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Mini Review

Chitosan as Reinforcement for Biopolymers - A Mini Review

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Abstract

It is nowadays urgent to find new packaging solutions that have a lower impact on the environment. Biopolymers (PLA, starch, PBAT) seem interesting to the design of the new packaging generation. These polymers have some drawbacks such as mechanical and barrier properties. Also, it could be interesting to add antimicrobial properties to packaging to increase the shelf life of food products. For those reasons, chitosan seems to be an interesting component to add to a biopolymer matrix. Chitosan is a polysaccharide derived from crustacean shells. Chitosan can be directly added to the matrix via thermomechanical processes, or it can be turned into thermoplastic chitosan with the combined effect of an acid solution, a plasticizer, heat, and shear. The chitosan intramolecular bonds are thus reduced. The second method seems to limit the agglomeration of chitosan in the polymer matrix and increase interfacial adhesion. The composite properties depend on the acid and plasticizer type and rate.

Keywords: Antimicrobial properties; Biopolymer; Chitosan; Composite; Plasticised chitosane

Introduction

Packaging is nowadays one of the main polluting fields, particularly because of plastic packaging [1,2]. Plastic world production was 367 million tons in 2020 [3]. It generates a massive amount of waste, which is not enough valorized [4]. As the field grows, it is urgent to find new packaging solutions that preserve food from spoiling and have a lower environmental impact. For those reasons, biopolymers seem promising to replace oil-based polymers currently used [5,6]. More precisely, biopolymers such as Polylactic Acid (PLA) [7,8], starch [9,10], Polybutylene Succinate (PBS) [11-13], Poly (Butylene Succinate-Co-Butylene Adipate) (PBSA) [12,13], and Polybutylene Adipate Terephthalate (PBAT) [14,15] are widely studied [16,17]. Those polymers can be transformed by thermomechanical processes (injection, extrusion, thermoforming), which is an advantage for industrial production. However, biopolymers also have drawbacks. Mechanical, barrier and optical properties can be weak for some applications. Design composites can be an interesting way to improve polymer's properties. To produce those structures, reinforcements are dispersed in polymers matrix. Cellulose, silica, clay, and alumina are the main studied reinforcements [18]. Nonetheless, chitosan has proved that it could be an interesting candidate due to its antimicrobial properties [19-23]. This property could increase the shelf life of food products and limit spoilage. Thus, this review aims to present the recent advances in biopolymers reinforcement with chitosan.

Chitosan

Chitosan is a polysaccharide derived from chitin by deacetylation (Figure 1); [24,25]. Chitin is extracted from shellfish skeletons and exoskeletons, mainly from crustacean shells. Seafood industry generates 80.000 tons of waste per year [26]. Consequently, it could be interesting to recover this material. Chitosan is biodegradable, biocompatible, non-toxic, antimicrobial. It is also chemically modifiable, which allows to adapt the properties [21,23]. It is insoluble in water but soluble in acidic conditions. Chitosan is usually defined by its molecular weight and its Deacetylation Degree (DD). Chitosan cannot be transformed by common plastics processes (injection, extrusion, thermoforming) because it is not thermoplastic. The degradation temperature is lower than the melt temperature. This is due to strong intermolecular bonds that prevent the melting, flow, and deformation [27]. Nonetheless, chitosan can be added to polymers as reinforcement by thermomechanical processes.

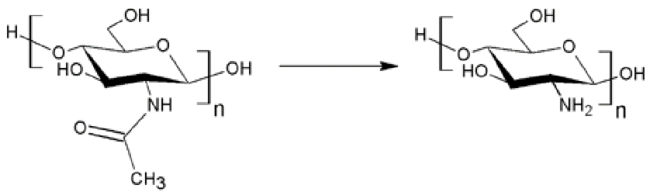

Figure 1: Chitin deacetylation reaction [24,25].

Raw Chitosan as Reinforcement for Biopolymer

Reinforcement of thermoplastic polymers by chitosan was studied by directly adding chitosan without any treatment. Correlo et al. mixed biopolyesters (PLA, PBS, PBSAT, PBSA, Polycaprolactone (PCL)) with chitosan (25 à 70 %wt.) via twin-screw extrusion and injection [28]. Clusters of chitosan are observed in samples (100-300µmx15-30µm). Chitosan clusters are larger than the initial size of chitosan, which suggests the chitosan agglomeration. Tensile strength reduction was observed and depend on the polymer considered: a diminution of 34 % and 11 % for 50 %wt. of chitosan in PBSA composite and PBAT composite was obtained, respectively. Those results suggest a weak interfacial adhesion. Bonilla et al. obtained similar results by studying PLA/chitosan (Mw=161kDa; DD=77 %) composites made by twin-screw extrusion and cast extrusion [29]. Chitosan seems well dispersed but obtained films present irregularities and rugosity because of chitosan particles. Matrix and polymer seem immiscible and non-compatible. However, antimicrobial properties were observed for chitosan-based films and allow a reduction of bacterial growth on pork meat. Díez-Pascual et al. have also studied composites with chitosan. Nanofibers were produced by electrospinning and were mixed with PBAT via solvent casting method [30]. Composites were considered efficient from 5 %wt. of chitosan against 4 pathogens (*Staphylococcus aureus, Bacillus subtilis, Salmonella enteritidis* and *Escherichia coli*). Other studies have demonstrated the antimicrobial properties of chitosan-based composites (PLA/starch/chitosan, PLA/chitosan, PCL/chitosan) [31-33].

Thermoplastic Chitosan Blend

Chitosan-based composites can present agglomeration and compatibilization issues. Produced Thermoplastic Chitosan (TPC) can be a good method to avoid those problems. Chitosan can be converted into TPC by the combined effect of heat, shear, and the presence of a plasticizer. This method is widely studied in starch's case (production of Thermoplastic Starch (TPS)) [9,10,34]. Small molecules are located between polymer chains by means of the thermomechanical process (generally twin-screw extrusion or internal mixer). Intermolecular bonds are reduced, and chains mobility is increased [27,35]. Chitosan can consequently melt. TPC production requires two components:

a. An acid solution, which allows the protonation of chitosan: acetic, hydrochloric, and lactic acid can be used [36]. Hydrochloric acid is a strong acid that is efficient but can degrade chitosan at a high rate. Acetic acid is a weak acid. Its action of protonation is less efficient than hydrochloric acid, but it cannot degrade chitosan [36-38]. The protonation reaction by lactic acid is presented in Figure 2. The sterically hindered caused by the acid leads to an increase in the space between molecular chains [36-38].

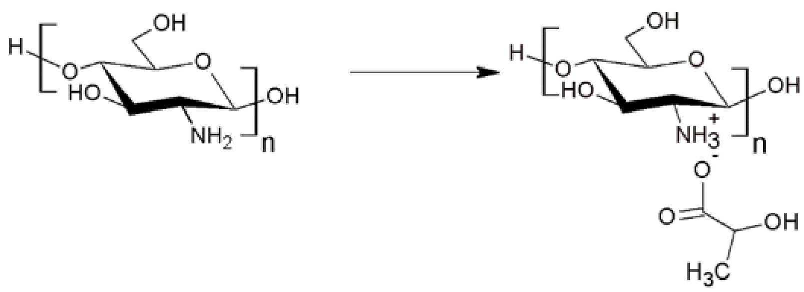

Figure 2: Chitosan protonation reaction by lactic acid [36-38].

b. A plasticizer, which increases the space between chitosan chains. It strengthens the acid role. Propylene glycol, polyethylene glycol, and polyols (glycerol, xylitol, sorbitol) can be used [35,38,39]. According to the authors, sorbitol gives better thermal and mechanical properties than glycerol and xylitol [35].

Both acid and plasticizer have an impact on chitosan crystal structure [35]. Some studies aim to improve TPS properties by adding Thermoplastic Chitosan (TPC). Deng et al. prepared TPC via casting method and mixed it with TPS by twin-screw extrusion [40]. TPC increases the viscosity of TPS and thus facilitates the processing. Hygroscopy and elongation are lower, and Young Modulus is higher than neat TPS. Mendes et al. studied the same blend and demonstrated that chitosan and starch are well dispersed, as there is no chitosan cluster [41]. Young modulus and elongation are also improved.

Moreover, some published work deals with oil-based polymer and TPS. Matet et al. studied the Polyethylene (PE)/Ethylene-Vinyl

Acetate (EVA)/TPC blend, which was produced by extrusion [35]. 90 % of chitosan areas are smaller than 10µm large, which means that the plastification works. The obtained films are yellowish. The Young modulus and elongation are reduced. The same authors in another study demonstrate that PE/chitosan composites have antimicrobial properties [42].

Conclusion

Chitosan is a widely studied polysaccharide because it is a biobased, biodegradable, non-toxic, and antimicrobial component. Chitosan can be added to a polymer matrix by thermomechanical processes. Some of those composites have antimicrobial properties, which can be interesting to increase the shelf life of food products. However, polymer matrix and chitosan are often non-compatible. That can lead to a reduction of polymers properties, such as mechanical properties. Recently, TPC production methods have been studied. TPC was mixed with other polymers to increase properties. A reduction of agglomeration was noted. This is promising for further designs of the next packaging generation.

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