FABRICATION OF CELLULAR MATERIALS

Robert K. Prud'homme, Ilhan A. Aksay, and Rajeev Garg

Department of Chemical Engineering and the Princeton Materials Institute
Princeton University, Princeton, NJ 08544

INTRODUCTION

Nature uses cellular materials in applications requiring strength while, simultaneously, minimizing raw materials requirements. Minimizing raw materials is efficient both in terms of the energy expended by the organism to synthesize the structure and in terms of the strength-to-weight ratio of the structure. Wood is the most obvious example of cellular bio-materials[1], and it is the focus of other presentations in this symposium. The lightweight bone structure of birds is another excellent example where weight is a key criterion. The anchoring foot of the common muscle[2] [*Mytilus edulis*] whereby it attaches itself to objects is a further example of a biological system that uses a foam to fill space and yet conserve on raw materials. In the case of the muscle the foam is water filled and the foot structure distributes stress over a larger area so that the strength of the byssal thread from which it is suspended is matched to the strength of interfacial attachment of the foot to a substrate. In these examples the synthesis and fabrication of the cellular material is directed by intercellular, genetically coded, biochemical reactions. The resulting cell sizes are microns in scale. Cellular materials at the next larger scale are created by organisms at the next higher level of integration. For example an African tree frog lays her eggs in a gas/fluid foam sack she builds on a branch overhanging a pond. The outside of the foam sack hardens in the sun and prevents water evaporation. The foam structure minimizes the amount of fluid that needs to be incorporated into the sack and minimizes its weight. However, as far as the developing eggs are concerned, they are in an aqueous medium, i.e. the continuous fluid phase of the foam. After precisely six days the eggs hatch, and the solidified outer wall re-liquefies and dumps the emerging tadpoles into the pond below. The bee honeycomb is an example of a cellular material with exquisite periodicity at millimeter length scales. The cellular structure provides strength through geometric regularity and functions as both honey storage vessels and incubators.

2. FABRICATION TECHNOLOGY

In this talk we will focus on man-made routes to cellular materials over the same range of length scales as nature provides.

Micro-scale cellular equilibrium structures: The easiest way to ensure uniformity is to produce structures that are at thermodynamic equilibrium. Recently, there has been a great deal of interest in using thermodynamically stable surfactant phases as templates for polymerizations[3,4]. Surfactants in solution can produce a variety of interesting structures as shown in the generic phase diagram[5] (Fig. 1). The cubic phase shown in figure is of particular interest because it consists of two interpenetrating phases with periodicity on the scale of 15 A to 250 A. The high viscosity of the cubic phase make them ideal candidates for polymerizations because the high viscosity inhibits rearrangements during polymerization. Strategies

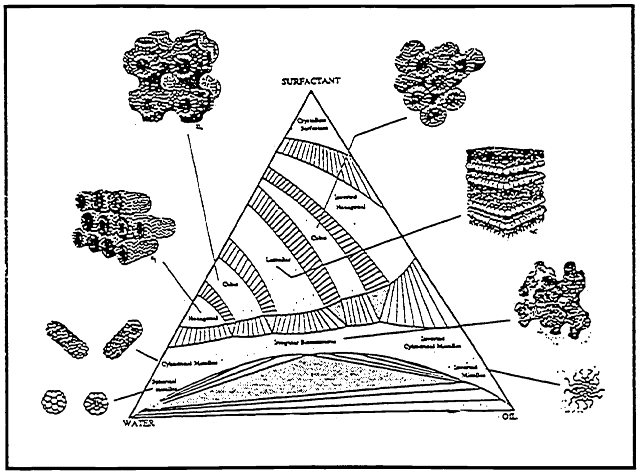

Fig. 1. Schematic of surfactant phase diagram showing surfactant strurctures (from ref 5).

for polymerizing these structures to make cellular materials includes polymerizing the aqueous phase, the organic phase, or the surfactant interface itself. The challenge in this area has been to polymerize the surfactant phase without disruption the equilibrium structures.

Micro-scale cellular kinetically determined structures: Using chemical kinetics, or transport phenomena to establish microstructure can not provide the exactly regularity of thermodynamically equilibrium structures, but the ability to tune kinetics means that microstructure can be tuned over a wider range of length scales. Industrial examples of micro-cellular materials include phase separated polymeric and inorganic materials used as chromatographic media[6]. Early examples were based on temperature induced phase separation of a polymer matrix with a lower molecular weight "porogen" that phase separated at a lower temperature. Upon cooling the polymer phase separated into a porous matrix from which the lower molecular weight species was extracted. Recently, very low density polymeric foams have been produced by phase separation of polymer solutions, followed by supercritical drying to create structures shown in Fig. 2 [7].

Controlling kinetics controls pore size. Since the kinetics involves competing thermal diffusion and mass diffusion it is not possible to create uniform bulk materials. Therefore these strategies are used primarily for small particle formation and for membranes. Similar strategies are used for inducing chemical composition variations during quenching of glasses. The phase separated network of the more soluble glass species is selectively dissolved away to leave micro-porous Controlled Pore Glass (CPG)[8]. Flocculation of inorganic silica particles (rather than precipitation from an initially homogeneous state) is used to create fractal ceramic networks for chromatography media. With subsequent supercritical drying, low density ceramic "aerogels" foams can be made[9].

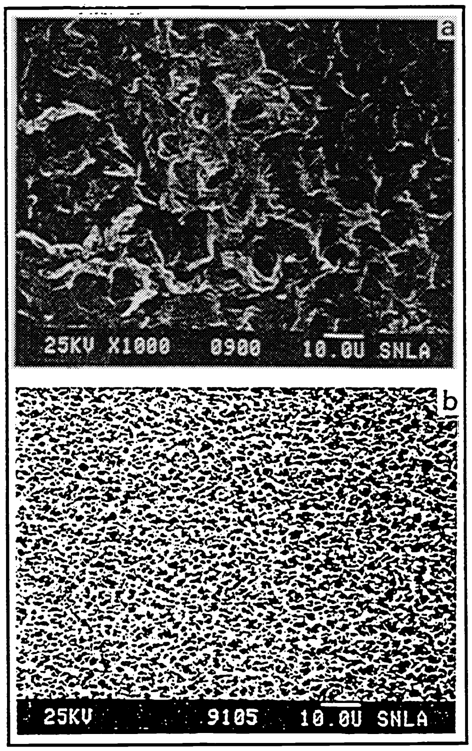

Fig. 2. Cellular structure of polymeric foams created by phase separation

Macro-scale kinetically determined materials: Cellular polymeric foams represent well over five million pounds per year in sales for items ranging from soft foams for seat cushions and bedding, to rigid foams for insulation and disposable hot beverage cups, to higher technology foams for the space shuttle heat shield tiles. Rubens has recently reviewed polymer foam production[10] . The cellular structure comes from the expansion of a gas phase in a continuous polymer phase. The gas phase may come from added "blowing agents" or from reaction products of the polymerization reaction as in the case of polyurethane foams. Control of cell size and structure involves the simultaneous control of several kinetic processes: gas bubble nucleation, gas diffusion, heat transfer, and polymer rheology as the foam structure solidifies either upon cooling or upon chemical reaction. Figure 3 shows the variation in

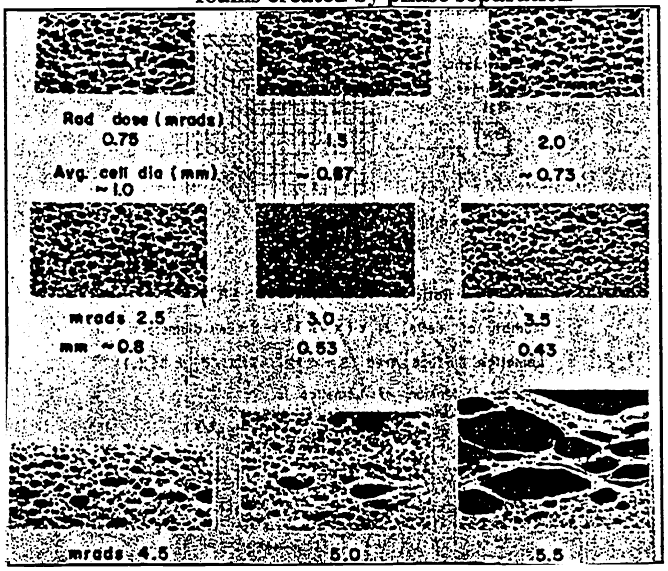

Fig. 3. Polyethylene foam structure as a function of radiation crosslinking dose (from ref 10).

cell structure with radiation dose (which crosslinks and increases the elastic properties of the polymer) for a polyethylene foam sheet[10]. The relationship between foam structure and foam mechanical properties is key in any application and there have been recent advances in the theory of structure-property relationships for foams[11]. While polymeric foams can be made in bulk with cell sizes from microns to millimeters they are analogs of the foam frog nests rather than the bee honey comb. They lack uniformity and control of orientation and pattern.

Macro-scale patterned cellular materials: At Princeton we have been working on techniques of macro-scale pattern formation using stereolithography that more closely approximate the bee honey comb . In this technique the ceramic "green body" (i.e. the ceramic object prior to sintering) is fabricated layer-by layer by coating a thin film of a ceramic slurry, and then laser curing the layer to define a pattern (Fig. 4). The layering is repeated multiple times to produce the three dimensional body.

The two dimensional sections are created from a three dimensional CAD (computer aided design) file and the motion of the laser beam to cure the two-dimensional section is controlled by a computer interpreting the CAD file. After layering and curing the entire object, the uncured regions are removed by washing and the final green body is ready for firing. Stereolithography has been widely used to create polymeric objects by curing transparent monomer liquids. While this provides a designer with a part having the shape of the desired object, it does not provide fully functional parts for demanding applications. Ceramic objects still had to be cast or injection molded which requires expensive and time consuming mold fabrication steps. The advance of stereolithography for the production of ceramic objects requires a detailed understanding of the laser light penetration and diffusion in the ceramic slurry. The curing of the photopolymerizable monomer or polymer in the continuous phase of the ceramic dispersion depends on the photon dose. The control of the laser beam rastering speed to deliver the correct photon dose requires expressions for the photon attenuation and lateral diffusion. A major part of our effort has gone into understanding light penetration using multiple scattering transport theories of light propagation[12]. With stereolithography our goal is to produce cellular materials with repeat length scales on the order of millimeters that can be fabricated into smart materials. One such example is the piezoelectric "rainbow" structures shown in Fig. 5. Our progress in this area will be presented at the workshop.

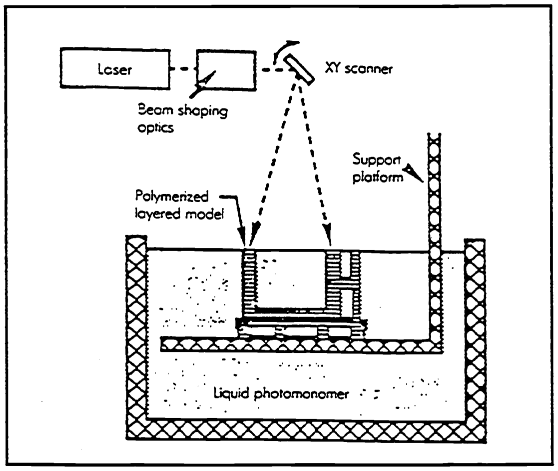

Fig. 4. Schematic of laser stereolithography apparatus showing laser, beam shaping and steering mechanism, monomer pool, and translation stage.

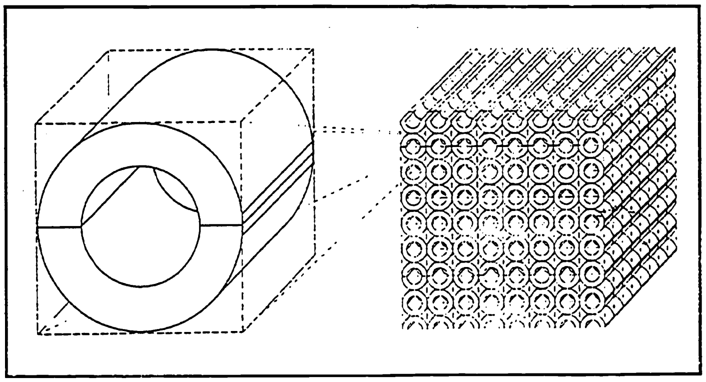

Fig. 5. Cellular piezoelectric rainbow structure for smart materials.

REFERENCES

1. J.F.V. Vincent, **Structural Biomaterials**, Princeton Univ Press, Princeton NJ, (1990).
2. J.H. Waite, Chem. and Industry, 607-611, 2 Sept., (1991).
3. C.T. Kresge, et al.,*Nature*, **359,** 710, (1992); J.S Beck, et al., *J. Am. Chem. Soc.*, **114**, 10834, (1992).

4. D. Anderson and P. Strom, *Phys. A*, **176**, 151, (1991); R. Laversanne, *Macromolecules*, **25**, 489, (1992).
5. H. Davis, J. Bodet, L. Scriven, and W. Miller in **Physics of Amphiphilic Layers**, Eds. J. Meunier, D. Langevin, and N. Boccara, Springer Verlag, Berlin (1987).
6. L.H. Tung, ed., **Fractionation of Synthetic Polymers**, Ch 6, Marcel Dekker Inc., NY (1977).
7. S.-W Song and J.M. Torkelson, *Macromolecules*, **27**, 6389-97 (1994); J.H. Aubert and R.L. Clough, *Polymer*, **26**, 2047-54.
8. W.J. Haller, *Chem. Phys.*, **42**, 686 (1965).
9. A.J. deVries, et al., *Anal. Chem.*, **39**, 935, (1967); K.K. Unger, **Porous Silica, its properties and use as a support in column liquid chromatography**, Elsevier Pub., NY (1979).; R.K. Iler, **The Chemistry of Silica**, John Wiley and Sons, NY, (1979).
10. L.C. Rubens, J. Polym. Sci.: Polym. Symp. **72**, 241-62, (1985).
11. W.E. Warren and A.M. Kraynik, Proc. Engr. Mechanics ASCE, Proc. 9th Conf. on Engr. Mech., May 24, 1992, College Station, TX, p.143-46., W.E. Warren and A.M. Kraynik, J. Appl Mech., Trans. ASME, **58** (2), 376-81 (1991).
12. P.F. Jacobs, **Rapid Prototyping and Manufacturing - Fundamentals of Stereolithography**, SME, Deabron, MI, (1992).