Abstract

Pectins are key component of plant cell walls, influencing rigidity, mechanical resistance, and tissue integration. Among pectins, rhamnogalacturonan I (RG-I) is particularly significant due to its complex structure and variability depending on the source. The structure of pectin molecules rich in RG-I primarily depends on the presence of rhamnose in the main chain of RG-I, to which other neutral sugars are attached. The insertion of a rhamnose unit can cause bends in the conformation of the RG-I main chain. Compared to the homogalacturonan (HG) linear chains, this may lead to reduced mobility of RG-I molecules in solution and, therefore, a decrease in the degree of interaction with other molecules. Consequently, this may result in different functional properties of RG-I, both in cross-linking in solution and mechanically in the cell wall. The diluted alkali-soluble pectin (DASP) fraction, in addition to linear homogalacturonan, is rich in RG-I. Therefore, this study hypothesized that the presence of rhamnose in diluted alkali-soluble pectin (DASP) affects the structure and crosslinking properties of this fraction and, thus, the mechanical properties of the materials in which they are present. The above hypothesis was verified in an experiment conducted on DASP pectins extracted from two horticultural plant sources (apple and carrot). The study examined the monosaccharide composition of pectins, their nanostructure, rheological properties in solution, and the mechanical properties of cell walls and cell wall analogues containing DASP fraction. Differences resulting from the plant species and those arising from enzymatic modifications aimed at removing rhamnose and RG-I pectin side chains in this fraction were analyzed. The aim of the dissertation was to assess the impact of rhamnose and the monosaccharide composition of diluted alkali-soluble pectin (DASP) on the cross-linking properties of this fraction and, thus, on the mechanical properties of the materials in which they are present.

The work comprises three main research stages. The first stage focuses on comparing the structural and rheological properties of the DASP fraction extracted from two plant sources: apples (Malus domestica Borkh.) and carrots (Daucus carota subsp. sativus). In the next step, a series of enzymes degrading the RG-I region and chemical hydrolysis were used to obtain information about the impact of specific elements on the structure and properties of pectins. Finally, the impact of the DASP fraction on cell wall mechanics was examined by incorporating native and enzymatically modified DASP into plant cell wall analogues and mechanical testing of cell wall material (CWM) also modified enzymatically.

The research showed that the diluted alkali-soluble pectin fraction is rich in the RG-I domain, with its proportion being significantly higher in carrot samples than in apples. Carrot DASP contains significantly more rhamnose but less arabinose than apple DASP. The DASP pectin solutions from the two studied sources exhibit elastic properties, with the presence of arabinose favoring the formation of

stronger gels (apple DASP samples), while the presence of rhamnose may be associated with greater resistance to mechanical deformation (carrot DASP

samples). It was demonstrated that arabinose in the RG-I side chains participates in the formation of the pectin network and affects the pseudoplastic properties and viscosity of DASP pectin solution. A significant increase in chain length after the removal of arabinose suggests that in certain conformations, they may limit the interactions of polymer chains. The insertion of rhamnose, the presence of arabinose attached to rhamnose, and the degree of acetylation arestructural parameters of the RG-I domain responsible for the differences in rheological properties of DASP pectin solutions derived from apple fruits and carrot roots. Rheological studies showed that the viscosity of DASP pectin solutions decreases with the degree of degradation of the RG-I domain and depends proportionally on molecular weight. The decrease in viscosity was accompanied by the formation of polymers with shorter chains but a high degree of linearity due to acid hydrolysis or the formation of polymers with a linear character due to selective enzymatic degradation of the RG-I domain. Mechanical studies, on the other hand, showed that the DASP fraction pectins, rich in RG-I, play a significant role in the mechanical properties of the plant cell wall. The degradation of the RG-I domain by means of depolymerization of the Rha-GalA main chain and the degradation of arabinose chains attached to rhamnose, cause a reduction in the Young's modulus of both the natural cell wall and cellulose-based bacterial cell wall analogues.

Keywords: pectins, DASP, rhamnogalacturonan I, AFM, enzymatic modifications, rheological properties, cell wall.