

## Microcellular Polymers: Novel Materials for the 21st Century

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### SUMMARY

Microcellular polymer's produced by gas nucleation, refer to closed cell thermoplastic foams with a very large number of very small cells—typically  $10^8$  or more cells per  $\text{cm}^3$  of order  $10\mu\text{m}$  in diameter. First produced in the early 1980's with the objective of reducing the amount of polymer used in mass produced items, these novel materials have the potential to revolutionize the way thermoplastic polymers are used today. Microcellular plastics have been produced from a number of polymers ranging in relative density from 0.1 to 1.0, containing  $10^8$  to  $10^{11}$  cells per  $\text{cm}^3$ , offering the engineer a new range of properties for design. The microcellular polymers appear to possess improved fatigue life and energy absorption characteristics as well as a higher specific strength. This paper reviews recent progress in this emerging technology and discusses the areas where this technology is likely to make an impact in the future.

### INTRODUCTION

Imagine solid polymers replaced by microcellular polymers with 20 to 40 percent reduction in material without compromising their function or required strength; also look forward to further composite microcellular materials with layers of solid and cellular materials designed to offer optimum mechanical and thermal properties with minimum use of polymer, created by processes without using any chemicals that are harmful to the environment. Such materials may well become a reality by the turn of the century!

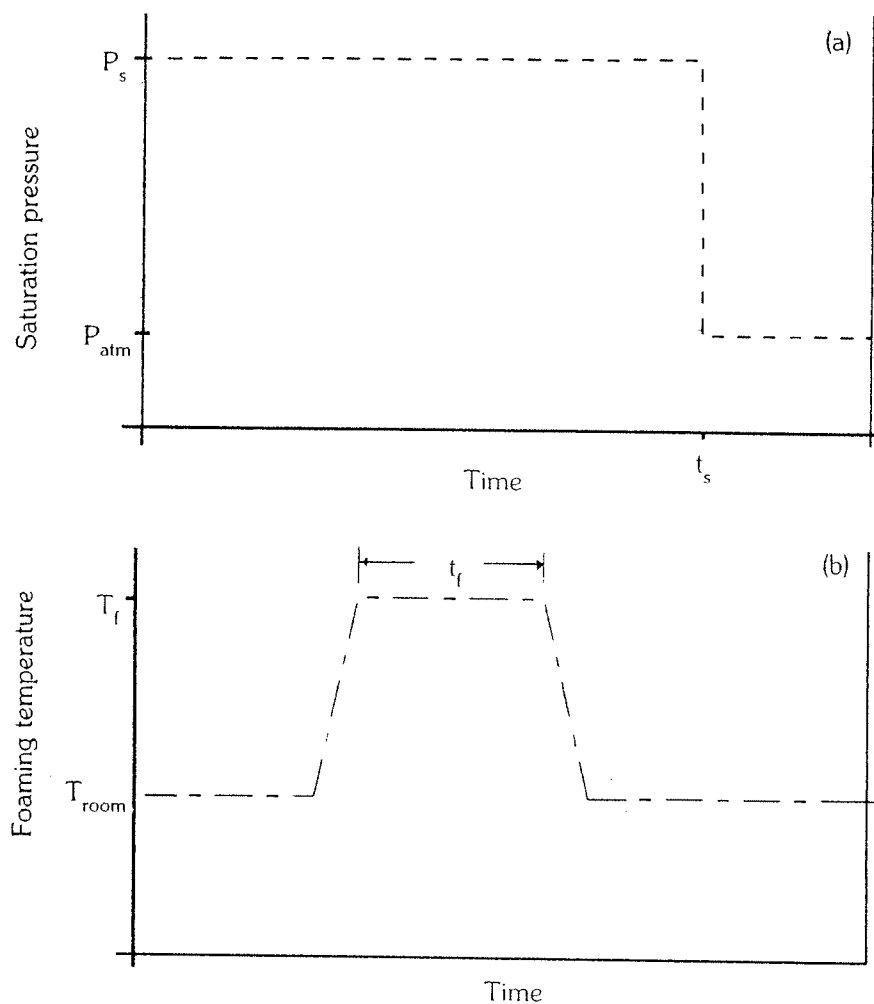
Microcellular polymers are closed cell plastic foams with a bubble density in excess of 100 million per  $\text{cm}^3$  and diameters of order  $10\mu\text{m}$ . The idea to introduce very small bubbles in plastics by gas nucleation was originally advanced by Professor Nam P. Suh of the Massachusetts Institute of Technology around 1980 as a means to reduce the cost of

many mass produced plastic items. The rationale was that if bubbles smaller than the critical flaws that already exist in plastics could be introduced in sufficient numbers, then the material density could be reduced while maintaining the essential mechanical properties. A process to create such microstructure has been developed<sup>(1)</sup>.

The basic microcellular process is a two-step process shown in Figure 1. In the first step, the polymer sample is saturated by a non-reacting gas in a pressure vessel at a pressure  $P_s$ . The time for saturation  $t_s$  is long enough to achieve a uniform concentration of gas in the polymer sample.

Achieving a uniform gas concentration is necessary in order to get a uniform bubble nucleation in the polymer. This step is usually carried out at room temperature although a higher temperature may be employed to

**Figure 1 Schematic of the microcellular process: (a) saturation of polymer with gas at room temperature; (b) bubble nucleation and growth at atmospheric pressure**



accelerate the diffusion of gas in the polymer. Upon saturation, the polymer sample is removed from the pressure vessel, producing a supersaturated sample. In the second step, the supersaturated sample is heated to the foaming temperature  $T_f$ , which is close to the glass transition temperature of the polymer. At this stage a large number of bubbles nucleate in the polymer. The specimen is held at the foaming temperature for a time  $t_f$ , which is chosen to allow sufficient bubble growth to achieve the desired density of the resulting foam. The growth rates of bubbles near the glass transition temperature are relatively low, and it is possible to arrest the bubble growth in a controllable manner once the desired growth has been achieved.

In Figure 2 Scanning Electron Micrographs of a number of polymers foamed by this process are shown. It can be seen that the microcellular structure is very homogenous. Bubbles are typically between 5 to 25  $\mu\text{m}$  in diameter, with the exception of PET in which the bubbles are an order of magnitude larger. The final average bubble size is primarily governed by the number of bubbles that nucleate, which in turn is strongly influenced by the concentration of gas after saturation in step one. The density of the foams can be controlled by choosing an appropriate gas saturation pressure, and using a suitable foaming time and temperature. These parameters are specific to a given gas-polymer system, and for the most part must be determined experimentally.

**Figure 2** Scanning electron micrographs showing examples of the structure created by the microcellular process: (a) PVC; (b) polycarbonate; (c) ABS; and (d) PET

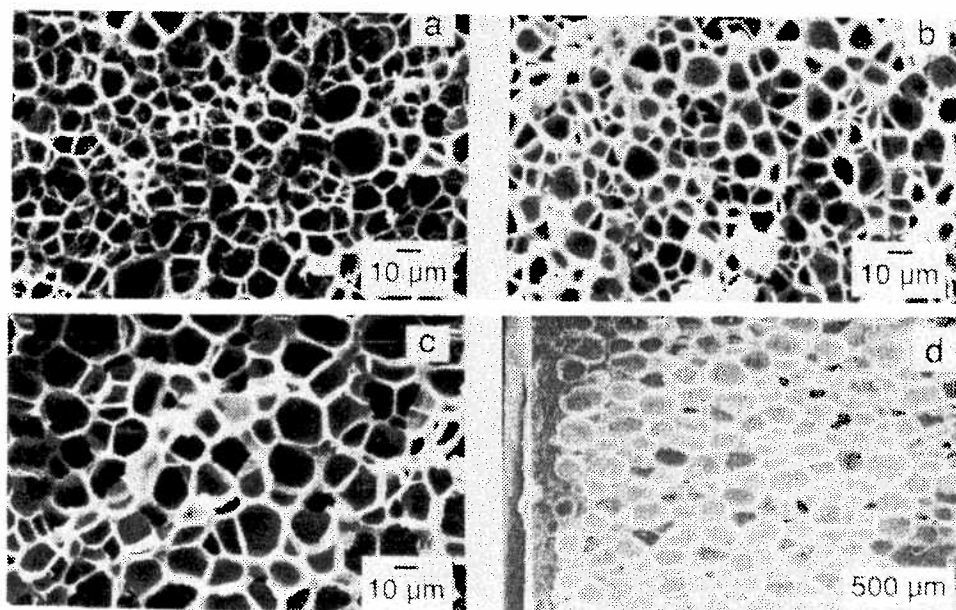
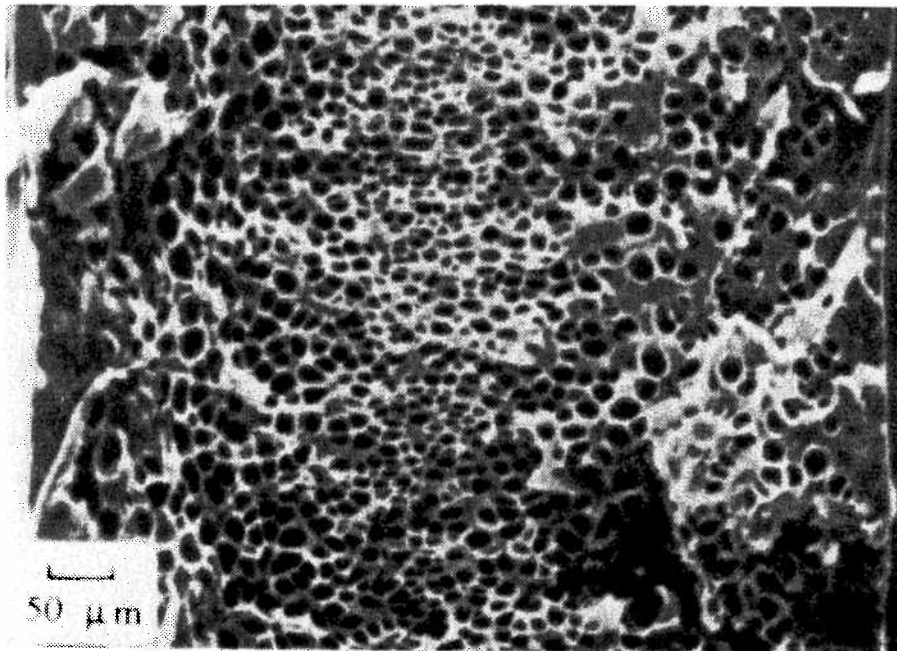


Figure 3 shows scanning Electron Micrograph of a polystyrene sample showing the full specimen cross section. This sample was originally 0.04 mm thick and grew to a thickness of 0.06 mm after foaming.

This example shows that thin sections of polymers normally made from solid polymer can indeed be foamed by the microcellular process.

In this paper a review of the state-of-the-art in this emerging field since its inception some 10 years ago is presented. First the key gas-polymer systems for which the process has been successful will be reviewed. Second, the progress in processing of these materials will be reviewed, and many process innovations since the original process was discovered will be described. Finally, I will conclude with my vision for the potential impact of microcellular materials.

**Figure 3 Overall view across a polystyrene sample originally 0.04 mm thick<sup>(7)</sup>. The thickness after foaming was 0.06 mm**



### OVERVIEW OF MICROCELLULAR POLYMERS

The basic microcellular process outlined above has been successful with a number of amorphous polymers. Semi-crystalline polymers have been difficult to foam by this process due to lower gas solubility in these polymers, and the fact that the crystalline portions of such polymers prevent the nucleation of bubbles. Some of the successful gas-polymer systems are discussed below.

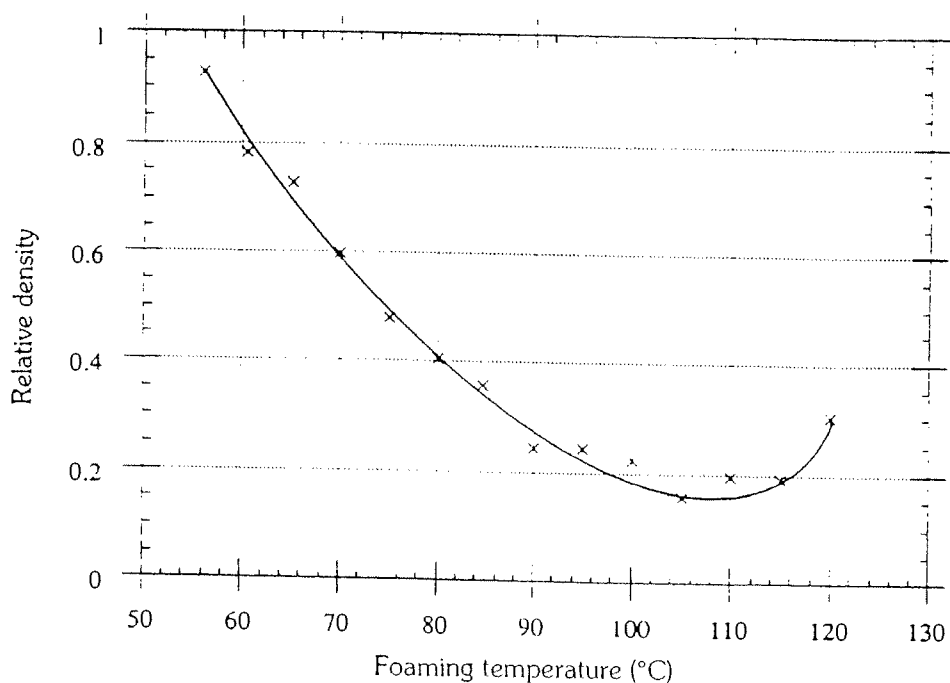
### POLY VINYL CHLORIDE (PVC)

Microcellular PVC foams have recently been produced by Kumar and Weller<sup>(2)</sup> using carbon dioxide as the nucleating gas. Bubble densities in the range  $10^7$ - $10^9$  per  $\text{cm}^3$  of polymer were achieved, and foams with relative density (density of the foam divided by the density of the polymer) in the range 0.15 to 0.94 have been produced.

The sorption data for carbon dioxide in PVC<sup>(2)</sup> shows that for 2 mm thick specimens of a rigid PVC formulation saturated at 4.8 MPa at room temperature the gas concentration at equilibrium saturation is approximately 75 mg of carbon dioxide per gram of PVC, or about 7.5 percent by weight. Thus a very high concentration of gas molecules exists in the polymer matrix at saturation. As a result, there is significant plasticization of the polymer, and the glass transition temperature drops from 78.2°C for original PVC to an estimated 14°C upon saturation<sup>(2)</sup>. Bubble nucleation and growth is therefore possible at very moderate temperatures, at or below the glass transition temperature of the original polymer. In the case of PVC, the lowest temperature at which microcellular foam was produced was 56°C.

Figure 4 shows the range of relative densities of the family of microcellular PVC foams produced by heating the saturated PVC specimens

**Figure 4** Plot of PVC foam relative density as a function of foaming temperature for specimens saturated with carbon dioxide at 4.8 MPa<sup>(2)</sup>



to different temperatures. The lowest density foams (15 to 20 percent of the solid PVC density) are produced in the 100-115°C temperature range. Note the nearly linear variation of foam relative density with foaming temperature in the range 56°C to 105°C, demonstrating that the foam density can be simply and accurately controlled by controlling the temperature to which the saturated plastic is heated.

### POLYCARBONATE (PC)

Creation of microcellular structure in polycarbonate was first reported in 1990 by Kumar, Weller and Hoffer<sup>(3)</sup>. Carbon dioxide, due to its high solubility in polycarbonate, was used to achieve very high bubble nucleation densities in the range  $1-10 \times 10^9$  per  $\text{cm}^3$  of polymer. Sorption data shows an equilibrium gas concentration of approximately nine percent by weight at a saturation pressure of 4.8 MPa. The number of bubbles nucleated was found to increase exponentially with increasing gas saturation pressure. A family of microcellular polycarbonate foams has been produced ranging in density from 10 to 99 percent of the density of solid polycarbonate.

The amount of gas absorbed by the polymer is directly proportional to the gas saturation pressure as suggested by Henry's law<sup>(4)</sup>:

$$C=HP_s$$

where

C = gas concentration at saturation,  $\text{cm}^3$  (STP) per gram of polymer

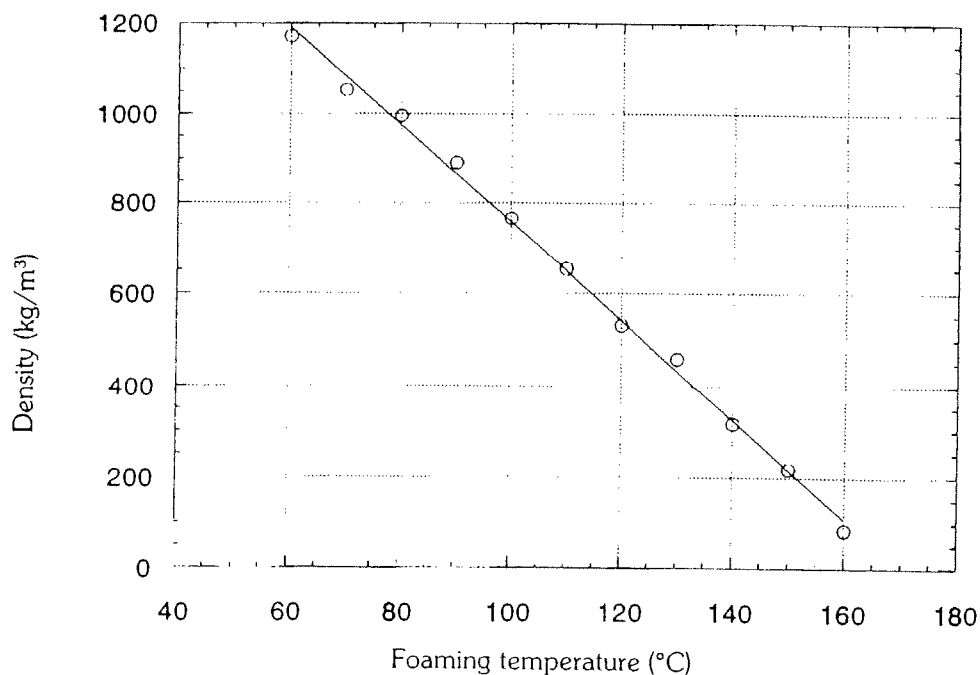
H = Henrys Law constant,  $\text{cm}^3$  (STP)/g Pa, and

P<sub>s</sub> = gas saturation pressure, Pa.

This relationship was tested by Kumar and Weller<sup>(5)</sup> for the carbon dioxide-polycarbonate system. They found that the linear relationship given by Eq. (1) holds very well for saturation pressures between 2 and 6.5 MPa which was the range of gas pressures explored.

The density of microcellular polycarbonate foams as a function of the foaming temperature is shown in Figure 5. Again, we see a linear relationship, suggesting that the foaming temperature is a critical parameter for controlling the density of the microcellular foams, and thus an effective means of in-process control of foam morphology.

**Figure 5** Plot of polycarbonate foam density as a function of foaming temperature for specimens saturated by carbon dioxide at 4.8 MPa<sup>(5)</sup>



### POLYSTYRENE (PS)

Microcellular polystyrene has been studied by a number of investigators<sup>(1,6,7,8,9,10,15)</sup>. Nitrogen has been the most effective gas to use with polystyrene and high impact polystyrene, although other gases such as helium and carbon dioxide have also been tried. Martini et al.<sup>(1)</sup> produced microcellular polystyrene with cells in the 5-25  $\mu\text{m}$  range and void fractions of 5 to 30 percent. Using higher nitrogen pressures for saturation, Kumar<sup>(10)</sup> extended the void fraction range to 80 percent. This is possible because the number of bubbles increases exponentially with saturation pressure, allowing for lower density foams to be produced while keeping the average bubble diameter in the microcellular range.

### POLYETHYLENE TEREPHTHALATE (PET)

Kumar and Gebizlioglu<sup>(11)</sup>, and Baldwin and Suh<sup>(12)</sup> have applied the microcellular process to foam PET using carbon dioxide. The results with PET have been most interesting. It has been found that with sufficiently

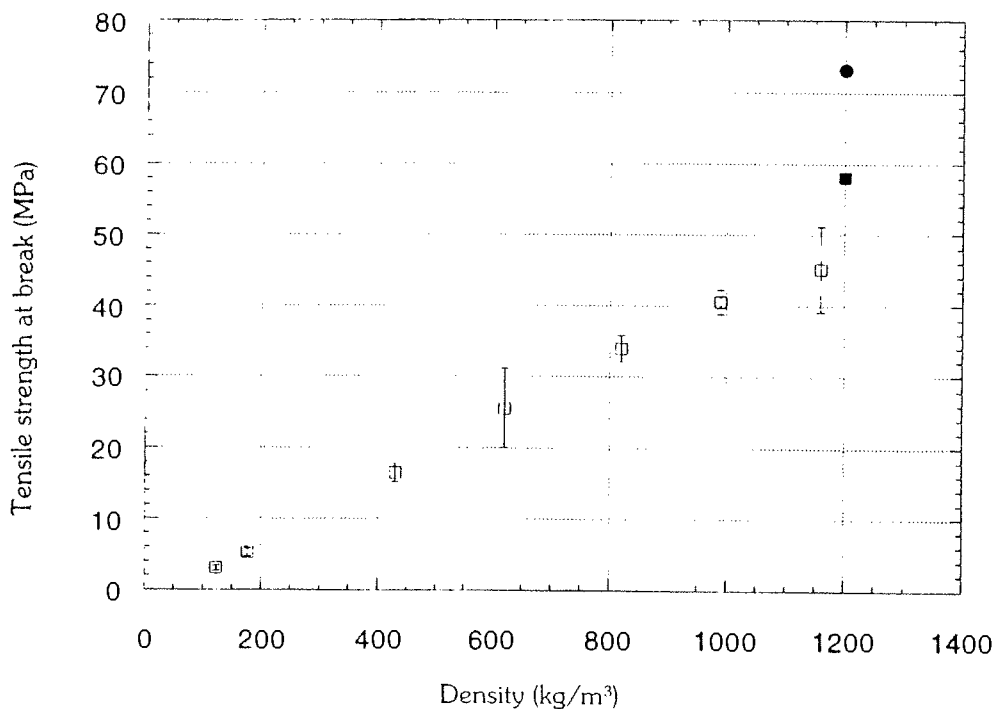
long exposure to high pressure carbon dioxide, PET begins to crystallize. The resulting PET foams have a significantly higher crystalline content, and although mechanical property data is not yet available, these foams appear to be much stronger than microcellular foams from other polymers at comparable relative densities.

## MECHANICAL PROPERTIES OF MICROCELLULAR POLYMERS

The mechanical property data available on microcellular polymers to date is limited. However, the available data shows that these novel materials may offer properties not previously available from conventional polymeric foams, and in many cases offer improved properties.

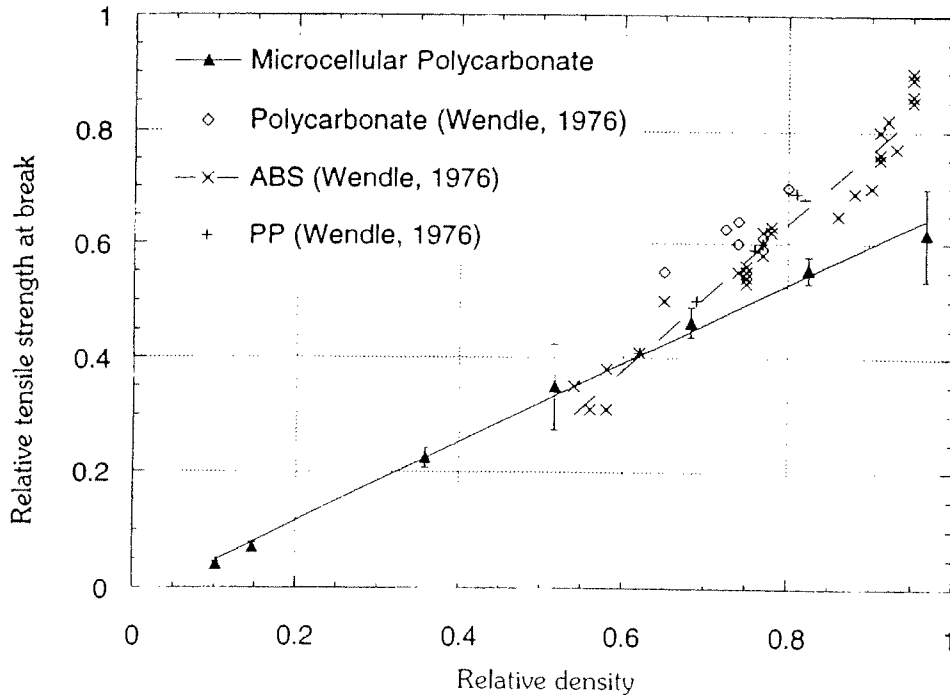
The tensile behaviour of microcellular polycarbonate has been studied experimentally<sup>(13,14)</sup>. It has been found that the strength of microcellular foams is directly proportional to the foam density as shown in Figure 6. As shown by the solid symbols in Figure 6, polycarbonate appears to lose

**Figure 6** Plot of tensile strength at break of solid and microcellular polycarbonate as a function of relative density. the error bars represent one standard deviation. Filled symbols are solid polymer; the filled circle is virgin polycarbonate, while the filled square is polycarbonate saturated with CO<sub>2</sub> but not foamed





**Figure 7 Plot of relative tensile strength at break of microcellular polycarbonate foams and some common structural foams as a function of foam relative density<sup>(14)</sup>**

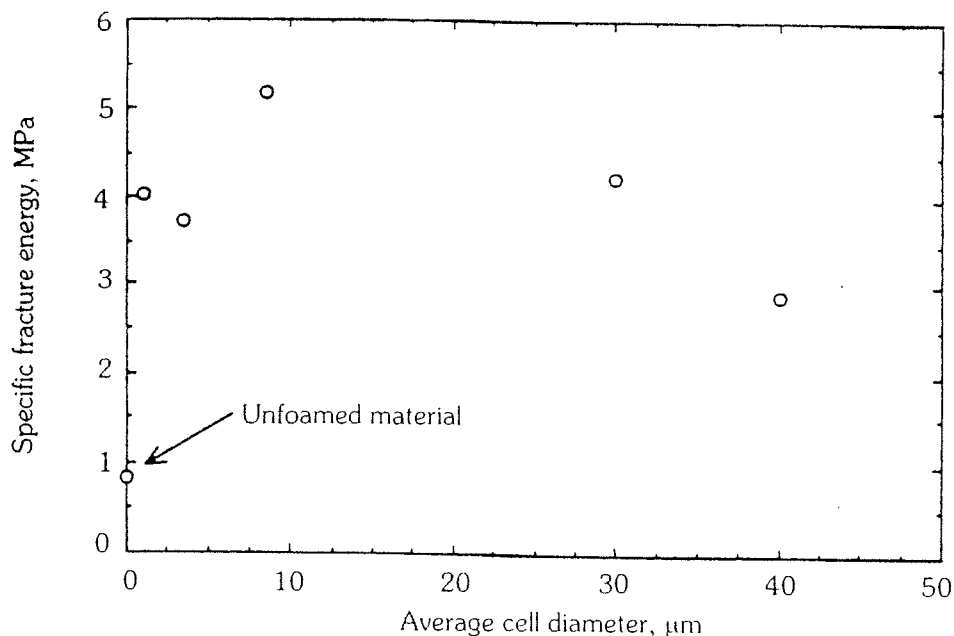


approximately 20 percent of its strength when saturated by 4.8 MPa carbon dioxide. The relative modulus of microcellular polycarbonate varies as the square of the foam relative density<sup>(14)</sup>.

Figure 7 shows the relative tensile strength of microcellular polycarbonate as a function of relative density. The relative strength for some common structural foams have also been plotted for comparison. It can be seen that the strength of microcellular foams, at a given relative density is comparable to that of structural foams. We also see that as the foam relative density decreases, the strength of structural foams decreases at a faster rate compared to the strength of microcellular polycarbonate foams. It is noteworthy that in the relative density range of 0.3 to 0.6, few data on structural foams was found, suggesting that in this density range microcellular foams may represent novel materials with properties not previously available.

Figure 8 shows Waldman's<sup>(15)</sup> data on the energy absorbed before fracture in uniaxial tension tests for microcellular polystyrene as a function of average bubble diameter. It can be seen that for the entire range of data, there is a five to seven-fold increase in the energy to fracture relative to

**Figure 8** Plot of energy to fracture in uniaxial tension tests as a function of average bubble diameter for microcellular polystyrene<sup>(15)</sup>



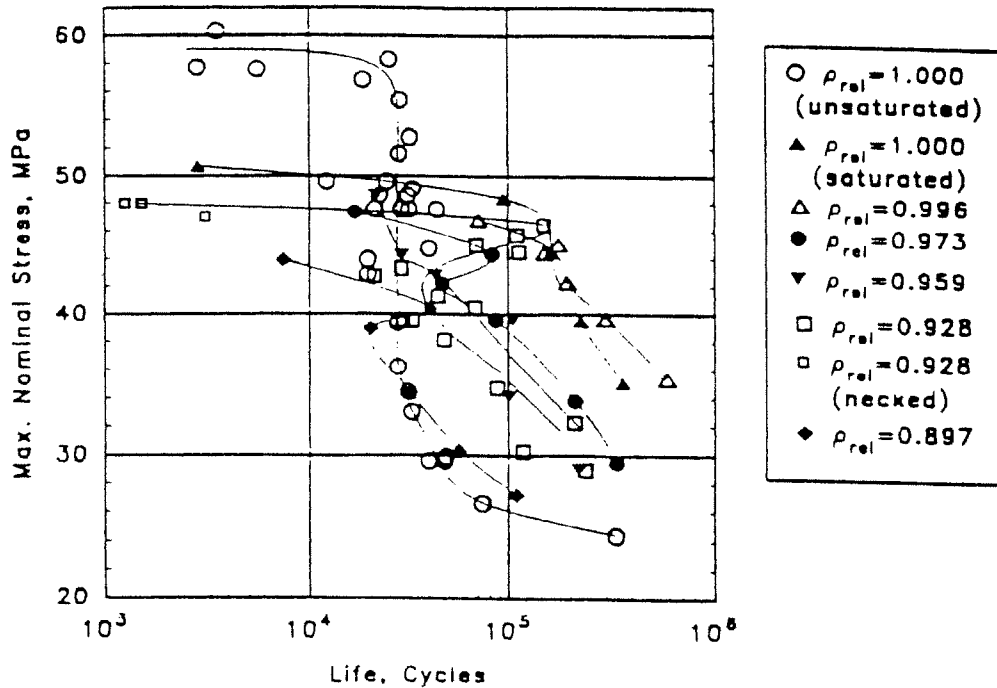
the solid polystyrene. A corresponding increase was observed in the strain to failure. It appears that, at least in polystyrene, the advance is a significant step toward production of microcellular polymers in a continuous process.

Kumar and Seeler<sup>(16)</sup> have characterized the fatigue behaviour of high density microcellular polycarbonate, with foam relative density ranging from .897 to 0.996. The fatigue data is shown in Figure 9. The  $\rho_{rel} = 1.00$  represents data on solid polycarbonate. The fatigue life of specimens with relative density of 0.923 exceeded the fatigue life of solid polycarbonate by up to a factor of four. Specimens with a relative density of 0.996 were found to have the highest fatigue life, exceeding the life of solid polycarbonate specimens by up to a factor of 17. Thus the introduction of a microcellular structure may provide a way to increase the fatigue life of a polymer.

## RECENT INNOVATIONS

Initially<sup>(1,6)</sup> it was believed that the bubble nucleation in the microcellular process is caused by the supersaturation of the polymer. Kumar<sup>(7)</sup> showed

**Figure 9** Fatigue life of high relative density microcellular polycarbonate foams<sup>(16)</sup>

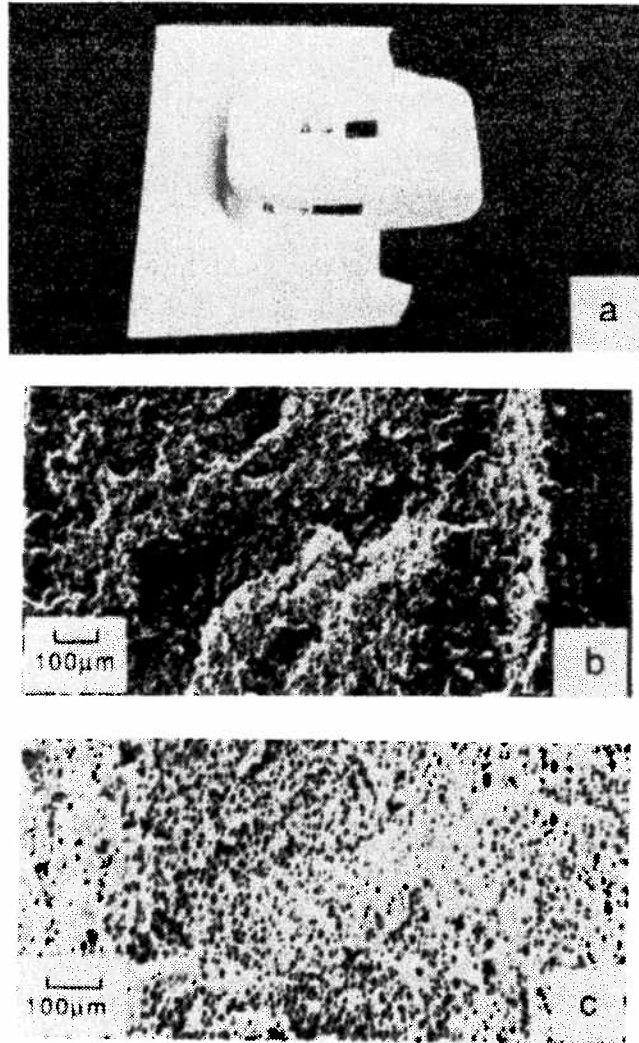


that the reduction in the solubility of the gas with temperature can provide a very significant driving force for bubble nucleation even without creating supersaturation condition. Thus an alternative to the process shown in Figure 1 would be to saturate the polymer at a certain temperature and pressure (this could be room temperature or an elevated temperature) and then raise the temperature of the polymer to cause bubble nucleation while maintaining the gas pressure at the level used for saturation. This principle has been employed by Park and Suh<sup>(17)</sup> to create microcellular structure in extruded filament. This advance is a significant step toward production of microcellular polymers in a continuous process.

A thermoforming process to produce microcellular parts was developed by Kumar<sup>(7,18)</sup>. In this process a polymer sheet saturated by gas is thermoformed using a heated mould. Thus the shape of the part is achieved first, and the foaming is completed later in the heated mould. Figure 10 shows a picture of a microcellular container produced by this process, which can be readily adapted to produce microcellular components by thermoforming from a plastic sheet.

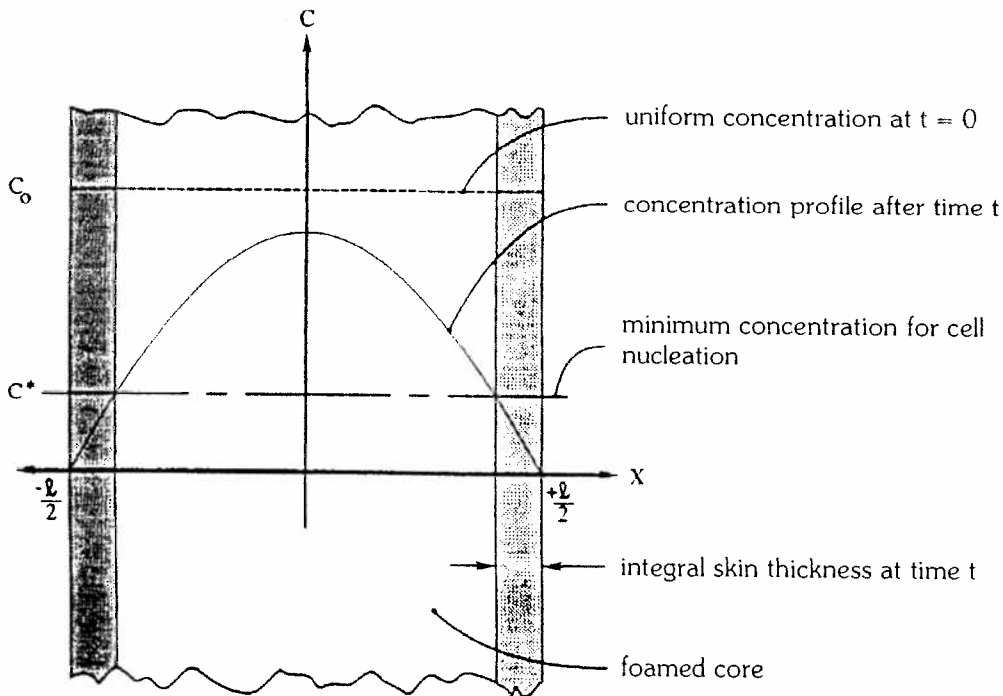
A skin of unfoamed polymer can be created on the microcellular foam by letting the gas diffuse out of the surface layers prior to foaming<sup>(19)</sup>. This

**Figure 10** Example of a microcellular part made by a modified thermoforming process: (a) photograph of a microcellular container; (b) scanning electron micrograph of a sample from container bottom; (c) from the container wall. The average cell size is approximately  $7\ \mu\text{m}$ <sup>(18)</sup>



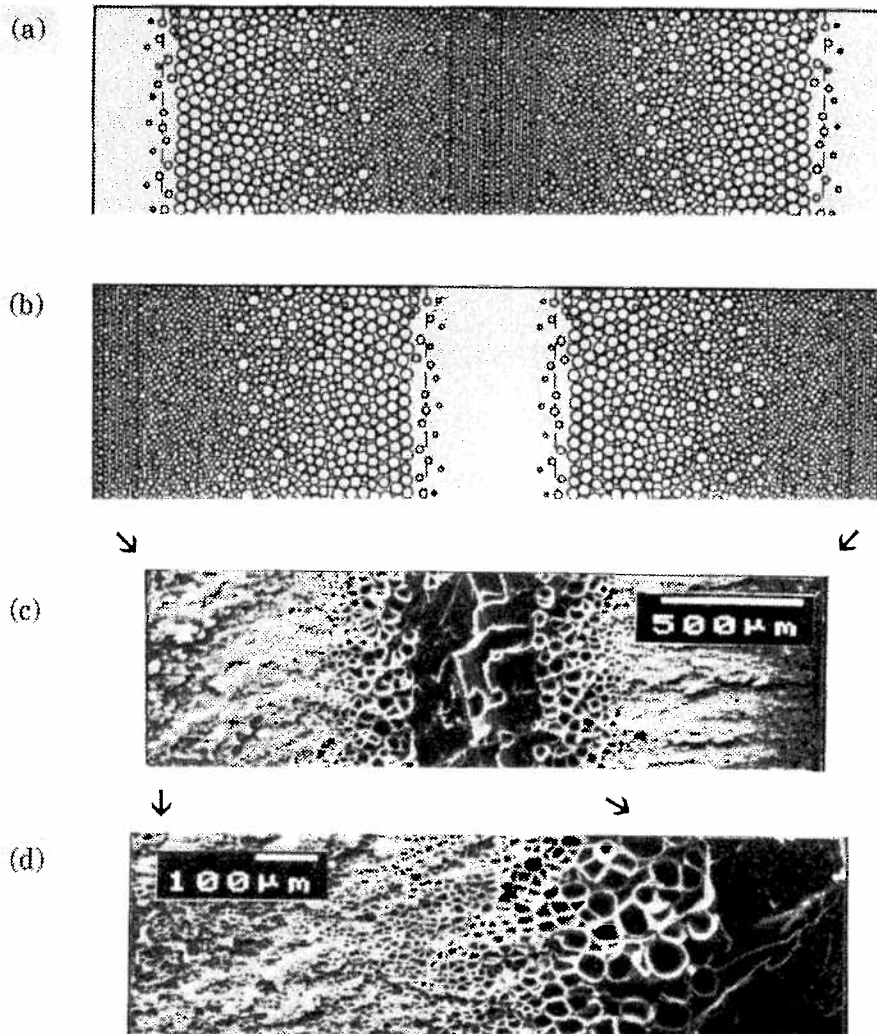
simple modification to the original process is illustrated in Figure 11. In the region where the gas concentration in the polymer drops below the minimum concentration needed for nucleation  $C^*$ , bubbles do not nucleate when the polymer is heated resulting in an unfoamed skin. The thickness of this solid skin can be easily controlled by monitoring the time allowed for gas desorption. Thus microcellular foams with a desired skin-core structure can be created for load bearing applications. In PET foams a crystalline skin integral to the foam core can be produced<sup>(11)</sup> creating a cellular composite material with higher specific strength.

**Figure 11** Schematic showing development of a skin region as a function of gas desorption time.  $C^*$  is the minimum concentration needed for bubble nucleation<sup>(19)</sup>



Research on non-destructive evaluation of the microcellular structure, and on development of sensors for in-process control of the microstructure has recently been initiated<sup>(20, 21)</sup>. The controllability of microstructure is demonstrated in Figure 12, where a scanning electron micrograph of a polycarbonate specimen with a solid unfoamed core surrounded by layers of microcellular polymer is shown. These advances point to the possible creation of composite structures designed to deliver the desired mechanical and thermal properties with smaller use of polymer.

**Figure 12** Illustration of control of microstructure: (a) schematic of foamed core with solid skin produced by the process shown in Figure 11; (b) schematic of an inverted structure with a foamed skin and a solid core; (c) and (d) scanning electron micrographs showing the structure in (b) produced in a polycarbonate specimen<sup>(21)</sup>



### IMPACT OF MICROCELLULAR POLYMERS

There is a recognized need for minimizing the consumption of our natural resources. Further, there is an increased awareness that in processing the natural resources the environment must be protected. Microcellular processes and materials address both of these concerns, and are therefore likely to strongly impact the way plastics are used in the future.

Wherever solid plastics are used today, there is the potential of significant reduction in the amount of material used by employing microcellular plastics. The savings in material and transportation costs

could potentially be very significant for a number of mass produced plastic items. In aircraft, for example, the weight saving by use of microcellular plastics could significantly enhance payload efficiency. And although the mechanical property data available so far is limited, there is an indication that the microcellular structure could improve the toughness and fatigue life of plastics. In the long run, I expect that these materials will be used in a number of applications, e.g. packaging, automotive, home construction, toys, aerospace, medical prostheses, telecommunications, to name a few. As no harmful chemicals are used in the microcellular process, it is likely that microcellular polymers will replace many cellular polymers now produced by processes that damage the environment. The ability to control the microstructure and create composite structures will greatly increase the range of applications of these materials. I expect that by the turn of the century, these novel materials will be in widespread use.

### ACKNOWLEDGMENTS

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### **BIOGRAPHICAL NOTE**

#### **Vipur Kumar**

Vipin Kumar came to the USA in 1970, after graduating from the Indian Institute of Technology in Kampur, India. After getting an MS and an MBA he worked for the ITT Corporation for nearly ten years. In 1984 he joined the Massachusetts Institute of Technology Polymer Processing Program where he first conducted research in the area of microcellular plastics. In 1988 he earned a PhD from MIT, and has since been on the Mechanical Engineering faculty at the University of Washington, Seattle, USA. In 1992 he started the Cellular Composites Consortium at the university, which he now directs.