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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

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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.

1. Chitosan

Chitin the precursor of chitosan, is a linear polymer of mainly β-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose units and low amounts of β-(1 → 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 & Aïder, 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).

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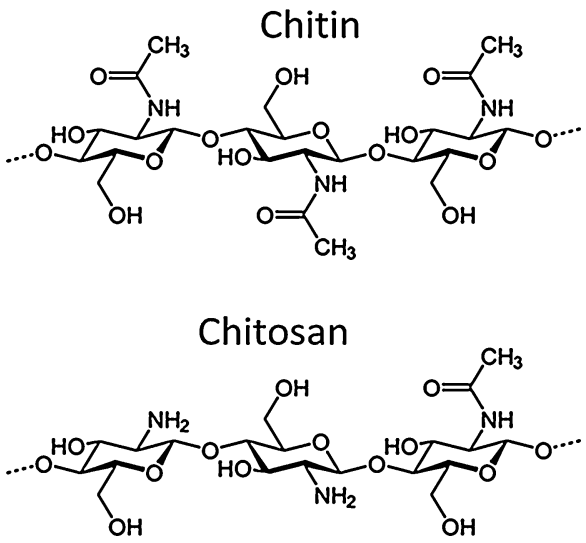

Fig. 1. Structure of chitin and chitosan.

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

better controlled, in comparison to the solvent evaporation process (Pelissari et al., 2011).

2.2.1. Solution blending

Blending chitosan with water soluble poly(vinyl alcohol) and subsequently cross-linking with glutaraldehyde is another approach to make edible antimicrobial films (He & Xiong, 2012; Tripathi, Mehrotra, & Dutta, 2009). Lin et al. prepared single or double network chitosan poly(vinyl alcohol) films through selective cross-linking using borate and tripolyphosphate. Borate has the special ability to cross-link poly(vinyl alcohol) through di-diol reaction (Lin, Liu, Shen, Yu, & Cheng, 2003). Tripolyphosphate can form cross-links with chitosan by strong electrostatic interactions (Mi, Sung, Shyu, Su, & Peng, 2003). These films showed a very high transparency and enhanced the water barrier properties.

Blends of chitosan with polyethylene oxide (PEO) and poly(*N*-vinyl-2-pyrrolidone) (PVP) with ratios chitosan varying from 0% to 100% were made and evaluated by Li, Zivanovic, Davidson, and Kit (2010). The physical properties of the blends were altered compared to films obtained by using just a single polymer. Clear films were obtained for blends with only 25 wt% PEO; addition of higher levels of PEO resulted in whitish, opaque appearance due to the formation of large PEO crystals. The addition of 75 wt% PEO resulted in a threefold enhancement in flexibility compared to pure chitosan films. PVP–chitosan blends with 25–75 wt% PVP appeared transparent but did not change significantly the flexibility. Although the WVP of chitosan–PEO blends was lower than for films of PVP–chitosan, blending chitosan with hydrophilic polymers did not appear to be an effective way to improve the WVP. Interestingly, PVP–chitosan blends showed a lower antimicrobial effect than PEO chitosan blends. This is explained by the linear polymer chain in PEO while the pyrolidone rings in PVP may obstruct the interaction of chitosan with the microbial cells.

Comparable to the incorporation of plasticizers and hydrophilic polymers in chitosan via solvent casting techniques, blends of chitosan with various hydrophobic polymers were made such as polyhydroxybutyrate (PHB) (Ikejima & Inoue, 2000), poly-ε-caprolacton (PCL) (Joseph et al., 2011), polylactic acid (PLA) (Suyatma, Copinet, Tighzert, & Coma, 2004) and starch (Xu, Kim, Hanna, & Nag, 2005). A typical procedure to blend chitosan via this solution technique is as follows. A 1–2 wt% chitosan solution in acetic acid (1–5 wt%) is mixed with a polymer solution in chloroform. This is stirred until a homogenous mixture is obtained. Subsequently, it is poured on a flat surface and the water solvent mixture is allowed to evaporate. Depending on the final composition, PCL based blends showed mainly phase separated morphologies but co-continues morphologies were obtained for one specific combination. Although due to the immiscibility of the two solutions, acidified water and chloroform, mixing ratios have to be taken into account. Unfortunately, none of these publications takes this into account which makes comparing impossible.

More homogenous blends were obtained by Ikejima and Inoue (2000) using one and the same solvent to dissolve both polymer and chitosan. Although homogenous blends were obtained, the use of 1,1,1,3,3,3-hexafluoro-2-propanol makes this route not economical feasible.

2.2.2. Extrusion blending

Different blends of chitosan with synthetic polymers are described changing from complete biodegradable to almost non-biodegradable. Correlo et al. (2005) performed a systematic study of the properties of melt processed blends of aliphatic polyesters and chitosan. PCL, poly(butylene succinate) (PBS), PLA, poly(butylene terephthalate adipate) (PBTA), and poly(butylene succinate adipate) (PBSA) were blended in various ratios with chitosan and the thermal, mechanical properties were studied. Using optical and scanning electron microscopy allowed them to investigate the morphology as well as the homogeneity. Interestingly, different blend ratios were described in combination with aliphatic polyesters. Although for polymer–chitosan combination different chitosan polymer ratios were used, comparison of the influence of blending on properties is still possible for the 50:50 ratio blends. The influence of chitosan on the thermal properties of the blend is different for each combination. Chitosan (50 wt%) in PLA slightly lowers the glass transition temperature (T_g) from 62 °C to 61 °C but largely influence the onset temperature for crystallization. The onset temperature is reduced from 107 °C to 89 °C although the melting temperature remains constant indicating that similar crystals are formed. In contrast to PLA, 50 wt% chitosan in PCL caused a slight increase in melting temperature (T_m) from 52 °C to 55 °C. The total crystallinity is reduced from 41.7% for pure PCL and 31.2% for the blend which is probably due to hydrogen bonding of the carbonyl group of the polyester and —OH and —NH_2 groups in chitosan. These interactions occur in the amorphous regions suppressing the extent of crystallization. Controversially to PCL, PBS and PBSA showed a melting point depression of about 5 °C when mixed with chitosan in a 50 wt% blend. For 25 wt% and 75 wt% chitosan blends in PBS, an increase in T_m and crystallinity was detected. This was contributed to strong intermolecular interactions between chitosan and polyester chains resulting in thinner lamellar thickness crystals. The depression of T_m for the 50 wt% blends of PBS and PBSA may be an indication that physical and thermal properties of such blends may not exhibit regular trends with compositions, as the processing conditions may have an important role on the final materials.

The influence of chitosan on the TS, tensile modulus and EB was investigated. In general can be stated that for all 50 wt% blends a decrease in TS and EB is found. The reduction in TS is roughly 25–30% for PBS and PCL blends but much higher for PLA and PBSA (roughly 52%). The reduction in TS was the lowest for PBTA, only 12%. This is mainly due to the thermodynamic immiscibility and inherent incompatibility of chitosan and polyester. Since the mechanical performance of filled polyester strongly depends on the strength and modulus of the filler, the tensile strength of a heterogeneous polymer blend depends on the tensile strength of the polyester matrix.

Another trend was observed for the tensile modulus which in all cases increased. This was, as comparable to TS, highest for PBS and PCL (69 and 79%, respectively) and the lowest for PLA and PBSA (both 35%). PBTA showed the smallest reduction in TS but a 50% increase in tensile modulus. The EB is strongly affected by blending chitosan. For all polyesters except PLA, a two order of magnitude decrease in EB was observed. The lowest decrease in EB for PLA is mainly due to the inherent brittle fracture behaviour of pure PLA and its T_g which is above room temperature. As expected, the chitosan remained in the continuous polyester phase since chitosan particles do not melt. However, particle agglomerates are visible indication that less effective mixing occurred. Some attempts have been made in order to improve the mixing by using another extrusion configuration. Reverse mixing elements improved mixing and prevented agglomeration of chitosan particles in the blend. Unfortunately, due to the high torque, these reverse mixing elements cannot be used for all blends.

The extrusion parameters related to starch chitosan film properties were extensively studied by Pelissari et al. (2011). The influence of the extrusion parameters on film blowing properties and on the obtained film were investigated via an experimental design approach. They concluded that an increase in screw speed of the extruder resulted in an increase in blow-up ratio of the film during film blowing, and WVP. An increase in screw speed resulted in a decrease of opacity, TS and EB of the films. Low die temperatures lead to an increase in TS, EB, Young's modulus and WVP. This

makes clear that depending on the purpose of the film, the process conditions has to be optimized.

Chitosan blends with non-biodegradable polymers (LDPE) in order to obtain anti-microbial films for food packaging have been studied. Zhang, He, Liu, and Qia (2009) investigated the influence of two types chitosan, water soluble hydroxypropyl chitosan (W-CS) and microdispersed chitosan (M-CS) with various loadings ranging from 0.1 wt% up to 2 wt% on EB and antimicrobial activity against *Escherichia coli*, *B. subtilis*, and *Proteus* sp. Although the mechanical properties were decreased with increasing chitosan content, the antimicrobial properties of chitosan remained and also increased with increasing chitosan content (Park, Marsh, & Dawson, 2010; Zhang et al., 2009). Opposite to these findings, Rodriguez-Nunez et al. (2012) found that chitosan polyamide blends did not show any antimicrobial activity, also when there was contact). They compared bilayer films and blends of polyamide and chitosan. The bilayer production was a two-step process; a chitosan solution was casted onto a polyamide 6/66 film. This bilayer showed contact antimicrobial activity to *Salmonella typhimurium* and *Staphylococcus aureus*.

2.2.3. Compatibilized blends

The usage of compatibilizers, additional low molecular weight compound or as block copolymer, is well described in order to facilitate homogeneous distribution of chitosan over the polymer matrix. Usage of other additives is described in order to improve sealing properties of the obtained films. Alternatively, reactive extrusion is used with a dual goal, homogeneous distribution of chitosan over the polymer matrix and avoiding migration out of the matrix.

Recently, Massouda and coworkers concluded that high M_w chitosan was not effective as antimicrobial agent. However, the antimicrobial activity was still present when spray dried chitosonium acetate was extruded with ethylene vinyl acetate (EVA) copolymers. They prepared a PE film and compared the influence of different concentration of chitosan. In an earlier patent, they also claimed remaining antimicrobial effect after extrusion blending of PE with chitosan-acetate with ethylene using an ethylene based block copolymer with amino-reactive groups. These polymers should be water insoluble and are further referred as 'ionomers'. Ionomers are defined as a polymer with inorganic salt groups attached to the polymer chain (Massouda, 2006; Massouda, Visioli, Green, & Joerger, 2012). Martinez-Camacho et al. (2013) prepared blends based on PE using ethylene acrylic acid (EAA) as compatibilizer. From tensile measurements, the TS decreased with increasing chitosan content, they concluded that nearly no interaction was present between PE and chitosan. The use of EAA did not lead to sufficiently high hydrogen bonding in order to improve the adhesion between chitosan and PE. Alternatively, polyacrylic acid groups, obtained after functionalization of PE with acrylic acid after plasma treatment of the PE surface, were evaluated for their antimicrobial properties.

2.2.4. Reactive extrusion blending

Like the use of compatibilizers, reactive compatibilizers can be used in order to improve the interfacial adhesion between the polymer matrix and chitosan. The difference between compatibilizers and reactive compatibilizers is the interfacial bond, physical (like electrostatic or hydrogen bonding) and covalent bonds, respectively. Prasanna and Sailaja (2012) used epoxy-functionalized LDPE as reactive compatibilizer for chitosan in LDPE blends. The mechanical properties were found to improve considerably, even for high loadings due to the addition of compatibilizer. The epoxy group reacts with the hydroxyl and amine/amide (amine can react twice with epoxide, fist an amide is formed which subsequently can react with another epoxy group) of chitosan. Due to the enhanced interaction between chitosan en LDPE, better stress transfer from the filler to the matrix leaded to significant improvement of TS and flexural strength although the EB decreased. Biodegradation and water absorption increased with increasing chitosan loading.

A promising way to functionalize (bio)-material surface in a controlled and versatile manner can be achieved with the layer by layer (LbL) technique. LbL build up proceeds by alternating adsorption of oppositely charged polyelectrolytes until a charge conversion occurs on the surface (Ai, Jones, & Lvov, 2003). Chitosan is a weak polybase with a p*K*a around 6.5 (Rinaudo, 2006) and alginate is a weak polyacid with a p*K*a between 3 and 4 (de Kerchove & Elimelech, 2006) and adsorption was studied as function of pH of the polyelectrolyte solution by Martins, Mano, and Alves (2010). Multi-layered films were obtained by sub sequential steps: immersion into the polyacid solution, rinsing solution and immersion in the polybase solution. The pH dependent character of polyelectrolytes enables the production of multi-layered systems with different viscoelastic properties.

2.3. Physicochemical characterization

Chitosan is blended in polymers for two different reasons, e.g. increasing the bio-based content in non-bio-based polymers like PE and polypropylene (PP) or for obtaining antimicrobial materials. Independent of the goal, the analysis performed on these films is mainly mechanical and thermal analysis. The antimicrobial effect of the films is evaluated mainly for edible films. For none of both applications, physicochemical analysis is described.

3. Future trends

In 2009 biobased plastics were only a small fraction (<1%) of the total polymer market. However, it is predicted that it could reach 20% by 2020 (Plackett, 2011). This underlines the fast development in application and production of biobased materials in packaging. Due to its antimicrobial properties chitosan is a promising polymer.

Many researchers are working on blends of chitosan with various polymers either for increasing the biobased content or for the antimicrobial effect of chitosan. In order to increase the biobased content, and preferably improving the mechanical properties of the material, good interfacial adhesion between chitosan and the polymer matrix is needed. For this reason, more focus should be spent on reactive extrusion at which the chitosan and polymer matrix will be covalently connected. Another advantage is that it is possible to direct the orientation of the —OH groups of chitosan to the polymeric matrix and the antimicrobial active groups to the outside of the plastic. In addition modification of chitosan to improve its properties like solubility and/or its antimicrobial activity will be another area for research the coming years. However, it is important to keep in mind that the costs of modification should be as low as possible to obtain an economical viable product.

If the potential antimicrobial activity of chitosan is of main interest than, two main prerequisites are important. First, the chitosan should be at the outside layer of the polymer matrix in order to have the antimicrobial moieties available for microorganisms (Figs. 2 and 3). As it will be obvious when chitosan is covered with the polymer matrix the antimicrobial properties will not be available anymore. Second, the chitosan should have any interaction with the polymer matrix in order to prevent dissolution and/or migration. Once the chitosan is migrated from the surface, the surface will lose its antimicrobial properties. For example polymer foils coated with chitosan already showed that delamination can occur, and, although plasma treatment enhanced the wettability of the PE

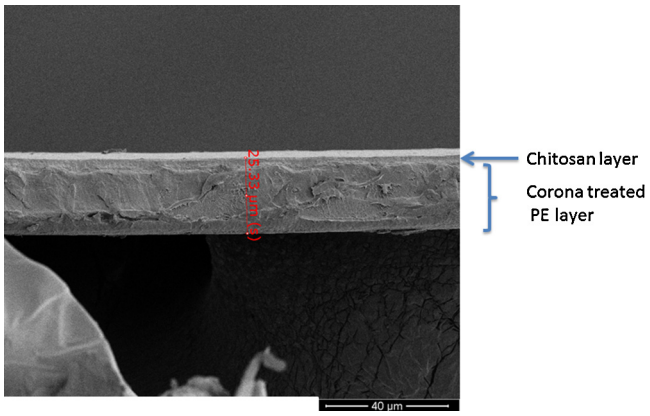

Fig. 2. Scanning electron microscopy analysis of chitosan coated corona PE prepared by solvent casting; magnification 2000×.

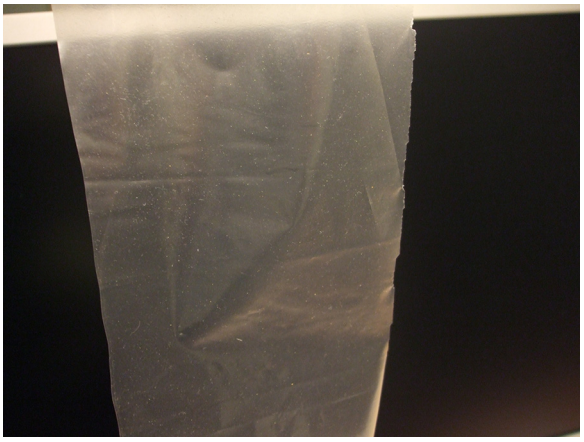

Fig. 3. Chitosan–PE multilayer film consisting of 5 wt% chitosan outer layer (each 5 μm) and a middle layer of corona PE (30 μm).

resulting in homogenous coated PE, delamination occurs mainly due to the poor interfacial adhesion.

Although chitosan is a research topic which attracts many researchers from different disciplines, a clear picture between processing and antimicrobial properties is still not present. From a chemical point of view, the research topic is often completely different than from microbiological and polymer processing point of view. This makes results obtained by different research groups more difficult to interpret. For example parameters which largely influence the properties of chitosan films and blends are: particle size, M_w of chitosan, DA and many more. On the other hand different types of chitosans are dissolved in acid solutions like acetic acid, propionic acid, and lactic acid at different concentrations. Especially during drying of the coatings, these effects will largely influence the final properties of the coating. Since the boiling point of water is lower than for acetic acid and lactic acid, first water will evaporate and the acid will remain present in the coating. As shown here, different parameters can play a role in the outcome of the results. Although the results obtained so far gives us answers, a better consensus of experiments to be performed will give us a leap forward in the future.

4. Conclusion

Chitosan, a biobased material, has interesting antimicrobial and film-forming activities. Its application in coatings, films and blends can contribute to food preservation and shelf-life extension. For films solvent casting can be used whereas for blends solution, extrusion compatibilizers and reactive extrusion blending can be applied. Reactive extrusion seem the most promising blending technique. To understand how chitosan has its optimal antimicrobial activity in films and blends more research is needed to understand: (1) how chitosan can be prevented from dissolution in films and blends; (2) the accessibility of chitosan; and (3) the influence of the processing parameters on the antimicrobial activity. At this moment a lot of research is performed and going on although a consensus in experimental setup to compare all research in the past and bright future will be needed.

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