



# Foaming of polymers with supercritical fluids: A thermodynamic investigation



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## ABSTRACT

The foaming of polymers using supercritical fluids was investigated, both, from a theoretical and an experimental point of view. Key thermodynamic phenomena that take place during the foaming process were described using the Non Random Hydrogen Bonding (NRHB) equation-of-state, such as the supercritical fluid solubility in the polymer matrix and the plasticization profile of the polymer–supercritical fluid system. Moreover, the NRHB model was combined with the classical nucleation theory in order to describe the energy barrier for nucleation. Subsequently, the foaming of the well-defined polystyrene–CO<sub>2</sub> system was experimentally studied. Porous polystyrene structures were prepared using supercritical CO<sub>2</sub> as foaming agent at various pressure and temperature conditions that refer to constant amount of dissolved fluid (CO<sub>2</sub>) inside the polymer matrix, or to constant initial energy barrier for nucleation. The experimental results, which were discussed in the light of the aforementioned theoretical investigation, reveal that at pressure and temperature conditions of constant equilibrium solubility of CO<sub>2</sub> inside the polymer matrix, the average pore diameter decreases with increasing foaming temperature, mainly due to the formation of more pores, which is a consequence of the decrease in the energy barrier for nucleation. Furthermore, at conditions that refer to constant initial energy barrier for nucleation, all the produced porous structures presented similar pore diameters and cell population densities, regardless of the foaming temperature. Finally, it is concluded that the energy barrier for nucleation determines the morphology of the final porous structure to a large extent, although other processing parameters, such as the foaming temperature (or pressure) and the amount of the dissolved fluid, may also influence the cell size.

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## 1. Introduction

Polymer foams attracted particular interest due to the wide range of applications that they find, which include thermal and sound insulation, shock absorbents, packaging materials, airplane and automotive parts, sporting equipment, microelectronic and optical devices [1–4].

For the production of porous polymers, supercritical fluids (mainly CO<sub>2</sub> and N<sub>2</sub>) can be used as physical blowing agents, which could substantially improve the conventional manufacturing techniques [5,6]. In this direction, porous polymers can be produced through the gas foaming method, which is mainly divided in two steps. In the first one, the polymer is saturated with a gas or supercritical fluid at constant temperature and pressure conditions. Subsequently, the system is led to a supersaturated state by rapidly increasing temperature (temperature induced phase separation) or

reducing pressure (pressure induced phase separation) resulting in the nucleation and growth of gas bubbles – cells – inside the polymer matrix [7,8]. The growth of cells continues until the viscosity of the polymer matrix is increased up to the point that the force opposing the expansion of the foam becomes sufficiently high or when the system passes from the rubbery to the glassy state (in cases of high  $T_g$  amorphous polymers and solid state foaming).

The foaming of polymers with supercritical fluids has attracted particular interest mainly for producing microcellular materials, which are porous polymer matrices with average pore diameter smaller than 10 μm and pore population density larger than 10<sup>9</sup> pores per cm<sup>3</sup> [7]. Compared to the corresponding compact materials, they present reduced bulk density, which induces materials saving and, consequently, reduction of cost. On the other hand, such materials often exhibit high toughness, high impact strength, high fatigue life, high stiffness to weight ratio, as well as low thermal conductivity [7]. Furthermore, foaming of polymers with supercritical CO<sub>2</sub> does not usually require the use of harmful organic solvents. Such an advantage renders the method suitable for processing polymers for various biomedical applications and

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especially for producing porous structures of biocompatible and biodegradable polymers, which could be used as scaffolds for tissue engineering applications [9–12].

Current foaming processes include batch or extrusion foaming and injection molding [5,13,14]. The batch foaming technique, sometimes mentioned as solid state foaming, allows the processing of polymers at significantly lower temperatures than those needed in extrusion or injection molding. Such reduction of the processing temperature leads to a substantial increase of the CO<sub>2</sub> solubility in amorphous polymers, which, subsequently, results in higher cell densities and smaller cell sizes [5,15,16]. Such foam characteristics, i.e. cell size and cell density, are also improved, simultaneously with the mechanical properties, upon the addition of a small portion of nanofillers inside the polymer matrix. Consequently, the foaming of nanocomposite polymer materials results in porous structures with improved mechanical properties, increased cell density and reduced cell size [14,17,18].

However, the batch foaming method is usually applied to amorphous polymers starting from saturation conditions that refer to the rubbery state. In the case of semicrystalline polymers, the final porous structure is often nonuniform due to the disability of the dissolved fluid to penetrate the polymer crystallites. The crystalline structure should be destroyed before foaming and, in this direction, one can take advantage of the melting point depression of the polymer due to the sorption of the supercritical fluid [19]. Consequently, there is a foaming temperature window, below the neat polymer melting point, where the method can be applied. The melting point depression of the polymer can be further assisted by the addition of a co-solvent [20,21].

From the materials point of view, most studies investigate the production of porous structures from usual thermoplastics or synthetic biodegradable amorphous polymers. On the other hand, fewer studies focus on the use of native biopolymers (such as cellulose, chitin or starch) due to the difficulty of processing such materials, although they are abundant and relatively cheap [22,23]. Such polymers present a unique crystalline and intramolecular structure, which is difficult to break. In such cases the so called hydrogel foaming technique could be an alternative [22,23].

Concerning the foaming of polymers with gases (or supercritical fluids), the most important properties of the polymer–gas (fluid) system that define the final porous structure are the degree of crystallinity of the polymer matrix (in case of semicrystalline polymers and solid state foaming), the initial (equilibrium) amount of the dissolved gas, the degree of supersaturation that is induced from the depressurization or the heating of the system, the surface energy between the gas nuclei and the surrounding polymer matrix and the plasticization profile of the polymer–gas system (i.e. the change in the glass transition temperature, which is induced by the sorption of the gas) [8,15,16,24].

The modeling of bubble nucleation inside the polymer matrix is usually performed on the basis of classical nucleation theory [25]. However, using this approach often several approximations are made, such as that only homogeneous nucleation proceeds inside neat polymer matrices, or that the interfacial tension between the gas nuclei and the supersaturated polymer matrix is equal to the surface tension, which is macroscopically observed at saturation [2,3,26]. Consequently, often the process is only qualitatively described and not accurate correlations are yielded rendering the modeling of bubble nucleation inside the polymer matrix as a challenging task [2,5,26]. Nevertheless, homogeneous nucleation theory proved able to describe the effect of pressure and temperature on nucleation [4,8].

In the present work, key thermodynamic properties of the polymer – supercritical CO<sub>2</sub> system are modeled with the Non Random Hydrogen Bonding (NRHB) theory [27], which is combined with the homogeneous nucleation theory. Findings of the theoretical

investigation are compared with experimental observations for the foaming (using the pressure quench method) of a well-defined system, i.e. polystyrene with supercritical CO<sub>2</sub>.

## 2. Theory

### 2.1. Nucleation theory

During the pressure quench, which induces the polymer supersaturation in the relevant foaming method, gas nuclei are produced inside the metastable polymer matrix. The development of such initial gas nuclei can be attributed to both homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs due the spontaneous gathering of gas molecules in the metastable polymer matrix, while heterogeneous nucleation occurs when the nuclei are produced on the boundaries of two phases, i.e. on the surface of solid particles (fillers or impurities), on preexisting gas cavities, or between areas of different density due to the dispersed crystallites or due to insufficient thermal processing during polymer molding.

However, in most cases of neat polymer foaming (and not polymer composite materials) the results are discussed assuming homogeneous nucleation. According to the classical homogeneous nucleation theory, the difference of the free energy of the system due to the formation of a gas nucleus inside the metastable polymer matrix can be written as the sum of the gain in the free energy related to the formation of the new phase and the cost of the free energy due to the introduction of the interface. Subsequently, in a closed isothermal system in chemical equilibrium, the difference of the free energy related to the formation of new phase cluster is given by the following relation [28,29]:

$$\Delta G = -\frac{4\pi r^3}{3}\Delta P + 4\pi r^2\gamma \quad (1)$$

where  $r$  is the radius of the spherical cluster,  $\gamma$  the interfacial tension, and  $\Delta P$  is the pressure difference related to the supersaturation of the system. The latter equation is derived assuming homogeneous nucleation and also that the new phase cluster has properties as a bulk phase in the same physical state. When  $\Delta G$  is plotted against cluster size, a curve that shows a maximum at a critical radius  $r_c$ , is obtained:

$$\frac{d\Delta G}{dr} = 0 \Rightarrow r_c = \frac{2\gamma}{\Delta P} \quad (2)$$

The maximum value of  $\Delta G$  for homogeneous nucleation is obtained by substituting Eq. (2) into Eq. (1), or:

$$\Delta G_{hom}^* = \frac{16\pi\gamma^3}{3\Delta P^2} \quad (3)$$

According to Kusaka et al. [26] the main difficulty of applying Eq. (3), is that the interfacial tension between a nucleus with critical size and the metastable polymer matrix is not directly measurable. Consequently, in most cases, in order to apply the classical nucleation theory such interfacial tension is approximated with the surface tension of the macroscopic interface at equilibrium.

$\Delta P$  in Eq. (3) is a pressure difference related to the supersaturation of the system. According to Gibbs [30] this pressure difference,  $\Delta P = P_\beta - P_\alpha$ , is the difference of the pressure that the nucleating phase would have, if it were present in bulk, at the same temperature and chemical potential with the metastable phase,  $P_\beta$ , minus the actual pressure of the metastable phase,  $P_\alpha$  [5]. In many cases such pressure difference is approximated with the actual pressure quench during the rapid depressurization of the system [8,16,28], however, with this approximation the energy barrier for nucleation is underestimated [5]. Nevertheless, such pressure difference,

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