A facile way of making inexpensive rigid and soft protein biofoams with rapid liquid absorption

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ABSTRACT

A novel and facile method to produce inexpensive protein biofoams suitable for sponge applications is presented. The protein used in the study was wheat gluten (WG), readily available as a by/co-product, but the method is expected to work for other cross-linkable proteins. The foams were obtained by high-speed stirring of pristine WG powder in water at room temperature followed by drying. Glutaraldehyde was used to crosslink the foam material in order to stabilize the dispersion, reduce its tackiness and improve the strength of the final foam. The foams were of medium to high density and absorbed readily both hydrophobic and hydrophilic liquids. The foam structure, consisting primarily of an open pore/channel system, led to a remarkably fast capillary-driven (pore-filling only) uptake of a hydrophobic liquid (limonene). Essentially all uptake occurred within the first second (to ca. 90% of the dry weight). In a polar liquid (water), the rapid pore-filling occurred in parallel with a more time-dependent swelling of the foam matrix material. Further improvement in the foam strength was achieved by making a denser foam or adding TEMPO-oxidized cellulose nanofibres. Soft foams were obtained by adding glycerol.

1. Introduction

Polymeric foams based on polystyrene, polyurethanes and/or polyolefins are widely used today as thermal insulation, shock absorption, and cushioning materials (Grand View Research, 2016). These polymeric materials are versatile and have good mechanical properties. Nonetheless, they have several disadvantages, including that the monomers are mostly petroleum-based and are not biodegradable, which makes them unsuitable for composting (Siracusa et al., 2008). A sizeable amount of research has therefore been undertaken to find sustainable bio-based alternatives. Naturally sourced polymeric materials that have been considered for use in fabricating biofoams include starches, nano-fibrillated cellulose, and proteins (Cervin et al., 2013; Chen et al., 2015; Svagan et al., 2008). A commonly reported process for the fabrication of biofoams is lyophilization, wherein the base material is dispersed in a solvent (typically water) and the suspension is frozen (Iannace and Sorrentino, 2015). The ice crystals are then sublimated under vacuum, giving rise to the formation of pores in the matrix (Wu et al., 2014; Wu et al., 2016). This process becomes problematic when producing large foam products due to the formation of a heterogeneous structure caused by uneven freezing and sublimation, although we have shown previously that larger foam products can be obtained by assembling smaller foam products through water welding (Wu et al., 2017). The lyophilisation process, however, is also associated with a high energy cost (Dordoni, 2012). An alternative method for the production of biofoams involves the use of supercritical carbon dioxide, but this method is also associated with high energy consumption (Hao et al., 2008; Quester et al., 2014). The supercritical carbon dioxide foaming technique can be used to make both open and closed cells (Yang et al., 2017), whereas freeze-drying normally yields more open than closed cells (Wu et al., 2016). Another method that has gained increased interest for the preparation of foams is the Pickering emulsion technique, wherein particles are used to stabilize the interface between the air and the liquid during foaming. This method generates mainly closed pores, which are 3–4 orders of magnitude larger than the particles used for stabilization of the interface (Horozov, 2008). Foams have successfully been made through this method using both inorganic and organic base materials, such as nano-fibrillated cellulose, protein particles, silica and even bacterial cells (Binks and Horozov, 2005; Lam et al., 2014). The main requirement for the Pickering method is that the particles used are amphiphilic, allowing them to be partially wetted by both the liquid and the gas phases (Pickering, 1907). Other foaming techniques also exist that can be or have previously been used for the production of biofoams (Zhang and Kessler, 2015).

One of the proteins available in large-scale quantities that has been studied as a candidate for bio-based foams is wheat gluten (WG) (Blomfeldt et al., 2010). One important advantage of using WG is that the raw material is obtained as a co-product from wheat starch and ethanol production (Wieser, 2007). WG-based products can be obtained using conventional plastic production techniques, e.g., extrusion, compression moulding and injection moulding (Cho et al., 2010a,b). They can be made either rigid or ductile, the latter with the use of a plasticiser. (Blomfeldt et al., 2011) If necessary, the strength and stiffness can also be improved using a crosslinker, e.g., a dialdehyde such as glutaraldehyde (GA) (Gerrard et al., 2002b; Reddy et al., 2008). GA forms covalent bridges mainly between lysine groups in the protein (Gerrard et al., 2002a). Reinforcement can also be achieved by the incorporation of fibres (preferentially biobased), such as bacterial cellulose fibres (Blomfeldt et al., 2011). It has also been shown that WG foams can be obtained with tailored properties and functionalities. The foams can be made antimicrobial (using a material such as Lanasol, a constituent of algae), electrically conductive (using nano-sized carbon black or carbon nanotubes) and flame-retardant (using in situ polymerized silica) (Wu et al., 2014; Wu et al., 2016).

In this work, a novel and simple method for creating medium- and high density porous WG materials is presented. The method is based on mechanical stirring of a water-WG dispersion without freeze-drying. WG powder is used as obtained directly from the wheat mill without pre-treatment, and the dispersion is prepared without any further denaturing of the protein through heating or pH adjustment. When the dispersion is mechanically stirred, it phase-separates into WG-rich and water-rich phases, and the latter is removed mainly through pores in the bottom of the mould. The final foam was obtained after a drying step. To improve the rigidity of both the dry and the wet state and to avoid a capillary force-generated collapse during drying, the material was crosslinked with GA. To produce a soft foam, the WG material was plasticised with the most commonly used plasticiser for proteins (glycerol). An investigation of whether both the rigid foam and the soft foam could be strengthened by the addition of cellulose nanofibrils (CNF, obtained by the TEMPO technique (Salajková et al., 2012)) was also performed. The choice of CNF was based on producing a composite foam with mainly biobased constituents. The effects of increasing the density of the foam using a higher content of WG was also investigated.

2. Experimental

2.1. Materials

Gluten was provided by Lantmannen Reppe AB, Sweden and contained 77.7 wt.% gluten (modified NMKL Nr 6, Kjeltec, Nx5.7) and 5.8 wt.% starch, as determined by the Ewers polarimetric method (ISO 10520:1997). The WG lipid content was 1.2 wt.% of the dry weight (Soxtec, Lidfett.OA.19, tecator AN 301). Glutaraldehyde (GA) in a 25% water solution was obtained from Sigma Aldrich (grade II), and the glycerol used was obtained from Alfa Aesar (ultrapure, HPLC-grade).

TEMPO-oxidized cellulose fibres (TEMPO) were prepared as described by Salajková et al. (2012) with oxidation on commercial wood pulp (hemicellulose content 13.8% and lignin content 0.7%, provided by Nordic Paper, Sweden). First, 40 g of pulp was suspended in 4 L of water with 0.64 g of 2,2,6,6-tetramethylpiperidinyl-1-oxyl and 4 g of sodium bromide. Oxidation was carried out by adding 4 mol/L NaClO to the suspension and keeping the pH constant at 10 with 0.5 M NaOH for 5 h. After oxidation, the reaction was quenched with ethanol, washed with water and centrifuged. The TEMPO cellulose was stored in a refrigerator at 4 °C until it was used. The cellulose had a dry content of 1.3% and a charge content of 10 equivalents. The fibres had a diameter of 2.4 ± 0.7 nm and a length of several micrometers; (Salajková et al., 2012) hence, the fibre aspect ratio was over 400.

2.2. Foam preparation

The foam was made by first preparing a mixture of glutaraldehyde and the other additives (glycerol and/or TEMPO, if used) in water and then adding wheat gluten (WG). The mixture was mechanically stirred for 2 min at 13,000 rpm in a Yellow Line Di 25 basic homogenizer from IKA equipped with an S25N-18G dispersion tool.

To determine the most suitable amount of GA, a series of samples (set 1) containing only WG and different amounts of GA was made and examined to identify the GA concentration that would provide the necessary reduction in tackiness while largely maintaining the sample size and shape during the drying step. The goal was to keep the glutaraldehyde concentration as low as possible. The mixtures were decanted into a cylindrical PET mould with a diameter of 2.5 cm and a height of 12 cm and then dried at room temperature for 24 h. Subsequently, the samples were removed from the mould and dried further in an open petri dish at ambient conditions. It should be mentioned that the drying time can be shortened significantly by using a heating step, which was not employed here. The bottom of all moulds used was perforated with a pin (diameter: 0.6 mm) to obtain ca. 10 holes/cm^2. This enabled drainage of water from the foam. The concentrations evaluated were 0, 0.05, 0.1, 0.25, 0.5 and 1 g of GA per 10 g of gluten. As reported in a later section, 0.25 g of GA (2.5 wt.%) per 10 g of gluten yielded acceptable properties and was therefore used in the second set of samples, into which glycerol and TEMPO fibres were added. In the sample for which the concentration of WG in the mixture was increased by 50%, the GA content (in grams) was kept the same as in the other samples (resulting in a GA concentration of 1.7 wt.% relative to the WG content), since the higher WG content made the foam more mechanically stable. The second set of samples (set 2), used in all further measurements, was produced in a cylindrical mould with a diameter of 4 cm and a height of 2.5 cm or in cubic moulds having a side of 2 cm. The cubic foams were used for the liquid absorption tests, and the cylindrical foams were used in all other tests. All mixtures were viscous, and a spatula was used to fill the moulds and remove any large voids. After drying for 24 h in the mould, samples were removed for further drying in an open petri dish at ambient conditions.

When TEMPO cellulose was used, the cellulose was dispersed in the glutaraldehyde solution using the homogenizer tool for a few seconds before adding WG. For the higher gluten-content samples, WG was added in two portions to improve dispersion and prevent it from forming large lumps.

The sample recipes (set 2) are given in Table 1. The chosen formulations were a reference base material (Reference), the same reference material containing 50% more WG (high-WG), a material with glycerol added to generate a soft product (Glycerol), a material with TEMPO cellulose added as a reinforcement (TEMPO) and one material combining TEMPO cellulose and glycerol (TEMPO/glycerol) to reveal any synergistic effects between the two additives. The amount of TEMPO cellulose used (1 wt.%) was based on previous successful production of freeze-dried WG using 1 wt.% of bacterial cellulose fibres (Blomfeldt et al., 2010). The content of glycerol used was similar to that used previously in WG foams (Blomfeldt et al., 2010; Cho et al.,

Table 1
Compositions of the materials fabricated (set 2).[a]

Sample	WG (g)	GA (g)	Glycerol (g)	TEMPO (g)
Reference	20	0.5	0	0
High-WG	30	0.5	0	0
Glycerol	20	0.5	6	0
TEMPO	20	0.5	0	0.2
TEMPO/glycerol	20	0.5	6	0.2

[a] 100 mL Milli-Q water was used in the recipes. For the TEMPO cellulose samples, less water was added to compensate for the water in the TEMPO cellulose gel.