Research Article

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Ultrasonic-modified montmorillonite uniting ethylene glycol diglycidyl ether to reinforce protein-based composite films

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Abstract: A novel biodegradable protein-based material (UMSPIE) that consists of natural polymer soy protein isolate (SPI), ultrasonic-modified montmorillonite (UMMT), and ethylene glycol diglycidyl ether (EGDE) was produced by solution casting. Fourier infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TG), and scanning electron microscopy (SEM) were used to characterize the chemical structure and micro-morphologies of as-synthesized protein-based composite films. The results showed that the interlayer structure of MMT was destroyed by ultrasonic treatment, and the hydrogen bonding between SPI chains and the ultrasound-treated MMT plates was enhanced. The synergistic effect of UMMT and EGDE on SPI molecules made the network structure of the UMSPIE film denser. In addition, the mechanical and barrier properties of the as-synthesized films were explored. Compared with pure soy protein film, the tensile strength of the UMSPIE film has an increase of 266.82% (increasing from 4.4 to 16.14 MPa). From the above, the modified strategy of layered silicates filling combining crosslinking agents is considered as an effective method to improve the functional properties of bio-based polymer composites.

Keywords: ultrasonic-modified montmorillonite, crosslinking agent, network structure

1 Introduction

Environmental and food safety problems due to disposable plastic packaging materials have been the focus of people’s attention. Researchers favor the development and use of materials, which are healthy, sustainable, and environmental friendly (1). There are natural polymers (such as protein, starch, chitosan, cellulose), which are excellent candidates to replace petroleum-based materials owing to their good biocompatibility, excellent biodegradable, abundant reserves (2,3). As one of the natural polymers, soybean protein isolate (SPI) has the potential to be used in food packaging due to its low price, extensive raw material sources, easy process, and good film formation. However, its inferior physical-mechanical properties have restricted its practical application. To overcome these challenges, numerous strategies have been explored to modify SPI-based films: ordinary methods including the physical method (4), the chemical method (5), enzyme treatment (6), and organic and inorganic blending (7).

As a typical layered silicate, montmorillonite (MMT) possesses a unique lamellar structure and adjustable interlayer spacing. And, it is used to improve the mechanical properties of composites because of their high surface area, low price, plentiful sources, and excellent mechanical properties (8,9). Research showed that the effect of nano-fillers on the performances of composites depends on the dispersion degree of the nano-filler in the matrix and the interaction between the nano-filler and the matrix (10). The higher the dispersion degree of the nano-filler in the matrix, the greater the influence. The stronger the interaction between the nano-filler and the matrix, the greater the effect is. However, due to the surface hydrophilicity of MMT, MMT nanosheets are easy to self-assemble and hard to sustain stability in water solution, which limits the application of MMT as nano-reinforced fillers (11). MMT nanosheets can be exfoliated by ultrasonic treatment to improve their dispersity and interaction with organic material by previous studies (12). Wang et al. (13) prepared...
1–5 nm MMT nanosheets by ultrasonic, which were added into the chitosan matrix to fabricate MMTNS/CS hydrogels. And, the results indicated that exfoliated MMTNS endowed as-synthesized hydrogels with a tremendous specific surface area. Tepmatee and Siriphanom (14) studied the effect of conventional intercalation and ultrasonic-assisted intercalation on preparing aluminum-pillared montmorillonite adsorbent and found that the ultrasonic-assisted method could improve the intercalation efficiency and increase the amount of intercalated $\text{Al}^{3+}$ in the MMT. Kaur et al. (15) studied MMT and CNCs as reinforcement materials modifying chicken feather keratin. Results indicated that the tensile strength of the composite was enhanced significantly with the addition of MMT.

Generally, synergistic enhancement is superior to a single modification. The use of crosslinking agents is also generally considered to improve the performance of proteins. Ethylene glycol diglycidyl ether (EGDE) is a common crosslinking agent because it has epoxy groups at both ends, which can react with amino, hydroxyl, carboxyl, and other active groups. SPI molecules contain a large of amino groups, which can form a dense three-dimensional network structure by the ring-opening reaction with the epoxy groups of EGDE (16,17). Wang et al. (16) prepared a soy protein isolate plastic with anionic waterborne polyurethane. The study revealed that the crosslinked SPI/WPU plastics with EGDE possessed excellent mechanical properties and water resistivity. In addition, EGDE was also used to crosslink hydroxyethyl cellulose and SPI to prepare composite sponges. The composite sponges exhibited uniformly interconnected porous structures on their surfaces and cross-sections (average pore size $\geq 220 \mu m$) and good mechanical property (18).

Accordingly, in this study, we investigated ultrasonic-modified MMT and EGDE into SPI-based composite film as a filling and a crosslinking agent, respectively. It was expected that the addition of ultrasonic-modified MMT and EGDE can improve the mechanical and barrier properties of SPI-based composite films. The prepared SPI-based composite films were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric (TG) analysis.

## 2 Materials and methods

### 2.1 Materials

Soy protein isolate (protein content >95%) was provided by Shandong Yuwang Ecological Food Co., Ltd. Montmorillonite (type: KSF, surface area: 20–40 m$^2$/g) was purchased from Shanghai McLean Biochemical Reagent Co., Ltd. EGDE was purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Glycerin (99% purity) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Sodium hydroxide was provided by Chengdu Kelong Chemical Reagent Co., Ltd. All materials were directly used as received without further purification.

### 2.2 Preparation of MMT and UMMT suspensions

1 g MMT was added into 99 g water and stirred for 24 h to fabricate 1% w/w MMT suspension. To obtain a 1% w/w UMMT suspension, 1% w/w MMT suspension was further processed by 500 W ultrasonic for 30 min.

### 2.3 Preparation of UMSPIE film

The preparation method of UMSPIE films was similar to the way described in the literature (7). SPI powders (2.5 g) were mixed with distilled water (47.5 g), and then glycerol (0.75 g) was added as a plasticizer. After magnetic stirring, 10% NaOH solution was added to regulate the SPI suspension pH to 9 ± 0.5, and 5% SPI solution was obtained after stirring and heating at 80°C for 30 min. Next, desired amounts of UMMT suspension and EGDE solution were mixed with 5% SPI solution by magnetic stirring for 10 min. Subsequently, the mixture was dispersed with ultrasonic treatment for 5 min with the power of 40 W to obtain a homogeneous solution. The solution was slowly poured into plastic Petri dishes to avoid the appearance of bubbles, and the plastic Petri dishes were uniformly dried in a constant temperature and humidity box (40°C and 40 RH%) for 24 h. For comparison, the same method was used to prepare undecorated SPI film and decorated SPI films modified by MMT or EGDE. Detailed ingredients of all protein-based composite films were exhibited in Table 1. All the obtained films were placed in a desiccator (humidity of 57 ± 2 RH%) for 48 h to stabilize moisture content, which is used for physical and mechanical properties testing and characterization analysis.

### 2.4 Measurement

#### 2.4.1 Measurement of mechanical properties

The mechanical properties of films include tensile strength (TS), elongation at break (EB), and elastic modulus ($E$). For
mechanic testing, SPI composite films were cut into strip samples with a width of 10 mm and a length of 80 mm. Then, the strip sample film was fixed on a general mechanical testing machine (AG-X Plus, Shimadzu Corporation, Kyoto, Japan), which was equipped with a 50 N sensor. The initial gap between the upper and lower clamps was 50 mm. The stretching speed was set to 50 mm/min. The TS was calculated as follows:

$$TS = \frac{F_m}{T \times W},$$  

(1)

where $F_m$ is the break longitudinal tensile force (N) of the film, $T$ is the thickness of the film (mm), and $W$ is the width of the film (mm).

The equation for calculating EB was as follows:

$$EB = \frac{L_m - L_0}{L_0} \times 100\%,$$  

(2)

where $L_m$ is the length of the film at the break (mm) and $L_0$ is the length of the film before testing (mm).

The equation for calculating $E$ was as follows:

$$E = \frac{\sigma}{\varepsilon},$$  

(3)

where $\sigma$ is the stress on the film (MPa) and $\varepsilon$ is the strain of the film (%).

### 2.4.2 Water content

Sample film was cut into a square sample of $20 \times 20$ mm and was weighed ($M_1$). Then, the film was placed in a dryer containing $P_2O_5$ (with a relative humidity of 0%) to dry (about 24 h). When the film weight reached a constant, the weight was marked ($M_2$). The water content (WC) was calculated as follows:

$$WC = \frac{M_1 - M_2}{M_1} \times 100\%. $$  

(4)

### 2.4.3 Moisture absorption

The moisture absorption (MA) of sample film was stated by the following procedure. The film sample ($20 \times 20$ mm) was dried until reaching a constant weight ($M_3$) in a dryer containing $P_2O_5$ (with a relative humidity of 0%). The dried sample was placed in a dryer containing calcium chloride saturated solution (80%) to absorb water. After 24 h, the film weight was marked ($M_4$). Then, we can calculate MA by the following formula:

$$MA = \frac{M_3 - M_2}{M_2} \times 100\%. $$  

(5)

### 2.4.4 Total solubility matter

The dried film ($20 \times 20$ mm) was added to a beaker containing 100 g of water. The beaker was shaken in intervals for 24 h at 25°C. The undissolved substance was removed and placed in the oven at 60°C to dry completely. The residuum was weighed and recorded as $M_5$. The total solubility matter (TSM) was calculated by the following formula:

$$TSM = \frac{M_5 - M_4}{M_2} \times 100\%. $$  

(6)

### 2.4.5 Water vapor permeability

The water vapor permeability (WVP) experiment was carried out at $25 \pm 2°C$. Sample film was horizontally sealed on the round test container mouth comprising $P_2O_5$ to create a 0 RH% condition, and the initial weighing of the test container was performed. Subsequently, the container was placed into a dryer with a saturated solution of calcium chloride (humidity: 80%) to maintain the
relative humidity difference of 0/80% on both sides of the films. The change in container weight was recorded at intervals of 1 h. The WVP was calculated as follows:

\[
WVP = \frac{\Delta M \times T}{s \times t \times \Delta p},
\]

where \(\Delta M\) is the weight increment of the container (g), \(T\) is the thickness of the sample film (mm), \(s\) is the permeation area of the sample film, \(t\) is the time interval for permeation (s), and \(\Delta p\) is the vapor pressure difference.

2.5 Characterization

X-ray diffraction (XRD) measurement was conducted on Smart Lab with monochromatic radiation of Cu, a voltage of 40 kV, and current of 40 mA. The diffraction angles were collected from 5° to 60° at a scan speed of 5/min. The micro-morphology of the different SPI composite films was evaluated by SEM imaging on a JSM-7500F field emission electron microscope with an acceleration voltage of 5 kV. And, the SEM imaging magnification was 5,000× and 2,000×. The microstructural changes of samples were observed by attenuated total reflectance FTIR (ATR-FTIR; Nicolet 6700 Nicolet Instrument Corporation, USA). The spectra were collected in the range of 4,000–400 cm\(^{-1}\). DSA100 contact angle measuring instrument (KRUSS Co., Ltd., Hamburg, Germany) was used to determine the contact angle of samples, and the experimental temperature was controlled at 25 ± 2°C. The sample (20 × 80 mm) was fixed on a horizontal slide, and then a digital microsyringe was used to drop 5 L of water droplets on the sample surface. The thermal performances of all SPI composite films were determined by thermogravimetric analysis (TGA; Q50, TA Instruments, Massachusetts, USA). The samples were placed in desiccators containing P\(_2\)O\(_5\) with a relative humidity of 0% to dry, and drying was stopped when the quality does not change. Then, under the condition of heating rate 10°C/min and nitrogen flow rate 60 mL/min, the samples were heated from room temperature to 600°C.

3 Results and discussion

3.1 Mechanical properties of films

The tensile strength (TS), elongation at break (EB), and elastic modulus (E) of prepared SPI-based films are studied (Figure 1a–c). After adding MMT, the TS of the MSPI film is higher than that of the original SPI film, which attributes the existence of the hydrogen bond interaction.
between MMT and SPI molecules when MMT slice layers are blended into the SPI matrix. However, MMT has strong hydrophilicity and self-accumulating ability, so only part of MMT interacts with SPI molecules. After ultrasonic treatment, the multi-layer structure of UMMT is disrupted and SPI molecules enter more easily into the layers of modified MMT, enhancing their hydrogen bonding interaction, causing the TS of UMSPIE film higher than that of MSPI film. In contrast to pure SPI film, the addition of EGDE significantly also improves the TS of the SPIE film. This is because the two epoxy groups at the end of EGDE molecules have the ring-opening reaction with –NH₂ in SPI molecules. A dense cross-linking network is formed between EGDE molecules and SPI chains. When UMMT and EGDE are added to the SPI matrix at the same time, the cross-linking interaction between UMMT, EGDE, and SPI molecules is further enhanced, making the three-dimensional structure of SPI film stronger. Compared to the pristine SPI film, the TS of the UMSPIE film achieves an increment of 266.82%.

### 3.2 Water-resistance properties of films

The WC, MA, TSM, and WVP of SPI composite films are investigated in Table 2. SPI molecules contain a large of polar groups, such as –OH, –NH₂, and –COOH. So, the pure SPI film is hydrophilic. It can be detected that the WCs of MSPI, UMSPIE, SPIE, and UMSPIE films have a decrement when compared with the original SPI film. The WC of the MSPI film decreased. It is because MMT interacts with SPI molecules forming hydrogen bond association. However, SPI molecules cannot greatly enter the interlayer of MMT, and a little aggregation of MMT exists in the solution. By contrast, the ultrasonic treatment can expand the interlayer spacing of MMT. Hence, UMMT has larger layer spacing, and the hydrogen bond interaction between UMMT and SPI molecules is enhanced. Thus, the UMSPIE film has lower water content in contact with MSPI film. The reason for the WC decreasing of SPI film is that the epoxy groups of EGDE molecules can react with the –NH₂ of the protein molecules and their long chains are entangled with each other, reducing the exposure of polar groups. The WC of UMSPIE film declines owing to the synergistic effect of UMMT and EGDE on SPI molecules. There are different degree decreases for the TSMs, MAs, and WVPs of the SPI-based composite films except for pure SPI film. The TSM, MA, and WVP of the UMSPIE film present a decrement of 40.29%, 34.75%, and 37.0%, respectively. It is because SPI molecules not only exist hydrogen bond interaction with UMMT but also have the ring-opening reaction with EGDE. The incorporation of the nano-filler and the cross-linking agent can make the SPI composite film to form a compact network structure and discourage the invasion of water molecules.

### 3.3 FTIR spectra of films

FTIR was used to investigate the chemical structure of SPI-based films. Figure 2 showed the FTIR spectra of SPI, MSPI, SPIE, and UMSPIE films. For all protein films, they were presenting similar spectra. Three characteristic amide bands at 1,629, 1,536, and 1,237 cm⁻¹ were assigned to hydrogen bonding of SPI molecules and glycerol (19). Compared to the native SPI film, after the incorporation of MMT, UMMT, and EGDE into SPI matrix, the absorption bands at 3,600−3,000 cm⁻¹ became broader and stronger (Figure 2; MSPI, SPIE, and UMSPIE). The variation was ascribed to strengthen the hydrogen bonding between MMT, EGDE, and SPI matrix. The absorption peak at 1,043 cm⁻¹ was attributed to C−O−C asymmetric stretching vibration, and it was weakened in the SPIE film and the UMSPIE film. The result corresponded to the previous study (17), demonstrating the occurrence of ring opening between EGDE and SPI.

### Table 2: WC, TSM, MA, and WVP of the SPI-based composite films

| Films | Water content (%) | Total soluble matter (%) | Moisture absorption (%) | Water vapor permeability (×10⁻¹⁹ g cm⁻¹ s⁻¹ MPa⁻¹) |
|-------|-------------------|--------------------------|------------------------|-----------------------------------------------|
| SPI   | 15.5 ± 1.5        | 81.9 ± 8.8               | 86.9 ± 14.9            | 7.81 ± 1.44                                  |
| MSPI  | 14.5 ± 1.7        | 68.7 ± 7.0               | 82.0 ± 9.9             | 6.42 ± 0.84                                  |
| UMSPIE| 13.8 ± 1.1        | 64.6 ± 11.7              | 77.2 ± 12.0            | 6.03 ± 1.36                                  |
| SPIE  | 13.2 ± 0.7        | 49.6 ± 11.3              | 62.0 ± 7.8             | 5.08 ± 1.31                                  |
| UMSPIE| 12.3 ± 1.5        | 48.9 ± 3.7               | 56.7 ± 2.9             | 4.92 ± 0.64                                  |
molecules. The cross-linking mechanism between MMT, EGDE, and SPI chains was provided in Scheme 1.

3.4 XRD patterns of films

Figure 3 shows the XRD pattern of MMT and SPI powders as well as SPI-based composite films. The XRD diagram for pure MMT revealed many sharp peaks, following previous results from other studies (20,21). The disappearance of the peaks meant the destruction of the layered structure. Two peaks at $2\theta = 8.8^\circ$ and $21.2^\circ$ appeared in the SPI powder, suggesting that there were some ordered structures due to the $\alpha$-spiral crystal structure and $\beta$-folded crystal structure of the SPI molecules (22). Compared with pure MMT, some sharp diffraction peaks disappeared for the MSPI film, indicating that the MMT structure has changed. It was ascribed that the MMT was intercalated by SPI molecules partially. However, when the ultrasonic-treated MMT contacts with the protein matrix, the sharp diffraction peaks of UMSPI practically vanish. The result implied that ultrasonic treatment destroyed the MMT platelets and even exfoliated them, the crystal plane spacing became wide, and the layered structure disappeared. After the addition of EGDE, the peak at $8.8^\circ$ disappeared in the patterns of SPIE and
UMSPIE, indicating that such ordered structures were destroyed by the crosslinking reaction. The crystallinity of the protein increased with the addition of MMT or UMMT. When UMMT and EGDE were added, the α-spiral crystal structure disappeared and the β-folded crystal structure widened.

3.5 Thermal stabilities of films

The thermal stability of different SPI-based composite films was examined with TG analyses. The typical weight-loss trends and derivative TG (DTG) curves of all composite films were observed; the data are detailed in Figure 4a and b and Table 3; the testing temperature was in the range from 30°C to 600°C. Three obvious weight losses of the SPI-based composite films were observed at the range of 30–150°C, 150–260°C, and 260–500°C, assigned to the evaporation of adsorbed water, the degradation of glycerol, and the thermal degradation of protein chains, respectively (23). At the third stage, the maximum temperature at the maximum degradation rate of the SPI film was 301.09°C and the SPIE film was 317.88°C. The raising was attributable to the occurrence of the ring-opening reaction between SPI and EGDE chains. In contrast with the virgin SPI film, the addition of nanoparticles increased the residual weight of composite films (MSPI or UMSPI), as montmorillonite contained non-volatile silicon or aluminum remaining in the films’ decomposition residuum.

Table 3: Thermal degradation data of the SPI-based composite films

| Samples | $T_{i1}$ ($^\circ$C)$^a$ | $T_{i2}$ ($^\circ$C)$^b$ | $T_{i3}$ ($^\circ$C)$^b$ | $T_{i4}$ ($^\circ$C)$^b$ |
|---------|----------------|----------------|----------------|----------------|
| SPI     | 116            | 246            | 267            | 301            |
| MSPI    | 125            | 245            | 266            | 308            |
| UMSPI   | 118            | 246            | 267            | 307            |
| SPIE    | 116            | 199            | 248            | 317            |
| UMSPIE  | 115            | 194            | 244            | 318            |

$^a$ $T_i$, degradation onset temperature. $^b$ $T_{max}$, temperature at the maximum degradation rate.
3.6 Surface morphologies of films

The SEM images of cross-sections of SPI-based composite films are shown in Figure 5. The rough surface containing cavities was observed at the fracture section of the pure SPI film, likely caused by the evaporation of gas (24). And there are some tiny cracks due to the complete dryness of the pure SPI film (Figure 5a). For the MSPI film, the tiny cracks disappeared. This was attributed to the hydrogen bond interaction between MMT and SPI molecules, which made the MSPI film internal closely. However, MMT layers were observed to scatter unevenly in the SPI matrix (Figure 5b) demonstrating that the compatibility between MMT and the SPI matrix was bad and only a bit of MMT layers was intercalated by SPI chains. Compared with MSPI film, the treated MMT was more evenly dispersed in the SPI matrix, which indicated that the ultrasonic treatment causes the MMT layer spacing to enlarge or the MMT plates to exfoliate. The SPI chains were more easily intercalated into the treated MMT layers (Figure 5c). After EGDE cooperates with the SPI matrix, the cross-section of the SPIE film becomes denser, with significantly lower roughness (Figure 5d). There was a close cross-linked network between EGDE and SPI molecules due to the occurrence of the ring-opening reaction, which reduced the roughness of the SPI composite film. When UMMT and EGDE were added to the SPI matrix as filler particles and crosslinker, respectively, synergistically acting on the UMSPIE film makes its cross-section denser (Figure 5e).
4 Conclusion

In this paper, a series of novel SPI-based composite films were prepared by the routine solution casting method. And, the effects of UMMT and EGDE on the protein-based film mechanical properties, moisture content, hygroscopicity, total dissolved substances, and water vapor transmittance were investigated. The results established that ultrasonic treatment could destroy the layered structure of MMT, which facilitated the intercalation of SPI molecules. Numerous MMT single layers were uniformly dispersed in SPI composite films. The hydrogen bond interaction between MMT and SPI molecules and then crosslinked by EGDE made SPI film becoming compact. The incorporation of the ultrasonic-modified montmorillonite and the crosslinking of EGDE significantly improved the tensile strength of the composite film. Besides, the SPI-based composites that contained modified montmorillonite and EGDE had improvements in barrier properties as well. Based on these facts, ultrasonic-modified montmorillonite combining EGDE reinforced SPI-based composites may be an appropriate candidate in the food packaging over the coming years.

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