Controlling the transition of emulsion process from dripping to jetting in a flow-focusing microcapillary device

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The monodispersed microspheres were fabricated using a flow-focusing microcapillary device. The emulsification of monomer TPGDA in water solution was controlled through the adjustment of internal and outer phase flow rates. Results showed flow rates and the interface of internal and outer phase contributed to the different emulsion processes and differences in product size. With the increase of Ca from 0.12 to 0.24, the mechanism changed from dripping to jetting. When Ca increase to a value between 0.24 and 2.4, the mechanism changed to periodical dripping. Only the dripping mechanism creates microspheres whose radius is determined by the orifice size.

1. Introduction

Microfluidics refers to the theories and applications of the control on the small volumes of fluids, which provides useful applications for creating monodispersed polymer microspheres [1-3]. In comparison with other methods, microfluidics is a versatile approach and enables accurate control over the microsphere size and internal structure [4-6]. The co-flow and flow focusing microcapillary devices are the most widely used (Fig. 1) when creating monodispersed polymer microspheres [7]. The microsphere created with these devices could be in different sizes and shapes, or with different physical and chemical properties, which could be used in optical imaging measurement [8], or in reaction engineering [9] and even bioengineering [10], etc. The most significant difference between the two types of devices is the flow direction. The internal phase (IP) and outer phase (OP) follow the same or the contrary flow direction when using a co-flow device. The co-flow devices are characterized by stable emulsion processes and better monodispersity, while the flow focusing devices are more flexible in the fabrication of smaller diameter microspheres, though more sensitive to the working condition of pressure and flow rate [11]. For microspheres under 100μm, the flow focusing devices are more suitable than the co-flow devices, which was first reported by Weitz in 2005 [12].

The emulsion process inside microcapillary devices is driven by the fluid prosperity, flow rate and tunnel size of the device [13]. There are three main types of emulsion mechanisms: dripping, jetting and squeezing [14] the factor that influences the emulsion mechanism is described by a capillary displacement ratio of the continuous phase, with the Capillary number (Ca) [15, 16] being defined by:

$$Ca = \frac{\mu U}{\gamma_{12}} \tag{1}$$

where μ refers to the dynamic viscosity, U refers to the fluid velocity and γ_{12} refers to the interfacial tension of the two phases.

The capillary displacement ratio of the continuous phase, Ca, defines the transition of one type of emulsion mechanism into another. If the material remains unchanged, the capillary displacement ratio will be dependent upon the flow rate of the continuous phase (the outer phase). This means the emulsion process can be controlled only when manipulating the flow rate of the continuous phase.

In this work, a flow focusing microcapillary device with an orifice diameter of 100μm was designed to create polymer matershperes. Through manipulating the flow rate of the internal and outer phases, the transition of the emulsion process from dripping to jetting was observed and the transition point of Ca was investigated to discuss the dripping-jetting mechanism.
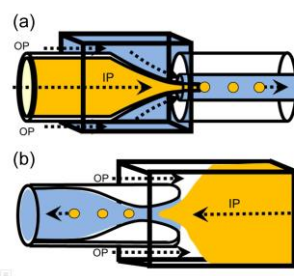

Fig. 1. The principle of the two microcapillary devices: (a) co-flow microcapillary device, (b) flow - focusing microcapillary device

2. Methods and analysis

The end of the capillary was heated by the flame of an alcohol lamp in order to make the upper pore shrink to about 100μm. The shape and size of the orifice are shown in Fig. 2(c).
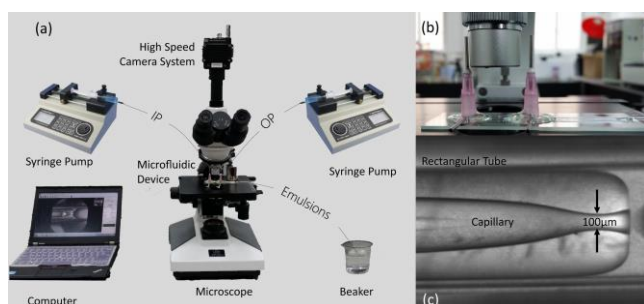

Fig. 2. (a) Experimental setup, (b) The flow-focusing microcapillary device, (c) Details of the orifice

The capillary was inserted into a rectangular tube to make a flow-focusing microcapillary device (Fig. 1). The IP and OP were pumped by two syringe pumps (Longerpump Co., Ltd, China) into the device and emulsified near the orifice. The emulsification process was recorded by a High Speed Camera System (HSCS) with a microscope. The experimental setup is shown in Fig. 2(a) and the flow-focussing microcapillary device in Fig. 2(b). The emulsions were solidified to solid microspheres under the exposure of ultraviolet light (wave length 365nm, power 400w).

Tripropylene Glycol Diacrylate (TPGDA) (TCI, Japan) and 2-Hydroxy-2-methylpropiophenone (HMPP) (Sigma-Aldrich, USA) were used as the base monomer solvent and photoinitiator was used for the oil phase. Pluronic F-127 (Sigma-Aldrich) and polyglycerol polyricinoleate (PGPR 90) (Danisco, Denmark) were used as the surfactants for the aqueous phase and the oil phase. Glycerol was used to adjust the viscosity and density during the aqueous phase. All reagents were of analytical grade and were unchanged. Monomer TPGDA comprising PGPR 90 [(5% (w/v)] and HMPP (1% (v/v)) was used during the IP. Aqueous solution with Pluronic F-127 [1% (w/v)], and glycerol [(5% (w/v)] were used during the OP.

To determine the essential index of C_a, some properties of the continuous phase were measured beforehand: the viscosity wass measured with a rotational rheometer (MARS III, Haake, Germany) and the interfacial tension γ_{12} was measured with a surface tensiometer (DCA-315, Thermo Cahn, U.S.).

3. Results and discussion

In this experiment, the two phases successfully emulsified under three combinations of flow rate for IP and OP, which is shown as following: Flow rate combination 1: IP/OP=300/2000 (μL/h); Flow rate combination 2: IP/OP=1000/4000 (μL/h); Flow rate combination 3: IP/OP=2000/20000 (μL/h).

All of the conditions were stable and repeated twice. The products were quite different in size and monodispersity due to the different emulsion mechanisms. The size and monodispersity of microspheres were analyzed from 200-microsphere samples after solidification with UV light exposure. The monodispersity is represented by the coefficient of variation (CV), which is defined by the following equation:

$$CV = \frac{(\sum_{i=1}^{N} \frac{(D_i - \overline{D_n})^2}{(N-1)})^{\frac{1}{2}}}{\overline{D_n}} \times 100\% \qquad (2)$$

where Di refers to the individial particle size, $\overline{D_n}$ refers to the average particle size and N refers to the sample number. In the sense of monodispersity, it is better to control the coefficient of variation under 10%, and 5% and below would be the best, which has already been discussed in previous reports on microsphere fabrication [17].

Fig. 3(a) represents the emulsification process under the flow rate combination of 300μL/h for IP and 2000μL/h for OP (combination 1). In this condition, the internal phase was sheared to form microspheres by the outer phase at the vicinity of the capillary orifice. The emulsions were created due to the dripping mechanism.

Fig. 4(a) shows the solidified microsphere sample under combination 1. The average size of solidified microspheres was 104.75μm, which was approximately the size of the orifice. The monodispersity was optimum (CV equals to 1.53%) because the emulsification process was controlled mostly by the size and shape of the orifice rather than the flow rate of the internal and outer phase. It produced 300μL/h microspheres in volume and 62312 pcs/h microspheres in number.

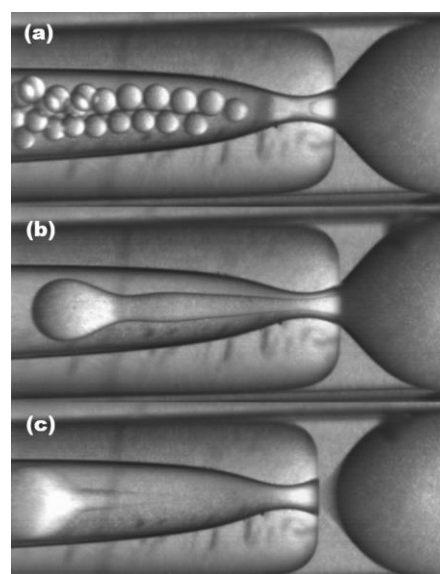*Fig. 3. The dripping and jetting emulsification process:(a) IP/OP=300/2000 (μL/h), (b) IP/OP=1000/4000 (μL/h), (c) IP/OP=2000/20000 (μL/h)*

Fig. 3(b) represents the emulsification process under the flow rate of 1000μL/h for IP and 4000μL/h for OP (combination 2). In this condition, the internal phase was sheared to form microspheres by the outer phase inside the capillary orifice. The emulsions were created due to the jetting mechanism.

Fig. 4(b) shows the solidified microsphere sample under combination 2. The average size of solidified microspheres was 348.12μm, which was approximately the inner diameter of the capillary where it was formed. The monodispersity was acceptable (CV equals to 3.78%), but not as good as the combination 1 because the emulsification process was controlled both by the flow rate of the internal and outer phase and the inner diameter of the capillary. It produced 1000μL/h microspheres in volume and 5658 pcs/h microspheres in number.

Fig. 3(c) represents the emulsification process under the flow rate of 2000μL/h for IP and 20000μL/h (combination 3). In this condition, since the two phase interface was mainly outside the capillary, the pushing of the internal phase forced the interface to periodically move forward and the internal phase was sheared to form microspheres near the capillary orifice. The emulsions were also created due to the dripping mechanism, but were not as stable as the first condition.

Fig. 4(c) shows the solidified microsphere sample under combination 3. The average size of solidified microspheres was 287.20μm, which was also approximately the inner diameter of the capillary where it was formed. The monodispersity was the least acceptable (CV equals to 13.16%) of the three combinations because the emulsification process was periodical and the flow was not as stable as that in the previous two combintaions. However, the yield of microsphere product was the highest due to the high inner phase flow rate. It produced 2000μL/h microspheres in volume or about 20155 pcs/h microspheres in number.

The emulsion process was controlled to shift from dripping to jetting and microspheres in various diameters were obtained, through the adjustment of internal phase and outer phase flow rates. Among the three combination of IP/OP flow rate, combination 1 was the most feasible application because the microsphere size could be controlled by adjusting the inner diameter of the orifice, resulting in better monodispersity. Combination 2 also displayed good monodispersity, making it acceptable to most applications. Combination 3 displayed the poorest monodispersity, however, its yield was the largest.

The transition between jetting and dripping under different flow rate could mainly be attributed to the different contact mode of the two fluids in the micro-tunnel system. The shear of the OP on IP would change accordingly with the flow rate combinations. In combination 1, the shear was conducted on the orifice (near the tip) in a continuous manner, while in combination 3, it acted in an intermittent manner. But in combination 2, the shear was conducted inside the orifice. Thus, different flow rate contributes to various emulsion processes.

The transition between jetting and dripping could be described by the Capillary number (Ca). According to equation (1), dynamic viscosity μ, fluid velocity U and the interfacial tension γ_{12} were measured or calculated to determine the value of Ca. In this work, $\mu=0.618P_a{\cdot}s$, $U_1=0.0707m/s$, $U_2=0.1414m/s$, $U_3=0.707m/s$, $\gamma_{12}=0.35$ N/m. Then $C_{a1}=0.12$, $C_{a2}=0.24$, $C_{a3}=1.2$.

It shows with the increase of Ca from 0.12 to 0.24, and the mechanism changed from dripping to jetting. This phenomenon is somewhat like that in microfluidic T-shaped junction, and it transition point of Ca is about 0.1 [18]. When Ca increase to a value between 0.24 and 2.4, the mechanism changed to periodical dripping, this is mainly because the two phase did not contact continuously.

Moreover, only the dripping mechanism creates microspheres whose radius is determined by the orifice size. The radius of microspheres with jetting or periodic dripping mechanism is determined by the inner diameter of the capillary. This phenomenon is important for microsphere production in that the product size is determined by either orifice or capillary diameter, so the size of the created microspheres is controllable and expectable, with proper selection of emulsion process by means of flow rate/pressure adjustment on the internal and outer phases.
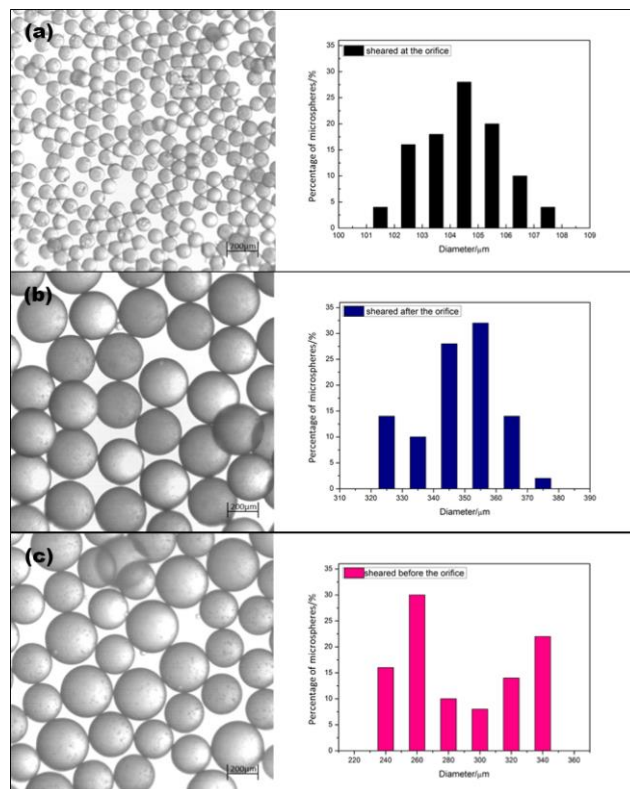

Fig. 4. The sampled microspheres and their size distribution (a) IP/OP=300/2000 (μL/h), (b) IP/OP=1000/4000 (μL/h), (c) IP/OP=2000/20000 (μL/h)

4. Conclusion

The emulsion process was controlled to shift from dripping to jetting and microspheres in various diameters were obtained, through the adjustment of internal phase and

outer phase flow rates. The flow rate combination of 300μL/h for IP and 2000μL/h for OP was the best in the sense of monodispersity of microspheres. The flow rate of 1000μL/h for IP and 4000μL/h for OP was also acceptable while the flow rate of 2000μL/h for IP and 20000μL/h for OP was the least acceptable, but larger in yield. The mechanism for the first and third combination was dripping, while that of the second one was jetting. The different flow rate of the two phases and the IP/OP interface contributed to the different emulsion processes. Results showed with the increase of Ca is from 0.12 to 0.24, and the mechanism changed from dripping to jetting, and when Ca increase to a value between 0.24 to 2.4, the two phase would not contact continuously, the mechanism changed to periodical dripping. Only the dripping mechanism creates microspheres whose radius is determined by the orifice size. The radius of microspheres with jetting or periodic dripping mechanism is determined by the inner diameter of the capillary. This work could be used as a reference for the selection of emulsion process to create microspheres with expected size and monodispersity.

Acknowledgements

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