



Innovative plasticized alginate obtained by thermo-mechanical mixing: Effect of different biobased polyols systems



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ABSTRACT

Plasticized alginate films with different biobased polyols (glycerol and sorbitol) and their mixtures were successfully prepared by thermo-mechanical mixing instead of the usual casting-evaporation procedure. The microstructure and properties of the different plasticized alginate formulations were investigated by SEM, FTIR, XRD, DMTA and uniaxial tensile tests. SEM and XRD results showed that native alginate particles were largely destructured with the plasticizers (polyols and water), under a thermo-mechanical input. With increasing amount of plasticizers, the samples showed enhanced homogeneity while their thermal and mechanical properties decreased. Compared to sorbitol, glycerol resulted in alginate films with a higher flexibility due to its better plasticization efficiency resulting from its smaller size and higher hydrophilic character. Glycerol and sorbitol mixtures seemed to be an optimum to obtain the best properties. This work showed that thermo-mechanical mixing is a promising method to produce, at large scale, plasticized alginate-based films with improved properties.

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1. Introduction

In the last years, polysaccharides-based materials have attracted great attention due to their large availability, renewability and biodegradability (Alcantara, Darder, Aranda, & Ruiz-Hitzky, 2014). Particularly, interesting results concerning the great potential of alginate have been obtained and reported (Paula et al., 2015). It is, for instance, a promising biopolymer for environmental applications due to its good film-forming properties (Lee & Mooney, 2012). Alginate, a salt of alginic acid, is mainly extracted from different species of kelp (brown algae) (Ertesvåg & Valla, 1998). Alginate is also extracellularly bioproduced by bacteria such as *Pseudomonas aeruginosa* or *Azotobacter vinelandii* (d'Ayala, Malinconico, & Laurienzo, 2008). With a worldwide production higher than 50,000 t per year (d'Ayala et al., 2008), alginate-based materials are developed for different fields such as the food industry, biomedical applications, waste water treatment or textile printing.

This polysaccharide is a copolymer consisting of D-mannuronic acid (M) and L-guluronic acid (G) joined by a β -1,4-linkage. M and G units compose homopolymeric M blocks, G blocks, and regions of alternating M and G blocks (Grant, Morris, Rees, Smith, & Thom, 1973). The proportion of M and G units has a strong effect on

the structure and properties of this biopolymer (Haug, Larsen, & Smidsrød, 1974; McLachlan, 1992).

Casting based on the dissolution of alginate in aqueous solution and then evaporating off the solvent is the conventional method of producing plasticized alginate films (Jost, Kobsik, Schmid, & Noller, 2014). Edible films and coatings based on alginate prepared by this method are the prominent concerns in the existing literature (Azeredo, Miranda, Rosa, Nascimento, & de Moura, 2012; Paula et al., 2015; Tavassoli-Kafrani, Shekarchizadeh, & Masoudpour-Behabadi, 2016; Xiao & Tong, 2013; Xiao, Tong, & Lim, 2012). However, films prepared with this method exhibit limited thickness and surface area. Additionally, this technique gives low productivity for industrial applications and hardly achieves the production of multiphase systems such as blends with more hydrophobic polymers (Epure, Griffon, Pollet, & Avérous, 2011; Matet, Heuzey, Pollet, Aji, & Avérous, 2013) or composites with reinforcement additives (Xie, Martino et al., 2013). The preparation of such multiphase systems with a good dispersion of the different phases is a key point to fulfill the requirements for a large range of applications. To overcome these shortcomings, thermo-mechanical mixing seems to be an ideal process technique to fabricate alginate-based films since this technique has been successfully applied in the preparation of different plasticized polysaccharides, also called thermoplastic polysaccharides, like starch (Avérous, 2004) or chitosan (Epure et al., 2011; Matet et al., 2013; Meng, Heuzey, & Carreau, 2014). According to our knowledge, this approach has

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never been used for the preparation of plasticized alginate. The few works reporting the thermo-mechanical processing of alginate actually concern its addition at relatively low amounts in plasticized starch and its possible role as plasticizer (Souza & Andrade, 2001; Weerapoprasit & Prachayawarakorn, 2015; Cordoba, A., Cuellar, N., Gonzalez, M., & Medina, 2008).

For thermo-mechanical mixing, a destructuring agent, such as water, is needed to disrupt the intermolecular bonds between polymer chains to reach a “molten state” under a thermo-mechanical input (Donovan, 1979). Besides, since the melting temperature of alginate is higher than its degradation temperature, like for most polysaccharides, plasticizers are added to lower its processing temperature. In addition, plasticizers are also added to increase the flexibility of neat alginate films, which are often too rigid and brittle, by increasing the interchain spacing and reducing the interactions between the chains (Bocque, Voirin, Lapinte, Caillol, & Robin, 2016). Water is a “natural” but volatile plasticizer for most of the carbohydrates, since this molecule exchanges easily with the environment by sorption/desorption phenomena (Ashikin, Wong, & Law, 2010). Thus, the addition of non-volatile plasticizers is often required to obtain plasticized polysaccharides with stable properties. Different non-volatile plasticizers have been examined in alginate materials processed by solvent casting such as glycerol (Ashikin et al., 2010; Avella et al., 2007; Benavides, Villalobos-Carvajal, & Reyes, 2012; Jost et al., 2014; Liakos et al., 2013; Maizura, Fazilah, Norziah, & Karim, 2007; Olivas & Barbosa-Canovas, 2008; Paşcalău et al., 2012; Paula et al., 2015; Pongjanyakul & Puttipatkhachorn, 2007; Rhim, 2004; Santana & Kieckbusch, 2013; Silva, Bierhalz, & Kieckbusch, 2009), sorbitol (Jost et al., 2014; Olivas & Barbosa-Canovas, 2008), xylitol (Santana & Kieckbusch, 2013), mannitol (Santana & Kieckbusch, 2013), poly(ethylene glycol) (PEG) (Lee & Min, 1995; Pongjanyakul & Puttipatkhachorn, 2007), low molecular weight sugar (Olivas & Barbosa-Canovas, 2008), or lactate (Parris, Coffin, Joubran, & Pessen, 1995). Most of these non-volatile plasticizers are biobased polyols. They have been particularly tested during the last decade for materials obtained by casting. Jost et al. (2014) showed that glycerol showed more obvious effect on the mechanical properties of alginate compared to sorbitol at the same loading level. Glycerol increased the permeability of alginate films to oxygen and water vapor while sorbitol did not affect the barrier properties to oxygen and water vapor. Olivas and Barbosa-Canovas (2008) found also that glycerol exhibited the most pronounced effect on the mechanical and thermal properties of plasticized alginate obtained by casting compared to other plasticizers. PEG with a molar mass of 8000 g/mol provided the lowest tensile strength and elongation at break due to the poor compatibility with alginate. Fructose and sorbitol showed the lowest water vapor permeability.

To the best of our knowledge, no work has been conducted on how biobased polyols affect the structure and properties of alginate films produced by thermo-mechanical mixing. Hence, the objective of this work was to prepare plasticized alginates using a conventional plastic melt-processing technique and to study the corresponding behaviors of these fully biobased materials. Since glycerol and sorbitol are the two main biobased polyols used to plasticize polysaccharide-based materials, the effect of each of these biobased polyols and their mixtures have been more particularly analyzed and compared on the morphology, thermal and mechanical properties of these innovative thermo-mechanically processed alginate-based materials.

2. Materials and methods

2.1. Materials

Sodium alginate (Scogin[®] MV Alginate) was kindly donated by FMC BioPolymer, Ireland.

The viscosity of 1% solution at 25 °C is quite high, 350–500 mPa s, which corresponds to a molar mass of 310–340 kDa according to the manufacturer. The sodium alginate particles are yellowish to light-brown in color and minimum 96.0% of alginate particles can pass through 25 mesh BS. Glycerol was purchased from Fisher Scientific, UK. Sorbitol (Merisorb 200) was kindly supplied by Tereos, France. Deionized water was used for all samples preparation.

2.2. Samples preparation

An internal batch mixer (Haake Rheomix-PolyLab OS, ThermoScientific, Germany) was used to obtain processed plasticized alginates. First, alginate was manually mixed with the desired amount of the corresponding polyol system, and deionized water. The formulations of the different polyol samples are listed in Table 1. The mixtures were equilibrated for one night before the kneading step. Then, the mixtures were kneaded at 80 °C, 100 rpm for 15 min with the internal mixer. These optimized parameters have been obtained after some preliminary tests. Finally, the resulting materials were compression molded to obtain films (thickness of approx. 0.5 mm) at 120 °C for 15 min, with 3 venting steps, under a pressure of 160 bar. The films thickness in this case, approx. 0.5 mm can be controlled by the mold.

Films prepared by solvent casting has also be prepared and compared with equivalent samples (same formulation) obtained by thermo-mechanical mixing. To obtain these films, a certain amount of alginate powder was dissolved in deionized water at 25 °C and stirred for 12 h to prepare 1.5 wt.% homogeneous alginate solution,

Table 1
Formulations of the different samples with the corresponding designations.

Samples designation	Alginate/Water (w/w)	Alginate/Glycerol (w/w)	Alginate/Sorbitol (w/w)
AW	50/50	–	–
AG20	50/50	80/20	–
AG25	50/50	75/25	–
AG30	50/50	70/30	–
AG40	50/50	60/40	–
AG50	50/50	50/50	–
AS20	50/50	–	80/20
AS25	50/50	–	75/25
AS30	50/50	–	70/30
AS40	50/50	–	60/40
AS50	50/50	–	50/50
AGS7030 ^a	50/50	75/17.5	75/7.5
AGS5050 ^a	50/50	75/12.5	75/12.5
AGS3070 ^a	50/50	75/7.5	75/17.5

^a The total amount of plasticizer is 25 wt.%.

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