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Loss of crystalline structure and swelling kinetics of maize starch and flour granules in glycerol excess: The role of the envelope structure

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ABSTRACT

Temperatures of loss of crystallinity and kinetics of swelling in glycerol excess were investigated on various maize flours and starch. The increase of amylose content in flour leads to a more persistent "crystalline" structure. This appears more clearly in differential scanning calorimetry (DSC) than in loss of birefringence, because a significant portion of the starch structure does not come only from amylopectin crystallites but also from helical arrangements. The effect of heating rate on the loss of order and on the glycerol/starch interactions was highlighted. Granule swelling tests in glycerol excess confirmed that the melting of crystallites is not a sufficient condition for complete dissolution of the granule. The granule swelling takes place in two steps for flours containing amylose, and occurs largely after gelatinization due to the importance of the granule envelope. The strength of this envelope, due to the presence of networks including proteins, lipids and amylose, is different between standard maize flour and starch. Tests in presence of lauric acid highlight the role of lipids on the granule envelope strength. The change in the viscosity of the granule/glycerol suspension during gelatinization is explained by granule swelling and can be described by a Krieger–Dougherty equation.

1. Introduction

Starch gelatinization has been studied for a long time (Olkku and Rha, 1978; Donovan, 1979; Ratnayake and Jackson, 2006), essentially in water, but also more recently in other liquids, like glycerol (Liu et al., 2011), NMMO (Koganti et al., 2011, 2015) and ionic liquids (Liu and Budtova, 2013; Mateyawa et al., 2013 Mateyawa et al., 2013). Different methods were used to characterize gelatinization kinetics and mechanisms, like differential scanning calorimetry (DSC), optical and electron microscopy, birefringence, wide angle X-ray diffraction, light scattering, viscosity measurements. DSC is one of the most popular and was largely used to explore the phase transitions in starch/water systems (Wootton and Bamunuarachchi, 1979; Russell, 1987; Zanoni et al., 1995; Spigno et al., 2004; Sopade et al., 2004). Combinations of rheology and microscopy can also be used (Tan et al., 2008). It is reported that suspension viscosity increases during gelatinization, then reaches a peak and decreases (Eliasson, 1986; Yang and Rao, 1998; Yu et al., 2006). By studying starches of different botanical origins or with various amylose/amylopectin ratios, it was possible to evidence the strong influence of this parameter (Russell, 1987; Tester and Morrison, 1990; Cooke and Gidley, 1992; Jenkins and Donald, 1998; Fredriksson et al., 1998; Liu et al., 2006; Chen et al., 2007; Blazek and Copeland, 2008; Liu et al., 2011; Chen et al., 2011). It was shown that the amylose content is very influent on granule swelling in water excess. The granule size, the heating rate (Patel and Seetharaman, 2006) and the addition of fatty acids (Blazek and Copeland, 2009) can also change granule swelling kinetics. Theses fatty acids do not have the same interactions with maize starches of different amylose content (Chang et al., 2013). Some explanations of the differences in swelling kinetics regardless to the amylose content were proposed by Debet and Gidley (2006, 2007),). They evidenced the role of the granule envelope structure on the swelling behavior. This structure is due to a network made of proteins and V-type crystallites, resulting from helical arrangements of amylose chains. The recent development of plasticized starch/thermoplastic blends (St-Pierre et al., 1997; Rodriguez-Gonzalez et al., 2003; Li and Favis, 2010), based on ternary starch/glycerol/water mixtures, recently led to the study of starch gelatinization in such media (Forssell et al., 1997; Nashed et al., 2003; Tan et al., 2004; Li et al., 2008; Liu et al., 2011). If the gelatinization of starch is well documented, it is less the case for flours. However, from an economic point of

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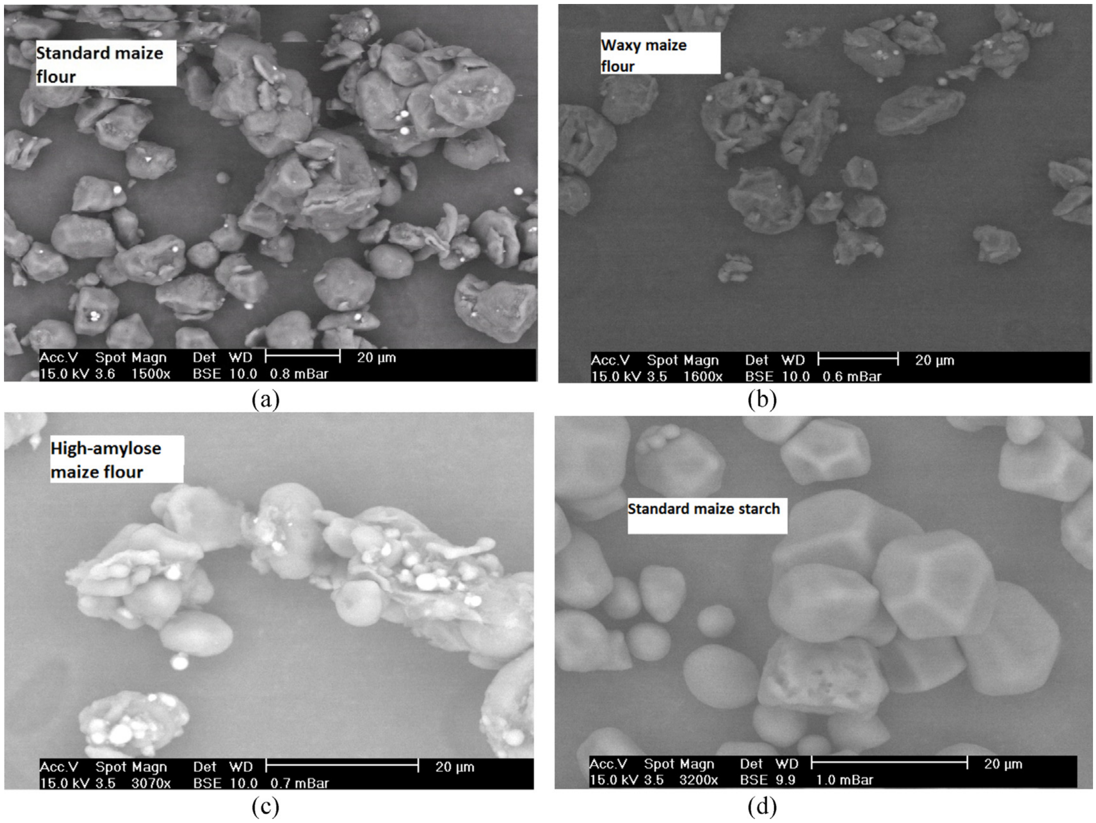

Fig. 1. SEM micrographies of the pristine granules. (a) standard maize flour, (b) waxy maize flour, (c) high amylose maize flour, (d) standard maize starch. The white spots on the flour pictures correspond to minerals (calcium, magnesium, phosphorus) (0.5–1.3 wt% on dry basis).

view, flour is less expensive than starch to be used in blend with a thermoplastic. Consequently, it is also interesting to look at flours behavior. Therefore, in the present study, we propose to characterize the mechanism of starch and flour gelatinization in glycerol suspensions, and to evaluate the swelling kinetics of starch and flour granules with different amylose/amylopectin contents in pure glycerol.

2. Materials and methods

Four starchy products, kindly provided by ULICE (Riom, France), were investigated in this study: three maize flours (standard, waxy, high amylose) and a standard maize starch. SEM pictures of these materials are shown in Fig. 1 and their main characteristics are given in Table 1. They differed either by the variety and/or the treatment, e.g., extraction of fats and proteins for the starch. The three varieties of maize flour essentially differed by their respective ratio of amylose and amylopectin: the waxy maize contained less than 1 wt% amylose (dry matter), whereas standard maize contained about 30 wt%, and high amylose maize (or amylomaize) 70 wt%. The initial water content was also different for the various starchy products: it varied from 8.4 wt% (waxy flour) to 12.3 wt% (standard starch). This initial water content was not modified during trials in glycerol excess. Experiments at the same water content may have been of interest, but were not carried out in the present study. Storage in closed bags of the samples in a freezer allowed to avoid changes in water content. It was effectively checked that the storage did not modify the water content. The global gelatinization process in glycerol excess is assumed to be not affected by small variations of the water content. This is of course fully different from plasticization of starch at low glycerol content, where small variations of the water content have an important effect on the plasticization process and the product rheological behavior. The lipid content in flours was globally proportional to the amylose amount. The protein content was almost zero in standard starch whereas it was quite high in flours (around 9 wt%).

Glycerol was chosen as starchy phase plasticizer. Its melting temperature was 17 °C, it is boiling at 290 °C, but may begin to evaporate around 170 °C. It had a density of 1.26 and a viscosity of 1 Pa s at 25 °C.

Lauric acid was also used in the study. It is a mono-fatty acid, with a melting temperature around 45 °C. It has no double bond and can create complexes with amylose.

Table 1
Starchy products density and composition (in weight% of dry matter) Data provided by ULICE.

	Standard maize starch	Standard maize flour	Waxy maize flour	High amylose maize flour
Raw density (g/L)	1470	1407	1449	1420
Amylose (wt%)	30	30	1	70
Water (wt%)	12.27	8.76	8.39	9.44
Proteins (wt%)	0.4	8.33	9.16	9.8
Lipids (wt%)	0.92	2.9	1.66	5.49
Ashes at 900 °C (wt%)	0.06	0.9	0.53	1.29