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Adsorption of hydrophobically modified anionic starch at oppositely charged oil/water interfaces

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Abstract

In this paper we study the adsorption at cationic emulsion droplets of starch which had been hydrophobically modified with octenyl succinic anhydride (OSA), a modification which also renders the starch anionic. Emulsions were formed with didodecyldimethylammonium bromide (DDAB) after which the OSA-starch was added. The emulsions were separated by centrifugation and the surface load of OSA-starch was determined through serum depletion. The results show the adsorbed amounts can become very high, in some cases reaching approximately 40 mg/m^2. The surface load correlates positively with the surface charge density of the starch which depends on the degree of substitution, rms radius and molar mass. Furthermore, the surface load obtained depends on the ratio between polymer surface charge density and the interface charge density which could be varied experimentally by combining various amounts of DDAB and dioleoyl phosphatidylcholine (DOPC) in the formation of the emulsion. The very high surface loads should correspond to very thick adsorbed layers. Thus, OSA-starch should be appropriate for encapsulation applications provided a suitable adhesion substance is employed.

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1. Introduction

Polymers play an important role in the stability of colloidal dispersions. If a polymer has affinity for the interface between a dispersed and a continuous phase it will adsorb and can generate stability. The adsorption properties and the ability to form a coherent interfacial layer are thus important in the understanding of polymer functionality in dispersions. The stability generated by adsorbed polymers is either of an electrostatic nature or more commonly of a sterical nature (or both). The ability to provide sterical stabilisation depends on its ability to protrude into the continuous phase and hence the size of the polymer and its solubility in the continuous phase are crucial for its stabilising properties.

Starch from various sources is a versatile high molar mass biopolymer which can be used in many technical applications. Starch can be hydrophobically modified with octenyl succinic anhydride [1] (OSA) which gives it surface active properties. However, the hydrophobic substituent (Fig. 1) also contains a carboxylic acid which can be negatively charged. The degree of substitution (*DS*) of OSA-starch for food applications is typically low (0.01–0.03) [2] and hence it could be considered a weekly charged polyelectrolyte.

OSA-starch can be used to produce oil-in-water emulsions as the sole emulsifier [3–5] in which case the hydrophobic character of the substituent is the most important for the adsorption at the interface. If the interface is charged or if the emulsion contains other charged molecules, for instance ionic surfactants or charged macromolecules, the ionic character of the substituent is likely to play an increasingly important role in the adsorption. There are several studies where oppositely charged emulsifiers have been shown to enhance polyelectrolyte adsorption at emulsified droplets. One example is the adsorption of chitosan at bile acid emulsified oil droplets by Fäldt et al. [6]. In recent years there has been an increased interest in the use of OSA-starch for encapsulation in various systems. In such applications a protective coat or layer is created from a polymeric material in order to protect the core material from the surrounding environment. In order for such a formulation to

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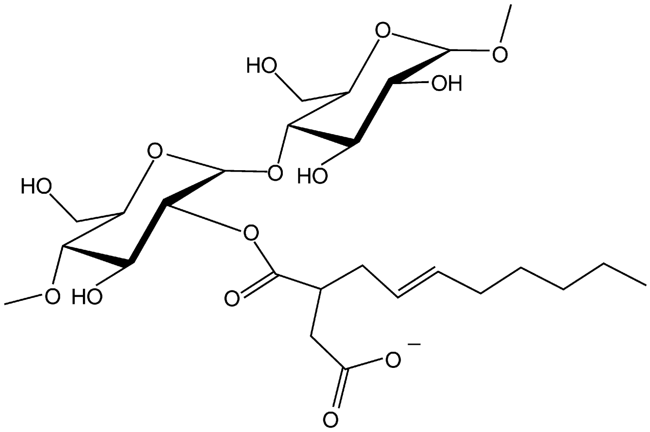

Fig. 1. Starch which has been hydrophobically modified with octenyl succinicanhydride (OSA). The figure shows the hydrophobic/anionic substituent esterified to the starch polymer backbone.

Table 1
Properties of the OSA-starch samples (from Ref. [13])

Sample	Molar mass (10^6 g/mol)	*DS*	Degree of branching	Properties after homogenisation	
				Molar mass (10^6 g/mol)	r_{rms} (nm)
B39-22	39	0.0224	0.0548	12	38
B27-21	27	0.0213	0.0502	8.6	44
B86-10	86	0.0104	0.0526	6.7	41
P23-14	23	0.0137	0.0352	8.8	32
P08-15	0.77	0.0148	0.0350	0.6	34
P34-076	34	0.0076	0.0354	11	42

work efficiently in an application the coating agent must have high affinity for the surface which is to be coated. Furthermore, the creation of a coherent and thick layer is also a requirement. Several studies in the area of encapsulation deals with the encapsulation of volatile substances and flavours [7–9]. O'Riordan et al. used OSA-starch to encapsulate bacteria but found no positive effect [10].

In the previous investigations [7–9] the adsorption have been driven by hydrophobic interaction. The purpose of this investigation is to describe the adsorption of OSA-starch at cationically charged emulsion droplets as a function of the physicochemical properties of the OSA-starch, i.e., degree of substitution (*DS*), molar mass, and polymer radius. Due to the anionic charge of the OSA-starch it is expected to interact strongly with the oppositely charged oil/water interface and thereby creating a denser and thicker adsorbed layer.

2. Materials and methods

The six OSA-starch samples were provided by Lyckeby Stärkelsen (Kristianstad, Sweden) and were of either native potato origin, containing 20% amylose and 80% amylopectin, or waxy barley origin, containing 7% amylose and 93% amylopectin. The molar degree of branching and the molar degree of substitution were determined with ^{1}H NMR (Table 1) and this method has been described elsewhere [4,5,11].

OSA-starch solutions of 1% (w/v) were prepared by dispersing 1.0 g of OSA-starch in a phosphate buffer (10 mM, pH 6.0) containing 20 PPM NaN_3 which was then diluted to 100 ml. The samples were then placed in a boiling water bath under stirring for 10 min after which they were left over-night at room temperature. The OSA-starch solutions where passed through a lab-scale high-pressure valve homogeniser three times at a pressure of 15 MPa. This makes the results of this study comparable to experiments carried out in the absence of low molecular weight emulsifiers in which the OSA-starch has to pass through the homogeniser [4,5]. It has been observed that homogenisation leads to a reduction in molar mass as well as changes in the internal structure of the OSA-starch [12,13]. The molar mass and radii distributions, average molar mass and the root mean square radius (r_{rms}) of the OSA-starch samples was determined after homogenisation by asymmetrical flow field-flow fractionation (AsFlFFF-MALS-RI) and is described elsewhere [13]. The properties of the various OSA-starch samples are given in Table 1. Didodecyldimethylammonium bromide (DDAB) was purchased from Sigma–Aldrich Corp. (St. Louis, MO, USA) and dioleoylphosphatidylcholine (DOPC) was purchased from Avanti polar lipids Inc. (Alabaster, AL, USA). The DDAB was dispersed in medium chain triglyceride (MCT) oil (Miglyol 812 F, Sasol, Witten, Germany) to a concentration of 3% (w/w) by heating the oil to 160 °C. In the experiments where DOPC was used the appropriate amount (to a total concentration of 3% w/w of polar lipids) was dispersed in the oil phase. An oil-in-water emulsion was prepared with 5% (w/w) of the MCT oil using a high shear mixer (Ystral X10/25, Ystral, Ballrechten-Dottingen, Germany) for 10 min. The continuous phase consisted of the buffer described above. The average droplet size (d_{32}) in the emulsions was determined by light diffraction using a Coulter LS130 (Beckman Coulter, High Wycombe, UK). The emulsion was then divided into aliquots to which different amounts of the OSA-starch solution was added. The samples where allowed to equilibrate for 5 h after which they were separated by mild centrifugation in two steps. The total OSA-starch content was determined by enzymatic degradation according to the method of Åman et al. [14]. The determination was carried out in the subnatant of the separated emulsion sample and in a reference sample containing the same initial OSA-starch concentration but no emulsion. As the method of Åman et al. was developed for nonmodified starches the recovery was slightly lower for the OSA-starch which was probably due to incomplete hydrolysis. The recovery varied between 85 and 89%. However by assuming that the recovery is equal in the emulsion sample and in the reference sample this error can be minimised.

2.1. Calculation of the surface load of OSA-starch

The adsorbed amount of OSA-starch is obtained from the difference between the amount in the reference sample containing no disperse phase and the amount in the subnatant after separation of the emulsion.

$$c_{\text{adsorbed}} = c_{\text{reference}} - c_{\text{sub}}. \tag{1}$$

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