**In Situ** Mechanical Testing of Nanostructured Bijel Fibers

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**ABSTRACT:** Bijels are a class of soft materials with potential for application in diverse areas including healthcare, food, energy, and reaction engineering due to their unique structural, mechanical, and transport properties. To realize their potential, means to fabricate, characterize, and manipulate bijel mechanics are needed. We recently developed a method based on solvent transfer-induced phase separation (STRIPS) that enables continuous fabrication of hierarchically structured bijel fibers from a broad array of constituent fluids and nanoparticles using a microfluidic platform. Here, we introduce an in situ technique to characterize bijel fiber mechanics at initial and final stages of the formation process within a microfluidics device. By manipulation of the hydrodynamic stresses applied to the fiber, the fiber is placed under tension until it breaks into segments. Analysis of the stress field allows fracture strength to be inferred; fracture strengths can be as high as several thousand Pa, depending on nanoparticle content. These findings broaden the potential for the use of STRIPS bijels in applications with different mechanical demands. Moreover, our in situ mechanical characterization method could potentially enable determination of properties of other soft fibrous materials made of hydrogels, capillary suspensions, colloidal gels, or high internal phase emulsions.

**KEYWORDS:** bijels, phase separation, particle-stabilized emulsion, micromechanics, tensile testing

Bicontinuous interfacially jammed emulsions (bijels) are a class of soft materials,1 formed by arresting the spinodal decomposition of a mixture via interfacial attachment and jamming of colloidal particles.2,3 Bijels have two interpenetrating, continuous networks of immiscible liquids, stabilized by a jammed layer of nanoparticles at their interface.4,5 This structure has rich possibilities in application; for example, the immiscible fluids can serve as reaction or separation media, and the nanoparticles could serve as catalysts or provide other functionalities.5,7 Moreover, by selectively polymerizing one of the bicontinuous liquids, solidified bijels can be used as sensors,9 filtration devices, tissue engineering scaffolds,9 and catalytic membranes.10

We recently reported a method to generate nanostructured bijels via solvent transfer-induced phase separation (STRIPS). In STRIPS, a homogeneous ternary fluid mixture of oil, water, and solvent is triggered to undergo spinodal phase separation by solvent removal. The interpenetrating network of fluids that develops during this process is arrested by the interfacial adsorption of nanoparticles suspended in the fluid mixture. This method complements the thermally induced phase separation method, which is limited to mixtures of fluids that can undergo thermal spinodal decomposition and to nanoparticles with particular wetting properties.1,11,12 With STRIPS, bijels can be fabricated with a broad palette of immiscible liquids and surface-active nanoparticles in a continuous process. In particular, nanostructured bijel fibers can be made continuously in microfluidics devices; in these settings, solvent removal occurs by predominantly radial fluxes, generating hierarchical architectures within the fibers.

Means to characterize the mechanical properties of bijels are needed to understand how they can be tailored via changes in constituents or hierarchical internal structures and to lend insight into mechanisms. The rheological properties of bijels made using the conventional method, for instance, have been shown to undergo transitions like those observed in colloidal gelation to form semisolid structures, and their mechanical properties depend on the surface tension, particle interactions, and the stage of bijel maturity.9,12−15 The mechanical properties of STRIPS bijels during their formation and their dependence on processing parameters, however, have not been investigated in detail. In this research, bijel fibers are characterized in situ within the microfluidics device as they are formed, facilitated by the ability to rapidly and continuously

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characterize a large number of samples and the exquisite control over flow fields and stresses afforded in microfluidics settings. The device and flow field are designed so that hydrodynamic stresses place the fibers under tension and result in the segmentation of fibers at well-defined sites within the device. Once they break off, these fiber segments are convected away, allowing for subsequent characterization of the fracture strength of bijel fibers at later stages of maturation. The in situ technique allows us to probe the dependence of bijel mechanics on parameters including the volume fraction of nanoparticles and the flow rates of the fluid phases in the microfluidic device. Finally, while we focus here on nanostructured bijel fibers, in principle, other soft fibrous materials could be readily characterized in such settings to characterize their elastic modulus and fracture strength.

RESULTS AND DISCUSSION

Formation of Bijel Fibers with Controlled Length. A STRIPS bijel fiber is formed in a microfluidic device by continuously injecting a ternary liquid mixture containing suspended nanoparticles through a small capillary into a larger capillary that carries a water stream (Figure 1). The ternary liquid mixture contains diethyl phthalate (DEP), ethanol, and water doped with silica nanoparticles and cetyltrimethylammonium bromide (CTAB). Although this mixture has a viscosity comparable to that of water while inside the inner glass capillary, it rapidly forms a viscoelastic thread that transitions with time to form a bijel fiber upon contact with the water stream. This occurs as ethanol enters the external water stream; the loss of solvent from the ternary phase causes DEP and water to phase separate, forming fluid interfaces and interpenetrating channels. Concomitantly, CTAB-modified silica nanoparticles attach to these interfaces, forming a jammed structure. Long bijel fibers form continuously when the flow rate of the outer stream \( Q_W \) is sufficiently low (Figure 1a). When \( Q_W \) exceeds some threshold, however, fibers pinch-off periodically (Figure 1b) to form reproducible segments that are not yet fully matured bijels. After detachment, the segments migrate downstream and continue to evolve via solvent loss to form bijel fibers of finite length. Characterization of these mature bijel segments is of tremendous importance, which will be discussed in the second part of this paper.

Figure 2a shows micrographs of the fibers produced at different flow rates of the external water phase at a fixed flow rate of the ternary liquid mixture \( (Q_t = 50 \, \mu L/h) \) (see also Supporting Information video 1). For water flow rates \( Q_W \) < 1.5 mL/h, a continuous thread forms. Increasing \( Q_W \) > 2 mL/h causes the thread to pinch-off periodically into segments; the greater \( Q_W \), the shorter the segments; for example, segments of 4 mm form at \( Q_W = 2.5 \, mL/h \); segments of 1 mm form at \( Q_W = 4 \, mL/h \), and very short segments, less than 0.4 mm long, form at \( Q_W = 13 \, mL/h \).

As shown in Figure 2, upon exiting the formation device, the segmented and continuous fibers retain their shapes, which range from small aspect ratio (length/diameter <10) blobs to elongated rods. Associated three-dimensional confocal microscopy images reveal the internal structure of STRIPS bijels, featuring a bicontinuous oil/water architecture that can be tuned by adjusting the CTAB and silica nanoparticle concentrations (Figure 2b). Figure 2c summarizes the dependence of fiber length on the ratio of \( Q_W \) and \( Q_T \). The topmost curve in Figure 2c marks the transition between continuous fibers to rods, which flattens logarithmically with increasing ternary flow rate. Thus, for \( Q_T \) greater than 500 \( \mu L/h \), fibers do not break into segments. Rather, in this regime, increasing \( Q_W \) simply decreases the diameter of the continuous fibers. For a lower \( Q_T \), the fiber breaks into segments. Lines of constant segment length (presented in terms of segment length to diameter) are shown in this figure. These lines also follow a logarithmic trend. Segments formed for flow rates below these lines have aspect ratios smaller than the aspect ratio that corresponds to the line. The iso-aspect ratio lines pack densely close to the transition curve. Thus, fibers with high aspect ratios (>200) can only be obtained in a narrow flow rate window.

To probe this dependence, we approximate the phase-separating fibers as solid-like materials. We calculate the axial velocity profile in the external water stream \( v_z(r) \) in cylindrical coordinates, where \( r \) is the radius from the axis of the channel. We also calculate the associated shear stresses and forces exerted on the fiber assuming no slip boundary conditions at the outer wall (located at \( r = R_2 \)) and the fiber surface (located at \( r = R_1 \)), so that \( v_{z,s}=0 \) and \( v_{z,s} = U \) (the velocity of the fiber), respectively.

\[
v_z(r) = -\frac{dp}{dz} \frac{(R_2^2 - r^2)}{4\mu} + \left\{ U + \frac{dp}{dz} \frac{(R_2^2 - R_1^2)}{4\mu} \right\} \frac{\ln(R_2/r)}{\ln(R_2/R_1)}
\]
In the bijel formation process, fluid dominates the corresponding to the water. Dark areas correspond to oil and bright areas to water domains.

Figure 2. Tunability of fiber length and morphology. (a) Snapshots of the fiber formation in the coaxial microfluidic channel. Numbers correspond to the water flow rates in mL/h.

(b) Three-dimensional confocal micrographs of continuous bijel fibers, bijel rods, and bijel blobs. (c) Fiber length dependence on the flow rates. The curves in the diagram correspond to flow rate combinations resulting in constant fiber lengths (expressed as aspect ratio ± standard deviation). The curves are obtained by fitting the experimental data shown in Figure 3a and Figure S6. For each flow rate combination, the standard deviation of a given aspect ratio is calculated from at least 20 measurements.

\[
T_{zz} \bigg|_{r=R_i} = \frac{\mu(U_0 - U)}{R_i} \frac{1}{\ln(R_2/R_i)}
\]

(2)

where

\[
U_0 = -\frac{R_i^2}{4\mu} \frac{dp}{dz} \left( \frac{R_z^2 - R_i^2}{R_i^2} - 2\ln(R_2/R_i) \right)
\]

and

\[
T_{zz} \bigg|_{r=R_i} = \frac{\mu}{R_i} \frac{dz}{dr}
\]

is the shear stress on the fiber exerted by the water phase, where \( dp/\text{dz} \) the axial pressure drop, \( U \) the fiber velocity, and \( \mu \) the dynamic viscosity of the outer continuous phase. \( U_0 \) physically represents the velocity of the fiber for which zero shear force is exerted on the fiber surface. The associated shear force on the fiber of length \( L_c \) is

\[
F_{zz} \bigg|_{r=R_i} = T_{zz} \bigg|_{r=R_i} 2\pi R_i L_c = \mu(U_0 - U)L_c \frac{2\pi}{\ln(R_2/R_i)}
\]

(3)

A feature of this simple flow field is that the sign of the shear stress can change, as shown schematically in Figure 1. If the fiber moves slowly (\( U < U_0 \)), the shear stress is dominated by the pressure driven flow and pulls in the +z direction. If, however, the fiber moves quickly (\( U > U_0 \)), the translating fiber dominates the flow field and the shear stress pulls in the −z direction. In the bijel formation process, \( U \) is determined by the complex phenomena associated with the balance of the rates of ternary fluid injection \( Q_S \), outer water flow rate \( Q_{W} \), orifice size, as well as the rates of ethanol loss and water uptake as the fiber migrates downstream. In the experiment, we measure \( U \) by high-speed video microscopy at the last few frames before pinch-off (within 5 ms of pinch-off, with precisions of typically ±2 mm/s; see Supporting Information), and \( dp/\text{dz} \) is calculated for a given water flow rate \( Q_{W} \) (see Supporting Information). We find that the transition from continuous to segmented fibers occurs at low, positive shear force. Notably, as fiber segments undergo pinch-off, no measurable elastic behaviors like stretching or retraction are observed.

What determines the pinch-off length \( L_c \)? The shear force on the fiber increases linearly with the fiber length (eq 3). When the fiber has length \( L_c \), the net force pulling downstream exceeds the fracture strength \( \sigma_{ij} \) of the fiber (subscript \( i \) denotes the initial stage of bijel formation), causing a segment of the fiber to break off. A bounding value for the length can be extracted from the balance at the cross section of the fiber where break off occurs:

\[
F_{zz} \bigg|_{r=R_i} = 2\pi R_i L_c T_{zz} \bigg|_{r=R_i} = \pi R_i^2 \sigma_{ij}
\]

(4)

These relationships imply \( L_c = \frac{R_i \sigma_{ij}}{2\pi \alpha_{ij}} \). Segmented fiber lengths \( L_c \) indeed depend strongly on \( Q_{W} \) (Figure 3a); these data, recast based on the hydrodynamic calculations, are shown in Figure 3b, in which \( L_c \) is plotted against the inverse shear stress. The predicted linear dependence of \( L_c \) on the inverse shear stress is confirmed; the slope of this line allows \( \sigma_{ij} \) to be inferred. From this analysis, we find that \( \sigma_{ij} \) for the segments during pinch-off ranges from 90 to 300 Pa and that \( \sigma_{ij} \) increases with \( Q_S \).

To understand the physical reason behind this trend, we analyze the pinch-off event at different \( Q_S \) values by carefully monitoring the relative grayscale of the fibers (ratio of the grayscale at some distance from the nozzle to that when bijel formation is complete (4 cm from the nozzle)) in the regions...
around the pinch-off. The relative grayscale increases as bijel matures owing to phase separation and interfacial particle jamming. Prior to pinch-off (Figure 3d, top), the relative grayscale increases more or less linearly with the distance from the nozzle. Upon pinch-off, the grayscale profile shows an abrupt dip due to the appearance of the bright background. We find that the relative grayscale measured at the ruptured ends increases with $Q_T$ (see lower x-axis in Figure 3c and Supporting Information) and that the pinch-off occurs further downstream as $Q_T$ is increased. Based on the location of pinch-off and the velocity of the fiber ($U$), we infer that the residence time for the region of the fiber that undergoes pinch-off also increases with $Q_T$ (see Supporting Information). Moreover, we observe thinning of the viscoelastic thread as $Q_T$ is increased, which would facilitate radial mass transfer of ethanol and thus lead to higher extent of phase separation, again consistent with the increased $\sigma_f$ with $Q_T$ (see Supporting Information). All of these observations indicate the region of the fiber that undergoes pinch-off undergoes a greater extent of phase separation with increasing $Q_T$, consistent with the trend seen in Figure 3c.

This analysis of the pinch-off phenomenon allows us to probe $\sigma_f$ in the early stages of bijel formation. However, pinch-off in the uniform cross section channel always occurs before the formation process is complete (Figure 2b). The tensile strength of the final material ($\sigma_f$) is a parameter of utmost relevance for subsequent applications of STRIPS bijel fibers. Fortunately, with small changes in device geometry, we can design flow fields to cleave mature bijel fibers.

**Fracture Strengths of Mature Bijel Fibers.** To characterize the tensile strength of mature bijel fibers, we apply tensile stress on fiber segments by flowing them through a conical constriction (Figure 4) far downstream from the nozzle (~5 cm from the device entrance). At this point, the grayscale profile (i.e., opacity) of the fiber no longer changes, indicating the completion of bijel formation.

Remarkably, as a fiber segment flows through the constriction, it breaks into two shorter pieces. This process does not always occur at the same location and strongly depends on the total length of the fiber segment and its position in the constriction (see Supporting Information and video 2); no elastic stretching or retraction is observed during these snapping events.

As a fiber segment, transported by the outer water stream, enters the constriction, both water and segment velocities increase (see Figure 4a), attaining maximum values at the narrowest point. At some critical location along the segment length, a piece breaks off and convects away. When this occurs, the remaining portion of the segment slows abruptly (see Figure 4a). This remaining portion can undergo a second breaking event as it accelerates again into the constriction.

The associated flow field is calculated within the lubrication approximation, based on the small slope in the conical region (see Supporting Information). The main outcome of this analysis is that eqs 1–3 are modified to leading order, with $R_2 =
R_{2(0)} - \beta z, where R_{2(0)} denotes the radius of the cylindrical capillary and \beta denotes the slope of the taper, and, as a result, U_0(z) can be derived (see Supporting Information). Calculation of the associated stresses T_{c,b} along the fiber segment reveals the source of tension that drives segment cleavage.

At the trailing end of the fiber, U > U_0(z), thus shear pulls in the -z direction, while at the leading end, U < U_0(z), so shear pulls in the +z direction. The fiber breaks near the location where the shear stress changes sign, labeled c in Figure 4c, to form a segment of length determined by the fracture strength. The shear force in the -z direction, \( F_{\text{left}} = 2\pi \int_0^b R_t(z) T_{c,b} dz + \int_0^c R_t(z) T_{c,b} dz \), includes contributions from the shear force on the fiber in the cylindrical region and at the entrance to the conical regions, whereas the shear force in the +z direction, \( F_{\text{right}} = 2\pi L c R_t(z) T_{c,b} dz \) (where \( d \) denotes the location of the fiber’s leading end) depends on the shear force in the rest of the conical region. The longer the fiber segment between c and d, the greater the tension in the fiber at point c. Snap-off occurs when the opposing shear forces exceed the fiber tensile strength:

\[
\pi R_t(z = c)^2 \sigma_{c,f} = 2\pi \int_0^b R_t(z) T_{c,b} dz + \int_0^c R_t(z) T_{c,b} dz - 2\pi \int_c^d R_t(z) T_{c,b} dz
\]

From this balance, we infer \( \sigma_{c,f} \). The tensile strength depends strongly on the weight percent of silica nanoparticles in the original ternary mixture, ranging from a few hundred Pa at 10 wt % silica particles up to 4000 Pa (comparable to calcium cross-linked alginate hydrogel) \(^{14} \) at 25 wt % silica particles (Figure 4c). We attribute this increase to the increased number of coagulated silica particles, most likely adhering to each other via various attractive interactions such as van der Waals, hydrophobic interactions, and capillary forces. We find that \( \sigma_{c,f} \) is only weakly dependent on CTAB concentration, in spite of the critical role the surfactant plays in altering the internal architecture of the fibers (see Supporting Information). These differences might affect other mechanical properties of the fibers, such as the bending modulus, as indicated by our observation that fibers prepared with higher CTAB concentrations have lower tendency to kink under their own weight when exiting the glass capillary channel into a vial filled with stagnant water.
CONCLUSIONS

Bijels are an emerging class of soft materials with promising applications in food science, reaction engineering, and membrane separation due to their unique structural, mechanical, and transport properties. Here, we introduce a microfluidic technique to form nanostructured STRIPS bijel fibers of controlled aspect ratio and to measure their mechanical strength in the initial stages of bijel formation. Moreover, using a tapered geometry, we apply tensile stress on bijel fiber segments to measure the fracture strength of mature STRIPS bijels. Using this method, we find that the tensile strength of the bijel fibers depends strongly on the nanoparticle concentration and can be tuned over 2 orders of magnitude. In future experiments, this microfluidic method will be used for the mechanical characterization of bijels made with different building blocks as well as the assessment of bijel postprocessing such as interfacial particle cross-linking. Moreover, this technique, we believe, is not limited to the characterization of bijels and has broad potential for the in situ mechanical characterization of other soft fibers, composed of hydrogels, colloidal gels, high-intermolecular phase emulsions, or capillary suspensions.

EXPERIMENTAL SECTION

Materials. Twenty-two nanometer SiO₂ nanoparticles (Ludox TMA), CTAB (BioUltra >99%), and diethyl phthalate (99.5%) were purchased from Sigma-Aldrich and used as received. Pure water and pure ethanol (200 proof, >99.5%) were used for all experiments.

Preparation of Suspensions/Solutions. The ternary liquid mixture comprises five main components: (i) pure ethanol, (ii) a solution of 200 mM CTAB in ethanol, (iii) a suspension of 22 nm SiO₂ silica nanoparticles in water at pH 3, (iv) pure water, and (v) DEP. The original SiO₂ suspension has a silica concentration of 44.2 wt % and a pH value between 5 and 7. We titrated this suspension to pH 3 by adding 1 M hydrochloric acid dropwise. As an example, we describe the preparation of a 5 mL solution for the generation of a bijel fiber with 25 mM CTAB and 10.4 wt % silica particles in a ternary mixture comprised of 40.8 vol % DEP, 40.8 vol % ethanol, and 18.4 vol % water. This mixture corresponds to 2.04 mL of DEP, 1.43 mL of pure ethanol, 0.6 mL of the 200 mM CTAB in ethanol solution, and 0.92 mL of the 44.2 wt % Ludox TMA suspension. Simply shaking a mixture containing all the components is enough to produce a clear liquid mixture containing silica nanoparticles. To increase the silica concentration further, the suspension was heated to 130 °C under a nitrogen stream to evaporate the ethanol and water. After the evaporation, we add 0.92 mL of the 44.2 wt % silica suspension and 2.04 mL of pure ethanol to obtain a dispersion with 18.8 wt % silica particles.

Microfluidic System. To produce STRIPS bijels and characterize their mechanical properties, we use a glass-capsule-based microfluidic device consisting of two concentric cylindrical glass capillaries glued onto a microscope slide. A round capillary with 80 μm outer diameter was centered in a round capillary with 300 μm inner diameter. Both capillaries were connected through dispensing needles to two separate syringe pumps. Into the larger capillary we pumped an aqueous solution with a pH value of 3 and 1 mM CTAB at laminar conditions (Re < 50). Through the 50 μm orifice of the smaller capillary, a ternary liquid mixture containing silica nanoparticles and CTAB was introduced. For the measurement of the final bijel fracture strength, the outer round capillary (300 μm) was tapered with a micropipette puller (Sutter P-97) at a distance 5 cm from the injection nozzle. For all experiments, the centered alignment of the injection nozzle was crucial.

Microscopy. An inverted light microscope (Nikon Diaphot 300) equipped with a high-speed camera (Phantom V7) was used to visualize the fiber formation and rupture at a frame rate of 500–8000 Hz. To visualize the three-dimensional structure of the bijel fibers, we added Nile red to the ternary mixture and collected fibers on a microscope slide. With a confocal microscope, we acquired confocal z-stacks and reconstructed the three-dimensional structure with the software ImageJ.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b02660.

Calculations on lubrication approximation validation, velocity and shear stress profiles, fiber velocity measurements during pinch-off, fracture strength dependence on Qw and the concentration of CTAB (PDF)

Video 1 (AVI)

Video 2 (AVI)

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Notes

The authors declare no competing financial interest.

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