



A coarse-grain force-field for xylan and its interaction with cellulose



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ABSTRACT

We have built a coarse-grain (CG) model describing xylan and its interaction with crystalline cellulose surfaces. Each xylosyl or glucosyl unit was represented by a single grain. Our calculations rely on force-field parameters adapted from the atomistic description of short xylan fragments and their adsorption on cellulose. This CG model was first validated for xylan chains both isolated and in the bulk where a good match was found with its atomistic counterpart as well as with experimental measurements. A similar agreement was also found when short xylan fragments were adsorbed on the (1 1 0) surface of crystalline cellulose. The CG model, which was extended to the (1 0 0) and (1 – 1 0) surfaces, revealed that the adsorbed xylan, which was essentially extended in the atomistic situation, could also adopt coiled structures, especially when laying on the hydrophobic cellulose surfaces.

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1. Introduction

In plants, the cell wall serves a variety of physical and biological purposes (Albersheim, Roberts, Seferoff, & Staehelin, 2010). Among these, one of its main functions is to provide support and mechanical strength to the plant and to ultimately organize its architectural design and diversity. The cell wall also possesses many biological and biophysical functions required for the plant development, ranging from the containment of the cell turgor pressure during the wall growth, the prevention of insect and pathogen invasion, the diffusion of signaling molecules, etc. All these roles rely on the unique nanocomposite ultrastructure of the wall that chiefly consists of slender crystalline cellulose microfibrils embedded in amorphous hemicelluloses, with or without lignin, depending on the class of the tissues (Carpita & McCann, 2002; Keegstra, 2010; Varner & Lin, 1989). An accepted scheme of this ultrastructure is that the hemicelluloses are laid along the cellulose microfibrils and when lignin is present, as in secondary walls, the hemicelluloses

act as a “coupling agent” between cellulose and lignin (Page, 1976; Terashima et al., 2009).

Among the known hemicelluloses, xylan stands out as being by far the most abundant. On an industrial scale, the beneficial influence of xylan on cellulose fibers is well documented, either during the cooking of the wood pulp (Yllner & Enstrom, 1956), or its beating (Roberts & El-Karim, 1983). On the other hand, the presence of xylan in lignocellulosics is detrimental for the enzymatic digestion of the cellulose fibers prior to biofuel production (Ohgren, Bura, Saddler, & Zacchi, 2007). At the laboratory scale, the selective adsorption of xylan on cellulose microfibrils has been extensively studied (Kabel, van den Borne, Vincken, Voragen, & Schols, 2007; Koehnke, Oestlund, & Brelid, 2011; Mora, Ruel, Comtat, & Joseleau, 1986). In particular, this affinity is well exemplified when the addition of xylan to the culture medium of bacterial cellulose leads to a spontaneous xylan adsorption at the surface of the nascent cellulose microfibrils, which thus cannot get assembled into ribbons as in the xylan-less control case (Atalla, Hackney, Uhlin, & Thompson, 1993; Tokoh, Takabe, Sugiyama, & Fujita, 2002). The ultrastructural visualization of deposits of xylan on cellulose microfibrils has been illustrated in many micrographs obtained with a battery of high-resolution microscopy techniques (Henriksson & Gatenholm, 2001; Linder, Bergman, Bodin, & Gatenholm, 2003; Mora, Ruel, Comtat, & Joseleau, 1986).

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Given its crucial role in the ultimate physical properties of the plant cell wall, the molecular description of the organization of xylan at the interface with cellulose is important. There are several spectroscopic studies that show that in wood cell wall, xylan as well as other hemicelluloses tend to be aligned, parallel to the cellulose microfibrillar direction (Liang, Bassett, McGinnes, & Marchessault, 1960; Marchessault & Liang, 1962; Olsson, Bjurhager, Gerber, Sundberg, & Salmen, 2011; Stevanic & Salmen, 2009). The co-crystallization of xylan on cellulose microfibrils was even described in one report (Marchessault, Settineri, & Winter, 1967), but this observation was criticized (Caulfield, 1968) and so far has not been reproduced.

In view of the difficulty of obtaining precise experimental data revealing the fine details of the interface of xylan and cellulose, modeling appears as a choice method to propose an energetically acceptable description of such an interface. In a previous report, we have simulated by molecular dynamics (MD) at the atomic scale, the adsorption of xylooligosaccharides at the (1 1 0) surface of an I β crystal of cellulose (Mazeau & Charlier, 2012). This study showed that such xylan fragments could not only be adsorbed in a parallel or antiparallel fashion with respect to the cellulose molecular axis, but also that inclined situations were also possible. Counter-intuitively, the most populated adsorbed conformation of the xylooligosaccharide backbone corresponded to the classical left handed 3_2 helices, suggesting that such helices could interact efficiently with a crystalline cellulose surface in spite of apparent conformational incompatibility. Adsorbed xylooligosaccharides could also explore the 2_1 helicity as well as non-helical geometries. Atomistic simulations, restricted so far to several tenths of nanoseconds, have been performed, using a short fragment of xylan of five xylose units, adsorbed on a very small cellulose surface of 18 nm² made of only eight chains of eight glucosyl units each. In addition, only the (1 1 0) surface of cellulose was considered, based on results from ¹³C solid-state NMR spectroscopy (Larsson, 2004; Larsson, Hult, Wickholm, Pettersson, & Iversen, 1999). However, recent WAXS data suggest that the (1 0 0) surface could also participate in the interaction of xylan on crystalline cellulose (Penttila et al., 2013).

Despite the interesting results obtained on rather small systems, an extensive characterization of the adsorption requires more realistic models including longer hemicellulose chains, wider cellulose surfaces, cellulose surfaces of different nature, and longer simulation times, which are beyond the reach of actual computing power.

To overcome such limitations, alternative methods have been developed for the simulation of biological systems as well as polymer in their various states. Among these new techniques, the coarse grain modeling has the capability of circumventing the limitations of atomistic simulations. The methods and applications of CG modeling in the field of biopolymers including polysaccharides have been reviewed at several occasions (Muller-Plathe, 2002; Noid, 2013; Saunders & Voth, 2013). Different CG models of cellulose were recently developed to answer critical problems that need to be solved for the use and processing of plant biomass. Along this line and referring to the cellulose component, one can quote (i) the determination of its intrinsic properties in both its crystalline and amorphous states (Glass, Moritsugu, Cheng, & Smith, 2012; Queyroy, Neyertz, Brown, & Mueller-Plathe, 2004; Shen & Gnanakaran, 2009; Srinivas, Cheng, & Smith, 2011; Wohlerl & Berglund, 2011; Wu, Zhan, Wang, & Ju, 2012) (ii) its ability to interact with external agents such as cellulases (Asztalos et al., 2012; Bu et al., 2009; Bu, Himmel, & Nimlos, 2010; Lin, Beckham, Himmel, Crowley, & Chu, 2013), (iii) its dissolution into organic solvents (Gross, Bell, & Chu, 2013), (iv) its swelling with agents such as ammonia (Bellesia et al., 2012), etc.

The basic idea of the CG approach is to group a number of atoms into a single grain. In the field of carbohydrates, the number of

grains that define a monosaccharide residue ranges from one to six. The choice of the CG scale depends on the desired level of structural information and on the desired scientific issue. CG models with many grains are able to describe the chemical specificity of carbohydrates, including the shapes of the pyranose ring, the accessible conformational states of the glycosidic bonds and even the rotation of the hydroxymethyl groups. Describing monosaccharides with a large number of grains requires however huge computational resources. At the opposite, CG models that scale glycosyl residues by a single grain are minimal models for the study of the structure and dynamics of large assemblies of polysaccharides. This scaling level is intuitively natural but presents some difficulties in its primitive form, as it is not able to distinguish different monosaccharides. In addition, it cannot handle the different shapes of the monosaccharides or the anisotropic interactions. Finally, reverse-scaling, i.e., deriving an atomistic description from the CG model, is difficult at this scaling level.

To our knowledge, only three CG models of the cellulose/hemicellulose interactions have been proposed. These models differ by the mapping level. A hyper-CG model, where cellulose was only represented by a flat surface and xyloglucan by beads having the Kuhn-length – i.e., 6 nm – has been developed to better understand the experimental extension forces between cellulose and xyloglucan measured by AFM (atomic force microscope) spectroscopy (Morris, Hanna, & Miles, 2004). In this system, the CG modeling was able to reproduce the observed plateaus when three chains of different lengths, with 40, 80 and 120 beads, were attached to the modeled tip. In another CG model, the cellulose microfibril is represented by a long stiff rod made of seven beads, whereas the xyloglucan is represented only by stretchable cross-links, placed at three points per rod (Manyuhina, Fasolino, & Katsnelson, 2007). This modeled system, which contained 288 rods, was generated to study the frustration effects induced by the xyloglucan particles on the co-orientation of the cellulose rods. Reorientation of these rods studied at different temperatures showed that the orientation correlation function presented a logarithmic time dependence, in agreement with the observed logarithmic creep motion in primary plant cell walls leading to the cell extension (Nieuwland et al., 2005). In the most precise CG model of the cellulose/hemicellulose complex developed so far, the beads of both polymers have a diameter of 1 nm, which is roughly the length of a disaccharide (Adler & Buehler, 2013). A generated cell wall model containing 10 cellulose microfibrils, each with 30 beads, and hemicelluloses made of 36 beads was developed. When stressed, this model was adapted to study the influence of the average orientation of the fibers on the mechanical response of the complex. In very good agreement with the experiments, it was found that a decrease in the microfibril angle had the effect of increasing the stiffness of the system. The CG mapping levels proposed so far of the association of hemicelluloses with cellulose are too coarse to address the question of the description of the adsorption, together with the interaction and organization of the hemicellulose at the exposed surfaces of the cellulose crystals.

In this report, which goes beyond our earlier atomistic study (Mazeau & Charlier, 2012), we present the development of a CG using a mapping scale where each bead has a diameter of 0.5 nm, corresponding to the size of a single anhydro sugar unit. Our new model is more accurate than the previous models that were capable of describing the cellulose–hemicellulose complexes. The model completes the existing ones and thus extends their possibilities in this particular field. Our long term objective is to integrate the description of non-spherical grains with anisotropic interactions (Zhu et al., 2013), to get rid of the limitations inherent to the scaling level. We feel that the tool that we are herewith developing will allow deeper investigation of the plant cell wall, but also the development advanced bio-sourced materials.

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