



Physicochemical and mechanical properties of pectin-carbon nanotubes films produced by chemical bonding

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ARTICLE INFO

Keywords:

Pectin
Carbon nanotubes
Chemical bonding
Biodegradable film
Mechanical properties

ABSTRACT

The aim of this study was to compare composites of pectin and carbon nanotubes (CNTs) prepared by chemical interaction (CI) or physical mixing (PM). CI-pectin-CNTs composite was produced by dispersing pectin and CNTs powder in ethanol, followed by refluxing at 60 °C. Biodegradable films of the pectin-CNTs composites were then produced and their mechanical, physicochemical and thermal properties were compared using rheological, tensile, oxygen permeation, integration, swelling and color tests. The CI-pectin-CNT films were more resistant to force, had greater stiffness and elongation at break and their water barrier properties were significantly greater than those of PM-pectin-CNTs. CI-pectin-CNTs films were lighter in color and showed greater integrity and swelling ratios. These confirmed substantial improvement of properties of pectin-CNTs films by chemical bonding as compared to physical mixing. Moreover, by chemical bonding the required level and hence the potential health risks of CNTs in biopolymer films and mixtures may be reduced.

1. Introduction

In recent decades demand for biodegradable polymers has increased due to their ability for degradation in nature as environmental friendly packaging materials (Lange & Wyser, 2003). Biodegradable refers to materials that under suitable situation of temperature, moisture, and oxygen availability are degraded with no adverse environmental impacts (Chandra & Rustgi, 1998; Kuorwel, Cran, Sonneveld, Miltz, & Bigge, 2014). With recent years' approaches towards environmentally friendly technologies for food packaging; biodegradable materials are gaining more attention. However, real applications of biodegradable materials for food packaging have been limited due to their weak mechanical and thermal characteristics and nano particles have been indicated to help overcome some of shortcomings of these films. Nano-composites are mixtures of polymers and particles, which are in nano scale range (Dadfar, Alemzadeh, Dadfar, & Vosoughi, 2011). Findings of nanocomposite research have indicated promising results to improve properties of biodegradable films in which nano particles act as filler or improver agents (Abreu, Losada, Angulo, & Cruz, 2007; Ray, Quek,

Easteal, & Chen, 2006). Nano scale particles can improve the mechanical and physical properties of biopolymers and enhance their tensile, elastic modulus and thermal resistance. Blending of polymers (biopolymer mixtures) or polymers with nanoscale particles such as nanoclay or carbon nanotubes (CNTs) may overcome some of these defects (Sorrentino, Gorrasi, & Vittoria, 2007).

Since 1991 when multi-walled carbon nanotubes (MWCNTs) were first introduced (Zhang, Wang, & Guo, 2005), they have attracted much attention for their interesting mechanical, thermal and electrical properties (Baughman, Zakhidov, & Heer, 2002; Qian, Dickey, Andrews, & Rantell, 2000; Popov, 2004; Ruoff, Qian, & Liu, 2003). Different researches have illustrated that, CNTs are materials with high stiffness-to-weight and strength-to-weight ratios and they could be employed in a variety of biomaterials such as proteins, polysaccharides and lipids (Cornwell & Wille, 1997; Krishnan, Dujardin, Ebbesen, Yianilos, & Treacy, 1998; Salvetat et al., 1999; Treacy, Ebbesen, & Gibson, 1996; Wong, Sheehan, & Lieber, 1997; Xie, Li, Pan, Chang, & Sun, 2000). According to anisotropy of graphite, the mechanical characteristics of carbon nanocomposites are dependent on the three

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<https://doi.org/10.1016/j.fpsl.2018.01.004>

Received 21 May 2017; Received in revised form 7 December 2017; Accepted 9 January 2018
2214-2894/ © 2018 Published by Elsevier Ltd.

dimensional carbon structure (Sothornvit, Hong, Jun, & Rhim, 2010) and small diameter of carbon nanotubes (Dresselhaus, Dresselhaus, Sugihara, Spain, & Goldberg, 1988).

Pectin, a structural heteropolysaccharide, is mainly extracted from renewable resources such as citrus fruits and apple pomace, is used in food and non-food systems as gelling and viscosifying agents. It has a linear structure rich in galacturonic acid and its molecular weight is about 50,000–150,000 Da. Pectin has several distinct homogalacturonans of linear chains of α -(1–4)-linked D-galacturonic acid. Pectin is a suitable biomaterial for its biodegradability and has a wide range of applications depending on its degree of esterification and polymerization (May, 2000). The physical properties of this biomaterial may be improved by adding nanoparticles such as nanoclay and CNTs, which are dispersed in the polymer matrix. They may enhance pectin biopolymer properties such as mechanical strength, high modulus, barrier properties against liquids, gases and vapors due to the interactions between biopolymer and nanoparticles at nanometric level (Dadfar, Alemzadeh, Dadfar, & Vosoughi, 2011). In fact, when nanoscale particles are added to the biopolymer, they will be scattered into a polymer matrix and provide multiple parallel layers, which force gases to pass through the polymer in a “torturous path” forming complex barriers to gases and water vapors (Dadfar, Ramezani, & Dadfar, 2009; Farahnaky, Dadfar, & Shahbazi, 2014).

The physicochemical and mechanical properties of biopolymer based films require substantial improvements to compete with synthetic polymers (Moridi, Mottaghitalab, & Hagh, 2011; Farahnaky, Dadfar, & Shahbazi, 2014) and nanoparticles have proved promising outcomes in improving physical properties of biopolymer films. Although, conjugations of biopolymers and nanoparticles have been used before for versatile uses in sensing materials (Uehar, 2010), so far most research on mixtures of biopolymers with nano particles (Moridi, Mottaghitalab, & Hagh, 2011), have focused on physical mixing in which nano particles are likely to clump and form clusters of micro scale ranges. CNTs usually form stable bundles, due to Van der Waals interactions, that are very difficult to disperse and align in polymer matrices (Gopal, Sravendra, Jae, Lin, & Hwa, 2010). This is due to difficulties in solubilizing CNTs and occurrence of phase separation and low levels of bonding between the functional groups of CNTs and biopolymers.

In the past attempts have been made to increase dispersion degree and stability of CNTs-biopolymer systems through functionalizing CNTs and using better mixing strategies (e.g. ultrasound assisted dispersion), however phase separation and the lack of adequate and homogenous dispersions of CNTs in biopolymer systems remain a major challenge for employing the maximum potential of CNTs in biopolymer systems and films (Sun, Fu, Lin, & Huang, 2002; Tardani & Mesa, 2015). Moreover, the real microstructures of mixtures of biopolymers and nanoscale particles prepared by physical mixing (i.e. dispersion of nano particles in biopolymers solutions or melts) have always been subject to debates and require further advancements. Chemical bonding between biopolymers and CNTs may offer a solution for proper dispersion of CNTs and to achieve homogenous mixtures for improving physicochemical properties of these films. Therefore, the objectives of this research are to investigate the effects of chemical bonding and physical mixing in composites of pectin (as a base biomaterial) and carbon nanotubes (as an additive) and compare rheological, mechanical and physicochemical characteristics of their thin layer films.

2. Materials and methods

2.1. Materials

Apple pomace pectin (analytical grade) and glycerol (99.9% purity) were purchased from Merck (Germany). Acetylene gas (98% purity) supplied by Parsballo (Fars, Iran) was used to synthesize carbon nanostructures. All other chemicals were of analytical grade, unless otherwise mentioned.

2.2. Preparation of carbon nanotubes

Highly purified (99%) multi-walled carbon nanotubes (MWCNTs, 40–60 nm) were synthesized by chemical vapor deposition (CVD) method at high temperatures of ~ 1200 °C in argon atmosphere using acetylene gas as the source of carbon and ferrocene (Merck, Darmstadt, Germany) as the precursor of iron nanoparticles. Based on the transmission electron microscopy image (not presented), the average size of the synthesized MWCNTs was estimated to be around 60 nm. The synthesized carbon nanostructures were then activated and purified up to 99% via introduction of oxygen to the production line, followed by reduction by H_2 as reducing agent and finally irradiation with ultraviolet (UV, $\lambda = 360$ nm, $P = 1200$ W) and microwave (Saadat, Karimi-Jashni, & Doroodmand, 2014; Rahimi, Doroodmand, Sabbaghi, & Sheikhi, 2013).

For physical fabrication of CNTs-based film, 0.65 g of pectin was physically mixed with 0.35 g of MWCNT powder, followed by vigorously shaking for ~ 2 h using a shaker. The mixture was used for film preparation as explained in the next section and the films will be named as physically mixed (PM) films and used as the control. Whereas for the chemical formation, powders of activated MWCNT/pectin, 0.65 g of pectin and 0.35 g of MWCNT powder were suspended in 20 mL of absolute ethanol, followed by refluxing at 60 °C for 12 h. Then the solid composite was separated from the organic media using a rotary pump and finally dried at 50 °C for about 24 h. This mixture was used for preparation of chemically mixed (CM) films as explained in the next section. Mechanical stability and also flexibility of CNTs-based films strongly depend on the degree of homogeneity of carbon nanostructure being interacted with pectin polymer macromolecules. In this study, however, the CNTs were automatically synthesized, purified and activated, but, reflux process was required to chemically control the mechanical stability of the CNTs-based composite.

2.3. Preparation of films

Nanocomposite films were prepared by casting method. One gram of each nanocomposite powder (PM or CI powders) as prepared in the previous section was slowly added to 100 mL distilled water at 90 °C and mixed using a hot plate magnetic stirrer. After the complete dispersion of particles, 0.30 g of glycerol was added and mixed thoroughly. To achieve a homogenous dispersion, it was then treated by power ultrasound for 6 min by an ultrasonic probe (75 W and 20 kHz) using power ultrasound (HD3200, Bandelin, Germany) and left overnight for complete hydration. An aliquot amount (22.0 g) of the prepared dispersion was poured into a plastic Petri dish (8 cm diameter) and transferred to an oven set at 50 °C and kept for 24 h. Dried films were then put in hermetically sealed boxes of saturated solutions of NaI and NaCl at room temperature (25 °C) until moisture sorption equilibrium reached. The films were then used for further experiments (Dadfar, Ramezani, & Dadfar, 2009).

2.4. Rheological properties

Viscosity of biopolymer solutions was measured using a Brookfield viscometer (model LV-DVII Pro, Brookfield Engineering Inc., USA) equipped with a temperature control unit and a cone and plate type geometry (CP51) at 25 ± 1 °C. 0.5 mL of prepared solution was loaded on to the plate and its rheological flow property was investigated in the shear rate range of $5\text{--}150$ s $^{-1}$.

2.5. Film thickness measurement

Thickness of the prepared films was measured using a digital micrometer (China) by averaging the thickness of five points of each test specimen. This parameter is necessary for further experiments such as water vapor permeability and mechanical properties tests (Martucci, &

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