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Flow and foam properties of extruded maize flour and its biopolymer blends expanded by microwave

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ABSTRACT

Maize flour and blends from starch and zein biopolymers were processed as dense materials by extrusion (120 °C, 300 $J \cdot g^{-1}$) and press-molding (140 °C, 10 min) at a constant moisture content (26% wb), and then foamed by microwave heating. The mechanical properties of foams, determined by a 3-point bending test, were governed by density, in agreement with an open solid foam model. The density and 3D cellular structure of the foams were determined by X-ray tomography. In the same interval of density [0.15, 0.3 $g \cdot cm^{-3}$], foams from microwaved materials had a finer cellular structure than directly expanded materials at extruder outlet. The study of melt rheological behavior with Rheoplast® (100–160 °C, SME ≤ 200 $J \cdot g^{-1}$) showed that protein content (0–15%) did not affect shear viscosity but increased elongational viscosity. This trend, similar to the one reported for the storage modulus in a rubbery state, could be attributed to dissipative effects in a starch/protein interphase, explaining the difference of expansion between starch, blends and flour.

1. Introduction

Maize is one of the main cereals used for food consumption. Starch has often been considered as a model substrate for studying its changes during processing, especially under low moisture contents, and thus foresees its functional and nutritional properties. Its structure–property relationships have been well established now, even for severe processing conditions like extrusion. As a particular domain of interest, its rheological properties have been thoroughly studied and they might be used in designing foods as well as materials for plastic substitution (Xie, Halley, & Averous, 2012).

This latter application has triggered studies on starch blend morphology and mechanical properties (Yu, Dean, & Li, 2006), but more scarcely with other biopolymers coming from cereals. Among those, proteins, and precisely zein, the major maize protein, has deserved specific attention (Madeka & Kokini, 1996; Shukla & Cheryan, 2001) in order to predict its behavior, during extrusion or thermal molding. More recently, Ghanbarzadeh et al. (2006) and Gomez-Martınez, Altskär, and Stading (2012) have determined the rheological properties of zein resins blended with plasticizers, like sugars, glycerol, or citric acid and the mechanical properties of their films. These works have been achieved in thermal conditions where viscoelastic zein melts could be achieved (≤100 °C). Conversely, during cereal processing with low plasticizer contents, like extrusion, temperature reached much higher values, favoring zein aggregation (Batterman-Azcona & Hamaker, 1998). Under such conditions, Chanvrier, Colonna, Della Valle, and Lourdin (2005) envisioned the morphology of starch–zein blends like dense composite materials. This assumption allowed explaining their mechanical behavior in the glassy state, by interactions between the matrix (amorphous glassy starch) with particles (zein aggregates) (Chanvrier, Della Valle, & Lourdin, 2006). The brittle behavior of the composites was attributed to the lack of adhesion between amorphous starch and zein aggregates. Habeych, Dekkers, van der Goot, and Boom (2008) confirmed this interpretation by studying the morphology of starch/zein blends processed with a specific conic shearing device. Chaunier, Della Valle, and Lourdin (2007) considered these blends as model systems for maize flour, to interpret the mechanisms of creation of maize flakes. They related the texture of these foods to the mechanical properties of the blends.

However, the effect of zein and other ingredients from maize flour on the rheological properties of molten starch has not been fully understood. One of the reasons for this lack of knowledge has been the difficulty of performing experiments for determining rheological properties in relevant processing conditions, because of the low water content and the sensitivity of starch to mechanical treatment (Xie et al., 2012). Meanwhile, the importance of these properties, and especially of elongational viscosity, has been established for long in polymer processing, like stretching, film blowing and foaming (Dealy & Wissbrun, 1990). So there is a need to determine the effect of zein on the

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elongational viscosity of starch melts to better control the creation of cellular structure by extrusion.

Regarding starchy extruded foams, the impact of processing on cellular structure could be studied more precisely thanks to X ray tomography (Lim & Barigou, 2004). Indeed, using this technique, Babin, Della Valle, Dendievel, Lourdin, and Salvo (2007) found that extruded foams with more homogeneous cellular structure were obtained from starches having larger elongational viscosity. They have also shown that this difference of cellular structure could explain the deviation from the model of cellular solids, which relates the mechanical properties of the foam to their density (Gibson & Ashby, 1997). One of the difficulties in applying the model of cellular solids has been the knowledge of the constitutive material, i.e. the dense parietal material, of the foam. One way to overcome this difficulty is to prepare foams by expanding the well characterized dense material, by microwaves. Zhou, Song, and Parker (2006) applied this method for wheat starch and flours added with salt and plasticizer. They have found a general agreement with the cellular solid model, although they did not characterize the dense material. They also found a great variety of cellular structure, as indicated by scanning electron microscopy (SEM). More recently, Kaisangsri, Kerdchoechuen, and Laohakunjit (2014) have prepared solid foams from low moisture blends of cassava starch with zein by molding at 200 °C. The addition of zein induced a decrease of the foam compressive strength and an increase of density, with a little change of their cellular structure, qualitatively described by SEM. For both works, no attempt was made to link the foam density and cellular structure with the rheological properties of the blends. So, there is a need to better understand how the cellular structure of starch/zein foams was created and check whether these blends could be used as model systems for maize flour.

Given this context, the aim of this work was to determine how the structure of maize biopolymer foams was affected by the rheological properties of the blends in molten phase, and how it influenced the foam mechanical properties. In this purpose, materials from maize flour and starch–zein blends were extruded and expanded by microwave. Their resulting cellular structure was investigated by X-ray tomography, and their shear and elongational viscosities were determined for different protein contents and different processing conditions, using capillary rheometry with pre-shearing, simulating extrusion process.

2. Experimental

2.1. Materials

Maize starch (Roquette F-62 Lestrem, France) had an initial moisture content of 13.5% (total wet basis). Zein powder, the main maize protein (Fluka BioChemika, Germany), was a mixture of two alcohol-soluble polypeptides of molecular mass of 25,000 and 29,000 Da; it contained 4% moisture (wb) and 1% ashes. Maize flour (M.C. Technologies, F-63 Ennezat, France) had 13% moisture (wb) and a a protein content of 6.6% (db), determined by the Kjeldahl method, and starch content of 83% (db), whereas the remaining mainly contained lipids and fibers. Maize gluten meal, Glutalys®, noted CGM (Roquette Frère, F-62 Lestrem, France) was the co-product during starch separation by wet milling of maize, composed of 70.3% proteins, 16.3% of starch, and less than 10% of lipids and fibers.

5 and 15% zeins were added to starch to make blends, to be compared with flours, because materials processed from these blends had a mechanical behavior close to the one of materials processed from maize flour (Chanvrier et al., 2005). Another blend of flour with 4% zein was also prepared to match the total zein content of the 85/15 starch/zein blend. Finally another blend was prepared by adding 21% CGM to starch. The lists of the resulting samples are reported in Tables 1 and 2.

In the following, the word “blend” means the blend of two of these components, zein or CGM, mixed with starch or maize flour. For processing and capillary viscosity measurements, starch, maize flour and the blends were moistened at a moisture content MC = 26% (wb) by addition of the necessary amount of water, during blending in a lab mixer (capacity 3 kg) and left for equilibrating 72 h at 4 °C.

2.2. Processing and sample preparation

Extrusion has been used to prepare dense samples, under conditions close to common industrial processing ones, before expansion by microwave. Samples of maize flour, starch, blends, with a moisture content MC = 26% (total wet basis), were extruded using a Scamia single screw machine (Rheoscam, France) with a flat die ($50 \times 30 \times 1 mm^3$), at 110 and 120 °C, for 5 $g \cdot mn^{-1}$, leading to a specific mechanical energy SME close to 400 $J \cdot g^{-1}$, and apparent shear rate in the die close to 10 s^{-1}. Under these conditions, at 120 °C, the melt did not expand at die outlet, at bare eye, and starch was amorphous, as checked by DSC, and formerly by X-ray diffraction (Chanvrier et al., 2006).

Some starch–zein blends with a wide range of zein content (0 to 50%, w/w) were also prepared by press-molding, for 10 mn, at 140 °C, 20 MPa, for further analysis and testing expansion capacity.

Extruded and thermo-molded samples were then conditioned until equilibrium under constant relative humidity (RH = 59%) before further processing by microwave, and analysis.

2 g of each sample was expanded by microwave heating using a single wave guide at 2.45 GHz (MES Technologies, F-94 Villejuif) and applying constant power of 1 kW for 15 s. Absorbed energy was about 270 $J \cdot g^{-1}$ and temperature reached about 150 °C, as measured by

Table 1
Main results of rheometry obtained for corn starch and blends melts processed with moisture content = 26% on Rheoplast®. Uncertainty on rheological data, due to repetition of experiments (= pre-shearing treatment + viscometry), was lower than 10%.

Material	Temperature (°C)	Rotation speed (rpm)	Residence time (s)	Consistency K ($Pa \cdot s^n$)	Flow index n	Starch transformation Degree (%)
Corn flour	100	100	15	54,500	0.2	84
	126			47,400	0.14	96
	140			36,700	0.18	100
	160			32,700	0.18	100
	116	100	15	49,700	0.21	85
		200	30	32,550	0.20	94
	128	100	15	46,100	0.20	100
		200	30	30,700	0.21	100
Corn flour + zein 4%	116	100	15	46,000	0.26	85
	128			38,800	0.20	100
Starch	128	200	30	30,670	0.21	100
Starch/zein 95/5%				31,050	0.28	100
Starch/zein 85/15%				18,200	0.30	100