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Evaluation of bionanocomposites as packaging material on properties of soft white cheese during storage period

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ABSTRACT

Novel bionanocomposites based on chitosan/poly(vinyl alcohol)/titanium nanoparticles (CS/PVA/TiO_2 nanocomposite) were prepared and used as packaging materials for soft white cheese. The prepared bionanocomposites were characterized using XRD, SEM, TEM and FT-IR. The CS/PVA/TiO_2 bionanocomposites exhibited good mechanical properties. Furthermore, the obtained bionanocomposites exhibited superior antibacterial activity against gram positive (*Staphylococcus aureus*), gram negative (*Pseudomonas aeruginosa, Escherichia coli*) bacteria and fungi (*Candidia albicans*). The soft white cheese was manufactured and packaged within the CS/PVA/TiO_2 nanocomposite films and stored at 7 °C for 30 days. The color, rheological and chemical properties of cheese were evaluated, also the influence of CS/PVA/TiO_2 bionanocomposites on microbiological analysis of soft white cheese was assessed, the results indicated that the total bacterial counts, mold & yeast and coliform decreased with the increasing storage period and disappeared at the end of storage period compared with control. Consequently, CS/PVA/TiO_2 bionanocomposite can be used in food packaging applications.

1. Introduction

Packaging materials offer a means to protect, preserve, products, market and distribute foods. They play an important role in how these products reach the consumers in a safe and healthy form without compromising quality. The packaging system, rely on a proper choice of the packaging material with appropriate gas and water vapor barrier, and mechanical properties, prevents product deterioration owing to physicochemical or biological factors and maintains the overall quality during storage and handling (Nerin, 2012). After their useful life, it is desirable for the packaging materials to biodegrade in a reasonable time period without causing environmental waste problems.

Among the extensively recognized natural polymers, chitosan has been one of the most attractive biodegradable owing to its biocompatibility and it has been extensively investigated for several decades for food packaging film, artificial skin, water engineering and so on, due to its good mechanical properties, biocompatibility, biodegradability, multiple functional groups as well as solubility in aqueous medium (Youssef, Abou-Yousef, El-Sayed, & Kamel, 2015; In this sense, chitosan based materials have some beneficial properties as packaging materials in improving food quality and extending the shelf-life through minimizing microbial growth in the product (Floros, Nielsen, & Farkas, 2000). It has been used to design and fabricate novel materials with functional properties useful in several fields, extending from waste treatment and medicine to food processing and packaging (Youssef, Abdel-Aziz, & El-Sayed, 2014).

In order to further impart new functionalities to chitosan for expanding its application fields, the use of suitable nanoparticles is highly demanded, hence titanium dioxide (TiO_2-NPs) nanoparticles is an effective biological material used widely in biomedical research because of its exclusive physiochemical nature (Hua, Cheuk, Wei-Ning, Chen, & Chang-Fa, 2007), and because it accelerates the formation of bone-like apatite through the Ti–OH site. Generally, particle size, specific surface area (SSA), chemical composition, structural property and solubility are fundamental in determining the toxicity of nanoparticles

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(Singh et al., 2007). Numerous examples of polymer-TiO_2 nanocomposites have been described in the literature, such as polystyrene/TiO_2 (Youssef, Kamel, & El-Samahy, 2013), TiO_2-poly (styrene-divinylbenzene)/maleic anhydride (Li et al., 2010), polypyrrole/TiO_2 (Yuvaraj, Park, Gal, & Lim, 2008), PMMA/TiO_2 (Haroun & Youssef, 2011), and polyaniline/TiO_2 (Youssef, 2014).

Chitosan combined to other polymers opened a window of research for altering or tailoring the property of interest. Blend systems with poly (vinyl alcohol) (PVA) hydrogel have been discovered for medical and pharmaceutical application attributable to the benefit of non-toxic, non-carcinogenic and bioadhesive properties (Mansur and Mansur (2007)). Chemical crosslinking is a highly versatile method to create and modify polymer nanostructure, where properties can be improved, such as mechanical, thermal, and chemical stabilities. PVA is a water soluble polymer with good physical and chemical properties (Wang, Wang, Xu, Zhang, & Shang, 2011). It could be blended with diverse synthetic and natural polymers as a result of its high hydrophilicity and processability (Han, Yan, Chen, & Li, 2011). The bio-inert character of PVA, determines its large use in biomedical field such as drug delivery, hemodialysis, and implantable medical device.

Storage of fresh white cheeses under aerobic conditions effects in rapid spoilage, frequently in less than 7 days, while active packaging may prolong storage life to 20–30 days. Additionally, soft and white cheeses constitute a major food safety anxiety attributable to their lower hurdle effect compared with hard cheeses, display a higher occurrence and potential for survival/growth of pathogens such as *Listeria monocytogenes* (Tsiotsias, Savvaidis, Vassila, Kontominas, & Kotzekidou, 2002). Cross-contamination may further occur during storage in retail or domestic refrigerators, which work quite commonly at extremely high temperatures (Sergelidis et al., 1997). Thus, controlling bacterial cross-contamination of fresh white cheeses, particularly after curd production, as well as during storage is a significant safety issue. Consequently, the use of active methods for both preservation and safety of white cheeses seems necessary.

The objective of the present study was to be a step toward using active food packaging materials instead of petrochemical based plastics in food packaging applications. The physical, chemical and mechanical properties of nanocomposite films consisting of chitosan, PVA and TiO_2-NPs were comprehensively investigated. To the best of our knowledge, this is the first report where such a system (CS/PVA/TiO_2 bionanocomposites) was prepared with different TiO_2-NPs concentrations and extensively characterized from a morphological, mechanical and thermal aspect. The prepared nanocomposite films were used for packaging soft white cheese for 30 days and the chemical and physical properties of cheese after the storage period were evaluated.

2. Materials and methods

2.1. Materials

Chitosan (CS) of medium molecular weight (average molecular weight M_v = 92,700 g mol^{-1}) and glacial acetic acid (HAc) used in this work were bought from Aldrich Chemicals. Poly (vinyl alcohol) was supplied from Sigma Aldrich. TiO_2-NPs (P_{25}) powders (Sigma Aldrich Co., St Louis, MO). Buffalo's milk containing 5% fat and 8.57% SNF (solid non-fat) was used for manufacturing soft white cheese. Chymosin rennet powder was obtained from Chr, Hansen's Lab., Denmark, and was used for manufacturing cheese. NaCl and $CaCl_2$ were used for salting soft white cheese and were obtained from Rankem Chemical Company. All materials were used as received.

2.1.1. Pathogenic strains

Bacillus cereus B-3711 and *Bacillus subtilus* were provided by the Northern Regional Research Laboratory Illinois, USA (NRRL). *Listeria monocytogenes* 598 was provided by the Department of Food Science, University of Massachusetts, Amherst, MA, USA. *Escherichia coli* 0157: H7 and *Staphylococcus aureus* were isolated and serologically identified by dairy microbiological Lab., National Research Center, Egypt. *Yersinia enterocolitica* was obtained from Hungarian National Collection of Medical Bacteria, OKI, Gyaliut 2-6, H-1966 Budapest, Hungary. *Aspergillus niger*, *Pseudomonas aeruginosa* and *Candidia albicans* were provided by the Institute of Applied Microbiology, University of Tokyo, Japan.

2.2. Film fabrication

A typical method for film preparation was carried out by mixing chitosan with acetic acid solution (2 wt% in water) at 50 °C in order to form 1 wt% homogenous viscous solution. Separately, 1 wt% PVA aqueous solution was attained by dissolving PVA powder in distilled water at 120 °C in water pass. CS/PVA blends were fabricated by mixing the two polymer solutions (50:50, v/v ratio). Then, the crosslinker reagent (glutaraldehyde) was gradually added under constant stirring. The final concentration of glutaraldehyde in the gel solution precursor was 1%. The composites with different ratios of TiO_2-NPs (2, 4, 8 wt%), were prepared by steadily adding the TiO_2-NPs suspension (1 mg/mL in water) to the CS/PVA solution and sonicating for 1 h at room temperature. The homogeneous CS/PVA/TiO_2 suspensions were poured onto Teflon dish and left undisturbed at room temperature for 72 h in order to evaporate the solvent and form the film. After that the films were peeled off from the mold and ready for use as packaging films and different characterizations.

2.3. Manufacturing of soft white cheese

Fresh buffalo's milk standardized to 5% fat, pasteurized at 63 °C for 30 min, cooled and adjusted to 37 °C, then calcium chloride and sodium chloride were added at the ratios of 0.02% and 2% (w/v), respectively. Then, the rennet was added and the coagulation was performed after 3 h. The milk was made into soft white cheese following the conventional method of Domiati cheese (Fahmi & Sharara, 1950). Cheese was divided into five portions, each portion packaged using nanocomposite films containing different TiO_2-NPs loadings (Control – 0, 2, 4 and 8% TiO_2-NPs) and stored under refrigeration at 7 °C for 30 days. The cheese samples were analysis chemically, microbiologically and rheological during the storage period.

2.4. Characterization

The prepared CS/PVA/TiO_2 bionanocomposites were characterized by usual techniques. The XRD patterns of the chitosan nanocomposites were carried out on a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with CuKα radiation source (λ = 0.15418 nm). The surface morphology and elemental compositions of the prepared nanocomposites were examined via scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM–EDX) (JSM 6360LV, JEOL/Noran). The images were obtained using an accelerating voltage of 10–15 kV. Also, the (SEM–EDX) (JSM 6360LV, JEOL/Noran was used to determine the ratios of inorganic materials in cheese ash. The structure of the prepared nanocomposites was examined using JEOL JEM-1230 (TEM) with acceleration voltage of about 80 kV. Fourier transform infrared spectrometer (FTIR) (Spectrum 100; PerkinElmer, USA) was used to record the spectra at 300 K in the range of 500–4000 cm^{-1} to confirm the incidence of