Abstract

The plant cell wall is a highly organized structure whose main components are polysaccharides such as cellulose, hemicellulose, and pectin. It surrounds plant cells, providing their shape and performing many key functions, including mechanical strength, extensibility, water and nutrient transport. The plant cell wall is a dynamic system that undergoes modifications during plant development, determining the mechanical properties of fruit tissue. Pectin degradation is considered a key factor influencing changes in mechanical properties, including loss of fruit firmness. However, there is still a lack of literature reports on the role of hemicelluloses in this process. Interactions between the plant cell wall components determine the above macroscopic functions. It is known that hemicelluloses, pectins, glycoproteins, and cellulose are in close contact within the wall, but research on these interactions is still ongoing.

It is known that native hemicelluloses are acetylated, which affects their physicochemical properties. In turn, pectins can be both methylated and acetylated. These substituents are a crucial component of the structure of non-cellulose polysaccharides and can significantly influence interactions with cellulose. In accordance with the fact that linear hemicellulose chains rich in hydroxyl groups show high affinity for cellulose, a research hypothesis was put forward that acetylation of non-cellulose polysaccharides hinders theirs interaction with cellulose microfibrils, thereby reducing the integrity of the plant cell wall and tissue. This hypothesis was verified by studies based on two apple varieties with different pre-harvest and post-harvest storage terms. The main objective of the doctoral dissertation was to determine the effect of the degree of acetylation of non-cellulose polysaccharides (hemicelluloses, pectins) on the mechanical properties and microstructure of plant tissue.

The doctoral dissertation covers three main stages of research. The first stage concerns quantitative research, a review of changes in monosaccharide composition, the degree of acetylation of pectin and hemicellulose fractions isolated from the cell walls of Idared and Pinova apples, and the correlation of these changes with the loss of firmness during fruit storage. The second stage presents qualitative research on changes in the structure of polysaccharides using FT-IR and Raman spectroscopy. In addition, Raman microscopy studies reveal the localisation of polysaccharides in the cell wall, with a distinction between acetylated and deacetylated hemicelluloses and low- and high-esterified pectins. The third is model adsorption studies aimed at demonstrating the interactions between hemicelluloses/pectins and cellulose and determining the effect of acetylation of non-cellulose polysaccharides on these interactions.

The study showed that Idared and Pinova apples had similar firmness during pre-harvest maturity and at harvest term, while during three months of storage, only Idared apples significantly softened. Pinova contained more branched pectins, while Idared was rich in linear homogalacturonans. The degree of acetylation of hemicelluloses soluble in LiCl-DMSO increased in the tested terms for Idared and Pinova apples. In addition to the correlation between the composition and structural characteristics of pectins, a negative correlation between acetylated hemicelluloses and apple firmness was demonstrated. FT-IR and Raman spectroscopy studies and PCA analysis confirmed changes in the structure of pectins and hemicelluloses. They emphasized the importance of changes in the degree of acetylation of hemicelluloses, especially acetylated glucomannan, occurring during cell wall remodeling in the tested terms. Raman mapping combined with image analysis was used to localize cell wall polysaccharides. Low-esterified pectins tended to accumulate in the corners of cell junctions, while highly esterified pectins were evenly distributed throughout the wall. Acetylated and deacetylated hemicelluloses in the cell wall were successfully distinguished. Acetylated hemicelluloses dominated the cell wall of apples after three months of storage, especially for the Idared variety. Hemicelluloses did not show specific clusters, however, a more even distribution in the wall was observed for acetylated hemicelluloses. Model adsorption studies showed only the adsorption of hemicelluloses: xylan, xyloglucan, glucomannan, and β-D-glucan on microfibrillar cellulose. The highest adsorption was observed for glucomannan. Acetylation of hemicellulose did not affect the kinetics of adsorption on cellulose, but caused an increase in adsorption for xyloglucan and glucomannan. This is due to the low degree of substitution of hemicellulose with acetyl groups, which do not constitute a steric hindrance in interactions with cellulose, but can reduce the self-association of polymer chains, which is a competitive process of these interactions. In addition, acetyl substituents may promote hydrophobic interactions with cellulose.

Keywords: acetylation, hemicellulose, pectins, plant cell wall, firmness, apples, FT-IR spectroscopy, Raman spectroscopy, Raman imaging, adsorption