Formation of core-shell droplets for the encapsulation of liquid contents

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Abstract

Accurate control of monodisperse core-shell droplets generated in a microfluidic device has a broad range of applications in research and industry. This paper reports the experimental investigation of flow-focusing microfluidic devices capable of producing size-tuneable and monodisperse core-shell droplets. The dimension of the core-shell droplets was controlled passively by the channel geometry and the flow rate of the liquid phases. The results indicate that microchannel geometry is more significant than flow rates. The highly controllable core-shell droplets could be subsequently employed as a template for generating core-shell microparticles with liquid core. Optical, electron microscopy and X-ray computed microtomography showed that the geometry of the core-shell droplets remains unchanged after solidification, drying and collection. The present study also looks at the thermal stability of core-shell particles depending on the particle size. The larger core-shell particles with a thicker shell provide a higher resistance to heating at elevated temperature. The high degree of control with a flow-focusing microfluidic device makes this a promising approach for the encapsulation, storage, and delivery of lipophilic contents.

Keywords

Core-shell particle, Oil flow rate, Polymer flow rate, Shell thickness, Thermal stability

1. Introduction

In recent years, droplets with a core-shell structure have attracted a considerable amount of interest due to their unique properties and potential applications. Monodisperse core-shell droplets can be used as a template to generate microcapsules using various solidification techniques such as photo or thermal polymerization, solvent evaporation, and ionic cross-linking (Xu and Nisisako 2020). Microcapsules of liquids are an important class of core-shell microcapsule with applications in food processing, cosmetics, controlled release as well as delivery of drugs, nutrients, and cells (Mytnyk et al. 2017; Wei et al. 2010). Conventional techniques for core-shell microcapsules production are layer-by-layer adsorption, polymerization, spray-drying, and electro-spraying (Galogahi et al. 2020). However, these techniques suffer from lack of control over the size, structure, and process parameters, high materials consumption and low encapsulation efficiency, restricting the potential of the generated particles (Chong et al. 2015; Liu et al. 2011; Nabavi et al. 2017; Nisisako et al. 2005; Utada et al. 2005). Furthermore, surfactants are required to be used in most conventional emulsion techniques. The use of surfactants can cause delamination, corrosion (Lu et al. 2011), protein-surfactant adducts (Xiong et al. 2008), impurities (Zheng et al. 2014), and quenching of fluorescence (Xie et al. 2009). The complete elimination of surfactants from the solutions is also cumbersome and time-consuming. Furthermore, the use of surfactants is not desirable for many clinical

applications (Hu et al. 2008). Surfactants may limit the potential development and practical applications of core-shell droplets. We therefore aim at surfactant-free formation of double emulsion in our encapsulation technique.

Microfluidic techniques could address the above challenges of conventional preparation techniques with well-controlled flow conditions (Nguyen et al. 1998). Droplet-based microfluidics provides a range of novel applications, including enhanced heat and mass transfer (Bandara et al. 2015). Core-shell droplets generated using droplet-based microfluidics are highly monodispersed and uniform. The generated droplets can be further controlled by various means (Yap et al. 2009). Microfluidic core-shell droplets are generated with a relatively precise and tunable control over the size, the shell thickness, and the shape of droplets. One of the most efficient geometries for the generation of size-tunable droplets is a flow-focusing geometry (Lashkaripour et al. 2019; Lee et al. 2009). However, the underlying physics and mechanisms of droplets generation in flow-focusing geometry has not yet been fully understood, hindering its performance in practical applications (Liu and Zhang 2011). To date, a large number of investigations focused on the role of physical and geometrical parameters of flow-focusing droplet generation (Costa et al. 2017; Lignel et al. 2017; Rahimi et al. 2019; Wang et al. 2019). For instance, Lee et al. (Lee et al. 2009) investigated experimentally the generation of tuneable droplets in flow focusing geometries. The authors defined relevant dimensionless parameters for flow-focusing microfluidic devices. By varying these parameters, they showed that single droplet formation depends on the viscosities, interfacial tension, flow rate of the fluids, and the device's geometry. Many studies have previously discussed single droplets generation in flow-focusing geometry and the effects of geometrical and physical parameters on droplet formation (Carneiro et al. 2016; Lashkaripour, Rodriguez et al. 2019; Lignel, Salsac et al. 2017; Ward et al. 2005). Liao et al. (Liao et al. 2018) and Wang et al. (Wang et al. 2019) investigated the effect of fluid flow rates on the size of core-shell particles with aqueous core in a flow focusing geometry. Furthermore, a variety of materials has been used to manufacture the devices with diverse geometry. Droplet formation mechanism and behaviour could vary with the materials used to fabricate the device, device geometry, fluid properties and operation conditions. Consequently, the results obtained are inconclusive. The challenge is to accurately determine the operating condition of the experiment based on optimised parameters to ensure the desired droplet size.

The present paper reports a PDMS-based microfluidic device for the controllable production of surfactant-free core-shell particles, using core-shell droplet as a template. We utilised flow-focusing microfluidic devices with a hydrophilic surface to generate the core-shell droplets, which enables the production of core-shell microparticles consisting of a HFE7500 fluorinated oil core and a polymer shell of trimethylolpropane trimethacrylate (TMPTMA). We demonstrated that the size of the core and the shell thickness can be tuned accurately and flexibly by adjusting the dimension of the channels and the fluid flows. One key parameter for the successful fabrication of core-shell particles with different sizes was the width of the main channel. We further investigated the formation mechanisms of HFE 7500 oil core droplets and proposed a model to predict the core size. The model predicts the core slug length as a function of geometrical and physical variables. Optical, scanning electron microscopy and X-ray computed micro tomography were utilised to investigate the morphology of the resulting core-shell particles. The results indicate that the core-shell structures remain stable during the collection and drying process. To further understand the robustness of the particles at elevated temperature, we also extend our studies to the behaviour of the core-shell particles under heating.

2. Materials and Methods

2.1. Materials

Fluorinated oil (HFE, Novec 7500 3M) with a surface tension of $\sigma_{oil} = 15.52$ mN/m, a viscosity of $\mu_{oil} = 1.31$ cP, a density of $\rho_{oil} = 1.63$ g/ml and a boiling point of 128°C was used as the liquid phase for the core (oil phase) (Rausch et al. 2015). The shell liquid (polymer phase) comprised of 0.06 g ethyl- 4(dimethylamino)benzoate (Merck), 0.05 g camphorquinone (Merck), and 10 g of trimethylolpropane trimethacrylate (TMPTMA, Merck). The surface tension, viscosity, and density of the polymer solution are $\sigma_{polymer} = 32.5$ mN/m, $\mu_{polymer} = 42$ cP, and $\rho_{polymer} = 1.07$ g/ml, respectively (Takei et al. 2019). An aqueous solution of 50% glycerol (Chemsupply, $\sigma_{polymer} = 67$ mN/m, $\mu_{polymer} = 6$ cP, and $\rho_{polymer} = 1.12$ g/ml) in distilled water was utilised as the outer continuous phase (Gregory 2018).

2.2. Microfabrication

We first used the PDMS-based microfluidic device introduced in our previous preliminary study to generate core-shell droplets (Teo et al. 2020). The device was fabricated using soft lithography. Two master moulds were prepared with respective channel widths of $100\text{ }\mu\text{m}$ and $200\text{ }\mu\text{m}$ and respective channel constriction with widths of $50\text{ }\mu\text{m}$ and $100\text{ }\mu\text{m}$ to investigate the effect of channel geometry on droplet size. The second device with the channel constriction width of $100\text{ }\mu\text{m}$ has an inlet neck of $70\text{ }\mu\text{m}$. The height h of all channels are $100\text{ }\mu\text{m}$ in both devices. A mixture of PDMS and curing agent (volume ratio of 10: 1) was poured onto the master mould. After curing at 75°C for 1 hour, the PDMS substrate was removed from the master mould. The inlets and outlet were created using a biopsy puncher. Subsequently, the PDMS substrate was bonded onto a glass substrate. Permanent bond was obtained after an air plasma treatment of both PDMS and the glass substrate in a low-pressure plasma cleaner. Finally, passing distilled water along the channels of the PDMS device keeps them sufficiently hydrophilic for the later experiments.

Figure 1 shows the fabricated device with the three cross junctions. The microchannels were visualised with food dye. The core-shell droplets are generated in three steps. First, the core droplets are formed at the first cross junction and dispersed into a flow of the shell prepolymer liquid. Hydrophobic TMPTMA monomer was chosen as the shell material, due to high thermal stability (Matsumoto et al. 2010) and high strength of its cross-linked network after polymerization (Takei et al. 2019). TMPTMA is commonly used in dentistry and does not show any evidence of toxic effects. The TMPTMA solution was prepared at a concentration of 98 mol% according to a previous report, and thus maintain the spherical shape and stable dimension of the core-shell particle after polymerization (Gorgannezhad et al. 2020; Sreejith et al. 2020). Next, the core droplets delivered into the second junction are encapsulated by the shell liquid to generate a core-shell droplet in a continuous phase of 50% glycerol solution. Glycerol increases the viscosity of the continuous phase, which results in a higher shear at the second junction and accelerates the pinch-off process of the shell layer. Finally, the core-shell droplets move through the channel to the third junction, where the droplets are separated further apart by 50% glycerol solution serving as the spacer fluid to prevent coalescence.

Figure 1 The PDMS microfluidic device with three cross junctions for the generation of core-shell droplets in the first device with the channel width of 100µm and channel constriction width of 50 µm. The core-shell droplets are produced in two steps. The core droplets are formed at the first cross junction, and are further encapsulated by the shell liquid to generate a core-shell droplet at the second cross junction. Finally, the core-shell droplets are delivered into the third junction and are further separated apart by the spacer fluid to prevent accidental coalescence.

2.3. Experimental setup and procedure

The PDMS device was placed on an inverted microscope (Nikon, Eclipse Ti) for real-time recording of the core-shell droplet generation. The video was captured with a 10× objective lens in brightfield mode. We employed a syringe pump interfaced to a computer for controlling the flow rates of all fluids. The flow rates of the core fluid and the shell fluid were varied and investigated to identify the effects of flow conditions on the core-shell emulsion. First, the core flow was varied from 60 to 140 µL/hr, while the flow rates of the shell fluid and glycerol solution at the second and the third cross junctions were maintained at 150, 800 and 1,600 µL/hr, respectively. Next, the flow rate of the shell fluid was varied from 130 to 190 µL/hr, while the flow rates of core fluid and glycerol solution at the second and third junctions were fixed at 100, 800 and 1,600 µL/hr, respectively.

2.4. Characterization of core-shell droplets and particles

All recorded videos were evaluated with the ImageJ software to determine the area of the core droplets A_{Core} and core-shell droplets $A_{\text{Core-shell}}$ and the separation distance in the channels. Subsequently, the equivalent radius of the droplets R_{eq} was calculated as $R_{\text{eq}} = \sqrt{A/\pi}$ where A is the droplet area. All the experiments and measurements were carried out three times. In each experiment, the area of 30 droplets was evaluated.

Figure 2 shows the model of the core-shell droplet in a microchannel with the channel height is less than the droplet diameter ($h < 2R_{\text{eq}}$). In this case, the droplet is considered as a discoid.

Figure 2 (a) Schematic illustration of core-shell droplet squeezed into a discoid shape between the channel walls and (b) side view of the droplet

Thus, the geometric parameters of the droplets can be directly derived from the height of channel h and the radius of the discoid R . The volume V_{discoid} of the core-shell droplets in both devices and the core droplets in second device with discoid shape can then be derived as (Nie et al. 2008; Teo et al. 2020):

$$V_{\text{discoid}} = \frac{\pi}{12} [16R^3 - (2R - h)^2 (4R + h)] \quad (1)$$

If the diameter of droplet is less than the channel height, such as in the case of the core droplet in the later experiments with a channel width of 100 μm , the droplets remain the spherical. Assuming the final hardened particle is a sphere, the radius of the core droplet R_{core} , the discoid core droplet R'_{core} , and the radius of discoid core-shell droplet $R_{\text{core-shell}}$ and the thickness of the shell T are determined as:

$$R_{\text{core}} = \sqrt{\frac{A_{\text{core}}}{\pi}} \quad (2)$$

$$R'_{\text{core}} = \sqrt[3]{\frac{3V_{\text{discoid}}}{4\pi}} \quad (3)$$

$$R_{\text{core-shell}} = \sqrt[3]{\frac{3V_{\text{discoid}}}{4\pi}} \quad (4)$$

$$T = R_{\text{core-shell}} - R_{\text{core}} \quad (5)$$

$$T = R_{\text{core-shell}} - R'_{\text{core}} \quad (6)$$

To ensure the accuracy of the above geometry estimation, data obtained with droplets along the channels using these equations was compared with the solidified particles diameter measured after collection and solidification. The results show that the difference in the core and core-shell droplet size and shell thickness gained through these two methods is less than 3%. Optical microscopy, scanning electron microscopy (SEM) (JEOL, JSM-6510LV) and X-ray computed microtomography were applied to investigate the morphology and geometrical properties of the core-shell particles. The core-shell droplets were collected at the outlet. The collected solution with core-shell droplets was exposed to UV irradiation for 5 minutes by an UV source at a wavelength of

$\lambda=365$ nm. After polymerisation of the shell layer and the formation of solid beads, the collected samples were air-dried at room temperature for 3 days. Optical microscopy images of the collected samples were taken with a microscope (Eclipse Ti2, Nikon) and a high-speed camera at a maximum frame rate of 320 fps at a full resolution of 2136×2136 pixels. SEM and optical images were analysed by the ImageJ software to measure the diameter of the core-shell droplet and core and shell thickness. The three-dimensional (3D) microstructure of core-shell particles was assessed with high-resolution X-ray microtomography. 3D imaging was obtained using an X-ray computed microtomography system (VersaXRM-500 High-Resolution 3D X-ray Tomography Microscope System, ZEISS® Xradia, Pleasanton, CA, USA). The measurement was conducted by applying a constant voltage of 40 kV and a power of 3 W, with air filter and 20 s exposure time. The source detector distance was adjusted to 20 mm, with a total magnification of $20\times$ resulting in a pixel size of $0.2891 \mu\text{m}$ and a field of view (FOV) of approximately $576 \mu\text{m} \times 576 \mu\text{m}$.

Microparticles with two sizes were prepared with the two microfluidic devices mentioned above. The samples were heated steadily from 27°C using a heater until a change in the particle surface was detected. The microparticles were kept at the constant temperature for 10 min under ambient atmosphere. If no change was observed, the temperature was increased by 5°C , followed by a 10 min at the constant temperature. During the heating process, particles were monitored and top view of them was recorded using a camera (Ximea xiQ-USB3 MQ013CG-ON) and a high-resolution magnification lens (Edmund Optics).

3. Results and Discussion

Figure 3 shows the impact of the change in oil flow rate on the core and core-shell droplet size and the shell thickness in the two microfluidic devices. The channel width of the first and second device was $100 \mu\text{m}$ and $200 \mu\text{m}$, respectively. Figure 3(a) shows that increasing the oil flow rate from $60 \mu\text{L/hr}$ to $140 \mu\text{L/hr}$ slightly increase the radius of the core in both devices. The formation of droplets in the flow-focusing geometry relies on the interplay between the shear and interfacial forces. The drop breaks up when the shear force overcomes the interfacial tension (Costa et al. 2017). A higher flow rate of the core phase allows more core liquid to accumulate before the breakup, resulting in a larger droplet. A slight increase of the core-shell droplet radius was observed in both devices, Fig. 3(b, c). With increasing flow rate, the thickness of the shell remains almost constant in the first device, while the thickness in the second device decreases gradually, Figs. 3(b, c). Comparing Fig. 3(b) and Fig. 3(c) indicates that the core and core-shell droplets radius were sensitive to the width of channels and larger droplets were produced in a broader channel. The radius of the generated core droplets and core-shell droplets increased by about 50%- 60% and 60%-80% respectively by doubling the channel width.

Figure 3 Core-shell droplet geometry as function of core flow rate: (a) Images from recorded videos showing formation of core droplets with changeable size at different oil flow rate in first device (1st Dev) and second device (2nd Dev); Influence of the oil flow rate on the radius of core-shell droplets $R_{core-shell}$ and the core R_{core} and the shell thickness T_{shell} in (b) in the first microfluidic device and (c) second microfluidic device. Scale bars depict 100 μm

Figure 3(a) shows that increasing the oil flow rate decreases the separation distance between the core droplets. Altering the flow rates also affects subsequently the number of core droplets encapsulated within the outer shell. At 60 μL/hr, the distance between the core droplets is larger than the major axis length of the core-shell droplets; hence we observed some droplets without core in both devices. The optimal oil flow rates and shell flow rates for achieving uniform core-shell droplets with a single core droplet was 100 μL/hr and 150 μL/hr and 70 μL/hr and 150 μL/hr in first and second device, respectively.

If the distance between core droplets is greater than the major axis length of the core-shell droplet, uniform droplets were generated. In the first device with the 100-μm channel width, the formation of compact core droplets at 140 μL/hr in the first junction led to the generation of unstable core-shell droplets containing two cores. Figure 4 depicts the radius of the encapsulated first and second core droplets with respect to the number of droplets. We observed that the radius of first core droplet remained unchanged while the radius of the second core gradually grew. However, further growth of the second core droplet beyond a threshold resulted in the coalescence of the two core droplets immediately after the formation in the second junction.

Figure 4 Variation of the radius of first and second core with the sequence number of core-shell droplets

Figures 5 show the influence of varying the shell flow rate on the geometry of the core-shell droplets. A high degree of control on the dimensions of the core droplet and the shell was achieved. Flow rates of the core and glycerol at the second junction and at the third junction were fixed at 100 $\mu\text{L/hr}$, 800 $\mu\text{L/hr}$ and 1,600 $\mu\text{L/hr}$, respectively. The droplet images in Fig. 5(a) indicate that the separation distance between the cores formed at the first junction remain constant in both devices. Increasing the flow rate of the shell from 130 $\mu\text{L/hr}$ to 190 $\mu\text{L/hr}$ resulted in a slight reduction in radius of both core and core-shell droplet in both devices. Increasing the polymer flow rate results in a shorter time for the growth of the core and the formation of shell layer.

Figure 5 Core-shell droplet geometry as function of shell flow rate: (a) Images from recorded videos presenting core droplets with varying radius at different polymer flow rate in the first device (1st Dev) and the second device (2nd Dev); The radius of core-shell droplets $R_{\text{core-shell}}$ and the core R_{core} and the shell thickness T_{shell} as a function of the polymer flow rate in (b) in the first microfluidic device and (c) second microfluidic device. Scale bars depict 100 μm

Furthermore, a higher flow rate of the polymer leads to a higher shear force between the two phases, contributing to a faster breakup and a smaller core droplet, Figs. 5 (a, b). Figures 5 (b, c) indicate an increase in the shell thickness with increasing polymer flow rate in both devices. Unlike the slight effect of polymer flow rate on the core and core-shell droplet size and shell thickness, experimental results clearly confirm that they can be remarkably affected by the channel geometry, Figs. 5 (b, c). The radius of the core and core-shell droplet of the second device were almost twice that of the first device.

In the above investigations, all measurements were conducted after the core-shell droplets were stabilised in the microchannel. The core-shell droplets are deformed while passing through the microchannel. Hence, we subsequently investigated the deformation of the core in the core-shell droplets along the channel between the second junction and the outlet. We employed the optimized oil and polymer flow rates achieved in our preliminary work (Teo et al. 2020). The optimum flow rates for oil, polymer and glycerol at the second and third junction were 100 $\mu\text{L/hr}$, 150 $\mu\text{L/hr}$, 800 $\mu\text{L/hr}$, and 1,600 $\mu\text{L/hr}$, respectively. Figure 6(a) shows the different position of core-shell droplet during the passage with respect to time. While the core-shell droplets move from the second junction to the outlet, image frames were extracted for the same droplet. The first image at 0 sec is the frame of the core-shell droplet just after the pinch-off, Fig. 6(a). The last image is the frame of core-shell droplets after stabilisation along the microchannel. The deformation of the core droplet is visible. The core-shell droplet protrudes into the glycerol phase and is sheared by the glycerol phase. The continuous phase pushes the core-shell droplet forward along the microchannel. While the droplet passes through the channel, the low interfacial tension

between the polymer and the core liquid allows the shape of the droplet to deform considerably. The deformation is also caused by the internal circulation of the polymer phase.

Figure 6 (a) A time series of images displaying the deformation of inner drop encapsulated into the shell between the second junction and outlet. (b) (i) Scanning electron microscopy image of an open hollow shell and (ii) X-ray image of an intact core-shell particle; (c) The flow rate of the inner phase in the first device with the width of 100 μm (oil); (d) The flow rate of shell phase (polymer) in the device with the width of 100 μm . The scale bar corresponds to 50 μm

The morphologies of core-shell particles were observed using SEM and X-ray computed microtomography (Fig. 6). The SEM images confirmed that the core-shell particles have a spherical shape and a smooth surface. As the SEM micrographs can only provide an image of the shell, X-ray computed microtomography was employed to analyse the entire core-shell structure after solidification and drying. The X-ray image confirmed the well-defined core-shell structure of particles, Fig. 6 (b,ii). The impacts of the flow rates of core and shell phases were further studied using scanning electron and optical microscopy. Figures 6 (c, d) show the scanning electron microscopy (SEM) images and optical images of samples at different core and shell flow rates. The core-shell droplets with different dimensions with corresponding flow rates could be observed with optical microscopy images (Figures 6 (c, d)), confirming the fabrication of size-tuneable core-shell droplets. Both SEM and optical images agreed with the data gained through measuring the size of the core-shell droplets along the channel.

We subsequently investigated the core droplet formation at the first junction in the flow-focusing geometry, Figure 7. The microchannel after the first junction has a width of w and a constriction region of width D . The values of w and D are 100 μm /50 μm and 200 μm /100 μm for the first and second device, respectively. The generalised behaviour of fluid flows in a flow-focusing microfluidic device can be described by a number of dimensionless numbers, which capture the geometrical and physical parameters such as flow rates, the interfacial tension, viscosities and densities of the fluids, and the dimensions in the device. In microchannels, the value of Reynolds and Weber numbers are typically relatively small due to the channel size and the low flow rate of the fluids; the inertial effect of the flow field can therefore be ignored (Costa, Gomes et al. 2017). On the other hand, the capillary number that represents the relative effect of viscous stress versus interfacial tension plays an important role in the process of droplet formation in microfluidic devices (Liu and Zhang 2009; Liu and Zhang 2011). The capillary number is defined as:

$$Ca = \frac{\eta_{\text{Polymer}} u_{\text{Polymer}}}{\sigma_{\text{Oil,Polymer}}} = \frac{\eta_{\text{Polymer}} Q_{\text{Polymer}}}{hw \sigma_{\text{Oil,Polymer}}}, \quad (7)$$

where η_{Polymer} , u_{Polymer} , and Q_{Polymer} are the viscosity, the inlet velocity, and the flow rate of the continuous phase (polymer), respectively. $\sigma_{\text{Oil,Polymer}}$ refers to the interfacial tension between the dispersed phase (oil) and the continuous phase (polymer). Good and Girifalco proposed a model for the interfacial tension for liquid-liquid systems (Good and Girifalco 1960):

$$\sigma_{\text{Oil,Polymer}} = \sigma_{\text{Oil}} + \sigma_{\text{Polymer}} - 2\Phi(\sigma_{\text{Oil}}\sigma_{\text{Polymer}})^{1/2}, \quad (8)$$

where σ_{Oil} and σ_{Polymer} are the surface tensions of the oil phase and the polymer phase, respectively; Φ is the interaction coefficient given as $\Phi = 4(V_{\text{Oil}}V_{\text{Polymer}})^{1/2}/(V_{\text{Oil}}^{1/2} + V_{\text{Polymer}}^{1/2})^2$, where V_{Oil} and V_{Polymer} are the molar volume of the oil phase and polymer phase, respectively. In our case, because of the small difference between $V_{\text{Oil}} = 256.5 \text{ ml/mol}$ and $V_{\text{Polymer}} = 293.86 \text{ ml/mol}$ the value of $\Phi = 0.99$ was considered as unity. The interfacial tension estimated from equation (8) is $\sigma_{\text{Oil,Polymer}} = 3.10 \text{ mN/m}$. The flow rate ratio of dispersed phase flow rate to continuous phase $Q_{\text{Oil}}/Q_{\text{Polymer}}$ is another important dimensionless parameter for droplet formation.

Two important factors affecting the size of core droplets at the first junction in a flow-focusing system are (i) wetting properties and properties of fluids interface, which can be influenced by the ratio of dispersed phase flow rate to continuous phase flow rate and the geometrical parameters; and (ii) the relative effect of viscous forces of the continuous phase versus interfacial tension represented by the capillary number (Tan et al. 2008). To predict the core slug or core droplet size at the first junction, we define the ratio of the slug length L to the width D of the constricted section as a function of geometrical parameters, $Q_{\text{Oil}}/Q_{\text{Polymer}}$, and the capillary number,

$$\frac{L}{D} = 1.3 \frac{h}{w} \left(\frac{Q_{\text{Oil}}}{Q_{\text{Polymer}}} \right)^{0.4} Ca^{-0.3} \quad (9)$$

We determined the constants of the equation experimentally through curve fitting across all experiments conducted by using both flow-focusing devices. For both set of experiments carried out for the two different geometries, we calculated the capillary number for each experiment using equation (7). Figure 7(b) shows the two sets of data obtained from two devices with different channel widths. Figure 7(b) indicates that this model fits well with experimental data across the range of investigated flow rates and channel geometries. The ratio of L/D increases with increasing ratio $Q_{\text{Oil}}/Q_{\text{Polymer}}$.

Figure 7 (a) Schematic illustration of the core droplet formation at the first junction of a flow-focusing microfluidic device, (b) the ratio of slug length to the channel contraction width as a function of ratio of dispersed phase flow rate to continuous phase flow rate.

We further studied the thermal stability of core-shell particles from the two devices. As mentioned above, the device width has significant impact on the particle geometry. The microfluidic devices mentioned above produced two particle samples with a considerable size difference. Particles were generated at the optimum flow rates. The overall radius of the particles and shell thickness were 57 μm and 16 μm in the first device and 96 μm and 33 μm in the second device, respectively. Figure 8 shows the temperature dependence of the core-shell particle size and the shell thickness. In the case of particles formed in the first device, which are smaller and have a thinner shell, the morphology of particles remains unaffected up to 92°C. Larger particles with thicker shell formed in the second device remain stable until 102°C. Both temperature values are below the boiling temperature of the oil at 128°C. Thus, the core-shell particles are substantially stable up to these elevated temperatures. At the critical rupture temperature, the particle shell ruptures and shrinks. The gradual shrinking of the solid shell could be attributed to the release of oil core and deflation of the polymeric shell due to the reduced pressure. Comparing the images of the first and second device before and after heating, we observed that the polymer shell of the larger particle is more robust against heating. This might be due to the thicker wall resisting the increasing pressure of the heated liquid core.

Figure 8 Core-shell particles produced in the first device: (a) before and (b) after heating up to 92°C; Core-shell particles produced in the second device: (c) before and (d) after heating up to 102 °C. The scale bar is 100 μm .

4. Conclusion

This paper presents the tuneable generation and the characterisation of core-shell particles in a flow-focusing PDMS microfluidic device. Varying the experimental parameters allowed for identification of the best condition to produce desirable core-shell particles, enabling the control of particle geometries and stability. A procedure was adopted for tuning precisely core-shell particle geometry based on fluid flow rate and device geometry. Independently varying oil phase and polymer phase flow, particles with different core number, core size and shell thickness were obtained. For the same flow rates, the experimental results indicate that the channel width is the most important parameter affecting core-shell particle geometry. The wider channels resulted in larger core and

core-shell droplets as well as a thicker shell. The investigation on the influences of a group of geometrical and physical factors on the size of the core droplets at the first junction showed that there is a reasonable relationship between the ratio of the core slug length to the channel contraction width and capillary number, the ratio of height to width of channel, and the ratio of dispersed phase flow rate to continuous phase flow rate. Equation 9 could describe this relationship well. The analytical results showed a good agreement with experimental data. The core-shell droplets can be polymerised and solidified to generate spherical particles with liquid core and polymer shell. In the end, the core-shell particles are displayed to be stable up to more than 90°C, retaining their original morphology. At a critical temperature, the shell was ruptured, and the core liquid was released. Larger core-shell particles with thicker shell provide more thermal stability.

Declarations

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