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Are modified pumpkin flour/plum flour nanocomposite films biodegradable and compostable?

Tomy J. Gutiérrez

Grupo de Materiales Compuestos Termoplásticos (CoMP), Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Facultad de Ingeniería, Universidad Nacional de Mar del Plata (UNMdP) y Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Colón 10850, B7608FLC, Mar del Plata, Argentina

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ABSTRACT

Nanocomposite films made from nonconventional food hydrocolloids: phosphated or methylated flours derived from pumpkin (*Cucurbita maxima*) with or without "*huesito*" plum (*Spondias purpurea*) flour, were obtained by the casting methodology. The films were characterized, and in addition two biomarkers of ecotoxicity, survival and weight changes, were determined for each one by means of a novel bioassay using the furniture weevil (*Tricorynus sp*, Coleoptera: Anobiidae). The films prepared from the methylated flours had a lower sensitivity to water, greater thermal resistance and higher crystallinity percentage than the phosphated flour films. However, these materials were very fragile, as well as being ecotoxic, thus limiting their compostability. Thus, although both the phosphated and methylated pumpkin flour-based films were biodegradable only the phosphated films can be considered as eco-friendly. The plum flour nanocomposite was included due to the anthocyanins it contains, with the aim of developing pH-sensitive films. Unfortunately, neither of the resulting nanocomposite films achieved this objective. Nevertheless, their mechanical and thermal properties were improved, and the ecotoxicity levels reduced, compared to the films prepared without the nanocomposite.

1. Introduction

The development and manufacture of food packaging (films and coatings) derived from hydrocolloids (starch, proteins, and gums) has boomed over the last three decades, as packaging made from these materials can extend food shelf-life, as well as providing a solution to the pollution caused by synthetic polymer-based packaging materials (Álvarez, Alvarez, & Gutiérrez, 2018). In recent years, flours in particular have attracted much attention as food packaging materials as they have biopolymer matrices that produce films with better physicochemical properties than those prepared from isolated starch or proteins (Pelissari, Andrade-Mahecha, Sobral, & Menegalli, 2013). This is mainly due to the chemical interactions that take place between the components of the flours (Gutiérrez & Álvarez, 2016). In addition, flour offers a higher yield compared to starch (Gutiérrez & Alvarez, 2017a). Flours as polymer matrices for the development of films also share some of the favorable characteristics of starch: they are economical, abundant, easy to obtain, renewable, and innocuous (Otoni et al., 2017). In this study, we propose the manufacture and use of pumpkin flour (*Cucurbita maxima*) as an unconventional biopolymer matrix for the development of films. According to the published literature only films based on pumpkin oil cake, a by-product obtained after extracting oil from pumpkin seed (*Cucurbita pepo* L.) by cold-pressing, have been manufactured, but there is no record of the use of pumpkin flour for film development (Popović, Peričin, Vaštag, Lazić, & Popović, 2012; Popović, Peričin, Vaštag, Popović, & Lazić, 2011).

According to the Food and Agriculture Organization of the United Nations (FAO, 2014) the world production of pumpkins occurs over an area of 1,775,000 hectares, with a production of 24.3 million tons/year. Since the year 2000 there has been an increase in production of 36.5%, from 17.8 to 24.3 million tons/year, with 48% undertaken by only two countries, China (28.7%) and India (19.3%). Argentina ranks among the top 10 producing countries, with an estimated production volume of between 420,000 and 450,000 tons in an area close to 25,000 hectares. Although this crop is developed throughout the whole of Argentina, Buenos Aires, Mendoza and Santiago del Estero are the main producing provinces. The FAO (2014) report also highlighted that more than 85% of total imports worldwide are absorbed by only seven countries, notably the United States with 41%. As for the main exporting countries, more than 90% of the total is undertaken by eight countries, led by Spain with 42.68%.

In spite of the aforementioned advantages of biopolymer-based films, their susceptibility to moisture and tendency towards brittleness are challenges that still need to be overcome (Gutiérrez, González Seligra, Medina Jaramillo, Famá, & Goyanes, 2017). In order to achieve this, several studies have produced modified flour biopolymer matrices

E-mail address: tomy.gutierrez@fi.mdp.edu.ar.

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to which composites are also added. As regards the composites, these are preferably in the nanometric size range, since this enables a stronger interaction with the matrix, resulting in materials that are less sensitive to humidity and more resistant (Bracone, Merino, González, Alvarez, & Gutiérrez, 2016). In this study, phosphation and methylation were performed to modify the polymer matrix. Phosphation has been shown to result in the development of less hydrophilic materials by 1) reducing the number of hydroxyl groups (polar sites) within the structure of the starch *via* the crosslinking reaction, and 2) increasing glycerol-phosphated starch interactions within the starch structure by the introduction of phosphate groups, which compensates for the polar sites within the matrix (Gutiérrez, Morales, Pérez, Tapia, & Famá, 2015). Methylation, on the other hand, reduces the moisture susceptibility of films due to the occurrence of a second-order aliphatic electrophilic substitution reaction (SN2) which replaces the hydroxyl groups in the starch structure by apolar groups such as methyl (-CH_3) (Sívoli et al., 2013).

The nanocomposite employed in this study was derived from "*huesito*" plum (*Spondias purpurea*) peel, and was included as a natural reinforcement material within the polymer matrices. The reasons for using plum peel to develop the nanocomposite were that 1) cellulosic materials are widely used as reinforcement materials in both natural and synthetic polymers, and the peel of the fruits is where the highest fiber content in the form of cellulose is found (Gutiérrez & Alvarez, 2017b), and 2) high concentrations of anthocyanins have been found in the peel of "*huesito*" plums (Ferreira de Almeida et al., 2017; Muñoz-López, Urrea-Garcia, Jiménez-Fernandez, Rodríguez-Jiménes, & Luna-Solano, 2018). Research done over the last five years has shown that the direct incorporation of anthocyanins into biopolymer matrices can produce pH-sensitive films when these are developed through the casting methodology (Choi, Lee, Lacroix, & Han, 2017; Gutiérrez, 2018a; Liu et al., 2017; Luchese, Frick, Patzer, Spada, & Tessaro, 2015; Luchese, Garrido, Spada, Tessaro, & de la Caba, 2018; Ma & Wang, 2016; Pereira, de Arruda, & Stefani, 2015; Prietto et al., 2017; Yoshida, Maciel, Mendonça, & Franco, 2014). It is the batochromic effect of the anthocyanins that makes these materials pH-sensitive, i.e. they change color depending on the pH of the medium.

One of the main advantages to using pH-sensitive films in food packaging is that they can alert the user to adulterations and contaminants in food, as well as informing him/her as to how fresh an item of food is or the duration of its shelf life, leading them to be dubbed "smart or intelligent" systems. This means that food packaging has become more than just a simple barrier to protect food, and is currently being developed as a warning system that could help to reduce the large amount of food that is wasted after harvesting (Gutiérrez & Alvarez, 2018).

In addition to characterizing the novel matrices used, this study focuses on investigating the biodegradability and compostability of the films developed. Frequently, studies assume that natural polymers are biodegradable and environmentally friendly. However, biodegradable materials are not necessarily compostable, and the international regulations that regulate these aspects in plastic materials are very clear (EN 13432, 2000; ASTM D5338 - 98, 2003; ISO 14855–1:2005, 2005; EN 14995, 2006; ISO 14855–2:2007, 2007). The current trend is towards the development of compostable materials, since they guarantee not only that the materials are biodegradable, i.e. they break down into small fragments, but also that the products of degradation do not represent a danger to the environment in terms of their ecotoxicity, i.e. they are compostable (Gutiérrez, 2018b). According to the ASTM D6400 (2004) standard, the methods for the evaluation of the ecotoxicity (compostablity) of polymers are mainly based on the use of plants, soil fauna (earthworms), aquatic fauna (Daphnia), algae (green algae) and microbes (luminescent bacteria). However, we propose a new simple approach to evaluate the ecotoxity of a polymer through an *in vivo* digestibility test using two biomarkers: weight change and survival in an insect. In this study we used the furniture weevil (*Tricorynus sp*, Coleoptera: Anobiidae), one of the most serious pests of starches, flours and cereals in storage silos worldwide (FAO, 1985; Lovera, Pérez, & Laurentin, 2017).

The hypotheses of this research work were: 1) bionanocomposites developed from plum peel will enable the development of pH-sensitive films with better physicochemical and mechanical properties, and 2) weight changes and survival of the furniture weevil can be used as biomarkers for the evaluation of the compostability of the developed materials. Taking into account these hypotheses, the following objectives were defined: 1) exhaustively analyze the properties of the plastic materials developed, and 2) assess their biodegradability and compostability.

2. Experimental

2.1. Materials

Native pumpkin flour (*Cucurbita maxima*) from the edible part of the pumpkin and "*huesito*" plum (*Spondias purpurea*) flour from the fruit peel were obtained by the method described by Pacheco (2001). The pumpkins and plums were acquired at a local market in Caracas, Venezuela. The flours were stored in dark containers for one week at room temperature (25 °C) before preparing the films, in order to avoid oxidative damage to the materials used. Food grade glycerol (Aldrich, product code - G7893) was used as a plasticizer, and the plum flour as a nanocomposite.

2.2. Modifications to the pumpkin flour

The modification reactions carried out in this study were methylation and phosphation to the native (unmodified) pumpkin flour. It is well known that these reactions are more successful when carried out in an alkaline medium preferably pH = 10. All the modifications were thus performed at this pH value. It is important to note that modification by phosphation is approved by the U.S. Food and Drug Administration (FDA, 2017) for food applications, whereas modification by methylation is not. However, according to Sívoli et al. (2013), the latter has low cytotoxicity. The maximum concentration of the modifying agent allowed by the FDA (2017) for starchy matrices intended for the food industry (3% w/w of sodium trimetaphosphate (STMP - $Na_3P_3O_9$) with respect to the weight of the starchy matrix) was used. It is worth remembering that chemical reactions are given using molar ratios rather than weight or volume ratios. Thus, the same number of moles (0.0294 mol) of the modifying agent was used for both phosphation and methylation. The modifications were also performed using the same weight (300 g) of native pumpkin flour, and the same amount of solvent (300 mL of distilled water) so that the concentration of the modifying agent was the same for both reactions (0.098 M).

2.2.1. Modification by methylation (esterification)

Methylated pumpkin flour was obtained using dimethyl sulfate ($(CH_3)_2SO_4$) as a modifying agent using the procedure described by Sívoli et al. (2013). Briefly, native pumpkin flour (300 g) and 2.8 mL (0.0294 mol) of $(CH_3)_2SO_4$ were suspended in 300 mL of distilled water, and the pH adjusted to 10 with a 2.5% NaOH solution. The slurry was then heated to 45 °C and shaken for 3 h, with the pH adjusted every hour so that it remained at 10. After 3 h the pH was lowered to 7 with 2.5% HCl solution. The slurry was then washed three times by suspension in distilled water, centrifuged at 1500 r/min for 15 min, and dried in a tray dehydrator (Mitchell, USA, Model 645159) for 24 h at 45 °C. The dried modified flour was then milled and passed through a 60-mesh sieve. This same method was used for modification by phosphation, changing only the modifying agent employed.

2.2.2. Modification by phosphation (cross-linking)

Phosphated pumpkin flour was prepared with STMP as the