



Characteristics of bio-nanocomposite films from tilapia skin gelatin incorporated with hydrophilic and hydrophobic nanoclays



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ABSTRACT

Properties of films from tilapia skin gelatin incorporated with hydrophilic and hydrophobic montmorillonite (MMT) nanoclays at various levels (0–10%, w/w) were investigated. Generally, mechanical properties were improved by the addition of hydrophilic nanoclay (i.e., Cloisite Na⁺) in the range of 0.5–5% (w/w). The lowest water vapour permeability was observed for films incorporated with Cloisite Na⁺ and Cloisite 20A at a level of 1% (w/w) ($P < 0.05$). The lowest L^* and the highest ΔE^* values were observed ($P < 0.05$) when the film was incorporated with Cloisite 15A at 10% (w/w). Generally, b^* value (yellowness) of resulting films increased with increasing amount of all nanoclays ($P < 0.05$). All films became less transparent with increasing levels of nanoclay incorporated ($P < 0.05$). Wide angle X-ray diffraction and scanning electron microscopic analyses revealed the intercalated/exfoliated structure of nanocomposite gelatin-based films incorporated with hydrophilic and hydrophobic nanoclays. Homogeneity and smoothness of film surface decreased with the addition of both nanoclays as revealed by SEM micrographs. Thermogravimetric and differential scanning calorimetric analyses indicated that the incorporation of nanoclays enhanced the rigidity and heat stability of the gelatin-based films differently, depending on the types of MMT-nanoclay used. Thus, the types and levels of nanoclay incorporated directly affected the properties of tilapia skin gelatin films.

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1. Introduction

Gelatin is a biopolymer, commonly being known for its film-forming ability and applicability for food packaging (Gomez-Guillen et al., 2009). Gelatins from aquatic animals are gaining attention due to health issues and religious constraints on gelatin from mammals (Karim and Bhat, 2009). Because of its good film-forming abilities, fish gelatin may be a good alternative to synthetic plastics for making packaging films to preserve food stuffs (Gomez-Guillen et al., 2009). Owing to the superior oxygen barrier property, fish gelatin-based film could prevent lipid oxidation in food systems (Bigi et al., 2000; Jongjareonrak et al., 2008). Additionally, it can be used as a smart packaging material, in which antioxidants or antimicrobials can be incorporated (Gomez-Guillen et al., 2007; Jongjareonrak et al., 2006). Although gelatin films have good mechanical properties, it could swell at high humid conditions, due to their hydrophilic nature. This is associated with loss in mechanical and barrier properties, thereby limiting their applications in food packaging (Martucci and Ruseckaite, 2009). To

tackle this problem, gelatin-based films must be modified. Over the years, several approaches have been developed to improve the barrier properties such as, incorporation of essential oils (Gomez-Estaca et al., 2010; Tongnuanchan et al., 2013) and fatty acid (Bertan et al., 2005; Limpisophon et al., 2010). Recently, the properties of gelatin based film were improved by the incorporation of nano-clays (Bae et al., 2009; Farahnaky et al., 2014; Shakila et al., 2012). As a consequence, gelatin films can compete with petroleum-based polymers as a biodegradable packaging material (Martucci and Ruseckaite, 2010a).

Polymer nanocomposites have received great interest because nanosized material fillers significantly improve polymer properties when compared with polymer alone or micro-scale composites (Bae et al., 2009). Nanocomposite films developed from biopolymers known as 'bio-nanocomposites' showed improved mechanical properties, thermal stability and barrier properties (Martucci and Ruseckaite, 2010b; Ray and Okamoto, 2003), due to the enhanced polymer-filler interfacial interaction. The improved water and gas barrier properties of nanocomposite films are believed to be due to the presence of dispersed silicate layers in organised manner with large aspect ratios in the polymer matrix. This forces water/gas travelling through the film via. an increased

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'tortuous path' of the polymer matrix surrounding the nano-fillers, thereby increasing the effective path length for diffusion (Ray and Okamoto, 2003; Rhim, 2007). Amongst various nano-fillers, layered silicates commonly known as the cationic clay minerals, especially the naturally occurring smectite clays, such as hectorite and montmorillonite (MMT) are widely used (Ray and Okamoto, 2003; Rhim et al., 2009; Sothornvit et al., 2009).

Nanoclays, Cloisite Na⁺ (hydrophilic) and Cloisite 20A (hydrophobic) have been used to improve mechanical and barrier properties of gelatin-based biopolymers (Bae et al., 2009; Farahnaky et al., 2014; Shakila et al., 2012). Rhim et al. (2009) reported that, hydrophobicity of organically modified nanoclays (Cloisite 20A and Cloisite 30B) and hydrophilicity of unmodified nanoclay (Cloisite Na⁺) have different impact on barrier properties of PLA-based films. Therefore, the relative hydrophobicity of nanoclays would have different impacts on the properties of resulting nanocomposite films. However, little information is available regarding the influence of hydrophobic nanoclays such as Cloisite 15A (highly hydrophobic), Cloisite 20A (moderately hydrophobic) and Cloisite 30B (least hydrophobic) on barrier properties of gelatin-based films, particularly for those from fish gelatin. Therefore, this study aimed to investigate the effects of different MMT-nanoclays at various inclusion levels on the barrier and mechanical properties of fish gelatin-based films.

2. Materials and methods

2.1. Chemicals

Fish skin gelatin from tilapia (~240 bloom) was purchased from Lapi Gelatine S.p.A (Empoli, Italy). MMT-nanoclays including, Cloisite[®] Na⁺, Cloisite[®] 15A, Cloisite[®] 20A and Cloisite[®] 30B were purchased from Southern clay products Inc. (Gonzlaes, TX, USA). Glycerol was procured from Merck (Darmstadt, Germany). All chemicals were of analytical grade. The general characteristics of these Cloisite[®] nanoclays are presented in Table 1.

2.2. Preparation of gelatin films

Gelatin films were prepared as per the method of Bae et al. (2009) with a modification. Firstly, gelatin solution was prepared by mixing the gelatin powder with distilled water to obtain protein concentration of 3% (w/v) as determined by the Kjeldhal method (AOAC, 2000). Thereafter, glycerol (25% of protein, w/w) was added into the gelatin solution as a plasticiser. Nanoclays including Cloisite Na⁺, Cloisite 15A, Cloisite 20A and Cloisite 30B were mixed with distilled water to obtain a final concentration of 0, 0.5, 1,

2.5, 5 and 10% (w/w, on dry protein basis). The mixtures were stirred at 1000 rpm (IKA Labor Technik stirrer, Selangor, Malaysia) for 5 min at room temperature. Nanoclay suspensions were then incubated at 60 °C for 1 h to delaminate the nanoclays in a temperature controlled water bath (W350; Memmert, Schwabach, Germany) with occasional stirring. Nanoclay suspensions were cooled down to room temperature and homogenised for 1 min at 5000 rpm (IKA Labor Technik homogeniser, Selangor, Malaysia). Gradually, nanoclay suspensions were dropped into the gelatin solution and the mixtures were homogenised for 30 s at 5000 rpm. The mixtures were degassed using a desiccator equipped with JEIO Model VE-11 electric aspirator (JEIO TECH, Seoul, Korea). The final volume was made up to 100 ml and referred to as film-forming suspension, FFS. FFSs were sonicated for intercalation/exfoliation of the gelatin and nanoclay for 30 min using the sonicating bath (Elmasonic S 30 H, Singen, Germany) and then the FFSs were gently stirred for 24 h at room temperature to obtain a homogenous suspension. Prior to casting, FFS were degassed for 10 min using the sonicating bath. FFS (4 ± 0.01 ml) were then cast onto a rimmed silicone resin plate (5 × 5 cm²), air-blown for 12 h at 25 °C, followed by drying in an environmental chamber (Binder GmbH, Tuttlingen, Germany) at 25 ± 0.5 °C and 50 ± 5% relative humidity (RH) for 24 h. Films obtained were manually peeled off and further subjected to analyses. Gelatin film without nanoclay was named as C (control) and those incorporated with Cloisite Na⁺, Cloisite 15A, Cloisite 20A and Cloisite 30B were referred to as Na⁺, 15A, 20A and 30B, respectively, followed by numbers representing the level of nanoclay used (0.5, 1, 2.5, 5 and 10%, w/w).

2.3. Analyses

Prior to testing, samples were conditioned in an environmental chamber for 48 h at 50 ± 5% relative humidity (RH) and 25 ± 0.5 °C. For WAXD, SEM, TGA and DSC studies, films were conditioned in a desiccator containing dried silica gel for 3 weeks at room temperature (28–30 °C) to obtain the most dehydrated films.

2.3.1. Thickness

The thickness of ten film samples of each condition was measured using a digital micrometer (Mitutoyo, Model ID-C112PM, Serial No. 00320, Mituyoto Corp., Kawasaki-shi, Japan). Ten random locations around each film sample were used for determination of thickness.

2.3.2. Mechanical properties

Young's modulus (YM), tensile strength (TS) and elongation at break (EAB) of film samples were determined as described by Iwata et al. (2000) using the Universal Testing Machine (Lloyd

Table 1
Characteristics of hydrophilic and hydrophobic nanoclays. Source: Southern clay products Inc. (Gonzlaes, TX, USA).

Nanoclays	Cloisite [®] Na ⁺	Cloisite [®] 15A	Cloisite [®] 20A	Cloisite [®] 30B
Chemical name	Natural bentonite	Bis (hydrogenated tallow alkyl) dimethyl, salt with bentonite	Bis (hydrogenated tallow alkyl) dimethyl, salt with bentonite	Alkyl quaternary ammonium salt bentonite
Chemical structure	Na _{0.33} (Al _{1.67} Mg _{0.33})Si ₄ O ₁₀ (OH) ₂	$\begin{array}{c} \text{CH}_3 \\ \\ \text{MMT} + \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{MMT} + \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{MMT} + \text{CH}_3 - \text{N}^+ - \text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$
Organic modifier	None	Dimethyl dihydrogenated tallow, quaternary ammonium (2M2HT)	Dimethyl dihydrogenated tallow, quaternary ammonium (2M2HT)	Methyl tallow, bis-2-hydroxyethyl, quaternary ammonium (MT2EtOH)
Modifier concentration	–	125 meq/100 g clay	95 meq/100 g clay	90 meq/100 g clay
Relative hydrophobicity	Hydrophilic	Highest hydrophobic	Moderately hydrophobic	Lowest hydrophobic
Moisture content	4–9%	<3%	<3%	<3%
Particle size	<25 μm (d ₅₀)	<10 μm (d ₅₀)	<10 μm (d ₅₀)	<10 μm (d ₅₀)
Bulk density	568 g/l	165 g/l	175 g/l	365 g/l
Density	2.86 g/cc	1.66 g/cc	1.77 g/cc	1.98 g/cc
X-ray results	d ₀₀₁ = 1.17 nm	d ₀₀₁ = 3.15 nm	d ₀₀₁ = 2.42 nm	d ₀₀₁ = 1.85 nm

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