

# Plasticized chitosan/polyolefin films produced by extrusion



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## ABSTRACT

Plasticized chitosan and polyethylene blends were produced through a single-pass extrusion process. Using a twin-screw extruder, chitosan plasticization was achieved in the presence of an acetic acid solution and glycerol, and directly mixed with metallocene polyethylene, mPE, to produce a masterbatch. Different dilutions of the masterbatch (2, 5 and 10 wt% of plasticized chitosan), in the presence of ethylene vinyl acetate, EVA, were subsequently achieved in single screw film extrusion. Very small plasticized chitosan domains (number average diameter  $<5 \mu\text{m}$ ) were visible in the polymeric matrix. The resulting films presented a brown color and increasing haze with chitosan plasticized content. Mechanical properties of the mPE films were affected by the presence of plasticized chitosan, but improvement was observed as a result of some compatibility between mPE and chitosan in the presence of EVA. Finally the incorporation of plasticized chitosan affected mPE water vapor permeability while oxygen permeability remained constant.

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## 1. Introduction

Environmental concerns have led plastic research towards the development of new materials based on natural polymers in order to decrease synthetic polymers consumption and impact on the environment. Bio-based materials such as starch, cellulose, protein-based plastics and chitosan have been studied for several years because of their good properties such as biocompatibility and biodegradability (Mekonnen, Mussone, Khalil, & Bressler, 2013). Development of bio-based plastics is also an ideal way to use waste from agriculture or industries such as agro-processing and fisheries. Since these bio-based materials frequently suffer from mechanical weaknesses, blending with another thermoplastic may be a way to increase the bio-content in polymers while producing plastics with good functional properties and economically viable.

Chitosan is the most important derivative of chitin and is obtained through its deacetylation. Chitin is a biopolymer found, for instance, in the cell wall of fungi or in the shell of arthropods such as crustaceans (e.g., crabs, shrimps or lobsters), and is the most abundant polysaccharide on earth after cellulose (Domard & Rinaudo, 1983; Roberts, 1992). Because of its natural origin,

non-toxicity, biocompatibility, biodegradability and antibacterial activity, chitosan has become a particularly interesting and attractive biomaterial in the last decades (Ravi Kumar, 2000; Rinaudo, 2006). Chitosan can be used in several areas such as food industry (food coatings or edible films to improve food conservation using its antifungal, antibacterial and antimicrobial activity), waste water treatment (filtration due to metal capture by chelation), cosmetics and biomedical applications such as drug delivery systems owing to its wound healing properties, or artificial skin due to its efficiency against bacteria and viruses and structural characteristics (Kittur, Kumar, & Tharanathan, 1998; Ravi Kumar, 2000; Rinaudo, 2006).

Chitosan films are generally produced by solvent casting, i.e. by dilution of chitosan raw powder or flakes in an acidic aqueous solution, casting in thin layers followed by solvent evaporation (Balau, Lisa, Popa, Tura, & Melnig, 2004; Dutta, Tripathi, Mehrotra, & Dutta, 2009). Films prepared using this technique present high brittleness because of the frictional force between polymer chains, a limited surface area and low production yield (Leceta, Guerrero, & de la Caba, 2013; Srinivasa, Ramesh, & Tharanathan, 2007).

To overcome these drawbacks, chitosan films should ideally be prepared through a molten route via film extrusion (Correlo et al., 2005; Martínez-Camacho et al., 2013) or internal mixing followed by compression molding (Mir, Yasin, Halley, Siddiqi, & Nicholson, 2011; Zhang, He, Liu, & Qia, 2009) like in the case of traditional thermoplastic polymers. However similarly to cellulose, chitosan exhibits a degradation temperature below its melting point, therefore chitosan-based materials prepared in typical

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polymer processing equipment incorporate solid chitosan particles in the form of powder or flakes. Those composite materials present a poor visual aspect (presence of large elliptical chitosan particles with dimensions of 40–300  $\mu\text{m}$  in length and 15–30  $\mu\text{m}$  in thickness (Martínez-Camacho et al., 2013)) and low mechanical properties (Martínez-Camacho et al., 2013; Mir et al., 2011; Zhang et al., 2009) due to incompatibility between chitosan which is hydrophilic and the hydrophobic polymer matrix.

Chitosan plasticization allows obtaining a deformable phase. Indeed, plasticization results in a lower glass transition temperature (Meng, Heuzey, & Carreau, 2014) by decreasing the number of intermolecular bonds between polymer chains (Sears & Darby, 1982), and can improve film flexibility and facilitate chitosan processing (Srinivasa et al., 2007; Suyatma, Tighzert, Copinet, & Coma, 2005). In addition, plasticization in the “molten” state can be achieved through thermo-mechanical kneading, and production of chitosan-based films using this technique may approach industrial fabrication conditions. Such a plasticization technique has been developed since the nineties to facilitate the processing of bio-based plastics such as thermoplastic starch (TPS) (Avérous, 2004), cellulose acetate (Quintana, Persenaire, Bonnaud, & Dubois, 2012), protein-based plastics (Hernandez-Izquierdo & Krochta, 2008), polyhydroxyalkanoates (PHAs) (Holmes, 1985) or poly(lactic acid) (PLA) (Garlotta, 2001). More recently, this technique that uses mechanical and thermal energy, has been adapted to chitosan in the presence of polyols and an acetic acid aqueous solution to achieve plasticization (Epure, Griffon, Pollet, & Avérous, 2011; Matet, Heuzey, Pollet, Ajji, & Avérous, 2013).

In our previous work, chitosan plasticization was performed through thermo-mechanical treatment in an internal mixer in the presence of water, acetic acid and glycerol, and the plasticized material was melt-blended with metallocene polyethylene (mPE) and ethylene vinyl acetate (EVA) (Matet, Heuzey, & Ajji, 2014). Our observations have however revealed that the resulting chitosan plasticization was only partial and that an ordered microstructure remained. In the present work, the thermo-mechanical treatment is improved by achieving for the first time an extrusion process in order to produce a chitosan-based film with a higher degree of chitosan plasticization. Indeed, the processing method can affect the outcome of plasticization since higher shear stresses were shown to allow a reduction of processing temperature and the water content required to achieve starch plasticization, as reported by Liu, Xie, Yu, Chen, and Li (2009). A one-step extrusion process was developed for starch plasticization by Favis, Rodriguez, and Ramsay (2003, 2005) ten years ago. This approach, applied to chitosan, may allow chitosan plasticization and its blend with a thermoplastic polymer in a single step. It should provide a better control of the thermal degradation of plasticized chitosan by reducing mixing time and hence contact time between the polymers at high temperature, and it should also improve the dispersion of the chitosan phase. In this work, chitosan is plasticized using a one-step extrusion process in the presence of glycerol and an acetic acid solution, and directly blended with metallocene polyethylene (mPE). This masterbatch is then diluted with mPE in the presence of ethylene-vinyl acetate (EVA), for compatibilization purposes, in order to prepare films with different chitosan content. Detailed characterization of the chitosan-based materials is provided, including morphology, optical, thermal, mechanical, and oxygen and water vapor barrier properties.

## 2. Materials and methods

### 2.1. Materials

Chitosan in powder form (grade ChitoClear<sup>®</sup>) was purchased from Primex (Iceland). Its degree of deacetylation (DDA) is 96%, its

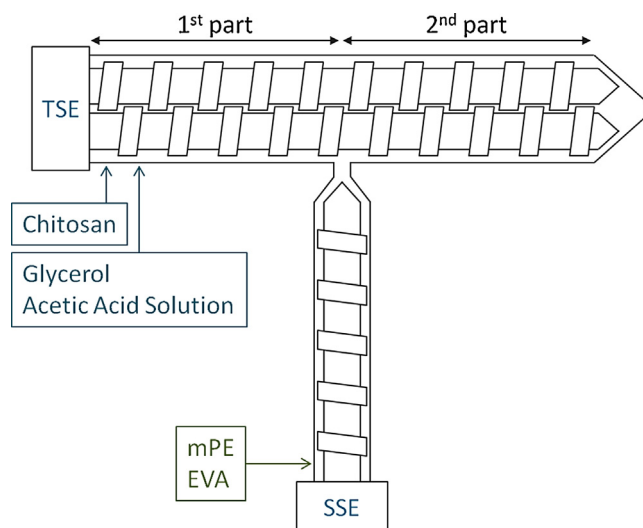


Fig. 1. Schematic representation of the one-step extrusion process.

weight-average molecular weight is in the range 250–300 kDa and it contains 0.1 wt% ash residue (according to the manufacturer's specifications). Glacial acetic acid and glycerol, used for chitosan plasticization, were purchased from Sigma-Aldrich and used as received.

Metallocene polyethylene (mPE) Affinity PL1880, with a melt flow index of 1 g/10 min at 190 °C (ASTM 1238), was purchased from Dow Chemicals (USA). The melting temperature is 99 °C, as determined by differential scanning calorimetry.

Ethylene vinyl acetate (EVA) Evatane 28-05, containing 28 wt% vinyl acetate, was obtained from Arkema (France). Its melting point is 72 °C and it presents a melt flow index of 5 g/10 min at 190 °C (ASTM 1238).

### 2.2. Sample preparation

The new procedure to prepare plasticized chitosan/polyolefin blend was based on the process developed by Favis et al. (2003, 2005). The specific screw profiles used were developed by Rodriguez-Gonzalez, Ramsay, and Favis (2003). The one-step extrusion process consisted in the use of a single-screw extruder (SSE) connected to a co-rotating twin-screw extruder (TSE) divided in 8 zones, as presented in Fig. 1. The SSE had a L/D = 26 with L = 495 mm (Brabender, Germany), while the TSE had a L/D = 28 with L = 960 mm (Leistritz, Germany). The SSE was used for the melting of the thermoplastic polymer (mPE) and its introduction in the TSE in zone 5. The TSE was divided in two functional parts: zones 1–4 were dedicated to chitosan feeding and plasticization and zones 5–8 to blending of plasticized chitosan and mPE.

Plasticized chitosan was prepared with 20 wt% chitosan, 60 wt% of a 3% v/v acetic acid solution and 20 wt% glycerol. Chitosan was fed in the first zone of the TSE at 0.75 kg/h. At the end of the first zone, the acetic acid solution and glycerol were fed together at 3 kg/h. Consequently, chitosan plasticization occurred in zones 2–4 of the TSE, at 105 °C and screw speed of 150 rpm. In the SSE, mPE was molten using a temperature range of 155 °C at the feeder to 180 °C at the connection with the TSE and screw speed of 110 rpm. The molten thermoplastic was introduced directly in zone 5 of the TSE at 4.5 kg/h. Then, plasticized chitosan and mPE were processed together in zones 5–8 at 130 °C and screw speed of 150 rpm. At the triple channel die exit, the extrudate was cooled in water and pelletized. A masterbatch containing 14 wt% of dry chitosan and 86 wt% of mPE was prepared, considering only the dry polymer

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