In-situ mechanical testing of nanostructured bijel fibers

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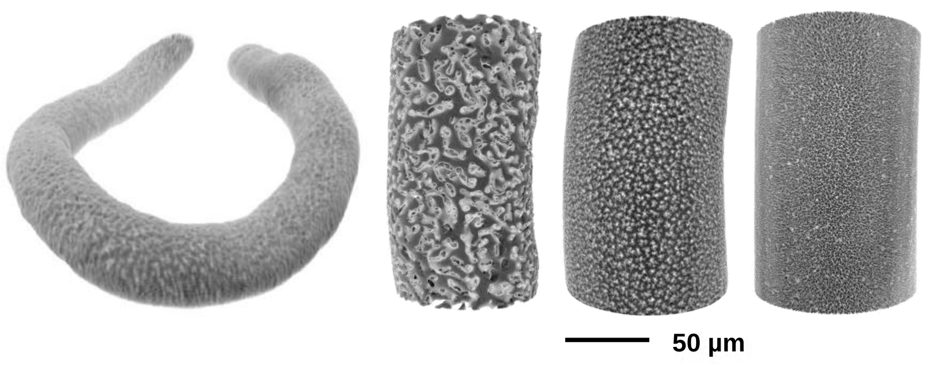
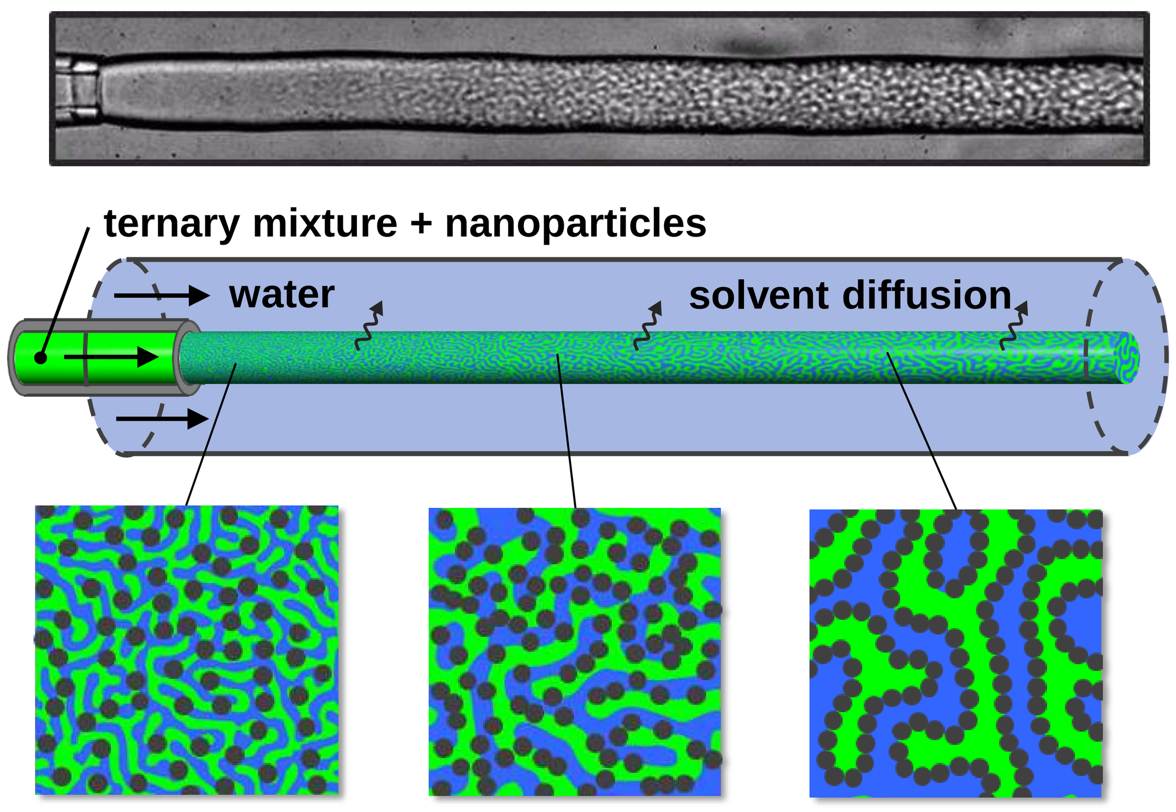
1. Abstract

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. 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.



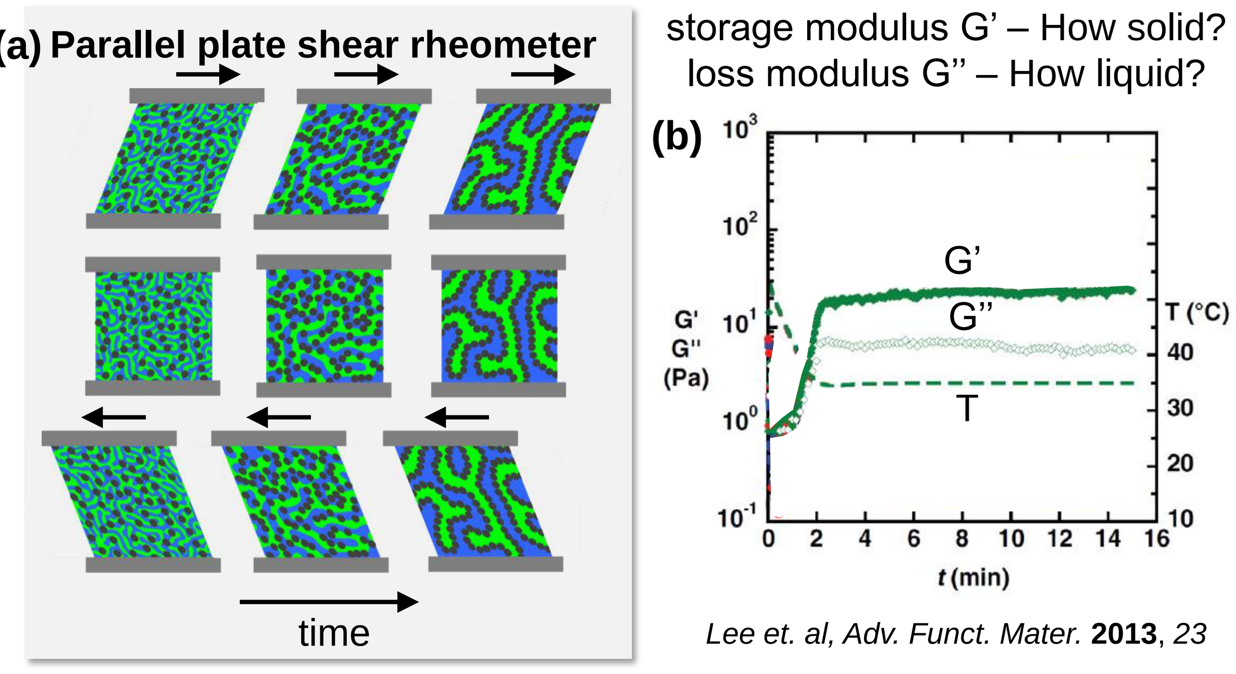
2. Bijels by ternary phase separation



Bicontinuous **i**nterfacially **j**ammed **e**mul**s**ion (**Bijel**)

A liquid mixture with nanoparticles is extruded into a water flow field. Diffusion of a solvent from the fiber to the water initiates a phase separation in the fiber. The coarsening oil/water channels in the fiber are arrested by the interfacial attachment and jamming of the nanoparticles, creating a semisolid material.

3. Measuring mechanical properties?



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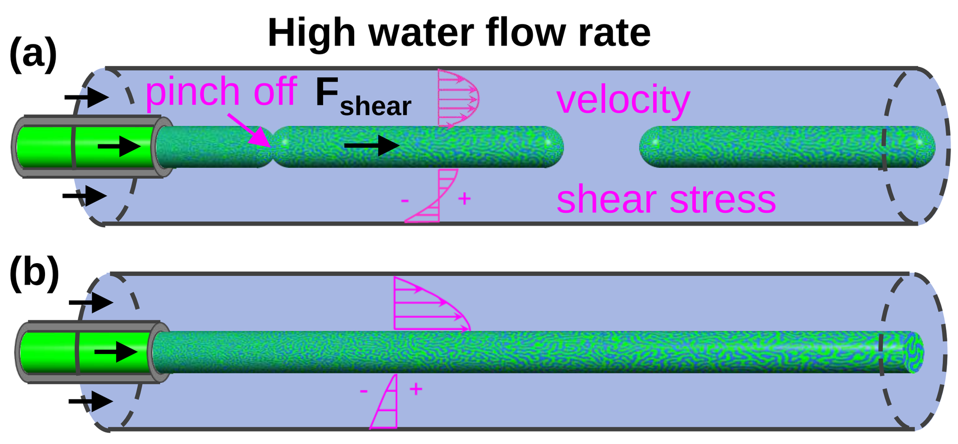
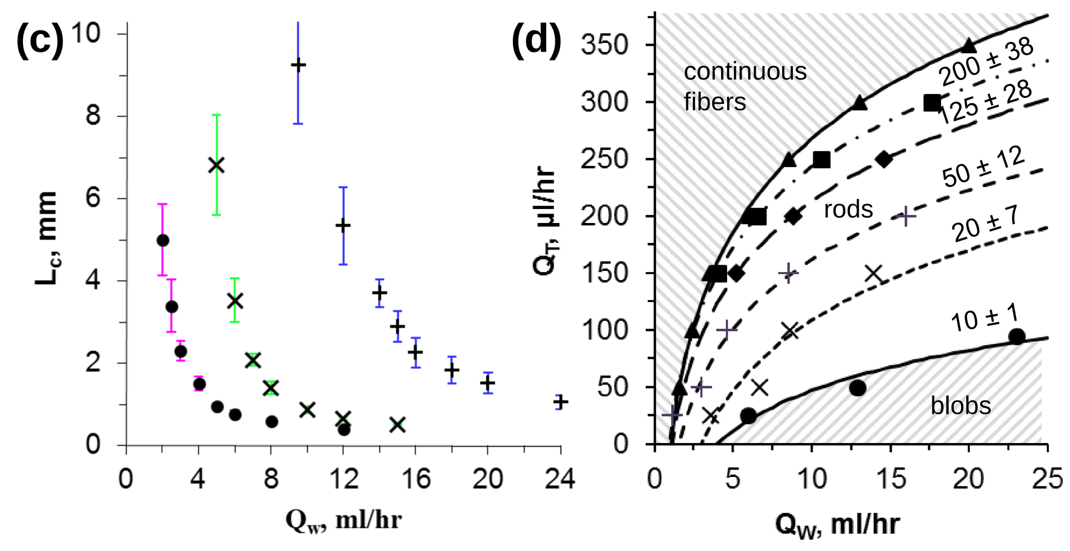
Previously, researchers have created bijels in a gap between two parallel plates upon rapidly cooling a mixture of oil, water and nanoparticles **(a)**. They were able to characterize the rheological properties of their bijels by periodical shearing (shear rheology). In these experiments the storage and loss moduli both increased during bijel formation **(b)**, meaning the material became both more solid and more viscous. However, the storage modulus exceeded the loss modulus by an order of magnitude, indicating that bijels can be treated as solids materials.

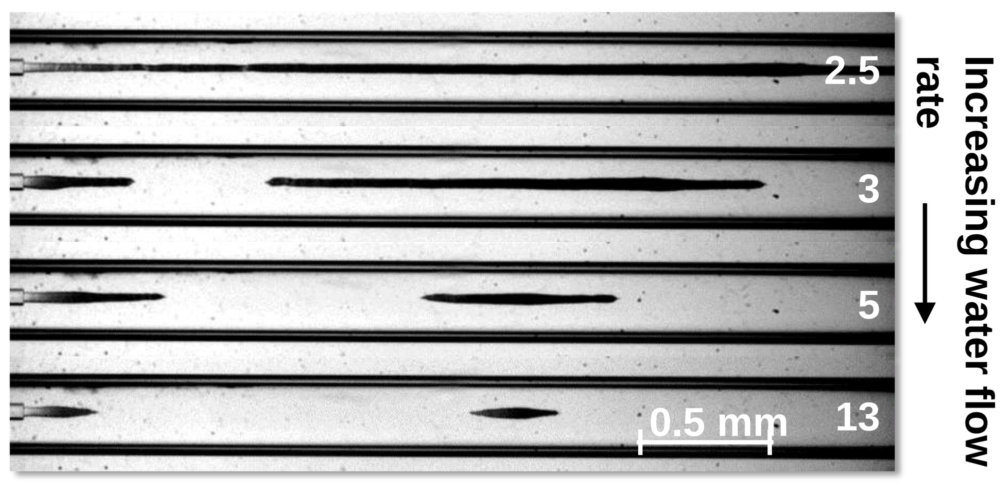
4. Fiber pinch-off behavior

Bijel fibers require new mechanical characterization methods since parallel plate rheology cannot be used. In our fiber extrusion experiment we find that increasing the flow rate of the water stream causes periodic pinch-off of equally long segments **(a)**. This phenomena is caused by the increasing shear stress exerted from the water stream on the fiber. When the velocity of the water equals the velocity of the fiber surface, continuous fibers are formed **(b)**. On the other hand, when the outer water flows much faster than the fiber, segmentation occurs **(a)**. The segment length then depends on the shear stress as we will show below.





In **(c)** we plot the fiber-segment length L_C for constant flow rates of the liquid mixture (Q_T) vs. the water flow rate (Q_W). A complex relationship for the fiber aspect ratio as shown in **(d)** is found.



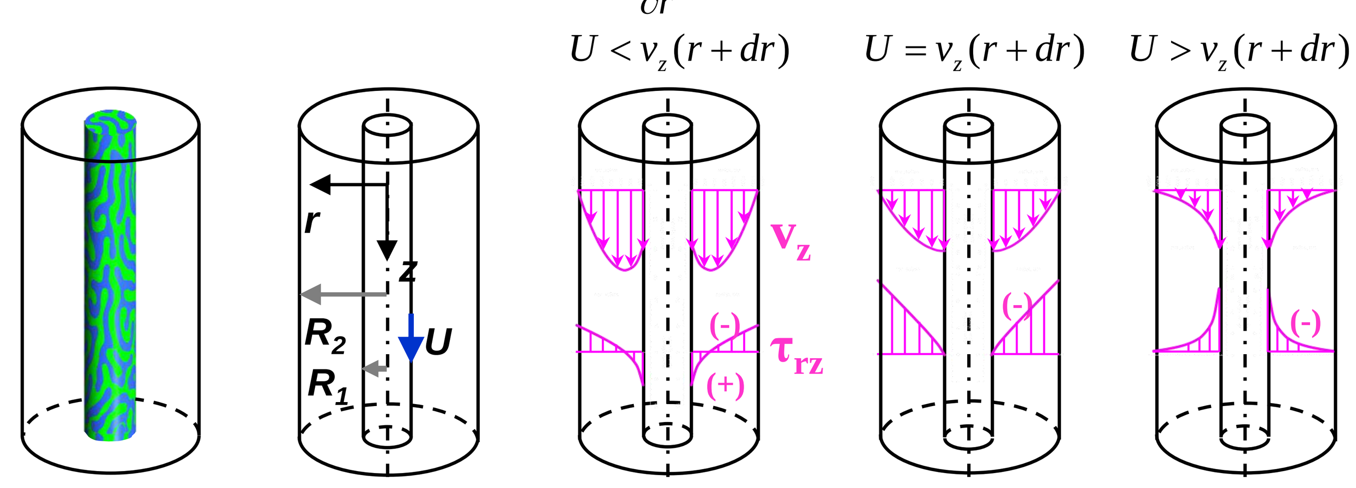
5. Fluid mechanics around fiber

To prove our hypothesis we have to calculate the radial distribution of the axial water velocity ($v_z(r)$) around the fiber. This can be done by solving the Navier-Stokes-Equation or a momentum balance. The equivalent geometry is a cylindrical annulus with an inner cylinder (fiber) moving at the velocity U (no slip) and the static outer wall at zero velocity:

Boundary conditions: $r = R_1 \rightarrow v_z = U \qquad r = R_2 \rightarrow v_z = 0$

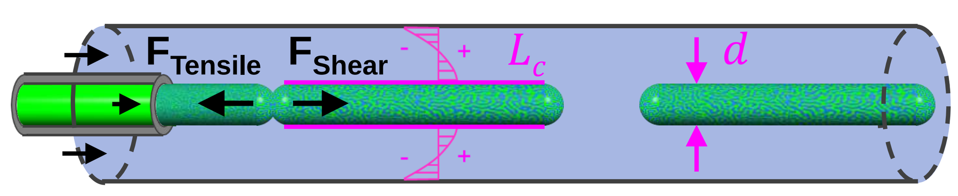
Axial velocity: $$v_z(r) = -\frac{dp}{dz}\frac{\left(R_2^2 - r^2\right)}{4\mu} + \left\{U + \frac{dp}{dz}\frac{\left(R_2^2 - R_1^2\right)}{4\mu}\right\}\frac{\ln(R_2/r)}{\ln(R_2/R_1)}$$

Shear stress: $$\tau_{rz}(r) = \mu\frac{\partial v_z}{\partial r}$$



The fiber can either move slower, at equal speed or faster than the water.

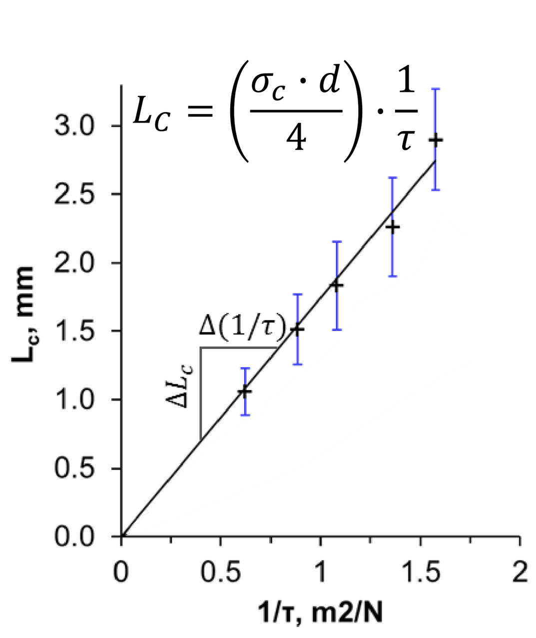
6. Mechanical strength at early stages of bijel formation



$$F_{yield} = F_{shear,c}$$

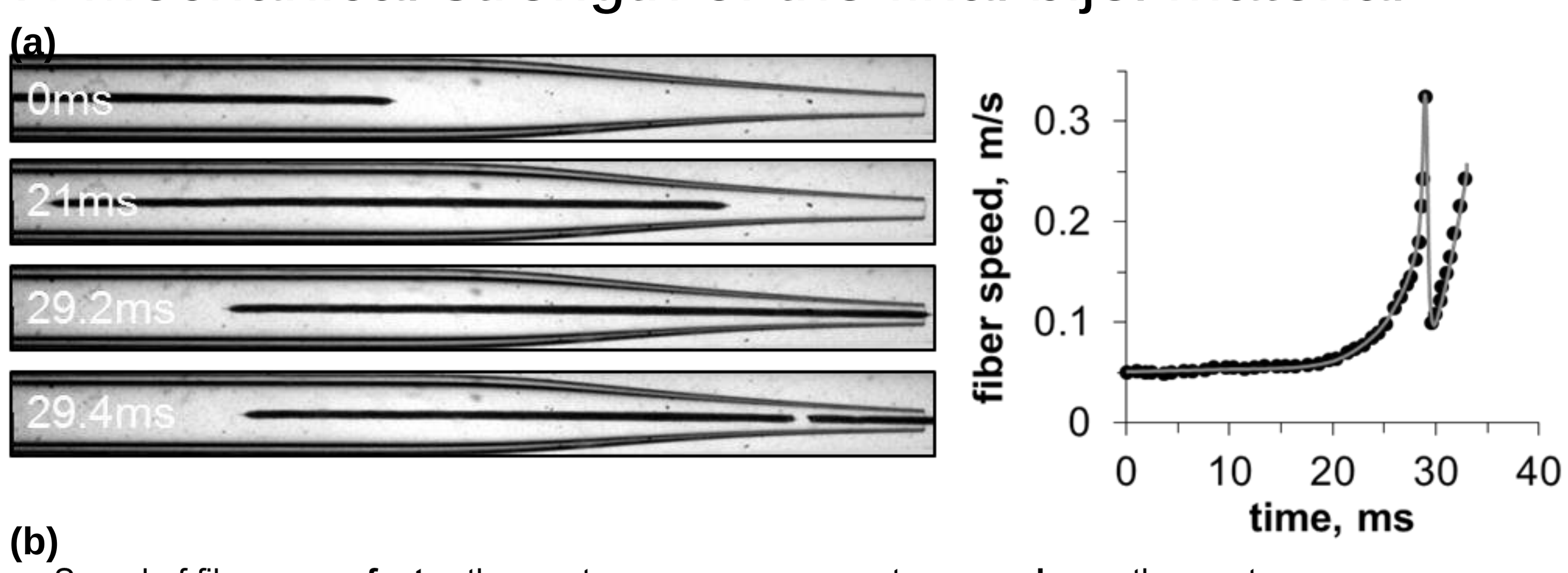
$$\sigma_c \cdot \frac{\pi}{4} \cdot d^2 = \tau \cdot \pi \cdot d \cdot L_c$$

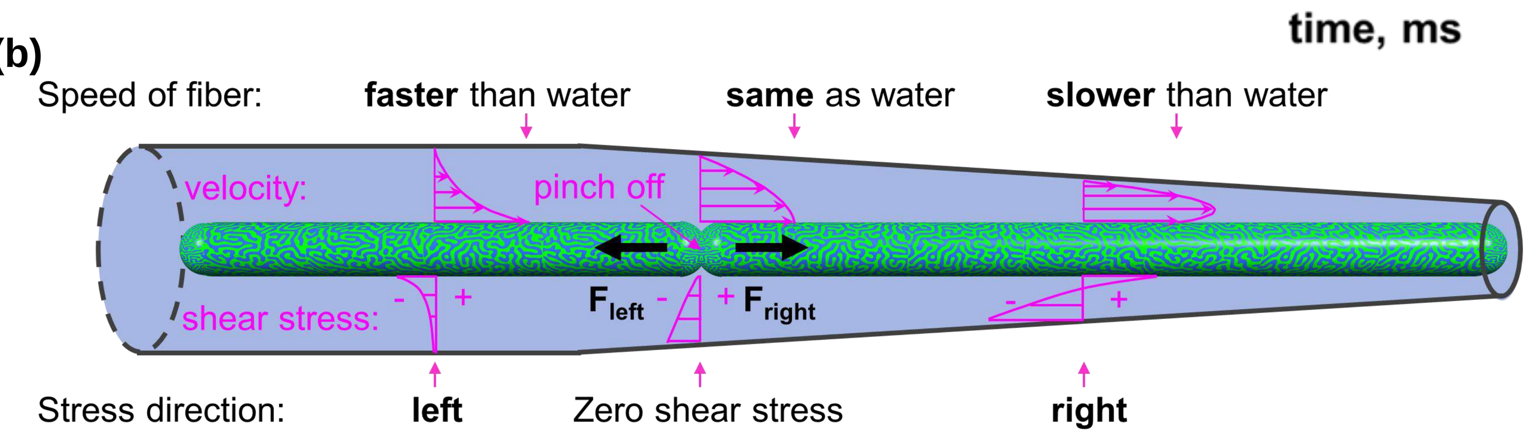
L_C Fiber length
σ_c Tensile strength
d Fiber Diameter
τ Shear stress

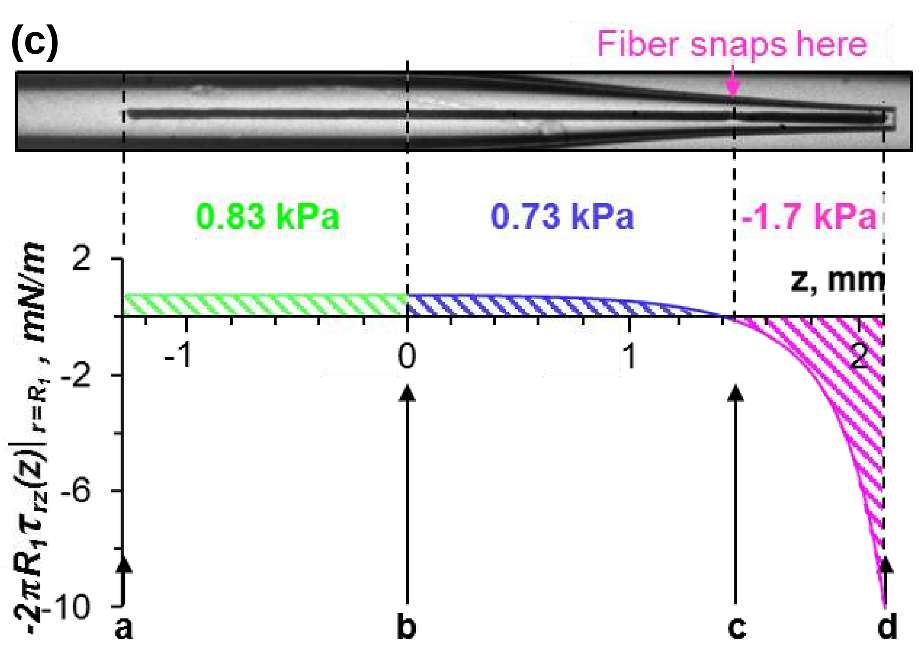


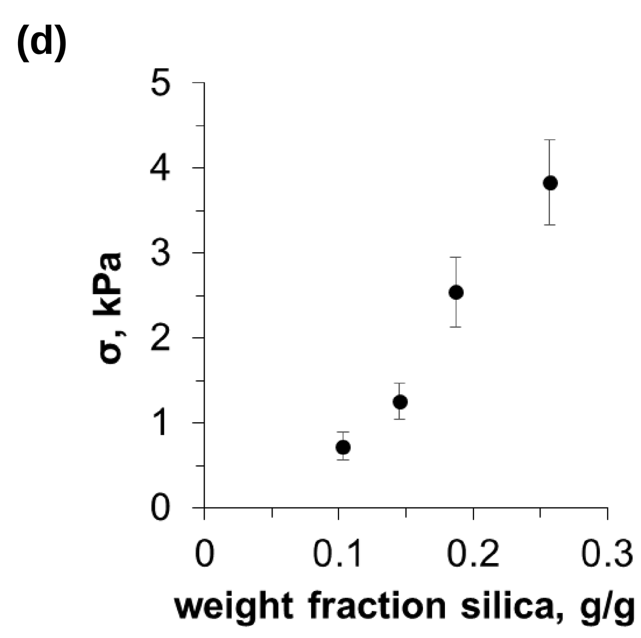
The literature tells us that bijels can be treated as solid objects (section 3). Thus, for the moment of fiber pinch-off we can set up a simple force balance between the fiber tensile strength and the shear force (see left). The resulting equation can be rearranged to yield a linear relationship between fiber segment length L_C and the inverse shear stress $1/\tau$. And indeed, plotting the measured fiber lengths for different calculated and inverted shear stresses (calculated with the equations in section 5) gives a linear relationship, confirming our hypothesis. The tensile strength of the fiber can now be inferred from the slope.

7. Mechanical strength of the final bijel material



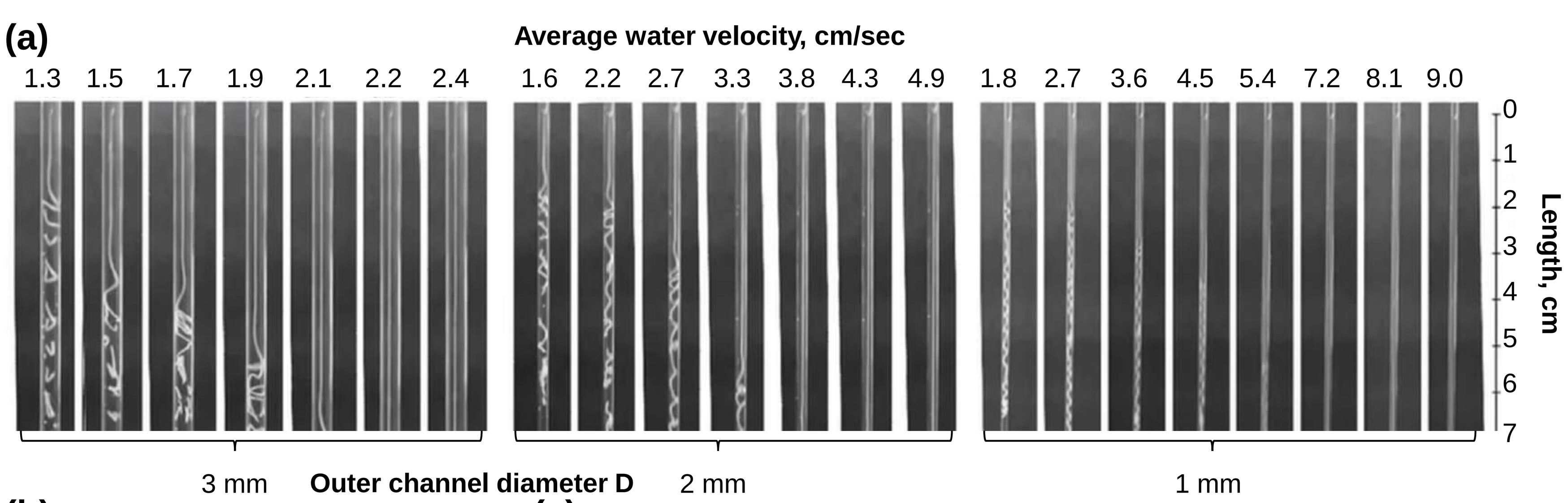


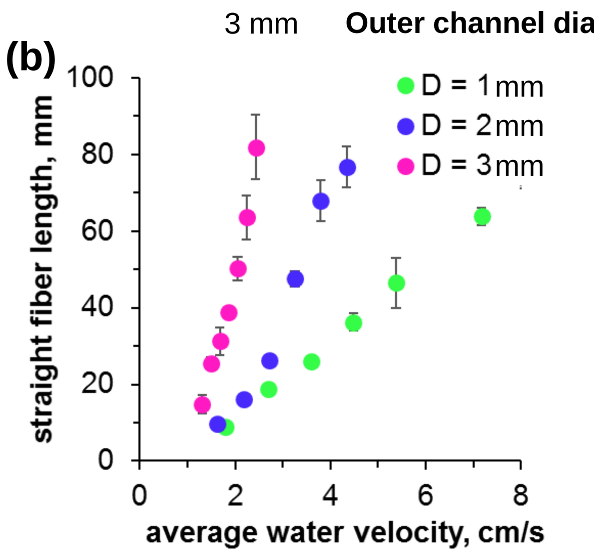


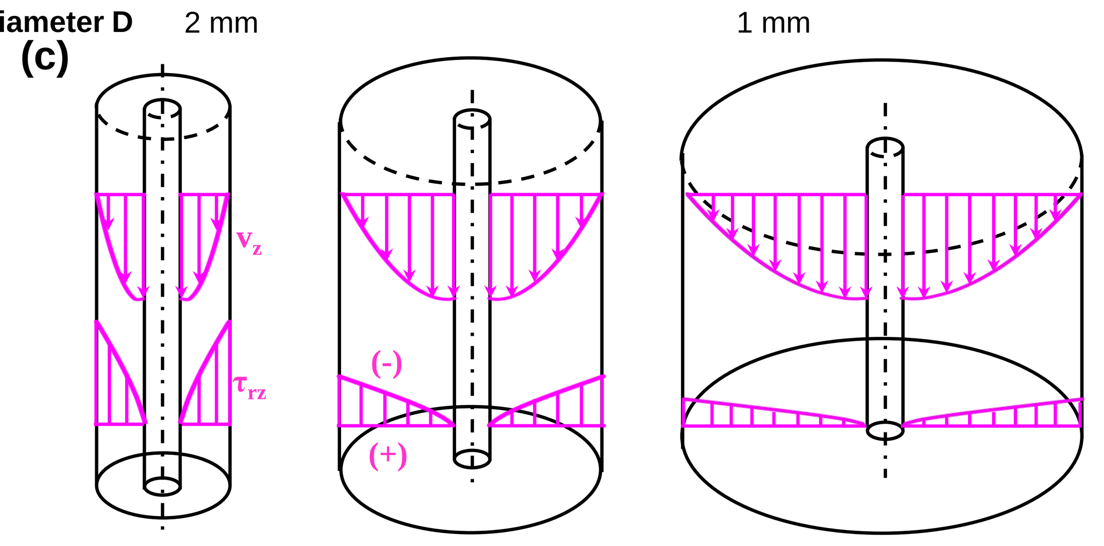


The limitation of the approach described in section 6 is that only bijels fibers that have not yet completed phase separation can be tested. However, measuring the mechanical strength of the final bijel is of great importance, since this is the material used in later applications. To measure the final mechanical strength, a fiber segment is transported by the water flow over a distance of several centimeters into a constriction. In the constriction, the segment accelerates and snaps into 2 segments **(a)**. Under the lubrication approximation we can use the same equations as in section 5 to calculate the shear stresses **(b)**. It turns out that this time the shear forces have opposite, because the front of the fiber moves slower, while the trailing end moves faster than the surrounding water. By calculating the forces **(c)** we find that the tensile strength of the fiber depends strongly on the nanoparticle concentration **(d)**.

8. Fiber Undulation behavior in the channel







Continuous straight fibers are useful for a variety of applications. But how to extrude continuous straight fibers? For sufficiently strong fibers moderately increasing the water flow rate does not cause pinch-off. Instead, increasing the average water velocity increases the straight fiber length before undulation occurs **(a)**. Moreover, the wider the channel, the lower the average water velocities required to keep the fiber straight **(b)**. The calculation of the shear stress in the different channels explains this **(c)**: In a narrow channel the fiber experiences strong forces when moving slightly off-center due to the sharp shear stress profile. This causes undulation by strong asymmetric shear stress profiles around the fiber. In contrast, in a wide channel the fiber barely notices when it moves off-center due to the shallow shear stress profile.

Publication from this work:

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