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Effect of carbohydrate type on the DVS isotherm-induced phase transitions in spray-dried fat-filled pea protein-based powders

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ABSTRACT

The objectives of research were to investigate the moisture sorption behavior of twelve spray-dried fat powders using dynamic vapor sorption (DVS) adsorption isotherms at twenty-three values of water activity (a_w) within the range of 0.005–0.95 and at 25, 30 and 35 °C. The model fat powders were formulated with high vegetable oil content (solid below 28–30° palm/rape blend oils, or rape oil), and a constant carbohydrate-to-protein-component ratio. The DVS isotherms showed good consistency in determination of the moisture-induced phase transitions of amorphous carbohydrate components in fat powders. Powders made with Nutriose demonstrated a constant moisture adsorption rate up to the a_w value of ~0.7, without phase transition upon humidification. Powders with trehalose, inulin and polydextrose in the range of a_w 0.3–0.7 went through a glass transition and most likely crystallized. It seemed that with more solid fat in powders, there was higher water activity and moisture content to induce phase transitions.

1. Introduction

Fat powders and microencapsulated oils have found broad applications in various fields. Recently, comprehensive reviews on microencapsulation techniques and application of encapsulated marine, vegetable, omega-3 and essential oils in various food and pharmaceutical products have been reported in the literature (Bakry et al., 2016; Rodríguez et al., 2016; Kaushik et al., 2015). Spray drying is the most commonly used technique for the encapsulation of bioactive oils and mixtures of different oils (Lee and Ying, 2008; Bakry et al., 2016). Industry has strong interest in manufacturing through spray drying both stable bioactive oil powders and drying several types of powdered fat products, such as creamers, milk replacers, milk fat replacers or vegetable fat powders with a fat content up to 80%.

The production of microencapsulated oil powders involves the selection of core and wall materials, design of the formulation (ratio of core to wall) and selection of the appropriate emulsification technology (Kaushik et al., 2015). However, only limited numbers of wall materials are compatible with this technology. These materials include proteins, carbohydrates, lipids and gums used either alone or in combination depending on the core material and the characteristics desired in the final product (Bakry et al., 2016; Rodríguez et al., 2016; Kaushik et al., 2015; Gharsallaoui et al., 2007).

Unlike proteins and some carbohydrates (gum arabic and modified emulsifying starches) that have excellent emulsifying properties and provide relatively high oxidative stability, most carbohydrates and hydrocolloids are unsuitable for use alone as a primary encapsulating wall material as they do not have emulsifying properties (Lee and Ying, 2008; Gharsallaoui et al., 2007). Moreover, most carbohydrates and hydrocolloids, except for small molecules of monosaccharides and oligosaccharides, are also highly viscous even at very low solid concentrations. Therefore, carbohydrates should be used in conjunction with proteins or emulsifying agents in order to encapsulate oil materials. Recently, the potential of legume protein, alone or in combination with other materials, for microencapsulation has been of particular interest in the literature (Nesterenko et al., 2013; Domian et al., 2017b).

Hence, there is a need to explore different wall materials that can be used in high temperature and high evaporation flux conditions which prevail in the spray-drying environment. The selection

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of wall materials for microencapsulation by spray drying has traditionally involved trial-and-error procedures. Powders are then evaluated for several properties, including encapsulation efficiency, size and morphology of particles, oxidative stability of oil material, and water reconstitution (Domian et al., 2017b). An important step is the selection of a wall material that meets required criteria in relation to appropriate bulk properties of powders and their physical stability under different storage conditions.

Knowledge of the equilibrium relationship between the moisture content in the powdered material and the relative humidity (RH) of the surrounding air at a given temperature is required to predict shelf life stability, and moisture transfer between ingredients or to optimize packaging (Al-Muhtaseb et al., 2002; Bhandari and Hartel, 2005). The moisture adsorption data can be further analyzed to provide a theoretical interpretation of powder microstructure and physical interaction between water molecules and the solid matter of a material (Al-Muhtaseb et al., 2002; Lewicki, 2004). The drawbacks of measurement of moisture sorption isotherms associated with the saturated salt slurry method have mostly been overcome by the introduction of humidity generating instruments. The dynamic vapor sorption (DVS) method is designed to measure the equilibrium moisture content of a material at any desired relative humidity and selected temperatures in a short period of time. Dynamic water sorption data from DVS can be compared with water sorption from the conventional water sorption method (Burnett et al., 2004; Li and Schmidt, 2011). Additionally, the high data resolution resulting from dynamic water sorption methods makes it possible to observe distinct inflection points in the curve that represent changes in sorption properties that accompany the glass transition (Carter and Schmidt, 2012) and sugar crystallization (Kelly et al., 2014, 2015; Kelly, O'Mahony et al., 2016; Nurhadi and Roos, 2016; Fan et al., 2017). The DVS system has been applied to measure the moisture sorption properties of fat powders (Kelly et al., 2014); however, limited attempts have been performed to examine the effect of temperature and isosteric heat of sorption as well as phase transition of carbohydrates other than lactose using this system.

In this work pea protein isolates were used in combination with some carbohydrates with sugar-replacing properties (Auerbach and Dedman, 2012) as alternative materials, in production of fat-fill powders by spray-drying emulsion. In our recently study (Domian et al., 2017a), based on glass transition temperatures (Tg was measured at the moisture content of the “as is” sample), we concluded that all obtained spray-dried fat-filled pea protein-based powders should be stable and avoid glassy transition during storage at room temperature in hermetic packages. Therefore, the objectives of the present work were (i) to investigate the moisture sorption behavior of obtained model multicomponent powders, formulated with four types of carbohydrate component and two different fat types, using a DVS equilibrium method at temperatures which can be found in storage (ii) to find the most appropriate mathematical model to describe the experimental adsorption data and (iii) to estimate the isosteric heat of adsorption.

2. Materials and methods

2.1. Materials

Shortening AMADA L containing palm oil, rapeseed oil and hardened palm oil (fatty acid composition: 42.2% saturated fatty acids (SAFA), 45.5% monounsaturated fatty acids (MUFA), 12.3% polyunsaturated fatty acids (PUFA); softening point: 28–30 °C) and rapeseed oil Maestro (fatty acid composition: 8.4% SAFA; 63.3% MUFA, 27.5% PUFA; liquid oil at 20 °C) were purchased from the Bunge Company Poland (ZT Kruszwica S.A., Poland).

Pea protein isolate NUTRALYS S85F (compositional specifications: protein 84 %db, moisture 7.6%) and wheat dextrin soluble fiber NUTRIOSE FB06 (compositional specifications: fiber rate AOAC 83 %db, monosaccharides 0.1%, disaccharides 0.2%, moisture 3.9%) were kindly donated by Roquette Poland Sp. z o.o. Polydextrose STA-LITE R90 (Tate & Lyle USA) (compositional specifications: average degree of polymerization DP 9–10, polydextrose 92 %db, glucose + sorbitol 5.6 %db, moisture 2.9%) was obtained from Brenntag, Poland. Inulin ORAFTI GR (Orafti, Belgium) (compositional specifications: average degree of polymerization DP $\geq$ 10, inulin 93 %db, glucose + fructose + sucrose 7 %db, moisture 2.1%) and trehalose (Hayashibara, Japan) were obtained from Hortimex, Poland. All chemicals used for analysis were of reagent grade.

Based on osmolality of the carbohydrate sample solutions (Rong et al., 2009), it was concluded that Nutriose showed the highest average molecular weight of the particles, followed by inulin, polydextrose and trehalose.

2.2. Experimental design

The experimental design consisted of twelve unique trials. The spray-dried fat-filled pea protein-based powders consisted of pea protein isolate, vegetable oil and carbohydrate components. The experimental design included three compositional variations – PR53, PR35 and R35–in which the oil fraction respectively was made up of a blend of palm and rapeseed oil (PR) at different ratios of 53 or 35% weight per weight (w/w) and rapeseed oil (R) at 35% w/w total solids. Each group of model fat-filled powders was formulated with four different carbohydrates (Nutriose (N), inulin (I), polydextrose (D), and trehalose (T)), wherein in all cases the carbohydrate-to-protein-material ratio was 5.3:1. The samples composition is summarized in Table S1.

2.3. Preparation of model emulsions and fat-filled pea protein-based powders

A model oil-in-water emulsion (target 30% w/w total solids, comprising pea protein, oil and carbohydrate components) were prepared as follows. Carbohydrate powder was dissolved in hot water (60 °C), pea protein isolate (PPI) was slowly added during mixing, and it was moved to cold storage (5 °C) for 12 h for hydration of components. The water phase was tempered to 60 °C before addition of the fat component. When a blend of palm and rapeseed oils was used, it was melted in a separate vessel before addition. The mix was agitated using Ultra-Turrax (IKA T18 Basic, Wilmington, USA) at 13,000 rpm for 2 min then homogenized using a 2-stage homogenizer (Panda 2K; Niro Soavi, Italy) with a first-stage pressure of 60 MPa and a second-stage pressure of 20 MPa. Emulsions were spray dried in a lab-scale Niro Spray dryer (Model MOBILE MINOR Niro A/S, Denmark) equipped with a rotary atomization system and co-current drying. An inlet air temperature of 150 ± 3 °C and an outlet air temperature of 60±2 °C were selected and disk rotation was approximately 20,000 rpm. Samples of powder were stored at 4 °C in sealed vacuum foil bags until analyses were carried out.

2.4. DVS water vapor isotherms

Water vapor isotherms were determined using the DVS equilibrium method. About 20 mg samples of powders were placed into a pan of the calibrated DVS Intrinsic analyzer (Surface Measurement Systems Ltd, London, UK). The samples were dried at 25, 30 or 35 °C to a constant mass under a stream of dry nitrogen (0% RH) for 480 min. The samples were then exposed to the following RH profile: 0–5% RH in 0.05, 0.25, and 2.5% RH increments, 5–95% RH