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Synthesis and characterization of zein-based cryogels and their potential as diesel fuel absorbent

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ABSTRACT

In this study, zein-protein based cryogels were synthesized by solution-based graft copolymerization of acrylic acid monomers onto zein protein backbones in the presence of an acrylamide crosslinker and initiators (sodium bisulfite and potassium persulfate). The grafting was confirmed by Fourier transform infrared spectroscopy. The thermal properties of the cryogels were assessed by thermogravimetric analysis and their morphology was studied by scanning electron microscopy and Brunauer–Emmett–Teller surface analysis. It was found that freezing the materials using liquid nitrogen at −196 °C before drying increased the surface area of the cryogels as compared to freezing at −20 °C. Dynamic mechanical analysis tests revealed that cryogels with increased acrylic acid content captured ambient moisture more quickly. The absorption capacity tests were performed in water and in diesel fuel. The highest equilibrium swelling of cryogels in distilled water reached 119.5 g/g of cryogel after 1 h while the highest equilibrium swelling in diesel fuel reached 49.8 g/g of cryogel in 15 min.

1. Introduction

Aerogels are absorbent materials recognized for their remarkably low density and high surface area [1]. The steps for the synthesis of aerogels usually include the synthesis of wet gels followed by a drying step. Common drying methods such as air drying and heat drying are not suitable as upon solvent removal, the surface tension of the solvent contained in the pores of the gel generates a high capillary pressure gradient enabling the collapse of the porous structure [2]. In order to avoid the disruption of the aerogels' structure, supercritical drying is traditionally used. Freeze-drying is another method that can produce porous matrices, and the obtained products are usually referred to as cryogels. The microstructure of cryogels prepared by freeze drying has been reported to differ in pore size, pore distribution and specific surface area as compared to aerogels, depending on the freezing temperature [3].

Bio-based polymers have gradually become an alternative to petroleum-derived polymers as new materials with improved physical properties are being developed. Moreover, polymers synthesized from proteins, plant starches, plant oils and polysaccharides can be designed to be fully biodegradable and biocompatible. The utilization of biomass feedstocks decreases the adverse environmental impacts as compared to petroleum-based polymers, especially when the biomass is considered as a byproduct from industrial processing [4,5]. For example, zein protein is the major storage protein of corn kernel and has been commercially produced from corn gluten meal, which is a byproduct from industrial corn starch production [6]. Zein has been used for applications in food packaging and encapsulation of nutrients [7,8]. Due to the high portion of nonpolar amino acids (approximately 55%), zein is insoluble in water, but the solubility can increase with the presence of alcohol, anionic detergents, high concentration of alkali (pH 11 or above) or urea [9]. Thus, zein has also been used for hydrophobic coatings that are resistant to microbial attack [9].

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Due to environmental and ecological concerns over the consequences of oil spills, several research groups have prepared sorbent materials to deal with these spills. For example, Hong et al. [10] produced a graphene-based aerogel with fluorinated functional groups which demonstrated excellent physical properties, such as high porosity, low density and high hydrophobicity. These aerogels could absorb up to 112 times their own weight in pump oil floating on the surface of water. Meng et al. [11] used microfibril cellulose to produce a sponge-like carbon aerogel which had a porosity of over 99%, ultra-low density (0.01 g/cm^3) and that could be reused. Lastly, Wu et al. [12] obtained aerogels by freeze-drying bacterial cellulose followed by pyrolysis to generate carbon nanofiber aerogels. These ultralight and flexible aerogels demonstrated high selectivity for oils with good reusability.

This study presents the synthesis of zein-based cryogels synthesized by graft copolymerization with acrylic acid. The objective of the present work was to study the effect of chemical composition and freezing temperature on the properties of the resulting cryogels. The wet gels were frozen at −20 °C and −196 °C before vacuum drying in order to investigate the effects of the freezing temperature and rate on the properties of the resulting cryogels. The physical properties of the cryogels were investigated by Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The evaluation of the absorption capacity of the cryogels was assessed in distilled water and oil (diesel).

2. Materials and methods

2.1. Materials

Zein proteins, acrylic acid (AA), sodium bisulfite (SBS), potassium persulfate (KPS), N,N′-methylenebisacrylymide (NMBA) and anhydrous ethanol were purchased from Sigma Aldrich (St. Louis, MO, USA). Hydrochloric acid and sodium hydroxide were purchased from EMD (Darmstadt, Germany). Diesel was purchased from Petro-Canada.

2.2. Methods

2.2.1. Hydrolysis of zein proteins

In this study, superabsorbent hydrogels were used as precursors for cryogels. Hydrophilic functional groups such as carboxyl groups are essential for the swelling properties of hydrogels. However, the carboxyl residues of aspartic acid and glutamic acid contained in zein are highly amidated [13]. Commercial zein contains approximately 25 wt% of asparagine and glutamine [9]. In order to synthesize hydrogels, a hydrolysis step was performed to deamidate the proteins and to increase the solubility of zein. To hydrolyze zein, hydrochloric acid was dissolved in 70% (w/w) aqueous ethanol to obtain a 0.37 M solution. Zein powder was added to the solution in a ratio of 1:10 (w/v). The mixture was stirred for 24 h at 70 °C. After the reaction, the pH of the solution was adjusted to 7 using sodium hydroxide. Thereafter, distilled water was added in excess to change the polarity of the solvent and to precipitate zein. The mixture was put in a freezer at 4 °C for at least 3 h to further precipitate zein. The proteins were collected after centrifugation and removal of the supernatant. To remove residual undesired salts (NaCl), distilled water was added and the mixture was stirred and re-centrifuged twice. The hydrolyzed zein proteins (HZP) were collected and freeze-dried.

2.2.2. Synthesis of zein-based cryogels

Zein-based hydrogel precursors were synthesized by graft polymerization technique with acrylate monomers as described in a previous study performed in our laboratory [14]. In a typical experiment, a solution of 70% neutralized AA was prepared by dissolving NaOH and AA in 16.7 g of 70% aqueous ethanol. A predetermined amount of crosslinker (NMBA) was dissolved in the AA solution. 1 g of HZP was added to 16.7 g of 70% aqueous ethanol and stirred for 5 min at 70 °C in a thermostat water bath. KPS and SBS initiators were added in a ratio of 2:1 (w/w) to the protein solution. After stirring for 5 min, the protein solution was mixed with the solution containing NMBA and AA. The mixture was incubated for 4 h at 70 °C in a water bath. After completion of the reaction, the obtained gel was immersed in distilled water for a total of 36 h. The distilled water was changed every 12 h. Thereafter, the gel was collected and subjected to different drying methods. The first one consisted in freezing the gel overnight at −20 °C, while the other method consisted in flash freezing using liquid nitrogen at −196 °C for 5 min. After freeze-drying, the cryogels were obtained and stored in a desiccator. The formulations and the drying method used in the synthesis of the cryogels are shown in Table 1.

Table 1
Formulations and drying methods of zein-based aerogels.

Sample	HZP (g)	AA (g)	KPS (g)	SBS (g)	NMBA (g)	Freezing temperature (°C)
1	1	2.7	0.75	0.375	0.03	−20
2	1	3.3	0.75	0.375	0.03	−20
3	1	3.9	0.75	0.375	0.03	−20
4	1	2.7	0.75	0.375	0.03	−196
5	1	3.3	0.75	0.375	0.03	−196
6	1	3.9	0.75	0.375	0.03	−196