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Mechanical, microstructure and permeability properties of a model bread crust: Effect of different food additives

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ABSTRACT

The aim of this study was to understand the action of different additives on the crust properties using a layer crust as a model. Moisture content, water vapor barrier properties, water sorption isotherms and mechanical properties were evaluated. Crust model showed multilayer internal structure. Glycerol (10% and 20%) and HPMC-10% increased moisture content, whereas linolenic acid and beeswax, glycerol-1%, HPMC-0.5% and citric acid significantly decreased it. Water vapor permeability (WVP) decreased with lipids and citric acid, due to their hydrophobic nature and crosslinking action, respectively. Hydrophobic additives lowered the WVP of the crust and provided water barrier properties and brittle texture. Crust mechanical properties were greatly correlated with water present as well as with composition of crust layer. Barrier properties of the crust layer were greatly dependent on the hydrophilicity or hydrophobicity of the additives, which determined the internal interactions between starch and proteins and the microstructure and mechanical properties.

1. Introduction

Crusty breads are much appreciated due to their crispy texture. Crust is the upper part of the breads formed during baking. Crust is constituted by a network comprising denatured gluten proteins and partially gelatinized starch granules. Different concepts have been applied to define the crust, e.g. dry, hard, dark and dense (Hug-Iten et al., 2003). In fresh state, bread crust is dry and crispy and exhibits a brittle noisy fracture, but those properties are transitory and change during staling (Gray and Bemiller, 2003), owing to the steady increase in water content and water activity (Cuq et al., 2003). Water acts as a plasticizer and decrease the bread Tg of the material. As a consequence, the mechanical properties of the crust associated to crispness changes and the crust becomes very soft and leathery (Roudaut et al., 1998), which cause consumer's rejection. Therefore, bread crust must have low moisture content (3–11.5% d.b.) and water activity (0.34–0.57) to keep its crispy texture (Cuq et al., 2003). Water uptake kinetic is strongly related to crispiness retention of composite products consisting of a dry crispy part and a more humid and soft part (Meinders and Van Vliet, 2011). Besides, water uptake is usually described by sorption isotherms and several mathematical models have been described for fitting sorption curves. Nevertheless, no approach has been presented considering the crust as a physical barrier and its diffusivity properties.

In addition, the composition of the product, morphology and crust thickness also play an important role in crispy texture perception. Some studies have been focused on strategies for prolonging the bread crust crispiness. With that purpose, enzymes (proteases, transglutaminase, *alpha*-amylase, amyloglucosidase and glucose oxidase) have been sprayed onto dough or bread crust surface (Primo-Martín et al., 2006; Primo-Martin et al., 2008; Altamirano-Fortoul et al., 2014). Those enzymes modified the starch–protein network, which had effect on the water holding capacity of the crust and in turn on the crispy texture behavior and cellular structure of crust. The potential of other additives has not yet been considered.

According to previous studies, crust acts as a barrier for water migration. Primo-Martin et al., 2009 proposed a crust model consisting on a very thin bread to discriminate between the fracture properties of the crust material and the gradient of water in the crust. However, the crust of the bread is not at equilibrium, because it is a complex system in which different reactions as well as changes in water activity/content occur during breadmaking. Considering that crust is a vitreous surface layer, in this study a model bread crust (crust layer) was developed using pregelatinized flour to simulate the bread crust. The aim of the present

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study was to investigate the effect of different bakery's additives (hydroxypropylmethylcellulose, vital gluten, diacetyl tartaric acid ester of mono-diglycerides, a protease from *Bacillus licheniformis* (Alcalase 2.4 LFG, 2.4 units/g), beeswax, linolenic acid, glycerol and citric acid), on water vapor permeability (WVP), water diffusion, mechanical properties and structure of the model crust layer.

2. Materials and methods

2.1. Materials

Pre-gelatinized wheat flour, provided by Harinera Villamayor (Huesca, Spain), was used for crust layer formulations. The wheat flour composition was (expressed as dried basis): 10.54% protein content, 10.91% moisture content, 1.03% fats and 0.58% ash content. Additives studied included hydroxypropylmethylcellulose (HPMC K4 M) from Dow Chemical (USA), vital gluten provided by Roquette (Keokuk, IL), diacetyl tartaric acid ester of mono-diglycerides (DATEM, Panodan® AB 100 VEG-FS KOSHER) from Danisco (Spain), a protease from *B. licheniformis* (Alcalase 2.4 LFG, 2.4 units/g) provided by Novozymes A/S (Bagsvaerd, Denmark), beeswax from Scharlau (Barcelona, Spain), linolenic acid provided by Sigma (Barcelona, Spain), glycerol and citric acid from Panreac (Barcelona, Spain).

2.2. Methods

2.2.1. Crust layer forming solution

Crust layer forming solutions were prepared using pre-gelatinized wheat flour blended with additives at different concentrations (Table 1) and in the presence of calcium propionate (0.1%, w/w) as preservative. All raw materials were mixed mechanically with water during 60 s and then were degassed. For beeswax based crust layer, the additive was suspended in 10 ml distilled water and boiled to mix it completely.

Crust layers were cast onto plastic trays (25.5 cm × 16 cm × 1.5 cm). In each case 134.20 g mixture was poured into each tray to minimize crust layer thickness variations. Preliminary tests were carried out to define the appropriate mixture amount for obtaining model crust of similar thickness to bread crust (~0.5 mm). Mixtures were allowed to dry at 37 °C for 12 h, after this time, drying continued at 20 °C for 39 h. Dried crust layers were stored in a desiccator containing saturated magnesium nitrate with 54.4% (RH) at 20 °C for further analysis. Conditions were selected to avoid microbial growing. Control crust layers were prepared in the same way without the presence of additives. Each crust layer formulation was prepared in duplicate.

Table 1
Additives concentrations applied in crust layer formulation.

Sample	Dosage % (w/w) flour basis
Control	–
Gluten	1
Protease	0.8
Hydroxypropylmethylcellulose (HPMC)	0.5
	10
Diacetyl tartaric acid ester of mono-diglycerides (DATEM)	0.3
Glycerol	1
	10
	20
Citric acid	1
Linolenic acid	0.3
Beeswax	0.3

2.2.2. Physicochemical analysis

Moisture content was determined following ICC standard method (1994) (ICC 110/1). Thickness of crust layers was determined using a digital micrometer (Mitutoyo, Kanagawa, Japan) with a sensitivity of 2 μm. The mean thickness was calculated from measurements taken at 10 different locations on each crust layer sample.

2.2.3. Water vapor permeability

Water vapor permeability (WVP) of the crust layers was determined according to the method ASTM E96 (ASTM, 1980). A cup having an internal diameter of 3.6 cm was filled with distilled water, sealed with the crust layer and then placed into different desiccators at 20 °C, and 54.4% RH. Changes in the weight over time were monitored to determine the steady state flux of water vapor through the crust layers. The cups were weighed every day during seven days.

2.2.4. Moisture sorption isotherms

Crust layer pieces of about 3 cm in diameter were transferred into a desiccator containing P_2O_5 to complete drying. Afterwards, crust layer specimens, in duplicate, were placed at 20 °C in desiccators containing saturated salt solutions with different relative humidity: $LiCl{\cdot}H_2O$ (11.3%), $KC_2H_3O_2$ (23.1%), $MgCl_2{\cdot}6H_2O$ (33.1%), $K_2CO_3{\cdot}2H_2O$ (43.2%), $Mg(NO_3)_2{\cdot}6H_2O$ (54.4%), NaCl (75.5%), KCl (85.1%), $BaCl_2{\cdot}2H_2O$ (91.2%) and K_2SO_4 (97.6%). Samples were weighed periodically till constant weight value was reached, where the equilibrium was assumed to be achieved. The experimental values were fitted by the GAB (Guggenheim–Anderson–deBöer) model

$$EMC = W_m Cka_w/[(1 - ka_w)(1 - ka_w + Cka_w)] \quad (1)$$

where EMC is the equilibrium moisture content on a dry basis, W_m represents the water content corresponding to saturation of all primary adsorption sites by one water molecule, and is called monolayer moisture content in BET (Brunauer, Emmett and Teller) theory, C is the Guggenheim constant, k refers to the factor correcting properties of the multilayer molecules corresponding to the bulk liquid, and a_w = water activity.

The root mean square (RMS, %) of the fitting is also included for each crust layer.

$$\%RMS = \left[\sqrt{\frac{\sum\left[\frac{M_{exp}-M_{cale}}{M_{exp}}\right]^2}{N}}\right] \times 100 \quad (2)$$

where N is the number of experimental points, M_{exp} is the experimental equilibrium moisture content value; M_{calc} is the calculated equilibrium moisture content value.

2.2.5. Mechanical properties: fracturability test

Crust layers were fractured using a texture analyzer with a 5 kg load (TA XTplus, Stable Micro Systems, Surrey, UK). Experiments were carried out using a HDP/BS blade set at 5 mm/s. The maximum force (N), the area (N/s), and the displacement at fracture (mm) were measured. Twenty replicates of each crust layer were conducted.

2.2.6. Microstructure

Structural analysis was performed by scanning electron microscopy (SEM) on samples. Crust layers were freeze-dried previously to the microscopy analysis. Crust layers were fixed with the aid of colloidal silver and then coated with gold (Baltec SCD005) at 10^{-2} Pa and an ionization current of 40 mA. The observation was