Preparation and Characterization of Whey Protein Film Incorporated with TiO$_2$ Nanoparticles

J.J. ZHOU, S.Y. WANG, AND S. GUNASEKARAN

ABSTRACT: Biodegradable titanium dioxide (TiO$_2$)/whey protein isolate (WPI) blend films were made by casting denatured WPI film solutions incorporated with TiO$_2$ nanoparticles. X-ray diffraction, UV-vis spectra, and fluorescence spectra of the films showed the successful incorporation of TiO$_2$ nanoparticles into the WPI matrix and indicated the interactions between TiO$_2$ and WPI. Mechanical tests revealed the antiplasticizing effect of TiO$_2$ nanoparticles on the WPI/TiO$_2$ film. Small amounts (<1 wt%) of added TiO$_2$ nanoparticles significantly increase the tensile properties of WPI film, but also decrease the moisture barrier properties. The addition of higher amounts (>1 wt%) of TiO$_2$ improves moisture barrier properties but lowers the tensile properties of the film. Microstructural evaluation confirmed the aggregation and distribution of TiO$_2$ nanoparticles within the WPI matrix and validated the results of functional properties of the WPI/TiO$_2$ film.

Keywords: mechanical properties, microstructure, TiO$_2$ nanoparticles, water vapor permeability, whey protein isolate films

Introduction

Plasticized, self-supporting films made of globular proteins are potentially useful as edible coatings and wrappings (Lefevre and others 2005). Whey proteins are widely used in food products because of their high nutritional value and their ability to form gels, emulsions, or foams (Foegeding and others 2002). The native whey proteins are globular protein complexes but become random coils upon denaturation and form 3-dimensional network when certain conditions are met. This functionality enables whey proteins to be good candidates for biodegradable films. However, films made using whey proteins without any modification have poor moisture barrier properties and relatively low mechanical properties compared with synthetic or other commercial food packaging materials and therefore have limited applications (Alcantara and others 1998; Perez-Gago and others 1999; Fugh-Berman 2000; Ouattara and others 2002; Shaw and others 2002; Yoshida and others 2002; Cisneros-Zevallos and Krochta 2003; Mei and Zhao 2003; Yoshida and others 2003).

High-performance composite materials are actively sought in the quest to add novel properties to polymer-based systems used in the food industry. Recently, the application of the nanocomposite concept is becoming a promising option to improve mechanical and barrier properties of biodegradable biopolymer based films (Avella and others 2005).

Titanium dioxide (TiO$_2$) is an inert, nontoxic, and inexpensive material with potential activity against a wide variety of microbes due to its photocatalytic activity. When TiO$_2$ is incorporated into a polymer matrix such as packaging material, it will provide protection against foodborne microorganisms as well as odor, staining, deterioration, and allergens on the presence of radiation of relatively low wavelength near the ultraviolet region. Thin TiO$_2$ films exhibit excellent mechanical and chemical durability in the visible and near-infrared region (Tazawa and others 2004; Okada and others 2006). Incorporation of TiO$_2$ into synthetic plastic matrix to increase the biodegradability has been investigated (Kubacka and others 2007). However, there has been no attempt to investigate the incorporation of TiO$_2$ nanoparticles into biopolymer matrix.

As a part of the project to develop a new biodegradable and antimicrobial nanocomposite food packaging materials using TiO$_2$, the purpose of this study was to fabricate TiO$_2$ nanoparticles incorporated WPI film and to characterize its physical, mechanical, and functional properties. The results of this study together with ongoing antimicrobial study in our lab are expected to gather the sufficient knowledge to develop a new biodegradable and antimicrobial nanocomposite food packaging materials by incorporating nanostructure TiO$_2$ into biopolymer polymeric hosts matrices as the alternative to synthetic plastics.

Materials and Methods

Materials

TiO$_2$ nanoparticle (anatase, particle size <20 nm) was purchased from Sigma-Aldrich (St. Louis, Mo., U.S.A.). Whey protein isolate (WPI, 98 wt% protein) was obtained from Davisco Foods Intl., Inc. (Eden Prairie, Minn., U.S.A.). All other reagents were of analytical grade. Deionized water was used for all sample preparations.

Preparation of TiO$_2$/WPI blend films

WPI (5%, wt/vol) was dissolved in deionized water, and glycerol (5%, wt/vol) was added to the WPI solution before degassing under vacuum. The solution was heated in a water bath at 90 °C for 30 min and rapidly cooled on ice, followed by vacuum degassing again to remove trapped air bubbles in the solution. Various amounts of TiO$_2$ nanoparticles (0.5% to 4%, w/w) were added to the
Preparation and characterization of whey protein film...

WPI film solutions. To control the dispersion of the TiO₂ nanoparticles in WPI polymeric hosts, both dispersion process and film forming process were carefully conducted to avoid nanoparticles aggregation that tends to negate benefits associated with the nanoscopic dimension. First of all, we choose very small size of TiO₂ nanoparticles (< 20 nm) and disperse them into prepared WPI solution very slowly with intense stirring at the same time, which therefore may help those nanoparticles form colloid composite with whey protein molecules in the film solution. The slow addition and intense stirring can also help added nanoparticles uniformly dispersed into whey protein matrices before they got opportunity to aggregate. Second, we conducted the film formation with a very mild and slow process in controlled temperature and humidity, expecting to obtain a homogeneous nanocomposite. The WPI solution with dispersed TiO₂ nanoparticles was cast on 18.5-cm glass Petri dish that has been coated with Sigmacote® silicone solution (Sigma-Aldrich). The WPI film solution was dried overnight at 35 ± 0.5 °C in an incubator under controlled relative humidity (RH ≈ 40 ± 1%). Dried films were peeled and stored at room temperature.

TiO₂/WPI blend film characterization

**Film solution surface charge measurement.** The surface charge of the denatured WPI film solution and WPI-TiO₂ film solutions were measured using the Zetaplas instrument (Brookhaven Instruments Corp., N.Y., U.S.A.).

**Film thickness.** Thickness of TiO₂/WPI blend films was determined using a micrometer (nr 2804-10, Mitutoyo, Japan). At least 10 measurements were made randomly at 5 locations on each film specimen and the mean value was used as the film thickness. Film specimens of 50 μm thickness were selected for all experiments.

**X-ray diffraction (XRD).** XRD patterns of the WPI/TiO₂ blend films were obtained using an X-ray diffractometer (Scintagge Pad V system with a Ge solid-state detector) with a nickel-filtered Cu Kα radiation beam in the angular range of 20 to 80 (2θ) at a voltage of 40 kV and current of 30 mA.

**Spectrophotometric analyses.** UV-vis spectrophotometer (Shimadzu UV-1601PC, Shimadzu Corp., Kyoto, Japan) was used to obtain transmission/absorption spectra of the TiO₂/WPI blend film in the wavelength range of 200 to 800 nm. The same size of film specimens with well-controlled thickness was carefully chosen, cut, and attached on the measuring cell for UV-vis spectrophotometer.

Fluorescent spectra were also recorded in the wavelength range of 200 to 600 nm and excitation wavelength 235 nm on a MOS-250 fluorescence spectrometer (Biologic, Claix, France).

**Water vapor permeability (WVP).** WVP of the WPI/TiO₂ films was measured using a cup method at approximately 25 °C and 100/50% RH gradient, following ASTM E96 methodology (Kumaran 1998). Films were sealed in plastic chambers (inside diameter of 10 cm and depth of 20 mm). The effective film area was 78.5 cm². Distilled water was used to create a 100% RH environment inside the chambers. The distance between the film and the water surface was 10 mm. WVP test chambers were placed in a temperature- and humidity-controlled incubator conditioned at room temperature and 50% RH. The cup was weighed periodically over 24 h at about 3 h intervals to determine moisture loss over time. The slope of the weight compared with time linear regression plot (Δw/t) was used to determine the water vapor transmission rate (WVTR, g/h m²)

\[
WVTR = \frac{\Delta w}{A} \quad (1)
\]

where Δw is the rate of weight loss (g/h) and A is area of the exposed film surface (m²). WVP (g mm/m²h kPa) was calculated using a modified method described by McHugh and others (1993):

\[
WVP = \frac{WVTR \times t}{\left(p_2 - p_1\right)} \quad (2)
\]

where p₁ and p₂ (kPa) are the partial pressure at the outer and inner surface of the film, respectively; t (mm) is the average film thickness.

**Mechanical properties.** Uniaxial tensile tests were conducted using a universal testing machine (Synergy 200, MTS System Corp., Cary, N.C., U.S.A.) following the standard ASTM D882 method (ASTM 2001). Films specimens were cut into strips with a test dimension of 50 × 10 mm and stored in the chamber at 22 ± 2 °C and 50% ± 5% RH overnight before measurements. The measurements were performed immediately after film specimens were removed from the storage chamber to minimize moisture variation. The specimen was mounted between grip heads with initial grip separation of 20 mm. The test was performed at a crosshead speed of 5 mm/min. Force deformation data were obtained and tensile strength (TS), elongation at break (E_b), and elastic modulus (EM) were calculated

\[
TS(MPa) = \frac{F}{A} \quad (3)
\]

where F is peak force at failure (N) and A is film cross-sectional area (0.5 mm²)

\[
E_b(\%) = \frac{l_b}{l_0} \times 100 \quad (4)
\]

where l₁ is measured elongation at break (mm) and l₀ is original specimen length (20 mm)

\[
EM(MPa) = \frac{\Delta F}{\Delta l/l_0} \quad (5)
\]

where ΔF and Δl are change in force and corresponding change in specimen length during initial linear deformation.

**Scanning electron microscopy (SEM).** The surface morphology of TiO₂/WPI films was visualized using a field-emission scanning electron microscope (JEOL JSM-6100, Tokyo, Japan) operated at an accelerating voltage of 10 keV. The film specimens were dried in vacuum at room temperature, mounted on a metal stub, and sputtered with gold for conductivity. The images were taken at 4500× magnification.

**Atomic force microscopy (AFM).** AFM imaging of the TiO₂/WPI film was conducted under ambient conditions using a multimode nanoscope (Digital Instruments, Santa Barbara, Calif., U.S.A.) operating in tapping mode. Micro-fabricated silicon cantilever tips with a resonance frequency of 299 kHz and a spring constant of 20 to 80 N/m were used.

**Statistical analyses.** All experiments were performed at least in triplicates. Data were analyzed by one-way analysis of variance (ANOVA). A 95% confidence level was applied for all statistical analyses.

**Results and Discussion**

TiO₂/WPI film X-ray diffractogram

The X-ray diffractograms of WPI film and WPI/TiO₂ blend films are displayed in Figure 1. An anatase characteristic structure of
TiO$_2$, indicated by star symbols, was found in TiO$_2$/WPI blend films ($2\theta = 26, 37, 48, 55, 63, 70$, and $75^\circ$). After refinement, the lattice constants, $a = 3.741$ Å and $c = 9.505$ Å, were obtained, which can be reconciled with anatase lattice TiO$_2$ standard (JCPDS card nr 21-1272). The average crystallite size from TiO$_2$ was estimated to be 80 nm based on the Scherrer equation, $D = \kappa \lambda / \beta \cos \theta$, where $D$ is the crystallite size, $\kappa$ is shape factor of average crystallite, $\lambda$ is the wavelength of the x-ray radiation, $\beta$ is the line width (obtained after correction for the instrumental broadening), and $\theta$ is the angle of diffraction (Murugan and others 2006). The average crystallite size is consistent with the average granule size estimated from AFM (Figure 2) at the same TiO$_2$ concentration (4, wt%). Considering the anatase TiO$_2$ nanoparticles used were 20 nm before incorporating into WPI, the bigger size of particles of anatase phase observed in TiO$_2$/WPI films can be attributed to the agglomeration of TiO$_2$ nanoparticles in WPI matrix.

The intensity of signal depends on the TiO$_2$ concentration incorporated into the WPI matrix. A clear signal of diffraction peaks starts to appear when 4 wt% TiO$_2$ content was present in the film, indicating the presence of crystalline anatase TiO$_2$ in the WPI film matrix. This result was confirmed by AFM images in Figure 2. The rest of the weak XRD peaks in Figure 1 are attributed to WPI crystalline phase. Since the majority matrix of the blend films is WPI, the similar pattern of XRD was found in all the film specimens with different TiO$_2$ concentrations, whereas only the intensity of the peaks varied.

**Microstructure**

Tapping mode AFM images yielded information about the surface features of the film, as good complimentary of SEM images. In this mode, the probe cantilever is oscillated at or near its resonant frequency. A granular morphology of 4% TiO$_2$ films from AFM image, depicted in Figure 2, is in good agreement with the results of XRD, suggesting the presence of crystalline grains of anatase of TiO$_2$ nanoparticles. The surface topography (a) and 3-dimensional images (b) of WPI/TiO$_2$ blend films exhibited the heterogenous surface (WPI matrix) with small patches of particles (TiO$_2$ nanoparticles or aggregates) in the size range of 0 to 200 nm (Figure 2A) protruded from WPI matrix surface in the size range of 0 to 80 nm (Figure 2B). The average surface roughness and peak-to-peak height are about 100 and 50 nm, respectively, which is in good agreement with XRD results. Some agglomerates (size $> 500$ nm) were also observed from AFM images.

The surface images obtained from scanning electron microscope (Figure 3) were compared with the surface structure of WPI/TiO$_2$ films of different TiO$_2$ concentrations with WPI film (white spots indicate TiO$_2$ crystals or agglomerates). The smooth structure of WPI film (Figure 3A) was observed whereas the granular structure on the surface of blend films appeared when TiO$_2$ was incorporated (Figure 3B and C). The discontinuous phase and more agglomerates can be clearly observed in the microstructure as the concentration of TiO$_2$ was increased (Figure 3C). It can also be seen from Figure 3C that TiO$_2$ in the higher concentration is almost distributed into the entire WPI matrix, behaving like a coating that may alter the film properties.

**Spectroscopy properties**

Figure 4 shows the UV-vis transmittance spectra of the WPI/TiO$_2$ film. Owing to the strong UV absorption of TiO$_2$ nanoparticles ($\lambda_{max} = 340$ nm), the transmittance of the blend films was much
lower than that of WPI film in the 300 to 400 nm UV region, whereas similar transmittance or absorbance under 300 nm was found due to the strong absorption of WPI around 290 nm and because the WPI concentration was constant and only the TiO$_2$ concentration varied. In the visible light region, the transmittance of WPI film was 80.1% at 700 nm, which looks very transparent. However, the transmittance of the WPI/TiO$_2$ films decreased dramatically in the visible region as the TiO$_2$ content was increased, which can also be seen from the opaqueness of the fabricated blend film as indicated by the picture in Figure 5.

As TiO$_2$ nanoparticles content reached 4 wt%, nearly all the visible and ultraviolet spectra were absorbed or scattered. The properties of high opacity and UV absorption of the WPI/TiO$_2$ blend films indicate the potential applications in food packaging by slowing the deterioration process.

Fluorescence spectroscopy is useful in providing important information about chemical and physical properties as well as changes in several types of complex food products (Munck and others 1998; Zandomeneghi and others 2005; Christensen and others 2006). Whey proteins are a mixture of several proteins including $\beta$-lactoglobulin, $\alpha$-lactalbumin, immunoglobulins, bovine serum albumins, and so on; the amino acid composition of all these component proteins consists of at least 1 tryptophan residue (Walstra and others 1999). Owing to the complexity of protein components and concentrations of each protein, the excitation and maximum emission wavelength of whey protein exhibits variations in the 280 to 295 and 330 to 350 nm region, respectively. A characteristic fluorescence emission spectrum was defined by its maximum emission wavelength and the tryptophan quantum yield. The maximum emission wavelength of 350 nm observed for WPI film was different from the typical WPI emission maximum wavelength of 331 nm. The difference can be attributed to the denatured state of WPI (Marangoni and others 2000) and the effects of added glycerol (Mao and others 2003).

Fluorescence is also a useful tool to identify the interactions among protein and other molecules in conjugates or blends (Andersen and Mortensen 2008). As shown in Figure 6, there is a significant quenching of fluorescence in WPI/TiO$_2$ blend films as compared to that in the WPI film. The more the TiO$_2$ nanoparticles are incorporated into the film, the more quenching of fluorescence intensity was found. The fluorescence quenching in WPI/TiO$_2$ film could be attributed to (1) photo-induced charge transfer from excited protein molecules to TiO$_2$ and (2) resonance energy transfer between species in the excited state, respectively, due to an overlap of emission and absorption spectra. The resonance energy transfer and photo-induced transfer are closely related to the charge of the participating donor and acceptor molecules and excitation energy required. The surface charge of denatured WPI and TiO$_2$ nanoparticles were $-45$ and 2.5 mV, respectively, determined by Zeta potential measurement, indicating that WPI is electron donor and TiO$_2$ is electron acceptor. The fluorescence quenching may be due to the electron transported from excited WPI to TiO$_2$ indicated by reduced emission intensity. The quenching effects of fluorescence intensity are more significant as more TiO$_2$ nanoparticles were incorporated.
Preparation and characterization of whey protein film . . .

into the WPI matrix. The low concentration of TiO$_2$ in the WPI matrix may result in less chance of electron transport path from WPI to TiO$_2$. When TiO$_2$ content increased, more physical contact between WPI and TiO$_2$ or between TiO$_2$ molecules were built and therefore improved the charge transfer, contributing to increased fluorescence quenching effect (Greenham and others 1996). A red shift of maximum emission peak to 390 nm was observed from 0.5% TiO$_2$ incorporated blend film as compared with peak at 350 nm of WPI film, indicating the conformational change of Trp or Tyr residues, which is in agreement with the published results that the fluorescent amino acids tyrosine and tryptophan are responsible for the intrinsic fluorescence of whey proteins (Pulgarin and others 2005).

**TiO$_2$/WPI blend film functionalities**

TS, EM, and $E_b$ values of WPI/TiO$_2$ blend film containing varied TiO$_2$ concentration are reported in Table 1. The incorporation of TiO$_2$ nanoparticles significantly affected the EM of WPI film ($P < 0.05$). In general, WPI-TiO$_2$ blend film has higher EM and TS but lower $E_b$ than WPI films. Previous studies have reported that the incorporation of a compound with a plasticizer effect generally decreases EM and TS of a biopolymer film and increases $E_b$ (McHugh and Krochta 1994; Sothornvit and Krochta 2001), indicating the antiplasticizing effect of TiO$_2$ in WPI matrix, that is, the WPI film became more brittle with TiO$_2$ addition.

WPI films with a small amount of TiO$_2$ (<1 wt%) had the highest EM and TS values, which may be attributed to the interactions between TiO$_2$ and WPI molecules. The possible interactions involve electrostatic attraction between negatively charged carboxylic or sulphhydryl groups from certain amino acids of WPI and positively charged Ti$^{4+}$–water complex during the preparation of WPI-TiO$_2$ film solution. Hydrogen bonding or O–Ti–O bonding may also contribute to the increase in tensile properties of blend films. Similar studies regarding interactions on ZnO–whey protein nanocomposite have been reported (Shi and others 2008).

It is interesting to see that the EM and TS values decreased when more TiO$_2$ nanoparticles (>1 wt%) were added. The possible reason for decrease in tensile properties might be inhomogeneous distribution of TiO$_2$ and aggregation of TiO$_2$ in the WPI matrix. TiO$_2$ is more hydrophobic than WPI molecules and therefore tends to aggregate when certain concentration is reached to reduce energy dissipated in the system, which is confirmed by our SEM, AFM, and XRD results. The aggregation will discontinue the aggregated protein domains and amorphous protein domains of the WPI film and consequently reduce tensile properties of the blend films. Similar results for lactoperoxidase incorporated WPI films have been reported (Min and others 2005).

From Table 1, although tensile strength of the blend film increased significantly, $E_b$ reduced as TiO$_2$ was added (especially >2 wt%), which may limit its application as food packaging material due to antiplasticizing effects of TiO$_2$. However, the highest TS

**Figure 5** — Film pictures of pure WPI film (left) and TiO$_2$/WPI blend film containing 0.5% TiO$_2$ nanoparticles (right), showing visualized different transparency.

**Figure 6** — Emission fluorescence spectra of (A) WPI film, (B) WPI/TiO$_2$ blend film containing 0.5 wt% TiO$_2$ nanoparticles, and (C) WPI/TiO$_2$ blend film containing 4 wt% TiO$_2$ nanoparticles (excitation wavelength is 235 nm).
Preparation and characterization of whey protein film...

and EM values were found when TiO2 concentration is 0.5% without a significant decrease in % (P > 0.05) compared with WPI film, suggesting the 0.5% is the optimum amount of TiO2 to reach the best mechanical properties of the blend films in our experimental conditions. The mechanical properties of blend films may otherwise be improved by changing concentration or type of plasticizer in the film (McHugh and Krochta 1994).

Figure 7 shows the effects of TiO2 nanoparticle concentration on WVP properties of blended films. Statistical analysis indicates a significant effect of TiO2 concentration on WVP (P < 0.05). When a small amount of TiO2 nanoparticles (TiO2 < 1 wt%) was added into WPI film, WVP increased compared with when no TiO2 was added, indicating less water barrier capability. This could be attributed to the decreased cross-linking in WPI film matrix due to the presence of TiO2 particles. Nevertheless, WVP of blend films decreased significantly as the concentration of TiO2 was increased beyond 1 wt%. The contradictory results can be explained as the low water solubility of TiO2 compared with WPI, suggesting the potential applications of TiO2 as the hydrophobic coating, as discussed in the SEM results (Figure 3), to improve the water barrier properties of biopolymer films. In addition, the prolonged tortuous pathway of water vapor caused by TiO2 nanoparticles concentration above certain concentration may also contribute to the WVP decrease (Bharadwaj 2001).

Since one of the main functions of food packaging is often to avoid or at least to decrease the moisture and gas transfer between the food and the surrounding atmosphere or between the 2 components of a heterogeneous food product, the water vapor permeability of the packaging material should be as low as possible (Gontard and others 1992). However, most of the biodegradable films made from biopolymers suffer from the low water barrier properties and therefore have limited applications. TiO2 coating on film surface may be an alternative to improve the water barrier properties.

In addition, water vapor permeability of biopolymer films is strongly correlated with the film thickness (Sezer and others 2007). To reduce or eliminate the effect of film thickness, the film thickness was carefully controlled in the range of 48 to 53 μm (Figure 7). However, the unavoidable difference in film thickness may still contribute to variations in WVP values.

**Conclusions**

The results indicate that TiO2 nanoparticles can be incorporated into WPI matrix to make WPI/TiO2 blend films. The TiO2 concentration in WPI matrix determines the functionalities of the film such as WVP and mechanical properties. Compared to WPI films, addition of low amount of TiO2 (<1 wt%) provides WPI/TiO2 films improves mechanical properties but decreases moisture barrier properties. When TiO2 addition exceeds 1 wt%, the mechanical properties suffer but water vapor permeability improves. The distribution of TiO2 nanoparticles and the interaction between TiO2 particles and between TiO2 and denatured WPI molecules are closely related to the physical properties, microstructure, and functionalities of the TiO2/WPI blend films. In summary, under the current processing conditions, 1% TiO2 nanoparticles can be regarded as the optimum concentration to make the TiO2/WPI blend films with relatively balanced physical properties and improved mechanical properties. However, the improvement of processing techniques may allow homogeneous distribution of TiO2 and prevent

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**Table 1** — Tensile properties of the whey protein isolate (WPI)–TiO2 composite films.

<table>
<thead>
<tr>
<th>TI02 concentration (wt%)</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
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<tr>
<td>EM (MPa)</td>
<td>31.44 ± 3.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>66.67 ± 2.82&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>63.09 ± 1.98&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>44.54 ± 2.26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>39.23 ± 3.65&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>TS (MPa)</td>
<td>1.69 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.38 ± 0.23&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>2.19 ± 3.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.88 ± 0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.78 ± 0.08&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>E&lt;sub&gt;b&lt;/sub&gt; (%)</td>
<td>55.56 ± 1.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>54.08 ± 0.98&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>40.11 ± 1.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.15 ± 0.56&lt;sup&gt;c&lt;/sup&gt;</td>
<td>12.14 ± 0.22&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
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</table>

<sup>a</sup>Values are recorded as mean ± standard deviations (3 replicates). Different letters within the same row indicate significant differences (α = 0.05).

<sup>b</sup>EM = elastic modulus; TS = tensile strength; E = elongation at break.

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**Figure 7** — Water vapor permeability (WVP) (line) and thickness (bars) of WPI/TiO2 blend films with different TiO2 nanoparticle concentrations.
nanoparticles from aggregation in the WPI matrix, making it possible to incorporate more TiO$_2$ into WPI polymeric matrices with desired mechanical and WVP properties. The composite film has the potential to be used as food-grade, biodegradable packaging materials.

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References


