



Tweaking the mechanical and structural properties of colloidal chitosans by sonication



Laidson P. Gomes^{a, b}, Hiléia K.S. Souza^{a, **}, José M. Campiña^{c, *}, Cristina T. Andrade^d, Vânia M. Flosi Paschoalin^b, António F. Silva^c, Maria P. Gonçalves^a

^a REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

^b LAABBM, Instituto de Química, Universidade Federal do Rio de Janeiro, UFRJ, Av. Athos da Silveira Ramos 149, CT, Bl A, sala 545, Ilha do Fundão, CEP 21941-909, Rio de Janeiro, Brazil

^c Centro de Investigação em Química da Universidade do Porto (CIQ-UP), Departamento de Química e Bioquímica, Faculdade de Ciências, Rua do Campo Alegre, 687, 4169-007, Porto, Portugal

^d Programa Ciência de Alimentos, Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J, 21941-598, Rio de Janeiro, RJ, Brazil

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ABSTRACT

Compared to the oil-derived plastics typically used in food packaging, biofilms of pure chitosan present serious moisture issues. The physical degradation of the polysaccharide with ultrasound effectively reduces the water vapor permeability in these films but, unfortunately, they also turn more brittle. Blending chitosans of different morphology and molecular mass (M) is an unexplored strategy that could bring balance without the need of incorporating toxic or non-biodegradable plasticizers. To this end, we prepared and characterized the mixtures of a high- M chitosan with the products of its own ultrasonic fragmentation. Biopolymer degradation was followed by dynamic light scattering (DLS) and the mechanical and structural characteristics of the mixtures were evaluated from different rheological methods and atomic force microscopy (AFM). The results indicate that, through the control of the sonication time and mixture ratio, it is possible to adjust the viscoelasticity and morphological aspect of the mixtures at intermediate levels relative to their individual components. In a more general sense, it is emphasized the importance of design and materials processing for the development of a novel generation of additive-free sustainable but functional bioplastics.

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1. Introduction

The growing societal demands on sustainability and environmental protection are expected to trigger a deep transformation of industrial manufacturing. In this sense, the harnessing of abundant biomass resources must pave the way towards a greener bio-economy. Natural biopolymers are suitable resources for bio-fabrication because of their good biodegradability, biocompatibility, and abundance. Chitosan (a polysaccharide obtained by N-deacetylation of chitin, its natural precursor) which is usually extracted from insect and marine crustacean shells (Aguila, Gomes, Andrade, Silva, & Paschoalin, 2012) is widely used in the

food and cosmetic industries due to its good processability as hydrogels, membranes, colloidal microparticles, nanoparticles, and so on (Calero, Muñoz, Ramirez, & Guerrero, 2010; Ikeda et al., 1993; Jayakumar et al., 2010; Laplante, Turgeon, & Paquin, 2006; Liu et al., 2012; Pan et al., 2002; Pillai, Paul, & Sharma, 2009; Rinaudo, 2006; Shukla, Mishra, Arotiba, & Mamba, 2013). Due to its great versatility, the use of chitosans in a new generation of nanobiomaterials for analysis (Borges, Campiña, & Silva, 2013), catalysis, tissue engineering (Kim et al., 2008), gene-delivery (Jayakumar et al., 2010), and other applications (Mizrahy & Peer, 2012; Payne & Raghavan, 2007), is being widely investigated.

Regarding its use in biofabrication, applications have been mainly restricted to thin films for food packaging and dressings for surgical wounds (Madhumathi et al., 2010; Sebti, Chollet, Degraeve, Noel, & Peyrol, 2007). Although the replacement of non-biodegradable plastics derived from crude oil by materials based

* Corresponding author.

** Corresponding author.

E-mail addresses: hsouza@fe.up.pt (H.K.S. Souza), jpina@fc.up.pt (J.M. Campiña).

on renewable and more sustainable resources, such as natural biopolymers, has been anticipated since the early 90s (Borman, 1990; Chiellini & Solaro, 1996; Hosokawa, Nishiyama, Yoshihara, & Kubo, 1990; Methven, 1990), the attempts to reproduce 3D objects of pure chitosan with the good organization (and structural properties) which usually characterize chitin systems in nature, have failed so far. In this respect, a significant step forward has been given very recently thanks to the development of a new manufacturing strategy that yields chitosan items in a variety of colors and shapes and with good mechanical properties for commercial exploitation (Fernandez & Ingber, 2014). In the particular field of food packaging, chitosan films have evidenced poorer mechanical properties and much higher moisture sensitivity than their oil-derived counterparts (Mima, Miya, Iwamoto, & Yoshikawa, 1983; Nadarajah, 2005). Unfortunately, the large retention of water turns these films unsuitable for their use in direct contact with foodstuffs (Olabarrieta, Forsström, Gedde, & Hedenqvist, 2001). To circumvent these issues, researchers have explored the use of different solvents (Nadarajah, Prinyawiwatukul, No, Sathivel, & Xu, 2006), chemically-derivatized chitosans (Nikolaev, Prokopov, Shulgina, & Vinogradov, 1987), or blending chitosan with synthetic or natural compounds (referred to as *plasticizers*) (Ziani, Oses, Coma, & Maté, 2008).

The compatibility, miscibility, morphology, and spinnability of chitosan blends have been extensively assessed in the literature (Azevedo, Retarekar, Raghavan, & Kumar, 2013; Fernandes et al., 2009; Homayoni, Ravandi, & Valizadeh, 2009; Kumar et al., 2010; Rao & Johns, 2008; Wrzyszczyński, Qu, Adamczak, Lindén & Rabek, 1995). For instance, Fernandes et al. (2009) found enhanced mechanical properties in chitosan/bacterial cellulose biofilms. Azevedo et al. (2013) reported a notable improvement of the elasticity in biofilms of chitosan/cellulose blends. In general, the properties of these blends are mainly determined by the compatibility between their components: i.e. whether inter- and intra-molecular interactions between the polysaccharide and the plasticizer lead to an intimate combination and to macroscopically uniform physical properties (Kumar et al., 2010). However, leaving apart the controversial migration of the plasticizer into the packaged food, the brittle nature of these biomaterials remains a challenge to overcome. Ultrasonic irradiation has emerged as a rapid, easy-to-use, and low-cost tool for the degradation of biopolymers such as starch (Tomasik & Zaranyika, 1995), pectins (Seshadri, Weiss, Hulbert, & Mount, 2003), etc. Whereas the chosen frequency mostly determines the energy available to trigger a random or a bond-specific chain scission (in chitosan it occurs, preferentially, through the β -(1 \rightarrow 4) linkage), the intensity and irradiation time (t_S) control the extension of the process (Baxter, Zivanovic, & Weiss, 2005; Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Rosiak, 2005; Kasaai, Arul, & Charlet, 2008).

Engineering films made of pure natural and biodegradable components with improved moisture resistance but still retaining good shear strength and flexibility, remains a challenge to improve the sustainability of the food packaging industry. In a recent paper, we demonstrated that the sonication of a chitosan with high degree of deacetylation ($DD = 90\%$) and molecular mass (M) induces a transition from a material mostly composed of colloidal microfibers (non-sonicated sample) to a morphology dominated by the presence of spherical nanoparticles (NPs) whose size is reduced upon increasing t_S (Souza, Campiña, Sousa, Silva, & Gonçalves, 2013). In parallel with this transition, the mechanical properties of the corresponding biofilms turned increasingly poorer (with a significant decline of the tensile strength and Young's modulus). Interestingly, the lowest water permeabilities were exhibited by the films prepared from the most degraded chitosans what suggests that the

high surface areas and surface-to-volume ratios characterizing the nanoparticulated systems may provide a physical barrier to water molecules.

Under the light of these results, one may wonder whether using mixtures of fibrous and nanoparticulated chitosans as film precursors would bring some balance by ensuring both reasonable mechanical properties, thanks to the presence of the microfibers, and enhanced moisture resistance potentially provided by the NPs (a graphical representation of the concept is shown in Scheme 1). In this work, we evaluate these prospects by preparing colloidal mixtures of high- M (non-sonicated) chitosans and their corresponding low- M counterparts (obtained by ultrasonic irradiation) at different ratios. The viscoelastic behavior and morphology of the mixtures have been investigated by means of rheological measurements and atomic force microscopy (AFM). The dynamic light scattering technique (DLS) has been used to estimate the size distributions of chitosan colloids before, NS , and after sonication for different times, S (t_S).

2. Experimental

2.1. Materials and solutions

For this investigation, a commercial ChitoClear[®] chitosan kindly supplied by Primex (Siglufjörður, Iceland) was used. This product is extracted from shrimp shells from the North Atlantic Ocean and further de-acetylated to a degree of $DD = 90\%$. Although the average M was declared to fall in the range 250–300 kDa, the viscosity-average molecular mass (M_V) is over 650 kDa as it was determined in a previous work (Souza et al., 2013). Hereinafter, we will refer to this high- M chitosan as CHIT90. Glacial acetic acid (Merck, purity: >99%), sodium acetate trihydrate (Merck, suprapur), sodium chloride (NaCl, Sigma–Aldrich, >99.9%), and ethanol (Aga), were all analytical grade and used without further purification. A 0.1 M acetate buffer solution pH 6.0 (ACB) was prepared in ultrapure water (18.2 M Ω s). When required, the pH was adjusted by addition of drops of glacial acetic acid or sodium acetate. CHIT90 was suspended at 3% (w/w) in this buffer and, after gently stirring for 2 h, stored at 4 °C (stock suspension). Before any measurement or ultrasonic treatment, aliquots of this stock were incubated at room temperature (RT) for 60 min. The equilibrated samples were, then, centrifuged for 20 min at 21,000 \times g (9 ACC, 20 °C) with a Beckman Coulter centrifuge Alegria 25R to remove the large aggregates. Thereby, a stable colloidal dispersion of CHIT90 was obtained.

2.2. Biopolymer degradation & DLS analysis

After centrifugation, 30 mg aliquots of the CHIT90 dispersion were placed in ice and ultrasonicated for a period of time between 0 and 30 min increased at 2 min per sample (the so called sonication time, t_S). A SONIC ultrasonic probe (model 750 W), equipped with a 1/2" tip, was used to this end (constant duty cycle and 40% amplitude). The ultrasonic degradation of CHIT90 was followed by dynamic light scattering (DLS). For these purposes, aliquots of the sonicated dispersions were diluted 100 times and placed in fluorescence quartz cuvettes (Hellma 111-QS, 10 mm light path). The measurements were acquired at constant temperature (20 °C) in a high-performance W130i DLS system (Avid Nano, UK) equipped with a 660 nm light source and operated at 90°. In a previous viscosimetric study (Souza et al., 2013), it was shown that the progressive sonication of CHIT90, under identical conditions to those applied in this work, results in a continuous decrease of the viscosity-average molecular mass (M_V) from a value of 660 kDa (non-sonicated sample) to 540 ($t_S = 5$ min), 327 (15 min), and

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