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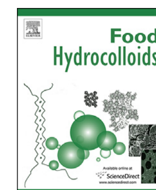

Characterization of films based on enzymatically modified chitosan derivatives with phenol compounds

Abdulhadi Aljawish*, Lionel Muniglia, Amira Klouj, Jordane Jasniewski, Joël Scher, Stephane Desobry*

Laboratoire d'Ingénierie des Biomolécules (LIBio), Université de Lorraine, 2 avenue de la Forêt de Haye, TSA 40602-54518, Vandœuvre-lès-Nancy, France

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Enzymatic modification of chitosan particles by the ferulic acid (FA) and ethyl ferulate (EF) oxidation products using *Myceliophtora thermophyla* laccase in mild conditions (pH 7.5, 30 °C in aqueous medium) was investigated. The chitosan derivatives showed an increase of degree of acetylation (DA), molecular mass (MM) and viscosity in comparison with chitosan.

Chitosan and its derivatives films were characterized in terms of physicochemical, surface, barrier, mechanical and antioxidant properties. The results showed that the chitosan derivative films were colored (yellow-orange) for FA and colorless for EF compared to colorless chitosan films. The oxidation products grafted onto chitosan increased the dry matter content, thickness and heterogeneous surface of chitosan derivative films. Owing to the hydrophobic character of oxidation products, chitosan derivative films showed a low capacity of moisture capture and sorption at different levels of relative humidity (RH). Low moisture content improved the barrier properties and decreased the mechanical properties of chitosan derivative films. Furthermore, the presence of phenol products onto chitosan improved the antioxidant properties of its derivative films. Despite the phenol content of FA-chitosan films was higher than that of EF-chitosan films; no significant change was noticed in thickness, water sorption isotherms as well as barrier and mechanical properties. Interestingly, FA-chitosan films showed higher antioxidant properties in comparison with EF-chitosan films. It could be concluded that the enzymatic grafting of phenol compounds onto chitosan is a promising process to create useful functional materials for industrial applications such as food packaging.

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1. Introduction

Recently, a growing interest was shown for the development of new active materials based on sustainable polymers such as chitosan, pectin, cellulose and starch. These new materials are used in industrial applications especially in foodstuffs such as edible films, packaging and coating which biodegrade during the storage with controlled conditions in order to relieve the growing materials waste problem (Dutta, Tripathi, Mehrotra, & Dutta, 2009). In fact, the chitosan and its derivatives represent an important potential as packaging material due to its film-forming material and antimicrobial activity (Vinsova & Vavrikova, 2011).

Chemically, chitosan is defined as a copolymer which consists of pyranose cycles of *N*-acetyl-D-glucosamine (GlcNAc) and N-glucosamine (GluN) linked with a glycosidic linkage and mainly obtained from deacetylation of chitin by chemical approach (alkaline conditions) (Ravi Kumar, 2000). As a natural resource, chitosan exhibits unique interesting properties such as biocompatibility, biodegradability and non-toxicity (Sabnis & Block, 2000). For these reasons, chitosan polymer is used in several important applications in the food packaging, agriculture, biomedical and cosmetics domains (Kim et al., 2006; Rinaudo, 2006). Among the several applications of chitosan, it is used in a variety of packaging needs (Srinivasa, Baskaran, Ramesh, Harish Prashanth & Tharanathan, 2002). Moreover, due to the capacity of good film-forming, chitosan can be used in the form of transparent films or coatings to improve the quality of fresh food and extend its shelf life (Arancibia et al., 2014). Although, chitosan films have a low permeability to

* Corresponding authors. Laboratoire d'Ingénierie des Biomolécules (LIBio), Université de Lorraine, 2 avenue de la Forêt de Haye, TSA 40602-54518, Vandœuvre-lès-Nancy, France.

E-mail addresses: ahjawish@yahoo.com (A. Aljawish), stephane.desobry@univ-lorraine.fr (S. Desobry).

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gases (CO_2 and O_2); they are highly permeable to water vapor at 50% of relative humidity (Hosokawa, Nishiyama, Yoshihara, & Kubo, 1990). Moreover, chitosan based-films are stable, flexible, tough and difficult to being torn apart (Dutta et al., 2009) and it received a special attention as antimicrobial agent for food preservation (Sabnis & Block, 2000).

In order to increase or improve the properties of chitosan films such as antimicrobial, antioxidant and/or mechanical properties, various active compounds were frequently incorporated such as essential oils of basil and thyme (Bonilla, Atares, Vargas, & Chiralt, 2012), ascorbic acid (Sun, Liang, Xie, Lei, & Mo, 2010), tocopherol (Martins, Cerqueira, & Vicente, 2012), ferulic acid and tannic acid (Benbettaieb, Karbowiak, Brachais, & Debeaufort, 2015). Practically, the modification of chitosan films with active compounds may be carried out by chemical and enzymatic approaches. Due to growing safety and environmental concerns, the modification of chitosan films using enzymes was investigated as an important alternative to non-specific and toxic chemical catalyzes (Couto, Sanroman, & Gubitz, 2005). This enzymatic process can maintain or improve its initial interesting properties creating new functional properties and thus expand the field of its potential applications. The enzymatic modification of chitosan is usually performed using oxidative enzymes such as polyphenol oxidases (PPOs) (tyrosinases and laccases) that convert phenols derivatives into free radicals (quinones, semiquinones). These active radicals can chemically react in reaction medium with the free amino groups of chitosan (nucleophilic function) to yield either Schiff-bases or Michael-type adducts (Chen, Kumar, Harris, Smith, & Payne, 2000; Payne, Chaubal, & Barbari, 1996; Shao, Kumar, Lenhart, Smith, & Payne, 1999; Vartiainen, Ratto, Lantto, Nattinen, & Hurme, 2008).

The present work reported the manufacturing and the characterization of films based on chitosan and its derivatives modified by enzymatic method. The chitosan derivatives were produced by the enzymatic grafting of ferulic acid (FA) and its ethyl ester (ethyl ferulate) (EF) onto chitosan particles according to (Aljawish et al., 2012). FA and EF were chosen because they are usually used as antioxidant additives in the food industry with known functional properties such as antioxidant and antibacterial activities (Ou & Kwok, 2004; Warner & Laszlo, 2005). The chitosan and its derivative films were characterized in terms of physicochemical, barrier, mechanical, surface and antioxidant properties.

2. Materials and methods

2.1. Chemical and enzyme

High molecular weight Chitosan (HMW, M_w 290–325 kDa), ferulic acid (FA) and ethyl ferulate (EF) (purity about 99%) were obtained from Sigma–Aldrich (France). Acetic acid was obtained from Prolabo (France). 2,2′-azino-bis(3-ethlyl-benzthiazoline-6-sulfonic) acid (ABTS), methanol, ethanol and acetone were obtained from Carlo Erba (Milwaukee, WI, USA).

Suberase® (Novo Nordisk, Denmark), an industrial laccase was obtained from the Society Novozymes under brown liquid form. This enzyme is a fungal laccase from *Myceliophthora thermophila* sp. Suberase® was partially purified according to method described previously (Aljawish et al., 2014) to remove inactive peptides or proteins and to avoid the interaction between the interesting phenols and phenols which were initially present with the industrial laccase.

2.2. Enzymatic synthesis of chitosan derivatives

Chitosan derivatives were synthesized by enzymatic grafting of the oxidation products of (FA) or (EF) onto chitosan particles using the *Myceliophtora thermophila* laccase (Aljawish et al., 2012). The reaction medium was consisted of 5 ml of FA or EF solution (50 mM), 45 ml of phosphate buffer (50 mM, pH 7.5) and 1 g of chitosan particles. The enzymatic process was started by adding 0.13 ml of Suberase® (13.5 U/ml of laccase) at 30 °C for 4 h in a magnetic stirred reactor. Then, the reaction medium was filtered under vacuum with a Sartorius filter (porosity 0.2 μm) in order to recover the chitosan derivatives. The obtained chitosan derivatives were washed with an abundant amount of phosphate buffer (50 mM, pH 7.5) and then methanol, ethanol and acetone to remove all traces of enzyme and substrates adsorbed on the chitosan derivatives. Finally, the chitosan derivatives were dried at room temperature and then kept in desiccators until use.

2.3. Characterization of chitosan derivatives

Degree of acetylation (DA%) was determined using infrared spectroscopy method (Brugnerotto et al., 2001) and UV spectrophotometric method (Liu, Wei, Yao, & Jiang, 2006).

Molecular weight (MW) of chitosan derivatives was measured by size exclusion chromatography (SEC-MALLS, Viscotek – Malvern, France) according to the method described earlier (Nguyen, Hisiger, Jolicoeur, Winnik, & Buschmann, 2009). Analysis assay was realized using a Viscotek A6000M gel column and OmniSEC 4.6 Software (Malvern) at 30 °C and a flow rate of 0.6 ml/min with injection volume of 100 μl. Values were calculated as the average ± standard deviation of three experiments.

Viscosity of chitosan derivatives was performed using cone-and-plate rheometer (Kinexes Malvern) with a fixed outer cylinder and rotating measuring bob. The radius of the rotating cylinder was 30 mm and the gap width was 0.052. Chitosan solution at 1% (w/v) was prepared in aqueous acetic acid (1%, v/v) at pH 3. The apparent viscosity was determined at steady shear rate (0.15 s^{-1}) and all measurements were performed in triplicates at 25 °C.

2.4. Preparation of films casting

Chitosan solution (1%, w/v) was prepared in aqueous acetic acid (1%, v/v) at pH 3 and then filtered with cellulose nitrate membrane filters with 5 μm pore size and 47 mm diameter (Whatman®, 7195-004, Germany). A vacuum (6×10^{-2} Pa) was used for 1 h to remove air bubbles from the systems (Yamato®). Chitosan films were made by pouring 18 g of chitosan solution on Petri dish equipped with Teflon sheet and left to dry at 20 °C and relative humidity 50% for 48 h under clean conditions. The films were stored in the desiccators containing phosphorus pentoxide (P_2O_5) until use.

2.5. Characterization of chitosan-based films

2.5.1. Determination of phenol content

The phenol content of chitosan films was determined according to the method described by Singleton, Orthofer, and Lamuela-Raventos (1999) with some modifications. One mg of each film was re-dissolved in 1 ml of acetic acid solution (1%, v/v). Then, 1 ml of the chitosan film solution was mixed with 1 ml of 10% sodium carbonate (Na_2CO_3). After 10 min at 38 °C, 1 ml of Folin-Ciocalteau reagent (1/3) was added to the mixture and stirred for 1 h in the dark at room temperature. The absorbance was measured at 660 nm using a UV–visible spectrophotometer (Shimadzu UV-1605). Gallic acid (40 μg/ml) and water were used as standard and blank, respectively. The phenolic content was calculated by the following Equation (1):

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