A Process for Making Microcellular Thermoplastic Parts

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A novel process to produce microcellular thermoplastic parts is described. This is achieved by integrating the deformation process in the foaming cycle in such a way that the cell nucleation and growth processes are effectively uncoupled from deformation. The nitrogen-polystyrene system is studied and the relationships between the essential process parameters are established. It is experimentally shown that the pressures associated with deformation do not reduce the number of bubbles nucleated. The process synthesized is demonstrated by making a microcellular polystyrene container.

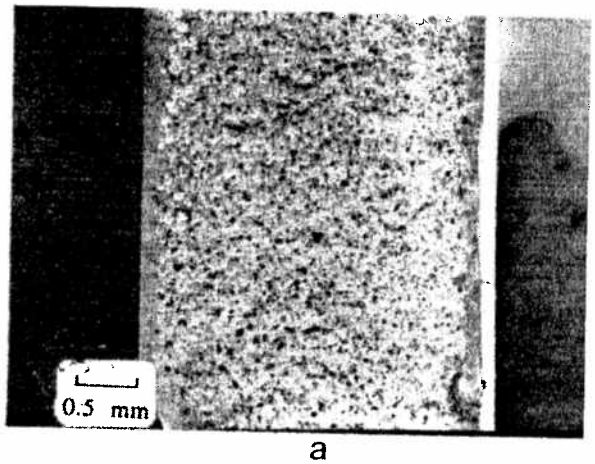
INTRODUCTION

Microcellular plastics refer to closed-cell thermoplastic foams with cell diameters on the order of 10 μm. This idea was originally conceived as a means to reduce the amount of plastic used in mass-produced items. The rationale was that if a sufficient number of voids smaller than the critical flaw size pre-existing in polymers can be produced, then the amount of plastic used could be reduced without compromising the mechanical properties. Such a process has been developed by Martini, *et al.* (1, 2) for amorphous polymers using a thermodynamic instability phenomenon to achieve the cell nucleation.

The basic process involves saturating the polymer with an inert gas below the glass transition temperature and at a high pressure. When the pressure is removed, a supersaturated specimen is produced, since the excess gas is unable to escape the glassy polymer matrix. As the specimen is now heated above the glass transition temperature, a very large number of bubbles spontaneously nucleate. The bubbles cannot expand very rapidly due to the high viscosity of the polymer near the glass-transition temperature, allowing us to obtain very small cells. *Figure 1a* shows an overall view across the thickness of a microcellular polystyrene disk showing the general uniformity of the structure. *Figure 1b* is a closeup of the structure, showing typical cell size and shape distribution.

Introducing a very large number (say 100 million per cm^3 or more) of very small bubbles leads to some interesting properties. For example, Waldman (3) has found microcellular polystyrene to have several-fold increase in impact strength, while maintaining a tensile strength in proportion to foam density. These properties make it possible to foam thin-walled (say 1 to 2 mm thick) parts which, if foamed by conventional means, could suffer an excessive loss of strength. Microcellular foams with density reductions of up to 75 percent have been produced by Kumar and Suh (4), demonstrating the possibility of considerable savings in material costs.

When a microcellular sheet is deformed to obtain a desired shape, the cells become grossly distorted and are sometimes destroyed in regions of large strain gradients (see *Fig. 2a*). To circumvent this problem, we may form the part first (say by injection molding) and then foam it using the microcellular process. This procedure results in gross distortions in part shape (see *Fig. 2b*) due to the relaxation of the residual stresses introduced in the part-forming operation when the part is heated to the glass transition temperature in the microcellular process. We therefore need a process by which the desired geometry can be obtained while preserving the microcellular structure. In this paper, we describe a strategy to uncouple deformation from cell nucleation and growth, enabling us to independently realize both geometry and the microcellular structure in a thermoplastic part.



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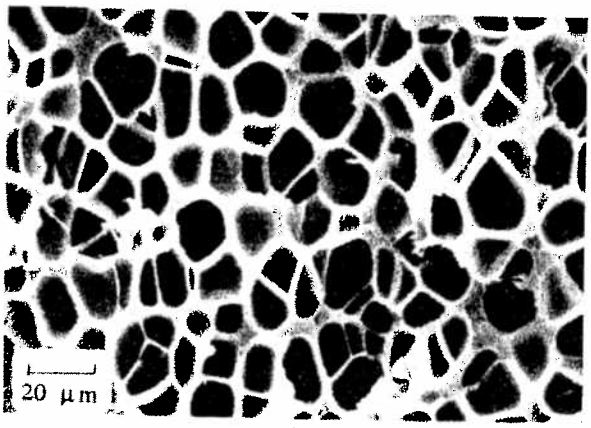

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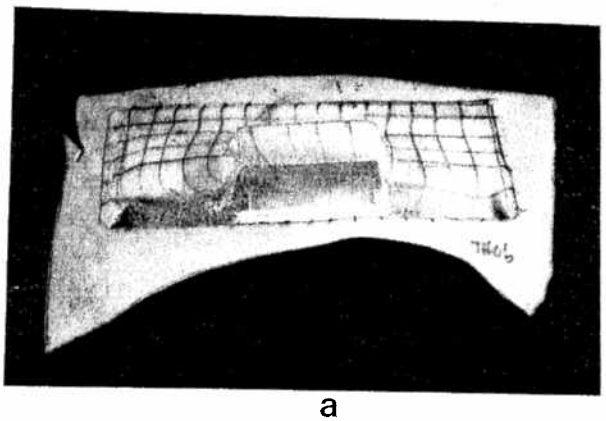
Fig. 1. Scanning electron micrographs of microcellular polystyrene foam: (a) overall view across sample thickness; (b) closeup showing structural details.



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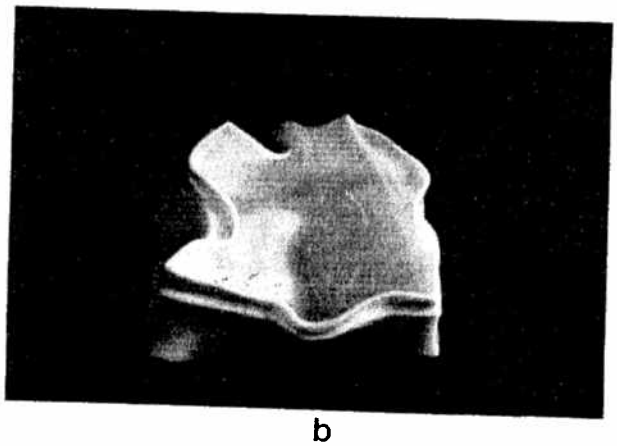

b

Fig. 2(a). Photograph of a microcellular polystyrene sheet that was later thermofoamed. Note the gross distortion in cell structure.

Fig. 2(b). Photograph of an injection molded polystyrene box that was microcellularly foamed. Note the distortion in geometry.

EXPERIMENTAL

A number of experiments were conducted in order to understand the essential physics of the phenomena involved in the microcellular process, and to establish the interrelationship among the key process variables and the process design parameters. The strategy for the experimental investigation was based on the axiomatic approach to design, Suh (5, 6); Kumar (7), and will not be further addressed in this paper. We will present some key experimental results here that have a direct bearing on the process for producing microcellular parts.

All experiments were conducted on DOW XP6065 polystyrene with an average molecular weight of 200,000. Circular disks of 50 mm diameter and 1.6 mm thickness were injection molded from the resin. These disks were saturated with nitrogen at room temperature in a pressure vessel maintained at the chosen saturation pressure for the experiment. The Henry's Law constant for solubility of nitrogen in polystyrene was measured to be 0.043 cm^3 (STP)/g atm. The average diffusion constant for nitrogen in polystyrene at room temperature was found to be 4×10^{-8} cm^2/s from desorption experiments using the analytical solution from Crank (8) for one-dimensional diffusion from a saturated disk. For the 1.6 mm thick polystyrene disks, it took three days to reach 98 percent of the limiting saturation, at which time the disks were removed from the pressure vessel and foamed in a glycerin bath maintained at 115°C. The microstructure of the resulting foam was studied on a Scanning Electron Microscope (SEM).

The number of cells nucleated per cm^3 of original (unfoamed) polymer, N_o, was determined as follows. First a micrograph showing 100 to 200 bubbles was obtained and the exact number of bubbles n in the micrograph was determined. Now if A is the area of the micrograph in cm^2 and M is the magnification factor, then $(n/(A/M^2))$ gives the area bubble density, or the number of bubbles per cm^2 of the foam. Assuming an isotropic bubble distribution, the square root of the area density gives a line-density, or the number of bubbles per cm in the foam. By cubing the line density, we can estimate the number of bubbles

per cm^3 of the foam N_f. Thus

$$N_f = \left(\frac{n\,M^2}{A}\right)^{3/2} \quad (1)$$

where

N_f = number of bubbles per cm^3 of foam
n = number of bubbles in the micrograph
A = area of the micrograph, cm^2
M = magnification factor of the micrograph

Let D be the average cell diameter in cm as determined from the SEM micrograph. Then in one cm^3 of foam, the volume occupied by the voids V_f is

$$V_f = (\pi/6)\, D^3 \cdot N_f \quad (2)$$

so that the volume $(1 - V_f)$ is occupied by the polymer. Thus N_f bubbles in one cm^3 of the foam must have nucleated in $(1 - V_f)$ cm^3 of the original polymer. We can therefore say that the number of bubbles nucleated per cm^3 of original unfoamed polymer is

$$N_o = N_f/(1 - V_f) \quad (3)$$

Unless otherwise specified, cell density reported in this paper is determined by *Eq. 3*.

CONTROL OF MICROCELLULAR STRUCTURE

From a design point of view, one may wish to aim for a certain foam density, or void fraction. Since the void fraction depends on the size of cells as well as the number of cells present, we need to control both of these variables.

Control of Cell Nucleation Density

Colton and Suh (9) studied the phenomenon of nucleation in amorphous polymers in the presence of a nucleating agent. The nucleation process is complex and depends on the solubility, concentration, interfacial energy of any additives present, and the concentration of the foaming gas. We investigated the effect of gas concentration on cell nucleation by saturating a number of polystyrene disks at different saturation pressures, and then foaming these disks by the microcellular process. Based on a simple thermodynamic model for nucleation (see **Appendix A**) we expected the cell density to increase as the saturation pressure was raised.

Figure 3 shows cell nucleation density in polystyrene as a function of the gas saturation pressure. We see that, at least over the range of saturation pressures used in this experiment, the cell nucleation density increases exponentially with the gas saturation pressure. Thus gas saturation pressure is a viable process parameter to control cell nucleation density.

Control of Cell Geometry

The rate at which cells grow at the foaming temperature (typically 10 to 20°C above the glass transition temperature of the polymer) is an important process parameter. This rate is a function of the polymer viscosity, surface tension, the pressure inside the bubble, and the external pressure under which the growth is allowed to occur. The pressure inside the bubble changes as the bubble grows, and is affected by the rate at which gas molecules diffuse into the bubble from the surrounding polymer matrix.

The rate of bubble growth in the nitrogen-polystyrene system was experimentally studied. A number of polystyrene samples were saturated with nitrogen at 13.8 MPa (2000 psi) and foamed at 115°C at atmospheric pressure for different lengths of time. *Figure 4* shows a plot of the average cell diameter as a function of foaming time. It is seen that the cell growth rate is highest in the beginning, and decreases as the cells grow and the driving force for growth is depleted. The cells reach maturity after approximately 100 s of foaming time, beyond which little further growth in the average cell size is observed. Most importantly, we see that it takes some 20 to 30 s to attain an average cell size of approximately 10 μm.

Figure 5 shows two micrographs from samples foamed under different external pressure conditions with strikingly different cell geometry. In *Fig. 5a* an external pressure was maintained during foaming

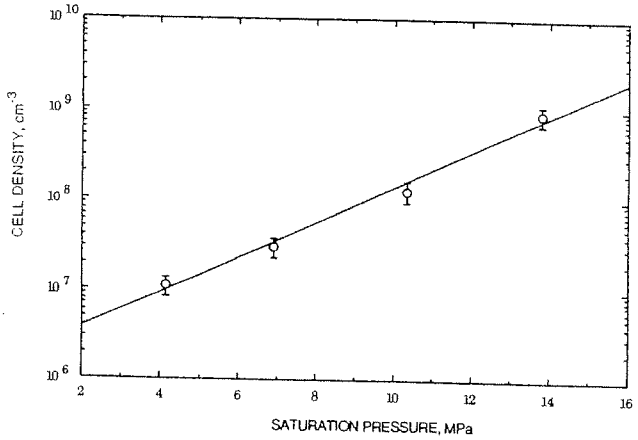

Fig. 3. Plot of cell nucleation density in polystyrene as a function of nitrogen saturation pressure.

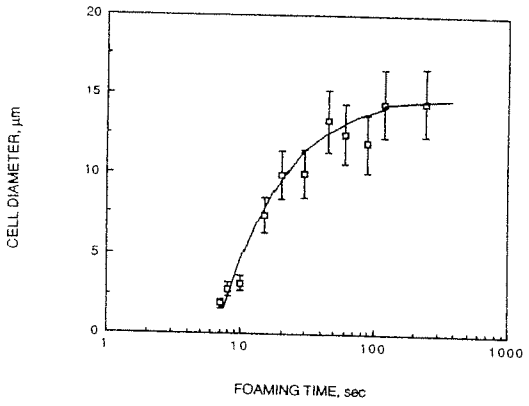

Fig. 4. Growth in average cell size as a function of time.

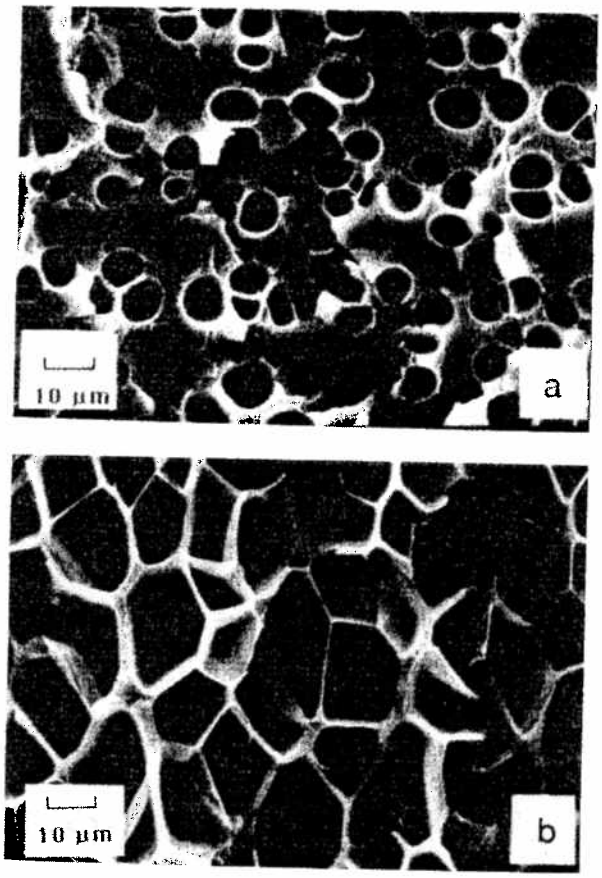

Fig. 5. Scanning electron micrographs of polystyrene samples nucleated under external pressure. In (a), the pressure was maintained during the cooling cycle, while in (b), the pressure was released before cooling began.

and subsequent cooling cycle. The external pressure limited the cell growth and spherical cells were formed. In *Fig. 5b* the external pressure was released before the cooling cycle began causing the cells to grow and touch each other until a honeycomb structure was formed. Thus the cell shape can be controlled if desired.

MANUFACTURE OF MICROCELLULAR PARTS

As mentioned in the **Introduction**, our overall goal was to develop a process in which deformation is integrated in the foaming cycle in such a way that both the microcellular structure and the part geometry can be obtained. One way to achieve this would be to obtain the part geometry first—say in a molding operation—and then subject the part to the microcellular process and a secondary deformation process in order to eliminate the shape distortions shown in *Fig. 2b*. Such a process will involve two heating and cooling cycles, and may be prohibitively expensive. We therefore searched for a process in which microstructure and part geometry could be attained within one thermal cycle.

Our goal could be realized if, starting with a sheet of plastic saturated with gas, we could obtain part geometry first, and then grow the microstructure. Since obtaining part geometry will require heating the plastic above the glass transition temperature, bubbles will nucleate and grow during deformation and the microstructure will probably be damaged. If we could somehow suppress the nucleation of bubbles until deformation was completed, and then nucleate and grow the bubbles, we would achieve our objective. Under these conditions, bubble nucleation will have to occur under a certain external pressure necessary to carry out the deformation step. How would the presence of an external pressure affect the number of cells nucleated?

Effect of External Pressure on Cell Nucleation

We investigated the effect of external pressure on cell nucleation density using the experimental setup shown in *Fig. 6*. Polystyrene disks were saturated with nitrogen at 13.8 MPa (2000 psi) and placed in the mold where they were subjected to a hydrostatic external pressure provided by a nitrogen cylinder. The mold was then heated by the plattens of a hydraulic press to 115°C, held for a few minutes, and then cooled down to the room temperature. The sample was then removed and examined. The external pressure was maintained throughout the heating and cooling cycle. This experiment was repeated at different external pressures, always using polystyrene samples pre-saturated at 13.8 MPa (2000 psi).

Figure 7 shows a plot of the cell density as a function of the external pressure. We see that the external pressure has no effect on the number of cells nucleated. As the external pressure reduces the degree of supersaturation which drives cell nucleation, we expected cell nucleation density to go down as external pressure increased. The experimental result is therefore surprising and counter-intuitive. There are two important implications of this result. First, the nucleation of cells cannot be suppressed by applying an external pressure during the heating cycle. Second, the pressures associated with deformations do not affect the number of cells nucleated in the microcellular process.

Effect of Gas Solubility on Cell Nucleation

Previous investigators believed that the driving force for nucleation is provided by the gas supersa-

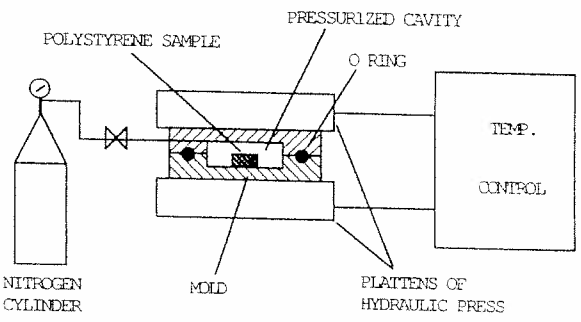

Fig. 6. Schematic of the experimental setup for study of cell nucleation under controlled hydrostatic pressure.

turation, Colton and Suh, (9). If this is true, then the presence of external pressure should certainly reduce the number of cells nucleated, since the external pressure reduces the degree of supersaturation. However, our experiments showed no effect of external pressure on the cell nucleation density, and therefore there must be an additional driving force that is compensating for the reduction in driving force due to the external pressure.

A decrease in the solubility of nitrogen in polystyrene as we heated our supersaturated sample from room temperature to the glass transition temperature could provide such a compensating driving force for nucleation. Data of Durrill and Griskey (10) shows that the solubility of nitrogen in polystyrene at the melt temperature is lower compared to room temperature solubility. No data were found, however, on solubility near the glass transition temperature.

We therefore measured the solubility of nitrogen in polystyrene in the range 20 to 115°C. The setup shown in *Fig. 6* was used again for the solubility measurements. Polystyrene samples were placed in the mold and pressurized with 10.3 MPa (1500 psi) nitrogen. The mold was heated to the desired temperature. At regular intervals, the samples were removed and weighed to the nearest 10 micrograms. After each reading, the samples were restored to the mold which was pressurized again to 10.3 MPa (1500 psi) and heated to the temperature at which the solubility was being determined. This procedure was repeated until two consecutive readings showed that the samples had saturated with nitrogen. Solubility in milligrams of nitrogen per gram of polystyrene was determined from the weight measurements and converted to the units of cm^3 (STP) per gram per atmosphere in which the Henry's Law constant is customarily reported. This experiment was repeated at a number of temperatures between 20 and 115°C, and the mold pressure was maintained at 10.3 MPa (1500 psi) in all experiments.

The solubility data are shown in *Fig. 8* which shows the Henry's Law constant as a function of temperature. We see that the solubility drops by nearly 40 percent as the temperature increases from room temperature to 100°C, the glass transition temperature for polystyrene. This data confirms our hypothesis that the reduction in gas solubility with temperature provides an additional driving force for cell nucleation. The large drop in solubility suggests that this driving force can be comparable to the driving force due to gas supersaturation, and at least partially explains the observations from *Fig. 7*, namely that the presence of external pressure does not reduce the number of cells nucleated. The exact nature of the effect of gas solubility on nucleation in a polymer near the glass transition temperature is still under investigation.

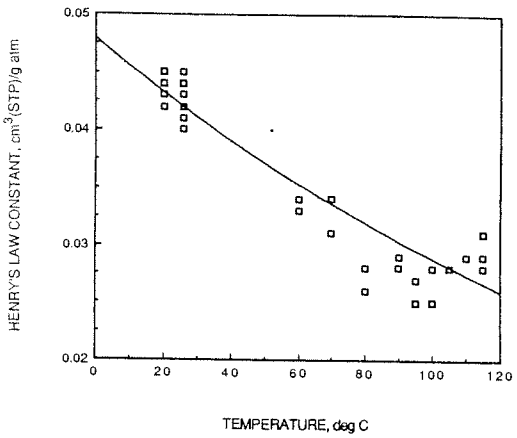

Fig. 8. Plot of solubility of nitrogen in polystyrene (expressed as the Henry's Law Constant) as a function of temperature.

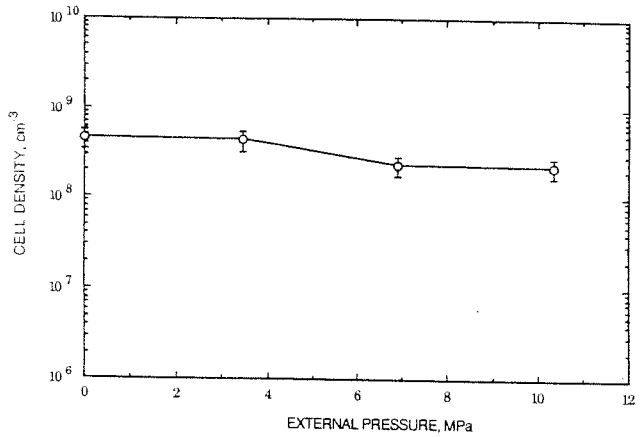

Fig. 7. Plot of cell density as a function of external pressure.

A Process to Produce Microcellular Parts

The experiments on the effect of external pressure on nucleation demonstrated that it is not possible to suppress cell nucleation by maintaining an external pressure as we originally thought. Therefore our proposed strategy of (starting with a saturated sheet of polystyrene) getting deformation first, and then obtaining nucleation and growth of bubbles cannot work.

The experimental results, however, suggest the following alternative process strategy. Since cells are bound to nucleate as soon as the gas saturated plastic is heated to the glass transition temperature, one could achieve deformation soon after cell nucleation while the cells are still very small, and then proceed to obtain cell growth (and the desired void fraction) at a higher temperature. This should be possible since it takes some 30 s for cells to grow to a size on the order of 10 μm (see *Fig. 4*) while deformation can be accomplished within 1 to 2 s.

The result that cell nucleation density is unaffected by an external pressure is a welcome one from the processing standpoint. It suggests that cell nucleation and deformation can be uncoupled in the sense that any external pressures associated in carrying out the required deformation will not affect the

number of cells nucleated, and thus our ability to control the cell density is not adversely affected.

The processing strategy is schematically shown in *Fig. 9*. The presaturated polymer sheet is heated to a temperature T_d above the glass transition temperature T_g at which the required deformation is carried out. The part geometry is obtained in a mold which is pre-heated to a higher temperature T_G at which the desired cell growth is achieved.

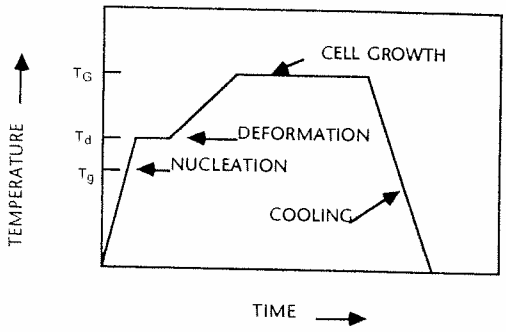

Fig. 9. Schematic of the proposed process for producing microcellular parts.

Process Demonstration

To study the feasibility of the processing strategy, a conventional thermoforming machine was equipped with a mold to produce a plastic container, and the bottom half of the mold was connected to a

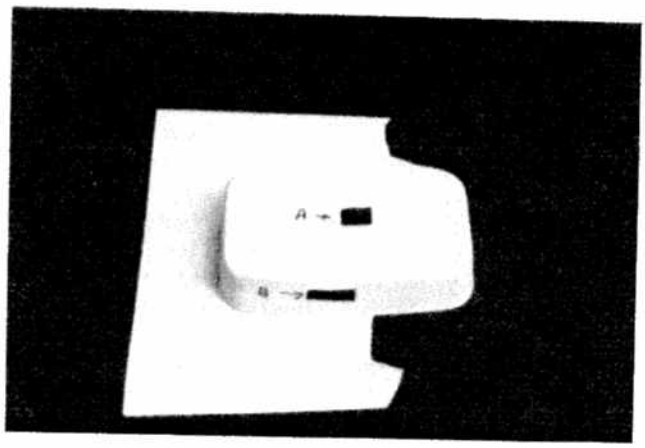

Fig. 10. Photograph of a microcellular container made by the process outlined in Fig. 9.

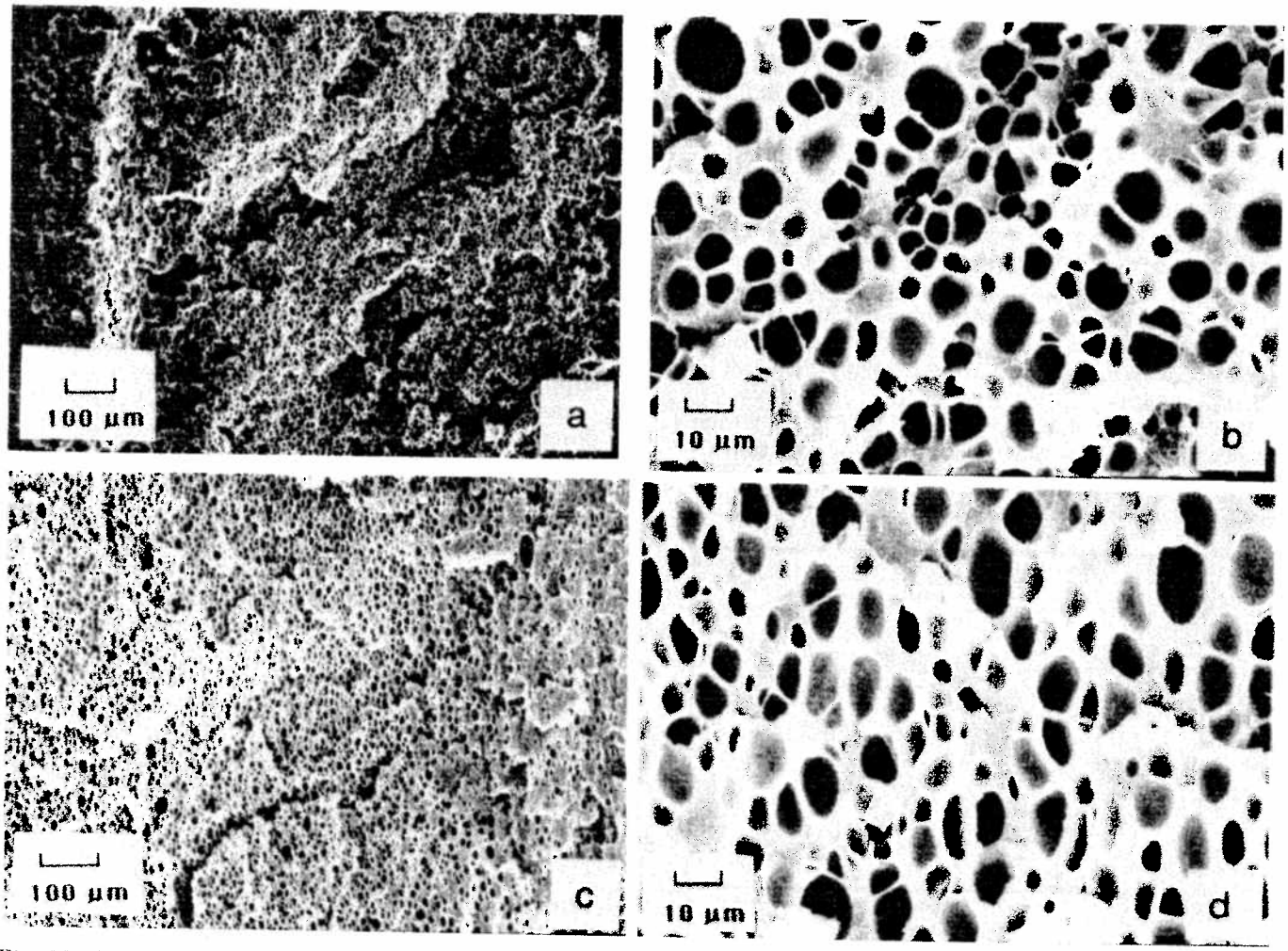

Fig. 11. Scanning electron micrographs of samples from the microcellular container: (a) sample from container bottom; (b) close-up of bottom; (c) sample from container wall; and (d) close-up of wall.

thermolator which could heat the mold to a desired temperature. A commercial grade high impact polystyrene sheet was saturated with nitrogen at 13.8 MPa (2000 psi) and placed in the thermoformer. The sheet was heated in an infrared oven and formed into a container using a heated mold in a plug-assist vacuum forming operation.

A sample from the bottom of the container and one from the wall of the container was studied under the SEM. *Figure 10* shows a picture of the container, and *Fig. 11* shows the micrographs from the samples. We see that microcellular structure has successfully been produced in the container, with an average cell size of approximately 7 μm.

This demonstrates the feasibility of the process-concept to produce microcellular thermoplastic parts.

CONCLUDING REMARKS

We have presented a process-concept that can be used to produce microcellular thermoplastic parts. In this process, the part geometry and the microcellular structure can be independently realized. The process uses one thermal cycle to achieve both the part shape and the microstructure.

Two key results from our experiments to understand the process physics enabled us to synthesize a process in which the deformation process is uncoupled from the cell nucleation and growth processes. The first result is from the experiments on the effect of external pressure on cell nucleation density, where we found that the number of cells nucleated is not affected by the external pressure under which nucleation takes place. This allows us to uncouple the deformation process from the cell nucleation process.

The second key result is from the experiments on cell growth in microcellular foams, where we learned that for cells to grow to a size of 10 μm near the glass transition temperature, it takes an order of magnitude longer (10 s or more) than the time it takes to achieve the required deformation (on the order of 1 s). This allows us to uncouple the deformation process from the cell growth process.

The feasibility of the process-concept was demonstrated by making a microcellular container from a high impact polystyrene sheet employing a conventional thermoforming machine. Although the process was developed on the nitrogen-polystyrene system, the basic idea can be extended to a variety of thermoplastics that can be foamed by the microcellular process.

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APPENDIX A

Effect of Saturation Pressure on Cell Nucleation

Bubbles in polymers may nucleate either homogeneously or heterogeneously. The specific mechanism depends upon whether a second phase is present in the polymer due to an insoluble additive or a nucleating agent. Homogeneous nucleation occurs when the dissolved gas molecules come together for a long enough time to produce a stable bubble nucleus. The homogeneous nucleation rate N_{HOM} is given by Colton and Suh (9) as

$$N_{HOM} = C_o f_o \exp(-\Delta G'/kT) \tag{A1}$$

where

C_o = concentration of gas molecules
f_o = frequency factor for gas molecules joining the nucleus
k = Boltzman's Constant
T = temperature in K
$\Delta G'$ = activation energy

The activation energy for homogeneous nucleation is given by

$$\Delta G' = \frac{16\pi\,\gamma^3}{3(p_s - p_o)^2} \tag{A2}$$

where

γ = surface energy of the polymer
p_s = gas saturation pressure
p_o = environmental pressure

The effect of gas saturation pressure on the cell nucleation density can be qualitatively seen from *Eqs A1* and *A2* respectively. *Equation A2* shows that a higher saturation pressure leads to a lower activation energy barrier leading to a higher nucleation rate as is evident from *Eq A1*. Thus a higher gas saturation pressure leads to a higher cell density.