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Fabrication and characterization of the bionanocomposite film based on whey protein biopolymer loaded with TiO_2 nanoparticles, cellulose nanofibers and rosemary essential oil

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A B S T R A C T

A bionanocomposite film based on whey protein isolate (WPI), cellulose nanofibers (CNFs), titanium dioxide (TiO_2) nanoparticles and rosemary essential oil (REO) was prepared by casting/evaporation method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The effects of various concentrations of CNFs (2.5, 5, 7.5 and 10%), TiO_2 (0.5, 1 and 1.5%) and REO (1.5 and 2%) were investigated on the physicomechanical, barrier analyses, antibacterial, and antioxidant properties of bionanocomposite films. The results showed that the simultaneous combination of mineral compounds (TiO_2) and phytochemicals (REO) with WPI/CNFs films had remarkable effects on the studied properties. Water resistance of WPI/CNFs composite films increased significantly with the addition of TiO_2 and REO. The results of FTIR spectroscopy showed suitable interactions between TiO_2 and REO with WPI/CNFs blend, while the results of SEM confirmed good and homogeneous dispersion of TiO_2 NPs into the films. Addition of CNFs (7.5%) and TiO_2 (1%) has led to a significant increase in tensile strength (TS) and Young's modulus (YM), while elongation at break (EB) reduced. However, the addition of REO, regardless of TiO_2 nanoparticles addition, decreased TS and YM, EB significantly increased. In addition, WPI/CNFs7.5% films that have been incorporated with both TiO_2 and REO, had shown lower EB and higher TS and YM. On the other hand, TiO_2 and REO incorporation reduced transparency and increased hydrophobicity of WPI/CNFs films. Simultaneous combination of TiO_2 and REO into WPI/CNFs films, showed a strong antibacterial activity against pathogenic and spoilage bacteria, especially Gram posetive bacteria. The developed films exhibited good morphology features, improved physicomechanical properties and appropriate antibacterial and antioxidant behavior due to the excellent dispersion of the TiO_2 and REO into the WPI/CNFs matrix, which are the important properties required for packaging applications. Finally, the results propose for the use of CNFs as a green reinforcement and good replacement for mineral reinforcement and use of these ecofriendly nanocomposite films in packaging industries.

1. Introduction

Materials used for packaging has become an important part of different industry (Siracusa et al., 2008). To improve safety, security and products quality, and also to extend the shelf life of products, materials with the following characteristics are favorable: having proper mechanical strength, having barrier properties against water, water vapor and oxygen, thermal stability, recyclability, biodegradability along with antimicrobial and antioxidant activities (Ghanbarzadeh et al., 2011). This has been recently investigated because of contamination of the packaging materials produced from petroleum products (Davis and Song, 2006; Teacă et al., 2013).

Plastics produced from petroleum derivatives have been applied extensively in packaging industry because of their low price, wide accessibility and their favorite features such as transparency, brightness and plasticity. However, the main problem regarding plastics is environmental contamination due to their overall non-biodegradability and inefficient decontamination procedures such as graving, burning

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etc. (Tharanathan, 2003). As consumer demands increase for durable products, investigating the issues related to the development of biocompatible materials with functional properties such as having edible, active and biodegradable films can be an appropriate approach to improve the quality of the products and to enhance their nutritional value (Kanmani and Rhim, 2014; Seligra et al., 2016).

Biodegradable polymers (natural and synthetic) are possible alternatives to conventional plastics. In recent years, biodegradable and edible nanocomposite films have attracted attention in the packaging industry, mainly due to natural and environmental factors (Moghaddas Kia et al., 2018; Müller et al., 2011; Zhang et al., 2018). They are produced by incorporating expletives (nanoparticles of inorganic or natural fillers) into a biopolymer matrix (Petersson et al., 2007; Zhang et al., 2016). Nanocomposite films can improve mechanical properties and heat resistant, gain barrier against water vapor, gases and increase antimicrobial activity. Due to the fact that biopolymers are cheap, biodegradable and biocompatible, they are considered an appropriate replacement for synthetic plastics (Azeredo et al., 2009; Li et al., 2009). Furthermore, nanocomposite films are appropriate structures for carrying chemical compounds such as nanoparticles, antimicrobials agents, antioxidants, enzymes or functional ingredients such as minerals, vitamins and probiotics (Assis et al., 2017; Kanmani and Rhim, 2014). The great advantage of nanocomposite films in packaging has triggered a lot of researches to design and produce numerous new biopolymers which can be used in packaging industry. Bionanocomposite films are made of natural ingredients, including proteins, lipids and polysaccharides alone or combined (Saberi et al., 2016; Tang et al., 2012). Several studies have shown that polysaccharides and proteins can be used as packaging material (Galus and Kadzińska, 2016; Ghanbarzadeh et al., 2011).

The application of whey protein in biodegradable films and coatings has received a great deal of attention. Whey protein is a yellow-green liquid separated from the curd during the production of cheese and casein, as the by-product of cheese (Azevedo et al., 2015; Henriques et al., 2016). Whey protein has a wide range of proteins (35–97%). Whey protein concentrates (WPC) have 35–90% protein and whey protein isolates (WPI) have more than 90% protein (Gonzalez-Jordan et al., 2016). It is extensively used as food supplements and in food products due to its high nutritional value and significant ability to form emulsions, coatings, films and gels (Sani et al., 2017). Whey proteins can produce transparent, flexible, colourless and flavourless biodegradable films (Li et al., 2011; Yoo and Krochta, 2011). Whey protein films has already been known as a barrier against oxygen penetration and provide special mechanical properties. In contrast, they have a relatively high permeability to moisture due to their hydrophilic amino acids. These features have made whey proteins a potential candidate to use and produce nanocomposite films with biodegradability and biocompatibility features (Li et al., 2011).

Among polysaccharides, cellulose is the most common natural polymer on earth and it is produced from different sources. Cellulose nanostructures have two forms: cellulose nanocrystals (CNCs) and nanofibers (CNFs) (Zhao et al., 2014). Cellulose nanostructures have been used as an alternative in the production of biodegradable films and coatings due to their biodegradability and biocompatibility characteristics (Pelissari et al., 2014; Vilarinho et al., 2016). CNFs are produced from agricultural wastes such fruits and vegetables' peels (Leite et al., 2017; Pelissari et al., 2014). Cellulose fibers are manufactured at a nanoscale called cellulose nanofibers (CNFs) and is used as nano-reinforcement along with other biopolymers (Khalil et al., 2012). Cellulose nanofibers in combination with biopolymer films improve mechanical and thermal properties and lower water and gas permeability. One important feature of cellulose nanofibers that distinguish them from other nano-boosters is their application in the production of composite films; this can be attributed to their inherent properties such as high mechanical strength, higher surface-to-volume ratio, low density, easy accessibility, full biodegradability and having a reasonable price, which has led to their application in the production of nanocomposite films (Abdul Khalil et al., 2016; Noshirvani et al., 2016; Sirviö et al., 2014).

New trends and perspective in nanotechnology has facilitated the path to use nanoparticles in the packaging industry (Li et al., 2016). Nanoparticles with sizes below 100 nm, in one or more dimensions, can increases the surface area the activity. Therefore, these particles are of importance because of their high activity and efficiency. Nowadays, nanoparticles are applied to improve the functional properties of nanocomposite films (Guimarães et al., 2015; Rhim et al., 2006). Titanium dioxide (TiO_2) is inexpensive, inert and non-toxic and is widely used as anti-radiation and anti-microbial due to its photocatalytic activity in biodegradable films. When TiO_2 is combined with polymer matrix, it exhibits proper chemical and mechanical durability and provides preservation against pathogenic and spoilage bacteria, aroma, deterioration and allergens in the presence of ultraviolet radiation. It has been used in different products as a mean to block light and to create a bright appearance (El-Wakil et al., 2015; Li et al., 2011; Zhou et al., 2009).

The application of essential oils (EOs) and plant extracts is considered as an alternative which does not require a particular packaging technology (Ribeiro-Santos et al., 2017b). These components can decrease spoilage products through antioxidant and antimicrobial activities; their ingredients are natural and have lower risk to human health and the environment compared to chemical preservatives(Ribeiro-Santos et al., 2017a; Souza et al., 2017). Rosemary (*Rosmarinus officinalis*) essential oil (REO) which is broadly known as a spice, is successfully used for pharmaceutical and food due to its antioxidant and antimicrobial properties (Raeisi et al., 2016; Sani et al., 2017). These components have been approved by FDA for safety and effectiveness before they enter the market (FDA, 2014).

To the best of our knowledge, there have been no other studies regarding photocatalytic disinfection properties of films produced by WPI, CNFs, REO and TiO_2 nanoparticles. The aim of the present study was to investigate the effects of CNFs, TiO_2 NPs and REO on structural, barrier, and mechanical properties of WPI/CNF/REO/TiO_2 bionanocomposite film.

2. Materials and methods

2.1. Materials

TiO_2 nanoparticles (anatase, purity > 99%, particle size ~10–25 nm) were purchased from US Research Nanomaterials, Inc., Houston (U.S. A). Whey protein isolate (WPI, 92 wt.% protein) was obtained from Davisco Intl., Inc. (Eden Prairie, Minn., U.S.A.). Commercial bleached softwood pulp was supplied by the Nano-Novin polymer company, Mazandaran, Iran. REO was procured by Barijessence Company, Kashan, Iran. 2, 2-diphenyl-1-picrylhydrazyl (DPPH) reagent and butylated hydroxytoluene (BHT) standards were purchased from Sigma-Aldrich (St. Louis, MO). Medium cultures were purchased from Micromedia, Canada. Bacterial strains were obtained from Biological and Genetic Resources Center, Tehran, Iran. All the applied reagents were of analytical grade and used without further purification. Deionized water was used for all sample preparations.

2.2. Preparation of CNFs by mechanical method

A quick, simple and single step mechanical method (Super disc milling) was used to prepare cellulose nanofiber, as displayed in Fig. 1, similar to (Zhang et al., 2015) method with some modifications. At first, alpha cellulose softwood pulp is washed and centrifuged several times with distillated water and then remained in a potassium hydroxide solution (5%) at 80 °C for one hour. After alkaline treatment, CNFs was prepared by passing a suspension of 1% alpha-cellulose from a milling machine (MKCA6-3; Masuko Sangyo Co., Ltd., Japan) at 1500 rpm, due to shear and compressive forces. Nanofiber suspensions was dehydrated