Production of High Internal Phase Emulsion with a Miniature Twin Screw Extruder

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ABSTRACT: Emulsions are traditionally prepared by batched emulsifying an oil phase and aqueous phase with a magnetic/mechanical stirrer, homogenizer, or ultrasonic machine, etc. Herein, high internal phase emulsions (HIPEs) produced with a miniature twin screw extruder were first investigated. Adding an oil phase (the mixture of styrene, divinylbenzene, and span 80) and aqueous phase to the inlet of a miniature twin screw extruder, a series of white and viscous HIPEs were obtained at the outlet of the extruder. With the screw rotation speed and the surfactant content varied respectively in the ranges of 50–200 rpm and 5–20%, a series of HIPEs having uniform droplet size were produced. Polymerizing these HIPEs caused a series of polymerized HIPES, which have a well-defined open-cell structure. The method developed herein shows that it is possible to prepare emulsions with oil and water by twin screw extrusion. Also, it may also cause a continuous preparation of HIPEs when the miniature twin screw extruder was replaced by an industrial extruder.

INTRODUCTION

High internal phase emulsions (HIPEs) have been widely used in many fields including food preparation, fuel, oil recovery, and cosmetics.1 If there are one or more monomers contained in the continuous phase of HIPE, the viscous liquid property of the emulsion allows polymerized HIPEs (polyHIPEs) with any shape.2,3 During the polymerization, the emulsion acts as a template for the resulting polyHIPE. A polyHIPE is a kind polymer foam with a tunable porous structure, low density, and very high pore volume, which make the materials have great potential applications in areas such as scaffolds for tissue engineering,4,5 as well as supports for catalysis,6,7 water treatment,8,9 supports for catalysis,10,11 and separation membranes.12

HIPEs are defined as emulsions containing internal phases over 74%, which lead to emulsions having nonuniform or polyhedral droplets.13 Emulsion is a mixture produced by dispersing liquid droplets in another liquid phase. It is normally prepared by emulsifying these two immiscible liquids with a magnetic/mechanical stirrer, homogenizer, or ultrasonic machine, which provides the necessary energy to achieve a metastable state by splitting one phase into another.

Conventional methods for manufacturing HIPEs include dissolving appropriate emulsifiers (surfactant14,15 or solid particles16–21) in the components that make up the continuous phase and then gradually adding dispersed phases to the continuous phase under continuous shearing, such as magnetic/mechanical stirring,22 homogenizing,23 and ultrasonic emulsification strategies.24–26 HIPEs prepared by different shearing methods would have different properties, which mainly performed in the difference in viscosity and stability of the emulsion and in the pore size and mechanical properties of the resulting polyHIPEs. Recent studies have focused on various shear-related issues, including a two-rod batch mixer27 and stirred cell membrane emulsification.28 However, although it is noted that the shearing methods reported normally prepare HIPEs in a batched way, a continuous and large-scale preparation method for fabrication of HIPEs is still to be explored.

Alternatively, a twin screw extruder has been widely used to continuously produce polymeric materials.32,33 Extrusion means forcing a material passing through a restricted orifice (i.e., a die). A twin screw extruder is normally composed of two rotating Archimedes screws, which are installed in a barrel to gradually increase the pressure and push the ingredients forward through the die, and the products are obtained in the die. The thermomechanical treatment in the barrel helps to texture the product, while the expansion in the die is responsible for the final product formation. The screw speed, screw shape, die size and shape, temperature, pressure, and water content are the most important parameters to control the process.34–37 Despite the high operating temperature (up to 200 °C), high pressure (over 10 MPa), and high shear rate, the extrusion polymer process, also known as hot melt extrusion, is widely used in industry because of its continuous, fast, simple, and versatile operation for converting raw materials into final products.38 Extrusion has been applied in the polymer industry for decades as a mass production process to produce many products, such as tubes, frames, plastic plates, and films. However, extrusion has only recently attracted attention to the formation of emulsion. Recently, a continuous emulsification technology, solvent-free extrusion emulsification (SFEE), was developed to prepare submicron particles (100–500 nm) from high-viscosity polymers (100–1000 Pa·s) by a twin screw extruder.38–40 Meanwhile, in most cases, emulsions are prepared by emulsifying an oil phase and aqueous phase.

In this study, a series of water-in-oil (W/O) HIPEs having uniform droplets were first prepared with a miniature twin screw
extruder (Figure 1). There is a circulation slot inside the machine, which is different from the traditional industrial twin-screw extruder. The presence of the circulation slot allows the mixture of oil and aqueous phases to recycle flow in the barrel of the extruder to overcome the shortcomings of the insufficient length of the screw and barrel. Herein, by adding an oil phase (the mixture of styrene, divinylbenzene, and surfactant span 80) and aqueous phase to the inlet of the extruder, a series of white and viscous W/O HIPEs were obtained at their outlet. The method developed herein may cause a continuous preparation of HIPEs and improve the performance consistency of the HIPE products and their resulting polyHIPEs when the miniature twin screw extruder was replaced by an industrial extruder. The difference in performance between different batches of emulsion made by a traditional emulsifying method is one of the important factors limiting the application of emulsion.

**EXPERIMENTAL SECTION**

**Materials.** Styrene (St, Shanghai Ling Feng Chemical Reagent Co., Ltd., China) and divinylbenzene (DVB, 80%, the remainder being m- and p-ethylstyrrene, Sigma-Aldrich) were purified by passing through neutral chromatographic aluminum oxide to eliminate the inhibitor. Sorbitan monooleate (KPS, Adamas-beta, China) was recrystallized before use. Sodium chloride was purchased as supplied. Potassium persulfate (KPS, Adamas-beta, China) was used. Deionized water was used.

**Preparation of HIPE and polyHIPE.** The HIPE was prepared with a twin conical screw miniextruder (Thermo Electron, MiniCTW). The maximum and minimum diameters of the conical screw were 13.4 and 4.4 mm, respectively. A mixture of St, DVB, and Span 80 (the volume ratio 4:1:X was used as oil phase; Table 1; X represented the volume ratio of Span80). An aqueous solution containing KPS and NaCl of 0.4 and 1.0 wt %, respectively, was added to a 50 mL beaker and an aqueous solution (20 mL, containing KPS and NaCl of 0.4 and 1.0 wt %, respectively) were added to a 50 mL beaker and homogenized with an Ultra Turrax T18 homogenizer (rotor diameter = 7 mm) at 12,000 rpm.

**Characterization.** The stability of HIPEs was detected by testing the backscattering of infrared light (λ = 880 nm) from the emulsion with an optical Turbiscan analyzer (Formulaction, France). Before testing, the HIPE was poured into a flat bottomed cylindrical glass tube with height and external diameters of 70 and 27.5 mm, respectively. Then, the tube was placed in the instrument, and the backscattering of light from emulsion was detected along the tube at 25 °C. The result was given as the average backscattering of the sample versus time.

| Table 1. Parameters of HIPEs and Their Resulting polyHIPEs |
|----------------|----------------|----------------|
| sample | emulsification method | rotation speed (rpm) | surfactant content (vol %) | $D$ (μm) |
| 1 | twin screw | 30 | 13 | 7.8 ± 1.9 |
| 2 | twin screw | 50 | 13 | 6.2 ± 1.1 |
| 3 | twin screw | 100 | 13 | 2.9 ± 1.3 |
| 4 | twin screw | 150 | 13 | 4.9 ± 2.1 |
| 5 | twin screw | 200 | 13 | 4.4 ± 3.4 |
| 6 | twin screw | 150 | 4.8 | 44.3 ± 6.2 |
| 7 | twin screw | 150 | 9.1 | 39.0 ± 5.8 |
| 8 | twin screw | 150 | 16.7 | 33.1 ± 3.9 |
| 9 | magnetic stirring | 800 | 13 | 13.2 ± 2.0 |
| 10 | homogenizing | 12,000 | 13 | 13.2 ± 2.0 |

The surfactant content corresponds to the oil phase. The polyHIPE was not obtained due to the instability of the HIPE and an aqueous solution (20 mL, containing KPS and NaCl of 0.4 and 1.0 wt %, respectively) were added to a 50 mL beaker and homogenized with an Ultra Turrax T18 homogenizer (rotor diameter = 7 mm) at 12,000 rpm.

The polyHIPE morphology was observed by a Hitachi S-3400 N fluorescence microscope, a resonant confocal microscope, a confocal microscopy (LSCM). The LSCM was equipped with an automated inverted confocal microscope, a resonant scanner, and an objective. Before observation, a fluorescent dye (Coumarin 6) was added to the organic phase, and a laser line (488 nm) was used to excite the dye. The average droplet size of the HIPE was calculated from confocal images using the image analysis software ImageJ released by the National Institute of Health (NIH, US). One hundred droplets were measured for each HIPE. The photographs of HIPEs were performed using a Nikon camera (SLR D90).

The polyHIPE morphology was observed by a Hitachi S-3400 N SEM. Also, the average void size ($D$) and interconnecting pore size ($d$) were determined from SEM images by measuring more than 100 voids with the ImageJ software.

The interconnectivity degree ($I$) of the polyHIPE was calculated by eq 1:

$$I(\%) = \frac{1}{4} \times n \times \left( \frac{d}{D} \right)^2 \times 100\%$$

where $n$ is the average number of interconnected pores per void, $d$ is the average interconnected pore diameter, and $D$ is the average void diameter. More than 100 voids and interconnected pores were correspondingly measured for each polyHIPE.

The compression test of polyHIPEs was run with a universal material experiment machine (LD104, SANS, China). Cylindrical monoliths having a diameter and height of 6.0 and 10 mm, respectively, were used. The compression test run at a velocity of 1.0 mm/min until half of the height of the monolith reached.
The compression modulus was obtained from the stress–strain curve.

RESULTS AND DISCUSSION

The screw speed was considered as one of the most important parameters for controlling the polymer processing.41 Herein, aiming to study the effect of the screw rotation speed on the HIPE and its resulting polyHIPE, a series of HIPEs were prepared with varied screw rotation speeds (30, 50, 100, 150, or 200 rpm) as shown in Figure 2. It was found that the HIPE underwent quick separation as soon as it reached the outlet of the extruder (Figure 2a) when the screw rotation speed was 30 rpm. Also, increasing the screw speed to 50 or higher, the HIPEs were stable after they were collected at the outlet of the extruder (Figure 2a,b).

Further analysis of the HIPEs 2–5 with Turbiscan analyzer (Figure 3) showed that the backscattering of these HIPEs increased with an increase in a screw rotation speed, which meant that the stability of the HIPEs was enhanced by increasing the screw speed.42−44 This conclusion was also confirmed by the images taken by laser scanning confocal microscopy (Figure 4) and the viscosity of the HIPEs measured by a rotational rheometer (Figure 5). One can see that increasing the screw rotation speed decreased the average droplet size of the HIPEs and increased the emulsions’ viscosity. The smaller the droplet size and the higher the viscosity, the more stable the emulsions.45−48

As shown in Figure 6 (samples 2−5), polymerizing these HIPEs caused a series of polyHIPEs having a well-defined open-cell structure, which was similar to those of the porous polymers from traditional emulsifying methods (e.g., magnetic stirring (sample 9) and homogenizing (sample 10) in Figure 5). Samples 9−10 were prepared with the same composition as those of samples 2−5. The SEM analysis showed that as the screw speed of the extruder increased, the void size distribution became narrower (Figure 7), which agreed to the observation of HIPEs by laser scanning confocal microscopy because the emulsion structure acts as a template for its resulted polyHIPEs.1
Compared to the polyHIPEs prepared with the same components and traditional methods such as magnetic stirring (Table 1 and Figure 5; sample 9) and homogenizing (Table 1 and Figure 5; sample 10), the average void sizes of the polyHIPEs prepared with a miniature twin screw extruder were much larger (2- to 3-fold and 5- to 7-fold of those in polyHIPEs prepared with magnetic stirring and homogenizing, respectively). This phenomenon could be due to the shear rate difference among these three emulsifying methods. Estimating from the rotation speed and diameter of the screw (length of magnetic stirrer or rotor diameter of homogenizer), one could find that the shear rates of the twin screw extruder, magnetic stirring, and homogenizing were thousands, tens of thousands, and hundreds of thousand millimeters per minute. They were orders of magnitude different in shear rates. Thus, polyHIPEs with a large void size, such as tens of micrometers, could be produced through a miniature twin screw extruder. A large void size is required when the polyHIPE is used in some fields such as tissue engineering.

As reported, the void size played an important role in the mechanical performance of porous materials. Therefore,
compression tests were run to check the effect of the void size on the mechanical performance of the polyHIPEs. The stress–strain curves of the polymers are shown in Figure 8, and their compression moduli are shown in Figure 9. However, one could see that the polyHIPE prepared with a screw rotation speed of 50 rpm, having the largest void size, had the poorest compression strength. With increasing the screw rotation speed from 50 to 200 rpm, the average void size of the resulting polyHIPEs decreased, and the compression strength increased. The phenomenon was consistent with the relationship between the void size and the compression modulus reported in the literature in which a quasi-linear dependence of Young’s modulus as a function of the pore size was mentioned when the internal phase volume fraction was kept constant. This may be due to the fact that the polyHIPE prepared with a higher screw rotation speed had a narrower void size distribution (Figure 7). A broader void size distribution may tend to cause stress concentration during the compression, which reduced the overall compression strength of the polyHIPE. Moreover, the compression modulus of the polyHIPEs prepared by a miniature twin screw extruder was compared with those of prepared by conventional emulsifying such as magnetic stirring and homogenizing (Figure 8). It could be found that the compression moduli of the polyHIPEs from a miniature twin screw extruder were poorer than those of the conventionally made polyHIPEs. This might also be contributed to narrow void size distributions obtained by magnetic stirring or homogenizing (Figure 6). When the void size distribution of the polyHIPE was broad, the stress concentration would be caused by the larger voids during the compression test, and the polyHIPE first broke in the large voids and then spread to the entire material. When the void size distribution of the polyHIPE was narrow, the stress will be evenly dispersed on each void of the polyHIPE, and the compression strength of the polyHIPE will be high.

As reported in the literature, the surfactant played a critical factor to tune the morphologies of HIPEs and the resulting polyHIPEs. Herein, the effect of the surfactant content on the HIPE was also taken into account. Four HIPEs (Table 1, samples 6, 7, 4, and 8) were prepared with surfactant contents of 4.8, 9.3, 13, and 16.7 vol %, respectively, relative to the continuous phase. The temperature of the barrel of the extruder was set at 30 °C, and the screw rotation speed for these samples was 150 rpm. The HIPE images performed by laser scanning confocal microscopy (Figure 4) showed that the droplet size decreased gradually with an increase in the surfactant contents, which caused a decrease in the void size of the polyHIPEs produced by polymerizing these four HIPEs (Table 1 and Figure 6). This phenomenon agreed to the effect of the surfactant content on the HIPE and its resulting polyHIPE prepared with traditional methods.

**CONCLUSIONS**

HIPEs were firstly produced with a miniature twin screw extruder. Also, polymerizing these HIPEs caused a series of polyHIPEs with a well-defined open-cell structure. It was found that the stability of HIPEs was enhanced with increasing the screw rotation speed and/or surfactant content, which caused a decrease in the droplet size of the dispersed phase and therefore a decrease in the void size of the HIPE-templated polyHIPEs. The method developed herein shows that it is possible to prepare emulsions with oil and water by twin screw extrusion. Also, it may also cause a continuous preparation of HIPEs when the miniature twin screw extruder was replaced by an industrial extruder.

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Notes
The authors declare no competing financial interest.

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**REFERENCES**

(1) Cameron, N. R. High internal phase emulsion templating as a route to well-defined porous polymers. *Polymer* 2005, 46, 1439–1449.
Soluble Porogenic Solvents: Span 80 as Surfactant.

Macromolecules

Emulsion-Derived (PolyHIPE) Solid Foams Prepared with Oil-Phase
Phase Emulsions (HIPEs): Preparation and Void Size Tuning.

Monoliths from 2-Hydroxyethyl Methacrylate Based High Internal
Streamlining Organic Free Radical Synthesis through Modern
Emulsions Stabilized Solely by Microgel Particles.

2009

monoliths from ionomer-stabilized high internal phase emulsions
Oxide

ACS Omega

Article

Macroporous Polymers Synthesized from Silica Particle Stabilized High
Biomaterials

templated porous polymers.

Angew.

structure for cartilage regeneration.

Polyester type polyHIPE scaffolds with an interconnected porous

Vukasovic

Emulsion Templating: Recent Advances.

Application for Catalyst of Fenton Reaction.

(15) Silverstein, M. S. Emulsion-templated polymers: Contemporary

(17) Kovac

(14) Wu, P.; Zhang, S.; Yang, H.; Zhu, Y.; Chen, J. Preparation of

(12) Zhang, S.; Chen, J.; Lykakis, I. N.; Perchyonok, V. T.

(20) Zheng, Z.; Zheng, X.; Wang, H.; Du, Q. Macroporous Graphene

(11) Hua, Y.; Zhang, S.; Chen, J.; Zhu, Y. Switchable release and

(6) Jiao, B.; Shi, A.; Wang, Q.; Binks, B. P. High-Internal-Phase

(8) Rather, A. M.; Manna, U. Facile Synthesis of Tunable and Durable

(7) Zhu, H.; Yang, X.; Cranston, E. D.; Zhu, S. Flexible and Porous

(39) Goger, A.; Thompson, M. R.; Pawlak, J. L.; Arnould, M. A.;

(38) Lawton, D. J. W. Solvent-free polymer emulsification inside a twin-

Extrusion Emulsification: Varying System Temperature.

Influence of twin-screw extrusion conditions on the dispersion of multi-

emulsions.

AIChE J.

Polymerization for oxidation of sulfides under visible light.

“2012

Chem. Mater.

Gel.

(31) Manga, M. S.; York, D. W. Production of Concentrated Pickering

(29) Forgacz, C.; Caubet, S.; Le Guer, Y. L.; Grassl, B.; El Omari, K.;

(28) Chen, X. W.; Wang, J. M.; Guo, J.; Wan, Z. L.; Yin, S. W.; Yang, X.

Hierarchical high internal phase emulsions and transparent oleogels
stabilized by quillaja saponin-coated nanodroplets for color performance.

Food Funct. 2017, 8, 823–831.

(30) Caubet, S.; Le Guer, Y.; Grassi, B.; El Omari, K.; Birot, M.;

Deleuze, H. Synthesis of Porous Emulsion-Templated Monoliths Using a Low-Energy Emulsification Batch Mixer. J. Polym. Environ. 2013, 21, 683–691.

(34) Sauceau, M.; Fages, J.; Common, A.; Nikitine, C.; Rodier, E. New challenges in polymer foaming: A review of extrusion processes assisted by supercritical carbon dioxide. Prog. Polym. Sci. 2011, 36, 749–766.

(35) Demongeot, A.; Groote, R.; Goossens, H.; Hoeks, T.; Tournilhac, F.; Leibler, L. Cross-Linking of Poly(butylene terephthalate) by Reactive Extrusion Using Zn(II) Epoxy-Vitrimer Chemistry. Macromolecules 2017, 50, 6117–6127.

(36) Zhou, Y.; Goossens, J. G. P.; Sijbesma, R. P.; Heuts, J. P. A. Poly(butylene terephthalate)/Glycerol-based Vitrimers via Solid-State Polymerization. Macromolecules 2017, 50, 6742–6751.

(37) Villmow, T.; Fötschke, P.; Pegel, S.; Häussler, L.; Kretzschmar, B. Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. Polymer 2008, 49, 3500–3509.

(38) Goger, A.; Thompson, M. R.; Pawlak, J. L.; Arnould, M. A.; Lawton, D. J. W. Effect of Viscosity on Solvent-Free Extrusion Emulsification: Varying System Temperature. Ind. Eng. Chem. Res. 2018, 57, 12071–12077.

(39) Goger, A.; Thompson, M. R.; Pawlak, J. L.; Arnould, M. A.; Klymachyov, A.; Lawton, D. J. W. Effect of Viscosity on Solvent-Free Extrusion Emulsification: Molecular Structure. Ind. Eng. Chem. Res. 2017, 56, 12538–12546.

(40) Goger, A.; Thompson, M. R.; Pawlak, J. L.; Arnould, M. A.; Lawton, D. J. W. Solvent-free polymer emulsification inside a twin-screw extruder. AIChE J. 2018, 64, 2113–2123.

(41) Elisa, P.; Coiai, S.; Augier, S. Control of macromolecular architecture during the reactive functionalization in the melt of olefin polymers. Prog. Polym. Sci. 2009, 34, 911–947.
(42) Mengual, O.; Meunier, G.; Cayréa, I.; Puech, K.; Snabre, P. TURBISCAN MA 2000: multiple light scattering measurement for concentrated emulsion and suspension instability analysis. *Talanta* 1999, 50, 445–456.

(43) Lemarchand, C.; Couvreur, P.; Vauthier, C.; Costantini, D.; Gref, R. Study of emulsion stabilization by graft copolymers using the optical analyzer Turbiscan. *Int. J. Pharm.* 2003, 254, 77–82.

(44) Mengual, O.; Meunier, G.; Cayre, I.; Puech, K.; Snabre, P. Characterisation of instability of concentrated dispersions by a new optical analyser: the TURBISCAN MA 1000. *Colloids Surf., A* 1999, 152, 111–123.

(45) Zhu, Y.; Zhang, R.; Zhang, S.; Chu, Y.; Chen, J. Macroporous Polymers with Aligned Microporous Walls from Pickering High Internal Phase Emulsions. *Langmuir* 2016, 32, 6083–6088.

(46) Fan, X.; Zhang, S.; Zhu, Y.; Chen, J. Macroporous polymers prepared via frozen UV polymerization of the emulsion-templates stabilized by a low amount of surfactant. *RSC Adv.* 2018, 8, 10141–10147.

(47) Pal, R. Rheology of high internal phase ratio emulsions. *Food Hydrocolloids* 2006, 20, 997–1005.

(48) Kim, H. S.; Mason, T. G. Advances and challenges in the rheology of concentrated emulsions and nanoemulsions. *Adv. Colloid Interface Sci.* 2017, 247, 397–412.

(49) Ceglia, G.; Mahe, L.; Viot, P.; Bernard, D.; Chirazi, A.; Ly, I.; Mondain-Monval, O.; Schmitt, V. Formulation and mechanical properties of emulsion-based model polymer foams. *Eur. Phys. J. E: Soft Matter Biol. Phys.* 2012, 35, 9708.

(50) Zhang, S.; Chen, J. Synthesis of open porous emulsion-templated monoliths using cetyltrimethylammonium bromide. *Polymer* 2007, 48, 3021–3025.