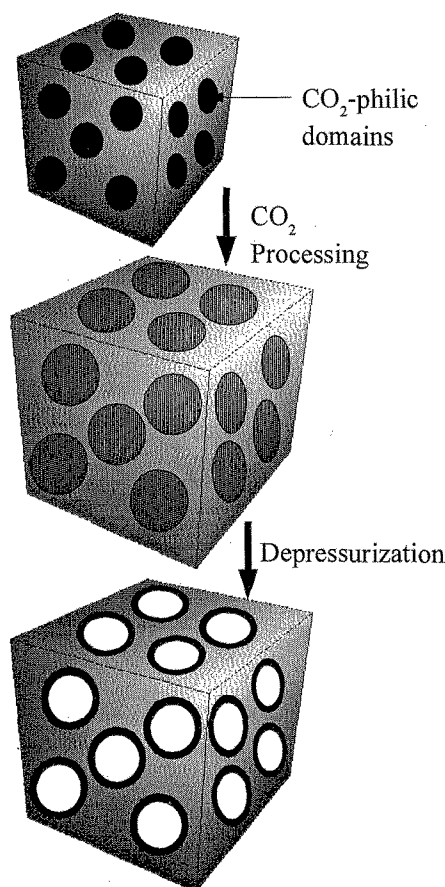


Figure 4. Schematic pictures of nanofoaming from block copolymer nanodomains. The dark gray domains of CO_2 -philic domains are swollen by CO_2 under CO_2 pressure as shown as hatched domains. After removing CO_2 , empty cells remain in polymeric monoliths.

3.4 Volume fractions of cells

Analytic ellipsometry was employed to confirm nanofoaming of the PS-PFMA block copolymer. This strategy is only valid when the cell size is much smaller than the wavelength of lights. Actually, the nanofoams are optically transparent and hence the ellipsometry experiment successfully measure the thicknesses and refractive indices before and after the CO_2 processing. As shown in Table 1, the refractive index measured by ellipsometry and volume fraction of cells which is determined by effective medium approximation significantly differ from those of the original copolymer indicated as pressure 0 MPa. The introduced volume indicate the same trend as the size of cells introduced into the polymeric monoliths. As shown in the

schematic pictures in Figure 4, the nuclei grows and increases both the volume and diameter of the cells.

Table 1 Pressure dependence of refractive index, n_{488} , and volume fraction of cells, Φ .

Pressure / MPa	0	7.5	10	15	20
n_{488}	1.49	1.4	1.38	1.35	1.24
Φ	0	0.18	0.2	0.28	0.49

3. CONCLUSIONS

A novel method of fabricating polymeric nanofoams using CO_2 -philic block polymer as nuclei for foaming in CO_2 was studied. Nanofoams with a diameter of 10–30 nm were observed on the cryo-fractured surface by SEM. In addition to that, this method has been proved to have a capability of controlling the size and volume of cells just by changing the saturation pressure of CO_2 .

4. REFERENCES

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