Open Porous Polymer Foams via Inverse Emulsion Polymerization: Should the Definition of High Internal Phase (Ratio) Emulsions Be Extended?

Angelika Menner,[†] Ronald Powell,[‡] and Alexander Bismarck*,[†]

Department of Chemical Engineering, Polymer & Composite Engineering (PaCE) Group, Imperial College London, South Kensington Campus, London SW7 2AZ, UK, and Halliburton Energy Services, 2600 South 2nd Street, PO Box 1431, Duncan, Oklahoma 73536-0470

Received December 19, 2005
Revised Manuscript Received February 2, 2006

In recent years high internal phase emulsions (HIPEs) with a continuous organic phase consisting of monomers, cross-linker, and surfactant gained increasing interest.[1] Lissant[2] was the first to define HIPEs as emulsions containing an internal phase volume of 70 vol % or greater. Nowadays, HIPEs are commonly defined as emulsions containing an internal phase volume of 74 vol % or greater, which causes the internal phase (i.e., droplets) of the emulsion to be of nonuniform size or deformed to polyhedra.[1,3−7] The liquid but highly viscous nature of HIPEs allows polymerized HIPEs (polyHIPEs) to be given any shape; i.e., no machining is required. During the polymerization of the continuous phase of HIPEs, the structure of the emulsion acts as a template for the resulting polyHIPE. PolyHIPEs are polymer foams with an open porous network structure, low foam densities, and a very high porosity, up to 95%.[5−7] PolyHIPEs are considered for numerous applications where high porosities and high degrees of pore interconnectivity are required.[8−13] Even though many applications have been explored, only limited progress in the exploitation of these materials has been made so far because of the poor mechanical performance of the material. The poor mechanical performance of polyHIPEs is mainly caused by their extremely low foam density.

Studies on concentrated emulsions such as HIPEs indicate that a minimum volume fraction of the internal droplet phase Φ_D of 0.74 is required to obtain emulsions in which the droplet phase is deformed and distorted and thereby each droplet is in contact with its neighboring droplets.[14−17] This leads to the characteristic high viscosity of HIPEs. During the polymerization of the continuous phase of a HIPE, pore throats form in the region of the contact points between neighboring droplets. The formation of the pore throats is a complex phenomenon which depends on many parameters, such as the volume fraction of the internal phase, the concentration of the surfactant, the droplet size, the tendency for Ostwald ripening, and the nature of the polymer forming throughout the polymerization.[2] Since the open porous structure is desired for polyHIPEs, the maximum continuous phase level is believed to be limited to 26 vol %, which causes the extremely low foam density of the resulting polyHIPE.

We focus on the question how to increase the foam density of polyHIPEs without affecting the interconnected pore network structure. This requires the increase of the maximum continuous phase level of HIPEs. The volume fraction of the continuous phase was 16 and 40 vol % for the concentrated emulsions **1** and **2**, respectively. The main component making up 50 vol % of the organic phase was divinylbenzene (DVB; Sigma Aldrich (Gillingham, UK)). The methacryloxypropyltrimethoxysilane (MPS; Sigma Aldrich) content in the continuous phase of both emulsions was 30 vol %. Furthermore, the organic phase contained 20 vol % of the nonionic polymeric surfactant Hypermer 1070 with an hydrophilic−lipophilic balance (HLB) of 6.7 (UNIQUEMA, Wirral, UK) and 1 mol % of the initiator α,α′-azoisobutyronitrile (AIBN; Sigma Aldrich). The organic phase was mixed in a reaction vessel fitted with an addition funnel and a glass paddle rod connected to an overhead stirrer. The stirring rate of 400 rpm was kept constant during the preparation of the emulsion. The aqueous phase, containing 0.034 mol/L of $CaCl_2 \cdot 2H_2O$ (Sigma Aldrich) as electrolyte to suppress Ostwald ripening, was slowly added to the stirring reagents. To obtain a highly viscous emulsion, the stirring rate was increased to 2000 rpm for 10 min. All chemicals were used as received without further purification. After preparation, the liquid formulations were poured into a mold and polymerized at 70 °C in an oven for 24 h. The polymerized samples were removed from the mold, purified, and dried to constant weight in a vacuum at 80 °C.

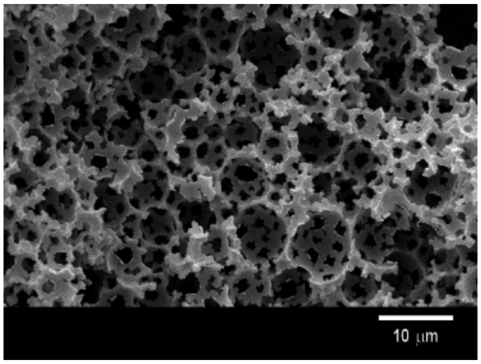

Figure 1. SEM image of polyHIPE **1**.

The polymerization of the emulsions **1** and **2** leads to the formation of white and chalky monoliths. The high degree of cross-linking explains the absence of a glass transition in the temperature region of 20−200 °C. During the polymerization of the emulsions **1** and **2** the organic polymer network was reinforced by an inorganic polysilsesquioxane network, which formed additionally via the hydrolytic condensation of the trimethoxysilyl groups of MPS.

PolyHIPE **1** was obtained via the polymerization of a typical HIPE with an organic phase level of 16 vol %. The density of the polymer matrix and foam density as well as percentage porosity of the polyHIPEs were obtained using pycnometry.[18] PolyHIPE **1** is a highly porous material (porosity of 89%) with a foam density of 0.138 ± 0.001 g/cm^3 and a density of the polymer matrix of 1.241 ± 0.007 g/cm^3. The morphology of the polyHIPEs was studied using scanning electron microscopy.[19] The SEM micrograph of **1** (Figure 1) has the characteristic open porous structure of polyHIPEs. The pore size of **1** is 5 ± 2 μm in diameter. The pores are interconnected via pore throats. Their size is relatively uniform and ranges from 1.5 to 2.5 μm. The surface area[20] of **1** is with 3.60 ± 0.13 m^2/g in the range commonly reported for polyHIPEs.[3]

[†] Imperial College London.
[‡] Halliburton Energy Services.
* Corresponding author: e-mail a.bismarck@imperial.ac.uk.

10.1021/ma052705x CCC: $33.50

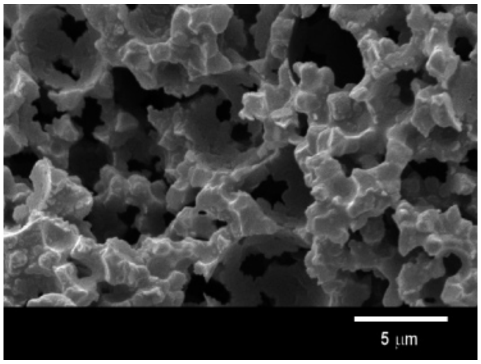

Figure 2. SEM image of polymer foam **2**.

The emulsion polymerized to **2** contained 40 vol % organic phase relative to the total volume of the emulsion. As discussed above, such emulsions do not classify as HIPEs. It was claimed that an internal aqueous phase volume exceeding 74 vol % is required to prepare polyHIPEs.[1−7] According to Masons,[16] the droplets in emulsions, such as **2** ($\Phi_D(\mathbf{2}) = 0.6$), should be transiently caged by their neighbors. If the structure of such an emulsion (at the gel point of the polymerization) acts as a template for the resulting polymer foam, it should lead to highly porous but closed cell foams due to the absence of a sufficient contact area of neighboring droplets. However, we find **2** (porosity of 70%) to be a highly porous foam with an open pore structure as shown in Figure 2. The pore diameters in polymer foam **2** range from 2 to 5 μm and the pore throat sizes from 1 to 2 μm. The density of the polymer matrix of foam **2** is 1.150 ± 0.001 g/cm^3. The foam density of **2** (0.309 ± 0.003 g/cm^3) is much higher as compared to that of **1** (0.138 g/cm^3), which is expected because of the variation of the organic phase levels of the polymerized emulsions. Polymer foam **2** possesses a surface area of 2.03 ± 0.04 m^2/g. All properties of **2** fit the characteristics reported for polyHIPEs[1−10] and those obtained for polyHIPE **1**. It seems that the polymeric nature of the surfactant Hypermer 1070 is much better suited to stabilize emulsions with 40 vol % continuous phase, such as emulsion **2**, against coalescence than the commonly used surfactant Span 80. The use of the Hypermer surfactant not only enhances the emulsion stability over a long period of time but also helps to stabilize the emulsions during heating, which is a requirement for the formation of highly porous and interconnected polymer foams such as **2**.

The mechanical properties of the resulting polymer foams **1** and **2** were determined using compression tests[21] in order to study the impact of the foam density on the mechanical performance of the polyHIPEs. The elastic modulus of **1** is with 3 MPa relatively low, which is mainly a result of the low foam density. Foam **2** has a much improved mechanical performance; an elastic modulus 24 MPa was measured. The stiffness of **2** increased due to the increased organic phase volume of 40 vol % of the concentrated emulsion polymerized to **2**, which causes the foam density to increase.

Our results show that increasing the continuous phase volume of HIPEs is a simple but very effective way to improve the mechanical properties of polyHIPEs without affecting the highly interconnected nature of the porous medium. Commonly these emulsions with reduced internal phase are not considered to be HIPEs, and the polymerization of their organic phase should not lead to highly porous and interconnected polymer structures. We therefore question the definition of HIPEs. Should the definition of HIPEs be extended? We believe an alternative definition should consider all emulsions containing a polymerizable continuous phase, which can act as a template for the formation of highly porous solids with interconnected pore network structures. Emulsions with an internal phase level of 60 vol % should be included. However, the lower limit for internal phase has yet to be found.

References and Notes

(1) Cameron, N. R. *Polymer* **2005**, *46*, 1439−1449.
(2) Lissant, K. J. *J. Colloid Interface Sci.* **1966**, *22*, 462−468.
(3) Cameron, N. R.; Sherrington D. C. *Adv. Polym. Sci.* **1996**, *126*, 163−214.
(4) Cameron, N. R.; Sherrington, D. C.; Albiston, L.; Gregory D. P. *Colloid Polym. Sci.* **1996**, *274*, 592−595.
(5) Williams, J. M. *Langmuir* **1991**, *7*, 1370−1377.
(6) Williams, J. M.; Gray, A. J.; Wilkerson, M. H. *Langmuir* **1990**, *6*, 437−444.
(7) Williams, J. M.; Wrobleski, D. A. *Langmuir* **1988**, *4*, 656−662.
(8) Wakeman R. J.; Bhumgara, Z. G.; Akay, G. *Chem. Eng. J.* **1998**, *70*, 133−141.
(9) Akay, G.; Erhan, E.; Keskinler, B. *Biotechnol. Bioeng.* **2005**, *90*, 180−190.
(10) Krajnc, P.; Leber, N.; Stefanec, D.; Kontrec, S.; Podgornik, A. *J. Chromatogr. A* **2005**, *1065*, 69−73.
(11) Akay, G.; Birch, M. A.; Bokhari, M. A. *Biomaterials* **2004**, *25*, 3991−4000.
(12) Bokhari, M. A.; Akay, G.; Zhang, S. G.; Birch, M. A. *Biomaterials* **2005**, *26*, 5198−5208.
(13) Bhumgara, Z. *Filtr. Sep.* **1995**, *32*, 245−251.
(14) Tausk, R. J. M.; Wilson, P. N. *Colloids Surf.* **1981**, *2*, 71−80.
(15) Das, K.; Mukesh, D.; Swayambunathan, V.; Kotkar, D. D.; Ghosh, P. K. *Langmuir* **1992**, *8*, 2421−2436.
(16) Mason, T. G. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 231−238.
(17) Babak, V. G.; Stebe, M.-J. *J. Dispersion Sci. Technol.* **2002**, *23*, 1−22.
(18) Density and porosity: The density of the polymer matrix (ρ_m) and foam density (ρ_f) as well as percentage porosity (P) of the polyHIPEs were obtained using pycnometry (Micromeritics GeoPyc 1360 V1.03, Micrometrics Limited, Dunstable, UK) in conjunction with helium displacement pycnometry (Micromeritics AccuPyc 1330 V3.00, Micrometrics Limited, Dunstable, UK). At least six foam samples were analyzed to obtain statistically relevant data.
(19) Scanning electron microscopy (SEM): The morphology, pore, and pore throat size of the polyHIPEs were studied using scanning electron microscopy (JEOL JSM 5610 LV, JEOL Ltd., Welwyn Garden City, UK). Prior to observation, each sample was sputtered with gold to ensure sufficient conductivity.
(20) BET surface area: The surface area of the polyHIPEs (about 0.2 mg material) was determined using nitrogen adsorption isotherms at 77 K applying the Brunauer−Emmet−Teller (BET) model. The measurements were carried out using a surface area analyzer (Micromeritics ASAP 2010, Micrometrics Limited, Dunstable, UK). Prior to the measurements, adsorbed impurities were removed via a “degassing” step.
(21) Mechanical properties: Compression tests were carried out on polyHIPEs **1** and **2** using a Lloyds universal testing machine (Lloyds EZ50, Lloyds Instruments Ltd., Fareham, UK). Six samples (25 mm diameter and 10 mm high) were compressed at a loading rate of 1 mm/min by means of a compression plate until a displacement of 5 mm of the initial test piece thickness is attained. The elastic modulus was determined from the initial slope of the stress−strain plot.

MA052705X