Journal of Food Engineering 167 (2015) 65–70

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Gelatin-based nanocomposite films: A study on montmorillonite dispersion methods and concentration

Christian H.C. Flaker *, Rodrigo V. Lourenço, Ana M.Q.B. Bittante, Paulo J.A. Sobral

Department of Food Engineering, FZEA, USP, Av. Duque de Caxias Norte, 225, 13635-900 Pirassununga, SP, Brazil

ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form 3 November 2014
Accepted 19 November 2014
Available online 29 November 2014

Keywords:
Zeta potential
Biodegradable films
Tensile strength
Water vapor permeability

ABSTRACT

Reinforcing films based on biopolymers with nanoparticles could improve their properties. The nanoparticles must be dispersed in water before addition in the film-forming solution, when produced by a wet technique as casting or spreading. Thus, the aim of this research was to study the quality of the dispersion of montmorillonite in water, and its effect on some properties of gelatin films produced using the best dispersion technique. The nanoparticles were dispersed in water with mechanical homogenizer, colloidal mill and ultrasonic processor; then, analyzed for determination of particle size and zeta potential. Subsequently, films were produced by spreading with different nanoparticles concentration, and characterized for determination of some physical and functional properties. The mechanical homogenizer was chosen to process the montmorillonite and to produce the nanocomposite films, which in general, were less glossy, less permeable to water vapor and more hydrophilic than control film. The tensile strength increased from 20 to 40 MPa in the nanocomposite films. The dispersion method used had a slight influence on the quality of dispersions and the critical concentration of montmorillonite was 5 g of MMT/100 g of gelatin.

1. Introduction

One of the possible alternatives to replace synthetic materials in food packaging is the development of films based on biopolymers. Gelatin is a biopolymer with excellent film-forming properties (Arvanitoyannis, 2002). Some works on gelatin-based films can be found in the literature. Denavi et al. (2009), Jongjareonrak et al. (2006), Sobral et al. (2001), Thomazine et al. (2005) and Vanin et al. (2005), among others, studied the physical and functional properties of gelatin based films depending on the gelatin origin, the plasticizer type and concentration, drying conditions or the thickness of films. Nevertheless, those films have good mechanical properties but low water vapor permeability and high sensitivity to ambient humidity (Rao, 2007).

Several authors have studied the improvement of properties of films based on biopolymers using nanoparticles as reinforcement. Tunc et al. (2007) using casting technique developed gluten films loaded with montmorillonite in concentrations varying from 0% to 10%, and observed decreased water vapor permeability. Angellier-Coussy et al. (2008) also reported significant improvement in the properties of films based on gluten with montmorillonite in concentrations of 0–5% produced by thermopressing. On the other hand, Chen and Zhang (2006) also prepared soy protein isolate based films with montmorillonite and observed that the structure of these nanocomposites was strongly dependent on the concentration of the nanoparticles. Finally, Luecha et al. (2010), working on zein based films produced by casting, observed that the critical concentration of montmorillonite to improve the mechanical properties was 5%.

Among the alternatives to improve the physical properties of films based on gelatin, the use of load of montmorillonite has been recently privileged. Zheng et al. (2002) prepared gelatin films incorporated with 30% montmorillonite by casting, and concluded that the nanoclay dispersion in the matrix improved the thermal and mechanical properties of the films. Rao (2007) produced films of gelatin and montmorillonite by coating on a PET substrate, with high modulus of elasticity, revealing that the state of exfoliation and content of particles, among other parameters, have great influence on the properties of the films. Montmorillonite–gelatin films without plasticizer produced by casting were developed by Martucci et al. (2007), who studied the state of exfoliation/intercalation of the nanoparticles in the matrix by atomic force microscopy, determining that high montmorillonite concentrations (>10%) favored agglomeration and reduced interactions between

* Corresponding author at: Faculty of Animal Sciences and Food Engineering, University of São Paulo, Av. Duque de Caxias Norte, 225, 13635-900, Brazil. Tel.: +55 19 3565 4186.
E-mail address: crisflaker@hotmail.com (C.H.C. Flaker).

http://dx.doi.org/10.1016/j.jfoodeng.2014.11.009
0260-8774/

matrix and particle. Bae et al. (2009) produced fish gelatin films reinforced with montmorillonite by casting and observed a significant increase in mechanical resistance (30–41 MPa) with 5% inclusion of nanoparticles due to good exfoliation caused by ultrasound. Vanin et al. (in press) studied the effect of montmorillonite concentration on mechanical properties of gelatin-based films in a more complex design producing films by spreading, and observed that the effect of nanoparticles concentration depends on the gelatin and plasticizer concentration.

Montmorillonite is considered as nanoclay, from the group of phyllosilicates, whose main characteristic is to have a crystalline structure on sheets of nanometer thickness, providing a large specific surface (Weiss et al., 2006). They have been frequently used in studies of protein-based nanocomposites (Angellier-Coussy et al., 2008; Bae et al., 2009; Chen and Zhang, 2006; Hedenqvist et al., 2006; Tunc et al., 2007). The interactions between gelatin and montmorillonite can be of the electrostatic type between the positive domains of the protein and the negatively charged layers of MMT; as well as hydrogen bonding between the NH groups of the gelatin and the Si–O of the montmorillonite (Luckham and Rossi, 1999). These two interactions benefit the intercalation and delamination of the particle layers among protein matrix (Chen and Zhang, 2006); and, in the case of film production by spreading, depend on the quality of dispersion of those particles in water before addition in the film-forming solution. However, commercially, montmorillonite is found in agglomerate form, that is, in micrometer scale and its application as reinforcement in films requires its dispersion in nanometric dimensions.

In overall, the works cited above aimed at studying the effect of the montmorillonite on the mechanical properties, or improving the water vapor barrier and stability to environmental humidity of polymeric films varying the concentration of montmorillonite, without discussing the eventual effect of the technique employed to disperse nanoparticles.

Considering that several authors observed some limitations in the reinforcement, partly due to problems in the filler dispersion within the polymer matrix, and no works on the effect of the nanoparticles dispersion before its incorporation into formulation were found in the literature, the aim of this project was to study the quality of the montmorillonite dispersion in water, in terms of particle size and zeta potential, and to analyze the effect of the montmorillonite concentration (MMT) on the barrier, surface and mechanical properties of gelatin films.

2. Material and methods

2.1. Material

Pigskin gelatin, type A, bloom 245 and molecular weight 5.2×10^4 Da (Gelita South America, São Paulo, Brazil) was used as biopolymer, and glycerol (Synth, Brazil) was used as plasticizer. An unmodified commercial MMT (Nanomer® clay||, PGV, Sigma) with an aspect ratio ranging from 200 to 400, was used as filler.

2.2. Montmorillonite dispersion

The montmorillonite particles were dispersed in distilled water (1 g/100 g of water) for 30 min, using three devices: Mechanical homogenizer UT (T25, IKA) at 20,000 rpm; colloidal mill CM (SPEX type) with 4 acrylic balls; or ultrasonic processor US (Sonics, 750 W) with a 1/2″|| probe. These dispersions were analyzed for determination of particle size and zeta potential, both techniques using the ZetaPlus equipment (Brookhaven Instruments Company, EUA), at natural pH and 25 °C, up to 18 h after preparation. Each data was an average of 10 measurements. The dispersion method of montmorillonite to produce the nanocomposite films was chosen as a function of particle size associated with the higher zeta potential.

2.3. Gelatin nanocomposite films

The film-forming solutions (FFS) were prepared with 5 g of gelatin/100 g of FFS and 30 g of glycerol/100 g of gelatin and the aqueous dispersions of montmorillonite prepared with the best technique studied as in Section 2.2. The nanoparticles concentration in nanocomposite films was adjusted to 1, 3, 5 and 7 g of MMT/100 g of gelatin, these values were selected since the observed improvements in the properties of the films were obtained with up to 10 wt% of MMT (Luecha et al., 2010; Vanin et al., in press; Martucci et al., 2007). Films without MMT were considered as the control treatment.

Films were produced by spreading 100 g of the FFS onto an acrylic plate (780 cm^2) and dried in oven at 30 °C for 24 h; then, conditioned in a relative humidity of 58% for 7 days. The nanocomposite films were characterized for determination of gloss, contact angle, microstructure by scanning electron microscopy (SEM) and atomic force microscopy (AFM), mechanical properties and water vapor permeability.

Gloss measurement was done using a glossmeter (Rhodopoint NGL 20/60) with 60° angle and in 10 points of the film dried surface, according to ASTM D2457 standard (Villalobos et al., 2005). The contact angle was measured according to ASTM D7334 standard, using an optical tensiometer Attension Theta lite (KSV Instrument, Finland). Films were analyzed at the surface by SEM; for the cross-section analysis, the films were cryo-fractured after immersion in liquid nitrogen, and analyzed without further preparation. The images were taken at random positions of the films with 2000× magnification. AFM was used to study the surface topography and roughness (as mean root square); analyses were performed in areas of 25 μm × 25 μm at random positions of films.

Mechanical properties were determined by tensile test (samples cut into 15 mm × 100 mm strips) with grip separation of 50 mm and speed rate of 1 mm/s, according to ASTM D882 standard (Thomazine et al., 2005), and by puncture tests (samples diameter 53 mm), with a 3 mm probe and velocity of 1 mm/s according to ASTM F1306 standard (Gontard et al., 1992). Both tests were carried out using a texture analyzer (TA.XT icon, SMS, Surrey, UK). The water vapor permeability (WVP) was determined gravimetrically, according to the standard ASTM E96 (Gontard et al., 1992); the area of permeation of film was 0.0032 m^2 and the water vapor partial pressure gradient was 3169 Pa at 25 °C.

All tests were executed in triplicate, and results submitted to ANOVA and Tukey tests ($\alpha = 0.05$). Statistical analysis was performed with SAS software.

3. Results and discussion

3.1. Dispersion of montmorillonite

Initially, the commercial montmorillonite (MMT) was dispersed in water using magnetic stirring of low shear stress (stir bar 20 mm × 6 mm, 1000 rpm), which caused some disruption of the structure of the commercial product: its particle size was around 500 nm, a typical value of this type of clay, according to Tombácz and Szekeres (2006).

The particle size distribution presented two populations for all dispersion treatments, centered at 130 and 500 nm. Analyzing the means values, it could be observed that after dispersion treatments, the nanoparticles size was about 43% smaller for US treatment (289.6 ± 4.0 nm); this reduction was a consequence of the cavitation