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Gravitational Effects on Closed-Cellular-Foam Microstructure

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Polyurethane foam has been produced in low gravity for the first time. The cause and distribution of different void or pore sizes are elucidated from direct comparison of unit-gravity and low-gravity samples. Low gravity is found to increase the pore roundness by 17% and reduce the void size by 50%. The standard deviation for pores becomes narrower (a more homogeneous foam is produced) in low gravity. Both a Gaussian and a Weibull model fail to describe the statistical distribution of void areas, and hence the governing dynamics do not combine small voids in either a uniform or a dependent fashion to make larger voids. Instead, the void areas follow an exponential law, which effectively randomizes the production of void sizes in a nondependent fashion consistent more with single nucleation than with multiple or combining events.

Introduction

POLYMERIC foams represent a large fraction of industrial material science, with applications ranging from thermal and sound insulation to building and packing structures as well as a variety of premium specialty uses.[1,2] Because of their low cost and high strength-to-weight ratio, the potential for foam production in space-related assembly and manufacture has attracted scientific interest.[3–6] The present rocket experiments examined foam formation in low gravity.[4] The results center on a statistical analysis of cellular location and size through a direct comparison between polyurethane foams produced under otherwise identical conditions in unit and low gravity.

Low gravity was produced during a sounding-rocket flight as reported previously,[3] and a quantitative comparison of structural properties enlarges the previous reports of efficient foam production in low gravity.[4] The aim of the original experiment was to determine the mixing efficiency of the reactants in the formation of hard urethane foams. As a function of observed gravity level, observations were made of the foam setting time, the final shape of the foamed material, and the ability of the foam to withstand re-entry and landing loads. The present work takes up the quantitative aspects of cellular geometry. Using image analysis techniques, we classify the cellular centers according to size and number and undertake to examine distributional differences that result from the gravitational history of the samples. In contrast with the previous reports,[3,4] the original aim of understanding the engineering parameters of foam production has been expanded to include the present concerns for predicting material properties such as void ratio, cellular size, and placement, along with some estimates of comparative foam strengths.

The scientific interest in these foams depends on detrimental influences of foam settling and restructuring during Earth-based processing. Gravitational effects on foams are well documented using a variety of experimental configurations. For vertically misaligned foam columns, a 1-deg angular tilt from the gravity vector leads to "pronounced effects on surfactant concentration" along the column length, with back circulation and fluid channeling.[7] In reduced gravity, a number of investigators have examined froth production,[8] chemical reaction on foams,[9–10] and metallic foaming.[11–13] In addition to gravity, other body forces such as magnetic fields[14] show a pronounced effect on bubbling of ionic metals such as Ni, Co, and Cu. From these results, some qualitatative conclusions can be drawn about how gravity affects foam formation. In brief, gravity 1) alters gas-bubble purging,[4] 2) leads to bubble coalescence from film drainage,[15–18] 3) increases surfactant requirements[15] for an equivalent suspension of solids, 4) increases bubble–particle collision velocities[15] during reaction, 5) alters the impeller–foam contact geometry and volume during rapid stirring,[4] and 6) changes the heat and mass transfer from convection during thermal reaction.[4,9,17] For hard foams that cure in several minutes, gravity-induced film drainage and thinning of bubbles is secondary to the large mass and heat transfer differences during chemical reaction.[9] For these reasons, careful consideration should be given to gravity effects in foam production, with particular attention to mixing and gas-void distributions in contrasting acceleration environments.

Materials and Methods

Experimental Foam Protocol

All experiments were conducted using a polyurethane foaming process.[3,4] The external foam volume was approximately 2300 cm^3. The foam underwent a progression of mixing, creaming, expansion, and hardening steps before being sampled for its internal properties. To summarize the production cycle and material selection, a two-part mixture was employed.

The polyurethane foam formulated for Consort I included a solution of sucrose-based polyol, catalyst, surfactant, and fluorocarbon blowing agent in one chamber and an oligomeric diisocyanate in another chamber. The diisocyanate was incompatible with the polyol and the catalyst, so that the components had to be stored apart until reaction was desired.

The following proportions (Fig. 1) were used: 1) polyol: Voranol 360© (Dow Corning), 100 g; 2) catalyst: DABCO 33LV0© (Air Products), 2.0 g; 3) surfactant: DC 193© (Dow Corning), 1.5 g; 4) blowing agent: Genetron 11© (Allied), 3.4–3.6 g; and 5) diisocyanate: PAPI-94© (Dow Corning), 92.5 g.

The materials from the two chambers were mixed shortly before the beginning of the low-gravity period. The resultant mixture was then driven through an exit funnel. Chlorofluorocarbon begins to come out of the solution at the cream time, which occurred 28–37 s after mixing. Within 10 s of the cream time, the material began to expand. A 10-to-20-fold volume increase was thus achieved 180–200 s after the initial mixing. The foam reached its final state after 120–180 s of additional curing. A successful experiment therefore depended on each stage of the process (total of 300–360 s) occurring in sequence in a low-gravity flight.

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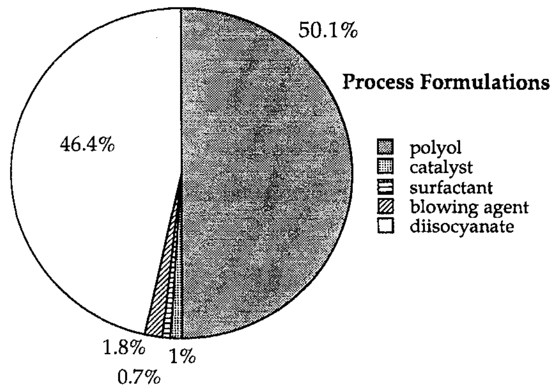

Fig. 1 Chemical formulation of hard-processed foams.

Spatial Analysis of Foam Microstructure

Upon recovery of the foam sample, cross sections were taken from a medial, nearly circular cut. The image of cellular orientation was recorded on video, then photographed for selected frames. The photographic images were digitized by tracing the ovoid cellular surface, then scanned with a spatial resolution of 512×512 pixels. The digital images were further analyzed for geometric parameters along the major- and minor-axis directions using a main image analysis program written in the computer language C. All images were thresholded to include cellular microstructure larger than 2 mm.

The outline and axial direction of each cell were determined using a chain coding algorithm and analyzed spatially as a best-fitted centroid. For each cell, the geometry was stored in the form of its ellipsoidal orientation with respect to vertical (arbitrary pixel units) as well as the number of cells in a frame, then calibrated (normalized) to the average value for all cells (average density, 50–200 cells per frame). As the spatial parameters changed with unit- and low-gravity processing, the geometric measures of cell orientation were plotted as a function of applied accelerations.

Low-Gravity Protocol

Low gravity was induced using a sounding rocket carrying the experimental payload, Consort I. It contained six experimental apparatuses and housed 149 experiments. The payload compartment was approximately 3.5 m long, 0.44 m in diameter, and 290 kg in mass. Based on accelerometer readings, approximately 7 min of low gravity were achieved. Following takeoff, the interior payload temperature remained constant at 20°C, whereas the reaction temperature for foam mixing, curing, and hardening stages varied from 20 to 48°C. The rocket interior maintained an air pressure of 1 atm.

Results and Discussion

Figure 2 shows the digitized foam cross sections from unit-gravity and low-gravity experiments. The total numbers of cells that registered above the size threshold were 53 in unit-gravity and 232 in low-gravity samples. The x and y centers for each void were found from their centroids; then a nearest-neighbor partitioning of the total foam area was divided according to standard Voronoi constructions.[19] This polygonalization of void centers creates a shape "grammar" to regionalize the foam surface. The Voronoi construction was originally developed as a contouring routine created to determine the most compact division of space with successive neighbors on a map. Because the space divisions give the minimum area between void centers, they may equivalently be taken as the void density. The objective behind classifying the foam microstructure using the most compact division method was to describe texture for interacting voids within a two-dimensional grid defined for nearest neighbors. From Fig. 2, for example, it is seen that smaller voids tend to cluster around large voids. This representation gives an intuitive and direct way to classify the neighborhood of void sizes.

Table 1 shows the results of statistical comparison for size and shape parameters. Overall the Earth-formed froth displayed more elongated, larger microstructure. Observations of the entire sample[4] concluded that both were well mixed and chemically uniform prior to hardening, but displayed different cellular sizes and shapes. To

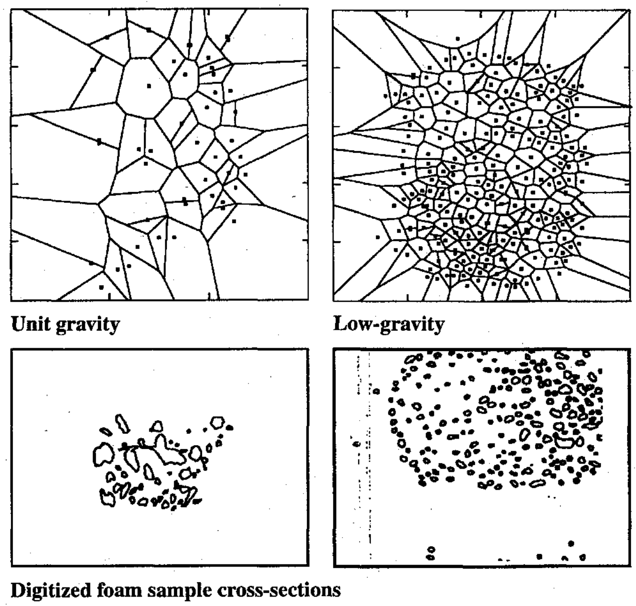

Fig. 2 Digitized foam sample cross-sections and their corresponding spatial distribution using a Voronoi construction; statistical distribution of cellular centers.

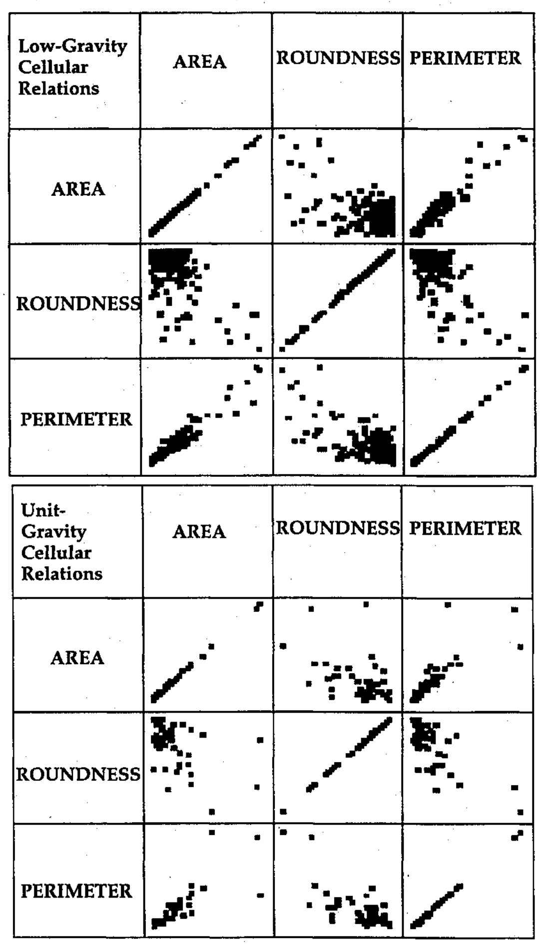

Fig. 3 Effect of void size on shape (roundness) and perimeter for both unit- and low-gravity processing.

make these results quantitative, cross sections were subjected to rigorous statistical reduction for size and shape parameters. In Figs. 2 and 3, average area, perimeter, and roundness are reported along with standard deviations and minimum/maximum. In general, the unit-gravity voids were formed with approximately twice the average radius of the low-gravity sample. The spread in sizes was much less uniform in unit gravity, with a consequent larger standard deviation. A roundness index (circle = 1.00) was applied to both samples

Table 1 Size and shape parameters for average quantities compared for unit- and low-gravity foam samples

	Area		Roundness		Radius		Total number	
Parameter	Low gravity	Unit gravity	Low gravity	Unit gravity	Low gravity	Unit gravity	Low gravity	Unit gravity
Average	102	1,350	0.90	0.75	6.12	12.7	231	53
Standard deviation	48	8,325	0.12	0.21	1.79	24.1		
Medium	92	140	0.94	0.80	5.61	7.76		
Maximum	346	60,796	1.00	1.00	16.7	180		
Minimum	51	50	0.43	0.06	4.00	3.99		

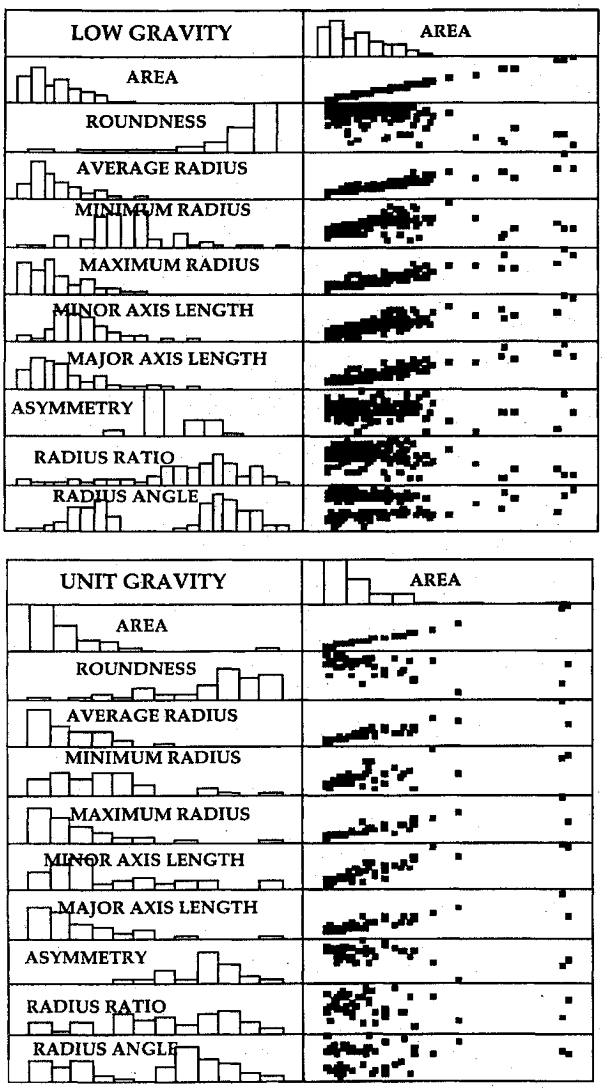

Fig. 4 Histograms and associated correlations between void size and geometrical shape parameters compared between low- and unit-gravity samples.

to identify any elongation properties associated with gravitational stresses during mixing or hardening of the foam. The unit-gravity sample showed a 17% lower roundness than the low-gravity one and a doubled deviation about the mean. Of particular interest is that although the small voids show comparable morphology in the two both samples, the larger voids account for the maximum in elongation and radius for the unit-gravity foam. These large voids are particularly detrimental to the expected material strength and thermal properties, the latter owing to the large differences in thermal conductivity between solid and air. As indicated in previous discussions,[4] the cause of elongation and size changes with gravity remains an active area of research.

In an effort to identify correlations between spatial distribution of voids and their size and shape, a complete correlation analysis was undertaken. Figure 3 compares the microstructure parameters of unit- and low-gravity foams for area, roundness, and

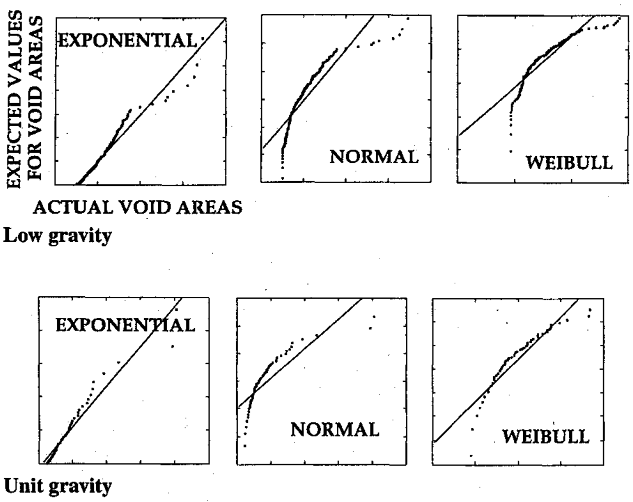

Fig. 5 Statistical distribution governing foam void areas in low- and unit-gravity samples.

perimeter. Roundness is inversely related to both area (correlation coefficient, −0.366 and −0.372, respectively, for unit- and low-gravity foams) and perimeter ($R = -0.518$ and −0.540). This finding suggests that larger voids tend to elongate more than smaller ones. This outcome could be anticipated if pancake-like slumping of material governs gravitational effects in larger voids more than in smaller ones. Figure 4 shows a complete histogram of the size and shape parameters. Table 2 compares the correlation coefficients for the matrix of geometric factors. In general, these results confirm the previous qualitative observation[4] that the larger void fraction in unit-gravity foam samples likewise favors a larger asymmetry between minor and major axes for each void shape. Both roundness and asymmetry factors correlate negatively with all major size classifications based on area and radius. Note that the radius ratio between major and minor axes is unimodal in low gravity, but bimodal in unit gravity. The asymmetry between unit-gravity samples, based on minor and major cross-sectional axes, suggests a preferred direction of elongation in the unit-gravity sample and is consistent with a pancake-like slumping of larger voids with applied accelerations.

The histogram for void areas in Fig. 4 was tested against three statistical distributions: exponential, Gaussian (see Fig. 5), and Weibull. In both unit- and low-gravity samples, the sizes appear to follow an exponential distribution and not to fit either a random (Gaussian) distribution or a Weibull distribution. The significance of these statistical laws concerns the formation of the voids themselves. For processed hard foams, the gravitational differences are highlighted between the various statistical distributions, as they fit the void size spectrum. Log–log values are shown for expectations (perfect fit) based on uniform, Weibull, and exponential distributions and compared with the actual (measured) foam voids. A linear relation implies that the underlying cause of the size fluctuations is consistent the assumptions of the governing statistical law. For example, the well-known (uniform) Gaussian model suggests that fluctuations are random with a bell-shaped signature distributed around the mean. An exponential distribution, on the other hand, is equivalent to Brownian noise, with a kind of thermal randomness that distinguishes (flattens) its fluctuations particularly at the small-scale end of the spectrum. A Weibull distribution is commonly found in systems engineering and can be thought to characterize a foam

Table 2 Matrix of Spearman correlation coefficients for unit- and low-gravity processed foam samples

	Area	Roundness	Av. radii	Asymmetry	Perimeter	Radius ratio	Radius angle
			Unit-gravity results				
Area	1.000						
Roundness	−0.372	1.000					
Av. radii	0.950	−0.403	1.000				
Asymmetry	−0.214	0.121	−0.241	1.000			
Perimeter	0.947	−0.518	0.983	−0.254	1.000		
Radius ratio	−0.213	0.923	−0.231	0.007	−0.339	1.000	
Radius angle	−0.022	−0.222	0.020	0.102	0.057	0.132	1.000
			Low-gravity results				
Area	1.000						
Roundness	−0.366	1.000					
Av. radii	0.961	−0.470	1.000				
Asymmetry	−0.074	0.080	−0.095	1.000			
Perimeter	0.958	−0.540	0.983	−0.087	1.000		
Radius ratio	−0.200	0.831	−0.299	−0.053	−0.347	1.000	
Radius angle	−0.046	0.053	−0.066	0.232	−0.061	0.070	1.000

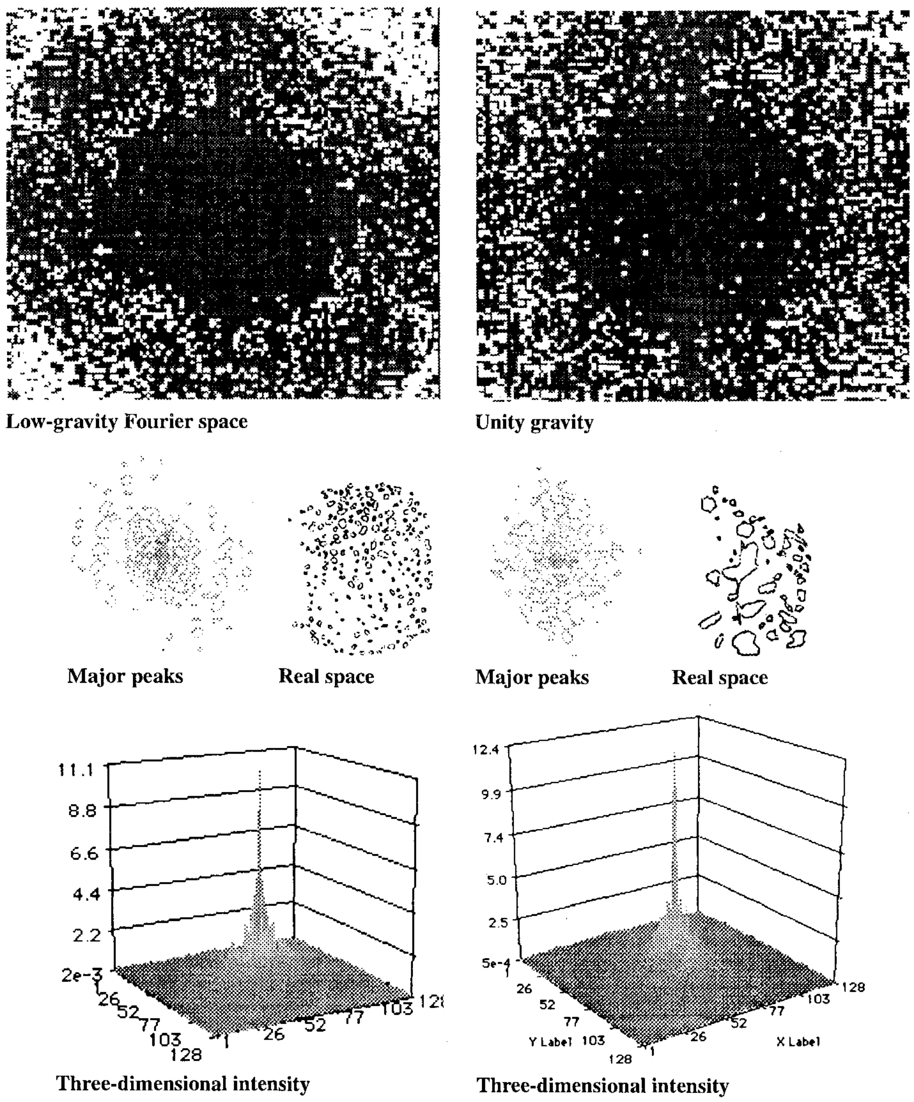

Fig. 6 Diffraction pattern of foam cross sections for unit- and low-gravity samples.

void formation mechanism that is subject to dependent failures. If one part of the system changes, other parts will rapidly follow suit according to a Weibull mechanism.

For the foam data, the best fit is found for exponential distributions. This suggests that thermal (random) interaction between void sizes is a good model for the foam images in both unit and low gravity. The failure of uniform and Weibull distributions is noteworthy since this observation effectively excludes both many independent random variables combining in a multiplicative fashion (uniform) and a dependent failure model where gravitational elongation of one void effectively captures the neighbors in a dependent fashion.

The spatial analysis of void production for different foam samples was concluded with a high-resolution diffraction picture taken from void areas. Diffraction patterns of foam cross sections for unit- and low-gravity samples are shown in Fig. 6. Photographic negatives of both foam samples were subjected to a Fourier transformation in two dimensions, and then spatial dissimilarities could be mapped into the frequency domain. The Fourier transform was achieved with a resolution of 128 × 128 pixels and shows the effects of size inhomogeneity as a more randomly arrayed set of intensity–frequency coordinates in the unit-gravity sample. The more uniform spatial distribution and smaller standard deviation in low-gravity void size appear as a narrower scattering pattern.

As noted[4] in the literature, the formation of voids in hard foams is not fully understood at present. Classification of the void area histograms, however, does indicate that an exponential distribution best fits the size fractions. This finding effectively excludes both a Gaussian and dependent failure model (Weibull distribution) and may finally bear on issues of whether the large voids form at the expense of combining smaller voids (e.g., Ostwald ripening). To summarize, the qualitative discussion of the more spheroidal voids and good mixing properties in low-gravity foams[4] now can be placed on a quantitative basis. Deductive evidence is found for considering the formation process itself as random in nature with a general exponential distribution for sizes.

In addition to foam applications in structural and insulation uses, low gravity may bear on the fundamental design of new processing technologies. Several biological and metallurgical examples of possible froth behavior warrant future consideration. Previous experimental evidence has supported the idea of higher particle transport in low gravity on uncured froths. The importance of particle transport in separating premium biologicals and viruses has been noted.[5] *E. coli* bacteria could not foam-float in unit gravity unless 5% sodium salt solutions were added. The successful 100% recovery of salted froths, however, was found to alter the morphology of bacteria[17] and also to concentrate the froth tailings with large amounts of salt. Such ionic salts and their frothing power would be less critical for low-gravity processing, and hence separations might be achievable in growth media alone. Similar effects of high osmolarity on more delicate cells (e.g., red blood cells) precludes salt as an aid to floating other large biologicals. Low-gravity foaming behavior with particle separations bears on adjunct processes such as metallic foam formation.[11–13,16] In particular, selectivity for splitting a mixed feed of variable sizes and floatabilities may hold promise not only for concentrating or stripping single components (e.g., proteins and viruses),[18] but also for separating whole cell types or large metallic complexes. In summary, we conclude that low-gravity processing of urethane foams can result in a quantitatively lower void size and elongation than in Earth-formed foams.

Concluding Remarks

The detailed analysis of spatial patterning among foam voids for low-gravity vs unit-gravity processing of hard urethane has quantitatively confirmed a number of significant observations. Low-gravity production yielded a (rms) 17% increase in the void roundness and an effective 50% reduction in average void radius. The standard deviation for all void size parameters revealed that a more homogeneous foam could be produced in low than in high gravity. The trend in void shapes reveals greater elongation and radial asymmetry for larger voids (negative correlation), independent of the processing environment.

Correlations between size–shape parameters are most notable between area and perimeter for both samples, with a positive coefficient of greater than 0.95. The resulting geometric relations govern both samples and seem a predictable product of geometric constraints for nearly circular slices. In contrast, however, the histogram for the axial-radius ratio (between major and minor lengths) reveals a bimodal distribution of ratios for the unit-gravity sample. This observation suggests that a directional preference for large elongations in large voids appears only in the unit-gravity environment. Hydrostatic pressure for large voids may account for this difference, and these issues are being actively investigated by systematically varying the gravity in a low-gravity aircraft for different fluid fractions.

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References

[1]Saunders, J. H., and Frisch, K. C., *Polyurethanes: Chemistry and Technology: Part 1,* Chemistry Editions, Wiley-Interscience, New York, 1962, pp. 261–343.

[2]Bruins, P. F. (ed.), *Polyurethane Technology*, Wiley-Interscience, New York, 1969, pp. 67–77.

[3]Wessling, F. C., and Maybee, G. W., "Consort I Sounding Rocket Flight," *Journal of Spacecraft and Rockets*, Vol. 26, No. 5, 1989, pp. 343–351.

[4]Wessling, F. C., McManus, S. P., Mathews, J., and Patel, D., "Foam Formation in Low Gravity," *Journal of Spacecraft and Rockets*, Vol. 27, No. 3, 1990, pp. 324–329.

[5]Noever, D. A., "Foam Fractionation of Particles in Low Gravity," *Journal of Spacecraft and Rockets*, Vol. 31, No. 2, 1994, pp. 319–322.

[6]Thomas, S., "Effects of the Earth Orbit Environment on Thin Wall Bubbles," *Journal of Spacecraft and Rockets*, Vol. 27, No. 4, 1990, pp. 438–445.

[7]Valdes-Krieg, E., King, C. J., and Septon, H. G., "Effect of Vertical Alignment on the Performance of Bubble and Foam Fractionation Columns," *AIChE Journal*, Vol. 21, No. 14, 1975, pp. 400–402.

[8]Grodzka, P. G., and Bourgeois, S. V., "Chemical Reactions in Low-G," AIAA Paper 78-166, Jan. 1978, p. 5.

[9]Naumann, R. J., and Mason, E. D., "Summaries of Early Materials Processing in Space Experiments," NASA TM-78240, Aug. 1979.

[10]Patten, J. W., and Greenwell, E. N., "Closed Cell Foams Produced from Sputter Deposited Aluminum–Experiments in Earth and Space," AIAA Paper 77-193, Jan. 1977.

[11]Pond, P. B., and Winter, J. M., "SPAR IX Postflight Engineering Report," *Space Processing Applications Rocket Project (SPAR) SPAR IX Final Report*, NASA TM-82549, Jan. 1984, pp. 1–11.

[12]Schaumlautfer, W., "TEXUS 5 Experiment: Metallschaumherstellungen," Dornier System, Final Rept. 5, Dusseldorf, Germany, March 1982.

[13]Skrylev, L. D., and Trigubenko, T. Z., "Magnetic Field Effects on Foam Floatation of Metallic Ions," *Zhurnal Prikladnoi Khimii*, Vol. 49, No. 18, 1976, pp. 1629–1635.

[14]Scheludko, A., Toshev, B. V., and Bojadjiev, D. T., "Attachment of Particles to a Liquid Surface," *Journal of the Chemical Society, Faraday Transactions*, Vol. 172, No. 16, 1976, pp. 2815–2825.

[15]Hudales, J. B. M., and Stein, H. N., "The Influence of Solid Particles on Foam and Fluid Drainage," *Journal of Colloid and Interface Science*, Vol. 140, No. 3, 1990, pp. 307–320.

[16]Steiner, L., Hunkeler, R., and Hartland, S., "Behaviour of Dynamic Cellular Foams," *Transactions of the Institute of Chemical Engineers*, Vol. 55, No. 8, 1977, pp. 153–163.

[17]Gaudin, A. M., Davis, N. S., and Bangs, S. E., "Floatation of *Escherichia coli* with Sodium Chloride," *Biotechnology and Bioengineering*, Vol. 4, No. 5, 1962, pp. 211–220.

[18]Morrow, A. W., "Concentration of the Virus of Foot and Mouth Disease by Foam Floatation," *Nature*, Vol. 222, No. 9, 1969, pp. 489, 490.

[19]Okabe, A., Boots, B., and Sugihara, K., *Spatial Tesselations: Concepts and Applications of Voronoi Diagrams*, Wiley, New York, 1992, pp. 335–362.

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