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Research Paper

Improving molar mass analysis of cellulose samples with limited solubility

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ABSTRACT

Fully dissolved cellulose samples are a requirement for reliable size exclusion chromatography (SEC). Although most of the standard dissolving pulps can be completely dissolved in the *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system, some cellulose samples (e.g., regenerated cellulose fibers) have poor solubility and therefore have a limited access to molar mass measurements. For improving the latter, different activation steps have been developed.

In order to obtain complete solutions for subsequent SEC analysis, the scope of this study was to further improve established methods by elucidating the major influential factors of sample preparation. In addition, the degree of stretching in artificial fibers was examined for viscose fibers. Therefore, activation steps in DMAc or dimethyl sulfoxide (DMSO) and subsequent dissolution in DMAc/LiCl were analyzed with swelling and dissolution kinetics. The time needed for maximum swelling was found to be the optimum activation time. Turbidity measurement was introduced to observe dissolution kinetics as an indicator of dissolution quality. Thus, the duration, as well as the number of steps toward dissolution, was optimized to enhance the throughput in the overall analysis of a large variety of hitherto poorly soluble cellulose samples. A comparison of the MMDs of completely soluble reference materials obtained with the intensified conventional method, and the developed method demonstrated that the latter has no adverse influence on the results.

1. Introduction

To determine the molar mass distribution (MMD) of natural and artificial cellulosic materials, size exclusion chromatography (SEC) combined with multi-angle light scattering (MALS) detection has been established as a valuable method for characterizing cellulose over the last 30 years (Ekmanis, 1986, 1987; McCormick, 1981; Turbak, El-Kafrawy, Snyder, & Auerbach, 1982). Although most of the standard dissolving pulps can be completely dissolved in the *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system, artificial and annual plant fibers and several pulps are often more difficult to dissolve.

Although regenerated cellulose fibers (i.e., lyocell and viscose fibers) consist of almost pure cellulose with low intrinsic viscosity (200–500 mL/g) and thus, a low degree of polymerization (DP), they are nevertheless hard to dissolve for the subsequent SEC analysis (Abu-Rous, Varga, Bechtold, & Schuster, 2007; Henniges et al., 2014; Siller, Ahn, Pircher, Rosenau, & Potthast, 2014). One explanation for the poor solubility could be the high orientation of cellulose chains resulting from spinning and stretching in the spinning process (Zhang, Shi, Liang, & Yao, 1999). This orientation leads to strong interactions between the cellulose chains and may prevent complete dissolution. In addition, only small nanopores are located on the surface of viscose fibers impeding a solvent attack in the core of the fibers (Abu-Rous, Ingolic, & Schuster, 2006). In contrast to viscose fibers, a porous skin layer consisting of residual hemicelluloses can be observed around the very compact core of lyocell fibers, and this dense core structure could prevent complete dissolution (Sjöberg, Rosenau, Potthast, & Kosma, 2005). Nevertheless, regenerated cellulose fibers can be dissolved after certain pre-activation, activation, and/or derivatization steps (Schelosky et al., 1999; Siller et al., 2014; Široká et al., 2012; Zhang et al., 1999).

In contrast to cellulose II fibers, cellulose I samples (such as softwood kraft pulps), also fully bleached with low lignin content, vary in solubility. One reason could be that cellulosic residues consisting of latewood fibers (and probably degraded proteins) remain partly undissolved in the DMAc/LiCl solvent system and lead to gel formation (Sjöholm, Gustafsson, Pettersson, & Colmsjö, 1997). This effect is assumed to be caused by glucomannan that becomes attached to the cellulose during pulping (Karlsson & Westermark, 1997; Ono et al.,

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Table 1
Pulp and fiber samples.

Sample	Description	Data
CO	Raw cotton lint fibers, milled to 3 mm	Viscosity 2010 mL/g, brightness 62.4% ISO, glucan content 93.2% (total sugars 94.3 %), ash content 0.95 %
PHK	Bleached softwood prehydrolysis kraft pulp	Viscosity 300 mL/g, glucomannan content 5.2%, Kappa number 0.36
CV 1 a/b	Viscose fibers, 40% stretching, with (a) and without (b) a textile finish	Titer 1.39 dtex, tenacity 22.3 cN/tex, elongation 17.9%
CV 2 a/b	Viscose fibers, 65% stretching, with (a) and without (b) a textile finish	Titer 1.32 dtex, tenacity 25.3 cN/tex, elongation 13.0%
CV 3 a/b	Viscose fibers, 85% stretching, with (a) and without (b) a textile finish	Titer 1.38 dtex, tenacity 22.9 cN/tex, elongation 11.3%
CLY	Lyocell fibers	Titer 1.3 dtex, length 38 mm

2016). Monodisperse dissolution (a requirement for reliable SEC measurement) would not be given under these circumstances.

Genuine cotton lint fibers have very poor solubility as they are not chemically treated with sodium hydroxide (Ghasemi, Alexandridis, & Tsianou, 2017). During the so called mercerization process, which is common in the textile industry, the outer layer of the fibers is removed, and a partial conversion from cellulose I to cellulose II occurs (Temming, Grunert, & Huckfeldt, 1972). The outer layer, the cuticle, mostly consists of pectin, fats, and waxes and serves as a water- and chemical-resistant coating for the cotton fibers (Schurz, 1980; Sczostak, 2009). Even though several solvents can at least partly dissolve the cuticle and the pectins and waxes contained in the primary cell wall the penetration of these solvents toward cellulose chains is additionally hindered by the dense cell wall structure of the secondary walls (Krässig, 1993; Sczostak, 2009), although complete dissolution of the cotton fiber is proposed to proceed from the lumen side (Le Moigne and Navard, 2010).

Non-cellulosic deposits from the lumen and the residuals of the protoplast in the lumen are non-soluble in DMAc/LiCl and thus remain undissolved (Temming et al., 1972).

For all cases described above, the solvent has to be able to break the intra- and intermolecular hydrogen bonds between the cellulose molecules. As this breakup is not immediately possible in the DMAc/LiCl solvent system (cellulose is not instantly soluble in the solvent), activation steps are required. As a standard activation procedure, swelling in water followed by solvent exchange via ethanol to DMAc is recommended by most common protocols. Although suitable for most dissolving pulps, this procedure has limited effects for the cellulose samples discussed above.

For viscose, Schelosky et al. (1999) described an activation procedure in a water/ethanol/LiCl solution (H_2O/EtOH/LiCl = 90/10/0.5) at 80 °C for 12 h, with subsequent washing in water and DMAc followed by the standard activation procedure. In addition, dissolution in DMAc/LiCl (9% w/v) was carried out for 2 h at 80 °C when the samples were incompletely dissolved. These suggestions for improving solubility were found to have an adverse impact on the MMD as improved solubility is not caused by activation and dissolution in heated H_2O/EtOH/LiCl and DMAc/LiCl, respectively, but by chain degradation of the cellulose using that method (Potthast et al., 2002). Thus, this protocol cannot be recommended as the average molecular weight of the cellulose decreases with heating before the SEC analysis. Nevertheless, activation at elevated temperatures is still deployed in recent works (Rebière et al., 2016).

As an alternative to operation at elevated temperatures, an extended solvent exchange procedure for viscose fibers was introduced by Siller et al. (2014). After the samples were washed with ethanol and DMAc, they were left in DMAc for an extended period of several days instead of overnight for the solvent exchange. Although solubility in DMAc/LiCl could be increased compared with most common protocols, complete dissolution did not occur in the majority of cases.

As insufficient activation procedures lead to poor solubility, another solvent with different properties is needed in order to increase the accessibility for DMAc/LiCl into the fibers. Dimethyl sulfoxide (DMSO) is known for its high swelling capacity (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998) and has been described as an effective activation agent to improve the solubility of viscose fibers (Siller et al., 2014).

In the present paper, we have further developed and investigated the DMSO-based protocol. For the measurement of the degree of solubility, the turbidity measurement was adopted from water quality evaluations as this tool is simple and effective for describing the clarity of solutions (World Health Organization [WHO], 2011). The method is based on light scattering measurement, and the ratio of scattered light by particles in the sample is compared to transmitted light through the sample (Kelley et al., 2014).

Based on Siller et al.'s (2014) previous work, DMSO was utilized as the solvent for activation. In this study, this approach was developed further, and an even faster single-step activation procedure was established. The effect of DMSO regarding the effects that can hinder complete dissolution is further investigated in this study. In addition, the influence of different degrees of stretching in viscose fibers on dissolution in DMAc/LiCl is examined in order to better understand why certain man-made cellulosic fibers are very hard to dissolve.

The new protocol is comprehensively tested for the activation and dissolution quality of cotton lint fibers in addition to different cellulose I and cellulose II samples. Advantages and disadvantages are shown and discussed.

2. Materials and methods

2.1. Cellulose samples and chemicals

Basic characteristics of cellulose samples used in this study are summarized in Table 1. All commercially supplied chemicals were of analytical grade. DMAc was supplied by VWR (Wien, Austria), DMSO and ethanol by Merck (Darmstadt, Germany), and LiCl by Sigma-Aldrich (Schnelldorf, Germany).

2.2. Standard activation and dissolution procedure

Air-dried cellulose samples (150 mg) were cut into small pieces that were a few millimeters long, suspended in deionized water, and disintegrated for 20 s in a kitchen blender. Water was removed with vacuum filtration (Büchner funnel), and the samples were washed with ethanol and DMAc. Samples were transferred into a 50 mL vial, which was subsequently filled with 20 mL DMAc. Placed on a rotary shaker, the vial was left overnight for solvent exchange. Excess DMAc was removed with filtration, and then the cellulose samples and 15 mL DMAc/LiCl solution (9% w/v) were added to a 15 mL cuvette (the size and shape required for the turbidity measurement). The cuvette was vortexed for 20 s and placed on a rotary shaker for dissolution. Dissolved samples were diluted 1:2.5 with DMAc (1 mL sample + 2.5 mL DMAc), centrifuged for 10 min at 4000 rpm, and stored in a refrigerator until the SEC analysis. Due to the high DP of the cotton lint fibers