



Early bubble coalescence in thermoplastic foaming

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ABSTRACT

In the underlying literature, bubble coalescence has been so far observed at the latest foaming stages, where bubble growing causes large extensional loads on the polymer film between two neighboring bubbles and eventually leads to the film rupture and to the merging of the two bubbles in a single one. This phenomenon is responsible for the coarsening of the foam morphology and, in turn, the worsening of the final foam properties. Here, the unanticipated, indirect, observation of a bubble coalescence phenomenon occurring at the very early stage of foaming, when most of the blowing agent is still solubilized in the polymer, is reported. Likewise, this phenomenon is responsible for a significant coarsening of the foam morphology. With the aim of investigating this phenomenon, a novel pressure vessel for foaming was utilized, capable of imposing two different cooling histories on two polymer samples, foamed at the same time. Results are presented on polystyrene foamed with carbon dioxide.

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1. Introduction

Physical polymer foaming has been attracting for decades the industrial and scientific interest due to the myriad of applications of these materials and to the numerous processing as well as material science challenges related to the inherent complexity of the foaming process. Most of the investigation on polymeric foams focused on the bubble nucleation and bubble growth [1–4], and on their effects on the final foam morphology [5–7]. Bubble coalescence in polymer melts or other fluids has been, in fact, an active research topic as well, both from the experimental and theoretical point of view since 1950 [8], with the main intent of controlling the foam structure (closed to open celled morphologies). For instance, Han and Ma [9] investigated the foam extrusion of low-density polyethylene, with talc as a nucleating agent and a fluorocarbon as blowing agent. They found that the bubble coalescence and the open celled fraction increased with increasing talc concentration and die temperature. In particular, the die temperature has been considered as the main factor, since the viscosity and melt strength of the polymer rapidly drop with the temperature. Similar relationships were found in the case of polystyrene (PS) [10–12]. In the state of the art, bubble coalescence has been so far considered as occurring because of prolonged growth against a weak polymer film, at the latest stages of the bubble growth, after cell impingement, and when most of the blowing agent had been diffused out of the polymer/blowing agent solution.

Herein, we present an insight into the foaming process with the observation of the bubble coalescence at early stage of growth, when most of the blowing agent is still in solution. This phenomenon, that may be described as “early” coalescence, as opposed to the so-far observed “late” coalescence, is as well responsible for a coarsening of the foam structure, possibly to a larger extent.

2. Materials and methods

To observe the early coalescence phenomenon, we made use of a novel pressure vessel, introduced in 2016 by our group as the “mini-batch”, capable of very high pressure drop rates and of imposing two different cooling histories to samples foamed at the same time. See Ref. [13] and the Supplementary Materials for details. Briefly, the pressure vessel, whose scheme is reported in Fig. 1a, is designed to minimize the volume to be evacuated [14], maintaining the capability of i) controlling the sample temperature, ii) measuring the pressure (and Pressure Drop Rate, PDR), iii) dosing a blowing agent and iv) releasing the blowing agent. As detailed in Fig. 1b, two kinds of foamed samples can be produced: 1) a sample, addressed to as “expelled” sample, exits the pressure vessel during the pressure release, dragged by the blowing agent stream; 2) a sample is hindered from doing the same as it is placed upstream, with respect to the blowing agent evacuation piping, of a metallic (retaining) net. The latter sample is addressed to as “retained”, and it is removed from the pressure vessel after around 20 s. In the Movies S1 and S2 in the Supplementary Materials clarify the sample expulsion and retention

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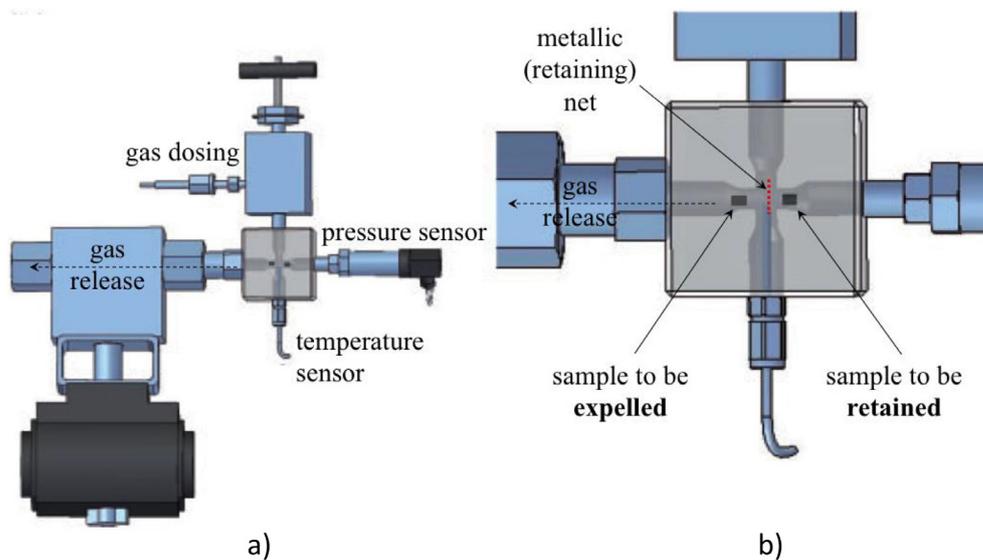
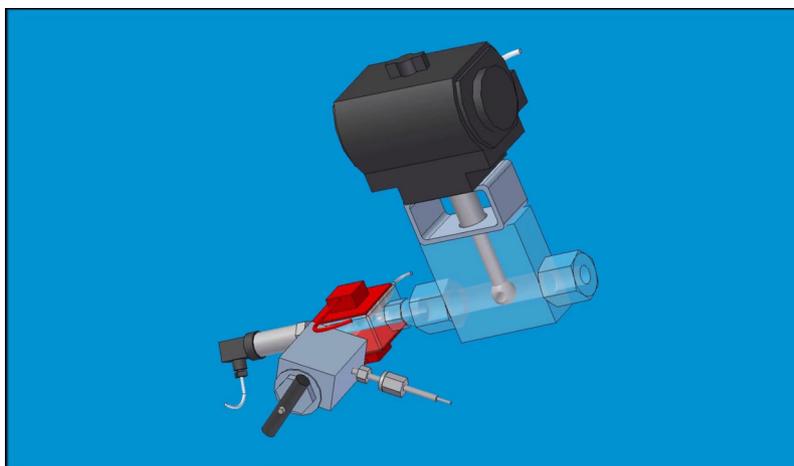


Fig. 1. Schemes of the pressure vessel. a) Overall view, with the pressure vessel in the center (gray) and the four connections (blue); b) details of the samples to be foamed (retained and expelled).

procedure, respectively. In a typical experiment, two polymeric granules are placed in the mini-batch upstream and downstream of the retaining net, for blowing agent solubilization (at saturation

temperature, T_{sat} and saturation pressure, p_{sat}). Afterwards, the pressure vessel is brought to the foaming temperature, T_{foam} , and finally pressure quenched by an actuated ball valve at a fixed *PDR*.



Movie S1.



Movie S2.

A PS (N2380) supplied by Versalis S.p.A., Mantova, Italy, was used as received. Talc (Imerys Talc, Toulouse, France; median particle size of 1.8 μm) was used in 1 wt% extruded mixtures, see Ref. [15] for details. CO_2 (SOL, Italy) was used as the blowing agent. Foam density (ρ) was measured according to ASTM D792, using an analytical balance (Mettler Toledo, Columbus, OH, USA). Foam morphology was investigated by a Scanning Electron Microscope (SEM). Cell density (N) was calculated as $N = (n/A)^{3/2} (\rho_p/\rho)$, where n is the number of the cells in the area, A , of the SEM micrograph, and ρ_p is the density of the solid sample.

3. Results and discussion

Fig. 2 shows SEM images of two samples, expelled (Fig. 2a) and retained (Fig. 2b), for a test conducted at $T_{\text{sat}} = T_{\text{foam}} = 100^\circ\text{C}$ and $p_{\text{sat}} = 10.0\text{ MPa}$ with CO_2 and foamed at $PDR = 300\text{ MPa/s}$. In Fig. 2b), the retained sample shows a fine morphology, with no apparent evidence of any cell collapse, with N of ca. 10^7 cells/cm^3 and $\rho = 0.2\text{ g/cm}^3$. Fig. 2a) reports the SEM image of the expelled sample, foamed at same conditions, but exposed to a more dramatic cooling history, as it is dragged out of the pressure vessel

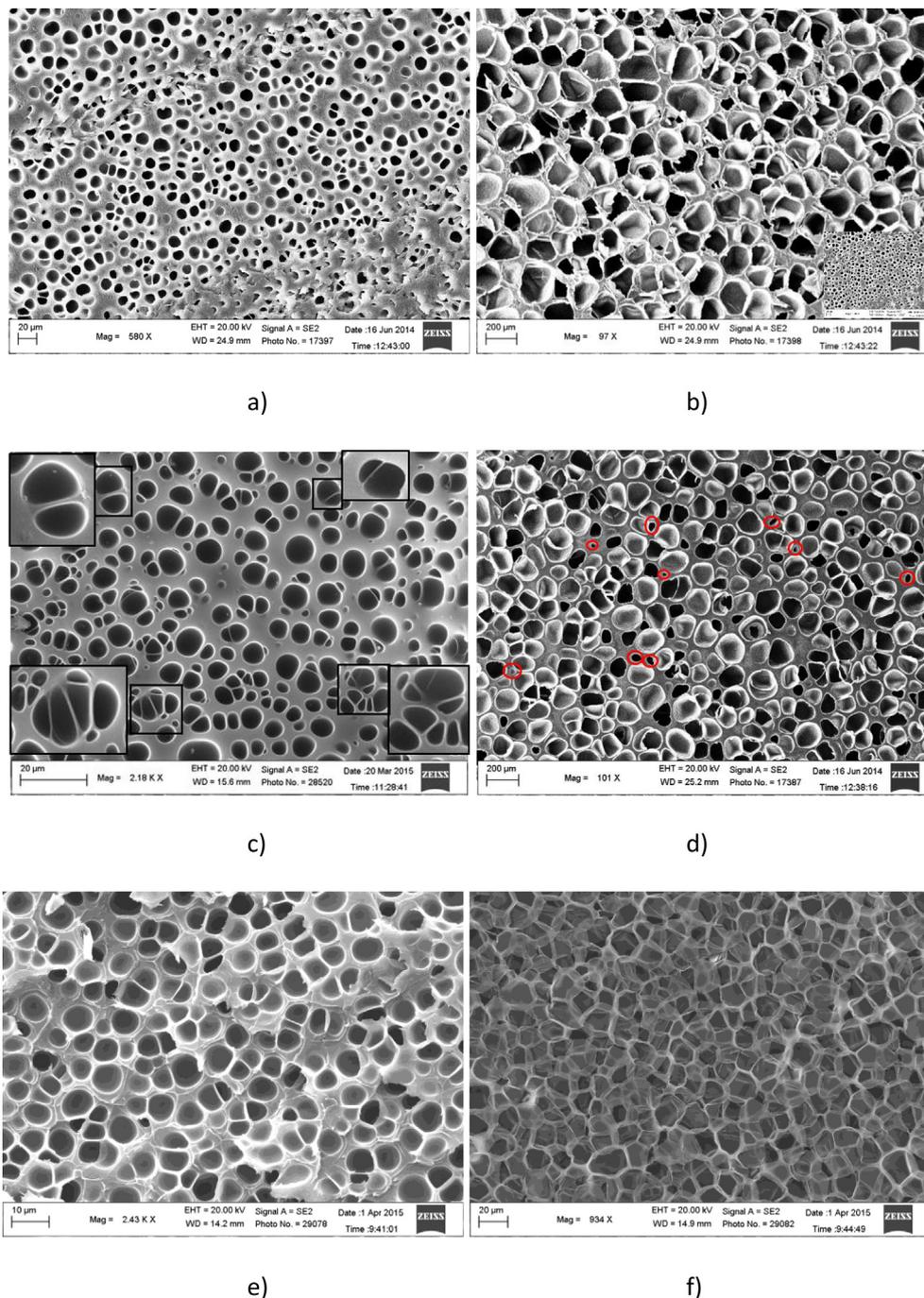


Fig. 2. SEM images of PS samples foamed with CO_2 at $T_{\text{sat}} = 100^\circ\text{C}$, $p_{\text{sat}} = 10.0\text{ MPa}$, $T_{\text{foam}} = 100^\circ\text{C}$. a) and b) neat PS foamed at $PDR = 300\text{ MPa/s}$; a) expelled; b) retained (inset reports (a)) at same magnification. c) and d) neat PS foamed at $PDR = 400\text{ MPa/s}$; c) expelled, with some insets evidencing bubbles which are keen to coalesce; d) retained, with few (circled in red) smaller cells possibly proving the earlier existence of smaller cells. Figure e) and f) talc filled PS samples, foamed at $PDR = 430\text{ MPa/s}$; f) expelled ($\rho = 0.7\text{ g/cm}^3$); e) retained ($\rho = 0.4\text{ g/cm}^3$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

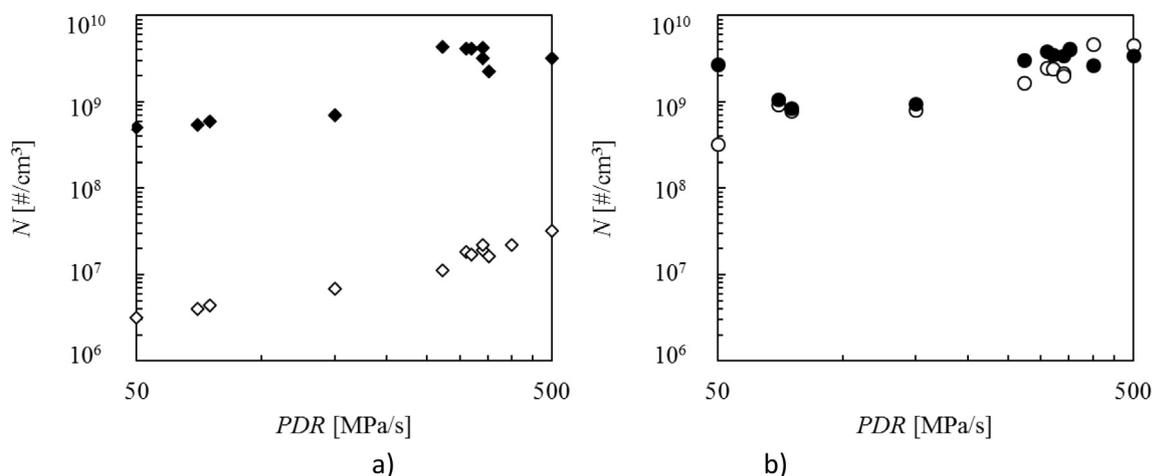


Fig. 3. a) N vs. PDR for neat PS samples: expelled (full rhombs), retained (empty rhombs). b) N vs. PDR for talc-loaded samples: expelled (full circles), retained (empty circles).

by the blowing agent. In this case $N = 10^9$ cells/cm³ and $\rho = 0.6$ g/cm³. Inset of Fig. 2b) shows a direct comparison at same magnification, evidencing the difference between the two morphologies. These differences have to be related to the cooling processes experienced by the two samples. As by the foam density, it is easily addressed by considering that the expelled sample is cooled much quickly than the retained sample, which means earlier growth-arrest, smaller expansion and higher foam density. Regarding the morphological difference, in the retained sample, despite the quick (within 20 s) removal, and despite no hint of any collapse is detectable in Fig. 2b, already extensive morphological changes occurred with respect to the expelled sample. We may speculate we (indirectly) observed an early bubble coalescence. In fact, in Fig. 2c) it is possible to observe, in an expelled sample, groups of neighboring cells, which, despite the relatively high foam density, are very close and separated by sub-micrometric polymer film [16]. This film is so thin that any additional load, deformation, or time at higher temperature (what, in fact, the retained samples experience) will induce its breaking, with the corresponding bubble merging – coalescence. Fig. 2d) shows an additional evidence of the early coalescence in retained samples, with large bubbles and, evidenced with red ovals, some smaller bubbles amid the larger ones. This bimodal bubble distribution could be the result of uncompleted disappearance, by early coalescence, of the early, high- N morphology, which is conversely set by fast quenching in the expelled samples. Early coalescence, in contrast with so-far observed late coalescence, occurred at the very early stages of growth, among bubbles which nucleated too close to each other and which, for this reason, cannot survive the incumbent growth (marked bubbles in Fig. 2c).

Another important difference between the early and the late coalescence is that, in the underlying literature, cell coalescence has been observed at higher temperatures (e.g. in the range 150–250 °C [12]) with respect to our observations (100 °C).

To verify the robustness of this speculation, tests were made in the PDR range 50–500 MPa/s. Results are reported in Fig. 3a) in terms of N vs. PDR , showing a rather persistent two-orders of magnitude difference between the expelled and the retained samples.

Finally, with the aim of clarifying the early coalescence observation, we investigated the use of nucleating agents, ubiquitous in

the foaming practice, to see how they interfered with the said early coalescence. To this aim, talc-loaded PS pellets were subjected to the foaming procedure described above, at same T_{sat} , p_{sat} and T_{foam} , in the PDR range 50–500 MPa/s. Results are reported in Fig. 3b). Two main comments emerge from the analysis of Fig. 3b), in comparison with Fig. 3a): i) for the expelled samples (closed symbols), the effect of the nucleating agent is null (within statistical difference); ii) the early coalescence is suppressed in the case of the presence of the nucleating agent, as no difference between retained and expelled sample is observed. When the nucleating agent is utilized, the morphologies of the retained samples are similar to the ones of the corresponding (at same PDR) expelled samples. Hence, we may conclude that *this* nucleating agent, instead of behaving as a nucleating agent, works as an “early-coalescence suppressor”. In the Fig. 2e and f, SEM of expelled and retained samples with talc are shown. The retained sample, Fig. 2f, loaded with talc can be seen as an “expanded” version of the frozen morphology of the expelled sample, with the same N but larger cells, thinner cell walls and a lower foam density.

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