doi:10.20396/revpibic.v0i0.id

XXVI Congresso de Iniciação Científica Unicamp
17 a 19 de outubro Campinas | Brasil

Wetting of Pristine and Functionalized Nanocrystalline Cellulose

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Abstract
Molecular dynamic simulations were used to investigate the wetting behavior of nanocrystalline cellulose allomorphs. Three 40ns independent MD simulations using CHARMM force field gave droplet profiles, whose contact angles were obtained with LBADSA plugin for ImageJ. Surface hydrophilicity was related to hydroxyl group availability for hydrogen bonding. Oxidation of C6 hydroxyl groups significantly boosts surface hydrophilicity, and even low levels of modification (~7%) leads to contact angles close to zero degrees. These data can be useful for biotechnological applications.

Key words:
Cellulose, molecular dynamics, hydrophilicity.

Introduction

Lignocellulosic biomass is a promising material for biofuel generation[1]. Its chemical and physical resistance (recalcitrance) towards enzymatic hydrolysis arises from complex interactions between water, lignin, cellulose and hemicelluloses[2]. Recalcitrance is a key factor to overcome in order to have an economically viable conversion of plant biomass into valuable chemicals[3]. The binding of enzymes to target substrates also depends strongly on the surface properties of cellulose.

In this context, we investigate the relative hydrophilicities of crystalline cellulose surfaces using MD simulations with CHARMM force field. Biomass structure and its deconstruction depends on surface properties of cellulose nanostructures, which are difficult to obtain experimentally at molecular level[4].

Results and Discussion

Contact angles and wetted area measurements were performed with ImageJ together with LBADSA plugin[5].

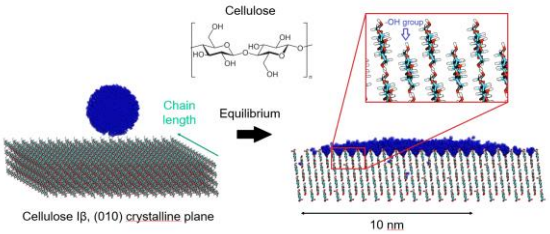

Image 1. Simulation systems consists of water and cellulose slabs exposing different crystalline planes.

The obtained contact angle values were rationalised based on hydrogen bonding.

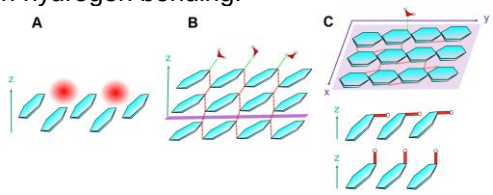

Image 2. Hydrogen-bond patterns of crystalline cellulose.

Grooved surfaces allow close contact between water and hydroxyl groups, leading to contact angles close to zero degrees (**A**). 3D hydrogen-bond networks in allomorphs II and III_I also results in hydrophilic planes (**B**). Distinc hydroxyl group orientations in Iα and Iβ controls intra/intermolecular hydrogen-bond ratio in cellulose chains and hence these cellulose allomorphs display both hydrophilic (zero contact angle) and hydrophobic planes (contact angles between 25 and 45º) (**C**).

Oxidation of a few percent cellulose C6 positions (~7%) reduces cooperativity in intramolecular hydrogen bond network and significantly boosts surface hydrophilicity.

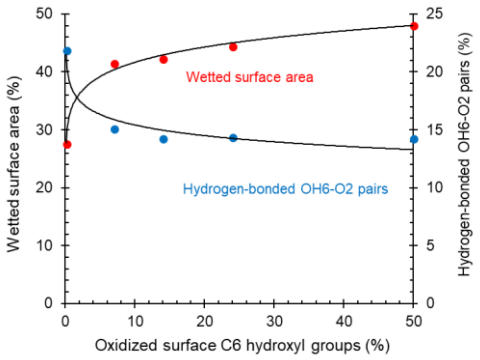

Image 3. Oxidation degree versus wetted area/ hydrogen-bonded hydroxyl groups for cellulose Iβ (110) face.

Conclusions

Molecular dynamics simulations allow hydrophilicity characterization of crystalline cellulose faces. Chemical modifications, even in small proportions, can lead to significative changes in hydrophilicity. This knowledge may improve our understanding about chemical interactions in plant cell walls and chemical treatment processes of cellulose, since it allows the development of more refined models.

Acknowledgement

This work has been supported by CNPq (144359/2017-0) and FAPESP (2013/08293-7).

[1] Matthews, J. F.; Skopec, C. E.; Mason, P. E.; Zuccato, P.; Torget, R. W.; Sugiyama, J.; Himmel, M. E.; Brady, J. W. Carbohydr. Res. **2006**, 341 (1), 138–152..
[2] Cosgrove, D. J.; Jarvis, M. C. Front. Plant Sci. **2012**, 3 (August), 1–6..
[3] Zhao, X.; Zhang, L.; Liu, D. Biomass Recalcitrance. Biofuels, Bioprod. Biorefining **2012**, 6 (4), 465–482.
[4] Dri, F. L.; Wu, X.; Moon, R. J.; Martini, A.; Zavattieri, P. D. Comput. Mater. Sci. **2015**, 109, 330–340.
[5] Stalder, A. F.; Melchior, T.; Müller, M.; Sage, D.; Blu, T.; Unser, M. Colloids Surfaces A Physicochem. Eng. Asp. **2010**, 364 (1–3), 72–81.

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