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Role of chitin nanocrystals and nanofibers on physical, mechanical and functional properties in thermoplastic starch films

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ABSTRACT

The purpose of this work was to evaluate and compare the role of different nano-chitin morphologies on the structural and functional properties of thermoplastic starch-based films prepared by casting-evaporation approach. The introduction of chitin nano-objects – nanocrystals (CHNC) and nanofibers (CHNF) in concentrations of 5–20% – in thermoplastic starch-based matrices resulted in the enhancement of the final properties of the nanocomposite films in a morphological-dependent manner. The obtained data clearly demonstrate that the nanocomposite films elaborated with chitin nano-objects showed superior mechanical, thermal, barrier and antifungal properties as compared to those prepared with unfilled thermoplastic starch films. Furthermore, chitin nano-objects content, shape and size, were found to be an important role to the final properties of the thermoplastic starch nanocomposite films. Our findings highlight the potential use of such chitin nano-objects in thermoplastic starch-based matrices to be applied in functional food coatings and packaging.

1. Introduction

Like cellulose, chitin is a supporting material in living organisms. Chitin is found in the exoskeleton of arthropods and cuticles of insects as crystalline nano-size fibrils embedded in a protein matrix (Chen, Lin, McKittrick, & Meyers, 2008; Ifuku & Saimoto, 2012; Pillai, Paul, & Sharma, 2009; Raabe, Sachs, & Romano, 2005; Zeng, He, Li, & Wang, 2012). Several routes to prepare chitin crystalline nano-size fibrils with different morphologies have been described (Fan, Fukuzumi, Saito, & Isogai, 2012; Fan, Saito, & Isogai, 2008, 2010; Goodrich & Winter, 2007; Nair & Dufresne, 2003a; Ifuku et al., 2009, 2010; Ifuku, Nogi, et al., 2011; Salaberria, Fernandes, Diaz, & Labidi, 2014). The isolation of these nano-size forms mainly include: (i) acid conditions (Fan et al., 2012, 2010; Goodrich & Winter, 2007; Nair & Dufresne, 2003a) resulting in chitin nanocrystals (CHNC), which are rodlike in appearance (Fig. 1A) with low aspect ratio; and (ii) mechanical treatments/disintegration (Fan et al., 2008, 2012; Ifuku et al., 2009, 2010; Ifuku, Nogi, et al., 2011; Salaberria, Fernandes, et al., 2014) resulting in chitin nanofibers (CHNF), which are fibrillar in appearance (Fig. 1A) with high aspect ratio, and have lower crystallinity than CHNC. These nano-size form of chitin fibrils have been found to play a fundamental role in nanocomposite materials as filler agents due to their usable form and intrinsic properties (Ifuku & Saimoto, 2012; Zeng et al., 2012). The physiochemical and biological properties of chitin nano-size fibrils — *i.e.*, their particularly small size, light weight, chemical stability, renewable and biodegradable character, and non-cytotoxicity — make these stunning nanomaterials tremendous candidates for use in food, packaging and biomedical applications (Ifuku & Saimoto, 2012; Zeng et al., 2012), especially given to their high antimicrobial activity (Butchosa et al., 2013; Salaberria, Fernandes, et al., 2014; Zhang, Li, & Liu, 2011). Contrarily to cellulose, chitin presents antimicrobial activity due to its chemical structure consisting of (1,4)-β-*N*-acetyl-D-glucosamine-repeating units.

Similarly to cellulose and starch nano-fillers, a wide variety of nanocomposite materials exploiting the attractive mechanical properties of chitin nano-size fillers have been investigated (Agulló et al., 2004; Avérous, 2004; Chang, Jian, Yu, & Ma, 2010; Mushi, Butchosa, Zhou, & Berglund, 2014; Nair, Dufresne, Gandini, & Belgacem, 2003; Nair & Dufresne, 2003b; Ifuku, Morooka, Nakagaito, Morimoto, & Saimoto, 2011; Ifuku & Saimoto, 2012; Ifuku et al., 2013; Junkasem, Rujiravanit, & Supaphol, 2006;

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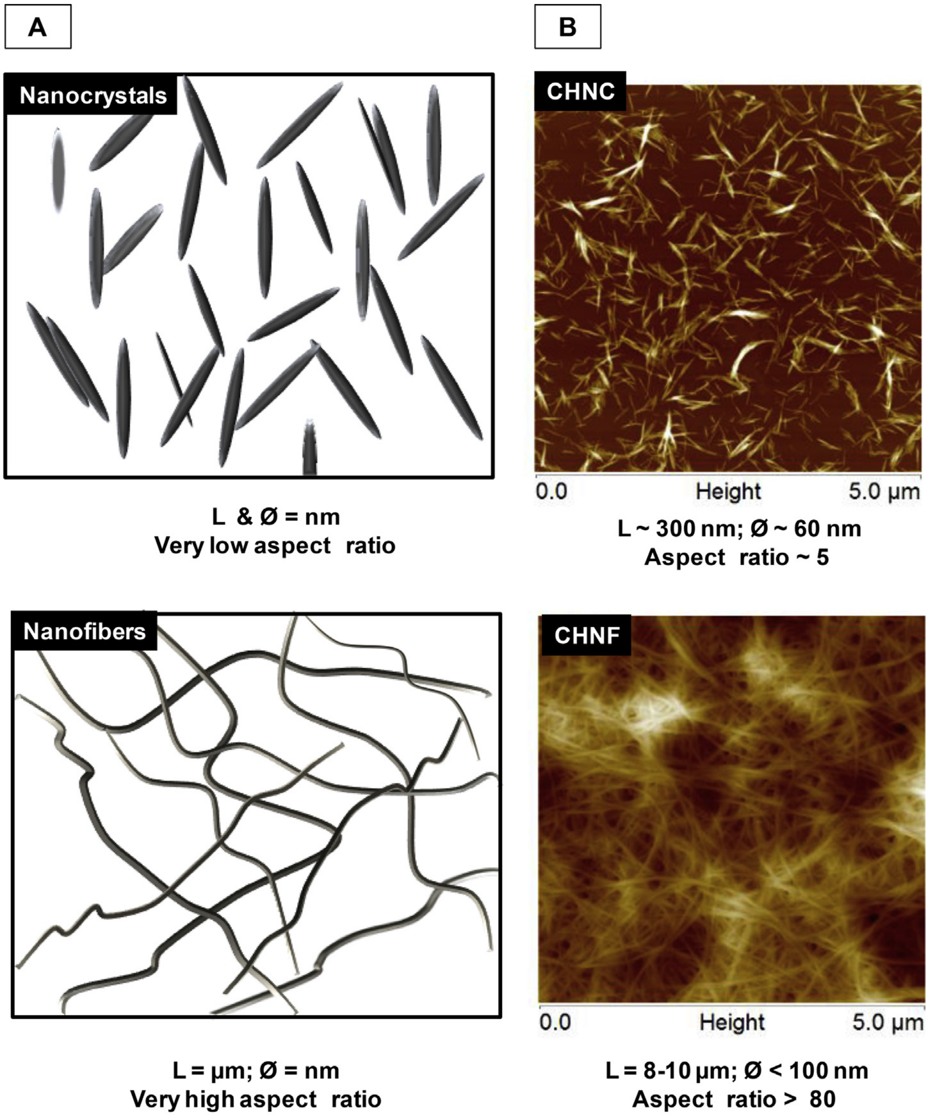

Fig. 1. A. A schematic of the two different chitin nanofibrils morphologies, *i.e.* nanocrystals (top) and nanofibers (bottom). B. AFM topography images, using a magnification of 5 × 5 µm^2, showing chitin nanocrystals (CHNC, top) and nanofibers (CHNF, bottom).

Junkasem, Rujiravanit, Grady, & Supaphol, 2010; Li, Li, Ke, Shi, & Du, 2011; Lu, Weng, & Zhang, 2004; Ma, Qin, Li, Zhao, & He, 2014a, 2014b; Morin & Dufresne, 2002; Nata, Wu, Chen, & Lee, 2014; Paillet & Dufresne, 2001; Salaberria, Fernandes, et al., 2014; Salaberria, Labidi, & Fernandes, 2014; Sriupayo, Supaphol, Blackwell, & Rujiravanit, 2005a, 2005b; Xie, Pollet, Halley, & Avérous, 2013; Yu, Dean, & Li, 2006; Zeng et al., 2012). Nonetheless, the exploitation of chitin nano-objects as a route to fabricate nanocomposites with high performance and specific functionalities is still a vast and quite untouched research field. In particular, the exploitation of the attractive antifungal and barrier properties of these nano-objects (Ifuku et al., 2013; Salaberria, Fernandes, et al., 2014).

Herein, we have investigated the effect of different nano-chitin morphologies – nanocrystals (CHNC) and nanofibers (CHNF) (Fig. 1) – on the structural and functional properties of thermoplastic starch-based films obtained by casting-evaporation approach. Starch was selected as polymeric matrix due to its renewable character, wide availability, low cost, non-cytotoxicity and biodegradability (Avérous, 2004; Xie et al., 2013; Yu et al., 2006). Moreover, another advantage in using starch is its chemical similarity with the chitin nano-objects, which could promote the matrix-nano-objects interactions. Although chitin nano-objects were already used to improve the weak mechanical properties of starch-based materials (Chang et al., 2010; Salaberria, Labidi, et al., 2014), the present work goes a step further, since our purpose is to exploit the antifungal and barrier properties of these nanomaterials. Moreover, the different nano-chitin morphologies were compared in terms of structural and functional properties.

Regarding the structural properties, the results were in good correlation with our earlier studies in which we demonstrated that the final properties of thermoplastic starch-based nanocomposite films were dependent of the content and type of chitin nano-size filler introduced in the matrix (Salaberria, Labidi, et al., 2014). Moreover, with the present work we found that the presence of chitin nano-objects in the thermoplastic starch films imparts fungal growth inhibition to the final nanomaterials in a morphological-dependent manner.