

SI.1 Compression instrument and loading

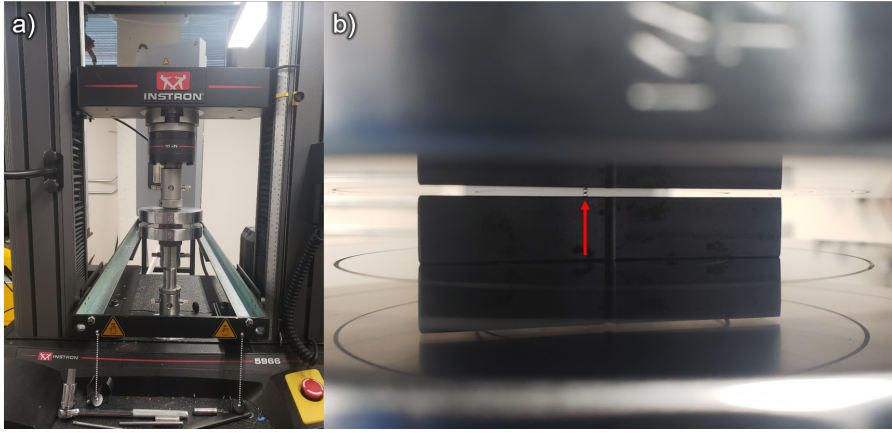


Fig. S1 a) Instron instrument used for compression testing b) microbead compressed between steel plate and steel jig used for loading

SI.2 Individual solvent screen bead sizes

Average sizes, sphericities, and deswelling ratios are listed with standard deviations for the solvent screen are listed below in Table S1 - individual trials for each solvent are listed in Tables S3-S6:

Solution	Precipitation	Extraction	D_{precip} [mm]	D_{bead} [mm]	Sphericity (precip.)	Sphericity (extract.)	$\frac{D_{bead}}{D_{precip}}$
8% cellulose	Ethanol	Ethanol	2.35 ± 0.29	1.28 ± 0.08	1.06 ± 0.04	1.06 ± 0.01	0.54 ± 0.08
8% cellulose	Water	Ethanol	2.76 ± 0.15	1.29 ± 0.07	1.03 ± 0.01	1.09 ± 0.02	0.47 ± 0.04
8% cellulose	Ethanol	Water	1.60 ± 0.08	1.52 ± 0.06	1.01 ± 0.17	1.07 ± 0.05	0.95 ± 0.06
8% cellulose	Water	Water	2.27 ± 0.15	2.12 ± 0.12	1.07 ± 0.04	1.24 ± 0.26	0.93 ± 0.08
8% cellulose	Eth:Water	Ethanol	2.60 ± 0.09	1.27 ± 0.05	1.05 ± 0.01	1.05 ± 0.03	0.49 ± 0.03
8% cellulose	0.1 M HCl	Ethanol	2.79 ± 0.07	1.34 ± 0.04	1.03 ± 0.03	1.10 ± 0.07	0.48 ± 0.02
7.2% cellulose	Ethanol	Ethanol	1.87 ± 0.13	1.01 ± 0.04	1.22 ± 0.10	1.27 ± 0.12	0.54 ± 0.04
7.2% cellulose	Water	Ethanol	2.16 ± 0.16	0.98 ± 0.04	1.10 ± 0.05	1.32 ± 0.29	0.45 ± 0.04
7.2% cellulose	Ethanol	Water	1.29 ± 0.09	1.07 ± 0.09	1.14 ± 0.07	1.28 ± 0.11	0.83 ± 0.09
7.2% cellulose	Water	Water	1.09 ± 0.09	1.14 ± 0.13	1.09 ± 0.03	1.08 ± 0.03	1.04 ± 0.15
7.2% cellulose	Eth:Water	Ethanol	1.70 ± 0.24	0.94 ± 0.08	1.24 ± 0.14	1.23 ± 0.11	0.55 ± 0.09
7.2% cellulose	0.1 M HCl	Ethanol	2.22 ± 0.14	0.93 ± 0.09	1.09 ± 0.06	1.12 ± 0.10	0.42 ± 0.05
2.7% lignin / 5.3% cellulose	Ethanol	Ethanol	1.42 ± 0.10	1.16 ± 0.07	1.45 ± 0.12	1.51 ± 0.27	0.82 ± 0.08
2.7% lignin / 5.3% cellulose	Water	Ethanol	2.19 ± 0.24	1.24 ± 0.13	1.14 ± 0.03	1.13 ± 0.04	0.57 ± 0.08
2.7% lignin / 5.3% cellulose	Ethanol	Water	1.53 ± 0.16	1.23 ± 0.12	1.26 ± 0.18	1.37 ± 0.14	0.80 ± 0.11
2.7% lignin / 5.3% cellulose	Water	Water	1.30 ± 0.04	1.07 ± 0.03	1.11 ± 0.11	1.13 ± 0.09	0.82 ± 0.04
2.7% lignin / 5.3% cellulose	Eth:Water	Ethanol	2.04 ± 0.25	1.19 ± 0.09	1.14 ± 0.10	1.16 ± 0.08	0.58 ± 0.09
2.7% lignin / 5.3% cellulose	0.1 M HCl	Ethanol	2.34 ± 0.09	1.24 ± 0.07	1.18 ± 0.05	1.26 ± 0.17	0.53 ± 0.04
4% lignin / 4% cellulose	Ethanol	Ethanol	1.50 ± 0.09	1.21 ± 0.04	1.23 ± 0.28	1.27 ± 0.56	0.81 ± 0.06
4% lignin / 4% cellulose	Water	Ethanol	1.76 ± 0.45	1.10 ± 0.08	1.32 ± 0.34	1.40 ± 0.10	0.62 ± 0.17
4% lignin / 4% cellulose	Ethanol	Water	1.41 ± 0.11	0.93 ± 0.10	1.25 ± 0.10	1.36 ± 0.20	0.66 ± 0.09
4% lignin / 4% cellulose	Water	Water	1.14 ± 0.19	0.89 ± 0.06	1.35 ± 0.25	1.42 ± 0.20	0.78 ± 0.14
4% lignin / 4% cellulose	Eth:Water	Ethanol	1.30 ± 0.25	1.02 ± 0.05	1.20 ± 0.12	1.19 ± 0.11	0.78 ± 0.16
4% lignin / 4% cellulose	0.1 M HCl	Ethanol	1.59 ± 0.46	1.29 ± 0.19	1.37 ± 0.37	1.26 ± 0.17	0.81 ± 0.26

Table S1 Average diameters before (D_{precip}) and after (D_{bead}) extraction, sphericities (determined by the ratio of major to minor axes), and deswelling ratios ($\frac{D_{bead}}{D_{precip}}$) of beads in the solvent screen, made from solutions with given concentrations of DP290 cellulose and Kraft lignin, extruded into a given precipitation solvent and extracted with given solvents.

Solution	Precipitation	D_{precip} [mm]
8% cellulose	Ethanol	1.98 ± 0.31
8% cellulose	Water	2.52 ± 0.21
7.2% cellulose	Ethanol	1.58 ± 0.16
7.2% cellulose	Water	1.63 ± 0.19
2.7% lignin / 5.3% cellulose	Ethanol	1.48 ± 0.13
2.7% lignin / 5.3% cellulose	Water	1.75 ± 0.26
4% lignin / 4% cellulose	Ethanol	1.46 ± 0.14
4% lignin / 4% cellulose	Water	1.45 ± 0.49

Table S2 Average diameters (D_{precip}) of before of $n=10$ beads in the solvent screen, made from solutions with given concentrations of DP290 cellulose and Kraft lignin and extruded into a given precipitation solvent. These samples were each divided in half and extracted in ethanol and water respectively.

SI.3 Extensional rheology

Extensional rheology of solutions of 8% wt DP290 cellulose, 8% wt DP230 cellulose, and 4% wt DP230 cellulose/4% wt Kraft lignin all in 70:30 DMSO:EMImAc are shown in Figure S2, showing the effect of shorter cellulose and substituting Kraft lignin into the solution on reducing breakup time and extensional viscosity at all Hencky strains. Apparent extensional viscosities are determined as $\eta_E = \frac{\sigma}{2dR(t)/dt}$, using a Savitsky-Golay filter with order 5 and window 25 to remove noise due to differentiation of discrete data. Radial decay profiles and extensional viscosity as a function of Hencky strain $\varepsilon_H = -\ln(R/R_0)$, where R_0 is the initial radius defined as 80% of the radius of the nozzle extruding the drop, are plotted below in Figure S2:

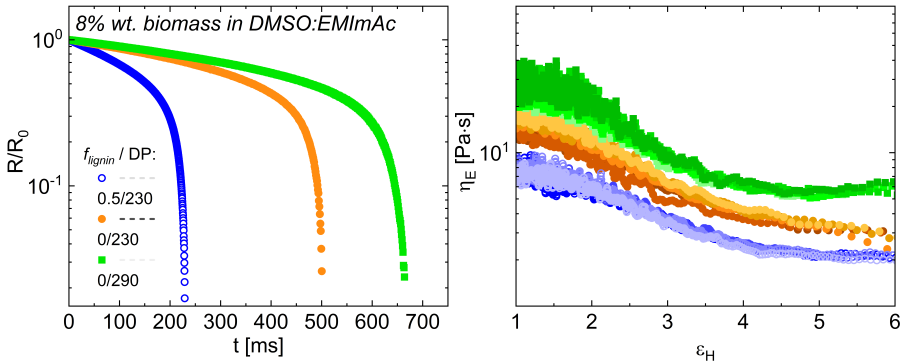


Fig. S2 a) Radial decay profiles of minimum radius R divided by initial radius R_0 for representative trials and b) apparent extensional viscosities η_E as a function of Hencky strain ε_H for all trials for solutions of 8% wt DP290 cellulose (green), 8% wt DP230 cellulose (orange), and 4% wt DP230 cellulose/4% wt Kraft lignin (blue)

Based on the small upturn in extensional viscosities for the 8% wt DP290 solution past a Hencky strain ε_H of around 5, we can see some evidence of elasticity in the solution, which is bad for processing, as elasticity results in an increase in stress in the sample flowing through the nozzle. These results explain our observation that the reduction in DP or the substitution of lignin allowed for use of smaller nozzles while maintaining a sufficient flow rate to avoid clogging (Figure S3).

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Precipitation	Extraction	D_{precip} [mm]	D_{bead} [mm]	Trial
Ethanol	Ethanol	2.81	1.33	1
Ethanol	Ethanol	2.32	1.28	2
Ethanol	Ethanol	2.34	1.16	3
Ethanol	Ethanol	1.98	1.34	4
Ethanol	Ethanol	2.31	-	5
Water	Ethanol	2.71	1.28	1
Water	Ethanol	2.73	1.20	2
Water	Ethanol	2.82	1.27	3
Water	Ethanol	2.98	1.39	4
Water	Ethanol	2.57	1.29	5
Ethanol	Water	1.62	1.47	1
Ethanol	Water	1.56	1.47	2
Ethanol	Water	1.68	1.50	3
Ethanol	Water	1.49	1.59	4
Ethanol	Water	1.67	1.58	5
Water	Water	2.24	2.12	1
Water	Water	2.42	2.28	2
Water	Water	2.44	1.95	3
Water	Water	2.10	2.13	4
Water	Water	2.15	2.14	5
Ethanol:Water	Ethanol	2.66	1.27	1
Ethanol:Water	Ethanol	2.66	1.34	2
Ethanol:Water	Ethanol	2.46	1.20	3
Ethanol:Water	Ethanol	2.64	1.27	4
Ethanol:Water	Ethanol	2.56	1.28	5
0.1 M HCl	Ethanol	2.90	1.36	1
0.1 M HCl	Ethanol	2.78	1.33	2
0.1 M HCl	Ethanol	2.78	1.28	3
0.1 M HCl	Ethanol	2.77	1.37	4
0.1 M HCl	Ethanol	2.72	1.38	5

Table S3 Individual diameters of beads from the solvent screen before (D_{precip}) and after (D_{bead}) extraction, made from an 8% wt solution of DP290 cellulose in 70:30 DMSO:IL, extruded into a given precipitation solvent and extracted with given solvents. For conditions where a bead was lost after extraction, the average was calculated without that bead.

Flow rates of biomass solutions through nozzles are limited by the inner diameter of the nozzle - therefore, for these viscous solutions, using too small of a nozzle can result in a flow rate so slow that the solution precipitates before dripping, due to ethanol vapor from the precipitation bath as well as water in the air, as depicted in Figure S3:

Precipitation	Extraction	D_{bead} [mm]	D_{precip} [mm]	Trial
Ethanol	Ethanol	1.92	1.06	1
Ethanol	Ethanol	2.03	0.99	2
Ethanol	Ethanol	1.93	1.00	3
Ethanol	Ethanol	1.80	1.03	4
Ethanol	Ethanol	1.69	0.96	5
Water	Ethanol	2.12	0.99	1
Water	Ethanol	2.21	0.99	2
Water	Ethanol	2.24	0.95	3
Water	Ethanol	1.90	0.93	4
Water	Ethanol	2.32	1.02	5
Ethanol	Water	1.22	1.06	1
Ethanol	Water	1.24	1.10	2
Ethanol	Water	1.30	1.01	3
Ethanol	Water	1.20	1.23	4
Ethanol	Water	1.39	0.98	5
Ethanol	Water	1.40	1.02	6
Water	Water	1.15	1.16	1
Water	Water	0.93	1.18	2
Water	Water	1.16	1.30	3
Water	Water	1.13	0.95	4
Water	Water	1.11	1.08	5
Ethanol:Water	Ethanol	1.70	0.90	1
Ethanol:Water	Ethanol	1.85	1.05	2
Ethanol:Water	Ethanol	1.29	0.92	3
Ethanol:Water	Ethanol	1.75	0.88	4
Ethanol:Water	Ethanol	1.92	-	5
0.1 M HCl	Ethanol	2.42	1.00	1
0.1 M HCl	Ethanol	2.04	0.88	2
0.1 M HCl	Ethanol	2.19	0.97	3
0.1 M HCl	Ethanol	2.23	0.98	4
0.1 M HCl	Ethanol	2.21	0.79	5

Table S4 Individual diameters of beads from the solvent screen before (D_{precip}) and after (D_{bead}) extraction, made from an 7.2% wt solution of DP290 cellulose in 70:30 DMSO:IL, extruded into a given precipitation solvent and extracted with given solvents. For conditions where a bead was lost after extraction, the average was calculated without that bead.

SI.4 Bead shape and calculation of stress and strain

Whereas the initial drop is approximately spherical, with a diameter determined by a force balance between surface tension and gravity of $D_{drop} \approx \left(\frac{6\sigma\cos(\theta)}{\rho_g} \right)^{1/3}$, the bead is deformed upon contact with the precipitation solvent surface, leading to a generally oblate spheroid shape compressed along the vertical axis. The radius of contact of the bead is calculated based on its curvature,[1] which can be calculated for an oblate spheroid with radii of $\frac{H}{2}$ and $\frac{H}{2}$ at its flattest point[2] as $\kappa = \frac{2H}{D_{bead}^2}$. Therefore, the radius

of curvature is $R_C = \frac{1}{2\kappa} = \frac{D_{bead}^2}{4H}$, or for a perfectly spherical particle ($H = D_{bead}$), $R_C = \frac{D_{bead}}{4}$. Plugging this value into Equation 1, the force on a perfect sphere where $H = D_{bead}$ would be $F_{sphere} = \frac{2}{3}E\sqrt{D_{bead}}x^{3/2}$, which is the form used for any beads which do not incorporate lignin, as these were very close to spherical.

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Precipitation	Extraction	D_{precip} [mm]	D_{bead} [mm]	Trial
Ethanol	Ethanol	1.46	1.17	1
Ethanol	Ethanol	1.34	1.06	2
Ethanol	Ethanol	1.46	1.24	3
Ethanol	Ethanol	1.29	1.16	4
Ethanol	Ethanol	1.55	-	5
Water	Ethanol	2.25	1.25	1
Water	Ethanol	1.78	1.07	2
Water	Ethanol	2.26	1.41	3
Water	Ethanol	2.22	1.30	4
Water	Ethanol	2.42	1.19	5
Ethanol	Water	1.55	1.06	1
Ethanol	Water	1.75	1.29	2
Ethanol	Water	1.52	1.32	3
Ethanol	Water	1.30	1.15	4
Ethanol	Water	1.54	1.33	5
Water	Water	1.29	1.06	1
Water	Water	1.33	1.04	2
Water	Water	1.27	1.10	3
Water	Water	1.27	1.11	4
Water	Water	1.37	1.04	5
Ethanol:Water	Ethanol	2.11	1.26	1
Ethanol:Water	Ethanol	1.87	1.22	2
Ethanol:Water	Ethanol	1.86	1.15	3
Ethanol:Water	Ethanol	1.89	1.05	4
Ethanol:Water	Ethanol	2.45	1.28	5
0.1 M HCl	Ethanol	2.42	1.31	1
0.1 M HCl	Ethanol	2.40	1.28	2
0.1 M HCl	Ethanol	2.20	1.23	3
0.1 M HCl	Ethanol	2.40	1.14	4
0.1 M HCl	Ethanol	2.28	1.24	5

Table S5 Individual diameters of beads from the solvent screen before (D_{precip}) and after (D_{bead}) extraction, made from a solution of 2.7% wt Kraft lignin and 5.3% wt DP290 cellulose in 70:30 DMSO:IL, extruded into a given precipitation solvent and extracted with given solvents. For conditions where a bead was lost after extraction, the average was calculated without that bead.

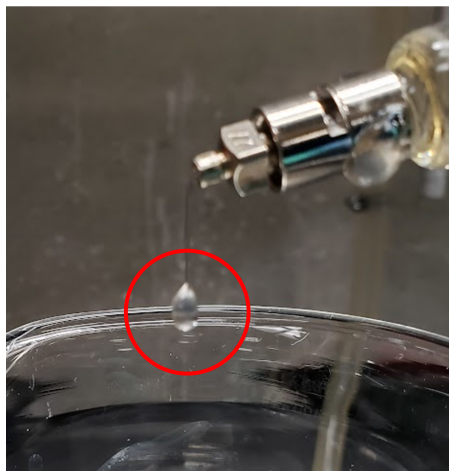
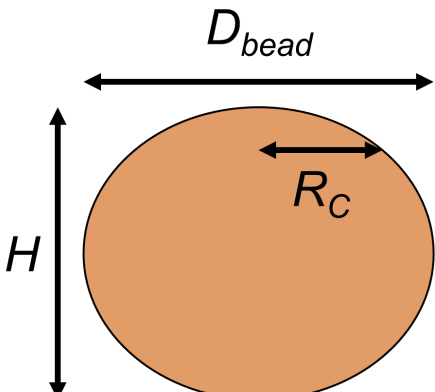


Fig. S3 A partially precipitated drop of 8% wt DP290 cellulose solution at the end of a 27 gauge nozzle

Precipitation	Extraction	D_{bead} [mm]	D_{precip} [mm]	Trial
Ethanol	Ethanol	1.42	1.23	1
Ethanol	Ethanol	1.54	1.20	2
Ethanol	Ethanol	1.60	1.25	3
Ethanol	Ethanol	1.43	1.15	4
Water	Ethanol	1.49	1.04	1
Water	Ethanol	2.08	1.02	2
Water	Ethanol	2.40	1.04	3
Water	Ethanol	1.44	1.19	4
Water	Ethanol	1.38	1.19	5
Ethanol	Water	1.45	0.92	1
Ethanol	Water	1.32	0.88	2
Ethanol	Water	1.36	0.84	3
Ethanol	Water	1.35	1.07	4
Ethanol	Water	1.59	-	5
Water	Water	1.35	0.86	1
Water	Water	0.89	0.85	2
Water	Water	1.26	0.94	3
Water	Water	1.18	0.96	4
Water	Water	1.01	0.83	5
Ethanol:Water	Ethanol	1.44	1.07	1
Ethanol:Water	Ethanol	1.45	1.04	2
Ethanol:Water	Ethanol	0.91	0.97	3
Ethanol:Water	Ethanol	1.52	0.99	4
Ethanol:Water	Ethanol	1.17	-	5
0.1 M HCl	Ethanol	1.38	1.63	1
0.1 M HCl	Ethanol	1.75	1.28	2
0.1 M HCl	Ethanol	1.28	1.14	3
0.1 M HCl	Ethanol	2.33	1.21	4
0.1 M HCl	Ethanol	1.22	1.19	5

Table S6 Individual diameters of beads from the solvent screen before (D_{precip}) and after (D_{bead}) extraction, made from a solution of 4% wt Kraft lignin and 4% wt DP290 cellulose in 70:30 DMSO:IL, extruded into a given precipitation solvent and extracted with given solvents. For conditions where a bead was lost after extraction, the average was calculated without that bead.



$$\kappa = \frac{2H}{D_{bead}^2}$$

$$R_C = \frac{1}{2\kappa} = \frac{D_{bead}^2}{4H}$$

$$F = \frac{2}{3}E \sqrt{\frac{D_{bead}^2}{H}} x^{3/2}$$

Fig. S4 Calculation of contact radius for oblate spheroid - the force on a perfect sphere where $H = D_{bead}$ would be $F_{sphere} = \frac{2}{3}E \sqrt{D_{bead}} x^{3/2}$

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This model does not account for other irregularities in the shape of microbeads, such as wrinkles due to contraction of the bead surface as formed in 4% wt beads (Fig S5) - consequently, moduli measured for these beads by single-particle compression tests are more variable, dependent on the geometry of the bead surface at the point of contact.

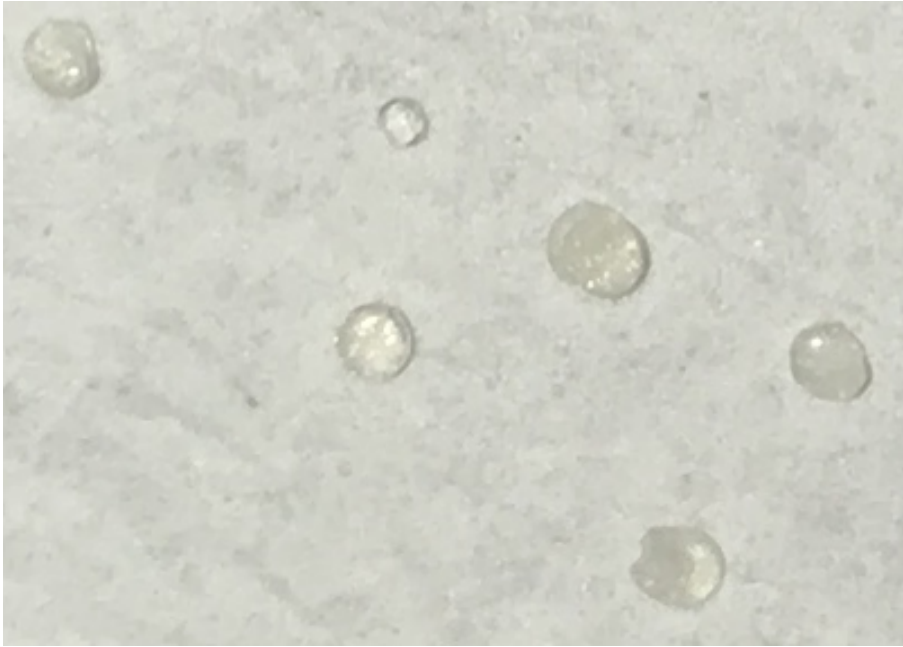


Fig. S5 Wrinkles on surface of a bead formed from 4% wt solution of cellulose, precipitated and extracted in ethanol, leading to variances in the measurement of Young's moduli by single-particle compression.

SI.5 Dye adsorption

While the microbeads have very little porosity when dry (as indicated by SEM images and swelling ratios), beads in solution are still capable of absorbing dyes from solution. However, based on preliminary experiments, adsorption of dyes depends on size, as shown in Figure S6 using a blue food dye comprised of Blue 1 and Red 40. While Blue 1 is the primary color in the dye, the microbead selectively absorbs the Red 40, indicating that size determines the adsorption of these two chemically similar compounds. Based on the average molecular diameters D_{avg} of the two dyes, calculated from a sphere with the volume determined from dye structures[3] in the absence of reliable bulk density data, the threshold for dyes that can be absorbed by the cellulose microbeads is on the order of 1 nm.

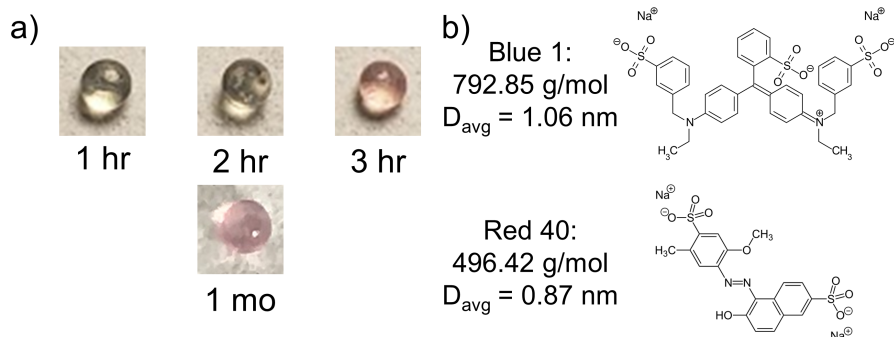


Fig. S6 a) 8% DP290 cell. beads in 0.1% vol. blue food dye (McCormick) containing FD&C Blue 1 and Red 40, with b) structures, molecular weights and average molecular diameters D_{avg} . Although both dyes are chemically similar, Red 40 is smaller, and is preferentially absorbed by the cellulose beads despite being the secondary component, indicating a size-based selectivity of adsorption with a threshold size on the order of ~ 1 nm.

SL.6 Stability of microbeads in model system

Images of microbeads submerged in 25% SDS and water after two months are shown in Fig. S7 for microbeads of $f_{lignin} = 0, 0.33, 0.5$. Lignin diffusion from the microbead is suppressed by the presence of SDS in water, as seen by the lighter colored images in the top row of Fig. S7.

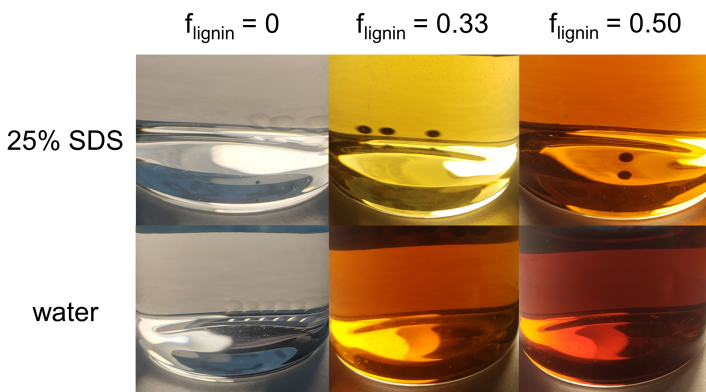


Fig. S7 Microbeads ($f_{lignin} = 0, 0.33, 0.5$) submerged in 25% SDS (top) and water (bottom) after 2 mo. Although lighting conditions vary between these images and those at the start of the stability test (Fig. 9), the same trend is evident, with SDS suppressing lignin diffusion from the bead.

Beads were removed from each solution weekly and dried overnight in a vacuum oven at room temperature to remove water, before undergoing mechanical compression tests. While this drying step prevented any further drying of beads during compression, it is unlikely that all water was removed from the interior of the bead, resulting in higher strains at break as compared to other beads not submerged in water, as a result of the plasticizing effect of this residual water.

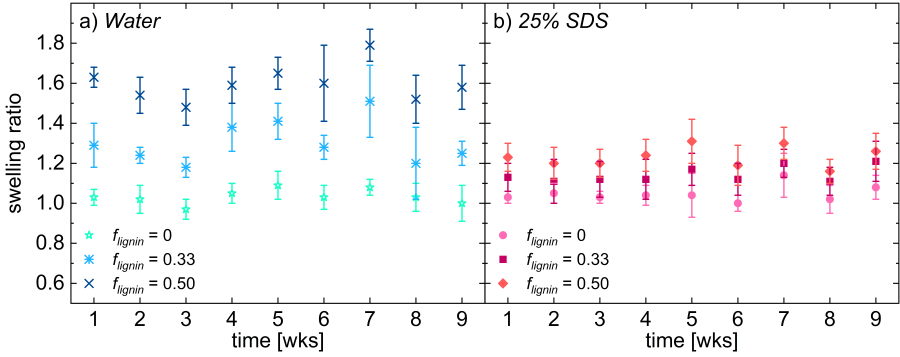


Fig. S8 Swelling ratios of microbeads (8% wt biomass, DP290 cellulose + lignin) submerged in a) water and b) 25% SDS, with $f_{\text{lignin}} = 0, 0.33, 0.5$. Swelling ratios remain nearly constant for 2 months. However, SR increases with f_{lignin} and generally decreases in SDS.

Solution	f_{lignin}	Slope $\times 10^3$	P-value
Water	0	1.83 ± 11.99	0.73
Water	0.33	4.67 ± 35.02	0.76
Water	0.50	6.17 ± 28.75	0.63
25% SDS	0	4.83 ± 12.62	0.40
25% SDS	0.33	8.00 ± 10.68	0.12
25% SDS	0.50	2.50 ± 16.39	0.73

Table S7 Slopes with 95% confidence intervals and associated p -values for linear fits of microbead SR in time. Microbeads with $f_{\text{lignin}} = 0, 0.33, 0.5$ were observed in water and 25% SDS, and swelling ratios did not change over 2 months, as indicated by the confidence intervals of the fit slopes all overlapping a value of 0 and by p -values indicating no significant difference from slopes of 0. Average values of these swelling ratios are shown as functions of f_{lignin} in Fig. 9.

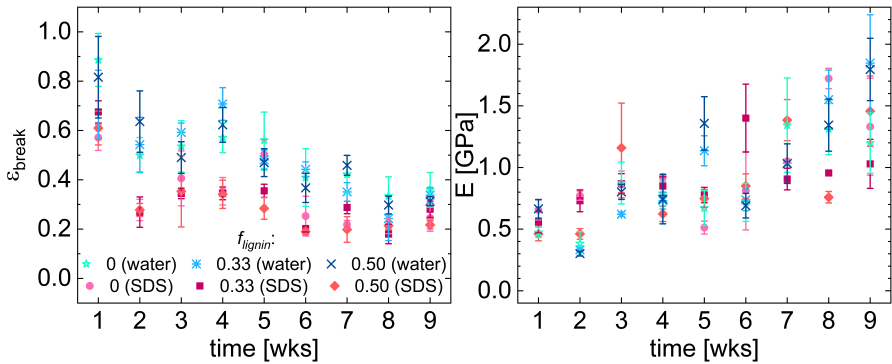


Fig. S9 a) Compression at break ϵ_{break} and b) moduli of microbeads submerged in water and 25% SDS, produced from 8% wt solutions of biomass (DP290 cellulose and Kraft lignin) with $f_{\text{lignin}} = 0, 0.33, 0.5$. All microbeads regardless of composition or environment exhibit lower ϵ_{break} values and higher moduli indicating brittleness due to aging, but there are some visible differences in ϵ_{break} trends depending on sample environment. ϵ_{break} is lower for all beads in SDS in a given week, but slopes after week 1 are approximately 50% steeper for beads in water than beads in SDS, indicating that SDS may slow mechanical degradation of microbeads.

Solution	f_{lignin}	Slope $\times 10^2$	P-value
Water	0	-4.99 ± 1.30	0.006
Water	0.33	-5.19 ± 1.10	0.002
Water	0.50	-5.57 ± 1.01	0.001
25% SDS	0	-3.30 ± 1.30	0.039
25% SDS	0.33	-3.47 ± 1.46	0.055
25% SDS	0.50	-3.71 ± 1.15	0.015

Table S8 Slopes with 95% confidence intervals and associated p -values for linear fits of microbead ε_{break} in time. Microbeads with $f_{lignin} = 0, 0.33, 0.5$ were observed in water and 25% SDS.

SI.7 Additional SEM images of microbeads

Additional SEM images of 8% wt, DP290 cellulose microbeads are shown in Figs. [S10-S12](#) below.

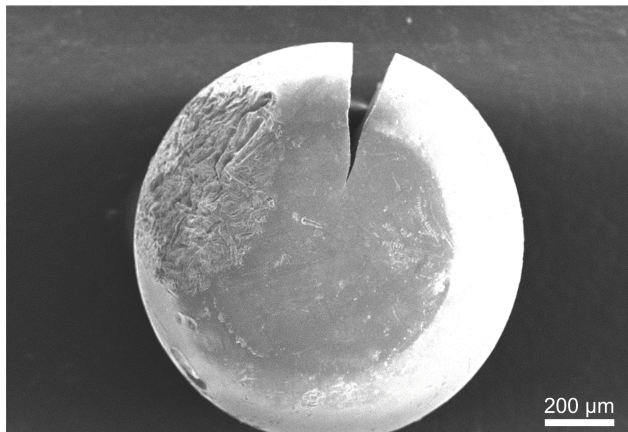


Fig. S10 Microbead formed from an 8% wt solution of DP290 cellulose after fracture - the bead is flattened in the center from the compression in a circle with contact radius R_C (Eq. 1) and has broken in a single smooth fracture from the edge to the center.

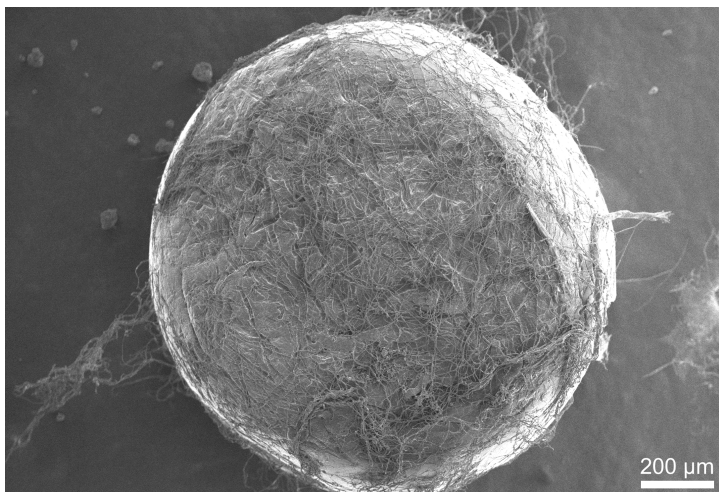


Fig. S11 A microbead (cellulose, DP290) precipitated and extracted in water, at 65x magnification. Many individual cellulose fibers are visible, indicating the swollen state of this microbead due to the presence of residual ionic liquid.

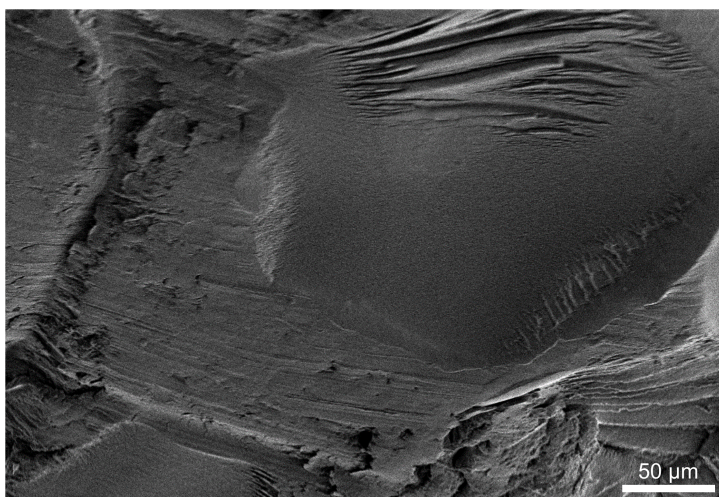


Fig. S12 A section of a microbead (from 8% wt DP290 cellulose) at 330x showing a dense internal structure free of regular pores.

SI.8 Energy-dispersive X-ray spectra

Energy-dispersive X-ray analysis (EDS) can identify residual ionic liquid in the microbeads, as microcrystalline cellulose does not contain nitrogen but 1-ethyl-3-methylimidazolium acetate (EMImAc) does. Thus the presence of nitrogen EDS peaks in beads precipitated and extracted in water confirms that these beads contain residual IL, which may explain their very low modulus.

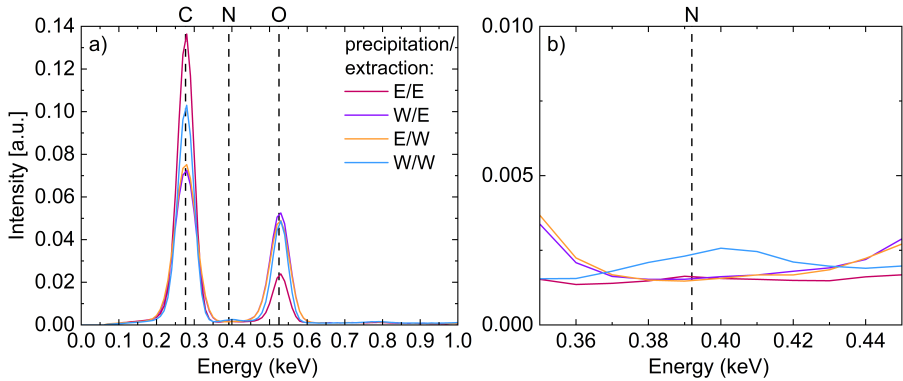


Fig. S13 a) Energy-dispersive X-ray spectra (EDS) normalized by the integral of the whole spectrum for beads precipitated/extracted in ethanol/ethanol (red), water/ethanol (purple), ethanol/water (orange), and water/water (blue). b) The nitrogen peak in these spectra is only present for beads both precipitated and extracted in water. Based on the presence of this small N peak, water/water beads contain residual ionic liquid, which may explain their very low modulus.

SI.9 Comparison between cellulose sources

Comparisons of force and stress curves between beads made from samples of DP230 and DP290 cellulose indicate that, contrary to expectations for an amorphous polymer, DP230 cellulose beads have higher moduli than DP290 beads, although they also break slightly earlier, as indicated by the location of the final downturns in the data. A direct comparison of the raw data for 8% cellulose solutions is shown in Fig. S14; here, the initial slope and overall force curve is higher for all DP230 trials than for the DP290 trials (Fig. S14a,b). The traces are more comparable in magnitude when compared as stress vs. compressive strain (Fig. S14c).

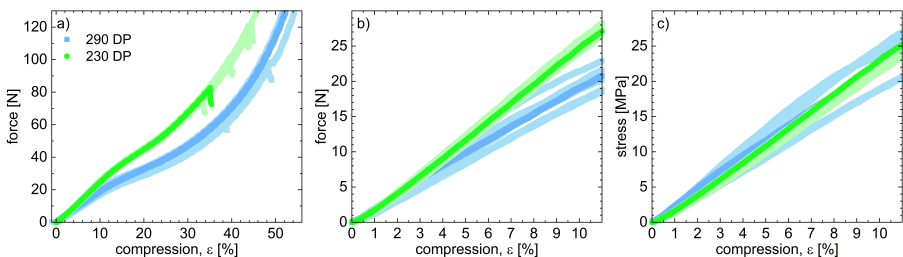


Fig. S14 Comparisons of all individual trials between beads formed from 8% wt solutions of DP290 cellulose and DP230 cellulose a) force vs. compression curves showing the points of fracture for the two samples, as indicated by sudden downturns in the data b) magnified force vs. compression curves showing differences in the initial contact regions c) engineering stress vs. compression curves, normalizing force data by different bead areas A

Fig. S15 shows a similar comparison to Fig. S14, but now comparing 8% wt DP290 cellulose microbeads to 7% wt DP230 beads, which have higher reported Young's moduli. Although larger forces and comparable engineering stresses are

measured for 8% wt DP290 beads than 7% wt DP230 beads at the same compression, the higher Young's moduli result from differences in bead shape. The effects of bead shape can be seen by converting equation 1 to terms of engineering stress and compression ϵ , resulting in the expression $stress = \frac{8}{3\pi} E \frac{H}{D_{bead}} \epsilon^{3/2}$. Because the 7% wt beads are slightly flatter, the $\frac{H}{D_{bead}}$ values are slightly lower, meaning that the moduli E of these beads can be higher despite similar engineering stresses.

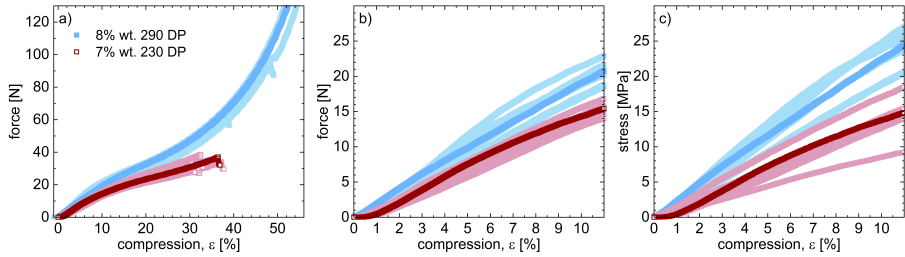


Fig. S15 Comparisons of all individual trials between beads formed from an 8% wt solution of DP290 cellulose and a 7% wt solution of DP230 cellulose a) force vs. compression curves showing the points of fracture for the two samples, as indicated by sudden downturns in the data b) magnified force vs. compression curves showing differences in the initial contact regions c) engineering stress vs. compression curves, normalizing force data by different bead areas A

The higher Young's moduli for the DP230 microbeads may be attributed to a number of factors. Whereas the broadly amorphous nature of cellulose after processing in this ionic liquid is established by experimental measurements,[4–6] actual degrees of crystallinity can vary based on the feedstock used.[6, 7] Because crystallinity is highly related to Young's modulus of cellulose samples,[6, 8–11] comparisons between different feedstocks cannot be used to draw conclusions about the effect of degree of polymerization, since this cannot be deconvoluted from the effect of crystallinity. Additionally, X-ray diffraction measurements suggest that the DP230 beads exhibit a higher degree of crystallinity than the DP290 beads (see SI.10 below).

While the final DP230 beads exhibit a higher degree of crystallinity than their DP290 counterparts (Fig. S16), the higher moduli of DP230 beads may also be explained by differences in density near the surface between the two samples, resulting from the lower surface tension of the DP230 cellulose solution (Table S9), indicating the possible formation of a denser "shell" at the surface of the precipitated drop which may persist after bead extraction. Both of these explanations are consistent with the observed compression curves, wherein the DP230 samples are initially stiffer than their DP290 counterparts, but fracture earlier.

Solution	γ [mN/m]
Solvent	45.79 ± 0.07
8% DP290 cellulose	45.48 ± 0.40
8% DP230 cellulose	44.63 ± 0.12
4% lignin / 4% DP230 cellulose	42.74 ± 0.65

Table S9 Surface tensions of solutions of biomass in 70:30 DMSO:ionic liquid by weight.

SI.10 X-ray diffraction

X-ray diffraction (XRD) can be used to assess crystallinity of beads with DP of 230 and 290 respectively. Although both peaks are broad, indicating the primarily amorphous nature of the cellulose after dissolution in ionic liquid, the sharper peak of the DP230 cellulose indicates that this cellulose sample is more crystalline even after regeneration from ionic liquid, which may explain in part the higher moduli measured in beads produced from this cellulose sample.

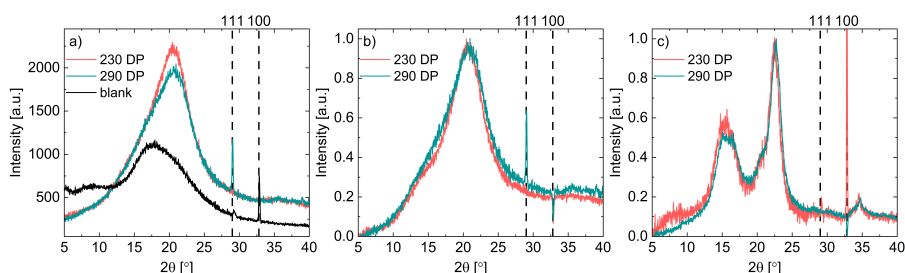


Fig. S16 a) X-ray diffraction (XRD) spectra of microbeads produced from 8% wt solutions of DP230 (orange) and DP290 (green) cellulose mounted on double-sided tape and silicon wafers, observed from diffraction angles of 5 to 40 degrees with a wavelength of 0.154 nm b) XRD spectra with the background removed, normalized to the maximum value in the spectrum and c) XRD spectra of DP230 and DP290 powders with the background removed, normalized to the maximum value in the spectrum.

While sharp peaks at 29 and 32 degrees correspond to the (111) and (100) directions of the silicon wafer, respectively, the broad peak around 21 degrees corresponds to the amorphous cellulose comprising both DP290 and DP230 beads. The degree of crystallinity cannot be calculated quantitatively for these samples, but the DP290 cellulose has a broader peak (full width at half maximum of 6.66 and 8.28 degrees for 230 and DP290 respectively, or an increase of 24%), indicating a lower degree of crystallinity as compared to the DP230 cellulose sample. The original powders in c), however, are crystalline, with the broader peaks around 15, 23, and 35 degrees corresponding to the (101), (002), and (004) peaks of crystalline cellulose I. Crystallinity indices were calculated using the peak height method[12, 13] from the normalized spectra as 0.74 for DP230 cellulose and 0.71 for DP290 cellulose.

SI.11 Individual compression trials

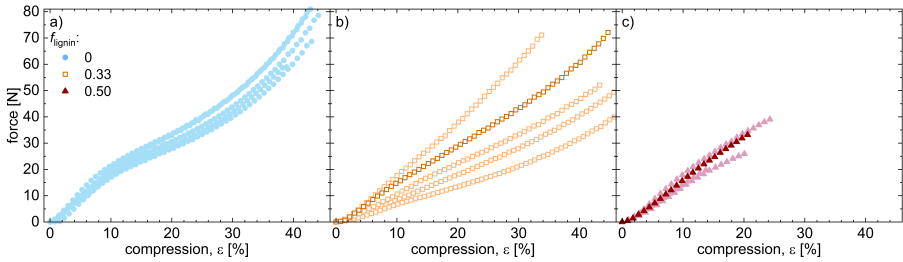


Fig. SI.17 All force/compression curves of 8% biomass solution beads with DP290 cellulose and mass fraction of Kraft lignin f_{lignin} of 0 (light blue), 0.33 (orange), and 0.50 (dark red). While there appears to be no trend in moduli with increasing fraction of lignin, the flatter shapes of beads with higher lignin content leads to higher moduli when fitting these curves to models of oblate spheroids (see SI.4), leading to increasing moduli with lignin content but earlier breaking points of the beads with more lignin. Differences in moduli were statistically significant (***, $p < 0.02$) between $f_{lignin} = 0$ and $f_{lignin} = 0.50$, but only significant to 90% confidence (*, $p < 0.01$) between 0 and 0.33 and between 0.33 and 0.50 (SI.13).

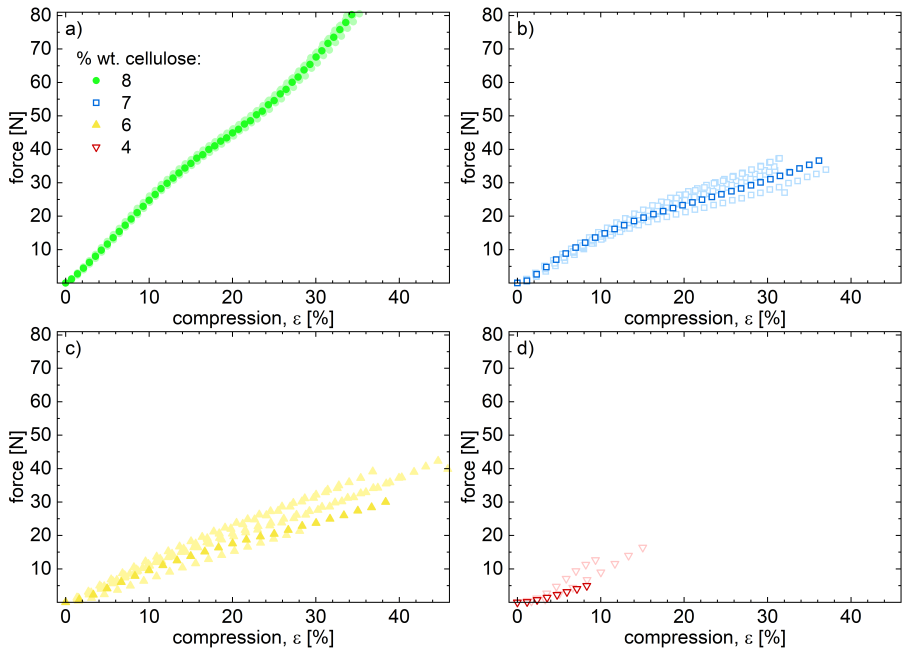


Fig. S18 All force/compression curves of 8% (green ●), 7% (blue □), 6% (yellow ▲), and 4% (red ▽) wt DP230 cellulose microbeads extracted in ethanol. Beads formed from higher concentrations were stiffer, with moduli of $E = 0.605 \pm 0.023$ GPa, 0.564 ± 0.020 GPa, 0.443 ± 0.020 GPa, and 0.349 ± 0.137 GPa for 8%, 7%, 6%, and 4% beads respectively. Due to the high variability of the 4% sample, the 4% and 6% samples were statistically similar ($p = 0.102$), but moduli of all other samples were significantly different (***, $p < 0.02$, [SI.13](#)).

SI.12 Bead diameters and moduli

Diameters and moduli of all bead samples are summarized below in Table [S10](#):

Development of microbeads from unmodified biomass with tunable size and competitive mechanical properties

Cellulose [% wt]	Lignin [% wt]	Gauge	DP	Precipitation	Extraction	E [GPa]	D_{bead} [μm]
8	0	22	290	Ethanol	Water	0.034 ± 0.010	1521 ± 58
8	0	22	290	Ethanol	Ethanol	0.448 ± 0.156	1277 ± 80
8	0	22	290	Water	Water	0.002 ± 0.001	2124 ± 118
8	0	22	290	Water	Ethanol	0.359 ± 0.054	1285 ± 70
5.33	2.67	22	290	Ethanol	Ethanol	$0.587 \pm 0.048^*$	1091 ± 71
4	4	22	290	Ethanol	Ethanol	$0.696 \pm 0.107^*$	1135 ± 126
8	0	22	230	Ethanol	Ethanol	0.428 ± 0.016	1287 ± 159
7	0	22	230	Ethanol	Ethanol	0.399 ± 0.014	1219 ± 46
6	0	22	230	Ethanol	Ethanol	0.313 ± 0.014	1092 ± 111
4	0	22	230	Ethanol	Ethanol	0.247 ± 0.097	1102 ± 210
7	0	26	230	Ethanol	Ethanol	0.131 ± 0.007	1139 ± 67
7	0	30	230	Ethanol	Ethanol	0.167 ± 0.053	976 ± 67

Table S10 Sizes and Young's moduli are listed for bead samples made from solutions with given concentrations of cellulose with a given degree of polymerization (DP) and of lignin, extruded from nozzles with a given gauge into a given anti-solvent and extracted with given solvents. Asterisks reflect potential inaccuracies in Young's moduli due to the flatter shape and lower curvature at contact of lignin-containing beads.

SI.13 P-values for differences in E

Sample 1	Sample 2	P-value
W/W	W/E	5.94E-05***
W/W	E/W	1.58E-02***
W/W	E/E	1.02E-06***
W/E	E/W	9.61E-05***
W/E	E/E	2.40E-01
E/W	E/E	4.31E-07***

Table S11 P-values calculated using two-sample, one-tailed Student's t-tests (assuming unequal variances) for differences in Young's moduli between sample pairs precipitated/extracted in combinations of water (W) and ethanol (E).

Sample 1	Sample 2	P-value
4	6	1.02E-01*
4	7	1.27E-02***
4	8	6.32E-03***
6	7	1.48E-06***
6	8	1.41E-07***
7	8	1.14E-03***

Table S12 P-values calculated using two-sample, one-tailed Student's t-tests (assuming unequal variances) for differences in Young's moduli between sample pairs produced from solutions with various concentrations (% wt) of DP230 cellulose.

Sample 1	Sample 2	P-value
0	0.33	9.15E-02*
0	0.50	1.50E-02***
0.33	0.50	1.03E-01*

Table S13 P-values calculated using two-sample, one-tailed Student's t-tests (assuming unequal variances) for differences in Young's moduli between sample pairs produced from solutions with various weight fractions of lignin (f_{lignin}).

SI.14 Variables and abbreviations

Variables:	
A	area of a microbead as measured by imaging
d	diameter of nozzle
D_{avg}	average diameter calculated from sphere with given molecular volume
D_{bead}	diameter of a dry and extracted microbead, determined by areas as seen from above
D_{drop}	critical size of pendant drop at breakup
D_{precip}	diameter of a microbead prior to extraction
D_{wet}	diameter of an extracted microbead after removal from solution
E	Young's modulus of microbead
E'	apparent Young's modulus of microbead
E_{plate}	Young's modulus of compression plate
F	force measured during compression
f_{lignin}	weight fraction of lignin in biomass in a given solution
H	height of microbead, determined by contact point during compression
n	number of samples in a given condition
p	statistical significance
R	minimum radius of liquid bridge at a given time in capillary thinning
R_0	initial radius of liquid bridge, defined as 80% of the radius of the extruding nozzle
R_C	contact radius during compression
SR	swelling ratio of wet microbead diameter normalized by dry microbead diameter
t	time
x	distance compressed
η_E	apparent extensional viscosity determined from capillary thinning experiments
ν	Poisson's ratio of microbead
ν_{plate}	Poisson's ratio of compression plate
ρ	density
σ	surface tension
θ	critical angle of pendant drop surface at breakup
ε	compressive strain on microbead
ε_H	Hencky strain

Abbreviations:

<i>DP</i>	degree of polymerization
<i>EDS</i>	energy-dispersive x-ray spectroscopy
<i>IL</i>	ionic liquid, 1-ethyl-3-methylimidazolium acetate
<i>PCCP</i>	personal care consumer product
<i>SDS</i>	sodium dodecyl sulfate
<i>SEM</i>	scanning electron microscopy
<i>XRD</i>	x-ray diffraction

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