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Development of egg white protein aerogels as new matrix material for microencapsulation in food

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ABSTRACT

Egg white protein hydrogels formed by heat coagulation were used to obtain aerogel structures by supercritical drying. Hydrogels were prepared from pasteurized and spray-dried egg white at different pH, ionic concentrations and protein content to modify the characteristics of the dried protein network. The largest BET-surface areas were found at low and high pH, the most mechanically stable aerogels – at alkaline pH. It was shown that the protein network is preserved during supercritical drying. Egg white as precursor for aerogels opens a new field of application for those proteins as microencapsulation material for sensitive or unpleasant tasting food additives.

1. Introduction

During the last years, a lot of research has been done on natural polysaccharide-based aerogels, which fulfill the requirements for food applications [1]. In principal, supercritical drying of an alcogel to an aerogel is an extraction of a solvent from a gel by supercritical carbon dioxide. The raffinate is represented by the aerogel. Extraction by supercritical carbon dioxide has become a well-established process in the food industry over the last years [2,3], indicating that there should be a potential to establish food-grade aerogels in industry, too. In this study, the irreversible heat coagulation of egg white proteins is used to form a gel which is afterwards supercritically dried to an aerogel. Aerogels based on natural proteins can provide new opportunities for life science and food applications because of their biocompatibility and biodegradability. Particularly hen egg white, which has been used for this study, is well-known as staple food and, therefore, most reliable for potential consumers. The general applicability of egg white protein as precursor for aerogels has already been shown by Kistler [4]. Furthermore, whey protein isolate out of milk [5,6] or soy protein isolate [7] were investigated as food grade aerogel precursors.

Egg white protein is a high quality protein source with high nutritive value. It offers versatile functional properties, for example foaming, emulsification, water-binding and heat coagulation [8–12]. Therefore, it is widely used in the food industry [8,12]. Native egg white consists of about 10 wt% protein and 90 wt% water [9]. The main protein fractions of egg white are Ovalbumin (54%); Ovotransferrin (12%) and Ovomucid (11%) [13]. When egg white is heated, the egg white proteins denature thermally and form a gel. This process is described as a 3-step mechanism: firstly, due to heat, the existing hydrogen bonds in particular between the polypeptide chains of the protein molecule break, the polypeptide chains unfold and hydrophobic reactive groups get exposed to the outside of the protein [9,11]. As a second step, the unfolded protein molecules rearrange due to hydrophobic and electrostatic interactions. Intermolecular disulfide crosslinking stabilizes the arranged protein network additionally. A gel is generated. Thirdly, the formed gel is cooled and gets more elastic because of the formation of hydrogen bonds, which stiffen the protein network [9,11,14]. The resulting gel structure is influenced by pH and ionic strength and the type of added salt [10,15].

The main objective of this study was to develop protein-based aerogels out of egg white as carrier material for food applications. The main requirements for such a carrier material consist of high specific surface area coupled with high mechanical stability.

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Therefore, the influence of pH, temperature, sodium chloride concentration and egg white source on the resulting aerogel structure was investigated.

2. Materials and methods

2.1. Materials

Pasteurized egg white and dried egg white powder were kindly donated from Ovobest Eiprodukte GmbH & Co., KG (Neuenkirchen-Vörden, Germany). Sunflower oil was provided from Bröckelmann + Co – Oelmühle GmbH + Co (Hamm, Germany). Sodium Chloride (purity ≥99%) was purchased from Carl Roth GmbH & Co., (Karlsruhe, Germany). Ethanol of analytical grade was purchased from Krayem GmbH (Ingoldstadt, Germany) and Merck KGaA (Darmstadt, Germany). Carbon dioxide of food grade was obtained from Yara GmbH & Co., KG (Dülmen, Germany).

2.2. Methods

2.2.1. Preparation of egg white protein gel samples

Commercially available pasteurized egg white was utilized as primary aqueous protein solution. Alternatively, a solution of dried egg white powder was prepared with deionized water, stored at 4 °C over night to allow for complete hydration and its protein content was adjusted to 10 and 15 wt%. The protein content was determined using the method of Dumas with an accuracy of ±0.1 wt% (Vario MAX CUBE, Elementar Analysensysteme GmbH, Hanau, Germany). The protein content of the powder solutions was determined for every new solution, the protein content of the pasteurized egg white randomly for new packages. The pH-values were adjusted with hydrochloric acid and sodium hydroxide to 2, 3.5, 4.6, 7, 9, and 11.5. To investigate the sodium chloride influence on the gel structure, additionally, sodium chloride was added to the liquid egg white in concentrations of 5 and 400 mmol/L in crystalline form and dissolved completely. The egg white protein solutions were then immersed dropwise into hot sunflower oil with a temperature of 80 and 90 °C, using a 0.9 mm syringe. After a time interval of 10 and 5 min, respectively, the hardened gel spheres were transferred into sunflower oil at room temperature for cooling. Gel spheres were dabbed with a lint free tissue to take away the major part of oil residue. The remaining small oil amounts on the surface of the gel spheres were dissolved in ethanol and removed during solvent exchange. For each variation, 20 gel spheres were produced.

2.2.2. Solvent exchange and supercritical drying of egg white gels

The solvent exchange from water to ethanol was started directly after gelation to avoid altering effects of the gel structure. The gels were put into 99.8% ethanol to mix the pore filling water inside the gels with ethanol. An ethanol to gel volume ratio of 50 was used. After 24 h, the gels were put into fresh ethanol. This was repeated at least three times to reach at least 97 wt% in the gel surrounding ethanol–water mixture. The ethanol concentration was measured indirectly by measuring the density of the ethanol–water mixture at 20 °C (Density Meter DMA 4500 M, Anton Paar, Ostfildern-Scharnhausen, Germany).

The supercritical drying was conducted at 12 MPa and 40 °C in a 250 mL autoclave for three hours using a continuous supercritical CO_2 flow (Fig. 1). At 12 MPa and 40 °C the system CO_2-ethanol is in the single phase region [16], and therefore, no phase boundary leading to capillary forces inside the gel could occur. Also the drying temperature was below the denaturation temperature of the egg white proteins [17] to avoid further changes of the protein structure.

First, the autoclave was heated to 40 °C by a thin electrical band heater. The alcogels were packed in filter paper, placed into the autoclave (A1 in Fig. 1) and soaked in ethanol to prevent shrinkage due to evaporation of ethanol from the alcogel network before exposure to supercritical CO_2. The system was pressurized to 11.0–12.0 MPa with CO_2 by a compressor (P1). The outlet regulating valve V7 was adjusted to a flow of CO2 of 2–4 NL/min, continuous CO_2 flow was provided for 3 h. Finally, the pressure was released slowly within 40–60 min at constant temperature (40 °C) until atmospheric pressure was reached.

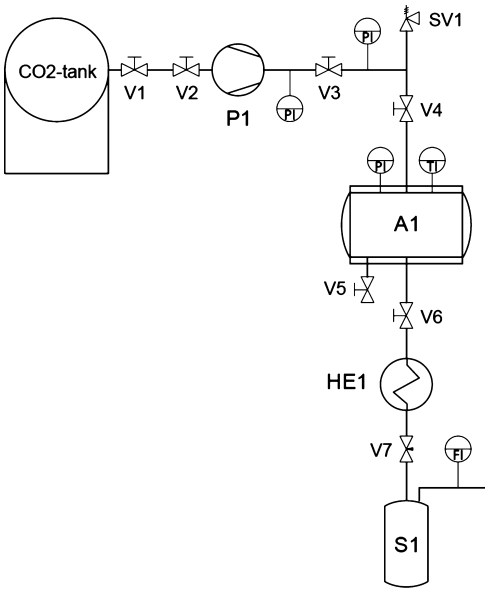

Fig. 1. Process flow diagram of the equipment used for the supercritical drying of protein aerogels. Tags: V1–V7 = valves; HE1 = heat exchanger for heating; P1 = compressor; A1 = 250 mL autoclave with sapphire window; S1 = separator; PI = pressure gauges; SV1 = safety valve; TI = thermocouple; FI = flow meter.

2.2.3. Physical characterization

Scanning electron micrographs of the samples were done at 5 kV using a detector for secondary electrons (Leo Gemini Zeiss 1530, Oberkochen, Germany). To analyze the internal structure of the aerogel spheres, the samples were crushed into smaller pieces which were then investigated. To avoid charging of the samples, they were sputtered with gold (7 nm thickness).

Low temperature N_2 adsorption–desorption analysis was used to investigate the physical properties of the aerogels (Nova 3000e Surface Area Analyzer, Quantachrome Instruments, Boynton Beach, USA). The specific surface area was determined using the BET (Brunauer–Emmet–Teller) method. The pore volume and mean pore diameter were estimated by the BJH (Barrett–Joyner–Halendia) method. All samples were degassed under vacuum at 40 °C for 20 h prior to analysis.

Bulk density was calculated from measured weight with a deviation of ±0.0001 g and from measured diameter of the aerogel spheres with an accuracy of ±0.05 mm. The measurements were repeated five times with different aerogel spheres.

Breaking and compression tests were done to analyze the mechanical stability (Texture Analyzer TA.XT plus, Stable Micro Systems, Godalming, UK). The spherical samples were compressed uniaxially to 8% strain or rather to the first fracture of the structure (0.01 mm/s test speed). In order to analyze the dry aerogel structure, the samples were dried additionally for 10 h under vacuum at 50 °C and then stored in an exicator with silica gel particles inside. The mechanical tests were done inside a tempered room (T = 20 °C). Each sample was measured directly after taken out of the exicator. Five replicates for each test were done.