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A novel lab-scale batch foaming equipment: The mini-batch

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Abstract

In this paper, we report the design of a new experimental apparatus for the study of the foaming process of thermoplastic polymers with physical blowing agents. The novel lab-scale batch foaming equipment is capable of achieving accurate control of the processing variables, namely, the temperature, the saturation pressure and the pressure drop rate and, furthermore, of allowing the achievement of very high pressure drop rates, the observation of the sample while foaming and the very fast extraction of the foamed sample. By recalling the considerations discussed by Muratani et al. (*J Cell Plast* 2005; 24: 15), the design converged into a simple, cheap, and very small pressure vessel, thereby denoted as mini-batch. We herein describe the overall design path of the mini-batch, its characteristics, configurations, together with some examples of use with polystyrene and CO_2 as the blowing agent.

Keywords

Batch foaming, pressure vessel, pressure drop rate, view cell, mini-batch

Introduction

In the last decades, general understanding of the foaming process of thermoplastic polymers with physical blowing agents settled around the delineation of the main processing variables and of their effects on the resulting foam, in terms of foam density and cell morphology. In the 80's in particular, the effect of the pressure

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drop rate, PDR (i.e. the rate at which the saturation pressure is reduced to ambient pressure by blowing agent release—in fact, the rate at which supersaturation of the blowing agent is achieved) was introduced as an important processing variable, being involved in the competition between the bubble nucleation and growth.[1,2] The reduction of the PDR, for instance, decreases the rate of stable nuclei formation, in turn increasing the chances for the blowing agent to inflate the formed bubbles, with a final coarsening of the cellular structure.[3–6] From the other side, since fine-celled foams possess, typically, better properties (among others, mechanical as well as thermal insulating), the correlation between the PDR and the final cell morphology was extensively studied by researchers and process designers, with the final aim of maximizing the PDR and, in turn, minimizing cell size.[7–11] In this context, numerous studies reported the design of foaming apparata allowing the possibility to release the blowing agent at several PDRs. Among others, Muratani et al.[12] minimized the volume of the pressure vessel in order to increase the PDR. In fact, standing the gas discharge system, the reduction of the volume of the vessel determined an increase of the PDR by reducing the amount of gas to be evacuated from the vessel itself.[13] Furthermore, they used an hydraulic press machine to close the upper lid of the pressure vessel in order to cool and quickly take out the sample after foaming. By using this reduced-volume pressure vessel, Muratani achieved values of PDR as high as 25 MPa/s, from a saturation pressure of 15 MPa. Guo et al. achieved much higher PDR values, i.e. 2500 MPa/s from a saturation pressure of 27.7 MPa, with a foaming system consisting of the vessel and an ad-hoc evacuating volume, characterized by optimized connections for the maximization of the PDR.[14] In particular, the apparatus proposed by Guo et al. was equipped with a sapphire window and a fast acquisition camera in order to observe the bubble nucleation. Nevertheless, unlike Muratani's apparatus, it was not possible to extract the foamed sample for further measurement. Chen et al.[15] achieved 150 MPa/s from a saturation pressure of 21.1 MPa with a pressure vessel capable of quick sample extraction and equipped with a tool for shearing the sample to investigate coupled effects of PDR and shear on the final foams (actually it was not equipped with a view cell for on-line foaming observation).

This paper presents a novel batch foaming apparatus that possess all of these *three important functions* to study the foaming process, namely: i) it allows a wide PDR range, in particular towards very high PDR; ii) it allows a very fast foamed sample extraction; iii) it has a view cell to observe the foaming "on air". Furthermore, it is very simple, cheap, versatile, since it allows multiple configurations, and environmentally friendly, for the very limited use of CO_2 and thermal energy for operation. In this paper, we report on the designing process (principle of operation), the equipment characteristics (apparatus) and capabilities (results), with some foaming data using the polystyrene (PS)-CO_2 system. The miniaturization approach led us to call this new equipment as "mini-batch".

Principle of operation

The mini-batch has been developed to satisfy the aforementioned three functions and uses the pressure vessel miniaturization approach as proposed by Muratani et al.[12] It has to possess all of the connections/ports needed to control the operations, namely, the temperature port to control the temperature inside the vessel (as close as possible to the sample), the gas dosing port, the pressure measurement port, and the gas release port. Our miniaturization approach, then, was simply to *eliminate the pressure vessel itself*, by using a cross to connect the different ports. In this way, standing the gas release system, the minimization of the gas volume to be evacuated maximizes the PDR. One important feature of this design is the use of a ball valve (activated by an electromechanical actuator) as a pressure discharge system. When open, a full, see-through pipe is created, and the gas to be released does not find any obstruction on its way out of the equipment, again for PDR maximization. As a side, yet important result, the foamed sample, if sufficiently small, may be transported by the gas flow through this un-obstructed pipe, towards the outside of the system, as like an instantaneous foam extraction system. The third important feature of this design is the possibility to look inside the batch while conducting all of the sequences for foaming. To do so, a view cell can be assembled on the apparatus, as it will be seen in the following. Creative use of available connections, view windows, full-flow quick connectors, sensors, etc. allows for a full versatility of the system. Finally, the simplicity of the design and the availability of standard pieces of equipment and connections render the mini-batch extremely cheap and easy to assemble and use. We are confident it will help the development of the knowledge of the foaming process and allow more people to be involved in this fascinating subject.

Apparatus

Three-dimensional (3D) rendering images of the mini-batch are reported in Figure 1. Figure 1(a) shows a view of the assembled vessel with the four ports of the cross (indicated with No. 1 in the figure) occupied by the temperature sensor (No. 3), the pressure sensor (No. 4), the gas dosing system (No. 5), and the gas release (No. 6). No. 2 indicates the two square heating elements (one on the top and the other on the bottom). Figure 1(b) and (c) shows a detailed view of the assembled vessel, with the cross rendered with a transparent material to show the sample positioning (dark colored polymer pellet) and the temperature sensor. The actual configuration is based on ½'' NPT threads, but ¼'' or other are possible, depending on the cross fitting. In the present case, the cross element is a mod. 15–24NFD cross from High Pressure Equipment Company, Erie, PA. Temperature was controlled by a PID thermoregulator (Ascon-New England Temperature Solutions, Attleboro, MA, model X1). A pressure transducer (Schaevitz-Measurements Specialties, Hampton, VA, model P943) was used to measure pressures and the pressure history was registered by using a data acquisition system

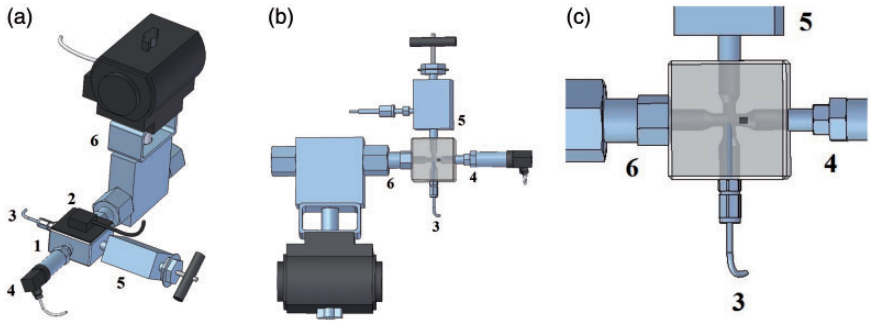

Figure 1. Three-dimensional rendering of the mini-batch in three views and magnifications. (a) assembled vessel, (b) assembled vessel, with the cross rendered with a transparent material. (c) zoom on the sample positioning. Refer to "Apparatus" section for the numbering.

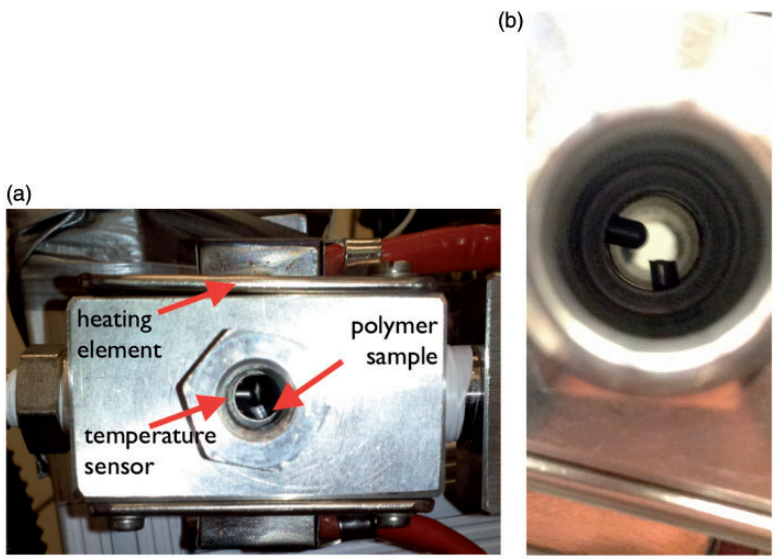

Figure 2. Pictures of the details of the mini-batch; (a) front view of the cross and, highlighted, some pieces; (b) view of the see-through pipe with the temperature sensor and the sample.

(DAQ PCI6036E, National Instruments, Austin, TX). The pressure release system consists of a discharge valve (High Pressure Equipment Company, model 10–80 NFH ball valve) and a pneumatic electrovalve.

Figure 2 shows two detailed pictures of the mini-batch. Figure 2(a) shows the heating elements, and how the sample and the temperature sensor are placed within the vessel (in this case, the front port has been left open for proper observation). Figure 2(b) shows again the temperature sensor and sample, but now in the "open"

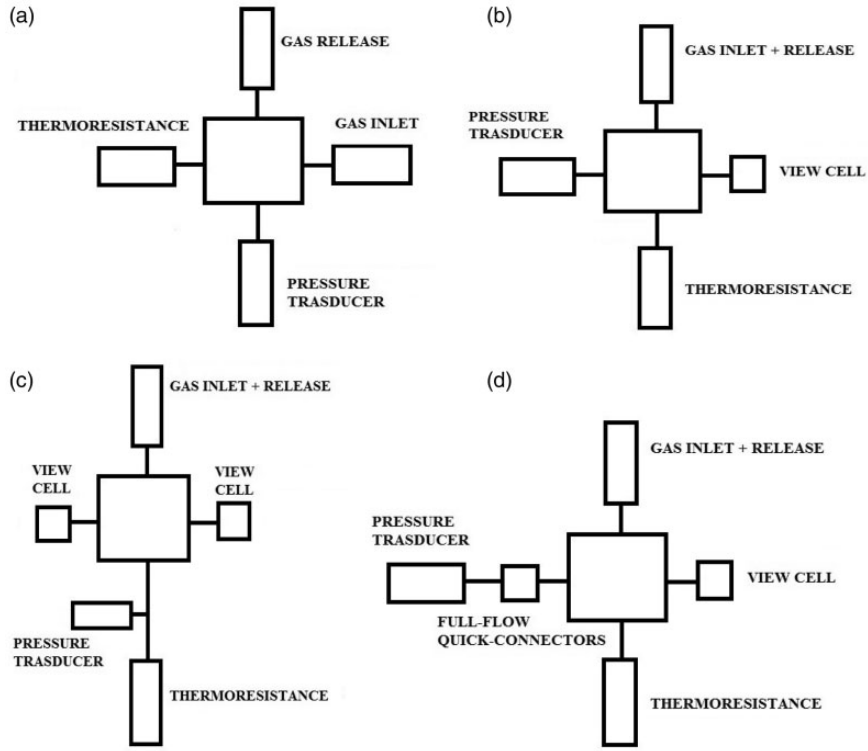

Figure 3. Schemes of the possible configurations of the mini-batch; (a) basic configuration, (b) view cell configuration, (c) two view cells configuration, and (d) a full-flow quick connector configuration.

position of the ball valve. It is evident, in this case, the full, see-through pipe, responsible for the fast evacuation of the gas and the extraction of the foamed sample.

Figure 3 shows some schemes of the possible alternative configurations of the mini-batch: (a) the cross has, connected to the four ports, the gas release system, the gas dosing valve, the pressure sensor, and the temperature sensor, alike in Figure 1; (b) a view cell is used (the gas dosing may be done from the same port of the gas release); (c) two view cells (to observe the sample in transmission, for better lighting) can be used (the pressure sensor is placed on the temperature sensor port with a T-fitting); (d) a full-flow quick connector can be used on the pressure transducer side.

As mentioned, a key feature of the mini-batch is the possibility to very fast extraction of foamed sample. To tell the truth, in our case, it is a foamed sample expulsion, rather than extraction. To clarify this point, Figure 4 shows a rendering of the details of the ball valve opening sequence: in (a), the mini-batch is closed (the ball valve is closed), ready for the pressure release, with the polymer sample

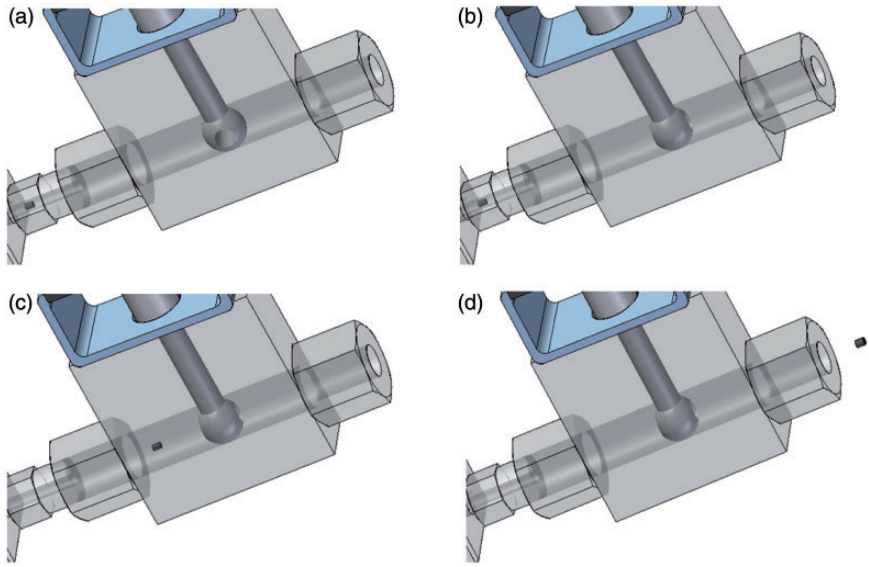

Figure 4. Schematic of the sample expulsion; (a) closed configuration; (b) open configuration; (c) open configuration, with the pellet dragged by the blowing agenttowards the exit; (d), open configuration, with the pellets expelled.

(dark colored) sitting in the cross; in (b), the ball valve has been rotated by 90° in open position; in (c), the pellet, dragged by the blowing agent evacuation, starts moving in the pipe towards the exit; in (d), the foamed pellet has been expelled. It is worth of note, here, that the sample is expelled at very high speed, and a collecting net has to be used in order not to loose the sample. Finally, it comes quite trivial the consideration about how fast is the sample expulsion with respect to conventional vessel and how fast could be the temperature quench in order to set the newly formed cellular structure, a very important aspect when dealing with foams that are keen to collapse or coalesce.

As a possible alternative to sample expulsion, of course, it is possible to retain the sample in the mini-batch, akin in a conventional pressure vessel, and remove it after some time, for example to study aging or to perform multiple pressure treatments. In this case, it is possible to use a metallic net between the sample and the blowing agent evacuation piping, as it is shown in Figure 5. In contraposition with ''expelled'' sample (as shown in Figure 4), we will call the sample kept in this way inside the mini-batch as ''retained''.

Results

The novel foam batch apparatus has been tested to verify the design by using PS and CO_2 as the foaming system. The PS used in this work is PS N2380 supplied by Versalis S.p.A., Mantova, Italy, used as received. The density and melt flow index

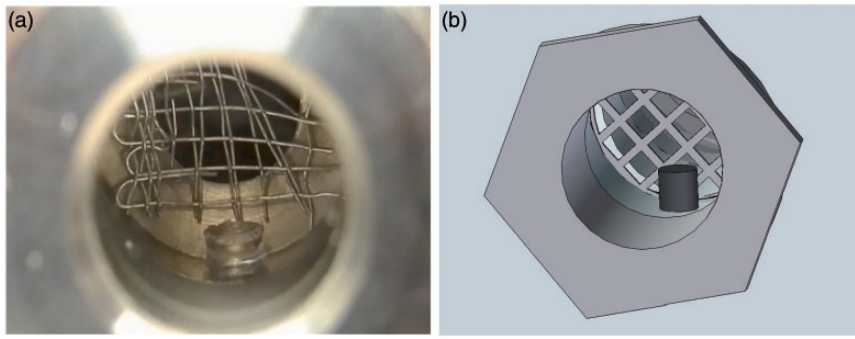

Figure 5. Retained sample; (a) picture of the actual configuration and (b) 3D rendering.

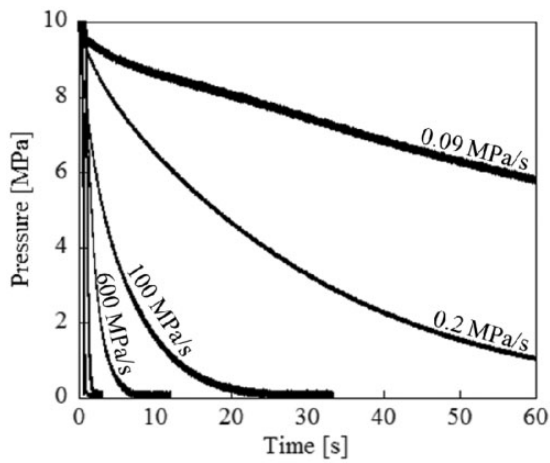

Figure 6. Selected pressure histories achieved by using several ball valve actuator pressures and/or several downstream pipings, from a saturation pressure of 10 MPa.

of the polymer, as provided by Versalis S.p.A., are 1.05 g/cm^3 and 2.0 g/10 min, respectively. Technical grade CO_2 was provided by Sol, Italy. For instance, by selecting several ball valve actuator pressures and/or several downstream pipings, we achieved a very wide PDR range (as shown in Figure 6, namely, up to 600 MPa/s from a saturation pressure of 10 MPa, and up to 1800 MPa/s, from a saturation pressure of 30 MPa; PDR was calculated as the highest absolute value of the derivative of the pressure history as the average on 0.004 s).

For proper comparison with other batch systems, in terms of relative pressure drop (the PDR over saturation pressure ratio), this means a maximum value of 60 s^{-1}; Guo et al.[14] reached a relative PDR of 90.2 s^{-1}, Chen et al.[15] of 7.1 s^{-1}, and Muratani et al.[12] of 1.7 s^{-1}. Figure 7 shows two pressure histories, together with

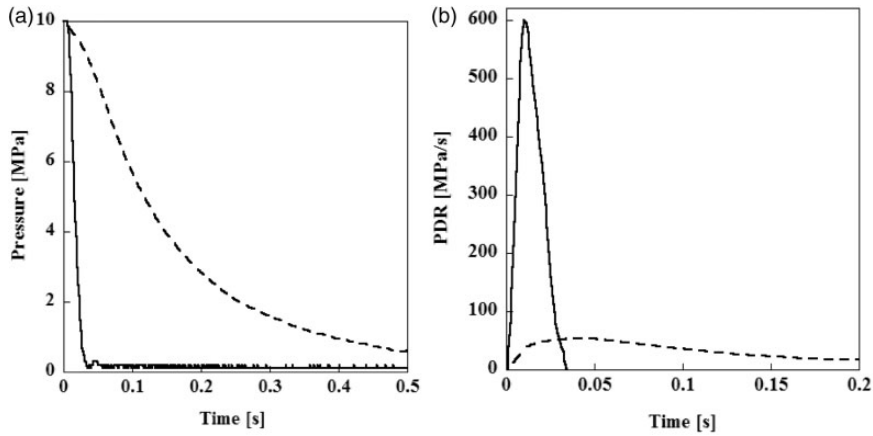

Figure 7. Pressure histories during a blowing agent release event for the mini-batch and for a conventional pressure vessel; (a) pressure as a function of time; (b) time derivative of the pressure. Solid lines, mini-batch; dashed lines, conventional pressure vessel.[3,4]

their time derivative, measured during a blowing agent release in the mini-batch and in a conventional pressure vessel.[3]

As it is possible to observe, the miniaturization approach led to a large reduction of the blowing agent evacuation time. It is worth of note, here, that we utilized the same ball valve in the two pressure vessels and that, hence, the very short blowing agent evacuation time is mostly due to the extremely low volume of the mini-batch (25 mL ca.).

As already reported in the ''Apparatus'' section, there is the possibility to both retain and expell the foamed sample. In particular, it is possible to concurrently foam two samples, one placed upstream of the separating net and other placed downstream. The samples would then be subjected to the same foaming conditions but to different extraction conditions, one very fast and the other slower (by using the full-flow quick connection the extraction time of the retained sample could be from few seconds to any longer time). This is a key feature of the mini-batch, giving the possibility to study with some greater detail the nucleation and growth phenomena. For instance, Figure 8 reports few scanning electron microscopy (SEM) micrographs showing the morphologies of selected foamed samples, both expelled and retained. Foaming conditions, final foam density, and cell number densities (calculated with respect to the unfoamed volume[16] as $N = \left(\frac{n}{A}\right)^{3/2} \times \left(\frac{\rho_s}{\rho_f}\right)$, where n and A are the number of the cells in the micrographand area of the micrograph (in square centimeter), and ρ_f and ρ_s are the densities of the foamed and solid sample, respectively, are reported in Table 1. As it is possible to observe by comparing Figure 8(a) and (b), the expelled samples show a finer morphology (cell number densities of expelled samples are 2–3 orders of magnitude higher than the corresponding retained sample) and higher densities (due to temperature quenching of

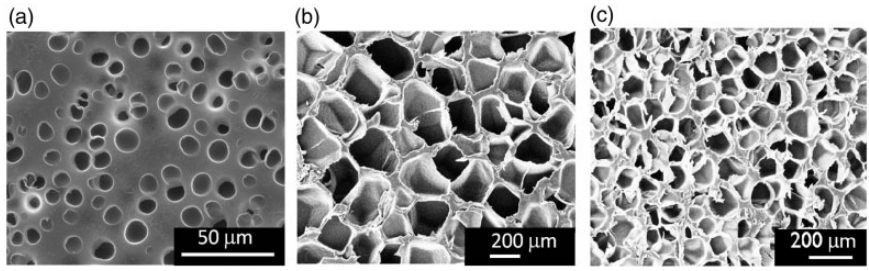

Figure 8. SEM micrographs of selected foamed samples; effect of foamed sample sample extraction, (a) expelled and (b) retained; effect of the PDR on the foam morphology, (b) low PDR and (c) high PDR, both retained; refer to Table 1 for foaming conditions and foam morphologies (all the samples were saturated with CO_2 at 100°C and 10 MPa).

Table 1. Results of selected foaming attempt; all the samples were saturated with CO_2 at 100°C and 10 MPa; different PDR were achieved by varying downstream piping.

Sample (refer to Figure 8)	a)	b)	c)
PDR (MPa/s)	270	270	600
Foam density (g/cm^3)	0.63	0.20	0.16
Cell number density (#/cm^3)	5.3×10^9	1.9×10^6	1.2×10^7
Type of extraction	Expelled	Retained	Retained

the expelled samples with respect to the retained samples). While the latter result is expected, the former is not a trivial result. To explain it, we could refer to a premature cell coalescence. This subject, however, is beyond the scope of this contribution and will be discussed in a forthcoming paper.

As an example of the effect of the PDR on the foam morphology, Figure 8 also reports a comparison of two samples foamed at different PDR, saturated in the same conditions (see Figures 8(b) and (c)). As expected, the cell number density increases and the cell diameter decreases with the increase of the PDR. A forthcoming paper will discuss about the effect of the PDR on the foam morphology of both the expelled and retained samples.

In order to show the utility of the view cell configuration (see Figure 3(b)), Figure 9 reports a sequence of images of a PS sample right after foaming. It is possible to follow the relatively slow growth and the volume and density time evolution.

Conclusions

In this work, a novel batch foaming equipment has been presented, based on the idea of miniaturization of the pressure vessel, in order to maximize the PDR. The new design, however, is very versatile and cheap and it has been proved to be useful

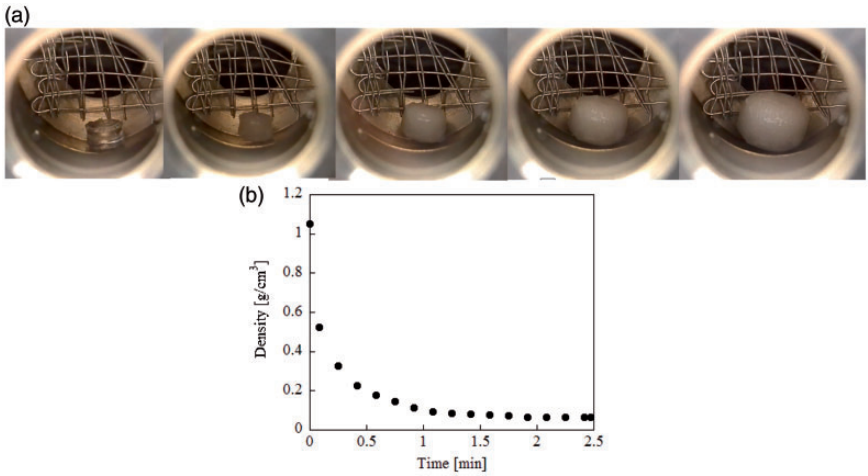

Figure 9. Foaming visualization of the retained sample, foamed at 80 MPa/s after saturation with CO_2 at 100°C and 10 MPa; (a) images of the sample and (b) the resulting density vs. time evolution.

as a new tool for studying the foaming process. In fact, we achieved PDR ranging from 30 to 1800 MPa/s, combined with the possibility to observe the sample while foaming and to expell the sample immediately at pressure release or to retain it in the pressure vessel. Several PS foams were produced by using CO_2 as blowing agent at different conditions of PDR and extraction conditions, with a wide range of final foam density and morphologies.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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