Food Hydrocolloids 85 (2018) 176–184

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Characteristics of the chemical processes induced by celluloses in the model and gluten dough studied with application of FTIR spectroscopy

Agnieszka Nawrocka*, Magdalena Krekora, Zbigniew Niewiadomski, Antoni Miś

Institute of Agrophysics Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin, Poland

ARTICLE INFO

Keywords:
Gluten network
Secondary structure
Water populations
Dehydration
FTIR
Celluloses

ABSTRACT

Fourier transform infrared spectroscopy (FT-IR) was used to study dehydration of the gluten network caused by supplementation of the model and gluten dough by celluloses differing in particle size and chemical structure. Wheat gluten and model flour reconstituted from wheat starch and wheat gluten was mixed with microcrystalline cellulose, Avicel microcrystalline cellulose PH 101 and PH 302, cellulose (20 μm) and 2-hydroxyethylcellulose in five concentrations: 3%, 6%, 9%, 12% and 18%. Analysis of the gluten dough – cellulose spectra shows bands connected with hydrated β-sheets (1594 cm^{-1}) and microvoids (3422 cm^{-1}) which indicate adequate hydration of the gluten network in the gluten dough. Contrary to gluten dough – cellulose, difference spectra of model dough – cellulose shows signs of gluten dehydration e.g. H-bonding in β-turns (1659 and 1665 cm^{-1}) and antiparallel-β-sheets (1683 cm^{-1}). Presence of the bands at ca. 1221 and 1313 cm^{-1} indicate incorporation of the celluloses into gluten network in the gluten and model doughs. Both phenomenon, incorporation of the celluloses accompanied by a decrease in their crystallinity as well as two-fold reduction of the water addition during preparation of supplemented doughs may contribute to the dehydration of gluten network.

1. Introduction

Gluten is a continuous, viscoelastic network that form during dough mixing process. Gluten contain two kinds of proteins – globular gliadins and polymeric glutenins. Glutenins are made up of high and low molecular weight subunits that are attached to each other via disulphide bonds and form mainly β-structures (β-sheets and β-turns). Dominant structure for gliadins is α-helix and they interact with glutenins via hydrogen bonds and noncovalent hydrophobic interactions (Wellner et al., 2005). Glutenins may also contain some amount of α-helices, while gliadins may form β-structures. Structure of the gluten network is closely connected with dough as well as bread quality. Supplementation of the bread dough with different compounds e.g. dietary fibre preparation (Nawrocka, Szymańska-Chargot, Miś, Wilczewska, & Markiewicz, 2016b, 2016c, 2017c, 2015; Bock & Damodaran, 2013), polyphenols extracts (Sivam, Sun-Waterhouse, Perera, & Waterhouse, 2012, 2013), or emulsifiers (Gomez, Ferrer, Anon, & Puppo, 2013) disturbs structure of the gluten network, changes its mechanical properties and hence decreases quality of the bread.

Spectroscopic methods like infrared spectroscopy, Raman spectroscopy, UV-VIS spectroscopy and fluorescence are regarded to be a good tool to study changes in the structure of gluten network caused by different additives. Fluorescence, similar to FT-Raman spectroscopy, was used to determine microenvironment of two aromatic amino acids – tyrosine and tryptophan (Wang et al., 2017; Wong et al., 2012). UV-VIS spectroscopy is applied the most often to determine content of disulphide bridges and free sulfhydryl groups in the gluten proteins (Xuan et al., 2017). Fourier transform infrared spectroscopy (FT-IR) and Fourier transform Raman spectroscopy (FT-Raman) are used mainly to study secondary structure of the proteins by analysis of the amide I band (1570–1720 cm^{-1}). In the case of the FT-IR, amide III band is also used to study this structure since it does not contain water oscillations like amide I band. Additionally, FT-IR provides information about water populations in the bread dough (Bock & Damodaran, 2013), whereas FT-Raman spectra shows conformations of disulphide bridges (tertiary structure) and the way hydrogen bonds are formed by two aromatic amino acids – tyrosine and tryptophan within the gluten network (Nawrocka, Szymańska-Chargot, Miś, Wilczewska, & Markiewicz, 2017a,b). Both spectroscopic techniques have been used to study changes in structure of gluten proteins in dough and/or bread supplemented with different compounds. Gluten structure in bread supplemented by pectins and polyphenols extracts was studied by Sivam, Sun-Waterhouse, Perera, and Waterhouse (2013) with use of FT-IR as well as FT-Raman spectroscopy. Infrared spectroscopy was also

* Corresponding author.
E-mail address: a.nawrocka@ipan.lublin.pl (A. Nawrocka).

https://doi.org/10.1016/j.foodhyd.2018.07.020
Received 5 March 2018; Received in revised form 26 June 2018; Accepted 14 July 2018
Available online 17 July 2018
0268-005X/

used to examine changes in the structure of gluten network during dough mixing by analysis of amide III band (Seabourn, Chang, Seib, & Mathewson, 2008). Bread dough mixing was also studied with using 2D CORR analysis of the raw NIR and MIR spectra by Ait Kaddour, Mondet, and Cuq (2008). Wang et al. (2014) determined an effect of frozen storage on the secondary structure of gluten proteins by using FT-IR spectroscopy.

Our previous studies concerning effect of dietary fibre polysaccharides on the structure of gluten network in a model and gluten doughs have shown that water-insoluble (microcrystalline cellulose and inulin) and water-soluble (pectins) polysaccharides caused opposite structural changes concerning mainly β-sheets and β-turns that form aggregates or β-structures connected by intermolecular H-bonds (Nawrocka, Krekora, Niewiadomski, & Miś, 2018). Additionally, thermal analysis indicated incorporation of the polysaccharides into gluten network (Nawrocka et al., 2017a, b). The aim of the present studies was to determine effect of celluloses characterized by different size and chemical structure on structure of the gluten proteins and mechanism of their incorporation into gluten network in gluten and model doughs.

2. Materials and methods

2.1. Materials

Wheat gluten, microcrystalline cellulose (MCC), cellulose 20 μm (C20), 2-hydroxyethylcellulose ($M_V \sim 90\,000$) (HEC) and sodium chloride were purchased from Sigma-Aldrich (Poland) and used as received. Avicel microcrystalline cellulose PH 101 (C101) and PH 302 (C302) was received from FMC BioPolymer (Ireland). Wheat starch was purchased from Cargill (the Netherlands). Double-distilled water was used.

2.2. Gluten dough (GD)/model dough (MD) – celluloses sample preparation

Gluten dough-celluloses (GD-MCC, GD-C20, GD-C101, GD-C302 and GD-HEC) samples were prepared according to the procedure described by Nawrocka, Szymańska-Chargot, Miś, Kowalski, and Gruszecki (2016a). Briefly, 7-g sample of the gluten-cellulose 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).

Model dough was prepared from a model flour that was reconstituted from two commercial components – wheat gluten and wheat starch in a constant weight ratio 15:80 (Nawrocka et al., 2016b). The simplified composition of the model flour was intentional because absence of the other components (polysaccharides, fats) in wheat flour facilitated to study structural changes caused by celluloses. The model dough – celluloses samples (MD-MCC, MD-C20, MD-C101, MD-C302 and MD-HEC) were prepared in similar way as in the case of gluten dough – cellulose. Because of twice lower water absorption of the model flour relative to wheat gluten, the only difference was in adding the twice lower amount of NaCl solution (4 mL) to prepare model dough. The celluloses contents in both doughs were 3%, 6%, 9%, 12% and 18%. Each sample was prepared in triplicate.

2.3. Gluten sample preparation to the FT-IR measurements

The gluten samples were washed out from unmodified and cellulose-modified gluten/model dough samples by using a Glutomatic 2200 (Perten Instruments, USA) according to the standard procedure ICC 155. 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 sample 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.

2.4. FT-IR spectra 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 (ATR) 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 (v.8.2, Thermo Fischer Scientific Inc., Madison, WI, USA). The analysed spectra were averaged over five registered spectra. The FTIR spectra of model doughs supplemented with 18% of C-20, C302 and HEC were not recorded because of difficulties with washing out the gluten from the model dough (unextractable gluten).

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 oscillations from amide I band and to obtain difference spectra in the OH stretching region (2500–4000 cm^{-1}) according to Nawrocka, Miś, and Niewiadomski (2017c).

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 – celluloses or model dough – celluloses mixture, respectively. All spectra were field-normalized in the amide I and amide III regions.

2.5. Determination of cellulose crystallinity index (CI) from FT-IR spectra

Crystallinity index (CI) of the studied celluloses was determined as the ratio of the bands' intensities at 1427 and 895 cm^{-1} (I(1427)/I(895)) according to O'Connor, Dupre, and Mitcham (1958). The CI ratio was calculated for both pure celluloses and celluloses in gluten and model doughs. Difference spectra were calculated in the case of both doughs. All FT-IR spectra after subtraction of D_2O spectrum were normalized against amide I band at 1630 cm^{-1}, which is the most intense band, using ORIGIN (v.9.0 PRO, OriginLab Corporation, USA). In order to obtain difference spectra, spectrum of the control sample (gluten washed out from the dough) was subtracted from the spectra of cellulose-modified gluten proteins.

2.6. Statistical analysis

The significance of the differences between the CI values was estimated using one-way analysis of variance (ANOVA) followed by Tukey's test ($\alpha = 0.05$). In all tables the results are presented as means with standard deviations of five replications.

3. Results and discussion

3.1. Characteristic of the studied celluloses

According to the manufacturer certificates, four studied celluloses (MCC, C20, C101 and C302) differ in the average particle size. MCC is a mixture of particles characterising whole volume range, whereas the average particle size for C20, C101 and C302 is 20, 50 and 90 μm. For all studied celluloses, the crystallinity index (CI) as the ratio I(1427)/I(895) was calculated. According to O'Connor et al. (1958), the bands at 895 and 1427 cm^{-1} can be assigned to crystalline and amorphous cellulose, respectively.

The crystallinity indexes for the pure celluloses are presented in