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Structural characterization of complexes prepared with glycerol monoestearate and maize starches with different amylose contents

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ABSTRACT

Morphology and different structural features of V-amylose complexes prepared with different concentrations (1%, 2%, 3%) of glycerol monostearate (GMS) and normal maize (NMS), waxy maize (WMS), and high amylose maize (HAMS) starches were evaluated using X-ray diffraction, differential scanning calorimetry, scanning electronic microscopy (SEM), atomic force microscopy (AFM), and transmission electronic microscopy (TEM). There was inclusion complex formation between all starches and GMS regardless of emulsifier concentration, with exception of WMS-2%GMS and WMS-3%GMS samples. All of the inclusion complexes displayed a V-type crystalline pattern and endothermic dissociation peaks between 115 and 120 °C. They also displayed faceted crystalline structures with a tendency of the crystals to aggregate and form agglomerates of various sizes. TEM images of the complexes showed an aggregated strand structure interwoven with the GMS. Emulsifier and amylose quantities directly influenced complex formation. At high GMS concentrations, there was higher tendency of emulsifier to self-associate rather than form complexes with amylose.

1. Introduction

Amylose-lipid complexes, which are responsible for important functional interactions in food systems, can be found naturally in starch or formed during its gelatinization in the presence of lipids and/or emulsifiers (Putseys, Lambert, & Delcour, 2010). In native starch, the amylose-lipid complex is in an amorphous state, but its crystallization becomes possible when the starch is heated in water (Morrison, Law, & Snape, 1993). Meanwhile, complexing with added lipids requires amylose to be accessible and to have enough mobility to undergo conformational changes (Conde-Petit, Escher, & Nuessli, 2006), which result in a single, left-handed helix with a V-amylose crystalline pattern (Putseys et al., 2010).

The amylose-lipid complex can exist in two forms according to its complexing temperature. Type I is formed at a low complexing temperature (<60 °C) and presents a low dissociation temperature (<100 °C), while type II or semicrystalline is formed at high temperature (>90 °C) and has a high dissociation temperature (>100 °C) (Gelders, Vanderstukken, Goesaert, & Delcour, 2004). The type II complex displays V- conformation, while the type I has been described as amorphous (Galloway, Biliaderis, & Stanley, 1989). However, Gelders et al. (2004) showed a semicrystalline V-pattern for type I complexes analyzed with 10% moisture, while a very weak V-pattern was obtained when the complexes were wet. Indeed, the X-ray spectrum appears to be highly dependent upon the conditions in which it is obtained. Cheetam & Tao (1998) reported that hydration induces an increase in the degree of crystallinity of starch but does not change the transition of crystal type.

A distinction is made between the two possible type II amylose-lipid complexes based on their degrees of crystallinity. They are referred to as type IIa and IIb complexes. The type IIb has a melting temperature that is higher than that of the type IIa, but both melting temperatures are above 100 °C (Karkalas, Morrison, & Pethrick, 1995).

The structural and physicochemical characteristics of amylose-lipid complexes vary according to the types of lipids and starches involved and conditions under which the complex is formed. The amylose content and the chain length of starch, as well as fatty acid chain length and the thermal treatment conditions used in the process are important factors that determine the inclusion complex

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formation (Chang, He, & Huang, 2013a; Fanta, Felker, Shogren, & Salch, 2006; Seo, Kim, & Lim, 2015; Villwock, Eliasson, Silverio, & Bemiller, 1999; Zhou, Ren, Zhang, Yoo, & Lim, 2013). Starches with a high amount of amylose have more molecules available to interact with the lipid and allow more complexes to be formed while long amylose chains favor more crystalline and stable complex formation (Exarhopoulos & Raphaelides, 2012; Gelders et al., 2004; Seo et al., 2015; Zhou et al., 2013). However, conformational disorders may occur if the amylose chains are too long, resulting in faults in the crystal structure (Gelders et al., 2004, Putseys et al., 2010). On the other hand, the lipids with long chain length are best for complex formation because they allow more hydrophobic interactions with the interior of the helix (Kawai, Takato, Sasaki, & Kajiwara, 2012; Putseys et al., 2010; Tang & Copeland, 2007).

Amylopectin is limited in its ability to form V-type complexes due to its highly branched structure. However, long branch chains of this molecule can also form helices that have been shown to complex with lipids (Chang et al., 2013a; Eliasson, 1994; Villwock et al., 1999). Inclusion complex formation between amylopectin and lipids has been shown by differential scanning calorimetry, X-ray diffraction (Chang et al., 2013a; Garcia & Franco, 2015; Villwock et al., 1999), and light microscopy (Chang et al., 2013a). However, complexing between waxy starch and lipids is less easily discernible than in maize starches with high amylose contents (Chang et al., 2013a; Exarhopoulos & Raphaelides, 2012; Villwock et al., 1999).

Starch-lipid inclusion complexes have been characterized mainly by their thermal properties and crystallinity (Chang et al., 2013a; Chang, He, & Huang, 2013b; Exarhopoulos & Raphaelides, 2012; Vasiliadou, Raphaelides, & Papastergiadis, 2015; Zhang, Huang, Luo, & Fu, 2012). A few reports have also shown the structural characteristics of these complexes using microscopic techniques such as scanning electron microscopy (SEM) (Exarhopoulos and Raphaelides, 2012; Fanta, Felker, & Shogren, 2002; Fanta et al., 2006; Zabar, Lesmes, Katz, Shimoni, & Bianco-Peled, 2009; Zabar, Lesmes, Katz, Shimoni, & Bianco-Peled, 2010), atomic force microscopy (AFM) (Lalush, Bar, Zakaria, Eichler, & Shimoni, 2005; Lesmes, Cohen, Shener, & Shimoni, 2009; Zabar et al., 2010), and transmission electron microscopy (TEM) (Godet, Bouchet, Colonna, Gallant, & Buléon, 1996; Richardson, Kidman, Langton, & Hermansson, 2004). These techniques have been applied to help elucidate the attributes of V-amylose complexes on the micro and nano scales and may provide new information even to previously studied starch systems.

SEM has revealed V-amylose complexes as faceted crystalline structures or spherocrystalline particles (Fanta et al., 2002; Fanta et al., 2006; Zabar et al., 2009, 2010). Previous reports have shown amylose-fatty acid complexes that are organized in crystalline lamellae as spherulites, which tend to aggregate in a radial direction from a central nucleus (Fanta et al., 2002; Fanta et al., 2006; Zabar et al., 2010). The increase in the degree of unsaturation of the fatty acid may lead to the formation of poorly defined complexes and decrease their thermal stability (Zabar et al., 2009). On the other hand, Fanta et al. (2006) reported that besides the influence of the fatty acid structure on the amylose helix conformation, the experimental conditions are also important to control spherulite morphology. Lalush et al. (2005) have also reported that the experimental conditions for inclusion complex formation affect the shape, size, and structural organization of the complexes.

Lalush et al. (2005), Lesmes et al. (2009), and Zabar et al. (2010) analyzed V-amylose complexes in AFM and reported that they are submicron-sized spheroids organized into packed lamellae that form aggregates that are microscopic in size. These aggregates were understood to be comprised of small, ~50–100-nm spherulites in

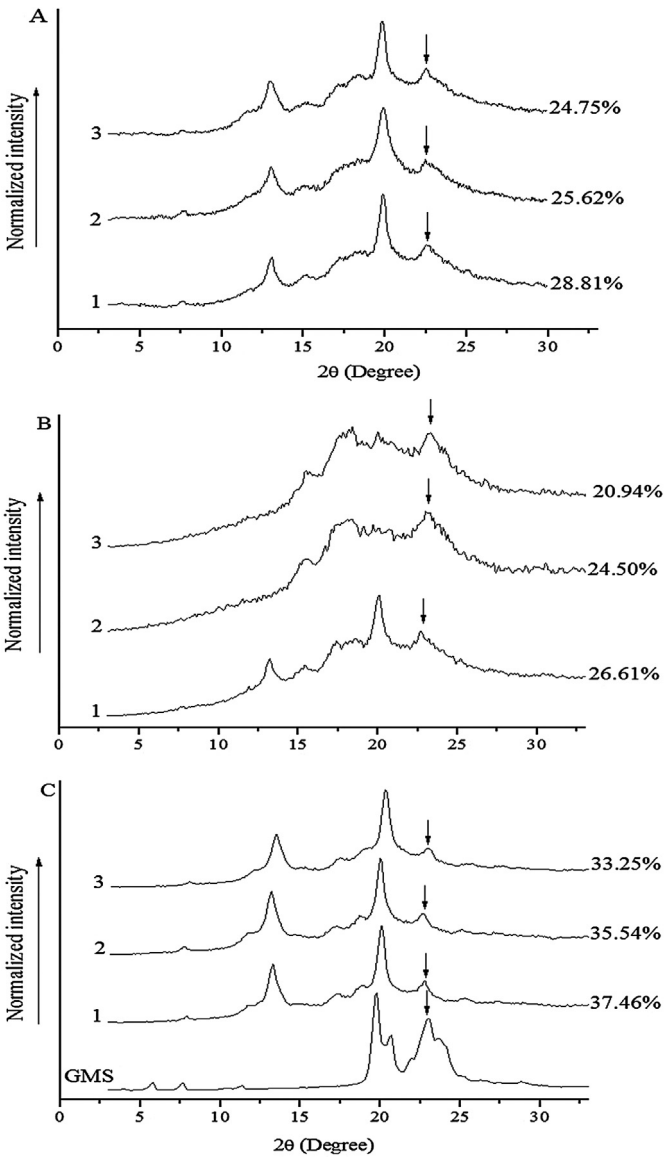

Fig. 1. X- ray pattern of the GMS, and X-ray pattern and relative crystallinity (%) of the starch-lipid complexes prepared with maize starches with different amylose contents and GMS in different concentrations: A: NMS, B: WMS, C: HAMS. (1): 1% GMS; (2): 2% GMS; (3): 3% GMS.

lamellae that are a few microns in length and ~10 nm thick, and a few other poorly-defined structures.

Morphology and the crystal thickness of amylose-fatty acid complexes were studied using TEM (Godet et al., 1996). Lamellar arrangements formed by the alternation of crystalline and amorphous areas were observed; the dimensions were found to be dependent on amylose DP and fatty acid chain length. Crystal thickness increased as the amylose and fatty acid chain lengths increased, reaching 4.5 nm. On the other hand, Richardson et al. (2004) investigated the effect of different kinds of emulsifiers on network formation and aggregation of amylose and starch gels using TEM. They observed that, at certain concentrations, the emulsifiers played an important role in amylose aggregation. The normal amylose network consists of thin strands. However, amylose was found to aggregate into thicker and more rigid strands at moderate emulsifier concentrations and to gather into unstructured, spherical aggregates at high emulsifier concentrations.

In a recent paper Garcia & Franco (2015) reported the effect of different glycerol monostearate (GMS) concentrations on both