Improving mechanical properties of a plasma based superabsorbent material through the addition of a crosslinker

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ABSTRACT

The main challenge for bioplastics is to achieve similar properties to those of traditional plastics. This research aims to improve the viscoelastic properties of superabsorbent materials based on a porcine plasma protein and glycerol, avoiding an excessively high soluble matter loss. For this purpose, glutaraldehyde was added in different amounts into the formulation. In this sense, the addition was made directly through mixing (0.2 and 0.4 wt.%) or through immersion of the bioplastic in a glutaraldehyde aqueous solution (0.01 and 0.025 wt.%). This helped to improve the mechanical properties of the protein-based plastics.

INTRODUCTION

A superabsorbent material (SAM) is one that is considered capable to absorb and retain more than 10 times (1000 %) its own weight in water without losing its integrity [1]. These materials are widely used in cosmetics and self-care industry, being commonly composed by traditional fuel-based plastics, which frequently contain acrylic derivatives. However, it should be born in mind the fact that those materials are toxic, highly pollutant and possess a very low biodegradability and consequently its deposition in the environment could cause serious environmental issues. Taking this into account, the possibility of replacing them by hydrophilic natural source-based plastics is being considered. Several studies have highlighted the possibility of using different protein sources either from animals or vegetables as main raw materials. This is the case of protein concentrates or isolates from soy[2–5] or porcine plasma[6–8], both of which are rich in hydrophilic amino acids which are related to high water absorption properties. In the particular case of the porcine plasma protein, a superabsorbent plastic has been obtained through injection moulding at mild temperatures, using glycerol as plasticizer, displaying a water absorption around 35 times (3500 %) its own dry weight[8]. However, in some particular cases, the soluble matter loss was considerably high which could compromise the integrity of the samples[7]. Thus, with the aim of avoiding the disintegration of the samples after the water immersion, the possibility of the inclusion of a crosslinker agent in the formulation of the materials may be considered. A widely employed chemical crosslinker is glutaraldehyde, which effectiveness has been already tested[9,10] , resulting for example in an improvement of the mechanical properties of crosslinked films[11]. The crosslinking produced by the action of glutaraldehyde can mainly take place by the intra or intermolecular covalent interactions between glutaraldehyde and the amino residues of lysine or residues of hydroxilysine of the protein chain[12,13].

The main objective of the present manuscript is the obtainment of a

superabsorbent material based on porcine plasma protein with reduced soluble matter loss values by the action of a chemical crosslinker such as glutaraldehyde. In order to observe the changes, some assays were carried out such as dynamic mechanical temperature analysis, water uptake capacity, and scanning electron microscopy.

MATERIALS AND METHODS

Materials

The porcine plasma protein (PPP) used in the present study (AproPork, Essentia Proteins (USA)) had a protein content around 74 wt.% (Kejdhal factor of 6.25) calculated with a LECO CHNS-932 Nitrogen analyser (Leco Corporation, St. Joseph, MI, USA). Moreover, the flour contained around 9 and 17 % of moisture and the ashes content, respectively. Glycerol (Gly) (Panreac Química S.A (Spain)) was employed as plasticizer and an aqueous solution 50 wt.% of glutaraldehyde (GTA) (Sigma-Aldrich Química, S.A. (Spain)) was used as crosslinker.

Sample preparation

Biobased-plastics were obtained through a two-step injection moulding procedure. In a first moment, raw materials were mixed in a Haake Polylab QC mixer rheometer (ThermoHaake, Karlsruhe, Germany) during 5 minutes at 50 rpm, giving rise to homogeneous blends. The ratio PPP/Gly was maintained equal to 1 for all samples. Likewise, GTA was added in the mixer rheometer in different quantities: 0 (reference), 0.2 and 0.4 wt.%. Then, the blends were conveniently injected in a Minijet Piston Injection Moulding System (ThermoHaake, Karlsruhe, Germany). Samples were rectangular shaped in a 1x10x60 mm mould, using a mould temperature of 60ºC. An injection pressure of 500 bar during 150 s was required during the process. Moreover, GTA was also introduced in in composition through immersion of the reference sample in a GTA-containing aqueous media, with concentrations from 0.01 to 0.025 wt.%.

Rheological characterization of blends

For blends, temperature sweep tests were performed in an RSA 3 rheometer (TA Instruments, USA) with the aim to know the influence of the addition of GTA in their rheological properties. Tests were carried out using an 8 mm diameter cylindrical geometry from 25 to 140ºC (heating rate: 5ºC/min), using a strain within the linear viscoelastic range and a constant frequency (1 Hz).

Water uptake and soluble matter loss

Water uptake capacities (WUC) as well as soluble matter loss (SML) of samples were estimated by differences between the weights of samples along different stages, using eq. (1) and eq. (2). In a first moment, samples were placed in an oven at 50ºC until constant weight (w_1). Consecutively they were submitted to immersion in an aqueous media (0, 0,01 or 0.025 wt.% GTA) for 24 h (w_2). Finally, swollen samples were dried in the oven until constant weight (w_3).

$$\text{WUC}\ (\%) = \frac{w_2 - w_3}{w_3} \cdot 100 \qquad (1)$$

$$\text{SML}\ (\%) = \frac{w_1 - w_3}{w_1} \cdot 100 \qquad (2)$$

Scanning electron microscopy

Selected plastic samples were freeze dried (-80ºC and 0.01 mbar) after the immersion stage. Small squared pieces of samples of approximately 2.5 mm of length were gold coated and observed with a magnification of 200x through Scanning Electron Microscopy (SEM) in a ZEISS EVO (USA). The observation parameters were set at 11-12 pA for the beam current, 6 mm as the working distance, and 10 kV for the voltage.

Statistical study

All measurements were carried out by triplicate. Results are expressed by the mean value and its deviation standard. The

software statgraphics was used for the statistical study.

RESULTS

Rheological properties of blends

The effect in the viscoelastic properties of the addition of GTA as a raw material in the mixing stage was studied through temperature sweep tests. From these results (Figure 1) it could be observed that the storage modulus (E') showed higher values than the loss modulus (E'') for the whole range of temperature. This resulted in tan δ (E''/E') values below one (data not shown), corresponding with a more solid-like behaviour, frequently observed in this kind of biobased plastics [6,14]. All samples presented a remarkable decrease in E' and E'', approximately from 50 to 62ºC, where a minimum for both viscoelastic moduli was detected. That decrease may be caused by the agitation and mobility of the protein chains enhanced by the effect of temperature[15]. From the minimum temperature on, an increase in both moduli was observed finally reaching a steady value when the essay temperature achieved 110ºC. This reinforcement was presumably produced by the aggregation of the albumin and globulins that make part of plasma protein. During this reinforcement, two different slopes were differentiated which could be attributed to the existence of diverse protein fractions with different responses to temperature and aggregation[16]. Analogous evolutions with temperature have been previously observed in plasma protein-glycerol systems[6–8].

It could be clearly observed that the presence of GTA in the sample increase remarkably the E' and E'' values through all the temperatures studied. The same effect was observed in other systems[12]. This strengthening may be produced by the already known crosslinking character of GTA which promotes the formation of linkages through the amino and sulfhydryl groups present in protein chains[17,18].

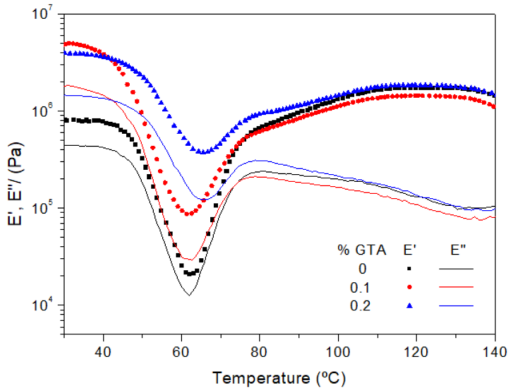

Figure 1. Temperature sweep test measurements performed (1 Hz and 5ºC/min) on PPP/Gly blends with different contents of GTA introduced through mixing.

Water absorption of bioplastics

The effect that the procedure employed to introduce GTA as chemical crosslinker in the bioplastic (mixing or immersion) was tested through water uptake capacity (WUC) measurements for plasma protein-based plastics (Figure 2). Reference sample, based solely on PPP and glycerol, showed a considerably higher water absorbance value which could be associated with its superabsorbent character (>1000 %)[6–8]. Observing the results when GTA was introduced through mixing when all ingredients were blended, a greater decrease was observed in WUC values as the quantity of crosslinker was higher, detecting values below the superabsorbent threshold when the added quantity of GTA was 0.2 %. Likewise, lower values of WUC were observed when GTA was included through immersion of the injected reference sample in an aqueous solution of GTA. When following this procedure, a concentration of GTA higher than 0.025 % in the aqueous solution hindered the water absorbance up to values lower than 1000 %. Thus, the decrease observed for higher contents of the chemical crosslinker may be related to the reinforcement in the structure which hindered penetration of water into the material, and consequently the swelling. The

water absorption of other protein source-based materials has been reported to directly correlate to the crosslinking degree in the samples[19,20] which is in agreement with the results obtained in the present study.

A similar evolution was observed when the soluble matter loss was calculated. Thus, higher values of SML were observed for reference samples. For those samples, the quantity of matter loss after immersion was considerably higher than the quantity of glycerol originally introduced in the sample formulation, which would indicate that some portion of the protein fraction from the material was solubilized during immersion, making it weaker[8]. On the other hand, when the GTA was included in samples, the SML values proportionally dropped up to the quantity of plasticizer. The decrease produces in SML when GTA was introduced in the sample was more remarkable if it was introduced through the immersion procedure.

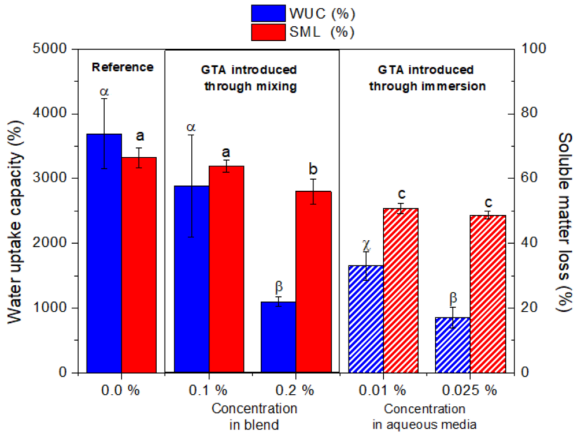

Figure 2. Water uptake capacities values for reference and samples with different quantities of GTA introduced through mixing (0.1 and 0.2 wt.%) or immersion (0.01 and 0.025 wt.%).

Scanning electron microscopy

In order to identify the influence of GTA in the structure of the plasma protein-based plastics, microscopy assays were carried out (Figure 3).

In reference samples, a relatively large porosity could be distinguished. They were presumably formed by solubilisation of the plasticizer and the penetration of water into the protein matrix structure during the immersion stage, just before the freeze-drying stage. Generally, it could be observed that the addition of GTA reduced noticeably the porosity of the samples. This fact could indicate a lower swelling which would justify the lower WUC values obtained from these samples, as it has been indicated in the WUC section. Likewise, the increase in the concentration of GTA added formed a packed and less porous structure.

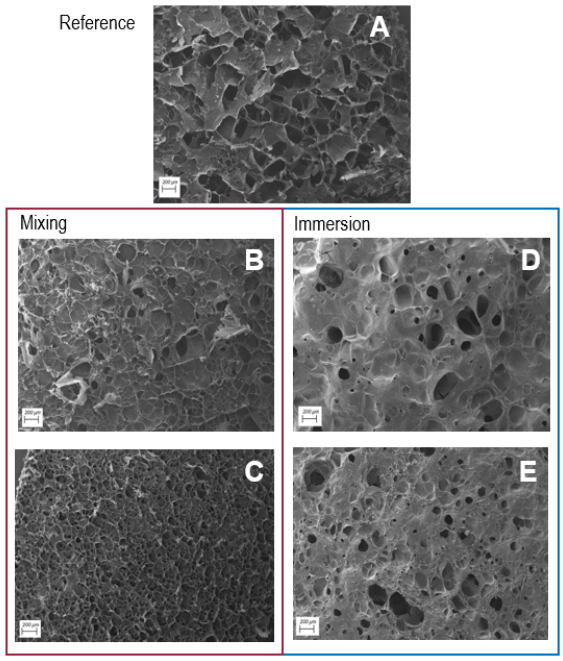

Figure 2. Micrographs for reference (A) and samples with different quantities of GTA introduced through mixing (0.1 (B) and 0.2 (C) wt.%) or immersion (0.01 (D) and 0.025 (E) wt.%).

CONCLUSIONS

The addition of glutaraldehyde either directly in the blend before injection or through immersion of the injected plasma protein-based plastic material had significant influence on the rheology of their blends, water uptake capacity and structure.

The introduction of glutaraldehyde in the mixing stage along with the rest of the components resulted in a reinforcement of

the structure which produced an increase in the viscoelastic moduli at all temperatures considered.

The water uptake capacity was always hindered when GTA was introduced, independently of the procedure followed, resulting in values lower than 1000 % (superabsorbent threshold) when a certain concentration of GTA was surpassed: 0.01 wt.% for mixing and 0.025 wt.% for immersion. Thus, the lower WUC values reached by the GTA-containing samples resulted in less porous structures as could be observed in the micrographs obtained.

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