

Mechanical and Water Barrier Properties of Soy Protein and Clay Mineral Composite Films

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Abstract Composite films were prepared with soy protein isolate (SPI) and various clay minerals by casting from polymer and clay water suspension. Effects of clay minerals on film thickness, moisture content (MC), tensile strength (TS), elongation at break (E), water vapor permeability (WVP), and water solubility (WS) were tested. Properties including thickness, surface smoothness, and homogeneity of films prepared with organically modified montmorillonite (O-MMT), Wamok clay (W-clay), bentonite, talc powder, and zeolite were comparable to those of control SPI films. TS increased significantly ($p < 0.05$) in films prepared with O-MMT and bentonite, while WVP decreased significantly ($p < 0.05$) in bentonite-added films. WS of most nanocomposite films decreased significantly ($p < 0.05$).

Key words: clay minerals, layered silicates, montmorillonite, soy protein, nanocomposite

Introduction

Synthetic petroleum-based polymers have been widely used in a variety of packaging materials, but have become a major source of waste disposal problem due to their poor biodegradability. One of the approaches to solve this problem is to use biodegradable polymers derived from biopolymers such as polysaccharides, proteins, and lipids (1). The targeted applications for the natural biodegradable polymers require that the materials have sufficient stiffness and strength during their useful life but eventually biodegrade. Achieving the required combination of properties from the biodegradable polymers is very difficult because of their inherent water sensitivity and relatively low stiffness and strength, especially in moist environments. However, biopolymer films prepared from polysaccharides (e.g., starch and cellulose) and hydrocolloids (e.g., pectin, alginate, and carrageenan) form strong films, but have poorer water resistance than synthetic polymers and thus absorb more moisture with associated swelling upon contact with water (1-4). All these contribute to a considerable loss of mechanical properties, which prohibiting straightforward use in most applications. Many research works have focused on improving the physical properties of biopolymer-based films by decreasing the hydrophilicity and increasing and stabilizing the mechanical properties.

One way of improving the moisture barrier properties of biopolymer films is to include additives that are hydrophobic in nature (5). Accordingly, lipid materials such as neutral lipids, fatty acids or waxes have been incorporated into biopolymer films to improve the moisture barrier properties of such films (6-11), although maintaining the mechanical properties is questionable.

Another approach to improving the physical properties of biopolymer-based films has focused on inducing inter-

molecular or intra-molecular cross-linking in the polymer matrix. The cross-linking of proteins has been reported to decrease solubility, improve mechanical strength, and barrier properties of the films (12). Property modification of the biopolymer-based films can sometimes be achieved by the addition of divalent or trivalent ions (e.g., cross-linking of alginate with calcium), adjustment of pH, exposure to irradiation, heat-curing or the use of cross-linking agents (1). The more commonly used covalent cross-linking agents are glutaraldehyde, glycerinaldehydes, formaldehyde, gossypol, and tannic and lactic acids (13). However, edibility and applications on food products of films treated with such cross-linking agents are highly questionable.

The other possible approach to modify the biopolymer film properties is to make hybrid films with organic polymer and clay minerals such as layered silicates, which are called nanocomposite films (14-17). The nanocomposite films consisting of inorganic nanolayers of layered silicate such as montmorillonite clay and organic polymers have recently evoked intense research interests in the material and polymer science areas. The impressive enhancements of the material properties of the nanocomposite films compared to the pure polymers can be achieved without the need for additional and cost-increasing processing or post-treatment procedures. Examples of such property enhancements include decreased permeability to gases and liquids, better resistance to solvents, increased thermal stability, and improved mechanical properties. Moreover, biodegradability is still retained, *i.e.*, after final degradation only inorganic, natural minerals (clay) will be left over (18, 19). The objective of this study was to examine the possibility of making nanocomposite films by blending soy protein with various clay minerals and test their effect on film properties.

Materials and Methods

Materials Soy protein isolate (minimum 90% protein on

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dry weight basis, Supro 620, SPI) was obtained from Protein Technologies International (St. Louis, MO, USA), and glycerol was purchased from Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Montmorillonite (Montmorillonite KSF; MMT) was purchased from ACROS Organics (Belgium, NJ, USA). Organically modified montmorillonite (Nanomer I.34TCN; O-MMT) was purchased from Nanocor Inc., (Arlington Heights, IL, USA). O-MMT, a clay surface-modified through onium ion exchange, is composed of 65-80 wt% montmorillonite clay and 20-35 wt% methyl dihydroxyethyl hydrogenated tallow ammonium. Wamok clay (W-Clay) was obtained from Haengnam Ceramic Co., Ltd. (Mokpo, Korea), and bentonite (OPAZIL AOK) from SÜD-CHEMIE Korea (Pohang, Korea). Bentonite is mainly used for paper-coating, and its major component is montmorillonite. Talc powder (Magnesium silicate hydrous, $3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$) and zeolite were purchased from Daejung Chemicals & Metals Co., Ltd. (Inchon, Korea) and Wako Pure Chemicals Industries, Ltd. (Osaka, Japan), respectively.

Particle size analysis Particle size of each clay mineral sample was analyzed using a particle size analyzer (Microtrac X-100, Honeywell Inc., Phoenix, AZ, USA).

Preparation of films SPI control films were prepared based on the film preparation methods of SPI film (20, 21). For the preparation of the SPI film solution, 5 g SPI was dissolved in 100 mL distilled water with 2 g glycerol as a plasticizer. Composite film solutions were prepared by adding 0.5 g each clay mineral into 100 mL distilled water with 2 g glycerol, and the mixture was stirred vigorously with a magnetic stirrer for 30 min and sonicated for 10 min. Five grams of SPI was then added to the suspension and stirred until the protein dissolved completely. Acidity of each film solution was determined using a pH meter (AB15, Fisher Scientific, Hanover Park, IL, USA) equipped with a standard combination electrode. All film solutions were heated for 20 min at 90°C in a constant-temperature water bath. The solutions were poured onto a leveled Teflon (Cole-Parmer Instrument Co., Chicago, IL, USA)-coated glass plate (24×30 cm) framed on four sides, spread evenly with a bent glass rod, and allowed to dry for about 24 hr at room temperature (c. $23\pm 1^\circ\text{C}$).

The resultant films were peeled from the plate and cut into 7×7, 2×2, and 2.54×10 cm pieces for measurements of water vapor permeability (WVP), water solubility (WS), tensile strength (TS) and elongation at break (E).

Film thickness Film thickness was measured using a micrometer (Dial Thickness gauge 7301, Mitutoyo, Japan) at a 0.01-mm accuracy.

Conditioning Film characteristics were determined after all sample films were preconditioned in a constant temperature humidity chamber (Model FX 1077, Jeiotech Co., Ltd., Seoul, Korea) set at 25°C with 50% RH for at least 48 hr to adjust the moisture content.

Transparency Transparency of the films (TP) was determined by measuring transmittance of films at 660 nm using a UV/VIS Spectrometer (HP8452AX, Hewlett Packard GMBH, Müllheim/Baden, Germany). A piece of film was attached

to the outside wall of a quartz cuvette and inserted into the holder to measure the percent transmittance of the film.

Tensile strength (TS) and percentage elongation at break (E) TS and E of each film were evaluated using a Model 4465 Instron Universal Testing Machine (Instron Engineering Corp., Canton, MA, USA) in accordance with ASTM method (22). For the tensile test, initial grip separation was set at 50 mm, and cross-head speed was set at 500 mm/min. TS was calculated by dividing the maximum load by the initial cross-sectional area of the film, and E was calculated by dividing the extension at rupture of the film by the initial length of the film (50 mm) multiplied by 100 (22). TS and E measurements for each type of film were replicated three times with individually prepared films as the replicated experimental units, each replicate being the mean of seven tested sampling units taken from the same film.

Water vapor permeability WVP ($\text{ng}\cdot\text{m}/\text{m}^2\cdot\text{sec}\cdot\text{Pa}$) was calculated as follows:

$$\text{WVP} = (\text{WVTR} \cdot L) / \Delta p$$

where WVTR is the measured water vapor transmission rate ($\text{ng}/\text{m}^2\cdot\text{sec}$) through a film, L is the mean film thickness (m), and Δp the partial water vapor pressure difference (Pa) across the two sides of the film. WVTR was determined gravimetrically using a modified ASTM Method E 96-95 (23). In calculating WVP, the effect of resistance of the stagnant air layer between the film underside and the surface of the water in cups was corrected by the method of Gennadios *et al.* (24).

Water solubility (WS) WS of film was defined as the content of dry matter solubilized after 24 hr of immersion. WS of each treated film was measured according to the method of Rhim *et al.* (25). Three randomly selected samples from each type of film were first dried at 105°C for 24 hr to determine the initial dry matter. Additional three pieces of the film were placed in a 50-mL beaker containing 30 mL distilled water. Beakers were covered with Parafilm (American National Can, Greenwich, CT, USA) and stored in an environmental chamber at 25°C for 24 hr with occasional gentle stirring. Undissolved dry matter was determined by removing the film pieces from the beakers, gently rinsing them with distilled water, and oven-drying them (105°C, 24 hr). The weight of water-soluble matter was calculated by subtracting the weight of undissolved dry matter from the weight of initial dry matter and expressed as a percentage of the initial dry matter content.

Statistical analysis Measurements of each property were triplicated for TS, E, WVP, and WS with individually prepared films as the replicated experimental units. Statistics on a completely randomized design were determined using the General Linear Models procedure in the SAS program (26). The significance of each mean property value was separated ($p < 0.05$) with Duncan's multiple range test.

Results and Discussion

Particle size of mineral clays Results of the particle size

Table 1. Percentiles [d(10), d(50), d(90)] of particle size and mean volume size (mv) of the clay minerals

Clays	d(10) (μm)	d(50) (μm)	d(90) (μm)	Mv (μm)
MMT	6.48	23.92	61.55	30.36
O-MMT	7.71	21.12	33.73	21.03
W-Clay	1.57	4.65	14.14	6.56
Bentonite	1.97	5.70	19.13	8.55
Talc	4.96	13.17	31.49	16.60
Zeolite	6.32	14.14	22.87	14.69

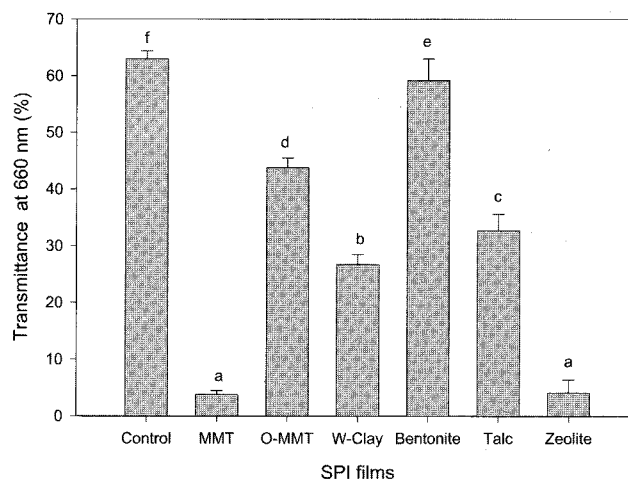
Table 2. pH of film solutions, thickness and moisture content (MC) of SPI and clay composite films¹⁾

Films	pH of film solution	Thickness (μm)	MC (% wb)
Control SPI	7.54 \pm 0.02 ^c	105.3 \pm 16.6 ^{ab}	19.3 \pm 1.2 ^{ab}
MMT/SPI	5.98 \pm 0.06 ^a	122.4 \pm 3.1 ^c	21.2 \pm 1 ^{bcd}
O-MMT/SPI	7.46 \pm 0.01 ^c	103.2 \pm 5.2 ^{ab}	19.6 \pm 0.9 ^{abc}
W-Clay/SPI	7.03 \pm 0.12 ^b	106.7 \pm 16.7 ^{ab}	21.0 \pm 1.8 ^{abc}
Bentonite/SPI	8.09 \pm 0.02 ^d	99.6 \pm 5.1 ^a	19.0 \pm 0.9 ^a
Talc/SPI	7.47 \pm 0.01 ^c	105.0 \pm 1.3 ^{ab}	20.5 \pm 0.3 ^{abc}
Zeolite/SPI	8.06 \pm 0.02 ^d	116.7 \pm 6.9 ^{bc}	20.9 \pm 0.6 ^{abc}

¹⁾Means of three replicates \pm standard deviations. Any two means in the same column followed by the same letter are not significantly ($p > 0.05$) different by Duncan's multiple range tests.

analysis of mineral clays used in this study are shown in Table 1. Mean volume size of the mineral clays ranged from 6.56 to 30.36 μm . Particle size of W-clay was the smallest and that of MMT was the largest. Differences in particle size of the clay minerals are expected to affect not only film-forming but also the film properties.

Film forming property The film-forming solutions were slightly acidic to slightly alkaline depending on the clay minerals used (Table 2). Acidities of the film-forming solutions such as control SPI, O-MMT/SPI, W-clay/SPI, and talc/SPI were neutral, while that of MMT/SPI was slightly acidic, and those of bentonite/SPI and zeolite/SPI were slightly alkaline. Although the pHs of the film-forming solutions differed depending on the clay minerals used, they were within the range of good film-forming for SPI-based films (27). Gennadios *et al.* (27) reported that the formation of a homogeneous free-standing SPI film could be achieved within the pH ranges of 1-3 and 6-12. Film formation did not occur between pH 4 and 5, but the film rather coagulated around its isoelectric point (pH 4.5). When moving away from the isoelectric point, the SPI proteins denature, unfold, and solubilize, exposing sulfhydryl and hydrophobic groups. These groups associate during drying, creating hydrophobic and disulfide bonding forces, which form a film structure. In addition, SPI films within pH ranges 6-11 had significantly higher TS and E, but lower WVP than films formed at pH ranges of 1-3. The solubility of amorphous silica is known to be very low at a pH less than 10 and increases sharply above 10 (28). SPI films are generally casted after adjusting the pH of the film solution to 10 (12, 27). However, in the present study, to test only the effect of various kinds of clay minerals, pH of the film solutions was not adjusted.

**Fig. 1. Transparency of SPI and clay composite films determined by transmittance at 660 nm.**

Flexible and free-standing films were formed from all films prepared. SPI films were transparent and pliable with greenish-yellow tint. The transparency (TP) of SPI films measured by transmittance was 63.0 \pm 1.4% (Fig. 1). By compositing with clay minerals, TP decreased significantly ($p < 0.05$). However, the degree of decrease in TP varied depending on the minerals used. Among the clay minerals tested, bentonite resulted in the most transparent films followed by O-MMT and talc powder. On the contrary, compositing with MMT and zeolite resulted in translucent films.

Film thickness In general, the thickness of biopolymer films depends on the solid content. The thickness of SPI films was not changed significantly ($P > 0.05$) by compositing with small amount of clay minerals (10% w/w of SPI) except zeolite and MMT (Table 2). The thicker films obtained by compositing with zeolite and MMT may be attributed not only to their particles but also to their incompatibility with the protein matrix. The incorporation of fillers such as mica, kaolin, calcium carbonate (CaCO_3), and talc into thermoplastics is a common practice in the plastic industry to improve the working properties of the plastics such as strength, rigidity, durability, and hardness (29). High-filling loadings or an incompatible filler with the polymer matrix, however, may adversely affect the film properties. Nanocomposite polymeric films based on layered silicates, such as montmorillonite (MMT) or hectorite, lead to new and large improvements in the polymer matrix in terms of mechanical, thermal, optical, and barrier properties, particularly at low clay content (as tiny as 1 wt %) in comparison with the more conventional microfillers (14-17). To reach this nanocomposite distribution, rendering of the naturally hydrophilic clay filler to be more compatible with the organic polymer matrix is often necessary. The natural forms of layered silicates such as MMT usually contain Na^+ or K^+ ions, which are hydrophilic in nature. Modifications of the silicate surface are generally achieved either by ion exchange reactions with organic cations (*e.g.*, alkylammonium ions) or by the introduction of copolymers containing at least one component with a high affinity for the silicate surface. It renders the normally hydrophilic MMT organophilic,

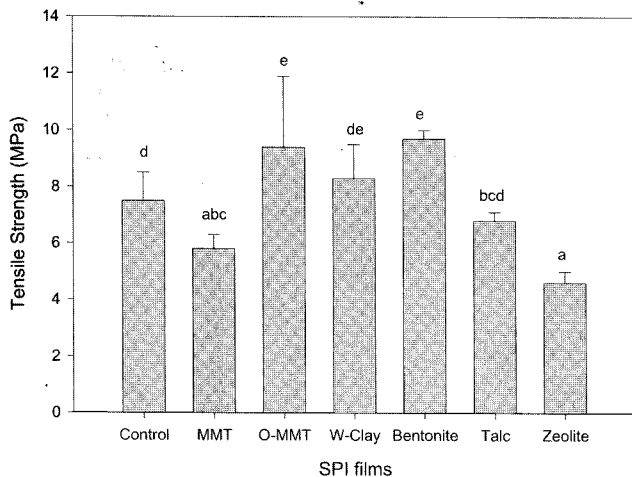


Fig. 2. Tensile strength (TS) of SPI and clay composite films.

resulting in an increasing compatibility with the organic polymeric matrix. In this study, homogeneous and smooth-surfaced films were prepared by blending with O-MMT and other clay minerals except MMT. The films composited with MMT were gritty in surface and the lack of film smoothness may have resulted in greater thickness readings. This result indirectly indicates that natural MMT is not compatible with the organic polymer matrix.

Tensile strength (TS) and elongation at break (E) TS and E of SPI films were changed by compositing with clay minerals (Fig. 2 and 3). The mean TS values of SPI films composited with O-MMT, W-clay, and bentonite increased ($P < 0.05$) by 25, 11, and 29%, while those of MMT, talc, and zeolite decreased by 23, 9, and 39%, respectively. This result also indicates the degree of compatibility of each clay mineral with the SPI polymer matrix. Generally, the incompatible polymeric composite with particulates causes a significant decrease in the mechanical strength due to the poor interfacial adhesion between the composited material and the polymer matrix. Furthermore, due to their high aspect ratio (often approaching 1,000), the introduction of intercalated or exfoliated layered silicate in the polymer matrix can dramatically enhance the mechanical properties of the film (14-17). The enhancement in TS of SPI films composited with O-MMT, W-clay, and bentonite may be directly attributed to the reinforcement provided by the intercalation of SPI in these clay minerals, as well as a fine dispersion of the particles in the SPI matrix. However, direct evidence for the development of such morphological structures can be confirmed through transmission electron microscopy (TEM) analysis.

The percentage elongation at break (E), a measure of the extensibility of films, generally shows an inverse relationship with TS, *i.e.*, it decreases as TS increases. E of SPI films composited with MMT, talc, and zeolite decreased significantly ($p < 0.05$) while the SPI films composited with W-clay and bentonite retained most of their resilience (Fig. 3). It is noteworthy that E of the SPI films composited with O-MMT, W-clay, and bentonite did not decrease significantly in spite of the increased TS. The increased TS and decreased E for soy protein films cross-linked by physical or chemical means have been reported (12, 25). Retained E,

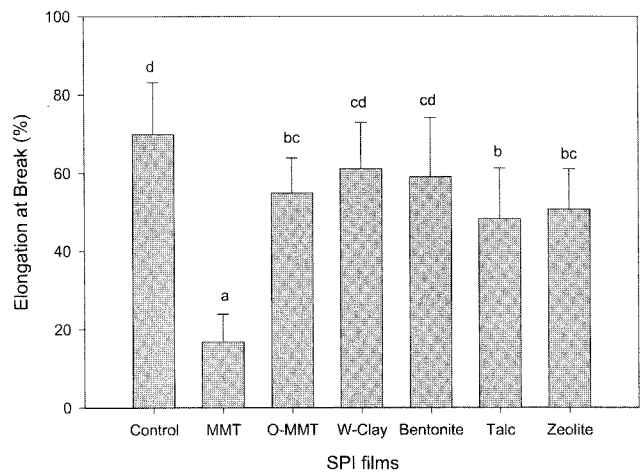


Fig. 3. Elongation at break (E) of SPI and clay composite films.

accompanied by increased TS in clay mineral-composited SPI films such as O-MMT, W-clay, and bentonite/SPI films could be attributed to the formation of a denser, tighter film structure and thus a stronger protein matrix retaining their resiliency.

Moisture content (MC) MC of SPI films, ranging from 19 to 21% (Table 2), was not changed significantly by compositing with clay minerals.

Water vapor permeability (WVP) WVP values of control and various clay mineral-composited SPI films were compared (Fig. 4). Compositing with clay minerals except MMT induced a decrease in WVP of SPI films ranging from 7 to 52% depending on the clay minerals used. Bentonite was the most effective in decreasing WVP, followed by zeolite, talc, W-clay, and O-MMT. It is noteworthy that the water vapor barrier of SPI films composited with bentonite increased two-fold compared to that of the control SPI films. This result further indicates that some specific structure, such as intercalation of SPI in clays, was developed in the films composited with clay minerals particularly with bentonite. Layered silicates are believed

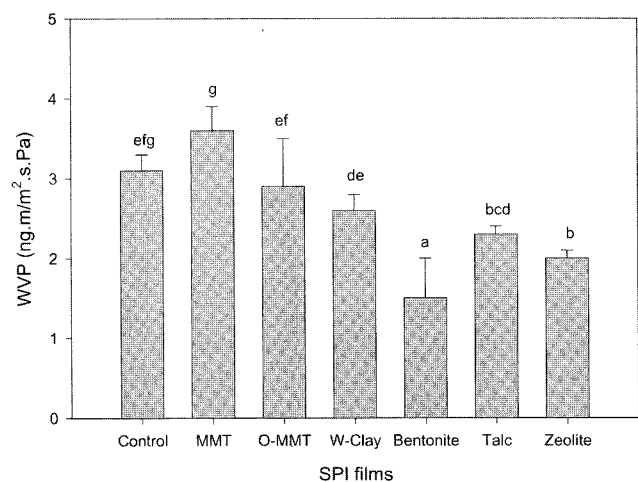


Fig. 4. Water vapor permeability (WVP) of SPI and clay composite films.

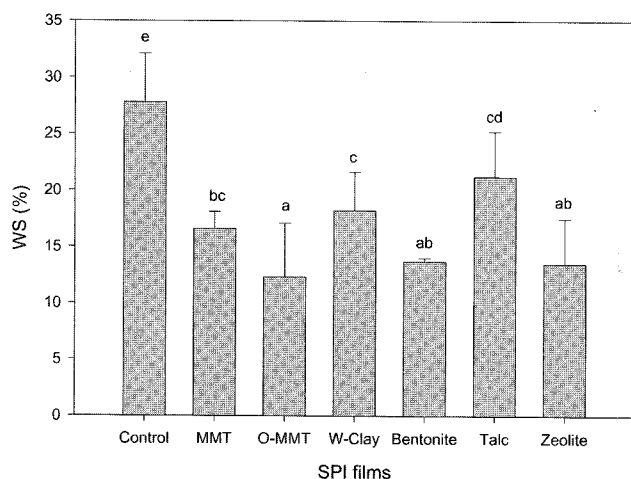


Fig. 5. Water solubility (WS) of SPI and clay composite films.

to increase the gas barrier properties of nanocomposite films by creating a tortuous path that retards the progress of gas molecule through the polymer matrix (30).

Water solubility (WS) Compositing with clay minerals improved the water resistance properties of the SPI film as evidenced by decrease in WS values (Fig. 5). WS of SPI films decreased significantly ($P < 0.05$) by compositing with clay minerals. The decrease in WS ranged from 24 to 56% depending on the clay minerals used. O-MMT was the most effective in improving the water resistance property of SPI films, followed by zeolite, bentonite, MMT, W-clay, and talc. The increase in water resistance may also have been due to the development of a polymeric composite structure with clay minerals. Direct evidence of such a nanocomposite structure could be confirmed through TEM analysis.

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