Vitrification conditions and porosity prediction of CO_2 blown polystyrene foams

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ABSTRACT

Experiments with CO_2-blown hanging polystyrene (PS) films were carried out. The porosity of foams decreased with decreasing film thickness, indicating thus effects of heat and/or mass transfer. Taking into account the Joule–Thomson effect, mathematical model based on a simplified heat balance for the system PS + CO_2 at the conditions of PS saturation with CO_2 on one side and at the conditions of foam vitrification at glass transition temperature on the other side was derived to estimate the foam porosity. The model was applied to data on CO_2-blown hanging films as well as literature data on foaming of PS particles. The trends of porosity dependence on saturation temperature and film thickness predicted by the model correspond to experimental results. The Joule–Thomson effect included in the modelling of the CO_2 foaming process significantly affects the foam porosity and improves the predictive capabilities of simple model based on enthalpy balance and thermodynamic data.

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1. Introduction

PS foams are used particularly as thermal insulators, food packaging and cushioning material. Among the conventional technologies of polymer foam production, the CO_2 blowing appears to be a well-established technique which does not leave any chemicals in the product. CO_2 is dissolved in the polymer under high pressure and foaming is induced by rapid depressurization when the mixture becomes supersaturated and CO_2 bubbles (cells) are formed. Small cell sizes (below 10 μm, preferably below 1 μm) and high porosity (>90%) are desired for improved insulation properties of the foam [1]. According to the cell sizes and number densities, microcellular foams are characterized by cell diameters in the range from 0.1 to 10 μm and number densities of cells ranging from 10^9 to 10^{15} cm^{-3} [2] and nanocellular foams by the cell size below 1 μm and cell density higher than 10^{15} cm^{-3} [3].

As shown in the recent review paper by Okolieocha et al. [3], the on-going research focuses on the move to microcellular and nanocellular foams, and the use of CO_2 as a physical blowing agent may be the way how to obtain in the future nanofoams of sufficiently high porosity. Presently, the best prepared CO_2-blown

foams are of either cell size less than 1 μm but with low porosity (volume expansion ratio less than 4, i.e., <75%), or high porosity but cell size of 10 μm and more.

Fundamental studies on CO_2 blowing of polymers carried out as batch process enable researchers to develop and refine mathematical models, which include the rates of both nucleation and bubble growth. Out of the recent studies, the models published by Khan et al. [4], Sun et al. [2], and Tsivintzelis et al. [5] can be named. Applying these sophisticated models, the cell size distribution was predicted [4], simultaneous prediction of cell size and cell density was carried out [2], and the effect of energy barrier for nucleation on the cell density was investigated [5].

An important property of a foamed polymer is its glass transition temperature T_g, above which the bubbles can grow because the polymer is in the rubbery state. As CO_2 molecules penetrate into the space between polymer chains, they alter the chain mobility and free volume characteristics, which results in the glass transition temperature depression. Li et al. [6] evaluated the current state of understanding for T_g, and qualitatively described the variation of T_g in the foaming process. In the period of polymer saturation with CO_2, T_g decreases and becomes lower than the temperature of the polymer + CO_2 mixture, T. In the course of depressurization, CO_2 diffuses from the polymer forming bubbles and T_g increases until it reaches the temperature of the mixture ($T = T_g$) and the bubbles cannot grow further – foam vitrification occurs.

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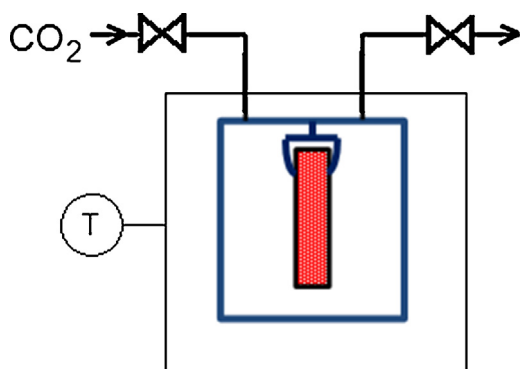
Fig. 1. Scheme of the pressure vessel with hanging polystyrene film, heated by the oil bath.

The temperature of the polymer + CO_2 mixture is fixed at the saturation temperature in the above mentioned models of foaming. However, the temperature of expanding gas decreases, which is known as the Joule–Thomson effect. In the course of depressurization, the increasing T_g will therefore become equal to the temperature of the mixture earlier than in the case of fixed saturation temperature. Besides, due to the polymer heat capacity, the temperature of expanding CO_2 outside the polymer will decrease faster than the temperature of the mixture of CO_2 and polymer; thus, the external cooling of the polymer + CO_2 mixture could affect the process.

In this study, CO_2 foaming of thin hanging PS films was carried out to examine the effects of saturation conditions and film thickness on the foam porosity. The results were interpreted with the help of simplified models based on the heat balance of the foaming process, which includes the Joule–Thomson effect. Publicly available experimental data are used in the thermodynamic description.

2. Experiments

PS films of thicknesses in the range from 0.11 to 0.90 mm formed by high temperature pressing were prepared from commercial PS pellets with molecular weight $M_w = 280$ kDa, density $d_{PS} = 1040$ kg/m^3 and glass transition temperature $T_{g1} = 100$ °C, purchased from the Sigma Aldrich company.

The scheme of the experimental set-up is shown in Fig. 1. The PS film was fixed in a high pressure vessel of 2.4 cm inner diameter and 5 cm height, which was placed in an oil bath maintaining the saturation temperature. The range of saturation temperatures was 40–102 °C. The vessel was pressurized to the saturation pressure (185–296 bar) with CO_2 (>99.9%, Linde, CZ) pumped from a pressure cylinder by high pressure pump from the company Ecom (CZ), whose head was cooled by a cryostat. The saturation pressure and temperature were applied for 1.5–19 h, in dependence on the film thickness, to ensure its equilibrated saturation with CO_2; the sorption time estimation is described elsewhere [7]. Then, the vessel was rapidly depressurized to ambient pressure within approximately 5 s.

The foam sample was analyzed via SEM and image analysis software NIS Elements. Its porosity was determined by dividing the area of the cells by the total area of the investigated part of the foam in the middle region of the film. The accuracy of the porosity evaluation was ±5 per cent points.

3. Mathematical models for the foam vitrification

Many simplifications were used to write the heat balance equations. The enthalpy of CO_2 absorbed in PS was assumed to be equal

to the enthalpy of the free CO_2. The pressure inside CO_2 bubbles was assumed to be equal to the pressure in and outside PS and uniform in the whole vessel. An instantaneous equilibration of the temperatures and CO_2 concentrations in a bubble and its surroundings was assumed. The CO_2 diffusion out of the PS film was neglected. The vitrification was assumed to occur exactly at the moment when the temperature in the mixture of polymer and CO_2 was equal to the glass transition temperature. The polymer was supposed to be saturated with CO_2, not over-saturated, at the moment of vitrification.

Disadvantage of this approach is that such a dynamic process is described in terms of equilibrium. Particularly the assumption of equal pressures is not realistic as the difference between the pressures inside the bubble and in its surrounding is substantial in the periods of nucleation and bubble growth, as mathematical models for polymer foaming prove. However, the pressure difference for larger bubbles in the vitrified polymer is supposed to be smaller. The discrepancy between the dynamics of the rapid foaming and the static character of the proposed models does not allow them to describe the process accurately. On the other hand, despite this inaccuracy, the direct comparison of saturation and vitrification condition is advantageous for studying the effects of saturation pressure, temperature, and polymer size on the porosity of polymer foams.

Two models for the foam vitrification in the course of rapid depressurization were derived. In the first model (model I), adiabatic process with no heat exchange between the PS and surrounding CO_2 was considered. In the second model (model II), the external cooling of the foamed PS film by CO_2 expanding outside the film was added to the heat balance equation.

3.1. Model I for adiabatic polymer foaming

3.1.1. Model equations and solution procedure

The expansion is supposed to be adiabatic and isentropic at the same time. The heat balance equation based on the assumption of no heat transfer between the polymer and its surroundings is:

$$S_0(H - H_0) + 100c_{PS}(T - T_0) = 0 \qquad (1)$$

where T is the temperature (°C), $S = S(P,T)$ is the solubility of CO_2 in PS (g/100 g PS), c_{PS} is the heat capacity of PS (kJ/kg·K), $H = H(P,T)$ is the enthalpy of CO_2 (kJ/kg), P is the pressure (bar) and the subscript 0 denotes the conditions of PS saturation with CO_2.

The vitrification conditions are indicated by subscript g. The relationship between the pressure P_g and temperature T_g is given by the pressure dependence of the glass transition temperature:

$$T_g = T_g(P_g). \qquad (2)$$

At the same time, the CO_2 enthalpy $H_g(T_g,P_g)$ and temperature T_g must fulfill Eq. (1), when substituted for H and T. The search for P_g in the interval $1 \le P_g < P_0$ satisfying these conditions is straightforward and the solution is found in a few iteration steps.

When the vitrification conditions are determined, the foam porosity ε (%) can be calculated from the difference in the solubility at saturation and vitrification conditions $S_0 - S_g$ and densities of CO_2 (d_g) and PS (d_{PS}):

$$\varepsilon[\%] = \frac{(S_0 - S_g)/d_g}{(S_0 - S_g)/d_g + (100/d_{PS})} \cdot 100. \qquad (3)$$

3.1.2. Calculation of PS and CO_2 properties

The values of CO_2 enthalpy H and density d were taken from the server of the U.S. National Institute of Standards and Technology (NIST) [8]. The heat capacity of PS at temperatures above T_g was estimated from the data published by Koh et al. [9] as $c_{PS} = 1.9$ kJ/(kg K).