Interfacial hydrogel formation and entropic effects in adsorption of mixed-linkage glucans on cellulose surfaces

Tuuli Virkkala[1], Vladimir Grachev[2], Eero Kontturi[3], Wim Thielemans[2], Tekla Tammelin[1]

[1]Biomaterial processing and products, VTT Technical Research Centre of Finland Ltd., PO Box 1000, FI-02044 Espoo, Finland.
[2]Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, Campus Kulak Kortrijk, Etienne Sabbelaan 53, BE-8500 Kortrijk, Belgium.
[3]Department of Bioproducts and Biosystems, Aalto University, FI-00076 Aalto, Finland.

tuuli.virkkala@vtt.fi

Cereal hemicelluloses, i.e., mixed-linkage glucans (MLGs) are interesting components for polysaccharide-based materials due to their unique gel formation tendency even at low concentrations[1]. While attractive interactions of annual plant hemicelluloses with cellulose surfaces have been shown priorly[2,3], several knowledge gaps on the plant cell wall component interactions in nature and technical materials exist. To reveal the mechanisms underlying the interconnections, we methodically probe MLG solution properties, adsorption at cellulose interfaces, and the thermodynamics of interaction using dynamic light scattering (DLS), quartz crystal microbalance with dissipation monitoring (QCM-D), and isothermal titration calorimetry (ITC), respectively. We show the intriguing solubility aspects and the pronounced interfacial hydrogel formation behaviour of MLGs adsorbed on cellulose nanocrystal surfaces (Figure 1). This is different from many other hemicellulose systems, which display polyelectrolyte-like adsorption. While entropy is accepted fairly universally as a driving force for polysaccharide adsorption, it is far from trivial to verify and has been demonstrated for few cellulose-hemicellulose systems[4,5]. Despite the experimental challenges resulting from the limited solubility and gelling tendency of MLGs, the entropic contribution in MLG-cellulose interactions is systematically evidenced. Additionally, we attempt to discuss the synergistic effect of entropy and MLG solubility on the adsorption, which is often only vaguely mentioned in similar studies. Overall, these findings point toward the wet-strength mediating and life-sustaining features of MLGs in nanocellulosic networks[2] being attributed to the interfacial hydrogel formation, as well as the hemicelluloses providing a hydrating layer in the plant cell wall.

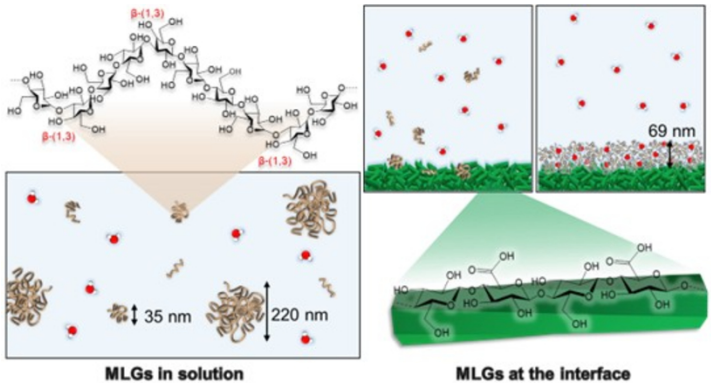

Figure 1. Schematic view and dimensions of mixed-linkage glucans (MLGs) in solution and adsorbing on a cellulose surface, forming a hydrogel layer at the interface. The chemical structures of MLG and cellulose are shown.

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