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BY THERMALLY INDUCED PHASE-INVERSION PROCESSES

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Preparation of Multishell ICF Target Plastic Foam Cushion Materials
by Thermally Induced Phase Inversion Processes

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ABSTRACT

Homogenous, low-density plastic foams for ICF targets have been prepared by thermally induced phase inversion processes. Uniform, open cell foams have been obtained by the rapid freezing of water solutions of modified cellulose polymers with densities in the range of 5 mg/cm^3 to 0.7 mg/cm^3 and respective average cell sizes of 2 to 40 micrometers. In addition, low-density, microcellular foams have been prepared from the hydrocarbon polymer poly(4-methyl-1-pentene) via a similar phase inversion process using homogenous solutions in organic solvents. These foams have densities from 2 to 5 mg/cm^3 and average cell sizes of 20 micrometers. The physical-chemical aspects of the thermally induced phase inversion process is presented.

I. INTRODUCTION

Several laboratories have recently been involved in the development of multishell fusion targets for laser interaction experiments.^{1,2} Initial designs consist of a D-T fuel filled hollow glass microspheres centered in the interior of an outer pusher-ablative shell (Fig. 1). Concentricity between the inner and outer shells must not vary over a 2% range. Between the two shells is a low-Z-cushion layer, which, depending on the particular design, requires densities from 0.01 to 1 g/cm³ or more. This cushion layer can be a gas, a small-cell plastic foam, or a full-density plastic.

Multishell fusion targets have been fabricated using a gas cushion layer with a thin plastic film supporting the inner shell.¹ Considerable effort has been extended to fabricate low-Z, low-density, micro-cellular foams for this cushion layer.^{2,3} In the study by Rinde and Stone a cellulose acetate foam was prepared by extrusion of an acetone solution of the polymer into a "phase-inversion" environment. This process is similar to the methods for making asymmetric, reverse-osmosis membrane for water desalination.⁴ Rinde and Stone were able to produce cellulose acetate foam strands with densities about 5 mg/cm³ and cell sizes of 1 to 2 micrometers.

Coudeville, et al.,² have reported the coating of stalk-mounted glass microspheres with a dextran foam with a density of 5 mg/cm³ and average cell sizes of 1 to 2 micrometers. Their freeze-drying process involved the rapid cooling of a water solution of the dextran polymer to

a temperature well below the freezing point of the water. The water was then removed via sublimation under reduced vacuum to give the polymer foam structure.

In a parallel study at this laboratory, plastic foams have been made from a water solution of the ammonium salt of carboxymethylcellulose (Figs. 2 and 3) via the freeze-dry process over a range of densities, that is, a density of 5 mg/cm^3 and cell sizes of 2 micrometers to a density of 1.6 mg/cm^3 and cell sizes of 10 micrometers. In addition, foams with a density of 0.7 mg/cm^3 (Fig. 4) were prepared from a water solution of methylcellulose.

II. THERMALLY INDUCED PHASE INVERSION PROCESSES

The freeze-dry process employed by Coudeville and in our laboratory falls into the general category of thermally induced phase inversion processes. In a phase inversion process, a solution of a polymer in a solvent is treated in such a manner as to force separation of the solvent from the polymer in a preferential manner such that a polymer matrix is formed in which is trapped discrete cells containing the solvent. Removal of the encased solvent droplets from the matrix gives the open cell plastic foam structure with the voids a replica of the solvent droplets. In a thermally induced process the solvent is selected from a class of poor (θ) solvents for the polymer. Controlled cooling of a polymer dissolved in a θ solvent can yield a polymer foam.

During the freezing step in a freeze-dry process solvent-polymer separation occurs at a temperature at which the solvent and the polymer no longer are miscible in each other. This temperature point has been

defined as the theta temperature or the critical miscibility temperature.⁵ For polymers having a broad molecular weight range, the theta temperature may not be a discrete point but a range of temperatures. Theta temperatures also vary with the concentration of the polymer in solution.

The mechanism for foam formation in this process is complex. As the temperature of the solution is lowered, the solvent becomes a poorer solvent for the polymer. Finally, as the theta temperature is reached, two distinct phases begin to develop, both phases having liquid characteristics. As the temperature is further reduced below the theta temperature, each phase begins to take on the unique characteristics of the major component of that phase until a distinctive heterogeneous mixture of the two components is reached (Fig. 5).

Factors which influence whether a foam matrix or a precipitate of polymer is formed as the temperature of the solution is dropped through the theta temperature are quite complex. Although many other factors may apply, factors such as intrinsic viscosities of the developing phases, frictional interactions of the polymer chains, rate of solvent drainage from the polymer matrix, and the critical surface tension between the developing phases can be considered to be the major contributors to the observed phenomenon. The effective interaction of these factors can to some extent be controlled by the rate at which the temperature is dropped through the theta temperature zone. In the case of water solutions of dextran and the chemically modified celluloses cooling rates in the range of 100 degrees Kelvin per second, or greater, tend to favor polymer foam

matrix formation, whereas considerably slower rates of cooling usually result in the formation of precipitates of the polymer in the solvent.

III. EXPERIMENTAL

Since dextran and the chemically modified celluloses contain an appreciable atomic percent of oxygen, we have embarked on a study to see if the thermally induced phase inversion phenomena of polymer solutions can be used to prepare low-density, microcellular, plastic foams from organic polymers containing only carbon and hydrogen (CH). Applying some of the fundamental principles as outlined in Section II, we have been able to develop CH polymer foams with densities in the range of 5 mg/cm^3 and cell sizes from 10 to 30 micrometers. In addition, we have developed a process whereby these delicate foams can be readily fabricated into desirable configurations via conventional micromachining techniques.

Poly(4-methyl-1-pentene), which is manufactured by Mitsui Petrochemical Co. in Japan under the trade name "TPX," is a linear polymer composed of only carbon and hydrogen and has a bulk density of 0.93 g/cm^3 (Fig. 6). The polymer is relatively insoluble in most common organic solvents, and only recently have theta solvents been published for TPX.⁶

It has been found that TPX can be heated with particular theta solvents to a temperature and for a period of time such that homogenous solutions are formed. Each solution is then allowed to cool in some desirable shape at a rate and to a temperature such that nonequilibrium liquid-liquid phase separation is initiated. As each solution is cooled,

it is necessary that no mixing or any other form of agitation be applied to the solution. Complete phase separation is observed when the solution develops a solid or gelatinous appearance. Cooling to room temperature results in a TPX foam matrix with the cells filled with the solvent.

If one selects a theta solvent which is a solid at room temperature, the process offers another distinct advantage in that the solid solvent dispersed in the TPX polymer foam matrix acts as a reinforcing agent for the delicate cell walls and, thus, the filled-foam structure can be mechanically shaped to relatively high tolerances before the solid solvent is removed. Table I lists the theta solvents found to be successful in preparing TPX foams of approximately 5 mg/cm^3 density.

TABLE I

Solvent	Physical State at Room Temperature	Boiling Point or Melting Point
Diphenylmethane	Liquid	264°C
Phenyl Ether	Liquid	259°C
Cyclohexylbenzene	Liquid	239°C
1-Phenyloctane	Liquid	261°C
Bibenzyl	Solid	49.6°C
Hexamethylbenzene	Solid	162°C

As a typical example a 5.5 wt solution of TPX in melted bibenzyl (1,2-diphenylmethane) is heated to 220°C until complete solution occurs.

The clear solution is then transferred into a 25 ml spherical glass flask preheated to 220°C in a programmable convection oven. A spherical flask was chosen in order to take advantage of uniform spherical radiation of the solution during cooling. The oven is programmed such that the cooling process is staged in order to allow the system to come to temperature equilibrium at periodic intervals. The flask and solution is first cooled to 180°C and held there for 30 minutes. The solution is then cooled at a rate of 1°C per minute to allow the reverse phase separation to occur. After holding the solution at 160°C for a few minutes the gelatinous mass is cooled to room temperature, solidifying the bibenzyl. The final, desired foam structure can then be formed by conventional machining techniques to tolerances of less than 2 micrometers, the solid bibenzyl serving as a reinforcing agent for the foam. The bibenzyl can be readily removed from the final part by leaching with methyl alcohol at room temperature while maintaining the dimensions established in fabricating the filled material.

From a study of the different theta solvents listed in Table I it was found that the rate of cooling of TPX solutions through the theta temperature is different from the different solvents. There seems to be no simple way to predict the rate for a particular solvent, each one being determined by trial and error.

IV. RESULTS AND DISCUSSION

In the above example the cooling rate between 180°C and 160°C is the critical portion of the process for the formation of the cellular foam

structure. This fact is best illustrated in the sets of stereophotomicrographs in Figs. 7 and 8. Figure 8 shows the type of foam structure obtained when the TPX-bibenzyl system is cooled at a rate of 0.7°C per minute. Note the rose-like structure of the foam resulting from nucleation and radial growth of the solid polymer from the nucleation site into rosettes as the solution cools.

The stereophotomicrographs in Fig. 7 show the foam structure when the cooling rate is held at 1.0°C per minute through the theta temperature. At this rate uniform spherical cells are formed. Figure 7 also shows the relatively smooth uniform flat surface obtained after a diamond-turned filled-foam blank is leached.

Preliminary studies on the freeze-drying of water-ammonium carboxymethylcellulose systems indicate that the molecular weight of the polymer and the viscosity of the solution (due to the degree of substitution on the cellulose backbone) play an important role in the cell size obtained in the process. Smaller cell sizes in the final foams are obtained with higher molecular weight polymers and higher viscosity solutions at the same weight percent concentration. This observation becomes obvious if these effects are compared with the factors outlined in Section II.

An increase in molecular weight results in an increase in polymer chain frictional interactions and, to some extent, an increase in the intrinsic viscosity of the developing polymer phase. These effects will in turn will slow down the rate of polymer diffusion during the phase separation period, and, thus, should lead to smaller cells.

Decreasing the solubility of the polymer in the solvent should contribute to both an increase in the intrinsic viscosity of the developing polymer phase and an increase in the rate of drainage of solvent from the polymer phase. These effects should also lead to smaller cell sizes. Based on this information work is currently underway to reduce the cell size of TPX and other hydrocarbon foams formed by the thermally induced phase inversion processes.

V. CONCLUSIONS

Thermally induced phase inversion process seems to be the best process for the preparation of low-density, microcellular plastic foams for fusion targets. Plastic foams with densities as low as 0.7 mg/cm^3 have been prepared by the controlled cooling of homogenous solutions of polymers in theta solvents. It is felt that the process has the potential of providing a wide variety of plastic foams for fusion target studies.

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FIGURE 1. CUTAWAY VIEW OF A TYPICAL MULTISHELL ICF TARGET.

FIGURE 2 CARBOXYMETHYLCELLULOSE FOAM; DENSITY = 5 mg/cm^3 ;
AVERAGE CELL SIZE = 2 MICROMETERS.

FIGURE 3. CARBOXYMETHYLCELLULOSE FOAM; DENSITY = 1.6 mg/cm^3 ;
AVERAGE MEAN FREE PATH DISTANCE BETWEEN RIBS = 10
MICROMETERS.

FIGURE 4. METHYLCELLULOSE FOAM; DENSITY = 0.7 mg/cm^3 ;
AVERAGE MEAN FREE PATH DISTANCE BETWEEN PIBS
= 40 MICROMETERS.

FIGURE 5. PHASE SEPARATION CHART.

SOLUTE-SOLVENT PHASE SEPARATION CHART

IPA

POLY(4-METHYL-1-PENTENE)

MW - 216,000

MP - 238°C

DENSITY - .83 g/cc

MELT INDEX - 8

FIGURE 7. TPX FOAM STEREO PHOTO MICROGRAPHS. COOLING RATE
= 1.0°C PER MINUTE.

FIGURE 8. TPX FOAM STEREO PHOTO MICROGRAPHS. COOLING RATE
= 0.2°C PER MINUTE.