Effect of Rubber on Microcellular Structures from High Internal Phase Emulsion Polymerization

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Abstract: A microcellular foam, which combines a rubber with the conventional formulation of styrene/divinylbenzene/ sorbitan monooleate/water system, was prepared using high internal phase emulsion (HIPE) polymerization. Although the open microcellular foam with low density from the conventional HIPE polymerization shows highly porous characteristics with fine, regular and isotropic structure, the one having much smaller cell size is desirable for various applications. In this study, a polybutadiene was introduced to reduce the cell size with comparable properties. Major interests were focused on the effects of rubber concentration and agitation speed on the cell sizes and compression properties. Scanning electron microscopy was used to observe the microcellular morphology and compression tests were conducted to evaluate the stress-strain behaviors. It was found that the cell size decreased as rubber concentration increased, reflecting a competition between the higher viscosity of continuous phase and the lower viscosity ratio of dispersed to continuous phases due to the addition of high molecular weight rubber into the oil phase of emulsion. A correlation for the average cell size depending on agitation speed was attempted and the result was quite satisfactory.

Keywords: microcellular foam, high internal phase emulsion (HIPE), polybutadiene, cell size, compression property.

Introduction

Emulsions in which the dispersed phase occupies more than the maximum packing volume fraction of about 74% for monodisperse spheres with identical sizes are referred to as high internal phase emulsions (HIPE).[1] Open microcellular foams with low density prepared by the HIPE polymerization of mixtures mainly composed of styrene and water, known as polyHIPE,[2] show highly porous characteristics with regular, spherical and isotropic structure. Here, the term called microcellular foam is defined as any polymeric foam with cell sizes smaller than the order of 10 μm. The cellular structure of HIPE foams is quite different from the oriented, irregular and anisotropic structure of commercial blown and extruded foams that generally contain closed cell morphology with cell sizes of the order of 100 μm. The HIPE foams are currently of interest because of their low density, microstructural and open cell, and high absorbency. A number of applications include polymeric membranes, ion exchange resin,[3,4] controlled release systems, absorbents and inertial confinement fusion targets.[5,6] The success in these applications strongly

depends on the microcellular structure having large surface area, i.e., small cell size. Over the years, many researchers have investigated the effects of polymerization conditions, such as sorbitan monooleate as a surfactant, divinylbenzene as a crosslinking agent, dodecane as a pore size controller, and the introduction of inorganic materials, on the cell sizes and properties of the foam.[7-11] The sizes of both the cell and the open window between adjacent cells can be controlled by changing the mixing method, the agitation speed, the surfactant concentration and the composition of the oil phase during the emulsion preparation. Naturally, it is recommended to prepare the foam having smaller cell size without any loss of mechanical properties. One of the simplest methods to get smaller cell size is to impose higher agitation speed during the preparation of emulsion mixture. Another way to attempt is to increase the viscosity of continuous phase, which might affect the cell size depending on the viscosity ratio of dispersed to continuous phases. Presumably, introduction of a high molecular weight rubber to the continuous phase is likely to be a good candidate to achieve this goal. Additional advantage of rubber introduction is that the combination of vinyl radical polymerization with dissolved rubber yields either a toughened structure or a rubber network structure. In this study, we introduced a polybutadiene to the oil phase in order to reduce the cell size while maintaining the

mechanical properties of original foam as far as possible. Scanning electron microscopy was used to observe the cell size as well as the microcellular morphology, and compression tests were conducted to evaluate the mechanical properties of the foams prepared.

Experimental

Materials. The monomers used were styrene (Showa Chemical) and divinylbenzene (DVB, Aldrich), where DVB is composed of 55% mixture of isomers containing ethylvinylbenzene as a main remainder. Styrene monomer was purified by a standard vacuum distillation method and divinylbenzene was washed with 10% NaOH aqueous solution to remove inhibitors and then with water before use. Polybutadiene (PB, Aldrich) as a rubber has monomer units of 36% cis, 55% trans and 9% vinyl and weight-average molecular weight of 420,000 g/mol. Sorbitan monooleate (SMO, Span 80) having the hydrophile-lipophile balance (HLB) value of 4.3 as a nonionic surfactant and potassium persulfate (KPS) as an initiator were also obtained from Aldrich Chemical Corp. Distilled water was used before use.

Preparation of HIPE Foam. The emulsion compositions and agitation speeds selected as experimental variables are listed in Table I. Other components were kept constant as 150 g of water, 3.8 g of DVB, 3.43 g of SMO and 0.2 g of KPS following the recipe used in the literature.[7] The oil phase consists of the monomers, rubber and surfactant. The aqueous phase consists of distilled water and initiator. Prior to the preparation of emulsion system, rubber was cut into small pieces and dissolved with styrene using a magnetic stirrer

for 3-12 hrs depending on the amount of rubber employed. The oil phase was charged into a 500 mL tall beaker at room temperature and mechanically stirred at a given speed. While the oil phase was stirred for 30 min, the aqueous phase was added dropwise from an addition funnel: the feeding time was 28 min and the emulsion mixture was stirred for an additional 2 min to produce the emulsion as uniform as possible.

The beaker containing the emulsion mixture was sealed with parafilm to minimize water evaporation, and polymerized for 48 hrs in a convection oven at 60 °C. The polymerized solid mass was obtained by cracking the beaker and carefully removing the fragments. The mass was placed in a convection oven at 60 °C and dried to remove water and residual volatiles for several days. Some portion of the dried mass was cut into small cubes having 1.5 cm length on each side for compression testing.

Characterization. The foam morphology was characterized with a scanning electron microscope (Jeol SEM 5200). SEM micrographs were prepared after coating the dried foam sample with gold for conductivity. The acceleration voltage was 20-25 kV. The cell size and size distribution of each sample could be obtained from the image analysis technique that statistically evaluates a number of cell sizes of SEM micrographs. From this information, the average cell size of each sample was calculated together with an error bar representing standard deviations above and below the average value. The compression stress-strain experiments were also performed using a universal testing machine (UTM, Lloyd LR 50 K) to evaluate the mechanical properties of the foams. The platen speed was 0.127 cm/min (0.05 inch/min).

Results and Discussion

Effect of Rubber on Cell Size. SEM micrographs were taken to examine the microcellular morphology of the foams obtained after the polymerization of emulsion system followed by subsequent processing. Figure 1 shows representative SEM micrographs of microcellular foams showing the effect of rubber concentration at the agitation speed of 500 rpm. Compared to the sample prepared without rubber shown in Figure 1(a), the sample prepared with rubber shown in Figure 1(b) has smaller cell size. Regular and isotropic morphology of the cell and the open window between adjacent cells seems to undergo a slight change to irregular and non-spherical structure as rubber is introduced, presumably because the phase separation between PS polymerized and PB employed within the oil phase has an effect on the mixture stability.[12]

Figure 2 represents the effect of rubber concentration on the average cell sizes of the foams prepared from R-series. It is shown that the average cell size decreases as rubber concentration increases. The average cell size of the sample prepared with 12% rubber (based on styrene and rubber solution) shows about 4 or 5 times smaller than that of the sample without rubber.

**Table I. Emulsion Compositions and Experimental Conditions**

Sample Code	Styrene Monomer (g)	Polybutadiene (g)	Agitation Speed (rpm)
R0S500	11.2	0.	
R1S500	11.088	0.112	
R3S500	10.864	0.336	500
R5S500	10.640	0.560	
R8S500	10.304	0.896	
R12S500	9.856	1.344	
R3S250			250
R3S500			500
R3S750			750
R3S1000			1000
R3S1250	10.864	0.336	1250
R3S1500			1500
R3S1750			1750
R3S2000			2000
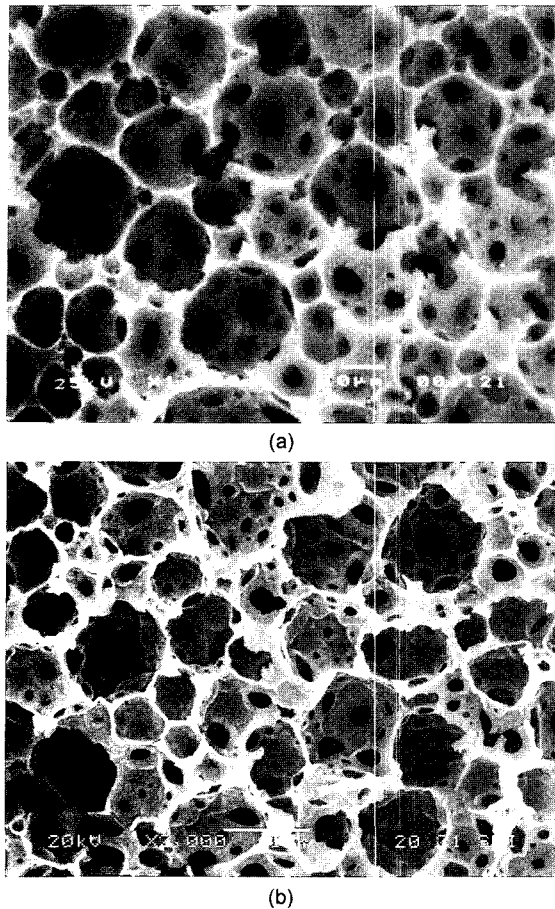
Figure 1. SEM micrographs of microcellular foams showing the effect of rubber concentration: The white horizontal bars indicate 10 μm. (a) R0S500 and (b) R5S500.
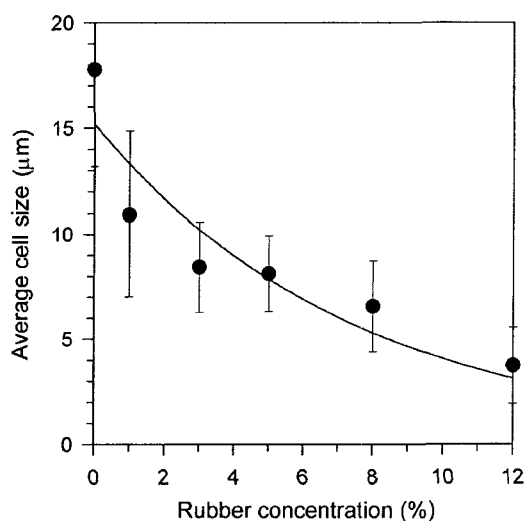
Figure 2. Effect of rubber concentration on the average cell size of the foams (R-series): The solid line is a regression fit from an exponential decay function with two parameters.
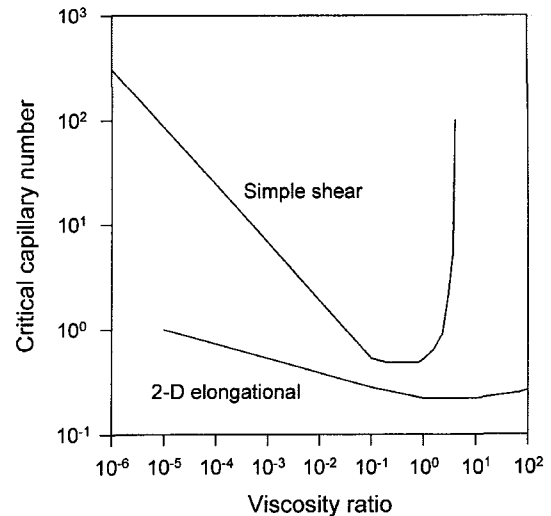
Figure 3. Critical capillary number for droplet breakup as a function of viscosity ratio.

The decreasing tendency of average cell size when rubber was added to the oil phase can be explained from the following diagram between the viscosity ratio and the critical capillary number shown in Figure 3.[13,14] Here, the viscosity ratio is defined as the ratio of viscosities of dispersed to continuous phases. The capillary number is the dimensionless number of external viscous force to surface force, and is given by

$$Ca = \frac{\mu_c \dot{\gamma} R}{\sigma} \qquad (1)$$

where μ_c is the viscosity of continuous phase, $\dot{\gamma}$ is the shear rate, R is the radius of droplet, and σ is the interfacial tension coefficient between two phases. Since the critical capillary number is the capillary number above which the breakup of droplet takes place, the maximum stable droplet size can be predicted from the relationship between the viscosity ratio and the critical capillary number. In simple shear flow, the critical capillary number when the viscosity ratio is less than unity increases with the exponent of 0.6 as the viscosity ratio decreases. It means the droplet under shear flow increases as the viscosity ratio decreases, provided that other conditions are constant. Our emulsion system consists of the aqueous phase as a dispersed phase and the oil phase as a continuous phase. If we roughly assume that the surfactant exists in the interface between two phases only and the aqueous and oil phases are made up of water and styrene, respectively, the viscosity ratio is nearly unity at room temperature since the viscosities of water and styrene are 1.0 and 0.8 cp at 20 °C, respectively. As rubber is introduced to the oil phase, the viscosity of continuous phase increases and the viscosity ratio decreases provided that the viscosity of dispersed phase is the same regardless of immiscible rubber. From eq. (1), droplet size is inversely proportional to the

viscosity of continuous phase at a given capillary number. Conclusively, the cell size decreases with an exponent of -0.4 as the viscosity of oil phase increases. As can be seen in Figure 2, the average cell size of the foam samples decreases as rubber concentration increases. The interfacial tension between two phases depending on rubber concentration should be considered to draw a quantitative analysis.

Effect of Agitation Speed on Cell Size. Representative SEM micrographs of microcellular foams showing the effect of agitation speed at the rubber concentration of 3% are shown in Figure 4. It is well known from the theory on the deformable droplet of immiscible two-phase system that an increase in agitation speed has a great influence on the size reduction of droplets. Compared to the sample prepared with low agitation speed shown in Figure 4(a), the samples prepared with higher agitation speed shown in Figure 4(b)-(d) produced much smaller cell size, indicating strong dependence on agitation speed. Except for the differences in average cell size and cell size distribution, the morphology of the cell and the open window between adjacent cells seems to be almost identical regardless of agitation speed.

The effect of agitation speed on the average cell sizes of the foams prepared from S-series is shown in Figure 5. It clearly shows that the average cell size decreased hyperbolically as the agitation speed increased. The solid and dashed lines in the figure were plotted based on the hydrodynamic analysis.[15,16] The Kolmogoroff length scale is defined as
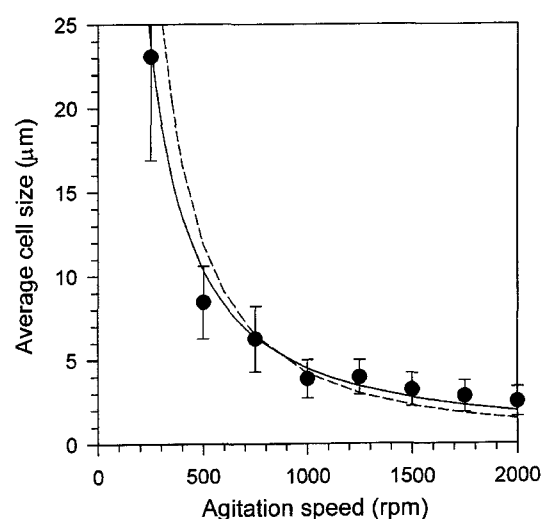
Figure 5. Effect of agitation speed on the average cell size of the foams (S-series): the solid line is a fit from a hyperbolic function with the exponent of -1.2, and the dashed line is a fit with the exponent of -1.5.

$$\eta = (v_c^3/\varepsilon)^{1/4} \tag{2}$$

where v_c is the kinematic viscosity of continuous phase and ε is the local energy dissipation rate per unit mass. If the maximum stable drop size (d_{max}) is smaller than η, the drop
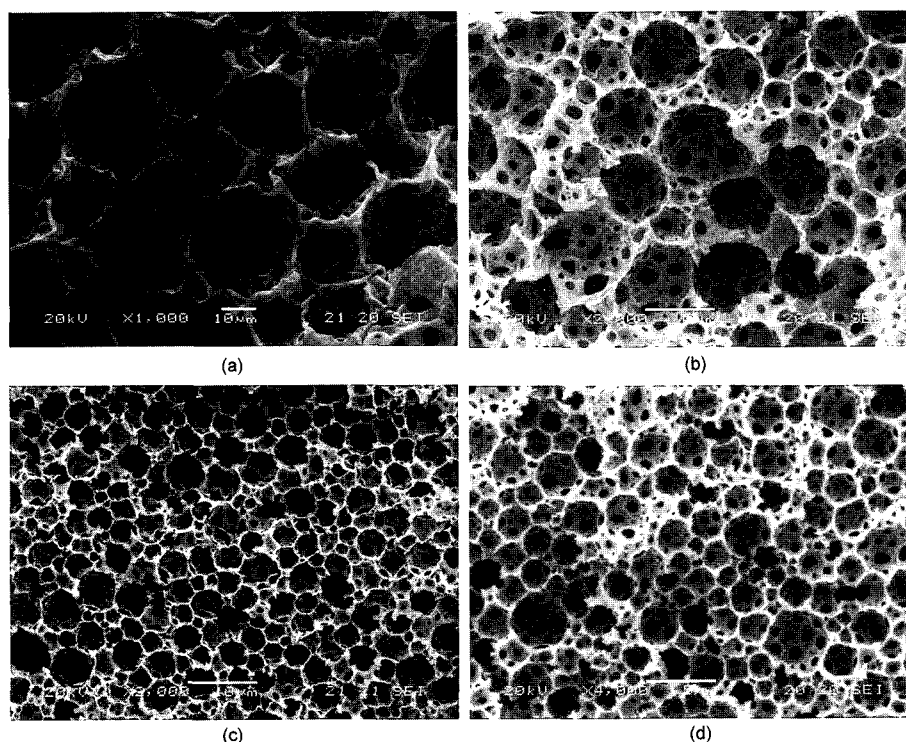
Figure 4. SEM micrographs of microcellular foams showing the effect of agitation speed: the magnifications are different. (a) R3S250, (b) R3S500, (c) R3S1000, and (d) R3S2000.

breakup would be dominated by viscous force and the drop diameter is proportional to $N^{-1.5}$, where N is the agitation speed. However, if d_{max} is larger than η, then breakup would be dominated by inertial force and the corresponding exponent on N is -1.2.

Although the theory was developed for highly agitated, dilute dispersion system without any coalescence, a correlation fit was quite satisfactory to our system as well. The average cell size of the sample prepared at the agitation speed of 1000 rpm showed about 5-6 times smaller than that of the sample at 250 rpm. Since our system is composed of highly concentrated emulsion, the probability of coalescence between droplets during mixing can exist inevitably but may be minimal because the droplets enclosed by surfactant are substantially stable.

Compression Properties. Representative compression stress-strain curves of the foam samples showing the effects of rubber concentration and agitation speed are shown in Figure 6. To distinguish the curves, the startups of strains were shifted horizontally to 0, 10 and 20% in the order of increasing rubber concentration and agitation speed, respectively. The graphs follow typical three stage foam compression behaviors including a linear elastic region, a plateau region and a bulk compression region. Since the crush strength and Young's modulus are the important mechanical properties in many practical applications, these two properties were measured from the compression stress-strain curves. The former was calculated from the break between linear and plateau regions and the latter was calculated from the slope of initial linear elastic region.[17] With the increasing rubber concentration up to 5% at the agitation speed of 500 rpm as shown in Figure 7, the crush strength decreased and Young's modulus increased. On the whole, it is estimated that both properties

are comparable to the unmodified foam without rubber. By introducing the rubber, foam mechanical properties were slightly modified to have weak but hard nature with much finer microcellular morphology. At more than 5% of rubber concentration, the modulus decreased gradually while the strength remained almost unchanged. Figure 8 represents the crush strength and Young's modulus showing the effect of agitation speed at 3% of rubber concentration. With the increasing agitation speed up to 1250 rpm, increasing tendency in both the strength and the modulus can be seen, while negative effect can be inferred with further increase of agitation speed. It is suspected that too higher speed causes the homogeneous mixing of the emulsion to be disturbed by air intake due to centrifugal force.
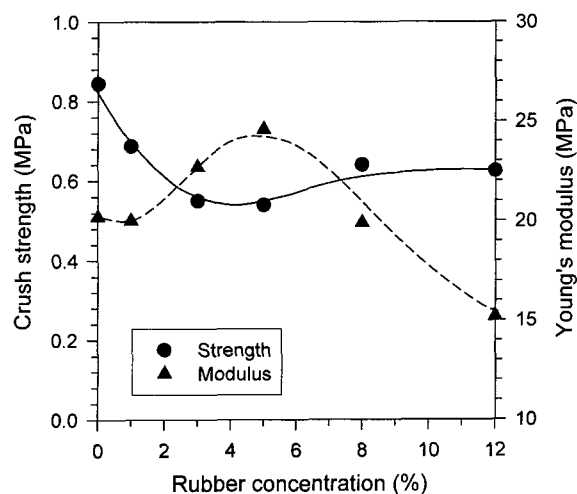

Figure 7. Crush strength and Young's modulus as a function of rubber concentration.
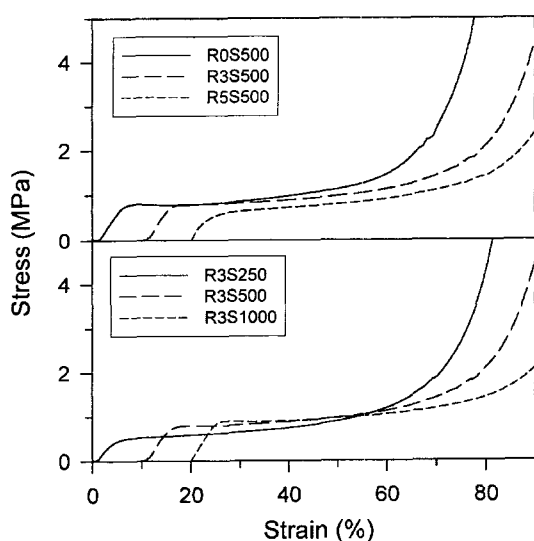

Figure 6. Compression stress-strain curves of microcellular foams showing the effect of rubber concentration.
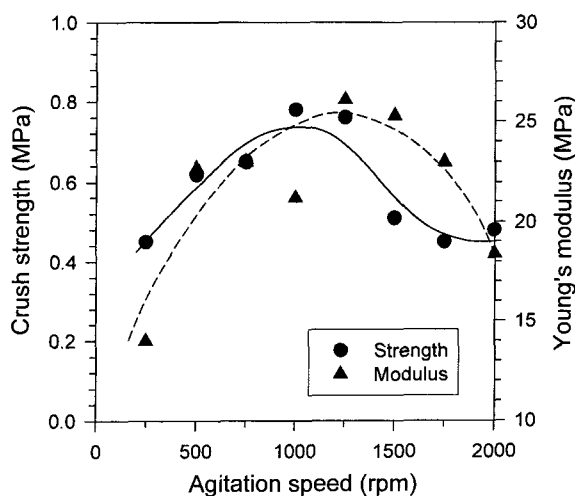

Figure 8. Crush strength and Young's modulus as a function of agitation speed.

Conclusions

Open microcellular foams modified by introducing a polybutadiene into the conventional water/styrene emulsion system were prepared using a HIPE polymerization technique. Compared to the foam prepared with the conventional formulation, the foams prepared in this study showed much finer microcellular morphology with comparable mechanical properties. The average cell size of the foams decreased as the rubber concentration increased. While the decrease in the viscosity ratio with less than unity gives an increase in cell size, the increase in the viscosity of continuous phase is responsible for the cell size decrease. It is confirmed that the latter played a dominant role in the cell size control due to the presence of dissolved rubber while compromised with the former. As is well known, the effect of agitation speed was dramatic in reducing the cell size of the foams. A hydrodynamic theory developed for highly agitated dispersion was applied to correlate the average cell size of the foams depending on agitation speed, and the correlation fit was quite satisfactory.

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