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Carbon nanoparticles/soy protein isolate bio-films with excellent mechanical and water barrier properties

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ABSTRACT

Different sized carbon nanoparticles (CNPs) were synthesized from glucose through a one-step hydrothermal process and soy protein isolate (SPI) films modified by the CNPs were prepared. Morphology and size distributions of the prepared CNPs were characterized by transmission electron microscopy. The effects of different sized CNPs (CNPA, CNPB, and CNPC) on mechanical properties of films were evaluated. Furthermore, the effects of different contents of CNPC with the smallest size on properties of films were analyzed including structure, morphology, moisture content, total soluble matter, water vapor permeability (WVP), mechanical properties, and thermal stability. The attenuated total reflectance-Fourier transform infrared results demonstrated that there were carboxyl and hydroxyl groups on the surface of CNPs. In addition, the CNPs led to a phase change of SPI matrix as shown in X-ray diffraction results. The tensile strength and modulus of SPI/CNPC films with 5.0 g CNPC increased by 82.97% and 79.74% compared to the unmodified one, respectively. In addition, SPI/CNPC films with 5.0 g CNPC exhibited the best water barrier property, which was a 48.36% decrease in WVP compared to SPI film.

1. Introduction

Nowadays, petroleum-based plastics are presenting more and more concerns since they are nonrenewable and nonbiodegradable (Tian et al., 2011). To solve these problems, biopolymers produced from natural resources, such as polysaccharides, proteins, and lipid are regarded as attractive alternatives for their renewability and biodegradability (Cao et al.,2007; Garrido et al., 2013; Shi and Dumont, 2014). Among all biopolymers, soy protein isolate (SPI), which contains 90–95% protein, has attracted more attention for the advantages of abundance, process ability, essential amino acids to human life, and film-forming capacity (Kumar et al., 2002; Song et al., 2011). Recently, SPI-based bio-films have attracted much attention for their biomedical and packaging applications, with the advantages of enhanced physical, mechanical and thermal properties (Dash and Swain, 2013). However, SPI-based films have some weaknesses such as brittleness and poor water resistance, which restrict the applications (Guerrero et al., 2014a; Liu et al., 2005; Rodriguez et al.,2006; Tummala et al., 2006).

Previous studies on the improvements of mechanical and water barrier properties of SPI-based films showed that the films can be modified by physical, chemical or enzymatic method. Although glycerol and sorbitol used mostly to improve the brittleness of SPI-based films, the tensile strength and water barrier properties are decreased (Coupland et al., 2000; Monedero et al., 2009; Ramos et al., 2013). Ultrasound and microwave are used to physically destroy the secondary structure of SPI, thus exposing more active side groups (Wang et al., 2013; Yang and Ma, 2009). Then the chemical modifiers were employed, involving acetamide (Liu and Zhang, 2006), PTGE and PAM (Xu et al., 2015), stearic acid (Lodha and Netravalia, 2005) or arylate (Kumar, 2010) and grafting with vinyl monomers(Li et al., 2010; Lu et al., 2011). Another approach is to prepare composite films by incorporating fillers as reinforcements, such as cellulose, lignin, and nanoparticles (Huang et al., 2004; Lu et al., 2004; Wu et al., 2009). Reports on incorporated nanoparticles include montmorillonite, nano-SiO_2, nano-TiO_2, starch nanocrystal, carbon nanotube, and rectorite nanoplatelets (Ai et al., 2007; Dash et al., 2012; González and Alvarez Igarzabal, 2015; Kumar et al., 2010; Song et al., 2011; Wang et al., 2012; Yu et al., 2007). Unfortunately, most of the nanoparticles mentioned above are water-insoluble and show bad compatibility with SPI, which need further modification. Carbon nanoparticles (CNPs) as a kind of nanoparticles have advantages over other nanoparticles due to the

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Table 1
Code and formulation of SPI/CNP films.

Sample code	SPI (g)	Glycerol (g)	Distilled Water (g)	CNPA (g)	CNPB (g)	CNPC (g)
SPI	4.0	1.2	80.0	0	0	0
SPI–CNPA	4.0	1.2	75.0	5.0	0	0
SPI–CNPB	4.0	1.2	75.0	0	5.0	0
SPI–CNPC	4.0	1.2	75.0	0	0	5.0
SPI–CNPC0.5	4.0	1.2	79.5	0	0	0.5
SPI–CNPC1.0	4.0	1.2	79.0	0	0	1.0
SPI-CNPC3.0	4.0	1.2	77.0	0	0	3.0
SPI–CNPC5.0	4.0	1.2	75.0	0	0	5.0
SPI–CNPC8.0	4.0	1.2	72.0	0	0	8.0

SPI–CNPC and the sample SPI-CNPC5.0 were the same one.

water-solubility, active functional groups on the surface, interfacial properties, good compatibility with SPI and nontoxicity.

CNPs emerged as a substitute for poisonous heavy metal fluorescent semiconductor nanocrystals have outstanding performance in optical and biochemical fields (Zhu et al., 2009; Guo et al., 2013). Up to now, various methods of synthesizing CNPs have been reported, such as arc dis-charge of candle soot, laser ablation of graphite, electrochemical oxidation of scrolled graphene layers, thermal oxidation of suitable molecular precursors, hydrothermal treatment of saccharide (Baker and Baker, 2010; Li et al., 2011; Peng and Travas-Sejdic, 2009; Zhu et al., 2009). Among all the methods, one-step hydrothermal method is efficient and easy to carry out (Ray et al., 2009). However, most researches have merely focused on fluorescent properties of CNPs and there are few on the application of CNPs in the modification of films. The water-solubility and the interfacial effect of CNPs can ensure good compatibility and strong interfacial absorption in SPI matrix. In addition, the large amounts of —OH and —COOH, which are on the surface of CNPs can easily interact with the active side groups, such as, $—NH_2$, —OH and —COOH in SPI (Wang et al., 2012) through hydrogen bond (Su et al., 2007). As a result, mechanical properties, water barrier properties, and thermal property could be enhanced.

In this research, we prepared CNPs with different sizes from glucose and SPI-based bio-films through an easy casting method. The aim of this research was to explore the effects of different sized CNPs (CNPA, CNPB, and CNPC) on mechanical properties of films were evaluated. Furthermore, the effects of different contents of CNPC with the smallest size on properties of films were analyzed including structure, morphology, moisture content, total soluble matter, water vapor permeability, mechanical properties, and thermal stability.

2. Materials and methods

2.1. Materials

SPI with 95% proteins was provided by Yuwang Ecological Food Industry Co., Ltd. (Shandong, China). Chemical reactants including glucose, glycerol and polyvinyl alcohol (PVA) were purchased from Beijing Chemical Reagents Co., Ltd. (China).

2.2. Synthesis of CNPs

CNPs were synthesized from glucose through a one-step hydrothermal method (Marta and Antonio, 2008; Zhu et al., 2009). In order to obtain three different sized CNPs, we optimized the hydrothermal carbonization process, including the temperature of the hydrothermal treatment and the reaction time.Finally the below three different conditions were chosen.

Briefly, 16 g of glucose was dissolved in 80 g distilled water and then 80 g of PVA solution (0.4%, wt%) were added under constantly magnetic stir (RH Basic, IKA, Germany). Averagely divide the mixture into mixture A, B and C. Then, the mixture (50 ml) A, B and C were sealed into three Teflon containers (100 ml) quipped with stainless steel autoclave and heated in three different ways to obtain CNPs with different sizes. Mixture A and B were heated at 180 °C for 5 h and 150 °C for 7 h, respectively (Marta and Antonio, 2008). Mixture C was treated in microwave-assisted hydrothermal synthesis system (MDS-6G, SINEO, China) at 180 °C for 20 min (Zhu et al., 2009). The purification of CNPs were conducted through a dialysis tube (1000 Da, molecular weight cutoff) for about 48 h. Different sizes of CNPs were coded as CNPA, CNPB, CNPC.

2.3. Preparation of SPI/CNP films

The CNP/SPI films were obtained through casting method. 4.0 g of SPI was dispersed in certain amount of distilled water under stirring and then 1.2 g of glycerol (30% of SPI, wt%) was added. Then, the required amount of CNP dispersion was added with severe stirring for 1 h to produce homogenous suspension. The pH values of these solutions were adjusted to 9.0 with 1.0 mol L^{-1} NaOH followed by heating in water bath at 85 °C for 30 min to disrupt the quaternary structure of proteins accompanied by a partial protein denaturation and subsequently poured onto Teflon plates. Film thickness was controlled by casting the same amount (40 g) of solution on each plate. The castings were dried in drying oven at 45 °C for 15 h and then peeled from the plates. Films were preconditioned at 50 ± 2% relative humidity (RH) and 25 ± 2 °C for a week before testing. Sample code and formulation are listed in Table 1.

2.4. Characterization of CNP and SPI/CNP films

2.4.1. Transmission electron microscopy (TEM)

TEM images of CNPA, CNPB and CNPC were performed on a JEM-1010 transmission electron microscopy (JEOL, Japan) operated at an acceleration voltage of 80 kV. Size distributions of CNPA, CNPB and CNPC were analyzed with nano measurer software (version 1.2.5).

2.4.2. Scanning electron microscope (SEM)

Morphology of the cross sections of films was observed using a SU8010 field emission scanning electron microscope (Hitachi Ltd., Japan) operating at an acceleration voltage of 5 kV. The films were frozen in liquid nitrogen and snapped immediately.

2.4.3. Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy

ATR–FTIR spectra were carried out on a Nicolet 6700 spectrometer (Thermo Scientific, USA), in the range of 4000–650 cm^{-1}, using an attenuated total reflectance accessory (ATR) with a diamond ATR crystal.