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Microfluidic production of endoskeleton droplets with controlled size and shape

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ABSTRACT

Oil-in-water emulsion droplets, containing an elastic endoskeleton that holds the droplets in various non-spherical shapes, are formed by crystallizing a portion of the oil phase into a network of wax crystals. Such structures have recently been found to provide enhanced active ingredient delivery and shape-changing responsiveness, but robust methods of producing such droplets are needed that enable control of droplet size and shape. A continuous microfluidic flow is used here to produce endoskeleton droplets whose size is controlled by fluid flow rate and whose shape is varied between spheres, ellipsoids, and rods by control of exit temperature. A wide range of anisotropic shapes is produced using a single flow channel geometry by allowing the endoskeleton droplet to relax its deformation by varying degrees in response to fluid interfacial tension. Flexible production of shaped endoskeleton droplets will expand their application in enhanced delivery, deposition testing, and additive manufacturing processes.

1. Introduction

Complex colloidal and supracolloidal particles with anisotropic shapes have been proposed as a way to design next-generation drug delivery vehicles, [1] control self-assembly [2], and, more generally, to design colloidal particles for specific functions [3]. The examination of custom-shaped colloids has moved from the realm of single-particle experiments to production of numerous monodisperse particles [4] as a result of innovative developments in molding [5] and microfluidics [6–9].

Droplet-based microfluidic techniques can produce complex colloids using uniform single or multiple emulsions as templates for solids like Janus particles [10], armored droplets [11–13] and bubbles, [14] liquid crystals [15], and differently-shaped microcapsules and colloidosomes [16]. However, many active ingredients in drug [17], food [18], laundry [19], and cosmetic [20] products need to remain in liquid droplet form for targeted delivery [21] to tissue, hair, and fabric substrates. Solidification processes that preserve a unique particle shape also lose droplets' ability to interact with surfaces by coalescence or wetting.

Recent work [22] showed that the yield stress of internal elastic microstructures, or endoskeletons, can arrest coalescence and preserve non-spherical droplet shapes, like rods [23], by balancing the interfacial Laplace pressure. The increased collision area of elongated droplets enhances their deposition onto substrates from a fluid flow, an application that was recently patented for personal cleansing and shampoo products [24]. Weakening the yield stress or increasing interfacial tension causes non-spherical droplets to collapse, change shape, and even wrap around nearby surfaces in response [23,25]. As consumer product use is often followed by a rinsing step, increasing interfacial tension, the shape change of anisotropic droplets has also just been patented as a way to enhance retention of droplets deposited on a surface [26].

Although spherocylindrical endoskeleton droplets have only been studied individually, dispersions of flattened cylindrical droplets have been made in microfluidic channels [27,28] and flattened droplets have been made by interfacial impact [29], yielding materials monodisperse in size and shape. However, little is known about the optimal needs for droplet shape in many applications, especially when shape-change is required, so a means to produce endoskeleton droplets with more robust control over shape is needed. Changing the shape of droplets molded in a microfluidic flow typically requires changes to the microchannel dimensions.

Another approach, explored here, is to allow the endoskeleton droplets to morph into a unique shape, once they exit a flow

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channel, based on the instantaneous balance of stresses on the drop. Endoskeleton droplets adjust their aspect ratio in response to a reduction in their yield stress, forming shapes with lower curvature and interfacial pressures [25]. Such an effect suggests a way to continuously tune droplet shape, and size, over the course of a microfluidic experiment. Controllably producing more complex distributions of sizes and shapes enables targeted delivery to a broad range of target geometries, such as lung surface tissue [30,31], and would also aid large-scale production of shaped droplets where dynamic shape adjustment occurs in flow [32].

In this work, we show how various spherocylindrical endoskeleton droplet shapes can be produced by a single microfluidic device using only changes in the operating conditions. Variations in fluid flow rates are used to control droplet size in the entry region of the device, where temperatures are higher than the melting point of the droplet's elastic microstructure. Channel exit temperature controls droplet shape by solidifying a specific fraction of the shape-preserving endoskeleton, arresting collapse of the droplet at a certain shape. The dynamic nature of the internal elastic network enables shape adjustment to occur after droplets are made, without losing all droplet shape anisotropy. Shapes can be produced with different dimensions than the channel used to make and mold the droplets, and subsequent solidification preserves their shape. This work expands the number of shapes possible for endoskeleton droplets and studies the limits on their consistent production. Structured emulsions enable new applications by combining the elements of shape and orientation, usually achieved only with solid particles, with the wetting and interaction behavior of liquid droplets.

2. Experimental details

Endoskeleton droplets were made of a mixture of hexadecane (99%, Sigma Aldrich) and petrolatum (Unilever). The rheological measurements of the wax-oil mixture were performed in the linear viscoelastic regime by oscillatory experiments using a TA-AR2000 rheometer in strain controlled mode at a strain of 0.1% and frequency of 1 Hz. The rheology of the mixture was characterized by measurement of the viscous modulus, G", and the elastic modulus, G'. The values of the viscoelastic moduli indicate the contribution of viscous, or fluid-like, behavior relative to elastic, or solid-like, behavior, respectively, during deformation. Droplets need a value of G' large enough to offset the interfacial tension and maintain a stable, non-spherical, shape [22]. The oil-wax mixture exhibited no elasticity above ~ 45 °C and was an easily handled Newtonian fluid at such temperatures, as shown in Fig. 1. When cooled below 45 °C, however, the viscosity and elasticity of the mixture rapidly increased as solid wax particles crystallized out of solution. A key transition temperature is 40 °C, where elasticity begins to dominate viscous behavior of the mixture during cooling based on the dominance of G' over G" in Fig. 1. We expect arrested shapes to form and be increasingly significant at temperatures below 40 °C. Droplet oil phase solid content is zero at high temperatures, because of mutual solubility; while room temperature droplet solid content can be varied between 10% and 50% based on the hexadecane:petrolatum ratio used.

Emulsion droplets were produced using a glass microfluidic chip (Dolomite 3000436) with rectangular channels 300 μm wide and 190 μm deep arranged in a T-junction geometry. At the junction, the channel width is reduced to match its depth as shown in Fig. 2. The droplets were formed at a temperature of ~ 70 °C in an aqueous 10 mM SDS (99%, Fluka) solution. Imaging of static droplet size and shape was carried out using a Moticam 10 MP camera on a Motic AE31 inverted light microscope. High-speed imaging utilized a Phantom v7.3 camera on the same microscope. Image analysis was performed using ImageJ [33] to quantify size and shape parameters by comparison with standard calibration slides. All images were

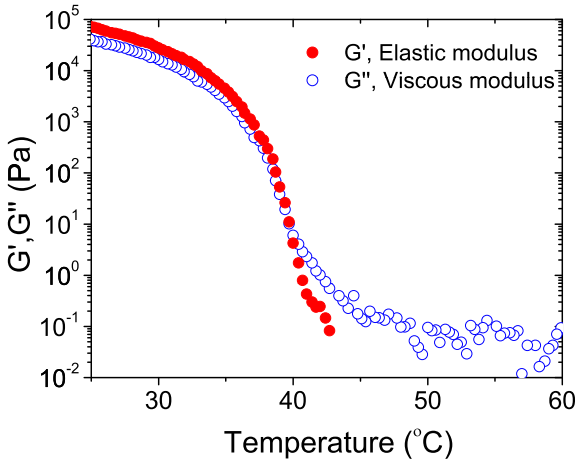

Fig. 1. Rheology of wax-oil mixture containing 35% solids as a function of temperature showing the steep increase in viscosity and elasticity as a result of crystallization of high molecular weight components of the wax near ~ 45 °C.

obtained using the Motic 10 MP except for Fig. 6a, that required the Phantom v7.3 operated at 10,000 frames/s.

The microfluidic chip was held by a metal chip holder (Dolomite 3000155) that, in conjunction with two linear connectors (Dolomite 3000024), supplied oil and aqueous phases to the chip. The flow of fluids in the chip was controlled by two Teledyne ISCO temperature-controlled syringe pumps. For the continuous water phase, a 500D pump module was used to achieve typical flow rates of 5–500 μL/min, while for the oil phase a 65DM pump module was used to achieve flow rates of 1–50 μL/min. The connectors and the chip can operate below 3 MPa and 100 °C while both pumps can operate below 25 MPa. Fluids moved from the pumps to the microfluidic chip through PTFE tubing with 0.5 mm internal diameter. The chip was placed on top of a hot plate and held at ~ 70 °C while the fluids in the syringe were kept at 70 °C by an external water circulation system. Tube length between pump and chip was kept below ~5 cm and the tube was held close to the hot plate to prevent cooling and premature structure formation.

Once the droplets were formed in the microfluidic chip, they traveled downstream from the junction and through a circular profile outlet tube (PEEK, Kinesis) whose internal diameter was selected from the range 75–500 μm based on the desired emulsion shape and

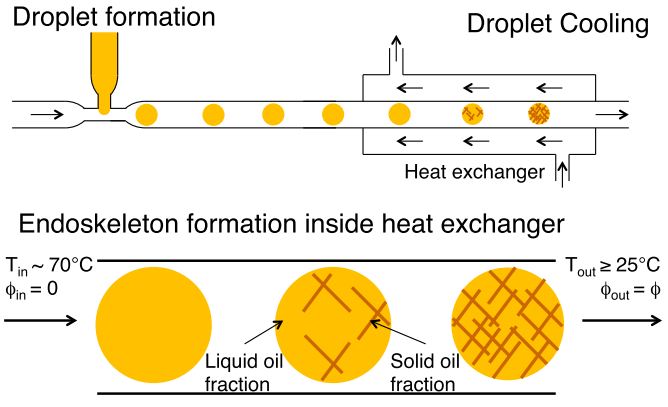

Fig. 2. Microfluidic setup used to produce structured droplets. In the first stage, oil droplets are formed in a T-junction at ~ 70 °C. Subsequently the droplets are transferred to a plastic tube and cooled in a heat exchanger down to a temperature of ~ 25 °C.