

PolyHIPE 발포체의 기공 크기에 대한 유체동력학적 해석

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Hydrodynamic Analysis on the Cell Size of PolyHIPE Foams

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Introduction

Open microcellular foams with low density prepared by the high internal phase emulsion (HIPE) polymerization of mixtures mainly composed of styrene and water, known as polyHIPE, show highly porous characteristics with regular, spherical and isotropic structure. The cellular structure of polyHIPE 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 . These HIPE foams are currently of interest because of their low density, microstructural and open cell, and high absorbency capabilities. A number of applications include polymeric membranes, ion exchange resin, controlled release systems, absorbents and inertial confinement fusion targets. 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. And, it is well known that the combination of vinyl radical polymerization with dissolved rubber yields a toughened material, possessing unique properties including higher toughness and impact strength. Another advantage of introducing a high molecular weight rubber is to increase the viscosity of oil phase, which substantially affects the cell size depending on the viscosity ratio between water and oil phases.

In this study, we introduced a polybutadiene rubber to the oil phase in order not only to endow the elastomeric property but also to reduce the cell sizes of the foams. The cell size variation due to rubber content and agitation speed could be explained by a hydrodynamic analysis describing drop breakup.

Experimental

Materials: The monomers used were styrene monomer (SM) and divinylbenzene (DVB), where DVB is composed of 55% mixture of isomers. SM was purified by a standard vacuum distillation method and divinylbenzene was washed with NaOH aqueous solution and then with water before use. Polybutadiene (PB) has monomer units of 36% cis, 55% trans and 9% vinyl and Mw of 420,000 g/mol. Sorbitan monooleate (SMO), potassium persulfate (KPS) and distilled water were used as received.

Preparation of PolyHIPE: Mixture of 15g comprised of SM and PB was used as styrene solution. Other components were fixed: 150g of water, 3.8g of DVB, 3.43g of SMO and 0.2g of KPS. Two types of code numbers, R-x-y or S-x-y, were used to identify the R- and S-series, where x stands for the PB % of styrene solution and y for the agitation speed. The oil phase consists of monomers, rubber and surfactant. The aqueous phase consists of distilled water and initiator. The oil phase was charged into a beaker and mechanically stirred at a given speed. While the oil phase was stirred, the aqueous phase was added dropwise. Total addition time was 30 min. Emulsion mixture was sealed with parafilm to minimize water evaporation and polymerized for 48 hours in a convection oven at 60°C. The polymerized mass was placed in an oven and dried to remove water and residual volatiles.

Hydrodynamic Analysis

In dispersion processes, the mixing impeller produces the flow fields that lead to drop breakup and provides bulk motion to homogenize composition in the vessel. Viscous, inertial and interfacial forces act on the surface of the drop and viscous forces also act inside it. The balance of the outside acting forces is expressed in the Weber (or capillary) number:

$$We = \tau d / \sigma \quad (1)$$

where d is the drop diameter and σ is the interfacial tension. The outside stress τ can be either inertial or viscous stress.

A drop exposed to a turbulent flow field will be subject to either inertial or viscous force. A criterion to determine which force is dominant is the Kolmogorov's length scale, i.e.

$$\eta = \left(\nu_c^3 / \varepsilon \right)^{1/4} \quad (2)$$

where ν_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 $d_{\max} \ll \eta$, then the

drop breakup presumably would be dominated by viscous force. However, if $d_{\max} \gg \eta$, then breakup would be dominated by inertial force.

Drop breakup by shear and elongational flows has different dependencies on the viscosity ratio of dispersed to continuous phases. From single-drop experiments, it is known that shear flow does not lead to drop breakup above the viscosity ratio of around 4, as depicted in Fig. 1. Since the critical Weber number is the Weber number above which the breakup of drop takes place, the maximum stable drop size can be predicted from the relationship between the viscosity ratio and the critical Weber number.

Results and Discussion

SEM micrographs were taken to examine the microstructural morphology of polyHIPE samples. Figure 2 shows representative samples showing the effect of rubber content at the agitation speed of 500rpm. Compared to the sample prepared without rubber, the sample prepared with rubber shows smaller cell sizes. Figure 3 shows the effect of rubber content on the average cell sizes of the samples prepared from R-series. The average cell size of the sample prepared with 12% rubber shows about 4 or 5 times smaller than that of the sample without rubber. Figure 4 shows some SEM micrographs showing the effect of agitation speed at the rubber content of 3%. The sample prepared with high agitation speed produced much smaller cell size, indicating strong dependence on agitation speed. Except for the size difference, the morphology of the cell and the open window between adjacent cells seems to be almost identical regardless of agitation speed. Figure 5 shows the effect of agitation speed on the average cell sizes of the samples prepared from S-series. It clearly shows that the average cell size hyperbolically decreases as the agitation speed increases. The solid line in the figure was plotted based on the drop breakup by viscous stress, where the drop diameter is proportional to the agitation speed with the exponent of -1.2 . The dashed line with the exponent of -1.5 was plotted based on the drop breakup by inertial stress. While the theory was originally developed for dilute dispersions neglecting coalescence and for a turbine agitator, correlation curves were quite satisfactory to our system as well. It is suspected that deviation mainly comes from coalescence due to highly concentrated emulsion system.

Acknowledgement

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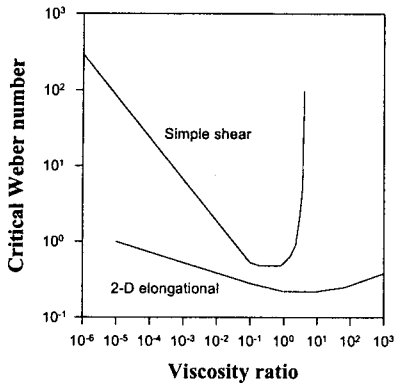


Fig. 1. Critical capillary number for drop breakup as a function of viscosity ratio.

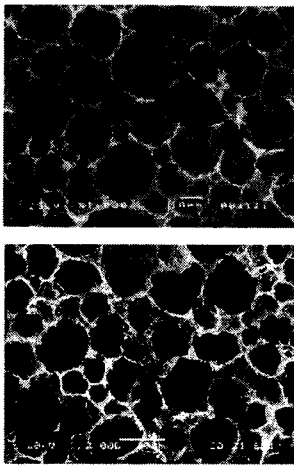


Fig. 2. SEM micrographs of polyHIPE foam: (a) R-0-500, (b) R-5-500.

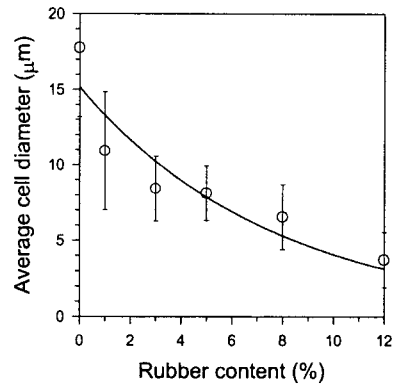


Fig. 3. Effect of rubber content on cell size (solid line: regression fit).

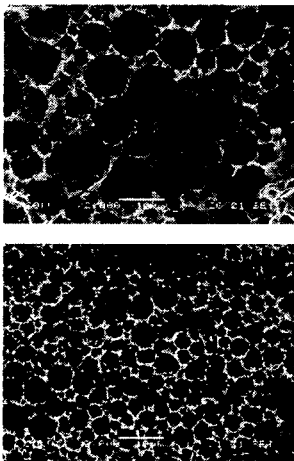


Fig. 4. SEM micrographs of polyHIPE foam: (a) S-3-500, (b) S-3-1000.

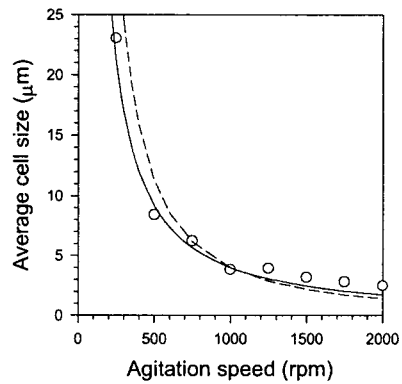


Fig. 5. Effect of agitation speed on cell size (solid line: exponent of -1.2 , dashed line: exponent of -1.5).