

# Soy Protein Isolate/Poly (Vinyl Alcohol) Films with IPN Structure by Crosslinkage of Ferulic Acid

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**Abstract:** Blend films from nature soy protein isolates (SPI) and synthetical poly (vinyl alcohol) (PVA) were successfully fabricated by crosslinkage of ferulic acid (FA) based on a solution-casting method. Structure analysis results indicated that FA had chemical reactions with both SPI and PVA, a three-dimensional interpenetrated polymer networks (IPN) had formed between SPI and PVA. The miscibility of SPI/PVA blends had improved by crosslinkage of FA. Moreover, the transparency of films had enhanced with the increasing of FA contents, which proved the INP structure of SPI/PVA blends could be adjusted by cross-linking degree. This method supplies a highlight potential usage of SPI as environmental-friendly packaging films.

**Keywords:** Biomaterials, polymers, soy protein isolate, poly (vinyl alcohol), ferulic acid, interpenetrating polymer network.

## INTRODUCTION

Soy protein isolate (SPI) is an abundant by-product of soybean oil industry, and today it is widely applied as a natural biomaterial to form films, fibers, foams and composites [1]. Because of the inherent hydrophilicity of natural proteins, pure SPI materials provide lower mechanical properties, lower barrier properties and higher moisture sensitivity without other secondary components. Blending is a promising approach to fabricate absolute "green" materials between SPI and other natural or synthetic biodegradable polymers [2]. In recent years, poly (vinyl alcohol) (PVA) has been applied as a blender to improve the mechanical properties or water moisture sensitivity of SPI materials [3]. It has been found that SPI/PVA blends have promising industrial applications in many fields because of their biodegradability, biocompatibility, chemical resistance and excellent physical properties [4]. Especially, SPI/PVA blend films have attracted lots of attention and they are regarded as a potential substitute for existing petroleum-based synthetic polymer films owing to their low cost, easy availability and complete biodegradability [5]. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the SPI and PVA [6]. It is well known that three-dimensional interpenetrated polymer networks (IPN) may offer new and improved applications for soy protein-based biomaterials [7]. From the synthetic standpoint, IPN structure materials could be obtained by one-pot or two-pot strategies [8].

For soy protein based blends, IPN structure is of two polymers binding with each other through strong interlocking cross-linked interaction, at least one of which (soy protein or the other blend polymer) is a cross-linked polymer network in the immediate presence of the other [9]. They have drawn much attention due to their excellent properties such as excellent thermal stability, mechanical properties, interpenetration and entanglements of polymer chains because of a synergistic effect induced by the forced compatibility of individual components [7].

The aim of this work was to prepare SPI/PVA blend films with IPN structure by crosslinkage of ferulic acid (FA). SPI/PVA films were prepared based on a solution casting and evaporation method. FA is a hydroxycinnamic acid derivative existing ubiquitously in the plant kingdom, which can cross-link with SPI by producing a resonance-stabilized free radical intermediate [10]. The structure, miscibility and light transmittance of the IPN films were discussed in relation to the FA addition.

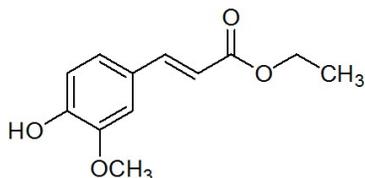
## EXPERIMENTAL

### Materials

SPI powder (Type C<sup>®</sup>), prepared by acid precipitation, was provided by Harbin High-technology Soy Protein Co. Ltd. It contained >90% protein and <5.0% moisture. PVA ( $M_w \approx 1.0 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$ , minimum degree of hydrolysis >87%) was purchased from SINPEC Shanghai Petrochemical Co. Ltd. Both PVA and SPI were vacuum-dried at 50 °C for 24 h before use. FA was purchased from Sigma Chemical CO, St Louis, MO, USA. Figure 1 shows the molecular

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structure of FA. Analytical grade sodium hydroxide (NaOH) pellets were used to prepare a 2.0 mol·L<sup>-1</sup> solution at room temperature.



**Figure 1:** Molecular structure of FA.

### Preparation of SPI/PVA Films Crosslinked by FA

SPI/PVA films were fabricated based on a solution casting and evaporation method [3-6]. SPI aqueous solution was prepared by SPI powder to 100 g of deionized water whose pH was adjusted to 10.0 with 2.0 mol·L<sup>-1</sup> NaOH solution, with continuous stirring at 200 r·min<sup>-1</sup> at 80 °C for 60 min. PVA aqueous solution (10 wt.%) was prepared by stir-heating in a water bath at 90 °C for 60 min. Mixtures, including the prepared SPI solution, PVA water solution and with various weight ratios of FA, were made as the film fabrication resins. The pH of the resins was again adjusted to pH=10.0 with 2.0 mol·L<sup>-1</sup> NaOH solution followed by heating at 80 °C with continuous stirring for 30 min. After defoaming in vacuum, the aqueous resin was poured onto a Teflon coated metal plate to fabricate SPI films. Uniform film thickness was obtained by casting the same amount of film forming solution on each plate in the same area. The Teflonoated metal plate with aqueous resin was oven dried at 50 °C for 6 h then cooled to room temperature. The films were then easily peeled from the plate and coded as SP-10, SP-20, SP-30, SP-40 and SP-50, which corresponded to the FA contents of 10, 20, 30, 40 and 50 mg/100g (SPI/PVA), respectively. The weight ratio of SPI/PVA is 90:10.

### Characterization

FTIR spectra of dried films were obtained using a Nicolet Magna 750 spectrometer with DTGS detector and Omnic 3.2 software. Scanning was carried out in the range 4000 to 400 cm<sup>-1</sup> with resolution 4 cm<sup>-1</sup>, and 128 scans were averaged for each sample.

X-ray diffraction patterns were obtained using a powder diffractometer (Rigaku D/max 2500v/pc, Japan) in the 2θ range 5 to 50° at 2°·min<sup>-1</sup> scan rate, with CuKα radiation of wavelength 0.1542 nm.

Thermal stability determination was performed with a Dupont SDT-2960 TGA instrument. Sample (50 mg)

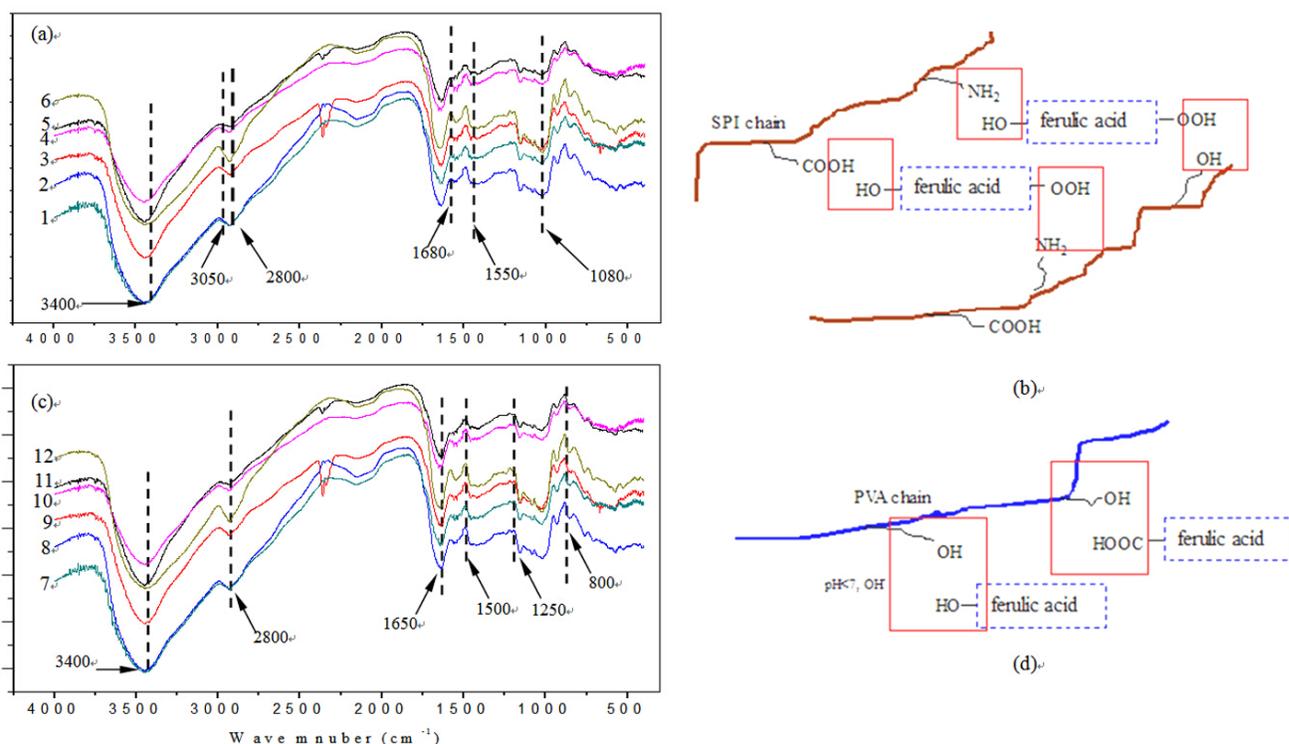
and reference material (α-Al<sub>2</sub>O<sub>3</sub>) were heated to 600 °C at 5 °C·min<sup>-1</sup> in flowing (40 mL·min<sup>-1</sup>) nitrogen.

The light transmittance (*T<sub>r</sub>*) of the films with thickness of 150 μm were performed on an ultraviolet-visible (UV-vis) spectrophotometer (UV-2550, SHIMADZU Co., Japan) at the wavelength of 800 nm.

### RESULT AND DISCUSSION

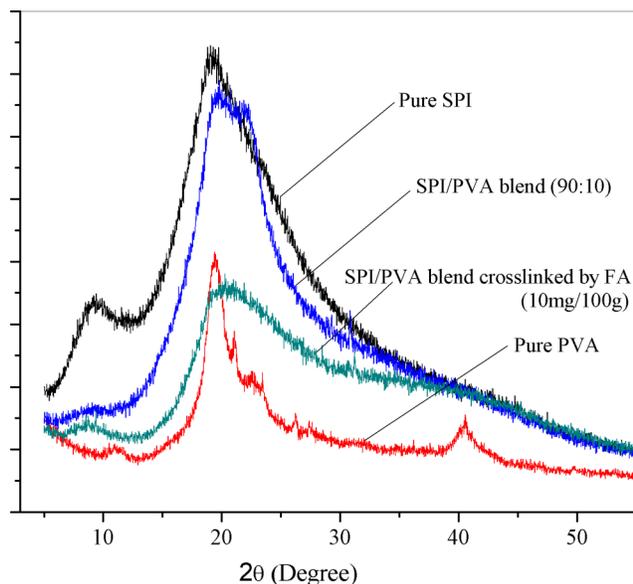
First of all, the molecular structures were measured to investigate the chemical reaction mechanism of SPI/FA and PVA/FA based on the identification of bands related to functional groups present in SPI and PVA. It needs to note that only hydrogen bonds exist between SPI and PVA [4]. Figure 2a shows the FTIR curves of pure SPI, SPI (100g) crosslinked by 10, 20, 30, 40 and 50 mg FA. For pure SPI (curve 1), the absorption of 3400 cm<sup>-1</sup> refers to the hydrogen-bond association between protein chains and moisture in protein. The absorption bands at 1680-1780 cm<sup>-1</sup> and 1150-1250 cm<sup>-1</sup> are attributable to -NH-, C-N stretching and N-H bending (amide II) vibrations, respectively. With the FA addition increasing (curve 2-6), the absorption peaks of -OH and -NH<sub>2</sub> groups both decreased. It implied that FA consumed both of -OH and -NH<sub>2</sub> groups by its own -OH and -OOH groups. Figure 2b illustrates the crosslinkage structure of SPI. In Figure 2c, pure PVA (curve 7) has a peak at 1500 cm<sup>-1</sup> due to deformation vibration of -CH<sub>2</sub> in -CH<sub>2</sub>OH and the -OH groups show absorption peak at 3400 cm<sup>-1</sup> [9]. The basic structure of PVA molecular is the -OH groups on carbon chains. With the increasing of FA in PVA (curves 8-12), a typical characterization of these spectra is the disappearance of the strong hydrogen-bond. It means that -OH groups of PVA had been consumed by -OOH and -OH groups of FA. Figure 2d sketches the molecular crosslinkage structure of PVA. Based on these results that we can concluded that INP structure had formed through both SPI and PVA crosslinked structures.

Figure 3 shows the XRD curves of pure SPI, pure PVA, SPI/PVA blend (90/10) and SP-10. First of all, PVA has a strong characteristic peak at 2θ=20°, which is agreeing with the results of our previous work [9]. Pure SPI gives a strong characteristic peak at 2θ values of around 22°. With the weight ratio of 90/10 for SPI and PVA, the blend has two strong peaks at 2θ value of about 19° and 22°. Blend films from SPI and PVA is partially crystalline materials because the the peaks intensity decreased a lot as compared with those of pure PVA and SPI. Interestingly, the crystalline



**Figure 2:** FTIR curves of SPI/PVA blend crosslinked by FA, (a) FTIR curve curves of pure SPI, SPI (100g) crosslinked by 10, 20, 30, 40 and 50 mg FA, (b) illustration of the crosslinkage structure of SPI by FA, (c) FTIR curve pure PVA crosslinked by 10, 20, 30 40 and 50 mg FA, and (d) illustration of the crosslinkage structure of PVA by FA.

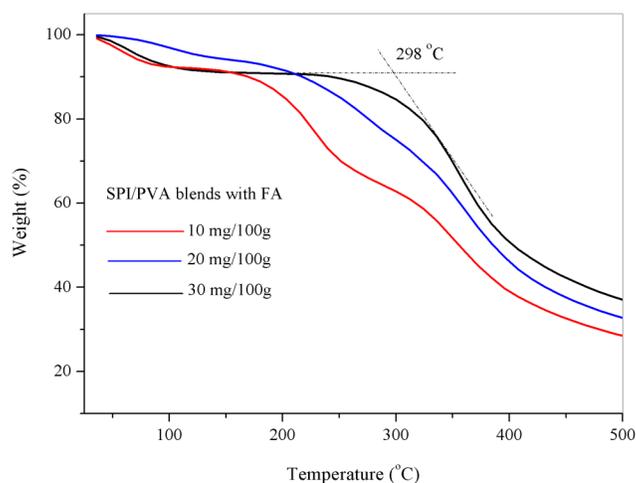
structure had been strongly destroyed by crosslinkage of FA as its strong characteristic peak decreased sharply.



**Figure 3:** XRD curves of pure SPI, pure PVA, SPI/PVA blend (90/10) and SP-10.

Figure 4 shows the TGA curves of SP-10, SP-20 and SP-30. We have reported that the SPI/PVA (90/10) had a decomposing temperature at about 230 °C higher than both of SPI and PVA [9]. The decomposing

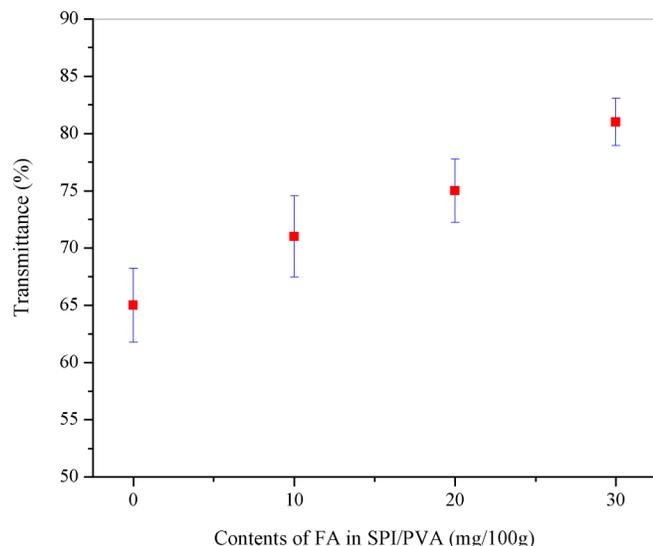
temperatures of SPI/PVA blends crosslinked by FA had increased with the increasing of FA content. Sample SP-30 even had a decomposing temperature of 298 °C. With the increasing weight of FA, the decomposing temperature decreased attributing the higher cross-linking degree. It means that IPN structure had improved the ability of thermal stability.



**Figure 4:** TGA curves of SPI/PVA blends of SP-10, SP-20 and SP-30.

Normally, the higher light transmittance of INP structure suggests good miscibility between two

components, as well as strong interpenetration and entanglements [7]. Figure 5 shows the light transmittance data of SPI/PVA (90/10) blend, SP-10, SP-20 and SP-30. The increase of transmittance can be attributed to the enhanced adhesion between SPI and PVA molecules, which is consistent with the XRD and TGA results. At the same time, the characterized optical property strongly supports the conclusion that INP structure had formed between SPI and PVA.



**Figure 5:** Light transmittance data of SPI/PVA (90/10), SP-10, SP-20 and SP-30.

## CONCLUSIONS

SPI/PVA blend films were successfully fabricated by crosslinkage of FA based on a solution-casting method. Structure analysis indicated that both SPI and PVA could be crosslinked by FA through chemical reactions. INP structure had formed through both SPI and PVA crosslinked structures. XRD tests showed that the crystalline structure of SPI/PVA had been strongly destroyed by crosslinkage of FA. TGA tests proved that the decomposing temperature of SPI/PVA blends decreased attributing the higher cross-linking degree with the increasing weight of FA. The higher light

transmittance of INP structure suggested good miscibility between SPI and PVA. The improvement in functional properties achieved in this work highlights the potential usage of SPI based films as packaging materials, medical materials or agricultural materials.

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