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# A comparative study of gelatin and starch-based nano-composite films modified by nano-cellulose and chitosan for food packaging applications

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ABSTRACT

Environmental concerns have led to extensive research for replacing polymer-based food packaging with bio-nano-composites. In this study, incorporation of nano-cellulose into gelatin and starch matrices is investigated for this purpose. Chitosan is used to improve mechanical, anti-fungal and waterproof properties. Experiments are designed and analyzed using response surface methodology. Nano-Cellulose is synthesized via acid hydrolysis and incorporated in base matrices through wet processing. Also, tensile strength test, food preservation, transparency in visible and UV and water contact angle are performed on the nano-composite films. DSC/TGA and air permeability tests are also performed on the optimal films. The results show that increasing nano-cellulose composition to 10% leads to increase the tensile strength at break to 8121 MN/m$^2$ and decrease the elongation at break. Also, increasing chitosan composition from 5% to 30% can enhance food preservation up to 15 days.

## 1. Introduction

The purpose of food packaging is prevention from contact of food materials with contaminating agents; physical, chemical or biological (Prasad & Kochhar, 2014), which is mainly performed through confining air and moisture availability. Glass, metal, paper, paperboard and various polymers including plastics have traditionally been implemented for this purpose (Tang, Kumar, Alavi, & Sandeep, 2012), among which plastics are considered as one of the main choices, during past decades due to processing convenience, high moisture and air resistance and low weight and cost properties (Accorsi, Cascini, Cholette, Manzini, & Mora, 2014). Various synthetic polymers are practiced for food packaging such as PVC, PA, PE, PET, PVA, etc. However, the growing demand for plastics has led to a global waste disposal crisis. The amount of plastic production in Europe has reached 311 Mt in 2014 with the highest demand in packaging industry (~40%). Although plastic recycling has reached 69.2% but ~8 Mt of plastic waste has been landfilled in European countries in 2014 (Plastics Europe Report, 2015).

Serious attempts have been made for replacement of synthetic polymers with relatively inexpensive, biodegradable and renewable material resources like natural polymers in food packaging application, though processing difficulties due to rigidity and stiffness has substantially hindered total and quick substitution. As a result, a deep need is felt for packaging films with biodegradable properties and yet significant flexibility and mechanical strength which entails fabrication of natural polymer nano-composites (Wang & Funk, 2012).

Biodegradable polymers derived from renewable resources are highlighted as the future generation of packaging materials (Petersen et al., 1999), including Poly (lactic acid) (PLA), starch, cellulose, chitosan, agar, alginate and various proteins. Despite biodegradable characteristics, renewable biopolymers have certain drawbacks regarding performance and processing costs (Petersen et al., 1999). However, they are generally cheaper, abundant and edible in some cases (Bengtsson, Koch, & Gatenholm, 2003).

Several studies have been performed to analyze the properties of starch films produced from different botanical sources (Mali, Grossmann, García, Martino, & Zaritzky, 2002; Mali, Grossmann, García, Martino, & Zaritzky, 2004; Mali, Sakanaka, Yamashita, & Grossmann, 2005). Certain plasticizers may be added to starch films in order to decrease brittleness. Although, mechanical and barrier properties of starch films depend on moisture (Krochta & Mulder-Johnston, 1997), this can be solved by the introduction of hydrophobic components in order to improve water vapor sorption properties. For example, glycerol is added to starch (plasticized wheat starch: PWS) to enhance processability via conventional extrusion. Poor mechanical strength and high sensitivity to moisture can also be overcome by associating starch with moisture resistant polymers with good mechanical properties, while maintaining biodegradability. PWS has been melt-blended with various biodegradable polyesters, such as poly (lactic acid) (PLA)

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(Martin & Avérous, 2001) and poly (butylene succinate adipate) (PBSA) (Avérous & Fringant, 2001) resulting in a significant improvement in properties.

Reduced water vapor transport is among important factors in the performance of starch as a packaging material which can be achieved through blending with polymers like chitosan. The higher hydrophobicity of chitosan compared with strach causes the film to obtain higher ressitance toward moisture along with the enhancement of mechanical strength. Strach-chitosan composite films are produced with improved trasnport properties and also the reduction of elongation to break and the enhancement of mechanical strength (Lopez et al., 2014). Chitosan has animicrobial properties besides biodegradability and intoxicity (Dutta, Tripathi Sh Mehrotra, & Dutta, 2009). While chitosan leads to the reduction of vapor transport, glycerol has an opposite effect. Also, glycerol results in the reduction of mechanical strength (Chillo et al., 2008; Pelissari, Grossmann, Yamashita, & Pineda, 2009).

Gelatin is another renewable polymer which has long been used as a packaging material consisting of a glued network of microcrystalline segments (Slade & Levine, 1988). Gelatin-Chitosan edible films with good mechanical strength and transport properties are prepared (Arvanitoyannis, Nakayama, & Aiba, 1998).

Addition of various nanomaterials to polymeric matrices has been another solution for the improvement of the desired packaging properties. Nano-clays have been added to various polymeric matrices in very small quantities (generally < 5 wt%) to improve film properties. Other nano-fillers have also been introduced to induce higher mechanical strength and barrier against gases and water vapor (Ghanbarzadeh, Oleyaei, & Almasi, 2015). Nano-fillers are capable of improving barrier and mechanical properties by decreasing filler dimensions and also reducing production cost due to lower material consumption (Rhim, Park, & Ha, 2013). Moreover, Nano-filler reinforcement leads to changes in polymer crystallinity (Azeredo, Mattoso, & McHugh, 2011). Mechanical strength and transport properties of chitosan-clay biodegradable films are investigated at various nano-clay proportions. Nano-clay leads to reduced transport and enhanced water absorption (Giannakas, Grigoriadi, Leontiou, Barkoula, & Ladavos, 2014). The addition of nanoclay to starch composite films has improved the mechanical strength and transport properties (Tang, 2008). Zeolites are also used as fillers in starch-based films. Studies show that zeolite leads to the enhancement of Young modulus and reduction of gas and vapor transport and also water solubility (Belibi et al., 2013).

Cellulose is another semi-crystalline high Mw natural nano-polymer virtually present in all plants with typical crystal lengths of 20–2000 nm. Even though the tensile properties of nano-crystalline cellulose are an order of magnitude below those of carbon nanotubes they are sufficiently high to justify them as fillers in bio-composite materials (Rousseau & Tolnai, 2010). Cellulose fibers are added to gelatin-based films enhancing film strength up to 5% (Santos et al., 2014). Nano-cellulose is also added to starch in order to enhance starch film properties. Based on the results, nano-cellulose leads to the improvement of mechanical properties up to 70% (Nasri-Nasrabadi et al., 2014).

Based on the literature review performed, a systematic study on the effect of nano-cellulose and chitosan on packaging performance of gelatin and starch-based nano-composite films is not performed. So, this study is aimed at the improvement of mechanical strength and barrier properties of gelatin and starch-based nano-composite films by incorporating various chitosan and nano-cellulose proportions in the host matrix. Based on the studies, it is expected that addition of nano-cellulose to the mixed polymeric matrix bring about mechanical strength as well as improved food preservation characteristics to gelatin and starch films.

## 2. Materials and methods

### 2.1. Materials

Starch ($\rho = 0.625\ g/cm^3$) and cellulose micro-fibrills ($\rho = 0.6\ g/cm^3$) were purchased from Sigma-aldrich. Chitosan (Mw = 60000–80000 g/gmol, $\rho = 0.3\ g/cm^3$) is provided by Acros Co. Gelatin ($\rho = 0.98\ g/cm^3$) and other reagents are also provided by Merck Co.

### 2.2. Methods

#### 2.2.1. Synthesis of nano-cellulose

Cellulose nano-crystals are obtained via acidic hydrolysis of cellulose microcrystals by dissolution of semi-crystalline regions in sulfuric acid and re-dispersion of the remaining materials in water. Details of the synthesis procedure can be found elsewhere (Abdollahi, Alboofetileh, Behrooz, Rezaei, & Miraki, 2013; Zhao et al., 2014)

#### 2.2.2. Preparation of nano-composite films

Single-layered films are prepared through film casting technique. A certain amount of chitosan is dissolved in a 10 mL of 2 V/V% acetic acid solution under stirring for 10–15 min producing a transparent solution. Also, a certain amount of nano-cellulose gel is dispersed in 20 mL deionized water and sonicated (200 W) for 10 min producing a homogeneous dispersion. A certain amount of polymeric base (starch or gelatin) is added to the mixed solution.

For starch films, the solution is heated to 60 °C and stirred vigorously for 10 min to produce a gelatinous solution. For gelatin films, the solution is heated to 40 °C and stirred vigorously for 15 min until total dissolution occurs. The separate solutions based on the polymer base and chitosan are mixed at 45 °C and glycerol is also added to the mixture and ultra-sonicated (50 W) for 2 min. The final solution is dried in oven at 55 °C for 12 h.

Double-layered films are prepared by producing the polymer base and chitosan solutions separately using the same procedure as stated in the preparation of single-layered films except that glycerol and nano-cellulose are added regarding dry mass of polymer and chitosan then ultra-sonicated separately. Here, first the chitosan layer is cast and dried. Thereafter, the starch or gelatin layers are coated over the first layer and dried in oven at 55 °C for 10 h.

#### 2.2.3. Design of experiments

Several parameters such as nano-cellulose composition, chitosan content, type of polymeric base and its weight% and glycerol content may influence the performance of nano-composite films to various degrees. As a result, these parameters are intended for optimization using a design of experiments procedure namely Response Surface Methodology (RSM), the results of which are shown in Table 1 as 24 individual experiments.

#### 2.2.4. Characterization

X-ray diffraction (XRD) is performed on cellulose nano/micro crystals to determine the variations in structure and crystallite size. Also, TEM micrographs are used to determine the size and morphology of nano-cellulose. Cellulose microcrystals are also observed using SEM technique. XRD equipment (D8 ADVANCE, BRUKER Germany) is used to perform XRD analysis.

Cellulose crystal micrographs were characterized using SEM (TESCAN-Mira III, Czceh Republic). Philips CM-30 was also implemented to perform TEM analysis. DSC/TGA and air permeability tests are also performed on the optimal efficiency films.