

A Model for the Unfoamed Skin on Microcellular Foams

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In microcellular plastics, an unfoamed skin that is integral with the foamed core can be created by allowing the nucleating gas to diffuse from the surfaces of a gas saturated specimen prior to foaming. In this paper, a semi-empirical model is proposed that predicts the skin thickness variation in microcellular foams as a function of gas desorption time. The model shows good agreement with experimental results on the polycarbonate-carbon dioxide system.

INTRODUCTION

The idea of introducing very small bubbles, of order 10 μm , into plastics was first developed by Martini, Suh, and Waldman (1,2) as a means to reduce the amount of plastic used to produce a part without compromising the mechanical properties. The basic microcellular process consists of two stages. In stage one, the polymer sample is saturated with a nonreacting gas in a pressure vessel at a temperature below the glass transition temperature of the polymer. In stage two, the saturated sample is removed from the pressure vessel, creating supersaturation, and heated to the glass transition temperature of the polymer. A large number of bubbles nucleate upon heating, and since bubble growth is limited by high polymer viscosity, it is possible to obtain 10 μm bubbles. The microcellular process works well with amorphous polymers. Most of the work on microcellular plastics to date has been done with polystyrene (2-5). Recently, the microcellular structure has been successfully produced in polycarbonate (6,7) and in PVC (8), using carbon dioxide as the nucleating gas.

By a simple modification of the original process, a smooth skin of desired thickness composed of original, unfoamed polymer that is integral with the foamed core can be created. This is achieved by simply delaying the heating of the saturated polymer in stage two for a sufficiently long time to allow gas to diffuse from the surfaces, causing the gas concentration to drop below that required for bubble nucleation. Figure 1 shows an assembly of overlapping micrographs of a polycarbonate specimen from the left edge to the specimen center. The sample was allowed to desorb for 6 h prior to foaming. A skin region, approximately 200 μm thick, can be seen at the left edge of the specimen. This technique to produce an integral skin was first used by Kumar (9) to create microcellular polystyrene foams with various

skin thicknesses. The possibility of creating an unfoamed polymer skin in this manner was also recognized by Hardenbrook, *et al.* (10), who incorporated a degassing device in their process. A smooth, integral skin offers many advantages. For example, it can be painted and decorated as desired. Furthermore, the strength and stiffness of the foam can be engineered to meet specific requirements by designing a skin of appropriate thickness. In this paper, we examine the key process parameters and present a theoretical model to predict the skin thickness in microcellular foams.

THEORY

Consider a thermoplastic sample that has been placed in an atmosphere where it is surrounded by a nonreactive gas at an elevated pressure. Over time, the sample will absorb the gas until it has become saturated. The concentration of gas in the sample at saturation is given by Henry's Law.

$$C_0 = HP_s \quad (1)$$

where

C_0 = concentration of gas in units of mg of gas per g of polymer,

H = solubility of the gas in the polymer at the saturation temperature, in units of mg of gas per g of polymer per MPa,

P_s = saturation pressure in MPa.

If the external pressure is removed from the sample, the gas absorbed will begin to diffuse out of the sample. This desorption process may be modeled using Fick's law.

For a plane sheet of thickness l , which is initially saturated at a gas concentration C_0 , and suddenly

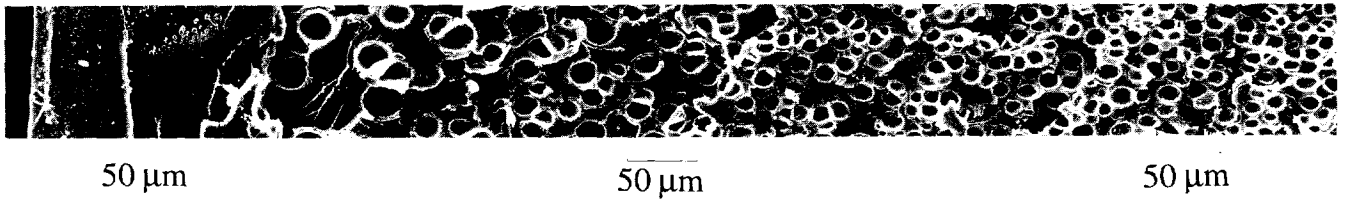


Fig. 1. Variation of the microstructure across the thickness in microcellular polycarbonate, showing an unfoamed skin region.

exposed to a concentration C_1 at the boundaries, the gas concentration at a distance x from the specimen center, after time t (see Fig. 2), assuming a constant diffusivity is given by Crank: (11)

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{2n+1} \exp\left(\frac{-\mathcal{D}(2n+1)^2 \pi^2 t}{\ell^2}\right) \cos\left(\frac{(2n+1)\pi x}{\ell}\right) \right] \quad (2)$$

where

C = concentration of gas at time t and distance x , mg/g

C_0 = initial gas concentration within the sample, mg/g.

C_1 = gas concentration at the boundary of the sample, mg/g

\mathcal{D} = diffusivity of the gas-polymer system, cm^2/s ,
 t = desorption time, s

ℓ = thickness of the sample, cm.

x = distance from the center of the sample, cm.

If a saturated sample is placed under atmospheric conditions, then we can assume that the gas concentration at the boundaries is negligible. This assumption is justified in view of the high saturation pressures used to achieve the initial gas concentration, C_0 , in the microcellular process (2, 4, 6, 8). Thus we can say that $C_1 = 0$ in Eq 2, and the concentration at time t and a distance x from the center of the specimen is given by

$$C = C_0 \frac{4}{\pi} \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{2n+1} \exp\left(\frac{-\mathcal{D}(2n+1)^2 \pi^2 t}{\ell^2}\right) \times \cos\left(\frac{(2n+1)\pi x}{\ell}\right) \right] \quad (3)$$

We now postulate that there is a minimum gas concentration, C^* , that is required for bubbles to nucleate. Depending on the time allowed for gas desorption, a skin region will be formed that consists of a layer of the polymer where the gas concentration had fallen below C^* before foaming. This is illustrated schematically in Fig. 2. If the gas concentration profile intersects the line $C = C^*$ at a distance $x = \xi$ from the center of the sample, then a skin of thickness δ

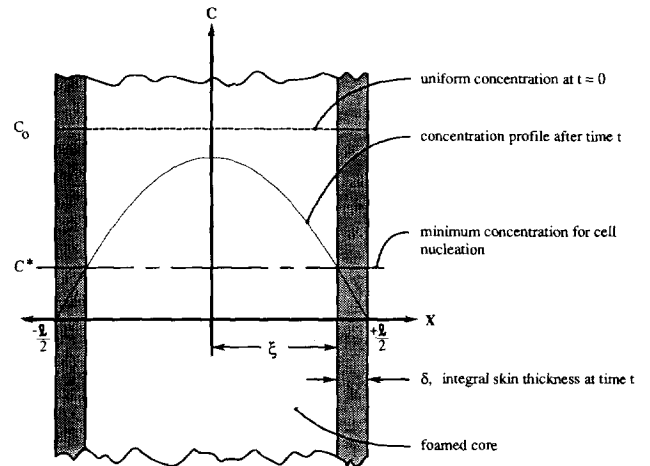


Fig. 2. Schematic showing the development of a skin region.

will be formed. Clearly both δ and ξ are functions of the gas desorption time t .

For a given desorption time t , the distance ξ can be found from Eq 3 by setting $C = C^*$ and solving for ξ using an iterative technique. Finally, the skin thickness δ is obtained from

$$\delta = \frac{\ell}{2} - \xi \quad (4)$$

EXPERIMENTAL

Polycarbonate samples were cut from GE Plastics' Lexan 9030 sheets, 1.50 mm thick, into approximately 3 cm x 3 cm squares. The samples were placed in a pressure vessel and saturated with carbon dioxide gas maintained at 4.8 MPa (700 psi) and 20°C. During saturation, the samples were periodically removed from the pressure vessel and weighed on a precision balance with an accuracy of 10 μg. Because the amount of gas absorbed by the samples was on the order of 10 mg, this method of monitoring gas sorption provided sufficient accuracy. The samples were considered saturated when two subsequent measurements, taken at least 6.0 h apart, were within 5% of each other. In our experiments, the samples became saturated in approximately 60 h. Upon saturation, the samples were removed from the pressure vessel and placed under atmospheric conditions, allowing gas desorption to occur. The samples were placed on edge during desorption to ensure that the same boundary conditions were applied to both sides. After 5, 10, 15, 30, and 60 min of desorption, the

samples were foamed by heating them in a glycerin bath maintained at 110°C, for 30 s. Beyond 60 min of desorption time, the samples were foamed at 1 h intervals, up to a desorption time of 6 h.

After foaming, the samples were placed in liquid nitrogen, and subsequently fractured to expose the internal microstructure. The fractured surfaces were made conductive by deposition of Au-Pd vapor, and were studied using scanning electron microscopy (SEM). For each sample, four SEM micrographs were taken of the edge region, two per side. The micrographs on a given edge were taken at least several millimeters apart to ensure an independent measurement. Once the micrographs were obtained, a line was drawn to define the edge of the sample. From this edge line, eight to ten perpendicular lines were drawn across the micrograph, approximately 1 cm apart. We defined the skin thickness, δ , as the distance from the edge line to the point where a perpendicular line intersects the first bubble. Figure 3 is a schematic of a micrograph indicating individual skin thickness measurements. After making skin thickness measurements on the four micrographs for each sample, a mean skin thickness and a standard deviation were established.

RESULTS AND DISCUSSION

Figure 4 shows scanning electron micrographs of the skin region in polycarbonate at increasing desorption times. In all micrographs, the left edge of the sample is shown, and the magnification is the same

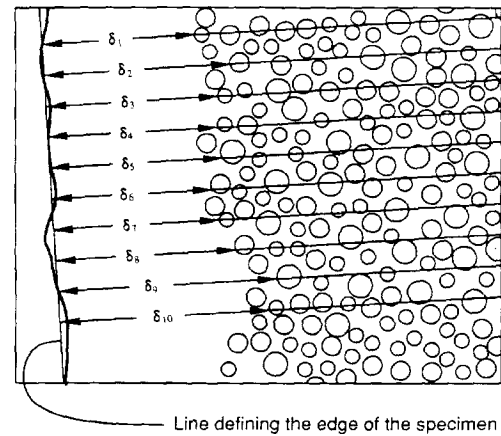


Fig. 3. Schematic showing the procedure used to determine the skin thickness from a scanning electron micrograph.

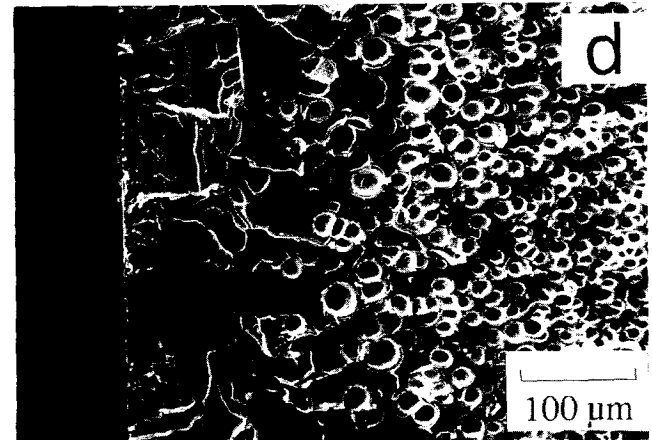
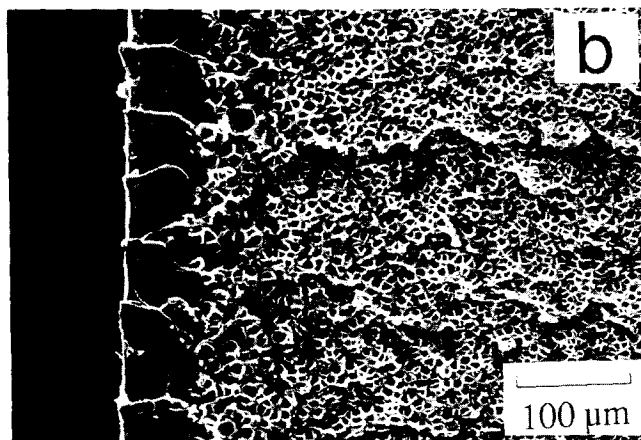
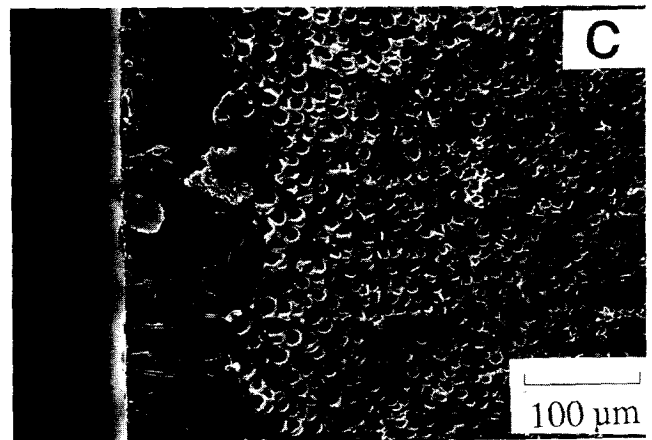
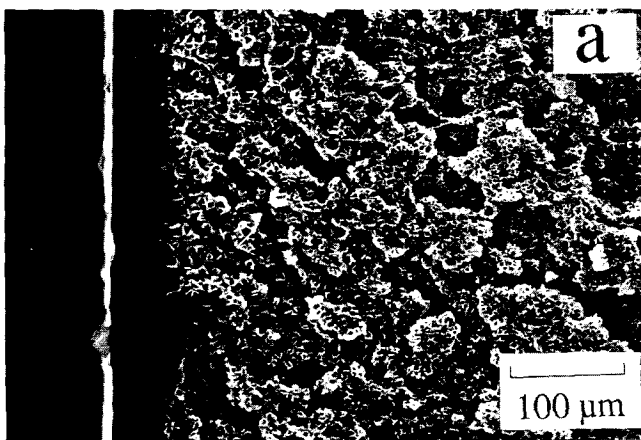


Fig. 4. Scanning electron micrographs showing the skin region in microcellular polycarbonate foam as a function of increasing desorption times. All micrographs were taken at a magnification of 200X. The desorption times are: (a) 5 min; (b) 30 min; (c) 2 h 10 min; (d) 5 h.

to aid in visual comparison. We can see that the skin thickness increases with desorption time, as a comparison of sample a and sample d would show. In addition to the increasing skin thickness, we can also see that the average cell diameter and the cell density change in the vicinity of the skin region as the desorption time increases. We can see that initially, the cell density is high and the average cell diameter is very small. As the desorption time increases, the cell density goes down and the average cell diameter goes up. This behavior is counter-intuitive, in that we might expect smaller bubbles in a given region with lower gas concentration. However, the average bubble size is strongly influenced by the number of bubbles that nucleate. Thus a sharp drop in the bubble density leads to larger bubbles (see sample d in Fig. 4), since fewer bubbles compete for the available gas volume at foaming conditions.

The behavior seen in Fig. 4 is intimately tied to the concentration profile within the sample at the time of foaming. In Fig. 5 we have plotted the concentration profile as given by Eq 3 at various desorption times for a polycarbonate sample. Note that the concentration profile has been shown only for a portion of the sample that is close to the edge, and that the gas concentration is given in units of mg CO₂/g polymer. The plot is based on an initial CO₂ concentration of 90 mg/g and an average diffusivity of 4.7×10^{-8} cm²/s (see Appendix). Because the value of the minimum concentration required for cell nucleation is not known for the polycarbonate-CO₂ system, we have plotted several assumed values of C* in Fig. 5. The theoretical skin thickness values as determined by Eq 4, corresponding to different C* values, have been plotted as the solid curves in Fig. 6, and compared to the experimental skin thickness data. The error bars shown in Fig. 6 represent one standard deviation for each sample determined from approximately 40 skin thickness measurements as previously described. From Fig. 6 we can see that a C* of approximately 30 mg/g fits the data well beyond a desorption time of 0.5 h. For times less than 0.5 h, we can see that the model underpredicts the actual skin thickness value. This discrepancy is likely due to a higher actual diffusivity at early desorption times compared to the average diffusivity used in the model. There are two factors that would tend to increase the gas diffusivity. First, the diffusivity in polymers is generally concentration dependent, and is therefore likely to be higher in the early stages of desorption. Second, when the sample is immersed in a glycerin bath for foaming (in this case 110°C), diffusion of gas from the sample surfaces occurs at the higher bath temperature for several seconds before the polymer foams, further depleting the gas concentration in the surface layers and increasing the skin thickness. Note that the model uses an average diffusivity measured at 20°C. Both of these factors affect the rate of diffusion from the surface layers, and their relative impact on the total skin thickness diminishes rapidly as the desorption time increases.

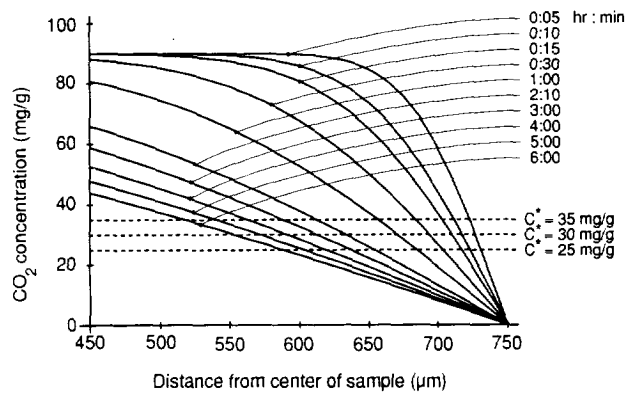


Fig. 5. Concentration profiles predicted by Eq 3 for 1.50 mm thick polycarbonate at various desorption times. Note that the concentration has been plotted only for the region close to the edge of the sample.

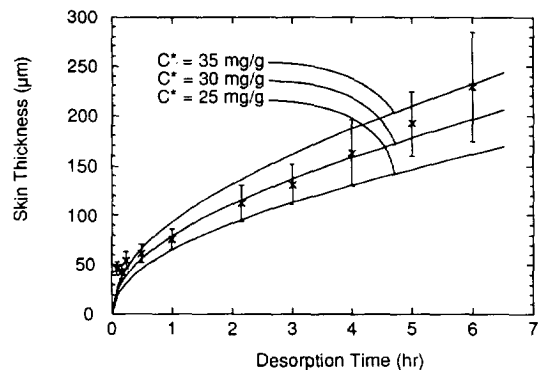


Fig. 6. Comparison of theory and experiment for the skin thickness of microcellular polycarbonate.

SUMMARY AND CONCLUSIONS

A smooth, integral skin made of the original polymer can be created in microcellular foams by allowing the gas to diffuse out of the surfaces of the saturated polymer prior to foaming. By controlling the gas desorption time, the thickness of the resulting skin can be controlled.

We have presented a model for predicting the skin thickness based on one-dimensional diffusion of gas from a saturated polymer specimen. The model shows good agreement with experimental data in the polycarbonate-CO₂ system, except in the early stages of desorption. In the early desorption stages, approximately 30 min in the polycarbonate-CO₂ system, the model underestimates the skin thickness because of the assumption of a constant diffusivity. Beyond the early desorption stage, the model predicts the skin thickness accurately. The model is especially useful for predicting the skin thickness in microcellular foams made from amorphous polymers.

APPENDIX

The average diffusivity of carbon dioxide in polycarbonate was measured in a desorption experiment. Polycarbonate samples, 3 cm × 3 cm × 1.5 mm, were

saturated with CO₂ at a given saturation pressure and 20°C. Upon saturation, the samples were withdrawn from the pressure vessel and weighed periodically on a precision balance with an accuracy of ± 10 μg, until the amount of carbon dioxide remaining in the samples was approximately 50% of the value at saturation. In our experiments, polycarbonate samples were saturated at two saturation pressures: 2.1 MPa (300 psi) and 5.5 MPa (800 psi), yielding different saturation concentrations at equilibrium.

For early states of diffusion, the amount of gas remaining in a plane sample at any time is related to the diffusion coefficient \mathcal{D} , by Crank (11)

$$\frac{M_t}{M_\infty} = 1 - \frac{4}{\sqrt{\pi}} \left(\frac{\mathcal{D}t}{l^2} \right)^{1/2} \quad (A1)$$

where

M_t = amount of gas remaining in the polymer

at time t , g.

M_∞ = amount of gas at equilibrium saturation, g.

\mathcal{D} = diffusion coefficient, cm²/s.

l = sample thickness, cm.

t = elapsed time in seconds.

If M_t/M_∞ is plotted against $\sqrt{t/l^2}$, then the slope R of the resulting straight line is given by:

$$R = \frac{4\sqrt{\mathcal{D}}}{\sqrt{\pi}} \quad (A2)$$

and the average diffusion coefficient can be found from:

$$\mathcal{D} = \frac{\pi R^2}{16} \quad (A3)$$

Figure 7 shows a plot of M_t/M_∞ as a function of $\sqrt{t/l^2}$ for our desorption experiments. From this data the average diffusion coefficient for a saturation pressure 2.1 MPa (300 psi) was determined to be 3.3×10^{-8} cm²/s. For a saturation pressure 5.5 MPa (800 psi) the average diffusion coefficient was determined to be 5.1×10^{-8} cm²/s. The diffusion coefficient is 4.8 MPa was estimated to be 4.7×10^{-8} cm²/s by interpolation.

ACKNOWLEDGMENTS

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NOMENCLATURE

C = Gas concentration, mg/g.

C_0 = Equilibrium gas concentration, mg/g.

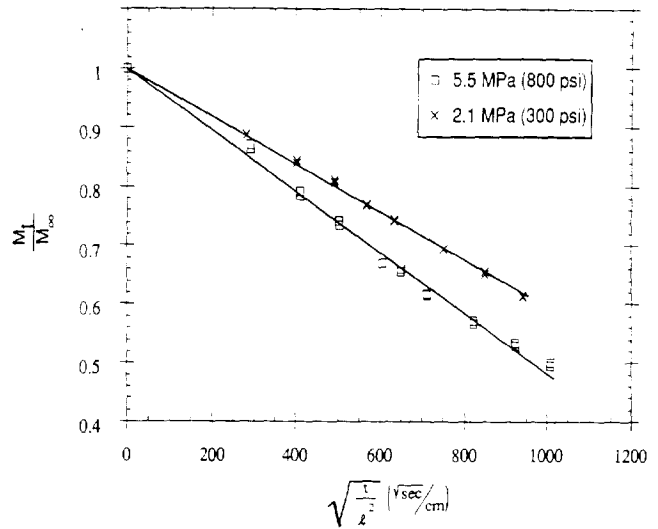


Fig. 7. Desorption plot for the polycarbonate-carbon dioxide system.

C_1 = Gas concentration at boundary of sample, mg/g.

\mathcal{D} = Diffusivity, cm²/s.

H = Henry's law constant, mg gas/g polymer MPa.

l = Thickness of sample, cm.

M_t = Mass of gas in sample at time t , g.

M_∞ = Mass of gas in sample at equilibrium, g.

P_s = Saturation pressure, MPa.

x = Distance from center of sample, μm.

δ = Skin thickness, μm.

ξ = Distance from center of sample to intersection of concentration profile and C^* lines, μm.

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