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Assessment of solvents for cellulose dissolution

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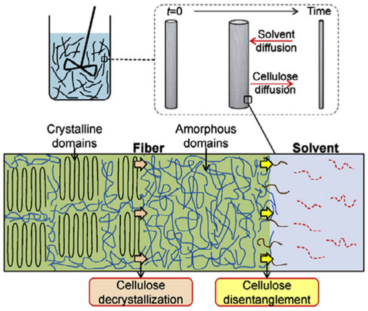
HIGHLIGHTS

- Characteristics of a good solvent for cellulose dissolution are defined.
- Solvent ability toward decrystallization and disentanglement controls the dissolution.
- Under disentanglement control, crystallinity has a small impact on the dissolution.
- Under decrystallization control, pretreatment improves the dissolution.

GRAPHICAL ABSTRACT



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ABSTRACT

A necessary step in the processing of biomass is the pretreatment and dissolution of cellulose. A good solvent for cellulose involves high diffusivity, aggressiveness in decrystallization, and capability of disassociating the cellulose chains. However, it is not clear which of these factors and under what conditions should be improved in order to obtain a more effective solvent. To this end, a newly-developed phenomenological model has been applied to assess the controlling mechanism of cellulose dissolution. Among the findings, the cellulose fibers remain crystalline almost to the end of the dissolution process for decrystallization-controlled kinetics. In such solvents, decreasing the fiber crystallinity, e.g., via pretreatment, would result in a considerable increase in the dissolution rate. Such insights improve the understanding of cellulose dissolution and facilitate the selection of more efficient solvents and processing conditions for biomass. Specific examples of solvents are provided where dissolution is limited due to decrystallization or disentanglement.

1. Introduction

Cellulosic biomass provides an abundant renewable feedstock that can be used for the production of valuable products such as polymers, chemicals, and fuels (Isikgor and Becer, 2015). Commonly used in the biorefinery is the pretreatment of biomass in order to deconstruct the crystalline cellulose using chemicals such as acids (sulfuric acid or hydrochloric acid), alkali (NaOH, KOH, Ca$(OH)_2$, or ammonia), organic solvents (ethylene glycol, glycerol, tetrahydrofurfuryl alcohol), or ionic liquids (Agbor et al., 2011; Karimi and Taherzadeh, 2016). For the preparation of materials such as fibers, films, and composites the direct dissolution of cellulose is often preferred (Kim et al., 2005; Reddy et al., 2014). Therefore, solvent treatment of cellulose is a necessary step in the efficient use of biomass (Medronho and Lindman, 2015; Zheng et al., 2009).

A relatively small number of solvent systems are known that can directly dissolve cellulose, and these involve rather uncommon chemicals and strict operating conditions (Heinze and Koschella, 2005): aqueous transition-metal complexes (e.g., cuprammonium hydroxide), aqueous alkali (e.g., LiOH or NaOH) solutions, aqueous concentrated salt solutions (e.g., $ZnCl_2$, ammonium, or sodium

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thiocyanate solutions), molten inorganic salt hydrates (Sen et al., 2013) (e.g., $LiClO_4 * 3H_2O$), inorganic salts dissolved in organic solvents (Dawsey and McCormick, 1990) (e.g., LiCl/N,N-dimethylacetamide (DMAc), ammonia/sodium or ammonium salt, or tetrabutylammonium fluoride (TBAF)/dimethyl sulfoxide (DMSO)), mixtures of organic solvents with sulfur dioxide and amines ($DMSO/SO_2$/diethylamine), amine oxides (e.g., N-methylmorpholine-N-oxide (NMMO)), and, more recently, ionic liquids (Mäki-Arvela et al., 2010) (e.g., 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) or 1-allyl-3-methylimidazolium chloride ([Amim]Cl)).

In cellulose dissolution, the solvent must diffuse into the structure of cellulose to affect both the amorphous and the crystalline regions (Zhang et al., 2006). The strong intermolecular interactions (hydrogen bonding and hydrophobic) among crystallized cellulose molecules need to be disrupted by the solvent, and the cellulose chains in amorphous regions should be disentangled from each other (Cheng et al., 2012; Keshk, 2015). Therefore, high diffusivity, aggressiveness toward disrupting the crystalline network, and capability to disentangle chains are necessary characteristics for an effective solvent for cellulose. Several solvents have acceptable diffusivity values and can penetrate and swell cellulose, however they cannot dissolve cellulose (Fidale et al., 2008; Mantanis et al., 1994). The insolubility of cellulose is not due to solvent diffusion and accessibility, rather it is believed to originate from the difficulty in overcoming the extended noncovalent interactions among cellulose molecules (Bergenstråhle et al., 2010). However, the mechanism of solvent diffusion into micron-diameter cellulose fibers is not well understood because of experimental difficulties in obtaining concentration profiles over time in such a small length scale.

Despite the fact that the dissolution of semicrystalline cellulose involves decrystallization, the effect of crystallinity on the dissolution process is controversial, and consequently the importance of solvent ability toward decrystallization is not clear (Medronho and Lindman, 2014). For example, it has been argued that the reason for faster dissolution in LiCl/DMAc of sisal pulp compared to cotton linters is the lower crystallinity and smaller crystallite size of sisal pulp (Ramos et al., 2011). In another study it has been shown that dissolution of cotton linter was considerably improved after pretreatment (e.g., mercerization) which resulted in a decrease in both crystallinity and average crystal size (Ramos et al., 2005). In contrast, it has been reported that "crystallinity does not seem to play a major role for solubility" (Le Moigne and Navard, 2010), and "if crystallinity would be the hampering factor, amorphisation should be the solution, we know this is not the case" (Glasser et al., 2012). These statements indicate that it is not sufficient for a solvent to only decrystallize cellulose, rather a solvent must be able to overcome the interactions that keep the chains entangled (Le Moigne and Navard, 2010). Therefore, it is not clear which solvent characteristics, i.e., aggressiveness in decrystallization or capability of chain disentanglement, are more important to render it suitable for cellulose dissolution and at which conditions these factors could be improved in order to dissolve more cellulose and faster.

To this end, this study aims to (i) assess solvent diffusion in micron-diameter cellulose fibers; (ii) identify conditions where cellulose dissolution is constrained by the lack of solvent abilities in decrystallization or in chain disentanglement; and (iii) present guidelines for selecting suitable solvents and processing conditions for cellulose dissolution. These aims are accomplished through a newly-developed phenomenological model (Ghasemi et al., 2016a) that captures the phenomena governing the dissolution of semicrystalline cellulose and can distinguish and quantify the individual effectiveness of solvent in decrystallization and disentanglement. The presentation of results and discussion follows the order of (i), (ii), and (iii).

The obtained insights about the impact of solvent characteristics in cellulose dissolution would facilitate the selection of more efficient solvents and the optimization of solvent-processing conditions, thus leading to enhanced utilization of biomass toward fuels and chemicals. The findings are also useful in suggesting efficient pretreatment conditions (FitzPatrick et al., 2010) for deconstructing cellulose, and also in the utilization of cellulose fibers to produce composites (Yousefi et al., 2015), membranes (He and Alexandridis, 2016), and carbon fibers (Li et al., 2015).

2. Materials and methods

2.1. Development of cellulose dissolution model to provide macroscopic and microscopic information

Cellulosic fibers are mostly cylindrical with micron-size diameters and lengths of up to several centimeters (Ioelovich, 2008). The fibers are composed of several cell walls with each wall consisting of microfibrils that are embedded in lignin and hemicellulose (Cosgrove, 2005). The microfibrils are mainly composed of cellulose chains held together by intermolecular interactions (hydrogen bonding (Nishiyama et al., 2008) and hydrophobic (Bergenstråhle et al., 2010)) and forming highly ordered crystalline regions. The amount and arrangement of microfibrils in each cell wall are different, and, consequently, properties such as degree of polymerization and crystallinity vary along the fiber cross section (Thomas et al., 2013).

In order to simplify the complex composition of cellulosic fibers, they are considered here to consist of two components: (i) crystalline domains which encompass all allomorphs of crystalline cellulose; and (ii) amorphous domains that mainly include the non-crystalline cellulose and also other biopolymers present in the fiber, e.g., hemicellulose and lignin. Consistent with its physical shape and geometry, the cellulosic fiber is considered a long semicrystalline polymer cylinder with a uniform cross section area. Since the fiber is almost uniaxially oriented and the cellulose chains are aligned on average along the fiber axis (Kljun et al., 2014), fiber properties such as degree of crystallinity are taken here to be constant over the fiber length, but different along the cross section due to the variant supramolecular and morphological structures of cell walls. Accordingly, in the developed model the cross section of cellulosic fiber was divided into several concentric regions with different thicknesses and properties based on the characteristics of plant cell walls (Ghasemi et al., 2016a).

The homogenous swelling and dissolution of cellulose fibers is depicted in Fig. 1. When the solvent diffuses into the cellulose both its amorphous and crystalline regions are affected, however, the amorphous domains are more accessible to the solvent because of their relatively higher disorder (Lindman et al., 2010). The solid cellulose is transformed to a gel-like medium and the fiber swells (El Seoud, 2009; Faelt et al., 2003; Wang et al., 2014). After a certain induction time, cellulose chains gradually become disentangled and move out of their network into the bulk solution (Lindman et al., 2010). Therefore, the dissolution of cellulose involves several steps including solvent diffusion, destruction and transformation of crystalline to amorphous domains (cellulose decrystallization), specimen swelling, cellulose chain disentanglement, and diffusion of disentangled chains toward the bulk solution. These steps are captured in the developed model using appropriate transport and kinetics equations, as outlined next (Ghasemi et al., 2016b).