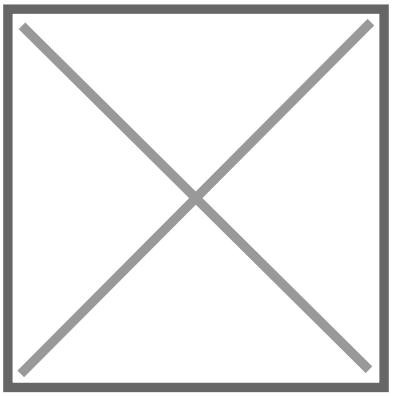

The Plant Cell Walls are Complex Nanocomposites of Polysaccharides

Description

Whether primary or secondary, the plant cell walls are built on the cellulose network organized around the cellulose microfibril unit (MF).

Depending on the developmental stage, the tissue type, and the cell wall layer, cellulose microfibrils (MFs) are differentially embedded in pectic polysaccharides, hemicelluloses and lignin. Many fundamental biological, physical, mechanical and chemical properties of plants depend on the fine organization of these structural polymer constituents at the ultrastructural and nanoscale levels. It is well accepted that the major load-bearing components in cell walls are MFs. Many fundamental biological, physical, mechanical and chemical properties of plants depend on the fine organization of these structural polymer constituents at the ultrastructural and nanoscale levels.

Primary walls

â?? The Xyloglucan-Cellulose interaction

In the growing primary walls, the main MFs are oriented transverse to the growth direction.Szymanski & Cosgrove, 2009 The strength of the cell wall is due to the interaction between cellulose MFs and the matrix polysaccharides. In the resulting scaffold, xyloglucan and arabinoxylan bind to cellulose surface and tie together the MFs into a strong network. It has been shown for a long time that XG interacts with cellulose forming non-covalent association mediated by hydrogen bonds.Valent & Albersheim, 1974 This privileged association involving the Î²-1,4-D-glucopyranosyl chain of cellulose and the highly substituted Î² -1,4-D-glucopyranosyl chains of XGs results in the extensive topochemical distribution of XGs coating cellulose microfibrils within the supramolecular cell wall edifice.McCann {et al.,} 1990Ruel & Joseleau, 1993Fujino {et al.,} 2000 This partly explains the load-bearing function of XGs. Cosgrove 1997 Chanliaud {et al.,} 2002 Several studies showed that the Xyl/Glc ratio affect the binding of XGs to cellulose, the less substituted XGs, the highest binding yields. Moreover, the terminal fucosyl residues of XGs differentially affect the binding, depending on the crystallinity of cellulose, suggesting that the surface status of native cellulose microfibrils affects the XG/Cellulose interaction.Abeces {et

al.,}1993Chambat {et al.,} 2005 The influence of XG side chains in the binding *in vitro* to cellulose was earlier rationalized by conformational dynamics simulations.Levy{ et al.,} 1997 The XyG backbone adopts a helical conformation in solution, which, together with the arrangements of side chains, prevents self-association in solution while at the same time favoring the adoption of a flat conformation upon interacting with cellulose.Levy {et al.,} 1991 Further computer simulation studies showed that every cellulose IÎ² surface was capable of binding xyloglucan oligomers.Hanus & Mazeau, 2006
The XG/Cellulose association may be modulated during anisotropic cell expansion by hydrolysis of XG through the action of endogenous XET in a process of selective primary wall loosening Fry {et al.,} 1992accompanied by mechanical constraints and changes in the orientation of cellulose microfibrils. Burgert & Frazl, 2009
However, the key tethering role of XG to cellulose microfibrils during growth has been recently questioned on the basis of two- and three-dimensional magic-angle-spinning (MAS) solid-state NMR and uniformly 13C-labeled nuclear magnetic resonance studies indicating that the interaction was actually weakly pronounced Dick-Perez {et al.,} 2011, and prompted a revision of the role of XG in the dynamics of the growing primary wall. Park & Cosgrove, (2012)

â?? The pectic network

In the classical models of primary walls, the Xyloglucan/Cellulose network is the load bearing component. On the other hand, the pectic polymers form another network. Carpita & Gibeaut, 1993 Several studies, including molecular modeling have shown that the arabinan and/or galactan side chains of pectins adsorb to cellulose microfibrils. Zykwinska {et al., } 2008 However, the cation-based cross-linking of acidic pectic polymers (essentially Ca2+) greatly influences the capacity of extension of the primary walls as well as their porosity. An important factor in this process is the methyl- de-esterification *in muro* of homogalacturonans by wall-bound methylesterases that modulates the extent of their binding capacity. As a result, the gel-forming pectins act as hydrophilic plasticizers between the microfibrils, keeping the growing cell wall both pliant and strong. Szymanski & Cosgrove, 2009.
Although the arrangement in vivo of the various pectic polysaccharides is not known, it is suggested that RG-I and RG-II form a continuous covalent cross-linking with the HG backbone. In complexing with boron to form a borate diol ester, two molecules of RG-II can establish crosslinks via their apiofuranosyl residues. Ishii {et al.}, 1999 A study of T1 relaxation time in two- and three-dimensional magic-angle-spinning (MAS) indicates that the interaction of pectin is restricted to the surface of microfibrils. Dick-Perez{ et al.,} 2011
It is suggested that arabinans are anchoring pectins in the wall and that galactans, in filling the gaps in the wall networks, may control the pore size. Voragen {et al., } 2003
Structural glycoproteins are found in most primary walls (1-5%). The most studied are the hydroxyproline-rich glycoproteins (HRGP), the arabinogalactan proteins (AGP), the glycine-rich proteins (GRPs), and the proline-rich proteins (PRPs). Their role in the cell development has been suggested to be their involvement in recognition and signaling.Showalter 1993 Ellis{ et al.,} 2010The case of these glycoproteins is not treated in the present review.

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Secondary walls

Secondary walls are divided into different layers, each layer having its own particular arrangement of cellulose MFs, which determine the mechanical and physical properties of the tissue. In the S1, S2, and S3 layers constituting generally the fiber walls, the MFs may be aligned at a particular angle to the cell axis. The MF angle increases, with regard to the cell axis, resulting in a highly anisotropic structure of the fiber wall.

- The Hemicellulose-Cellulose interaction

The role of hemicelluloses in secondary walls, illustrated here with wood cell walls, is mostly a mechanical function of support in fibers and tracheids, and therefore differs greatly from the role of hemicelluloses and pectins in the expending primary walls. A common standpoint is that cellulose fibrils are coated with hemicelluloses and that the complex is embedded in a lignin-hemicellulose matrix, as visualized by the technique of immunolabeling in transmission electron microscope. Ruel &Joseleau, 2005 In the coating, the D-pyranosyl backbone of the hemicellulose forms a strong non-covalent hydrogen-bond association with cellulose microfibrils. Additionally, the charged carboxyl groups of glucuronoxylans are arranged face-to-face in such a way that repelling forces prevent aggregation of the cellulose microfibrils and favor their parallel arrangement DammstrÃ¶m {et al.,} 2009The O-acetylation degree of xylans may modulate the binding to cellulose. However, the hemicelluloses show a much lower degree of orientation than that of cellulose. SalmÃ©n{ et al., } 2012

A modeling study by molecular dynamics simulations of the interaction of xylan fragments having 5 skeletal Î²-(1-4) xylosyl residues (X5) onto the (110) surface of cellulose microfibrils illustrated the affinity of the selected xylan fragments for crystalline cellulose. Mazeau & Charlier 2012 The calculations confirmed that xylan in solution is readily adsorbed on cellulose microfibrils and that the xylan fragments have a tendency to get aligned with respect to the molecular axis of cellulose in the microfibrils. Curiously, the study concluded that substitution of the X5 backbone by either GlcpA and/or Araf side chains had no major influence on either the conformation or the efficiency of the interaction. In an attempt to quantify the strength of the interaction at the interface between cellulose and hemicellulose, another molecular dynamics (MD) simulation study Zhang {et al.,} 2015 emphasized the contact area as well as hydrogen bonds, together with the covalent bonds in backbone of hemicellulose chain as the various controlling parameters at the interface.

The other main hemicelluloses of the woody plants secondary walls are glucomannans and galactoglucomannans. As well as the close affinity between mannans and cellulose. Chanzy{ et al.,} 1982, and due to the configuration of their sequences of Î²-(1-4)-linked D-mannopyranosyl interspaced by single Î²-(1-4)-D-glucopyranosyl residue, GM and GGM closely associate to cellulose. There is a hierachical organization in the secondary wall that is influenced by the degree of acetylation of the hemicelluloses which results in a parallel arrangement of xylans relative to cellulose and glucomannan, and in wich xylans may more interact with the accessible glucomannan than the cellulose itself. Ã kerholm &SalmÃ©n 2001 SalmÃ©n, 2015 The close interaction of hemicelluloses with the surface of cellulose microfibrils was evidenced by spectroscopic techniques such as dynamic infrared DammstrÃ¶m {et al.,} 2009 and microscopic techniques such as atomic force microscopy FahlÃ©n & SalmÃ©n 2004 and immuno-transmission electron microscopy using antibodies directed against xylans and glucomannans .Joseleau 2007Maeda {et al.}, 2013

The reticulation of cell wall polysaccharides through phenolic substances, and particularly lignin Ruel {et al.}, 2002, is an important factor of terrestrial plant mechanical resistance. This aspect will not be dealt with in this review, and will the included in another review to be published in Glycopedia by K Ruel and J-P Joseleau).

Category

1. News