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Fabrication and manipulation of polymeric magnetic particles with magnetorheological fluid

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ABSTRACT

Polymeric magnetic microparticles have been created using a microfluidic device via ultraviolet (UV) polymerization of double emulsions, resulting in cores of magnetorheological (MR) fluids surrounded by polymeric shells. We demonstrate that the resultant particles can be manipulated magnetically to achieve triggered rupture of the capsules. This illustrates the great potential of our capsules for triggered release of active ingredients encapsulated in the polymeric magnetic microparticles.

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1. Introduction

Functional composite particles, which are made of an inorganic material incorporated to a polymer network, are of great interest to biotechnology, optics and cosmetics [1]. Specifically, microparticles with a magnetic core are widely used in many applications such as treatment of hyperthermia [2], drug delivery [3], contrast enhancement for magnetic resonance imaging [4] and fluid flow modifications [5]. The magnetic properties of these materials make them susceptible to a non-uniform external field and enable their manipulation under controlled magnetic field. The high potential of these particles can be further realized by improving both the process of particle fabrication as well as the development of particles with new structures.

Microfluidic technologies offer an approach to create particles using emulsions as a template. With microfluidic devices, emulsion drops are fabricated one drop at a time. One way to prepare these drops is by co-flowing two immiscible fluids for droplet formation; the resultant particles have high size uniformity. In addition, the size and shape of the created droplets can be conveniently varied by controlling the flow rates of the fluids. Moreover, the approach also enables fabrication of higher-order emulsions such as water-in-oil-in-water (w/o/w) double emulsions. If in the emulsion one of the phases is a polymer, the

emulsions could be used as a template for generation of polymeric particles [6].

To provide a magnetic behavior to the particles, one approach is to directly coat polymeric particles with a layer of magnetic nanoparticles through surface chemistry techniques [7] or dispersion polymerization [7,8]. Another approach is to encapsulate magnetic nano- or micro- particles suspended in a carrier fluid in a polymeric matrix that form the particles. Common magnetic particle suspensions include magneto-rheological (MR) fluids and ferrofluids. MR fluids are suspensions of magnetic particles in a carrier liquid with some additives to stabilize the medium. Particle sizes are between 1 and 10 μm, which are too heavy for Brownian motion to keep them suspended, so due to the different densities between the particles and the carrier fluid, particles tend to sediment in MR fluids. Due to the high sensitivity of the magnetic particles, MR fluids exhibit a rapid response when a magnetic field is applied. Typical response time is on the order of milliseconds [9]. The fast response time makes MR fluids suitable as dampers and shock absorbers in applications ranging from helicopters to prosthetic legs [10,11]. From the point of view of the inner structure, in the absence of an external field, a MR fluid is a suspension. When a magnetic field is applied; a magnetic dipole moment is induced in the particles parallel to the magnetic field, and, as a result, particles tend to align to form ordered structures. The application of this field causes the microstructure of the fluid to change from a liquid-like state to a more structured state, giving rise to significant variations not only in viscosity but also in its inner order as exhibited by the particle rearrangement. At sufficiently high particle concentration, the original medium

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turns from an isotropic state to an anisotropic state, where particles aggregate to form chain-like structures. However, ferrofluids primarily consist of nano-size particles suspended in a carrier liquid so they are suspended by Brownian motion and generally will not settle. When a magnetic field is applied, Brownian motion prevents formation of a solid structure, so the mechanical properties do not change as much as in a MR fluid.

In this work, polymeric magnetic microparticles are prepared using a microfluidic device via UV polymerization of double emulsions in which the core is a MR fluid and the shell is a polymer. We demonstrate magnetically triggered release of the MR fluids from the core-shell microparticles.

2. Materials and methods

2.1. Materials

We prepare oil-in-water-in-oil (o/w/o) double emulsions as template for the polymeric magnetic microparticles. By adjusting the flow conditions and the choice of materials involved, we form a stable double emulsion encapsulating the MR fluid in the cores. The inner phase in all experiments is a MR fluid provided by Liquid Research, with a 20% of volume fraction of carbonyl iron particles from 1 to 10 μm suspended in a proprietary hydrocarbon oil. The continuous phase is a PDMS oil with surfactant Dow Corning 749 at 2% w/w for stabilizing the emulsion, while the shell of the double emulsions consists of a photoinitiator of Darocur 1173 (Ciba) at 5% w/w, oligomer and surfactant at optimized concentrations for stable double emulsions. PEG Dimethacrylate (Sigma-Aldrich) and PEG Diacrylate (Sigma-Aldrich) were tested as oligomers while Tween 20 (EMD), Tween 80 (Sigma-Aldrich), Pluronic L121 (BASF) or Pluronic 168 (BASF) were added at weight fractions of 2% w/w or 5% w/w for emulsion stabilization.

2.2. Capillary microfluidic devices

A glass capillary device is used for making double emulsions. Capillary microfluidic devices consist of coaxial assemblies of glass capillaries on glass slides [6,12]. The advantages of these devices are that the wettability can be easily controlled by a surface reaction with an appropriate surface modifier and the capability of creating three dimensional flows easily. Specifically, the device used in this work consists of two circular capillaries,

one for the inner fluid and the other one for collection of the prepared emulsions, arranged end-to-end within a square capillary. The inner diameter of the square capillary is about 1.05 mm and the outer diameter of the circular capillaries is 1 mm. We align these capillaries under an optical microscope to achieve coaxial configurations of them. The capillaries are tapered using a micropipette puller (Sutter Instruments) to achieve desired diameters of them. In a typical device in this work, the tip diameters of the collection tube and the inner capillary are about 240 μm and about 120 μm respectively. The nozzle size of the capillaries has been optimized to avoid clogging of the nozzle by the MR fluids. Another important parameter is the distance between the capillaries; in this work, the distance between the capillaries is about 180 μm . To avoid clogging and to form the double emulsion drops continuously, the distance between the capillaries and the size of the tip of the inner capillary must be at least a hundred microns. These dimensions are larger than those in typical capillary microfluidic devices for creating double emulsions with fluids with viscosities close to that of water.

To generate double emulsions, the inner fluid is pumped through the tapered circular capillary while the middle fluid, which is immiscible with the inner and outer fluids, flows through the interstices between the square capillary and the capillary for the inner fluids in the same direction as the flow of the inner fluids. The outermost fluid flows through the interstices of the square capillary and the collection capillary in the direction opposite to the flow of the inner and middle fluids. When the three fluids enter the collection tube, a double emulsion is formed, as shown schematically in Fig. 1a and in the optical microscope image in Fig. 1b.

We use syringes (Hamilton gastight, 10 cc) for injecting the fluid phases. The flow rates were controlled with syringe pumps (Harvard Apparatus). The range of flow rates used is 1750–2000 $\mu\text{L/h}$ for the outer phase, 500–600 $\mu\text{L/h}$ for the middle phase and 75–100 $\mu\text{L/h}$ for the inner phase. Due to the high volume fraction of the inner phase and therefore the high viscosity, the flow rate of the inner phase has to be low to avoid pressure buildup that leads to breakage of the syringes during operation. Among the three different phases, the stability of the double emulsion generation is most sensitive to changes in the flow rate of the inner phase. For instance, when the flow rate of the inner phase is higher than 200 $\mu\text{L/h}$, double emulsions fail to form.

With the appropriate device geometry and fluid flow rates, monodisperse double emulsions can be stably and reproducibly generated for as long as 3 h.

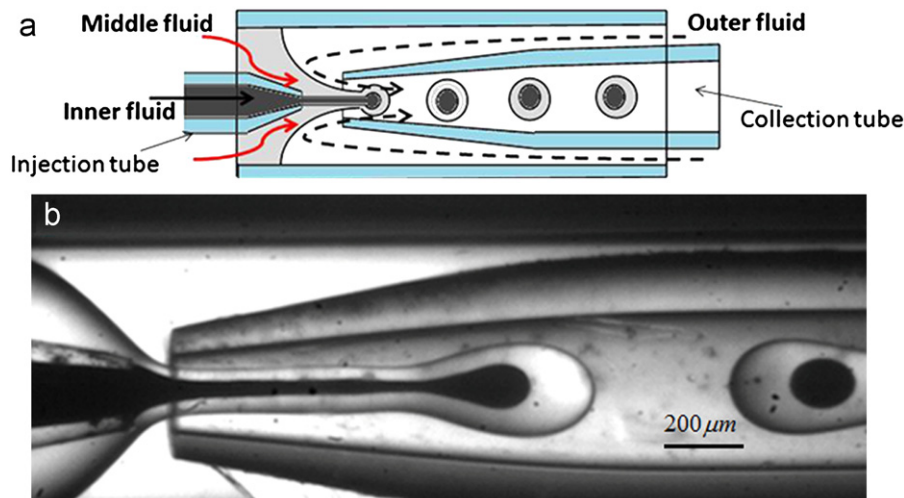


Fig. 1. (a) Schematic of a capillary microfluidic device for generating double emulsions; and (b) optical micrographs of a device at work.

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