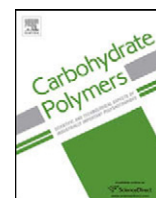




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Physicochemical design of the morphology and ultrastructure of cellulose beads

Jani Trygg^{a,*}, Pedro Fardim^a, Martin Gericke^a, Ermei Mäkilä^b, Jarno Salonen^b

^a Åbo Akademi, Laboratory of Fibre and Cellulose Technology, Finland¹

^b University of Turku, Department of Physics, Laboratory of Industrial Physics, Finland

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ABSTRACT

Cellulose was dissolved in NaOH–urea–water and beads were prepared by coagulation into nitric acid as well as saline solution. Morphology and ultrastructure of the beads were modified by controlling the molarity of the acid (0–10 M) and temperature (5–50 °C) of the coagulation media and the cellulose concentration (3–7%). The beads were characterized by optical image analysis (shape, volume, and size distribution) and weight (total porosity). Cross-sections of CO₂ critical point dried beads were studied by field emission scanning electron microscopy (FE-SEM) and specific surface areas of 336–470 m² g⁻¹ were determined from nitrogen adsorption isotherms. Pore size distribution was analyzed using solute exclusion technique. Our results demonstrate that the ultrastructure can be controlled by alteration of the coagulation conditions. Changes in size, shape and surface area were substantial. Also generation of micro- ($\leq 2 \text{ \AA}$), meso-, or macropores (>math>\geq 50 \text{ \AA}</math>) can be favored.

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1. Introduction

Cellulose gained increasing interest in research due to its attractive properties, such as abundance, biodegradability, and renewability. The polysaccharide can be chemically modified in different ways to obtain derivatives with specific properties, ranging from hydrophilic to hydrophobic, from non-charged to an-, or cationic (Heinze, Liebert, & Koschella, 2006; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). Moreover, cellulose can be shaped into well defined objects such as fibers of different geometry, films, sponges, or spherical particles that are also known as cellulose beads (Gavillon & Budtova, 2008; Lönnberg, 2005).

Cellulose beads are versatile materials for numerous applications, especially when they have been chemically modified in order to support their performance. They are excellent filling materials for chromatographic columns because they can withstand high flow rates due to the spherical shape (De Oliveira & Glasser, 1996; Kaster, de Oliveira, Glasser, & Velander, 1993). Thus, cellulose beads could be employed as stationary phase for size exclusion chromatography and as selective adsorbents for biological substances such as proteins, endotoxins, and viruses (De Oliveira & Glasser, 1996; Xia, Lin, Wang, Chen, & Yao, 2008; Yamamoto & Miyagawa,

1999). Ionic cellulose beads found use in ion-exchange and water treatment (Hirota, Tamura, Saito, & Isogai, 2009). Also pharmaceutical applications have been reported. Cellulose beads could be loaded with drugs that are gradually released from these materials afterwards (Volkert, Wolf, Fischer, Li, & Lou, 2009; Wolf, 1997).

In general, preparation of cellulose beads involves three steps: dissolution, shaping, and regeneration of the polysaccharide. Different procedures have been developed, mainly differing in the solvent applied and the technique utilized to obtain spherical particles. Cellulose beads have been prepared for instance by dropping (De Oliveira & Glasser, 1996), jet cutting (Pinnow, Fink, Fanter, & Kunze, 2008), spinning drop atomization (Rosenberg, Suominen, Rom, Janicki, & Fardim, 2007), spraying (Chen & Tsao, 1976) and dispersion (Luo & Zhang, 2010; Motozato & Hirayama, 1984; Peška, Štamberg, & Hradil, 1976). Many different solvents for the dissolution, shaping, and chemical derivatization of cellulose have been reported (Liebert, Heinze, & Edgar, 2010). Nevertheless, cellulose beads have been mostly prepared, via one of the above described techniques, by exploiting the viscose process or by utilizing organosoluble cellulose acetates as a starting material (Štamberg, Peška, Paul, & Philipp, 1979; Motozato & Ishibashi, 1981; Rosenberg et al., 2007; Thümmeler et al., 2011). Although both processes have been brought to commercial applications, they show several disadvantages that hamper the utilization of cellulose beads (Motozato & Ishibashi, 1981; Peška, Štamberg, & Blace, 1977). Cellulose is temporarily converted into a more or less stable derivative. The substituent, rendering the polysaccharide soluble, is first introduced and finally removed again from the final material, which is inefficient and implies the use of excess chemicals and the

* Corresponding author. Current address: Åbo Akademi, Fibre and Cellulose Technology, Porthansgatan 3, 20500 Turku, Finland.

E-mail address: jtrygg@abo.fi (J. Trygg).

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production of additional waste. In addition, the use of toxic CS₂ in the viscose process raises considerable environmental and safety issues.

Utilization of non-derivatizing and environmental friendly solvents is a more convenient approach for shaping of cellulose. Aqueous systems such as NaOH–water, NaOH–urea–water and NaOH–ZnO–water have raised a lot of interest for this purpose (Egal, Budtova, & Navard, 2008; Jin, Zha, & Gu, 2007; Liu, Budtova, & Navard, 2011; Zhang, Ruan, & Gao, 2002). Preparation of cellulose beads from these novel solvents has been reported as well using either dispersion or dropping techniques (Luo & Zhang, 2010; Rosenberg, Rom, Janicki, & Fardim, 2008; Sescousse, Gavillon, & Budtova, 2011). Later are of particular interest because they enable preparation of comparably large beads (from several 100 μm up to 1–2 mm) in large batches, if sophisticated technical devices such as spinning drop atomization are applied.

In the present comprehensive study, cellulose beads were prepared from NaOH–urea–water solution via dropping technique. The aim was to understand the influence of different preparation parameters on the macroscopic (e.g., size, shape, and density) and microscopic (e.g., inner morphology and pore size distribution) bead properties. Studying ways to control these parameters is vital for any application, novel as well as already established ones, since they determine the performance of the cellulose beads. Based on the gained result it is possible to obtain tailored materials that may be utilized in different areas.

2. Experimental

2.1. Materials

Dissolving pulp (Cellulose plus) was purchased from Domsjö Fabriker, Sweden. The pulp had a α -cellulose content of 93% and contained 0.6% of lignin (Domsjö, 2007). Intrinsic viscosity of the delivered pulp was reported to be $530 \pm 30 \text{ cm}^3 \text{ g}^{-1}$ according to SCAN-CM 15:99 standard after two stage sodium based cooking. Pulp was Total Chlorine Free (TCF)-bleached. Urea (99.5%) and nitric acid (65%) were purchased from Merck KGaA, NaCl (100.0%) and acetone (99.5%) from J.T. Baker, and NaOH (97%) from Fluka Analytical. Dextrans were purchased from Sigma–Aldrich and used as received.

2.2. Pretreatment of the pulp

The Pulp was pretreated in ethanol-hydrochloric acid for 2 h at 75 °C as described earlier (Trygg & Fardim, 2011). Intrinsic viscosity of the pretreated pulp was measured according to standard ISO/FDIS 5351:2009 and viscosity average degree of polymerization was calculated (Immergut, Schurz, & Mark, 1953). 0.2 M cupriethylene-diamine (CED) solution was dropped on the pretreated pulp fibres and optical microscopy was used to detect any ballooning (Cuissinat & Navard, 2006). The Pulp was dried in an oven at 60 °C overnight and stored at room temperature.

2.3. Dissolution of cellulose in NaOH–urea–water

Pretreated pulp was mixed with a solution of 7% NaOH and 12% urea in water so that the dry content of cellulose was 4%, 5% or 6% from the total weight of the final solution. Humidity of the pulp varied between 2% and 7% and this was included in the amount of water in solution. After 10 min of vigorous stirring the suspension of pulp and solvent was cooled to –10 °C and stirring was continued for half an hour. The solution became visually transparent approximately in 15 min from the beginning of the cooling.

2.4. The determination of gelation times

Gelation times of the 4–6% cellulose in NaOH–urea–water solution were determined using an Anton Paar Physica MCR 300 rotational rheometer with DG 26.7 double-gap cylinder. Temperature was set to 20 and 25 °C with a TEZ 150P thermostat with external water cycle. G' and G'' were measured with amplitude of 1% and frequency of 1 rad/s and gelation times were taken from the crossing point of both moduli.

2.5. Preparation of cellulose beads

Cellulose solutions were directly taken from the cooling device (–10 °C) and extruded through Eppendorf 5 ml syringe tip into the coagulation solutions. Height of the tip was manually adjusted in situ 1–2 cm above the surface to gain as spherical beads as possible. Beads were prepared in beakers of the same geometry (1 dm³, \varnothing 11.5 cm) in order to exclude possible effects due to changes of the surface tension of the coagulation media, sinking height, etc. Stirring was applied only occasionally to even concentration gradients. Each coagulation experiment took less than 10 min, which is notably shorter than gelation times of cellulose solutions (see Section 3.1).

Temperature, cellulose content, and concentration of the coagulation media were varied separately while keeping the other variables constant. Concentration of cellulose was 5% from the total weight of the solution, unless otherwise mentioned. Since cellulose solution is highly alkaline, high volumes of the acidic coagulation media was used in order to minimize the neutralization. Maximum allowed change was 0.5 M of the initial acid concentration except for the 0.5 M nitric acid solution where the change was 0.1 M. When coagulating in 10% NaCl solution, the final NaOH concentration did not exceeded 0.35 M.

Effect of the temperature of the coagulation media was studied with 2 M nitric acid solution and 10% NaCl solution at 5, 25 and 50 °C. Beads coagulated at 5 and 25 °C were kept at that temperature for the whole coagulation time and beads coagulated at 50 °C were kept at that temperature for 2 h and then cooled to 25 °C.

Effect of the acid concentration on the coagulation of the cellulose solution was studied with 0.5, 2, 4, 6, 8 and 10 M nitric acid at 25 °C. 2 M nitric acid at 25 °C was also used to coagulate 4% and 6% cellulose solutions.

Coagulated beads were left in acid overnight and in saline water for two nights. After one night the saline water was changed. All the beads were washed under running tap water for 30 min, distilled water for 15 min and stored in distilled water at room temperature for further use.

2.6. Critical point drying

In order to study the surface area of the beads and their structure (see Sections 2.7 and 2.8), water was exchanged to acetone by a step-wise procedure and beads were critical point dried with a Critical Point Dryer (Balzers Union Limited, Liechtenstein) using liquid CO₂ to maintain the porous structure. Some beads were cut half before being critical point dried (CPD).

2.7. Field emission scanning electron microscopy

Interior, edge, and surface morphology of the coagulated cellulose CPD beads were examined using a Leo Gemini 1530 field emission scanning electron microscope (FE-SEM) with an In-Lens detector. The whole beads as well as their cross-sections were coated with carbon in Temcarb TB500 sputter coater (Emscope Laboratories, Ashfold, UK). An optimum accelerating voltage for

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