Food Hydrocolloids 45 (2015) 256–263

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Preparation and characterizations of Pickering emulsions stabilized by hydrophobic starch particles

Xiaoyan Song [a, b, *], Yaqiong Pei [b], Mingwu Qiao [b], Fenglian Ma [b], Hongtao Ren [b], Quanzhi Zhao [a]

[a] Collaborative Innovation Center of Henan Grain Crops, Henan Agricultural University, Zhengzhou 450002, PR China
[b] College of Food Science and Technology, Henan Agricultural University, Zhengzhou 450002, PR China

ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form
20 November 2014
Accepted 3 December 2014
Available online 11 December 2014

Keywords:
Rice starch particles
Hydrophobic modification
Pickering emulsions
Preparation conditions
Rheological property

ABSTRACT

Soybean oil–in–water (O/W) Pickering emulsions were prepared using octenyl succinic anhydride (OSA) modified *indica* rice starch as particle stabilizers. The major factors affecting the emulsion stability were studied systematically. The rheological behaviors of the emulsions were also investigated by means of rheometer. Results indicated that the suitable parameters for the preparation of O/W Pickering emulsions stabilized by rice starch particles were selected as follows: concentration of starch particles 4.0 wt. % (degree of substitution 0.0287), soybean oil fraction 50 vol. %, pH of emulsion system 6.0–7.0. NaCl and sucrose concentrations had no obvious effect on the cream volumes of emulsions from 0 to 200 mmol/L. The rheological properties revealed that the Pickering emulsions showed a phenomenon of pseudo –plastic fluid characteristics. The elastic modulus (G') was always higher than loss modulus (G'') at frequencies of 0.01–10 Hz. Moreover, G' and G'' showed increasing trend with the increase in starch particle concentration. Microstructure of the Pickering emulsions showed that starch particles accumulated at the oil–water interface in the form of a densely packed layer. These results implied that an inter–droplet network probably formed, making the emulsions a gel–like behavior.

1. Introduction

Emulsions are formed from two immiscible liquids, with one dispersed as droplets in another. A system that consists of oil droplets dispersed in an aqueous phase is called an oil–in–water (O/W) emulsion (Bortnowska, 2012). O/W emulsions are common in food industry, such as cream in espresso, mayonnaise and homogenized milk. Food emulsions are generally stabilized by surfactants, proteins and hydrocolloids. Recently, particle stabilizers have been the focus of considerable research in food industry due to their properties such as strong interfacial stability, non–toxic, eco–friendly, and low cost (Yu, Lin, & Li, 2013). Particle stabilizers have been used in cosmetics and personal products for many years (Lee, Chan, & Mohraz, 2012). The emulsions stabilized by particles were called Pickering emulsion after S.U. Pickering, who observed this phenomenon over a century ago (Pickering, 1907).

The particle stabilizers widely used for Pickering emulsions were silica, alumina, wax, chitin, clay particles, titanium oxides, etc. (Binks & Rocher, 2009; Chen et al, 2011; Gao et al., 2009; Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011). Although there were a lot of studies conducted on particle stabilizers, fairly few were directly related to food (Dickinson, 2012). Some potentially food–compatible particle stabilizers that have been used in O/W Pickering emulsions include chitin nanocrystals (Tzoumaki et al., 2011), cellulose nanocrystals (Capron & Cathala, 2013; Wege, Kim, Paunov, Zhong, & Velev, 2008), fat crystals (Rousseau, 2013), protein (de Folter, van Ruijven, & Velikov, 2012; Liang & Tang, 2014), and flavonoid (Luo et al., 2012). Recent studies have demonstrated that hydrophobically modified starch with small granule size and regular shape could be used as particles to stabilize O/W emulsions (Marku, Wahlgren, Rayner, Sjöö, & Timgren, 2012; Tan et al., 2012; Timgren, Rayner, Sjöö, & Dejmek, 2011; Yusoff & Murray, 2011). Moreover, the modified starch could reduce the oxidation rate of sunflower oil in O/W emulsion (Kargar, Fayazmanesh, Alavi, Spyropoulos, & Norton, 2012).

Starch is an accepted food ingredient and pharmaceutical excipient. Starch granules can be isolated from a variety of plants, which are abundant, inexpensive, and renewable. However, native

Abbreviations: DS, degree of substitution; D_{50}, median particle diameter; D_{av}, average particle size; D_{90}, 90% particles is less than this size; OSA, octenyl succinic anhydride; O/W, oil–in–water.

* Corresponding author. Henan Agricultural University, Wenhua rd. No. 95, Zhengzhou 450002, Henan Province, PR China. Tel./fax: +86 371 63558150.
E-mail address: songxiaoyan2737@163.com (X. Song).

http://dx.doi.org/10.1016/j.foodhyd.2014.12.007
0268-005X/

starch granules are not hydrophobic, and thereby generally not suitable to adsorb to the oil–water interface during emulsification. The hydrophobicity of native starch granules can be increased by octenyl succinic anhydride (OSA) modification (Rayner et al., 2014). OSA modified starch is one of anion starches, which contains $-COO^-$ groups and negative charges. The modified starch could be used to stabilize O/W Pickering emulsions if they remain intact granule structure and are predominantly wetted by the aqueous phase. Our previous work demonstrated that rice starch had no change on the crystalline pattern and granule structure after OSA modification (He, Song, Ruan, & Chen, 2006; Song, He, Ruan, & Chen, 2006). The modified starch could be used as particle stabilizers to form O/W emulsions with the average droplet sizes of 10–70 μm (Song, Pei, Zhu, Ding Fu, & Ren, 2014).

Rice starch consists of tiny granules with a narrow size distribution (2–8 μm), which makes it an excellent candidate material for preparing particle stabilizers. However, little work has been reported on the preparation conditions affecting the stability of the emulsion stabilized by rice starch particles (Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013). Moreover, environmental variables such as pH, shear strength, NaCl and sucrose concentration may affect stability of the food emulsion and hydrophobic starch particles, altering the range of their mutual interactions. In this study, the hydrophobic starch particles modified from *indica* rice were used as particle stabilizers. The effect of preparation conditions on the stability and rheological properties of the soybean oil–in–-water emulsions were investigated, which is significant for the development of new starch-based particle stabilizers in the food and related industries.

2. Materials and methods

2.1. Materials

The *indica* rice starch used for this study was Te–you 2035. The approximate composition of Te–you 2035 was as follows: amylose content 18.0 ± 0.2%, crude protein content 0.3 ± 0.1%, and moisture content 8.7 ± 0.2%. The particle size distributions of Te–you 2035 starch granules are D_{50} 4.7 ± 0.1 μm, D_{av} 5.0 ± 0.2 μm, and D_{90} 7.6 ± 0.2 μm, respectively. OSA was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Soybean oil was purchased from Yihai Kerry Investment Co., Ltd. (Shanghai, China). The other chemicals were all analytical grade.

2.2. Preparation of hydrophobic starch particles

Rice starch (30.0 g, dry basis, db) was mixed with 70 mL distilled water. Five percent of OSA (in proportion to starch, w/w) were slowly added in 2 h. The starch slurry was adjusted to pH 8.4 during the reaction using a 3% NaOH solution. The hydrophobic modification was lasted for 5 h at 35 °C. Then pH value of the slurry was adjusted to 7.0 using 3% HCl solution. The mixture was centrifuged and washed two times with distilled water and two times with alcohol/water (70:100, v/v), respectively. The deposition was oven–dried at 45 °C for 24 h, and then passed through a 120–mesh nylon sieve (125 μm opening).

2.3. Degree of substitution measurement

Titration method was used to calculate the degree of substitution (DS) according to the report of Song et al. (2006). DS was calculated by the following equation:

$$DS = \frac{0.162 \times (A \times M)/W}{1 - [0.210 \times (A \times M)/W]} \quad (1)$$

where A is the titration volume of standard NaOH solution, mL; M is the molarity of standard NaOH solution; W is the dry weight of OSA starch, g.

2.4. Preparation of Pickering emulsions

Hydrophobic starch particles were suspended in 100 mL distilled water in a 250 mL glass beaker. Then the starch solution was mixed with different amounts of soybean oil using a high speed homogenizer (IKA T18, IKA–Werke GmbH & Co. KG, Germany) at 11,000 r/min for 2 min with 20 s intervals.

2.5. Stability of Pickering emulsions

Emulsion samples (25 mL) were placed in the sealed graduated test tubes respectively. Storage stability was determined as the volume of emulsion stored for 6 h, 1 d, 5 d and 35 d at room temperature (25 °C). Another 25 mL of the emulsions were placed in the colorimetric tubes at the same time, and then the photographs were taken after stored at room temperature for 35 days using a digital camera (Digital Ixus 115 HS, Canon, Japan).

2.6. Morphology of the Pickering emulsion droplets

The morphologies of the Pickering emulsion droplets were analyzed by an optical microscope (Eclipse 80i, Nikon Instruments Inc., Japan) fitted with a digital sight (DS–Fi1, Nikon Instruments Inc., Japan). The emulsions were stored for two days at room temperature and then were stained by iodine solution (0.2 g iodine and 2.0 g potassium iodide were dissolved in 100 mL distilled water). A small drop of the stained emulsion was place in a microscope slide with cavity. Micrographs of the samples were taken at 100 × and 1000 × magnifications, respectively.

Table 1
Effect of OSA starch particle concentration on the cream volumes and droplet size distribution of the emulsions.

Starch particle concentration wt. %	Starch amount relative to oil mg/mL	Cream volume of emulsion/mL[a,b]				Droplet size distribution/μm		
		6 h	1 d	5 d	35 d	D_{50}	D_{av}	D_{90}
0.5	15	9.5 ± 0.5f	9.5 ± 0.5d	9.1 ± 0.7e	6.8 ± 0.8e	ND[c]	ND	ND
0.7	21	10.8 ± 0.4e	10.8 ± 0.3c	9.8 ± 0.4de	9.6 ± 0.1d	28.0 ± 0.9a	29.5 ± 1.1a	50.3 ± 1.5a
1.3	38	11.9 ± 0.5d	10.9 ± 0.5c	10.6 ± 0.7cd	10.2 ± 0.3cd	27.7 ± 0.6a	28.8 ± 0.9b	46.2 ± 2.1b
2.0	59	12.4 ± 0.3d	11.9 ± 0.5b	10.9 ± 0.9c	10.5 ± 0.8bc	26.3 ± 0.6b	27.6 ± 0.7c	45.4 ± 3.4b
3.0	89	13.8 ± 0.7c	12.6 ± 1.3b	12.2 ± 0.6b	11.3 ± 0.7b	21.9 ± 0.3c	22.6 ± 0.8d	38.5 ± 3.1c
4.0	118	16.1 ± 0.3b	15.9 ± 0.2a	15.6 ± 0.3a	14.2 ± 0.8a	20.9 ± 0.6c	22.2 ± 1.0d	38.5 ± 0.9c
5.0	148	17.1 ± 0.5a	16.6 ± 0.5a	16.5 ± 0.5a	14.8 ± 1.1a	19.3 ± 0.9d	20.1 ± 0.7e	39.7 ± 1.9c

[a] Mean of 3 determinations ± standard deviation.
[b] Values with the different letter in the same column are significantly different ($P < 0.05$).
[c] ND, not detected.