European Polymer Journal 85 (2016) 164–174

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

A natural-based polymeric hydrogel based on functionalized soy protein

A.A. Cuadri [a], C. Bengoechea [b], A. Romero [b], A. Guerrero [b,*]

[a] Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro²TecS), Campus de 'El Carmen', Universidad de Huelva, 21071 Huelva, Spain
[b] Departamento de Ingeniería Química, Universidad de Sevilla, Facultad de Química, 41012 Sevilla, Spain

ARTICLE INFO

Article history:
Received 3 July 2016
Received in revised form 12 October 2016
Accepted 16 October 2016
Available online 18 October 2016

Keywords:
Hydrogels
Bioplastics
Protein acylation
Soy protein isolate
Water uptake capacity
FTIR

ABSTRACT

Even if most superabsorbent polymers (SAP) used nowadays are synthetic, natural-based SAP hydrogels have been gaining recently special attention due to their biocompatibility and degradability. The present manuscript studies the feasibility of obtaining hydrogels via soy protein functionalization using ethylenediaminetetraacetic dianhydride (EDTAD) as COO^- donor. The acylation of the protein was further confirmed by FTIR. Then, TGA tests and mainly the determination of the water imbibing capacity (WIC) of the modified protein samples related a higher extent of acylation reaction to a significant higher increase in the hydrophilic character of the soy protein. Using this functionalized protein as basis and glycerol as plasticizer (50 wt.%), bioplastics were obtained through small-scale injection molding. These samples displayed a water uptake capacity up to 2163 wt.% higher than that of the corresponding bioplastic based on the unmodified protein used as a reference. This increase in water uptake was observed to be greater as the degree of functionalization was higher. Correspondingly, scanning electron microscopy (SEM) images corroborated that larger porous regions were developed in the acylated bioplastics. On regards to their mechanical properties, an increase in the functionalization degree led to SAP materials with lower Young's Modulus and higher extensibility than those of the reference sample.

These results prove the potential of natural ingredients as proteins in the formulation of hydrogel that might overcome environmental issues related to the non-biodegradability of those based on acrylic derivatives.

1. Introduction

Superabsorbent polymer (SAP) hydrogels are highly cross-linked macromolecules that can absorb and retain a significant amount of water or biological fluids (as high as ~10–1000 times their own weight) [1,2]. Regarding their applications, SAP materials are momentous collection of resources with incredible purposes in engineering, biological and pharmaceutical sciences [3], highlighting the uses for water retention in agriculture and horticulture soils [4] and, mainly, for disposable diapers and feminine hygiene products [5].

Generally, SAPs are divided into synthetic and natural-based polymers. The first ones are frequently produced from acrylic acid, its salts, and acrylamide via solution or inverse-suspension polymerization techniques [6]. Even though syn-

* Corresponding author.
E-mail address: aguerrero@us.es (A. Guerrero).

http://dx.doi.org/10.1016/j.eurpolymj.2016.10.026
0014-3057/

thetic SAPs hydrogels exhibit large water uptake capacities, the broader use of these materials are strongly limited by their poor biodegradability and high cost [1]. Clearly then, there is a growing need to develop natural SAPs that, in addition to overcome these drawbacks, should present both great water uptake capacity and processability properties.

In this sense, some studies reported the synthesis of bio-based SAP hydrogels prepared from cellulose [7], starch [8], carrageenan [9], gelatin [10], chitosan [11–13], canola protein [1], alginate [14], guar gum [15,16] and collagen [17,18]. Following with the natural-based SAP, the employ of proteins as feedstock results in a promising alternative. Proteins contain more than 20 different aminoacids [19] characterized by numerous reactive groups that can be used as sites for chemical modifications and cross-linking to develop polymeric structures [20]. In addition to that, proteins may be the most under-rated and underutilized feedstocks with respect to their applications [1] and, consequently, its use as natural-based SAP materials provides substantial added value.

Among them, soy protein presents considerable advantages such as: (1) is the major coproduct of soybean oil and is one of the cheapest proteins in nature [21], (2) shows high hydrophilic character [22], and (3) in combination with a plasticizer (i.e., glycerol) displays excellent processability properties, allowing us to produce many kinds of shaped products (e.g. by injection molding) [23]. All this makes of the soy protein an adequate starting material for the manufacture of natural-based SAP hydrogels. However, the previous studies found in the literature based on soy-protein bioplastics [22–24] reported water uptake capacities that did not fall within the required level for SAP materials.

Therefore, more emphasis should be conducted on improving the water absorption capacity of the soy protein. A valuable way of getting it could be through the functionalization of the protein matrix, giving rise to the presence of new water-solubilizing groups. One of the most common chemical modifications used for proteins is the acylation of the amino acid residues with acid anhydrides [25]. On these grounds, Hwang and Damodaran [20,26] reported that the modification of lysyl residues using ethylenediaminetetraacetic dianhydride (EDTAD) is able to incorporate a large number of carboxylate anions (COO^-) into the soy protein molecule, creating numerous sites for water binding and, consequently, increasing its hydrophilic character. Nevertheless, these studies were just limited to calculate the water uptake capacity of the synthetized SAP hydrogels, which resulted in an insufficient characterization for their potential future applications.

The main goal of the present work is to develop and characterize natural-based SAP plastics via soy protein functionalization with EDTAD. More precisely, this research seeks to assess the effect that functionalization degree exerts on the thermomechanical response of their corresponding soy/plasticizer blends, as well as the water uptake capacity and tensile properties for the soy protein SAP plastics processed through injection molding.

2. Material and methods

2.1. Materials

Soy protein isolate (SPI), with the trade name of SUPRO 500E IP, was supplied by PROANDA (Proveedora Andaluza, S.L., Sevilla, Spain). Its specifications, provided by the supplier, were: max. 6.0% moisture, min. 90.0% protein, max. 1.0% fat, max. 5.0% ash and pH (5% slurry) in the range of 6.9–7.4. Glycerol (GL) and ethylenediaminetetraacetic dianhydride (EDTAD), from Panreac Química, S.A., were used as protein plasticizer and SPI COO^- donor, respectively.

2.1.1. Protein functionalization

The acylation of SPI was performed according to the procedure reported by Hwang et al. [20,26]. The pH of a 4 wt.% solution of SPI was adjusted to 12 by adding the amount necessary of a 3.0 N NaOH solution and heating for 30 min at 65 °C. The solution was then cooled down to room temperature and modified by the addition of the corresponding different amounts of EDTAD that result in a EDTAD/SPI mass ratio of 0.05, 0.10 and 0.15. Throughout the chemical modification, the pH of the protein solution was kept constant at 12.0 adding conveniently 1.0 N NaOH for 3 h while stirring. After that, the pH was decreased to 7.0 by the addition of 6 N HCl to prevent further modification. Finally, the protein solution was dialyzed against deionized water overnight to remove salts, mainly the sodium salt of EDTA, and the acylated SPIs were recovered by freeze-drying with a Telstar CRYODOS-80 (Telstar, Life Science Solutions, Madrid, Spain).

Regarding their nomenclature, the acylated SPIs prepared with EDTAD/SPI mass ratio of 0.05, 0.10 and 0.15 will hereinafter be referred to as aSPI-0.05, aSPI-0.10 and aSPI-0.15, respectively.

2.2. Sample preparation

Blends containing 50 wt.% protein (unmodified SPI or acylated SPI systems) and 50 wt.% GL were properly manufactured by a thermomechanical procedure that consisted of two stages:

(a) The ingredients were mixed in a two-blade counter-rotating batch mixer Haake Polylab QC (ThermoHaake, Karlsrube, Germany) at room temperature and 50 rpm for 10 min, at adiabatic conditions. During mixing, only a slight increase in temperature (always lower than 2 °C) was detected whereas no significant increase in torque was observed, which excludes any significant contribution of shear induced crosslinking over the mixing stage. The final pH value of these protein/plasticizer blends, which was measured by a Crison pH 25 pH meter in combination with a puncture electrode