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# Amorphous–amorphous phase separation in hydrophobically-modified starch–sucrose blends I. Phase behavior and thermodynamic characterization

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ABSTRACT

The glass transition of amorphous powders consisting of blends of octenyl-succinic anhydride (OSA) modified starch, and sucrose was studied as a function of blend composition and water content. Polarized light microscopy, differential scanning calorimetry (DSC) and water vapor sorption analysis were performed on four blends varying in their modified starch to sucrose ratio. The thermograms of the blends exhibit either a single glass transition event, characterized by a quite broad temperature range, or two glass transitions. This hints at a limited degree of phase separation into two amorphous phases within the blend matrix, most likely at the microscale. The results from dynamic water vapor sorption studies indicate that, in the phase-separated blends, the sucrose-rich phase constitutes the dispersed phase, while the continuous phase is formed by the phase rich in OSA starch. Our findings open up new ways to engineer glass encapsulation systems with composite structure, which can provide for a high level of protection of encapsulated bioactive compounds as well as defined release properties.



## 1. Introduction

The interest of the food and nutritional supplements industries in developing innovative products fortified with nutrients and other functional ingredients (Betoret, Betoret, Vidal, & Fito, 2011; Hasler, 2002; Parada & Aguilera, 2007) is growing, driven by the increased attention of consumers to their potential health benefits and promise to reduce the risk of diseases (Boon, McClements, Weiss, & Decker, 2010; Mohamed, 2014). The incorporation of bioactive compounds, such as vitamins and antioxidants, into food systems is made challenging by the need of matching several requirements that from a technological, market, safety, sensory and physiological point of view are often incompatible. For example, most bioactive molecules are poorly soluble in water, but in the majority of cases the target consumer products require water dispersible formulations (Williams et al., 2013). Additionally, the potential health benefits of such bioactives are often compromised by factors like lack of stability during processing and storage, as the bioactive compounds are often highly sensitive to temperature, oxygen and light, and low permeability and solubility within the gut (Salentinig, Sagalowicz, Leser, Tedeschi, & Glatter, 2011; Tedeschi, Clement, Rouvet, & Valles-Pamies, 2009; Wadsäter, Barauskas, Nylander, & Tiberg, 2014; Yeap, Trevaskis, & Porter, 2013). Several formulation and process technological approaches have been adopted to address these challenges. Especially the use of encapsulation systems has offered the possibility of both protecting and releasing in a controlled manner the often-sensitive bioactive ingredients depending on the compatibility properties of the bioactive and the desired application (Gibbs, Kermasha, Alli, & Mulligan, 1999; Garti, 2008; Madene, Jacquot, Scher, & Desobry, 2006; McClements, Decker, Park, & Weiss, 2008; Zuidam & Nedović, 2009).

In applications at low and intermediate water contents, a high level of protection can be achieved by encapsulating sensitive bioactives in matrices of low molecular-weight carbohydrates in the glassy state (Ubbink, 2016; Ubbink & Kruger, 2006). Carbohydrates in the glassy state specifically constitute very good barriers against the diffusion of gases, such as oxygen (Whitcombe, Parker, & Ring, 2005), nitrogen (Schoonman, Ubbink, MacInnes, & Watzke, 2002) and hydrophobic organic compounds (Flink & Karel, 1972). In

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addition, glassy carbohydrates can preserve and stabilize the conformations and structures of biomolecules, in particular proteins, peptides (Carpenter & Crowe, 1989; Crowe, Carpenter, & Crowe, 1998) and self-assembled surfactant complexes, during long-term storage in low-water content systems (Crowe et al., 1998; Crowe, Oliver, Hoekstra, & Crowe, 1997).

An important limitation of encapsulation systems based on glassy carbohydrates is that they are functional only at low water contents and concomitantly low water activities, as glassy carbohydrates are plasticized by water (Slade, Levine, & Reid, 1991). Upon increasing the water content beyond values corresponding to a water activity in the range of approximately 0.2–0.4 (depending on the composition of the carbohydrate glass), the barrier properties of the carbohydrate glass quickly diminish and the encapsulation system ceases to effectively protect the encapsulated bioactive ingredient (Ubbink, 2012). When the water content and water activity are further increased, the glassy matrix passes through the glass transition and becomes rubbery, and generally may be further diluted as to obtain a solution or aqueous dispersion (Roos, 1995; Ubbink, 2012). Glass encapsulation systems consequently offer little perspective for modulating the release of bioactives, as the fundamental trigger for the release of the encapsulated bioactive is water (Ubbink, 2012; Ubbink & Kruger, 2006).

The high sensitivity of glass encapsulation systems to water is related in a complex way to the physics of their matrices, as apart from the glass transition, the barrier properties of the matrix in the glassy state need to be considered. In the physics of amorphous carbohydrates, several relaxation modes are relevant for the behavior in both the glassy and rubbery states. The two most important ones, which are known as the α– and the β-relaxations, impact the behavior of amorphous carbohydrates, but in qualitatively different ways (Cicerone & Douglas, 2012; Slade & Levine, 1995). The α-relaxation, implied in global rearrangements of the matrix, arrests at the glass transition temperature. The β-relaxation may comprise multiple relaxations, collectively also known as the secondary relaxations.

The secondary relaxations include the Johari-Goldstein relaxation ($\beta_{JG}$) and γ-relaxation (Kaminski et al., 2009) or the "fast" β-relaxation ($\beta_{fast}$) (Cicerone & Douglas, 2012). These secondary relaxations bear on mobility modes in both the rubbery and the glassy state, which relate to highly localized, small movements and vibrations and generally shows an Arrhenius-type of temperature dependence. It is thought that these highly localized modes related to the secondary relaxations allow the migration of small molecular species, most importantly water and oxygen, through the glassy matrix.

For optimal barrier properties in the glassy state, the relaxation times of the secondary relaxations should thus be as long as possible. The common way to achieve this is by adding a significant fraction of low molecular weight compounds, so-called compatible solutes, to the encapsulation matrix (Cicerone & Douglas, 2012; Ubbink, 2016). These low molecular weight compounds give rise to a more densely packed matrix in the glassy state, which is likely to be one of the mechanisms by which the glassy-state dynamics are influenced (Ubbink, 2016). However, these low molecular weight compounds also significantly lower the glass transition temperature of the encapsulation matrix (Kilburn et al., 2004; Kilburn, Claude, Schweizer, Alam, & Ubbink, 2005; Roussenova, Murith, Alam, & Ubbink, 2010; Townrow, Kilburn, Alam, & Ubbink, 2007; Townrow, Roussenova, Giardiello, Alam, & Ubbink, 2010). Consequently, when developing glass encapsulation systems, a compromise needs to be found between optimal barrier properties in the glassy state, and the temperature and water content regime in which the encapsulation matrix is in the glassy state (Ubbink & Kruger, 2006).

Conversely, systems for the controlled release of bioactives are generally based on biopolymers and biopolymer complexes of intermediate and high molecular weight, often possessing surface-active properties, or on self-assembled lipid complexes (Garti, 2008; McClements et al., 2008; Risch & Reineccius, 1995; Williams et al., 2013; Zuidam & Nedović, 2009). These biopolymer and surfactant complexes are useful as controlled release systems as the release of the active can be made to sensitively depend on a number of triggers, such as temperature, ionic strength, pH and osmotic pressure (Garti, 2008; McClements et al., 2008). Since in addition they can be made not to dissolve in water, their surfaces can be modified for a targeted release, e.g. in the gastrointestinal tract (Garti, 2008; McClements et al., 2008).

Ideally, one would therefore design an encapsulation system, which has the flexibility with respect to the release mode of a controlled release system, combined with the protection offered by a glass encapsulation system. A possible avenue to realize this combined aim is to formulate systems showing amorphous–amorphous phase separation, in which the various phases exhibit distinct functionalities.

Systems exhibiting multiple, incompatible amorphous phases widely occur in foods and pharmaceutics. For instance, liquid emulsions of a hydrophobic ingredient encapsulated in a glassy carbohydrate are characterized by two amorphous phases, although in metastable states. Systems showing distinct amorphous phases separated by a first-order phase transition of a single component, so-called polyamorphous systems, have also attracted attention, but are not common in foods and pharmaceutics (McMillan, 2004; Poole, Grande, Angell, & McMillan, 1997). In addition, amorphous systems display a continuous spectrum of different realizations of the glassy state with variations for e.g. in density or specific heat (Hancock, Shalaev, & Shamblin, 2002). In the pharmaceutical area, significant efforts are being devoted to formulating poorly soluble drugs into what is designated as solid dispersions (Leuner & Dressman, 2000; Newman, Knipp, & Zografi, 2012). These solid dispersions, in which the drug is present in amorphous state in ideally a molecular mixture with the excipient, often show an enhanced bioavailability with respect to conventional formulations, containing the drug in crystalline form (Leuner & Dressman, 2000; Newman et al., 2012). Because of the often-disparate physico-chemical nature of the drug and the excipient, pharmaceutical solid dispersions tend to be sensitive to phase separation, initially into two amorphous phases, but subsequent crystallization of the drug in the dispersed phase is often observed (Rumondor, Wikstrom, Van Eerdenbrugh, & Taylor, 2011). Similarly, crystallization of one of the components in an amorphous–amorphous phase separated food system may be observed (Sun & Davidson, 1998).

In this paper, our approach is different. Although our aim is to use the phase-separated matrices for encapsulation of bioactive ingredients, we are at present not concerned by the physical state of the active. Conversely, we focus on the formulation of a multiphase amorphous matrix with specific encapsulation and release properties. We will explore the materials science basis for formulating such systems by blending a high-molecular weight amphiphilic carbohydrate, octenyl-succinic anhydride (OSA) starch with a disaccharide, sucrose.

Octenyl-succinic anhydride starch is a hydrophobically-modified starch (HMS), and is commonly used in the preparation of oil-in-water (O/W) emulsions of liquid hydrophobic active