Polymer Bulletin

Mechanical Properties, Biodegradation and Water Vapor Permeability of Blend Films of Soy Protein Isolate and Poly(vinyl alcohol) Compatibilized by Glycerol

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Summary

Novel blend films of soy protein isolate (SPI) and poly(vinyl alcohol) (PVA) compatibilized by glycerol were fabricated by preparing a solution, and then casting it on a Teflon-coated metal sheet. Mechanical, biodegradation and water vapor permeability of the blend properties were systematically investigated with various methods. SEM analysis results release that the SPI/PVA/glycerol film degrades at a slower rate than pure SPI. The mechanical test showed that the stress at yield point, stress at break point and Young's modulus were decreased and percentage elongation at yield point and percentage elongation at break point and of SPI/PVA were increased obviously than pure SPI films. The blend plastics were softened and became semi-rigid contributing to the plasticization of glycerol and the crystalline partion of PVA was destroyed by glycerol. Water vapor permeability of SPI/PVA/glycerol showed the minimum at the component of SPI/PVA (100/35) compatibilized by 3.5% of glycerol.

Introduction

In recent years, the development of environment-friendly and biodegradable materials from nature polymers, especially agriculture products, has received increasing attention in an attempt to substitute existing polymers [1]. Among various cellulose, starch and protein materials, soy protein isolate (SPI) has been applied in packaging film or edible film formation for its excellent film forming abilities, good biodegradable performance, high barrier properties against oxygen and oil movement in low relative humidities [2~9]. However, two inherent problems with soy protein based plastics that have limited their usage are their low mechanical properties and high moisture sensitivity [10]. Pure SPI films also tend to be brittle. Various physical, enzymatic, chemical and physicochemical attempts have been made to modify SPI films so as to improve their mechanical properties and increase the moisture resistance. Physical treatments, including the γ-radiation [11,12], ultraviolet [13], protein ultrafiltration [8], heat effects [14,15] and high pressure [16], mainly promote cross-linking within the protein film network. SPI materials without other secondary

components do not show satisfactory physicochemical and mechanical properties for industrial applications [17]. That is to say that adding other molecule may be an important role in properties of SPI film, as well as film forming conditions and film ingredient. Thus, methods such as blending with biodegradable polymer [18-20] have been developed.

The objective of this work is to prepare blend cast films from SPI and long-chain molecules of poly(vinyl alcohol) (PVA) compatibilized by glycerol for increasing the mechanical properties and moisture resistance of SPI film. Natural macromolecules are generally degradable in biological systems by hydrolysis and subsequent oxidation. PVA is susceptible to biodegradation by microorganisms and hydrolytic enzymes, and probably is the most readily biodegradable one of vinyl polymers [21]. Thus, the blends of biodegradable synthetic PVA and nature SPI may have supplied potential applications in the waste disposal of plastics. Also, literature has showed that blend fibers of SPI and PVA have biocompatibility [22]. Therefore, the novel blend films of complex system of SPI/PVA compatibilized by glycerol are expected to be an important method for combining the advantages of both components and may have better properties than either component.

Experimental

Materials

Soy protein powder (Type A$^{©}$) with moisture content of 2.0 % and more than 90% protein, prepared by acid precipitation, was provided by Harbin High-technology Soy Protein Co. Ltd, China. Poly(vinyl alcohol) (PVA 1799, Mw = 9,000) was purchased from SINPEC Shanghai Petrochemical Co. Ltd. Glycerol (1,2,3-propane-triol, Analytical grade, 95% purity) and sodium hydroxide (NaOH, Analytical grade) were acquired from Tianjin Chemical Co. Ltd, China. NaOH pellets, along with de-ionized water, were used to prepare a solution of 1.0 mol/L at room temperature.

Preparation of SPI films

SPI aqueous solution was prepared by adding 5g SPI powder to 100g of de-ionized water, followed by adjusting its pH value to 10.0 at 80°C by using 1.0mol/L NaOH solution under continuous agitation at a stirring rate of 200 rpm for 60min. The pH value was monitored using an electronic pH-meter (660 Type, Lengpu Co. Shanghai). The reason for tuning pH to 10.0 is well known, i.e., the maximum protein unfolding and rearrangement status can be resulted [23]. In addition, the pH value might cause high lysino-alanine linkage formation and high hydrolysis of asparagines and glutamine primary residues. 10% (*wt.%*) PVA aqueous solution was heated under stirring in a water bath at 90°C for 90min. Then, a series of solutions consisting of the prepared SPI solution, 10% PVA solution and glycerol (1~4%) were obtained as the film dope. Again, its pH value was properly adjusted to 10.0 with the 1.0mol/L NaOH solution at 80°C in 30min. At last, the dope, after vacuum treatment, was poured on a Teflon-coated metal plate to form SPI film. Uniform film thickness could be achieved by casting the same amount of film-forming solution on each plate. The nascent films were dried in an oven at 40°C for 6h and then cooled down to room temperature in 24h. Dried films were peeled off integrally from the metal plate. Samples were cut for mechanical properties, surface morphologies, thermal properties, moisture sorption

and water vapor permeability measurement. The samples with a weight ratio of 0, 10, 20 and 40 PVA over 100 SPI are coded as P-0, P-10, P-20, P-30 and P-40, respectively.

Characterization

Pure PVA and pure SPI in powder form and SPI/PVA blends with/without glycerol in film form were examined to obtain their X-ray diffraction patterns by using a powdery diffractometer (Rigaku D/max 2500v/pc, Japan).The samples were scanned from 5 to 60° (2θ) at 1°/min by using the Cu KαX-ray radiation of 0.1542nm. The patterns were analyzed to estimate the percentage of the crystallinity of the samples.

The thermal analyses of films were carried out on a DSC analyzer (Perkin-Elmer, DSC7). Under a nitrogen atmosphere, all samples first were equilibrated to 20°C and heated to 200°C, then quenched to 20°C and heated to 200°C at a rate of 5°C/min. All data reported in this study were obtained from the second DSC scan.

The surface morphologies and microstructure of the samples were characterized using a scanning electron microscope (SEM, XL30 PHILIPS) at an accelerated voltage of 5 KV. The samples were adhered to the SEM holder by double-side electrically conductive carbon tape and then coated with thin gold layers about 200 Å before observation.

Five samples (25×100mm) for each film were tested for mechanical properties. The values presented here were all average of five samples. Before testing, all the samples were conditioned for 2 days in an environmental chamber at 50% relative humidity (RH) and 25°C. The tensile fracture interface of the films was observed by an optical microscope (MiVnt Image analyze system, China). Thickness of samples were measured with a micrometer having a sensitivity of 1μm. Tensile strength (TS) and percentage of elongation at break (E) were determined with an AG-IS model analyzer (Shimadzu, Japan) according to ASTM D882-97 (ASTM, 2000b) procedure at the strain rate of 5mm/min. Other tensile properties, such as Young's modules, fracture strain, fracture stress, yield stress and energy to break were calculated from the tensile stress-strain plots by a computer software. Toughness was integrated as the area under the stress-strain curve.

Water vapor permeability of films was measured using the ASTM method (ASTM standard test method for water vapor permeability of materials, 1993). Water vapor permeability (WVP) (g mm/m^2 h kPa) was calculated from,

$$WVP = \frac{WVTR \cdot L}{\Delta p} \tag{1}$$

where WVTR was the measured water vapor transmission rate (g/m^2 h) through the film; L was the film thickness (mm); and the Δp was the partial water vapor pressure difference (kPa) across the two sides of the film.

Results and discussion

X-ray diffraction (XRD)analysis

Fig.1 shows the X-ray patterns of the pure SPI powder, pure PVA powder, P-10, P-40 and P-10 with 2*wt.%* glycerol. It can be seen that SPI gives two strong characteristic

peaks at 2θ values of around 9° and 19° whereas pure PVA results in only one strong peak at 2θ value of ca. 20°. The two blends of PVA/SPI are also seen to have a strong peak at 2θ value of about 19° but the peak intensity decreases a lot as compared with those of neat PVA and SPI. This in turn indicates that the crystalline structure of either SPI or PVA has collapsed after blending. Fig.1(e) shows that the XRD characteristic peak is gentle and its intensity is decreased after the PVA/SPI blend compatibilized by glycerol, indicating that the presence of glycerol reduces the crystallinity of PVA/SPI blend.
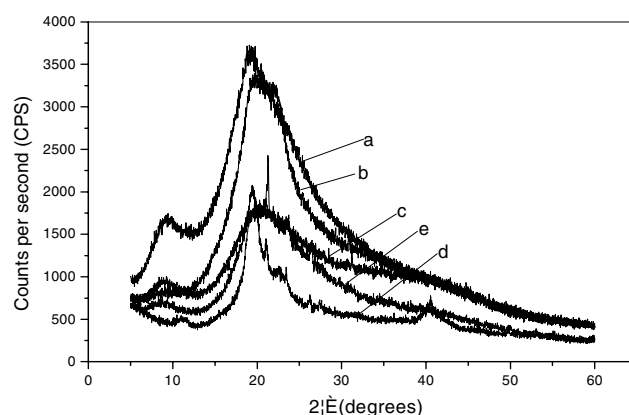

Fig.1. X-ray diffraction pattern of (a) pure SPI powder, (b) pure PVA powder, (c) P-10 (d) P-40 (e) P-10 with 2*wt.%* glycerol.

Thermal analysis of blend films

For the purpose of SPI processing and applications, the glass transition behaviors of soy protein plasticized with glycerol have been widely investigated. Literatures report no consistent result about its glass transition temperature (T_g). For example, pure SPI without any plasticizers presents a T_g value of about 150°*C* obtained by dynamic mechanical thermal analysis (DMTA), while the T_g of SPI with 25 *wt.%* glycerol decreases to -50°C [24-27]. More recently, Chen and Zhang have investigated the glass transition behaviors and microstructures of SPI by using differential scanning calorimetry (DSC) and small angle X-ray scattering [28]. Interestingly, their results revealed that there are two glass transitions for the SPI/glycerol system. All these researches imply that the microstructure and glass transition of SPI plasticized by glycerol are still uncertain, due to its structural complexity [29].

In order to know the difference in the thermal behavior, the SPI/PVA plasticized by 2.0 *wt.%* glycerol is analyzed by DSC. The T_g and melting temperature (T_m) thus obtained are shown in Table.1. T_g is observed to decrease from 136.5 to 97.5°C whereas T_m increases from 157.4°C to 179.8°C as the weight ratio of PVA/SPI increases to 40/100. These results agree very well with the XRD analysis result discussed earlier, i.e., blending SPI and PVA has destroyed their respective crystalline structures. The DSC analysis indicates the co-existence of both glycerol and PVA may have changed the aggregate structure of SPI.

Table.1 Glass transition temperature (T_g) and melting temperature (T_m) of pure SPI powder, P-10 and P-10 with 2*wt.*% glycerol.*

PVA content	DSC	
(*wt.%*)	T_g (°C)	T_m (°C)
P-0	136.5	157.4
P-10	120.4	160.1
P-20	111.9	165.7
P-30	101.3	170.5
P-40	97.5	179.8

*PVA: T_g=85°C, T_m=225.0°C

Morphologies of biodegradable films

The biodegradation of blend films can be achieved by observing their surface changes over the whole evolution process. Fig.2 shows SEM observations of P-10 films in 0, 10, 20 and 30 days, respectively. As seen in Fig.2(a), the film shows a relatively smooth and clean surface except for a few scratches produced as cast. After 10 days, the surface has many ripples (Fig.2(b)). This may be attributed to the partial
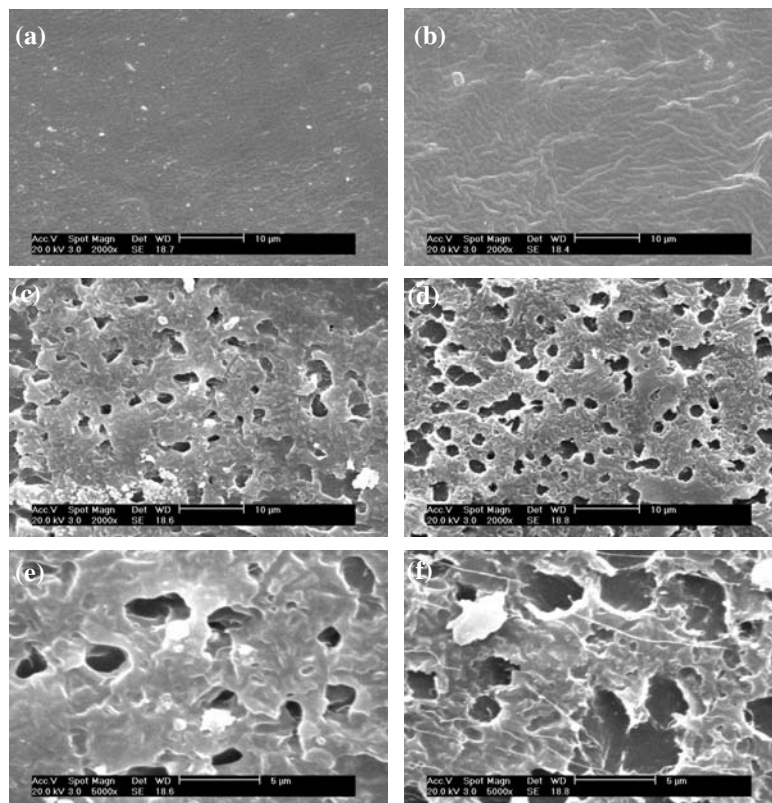

Fig.2. SEM photographs of the P-10 blend films, (a) 0 day, (b) 10 days, (c) 20 days, (d) 30 days, P-10 compatibilized by glycerol (e) 30 days, (f) 40 days.

biodegradation of both SPI and PVA molecules by microbes. After 20 days elapse, some holes are observed to form in the film (Fig.2(c)). There are about 3-4 holes in 10×10um and the hole diameter is in the range of 1-2 um. At the end of 30 days, the entire film is covered with more holes at a diameter of larger than 4-5um (Fig.2(d)). In addition, lots of neighboring holes are melted together to form even larger holes. A gradual increase in surface roughness, including deformation, wrinkles and cracks, is observed in the porous film.

More attention may be paid to the degradation of SPI/PVA/glycerol films. Fig.2(e) and (f) show the degradation behavior of these films in 30 and 40 days, respectively. Compared with its counterpart (Fig.2(d)), the SPI/PVA/glycerol film has fewer holes and less disfigurement, indicative of slower degradation and the significant compatibilization of added glycerol. After 40 days, the biodegraded holes become enlarged and the region without holes seems to begin decomposing.

Mechanical properties

Fig.3 shows the optical microscope morphologies of rupture samples after tensile tests. Fig.3(a) shows a typical brittle breakpoint of pure SPI film. With the increasing of PVA content in SPI, the blend materials are becoming less brittle, as shown in Fig.3(b~d). However, the percentage elongation at breakpoint is not enlarged apparently. Plasticizing effects of glycerol on surface morphologies of P-20 are shown in Fig.3(e~g). Upon compared to the sheet without glycerol, a plastic deformation appears as evidenced by increased percentage elongation at break. These results agree very well with the literature [30]. As a plasticizer, glycerol may reduce the interaction between protein molecules and meanwhile increase the flexibility, extensibility and processibility of SPI films.

The effect of added PVA on SPI mechanical properties is given in Table.2. Long-chain PVA molecules, containing many –OH groups, will form strong intra- and inter-molecules interactions with protein molecules. These interactions may include hydrogen-bonding, dipole-dipole and charge effects. In addition, blending long molecules in SPI could bring about molecular entanglements, which in turn will improve the mechanical properties of SPI. The decreasing of crystallinity of blend of SPI/PVA may be explained for it.

The effect of glycerol on mechanical properties of SPI/PVA blend can be seen from Table.3. Both of the percentage elongation at yield point and the percentage
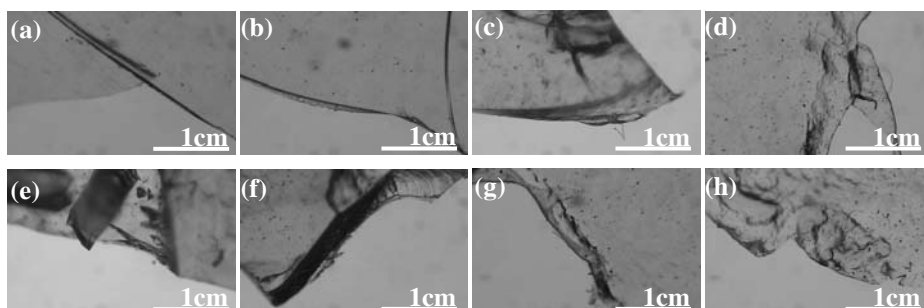

Fig.3. Optical photographs of fracture interface of (a) pure SPI film, (b) P-10, (c) P-20, (d) P-30, and (e-h) P-20 with 1%, 2%, 3% and 4% glycerol.

elongation at break point are enlarged after adding 2*wt.%* glycerol, as comparing Table 3 with Table 2. Also, Young's modules and yield stress decrease, indicating that the blend becomes softened. This could be contributed to the plasticization of glycerol.

Table.2 Effect of PVA concentration on mechanical properties of SPI films.

Samples	σ_y[a] (Mpa)	σ_b[b] (Mpa)	P.E.Y.[c] (%)	P.E.B.[d] (%)	Strength (Mpa)	E[e] (Mpa)	Toughness (Mpa)
P-0	41.6	41.2	1.2	1.3	41.6	1227	0.5
P-10	32.9	28.6	2.4	70	34.2	1009	20.0
P-20	20.6	16.3	3.5	76	21.0	300	17.2
P-30	2.0	8.8	4.3	80	10.1	154	16.1
P-40	1.6	7.9	4.7	80	7.4	120	10.5

[a]σ_y is the stress at yield point, [b]σ_b is the stress at break point, [c] P.E.Y. is the percentage elongation at yield point, [d] P.E.B. is the percentage elongation at break point, [e] E is *Young's* modulus.

Table.3 Mechanical properties SPI/PVA blend films compatibilized by glycerol (2.0 *wt%*).

Samples	σ_y (Mpa)	σ_b (Mpa)	P.E.Y. (%)	P.E.B. (%)	Strength (Mpa)	E (Mpa)	Toughness (Mpa)
P-0	39.7	40.2	2.0	2.7	40.3	1124	0.5
P-10	30.8	27.5	2.5	80	45.8	924	21.1
P-20	18.5	14.3	4.0	90.7	50.2	250	21.8
P-30	1.9	1.2	4.5	95.2	52.1	150	22.2
P-40	1.5	0.8	5.0	102.0	55.1	106	25.0

Water Vapor Permeability (WVP)

Besides mechanical parameters, WVP is another important and widely studied one of SPI films. Fig.4 shows the WVP values of various SPI/PVA films with/without glycerol. WVP of samples ranges between 7.25 and 12.5 (g mm/m^2 h kPa), and are significantly affected by either PVA or glycerol. Pure SPI film has a WVP of 10.1 (g mm/m^2 h kPa) and this value does not change much by only adding glycerol from 1% to 4%. Obviously, with increasing PVA content, all the curves show a two-step change. Firstly, the WVP values decreases with the increasing of weight of PVA. At the point of P-20, the minimums are 7.2, 7.9, 8.5, 8.9 and 9.5 corresponding to 0,1, 2, 3 and 4% glycerol, respectively. Secondly, the curves increase with more addition of PVA. Especially, the P-20 compatibilized by 4% glycerol has a WVP value of 12.5 (g mm/m^2 h kPa), which is 120% over pure SPI. Thus, it can be imagined that the proper component of film is P-20 compatibilized by glycerol. However, such film had poor structural integrity as evidenced by its lower TS and E values. In contrast, glycerol greatly reduces WVP while also increases film extendibility. However, such film had poor structural integrity as evidenced by its lower *TS* and *E* values. Nevertheless, the influence of amount of glycerol on mechanical properties is less than on WVP. Thus, the P-20 compatibilized by 4% glycerol still may be a perfect point of constitute. These might have results from the cross-linkage between glycerol molecules and SPI reducing the interstitial spaces in protein matrix, thus allowing for decreasing diffusion rate of water molecules through the films.
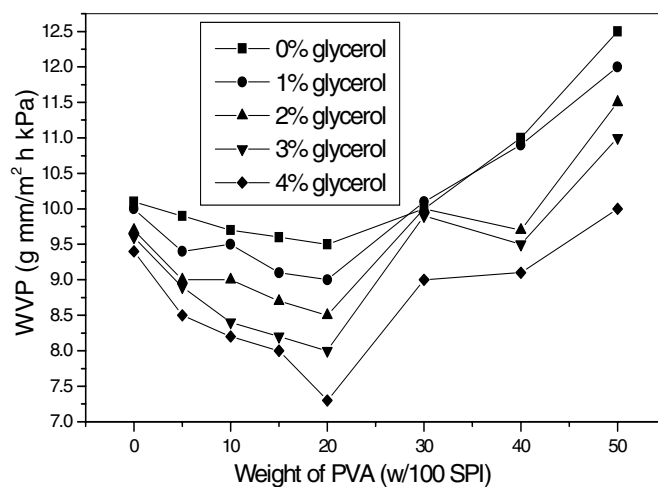
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Fig.4. Water vapor permeability (WVP) at 25°C of SPI/PVA films with various (*wt.%*) glycerol.

Conclusions

This study showed the potential application of PVA/SPI compatibilized by glycerol films in packaging, mulching and other industrial precuts. The enhancement of mechanical and WVP properties is contributed to the improvement of cross-linking degree of SPI molecules. Amino acid in SPI, which vary in composition and conformation, are expected to exhibit various degree of responsiveness to interaction with glycerol. Also, the long-chain molecules of PVA blending with SPI will cause entanglement and intermolecular hydrogen bonding. Therefore, the biodegradable period could be prolonged and mechanical properties are improved.

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