Development of bio-based superabsorbent polymeric matrices based on functionalized soy protein

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ABSTRACT

As a promising alternative to acrylic superabsorbent polymers (SAP), this work studies the feasibility of obtaining natural-based SAP materials via soy protein isolate (SPI) functionalization, using ethylenediaminetetraacetic dianhydride (EDTAD) as acylating agent. Different SAP samples were characterized by dynamic mechanical thermal analysis (DMTA) and water uptake capacity measurements.

INTRODUCTION

Superabsorbent polymer (SAP) materials 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) to form hydrogels[1,2]. Regarding their applications, SAP materials are momentous collection of resources with incredible applications 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].

SAPs are generally classified into synthetic and natural-based polymers. The former are frequently produced from acrylic acid and its derivatives[6,7], 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.

Soy protein isolate (SPI) would seem to be an adequate starting material for the manufacture of natural-based SAP materials when considering: (1) SPI is the main coproduct of the soybean oil industry, being available at an affordable price[8]; (2) SPI shows a high hydrophilic character, due to the high presence of aspartic and glutamic acids in its composition[9]; and (3) SPI, in combination with a suitable plasticizer (i.e., glycerol), displays excellent processability properties, allowing the production of different shaped products (e.g. by injection molding)[10].

A valuable way of improving the water absorption capacity of SPI could be through the functionalization of the protein matrix, giving rise to the incorporation 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. In this sense, SPI modification with 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[11].

Therefore, this work deals with the development and characterization of natural

SAP materials based on acylated SPI using EDTAD as acylating agent, therefore being regarded as a valuable green alternative to non-biodegradable SAPs. The effect of new COO^- groups incorporated into the protein matrix on dynamic mechanical thermal analysis (DMTA) as well as on the water absorption capacity was evaluated.

MATERIALS AND METHODS

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 EDTAD, from Panreac Química, S.A., were used as protein plasticizer and COO^- donor, respectively.

Protein functionalization

The acylation of SPI was performed according to the procedure reported by Hwang and Damodaran[11]. 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 ºC. The solution was then cooled down to room temperature and modified by the addition of the corresponding amount of EDTAD that result in an EDTAD/SPI mass ratio of 0.15. The pH of the protein solution was kept constant at 12.0 throughout the chemical modification, 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 equipment (Telstar, Life Science Solutions, Madrid, Spain).

Sample preparation

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

(a) The ingredients were mixed in a two-blade counter-rotating batch mixer Polylab QC (ThermoHaake, Karlsrube, Germany) at room temperature and 50 rpm for 10 min, at adiabatic conditions. Only a slight increase in temperature (always lower than 2 ºC) was detected during the mixing process, whereas no significant increase in the recorded torque was observed, which excludes any significant contribution of shear induced crosslinking over the mixing stage. Samples were stored in sealed plastic bags at room temperature either for 1 h or 24 h (ageing time), prior further processing.

(b) The blends, after ageing for 24 h, were subsequently processed by lab-scale injection molding using a MiniJet Piston Injection Molding System (ThermoHaake, Karlsrube, Germany) to obtain 60x10x1 mm rectangular shaped bioplastic specimens. The temperature, pressure and time in the pre-injection cylinder and in the mold were: 50/120 ºC, 500/500 bar and 10/500 s. For the acylated SPIs, the pressure profile selected was 500/250 bar in order to obtain homogeneous bioplastic specimens.

The blends and bioplastics obtained from unmodified or acylated SPI will be denoted as SPI/GL and aSPI/GL-0.15, respectively.

Characterization

DMTA tests were performed on the protein/plasticizer blends obtained after mixing with a RSA3 (TA Instruments, New Castle, USA) in compression mode using cylindrical plates (8 mm diameter). Temperature sweep tests were conducted at a constant frequency of 1 Hz and strains within the linear viscoelastic region (LVR). The selected temperature ramp was set at 3 ºC/min with a temperature range from 0 to 130 ºC. All the samples were coated with Dow Corning high vacuum grease to minimize water loss.

Water uptake of bioplastics was determined according to UNE-EN ISO

62:2008 using 20x10x1mm specimens immersed in distillate water for 24 h. The water uptake percentage was calculated as:

$$\text{Water uptake}\,(\%) = \frac{m_2 - m_1}{m_1} \times 100 \qquad (1)$$

where m_1 is the initial weight of the probe immediately weighed after being dried in an oven at 50 ºC for 24 h and cooled in a desiccator; and m2 refers to the weight of the probe just after 24 h of water immersion.

RESULTS AND DISCUSSION

With the aim of studying the effect that ageing time (1 h or 24 h) may exert on the rheological response SPI-based blends to be processed by injection molding, results from temperature ramp DMTA compression tests were displayed in Figures 1 and 2 for the reference system (SPI/GL) and the acylated sample (aSPI/GL-0.15), respectively.

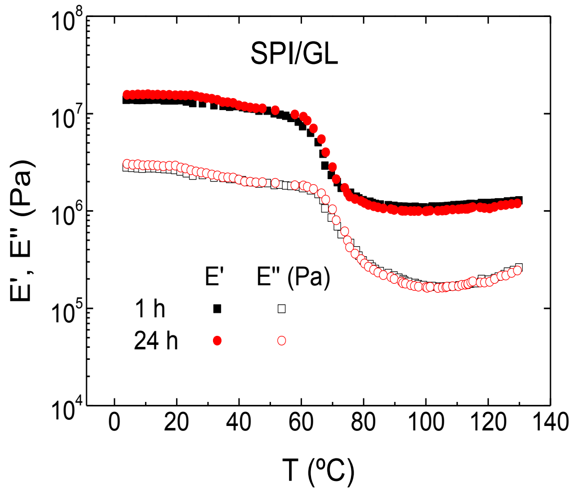

Figure 1. E’ and E’’ response from DMTA in compression mode for the reference (SPI/GL) blend, prior to the injection molding, after 1 h and 24 h of ageing time.

Thus, after 1 h, both moduli decrease progressively with increasing temperature until reaching their minimum value at ca. 50 ºC. Then, after a slight increase, between 50 ºC and 60 ºC, both moduli keep decreasing continuously with temperature in the intermediate-high temperature range (i.e. 60–130 ºC). Interestingly, it is found how the same blend (aSPI/GL-0.15) shows higher thermomechanical properties in the low-intermediate range (i.e. 0–60 ºC) after ageing for 24 h.

However, E’ and E’’ values become quite coincident for the two ageing times at the intermediate-high temperature range. This fact suggests that a maturation period is required for the aSPI/GL blends, probably involving some kind of reorganization of glycerol molecules in the blend that seem to lead to a reduction in plasticizing efficiency.

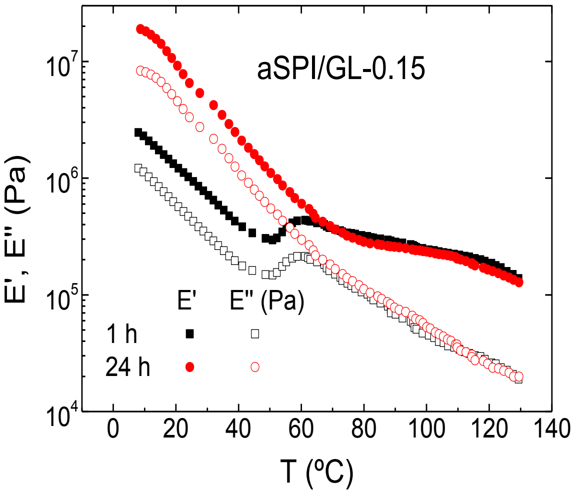

Figure 2. E’ and E’’ response from DMTA in compression mode for the acylated (aSPI/GL-0.15) blend, prior to the injection molding, after 1 h and 24 h of ageing time.

Moreover, it is expected that the protein-glycerol interactions from the acylated SPI, which has a more hydrophilic character as a consequence of the presence of a large amount of COO^- groups, differ considerably from those coming from the unmodified SPI, with lower hydrophilic properties (Figure 1). It seems that, for obtaining acylated SPI/GL blends with higher E’ and E’’ moduli at the range of low-intermediate temperature, a higher ageing period (e.g. 24 h) is needed. These results suggest that the ageing time needed for the functionalized SPI might be required for the formation of interactions between new carboxyl groups in the protein and hydroxyl groups of the plasticizer[12].

The effect that protein functionalization exerts on their corresponding rheological response was evaluated for samples after ageing for 24 h (Figure 3). The evolution of E' along heating (Figure 3) for the acylated SPI/GL blend was qualitatively similar and has been previously described (Figure 2). As may be seen, the acylated blend displays poorer viscoelastic properties in the whole range of temperature compared to the reference blend, showing lower E' values.

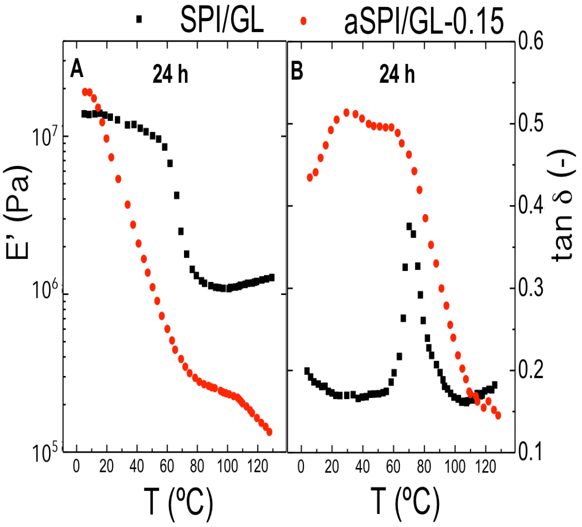

Figure 3. E' (A) and tan δ (B) responses from DMTA in compression mode for the reference and acylated blends, prior to the injection molding, after 24 h of ageing time.

Moreover, Figure 3B shows the tan δ profile for these systems. Some authors[13,14] reported that glycerol-plasticized soy protein materials could be visualized as blends of plasticizer-rich and protein-rich domains that lead to occurrence of two α-relaxation events. The first one is assigned to the plasticizer-rich phase and appears at temperatures lower than 50 ºC, whereas the peaks on tan δ curves shown in Figure 3B can be attributed to the glass transition of protein-rich domains. SPI/GL blend shows one single peak at about 68 ºC, in the testing temperature range. The behaviour found for the SPI/GL blend, showing a unimodal tan δ profile, has been previously reported and has been related to a good compatibility between protein and glycerol[9]. With regards to the acylated SPI-GL blend, its tan δ profile became wider and less prominent, which suggests a change to a broad range of functionalized protein-rich domains. This increase in tan δ values for acylated SPI blend, which is reflected in softer samples, over a broader temperature range, together with their higher sensibility to temperature, may be regarded as a favourable factor which facilitates their lab scale injection molding. In addition, it also allows us to prepare protein/glycerol blends with higher acylated protein concentrations.

Finally, Table 1 shows the results from the water uptake measurements obtained after immersion of bioplastic samples for 24 h. Regarding their water uptake capacity, bioplastic samples are strongly enhanced for those prepared from acylated SPI (with values of up to 3650 wt.%) compared to the moderate value obtained for the reference sample (160 wt.%).

Table 1. Water uptake values obtained for SPI/GL and aSPI/GL-0.15 samples after swelling and re-swelling tests.

	Water uptake (wt.%)	Water uptake after re-swelling (wt.%)
SPI/GL	161 ± 10	130 ± 9
aSPI/GL-0.15	3644 ± 204	3592 ± 198

On the other hand, the SAP-materials after their first water immersion were lyophilized and again subjected to water immersion for 24 h (named as re-swelling). Interestingly, no significant differences between water uptake and re-swelling capability are found in Table 1. In addition to that, no water-soluble loss matter (no data shown) was observed for the acylated samples after the second water immersion. This is particularly relevant from a practical point of view, since these findings imply that SPI superabsorbent materials can be re-used at least twice without losing their water uptake capacity.

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