

Foaming Behavior of Polystyrene with Supercritical Carbon Dioxide

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ABSTRACT The foaming behavior of commercial polystyrene using SC CO₂ as the blowing agent has been studied at the pressure of 30~60 MPa. A technique of rapid decompression was used in this work. The effects of pressure and temperature on foaming behavior were investigated. A high saturation pressure increased cell density and a low foaming temperature (above the depressed T_g) produced foams with small cells. This research showed that different cell morphology was obtained at optimum pressure and temperature. It was found that open-celled structures of the foam can be prepared at saturation pressure of 50 MPa and foaming temperature of 125 °C. Foams having a regular distribution with three different cell sizes can be created by saturating at 60 MPa and 50 °C. Moreover, different volume expansion ratios of foams could be obtained through the selection of foaming temperature. All these results indicated that polystyrene can be foamed into various microcellular morphology.

Key words Decompression; Foam; Microcellular; Polystyrene; Supercritical carbon dioxide

Introduction

Microcellular foams are defined as having average cell sizes in the range of 1-10 μm, cell densities on the order of 10⁹-10¹⁵ cells/cm³, and specific volume reduction ranging from 5% to 95%. These novel materials are characterized by outstanding properties such as high impact strength, high toughness, long fatigue life, high thermal stability, low dielectric constant and low thermal conductivity as well as reducing materials costs. These unique properties make polymeric foams ideal for a large number of applications, including packing materials, insulations, airplane, automotive parts, sporting equipment, and filtration membranes, etc¹⁻⁴.

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Supercritical fluids (SCFs) are matters whose temperature and pressure stay above their critical points, which are characterized by some physicochemical properties such as large diffusivity, low viscosity and zero surface tension. Among various SCFs, supercritical carbon dioxide (SC CO₂) is most frequently used because of its easily attainable critical parameters (T_c=31.05 °C, P_c=7.38 MPa). Moreover, CO₂ is also nontoxic and nonflammable. A few polymeric foams have been prepared using SC CO₂ as the blowing agent, such as poly(methyl methacrylate)⁵⁻⁶, polypropylene⁷⁻⁸, poly(vinyl chloride)⁹, polycarbonate¹⁰⁻¹¹, polysulfone¹²⁻¹⁴, poly(ether imide)¹⁴, polyethylene¹⁵⁻¹⁶ or their blends¹⁷⁻¹⁹. Generally, there are four steps involved in a foaming process: polymer-gas solution, cell nucleation, cell growth and cell stabilization.

Arora et al.²⁰⁻²¹ investigated microcellular polystyrene considering the variables of temperature, pressure and depressurization rate. They found that higher temperatures produced larger cells and higher pressures increased cell density. Stafford et al.²² studied the effects of molecular weight and polydispersity on the microcellular structures of polystyrene. They found that molecular weight and polydispersity did not significantly affect the foaming process, but the presence of a low molecular weight component was found to greatly influence the final structures of the foam. Reverchon et al.²³ reported the function of temperature, pressure and contact time on the foaming of polystyrene. They found that the foams morphology, cell size and sample volume were controlled by the process conditions. However, in their study, the saturation pressures were mostly below 30 MPa.

Higher saturation pressures can lead to higher cell densities and hence smaller cells. Higher cell density and smaller cell size can improve the mechanical properties of foam. In some aspects, it can present special properties. So in our study, the effect of pressure of 30~60 MPa on the microcellular structures was mainly investigated. Moreover, the polystyrene which was chosen as the substrate is commercial product. It is widely used in packing materials which are foamed by chemical blowing agent in industry.

Experimental

Materials

Polystyrene (PG-33) was purchased from Zhenjiang Qimei Chemical Engineering CO.,Ltd. (Jiangsu, China) in the form of pellets and used as plaques compressed at 170 °C into 3 mm thickness. The molecular weight was measured by gel permeation chromatography with THF as the mobile phase and found M_n to be 90 000 with a polydispersity of 2.7. The glass transition temperature was determined by differential scanning calorimetry and found T_g to be 90 °C. The density was 1.04 g/cm³. CO₂ with a purity of 99.95% was provided by Ruili Air Product CO., (Shanghai, China).

Foam processing

Foams were prepared in a high-pressure vessel as shown in Figure 1. The internal volume of the vessel was 170 mL, which was heated with an electronically controlled set-up. Polystyrene, in the form of 3 mm thick plaques were weighed and placed in the high-pressure vessel. The vessel was heated to the experimental temperature and filled with SC CO₂ up to the desired pressure using a high-pressure pump. The vessel was then maintained at the desired pressure and temperature for 3 h. At the end of this experiment, the vessel was depressurized to atmospheric pressure at a rate of ~ 10 MPa/s, while holding the constant temperature. Then the vessel was opened quickly, and the samples were removed for characterization.

Foam characterization

The foams were characterized to determine cell size and cell shape by scanning electron microscopy (SEM). Samples were cryofractured after immersion in liquid N₂, sputter coated with gold and viewed using a TEOL 2150 SEM. The resulting micrographs were analyzed by Image-Pro Plus 6.0 software to determine cell diameter (D) and to calculate cell density (N_0).

The cell diameter (D) is the average cell size measured from the micrographs, which were more than 100

cells. It was calculated using the following equation:

$$D = \frac{\sum d_i n_i}{\sum n_i} \quad (1)$$

Where n_i was the number of cells in the micrographs with an equivalent cell diameter of d_i .

The cell density (N_0), defined as the number of cells per unit volume of the unfoamed polymer, was determined from SEM micrographs. The cell density N_f , defined as the number of cells per unit volume of the foam, was calculated by:

$$N_f = \left(\frac{nM^2}{A} \right)^{3/2} \quad (2)$$

Where n was the number of cells in the micrograph, A was the area of the micrograph (cm^2), and M was the magnification factor.

$$V_f = \left(\frac{\pi}{6} \right) D^3 N_f \quad (3)$$

Where V_f is the void fraction of the foamed polymer. The cell density N_0 was then calculated according to the following equation:

$$N_0 = \frac{N_f}{1 - V_f} \quad (4)$$

The cell density N_0 can also be calculated in terms of the equation of (5), where ρ_0 was the density of the original polymer, ρ_f was the density of the foamed polymer.

$$N_0 = N_f \cdot \frac{\rho_0}{\rho_f} \quad (5)$$

Results and Discussion

Effect of pressure on solubility of CO₂

The solubility of CO₂ in polystyrene directly affects the foaming ability, because CO₂ has a great plasticization effect on polystyrene. The adsorption of CO₂ in polystyrene at the pressure of 30~60 MPa

and the temperature of 60 °C and 85 °C were studied. The gravimetric method was used to measure the solubility. In this experiment, samples were weighed and placed in the vessel, which was heated to the experimental temperature and filled with CO₂ to the desired pressure. After decompression, the samples were removed and immediately transferred to a balance to record mass loss as a function of time. A series of adsorption experiments at different pressure were studied. According to Fickian diffusion kinetics, there was a linear relation between the mass uptakes and the square root of the desorption time. So the mass uptake of CO₂ at the end of the sorption can be obtained by linear extrapolation to zero desorption time. The mass uptakes of CO₂ in polystyrene at different pressure were shown in Figure 2. The two sorption isotherm indicated the same trend. It presented a curve relationship between the solubility and the pressure, and it didn't completely follow Henry's law ($C=HP$). Henry's law may be accurate enough at low pressure region, but there was not a linear relationship between the solubility and the pressure at high pressure region. From Figure 2, a maximum mass uptake of CO₂ was 14.2% which was adsorbed at 60 MPa and 60 °C. The glass transition temperature of polymer can be depressed by the plasticization effect of CO₂. For example, the Tg of polystyrene can be depressed to 40 °C by CO₂ at 8 MPa of pressure²⁴. In our experiments, when the saturation pressure increased, the Tg of polystyrene decreased. However, during the foaming process, the foaming temperature should be above the depressed Tg. So it is greatly significant to know the adsorbed behavior of CO₂ in polystyrene at different saturation pressure.

Effect of temperature on volume expansion ratio

The volume expansion ratios of polystyrene foam were investigated at temperature of 50~100 °C and pressure of 60 MPa. The expansion ratio was obtained by measuring the volume of the sample before and after the foaming experiment. The effect of temperature on the volume expansion ratio at the constant pressure was shown in Figure 3. For a given saturation pressure of 60 MPa, the volume expansion ratio was

increased with increasing temperature. In this work, the maximum volume expansion ratio was 8.7 times at foaming temperature of 100 °C using the technique of rapid decompression. But when the foaming temperature exceeded 125 °C at the saturation pressure of 30~60 MPa, the shape of foam may be easily deformed and shrunk because of cells coalescence. The volume expansion of foam depends on the cell size and cell density. For a given cell density, an increase in cell size necessarily leads to an increase in volume expansion ratio²⁵. From Figure 6, it was found that a higher foaming temperature could produce foams with larger cells. So the volume expansion ratio can be increased as the temperature increasing as shown in Figure 3. Any factor that affects cell size may have an effect on volume expansion. In other words, the foams with different volume expansion ratios could be obtained through the selection of different foaming temperature.

Effect of pressure on cell density

The effect of saturation pressure on cell density has been studied at a constant temperature of 80 °C. The saturation pressure were changed from 30 MPa to 60 MPa, and the cell density N_0 was calculated according to the equations of (2) ~ (5). The results have been shown in Figure 4. An evident trend that cell density increased with increasing pressure could be seen from Figure 4. When the saturation pressure was 60 MPa, the cell density of foam could be up to 3.7×10^9 (Figure 6 d) which was higher than the value previously reported about microcellular commercial polystyrene²². According to the homogeneous nucleation theory, the cell size decreases with increasing saturation pressure. Because the amount of CO₂ incorporated into the substrate increases with increasing pressure, and the substrate is easily up to supersaturation upon releasing pressure. As the pressure drop increases, the energy barrier to nucleation decreases, leading to more cells being nucleated. So in this work, high cell density would be generated.

Effect of temperature on average cell diameter

The effect of foaming temperature on average cell diameter has been studied at a constant pressure of 60 MPa. The foaming temperature varied from 50 °C to 100 °C, and the average cell diameter D was calculated in terms of the equation of (1). The results were shown in Figure 5. A clear trend of increasing cell sizes with increasing temperature could be seen from Figure 5. Cell morphology of microcellular polystyrene were shown in Figure 6.

In Figure 6 (a), the cell diameters are not uniform. There were three different cells dispersing in this foam. The cell diameters of the foam can be decreased to ~1 μm . This microcellular structure indicated that phase separation took place during the process of the depressurization. The foaming process may present three depressurization stages. So the phase separation led to the formation of the regular distribution with three different cell sizes. In Figure 6 (b, c, d, e), uniform cells distributed in the foams. When the foaming temperatures were below 80 °C, the cell sizes were less than 7 μm . When the foaming temperature was 100 °C, the cell size could be up to 21 μm . So the cell sizes were increased with increasing temperature. But the thickness of cell walls decreased as the temperature increasing.

There is a relationship between cell size and the properties of foam. In some aspects, small cell size would show better properties than big cell size, including mechanical strength, optical, thermal, and electrical properties. Cell size was greatly influenced by foaming temperature. Because when the foaming temperature was increased, the polymer viscosity and surface tension decreased, and the mobility of the polymer chains increased, and this permitted the cells to grow larger²⁶⁻²⁷. According to our results about various foaming polymer, the foaming temperature may be related to the crystallinity of the polymer. If the polymer is amorphous, the foaming temperature should be above its glass transition temperature (the depressed T_g). If the polymer is crystal, the foaming temperature may be close to or above the melting temperature of the polymer.

Open-celled structures of foam

In this paper, an open-celled structure of foam has been developed. There are several approaches of preparing open-celled polymer foams such as immiscible polymer blending, pore opener method²⁸ and gas concentration threshold. In this work, a bubble coalescence model²⁹ was used to produce open-celled foam. Typically, the morphology of closed-celled foam was characterized by uniform cell sizes with thin walls separating the cells (Figure 6). To create open-celled morphology in this foam, the thin walls between cells must be broken. If these cell walls rupture spontaneously, the open-celled structure can be generated without additional processing steps, equipment or additives. Open-celled foam allows particles and fluids to flow through the material, so it can be used as a filter or membrane.

In this experiment, the substrates were saturated by SC CO₂ at pressure of 50 MPa. The depressurization time was properly prolonged by reducing the depressurization rate. The cells would grow larger during the process of the depressurization and the cell walls in this foam were unstable and eventually thin to rupture. So cell coalescence occurred during the depressurization time. When the foaming temperature was 125 °C, the foam presented partially open-celled structures. The cell morphology of open-celled foam was shown in Figure 7 (a, b). The open cells were marked by white arrowhead. Pores were generated within walls of the cells, and these cells were connected. Water intrusion measurement was conducted to confirm the open-celled structure using a self-made device. A schematic drawing of the device was shown in Figure 8. Water can not intrude the foam under atmosphere pressure because of the capillary effect. So the external force was performed to counteract the capillary resistance in order that water can intrude the foam. Connectivity was confirmed by comparing the volume of water (ΔV) intruded the foam under the same conditions. Compared to other foams (in Figure 6), this foam intruded larger volume of water. This was a strong indication that the observed pores were open and connected the cells to allow more water into the

foam.

Conclusion

The foaming behaviour of commercial polystyrene has been studied at pressure of 30~60 MPa. The microcellular structures of the foams can be controlled by altering the saturation pressure and the foaming temperature. A high saturation pressure increased the cell density and a low foaming temperature produced foams with small cells. Particularly, three different cell sizes of microcellular morphology and open-celled structures were obtained at optimum pressure and temperature using the technique of rapid decompression.

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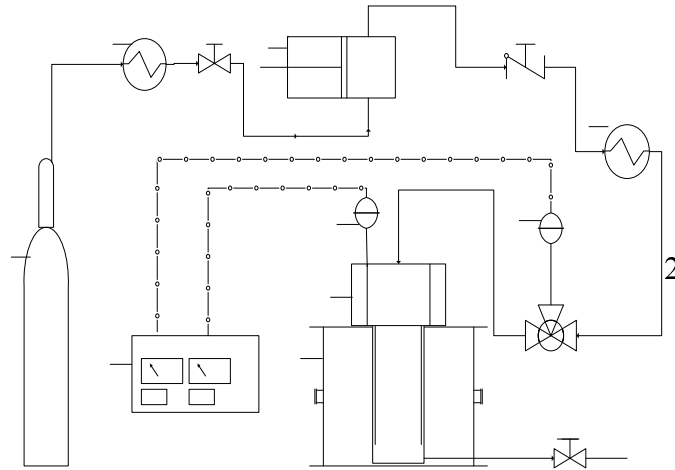


Figure 1 Schematic drawing of foaming process apparatus.

1. CO₂ cylinder 2, 4. Change heater 3. High-pressure pump 5. Pressure transducer 6. High pressure vessel
 7. Heating set-up 8. Discharge valve 9. Temperature transducer 10. Controller

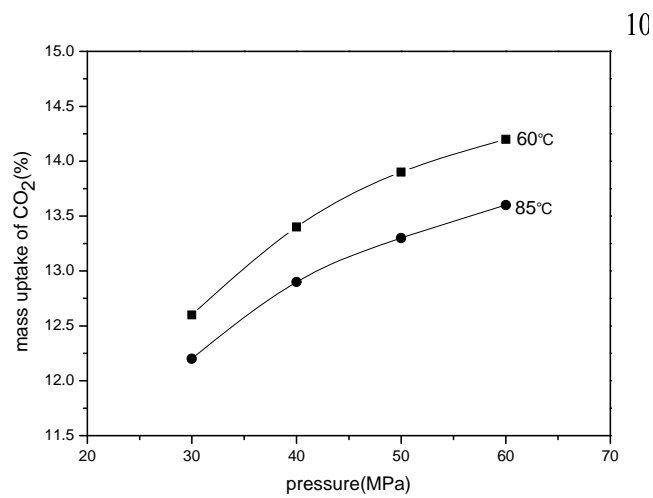


Figure 2 Effect of pressure on solubility of CO₂ in polystyrene at 30~60 MPa

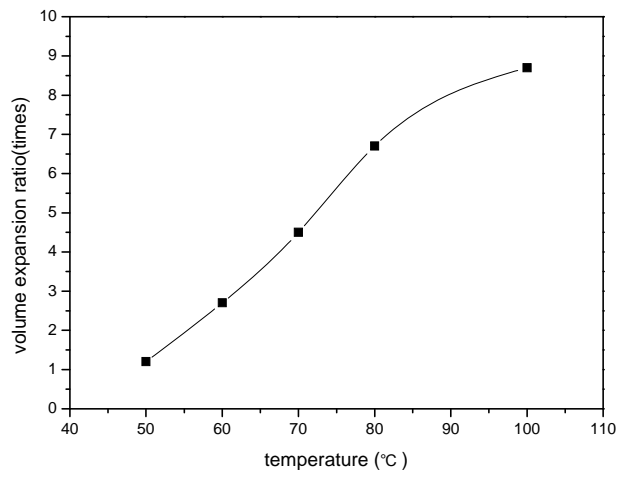


Figure 3 Effect of temperature on volume expansion ratio at 50~100 °C and 60 MPa

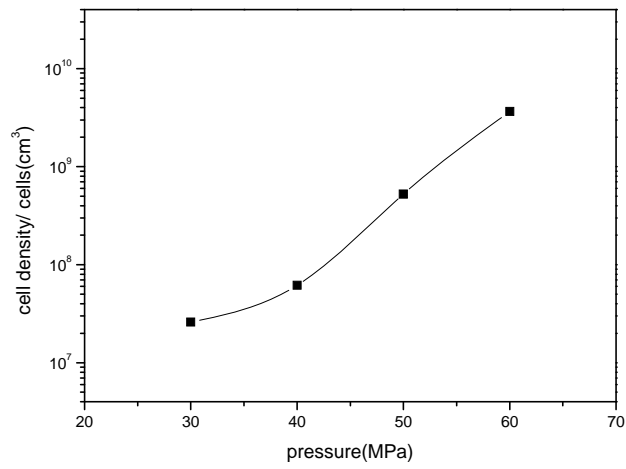


Figure 4 Effect of pressure on cell density at 30 ~ 60 MPa and 80 °C

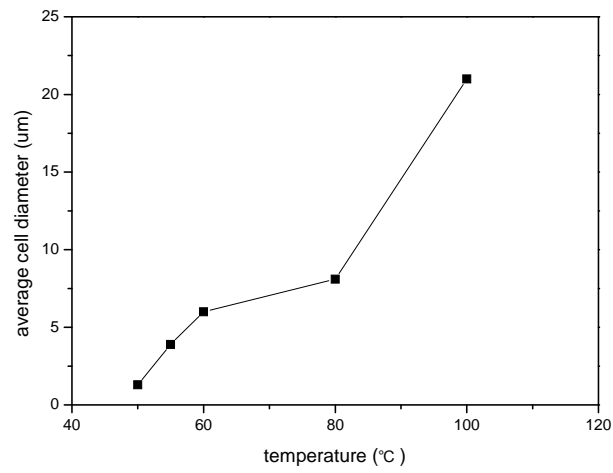
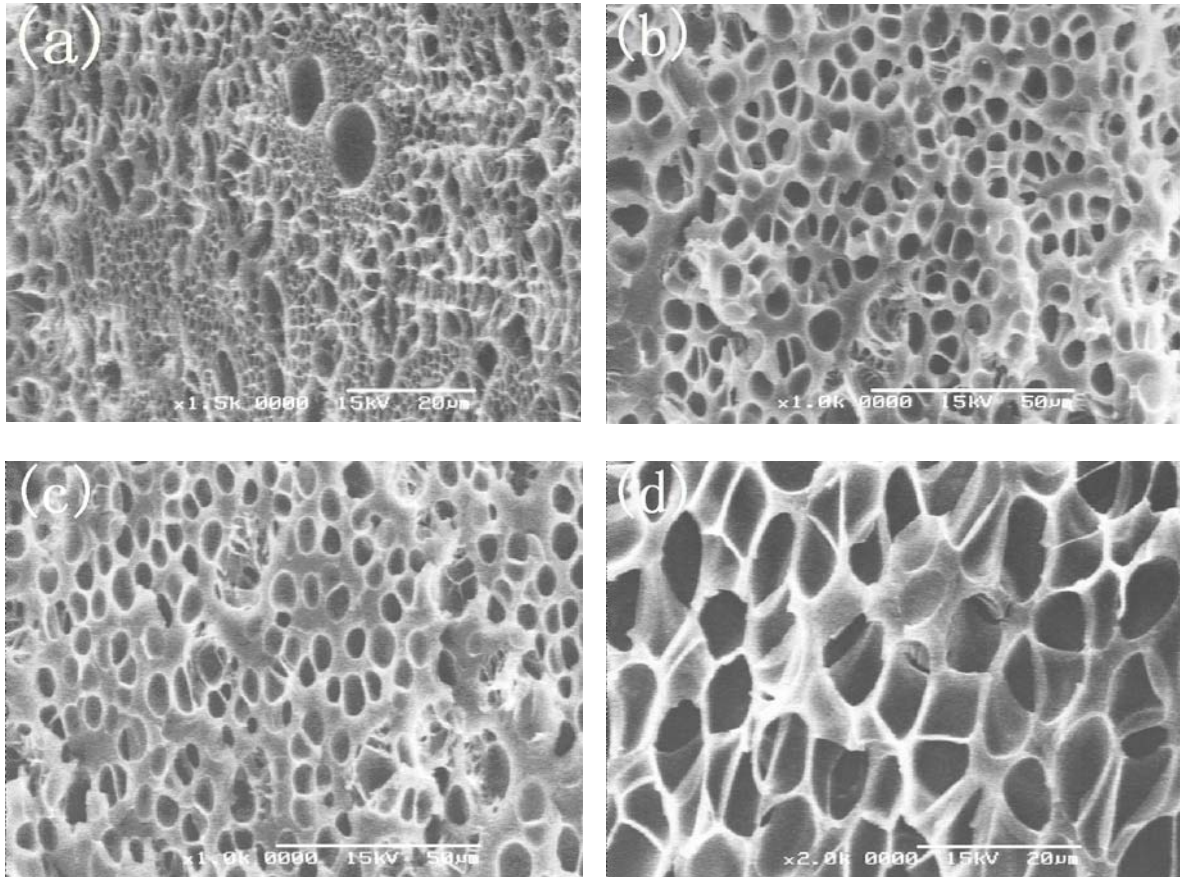


Figure 5 Effect of temperature on average cell diameter at 50 ~ 100 °C and 60 MPa



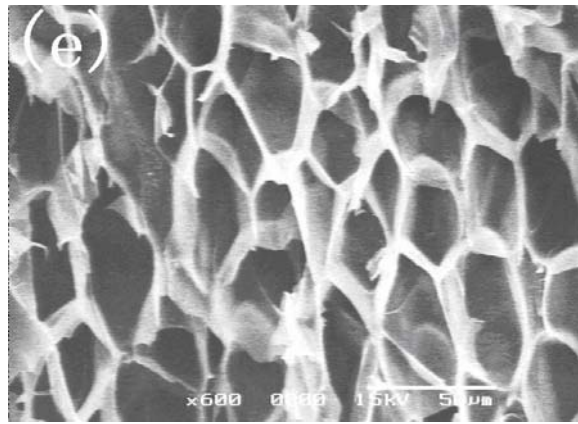


Figure 6 Cell morphology of microcellular polystyrene foamed at 60 MPa with different foaming temperature: (a) 50 °C, (b)55 °C, (c) 60 °C, (d) 80 °C, (e) 100 °C

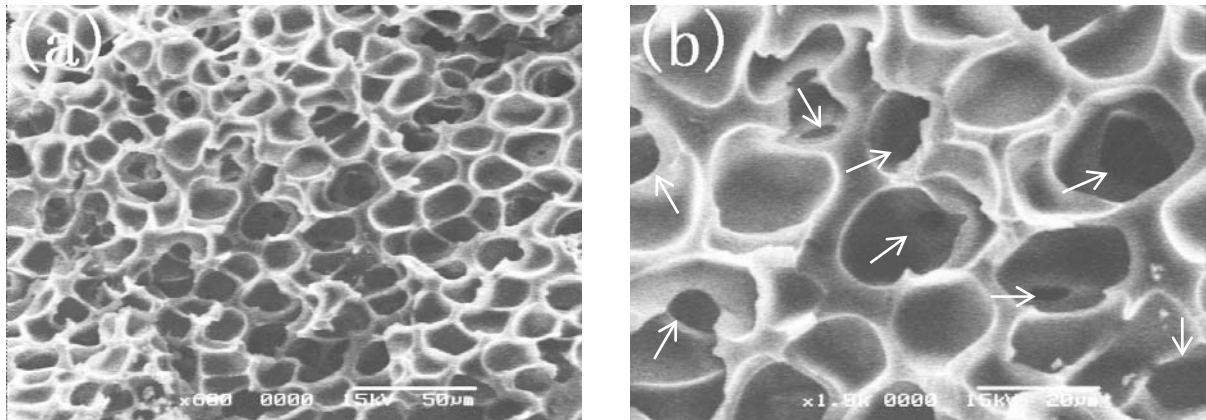


Figure 7 Cell morphology of open-celled polystyrene foamed at 50 MPa and 125 °C: (a) micrograph of foam (b) higher magnification of (a)

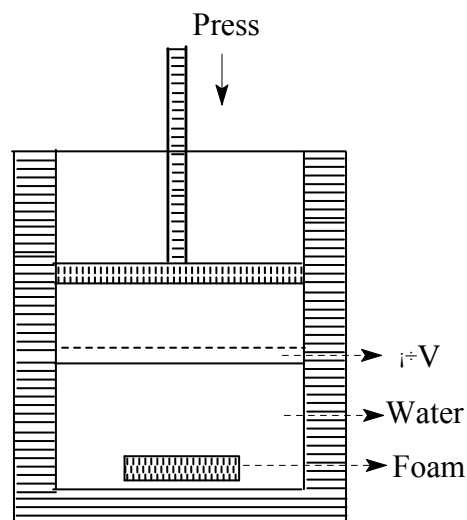


Figure 8 Schematic drawing of the water intrusion device