Assessment of solvents for cellulose dissolution

Mohammad Ghasemi, Marina Tsianou*, Paschalis Alexandridis*

Department of Chemical and Biological Engineering,
University at Buffalo, The State University of New York (SUNY),
Buffalo, New York 14260-4200, USA

* Corresponding authors.

E-mail addresses: mtsianou@buffalo.edu (M. Tsianou), palexand@buffalo.edu (P. Alexandridis).

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.

Keywords: Biomass processing, decrystallization, [disentanglement](#), dissolution kinetics, pretreatment

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, $\text{Ca}(\text{OH})_2$, 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 thiocyanate solutions), molten inorganic salt hydrates (Sen et al., 2013) (e.g., $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$), 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 (Bergenstrhle 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 Figure 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).

2.2. Phenomenological model of semicrystalline cellulose dissolution

The cellulose fiber is considered as a long cylinder; diffusion of the solvent and cellulose chains takes place only in the radial direction (r), therefore the swelling and dissolution of the fiber is uniform in the other directions (i.e., θ and z). Three components are present in the system: solvent (with volume fraction, ϕ_s), crystalline domains of cellulose (ϕ_p^c), and amorphous domains of cellulose (ϕ_p^a), where $\phi_s + \phi_p^a + \phi_p^c = 1$.

The diffusion of solvent in the cellulose fiber is governed by a nonlinear differential equation:

$$\frac{\partial \phi_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D_s(\phi_s, \phi_p^c) \frac{\partial \phi_s}{\partial r} \right) \quad 0 < r < R(t) \quad (1)$$

where $R(t)$ is the fiber radius at time t and $D_s(\phi_s, \phi_p^c)$ is the diffusion coefficient of the solvent in the fiber:

$$D_s = \phi_p^c D_{sc0} + (1 - \phi_p^c) D_{sa0} \exp(a_s \phi_s) \quad (2)$$

where D_{sc0} and D_{sa0} are the diffusion coefficients of solvent in the crystalline domains and in the glassy amorphous domains, respectively. The factor a_s reflects the steepness of the glassy-rubbery transition of cellulose.

The rate of solvent-induced decrystallization of cellulose is considered proportional to the concentrations of the solvent and the crystalline domains (second order reaction) (Ghasemi et al., 2016b; Ramos et al., 2011).

$$\frac{\partial \phi_p^c}{\partial t} = -k_{dec} \phi_s \phi_p^c H(\phi_p^c) \quad (3)$$

where H is the Heaviside step function ($H = 0$ for $\phi_p^c < 0$ and $H = 1$ for $\phi_p^c \geq 0$). The ability of solvent molecules to transform the crystal lattice into amorphous domains is captured by the decrystallization rate constant (k_{dec}) which depends on cellulose properties (e.g., molecular weight, type and size of crystallites), solvent properties, and external parameters such as temperature.

The disentanglement rate (r_{dis}) captures the effectiveness of the solvent molecules in disentangling cellulose chains. r_{dis} depends on properties of cellulose and solvent as well as temperature. Diffusion of disentangled cellulose chains toward the bulk solution is modeled by considering a diffusion boundary layer (with thickness δ) around the fiber:

$$\frac{\partial \phi_p^a}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D_p \frac{\partial \phi_p^a}{\partial r} \right) - \frac{dR}{dt} \frac{\partial \phi_p^a}{\partial r} \quad R(t) < r < R(t) + \delta \quad (4)$$

where ϕ_p^a and D_p are the volume fraction of the dissolved cellulose and the diffusion coefficient of disentangled cellulose chains, respectively.

The rate of change of the fiber diameter (dR/dt) is derived by applying mass conservation around the evolving volume of the cylindrical fiber:

$$\frac{dR}{dt} = \frac{D_s(\phi_{s,i})}{1 - \phi_{s,i}} \left(\frac{\partial \phi_s}{\partial r} \right)_{R(t)^-} - \left(\frac{-1}{(1 - \phi_{s,i})R} \right) \frac{d}{dt} \left[\int_0^{R(t)} (1 - \phi_s) r dr \right] \quad (5)$$

where $\phi_{s,i}$ is the volume fraction of solvent at the fiber-solvent interface; $\phi_{s,i}$ is constant over time, corresponding to quasi-equilibrium condition, and is estimated here from the thermodynamics of swollen polymer networks (Ghasemi et al., 2016b).

The first term on the right-hand side of Eq. (5) indicates the entering flux of the solvent at the fiber surface, which corresponds to the fiber rate of swelling (ROS). The second term is proportional to the rate of change of the total volume of solid (crystalline and amorphous domains) in the fiber, rate of fiber dissolution (ROD). Therefore, the rate of change of the fiber radius can be expressed as the difference between ROS and ROD: $dR/dt = \text{ROS} - \text{ROD}$.

The resulting moving boundary problem consists of coupled nonlinear differential equations which are solved numerically using known initial conditions and dissolution properties of the system, as described in detail elsewhere (Ghasemi et al., 2016b).

This model has been found capable of capturing cotton fiber diameter and crystallinity over time during swelling and dissolution with [Bmim]Cl (Figure 2) (Ghasemi et al., 2016a).

Characteristics of cotton fibers and model parameters for this system are listed in Table 1 (Ghasemi et al., 2016a). There are only two adjustable/fitting parameters (k_{dec} and r_{dis}) in the model, and all other parameters are obtained independently.

The solvent-induced decrystallization and chain disentanglement are inter-related. However, since there may be different types of interactions which affect disentanglement than those that affect decrystallization (Ghasemi et al., 2016a), in the model the ability of solvent molecules in decrystallization (k_{dec}) should be distinguished from their capability in chain disentanglement (r_{dis}). If a solvent can decrystallize cellulose but cannot disentangle the chains, then the crystallinity of cellulose is decreased, however, no dissolution takes place (the chains still remain entangled with each other), as in the case of [Bmim]Cl at 70 °C (see Figure 2). On the other hand, if a solvent can only disentangle the chains, then only the amorphous regions of cellulose can dissolve. Therefore, in order to molecularly dissolve cellulose, the solvent must be able to both decrystallize and separate the cellulose chains from each other.

Note that, while the cellulose degree of crystallinity can be measured by different methods, it is difficult to estimate the disentanglement behavior of cellulose chains due to the complex network of cellulose. However, results from this model have revealed that the effectiveness of solvent molecules toward cellulose chain disentanglement (captured by the disentanglement rate, r_{dis}) is the only factor that determines the decrease of the fiber radius (Ghasemi et al., 2016a).

Therefore, the velocity of the fiber radius decrease allows the experimental determination of the disentanglement rate of cellulose in homogenous swelling and dissolution at different solution conditions (Ghasemi et al., 2016a).

3. Results and discussion

3.1. Mechanism of solvent diffusion in semicrystalline cellulose

The model provides internal information on the micrometer-diameter fibers during dissolution. Specifically, the model predicts the concentration profiles of solvent and cellulose (amorphous and crystalline) over time, profiles which are difficult or even impossible to measure experimentally. This information coupled with the time variation of the fiber solubility intimates the mechanism of solvent penetration into the cellulosic fibers.

The concentration profiles of solvent, crystalline and amorphous domains of cellulose for the case when 7.14 μm diameter cotton fibers are dissolved in [Bmim]Cl at 80 °C are presented in Figure 3 for different dissolution times (5 sec, 5, 25, and 45 min). Upon solvent diffusion, the volume fraction of solvent in the fiber increases over time and eventually reaches the highest possible value (which here is 0.75). Figure 3a reveals that the solvent concentration profile is initially steep, because the diffusion resistance increases as the solvent moves inward. As the solvent penetrates into the fiber, the complex interaction network of crystalline cellulose is destroyed, resulting in the transformation of crystalline domains into amorphous, and, consequently, the concentration of crystalline domains decreases over time. For example, after 25 min the outer fifth of the fiber is in the amorphous state, and the concentration of crystalline domains increases toward the inside of the fiber and reaches 46% in the fiber center (Figure 3c). At this time, the average crystallinity of the fiber is 19% (Figure 2). In the case that is considered here, the fraction of dissolved fiber increases approximately linearly with time (Figure 4 at 80 °C). This behavior, combined with the very steep initial concentration profile of the solvent (Figure 3a), indicates that the diffusion mechanism of [Bmim]Cl in cotton fiber at 80 °C is similar to Case II transport (Lustig et al., 1992), i.e., the solvent diffusion is rapid compared with the relaxation of glassy cellulose. Similar results have been obtained for the diffusion of methanol in glassy poly(methyl methacrylate) (Thomas and Windle, 1978) and in the decrystallization and dissolution of semicrystalline poly(vinyl alcohol) (Mallapragada and Peppas, 1997) and poly(ethylene oxide) (Hermes et al., 2015) in water.

3.2. Decrystallization time and dissolution time

The model also provides macroscopic/integrated information about the kinetics of fiber dissolution. Specifically, the model determines the total dissolution time, TDT (when the fiber is completely dissolved) and the fiber decrystallization time, DcT (when all the crystalline domains are converted into amorphous) from the predicted fraction of dissolved fiber and fraction of converted crystalline cellulose domains (see Figure 4). The total dissolution time directly reflects the dissolution rate of cellulose, with small TDT values indicating faster fiber dissolution. The decrystallization time captures the rate of cellulose decrystallization. Therefore, the determination of TDT and DcT values for different solution conditions through running the model allows an investigation on the impact of solvent characteristics (e.g., aggressiveness in decrystallization and capability in disentanglement) on the progress of cellulose dissolution.

3.3. Method of approach

In order to examine how the solvent effectiveness in decrystallization affects the cellulose dissolution, various hypothetical solvent systems are considered here which have different abilities in cellulose decrystallization but the same capability toward chain disentanglement. To this end, different values have been assigned to the decrystallization rate constant (k_{dec}) (from 2.5×10^{-5} to 2.5×10^{-1} 1/s), while the other parameters are the same as [the experimental case for dissolution of cotton fiber with \[Bmim\]Cl at 80 °C \(Table 1, \$r_{dis} = 2.5 \times 10^{-10}\$ m/s\)](#). Small k_{dec} values correspond to solvent systems that are not very successful in cellulose decrystallization (e.g., [Bmim]Cl at 70 °C where $k_{dec} = 2.5 \times 10^{-5}$ 1/s), while large k_{dec} values reflect solvent systems that are aggressive in cellulose decrystallization (e.g., [Bmim]Cl at 80 °C where $k_{dec} = 2.5 \times 10^{-3}$ 1/s).

Similarly, in order to understand the importance of the solvent effectiveness in cellulose chain disentanglement, cellulose fibers are considered in hypothetical solvent systems which have different ability to disentangle chains (r_{dis} varies from 2.5×10^{-12} to 2.5×10^{-8} m/s) but the same capability in cellulose decrystallization ($k_{dec} = 2.5 \times 10^{-3}$ 1/s). Small r_{dis} values correspond to solvent systems that cannot disentangle the cellulose chains well (e.g., [Bmim]Cl at 70 °C with $r_{dis} = 0$, in which no dissolution takes place and the fiber only swells, see Figure 2), however large r_{dis} values reflect solvent systems that are successful in disentangling cellulose chains (e.g.,

[Bmim]Cl at 80 °C with $r_{dis} = 2.5 \times 10^{-10}$ m/s in which cellulose fibers are completely dissolved after 129 min, see Figure 2). The specific cellulose-solvent interactions (e.g., hydrogen bonding, dipolar, and hydrophobic interactions) that affect the solvent quality in the swelling/dissolution of cellulose have been captured in the model through the k_{dec} and r_{dis} values. Thus, a broad range of k_{dec} and r_{dis} values has been selected in order to cover the majority of solution conditions that may be encountered during cellulose dissolution. The calculated TDT and DcT values for a cellulose fiber are used to compare the impact of these hypothetical solvent systems on the overall kinetics of cellulose dissolution. The results are presented next (Sections 3.4 and 3.5).

3.4. When cellulose decrystallization controls the dissolution process

In order to select a solvent that can dissolve higher amounts of cellulose and faster, it is important to know how the solvent ability to decrystallize cellulose affects the kinetics of dissolution. The impact of this important solvent feature on the kinetics of cellulose decrystallization and dissolution as reflected in DcT and TDT, respectively, is shown in Figure 5a. Increasing the effectiveness of solvent toward decrystallization always decreases the decrystallization time. It also results in faster cellulose dissolution for small k_{dec} values, while it does not affect TDT for high k_{dec} values. For solvent systems where increasing k_{dec} decreases TDT, the fiber remains crystalline up to nearly the end of the process ($TDT \approx DcT$). For these cases the solvent molecules are not efficient enough to destroy the cellulose crystalline domains fast, and consequently the dissolution can be constrained by decrystallization. This happens for $k_{dec} < 9 \times 10^{-4}$ 1/s at a fixed $r_{dis} = 2.5 \times 10^{-10}$ m/s, the left side of the dashed line in Figure 5a. However, when solvent molecules are very aggressive in decrystallizing cellulose, the fiber becomes amorphous much earlier than its dissolution time ($DcT < TDT$), and so the solvent ability to disentangle the amorphous cellulose chains controls the kinetics of dissolution. This occurs when $k_{dec} > 9 \times 10^{-4}$ 1/s, on the right of the vertical dashed line in Figure 5a. At these conditions, a decrease in the decrystallization rate (by decreasing either the cellulose crystallinity or the decrystallization constant, k_{dec}) does not have much impact in increasing the time needed to dissolve the cellulose chains (TDT is almost constant).

The results of Figure 5a provide insights about experimental observations that signify when the dissolution process is hampered by the lack of ability of solvent in cellulose decrystallization.

Decrystallization controls the cellulose dissolution when one or more of the following is observed: (i) a small change in solvent ability to destroy the crystal domains results in a considerable impact on the kinetics of dissolution; (ii) cellulose remains in the crystalline form almost until the end of the dissolution process; (iii) using another cellulose sample with lower crystallinity results in a remarkable decrease in the total dissolution time (or an increase in the dissolution rate); and (iv) pretreatment of cellulose (such as mercerization) that decreases its crystallinity but without dissolution results in a faster dissolution.

For example, it was experimentally observed that LiCl/DMAc can dissolve better cellulose fibers having lower crystallinity and crystallite size (Ramos et al., 2011). This signifies that the decrystallization step is important in the dissolution of cellulose in LiCl/DMAc. Therefore in this system it is necessary to focus on increasing the cellulose-solvent interactions which result in decrystallization; this could be done by changing solution condition, such as temperature, or adding co-solvents. Furthermore, the crystallinity of cellulose can be reduced at first by pretreatment like mercerization (Ramos et al., 2005). Another example is cellulose dissolution followed by acetylation with 50 wt% acetic anhydride in pyridine which had an efficiency of 8.8% when there was no pretreatment, however, after pretreatment with chloroform/pyridine or with ethanol/chloroform the efficiency increased significantly and became 26% and 28%, respectively (Krässig et al., 1986).

3.5. When chain disentanglement controls the dissolution process

For complete dissolution of cellulose the solvent should be able to disentangle the cellulose chains (Medronho and Lindman, 2014). For this reason, the impact of solvent capability in disentanglement on the kinetics of cellulose dissolution, as captured by the fiber total dissolution time and the decrystallization time, has been examined. The results are shown in Figure 5b. Increasing the solvent effectiveness in disentanglement always decreases the total dissolution time of cellulose. For small r_{dis} values the ability of solvent to destroy the crystalline network of cellulose is stronger than the solvent effectiveness in separating the chains, consequently, the fiber becomes completely amorphous much earlier than its dissolution time ($TDT > DcT$). Therefore, at this condition the cellulose dissolution is mainly controlled by chain disentanglement. On the other hand, in solvent systems which are very active in chain

disentanglement, the entangled amorphous domains become disentangled very fast, while the solvent is not capable to sufficiently destroy the crystalline domains. Therefore, in these cases the dissolution is constrained by decrystallization, and the fiber remains mostly crystalline till the end of the process ($TDT \approx DcT$). These results indicate that when increasing r_{dis} at a constant k_{dec} there is a certain r_{dis} value at which the relative contributions of disentanglement and decrystallization in controlling the kinetics of cellulose dissolution differ. This r_{dis} value is 7×10^{-10} m/s at $k_{dec} = 2.5 \times 10^{-3}$ 1/s, indicated by the vertical dashed line in Figure 5b. Therefore, for solvent systems with $r_{dis} < 7 \times 10^{-10}$ m/s the dissolution is controlled by the ability of solvent to disentangle chains, while for solvents with $r_{dis} > 7 \times 10^{-10}$ m/s the disentanglement rate is sufficiently high and the efficiency of the solvents in decrystallization is the dominant factor.

Note that increasing r_{dis} results in a faster disentanglement of amorphous domains; consequently the crystalline domains become more accessible to solvent and the rate of decrystallization increases (Ghasemi et al., 2016a). This enhancement of decrystallization rate results in a considerable decrease in DcT for the decrystallization-controlled conditions (right side of the vertical dashed line in Figure 5b), while it results in a negligible increase in DcT when decrystallization is less important (disentanglement-controlled conditions, on the left of the dashed line in Figure 5b).

The results discussed above provide insights on conditions when the cellulose dissolution is controlled by chain disentanglement and on how the cellulose solubility at such conditions can be increased. Cellulose dissolution is controlled by the ability of solvent to disentangle chains when: (i) increasing the solvent capability to disentangle chains does not have a considerable impact on the decrystallization time; (ii) cellulose fibers become completely amorphous much earlier than the total dissolution time; (iii) another low- or high-crystallinity cellulose sample has similar overall kinetics of dissolution; (iv) pretreatment of cellulose to decrease its crystallinity does not have a considerable effect on the total dissolution time.

For example, [Bmim]Cl at 80 °C decrystallizes cellulose much faster than it dissolves it (Jiang et al., 2012), indicating that decrystallization does not play a major role in this solvent. Two samples of cellulose pulp with different degree of crystallinity have been shown to have approximately similar overall dissolution kinetics in 1-ethyl-3-methylimidazolium acetate-water (10 wt%) as evidenced by very similar dissolution enthalpy values (103 and 99 J/g for samples

with crystallinity of 61 and 20%, respectively), revealing that in this solvent system decrystallization is not the only factor affecting cellulose dissolution, rather disentanglement might play a major role in dissolution (Parviainen et al., 2014). In this condition, the only way to increase the dissolution rate is by promoting cellulose-solvent interactions which result in chain disentanglement. Crystallinity and chain accessibility have almost no impact on the progress of dissolution.

3.6. When cellulose overall dissolution kinetics are limited by solvent characteristics

The results presented in Sections 3.4 and 3.5 indicate that at a fixed disentanglement rate of 2.5×10^{-10} m/s there is a certain decrystallization constant value ($k_{dec} = 9 \times 10^{-4}$ 1/s), and at a fixed decrystallization constant of 2.5×10^{-3} 1/s there is a certain disentanglement value ($r_{dis} = 7 \times 10^{-10}$ m/s), at which the contributions of decrystallization and disentanglement in controlling the cellulose dissolution mechanism fundamentally change, resulting in a change of dissolution kinetics from disentanglement-controlled to decrystallization-controlled (or vice versa).

In order to identify over a broad range of solvent systems the conditions where the relative contributions of decrystallization and disentanglement to the kinetics of cellulose dissolution change, for each k_{dec} value the relevant r_{dis} value has been determined (as in Section 3.4), and for each r_{dis} value the corresponding k_{dec} has been identified (as in Section 3.5).

The obtained results are plotted in Figure 6 which indicates the controlling mechanism of cellulose dissolution over a broad range of solvent abilities in terms of decrystallization and disentanglement. In the region above the line, solvents are more active in overcoming intermolecular interactions which result in destroying the cellulose crystalline structure, consequently the kinetics of cellulose dissolution in this region are mostly controlled by chain disentanglement. However, for solution conditions corresponding below the line, solvents are more aggressive in disentangling the chains than in disrupting the crystallites, hence, cellulose decrystallization is the controlling step in this region.

This graph also helps clarify the controversial effect on cellulose dissolution of crystallinity, which in some systems has reportedly a considerable impact while in other systems has almost no effect. Accordingly, if in a solvent system (e.g., [Bmim]Cl (Jiang et al., 2012) or 1-ethyl-3-

methylimidazolium acetate-water (Parviainen et al., 2014)) the crystallinity of samples does not affect the kinetics of dissolution, this means that the process at that condition is controlled by disentanglement and the solvent is more capable of disrupting the crystalline cellulose compared to disentangling chains (region above the line). However, if in another system (e.g., LiCl/DMAc (Ramos et al., 2005; Ramos et al., 2011)) it is observed that crystallinity or sample pretreatment (which results in a decrease in the amount and size of crystallites) affect the kinetics of dissolution, this means that this solvent has weak ability to disrupt the crystalline network of cellulose, and so the dissolution progress is mainly limited by decrystallization (region below the line).

Together these results suggest that if a solvent can destroy the crystalline structure of cellulose but cannot dissociate and disentangle the cellulose chains, then such a solvent cannot be considered as effective and the solution condition would fall above the line of Figure 6 with a relatively large perpendicular distance from it. Similarly, if a solvent can disentangle the chains but is not efficient enough toward cellulose decrystallization, then this system would be represented by a point below the line (with a large perpendicular distance from it). Therefore, the solvent effectiveness in both cellulose decrystallization and in chain disentanglement is important: a good solvent for cellulose dissolution corresponds to points that are close to the line and have a relatively upper/right position (both r_{dis} and k_{dec} values must be high).

3.7. Closing remarks

The dissolution of crystalline cellulose involves three main inter-related phenomena: solvent diffusion, solvent-induced decrystallization, and disentanglement of chains. However, the diffusion mechanism of solvent in micron-diameter fibers is not well understood. Furthermore, there is insufficient understanding about how solvent characteristics such as capability in decrystallization and aggressiveness in disentanglement, affect the (in)solubility of cellulose. These issues are addressed here with the help of a newly-developed phenomenological model.

Information about solvent diffusion in cellulose has been obtained via the calculated concentration profiles inside micrometer-diameter fibers (Section 3.1). The diffusion mechanism of [Bmim]Cl in cotton is found similar to Case II transport, information that can be useful in the production of cellulose-reinforced composites (Bhatnagar and Sain, 2005).

Macroscopic information regarding the kinetics of cellulose dissolution is captured by the cellulose fiber total dissolution time (TDT) and decrystallization time (DcT) calculated by the model (Section 3.2). An analysis of TDT and DcT values for different solvent systems allows an assessment of the impact on the progress of dissolution of solvent characteristics such as capability in decrystallization and aggressiveness in chain disentanglement (Section 3.3).

Solvent systems have been identified where the dissolution process is controlled by either decrystallization or disentanglement. Solvents that are protic, such as methanol, ethanol, and dioxane, or aprotic, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO) (Antoniou et al., 2010; Fidale et al., 2008), solvent systems comprising a combination of dipolar aprotic solvents with certain strong electrolytes, such as tetrabutylammonium chloride or bromide/DMSO and LiBr/DMAc (El Seoud et al., 2013), and ionic liquid solvents with pyrrolidinium or piperidinium cation, instead of [Bmim]⁺, and containing Cl[−] anion (Kosan et al., 2010), are poor solvents for semicrystalline cellulose because such solvents cannot decrystallize and disentangle cellulose chains well (they only cause partial swelling).

In solvents such as LiCl/DMAc (Ramos et al., 2011), TBAF/DMSO (Östlund et al., 2009), and 50 wt% acetic anhydride in pyridine (Krässig et al., 1986), where decreasing the sample crystallinity has a considerable impact on its dissolution or where cellulose remains in crystalline form until the end of the process, dissolution is constrained by the lack of solvent ability to decrystallize cellulose (Section 3.4). In this case, pretreatment of cellulose to decrease its crystallinity and increase the solvent accessibility would improve the efficiency of such solvents in dissolving cellulose.

In solvents where cellulose becomes completely amorphous during the dissolution (e.g., [Bmim]Cl at 80 °C (Jiang et al., 2012)) or where the degree of crystallinity does not have much of an effect on the overall dissolution kinetics (e.g., 1-ethyl-3-methylimidazolium acetate-water (Parviainen et al., 2014)), the dissolution is controlled by the solvent ability to disentangle cellulose chains (Section 3.5). In this case, pretreatment cannot facilitate dissolution and there is a need to use solvents which are aggressive toward chain disentanglement (e.g., LiCl/DMAc (Ramos et al., 2011), TBAF/DMSO (Östlund et al., 2009), and 50 wt% acetic anhydride in pyridine (Krässig et al., 1986)).

The parameter space has been mapped out (Figure 6) where cellulose dissolution is limited either due to solvent inability to disrupt the crystalline network or due to solvent lack of effectiveness in untangling cellulose chains. These results provide guidelines for the selection of solvent systems and experimental conditions that can improve the extent and speed of cellulose dissolution (Section 3.6).

The approach presented here for the analysis of swelling and dissolution of a single cellulose fiber can be extended to describe the time evolution of a distribution of particle sizes and degrees of crystallinity as encountered in large scale processing for biomass pretreatment or enzymatic hydrolysis.

4. Conclusions

In conclusion, this study (i) assesses the diffusion mechanism of solvent in micron-diameter semicrystalline cellulose fibers; (ii) identifies conditions where the dissolution of cellulose is limited due to the lack of solvent ability either toward decrystallization or toward disentanglement; (iii) interprets experimental observations that signify decrystallization control or disentanglement control of cellulose dissolution, and recommends conditions that would favor more and faster cellulose dissolution. Beyond the novel elements identified above, the approach and results reported in this study could facilitate the enhanced conversion of recalcitrant biomass, and would be useful in designing pretreatment processes for cellulosic biomass hydrolysis.

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Table 1. Physical properties of cotton fiber swelling and dissolution in [Bmim]Cl.

Parameters	70 °C	80 °C
Initial average fiber diameter, R_0 (μm) ^a	7.14	7.14
Initial average degree of cellulose crystallinity ^a , d_c	0.69	0.69
Degree of cellulose polymerization ^a	514	514
Diffusion coefficient of disentangled cellulose chains in solution, D_p (m^2/s) ^b	1.35×10^{-13}	1.53×10^{-13}
Diffusion coefficient of solvent in glassy cellulose, D_{sa0} (m^2/s) ^b	2.65×10^{-15}	3×10^{-15}
Steepness of the glassy-rubbery transition of cellulose ^b , a_s	2	2
Diffusivity ratio of solvent in crystalline to amorphous domains ^c , D_{sc0} / D_{sa0}	0.1	0.1
Solvent volume fraction at the surface of the swollen gel-like fiber ^b , $\phi_{s,i}$	0.83	0.75
Dissolution induction time, t_{ind} (min) ^d	-	2
Ratio of boundary layer thickness to the fiber radius ^c , δ/R	0.05	0.05
Disentanglement rate, r_{dis} (m/s) ^e	0	2.5×10^{-10}
Decrystallization rate constant, k_{dec} (1/s) ^e	1×10^{-5}	2.5×10^{-3}

^a Given in the experimental work (Jiang et al., 2012).

^b Calculated using appropriate equations (Ghasemi et al., 2016a).

^c Considered based on the dissolution conditions (Ghasemi et al., 2016a).

^d Considered to be the first instance at which the concentration of dissolved cellulose chains was experimentally detected (Cai et al., 2012; Jiang et al., 2012).

^e Obtained from fitting the model to experimental data (refer to Figure 2) (Ghasemi et al., 2016a).

Figure 1. Schematic representation of dissolution of cellulose fibers.

Figure 2. Comparison of modeling results (lines) with the experimental data points (Jiang et al., 2012) for the time evolution of dimensionless diameter ((■) at 70 °C and (●) at 80 °C) and degree of crystallinity ((♦) at 70 °C and (▲) at 80 °C) of cotton fiber immersed in [Bmim]Cl as solvent.

Figure 3. Model predicted volume fractions of solvent (solid blue lines), crystalline domains (thick red lines), and amorphous domains (dashed black lines) of cellulose (cotton) fiber in [Bmim]Cl at 80 °C plotted as a function of the dimensionless radial position at different dissolution times: (a) 5 sec, (b) 5 min, (c) 25 min, and (d) 45 min.

Figure 4. Model predicted fraction of dissolved fiber (FDF) and fraction of converted crystalline domains (FCCD) in the swelling and dissolution of cotton fiber in [Bmim]Cl at 70 and 80 °C. The arrows indicate the DcT (decrystallization time) and TDT (total dissolution time) of the fiber. At 80 °C the dissolution commences after a certain induction time (2 min) and continues until the entire fiber is completely dissolved (TDT = 129 min). In the case of 70 °C, no dissolution takes place, and thus FDF remains equal to zero. The model parameters are presented in Table 1.

Figure 5. (a) Effect of decrystallization constant (k_{dec}) on the total dissolution time (TDT) and on the decrystallization time (DcT) of cellulose fibers at a fixed disentanglement rate ($r_{dis} = 2.5 \times 10^{-10}$ m/s). On the left side of the vertical dashed line, the dissolution process is controlled by the decrystallization of cellulose, whereas on the right side, the controlling step is cellulose chain disentanglement. (b) Effect of disentanglement rate (r_{dis}) on the total dissolution time (TDT) and on the decrystallization time (DcT) of cellulose fibers at a fixed decrystallization constant ($k_{dec} = 2.5 \times 10^{-3}$ 1/s). On the left side of the vertical dashed line, the dissolution process is controlled by cellulose chain disentanglement, whereas on the right side, the controlling step is cellulose decrystallization.

Figure 6. Determining factors of cellulose dissolution kinetics expressed in terms of solvent capabilities toward decrystallization and disentanglement. In the region above the line, the dissolution process is mostly controlled by the disentanglement of cellulose chains, while for conditions corresponding below the line cellulose decrystallization is the more dominant step. The desired conditions for a solvent that is effective toward cellulose are the upper/right corner of the plot (both r_{dis} and k_{dec} values must be high).