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# Foam-like materials based on whey protein isolate

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ABSTRACT

Low density materials from sustainable whey protein were fabricated through a simple, environmentally-friendly freeze-drying process. Aerogels produced solely from whey protein show poor mechanical properties, consistent with those of films produced from that biopolymer. The compressive moduli of these lamellar materials were increased by more than an order of magnitude by crosslinking, and further increased with increasing aerogel densities. Blending whey protein with alginate allowed for the production of bio-based aerogels with higher mechanical properties than those produced with whey alone, though thermal properties were slightly decreased by blending.



## 1. Introduction

Bio-based polymers are of increasing interest as fossil fuel resources become more costly. Use of materials, such as cellulose, sugar cane, animal proteins, and plant starches and oils, as alternatives to petrochemicals can decrease overall carbon footprints for consumer and industrial products, as well as reducing their environmental impacts [1–4].

Whey is the liquid remaining after milk has been curdled and strained for cheese production, and is composed primarily of β-lactoglobulin (>50% of the total whey protein), α-lactalbumin, bovine serum albumin (BSA), and immunoglobulins [5,6]. Whey protein is widely used in the food industry, with applications including processed meats, bakery products, pasta, ice cream, and infant foods [7]. As a by-product of the manufacture of cheese or casein, the broad availability in western countries makes whey protein a good feedstock candidate for the production of environmentally friendly-materials. Due to its comparatively low molecular weight and specific molecular conformation, whey protein possesses limited mechanical strength and is therefore seldom used other than in the food industry. Modification of the whey protein structure and blending with other materials, including plasticizers, crosslinkers, and other polymers, are possible methods to improve its final properties; in the absence of plasticization, whey protein isolate is known to be a brittle material [8,9].

Heat-induced gels can form when heating whey protein. Denatured whey proteins aggregate irreversibly and eventually form a space-filling, crosslinked gel structure. The gelation mechanisms and associated processes have been extensively studied [10–17]. The higher the ionic strength is, the lower the critical protein concentration necessary for gel formation other than near the isoelectric pH. By means of such facile crosslinking, the mechanical properties of whey protein can be enhanced. We have previously reported an environmentally-friendly process for the preparation of low-density polymer/clay aerogels from aqueous mixtures [18–20], showing great potential as alternatives to polymeric foam and balsa wood. An especially striking family of such aerogels is those produced

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from alginate/clay, exhibiting extremely high mechanical strengths and moduli [20].

In the current work, we report a family of low density materials based on whey protein. Gelation of the whey protein, as well as blending with alginate are explored as methods to enhance the mechanical properties of these whey protein aerogels.

## 2. Experimental

### 2.1. Materials

Whey protein isolate (WPI), BIPRO with a protein content of >95%, was supplied by Davisco Foods International, Inc. The main proteins are beta-lactoglobulin with a $M_W$ of ~18,000 Daltons and alpha-lactalbumin at ~14,000 Daltons, and used without further modification. Ammonium alginate and sodium chloride (Fisher Scientific), and sodium montmorillonite ($Na^+$-MMT, PGW grade, Nanocor Inc.) were used as received. Deionized water was produced using a Barnstead RoPure reverse osmosis system.

### 2.2. Aerogel preparation

Percentages of WPI, alginate and clay structural components in aqueous suspensions given prior to freeze-drying. For pure WPI aerogels, WPI powder (10, 15, 20 and 25 g, noted as WPI10, WPI15, WPI20 and WPI25) was dissolved into 100 ml DI water. The solutions were poured into 5 g polystyrene vials and frozen in a solid carbon dioxide/ethanol bath. Equivalent batches were prepared for gelling with 100 mM NaCl aqueous solutions, providing sufficient salt to induce gelation of thermally denatured WPI. The WPI solutions were then heated at 80 °C for 30 min to form gels, which were then frozen in a solid carbon dioxide/ethanol bath.

For WPI10A2.5C2.5, 2.5 g of $Na^+$-MMT was blended with 100 mL of DI water on the high speed setting of a Waring model MC2 mini laboratory blender for 1 min to obtain a 2.5 wt% clay aqueous suspension. 2.5 g alginate and 10 g WPI were then dissolved into the clay suspensions. These mixtures were then poured into 5 g polystyrene vials and frozen in a solid carbon dioxide/ethanol bath. The preparation of WPI10A5 (10 g WPI, 5 g alginate) followed the same procedure as was used to produce WPI10A2.5C2.5.

The frozen samples were dried in a VirTis Advantage freeze dryer, with an initial shelf temperature of 25 °C, condenser temperature of −87 °C and an eventual vacuum of <10 mbar applied to sublime the ice. The freeze drying process was allowed to proceed for 3–4 days to ensure complete solvent removal.

### 2.3. Characterization

The densities of the dried aerogels were calculated from the mass and dimension measurements using mass measurements and digital calipers.

Compression testing was conducted on the cylindrical specimens (~20 mm in diameter and height) using an Instron model 5565 universal testing machine, fitted with a 1 kN load cell, at a crosshead of 10 mm $min^{-1}$. Five samples of each composition were tested for reproducibility, run to 75% compressive strain. The initial compressive moduli were calculated from the slope of the linear portion of the stress–strain curve.

The morphological microstructure of the aerogels was characterized with HITACHI S-4500 scanning electron microscope at acceleration voltage of 5 kV. The samples were prepared by fracturing in liquid nitrogen, and then coated with platinum before testing.

The thermal stabilities were measured on a TGA Q500 thermogravimetric analyzer (TA Instruments) under a nitrogen flow (40 mL $min^{-1}$). Approximately 5 mg samples were placed in a platinum pan and heated from ambient temperature to 600 °C at a rate of 10 °C $min^{-1}$.

## 3. Results and discussion

Whey protein isolate (WPI) is very easy to dissolve in water up to 25% solids concentrations. The addition of other materials, such as alginate or clay, further increases solution viscosity, leading to an unwanted tendency to trap air bubbles in the mixture. Much like blending of egg whites in cooking operations, the applied mixing force tends to denature the WPI protein, while generating foam-like bubbles. Caution needs to be taken in the production of such mixtures, as trapped bubbles will lead to imperfection in the freeze dried aerogels.

Our previous research has shown a linear dependency of aerogel bulk densities and mechanical properties on the starting polymer content in the aerogel [19,21]. As shown in Fig. 1, the compressive moduli of pure WPI aerogels show a monotonic increase with increasing polymer content, consistent with previous experience. The densities of WPI10A2.5, WPI10A5 and WPI10A2.5C2.5 were much lower than expected, only 50–70% of their theoretical values, which we attribute to trapped air bubbles which freeze dry into structural voids. Because of these bubbles, thermal gelation of WPI composites failed: during heating, the trapped bubbles would expand and cause flaws in the aerogel structure.

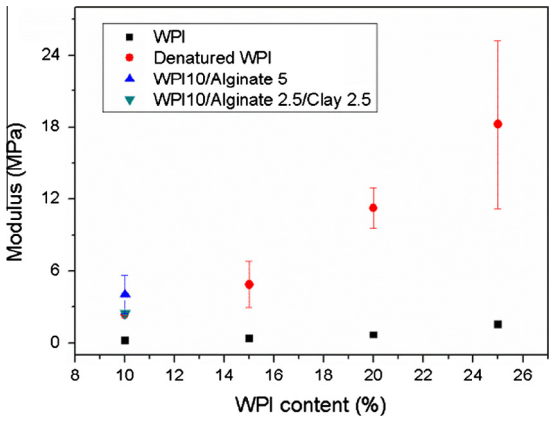


**Fig. 1.** Compressive modulus of WPI aerogel.