Extrusion of Microcellular Polysulfone Using Chemical Blowing Agents

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ABSTRACT: Microporous polysulfone hollow fibers were developed with the help of chemical blowing agents by means of extrusion. Two chemical blowing agents, azodicarbonamide and 5-phenyltetrazol, were selected, and the foam morphology dependent on the concentration of blowing agent was examined by scanning electron micrograph. By means of changing the processing parameters, e.g., temperature and screw speed, the structures of the foam, usable as membrane, can be controlled. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1753–1760, 1998

Key words: microcellular foams; extrusion; membranes; polysulfone; chemical blowing agents

INTRODUCTION

Microcellular foams are defined as any polymeric porous material with average cell sizes on the order of 10 μm. They are characterized by cell nucleation density larger than 10^8 cells per cubic centimeter of unfoamed material.[1] With a large number of cells, a substantial reduction in density relative to the original material is possible. The rationale behind their development was that if bubbles could be introduced into the polymer matrix which were smaller than the critical flaws inherent to the material, then the density could be reduced without significantly affecting the mechanical properties.

Conventionally foamed plastics with chemical blowing agents (CBAs) nucleate large cells in limited numbers on the order of 10^7–10^6/cm³. They are widely used in everyday life, e.g., as wrapping material with good conduction of warmth and good shock absorption or as model parts which need only little raw materials per volume compared with massive materials. The aim of this investigation was to study the possibility of transferring foam technology onto the manufacturing of porous hollow fibers, because microcellular foams with connected pores can also be used as porous membranes. Separation processes using porous membranes are called "filtration." Filtration that separates particles with a diameter of 0.05 to 10 μm is called "microfiltration," and with 1 nm to 0.05 μm diameter "ultrafiltration."[2] Microfiltration is mainly used to sterilize solutions in the food, beverage, and pharmaceutical industries, or when solvents without particles are required (in the electronic and cosmetic industries) and for regaining materials (in the chemical industry). Ultrafiltration membranes are typically applied to reject dissolved macromolecules; e.g., in the pharmaceutical industry to separate enzymes and antibiotics. Moreover, porous membranes can be used as support of so-called composite membranes.

The most important industrial production method for porous membranes is the phase-inversion process.[3] The formation of pores is based on addition of a nonsolvent in order to induce phase separation in a homogeneous polymer solution. It

is a problem to eliminate totally the solvent and the nonsolvent from the formed membrane structure. They have the effect of a softener even in traces, which may considerably influence the structure and transportation properties of the membranes.[4]

Until now only few continuous solvent- and non-solvent-free production methods for porous membranes have been known. Some of these methods are based on the extrusion of thermoplastic melts with the help of a softener.[5] Furthermore, methods are known in which porous membranes are produced by means of extrusion followed by biaxial stretching of partly crystalline polymer films or hollow fibers.[6] The above-mentioned processes must be carried out by thermic or mechanical after-treatment. Therefore a new process shall be developed in which porous membranes can be produced without the use of softeners and expensive thermic or mechanical after-treatment during the extrusion. The new process shall have the following advantages:

- no use of solvents;
- no posttreatment;
- in principle, usable for all amorphous and partly crystalline thermoplastics; and
- high velocity of extrusion.

Therefore, the formation of microcellular foams in the shape of hollow fibers was studied by extrusion with CBAs. The foams with isolated cells (pores) are not fit for a use as porous membranes. For such a use the following foam structure is requested:

- small cell size of about 100 nm to 10 μm;
- homogeneity of cell size;
- open cells and great numbers of cells.

The chemical foam-producing method described in this work is based on the production of foaming gas by thermic decomposition of organic compounds molten in polymers. The process is carried out in an extruder using high-grade shear at high pressure. Sinking of pressure, accompanied by expansion of gas in polymer, will cause a porous, hollow fiber. The use of a CBA is advantageous because only small variations in comparison with compact extrusion procedures are requested.
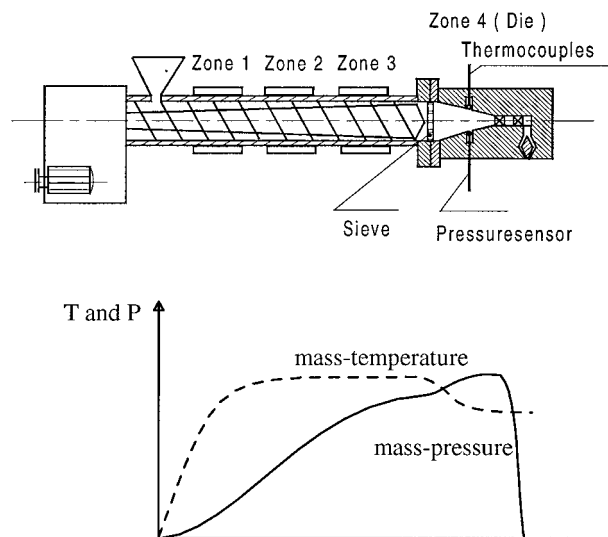
Figure 1   Construction of the one-screw extruder and a scheme of the mass pressure and temperature profile.

EXPERIMENTAL

Material

The polysulfone (PSU) used in this work was UDEL 3500 (Amoco Co., Belgium), having a glass transition temperature of 190°C, a melt index of 3.5 (g/10 min) at 343°C/0.3 MPa, and a density ρ_{PSU} of 1.24 g/cm³.

Two different types of chemical blowing agents were used:

1. Azodicarbonamide (ACA; Merck Schuchardt, Germany), a powdered yellow compound that decomposes at 205–215°C. The gas yield is about 200–220 mL/min and consists of nitrogen, carbon monoxide, carbon dioxide, and some ammonia.[7]
2. 5-Phenyltetrazole (5-PT; Aldrich, Germany), which decomposes at 240 to 250°C. Gas yield is about 210 mL/g. The decomposition gases are almost all nitrogen.[8]

The polymer was dried for 16 h at 150°C and then mixed with the blowing agents in the ratio of 0.5–2.0 wt % by tumbling for about 10 min; the mixture was then extruded.

Extruder Setup

Figure 1 shows a schema of the extruder setup. In addition, the typical course of mass- and gas-

Table I   Experimental Conditions at Extrusion of PSU

CBA	Screw Speed (rpm)	Temperature (°C)		
		Zone 1	Zone 2 + 3	Zone 4
ACA	10	330	340	310
5-PT	10	340	350	320

pressure and the temperature profile inside the extruder related to the different zones are shown.

The extruding installation consists of a one-screw extruder (GIMAC, Italy) with a conical screw; three heating elements at the cylinder and more heating elements around the die, with a heating capacity up to 400°C; thermoelements for the mass temperature measuring; a pressure sensor for pressures up to 700 bar; the die with feeder pipe for supporting air; a waterbath; and a mechanism for winding up. A temperature steering gear cupboard with a steering program is also part of the installation. The extruder screw has a diameter of 1.4 cm. The length of the cylinder room is 33.5 cm. Without the screw volume, the interior of the cylinder has a free volume of 25.0 cm^3.

Sample Preparation for SEM Analysis

Specimen hollow fibers were fractured in liquid nitrogen. After sputtering with palladium the surfaces of the fractured specimens were observed with a JEOL JSM 6400 F scanning electron microscope (SEM).

Determination of Cell Density and Cell Size

Micrographs showing 50–100 bubbles were used to count the exact number of bubbles. The cell density of the foams was calculated using the method suggested by Kumar and colleagues.[9] The number of bubbles nucleated per cubic centimeter of the foam (N_f) can be expressed by taking the cube of the linear bubble density as

$$N_f = \left(\frac{nM^2}{A} \right)^{3/2} \qquad (1)$$

where n is the number of bubbles seen in the micrograph, A is the area of the micrograph (cm^2), and M is the magnification factor.

The average cell diameter (D) was obtained from averaging the major and minor diameters of

50–100 cells in a SEM micrograph. The void fraction (V_f) in the foam can be estimated by multiplying the volume of an average cell by the number of cells per cubic centimeter of the foam:

$$V_f = \frac{\pi}{6} D^3 N_f \qquad (2)$$

The number of cells nucleated per cubic centimeter of unfoamed polymer N_0 (cell density), was then determined from

$$N_0 = \frac{N_f}{1 - V_f} \qquad (3)$$

Determination of Foaming Grade

The foaming grade was determined by the foam density ρ_{Foam}. The foaming grade can be calculated according to

$$\text{Foaming grade} = \left(1 - \frac{\rho_{\mathrm{Foam}}}{\rho_{\mathrm{PSU}}} \right) \times 100\% \qquad (4)$$

The foam density (ρ_{Foam}) was determined by exact measuring of the volume and the weight of a foamed hollow fiber.

RESULTS AND DISCUSSION

Effect of CBA Content on Cell Morphology

The experimental conditions with two CBAs are shown in Table I. The cylinder temperatures (zones 1 to 3) are higher than in zone 4, so that the blowing agents will be completely decomposed. Because the decomposition temperature of 5-PT is higher, the processing temperature of 5-PT must be higher than that of ACA.

The effects of CBA content on cell density are shown in Figure 2. It must be clearly recognized that according to the increasing amount of blow-
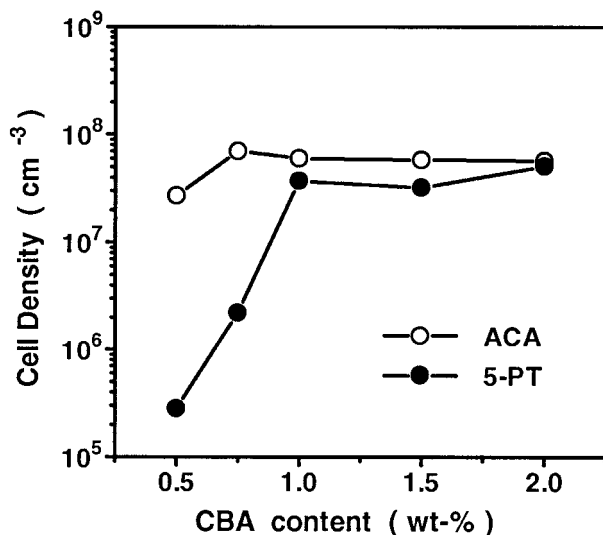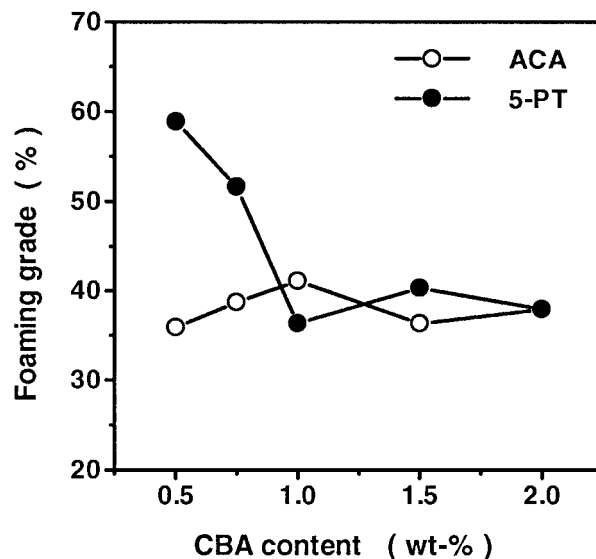
Figure 2 Relation between CBA content and cell density.

ing agent, the cell density first grows, then with a certain concentration reaches a level. The ACA curve shows a bend at 0.75 wt %. From 0.5 to 0.75 wt % ACA the cell density grows from 2.7×10^7 to 7×10^7. Foams with 5-PT generally have a little lower cell density than those with ACA but an enormous growth between 0.5 and 1.0 wt % 5-PT.

The average cell diameter was plotted against the CBA content (Fig. 3). Contrary to the cell density, the average cell diameter decreases remarkably with the increase of blowing agent
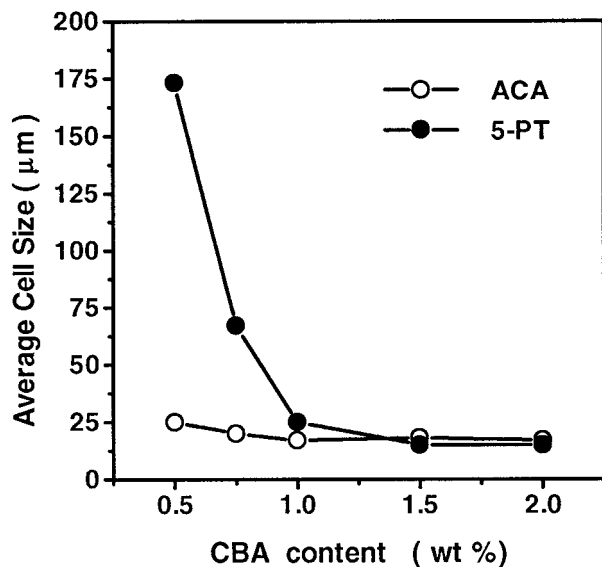
Figure 3 Relation between CBA content and average cell size.

**Figure 4** Relation between CBA content and foaming grade.

amount. Beginning at 1.0 wt %, it reaches a limit value of about 20 to 25 μm.

The foaming grade using 5-PT (Fig. 4) decreases between 0.5 and 1.0 wt % 5-PT from 59 to 35%. The foaming grade with ACA is between 35 and 41%.

A deficit of blowing agent produces a too-low cell density. The amount of gas grows with the concentration of the blowing agent, if the process is tuned to blowing agent and polymer. Loss of diffusion limits the efficiency of the blowing agent. A surplus of blowing agent does not cause greater growing of cell density because the solubility of gas at high temperature is limited. Therefore a surplus of gas cannot be dissolved in the melt; it escapes from the die.

The foam structures of a PSU/ACA and of a PSU/5-PT system show some differences. A comparison of Figures 2 and 3 demonstrates that at a smaller blowing-agent concentration of 0.5 to 0.75 wt %, the cells in the PSU/ACA system are substantially smaller and the cell density is substantially higher than in the PSU/5-PT system.

Comparing the morphology of the hollow fibers (Figs. 5 and 6) it is obvious that the cellular pores of PSU using 5-PT have a higher diameter than those using ACA. It can also be seen that cell walls are relatively thick. Most cells are closed and partly linked with other cells because of the different types of blowing agents and the different gases thereby set free. While the decomposition of ACA frees N_2, CO, CO_2, and NH_3, the decompo-
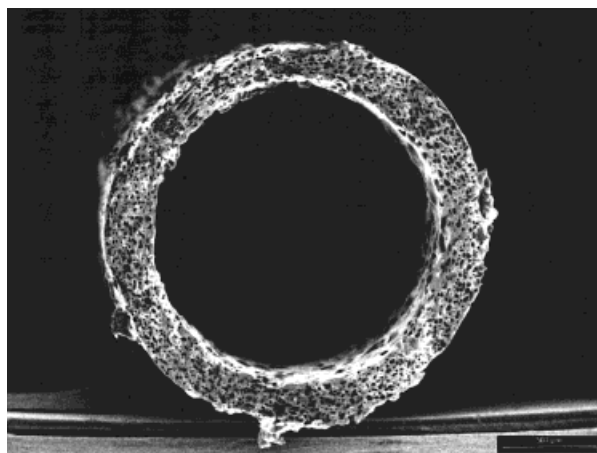
(a)
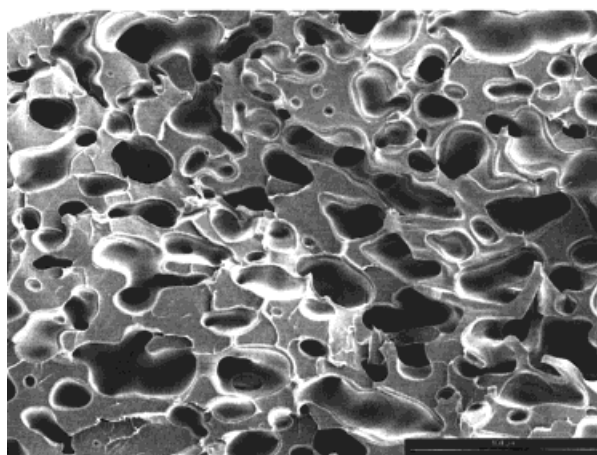
(b)

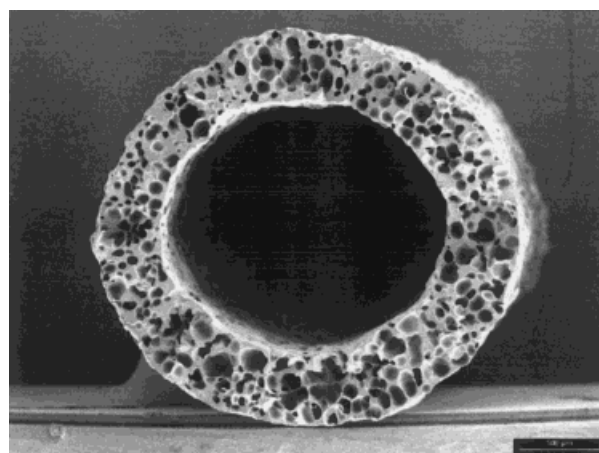**Figure 5** SEM micrographs of PSU hollow fibers with 0.75 wt % ACA. (a) ×40; (b) ×300.

sition of 5-PT produces only N_2. The solubility of CO_2 or N_2 in most of the polymer melts at 200°C and 27.6 MPa is about 11 or 2 wt %, as Durril and Griskey have calculated.[10,11] Less solubility of N_2 in the melt causes smaller cell density. While the surplus of N_2 in the melt is under shear mixed with the polymer melt in the extruder, it causes bigger cavities and at last escapes from the die. The diffusion of small bubbles into greater ones is promoted, so coarse cells arise.

Effect of Temperature on Cell Morphology

To examine the influence of temperatures on foam structures, PSU with 1.0 wt % ACA and 5-PT were extruded with different temperatures of the die (zone 4). The cylinder temperatures remained for ACA at $T_1 = 330°C$, $T_2 = T_3 = 340°C$, and for 5-PT at $T_1 = 340°C$, $T_2 = T_3 = 350°C$, so the blowing agents decomposed completely. The screw speed was 10 rpm. At lower temperatures under 300°C an extrusion cannot be performed because the viscosity of the polymer melt is too high and the melt does not flow fluidly. At high temperatures above 350°C the polymer PSU reacts with the blowing agent and decomposes. This causes black stripes in the hollow fibers, or it even blocks the die's aperture.

The dependence of cell density on temperature of the die and the mass pressure are shown in Figure 7. Figure 8 shows the relation between average cell magnitude and temperatures of the die.
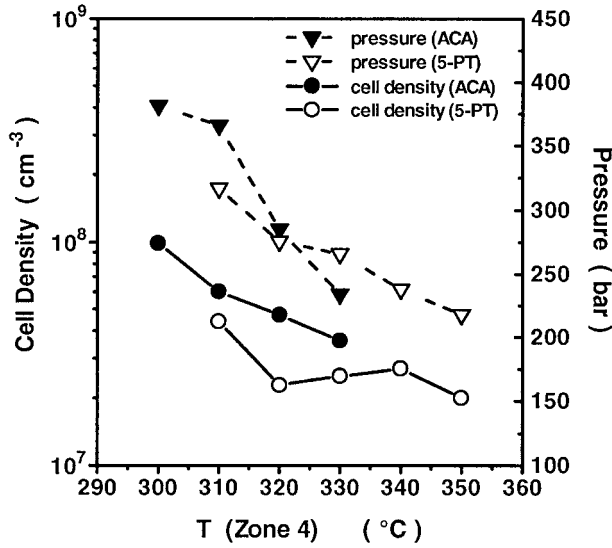

(a)
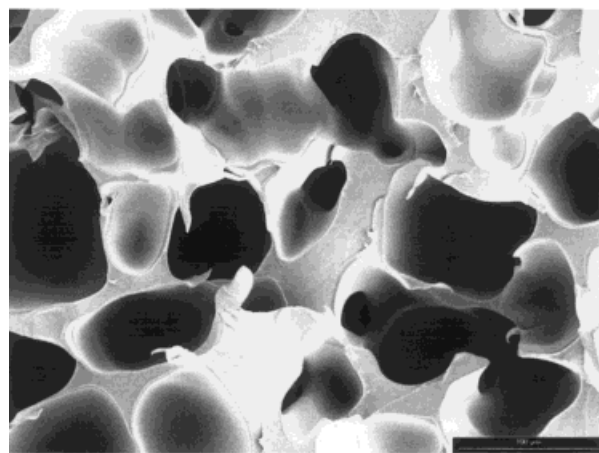
(b)

Figure 6 SEM micrographs of PSU hollow fibers with 0.75 wt % 5-PT. (a) ×40; (b) ×300.

Figure 7 Relation of die temperature to cell density and mass temperature.

Figure 8 Relation of die temperature to average cell size.

Within the range of temperatures in the die, the cell density grows with diminishing temperature. The reason for higher cell density at low temperatures is the growing mass pressure at the same time and the thereby-caused higher gas solubility. An estimation of the absorption of dissolved gases in relation to pressure is described by Henry's Law:

$$c_g = H p_g \qquad (5)$$

where H is Henry's constant. The equation says that the gas concentration (c_g) in the polymer is proportional to the gas pressure (p_g).
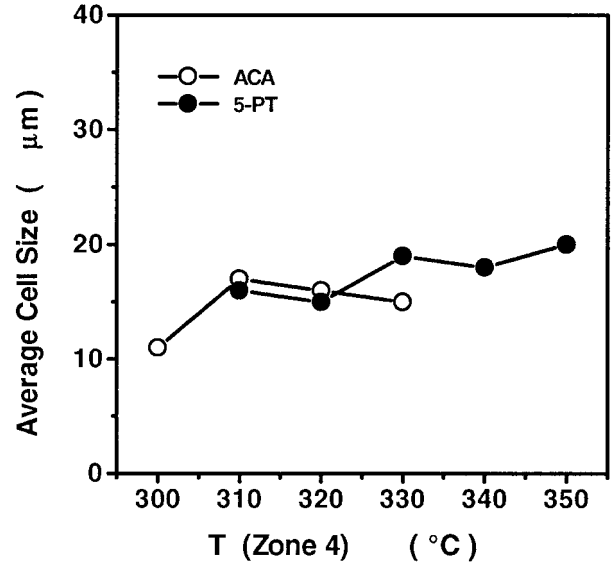
Furthermore the solubility (S) of a gas in the polymer depends on the temperature according to the Arrhenius relation:

$$S = S_0 \exp\left(-\frac{\Delta E_L}{RT}\right) \qquad (6)$$

where S_0 is the solubility constant and ΔE_L the solvent enthalpy. Because the solvent enthalpy is mostly negative, the solubility grows with decreasing temperature, which is advantageous for the origination of small cells and high cell density during the process of extrusion.

Effect of Screw Speed on Cell Morphology

In order to determine the effect of the screw speed on foam quality, PSU with 1.0 wt % ACA was extruded at a constant temperature profile with varied screw speeds. The temperature profile is as follows: in cylinder zones $T_1 = 330°C$, $T_2 = T_3 = 340°C$; and in the die $T_4 = 340°C$.

The dependence of cell density and pressure with screw speed are shown in Figure 9. The pressure rises continuously with growing screw speed. The cell density reached a maximum of 1.3×10^8 cells/cm^3 at 15 rpm. Further increase in screw speed caused a diminution of cell density.

Figure 10 shows the dependence of the average cell size on screw speed. The average cell size is at a minimum of 10 μm with the screw speed of 15 rpm.
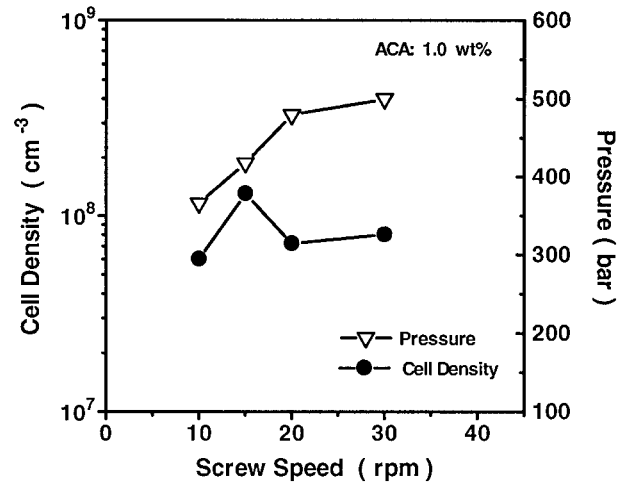
Figure 9 Cell density and die pressure versus screw speed for PSU foam with 1.0 wt % ACA.
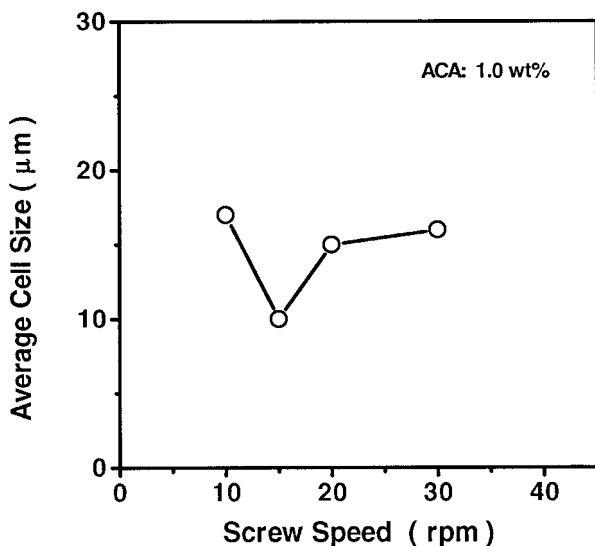
Figure 10 Average cell size versus screw speed for PSU foam with 1.0 wt % ACA.

Figure 11 shows two SEM micrographs of PSU and 1.0 wt % ACA with a screw speed of 15 to 30 rpm. Raising of the screw speed in a one-screw extruder always leads to two coupled alterations of the processing parameters: as the duration of the stay in the extruder diminishes, the pressure grows. As in practice, the amount of gas output and the blending of gases with the polymer melt is in proportion to the duration in the extruder and therefore with the screw speed; an increase of the screw speed is equivalent to a smaller foaming grade.

While a reduction of the duration in the extruder causes a coarse cell structure, a raising of the pressure is advantageous for the cell structure. In other words: an increase of the screw speed, which causes an increase of the pressure inside the extruder, leads to a finer cell structure. These two effects of the duration are contrary. An optimal duration for this specific system can be adjusted.

CONCLUSIONS

In this work the manufacturing of microporous PSU hollow fibers with the CBAs ACA and 5-PT by extrusion is described. The experimental results lead to the following conclusions:

1. It is possible to produce microcellular foams with CBAs by means of extrusion. Using PSU and 1.0 wt % ACA, foams with an average cell size of 15–20 μm and a cell density of 10^7–10^8 cells/cm^3 were produced.
2. Experiments proved that for PSU the effective ACA and 5-PT concentrations amounted to about 1.0 wt %. Higher blowing agent concentrations than 1.0 wt % did not cause a higher cell density.
3. For the foam extrusion with CBAs it is proved to be advantageous to have high temperature in the extruder cylinders and lower die temperatures. Within the possible range of temperatures the cell density grows according to a diminishing temperature of the die.
4. For PSU/ACA systems, a screw speed of 10–20 rpm causes a finer cell structure.
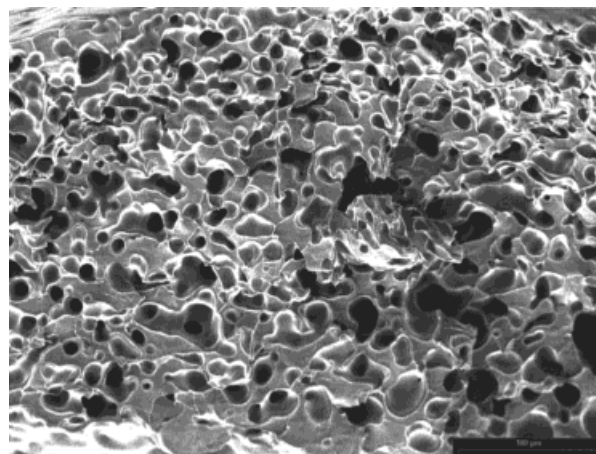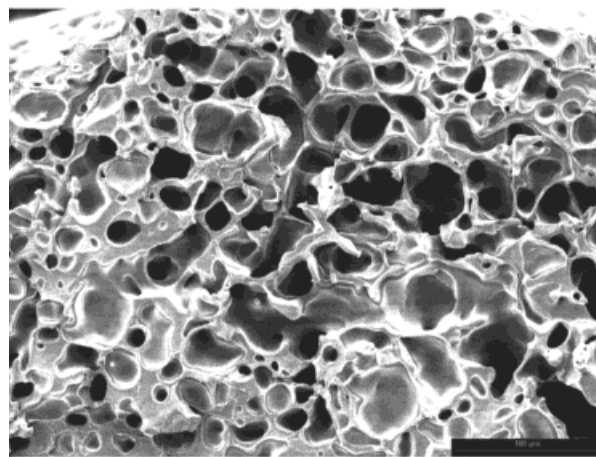
Figure 11 SEM micrographs of PSU hollow fibers foamed with 1.0 wt % ACA at different screw speeds: (a) 15 rpm; (b) 30 rpm.

Screw speeds higher than 20 rpm cause a coarse cell structure.

5. Foams made of different CBAs have different structures. Under the same conditions of production, the PSU/ACA system generally has a finer cell structure than the PSU/5-PT system.

6. Hollow fibers with connected pores and fine cell structure let us expect an application as porous membranes.

REFERENCES

1. J. E. Martini, F. A. Waldman, and N. P. Suh, US Pat. 4,473,665 (1984).
2. E. Staude, *Membranen und Membranprozesse,* VCH, Weinheim, 1992.
3. H. Strathmann, *Trennung von molekularen Mischungen mit Hilfe synthetischer Membranen,* Steinkopff Verlag, Darmstadt, Germany, 1979.
4. C. M. Hansen, *Farbe Lack,* **7,** 169 (1969).
5. B. M. Riggleman, M. E. Cohen, and M. A. Grable, US Pat. 3,745,202 (1973).
6. Mitsubishi Rayon Co. Ltd, Jpn. Pat. 01 014 315 (1989).
7. R. A. Reed, *Brit. Plast.,* **33,** 468 (1960).
8. R. L. Heck, *Plastics Compounding,* **4,** 52 (1978).
9. V. Kumar, J. E. Weller, and H. Y. Hoffer, *Symposium on Processing of Polymers and Polymeric Composites,* Vol. ND-19, ASME Winter Annual Meeting, Dallas, TX, 1990, p. 197.
10. P. L. Durril and R. G. Griskey, *AIChE J.,* **12,** 1147 (1966).
11. P. L. Durril and R. G. Griskey, *AIChE J.,* **15,** 106 (1969).