

Research Article

Physical-Chemical Properties of Edible Film Made from Soybean Residue and Citric Acid

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Received 27 December 2017; Accepted 19 April 2018; Published 6 June 2018

Academic Editor: Ana Moldes

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The effect of citric acid on the properties of soybean enzyme-assisted aqueous extraction processing (EAEP) residue edible film was studied. The washed soybean EAEP residue was produced by the process of EAEP. It was determined that the washed soybean EAEP residue is rich in fibers ($76.10 \pm 1.03\%$) and has lower oil and protein contents ($7.74 \pm 0.11\%$ and $3.50 \pm 0.20\%$, resp.). Edible films intended for food packaging have been produced from the washed EAEP residue combined with glycerol, different concentrations of citric acid (0%, 10%, 15%, 20%, 25%, and 30%), and sodium hypophosphite. The spectra have evidenced that the cross-linking reaction of citric acid and fibers has taken place in the residue. 30-CA films showed the highest tensile strength (17.52 MPa) and the lowest water vapor permeability ($7.21 \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$). Also, it indicated that citric acid can cross-link with the hydroxyls of polysaccharide and improve the compatibilization between the polymeric molecules to improve the intermolecular interaction between polysaccharide molecules, so that the water uptake is reduced. The smooth surface and better translucency of the films suggest that the EAEP residue films treated with citric acid are suitable for application in food packaging.

1. Introduction

Soybean is one of the most dominant oilseeds in the world. A large number of soybean residues which contain mostly crude fiber are generated in the process of extracting oil, protein, or other soy products from soybeans. In recent years, some studies have analyzed different sources of fiber to prepare edible films. Pinecone nanocellulose fibers have been produced by using chemical and mechanical treatments for making nanocellulose films [1]. With the huge development in film processing, the films made of carrot fiber and commercially low methoxyl pectin were developed, and the effect of different sizes on the performance of composite films was explored [2]. Wheat straw hemicellulose films had been mixed with glycerol and different concentrations of citric acid [3]. Due to the large amount of production and relatively low market values of soybean fiber

besides its rich residues, it has a great potential as a raw material for preparing films. For environmental and health considerations, enzyme-assisted aqueous extraction processing (EAEP)—an environmentally friendly way to extract soybean oil—has been developed [4]. EAEP results in four fractions: free oil, an oil-in-water emulsion, a liquid fraction (skim), and a residual fraction. The surplus amount of residues is the limitation of EAEP as it produces 2.8 L of residues when extracting 1 L of oil [5]. The insoluble fiber produced by EAEP is a potential material for producing edible films due to the large amount of fiber content. Using the EAEP residue to prepare edible films could improve the values of coproduct of EAEP and reduce its limitation.

Films prepared by polysaccharides have good oxygen barrier properties; on the other hand, the water vapor barrier property and moisture resistance are poor, due to the hydrophilic properties of polysaccharides [6]. Water barrier

property is a very important property of food packaging films, which could be improved by cross-linking. Cross-linking can form a three-dimensional network structure, thus reducing the mobility of the structure and enhancing the water barrier and mechanical properties. The cross-linking was formed by covalent, electrostatic, or hydrophobic bonds, or dipole-dipole interactions [7, 8]. Citric acid can be used as a cross-linking agent in the production of polysaccharide films [9–12]. The mechanism of cross-linking was that the hydroxyl groups of the polysaccharide and the two carboxyl groups of the citric are cross-linked by covalent intermolecular diester linkages [3, 12]. During the cross-linking reaction, high temperature and use of catalyst are very important conditions, where the reaction temperature should be always above 100°C and the catalyst used should be sodium hypophosphite (SHP) [10, 12].

Therefore, the aim of this study was to promote a novel method for preparing an edible film by using the soybean EAEP residue and to evaluate the physical properties of films made by the soybean EAEP residue as affected by citric acid content.

2. Materials and Methods

2.1. Materials. Full-fat soybean flakes (variety Dong-Nong 47) harvested in 2017 were provided by Heilongjiang Jiusan Oil & Fat Co. (Harbin, China). Protease (Protex 6L) was obtained from Novo Nordisk A/S (Bagsvaerd, Denmark). All the analytical-grade chemicals such as sodium hydroxide, hydrochloric acid, glycerol, citric acid, and sodium hypophosphite were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. EAEP Residue Preparation. Minor modifications such as crushing the full-fat soybean flakes and sieving through 60 mesh sieves have been made in the EAEP based on our previous research. The soybean flakes and water were collected into a beaker, mixed in the ratio of 1:5 (wt/vol), and then kept in a water bath at 55°C. 2% Protex 6L (v/w, based on the dry weight of the samples) was added when the pH of the slurry was adjusted to 9 by 2 N NaOH [13]. The reactions were carried out at the stable temperature and pH, and the reaction mixture was continuously stirred for 3 hours. After reaction, the slurry was centrifuged and oil, skim, cream, and residual fraction were obtained. The residue was dissolved in deionized water (4:1 v/w, water:residue) at room temperature under stirring, and then, the mixture was centrifuged, the aqueous phase was discarded, and the residue was recovered. This process has been repeated three times, in order to decrease the water-soluble substances like sugars [2]. The final residue was dried in an oven at 40°C for 24 h.

2.3. Composition Analysis of Residue. The moisture content of the EAEP residue was determined according to AOAC Official Method 945.15 Moisture in Cereal Adjuncts. The oil content (%) was determined according to the method of Soxtec Extraction-Submersion as described in AOAC 2003.06. The protein content (%) was determined according

to the Kjeldahl method with the nitrogen conversion factor of 6.25 (AOAC 988.05). The ash content (%) was estimated by AOAC 923.03. Cellulose, lignin, and hemicellulose were determined according to the method described in [1].

2.4. Film Formation Processes. Edible films using the EAEP residue were prepared by the following procedure. The film solution was taken in a glass beaker which contained EAEP residue (4 g/100 ml), 62.5% glycerol (w/w, on EAEP residue basis), different concentrations of citric acid (0%, 10%, 15%, 20%, 25%, or 30% w/w, on a EAEP residue basis), sodium hypophosphite (50% w/w on a citric acid basis), and 100 ml deionized water. Then, the solution was centrifuged at 500 rpm for one hour in order to reach homogeneous solution and the air bubbles were removed using a vacuum pump. Then, the solution was poured on glass plates to a final wet thickness of 0.86 mm. The plates were placed in the horizontal position for 24 h at room temperature. After drying, the films were removed from glass plates and cured at 130°C for 10 min using a fan oven. The six films were conditioned in plastic bags at room conditions: $25 \pm 1^\circ\text{C}$ and $28 \pm 2\%$ RH.

2.5. Film Thickness. Film thickness was measured with a digital micrometer (Mitutoyo Manufacturing, Tokyo, Japan) at 7 random locations which contains an intermediate point and the average value was calculated.

2.6. Water Vapor Permeability (WVP) Analysis. The water vapor permeability of film samples was analyzed according to the ASTM E96-95 method with a minor modification. The samples were sealed on acrylic sample cells (4.4 cm in diameter and 2.1 cm in height) and calcium chloride was added to the cells to ensure 0% RH inside the cells. The amount of calcium chloride was added in such a way that the plane of the calcium chloride was 10 cm below the edge of the cells. The initial weight of the cells with films was measured, and then, the cells were placed in a desiccator containing saturated solution of NaCl ($75.0 \pm 2\%$ RH).

2.7. Mechanical Properties Analysis. The tensile strength (TS) and elongation at break (EB) of EAEP residue films were measured by SUNS 6102 Universal Testing Machine (Shenzhen, China) according to the ASTM standard method D882-12. The films were cut into strips with 13 mm wide and 170 mm long and conditioned at the environment of 50% RH and 25°C temperature for 48 h before measurements. The 100 N load cell was used to determine the mechanical properties of samples. The initial grip distance was 100 mm and the crosshead speed was 5 mm/min. The reported values were the average of eight measurements of each film.

2.8. Glass Transition Temperature (T_g). The T_g of EAEP residue films was determined by using the modulated differential scanning calorimeter (MDSC, TA Instruments, USA) [14]. A piece of equilibrated film sample (about 10 mg) was placed into a hermetical aluminum DSC pans. An empty

TABLE 1: Chemical composition of EAEP residue.

Chemicals	EAEP residue	Washed EAEP residue
Moisture (%w/w)	7.91 ± 0.15	8.16 ± 0.12
Oil (%w/w)	8.34 ± 0.14	7.74 ± 0.11
Crude protein (%w/w)	9.98 ± 0.25	3.50 ± 0.20
Ash (%w/w)	4.31 ± 0.27	4.34 ± 0.29
Total dietary fiber (%w/w)	69.45 ± 1.17	76.10 ± 1.03

pan was used as reference. The film was cooled to -80°C by using liquid nitrogen and then it was heated to 270°C at a rate of $10^{\circ}\text{C}/\text{min}$.

2.9. Water Solubility. The films were cut into $2\text{ cm} \times 2\text{ cm}$ pieces and dried at 103°C for 24 h by using a fan oven and weighted [11]. The pieces of films were immersed in 50 mL distilled water with constant stirring at 25°C for 6 h. After immersion, film pieces were then taken out and dried at 70°C to determine the final dry weights of films. Total soluble matter was calculated from the initial and final dry weights of films and reported on dry weight basis.

2.10. Scanning Electron Microscopy (SEM) Analysis. The surface morphologies of the films were observed by SEM. Prior to the observation, the samples were coated with gold-palladium in a Denton Desk II sputter coating unit (Denton Vacuum, USA, Moorestown, NJ). The images were obtained on a Hitachi SU8020 SEM instrument (Tokyo, Japan) with an accelerating voltage of 1.0 kV.

2.11. Film Color and Opacity. The color parameters (CIE L^* , a^* , and b^* coordinates and opacity) of the EAEP residue films were analyzed by using a color meter (ZE-6000 color meter, Nippon Denshoku Industries Co., Ltd, Tokyo, Japan). The color values were expressed as L^* (lightness), a^* (red-green), and b^* (yellow-blue).

2.12. Fourier Transform Infrared (FTIR) Analysis. The FTIR analyses of the composite films were performed with a Nicolet 6700 spectrometer (Nicolet 6700, Thermo Electron Co., USA) in the 500 cm^{-1} to 4000 cm^{-1} wavelength range. The number of accumulated scans and resolution were 32 and 4 cm^{-1} , respectively. The collected spectral data were analyzed with the Thermo Scientific™ OMNIC™ (OMNIC Series Software, Madison, WI, USA) program.

2.13. Statistical Analysis. All experiments were conducted in triplicate, and the results were presented as mean ± standard deviation. The statistical analysis was performed using the one-way analysis of variance (ANOVA) at $p < 0.05$ using SPSS software (version 17.0, SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. Chemical Composition of EAEP Residue. Chemical composition of the EAEP residue was evaluated and is

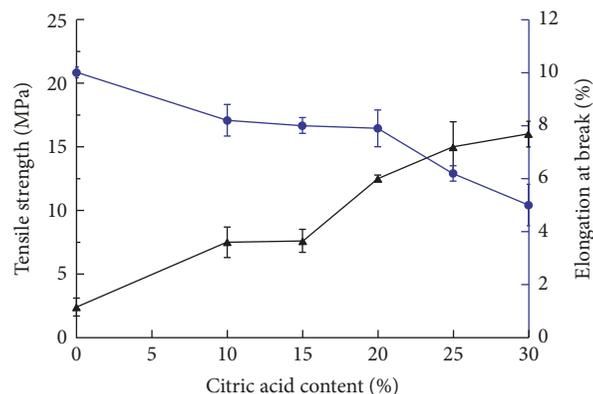


FIGURE 1: Tensile strength and elongation at break of the film as affected by citric acid concentration.

reported in Table 1. Results of the chemical composition of the EAEP residue are presented in Table 1. According to the process of forming film, the washed EAEP residue has the best capability to form a good film, followed by the EAEP residue. On the other hand, it is difficult to form a film using the okara. Compared with the okara, the chemical contents of the EAEP residue have lower values except the moisture and the total dietary fiber [15], which presented of a great importance in formation of the edible film. Maybe the film has a good texture property as a result of the decrease of oil and crude protein and the increase of total dietary fiber. After washing, the chemical contents of the residue have a significant change, especially total dietary fiber and crude protein. The total dietary fiber increases from 69.45 ± 1.17 (%) to 76.10 ± 1.03 (%), and the crude protein decreases from 9.98 ± 0.25 (%) to 3.50 ± 0.20 (%). Meanwhile, the oil also decreases slightly from 8.34 ± 0.14 (%) to 7.74 ± 0.11 (%). A large amount of oil and crude protein have a negative effect on the formation of film, which is consistent with the former result. Different mechanisms have been proposed in the literature to explain the cross-linking of fiber. According to [16], a mechanism was proposed based on anhydride intermediate formation. Firstly, the reaction of polyfunctional carboxylic acids with cellulose is due to the attachment of the polyfunctional carboxylic acid via esterification with a cellulosic hydroxyl group. Its further reaction—via esterification—with another cellulosic hydroxyl group produces the bridging cross-links of the fiber. Citric acid acts as a cross-linking agent during the cross-linking of fiber [3]. Therefore, the content of total dietary fiber is key to the formation of films.

3.2. Mechanical Properties. Tensile strength and elongation at break of the films with different concentrations of citric acid were measured. In addition, the films were prepared by casting, so the deviation of the mechanical parameters was a quite high [17]. As shown in Figure 1, it can be observed that the films treated with citric acid and the films untreated with citric acid were different in mechanical properties. The tensile strength of the 0-CA film was 2.62 MPa, which is the lowest value compared to other EAEP residue-based films. The tensile strength value increased from 8.59 MPa to 17.51 MPa with the

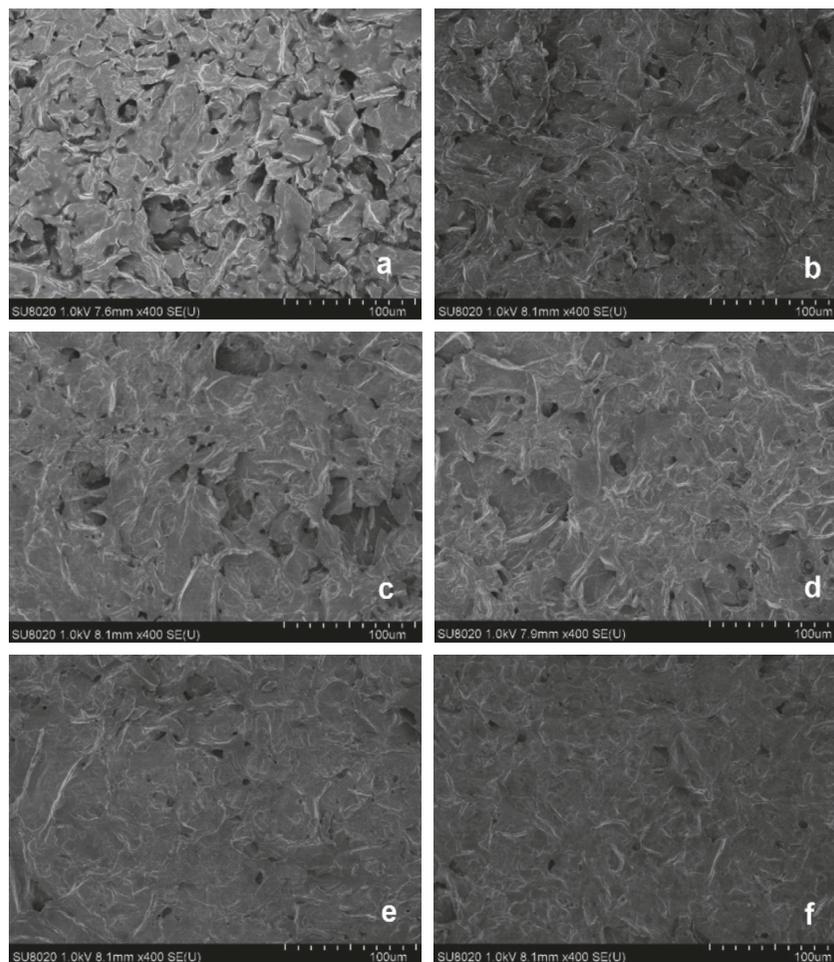


FIGURE 2: SEM images of films with citric contents of 0% (a), 10% (b), 15% (c), 20% (d), 25% (e), and 30% (f).

increase in the citric acid content from 10% to 30%. The tensile strength values for all were higher than the lower acceptable limit for packaging films (4 MPa) [18]. However, the result of elongation at break is exactly opposite to that of the tensile strength. The value of elongation at break was the highest in the 0-CA film, which is 9.37%. The addition of citric acid increases the tensile strength and decreases the elongation at break, respectively. The films with higher tensile strength were obtained when EAEP residue films were treated with higher concentration of citric acid. However, using the higher concentration of citric acid, the decrease in elongation at break was observed. This result may be because of the cross-linking reaction of citric acid and the fibers in the EAEP residue. Citric acid can cross-link with the hydroxyls of polysaccharide, improve the compatibilization between the polymeric molecules, and improve the tensile strength of polysaccharide films [19, 20]. It was demonstrated that citric acid acts as a cross-linking agent in the films and the result was consistent with some previous studies [20, 21]. In addition, it was observed that when the amount of citric acid was more than 20%, the trend of tensile strength and elongation at break of the sample films was relatively gentle. This may be due to the cross-linking reaction between the fibers and citric acid that tends to be saturated.

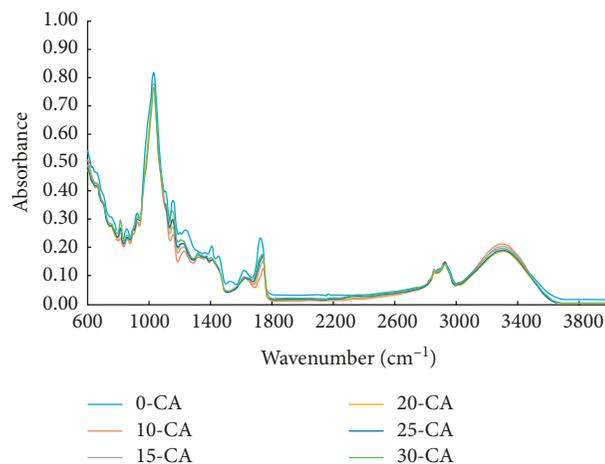


FIGURE 3: FTIR spectra of soybean EAEP residue films treated with citric acid and films untreated with citric acid.

3.3. Microscopy of EAEP Residue Films. Figure 2 shows the microstructure of the EAEP residue films added with different concentrations of citric acid. Microstructure can reflect the homogeneity and compactness of the films. The addition of citric acid made the surface of the

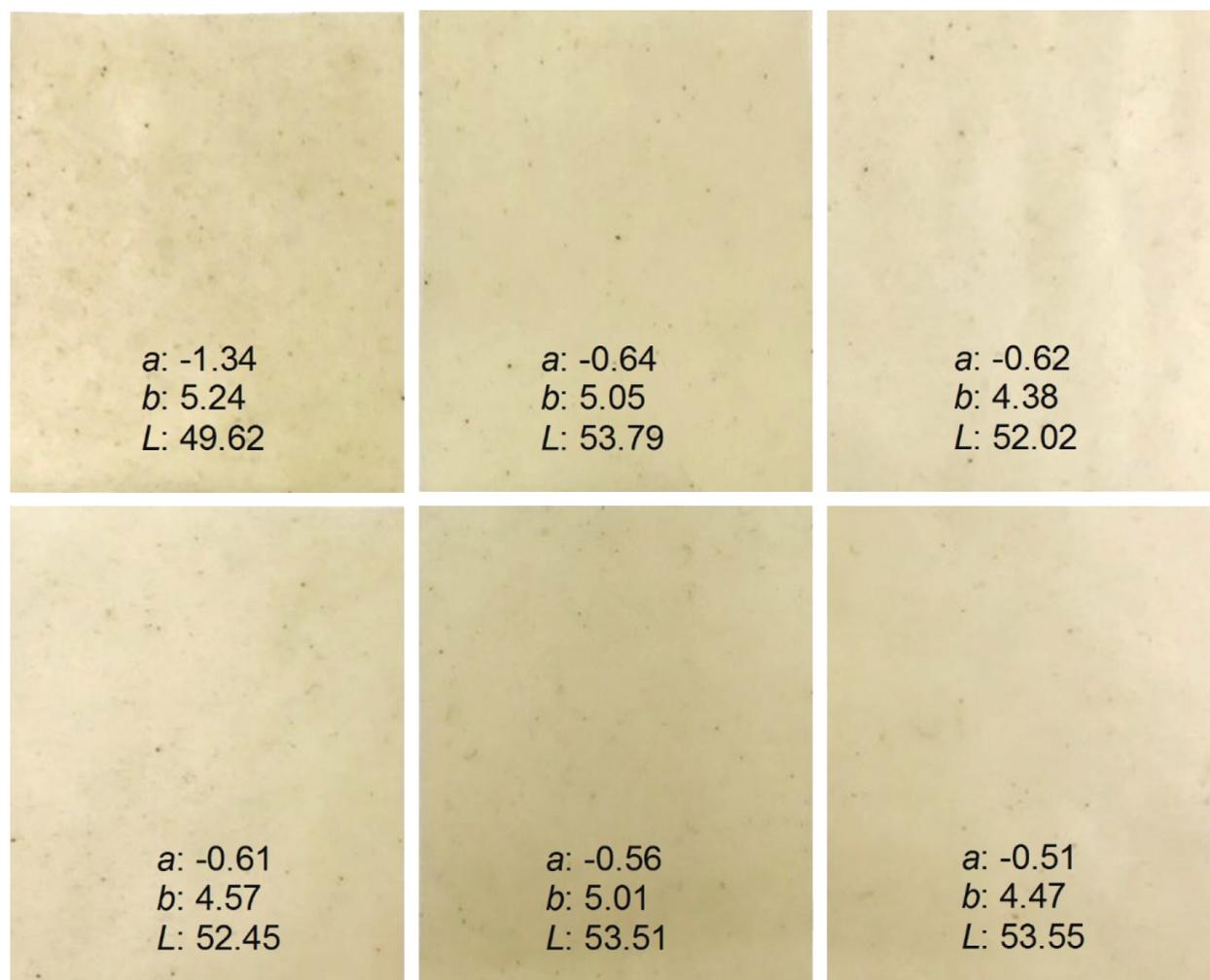


FIGURE 4: Apparent morphology of the film and the color parameters.

starch-chitosan films rough [9]. Also, the presence of citric acid resulted in a rough surface of the wheat straw hemicellulose films [3]. When 0-CA was used as a control sample, the surface structure showed a rough but uniform morphology (Figure 2(a)). However, when the citric acid was added during the preparation of the membrane, the surface of the sample was smoother than the control sample, but the homogeneous state was not as good as the control sample. In the image of the control sample, the average size of the gaps on the surface was about $17\ \mu\text{m}$. The average size of the gaps on the surface of the 10-CA, 15-CA, 20-CA, 25-CA, and 30-CA films was about $14\ \mu\text{m}$, $13\ \mu\text{m}$, $11\ \mu\text{m}$, $8\ \mu\text{m}$, and $5\ \mu\text{m}$, respectively. It could be found that the microstructure of the films' surface became smoother with the increase in the citric acid content. The tensile strength of edible films was stronger with the increase in homogeneity and density of the edible films [22]. The results of the studies are in agreement with the previous results [23], as it showed that the tensile strength of the films has increased from $8.59\ \text{MPa}$ to $17.52\ \text{MPa}$ as the citric acid content increased from 10% to 30% with the surface of the films becoming smoother.

3.4. FTIR Analysis of EAEP Residue Films. FTIR reflects the interaction between the edible film raw materials and the interaction between polysaccharides and citric acid molecules which will directly affect the characteristics of the edible film [3]. The FTIR spectra of untreated EAEP residue films and the EAEP residue films cross-linked treated with different citric acid concentrations are shown in Figure 3. The FTIR absorbance patterns of all the films were quite similar with some differences in the untreated EAEP residue film. One pronounced peaks were at about $3300\ \text{cm}^{-1}$ and with characteristic of the OH- stretching [24]. The intensity of these peaks is lower in the EAEP residue film with no citric acid addition and higher in the EAEP residue film with higher concentration of citric acid. This is probably due to citric acid containing hydroxyl bonds, and therefore, the addition of citric acid will make this peak increase slightly. The appearance of the peak at $1740\ \text{cm}^{-1}$ in the EAEP residue with citric acid added films is assigned to ester carbonyl bonds [21]. The intensity of these peaks is increasing with the addition of citric acid from 10% to 20%. When the citric acid addition is from 20% to 30%, the peak did not change obviously. The peak appearance shows

a change in the chemical structure after the addition of citric acid, indicating that there was some cross-linking that may have taken place between citric acid and the fiber. The decrease in intensity was observed in the band at 1626 cm^{-1} (absorbed water in the films) when citric acid was present, probably because some of the hydrophilic groups were involved in the cross-linking, and thus, the films absorbed less water [25]. This is consistent with the result of tensile strength and the WVP.

3.5. Color. Color parameters obtained from EAEP residue films are shown in Figure 4. Compared to the values of the blank film (0-CA), the value of a was increased and the value of b was decreased after the addition of citric acid. The a value of the blank film was -1.34 , and the value of a was significantly increased ($p < 0.05$) to -0.61 when 10% citric acid was added. The a value was increased slowly with the increase in the citric acid content. The b value was also significantly reduced ($p < 0.05$) at the time of citric acid addition and decreased slightly with the increase in the citric acid content. Regarding the L value of films, the addition of citric acid increased the L values of films as compared to the blank film, but with the addition of citric acid, there was no significant tendency.

3.6. Glass Transition Temperature. The relationship between T_g and citric acid content of the films is shown in Figure 5. Compared to the film untreated with citric acid, the T_g of the citric acid-treated films was decreased significantly ($p < 0.05$). The decrease of T_g may be due to the intermolecular forces between the polymer chains that are weakened by plasticization [14]. Therefore, it can be indicated that citric acid has the function of plasticizer during the reaction process of the product of EAEP residual film. Moreover, the T_g of citric acid-treated films has increased from 72.1°C to 79.5°C with the increase in the citric acid content from 10% to 30%. The increase of T_g may be due to the cross-linking reaction between citric acid and fibers. Therefore, citric acid in the production of the residual film was used not only as a plasticizer but also as a cross-linking agent.

3.7. Water Vapor Permeability. WVP of 5-CA films was $8.33\text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ which had the highest value compared to all films as shown in Figure 6(a). WVP decreased from $8.79\text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ to $7.21\text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ with the increase in the citric acid content from 0% to 30%. This is due to the addition of citric acid as it led to the occurrence of the cross-linking reaction between citric acid and the fiber in the EAEP residue. The cross-linking can improve the intermolecular interaction between polysaccharide molecules, so that the water uptake is reduced [26]. Moreover, the addition of the plasticizer could lead to the increase in water vapor permeability. In the present study, the water vapor permeability does not decrease with the increase in the citric acid content,

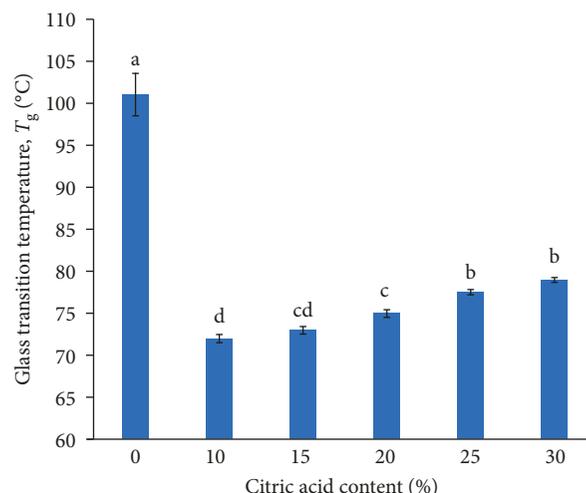


FIGURE 5: Glass transition temperature of the film.

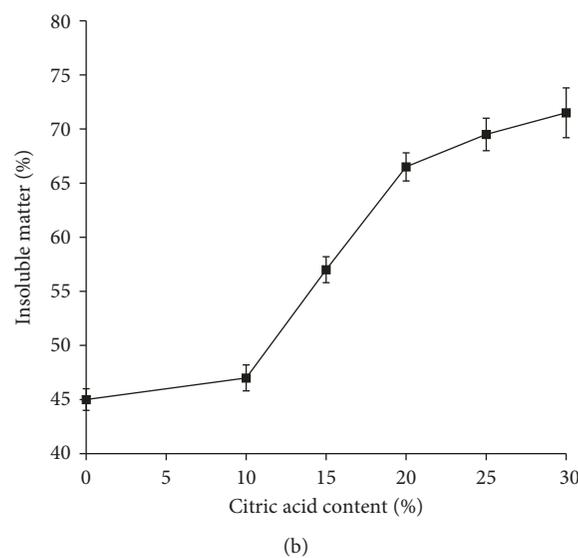
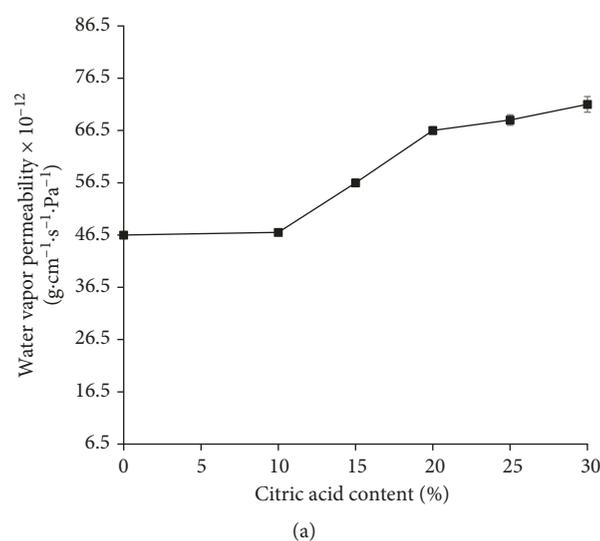


FIGURE 6: Water vapor permeability of the film as affected by citric acid concentration (a) and insoluble matter of the film as affected by citric acid concentration (b).

indicating that citric acid in the process of making EAEP residue acts as the cross-linking agent is stronger than the other plasticizers.

3.8. Water Solubility. Figure 6(b) shows the water solubility of the EAEP residue film samples. It can be clearly observed that the content of the insoluble matter was significantly increased after the films treated with citric acid. When the content of citric acid was 30%, the insoluble matter has increased to 71.67%. This dramatic effect of citric acid on the water solubility may be due to the citric acid and fiber in the residue that occurs in the cross-linking action formed denser structure, so that its water absorption decreased. During the cross-linking process of citric acid and fiber, a part of the hydroxyl group may be replaced by the hydrophobic ester group, which is also a reason for the increase of insoluble matter [20, 27].

4. Conclusions

In conclusion, the data and analysis from this study showed that varying concentrations of citric acid influence the physical and mechanical properties of films. The cross-linking reaction remarkably improved the properties of films, such as tensile strength (17.52 MPa) and water vapor permeability ($7.21 \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$). The resulting films were transparent, smooth, and hydrophobic surfaces, which are the essential properties for food packaging applications, highlighting the potential use of these films as active packaging.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge the support of this study by the National Key Research and Development Program of China (2016YFD0401402) and National Natural Science Foundation of China (nos. 3143000560, 31301501, and 31571876) with special thanks for the Fok Ying Tung Education Foundation (no. 151032).

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