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Synthesis and properties of canola protein-based superabsorbent hydrogels

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ABSTRACT

The present work reports, for the first time, the synthesis and characterization of canola protein-based hydrogels. These hydrogels were synthesized by solution based graft copolymerization of acrylic acid monomers on the canola protein backbones in the presence of a crosslinker (*N,N′*-methylenebis (acrylymide)) and initiators (sodium bisulfite and potassium persulfate). The grafting was confirmed by means of Fourier transform infrared spectroscopy. The contributions of the crosslinker, initiator and neutralization degree to the hydrogel were investigated by applying differential scanning calorimetry, thermogravimetric analysis, swelling test, scanning electron microscope. The macromolecules exhibited extraordinary water absorbency capacity in distilled water. The highest equilibrium swelling of hydrogel in distilled water reached 448 g/g of hydrogel in 48 h. The swelling properties of the optimized hydrogel were also studied at various pH and saline concentrations. The hydrogels responded spontaneously to these changes, which may confer them the title of smart materials.

1. Introduction

Hydrogels are highly cross-linked macromolecules which can undergo a change in volume (swelling/shrinkage) based on changes in environmental conditions, such as temperature, pH, ionic strength and the nature of the solvent. These spontaneous physical changes in response to changes in the environment conferred them the title of smart materials [1,2]. Superabsorbent polymer (SAP) hydrogel is one type of hydrogel that can absorb and retain a large amount of water or biological fluids in their polymeric structures [3]. Due to this characteristic, SAP materials are widely used in various areas, for example in hospital products, for water retention in agricultural and horticultural soils, in incontinence products, disposable diapers, and feminine hygiene products, for liquid radioactive waste treatment, in food packaging, biomedical products, and so forth [3–6].

Generally, SAPs are divided into synthetic and natural-based polymers. Synthetic hydrogels are usually made from petroleum-based hydrocarbons such as poly(hydroxyalkyl methacrylates), polyacrylate, polyacrylamide, and polymethacrylamide and its derivatives poly(N-vinyl-2-pyrolidone) and polyvinyl alcohol [7]. Even though synthetic hydrogels exhibit several advantages such as large water absorption capacities, and reasonable gel strength and cost; the broader use of synthetic hydrogel is limited by their toxic character and poor biodegradability. Therefore, natural-based SAPs have gained significant attention because of their nontoxicity, biocompatibility, and biodegradability [8]. This resulted in an increased number of studies reporting the synthesis of bio-based hydrogels synthesized from cellulose, starch, gelatin, chitosan, carrageenan, pectin, and proteins among others [9–12].

Of these natural polymers, proteins may be the most under-rated and underutilized feedstocks with respect to their industrial applications. Although proteins have been studied as starting material for the manufacture of films

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and composites [13–16], their potential as structural elements is still not well recognized. Proteins are characterized by numerous reactive groups, which can be used as sites for chemical modifications and cross-linking to develop polymeric structures [7]. An efficient way to obtain protein-based SAP hydrogels is through graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers within different initiator systems [17]. Addition of vinylic monomers enhances the hydrophilic character of proteins, which consequently improves the water absorption capacity of the resulting protein-based SAP hydrogels. To the best of the knowledge of the authors, collagen and cottonseed proteins are the only proteins which have been investigated for the synthesis of SAP hydrogels by the graft polymerization technique [17–22].

Canola is the third most widely grown commercial genetically modified crop after soybean and maize [23]. Canola proteins are extracted from canola meal, one of the by-products of the vegetable oil refining industry. These proteins are mostly utilized for low-value animal feed. Our research group saw an interesting potential in canola proteins since their amino acid composition is similar to soy proteins, which are utilized for many applications where polymers are involved. Therefore, in our previous study, we synthesized canola protein-based films [24]. These films showed water absorption capacities of up to 1150 wt.%. It should be noted that the films had not been designed for water retention applications. The high hydrophilicity of these canola protein-based films suggested that canola proteins could be excellent candidates for the synthesis of SAP hydrogels.

In this paper, we report the synthesis and characterization of canola protein-based SAP hydrogels by the graft polymerization technique with acrylate monomers, in order to broaden the non-food applications of canola protein. The swelling behavior of these hydrogels in different media shows their potential application as smart materials for controlled delivery applications, such as slow-release fertilizers for the agricultural sector.

2. Materials and methods

2.1. Materials

Hydrolyzed canola protein (HCP) (*Vitalexx*®) with a protein content of 77% (dry basis) was provided by BioExx Specialty Proteins Ltd. (Toronto, ON, Canada). Acrylic acid (AA), sodium bisulfite (SBS), potassium persulfate (KPS), *N,N′*-methylenebis (acrylymide) (NMBA) and anhydrous ethanol were of analytical grades and purchased from Sigma Aldrich (St. Louis, MO, USA). Sodium chloride and hydrochloric acid (ACS reagent grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Sodium hydroxide was purchased from EMD (Damstadt, Germany).

2.2. Preparation of hydrogels

In a typical experiment, hydrolyzed canola protein-*poly* acrylic acid (HCP-PAA) hydrogel were prepared as follows: 0.06 g of NMBA in 5 ml H_2O was added to 10 g of partially neutralized (70 mol%) AA. Hydrolyzed canola proteins (3 g) were dissolved in 25 ml of distilled water at 70 °C in a thermostat water bath with agitation using a magnetic stirrer for 5 min. Thereafter, initiators (2 g KPS and 1 g SBS) were added to the protein solution. After stirring for 10 min, the protein solution was mixed with the prepared AA and NMBA solution. The mixture was incubated in a water bath at 70 °C for 60 min for completion of the reaction. The resulting gel was immersed in an excess of non-solvent ethanol (200 ml) to dewater it. After 3 h, the ethanol was decanted. The gel was cut into small pieces and re-immersed with 100 ml fresh ethanol for 24 h. Afterwards, the gel was filtered and dried in an oven at 70 °C for 24 h after which, the dried gel pieces were treated with liquid nitrogen before being ground into powder. Finally, the powdered hydrogel was stored away from moisture, heat and light. To study the effects of the crosslinker, initiators and the neutralization degree on the swelling properties, hydrogels with different compositions were synthesized as described in Table 1.

2.3. Infrared analysis (FT-IR)

The FT-IR spectra of the HCP, hydrogels and additives were conducted in triplicate on a Nicolet iS5 FT-IR spectrometer (Thermo, Madison, WI, USA). The spectra were recorded at 32 scans and 4 cm^{-1} resolution in the 4000–400 cm^{-1} range. The spectra were analyzed using the OMNIC software package (version 8.2, Thermo Nicolet Corp).

2.4. Differential scanning calorimetry (DSC)

Around 10 mg of HCP and hydrogels were compressed in hermetic aluminum pans and scanned in duplicate using a DSC (Q100, TA Instruments, Inc., New Castle, DE, USA) under a steam of nitrogen (50 ml/min). Samples were heated from 0 °C to 200 °C at a rate of 10 °C/min to remove the thermal history. Samples were then cooled to 0 °C at a rate of 10 °C/min. The samples were then reheated from 0 °C to 350 °C at a rate of 10 °C/min.

2.5. Thermogravimetric analyzer (TGA)

A thermogravimetric analyzer (TGA) (Q500, TA Instrument, Inc., New Castle, DE, USA) was used for analyzing the thermal properties of the HCP powder and HCP based hydrogel. The thermogravimetric analyses were carried out under a stream of nitrogen at a flow rate of 60 ml/min. Samples weighing between 5 and 10 mg was heated from room temperature to 1000 °C at a constant rate of 20 °C/ min. The HCP powder and selected hydrogel samples were tested in duplicate.

2.6. Swelling measurement

The water uptake of hydrogel was determined as follows: In the first step, No. 2 coffee filter cone (Loblaws, Toronto, ON, Canada) was weighed and recorded as the original bag weight (M_1). The bag was then immersed in distilled water for 2 h and hung in the air for 20 min to remove the excess water. The bag was weighed again and the