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Material Performance

Natural superabsorbent plastic materials based on a functionalized soy protein

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ABSTRACT

A natural superabsorbent polymer (SAP) material based on an acylated soy protein was studied as a green alternative to non-biodegradable SAP. In order to obtain the natural SAPs, different amounts of succinic anhydride were used as acylating agent. Once the functionalized protein was obtained, it was mixed thoroughly with glycerol and then molded through a lab-scale injection molding device. Water uptake of samples obtained reached values much higher than those based on unacylated protein. Moreover, a greater extent of the acylation reaction led to higher water uptake values for the corresponding SAPs, probably related to their higher hydrophilic character. Water imbibing capacity measurements and thermogravimetrical analysis (TGA) seemed to confirm this. The presence of larger porous regions in acylated samples observed in SEM images could also play a role in their higher water uptake values.

Furthermore, an increase in the extent of acylation reaction led to plastics with lower Young's modulus and higher extensibility.

1. Introduction

Superabsorbent polymer (SAP) materials are defined as hydrophilic three-dimensional polymer networks that can absorb and retain a significant amount of water or biological fluids (as high as ~ 10–1000 times their own weight) [1–3]. Regarding their applications, the super-swelling characteristics of SAPs makes them ideal materials in engineering, biological and pharmaceutical products [4], highlighting the uses for water retention in agriculture and horticulture soils [5] and, mainly, for disposable diapers and feminine hygiene products [6].

SAPs are generally classified into synthetic and natural-based polymers. The former are frequently produced from acrylic acid and its derivatives [7,8], issues related to their poor biodegradability and high costs having been pointed out [1]. As a consequence, there is a growing need to develop natural SAPs that overcome these drawbacks, showing both great water uptake capacity and processability.

In this sense, some studies have reported the synthesis of bio-based SAP materials prepared from polysaccharides such as cellulose [9], starch [10], carrageenan [11] or gelatin [12]. However, the low efficiency when compared to synthetic SAPs together with the resulting high cost of production are factors that limit the application of polysaccharides-based SAPs [13,14]. On the other hand, the use of proteins might be a promising alternative in the production of natural SAPs, in spite of the relatively moderate water uptake capacity shown by most of them under native conditions. Proteins contain more than 20 different aminoacids [15] characterized by numerous reactive groups that can be used as sites for chemical modifications and cross-linking to develop polymeric structures [16]. In addition to that, proteins may be the most underrated and underutilized feedstocks with respect to their applications [1] and, consequently, their use as natural-based SAP materials would provide substantial added value.

Soy protein would seem to be an adequate starting material for the manufacture of natural-based SAP materials when considering the following facts: (1) it is the main coproduct of the soybean oil industry, being available at an affordable price [17]; (2) it shows a high hydrophilic character, due to the high presence of aspartic and glutamic acids in its composition [18]; and (3), in combination with a plasticizer (i.e., glycerol), it displays excellent processability

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properties, allowing the production of different shaped products (e.g. by injection molding) [19].

However, previous studies found in the literature based on soy-protein plastics [18–20] reported water uptake capacities that did not fall within the level required for SAP materials. Correct functionalization of the protein matrix, which would give rise to the presence of new water-solubilizing groups, would improve the water uptake capacity of the material. One of the most common chemical modifications used for proteins is the acylation of the amino acid residues with acid anhydrides [21]. On these grounds, Hwang and Damodaran [16,22] reported that the modification of lysyl residues using ethylenediaminetetraacetic dianhydride (EDTAD) as acylating agent 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. In this research, we propose the use of succinic anhydride (SA) as an alternative acylating agent. Even if SA possesses half the anhydride groups present in EDTAD, its much lower cost (~290 $/lb) compared to EDTAD (~4275 $/lb) would surely play a decisive factor in its eventual industrial application. On this basis, Yoshimura et al. have reported the use of SA in the manufacture of SAP materials made from chitin [23], cotton cellulose [24] and starch [25], whose synthesis involve the use of chemical reagents (e.g. dimethyl sulfoxide, lithium chloride). These SAP materials were solely characterized in terms of their water uptake capacity. Interestingly, the novelty of this research lies in obtaining SAP materials from soy protein and SA as acylating agent, but without the use of those chemical reagents, therefore being a green alternative to non-biodegradable SAP.

Therefore, the main goal of the present work is the production and characterization of natural SAP materials based on an acylated soy protein, obtained through functionalization with SA. Also, broader characterization of the natural SAP plastics processed through injection molding is made through different techniques: dynamic mechanical thermal analysis (DMTA), tensile tests, water uptake capacity measurements and scanning electron microscopy (SEM).

2. Material and methods

2.1. Materials

Soy protein isolate (SPI), under 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 succinic anhydride (SA), from Panreac Química, S.A., were used as protein plasticizer and SPI acylating agent, respectively.

2.1.1. Protein functionalization

The acylation of SPI was performed according to the procedure reported by Zhao et al. [21]. Firstly, a 4 wt% solution of SPI was dispersed in distilled water for 1 h using a magnetic stirrer. Subsequently, the pH of the solution was adjusted to 8 by adding the amount necessary of a 3.0 N NaOH solution. Then, it was modified by the addition of different amounts of SA according to SA/SPI mass ratios of 0.04, 0.08 and 0.12. The pH of the solution was kept between 7.5 and 8.5 adding conveniently 3.0 N NaOH while stirring. After pH was stabilized around 8, the solution was kept stirred for 1 h. Afterwards, pH was decreased to 7.0 by the addition of 3 N HCl to prevent further modification. Finally, the protein solution was dialyzed against deionized water for 48 h to remove impurities and excess reagents, recovering the acylated SPIs through freeze-drying using a Telstar CRYODOS-80 (Telstar, Life Science Solutions, Madrid, Spain).

The acylated SPIs prepared with SA/SPI mass ratio of 0.04, 0.08 and 0.12 will hereinafter be referred to as aSPI-0.04, aSPI-0.08 and aSPI-0.12, 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, under 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 would exclude any significant contribution of shear-induced cross-linking over the mixing stage. The final pH value of these protein/plasticizer blends was measured by a Crison pH 25 pH meter in combination with a puncture electrode (Crison Instruments S.A., Barcelona, Spain). The values of pH were 8.0 ± 0.5 and 8.4 ± 0.5 for those blends prepared from unmodified SPI and acylated SPIs, respectively. Samples were stored in sealed plastic bags at room temperature for 24 h, prior further processing.
b) The blends were processed after storage for 24 h by lab-scale injection molding using a MiniJet Piston Injection Molding System (ThermoHaake, Karlsrube, Germany) to obtain 60 × 10 × 1 mm rectangular shaped plastic specimens. Based on previous studies searching SPI/GL plastics with optimized water uptake capacity [18], moderate processing conditions were selected. Thus, the temperature, pressure and time in the pre-injection cylinder and in the mold were respectively: 50/120 °C, 500/500 bar and 10/500 s. For the acylated SPIs, the pressure profile selected was 500/250 bar in order to obtain homogeneous plastic specimens.

The plastic materials obtained from unmodified SPI will be referred to as SPI/GL, and those prepared from acylated SPIs as aSPI/GL-0.04, aSPI/GL-0.08 and aSPI/GL-0.12, depending of its SA/SPI mass ratio.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of protein samples were recorded on a Jasco FT/IR 4200 spectrometer (Jasco Analytical Instrument, Japan) from finely ground sample (~10 wt %) in KBr pellets. The spectra were obtained in a wavenumber range of 400–4000 cm^{-1} at 4 cm^{-1} resolution in the transmission mode.

2.3.2. Thermo-gravimetric analysis (TGA)

TGA tests were conducted in a Seiko TG/DTA 6200 (Seiko Instruments Inc., Japan). Temperature ramps were carried out using 5–10 mg of protein samples at 10 °C/min, from 30 to 600 °C, under N_2 atmosphere. From these tests, the water loss due to the free and bonded water was calculated in the temperature range from 30 to 150 °C.

2.3.3. Water imbibing capacity (WIC)

The WIC of all protein samples was measured in a Baummann apparatus according to a method modified by Wagner et al. [26]. A glass Buchner funnel equipped with a borosilicate filter (ROBU Glasfilter-Geraete GmbH, Germany) was connected to a horizontal