



Tuning of cellulose fibres' structure and surface topography: Influence of swelling and various drying procedures



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ABSTRACT

Presented study deals with the pre-treatment of cellulose fibres with the aim to activate their surface and to enlarge their pore system, leading to an enhancement of fibres' affinity for subsequent functionalization processes. Swelling of fibres in aqueous solutions of sodium hydroxide opens their fibrillar structure, while freezing and freeze-drying retain this enlargement of the pore system, in contrast with conventional air or elevated temperature drying. Effect of different pre-treatment procedures on fibres' supramolecular structure, enlargement of their pore system, surface topography, zeta potential and mechanical properties was investigated. Degree of enhancement of the pore system depends on the concentration of sodium hydroxide and type of freezing; higher alkali concentrations are more effective, but at the cost of extensive deterioration of mechanical properties. Swelling of fibres in lower concentrations of NaOH, in combination with freeze drying, offers an acceptable compromise between enhancement of the fibres' pore system, changes in surface potential and tensile properties of treated fibres. Design of a suitable regime of swelling and drying of cellulose fibres results in an effective procedure for controlled tuning of their surface topography in combination with an increase of the available internal surface area and pore volume.

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1. Introduction

Accessibility of cellulose, as far as the structure of the substrate is concerned, depends on the available inner surface, supramolecular order and fibrillar architecture (Klemm, Heinze, Heinze, & Wagenknecht, 1998). Activation procedures for enhancement of cellulose substrates accessibility and reactivity act through opening and widening of voids on the surface and internal pores, by disrupting fibrillar aggregates and thus forming additional available surface. More aggressive activation methods can also lead to defects of the crystalline structure and change of the crystallites' size. Activation of some sort is always required when processing cellulose fibres; enlargement of pores and widening of interfibrillar interstices allows for better penetration of chemical reagents

into the fibres structure. One of the most common procedures for the activation of cellulose fibres by opening of pores and making available higher surface area is swelling in aqueous solutions of sodium hydroxide. Activation with sodium hydroxide can, depending on the concentration of the swelling agent and temperature conditions, reach different levels of the fibres supramolecular structure and, consequently, cause more or less pronounced changes. Another important aspect of the swelling processes, with which one wishes to enhance the available inner surface, is the subsequent drying of the material. This can lead from a highly water-swollen state to a state of significantly reduced accessibility and reactivity, where an available interfibrillar surface is reduced. This phenomenon is known as hornification. After the dehydration of the cellulose sample, new hydrogen bonds are formed which interconnect the fibrils and decrease of the surface of the interstices (Krässig, 1993; Park, Venditti, & Pawlak, 2006). Majority of the scientific work which concerns itself with hornification of cellulose deals in the field of native, i.e. natural cellulose substrates; while there is a number of publications on the subject of treatment of regenerated cellulose fibres with alkali solutions (Široký, Blackburn, Bechtold, Taylor, & White, 2011) and changes that occur upon wetting and drying (Kongdee, Bechtold, Burtscher, & Scheinecker, 2004), effect

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of alkali swelling in combination with freeze drying has not been investigated as a viscose fibre treatment process. In the present study we aim to analyze the effects and efficiency of the activation of viscose fibres with aqueous solutions of sodium hydroxide in order to develop a pre-treatment process for fibres, which will be used as a base for subsequent growth of nano particles and imparting conventional regenerated cellulose fibres with new properties (Hribernik et al., 2007). In order to retain the effects of swelling after drying, i.e. increase in pore size and inner surface area, we have implemented a freeze drying procedure to avoid the occurrence of the hornification; in addition, attempt at gaining new insights into the processes behind swelling of cellulose fibres and its influence of fibres' properties was made. These processes are crucial in processing of cellulose fibres, since swelling (and its consequence) can be efficiently harnessed as an integral part of a functionalization process. Freeze drying itself is a process of sublimation of frozen water from a sample under vacuum conditions. Two of the most important differences between freeze drying and other types of drying are: with freeze drying material solidifies before the actual drying and the removal of water from the material occurs with a process of sublimation, i.e. direct transition from ice into vapour. By freezing the sample we achieve a partial dehydration of the sample, its solidification and the shaping of the samples morphology. Any other drying procedure involves water in its liquid state, which is removed via evaporation. Freeze-dried products are porous, but whether or not a sample is able to retain such a structure, depends on its rigidity. Rigidity, in regard of freeze drying, is closely connected with the structural stability of the material, i.e. their ability to sustain their own weight and to resist the influence of external forces on the geometry of the material.

We have used different concentrations of sodium hydroxide as well as different freezing rates, in order to investigate combining effect of the structure activation with shape of the ice crystals on the resultant pore system and surface morphology of treated fibres. Investigated parameters of the supramolecular structure were correlated with fibres' electrokinetic properties, giving us information on their surface behaviour and hydrophilic/hydrophobic character. Investigation of mechanical properties was also carried out and studied from the point of view of changes in the fibres' structure after activation and drying. On the basis of these findings we will be able to expect the behaviour of activated viscose fibres in subsequent applications in reaction mixtures where coating with nano particles will proceed. Pore enhancement and activated surface will prove beneficial in this regard.

2. Materials and methods

2.1. Materials and pre-treatment procedure of regenerated cellulose fibres

Viscose fibres (regenerated cellulose fibres, supplied by Lenzing, Austria) were treated in aqueous solutions of sodium hydroxide (NaOH; Merck) and were subsequently dried with different drying procedures. Two concentration of sodium hydroxide were used, 5 wt.% NaOH and 18 wt.% NaOH. 3 g of fibres were dipped inside a metal grid basket into 100 mL of NaOH solution and left swelling for 5 min. Fibres were then rinsed with hot and cold water, wrung and neutralised with 50 mL of 0.2 M solution of hydrochloric acid (HCl; Riedel de Haen) and then again rinsed with cold water. Fibres were then transferred into a beaker containing a larger amount of distilled water and were being slowly stirred. Distilled water bath was being replaced with a fresh one until the conductivity of water was below 1 $\mu\text{S}/\text{cm}$. Swollen and rinsed, but still wet fibres were then dried at ambient conditions (1st procedure) and freeze-dried (2nd procedure). In the second procedure (freeze-drying), fibre samples

were frozen in two ways; slow freezing in a refrigerator (at -20°C) and rapid freezing with liquid nitrogen (at -196°C ; liquid nitrogen was kept in an unpressurized container). For slow freezing, fibres were left in a freezer for approximately two days, while rapid freezing was done instantaneously with dipping fibres, cased in a plastic tube, into a Dewar vessel filled with liquid nitrogen. Fibres were immediately transferred into a vacuum chamber of a freeze-drier Lyotrap Mini (LTE); temperature of the freeze-drier chamber was maintained at -35°C . Sublimation of ice from the fibre samples was completed in less than three days. Designation of the alkali-swollen and differently dried viscose fibres is given in Table 1.

2.2. Analysis and characterization of regenerated cellulose fibres

Carl Zeiss FE-SEM SUPRA 35 VP field-emission electron microscope was used for observation of the surface morphology of treated viscose fibres. Samples were attached by means of carbon conductive tape onto brass specimen holders. The images were recorded with an acceleration voltage of 1 kV at a working distance of 4.5 mm.

Wide angle X-ray scattering analysis was carried out with Siemens D5000 diffractometer (Cu-K α radiation; 1,5406 Å), from 5° to 75° 2θ scattering angle, measuring with a 0.04° step and a 5 s interval. Wide angle scattering patterns of samples were recorded in the range of diffraction angles from 5° to 35° , where the most intense interference reflexes of cellulose II occur. Untreated and NaOH-treated/dried fibres samples were pressed into pellets for the means of WAXS analysis; resultant spectra were deconvoluted with PeakFit software, using Lorentzian function for crystalline peaks and Gaussian function for the fitting of amorphous fraction. Values of integrated deconvoluted peak areas were also extracted from PeakFit software. Crystallinity index is expressed as a ratio between integrated areas of crystalline peaks and integrated total area of the scattering spectra (Park, Baker, Himmel, Parilla, & Johnson, 2010). Following equation was used:

$$\text{CI}[\%] = (\text{Sc}/\text{St}) \times 100 \quad (1)$$

where Sc stands for "integrated area of crystalline peaks" and St stands for "integrated total area of the scattering spectra".

Small angle X-ray scattering (SAXS) investigations have been conducted with a Kratky-Compact-Camera using a position sensitive detector. Pore characteristics are determined according to the theory of Porod by assuming a 2 phase system of cellulose and pores (Glatter & Kratky, 1982). After corrections and lupolen calibration the volume fraction of the voids, the average pore dimensions (intersection length) and the specific internal surface have been determined. Prior to investigation of the fibres' pore structure with SAXS analysis, additional swelling with water and subsequent solvent exchange with ethanol was performed.

Linear mass density and tensile properties of fibres were determined with Vibroskop 400 and Vibrodyn 400 apparatuses (Lenzing), respectively. Gauge length between the clamps was 2 cm, rate of extension was 20 mm/min and pre-tension weight used was 100 mg. 25 breaking tests were performed for each sample. For means of determination of tensile properties in wet state, clamped fibres were submerged in a vessel with distilled water for 10 s before the extension. Testing was performed according to EN ISO 5079: 1999 (Determination of breaking force and elongation at break of individual fibres).

For the determination of the zeta potential, oscillating EKA apparatus (Eka Oszi) was used, where the streaming potential of samples is determined by an oscillating flow of electrolyte solution through or alongside the sample surface (Reischl, Köstler, Kellner, Stana-Kleinschek, & Ribitsch, 2008). 1 g of each sample was soaked in 10^{-3} M KCl solution for one hour; duration of this pre-treatment enables full swelling of the fibres and thus no additional structural

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