



On the efficiency of oleic acid as plasticizer of chitosan/clay nanocomposites and its role on thermo-mechanical, barrier and antimicrobial properties – Comparison with glycerol



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ARTICLE INFO

Article history:

Received 14 November 2015

Received in revised form

8 January 2016

Accepted 9 January 2016

Available online 15 January 2016

Keywords:

Chitosan

Na-montmorillonite

Plasticizers

Permeability properties

Antimicrobial properties

Heat-pressing

Chemical compounds studied in this article:

Chitosan (PubChem CID: 3086191)

Glycerol (PubChem CID: 753)

Oleic acid (PubChem CID: 445639)

Sodium bentonite (PubChem CID:

72941614)

Acetic acid (PubChem CID: 176)

ABSTRACT

The current study directly compares oleic acid's and glycerol's functionality as plasticizer and evaluates their compatibility and synergies with chitosan and/or Na-montmorillonite (NaMMT) in order to obtain films with antimicrobial and barrier properties and adequate performance for packaging applications. The effect of processing on the performance of the obtained films is also evaluated applying the solution casting and the heat-pressing methodologies. Overall it is shown that glycerol is more effective as plasticizer resulting in as high as 70% strain, compared to 26% strain obtained after 30 wt.% oleic acid's addition. Furthermore, glycerol offers higher stability against water sorption with up to 15 times lower weight gain in films containing 30 wt.% glycerol. On the other hand oleic acid offers better barrier to water vapour transition with up to 3 times lower permeability rates. At the same time oleic acid addition improves the antimicrobial response of plain chitosan with up to 75% lower relative bacterial growth while glycerol's addition does not lead to statistically significant changes. NaMMT contributes towards plasticization acting as plasticizer's carrier diminishing the phase separation phenomena and leading into films with very broad Tg transitions at higher plasticizer contents (20 and 30 wt.%). Heat-pressing on the other hand offers great stability to water sorption with up to 40 times lower weight gain but inhibits the antimicrobial activity of the films which demonstrate measurable initial specific bacterial growth rate compared to almost 100% inhibition found in all "unpressed" films.

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1. Introduction

Petrochemical-based plastics are widely used in food packaging applications because of their good mechanical performance, good barrier to oxygen, low cost and easy processibility. However, in recent years there has been a tremendous shift of the research interest towards biodegradable and/or biobased packaging materials mainly due to environmental concerns (Babu, O'Connor, & Seeram, 2013; Imre & Pukánszky, 2013). Next to that the research community is focusing nowadays on the development of active

packaging, targeting to extend the shelf life of the packed food or to improve its sensory properties, while maintaining its quality (Ozdemir & Floros, 2004). Antimicrobial packaging is an example of active packaging (Appendini & Hotchkiss, 2002).

Chitosan, the cationic (1-4)-2-amino-2-deoxy- β -D-glucan, is industrially produced in various quality grades from chitin, the second most abundant polysaccharide in nature (Muzzarelli et al., 2012). Due to chitosan's film forming ability, biodegradability, biocompatibility, antimicrobial properties and absence of toxicity, chitosan based films have been proposed as interesting alternatives in food active packaging (Aider, 2010; Lago et al., 2014; Leceta, Guerrero, Ibarburu, Dueñas, & de la Caba, 2013; Tripathi, Mehrotra, & Dutta, 2008). Tremendous literature support the essential importance of polycationic structure of chitosan in

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antimicrobial activity as reviewed by (Kong, Chen, Xing, & Park, 2010).

Key drawbacks for the widespread use of chitosan based films are related with their relatively poor water barrier properties, fairly brittle nature, as well as the differences in the morphology/crystallinity of the films upon preparation/processing. Different preparation methodologies and post-processing techniques (heat, vacuum, microwave treatment, homogenization, etc.) have been proposed in order to effectively control the performance of chitosan based films (Grigoriadi, Giannakas, Ladavos, & Barkoula, 2015; Mayachiew & Devahastin, 2008; Thakhiew, Champahom, Devahastin, & Soponronnarit, 2015; Thakhiew, Devahastin, & Soponronnarit, 2010; María Vargas, Perdonés, Chiralt, Cháfer, & González-Martínez, 2011). Physical crosslinking via thermal treatment has been suggested to positively influence the strength and barrier properties of the prepared films (Grigoriadi et al., 2015; Thakhiew et al., 2015).

At the same time many studies have been devoted on improving the mechanical and barrier properties of chitosan based films by adding plasticizers and/or various types of nanoparticles (i.e. layered silicate and more recently silver compounds) (Epure, Griffon, Pollet, & Avérous, 2011; M. Lavorgna et al., 2014; Marino Lavorgna, Piscitelli, Mangiacapra, & Buonocore, 2010; Srinivasa, Ramesh, & Tharanathan, 2007; Suyatma, Tighzert, Copinet, & Coma, 2005; Xie et al., 2013; Ziani, Osés, Coma, & Maté, 2008). The most commonly used plasticizer so far in chitosan based films is glycerol at contents varying between 10 and 40 wt.% while few studies have reported the plasticization effect of other polyols (sorbitol, xylitol, ethylene glycol, propylene glycol, polyethylene glycol), saturated and unsaturated fatty acids (stearic, palmitic acids, oleic acid and olive oil) and very recently ionic liquids (Aguirre-Loredo, Rodríguez-Hernández, & Chavarría-Hernández, 2014; Boesel, 2015; Fundo, Galvis-Sánchez, Delgadillo, Silva, & Quintas, 2015; Matet, Heuzey, Pollet, Ajji, & Avérous, 2013; Perdonés, Vargas, Atarés, & Chiralt, 2014; Mariana Pereda, Amica, & Marcovich, 2012; Rodríguez-Núñez, Madera-Santana, Sánchez-Machado, López-Cervantes, & Soto Valdez, 2014; Srinivasa et al., 2007; Suyatma et al., 2005; María Vargas, Albors, Chiralt, & González-Martínez, 2009). Nowadays market looks into the replacement of conventional plasticizer with natural and/or biodegradable ones alongside with the use of biopolymers (Vieira, da Silva, dos Santos, & Beppu, 2011).

Next to the plasticization efficiency, the compatibility of the plasticizer with the polymer is of key importance. Another essential characteristic for food packaging applications is related to the toxicity and migration that is found to be low in natural-based plasticizers (Vieira et al., 2011). The replacement of glycerol with lipid compounds in chitosan based films may provide a solution towards plasticization and at the same time additional water barrier due to the hydrophobic nature of lipids. Oleic acid (cis-9-octadecenoic acid) is one of the major component of oils (olive, castor and peanut oil) used in pharmacy and medicine (Misra, Jain, Tandon, Wartewig, & Gupta, 2006). Chitosan/oleic acid films for packaging applications have been recently prepared (Aguirre-Loredo et al., 2014; Bonilla, Vargas, Atarés, & Chiralt, 2014; Misra et al., 2006; Perdonés et al., 2014; Ramos-García et al., 2012; Souza, Monte, & Pinto, 2011; María Vargas et al., 2009; María Vargas et al., 2011) and the reported results suggested promising water barrier properties with however considerable reduction of the mechanical properties. Control of pathogenic microorganism has been also reported for the prepared chitosan based films.

Since increased amount of plasticizer may have negative side effects on the performance of the films due to variations in film's thickness, moisture content and blending efficiency, the idea of the current study was to use different amounts of oleic acid (10, 20 and

30 wt.%) and prepare chitosan based films with or without the addition of sodium montmorillonite (NaMMT). According to our knowledge the combined use of oleic acid with clay in chitosan based nanocomposites has not been reported so far. The same amount of glycerol with or without NaMMT has been added in chitosan for direct comparison of the two plasticizers and evaluation of their compatibility and synergies with chitosan and/or NaMMT. Since mixing of hydrophobic compounds with hydrophilic chitosan may result in incompatibility evidenced by phase separation two processing methodologies have been followed, i.e. the solution casting and the heat-pressing methodology. The aim was to propose the appropriate amount/type of plasticizer and the appropriate preparation methodology to: (i) effectively control the extensibility and barrier properties of chitosan based films, (ii) avoid phase separation and (iii) maintain the inherent antimicrobial properties of chitosan.

2. Experimental

2.1. Materials and solution preparation

Medium molecular weight chitosan (CS), 190–310 kDa (MMW) with a deacetylation degree greater than 75%, hydrophilic bentonite nanoclay with code name PGV Nanomer® (NaMMT) and glacial acetic acid (HAc) were purchased from Sigma–Aldrich. Glycerol and Oleic Acid were purchased from Carlo Erba.

Polymer blends and nanocomposite films were prepared via a reflux-solution methodology according to our previous publications (Giannakas, Grigoriadi, Leontiou, Barkoula, & Ladavos, 2014; Grigoriadi et al., 2015). As demonstrated in these publications the application of the reflux treatment was beneficial for the preparation of chitosan/NaMMT films since it facilitated the intercalation of chitosan chains in the clay galleries and led to significant decrease of the chitosan's hydrated crystallinity improving the mechanical and the water barrier properties of the films. Chitosan solution (in 1 v/v% HAc solution) was mixed with the appropriate amounts of NaMMT and glycerol or oleic acid in order to reach a final clay concentration of 5wt.% and a plasticizer concentration of 10, 20 and 30 wt.%. The amount of Chitosan, clay and plasticizer used for each sample are tabulated in Table 1. The Chitosan-clay and Chitosan-plasticizer-clay mixtures were refluxed for 1 h and then casted onto plastic dishes (14 cm diameter). The castings were dried at ambient conditions (~22 °C) for ~5 days and then the plastic plates were peeled off. Two set of specimens were prepared for testing. The first set included the as-received castings denoted hereafter as

Table 1

Designation and amounts (wt.%) of Chitosan (CS), oleic acid (OL), glycerol (GL), and Na-Montmorillonite (NaMMT) used for the preparation of chitosan based films.

Code name	CS wt.%	OL wt.%	GL wt.%	NaMMT wt.%
CS	100	0	0	0
CS5MMT	95	0	0	5
CS10OL	90	10	0	0
CS20OL	80	20	0	0
CS30OL	70	30	0	0
CS10OL5MMT	85	10	0	5
CS20OL5MMT	75	20	0	5
CS30OL5MMT	65	30	0	5
CS10GL	90	0	10	0
CS20GL	80	0	20	0
CS30GL	70	0	30	0
CS10GL5MMT	85	0	10	5
CS20GL5MMT	75	0	20	5
CS30GL5MMT	65	0	30	5

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