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Dehydration of gluten matrix as a result of dietary fibre addition – A study on model flour with application of FT-IR spectroscopy

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ABSTRACT

Nowadays, consumers demand dietary fibre-enriched products of appropriate taste, texture, smell and appearance. Unfortunately, addition of the dietary fibre supplements to bread significantly reduces its quality which is connected with changes in the structure of gluten proteins. Structural changes as well as changes in the water state of gluten matrix induced by eight dietary fibres were observed by using Fourier transform infrared spectroscopy. To facilitate this the difference spectra were calculated by subtraction of the control (gluten only) infrared spectrum from the spectra of gluten-fibre mixtures. The presence of positive bands at ca. 1597 and 1235 cm^{-1} indicated aggregation of gluten proteins into hydrogen bonded β-sheets. These β-sheets can be formed by other β-sheets, antiparallel-β-sheets, β-turns and/or α-helices. The aggregation is probably induced by partial dehydration of gluten matrix due to competition for water molecules between gluten proteins and fibre polysaccharides. This assumption is confirmed by the presence of the negative band at 3237 cm^{-1} and decrease in the intensity of the band at 3051 cm^{-1}. These bands are assigned to the weak and strong H-bonds in the gluten matrix, respectively. The results indicated that both weak and strong H-bonds are necessary to dough formation of adequate rheological properties.

1. Introduction

Gluten proteins, gliadins and glutenins, form a continuous, viscoelastic network within dough. Glutenin polymers are made up of high and low molecular weight subunits that are attached to each other via disulphide bonds, whereas gliadins interact with the glutenin polymers via noncovalent hydrophobic interactions and hydrogen bonds. Structural analysis shows that a dominant structure for a native gluten and gliadin fraction is α-helix, whereas antiparallel-β-sheets and β-turns are characteristic for glutenins (Wellner et al., 2005). Structure of the gluten proteins is strictly connected with the dough and bread quality. Glutenins provide strength and elasticity for bread dough development whereas gliadins impart viscosity to dough (Sivam et al., 2012).

To study structure of the gluten proteins spectroscopic techniques such as Fourier transform Raman spectroscopy (FT-Raman) and Fourier transform infrared spectroscopy (FT-IR) are used. These two spectroscopic methods are regarded as complementary. The FT-Raman spectroscopy gives information about secondary structure (amide I band), tertiary structure (disulphide bridges) and environment of the aromatic amino acids – tyrosine and tryptophan (Nawrocka et al., 2015). FT-Raman spectroscopy was applied to study interactions between emulsifiers (e.g. sodium stearyol lactylate and diacetyl tartaric acid esters of monoglicerides) and the gluten network in the dough (Gomez et al., 2013). The emulsifiers induced an increase in α-helix conformation and a decrease in β-sheet, β-turns and random coil. This behaviour was also confirmed by changes in stretching modes of disulphide bridges, low exposure of tyrosine residues, and low burial of tryptophan residues to a more hydrophobic environment. Sivam et al. (2013) used both FT-Raman and FT-IR spectroscopy to study influence of pectin and polyphenols extracts on gluten structure in bread. Results showed that adding these compounds caused an increase in the β-sheets content at the expense of β-turns, and an increase in unordered structures especially in the presence of berry polyphenols. Both hydrophobic and hydrogen bonding interactions occurred among bread components and the added pectin and polyphenols. Sivam et al. (2012) also studied an effect of the polyphenols and pectin

Abbreviations: αH, α-helix; APL, apple fibre; βS, β-sheet; βT, β-turns; CAC, cacao fibre; CAR, carob fibre; CHB, chokeberry fibre; CRB, cranberry fibre; CRR, carrot fibre; FLX, flax fibre; OAT, oat fibre.

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on the gluten proteins but in the model systems simulating real finished breads by using FT-IR spectroscopy. The studies showed that all components used as bread constituents influenced the conformational changes in gluten proteins. The changes were evidenced from the associated alterations in the amide I and II bands. Infrared spectroscopy was also used by Seabourn et al. (2008) to examine changes in the secondary structure of gluten proteins during dough mixing. Analysis of the amide III band revealed an increase in contribution of α-helix, β-sheet and β-turn during mixing. Using FT-IR spectroscopy it can be studied not only secondary structure of the proteins but also the state of water in the dough. Studies of Bock and Damodaran (2013) showed that changes in relative hydrogen bonding properties and water mobility can be deduced from shifts of the OH stretching absorption band (3000–3800 cm^{-1}).

There are two main hypotheses describing worsening dough viscoelastic properties and bread quality as a result of dietary fibre addition. One of them implicates competitive water binding by the dietary fibre as a major factor affecting dough quality (Collar et al., 2007). The second one assumes that the addition of the dietary fibre physically disrupted the gas cells and gluten network (Gan et al., 1989). Bock and Damodaran (2013) combined these two hypotheses in one. The authors claimed that competitive water binding by dietary fibre may cause redistribution of moisture in wheat dough. This may result in partial dehydration of gluten, which may in turn cause conformational changes in gluten matrix. Thus, the objective of this study was to determine changes in the secondary structure of gluten proteins and the state of water in the gluten matrix as a result of addition of eight dietary fibre supplements.

2. Materials and methods

2.1. Materials

Wheat gluten and sodium chloride were purchased from Sigma-Aldrich and used as received. Wheat starch was purchased from Cargill (the Netherlands). Chokeberry (CHB), cranberry (CRB), apple (APL), carrot (CRR), cacao (CAC), oat (OAT), and flax (FLX) fibres were received from Microstructure (Warsaw, Poland). The carob fibre (CAR) was a natural extract produced from the carob pulp (Carob General Applications, Valencia, Spain). Double-distilled water was used.

2.2. Dough sample preparation

A model flour that was reconstituted from two commercial components: wheat gluten and wheat starch was used to study the gluten-fibre interactions. The pure wheat gluten was applied to provide gluten proteins of definite structure. The starch and gluten were combined in constant weight proportion 80:15 (at the same moisture basis). The simplified composition of the model flour was intentional because absence of the native fibre compounds in wheat flour facilitated to study structural changes in gluten proteins as a result of fibre fortification. For fortification purposes, commercial fibre preparations produced from various plants (fruits, vegetables, cereals etc.) were used. All studied fibre preparations were micronized to avoid influence of the non-uniformed distribution size of particles on gluten-fibre interactions. Fibre-flour blends were made by substituting 3, 6, 9, 12 and 18% w/w model flour by single fibre preparation (at the same moisture basis). Doughs from the model flour (Control) and fibre-flour blends with 2% w/w sodium chloride addition relative to the blend mass were kneaded for 5min. in 300-g mixer of a Farinograph-E (Brabender, Germany). Amount of added water was adjusted to optimal water absorption (500 FU).

2.3. Gluten sample preparation to the FT-IR measurements

The gluten samples were washed out from unmodified and modified by fibre dough samples by using Glutomatic 2200 (Perten Instruments, the USA). Next, gluten samples were freeze-dried for 24 h and pulverized.

After pulverizing, gluten samples of definite weight were moisturized by 10% aqueous solution of deuterium dioxide (D_2O) for five hours. The samples were put in the desiccator with a vessel with the D_2O solution. 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 the amide I band.

2.4. Fourier transform infrared spectra (FT-IR) collection and data manipulation

The FT-IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA) equipped with a diamond attenuated total reflectance attachment. The FT-IR 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 software (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 get rid of water bands according to Reszczynska et al. (2015). The difference spectrum is shown in Fig. 1.

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 FT-IR amide I and amide III bands was assigned according to Pelton and McLean (2000) and Cai and Singh (1999), respectively. To determine changes in secondary structure of gluten proteins (amide I and amide III bands) difference spectra were calculated. A spectrum of gluten washed out from model dough (Control) was subtracted from spectrum of gluten-fibre mixture. All spectra were field-normalized in the amide I and amide III region.

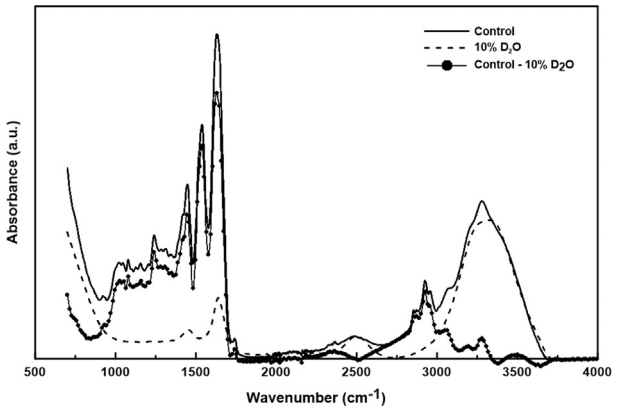

Fig. 1. Fourier-transform infrared spectra of control sample (solid line), 10% aqueous solution of D_2O (dashed line), and difference spectrum of these two (circles).