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# Development of eco-friendly biodegradable superabsorbent materials obtained by injection moulding

V. Perez-Puyana [a], M. Felix [b, *], A. Romero [c], A. Guerrero [b]

[a] Departamento de Ingeniería Química, Universidad de Sevilla, Facultad de Química, 41012 Sevilla, Spain
[b] Departamento de Ingeniería Química, Universidad de Sevilla, Escuela Politécnica Superior, 41011 Sevilla, Spain
[c] Departamento de Ingeniería Química, Universidad de Sevilla, Facultad de Física, 41012 Sevilla, Spain

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ABSTRACT

The development of eco-friendly materials requires a deep knowledge of physical, chemical and functional properties of biopolymers and fillers. Soy protein (SPI), which is one of the cheapest protein in global markets, was used in combination with montmorillonite (MMT-$Na^+$) to obtain fairly attractive green biocomposite superabsorbent materials, leading to biodegradable superabsorbent materials. Natural MMT-$Na^+$ was used since it is widely available as micron-size tactoids and gives rise to highly functional nanoparticles. However, the dispersion of such particles within a polymer structure is complex, showing a high impact on techno-functional properties. An easy-scalable processing technique was used with a mixing stage to obtain dough-like materials which were subjected to an injection-moulding process that led to biodegradable biocomposite materials. The structure of dough-like materials was characterized by scanning electron microscopy and X-Ray diffraction, whereas mechanical properties of green biocomposites were evaluated by dynamic mechanical analysis (DMA) and tensile tests. Moreover, the techno-functionality of the new materials obtained was determined by means of water uptake capacity (WUC). Results suggested that the addition of nanoclay led to an increase of the elastic modus although the overall improvement of mechanical properties is not clear. Interestingly, water uptake capacity was greatly enhanced. In this sense, these green biocomposites could be considered as an excellent candidate for the development of novel bio-based superabsorbent materials.


## 1. Introduction

Plastic materials have many different applications according to their extraordinary properties (Plastics-Europe, 2008). Furthermore, the combination of different materials with different specifications allows to modulate their properties, modifying the features of the final product (Sehaqui et al., 2011). However, most plastics present two main disadvantages: their non-renewable source (petroleum) and non-recyclable character, which cause huge wastes. Because of that, the use of bio-based materials instead of those based on synthetic polymers is seen as a promising way to reduce pollution (Lee et al., 2014). New challenges in this field are devoted to the research of new technologies which would allow the development of renewable materials for the existing requirements. In addition, the fabrication of these new materials by using proteins or polysaccharides (renewable resources) is seen as an interesting alternative (Wang and Sain, 2007). The development of new protein-based materials, for the production of bioplastics, is focusing researchers in this field to investigate promising applications other than those related to the food, medical or agriculture industries. As an example, biopolymers are being used for the replacement of PVC pipes or the coating of cell-phones (Mano et al., 2003).

Conventional plastics control the market, with the production of 240,000 million tons (Plastics-Europe, 2008), although the production of bioplastics in Europe is continuously growing, reaching 509,000 tons in 2013 (Martínez et al., 2003). Bioplastics are based in two main elements: a polymer matrix and a plasticizer, although some additives could be added to endow the bioplastics with specific properties.

* Corresponding author.
*E-mail address:* mfelix@us.es (M. Felix).

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Protein isolates from soy bean (SPI) constitute the biggest by-product from the soybean oil industry, being one of the cheapest proteins in global markets. Interestingly, their hydrophilic amino acids lead to superabsorbent properties (Tian et al., 2010). SPI systems have been used for the development of bio-materials, showing suitable properties such as high elastic modulus and high water uptake capacity (Liu et al., 2005; Song et al., 2011). Moreover, these properties have been improved through the addition of lamellar nanofillers (Alexandre and Dubois, 2000; Angellier-Coussy et al., 2013; de L. Freitas et al., 2017; Guillard et al., 2013). Related to this, natural montmorillonite (MMT-$Na^+$) is commonly used (Peelman et al., 2013). The structure and arrangement of these particles cause the formation of plates, with maintain a 1 nm gap between them, forming layers (Bagheri Marandi et al., 2011). One of the key factors is the efficient arrangement of these nanoclays in biopolymer matrices, where improving the mechanical properties of biocomposites have been related to the exfoliation of nanoclays (Yang et al., 1999). In this sense, it has been demonstrated that the arrangement of these particles within the polymer structure is complex. Several factors, such as the protein/plasticizer ratio, the amount of filler used or some processing variables, such as the moulding time or temperature, can modify the properties of the final bioplastics (Felix et al., 2018).

Previous studies have been focused on analysing the influence of different additives on the properties of biocomposites (Laadila et al., 2017; Selvaraju et al., 2017). However, in the literature there are no data about the evaluation of the effect of nanoclays on the properties of superabsorbent materials. Thus, the main novelty and objective of this work was the development of a new family of green superabsorbent materials based on soy protein isolate (SPI) and montmorillonite (MMT-$Na^+$), which were processed by injection moulding. The structure of the blends (after the mixing stage) was characterized by scanning electron microscopy and X-ray diffraction. The biocomposites were characterized by dynamic mechanical thermal analysis, tensile tests and water uptake capacity (WUC).

In this study, MMT-$Na^+$ concentrations were modified in order to obtain biocomposites with suitable mechanical and water absorption properties.

## 2. Materials and methods

### 2.1. Materials

Soy Protein Isolate (SPI) Supro500E (91 wt% of protein content) was purchased from Protein Technologies International (Leper, Belgium). Glycerol (GL), supplied by Sigma-Aldrich (St. Louis, Missouri, USA), was used as the plasticizer. Cloisite®-$Na^+$ was selected as the nanoparticle to be introduced and named as MMT-$Na^+$ (Southern Clay Products, Inc., USA).

### 2.2. Preparation of dough-like materials

The biocomposite materials were processed by a thermo-mechanical two-stage process: the blends were obtained by the mechanical mixing of SPI, the plasticizer (ratio 50/50) and MMT-$Na^+$, and subsequently the dough-like materials were injected (Fernandez-Espada, 2016; Fernández-Espada et al., 2016a). Hence, the first stage consisted of a mixing at 25 °C, 50 rpm and 60 min in a rotating batch mixer (HaakePolylab QC; ThermoScientific, Germany). The samples were produced by adding different nanoclay (montmorillonite) concentrations to the dough-like materials with a protein/glycerol ratio of 50/50: 0 wt% (0%), 3 wt% (3%), 6 wt% (6%) and 9 wt% (9%).

### 2.3. Characterization of dough-like materials

#### 2.3.1. Dynamic mechanical thermal analysis (DMTA)

A RSA3 rheometer (TA Instruments, USA), equipped with 8 mm parallel plates (for compression measurements) was used to determine the viscoelastic properties of the samples. E', E" and tan δ were obtained after applying compression tests combined with a thermal cycle. Prior to temperature ramp tests, strain sweep tests were carried out to determine the linear viscoelastic region (LVR). Subsequently, temperature ramp tests were performed from 20 to 150 °C (3 °C/min), where temperature was controlled using a Chiller PGC-100 (Polycold, Seattle, USA). All these measurements were carried out at constant strain amplitude (0.2%) within the LVR.

#### 2.3.2. X-ray powder diffraction (XRD)

XRD studies, with a scanning range between 2 and 40°, and a step size of 0.05°, were performed in the dough-like materials obtained after the mixing step. The equipment used was a D8 Discover (BRUKE, USA) (40 kV, 30 mA) equipped with Cu-$K_\alpha$ radiation ($\lambda = 0.1516$ nm).

### 2.4. Preparation of biocomposites

Once the dough-like materials were prepared, they were injected into a mould by means of MiniJet Piston Injection Moulding System (ThermoHaake, Germany), obtaining biocomposite probes. Suitable processing conditions were selected on the basis of rheological properties found in previous studies. Thus, the mould temperature was 70 °C and the injection pressure 500 bar over 20 s (200 bar as post-injection pressure was selected over 200 s) (Fernández-Espada et al., 2016a, 2016b). Two different specimens were produced: one was a 60 × 10 × 1 mm rectangular shaped and the other had the shape of a dumb-bell.

### 2.5. Characterization of biocomposites

#### 2.5.1. Rheological measurements

A RSA3 rheometer (TA Instruments, USA) fitted with a dual cantilever geometry (for flexion experiments) was used to carry out two different tests: (i) frequency sweep test (in a frequency range between 0.02 and 20 Hz) at room temperature and (ii) temperature ramp (in a temperature range between 20 and 140 °C at 3 °C/min and 1 Hz). All measurements were carried out within the linear viscoelastic range, studying the viscoelastic properties of the composites.

The critical stress was calculated in previous stress sweep tests. A stress was selected in order to perform the frequency sweep and temperature ramps into the LVR (0.2%).

#### 2.5.2. Tensile strength measurements

Stress-strain curves were obtained according to ISO 527 at room temperature (ISO, 2012). Three different parameters were obtained from these curves: (i) The Young's Modulus, (ii) Strain at Break and (iii) maximum tensile strength. Five replicates for each system were obtained. The device used was an Insight 10 kN (MTS, USA).

#### 2.5.3. Scanning electron microscopy (SEM)

After water immersion over 24 h at 25±1 °C, the biocomposites were lyophilized and then observed under SEM with JSM 6460 LV (JEOL, Japan) with a secondary electron detector (using 20 kV as voltage).

#### 2.5.4. Water uptake capacity (WUC)

The water uptake capacity of the composites was tested at 25±1 °C according to the standard ASTM D570 method for