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On the external morphology of native cellulose microfibrils

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ABSTRACT

This study is based on the working hypothesis that the external morphology of the cellulose microfibrils is correctly represented by a combination of eight surfaces issued from four lateral cleavage planes of the I-α and I-β allomorphs. Models of these surfaces have been generated and investigated before and after relaxation, thus allowing one to predict, for each of these, their roughness, the accessibility of the hydrophilic and hydrophobic groups as well as their surface and attachment energies. Results showed that the ensemble of eight surfaces could be divided into three families. The first family contains four hydrophilic and moderately rough surfaces, which dominate the external morphology of the microfibrils and are thus responsible for their macroscopic properties. Surfaces of the two other families are of minor importance in the external morphology as they are located at the corners of the cellulosic macrocrystals. They are either flat and hydrophobic or rough and hydrophilic. The flat surfaces are of high biological and technical significance as they are specifically recognized by hydrophobic substances, including the cellulose binding modules of cellulases. Relaxation resulted in a significant disorganization of the rough surfaces whereas the other surfaces remain close to their original organisation. The interpretation of the surface and attachment energies of the surfaces, evidences the major influence of the biosynthetic process in the design of the external morphology of the cellulose microfibrils, as opposed to the classical kinetic and thermodynamic crystal growth mechanism.

1. Introduction

Many of the functional properties of cellulose depend on its capacity to interact with diverse entities, ranging from small molecules to elaborate macromolecules, possessing various polarities. Example of this diversity is illustrated with the adsorption of hydrophilic hemicelluloses on cellulose microfibrils, a critical step for the development of lignin within maturing wood cells (Carpita & Gibeaut, 1993). In another documented case, it is the specific adsorption of the hydrophobic cellulose-binding module (CBM) of cellulases that enhances the biodegradation yield of cellulosic biomass (Himmel et al., 2007). Thus, the surface characteristics of cellulose present multiple facets and it is important to know their details if one want to find new end uses for cellulose. For instance, in the evolving field of cellulose-based nanocomposites, it is clear that the mechanical properties of these new materials will be optimized if the chosen matrix is well adapted for a strong compatibility with the cellulose surfaces.

With cellulose, the adsorption and adhesion phenomena depend on the organization of the glucan chains located at the surface of the cellulose microfibrils. The crystalline core of these microfibrils has been extensively studied (Nishiyama, 2009): it consists of slender crystalline phases made of two allomorphs, namely the one chain triclinic I-α and the two chain monoclinic phase I-β. The long crystals are regularly interrupted by short amorphous zones: for instance, in ramie cellulose, the crystals are about 300 glucosyl units long, whereas only 4–5 units occur in the amorphous regions (Nishiyama, Kim, et al., 2003). Much less is known about the surface of the cellulose microfibrils. Given the 2_1 helical conformation adopted by the cellulose molecules together with the equatorial orientation of the hydroxyl groups, one may anticipate that the cellulose microfibrils expose a variety of surfaces possessing a spectrum of characteristics. Inverse gas chromatography experiments give an average surface energy of 50–70 mJ m^{-2} (Aulin et al., 2009; Erbil, 1996; Forsstroem, Eriksson, & Waagberg, 2005; Mills, Gardner, & Wimmer, 2008; Swaminathan, Cobb, & Saracovan, 2006; Trejo-O'Reilly, Cavaille, Belgacem, & Gandini, 1998). This value, which is often used for estimating the compatibility of cellulose with potentially adsorbable molecular species, fails to reflect the diversity of the values that are present when going from one surface to the other.

The ultrastructural description of the surface of the cellulose microfibrils relies on specific microscopy techniques. Transmission electron microscopy, operated either in microdiffraction or in diffraction contrast modes, can reveal the cross-section of large crystalline microfibrils such as those of *Valonia*, *Micrasterias* or tunicin and identify their surfaces (Daele, Revol, Gaill, & Goffinet,

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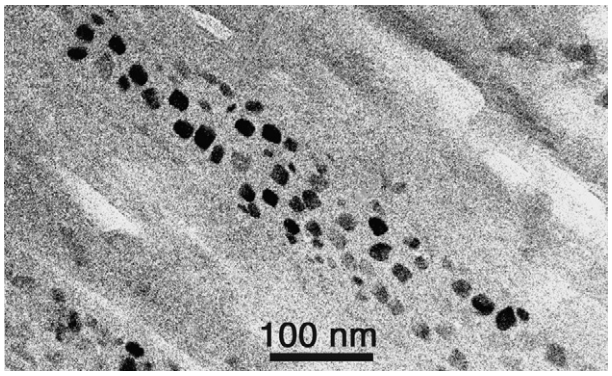

Fig. 1. Diffraction contrast electron micrograph image of *Valonia ventricosa* cell wall section with the microfibrillar orientation perpendicular to the plane of observation. Each microfibril is seen as a black squarish section, with sides of the order of 20 nm, corresponding to the (0 1 0) and (1 0 0) planes in the cellulose I-α system. The microfibrils are organized in crisscrossed layers with surface along the (1 0 0) plane in the I-α allomorph definition and (1 −1 0) in the I-β definition.

1992; Hanley, Giasson, Revol, & Gray, 1992; Helbert, Nishiyama, Okano, & Sugiyama, 1998; Helbert, Sugiyama, Kimura, & Itoh, 1998; Kim, Herth, Vuong, & Chanzy, 1996; Revol, 1982; Sassi & Chanzy, 1995; Sassi, Tekely, & Chanzy, 2000; Sugiyama, Harada, Fujiyoshi, & Uyeda, 1985). In *Valonia*, which has been the most studied, the microfibril sections are squarish (Fig. 1), with four developed surfaces defined by the hydrophilic (1 1 0) and (1 −1 0) planes for the I-β allomorph and/or the (1 0 0) and (0 1 0) planes for the I-α phase, according to the unit cell definitions of Sugiyama, Vuong, and Chanzy (1991). As observed by several authors and illustrated in Fig. 1, the corner of the crystals are frequently blunt, and thus secondary surfaces, corresponding to other planes are also present. The minor (1 −1 0) surface of the I-α phase of *Valonia* is one of them. This hydrophobic surface is quite important since it was proven to be the binding site for the CBM of the Cel7A cellulase from *Trichoderma reesei* (Lehtio et al., 2003; Xu et al., 2009), the first step leading to the digestion of crystalline cellulose by this effective enzyme.

High resolution AFM should be the technique of choice to describe the molecular details of the surfaces of cellulose. Due to experimental difficulties, only few high-resolution AFM images have been published so far, describing only the (1 0 0) triclinic surface of *Valonia* microfibrils (Baker, Helbert, Sugiyama, & Miles, 1998, 2000). In these images, a regular organization of the glucan chains is perceptible, indicating a *gt* conformation of the exposed hydroxymethyl groups, different from the *tg* situation of these groups within the core of the crystal. This interpretation is partly supported by either molecular dynamics (Bergenstrahle, Wohlert, Larsson Per, Mazeau, & Berglund Lars, 2008; Heiner & Teleman, 1997; Heiner, Kuutti, & Teleman, 1998) or by solid-state ^{13}C NMR measurements (Newman & Davidson, 2004), which clearly indicate a mixture of *gg* and *tg* conformations, together with some disorganization of the surface hydroxymethyl groups.

Taken together the aforementioned experimental descriptions of the cellulose surface are limited and the properties of most of the native cellulose surfaces exposed to the external environment remain to be ascertained. Molecular modelling can be used in this context to complement the paucity of experimental data. We have recently created molecular models of one amorphous and four organized cellulose surfaces from the I-β crystal, namely the (1 1 0), (1 −1 0), (0 1 0) and (1 0 0) (Da Silva Perez, Ruggiero, Morais, Machado, & Mazeau, 2004; Mazeau & Vergelati, 2002). These models were used to characterize some of the surface properties of native cellulose microfibrils. Remarkably, the dynamics of the surface chains of the (1 1 0) and (1 −1 0) surfaces differed significantly (Bergenstrahle, Wohlert, et al., 2008), and the contact angle of a water drop on the (1 1 0) and (1 0 0) surfaces was also substantially different (Mazeau & Rivet, 2008). These models have proven useful to predict the adhesion of synthetic polymers on cellulose by either selecting suitable polymers (Chauve, Heux, Arouini, & Mazeau, 2005) or modifying the surface of cellulose (Bergenstrahle, Mazeau, & Berglund, 2008) to accommodate them.

The modelling reports have so far been only fragmentary, with the consequence that many features of the potential cellulose crystalline surfaces are still lacking. The goal of the present paper is therefore to model in a comprehensive way the basic cleavage surfaces of native cellulose crystals. Eight surfaces of lowest Miller indices: four surfaces for each of the I-α and the I-β phases were selected as being the most probable in terms of crystal growth theory (Donnay & Harkei, 1937). For each individual surface, this paper focuses on the prediction of the roughness, the accessibility of the hydrophobic and hydrophilic groups, together with surface and attachment energies.

2. Experimental

The calculations were done with the *Cerius*^{2} molecular modelling package (Accelrys Inc.), at the Centre d'Expérimentation et de Calcul Intensif (CECIC), Grenoble, France.

2.1. Models

Graphical illustrations of the surfaces and the procedure used for their building are presented in Figs. 2 and 3, showing the definitions of the cleavage planes in the I-α and I-β crystalline systems (Fig. 2) and the build up of the models in the case of cellulose I-β (Fig. 3).

Coordinates, taken from the CIF files of the I-α (Nishiyama, Sugiyama, Chanzy, & Langan, 2003) and I-β (Nishiyama, Langan, & Chanzy, 2002) crystal structures, were used in this study. The I-α lattice parameters were first redefined in order to have the *c* axis of the unit cell coincident with the chain axis. Four infinite bulk models were built: two for the I-α phase and two for the I-β phase. Their surfaces are defined according to their Miller indices followed by a Greek letter, which refers to the considered allomorph: for example, the surface (1 1 0) of the I-β allomorph is indicated as (1 1 0)β, etc. In the case of cellulose I-β, they had the crystallographic planes (1 0 0) and (0 1 0) or (1 1 0) and (1–10) parallel to the *ac* and *bc* planes of the parent unit cell (Fig. 3). In the models, each individual cellulose chain was defined with eight independent residues. These four models were then duplicated to obtain the super cells P1, defined along *a*′, *b*′ and *c*′ parameters. Covalent bonds between one end of the mother chain and the other end of the image chain across the periodic box were created to model infinite chains of cellulose. The P1 cells were then relaxed by molecular dynamics in the NPT ensemble according to the protocol described elsewhere (Mazeau, 2005; Mazeau & Heux, 2003).

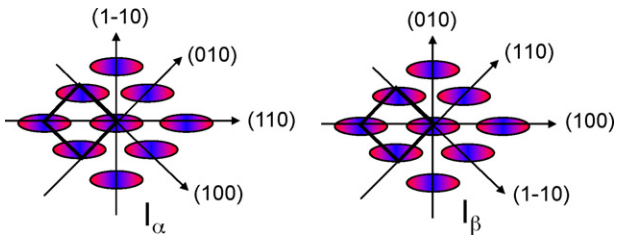

Fig. 2. Schematic representation of glucan chains in a crystalline organization representing the two native allomorphs of cellulose projected perpendicular to the chain axis. The arrows indicate the cleavage planes together with the Miller indices of the corresponding surfaces.