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Influence of molar mass distribution on the final properties of fibers regenerated from cellulose dissolved in ionic liquid by dry-jet wet spinning

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ABSTRACT

Regenerated cellulose fibers were produced by dry-jet wet spinning from cellulose/1,5-diazabicyclo [4.3.0]non-5-ene-1-ium acetate solutions. Cellulose blends with different molar mass distribution but fixed intrinsic viscosity were employed as starting materials to investigate the influence of the cellulose molecular structure on the spinnability and the mechanical properties of the resulting fibers. The cellulose/ionic liquid solutions were prepared from blends constituted of cotton linters and spruce sulfite pulp representing a polydispersity index from 2.0 to 5.9. Dynamic shear rheology was performed on the solutions to examine the effect of cellulose chain distribution on the visco-elastic behavior and to select the adequate temperature for stable spinning. The mechanical and physical properties of the resulting fibers were determined by tensile tests and birefringence measurements. Cellulose solutes having a share of high molecular weight cellulose (DP > 2000) higher than 20% and a minimum polydispersity index of 3.4 showed enhanced spinnability. Higher draw ratios were accessible, resulting in improved cellulose chain total orientation and high-tenacity fibers.

1. Introduction

The past decades have witnessed a constant population and income growth, which constitute the key factors driving consumption of goods such as household products, textiles and clothing. Material prosperity and improved health standards, particularly in the developing countries, contribute to a significant rise of the fiber consumption per capita. It is estimated that the emerging markets will continue growing and reach the current European level of fiber consumption of 25 kg per capita by 2020 [8].

In 2013, the total fiber consumption rose by 2.8% to 92.3 million tons of which 41% were cellulosic fibers (natural and man-made cellulosic fibers). The production of natural fibers, which are mainly represented by cotton, has decreased since 2011 by 3.0% to 32.0 million tons in 2013 [30]. A stagnant or limited cotton production is predicted for the coming years due to the abatement of arable land needed for food production and the limitations in water availability in the cotton growing countries Haemmerle [12] estimates a drop to 26 million tons by 2030. The same study foresees an annual fiber production of 133.5 million tons in 2030 with an estimated share of 33–37% of cellulosic fibers. The cellulosic fiber consumption per capita in 2030 will increase to 5.4 kg, of which only 3.1 kg can be covered with cotton. This future cellulose gap can thus only be filled by increasing the production of man-made cellulosic fibers (MMCFs). MMCFs are the most ideal substitutes for cotton as they demonstrate properties similar to cotton like absorbency and moisture management, which are the major characteristics of cellulosic fibers that cannot be met adequately by synthetic fibers [8,12].

MMCFs are presently mainly produced by means of two processes: the viscose process developed in the late 19th century and the more recent Lyocell process which emerged in the early 1990s. The viscose fibers are still the largest commercial type of cellulosic fibers despite the well-known environmentally-unfriendly aspects of the process [34]. The only alternative that has been developed and commercialized so far is the more environmentally-benign Lyocell process, which employs the non-derivatizing solvent *N*-methylmorpholine *N*-oxide (NMMO) [10]. However, certain aspects of this process, such as the thermal instability of the solvent and the

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high power consumption required for the recovery of the large amount of water used in the process are still problematic and render the process more expensive than the viscose process. There is, thus, a need for more cost-effective and eco-efficient production of regenerated cellulose fibers from non-derivatizing solvents [15,25]. Ionic liquids (ILs), which have been developed and thoroughly investigated during the past decades, offer a particularly interesting new type of direct solvents for cellulose processing [5,9,19,26]. ILs, consisting entirely of anions and cations, have been proven to be effective solvents for organic and inorganic compounds and polymers. Their low melting point, low vapor pressure and thermal stability render them attractive for industrial processes. IL spinning appears to be a promising substitute to the NMMO process as it applies similar technologies and offers safer processing conditions [15,16,32].

The Ioncell-F(iber) process, employing ILs as cellulose solvent, is a recently developed process presented as an alternative to the currently common viscose and Lyocell processes for the production of MMCFs [16,22]. The Ioncell-F process utilizes the same technique as the NMMO process and is thus also classified as a Lyocell-type process. In this process, cellulose is first dissolved in an IL without any derivatization and then regenerated as continuous filament by dry-jet wet spinning. In a dry-jet wet spinning process, a polymer solution is extruded at mild temperature through a spinneret via an air gap into an aqueous coagulation bath. The fluid filament is drawn immediately after the extrusion in the air gap, which induces the orientation of the polymer chains governing the properties of the resulting fibers. The final properties of the fibers are thus strongly influenced by the chosen spinning parameters (extrusion velocity, draw ratio, air gap, spinneret geometry) as well as the properties of the raw material (cellulose and hemicellulose contents, intrinsic viscosity, molar mass distribution) [23].

Cellulose is a linear polysaccharide which is present in the cell wall of plants with a wide range of average degree of polymerization depending on the cellulose source. Intrinsic viscosity measurement is a well-established, fast and convenient method to estimate the average DP of cellulose. However, the determination of DP provides no element regarding the molar mass distribution (MMD) and the different molar mass mean values M_n, M_w of a polymer. MMD is a fundamental polymer characteristic to be determined for industrial processes in which rheological behavior is of importance [7]. The MMD and the polydispersity index (PDI) of cellulose dissolved in ionic liquid have a significant influence on the rheological behavior of spinning solutions, which is important to consider to anticipate its processability [13,27]. Furthermore, the strength properties of the produced fibers are highly connected to the intrinsic characteristics of the original cellulose and to the way the cellulose chains, of different length, are oriented and entangled during the regeneration process.

This study investigates the spinnability of cellulose blends dissolved in 1,5-diazabicyclo[4.3.0]non-5-ene-1-ium acetate ([DBNH]OAc) and the physical and mechanical properties of the resulting cellulose fibers. First, the preparation of cellulose blends with a wide range of PDI and their dissolution in [DBNH]OAc are described. Further, the visco-elastic properties of the resulting polymer solutions are assessed by dynamic shear rheology and analyzed to anticipate the appropriate spinning temperature. The spinnability of the different solutions is afterwards described in terms of extrusion quality, ability of the fluid filaments to be stretched and the resulting fiber quality. The produced fibers are analyzed in terms of tensile properties and cellulose chain orientation. The fibers from the successful cellulose blend spinning are compared to the fibers spun from a commercial pulp for a better understanding of the role of the MMD on the visco-elastic behavior and on the final properties of the resulting cellulose fibers.

2. Material and methods

2.1. Raw materials

Six blends of varying MMD with a fixed intrinsic viscosity (ca. 420 ml/g) were prepared by combining two pulps with different MMD properties. Cotton linters and spruce sulfite pulp of different starting intrinsic viscosity were employed as raw materials in this study. The pulps are denoted by their origin (CL for cotton linters and S for spruce sulfite pulp) followed by their intrinsic viscosity. For example, CL729 indicates a cotton linters pulp with intrinsic viscosity of 729 ml/g. CL729, S1521 and S577 were delivered in sheet form, ground by means of a Wiley mill and used without any chemical modification. CL420, CL415, CL318, S218 and S174 were obtained by caustic degradation of CL729 and S577 [17]. The sodium hydroxide concentration (0.9 mol/l), the liquor-to-pulp ratio (weight:weight, 20:1) and the degradation temperature (185 °C) were kept constant while the incubation time was increased to reduce gradually the resulting intrinsic viscosity. The different pulps have been selected in order to form blends with a wide range of PDI. The blends were prepared by suspending the two pulps in water, stirring the suspension for 15 min by means of an ultra-turrax disperser, removing the water by Büchner filtration and drying the resulting cake at room temperature.

For comparison purposes, a commercial *Eucalyptus urugrandis* prehydrolysis kraft pulp (intrinsic viscosity 424 ml/g, $M_n = 79.8$ kDa, $M_w = 268.6$ kDa, polydispersity 3.4, Bahia Speciality Cellulose, Brazil) was employed as cellulose solute. The pulp was delivered in sheet form and cut to a powder by means of a Wiley mill.

2.2. Intrinsic characterization

The intrinsic viscosity of the blends was determined in cupriethylenediamine (CED) according to the standard method SCAN-CM 15:99.

Cellulose MMD was characterized by gel permeation chromatography (GPC). The GPC-system consisted of a pre-column (PLgel Mixed-A, 7.5 × 50 mm), four analytical columns (4 × PLgel Mixed-A, 7.5 × 300 mm) and a RI-detector (Shodex RI-101). After a solvent exchange sequence, to remove the residual water and activate the sample in *N,N*-dimethylacetamide, the samples were dissolved in 90 g/l LiCl/DMAc at room temperature under constant slow speed magnetic stirring. The dissolved cellulose samples were then diluted in pure DMAc to reach a concentration of 1 mg/ml in 9 g/l LiCl/DMAc. Filtration with 0.2 μm syringe filter was carried out and a volume of 100 μl was separated at 25 °C at a flow rate of 0.750 ml/min with 9 g/l LiCl/DMAc as eluent. Pullulan standards with molecular weights ranging from 343 Da to 708,000 Da were selected for the calibration. A correction of the molar mass distribution obtained by direct-standard-calibration was done with an algorithm calculating cellulose-equivalent molar masses of pullulan standards ($MM_{cellulose} = q \times MM^{P}_{pullulan}$, with $q = 12.19$ and $p = 0.78$) as suggested by Refs. [3,4].

2.3. [DBNH]OAc synthesis

[DBNH]OAc was prepared by neutralization of 1,5-diazabicyclo [4.3.0]non-5-ene, DBN, (99%, Fluorochem, UK) with acetic acid (glacial, 100%, Merck, Germany). Both components were used as received. Equimolar amount of acetic acid was slowly added under external cooling due to the exothermic nature of the reaction. After addition of the required amount of acetic acid, the solution was further stirred for 1 h at 80 °C. [DBNH]OAc crystallizes at room temperature and shows a melting temperature of 65 °C.