

PRODUCTION OF CONTROLLED MICROPOROUS POLYMERS BY SUPERCRITICAL CO₂

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The foaming of atactic and syndiotactic polystyrene has been studied using a technique based on the saturation and rapid decompression of supercritical CO₂-saturated samples. The resulting microcellular structures have been controlled manipulating the process conditions. The experiments were performed at various foaming temperatures while holding the other variables constant, showed that higher temperatures produce larger cells. Larger saturation times assure an homogenous microcellular structure and produced smaller pores.

INTRODUCTION

Supercritical fluids are widely used as alternative to liquid solvents in several fields: extraction, fractionation, chemical reaction, micronization, polymer synthesis, etc. They have also recently proposed for the preparation of microcellular foams. Microcellular polymers are of interest due to the potential use in the areas of separation membranes, thermal and electrical insulation, biomedical materials and adsorbents.

Some techniques have been developed to prepare microcellular foams using supercritical fluids; they rely on the same principles: 1) the polymer is saturated with the blowing agent at high pressure; 2) the polymer/gas mixture is quenched into a supersaturated state by either reducing pressure or increasing temperature; 3) nucleation and growth of gas cells dispersed throughout the polymer sample evolves. Noncontinuous and continuous foaming techniques have been used. Two alternatives have been proposed for noncontinuous processing; the first alternative consists of saturating the polymer with CO₂ at room temperature and subsequently remove it by heating to a temperature above the normal polymer glass transition in a high temperature bath [1-3]. In the second alternative the polymer is saturated with CO₂ at relatively high temperature and pressure (in the supercritical condition) followed by rapid depressurization to atmospheric pressure [4-7]. This method takes advantage of the depression of glass transition temperature induced by the presence of CO₂.

These techniques have been used to foam various polymers as Poly(ether imide) [1,2], Poly(ether sulfone) [1,2], atactic Polystyrene [3,6-7], Poly(methyl methacrylate) [4,5] and the effect of parameters such as saturation pressure, time and temperature have been investigated [1-3,5,6].

The supercritical foaming of polystyrene has been studied by some authors. Sumarno et al. [3] applied the first technique to atactic polystyrene and investigated the effects of saturation pressure and temperature on the microcellular structure. They found that the

increasing of saturation pressure cause an increase of the cell density and a decrease of the cell diameter. The solubility of CO₂ decreases with an increase in temperature and the decrease of the amount of gas in the polymer causes a decreasing of cell density. They found that at lower temperatures, the microcellular polymers shows smaller cell diameter and higher cell density. Arora et al. [6] used the second process to characterize microcellular atactic polystyrene varying saturation pressure, temperature, depressurization profile and rate, and vessel geometry. They worked in a temperature range between 40 and 120°C at 230 bar and obtained foams with pores ranging between 0.5 and 20 μm. They found that higher foaming temperatures produce foams with larger cells. Higher saturation pressures increase the nucleation density, leading to smaller cells. They also worked between 150 and 420 bar at 100°C and obtained cells with diameter between 5 and 35 μm. The size of the vessel in which the material is foamed can restrict the growth and hence affects cell size, cell shape, and foam density. Reduction of the rate of depressurization allows for a longer period of growth and, therefore, produces larger cells.

Stafford et al. [7] investigated the effect of molecular weight, polydispersity and low molecular weight components on the microcellular structure of polystyrene. They concluded that molecular weight and polydispersity do not significantly affect the foaming process. However, the presence of a low molecular weight component was found to greatly influence the final structure of the foam. The results available in the literature seem very interesting from the point of view of controlled foams generation. Therefore, in this work we tested a supercritical CO₂ assisted foaming process to verify its performance. We used atactic and syndiotactic polystyrene as model compounds testing the influence of temperature and of the saturation time on dimensions and distribution of the cells generated.

EXPERIMENTAL SECTION

Materials

We used atactic and syndiotactic polystyrene in form of pellets (D = 3mm, H = 2.5mm). CO₂ (purity 99%) was purchased from S.O.N. (Società Ossigeno Napoli, Italy) and used as received.

Foam preparation

Foams were prepared in a home-made laboratory apparatus equipped with a 316 stainless steel cylindrical high-pressure vessel (200 mL) where CO₂ contacted the sample in a single pass bed. The vessel was immersed in a thermostated oven. Polystyrene was placed in the vessel that was then heated and filled with supercritical CO₂ up to the desired pressure using a high pressure pump (Milton Roy – Milroyal B). The vessel was maintained at the desired temperature and pressure for the time of the experiment. At the end of this period the vessel was depressurized in about 20 s opening a fast discharge valve.

Foam Characterization

Foams were characterized to determine cell sizes. The cellular structure was examined by cryofracturing the specimen at liquid N₂ temperature, sputter-coating with gold and viewing it with a scanning electron microscope (SEM) mod. LEO 420. Sigma Scan Pro and Microcal Origin softwares were used to measure the average value of the pores and calculate the distribution of cell diameters.

RESULTS AND DISCUSSION

Using the technique of saturation at high pressure and temperature [6] several variables can be moved to influence the foam morphology. We analysed: (a) foaming temperature: the temperature of the sample during the foaming; (b) saturation time: residence time of the CO₂ in contact with the sample.

Temperature

Since this method of foaming relies on the depression of glass transition temperature (T_g) of the substrate by supercritical CO₂, the temperature at which the material is foamed can have a significant effect on the cells produced. The effect of the foaming temperature on the foam structure of polystyrene was studied at a constant pressure of 230 bar. A selection of SEM images with foaming results is reported in **Figures 1a – 1d**. From these images, (produced at the same magnification) it is evident the large increase of cell size with temperature; i.e., cells ranging from about 5µm to more than 50µm are generated operating in the range from 55 to 125°C.

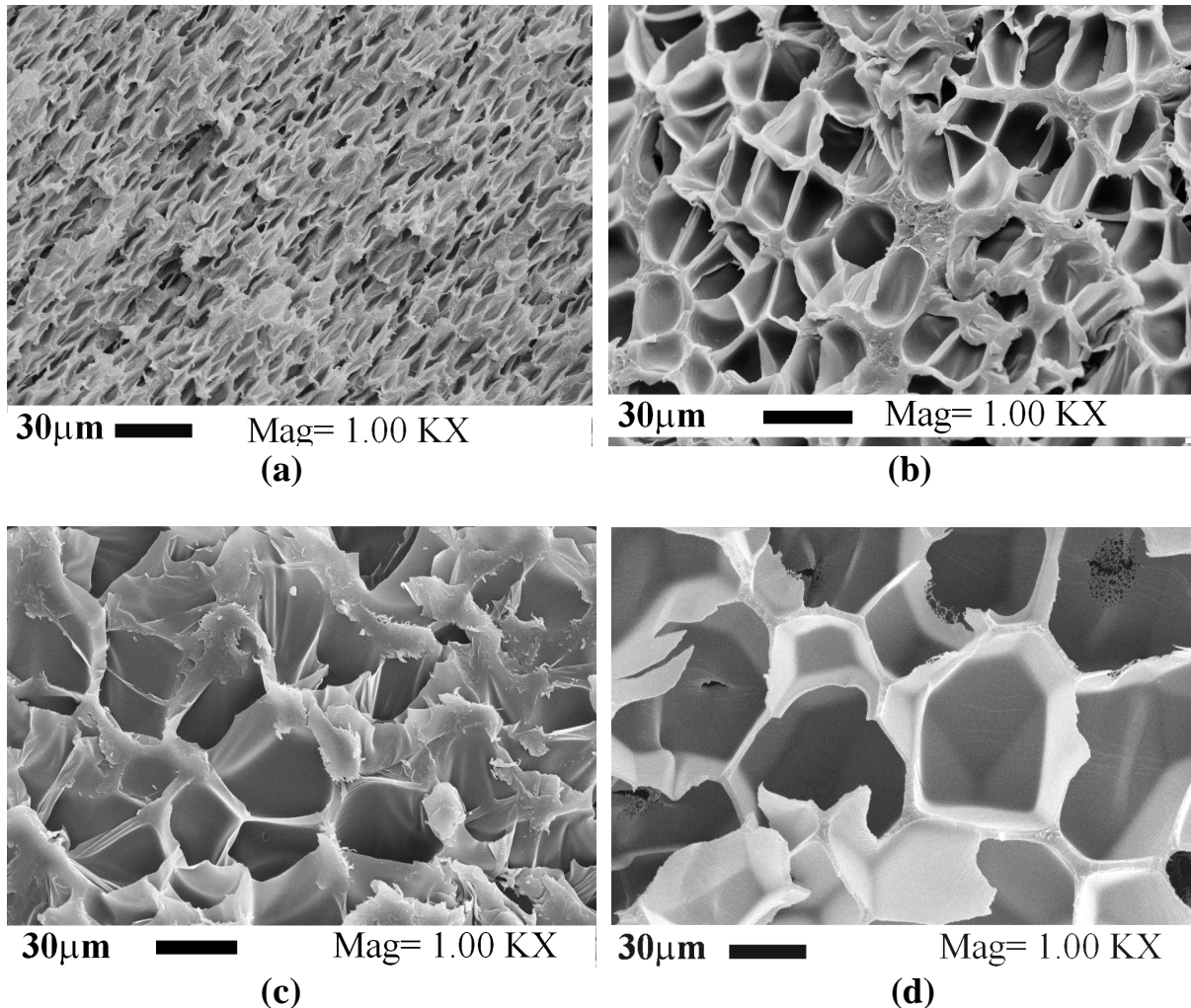
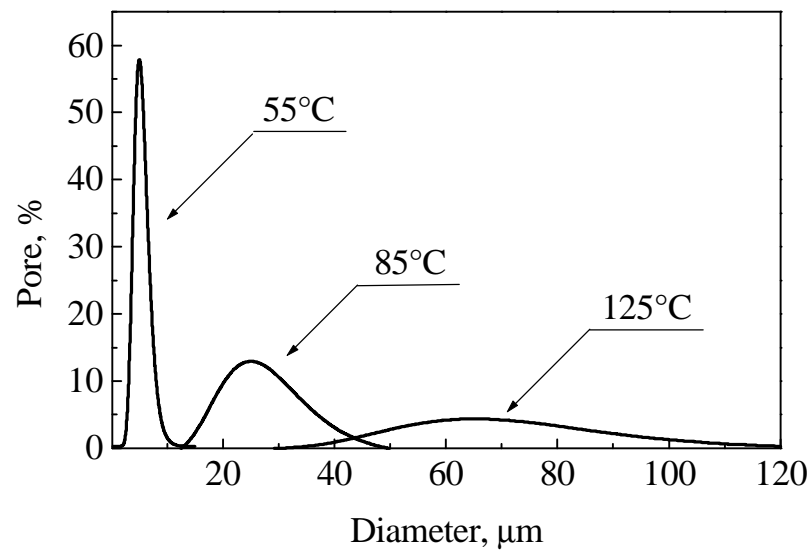


Figure1: Effect of temperature on the foam structure (saturation time = 240 min).
2a : 55°C; 2b : 75°C; 2c : 85°C; 2d : 125°C.

We have seen that typical cell size distribution obeys to Gaussian distribution: i.e, the distribution is symmetric. The cell size distributions at different foaming temperature have been calculated from SEM images and are shown in **Figure 2**. It is quantitatively visible the effect of temperature on mean cells size that increases from 5 to 65 μm (Figure 2).

However, not only the mean cell size increase with temperature, but also cell size distribution enlarges; thus, at higher temperatures, a less uniform foam is obtained.



These results can be explained taking into account the effect of temperature on the viscosity of the polymer. An increase of temperature leads to a decrease of the viscosity of the material and to an increase of diffusivity of CO_2 within the substrate. These factors lead to more rapid cell growth. Moreover, an increase of temperature decreases the solubility of CO_2 in the polymer and this factor leads less nucleation site and more space for cells to growth.

Arora et al. [6] produced smaller cells with diameter down to $10\mu\text{m}$ at a foaming temperature of 100°C . Probably, this difference depends on the higher pressure used by these authors and on the reactor they used that constrains cell growth.

Saturation Time

The effect of saturation time with supercritical CO₂ has been studied at fixed saturation pressure (230 bar) and temperature (85°C) in a range between 60 and 240 min.

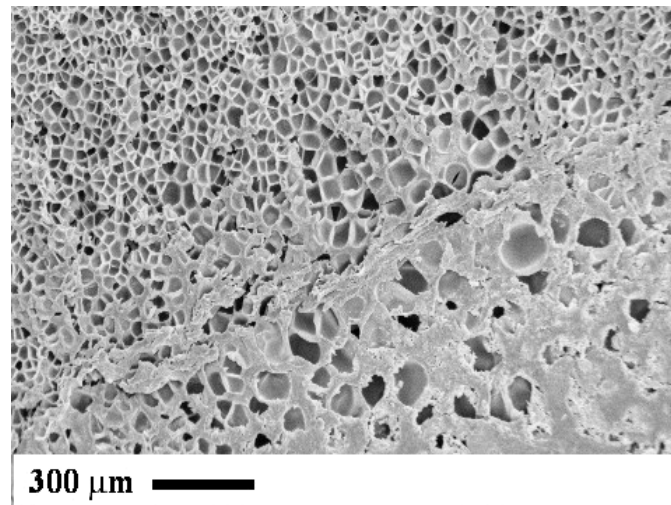


Figure 3: Microcellular structure obtained with a saturation time of 60 min.

Figure 3 shows the polystyrene foam structure obtained when the CO₂ saturation has been stopped at low times (60 min). Looking at the sample from the left top to the right bottom (that corresponds to a movement from the external to the internal of the pellet) small uniform cells can be observed on the left, whereas, progressively larger cells have been produced on the right side of the sample. The explanation of this result is simple; at short diffusion times penetration of CO₂ in the sample was not complete and uniform. Where the concentration of CO₂ is higher (external part) smaller cells have been produced; whereas large cells are produced in the internal part in which CO₂ concentration is lower. This result is in agreement with the classical theory of the homogenous nucleation [8]: large amount of gas leads to a large number of sites of nucleation that have less space for growing and limit their growth each others. A smaller amount of gas in the polymer produces fewer but larger cells.

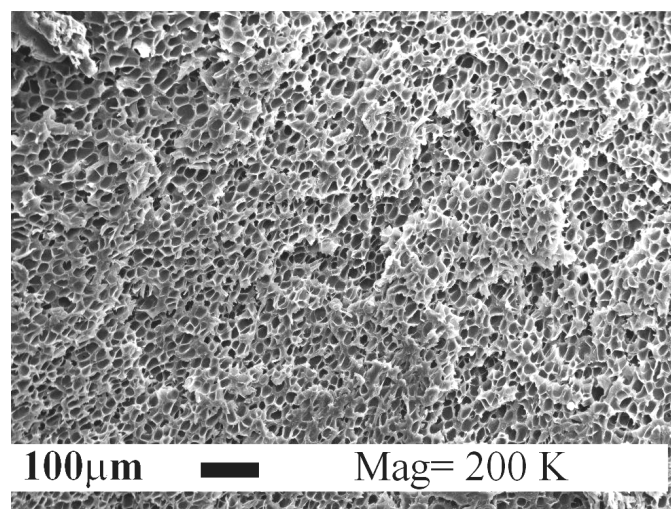


Figure 4: Microcellular structure obtained with a saturation time of 240 min.

Thus, increasing the saturation time, the porous structure becomes more uniform and the cell size decreases (**Figure 3 - 4**). The minimum time to assure the saturation of the pellets resulted of 150 min [9].

In the last part of the work we tried to foam also syndiotactic polystyrene that is characterized by a partial crystalline structure.

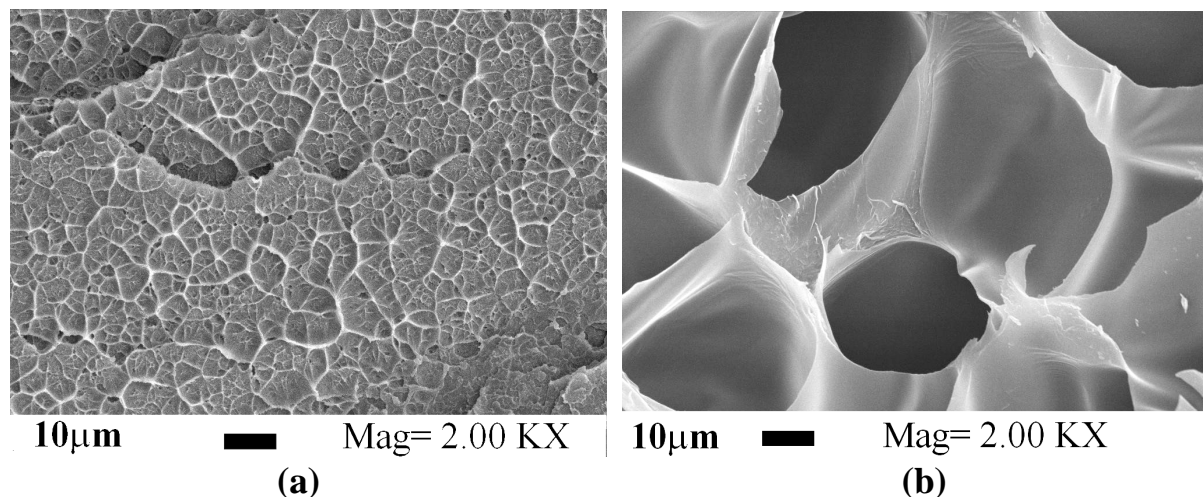


Figure 5: Syndiotactic (5a) and atactic (5b) polystyrene processed at 85°C, 230 bar and 240 minutes

The analysis of SEM images in **Figure 5 a-b** evidences that syndiotactic polystyrene (**5a**) presents a different microcellular structure. Probably, the crystalline part of the polymer tends to limit the growth of the pores that can grow only in the amorphous part. Therefore, at the same process conditions, syndiotactic polystyrene presents smaller pores than those produced in atactic polystyrene (**5b**).

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