ABSTRACT

Here we describe a novel approach to generate monodisperse silicone microdroplets via microfluidic based microemulsion. Through a flow-focusing configuration, a continuous flow of commercially available silicone precursor solution has been successfully dispersed into discrete microdroplets with narrow size distribution, which are future solidified into stable microparticles by subsequent thermal curing. As a proof-of-concept demonstration of their superior capabilities, we also integrate a type of oxygen dye into these silicone microbeads and apply these microparticles as non-invasive and real time oxygen sensors.

KEYWORDS: Droplet Microfluidics, Silicone, Microparticle, Oxygen Sensor

INTRODUCTION

Microfluidics is a promising technique for synthesizing monodisperse polymer microparticles with tailored properties, and has been employed for a wide range of polymer systems [1]. In particular, silicone is an optically transparent, porous and soft polymeric elastomer with excellent mechanical stability, gas permeability, and chemical compatibility. To our knowledge, however, production of uniform silicone microparticles remains an unsolved challenge using traditional microfluidic methods. The viscosity of commercial silicone formulations is unexpectedly high, making it difficult to emulsify them into discrete droplets [2]. Additionally, because of their low surface energy, silicone microdroplets tend to clump and collapse spontaneously into bigger aggregates [3]. As a result, harvesting individual microparticles with controlled size distribution is a significant challenge. Moreover, microfluidic devices are themselves commonly based on silicone soft lithography, and therefore formation of silicone microdroplets is also difficult considering the surface wetting requirement during microfluidic emulsification [1].

Here we report a novel microfluidic strategy with the capability to address all of these issues. The viscosity of the dispersed phase has been reduced by varying the content faction of prepolymer components in silicone formulations. Additionally, microfluidic devices are intentionally fabricated on an alternative substrate, hydrophilic poly(methyl methacrylate) (PMMA) thermalplastics, to avoid the high affinity between dispersed flow and microchannel surface. On such PMMA devices, we use a planar flow focusing configuration to disperse the less viscous silicone precursors into monodisperse droplets by contacting with a flow of aqueous continuous phase, and 5 wt% sodium dodecyl sulfate (SDS) has been added to effectively stabilize these generated silicone droplet precursors. These produced droplets are then collected in a glass vial and subsequently converted into stable microbeads through additional thermal crosslinking(Figure 1 and Figure 2).

These inert, monodisperse, transparent, and porous microbeads offer enormous opportunities in various application fields, and their functional properties can be easily modified by incorporating various encapsulants of interest. As a proof of concept, we have integrated an oxygen-sensitive dye, Pt(II) meso-tetrakis(pentafluorophenyl)porphine (PtTFPP), into the microbead matrix. The principle of the PtTFPP sensor is based on oxygen-dependent quenching of phosphorescence, providing a direct optical measurement of local O2 concentration [4]. The porous silicone matrix enables the fast exchange of O2 molecules, while the narrow size distribution of the beads ensures reproducible measurements from particle and particle. As depicted in Figure 3, the phosphorescent intensity changes in real-time oxygen.

Figure 1. Schematic illustration for production of silicone microbeads for oxygen sensors. (a): Microfluidic generation of silicone droplets by emulsifying silicone mixture on a PMMA microfluidic device. (b): Off-chip curing of generated droplet precursors was done at 70 °C in a glass vial. (c): Rinsing and harvest of individual cured microbeads. (d): Applying silicone microbeads for oxygen sensing.
time when the microbeads are exposed to varying O₂ concentrations.

EXPERIMENTAL
The Sylgard 184 silicone elastomer kit was obtained from Dow Corning. Sheets of PMMA were purchased from Piedmont Plastics. Surfactant SDS was purchased from TCI America. The PtTFPP was purchased from Frontier Scientific.

The continuous phase was prepared by dissolving 5 wt% of SDS in distilled-deionized (DI) water. The dispersed phase was a mixture of Sylgard Parts A and Part B at a weight ratio of 6:4. For mixing dye into the dispersed phase, PtTFPP was first dissolved in toluene and this solution was mixed with Sylgard Part A. The mixture was placed under vacuum overnight at 90°C to evaporate the toluene (final concentration of PtTFPP in the mixture was 0.5 wt%).

The microfluidic chip comprised with a Flow-Focusing droplet generator was prepared on a planar PMMA substrate according to the steps described before [5]. Commercial plastic PVC tubing was used to connect the needle ports on the PMMA chip with syringes. Precision syringe pumps (PHD 2000, Harvard Apparatus) were used to control the infusion of fluids into the chip. Typical infusion rates were 50 μL/min for the continuous phase and 1 μL/min for dispersed phase.

Optical characterization of the beads was performed using either a Nikon Eclipse LV-100 Profilometer microscope or a Nikon Eclipse TE2000s inverted microscope. Scanning Electron Microscopy (SEM) was done using a Hitachi SU-70 instrument. Beads were sputter-coated with a layer of gold for 90 s before SEM imaging.

For characterization of oxygen sensing performance, dye-incorporated microbeads were placed in a modified multwell plate equipped to allow continuous gas flow. Beads were exposed to gas with different partial pressures of oxygen (P_{O₂} = 0 atm, 0.01 atm, 0.05 atm, 0.1 atm and 0.2 atm), which were obtained by mixing nitrogen and air. The emission intensity from the beads was captured on an inverted microscope (Zeiss Axiosvert Z1, Thornwood NJ). A green LED (Thorlabs, Newton NJ) was used to illuminate the microbeads and images were captured using a CCD camera (CoolSnap HQ, Tucson AZ) with an integration time of 100 ms.

RESULTS AND DISCUSSION
The first step involved in microfluidic particle production is the generation of discrete microdroplets from two immiscible flows. This dynamic process is heavily influenced by parameters such as fluidic viscosities, interfacial tension, and flow rate ratios. We used Dow Corning Sylgard 184, a common silicone elastomer kit, as the dispersed phase. Sylgard 184 composes two resin parts which are mixed and thermally cured to achieve the final polymer structure. However, in our microfluidic systems we have found that it is difficult to disperse a mixture at the vendor recommended 10:1 ratio (Part A, 5000 cSt and Part B, 110 cSt, where blend viscosity is calculated to be 3221 cSt by the Refutas equation). Accordingly, we decreased the blend viscosity by increasing the content of less viscous Part B, with successful fluid injection and stable droplet generation achieved when using a blend at a mass ratio of 6:4 by weight (which an estimated blend viscosity of 827 cSt). Moreover, in order to achieve stable droplet formation, we have selected PMMA as our microchip substrate. PMMA is moderately hydrophilic, with a contact angle of water on a clean virgin PMMA surface of 70°-75°. Furthermore, our PMMA wafer and cover plates are treated by UV/ozone exposure before thermal bonding, which enhances the hydrophilicity of microchannels to achieve a contact angle of ~50° following 8 min UV/ozone exposure, and further helps the oil/water droplet generation.

In the fabricated PMMA devices, a planar flow-focusing configuration has been used for droplet generation, with the silicone precursor flow injected through the center channel and the continuous phase consisting of 5 wt% of the ionic surfactant sodium dodecyl sulfate (SDS) in water injected from the two side channels. As shown in Figure 2a, the silicone droplets were generated following a typical “dripping” mode: two continuous water flows from the two side channels spatially constrain the centre silicone flow into a thin thread as it is injected through the downstream orifice. As the center flow expands laterally while exiting the orifice, hydrodynamic instability induced by the continuous phase results in break-up of the dispersed silicone phase and formation of a spherical droplet. After breaking up, the silicone flow retracts to the tip of center channel, with successive cycles of droplet production repeated. Besides droplet production, another important requirement is stabilization of the vulnerable silicone prepolymer droplets from coalescence and aggregation. In our experiments, the addition of SDS into the continuous phase was found to solve this problem. SDS not only assists the

Figure 2. (a) Microscopic imaging showing the formation process of silicone droplets. (b) Generated silicone droplets stabilized in the collecting vial. (c) Microscopic view of monodisperse silicone microparticles. (d) SEM view of the cured silicone microparticles.
droplet formation process by reducing the interfacial tension, but also prevents possible clumping and coalescence of silicone droplets by providing a repelling barrier on the droplet surfaces. A glass vial filled with 10ml of SDS solution was used for droplet collection. As depicted in Figure 2b, silicone droplets remain intact even when densely stacked. After accumulating a desired amount of droplets, the collecting vial was then transferred to a heated oven at 70 ºC and additional overnight curing was done for full crosslinking of the droplets into solidified microbeads.

There are two important factors contributing to the high performance of our silicone microbead oxygen sensors. First, the high gas permeability of silicone materials (800 Barrer) allows rapid exchange of O₂ molecules through the entire bead matrix and thus ensures our sensor’s fast response and high sensitivity. Additionally, narrow size distribution of such sensors provides excellent reproducibility among groups of individual particles.

Characterization of the oxygen-sensing silicone microbeads was performed by placing the microbeads in water and equilibrating the headspace with either pure nitrogen (0% O₂) or its mixture with air (21% O₂). The beads were then observed with an inverted fluorescence microscope and the emission intensity was quantified under different O₂ concentrations. As depicted in Figure 3, the intensity dropped dynamically with increasing O₂ content, with the microbead showing high phosphorescence without O₂ and a significant reduction in intensity when the concentration of O₂ was raised. We have verified that the relationship between oxygen partial pressure Pₓ and Intensity has been plotted, which can be applied to calculate the real-time oxygen levels of unknown O₂ concentration in solution.

CONCLUSION

In summary, we have shown a novel approach to produce monodisperse silicone microbeads through a microfluidic synthesis method, and functionality of the resulting silicone microbeads can be easily tuned by incorporating corresponding desired components. Considering many advantageous properties these silicone microparticles process, we believe that they can used as excellent substitutes of traditional microparticles (silica/polylatex microbeads) in many application fields.

ACKNOWLEDGEMENTS

This work was funded by grants from the UMD Center for Energetic Concepts Development and from DARPA.

REFERENCES


CONTACTS
* Srinivasa Raghavan, tel: +1-301-4058164; sraghava@umd.edu
* Don L. DeVoe, tel: +1-301-4058125; ddev@umd.edu