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MICROCELLULAR FOAMS PREPARED FROM DEMIXED POLYMER SOLUTIONS

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ABSTRACT

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Low-density, microcellular polymer foams have numerous applications as structural supports in high-energy physics experiments, in catalysis, ion exchange, and filtration, and for a variety of biomedical uses. A versatile method to prepare such foams is by thermally-induced phase separation (TIPS) of polymer solutions. Demixed solutions can be transformed into a foam by freezing the demixed solution and removing the solvent by freeze-drying. The morphology of these foams is determined by the thermodynamics and kinetics of phase separation. A model of both the early and late stage structure development for demixed polymer solutions will be presented. For semi-crystalline polymers, gels can be prepared by crystallizing the polymer from solution, either a homogeneous solution or a demixed solution. Foams can be prepared from these gels by the supercritical extraction of the solvent. By understanding and utilizing the phase separation behavior of polymer solutions, engineered microcellular foams can be prepared. To design the foams for any application one must be able to characterize their morphology. Results will be presented on the morphological characterization of these foams and the relationship of the morphology to their processing history.

INTRODUCTION

687 million kilograms of polystyrene foams were manufactured in the U.S. during 1989 [1]. A great deal of this product was prepared by a physical process wherein a blowing agent (usually 6% pentane) was diffused into polystyrene beads and expanded at elevated temperature (above the glass transition temperature of polystyrene, $T_g = 100^\circ\text{C}$). In this process each bubble nucleation site becomes the center of a foam cell which has roughly a spherical shape and a diameter in the range of 50 to 150 micrometer (μm) [2]. These foams enjoy great usage in packaging where their insulating and shock absorbing capabilities are exploited. About 14% of the polystyrene foam produced in 1989 was in the form of cups, such as coffee cups [1]. Figure 1 shows a scanning electron photomicrograph (SEM) of a

Fig. 1. Scanning electron photomicrograph of a polystyrene foam obtained from a coffee cup. The bar in the photograph is 1000 micrometers.

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polystyrene bead foam obtained from a coffee cup. The cells have diameters of about 100 μm . What if one wanted to make a package with a thickness of only 200 μm ?

This is not as uncommon of a request as one might think. A number of targets for high energy physics experiments require low-density foam coatings or small low-density foam supports with dimensions smaller than a millimeter (1000 μm). An example would be a target for inertial confinement fusion (ICF) containing deuterium-tritium fuel [3,4,5]. The foam coatings within such a target could be made with a conventional foam but since the entire thickness would contain as few as 2 or 3 cells it would look very nonuniform, i.e. the fluctuations of density within the foam (varying from about 1.0 g/cc in the solid phase to about 0.0 g/cc in the gas phase) would occur on a length scale comparable to the size of the part. This is undesirable for these physics applications which require structural supports which are very homogeneous. To address the need for small-celled foams, numerous authors [3,6,7] have studied other types of phase-separation processes which can create finer-scaled structures. These foams have been termed microcellular.

PROCESS DESCRIPTION

Foams are two phase systems which consist of a continuous polymer phase and either a continuous or discontinuous gaseous phase. Most foams begin as a single phase and undergo some type of phase separation to create the foams' structure. In the polystyrene foam (coffee cup) described above the polymer contains dissolved solvent (i.e. pentane), which phase separates by a nucleation process when the temperature is raised. To prepare a microcellular polymer foam, we take advantage of different types of phase separation processes which create finer structures. Two types of phase separation processes utilizing polymer solutions are liquid-liquid phase separation and polymer crystallization. Sometimes both can occur during the thermal processing of a polymer solution. A generic phase diagram (temperature-composition) of a monodisperse polymer solution showing these types of phase separations is shown in Fig. 2.

Fig. 2. Typical temperature-concentration phase diagram for a polymer and a solvent which can both independently crystallize and can also liquid phase separate.

At high temperature the polymer is in solution and only one phase exists on this phase diagram. As the temperature is reduced, polymer crystals grow from solution when the equilibrium crystallization curve is crossed. This temperature usually depends upon the concentration of the solution and can be described by polymer solution thermodynamic theories such as that due to Flory [8]. The solution may also undergo a liquid-liquid phase separation which results in the formation of two liquid phases in equilibrium; one phase is typically nearly pure solvent and the other phase is a semi-dilute or concentrated polymer solution. The asymmetry in the liquid-liquid phase separation is a manifestation of the polymers high molecular weight compared to that of the solvent. Liquid-liquid phase separation of a polymer solution can also be described by polymer solution thermodynamic theories [8]. Both of these phase separation processes are termed thermally-induced phase separations (TIPS) because of the convenient quench used to induce phase separation.

The region of liquid-liquid phase separation can be further divided into two types which depend upon the kinetics of phase separation, the nucleated region which occurs between the binodal and spinodal curves on the phase diagram, and the region of spinodal decomposition which occurs below the spinodal curve. The nucleated region is characterized by phase separation occurring by the nucleation of a second phase. To the left of the critical point the nucleated phase would be a polymer-rich phase, while to the right of the critical point the nucleated phase would be a solvent-rich phase. In both cases only nuclei of a sufficient size would be stable enough to persist because of the energy associated with the interfacial area. Hence, nucleation is characterized by a lag time, prior to which few nuclei have grown to a sufficient size to be stable. The spinodal region is characterized by the critical nuclei size being exactly zero, and hence no lag time is associated with phase separation in this region. In addition, at high enough concentrations, phase separation in the spinodal region is characterized by the presence of bicontinuous phases, rather than discrete droplets usually associated with nucleation and growth.

Finally, for some polymer solutions the freezing point curve of the solvent can be crossed. This usually depends upon polymer concentration as there is a freezing point depression with any dissolved component in a solution (such as the polymer). Under the binodal, however, the freezing point is always constant because of the thermodynamic requirement that the solvent chemical potential be identical in the two equilibrated phases. This fact is often used to identify the binodal region; i.e. under the binodal the solvent freezing point remains constant.

If the TIPS process results in the formation of a continuous polymer-rich phase, then a microcellular foam can be prepared with two additional processing steps. First the morphology of the phase-separated solution must be preserved either through vitrification or crystallization of the polymer. This step preserves the small-scale morphology of the demixed solution. If the quench results in vitrification or crystallization of the polymer, without the solvent crystallizing, then a polymer gel results. If the solvent is crystallized it normally excludes polymer from the crystals. The polymer therefore becomes more concentrated and vitrifies, which also renders it immobile. After either of these possibilities, solvent freezing or solution gelation, the solvent must be removed.

In a freeze-drying process, the frozen solvent is removed by sublimation under vacuum. After solvent removal only polymer remains which has a morphology closely related to that of the phase-separated solution. Super-critical extraction is another technique in which the solvent can be removed while preserving the desired morphology. If the

liquid in a gel is taken above its' critical point, then it can be removed in the single phase region without any liquid/vapor meniscus and the related interfacial tension. In the absence of interfacial tension, the solvent leaves the gel without collapsing the gel morphology. In actual practice, the original solvent is often exchanged for one which is amenable to freeze-drying or to super-critical removal. In the latter case, super-critical carbon dioxide has been invaluable [7,9].

MODEL FOAMS

Polystyrene microcellular foams have been prepared using the TIPS process with a wide range of controlled morphologies. The morphologies can be directly correlated to the solution phase diagrams and processing conditions. By controlling how the phase separation occurs, foam morphology, cell size, and density can be engineered for a specific application [6,9,10].

Figure 3 shows a phase diagram (cloud point curve) determined for polystyrene ($M_w=2.23 \times 10^6$, $M_w/M_n=1.12$) in cyclohexane. This polymer is not crystalline but does have a region of liquid-liquid phase separation which is indicated by the cloud point curve shown in the figure.

The freezing point curve of cyclohexane in the solution is also shown. If a solution with a concentration near critical is quenched through the cloud point curve, and then frozen and freeze-dried, a foam with a morphology consistent with a spinodal structure is obtained (bicontinuous phases). The cell sizes obtained for fast quenches are consistent with predictions of spinodal wavelengths for demixed polymer solutions [6]. The cell size can be varied by varying the quench rate through the cloud point curve. Fig. 4 shows the cell sizes which can be obtained from four different quench rates. This variation is possible because when the solution enters the two-phase region a demixed structure forms via a preferred kinetic route. The equilibrium state, however, corresponds to two separate solutions, each of which has the tie-line concentrations. The structure which initially forms in the two-phase region will evolve to this equilibrated structure. By freezing the solution at different times (i.e. by varying the quench rate) different structures can be preserved during this evolution. A model for the structural coarsening of demixed polymer solutions has been presented which is based upon a diffusive coarsening mechanism with the structural size growing with time to the $1/3$ power [10].

Using different polystyrene concentrations, foam morphologies which resemble those expected for a nucleated process can be obtained. Below the critical concentration, phase separation proceeds by the nucleation of droplets of the polymer-rich phase. A foam prepared in this region has the

Fig. 3. Cloud point curve of a solution of polystyrene (molecular weight of 2.23×10^6) in cyclohexane solvent.

Fig. 4. Scanning electron photomicrographs of polystyrene foams obtained from 3%w/v solutions of polystyrene ($M_w = 2.2 \times 10^6$) in cyclohexane quenched at different rates. The quench rates were varied by holding each solution in the two-phase regions for 1, 3, 5, or 7 minutes prior to freezing the solution.

morphology shown in Fig. 5. As is seen, the morphology consists of polymer balls weakly connected together, which is consistent with a nucleation process. At concentrations higher than the critical concentration, one expects that the phase separation will proceed by the nucleation of the solvent-rich phase. In the dried material then, one expects to see roughly spherical voids which correspond to the solvent-rich regions of the demixed solution. Fig. 6 shows a foam prepared in this region and one does indeed see that the morphology has a more traditional foam-like morphology with roughly spherical voids.

In Fig. 7 schematic phase diagrams for polystyrene in different ratios of the cosolvent mixture 1,4-dioxane and isopropanol are shown. Below the phase diagrams are SEM photomicrographs obtained

Fig. 5. Polystyrene foam prepared from a 1%w/v solution in cyclohexane (lower than critical). The phase separation was expected to occur by polymer droplet nucleation.

from foams made from 5%w/v solutions in the various cosolvent mixtures. By changing the solvent ratios, one can vary the foam morphology from one that is anisotropic to one that is isotropic. One can vary the cell sizes of both the anisotropic and the isotropic morphologies. In a solvent composed of 80% 1,4-dioxane and 20% isopropanol, the phase diagram consists of just the freezing point curve of 1,4-dioxane from solution. There is no region of liquid-liquid phase separation. As 1,4-dioxane freezes, dendritic crystal growth excludes polymer which is displaced to the grain boundaries. This results in the anisotropic morphology shown. As more non-solvent (e.g. isopropanol) is added to a solution, the solvent quality worsens and eventually a region of liquid-liquid phase separation occurs.

Fig. 6. Polystyrene foam prepared from a 10%w/v solution in cyclohexane (higher than critical). The phase separation was expected to occur by solvent droplet nucleation.

Fig. 7. Schematic phase diagrams and foam morphologies obtained from solutions of atactic polystyrene ($M_w = 2.2 \times 10^6$) in a cosolvent of 1,4-dioxane and isopropanol in different ratios: left 80% 1,4-dioxane and 20% isopropanol, center 60% 1,4-dioxane and 40% isopropanol, right 55% 1,4-dioxane and 45% isopropanol.

For low concentrations of isopropanol only a small region exists as shown in the schematic phase diagram for 60% 1,4-dioxane and 40% isopropanol. A quench of a solution through this region is therefore necessarily quick and a small-celled foam results. If additional nonsolvent is added to the solution the region of liquid-liquid phase separation is larger as depicted for the cosolvent of 55% 1,4-dioxane and 45% isopropanol. If a solution is quenched through this region the quench will be relatively slower since the distance to traverse through the region of liquid-liquid phase separation is greater. Hence, the foam cell size obtained is larger as is shown in the photomicrograph. By changing the solvent, the polymer concentration, or the quench a great many thermodynamic histories can be obtained for a given polymer solution, each of which may result in a different foam morphology.

Isotactic (crystallizable) polystyrene (iPS) has been utilized to prepare microcellular foams with even smaller cell sizes and higher surface areas [9] than obtained with atactic (noncrystallizable) polystyrene. Figure 8 shows a SEM photomicrograph of an iPS foam at very high magnification which demonstrates the ability of this system to produce extremely small-celled and high surface area foams. The phase diagrams have been established for some solutions. One example is that of an iPS of molecular weight 160000 in nitrobenzene solvent, which is shown in Fig. 9. This phase diagram has some of the features depicted in Fig. 2 [9]. At quite high temperatures a crystallization curve is found below which polymer crystals grow from solution. The rate of crystallization is very slow for this polymer. However, if sufficient time is allowed for polymer crystals to grow, they will physically interact and the solution will gel. The solvent in the gel can be extracted by replacing it with supercritical CO₂, which is then removed as described above. The dry-gel (foam) has a morphology as shown in Fig. 10. This is a common morphology obtained for polymer crystallization from solution.

Fig. 8. Dried gel of isotactic polystyrene formed from a solution in nitrobenzene and quenched into the spinodal region. The gel was dried by exchanging the solvent with supercritical CO₂.

Because of the slow crystallization kinetics of this polymer, large supercoolings of the solutions are possible. At sufficient supercoolings, a different phase boundary can be crossed which has been interpreted as a buried spinodal [9]. Below the spinodal liquid-liquid phase separation occurs quickly and the structure formed is immediately gelled because of polymer crystal growth. Dried gels formed in this region have a morphology as shown in Fig. 8. This morphology is consistent with a spinodal process

and similar to that obtained with atactic polystyrene quenched near the critical point.

At even larger supercoolings, the solvent (in this case nitrobenzene) can be frozen. As in the case of atactic polystyrene, foams formed by quenches directly into this region are anisotropic due to dendritic crystal growth as shown in Fig. 11. Foams formed by quenches through the spinodal region and ending in solvent freezing, can have either morphology depending upon the strength of the gel formed in the spinodal region.

Polystyrene micro-cellular foams prepared using the TIPS process have been studied in some detail and excellent correlation between the solution phase diagrams, the kinetics of phase separation, and the observed morphologies was obtained. Numerous other microcellular polymer foams have also been prepared with this method. Usually this has been accomplished without detailed knowledge of the phase diagram and kinetics. In some cases the techniques developed for polystyrene foams have been successfully applied to other systems. A number of other microcellular foam systems have been developed for specific applications which take advantage of the unique mechanical or chemical properties of the polymer chosen. To effectively use these materials in any of the applications it is necessary to characterize the cell size distribution. This is not an easy task since often the cells are very random or the walls are nonuniform or strut-like.

CHARACTERIZATION

An exact stereological relationship exists between the surface area per unit volume, S_v , of a material and the number of intersections of test line of unit length with the surfaces, P_L [11,12,13].

$$S_v = 2 P_L$$

(1)

Fig. 9. Phase diagram of isotactic polystyrene ($M_w=1.6 \times 10^5$) in nitrobenzene: spinodal region, $\circ$; polymer crystallization, $\bullet$; atactic polystyrene cloud point ($M_w=2.2 \times 10^6$), Δ ; nitrobenzene freezing, $\blacksquare$; gel melting points by DSC, $\blacksquare$.

Fig. 10. Dried gel of isotactic polystyrene ($M_w=1.6 \times 10^5$) formed in nitrobenzene in the region of polymer crystallization. The solvent was exchanged with supercritical CO_2 .

Fig. 11. Dried gel of isotactic polystyrene ($M_w=1.6 \times 10^5$) formed in nitrobenzene in the region of solvent freezing. The solvent was exchanged with supercritical CO_2 .

We define N_L as the number of intersections of the solid phase of the foam per unit length of test line. For a low-density foam, a test line will almost always intersect both sides of the solid phase (once entering and once leaving) and therefore, N_L is equal to one half of P_L . Typical applications of these stereological relationships involve placing test lines on a photograph of a foam, counting the number of surface intersections, P_L , or solid phase intersections, N_L , and then calculating the surface area per unit volume or some other property related to these quantities. Our technique is to physically measure the surface area, with a nitrogen adsorption technique or with mercury intrusion, and with this measurement to calculate P_L or N_L . The motivation behind this is that $1/N_L$ is equal to the average distance between the solid phases of the foam, d :

$$d = 1/N_L = 4/S_v \quad (2)$$

This is an exact morphological feature which can be calculated from a measured value of the surface area per unit volume, S_v . The average distance between the solid phases of a foam can be thought of as a generalized cell size. This is a particularly useful property to characterize a foam which has a morphology that does not consist of easily-defined cells.

For a single surface area measurement obtained from BET nitrogen adsorption a single average cell size is obtained. This is called the surface-area-average cell size [12], and is defined as,

$$\langle d \rangle_s = [\sum d_i S_i] / \sum S_i , \quad (3)$$

where S_i is the surface area of the cells having average spacing between surfaces of d_i . For rigid foams, such as carbonized polyacrylonitrile (PAN) [14], a cell size distribution exists which can be determined through mercury intrusion experiments. Various average cell sizes can be determined from the intrusion profile including the surface-area-average and the volume-average cell size, which is defined as [13],

$$\langle d \rangle_v = [\sum d_i V_i] / \sum V_i , \quad (4)$$

where V_i is the volume of cells having average spacing between surfaces of d_i . Figure 12 shows a typical intrusion curve for a bimodal cell size distribution carbon microcellular foam prepared from PAN. Such techniques to characterize the cell size distribution of microcellular foams are invaluable to the development of microcellular foams, to comparisons of the cell size distribution of a foam to models of foam formation, or to relate the performance of a foam to its morphological structure.

Fig. 12. Mercury intrusion curve of a carbon microcellular foam of density 0.057g/cm³. The bimodal cell size distribution is evident from the intrusion curve and also from photomicrographs of the foam.

CONCLUSIONS

A large variety of polymers can be made microporous using the TIPS process. The morphology of these foams is determined by the thermodynamics and kinetics of phase separation. Hence, by controlling the phase separation process, one can engineer the morphology of the foams for a given application. Foam morphology can be varied from an anisotropic-tubular morphology to a very isotropic strut-like morphology. For a given morphology, the cell size can also be varied. With the TIPS process, microcellular foams have been prepared with a cell size below $0.1\ \mu\text{m}$, and a corresponding surface above $300\ \text{m}^2/\text{g}$. These foams have a large number of potential applications which span the range from somewhat esoteric uses such as high energy physics targets to biomedical uses.

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