



Chitosan films and blends for packaging material



Lambertus A.M. van den Broek*, Rutger J.I. Knoop, Frans H.J. Kappen, Carmen G. Boeriu

Wageningen UR Food & Biobased Research, PO Box 17, 6700AA Wageningen, The Netherlands

ARTICLE INFO

Article history:

Received 18 December 2013
Received in revised form 18 July 2014
Accepted 19 July 2014
Available online 29 July 2014

Keywords:

Packaging
Biopolymer
Chitin
Chitosan
Antimicrobial

ABSTRACT

An increased interest for hygiene in everyday life as well as in food, feed and medical issues lead to a strong interest in films and blends to prevent the growth and accumulation of harmful bacteria. A growing trend is to use synthetic and natural antimicrobial polymers, to provide non-migratory and non-depleting protection agents for application in films, coatings and packaging. In food packaging, antimicrobial effects add up to the barrier properties of the materials, to increase the shelf life and product quality. Chitosan is a natural bioactive polysaccharide with intrinsic antimicrobial activity and, due to its exceptional physicochemical properties imparted by the polysaccharide backbone, has been recognized as a natural alternative to chemically synthesized antimicrobial polymers. This, associated with the increasing preference for biofunctional materials from renewable resources, resulted in a significant interest on the potential for application of chitosan in packaging materials. In this review we describe the latest developments of chitosan films and blends as packaging material.

© 2014 Elsevier Ltd. All rights reserved.

1. Chitosan

Chitin the precursor of chitosan, is a linear polymer of mainly β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose units and low amounts of β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose residues. The polymer is highly acetylated and is insoluble in water. It is one of the most abundant biological materials in the world and is after cellulose and next to lignin the most biosynthesized polymer. When the degree of *N*-acetylation (DA) is lower than 50% it is entitled chitosan (Fig. 1). Typically the DA of chitosan is between 0.05 and 0.30 (Kardas et al., 2012; Kasaai, 2009; Yeul & Rayalu, 2013).

Chitin is mainly isolated from crustacean wastes (Alishahi & Aider, 2012). It is tightly bound in complexes with other substances, like proteins and minerals. At industrial scale, an acid treatment (decalcification) followed by an alkaline treatment (deproteination), or just in reversed order, and a decolourization step are

used to obtain chitin. In order to prepare chitosan, an additional alkaline treatment is performed to deacetylate chitin. Different factors, like alkali concentration, incubation time, ratio chitin to alkali, temperature, atmosphere, type of chitin source (including polymorph type), particle size, heterogeneous/homogeneous *N*-deacetylation, and single or multiple process play a role in the alkaline *N*-deacetylation of chitosan and thus affecting the properties of chitosan. At this moment, research is directed to more environmental biological methods like the use of enzymes and/or microorganisms that can be applied in the different isolation steps. For deproteination proteases like trypsin, chymotrypsin and papain can be used or microorganisms such as *Aspergillus niger*, *Bacillus subtilis* and lactic acid bacteria. In addition, lactic acid bacteria can also be used for demineralization. Alternative chitin or chitosan sources are fungi, yeast, protozoa, green microalgae, and insects, although their industrial application is limited (Arbia, Arbia, Adour, & Amrane, 2013; Barikani, Oliaei, Seddiqi, & Honarkar, 2014; Gortari & Hours, 2013; Kardas et al., 2012). Most chitosans (depending on e.g. DA and M_w) are insoluble in water and also in most common organic solvents. However, they can be easily dissolved in acidic aqueous solutions below pH 6.3, although at concentrations above >2 wt% they become very viscous (Kaur & Dhillon, 2014; Yeul & Rayalu, 2013).

Chitosan, having cationic groups along the backbone, has been shown to have antimicrobial properties against bacteria, yeasts, moulds and fungi (Friedman & Juneja, 2010; Rabea, Badawy, Stevens, Smagghe, & Steurbaut, 2003). The mechanism through which chitosan acts as an antimicrobial compound is not fully elucidated, however, two main hypotheses (I and II) have been

Abbreviations: DA, degree of *N*-acetylation; DDA, degree of de-acetylation; EB, elongation at break; EAA, ethylene acrylic acid; EVA, ethylene vinyl acetate; T_g , glass transition temperature; HDPE, high density polyethylene; LbL, layer by layer; LDPE, low density polyethylene; T_m , melting temperature; M-CS, microdispersed chitosan; PBS, poly(butylene succinate); PBSA, poly(butylene succinate adipate); PBTA, poly(butylene terephthalate adipate); PCL, poly- ϵ -caprolacton; PE, polyethylene; PEO, polyethylene oxide; PLA, polylactic acid; PHB, polyhydroxybutyrate; PP, polypropylene; PVP, poly(*N*-vinyl-2-pyrrolidone); TS, tensile strengths; W-CS, water soluble hydroxypropyl chitosan; WVP, water vapour permeability.

* Corresponding author. Tel.: +31 317 480104; fax: +31 317 483011.
E-mail address: Ben.vandenbroek@wur.nl (L.A.M. van den Broek).

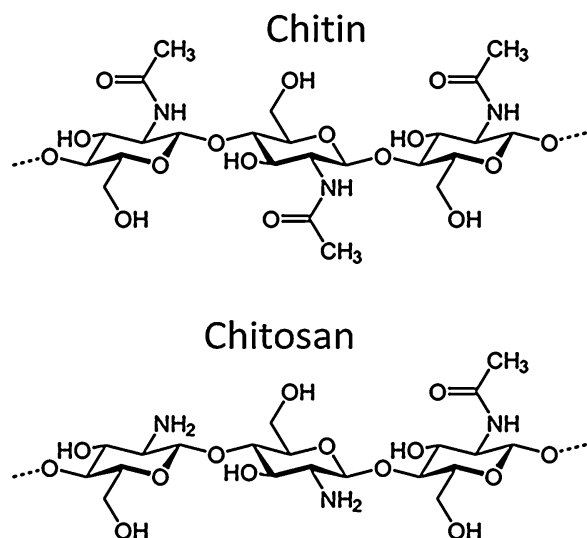


Fig. 1. Structure of chitin and chitosan.

proposed (Benhabiles et al., 2012; Jing et al., 2007) whereas some authors have proposed a third one (III) (Goy, de Britto, & Assis, 2009; Martinez-Camacho et al., 2010). These are:

- (I) The polycationic nature (positive charge) of chitosan that interferes with the bacterial metabolism by electrostatic stacking (negative charge) at the cell surface.
- (II) Low molecular weight chitosan that can enter the cell's nucleus blocking the transcription of RNA from DNA due to adsorption to DNA molecules.
- (III) Chitosan working as chelating agent of essential minerals.

Therefore, chitosan treatment can offer protection against contamination and microbial spoilage. The good film forming properties of chitosan allows the production of films, coating material or membranes semipermeable to gases. For example it is known that these films possess low oxygen permeability (Aider, 2010; Martinez-Camacho et al., 2010). In addition, chitosan has unique properties such as biodegradability, biocompatibility, non-toxicity and it is renewable (Barikani et al., 2014). Furthermore, it is inexpensive and commercially available. Low material cost is needed as the contribution of packaging material to the total product costs is highly significant (Aider, 2010). Chitosan films can be divided into edible films or coatings (<30 μm), for application directly on food in order to improve food safety and shelf life, films (>30 μm) and blends. Blends can be homogenous or heterogeneous mixtures. Edible films or coatings are very well described by others (Elsabee & Abdou, 2013; Goy et al., 2009). Our aim is to focus on processing of chitosan films and blends and their properties.

2. Chitosan films and blends

Films of pure chitosan can be obtained only via solvent casting from acidified water. However, for blending more possibilities are available such as solvent blending, extrusion blending and reactive extrusion blending all leading to different morphologies, e.g. homogenous dissolved in the polymer matrix or inhomogeneous present (like a filler) (Sorrentino, Gorrasi, & Vittoria, 2007). Due to the extensive hydrogen bonding of chitosan it degrades prior to melting. Dissolving chitosan in an appropriate solvent is necessary to impart functionality. However, for each solvent system, polymer concentration, counter ion concentration, temperature and pH must be known (Fernández-Saiz & Lagaron, 2011). For thin films,

solution casting is a suitable option, for foils, extrusion is the most economical option.

2.1. Pure chitosan films

Pure or partly plasticized chitosan films can be obtained from solvent casting. In this process chitosan is dissolved in suitable solvents, in most cases slightly acidified water, and a plasticizer is added. The solution is poured on a flat surface and the solvent is allowed to evaporate. A comprehensive research was performed by Kim, Son, Kim, Weller, and Hanna (2006) in which the solvent and pH of the solution was varied for low (78.9%) and high (92.3%) degree of de-acetylation (DDA). The main focus of their research was the water vapour permeability (WVP) of the obtained films in combination with the mechanical properties. The WVP was significantly affected by the DDA of chitosan, solvent pH and type of acid (formic acid, lactic acid, acetic acid and propionic acid), which interacted strongly with each other. Higher WVP was measured for highly de-acetylated chitosan than for chitosan with lower DDA. Films obtained from lactic acid and formic acid showed higher WVP compared to acetic- and propionic acid. The WVP for films formed at pH 4 and 5 showed higher WVP than for pH 3. Tensile strengths (TS) were significantly affected by the DDA, pH and acid type. The elongation at break (EB) was strongly affected by the acid type and pH but not by the DDA. The effect of storage time and temperature on mechanical and barrier properties on chitosan based films was investigated by Kerch and Korkhov (2011). The mechanical properties of chitosan films and the WVP rate increased with storage time, M_w of chitosan and decrease of storage temperature. Increased plasticizer content resulted also in improved mechanical property as the material became less brittle. Water vapour uptake of chitosan films decreased during storage at room temperature but increased during storage at temperatures below 4 °C. Depending on the M_w of the chitosan and the plasticizer content, different TS and EB were reported. These differences, however, makes comparison between the values difficult although TS and EB values are the most important characteristics for film applications. TS between 23 and 66 MPa were reported and these values are slightly higher than for high density polyethylene (HDPE) and low density polyethylene (LDPE). Reported EB are in between 46% and 66% which is comparable to HDPE, LDPE and cellophane (Butler, Vergano, Testin, Bunn, & Wiles, 1996). Unfortunately, the high sensibility of chitosan films to humidity limits the application for food packaging. Because chitosan films and coatings are created from diluted acid solutions, they can remain water sensitive, or even water soluble, which limits their range of applications. Cross-linking of chitosan with various reagents like genipin, glutaraldehyde, formaldehyde etc. is an alternative method to prevent dissolving and/or swelling of chitosan based films (Dutta, Tripathi, Mehrotra, & Dutta, 2009).

Improved antimicrobial coatings/films were obtained by solution blending of chitosan with various antimicrobial agents like cinnamon oil (Ojagh, Rezaei, Razavi, & Hosseini, 2010), tetrahydrocurcuminoid derivatives (Portes, Gardrat, Castellan, & Coma, 2009) and tea tree essential oil (Sanchez-Gonzalez, Gonzalez-Martinez, Chiralt, & Chafer, 2010).

Chitosan films are not thermoplastic because it degrades before the melt and, as such, cannot be extruded, moulded, stretched or heat-sealed as in the case of conventional thermoplastic packaging polymers. This increases the cost of the films and limits their applications (Pelissari, Yamashita, & Grossmann, 2011).

2.2. Blends

Blending of chitosan with thermoplastic polymers represents an alternative route to obtain more humidity resistant materials. Blending mainly lead to films which final material properties can be

Download English Version:

<https://daneshyari.com/en/article/1385688>

Download Persian Version:

<https://daneshyari.com/article/1385688>

[Daneshyari.com](https://daneshyari.com)