



# Enhanced mechanical properties of chitosan/nanodiamond composites by improving interphase using thermal oxidation of nanodiamond



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## ARTICLE INFO

### Article history:

Received 22 February 2017  
Received in revised form 12 March 2017  
Accepted 13 March 2017  
Available online 16 March 2017

### Keywords:

Chitosan  
Nanodiamond  
Interphase  
Mechanical properties  
Composite

## ABSTRACT

Polymer composite films based on chitosan (CS) and nanodiamond (ND) were prepared using solution casting method. ND with variable contents of carboxylic functional group was prepared using thermal oxidation at temperature of 420 °C under air atmosphere at various durations of 1.5 and 4.5 h. The interfacial interaction between NDs and CS and morphological evolution of CS in presence of NDs were investigated by Fourier transform infrared (FTIR), differential scanning calorimeter (DSC) and X-ray diffraction (XRD) analyses. A significant improvement in tensile strength (~85%) and tensile modulus (~125%) of CS was achieved by oxidized ND (OND) obtained at higher oxidation time of 4.5 at low concentrations (below 1.5 wt%). Theoretical analyses based on micromechanical models showed that the ND with higher degree of carboxylic functionality provided thicker and stronger interphase region which was reflected in higher mechanical properties. The equilibrium water uptake of CS decreased by incorporating ND and increasing its degree of carboxyl functionality.

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## 1. Introduction

Naturally occurring biopolymers such as polysaccharides, silk, lignin and gelatin have attracted tremendous attention particularly because of global concerns for sustainable development and environmental preservation (Williams & Hillmyer, 2008). Natural biopolymers are plentiful in nature, sustainable, biocompatible and readily degradable by natural composting process (Fernandes et al., 2009). Chitosan (CS) is a natural polysaccharide containing  $\beta$ -(1-4)-2-amino-2-deoxy-D-glucopyranose (Jiang, James, Kumbar, & Laurencin, 2014) which is simply obtained by deacetylation of chitin, the second most plentiful natural polymer next to cellulose.

CS has many interesting characteristics such as nontoxicity, hydrophilicity, biodegradability, biocompatibility, adsorption ability of impurities from wastewater by complex formation via amino and hydroxyl groups. Additionally, CS can be easily formed from the solution due to its dissolution ability in acids originated by the amino groups in its molecular structure (Busilacchi, Gigante, Mattioli-Belmonte, Manzotti, & Muzzarelli, 2013; Hsu et al., 2011;

Kim et al., 2011; Lai, Daear, Löbenberg, & Prenner, 2014; Muzzarelli, 2012; Wu, Pan, Bao, & Li, 2011). These features have made CS an ideal candidate for a broad range of applications such as food packaging films (García, Casariego, Díaz, & Roblejo, 2014), drug delivery (Justin & Chen, 2014), tissue engineering (Duan, Liang, Guo, Zhu, & Zhang, 2016; Venkatesan, Qian, Ryu, Kumar, & Kim, 2011), electrochemistry (Kulys & Stupak, 2008), conducting biomacromolecules (Huang et al., 2013) and separation membrane (Karim, Mathew, Grahn, Mouzon, & Oksman, 2014). CS has also been greatly used in diverse biomedical applications that imply a contact with bloodstream including artificial organs, biodegradable medical devices and disposable clinical apparatus such as vascular prostheses, heart valves, blood pumps and plasma separators (Balan & Verestiuc, 2014; Chen, Yuan, Song, Wu, & Li, 2008; Ishihara, Fukumoto, Iwasaki, & Nakabayashi, 1999; Polk et al., 2010).

Despite several attractive properties of CS, this biopolymer suffers significantly from poor mechanical properties restricting it from wide-range applications where good mechanical performances are essential. Blending with synthetic polymers, chemical modification or incorporation of suitable reinforcements are different methods to improve the mechanical properties of CS. The recent investigations have shown that the incorporation of inorganic nanoparticles such as clay (Wang, Shen, Tong et al., 2005; Wang, Shen, Zhang, & Tong, 2005), single-layer graphene (Du

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et al., 2014; Han, Yan, Chen, & Li, 2011), carbon nanotube (CNT) (Salam, Makki, & Abdelaal, 2011), hydroxyapatite (Lima, Resende, de Almeida Soares, Anselme, & Almeida, 2013) and metal nanoparticles (Seo et al., 2014) into CS is greatly effective in enhancing physico-mechanical properties while many useful properties such as improved gas barrier properties and retained transparency are simultaneously achieved. However, the maximal improvement in mechanical properties of CS nanocomposites can be achieved when the nanoscale dispersion of nanoreinforcement in CS matrix as well as chemical and/or strong intermolecular interactions between CS and nanoreinforcements are attained.

Presently, carbon-based nanoparticles such as CNT and graphene are known as promising nanoreinforcements for CS due to their unique mechanical, structural and multifunctional features. However, the lack of functional groups on the surface of these carbon-based nanoparticles makes challenging their dispersion and interfacial interaction in CS. Therefore, surface functionalization is of prime importance for CNT and graphene-based polymer nanocomposites. Fortunately, CS molecule contains many amino ( $-NH_2$ ) and hydroxyl ( $-OH$ ) groups which can be easily protonated in acidic solutions leading to polycationic molecule. Therefore, attachment of acidic groups, which can be negatively charged in water, on the surface of such carbon-based nanoreinforcements can favor their interaction with CS matrix more efficiently. Consequently, chemical derivatives of graphene such as graphene oxide (GO) and CNT such as acid treated CNT, bearing carboxyl ( $-COOH$ ) groups, can be much effective in CS nanocomposites (Pan, Wu, Bao, & Li, 2011; Wang, Shen, Tong et al., 2005; Wang, Shen, Zhang et al., 2005; Yang, Tu, Li, Shang, & Tao, 2010). However, the wet chemistry techniques along with their rigorous purifications (Hu, Kulkarni, Choi, & Tsukruk, 2014; Xie, Mai, & Zhou, 2005) used to obtain GO and oxidized CNT limit their applications on an industrial scale.

Nanodiamond (ND) particles are known as carbon-based nanoparticles that were first produced by detonation process in the 1960s (Rabiei & Shojaei, 2016). More recently, research interests in ND particles have increasingly progressed due to their remarkable mechanical, thermal and biological properties along with large specific surface area (larger than  $200\text{ m}^2/\text{g}$ ) and hydrophilic surface due to the presence of many oxygenated functional groups (Alishiri, Shojaei, & Abdekhoodaie, 2016; Barras, Szunerits, Woisel, & Boukherroub, 2011; Burns, Naclerio, Khan, Shojaei, & Raghavan, 2014; Liang, Ozawa, & Krueger, 2009; Mochalin, Shenderova, Ho, & Gogotsi, 2012; Rabiei & Shojaei, 2016). These valuable properties provide great potential for ND as a component of high performance multifunctional materials.

Exterior surface of pristine ND particles is mainly covered by many oxygen-containing groups including  $-COOH$  (carboxylic),  $-O-C=O$  (lactone),  $>C=O$  (carbonyl) and  $-C-O-C$  (ether) (Kharisov, Kharissova, & Chávez-Guerrero, 2010; Panich et al., 2006), making the ND surface chemistry more tunable. Osswald et al. (2006) showed that air oxidation of pristine ND at high temperatures, i.e. between 400 and  $430^\circ\text{C}$ , improves the purity of ND, in terms of removing amorphous and graphitic portions of ND, and converts the original oxygen-containing functional groups on the pristine ND to carboxylic acids and cyclic acid anhydrides (that this latter one can be easily hydrolyzed by water and turns to carboxylic acid). Thereafter, Li and Huang (2010) reported that the air oxidation leads to significant enhancement of carboxylic acid group ( $-COOH$ ) on the ND surface which is chemically active and favors the formation of charge-transfer complexes with amino-containing surfactants. Basically, air oxidation process offers an efficient and environment friendly single-step dry chemistry process for purification of ND and homogenization of its surface chemistry, making it well-accepted technique on an industrial scale.

As the CS matrix contains many amino groups, it appears that ND is able to disperse uniformly in the CS matrix and interact well

with it. Therefore, considering high mechanical properties of ND, it would have great potential to improve the mechanical properties of CS and broaden its applications in different fields. To our knowledge, CS/ND composites dealing with the mechanical properties have not been reported in literature so far. Therefore, the present study is to explore the reinforcing efficiency of ND in CS/ND composites. In this context, we will show how the simple and environment friendly air oxidation technique is efficient in controlling the interfacial interaction in CS/ND composites and its mechanical properties.

## 2. Experimental section

### 2.1. Materials and processes

CS with medium molecular weight having deacetylation degree of 75–85% and with molecular weight of 180,000–280,000 Da was purchased from Sigma-Aldrich. Anhydrous acetic acid was also obtained from Merck. ND powder (purity 98–99%, average single particle diameter of 4–6 nm, surface area of  $282\text{ m}^2/\text{g}$  and density of  $3.05\text{--}3.3\text{ g}/\text{cm}^3$ ) was obtained from NaBond Technologies Co., China. As-received ND was oxidized at high temperatures under air conditions for surface homogenization of ND and enhancing its surface carboxylic acid groups, as described in literature (Aris, Shojaei, & Bagheri, 2015; Jiang & Xu, 1995). To do this, desired amount of as-received ND or untreated ND, referred to as UND hereafter, were poured in crucible and then placed in the furnace (S302AU, CARBOLITE Company) at  $420^\circ\text{C}$  for two different times of 1.5 h and 4.5 h. OND-1.5 and OND-4.5 are used as designations for NDs oxidized for 1.5 h and 4.5 h, respectively. ONDs were put in the desiccators to prevent absorption of humidity.

CS solution of 1% (w/v) was prepared by mixing 10 g of CS in 1000 ml of 2% (v/v) aqueous acetic acid solution for 1 h under stirring at 1000 rpm. Desired amounts of NDs powder were separately suspended in distilled water and sonicated for 1 h to enhance dispersion of NDs in the suspension. ND suspension was added to CS solution and then the CS/ND suspensions were stirred for 3 h at 1000 rpm to achieve a uniform suspension. Finally the CS/ND suspension was sonicated for 1 h and in the latest step it was placed in vacuum oven at room temperature to remove the bubbles. Eventually, the CS/ND suspensions were dried at room temperature for 5 days to get films with an average thickness of 0.7 mm, followed by drying under vacuum at  $50^\circ\text{C}$  overnight. Composite films with different ND contents (0.1, 0.5, 1, 1.5 wt% with respect to CS) were obtained by solution evaporation method in a plastic dish.

### 2.2. Measurements and characterizations

Fourier transform infrared (FTIR) spectroscopic analysis was performed by an ABB Bomem M-B100 spectrometer, to characterize the surface chemistry of NDs and chemical interactions in CS/ND composites. Thermal transition behavior of the neat CS and CS/ND composites was investigated using a TA Instrument (Q100) differential scanning calorimeter (DSC). The samples of 4–5 mg were placed into standard aluminum pan and transferred into the DSC heating chamber. The DSC thermograms were recorded under nitrogen atmosphere with heating rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $250^\circ\text{C}$ . The water contact angle of the samples was measured by Kruss G10 on cantaloupe rind by the sessile drop method. The data recording was triggered by the initial contact between the liquid droplet and the rind surface. All measurements were carried out under ambient conditions. The morphology of the samples was investigated by scanning electron microscopy (SEM, LEO model 1455VP, UK) at an accelerating voltage of 30 kV on the fractured surfaces coated with gold. Strips were immersed in

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