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# Physical and mechanical properties of gelatin–clay nanocomposite

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ABSTRACT

Nanoclay particles were included in a gelatin matrix and gelatin–clay nanocomposites with different clay levels were produced, successfully. Mechanical properties of gelatin–clay nanocomposite films were measured using a texture analyzer by tensile test. Water vapor permeability, solubility, opacity, and color parameters were also determined. In the absence of nanoclay water vapor permeability was 0.86 g mm/kPa $m^2$ h and with addition of 18% nanoclay it decreased to 0.42 g mm/kPa $m^2$ h. Tensile strength of films was directly proportional to clay content, while addition of clay caused a reduction in elongation and water vapor permeability of films. Nanoclay was able to improve some physical and mechanical properties of gelatin biofilms.



## 1. Introduction

Biopolymers are obtained from different sources such as proteins, polysaccharides and lipids. Biopolymers, because of their renewability and abundance are considered as good alternatives for non-biodegradable petroleum based plastics (Bae et al., 2009; Koh et al., 2008; Krochta and De Mulder-Johnston, 1997; Martucci and Ruseckaite, 2009). Biopolymer films have many applications due to their being environmentally friendly and possibility of using them in various industries such as food packaging (Guerrero et al., 2011; Irissin-Mangata et al., 2001; Martucci and Ruseckaite, 2010; Sothornvit et al., 2010). Compared to polysaccharides, proteins are better in the case of film formation and being stronger and impermeable (Rhim et al., 1998; Wang et al., 2010; Pereda et al., 2011; Sothornvit et al., 2010). In order for biopolymers to be appropriate for packaging, their mechanical and permeability properties need to be improved. Proteins and polysaccharides have good ability for film forming but their mechanical and water vapor barrier properties are relatively poor. Therefore, these properties should be improved (Bigi et al., 2002; Chiou et al., 2009; De Carvalho and Grosso, 2004; Zenkiewicz and Richert, 2008). Plasticizers are used for producing more flexible films; however, they have negative effects on water vapor permeability (McHugh and Krochta, 1994; Hoque et al., 2011; Vanin et al., 2005).

Gelatin raw materials are inexpensive and abundant worldwide (Bae et al., 2009; Vanin et al., 2005). Gelatin is produced from chemical denaturation of collagen (Martucci and Ruseckaite, 2010). It is a complex polypeptide and used in different cases such as pharmaceuticals, photography, cosmetic and widely in food industry. Gelatin film, on its own, is permeable to water vapor so, it is not suitable for packaging of foods because water can escape or enter in foods with low or high moisture content foods, respectively (Martucci and Ruseckaite, 2010). There are various methods such as chemical cross-linking to overcome this problem (Lien et al., 2008; Bigi et al., 2002). Other methods are physical modification and lamination, both regarded as important and promising approaches (Martucci and Ruseckaite, 2010; Orozco et al., 2010).

Many attempts have been made to improve the poor mechanical and physical properties of biopolymer films by enzymatic, physical, chemical and physicochemical methods. However, so far few biobolymer based packaging materials have been commercialized and still the majority of packaging materials are petroleum based with negative environmental impacts (Guerrero et al., 2011). Nanomaterials are the materials with at least one dimension in the nanometer range. Because of superior physical and mechanical properties of nanomaterials compared to micro and milli scale materials, in the recent years, nanomaterials have attracted substantial attention from both academic and industrial researchers. Nanomaterials have shown new and promising characteristics to overcome the shortcomings of biopolymer based packaging materials.

Layered silicates can be added to gelatin for physical modification. This can increase barrier and mechanical properties of different films (Chen et al., 2003; Haug et al., 2004; Rao, 2007). Nanoclay is one type of layered silicates and montmorillonite (MMT) is the most popular nanoclay. MMT is a laminated silicate with layer

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thickness of about 1 nm. MMT is hydrophilic and therefore incompatible with polymers and it has to become hydrophobic. In the interlayer space, sodium cations are replaced with long chain organic cations and thus hydrophilic nanoclay is converted to hydrophobic nanoclay that is compatible with polymers (Dadfar et al., 2009; Dadfar et al., 2011; Lin et al., 2007).

Composite refers to materials composed of two phases. One phase can play a role as filler and another one is dispersed phase. Composite is called nanocomposite if the size of filler phase is less than 100 nm. Gelatin nanoclay is a type of nanocomposite with clay as a filler phase. Nanosized clay can act as a reinforcing factor and improves mechanical properties and heat stability and decreases water vapor permeability (Dadfar et al., 2009; Dadfar et al., 2011; Rao, 2007). The aim of this research is to produce gelatin–clay nanocomposite with the aid of ultrasound and study its physical and mechanical properties.

## 2. Materials and methods

### 2.1. Materials

Type of clay used was Cloisite® 20A and was supplied by Southern Clay Products, Inc. (Gonzales, TX, USA). Cloisite® 20A is a natural montmorillonite modified with a quaternary ammonium salt. It is used an additive for plastics and rubber to improve various physical properties, such as reinforcement, synergistic flame retardant and barrier. Moisture content was less than 2%. Its weight loss on ignition was 38%, its density was 1.77 g/cc and X-ray results showed that $d_{001}$ = 24.2 Å. Organic modifier used for its production was di-methyl, dehydrogenated tallow, quaternary ammonium (2M2HT), according to the supplier.

### 2.2. Preparation of gelatin–clay nanocomposite

The nanoclay solution was prepared with addition of 2 g glycerol in 80 ml of 55 ± 5 °C distilled water and stirred for 15 min. Different percentages of clay (0, 2, 6, 10, 14, 18 g clay/100 g gelatin) were then added and stirred for 40 min. Clay nanoparticles were dispersed uniformly with the aid of an ultrasound equipment operating at 40 kHz (Bandelin 400, Germany) for 5 min.

The gelatin solution was prepared separately. Firstly, 10 g bovine gelatin was dissolved in 40 ml of distilled water at room temperature and temperature rose to 60 ± 5 °C using a heater stirrer. The solution was then stirred at this temperature for 2 h. The gelatin solution was then left to cool down to 30 °C. The appropriate amount of the prepared clay solution was added to gelatin solution and mixed thoroughly. This solution was used for further film casting.

### 2.3. Film casting

After preparation of the solution, 10 ml of gelatin-nanoclay solution was poured into a plastic plate with the radius of 3.7 cm and surface area of 42.987 $cm^2$. Plates were maintained at 25 °C in an incubator for 36 h. After drying, films were peeled off from the plate surface and left to equilibrate at a specific relative humidity in a closed box containing a saturated salt solution. The films were then ready for further tests.

### 2.4. Film thickness

Film thickness was required for tests such as water vapor permeability and mechanical properties. Therefore, thickness of the films was measured to the nearest 0.001 mm with a digital micrometer (Micrometer, China). Average of thickness of films was about 170 ± 20 μm.

### 2.5. Scanning electron microscopy

Square cuts of the produced films were coated with gold using an ion sputter coater (Fisons Instruments, UK). The coated samples were viewed and photographed using a scanning electron microscope (model 5526, Cambridge, UK) at 20 kV.

### 2.6. Mechanical properties

Films were transferred to a closed container with relative humidity of 40% and left for equilibrium at 25 °C for 48 h before mechanical testing. Films were cut into rectangles with length of 5 cm and width of 1.4 cm. Then two predefined small cuts were made in the middle and two sides of each film before being placed between the two jaws of tensile rig. The tensile test was then performed by pulling off the film at pretest speed test, test speed, post test speed of 1, 1 and 10 mm/s using a texture analyzer (Texture Analyzer TA.xt2, Stable Microsystems, Surrey, UK). The net length between the jaws was almost constant for all films and about 20 mm. The texture analyzer was run at auto force mode with the trigger force of 5 g. From stress–strain curves three parameters were calculated: (1) tensile strength was calculated as maximum stress, (2) Young's modulus (the initial slope of stress-stain curves at the linear part, and (3) elongation at break where the film is torn.

### 2.7. Water vapor permeability (WVP)

The water vapor permeability of the films was measured using an aluminum cup (height and diameter of 2.1, 5.6 cm, respectively). The cup was filled with 10 g of silica gel and covered with a film specimen. The cup covered with the film was placed in a container containing a super saturated salt solution (75% RH) at 25 °C. The cup was then weighed eight times at 3 h intervals. WVP was calculated from the mass change versus time according to the method described by Chiou et al. (2009).

### 2.8. Swelling test

Square cuts of the produced films with the width and length of 2 and 2 cm were immersed in 0.1-M NaCl aqueous solution for 30 min and 25 °C. Then samples were taken out and put between 2 filter papers for 5 min to separate excess surface water. Swelling ratio was calculated using the following equation:

$$Sw(\%) = \frac{M_f - M_i}{M_i} \times 100$$

where $M_f$ is the weight of the swollen sample and $M_i$ is the weight of the dried sample.

### 2.9. Opacity

The opacity of gelatin-nanoclay films was measured using a UV–visible spectrophotometer (UNICO UV–2100 Spectrophotometer). Films were cut into rectangular strips and placed on the two outer sides of a spectrophotometer cell and light transmission was read at the wavelength of 550 nm (Martucci and Ruseckaite, 2010).

### 2.10. Color

*L*, *a* and *b* color parameters of the films were evaluated using digital photography followed by image analysis by Photoshop soft-