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FTIR studies of gluten matrix dehydration after fibre polysaccharide addition

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ABSTRACT

FTIR spectroscopy was used to determine changes in secondary structure, as well as water state, in gluten and model doughs supplemented by four fibre polysaccharides (microcrystalline cellulose, inulin, apple pectin and citrus pectin). The gluten and model doughs were obtained from commercially available wheat gluten and model flour, respectively. The polysaccharides were used in five concentrations: 3%, 6%, 9%, 12% and 18%. Analysis of the FTIR spectra indicated that polysaccharides could be divided into two groups: first – microcrystalline cellulose and inulin, second – apple and citrus pectins that induced opposite structural changes. Changes in secondary structure concern mainly β-sheets and β-turns that form aggregated β-structures, suggesting dehydration of the gluten matrix as a result of competition for water between gluten proteins and polysaccharides. Moreover, the positive band at ca. 1226 cm^{-1} in the spectra of pectin-modified samples indicates formation of 'ether' type hydrogen bonds between gluten proteins and pectins.

1. Introduction

Among wheat proteins, gliadins and glutenins (gluten proteins) are the most important because they participate in formation of viscoelastic network called gluten in dough. Structure of gluten proteins is strictly connected with the wheat dough and bread quality. Changes in the structure of gluten proteins may be caused by different additives like dietary fibre preparations (Nawrocka, Miś, & Niewiadomski 2017; Nawrocka, Miś, & Szymańska-Chargot, 2016; Nawrocka, Szymańska-Chargot, Miś, Kowalski, & Gruszecki, 2016; Nawrocka, Szymańska-Chargot, Miś, Wilczewska, & Markiewicz, 2016; Nawrocka et al. 2015), hydrocolloids (Correa, Ferrer, Anon, & Ferrero, 2014; Linlaud, Ferrer, Puppo, & Ferrero, 2011; Secundo & Guerieri, 2005; Xuan et al., 2017; Zhou et al., 2014), emulsifiers (Ferrer, Gomez, Anon, & Puppo, 2011; Gomez, Ferrer, Anon, & Puppo, 2013) etc. Observed structural changes concern secondary structure, conformation of disulphide bridges, environment of two aromatic amino acids (tyrosine and tryptophan) and populations of water. As for the secondary structure, formation of aggregates or aggregated β-structures in the form of parallel or antiparallel-β-sheets connected by inter- and/or intramolecular hydrogen bonds have been observed. Disulphide bridges change conformation from gauche-gauche-gauche (energetically stable) into trans-gauche-gauche and trans-gauche-trans (less energetically stable). Tyrosine and tryptophan residues become buried forming intramolecular H-bonds within the protein complex. All these structural changes indicate aggregation or abnormal folding of the gluten proteins as a result of wheat dough supplementation by dietary fibre preparations (Nawrocka et al., 2015; Nawrocka, Szymańska-Chargot, Miś, Kowalski, et al., 2016; Nawrocka, Szymańska-Chargot, Miś, Wilczewska, et al., 2016; Nawrocka, Miś, & Szymańska-Chargot, 2016). In addition, analyses of water populations revealed decrease in the number of strong and weak hydrogen bonds between gluten proteins and water molecules and lack of the free water in the gluten network (Nawrocka, Miś, & Niewiadomski, 2017).

The structural changes observed after wheat dough supplementation by dietary fibre preparations and hydrocolloids probably result from dehydration of gluten networks. The dehydration is regarded as an effect of competition for water between gluten proteins and polysaccharides that is connected with redistribution of the water in the wheat dough (Bock & Damodaran, 2013). This hypothesis has been confirmed by Xuan et al. (2017) and Nawrocka, Miś, & Niewiadomski (2017). In the first studies, hydroxypropylmethylcellulose was used to show decrease in the water mobility in wheat dough and a weakening of the gluten network in the conditions of higher water mobility. Supplementation of the model (gluten-starch) dough by dietary fibre preparations in the second studies caused a decrease in the amount of strong and weak hydrogen bonds between gluten proteins and water molecules which are necessary to obtain gluten network of proper structural and viscoelastic properties. Thus, the aim of the present studies was to determine how supplementation of gluten and gluten-

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starch (model) dough with fibre polysaccharides, characterized by different water holding capacity and water solubility, affect secondary structure and water populations in gluten network by using Fourier transform infrared spectroscopy (FTIR). Microcrystalline cellulose, inulin, apple pectin and citrus pectin were chosen to use in the studies because they are regarded as main components of the dietary fibre preparations. Moreover, TGA and DSC studies (Nawrocka, Szymańska-Chargot, Miś, Wilczewska, & Markiewicz, 2017a, 2017b) showed interactions between gluten proteins and the polysaccharides and hence another aim was to show that not only had dehydration of gluten networks taken place during the mixing process but there are also observed interactions between particular dough components. Two kinds of doughs (model and gluten dough) were used in the present studies to prove whether the starch protect the gluten proteins against undesirable structural changes.

2. Materials and methods

2.1. Materials

Wheat gluten, microcrystalline cellulose (MCC), inulin (IN), sodium chloride were purchased from Sigma-Aldrich (Poland) and used as received. Wheat starch was purchased from Cargill (The Netherlands). Apple pectin (AP) and citrus pectin (CP) were received from Herbstreith & Fox KG (Germany). According to the manufacturer certificates, degree of esterification and galacturonic acid content are 68% and 79%, respectively, for apple pectin, and 71% and 87%, respectively, for citrus pectin. Double-distilled water was used for all experiments.

2.2. Gluten dough (GD) – Polysaccharide sample preparation

Gluten dough – polysaccharide (microcrystalline cellulose, inulin, apple and citrus pectin) samples were prepared according to the procedure described by Nawrocka, Szymańska-Chargot, Miś, Kowalski, et al. (2016). Briefly, 7-g sample of the gluten – polysaccharide mixture with 8 ml of 2% aqueous solution of NaCl were mixed for 3 min in the vibrating kneader SŻ-1 (Sadkiewicz Instruments, Bydgoszcz, Poland). The polysaccharides contents were 3%, 6%, 9%, 12% and 18% w/w in relation to the gluten – polysaccharide mixture weight (at the same moisture basis equal 14%).

2.3. Model dough (MD) – Polysaccharide sample preparation

The model dough – polysaccharide samples were prepared according to the method described by Nawrocka et al. (2017b). Briefly, a model flour, which was reconstituted from two commercial components: wheat starch and wheat gluten in a constant weight proportion 80:15 (at the same moisture basis), was used in the present studies. The pure wheat gluten was applied to provide gluten proteins of definite structure. The polysaccharides contents and the samples preparation method were the same as in the case of gluten dough – polysaccharide samples. In the case of samples modified by apple and citrus pectins, there were prepared samples with only 3 and 6% content of the pectins. The higher contents of pectins caused problems with washing out of the gluten that became unextractable.

2.4. Gluten sample preparation to the FTIR measurements

The gluten samples were washed out from unmodified and modified by polysaccharides gluten dough and model dough samples using Glutomatic 2200 (Perten Instruments, USA) according to the standard procedure ICC 155. The gluten was washed out to get rid of starch and polysaccharides, which did not react with gluten proteins, from both doughs and to provide the same experimental conditions. Next, gluten samples were freeze-dried for 24 h and pulverized.

Freeze-dried gluten samples were prepared for FTIR measurements according to the method described by Nawrocka, Miś, & Niewiadomski (2017). Briefly, after pulverizing, gluten samples of definite weight were moisturized by 10% aqueous solution of deuterium dioxide (D_2O) for five hours. The gluten samples were weighed before and after humidification to determine whether the samples absorbed the D_2O solution. Increase in the sample weight and presence of the IR band at 2485 cm^{-1} indicated absorption of the D_2O solution. The samples were moisturized by the D_2O solution to get rid of the water bands especially from amide I band.

2.5. Fourier transform infrared (FTIR) spectra collection and data manipulation

The FTIR spectra were recorded with a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Madison, WI, USA) equipped with a diamond attenuated total reflectance (ATR) attachment. The FTIR spectra were recorded between 4000 and 400 cm^{-1} at 4 cm^{-1} intervals. Each spectrum resulted from 128 scans to obtain optimal signal-to-noise ratio. Each spectrum was corrected with a linear baseline using OMNIC (v.8.2, Thermo Fischer Scientific Inc., Madison, WI, USA). The analysed spectra were averaged over five registered spectra. All spectra were normalized at the band of D_2O (2485 cm^{-1}). A spectrum of 10% aqueous solution of D_2O (treated as an internal standard) was subtracted from all samples spectra to obtain difference spectra in the OH stretching region (2500–4000 cm^{-1}) according to Nawrocka, Miś, & Niewiadomski (2017).

Structural analysis of the amide I band (1570–1720 cm^{-1}), amide III band (1200–1340 cm^{-1}) and OH stretching region (2500–4000 cm^{-1}) was conducted by using ORIGIN (v.9.0 PRO, OriginLab Corporation, USA). The secondary structure from the amide I and amide III bands were assigned according to Pelton and McLean (2000) and Cai and Singh (1999), respectively. To determine changes in secondary structure of gluten proteins the difference spectra were calculated in both amide I and amide III bands. A spectrum of gluten washed out from gluten or model dough (control samples) was subtracted from spectra of gluten – polysaccharide or model flour – polysaccharide mixtures, respectively. All spectra were field-normalized in the amide I and amide III regions.

3. Results and discussion

3.1. Amide I band (1520–1720 cm^{-1})

Deconvoluted amide I band of the control samples (gluten proteins washed out from the gluten and model dough) are presented in Fig. S1 in the Supplementary Material. Both spectra are deconvoluted by three Gaussians with maxima at 1619, 1650 and 1678 cm^{-1} that can be assigned to β-sheets (βS), α-helix (αH), and β-turns (βT), respectively. The secondary structure of both control samples contains approximately 45% of β-sheets, 44% of α-helix and 11% of β-turns. Similar results were obtained by Nawrocka, Miś, & Niewiadomski (2017) who reported the same modifications induced by dietary fibre preparations.

Difference spectra of the amide I region as effects induced by fibre polysaccharides are shown in Fig. 1. Panels a and c of Fig. 1 present the interactions between MCC and IN, respectively, and gluten proteins in the gluten dough. All difference spectra show four negative bands at 1665, 1676, 1685, and 1695 cm^{-1} that can be assigned to hydrogen bonded β-turns, non-hydrogen bonded β-turns and/or antiparallel-β-sheets, and hydrogen bonded antiparallel-β-sheets (the last two), respectively (Secundo & Guerieri, 2005). The number of these structures slightly decreases with increasing content of the MCC and IN. Differences in the bands position are observed in the spectral region 1570–1650 cm^{-1} and depend on the polysaccharides' concentration. Generally, if there are present positive bands at 1622 (H-bonded β-sheets), 1630 (β-sheets) and 1648 cm^{-1} (β-turns/α-helix/random coils), the negative band at 1593 cm^{-1} (hydrated β-sheets and/or