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Preparation and properties of Starch-g-PLA/poly(vinyl alcohol) composite film

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ABSTRACT

Starch/lactic acid graft copolymer (Starch-g-PLA) was prepared by the in situ copolymerization of starch grafted with lactic acid catalyzed with sodium hydroxide, and then mixed with poly(vinyl alcohol) (PVA) to get composite films. The structures of the graft copolymer and composite films were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mechanical properties, water resistance, and thermal stability were also investigated. It was found that the compatibility of Starch-g-PLA and PVA was better than that of starch and PVA in the composite films. The tensile strength and elongation at break of the Starch-g-PLA/PVA composite film increased by 69.15% and 84.22%, respectively, while the water absorption decreased by 50.39%, which overcame the shortcomings of hydrophilicity and poor mechanical properties of Starch/PVA film. Thermogravimetric analysis (TGA) also showed that the thermal stability of Starch-g-PLA/PVA film was improved compared with Starch/PVA film.

1. Introduction

Plastic products from synthetic polymers are not easily degradable and cause serious environmental problems, so biodegradable plastics made of renewable raw materials have attracted much attention for sustainable development (Queiroz & Collares-Queiroz, 2009; Yu, Dean, & Li, 2006; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008; Zia, Zuber, Barikani, Jabbar, & Khosa, 2010). Starch, as an abundant and inexpensive natural polymer with good biodegradability, has been applied in the field of degradable plastics (Lu, Tighzerta, Dole, & Erre, 2005). However, starch-based films cannot be used widely due to its water sensitivity and poor mechanical properties (Follain, Joly, Dole, & Bliard, 2005). So development of new methods which can improve the properties of starch-based films is an urgent task for researchers.

At present, blending starch with synthetic polymers is extensively used and is regarded as an efficient method. However, the biodegradability of starch-based films decreased with the addition of the non-degradable synthetic polymers. Therefore, blending starch with biodegradable synthetic polymer PVA has been studied as a potential biodegradable polymer (Sin, Rahman, Rahmat, & Khan, 2010; Sin, Rahman, Rahmat, & Mokhtar, 2011; Sin, Rahman, Rahmat, & Samad, 2010; Xiao & Yang, 2006; Zhai, Yoshii, & Kume, 2003; Zhai, Yoshii, Kume, & Hashim, 2002). The properties of Starch/PVA blend films have been reported by researchers (Chiellini, Corti, & Solaro, 1999; Tudorachi, Cascaval, & Rusu, 2000), but their applications are limited by the lack of water resistance and the poor mechanical property of the Starch/PVA blended films. This might result from a poor compatibility between starch and PVA and resultant phase separation during film preparation (Lawton, 1996; Lawton & Fanta, 1994).

The effective methods, which can increase the compatibility between starch and synthetic polymers and improve the properties of the film, include adding a compatibilizer to the blends and chemical modifications of the synthetic polymers and starch. A number of methods are available in starch modification, including esterification, oxidation, etherification, crosslinking and so on (Kim & Lee, 2002; Kim, Na, Park, Yoon, & Ihm, 2002; Xu, Miladinov, & Hanna, 2005; Zhao et al., 2006). However, no information is available on the Starch-g-PLA/PVA film. Therefore, the objective of this work is to prepare the biodegradable copolymer Starch-g-PLA by modifying starch with lactic acid, and to prepare composite film by mixing Starch-g-PLA with PVA to avoid phase separation and improve the mechanical properties of the blend films. The structure and morphology of the starch/PVA, and the Starch-g-PLA/PVA films (with or without crosslinking) are characterized. The mechanical properties, water resistance performance and thermal stability of the crosslinked Starch-g-PLA/PVA composite films are all improved significantly.

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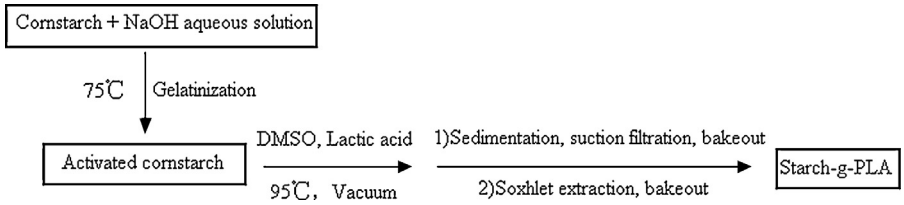

Chart 1. The process of preparation of Starch-g-PLA copolymer.

2. Experimental

2.1. Materials

Cornstarch was obtained from Beijing Yulixing Co. Ltd; lactic acid (A.R.), dimethyl sulfoxide (A.R.) were all purchased from West Long Chemical Co. Ltd. Acetone (A.R.), glycerine (A.R.), and ammonium chloride (A.R.) were obtained from Beijing Chemical Works, and PVA was obtained from Fuchen Chemical Reagent Works (Tianjin) with the polymerization degree of 1750.

2.2. Sample preparation

2.2.1. Preparation of Starch/lactic acid graft copolymer (Starch-g-PLA)

Starch-g-PLA was prepared as flow Chart 1. 5 g raw cornstarch was dispersed in 30 ml 0.40 mol L^{-1} NaOH aqueous solution and the mixture was heated to 75 °C for gelatinization for about 1 h. Then 15 ml dimethyl sulfoxide and 25 ml lactic acid were added to the flask. The graft copolymerization was carried out at 90 °C under vacuum for 9 h. Then the system was cooled down to room temperature, and the product was washed twice with acetone under vigorous stirring to remove unreacted lactic acid monomer, and dried in vacuum oven at 80 °C. The dried product was further purified by Soxhlet extraction with acetone for 48 h to remove the unreacted lactic acid monomer completely as well as the PLA homopolymer. The final product was dried at 80 °C under vacuum oven to get the grafting degree. The final product with a grafting degree of 33.6% was thus obtained (Wang et al., 2012). The grafting degree is calculated as follows:

$$\text{Grafting degree} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 is the weight of dried raw cornstarch and m_1 is the weight of purified Starch-g-PLA copolymer.

2.2.2. Film preparation

Starch-g-PLA/PVA composite films were produced as flow Chart 2. 5 g PVA was poured into a flask with 50 ml distilled water, and then it was stirred at 95 °C for 30 min, then 3 g Starch-g-PLA was slowly added under continuous stirring for 20 min for uniformity. Subsequently, glutaraldehyde (1.5%, w/w, on dry basis of the weight of Starch-g-PLA and PVA) and glycerine (10%, w/w, on dry basis of the weight of Starch-g-PLA and PVA) were added in turn and continuously stirred for another 25 min at 85 °C. Then ammonium chloride was added to neutralize the remanent glutaraldehyde. After that, the mixture was removed from the heat and cast onto a polytetrafluoroethylene plate. Finally, the blend was dried at 65 °C for 5 h, then the film was peeled off for evaluation. Starch and Starch/PVA films were also prepared in the same way.

2.3. Characterization

The IR spectra were obtained on a Perkin-Elmer 100 FT-IR spectrometer (America) with the wave range from 4000 to 400 cm^{-1}. The sample was scanned 32 times, and the scanning resolution was 16 cm^{-1}. The X-ray diffraction (XRD) curves of samples were recorded with a Rigaku D/max-RB diffractometer (Japan) with a Cu Kα radiation (λ = 1.5406 Å) operating at 40 kV and 100 mA, and scans were made in the range of $2\theta = 5°$ to 50° by steps of 0.02°. The films were dried at 60–80 °C for 2 days under vacuum and then the SEM pictures were got by an LEO-1450 electronic microscopy (Germany). TGA was performed on a thermogravimetric analyser Q600 SDT (America) at a heating rate of 20 °C/min over the temperature range from 30 to 500 °C and the data was computed by the Pyris software.

2.4. Mechanical properties and water absorption tests

Tensile strength and elongation at break were determined as mechanical indexes of the film. All the tested films were cut into 100 mm × 15 mm strips, film thickness was measured with a micrometer caliper. Tensile strength and elongation at break were measured on CMT4304 intelligent electronic tensile tester (MTS Industrial System, Ltd., China) with a stretching speed of 100 mm/min. Tensile strength and elongation at break were averaged from three tests.

The water absorption capacity of the films was measured by the Chinese standard method GB/T1034-70. The 50 mm × 50 mm films were first dried in a vacuum oven at 50 °C for 24 h, and then cooled in a desiccator and weighed immediately. Then the films were fully immersed in a container filled with distilled water at room temperature for the equilibrium (24 h). After taking out the films from the container, the water on the surface of the films were removed with filter paper, and then the film was weighed. The ratio

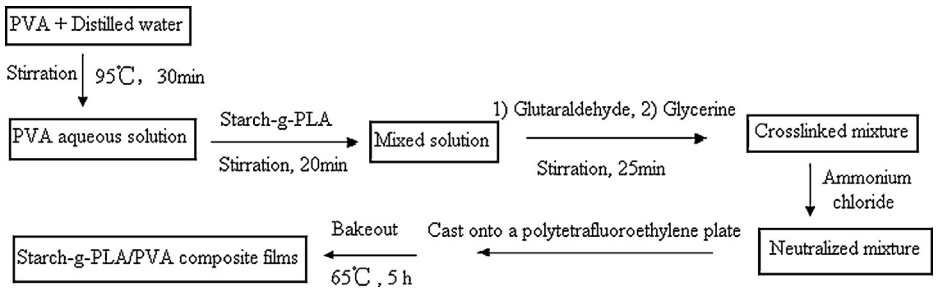

Chart 2. The process of preparation of Starch-g-PLA/PVA films.

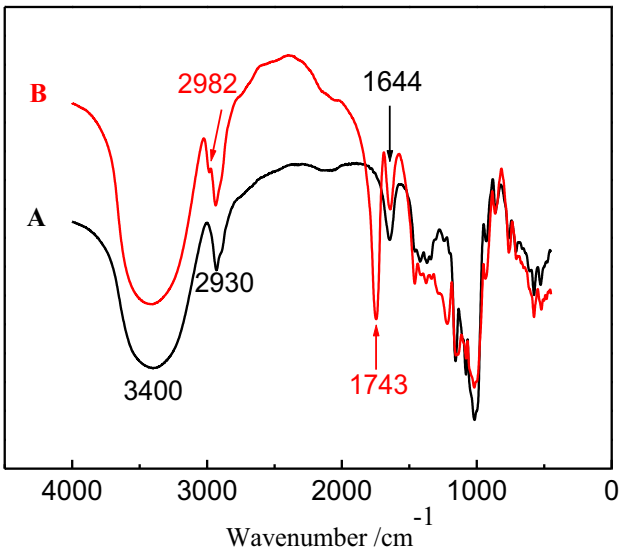

Fig. 1. IR spectra of starch (A) and Starch-g-PLA copolymer (B).

of water absorption (*WA*) is calculated using the following equation.

$$WA\% = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

where W_1 was the initial dry weight of the film and W_2 the weight of the film at the adsorbing equilibrium.

3. Results and discussion

3.1. FT-IR analysis

The IR spectra of cornstarch (A) and Starch-g-PLA (B) are shown in Fig. 1. The IR spectra of cornstarch (Fig. 1A) show a strong and broad absorption peak at 3400 cm^{-1} which is the characteristic absorption peak of the stretching vibration of —OH. The peaks at 2930 cm^{-1}, 1644 cm^{-1}, and 1160–1010 cm^{-1} are respectively assigned to the vibrational absorption of C—H bond, intramolecular hydrogen bond and C—O bond in starch, while the peaks at 570.6 cm^{-1}, 762.5 cm^{-1}, 862.4 cm^{-1} are the swing vibrational absorption peaks of C—H bond of starch (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Xiong, Tang, Tang, & Zou, 2008). Compared to the spectra of starch (Fig. 1A), the IR spectra of Starch-g-PLA (Fig. 1B) show new strong absorption peaks at 1743 cm^{-1} and 2982 cm^{-1}, which are assigned to carbonyl of ester and C—H bond in poly(lactic acid) chain, while the other peaks are almost unchanged (Gong, Wang, & Tu, 2006). These results demonstrate that the lactic acid has been successfully grafted onto the framework of starch to form the Starch-g-PLA copolymer.

The IR spectra of PVA and Starch-g-PLA/PVA films are shown in Fig. 2. As seen from the IR spectra of PVA, the peaks at 3427 cm^{-1} and 2940 cm^{-1} are assigned to stretching vibrational peaks of —OH and C—H, respectively. The peak at 1142 cm^{-1} is the stretching vibrational absorption peak of C—C bond related with the crystallized form, and the peak at 1099 cm^{-1} is the asymmetric stretching vibrational peak of C—O. In the IR spectra of Starch-g-PLA/PVA film, the characteristic peaks of PVA and Starch-g-PLA copolymer both appear, while the position, shape and intensity of some peaks change partly. And the characteristic peaks of C=O (about 1700 cm^{-1}) or C—H (2820 and 2720 cm^{-1}) assigned to aldehyde group does not exist, demonstrating the complete consumption of glutaraldehyde monomer.

3.2. XRD analysis

The X-ray diffractogram of starch, Starch-g-PLA copolymer and Starch-g-PLA/PVA film are shown in Fig. 3. The starch (A) shows sharp peaks at $2\theta = 15.0°$, 17.3°, 20.0° and 23.0°, demonstrating crystallization in starch (Chen et al., 2005; Xiong et al., 2008). In contrast, Starch-g-PLA copolymer (B) shows a dispersion band at around $2\theta = 18.5°$ with the absence of the above four peaks, indicating that the Starch-g-PLA copolymer is amorphous. In contrast, the Starch-g-PLA/PVA film also displays a weak and sharp peak at $2\theta = 19.0°$, which indicate that the addition of PVA had no influence on the internal structure of the film, but the intensity of the diffraction peak decreased, the little crystal just favor to enhance the mechanical performance of Starch-g-PLA/PVA composite film as illustrated below (Xiong et al., 2008).

3.3. SEM analysis

The scanning electron microscopy images of PVA, Starch/PVA film, non-crosslinked Starch-g-PLA/PVA film and crosslinked Starch-g-PLA/PVA film are shown in Fig. 4. The surface of the PVA film has a regular lattice structure (Fig. 4a). The Starch/PVA film (Fig. 4b) is rough and the arrangement is irregular, existing a large number of particles, which demonstrate that the starch and PVA cannot dissolve each other sufficiently. Non-crosslinked

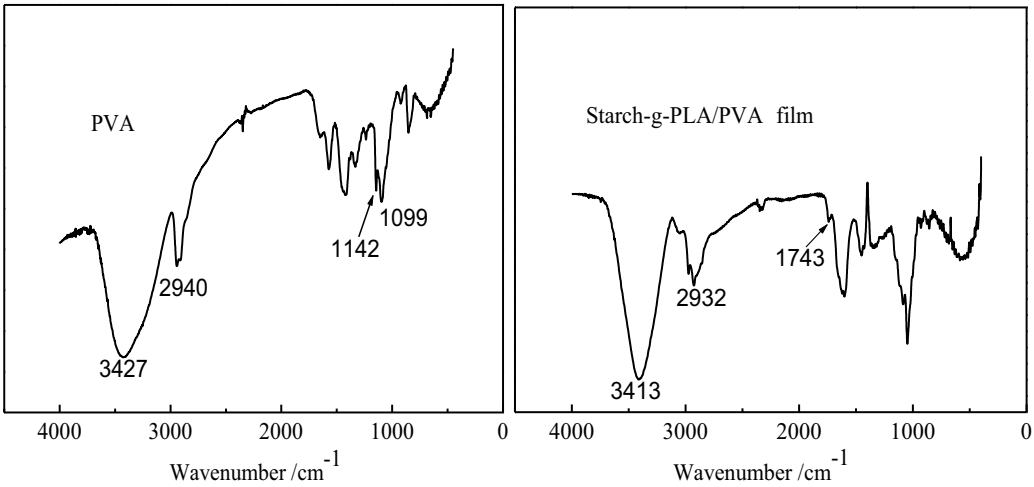

Fig. 2. IR spectra of PVA and Starch-g-PLA/PVA film.

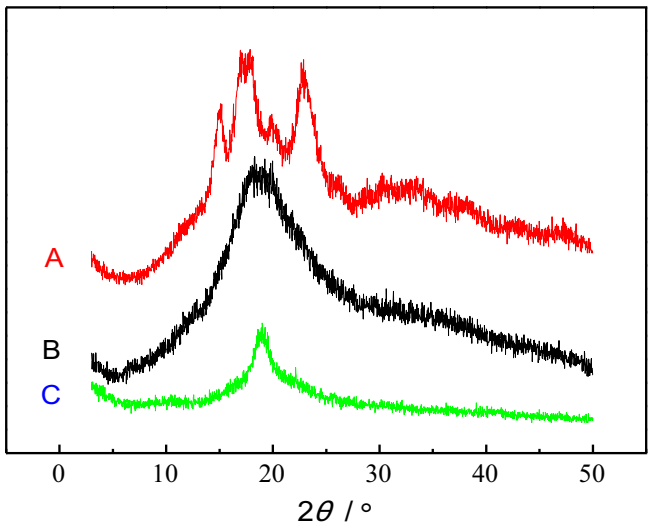

Fig. 3. X-ray diffractogram of starch (A), Starch-g-PLA copolymer (B) and Starch-g-PLA/PVA film (C).

Starch-g-PLA/PVA film (Fig. 4c) is comparatively smooth, and the distribution is more uniform with some particles still existing locally, demonstrating that the compatibility of the PVA and Starch-g-PLA copolymer is still poor without crosslinking. In comparison, the compactness and regularity of the crosslinked Starch-g-PLA/PVA film (Fig. 4d) is clearly the best, demonstrating that glutaraldehyde, as a crosslinking agent, significantly improves the compatibility of the two phases. So the comprehensive performance of the crosslinked Starch-g-PLA/PVA film is superior to other films as shown below.

3.4. Physical properties

The data in Table 1 shows that the tensile strength and elongation at break of the crosslinked Starch-g-PLA/PVA film increased by 69.15% and 84.22%, respectively, compared with the Starch/PVA film. The ratio of water absorption decreased by 50.39%, in which the mechanical performance and the water resistance are all improved clearly compared with reported results (Zhao et al., 2006). The reasons for such improvement is speculated as the destruction of crystallization of the starch molecule and the formation of network structures of the composite film.

3.5. Thermal stability of films

The thermogravimetric analysis of PVA, Starch/PVA, and Starch-g-PLA/PVA films are shown in Fig. 5. Fig. 5 indicates that the weight-loss curves of PVA, Starch/PVA and crosslinked Starch-g-PLA/PVA have no clear distinctions below 250 °C, only the loss of moisture and species of low molecular-weight occurs. But at higher temperature rising, clear distinctions for the decomposed curves of PVA, Starch/PVA and crosslinked Starch-g-PLA/PVA appear. As is shown in Fig. 5, the decomposition temperature are found to be 262 °C (PVA), 298 °C (Starch/PVA), and 317 °C (crosslinked Starch-g-PLA/PVA), respectively, for obtaining the same 60% residual weight of the total amounts. On the other hand, when the temperature rises to 262 °C, the residual weights of PVA, Starch/PVA and cross-linked Starch-g-PLA/PVA are found to be 60%, 76% and 80% respectively. These results indicate that the thermal stability of the crosslinked Starch-g-PLA/PVA film is markedly superior to that of PVA and Starch/PVA films.

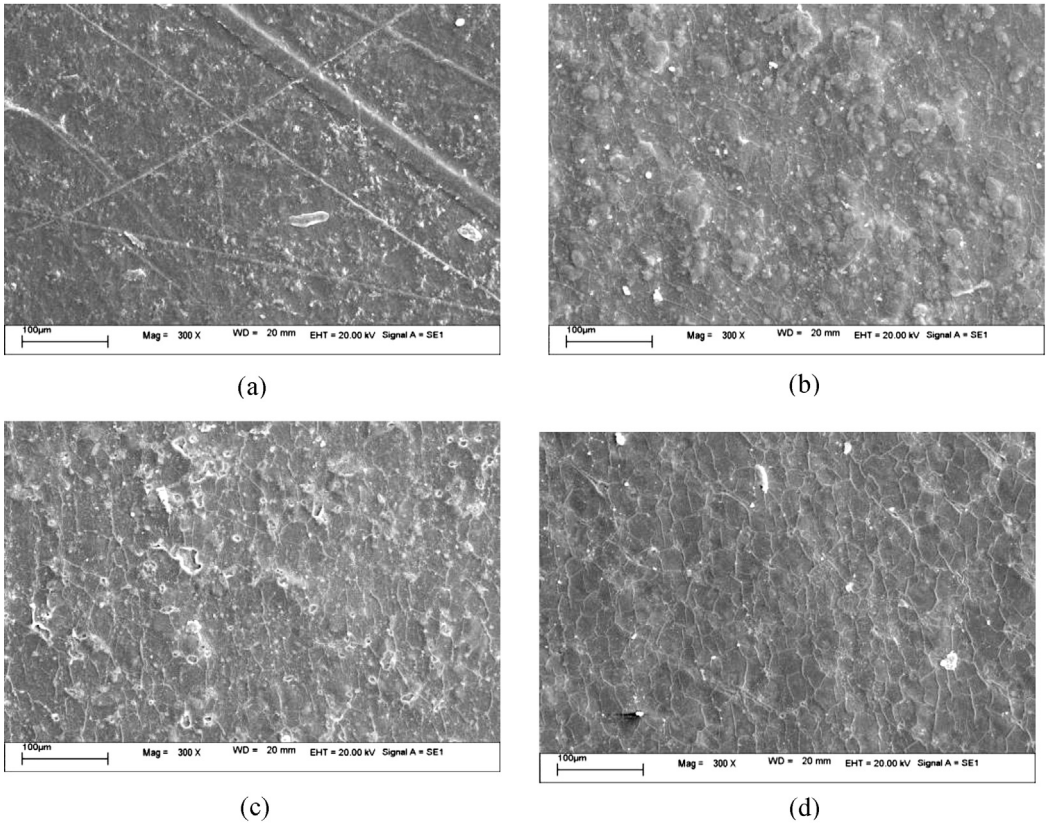

Fig. 4. SEM images of films: (a) PVA film, (b) Starch/PVA film, (c) non-crosslinked Starch-g-PLA/PVA film and (d) crosslinked Starch-g-PLA/PVA film.

Table 1
The physical properties of Starch/PVA film and Starch-PLA/PVA film.

Items	Starch/PVA film	Starch-g-PLA/PVA film	Change values	Extent change (%)
Tensile strength (MPa)	11.80	19.96	+8.16	+69.15
Elongation at break (%)	113.10	208.35	+95.25	+84.22
Water absorption (%)	142.30	70.59	−71.71	−50.39

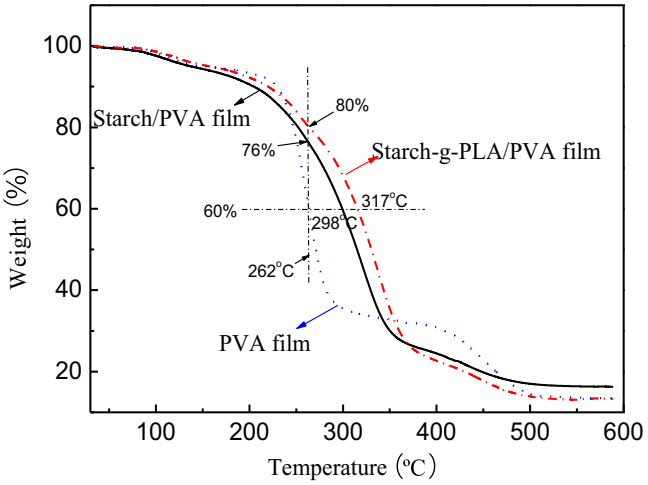

Fig. 5. Thermogravimetric analysis curves of PVA, Starch/PVA and Starch-g-PLA/PVA films.

4. Conclusions

Starch-g-PLA copolymer was prepared by the in situ copolymerization of starch grafted with lactic acid catalyzed with sodium hydroxide. As a step further, Starch-g-PLA/PVA composite film was achieved by blending Starch-g-PLA with PVA at elevated temperature. The mechanical properties, water resistance and thermal stability of the cross-linked film were improved significantly compared to the Starch/PVA film. The tensile strength and elongation at break of the film increased by 69.15% and 84.22%, respectively, while the absorption of water was decreased by 50.39%. The reasons for such improvement were hypothesized as the results of the improved compatibility and miscibility of Starch-g-PLA and PVA. Crosslinking was also highly effective in enhancing the mechanical properties, water resistance and thermal stability of the composite film.

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