Experimental study of plasticization and foaming of polymer materials in supercritical carbon dioxide

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Abstract. A laboratory system for the development of new approaches to the experimental study of nucleation and formation of three-dimensional structures in nonequilibrium "polymer - supercritical fluid" heterogeneous systems has been designed and produced. The system is designed to conduct a comprehensive analysis of these processes at various stages starting from supercritical fluid plasticization of the initial polymer, followed by its subsequent nucleation and passage to the glass transition stage of the foamed polymer matrix, providing an opportunity for adequate interpretation.

1. Introduction

Currently, advanced technologies based on implementation of supercritical fluids (SCF) are widely used to perform and study a huge variety of different physical-chemical processes [1]. An unique combination of supercritical carbon dioxide (scCO2) properties (e.g., high diffusion rate and ability to act as a fairly strong non-polar solvent) at the pressure above 7.4 MPa and the temperature higher than 31°C, provide an effective extraction of various chemical compounds from amorphous and semi-crystalline polymers, as well as their impregnation and structural modification. SCF processing of polymeric materials which can be plasticized in scCO2 is of particular interest. Under release of the carbon dioxide pressure, these polymers can form both isolated and interconnected porous micro- and macrostructures with certain geometric characteristics. By altering the pressure and temperature of scCO2, as well as their change rate during the experiment, it is possible to form highly porous (≥60 vol. %) structures of predetermined architectonics from bioresorbable polymer materials, which can be used in tissue engineering and regenerative medicine [4].

At the same time, most well-known works on the research and development of SCF processes relating synthesis of highly porous polymer functional materials, describe the study and analysis of elementary physical processes within the systems in terms of qualititative approaches. This is mainly due to the problems associated with difficulties in diagnostics of non-equilibrium physical processes in heterogeneous "polymer - supercritical fluid" systems. Furthermore, the theoretical understanding of these processes was not always adequate.
In the present work, we conducted a comprehensive experimental study of the influence of technological parameters (initial values of the scCO2 temperature and pressure as well as the rate of their changes) of the SCF synthesis of polylactide structures on the surface morphology and architectonics of biodegradable scaffolds, comprising a theoretical analysis of the results and empirical data.

2. Experimental setup
To study the processes of SCF plasticization, nucleation and foaming of amorphous D,L-polylactide Purasorb PDL 04 (Corbion, Netherlands), we used an original experimental setup, including a set of optical systems for real-time diagnostics of the formed structures [5].

![Figure 1. General view of experimental set-up.](image1)

![Figure 2. High-pressure reactor.](image2)

The apparatus (figure 1) includes the following main elements: the CO2 inlet system (1), an optical high-pressure reactor (2), a video recording system (3), a system for monitoring pressure and temperature inside the reactor (4). The optical high-pressure reactor (figure 2) is a modification of the previously developed modular high-pressure reactor [6]. Six optical ports have a form of a hexagonal pattern and are located in the central part of the reactor. The cover and the bottom modules of the reactor also have optical ports. This arrangement provides the maximum number of ports required for studying various processes in the scCO2 environment with a simultaneous use of several optical (laser, visual, etc.) diagnostic techniques [7]. At the bottom of the reactor there are six high pressure ports for connecting the temperature and pressure gauges, as well as the valves and inlet/outlet pipelines. To register the SCF parameters inside the high-pressure reactor, the pressure sensors and K-type thermocouples are used. They are connected to the TPM200 digital meter (OVEN, Russia), which records all the data at a required acquisition rate.

All the thermoregulators, as well as the temperature and pressure gauges are connected to the OwenCloud service, which allows for a remote control and automatic measurements. With the help of the enlightening modules made of LED strips, uniform illumination of the inner volume of the high-pressure reactor with both direct and diffused light is achieved to obtain clear and contrast images.

3. Experiments
An experimental study of polymer sample plasticization and foaming was carried out in line with the following procedure. An amount (~20 mg) of fine powder (the mean particle size ca. 50 - 100 μm) of preliminarily cryomilled initial D,L-polylactide granules was placed in a glass mandrel that was fixed on a metal holder using metal clamps and a drop of cyanoacrylate-based glue. After that, a holder with the sample was placed in a high-pressure reactor preheated to the predetermined temperature (from 35
to 85°C) that was purged with carbon dioxide (to remove the atmospheric air) and then sealed. After that within 5-10 minutes (depending on the selected density of carbon dioxide), there was a gradual increase in the CO₂ pressure to the required values. The standard residence time of the samples in stationary conditions after the end of the pressurization process was usually 30-45 minutes. However, at the low density of scCO₂, the samples had to be kept longer (about one hour) providing uniform CO₂ diffusion into the polymer volume.

After holding the sample for a preselected time, the precision needle valve was opened synchronously with a video recording started simultaneously from two digital video cameras, as well as the temperature and pressure values acquisition. At the same time, a "timer" countdown program was started. An example of frame images recorded by the video cameras during the experiment is shown in figure 3.

**Figure 3.** An example of images recorded during the polymer foaming. The initial pressure P = 14 MPa, temperature T = 37°C. The time for recording frames is 25 minutes from the start of the CO₂ pressure release.

The computer program calculated the value of the carbon dioxide pressure occurred at the current time in the reactor, providing the constant release rate throughout the entire process of its decompression. If necessary, using an adjusting screw (in the manual mode), the speed of the SCF flow can be slightly adjusted to match the calculated values. Upon completion of the discharge, the reactor was opened, and the sample was removed from the holder and marked.

**4. Results**
The fabricated samples are shown in figure 4. The parameters of the experiments at which plasticization and foaming of polymers was performed are given in table 1.
5. Discussion of the results
Formation of the polymer foam under slow depressurization of the "polylactide - carbon dioxide" system includes the following characteristic stages: 1) nucleation and gradual accumulation of bubble embryos in the volume of plasticized polymer until they come close to each other; 2) expansion of foam until reaching the glassy state in the plasticized polymer at sufficiently low pressure. The second stage of
foam formation can be considered in terms of the foam state equation pioneered by S. Ross [8]. This state equation in its initial form is somewhat similar to the equation of state for an ideal gas, with exception of an additional term on the left side [8, 9]:

\[ P_{\text{ext}} V_f + \frac{2\sigma S}{3} = N_n T \]  

(1)

where \( P_{\text{ext}} \) is the external pressure, \( V_f \) is the volume occupied by the foam, \( \sigma \) is the surface tension of the polymer-gas interfaces, \( S \) is the total area of the interfaces, \( N_n \) is the total number of gas molecules in the foam volume, and \( T \) is the thermodynamic temperature. Despite its simplicity and somewhat debatable character, this equation allows for a reasonable interpretation of experimentally observed general tendencies in the foam behavior. Let \( N_e \) be the total number of bubble embryos occurring in the system at the end of the first stage (nucleation and embryo accumulation). Assuming that \( V_f \) significantly exceeds the initial volume of the plasticized polymer, we can rewrite equation 1 in the following form:

\[ P_{\text{ext}} \frac{4\pi}{3} N_e \langle R \rangle^3 + \frac{8\pi \sigma K}{3} N_e \langle R \rangle^2 = N_n T \]  

(2)

where \( \langle R \rangle \) is the average bubble radius in the expanding foam at the current state and \( K \) is the dimensionless factor taking into account the foam architectonics. For further analysis, let us rewrite equation 2 in the following form:

\[ K_1 P_{\text{ext}} \langle R \rangle^3 = K_2 \frac{T}{N_e} - K_3 \sigma \langle R \rangle^2 \]  

(3)

where \( K_1, K_2, K_3 \) are constants. Figure 5 displays the graphical interpretation of the solution to this equation for the fixed values of external pressure, temperature, and surface tension. It is seen that, under these conditions, an increasing number of bubbles causes a decrease in the average radius of the bubbles. The reason for such behavior is obvious: an increasing number of bubbles in the foam volume causes an increasing energy consumption associated with an increasing total area of interfaces, and contribution of the first term to the left side of equation 1 becomes smaller. This trend is clearly seen in figure 4: the samples with a smaller number of bubbles in the foam volume (see, e.g., panels 11, 14) are characterized by larger sizes of bubbles and, accordingly, larger values of \( V_f \) (as the foam volume is proportional to \( \langle R \rangle^3 \)).
Figure 5. Graphical interpretation of the solution to equation 3. Curve 1 corresponds to $K_p R^3$, and curves 2 - 4 correspond to $K_{2}(T/N_{eq}) - K_\sigma R^2$.

6. Conclusions
In the course of our study, high efficiency of the laboratory setup developed for a comprehensive study and real-time analysis of the SCF plasticization, nucleation and foaming of amorphous D, L-polylactide was demonstrated. The considered phenomenological model satisfactorily agrees with the results of scCO$_2$ foaming of D,L-polylactide under condition of slow depressurization.

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