Supporting Information

Development of mechanical properties of regenerated cellulose beads during drying as investigated by atomic force microscopy

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Materials and methods

Materials

Domsjö dissolving pulp (Domsjö Fabriker AB, Sweden) was used to prepare the cellulose/DMAc/LiCl solutions and the regenerated gel beads. The fibres contained 96% glucose,¹⁻⁴ and their charge density was reported to be 29 μ eq/g.⁵ Lithium chloride (LiCl, puriss p.a., anhydrous \geq 99%), *N*,*N*-dimethylacetamide (DMAc, puriss p.a., \geq 99.5%), 12-mercaptododecane thiol (96%), and ethanol (96 vol%) were purchased from Sigma-Aldrich and used as received.

Preparation of cellulose/DMAc/LiCl solution

To prepare the cellulose beads, cellulose/DMAc/LiCl solution was first prepared according to the previously described protocol.^{2-4,6} The dissolving pulp was pre-washed to remove metal ions and dissolved colloidal substances (carbohydrates, lignin, and extractives). Water saturated dissolving pulp containing 1.5 g of dry mass was solvent-exchanged to ethanol and subsequently to DMAc through multiple washing/filtration steps. The solvent-exchange was performed over 2 days for each solvent, the solvent being changed at least twice a day in 150 mL each time. After the solvent exchange, 100 ml of DMAc was heated to 105 °C for 20 min in an oil bath and 7 g of LiCl was heated in an oven at 105 °C for 30 min to release entrapped water. The dehydrated LiCl was added to the heated DMAc and then allowed to cool to 65 °C to which the DMAc saturated pulp was added. After stirring overnight, a transparent 1.5 wt% cellulose solution was obtained.

Preparation of swollen cellulose beads

3 mL Cellulose/DMAc/LiCl solution was drop-wise precipitated into a still ethanol bath, where the cellulose solution solidified and formed spherical beads as shown in Fig. S1. The precipitation was performed using an infusion pump (Harvard Apparatus, Holliston, MA, model PHD 2000) with 1.2 mm needle diameter to obtain identically sized beads. The beads were kept still to equilibrate for 24 h in the ethanol bath. The beads were then divided into two fractions; i) beads washed with Milli-Q water and ii) beads washed with ethanol. Both fractions were washed with their respective solvents for at least 7 days to ensure a proper removal of the cellulose DMAc/LiCl. Beads obtained by washing with water or ethanol are named water swollen and ethanol swollen beads, respectively.



Fig. S1 Schematic illustration of cellulose swollen beads preparation method.

Characterization techniques

Atomic force microscopy (AFM)

AFM indentation measurements were performed with a MultiMode IIIa with PicoForce extension, Veeco Instruments. Measurements were conducted during the bead drying process at 21 °C and relative humidity of 24% (see Fig. 1a). Swollen cellulose beads were placed on a silicon wafer (with a native oxide layer) and adhered by the capillary force from the liquid interface between the beads and the substrate in the wet state and the subsequent adhesion that emerged following evaporation of the meniscus.

Spherical gold particles, prepared as described by Pettersson et al.,⁷ were used as indentation probes.⁸ The gold particles were glued to tip-less cantilevers that were calibrated for its normal spring constant using a method based on thermal fluctuation with hydrodynamic damping.^{9,10} To minimize capillary

forces and water to spread on the probe and cantilever during measurements of the wet cellulose beads both the probe and cantilever were coated with a hydrophobic mercaptododecane thiol (1 mM in ethanol for 12 h) prior to use. The inverse optical lever sensitivity (invOLS), used to convert the cantilever deflection into force were determined using a clean hard silica surface. The normal spring constant of the tip-less cantilever used (NSC12 tip-less, MikroMasch , nominal length 110 μ m) was selected to enable capture of the full force profile within the linear part of the detector response.¹¹ The indentation was performed ramping the probe at a speed of 36 μ m/s to obtain complete force curves.

Optical Microscope

An optical camera (AM7013MZT, Dino-Lite Premier Digital Microscope) was used to monitor the diameter of the cellulose bead during the AFM indentation measurements and during the drying at 21 °C and 24% RH (AFM room). This drying experiments were also repeated several times in another lab (at 22 °C and 28% RH) for optical microscopy. From Fig. S2a and S2b it is clear that swollen beads dry similarly under these two different conditions. This was observed in both the water swollen and the ethanol swollen beads.



Fig. S2 The diameters of (a) water swollen and (b) ethanol swollen beads measured from the side-view optical microscopy images in AFM room, as well as those measured in the another lab.

Thermogravimetric analysis (TGA)

Thermal stability of the cellulose beads after 4 hours of drying in AFM room was studied by TGA using a TGA/DSC 1 STAR Mettler Toledo system. The dry beads were heated from 40 to 110 °C with a heating rate of 10 °C/min, then kept at 110 °C for 60 min, and after that the temperature was increased to 650 °C with a heating rate of 10 °C/min. The measurements were performed under a nitrogen atmosphere.

The TGA curves of the beads dried from water and ethanol are presented in Fig. S2. It is observed that the two curves are overlapping at a lower temperature range (< 200 °C). The flat region between 110 °C

and 200 °C indicates that the remnant solvents are fully removed from the beads and no thermal degradation occurs in this temperature region. From 200 °C on, a decrease of the weight for the bead dried from ethanol is observed. It means that its onset decomposition temperature T_{onset} is 200 °C. However, for the bead dried from water, T_{onset} is around 280 °C, which is significantly higher than the one measured for the bead dried from ethanol. Different T_{onset} has been reported by Xu et al.¹² and Mahadeva et al.¹³ for other regenerated celluloses dissolved by different solvent systems. The rapid decomposition of cellulose occurs in the temperature range from 280 °C to 350 °C for both types of dry beads. The residual mass reported at 350 °C is about 40 wt% for the beads dried from water and 35 wt% for the beads dried from ethanol. The weight loss over this temperature range is mainly caused by the depolymerization of cellulose, like the breaking of glycosidic bonds and part of the glucose units in the cellulose molecules.¹⁴⁻¹⁶ Above 350 °C, the mass loss rate of dry beads decreases until the end of the TGA measurement at 650 °C. Similar residual mass of the beads dried from water and ethanol is reported, it is 24 wt% and 21 wt%, respectively.



Fig. S3 The TGA curves of the beads dried from water and ethanol.

Scanning Electron Microscope (SEM).

The microstructures and morphologies inside the totally dried beads were imaged using an S-4800 field emission scanning electron microscope (FE-SEM) (Hitachi, Tokyo, Japan) instrument operating at high vacuum. Dried beads were immersed in liquid nitrogen, crushed with a metal rod, air-dried, glued onto a sample holder using conductive carbon tape, and then coated with Pt/Pd in a Cressington 208 HR sputter coater (Cressington Scientific Instruments, Watford, UK) for 20 s to reduce specimen charging during the SEM imaging.



Fig. S4 SEM images of dried beads from (a) water swollen and (b) ethanol swollen cellulose beads.

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