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Preparation and characterization of tunable oil-encapsulated alginate microfibers

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ABSTRACT

A single-step microfluidic approach was developed which allowed a wide range of oil-loaded calcium-alginate microfibers to be fabricated at the same compositions but with different morphologies. A framework for characterization of wavy fibers was developed which linked the fiber morphology and tensile strength to the encapsulation type and geometry. The geometry of oil encapsulates as well as the fibers surface morphology were conveniently tuned via the gelation reaction dynamics and phase flow rates. A 2D mathematical reconstruction of the fiber's surface revealed that fibers having spherical and ellipsoid encapsulates enjoyed the highest surface roughness. Tubular fibers endured the highest tensile force before failure, compared to fibers with other encapsulate geometries at a fixed alginate phase ratio (ϕ_{alg}). Fibers with increased ϕ_{alg} withstood a higher tensile force. However, the strength of fibers reduced if the increase in ϕ_{alg} altered the encapsulate geometry from tubular to discrete oil segments. Tubular fibers also underwent maximum elastic and plastic deformation prior to failure, among all fibers.

1. Introduction

Microfibers of calcium alginate, a biocompatible hydrogel material, are widely used for several biomedical applications such as wound healing [1,2,3], and cell encapsulation [4]. These fibers are also commonly used for making complex fibrous networks, such as 3D scaffolds used in tissue engineering [5,6,7,8,9]. Microfibers in such applications are often subjected to frequent and enduring tensile loading during their handling and usage [10] and thus require superior physical and mechanical properties [11].

With a recent surge in technological innovations, an increasingly wide variety of novel hydrogel fibers are being reported. These compound microfibers are often tailored to possess highly structured interiors in the form of encapsulates [12] with a precisely tuned composition [13]. Such features are ideally suited for conferring multi-functionality to hydrogel microfibers [14]. For example, compound alginate microfibers have been used as micro-carriers of a range of hydrophobic encapsulates, such as multi-cellular aggregates [14], oil-soluble drugs [15], and magnetic oil droplets, for advanced fiber manipulation and assembly operations [16] and also for hierarchical storage and triggered release of encapsulates [17,18]. The presence of encapsulates can also alter the surface morphology of fibers and increase their surface area, advantage of which has been taken in wettability related applications such as enhancing water collection ability [19].

Given the wide range of applications, these compound microfibers are required to possess desirable physical features and mechanical properties, such as low spillage ratio and high tensile strength. However, the encapsulation of a liquid phase in a fiber reduces the fiber strength, since a part of the solid polymer is replaced by the encapsulated liquid phase. Furthermore, the fibers morphology can vary from segmented to tubular shapes with changing encapsulate geometry. Therefore, a comparative study to analyse the impact of encapsulate geometry on fiber properties is of high significance.

While there have been several studies on mechanical properties of synthetic fibers [20], and also simple and composite hydrogel fibers [21,22,23], reports on mechanical testing of compound hydrogel microfibers are extremely scarce in the literature. This is due to the fact that production of compound fibers by conventional techniques is restricted to either segmented hydrophobic encapsulates [14,15,16,17], or tubular hydrophilic encapsulates [13,15,24]. In a rare report, He et al. [15] conducted the uniaxial tensile testing of individual chitosan microfibers with segmented and tubular encapsulates, formed using different types of internal phase, and analysed the effect of shell thickness on the fiber strength. However, this lack of consistency in production of variety of encapsulate geometries can limit the compara-

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tive studies of microfibers produced by different techniques and also translate into further uncertainty due to the change of encapsulate phase.

Here we report an extensive investigation into the tensile testing of a wide range of oil-encapsulated alginate microfibers, to highlight the impact of encapsulate geometry and the alginate phase ratio (ϕ_{alg}), in addition to the shell thickness, on the fiber properties. In this report, we employ our recently developed flexible one-step encapsulation method [12,18] to fabricate oil-loaded microfibers with a whole range of encapsulate geometry, which can provide a sound platform for comparative characterization of microfibers structures. We show how fiber morphology can be tuned by controlling the rate of gelation during encapsulation. We also report a detailed framework for characterization of oil-encapsulated fibers, which shows how encapsulation geometry and surface morphology can affect the mechanical strength of the resulting fibers, which is of prime importance for biomedical applications of microfibers.

2. Experimental section

2.1. Materials

Sodium alginate and calcium chloride (Sigma Aldrich) were used as received. De-ionized water was used as the middle and external phase. Octane (99%, Sigma Aldrich) was used as received as the model inner oil phase. A water-soluble dye (trypan blue) was used in the alginate phase for contrast imaging, unless mentioned otherwise.

2.2. Device and procedure

Fig. 1a shows a schematic of the glass capillary microfluidic device used to achieve the single-step oil encapsulation within alginate fibers. Two glass capillaries, circular (ID: 0.56 mm, OD: 1 mm) and square (IL: 1 mm, OL: 1.5 mm), were pulled using a pipette puller (P-1000, Sutter Instrument, Novato, USA). The tapered tips were cut to the desired sizes, and the inner tip (ID: 40 μm, OD: 60 μm) was coaxially aligned with the outer tip (ID: 150 μm, OD: 175 μm) at the same level. The coaxially aligned capillary setup was introduced vertically into a wide cuvette, which housed the quiescent outer aqueous calcium chloride solution, as shown in Fig. 1a1. The middle aqueous alginate phase was introduced through the interstitial spaces between the middle and inner capillaries, into the outer phase to form calcium alginate fibers. The oil phase was pumped (using a syringe pump from Harvard Apparatus) through the inner capillary, which produced oil-loaded alginate fibers, an example of which is shown in Fig. 1b. The fibers were collected at the top of the cuvette, facilitated by the buoyancy force exerted by the encapsulated oil phase. This buoyancy-assisted microfluidic setup has previously been used to generate oil-loaded alginate microfibers with asymmetric oil-encapsulates [18], and millimetric core-shell drops with tunable shell thickness [25,26]. A high-speed video recording camera (Photron FastCam SA-5 monochrome) was used to record fiber formation.

The tensile testing of the fibers was conducted with the help of an extremely sensitive force-sensing device (DCA-100, First Ten Angstroms), which is controlled via its computer software. The device has an immobile jaw holding a metal hanger on its top section, which is coupled with a built-in force sensing mechanism. The bottom stage, which is integrated with a stepper motor, can be moved upwards or downwards in the vertical direction at a desired velocity. All the fibers were cut to a fixed length, which were mounted using a metal hanger at the top and glued at the bottom. The glue (Devcon 5-minute epoxy) was left overnight to harden completely before conducting the testing.

3. Results and discussion

3.1. Factors affecting fiber and encapsulate morphologies

We employed the flexible single-step microfluidic encapsulation approach recently developed by us to fabricate oil-in-alginate fibers with a tunable encapsulate geometry ranging from spherical and ellipsoidal to plug-like and tubular (Fig. 1a) [18,12].

The assigned nomenclatures for fibers are shown in Fig. 1b. Fig. 1c

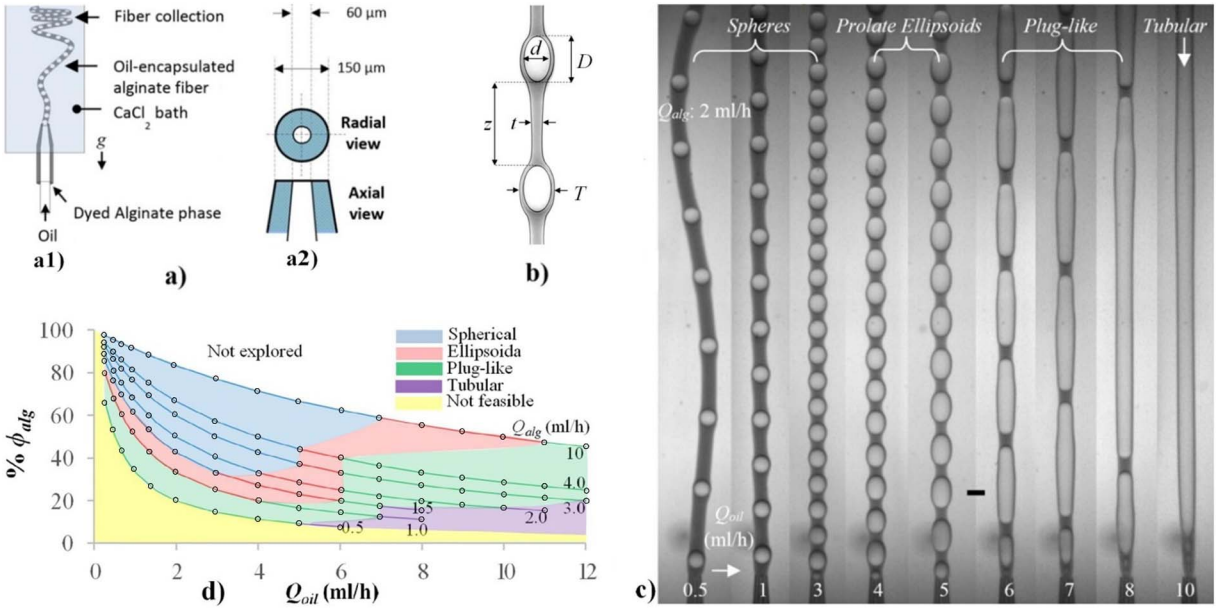

Fig. 1. (a) A schematic of the one-step microfluidic device, which was used to produce oil-encapsulated alginate fiber, is shown in (a1). The coaxial alignment and dimensions of the tapered glass capillary tips are presented in (a2). (b) An optical micrograph of a produced oil-loaded microfiber, which also shows the various nomenclatures assigned to its geometry. A water-soluble dye (trypan blue) was used in the alginate phase. (c) The variations in the shape of the oil segments encapsulated within the alginate fibers with Q_{oil} at a given middle alginate phase flow rate (Q_{alg} = 2 ml/h). The encapsulate geometry was tuned from a segmented encapsulation (having spherical, ellipsoidal or plug-like shapes) to a continuous (tubular) encapsulation. Scale bar: 200 μm. (d) The phase map for alginate microfibers at different flow conditions. The *x*-axis is Q_{oil}, while the y-axis indicates the alginate phase ratio ($\phi_{alg} = Q_{alg}/(Q_{alg}+Q_{oil})$). The solid lines represent fixed Q_{alg} but variable Q_{oil}. The investigated flow conditions are marked by circular symbols. All data obtained by using 1 wt% alginate and 4 wt% $CaCl_2$ concentrations.