Synthesis and characterization of a new soy protein isolate/Polyamic acid salt blend films

Lianjun Song · Junli Zhi · Pingan Zhang · Qiuyan Zhao ·
Ning Li · Mingwu Qiao · Jie Liu

Revised: 18 December 2013 / Accepted: 1 April 2014 / Published online: 12 April 2014
© Association of Food Scientists & Technologists (India) 2014

Abstract In this study, a new method was developed to produce biodegradable material using soy protein isolate (SPI) as matrix. The blend films were successfully prepared by casting the aqueous dispersions of SPI and polyamic acid salt (PAS) solution. The effects of blending and PAS content on the structure of the resultant films were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) analyses, scanning electron microscopy (SEM). Furthermore, film thickness, water vapor permeability (WVP), water barrier and mechanical properties were measured. The result showed that there exists strong intermolecular interactions between SPI and PAS, which played an important role in forming a homogeneous structure of the blend films. Moreover, the incorporation of PAS enhanced the water barrier and mechanical properties of the films. This is a simple way to prepare biodegradable films compared with other methods and the blend films have the potentiality to be used as food packaging and biomedical materials instead of synthetic polymer.

Keywords Soy protein isolate · Polyamic acid salt · Synthesis · Structure

Introduction

In recent years, biodegradable materials have received an increasing attention, since plastic materials have led to serious environmental concerns (Silva et al. 2007; Lithner et al. 2011; Ezrin 2013) and the oil price is increasing (Sothornvit et al. 2010; Arora et al. 2012; Ratti and Vespignani 2013).

Therefore, a variety of natural polymeric materials have been widely studied in the fields of food industry, packaging, pharmaceutical and biomedical sciences (Dutta et al. 2009; Mesquita et al. 2010).

Among the natural materials, SPI, of which the protein content is more than 90 % (Tian et al. 2010) have get a great concern from the researcher, for it is abundant and have a good film-forming ability (Wu and Zhang 2001; Rhim et al. 2006). Many researchers have confirmed SPI-based film have a certain mechanical strength and oxygen, water barrier properties in the presence of the plasticizer (Glycerol usually) (Monedero et al. 2010; Park et al. 2001), which is essential in food packaging. However, the brittleness and water sensitivity of protein films limit their further applications. An improvement in the toughness and water resistivity of soy protein material is essential for their successful applications (Wang et al. 2005). Thus many efforts have been made to enhance the toughness of SPI films through different kinds of modification, including chemical cross-linking with Gen (González et al. 2011), Cod gelatin (Denavi et al. 2009), Agar (Tian et al. 2011), Carboxymethyl cellulose (Su et al. 2010) and so on, reinforcing the SPI matrix with natural fibers such as ramie fiber (Lodha and Netravali 2005; Kumar and Zhang 2009), jute (Behera et al. 2012), joint enhancing by nano-materials and natural fibers (Huang and Netravali 2007; Huang et al. 2009), or blend with other synthetic polymers (Wang et al. 2005).

Among the above methods, blending with synthetic polymers is an effective method for modification of SPI films, because the chain of SPI contains a variety of active groups, which can react with the polymers. However, it is difficult to make the SPI solution and the hydrophobic polymers co-solvent due to the polarity difference (Wu et al. 2009). So the polymers which can be used are rare and the study in this area is few. To date, it is just only waterborne polyurethane (WPU) that was reported to be successfully used to improve

L. Song (✉) · J. Zhi · P. Zhang · Q. Zhao · N. Li · M. Qiao · J. Liu
College of food science and technology, Henan Agricultural
University, Henan 450002, People's Republic of China
e-mail: slj69@126.com

the performance of SPI films (Tian et al. 2010; Zhang et al. 2012).

Polyimide is a kind of polymer materials with excellent performance. Owing to its unique rigid rod-like structure in the main chain, it has excellent mechanical properties, thermal stability, and dimensional stability and so on. Now the films made from polyimide have been widely used in many fields. Polyamic acid salt is the precursor during the synthesis of polyimide film, which contains rich amide and carboxyl groups. More importantly, PAS is water-soluble; this make it feasible to blend SPI with PAS, and obtaining the SPI films with better mechanical and water-blocking properties is also possible.

Thus, in order to increase the Tensile strength (TS) Elongation at break (E) and Water vapor permeability (WVP), which are desirable improvements in considering such films for packaging applications, SPI/PAS blend films were prepared by a method of casting. And tensile testing, Swelling experiment, water vapor transmission test were conducted. The structure, morphology, thermal property were studied and the effects of PAS amount on the structure and properties of blend films were also discussed.

Materials and methods

Materials Commercial soy protein isolate (SPI) with a protein content of 92 % was purchased from DuPont-Yunmeng Protein Technology Co. Ltd. (Yunmeng, China). Glycerol and ammonia solution are both analytical grade. Pyromellitic dianhydride (PMDA) was purchased from Aladdin Co. Ltd. (Shanghai, China) and M-phenylenediamine (m-PDA) from Guangfu Fine Chemical Research Institute (Tianjin). Triethylamine and Dimethylacetamide (DMAC) was provide from YongDa Chemical Reagent Company (TianJin).

Preparation of the SPI/PAS blend films Alkaline soy protein solution was prepared according to the method provided by Brandenburg et al (1993). SPI (7 g) and glycerol (3.5 g) were dissolved in 100 ml deionized water with a constant stirring of 3 h. The pH value of the solution was adjusted to 10 ± 0.1 with 1 M ammonia solution. Then the solutions were heated for 20 min at 90 °C to denature the soy protein.

The m-PDA (1.08 g, 0.01 mol) and DMAC (20 ml) were introduced into a beaker, a 50 °C constant-temperature water bath and a magnetic stirring were used to make it dissolve completely. Then PMDA (2.20 g, 0.01 mol) was added to the solution in batches and the time was controlled in 2 h. The solution was stirred for 30 min again and triethylamine solution was added to it. After that, the solution was strongly stirred for another 6 h to make reaction sufficient. Next, the

solution obtained by previous steps was poured into acetone solution and the PAS precipitated in the form of solids. After standing for some time, the upper acetone was removed and the Gansi were continued to stand in the air for 1–2 days to make the acetone evaporate. Then deionized water was added to dissolve the precipitate and then PAS solution were prepared. By changing the amount of reactant, different concentrations of the PAS solution were obtained.

The PAS solution was added to the soy protein solution and stirred, followed by drawing a certain volume of the mixture into a homemade glass box (the dimension was $28.0 \times 15.0 \times 1.0$ cm), the box was dried in an oven at 70 °C for an hour then 100 °C for 2 h. Finally, a series of blend films were obtained. Specially, the pure SPI films without blending were prepared by the same process, and the films were coded as SP0, SP25, SP50, SP75, and SP100 respectively.

Film thickness Film thickness was measured with a hand-held micrometer (0–25 mm, Shanghai Measuring & Cutting Tool Factory). For each film, nine different points were tested and averaged.

Color measurements Color values of the films were measured with a portable colorimeter (CR 400, Konica Minolta, Japan). The specimens were placed on a white standard plate ($L=95.67$, $a=-0.05$, $b=2.82$), and the L , a , b color values were measured. L values range from 0 (black) to 100 (white); a values range from -80 (greenness) to 100 (redness); and b values range from -80 (blueness) to 70 (yellowness). Three measurements were taken on each specimen, and each type of films was replicated three times.

Structural characterization In order to confirm the change in the internal structure of the film, FTIR analyses of blend films were performed on a FTIR spectroscopy (NICOLET 6,700), all samples were scanned from 4,000 to 400 cm^{-1} . The XRD measurement was conducted on an X-ray diffractometer (Rigaku D/MAX-3B), the Bragg angles were 10 °C–45 °C and the scanning rate was 2°/min. In addition, The microscopy observation of the films was carried out on an SEM (HITACHI S-3,400 Japan). And before the examination, the samples were dried under vacuum, rolled into tight rolls, and the fractured surfaces of the rolls were coated with gold.

Differential scanning calorimetry (DSC) Thermal properties of the films were studied by a differential scanning calorimetry (TA, Q20). Each samples of 6.0 mg were equilibrated at 25 °C for 2 min, and then heated to 200 °C at a rate of 10 °C/min.

Swelling experiment The method of Zhang et al. (2012) was used to determine the swelling properties of the film. Films were cut into 2.0×2.0 cm, and dried to constant weight. Then the dried samples were immersed into the deionized water at 25 °C for 6 h. At specific time intervals, the samples

were taken out of the water, absorbed excess moisture with cotton and weighed. The water swelling ratio of test sample was calculated as follow:

$$\text{Water swelling ratio} = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

Where m_t is the weight of the test sample at time of t and m_0 is the initial weight after drying. All experiments were carried out in six replicates.

Mechanical property A texture analyzer (TA-XT2i, SMS, Britain) was used to measure the tensile properties of the films according to ASTM standard method D882 (ASTM D882 2002). Before the test, films were cut in rectangular strips, the length and width are 50 mm and 10 mm. Then the specimen were stored in chamber at 25 °C and 50 % RH for 48 h. The initial grip separation was set at 50 mm, the pre-test, test, and post-test speed were set at 1, 5, and 10 mm s⁻¹, respectively. The tensile strength (TS) and Elongation at break (E) were calculated according to the method described by ASTM-D882. Measurements were performed at least in twenty replicates.

Water vapor permeability (WVP) A modified cup method based on the ASTM standard method (ASTM E 96–00) was used to decide the WVP (González et al. 2011). Each specimens (without physical defects such as cracks, bubbles or pinholes) were conditioned for 48 h in a chamber at 25 °C and 50 % RH before being determined. Then it was sealed onto an cup, which is filled with silica gel (0 %RH) and the mouth area *ie* test area is 45 cm². The test cups were placed in a humidity chamber at 25 °C and 50 % RH, and the weight changes were recorded at intervals of 1 h during 12 h. Linear fit was used to get the slope of the fitting straight line from the graph of mass versus time.

The water vapor transmission rate WVTR (kg s⁻¹ m⁻²) and the WVP (kg m Pa⁻¹ s⁻¹ m⁻²) was calculated as follow:

$$\text{WVTR} = F/A \quad (2)$$

Fig. 1 FTIR spectra of SPI and SPI/PAS blend films

Fig. 2 XRD patterns of SPI and SPI/PAS blend films

$$\text{WVP} = (\text{WVTR} \times e) / [SP \times (RH_1 - RH_2)] \quad (3)$$

Where F is the slope of fitting straight line (kg s⁻¹). A is the test area. e is the film thickness (m). Sp is the saturation vapor pressure at test temperature (Pa), RH_1 is the relative humidity in the test chamber and RH_2 is the relative humidity in the cup (nominally 0 %). All samples were measured in six replicates.

Results and discussion

Structure and miscibility To confirm the interaction between SPI and PAS, FTIR measurements were carried out for all films. As shown in Fig. 1, The amine stretching band region displayed two peaks at 3,450 cm⁻¹ and 3,133 cm⁻¹, which was assigned to –NH– stretching of the primary amide in SPI. For SP0, the characteristic absorbing peaks of amide I, corresponding to C=O stretching, were observed at around 1,650 cm⁻¹. And the amide I peaks blue-shifted to higher

Fig. 3 DSC thermograms of the SPI/PAS blend films on the heating scan

Fig. 4 Macroscopic appearance of the films (SP0-SP100 from left to right)

wave numbers after mixing with PAS. From $1,660\text{ cm}^{-1}$ of SP25 to $1,712\text{ cm}^{-1}$ of SP100, this indicated the strong intermolecular interactions between SPI and PAS. But whether the $-\text{NH}-$ of amide bond in PAS provided proton is still unknown. To conclude, FTIR confirmed that the strong bonding reaction occurred between soy protein and PAS in the blend films and the interactions increased with an increase of PAS.

The X-ray diffraction of different films was shown in Fig. 2. For SP0, there existed a broad peak between $10-40^\circ$. And compared with pure SPI film, the blend films showed some new characteristic crystalline peaks, which indicated that the blending made the structure of the original amorphous SPI films changed. For SP25, three weak typical diffraction peaks were found at 18.92° , 19.42° and 21.24° , while the diffraction peaks of SP50 were observed at 19.38° , 20.77° . For SP75 and SP100, the peak values were 17.14° and 17.01° respectively. The result confirmed the interactions between SPI and PAS. Broadly speaking, the comparative intensity of the peaks and the peak area became larger with the increases of PAS, indicating the increase of the crystallinity.

In order to further confirm the interactions and investigate thermal behavior of the film, DSC analyses were carried out. Fig. 3 shows the DSC curves for the films. For SP0, no apparent melting peak was found for the lack of crystal structure and the low sensitivity of DSC. But for the blend films, the melting peak appeared at around 120°C , and the melting temperature was significantly higher than the 50°C of SPI/WPU blend films previously reported, though the peak shape were not particularly sharp (Zhang et al. 2012). This

Table 1 L , a and b color values of different films

Film	L	a	b
SP0	91.05 ± 0.50^a	-1.54 ± 0.22^d	15.25 ± 1.22^c
SP25	84.03 ± 1.41^b	-0.66 ± 0.28^d	49.05 ± 1.14^d
SP50	74.56 ± 1.18^c	6.12 ± 0.38^c	57.50 ± 0.68^c
SP75	66.67 ± 0.97^d	15.00 ± 0.62^b	64.05 ± 0.97^b
SP100	56.91 ± 1.64^e	18.22 ± 0.83^a	67.82 ± 1.38^a

^a Any two means in the same column followed by the same letter are not significantly different ($P \leq 0.05$)

Fig. 5 SEM images of SP0 (a), SP25 (b), SP50(c), SP75 (d), SP100 (e)

phenomenon confirmed the reactions and indicated that the film has a good thermal stability. On the other hand, with the

Fig. 6 Swelling characteristics of SPI and SPI/PAS films

addition of PAS, the melting peak area showed an increasing trend, demonstrated that the crystallinity of the films increased, which was consistent with the results of XRD.

Figure 4 shows the macroscopic appearance of the films and Table 1 shows the color values of them. The L value decreases with the PAS addition, while the a and b value increases largely, which is different from SPI film treated by Sodium dodecyl sulfate (SDS), as the effects on L and a color values are practically inconsequential (Rhim et al. 2002). It shows that the brightness of the films decreases and yellowness increases, which may be unfavorable factors in food packaging.

Figure 5 shows the SEM images of pure SPI plastics and blend films and they are different from the SPI film reinforced by fiber in general (Kumar and Zhang 2009; Lodha and Netravali 2005). The fracture surfaces of SP0 film were rough and have many raised skeleton structures, which may be due to the original protein structure that is not completely destroyed and left behind. With the incorporation of PAS, the fracture surface structure has undergone great changes. For SP25, the surface became smoother and the skeleton structures disappeared, replaced by layered structure that is similar to the films prepared by Tian et al. (2010) which suggested the entanglement and strong radical reaction between SPI chain and PAS. With the addition of PAS, the films possessed more even and homogeneous fracture surface as illustrated in Fig. 5 (c, d, e). It is believed that the methods used in this work resulted in the successful intermolecular

Fig. 8 Effect of PAS content on tensile strength(■)and elongation at break(▲)at 25 °C, 50 %RH

reactions between soy protein and PAS. On the other hand, since polyamic acid is an insoluble polymer, it cannot react with soy protein denatured at alkaline conditions, thereby the PAS was introduced. And the blending of PAS with soy protein solution lead to a much better interfacial contact and the fine compatibility. This also proved that the method in this study is quite feasible.

Water resistance and mechanical properties In order to study the water resistance property of the films, all samples were submitted to swelling experiments. At the first hour, water expansion ratio was calculated every 10 min. And for the remaining 5 h, it was calculated every 1 h. The resulting swelling curve was shown in Fig. 6. The pure SPI film presented a high ratio, and it was obviously lowered after mixing with PAS, which indicated that the blend films had better water resistance properties. This can be due to the radical reaction between SPI and PAS, which restricts the penetration of water into the polymer matrix. For all films, the ratio showed a decreasing trend on the whole, which is very different from previous study (Tian et al. 2010). This may be caused by dissolution of the soluble matter in the film, such as water-soluble protein, hydrophilic unbound. Especially for SP0 and SP25, the ratio increased initially and then decreased. This may due to the strong hydrophilicity of SPI, and it require a longer time to reach a equilibrium of water uptake. It was also found that after immersing into water for 6 h, the SP0 film fell into disrupt fragments, the SP25 has a slight volume expansion (Fig. 7). While the other films could

Fig. 7 Pictures of different films after immersing into the water for 6 h (SP0-SPI100 from top to bottom)

Fig. 9 The effect of PAS content on the WVP of the films

retain the original integrity. This also indicated that the blend films had a better water resistance property.

Figure 8 showed the mechanical properties of the films. For the pure SPI film, the value of TS was 5.82 MPa as shown in, which is higher than the results of González calculated according to the ASTM D882-02. For the blend films at test conditions, the TS increased with an increase of PAS content, and the E exhibited the similar trend. when the concentration of PAS is 25 %, both of the values were significantly improved, and generally higher than the SPI films added with other biological polymers (Galus et al. 2013; Denavi et al. 2009) or reinforced by chemical crosslinking (González et al. 2011). This means that a small amount of PAS will be able to improve the mechanical properties of blend films. With the amount rises again, the values of TS increased significantly but the E were not significantly different.

The mechanical Properties of pure soy protein materials were not good. But in our findings, SPI/PAS blend films exhibited a better mechanical property than most

films improved with other methods, films reinforced by fiber and carboxymethyl cellulose(CMC) excepted (Behera et al. 2012; Huang and Netravali 2007; Su et al. 2010). This may be due to the polymerization of the different groups that changed the rigidity and flexibility of the molecular chains.

Water vapor barrier property Good water vapor barrier performance is very important to the materials used in packaging. Owing to the hydrophilicity of SPI, its water vapor barrier property was very low and the WVP of the SP0 film was $(4.34 \pm 0.17) \times 10^{-10} \text{ gmPa}^{-1} \text{ s}^{-1} \text{ m}^{-2}$, showing a little stronger water vapor barrier behavior than the pure SPI films reported previously (Zhang et al. 2012). Figure 9 shows the WVP of the different blend films. Generally, the values were lower than the SPI films treated by SDS, but they were higher than cross linked SPI (Rhim et al. 2002; González et al. 2011). With the increase of PAS, the values of the WVP decreased, and the difference between the values is significant as shown in Tables 2, which indicated that the incorporation of PAS improved the water vapor permeability of the films greatly. Especially, when the PAS content is 25 %, the WVP value reduced more, which was in good agreement with the TS values. This may be attributed to its homogeneous structure (Fig. 5) as well as the strong interactions between SPI and PAS.

Conclusion

The functional properties of pure SPI films can be modified by incorporation of PAS. And there exist strong interactions between SPI and PAS, which were confirmed by FTIR, XRD and DSC. Furthermore, compared with most films improved by some other methods, such as crosslinking, adding biological polymers or compounds, the SPI/PAS films possess better mechanical performance and improved moisture barrier ability. It suggests that the new blend films have a greater potentiality to be used as bio-materials.

Table 2 The values of film thickness, tensile strength (TS), elongation at break (E) and water vapor permeability (WVP) for all films

Film	Thickness ($\mu \text{ m}$)	TS (MPa)	E (%)	WVP($\times 10^{-10} \text{ gmpa}^{-1} \text{ s}^{-1} \text{ m}^{-2}$)
SP0	62.88 $\pm$ 2.61 ^a	5.82 $\pm$ 0.73 ^a	22.16 $\pm$ 1.93 ^b	4.34 $\pm$ 0.17 ^a
SP25	62.05 $\pm$ 4.75 ^a	9.02 $\pm$ 0.53 ^b	35.73 $\pm$ 0.93 ^a	3.52 $\pm$ 0.15 ^b
SP50	63.28 $\pm$ 1.49 ^a	9.06 $\pm$ 0.92 ^b	36.23 $\pm$ 0.95 ^a	3.30 $\pm$ 0.04 ^c
SP75	62.69 $\pm$ 3.52 ^a	9.51 $\pm$ 0.25 ^c	37.20 $\pm$ 1.56 ^a	3.14 $\pm$ 0.15 ^d
SP100	63.17 $\pm$ 2.44 ^a	10.08 $\pm$ 0.09 ^d	39.96 $\pm$ 0.3 ^a	2.78 $\pm$ 0.10 ^c

^a Any two means in the same column followed by the same letter are not significantly different ($P \leq 0.05$)

Acknowledgments Authors are thankful to College of science of Henan Agricultural University, Caoyuan Niu for constant encouragement. We are also thankful to Henan Agricultural University, College of food science and technology. And the funds of this study was provided by Education Department Project of Henan Province.

References

- Arora V, Tyers R (2012) Asset arbitrage and the price of oil. *Econ Model* 29:142–150
- ASTM Standard. D882-02 (2002). Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International Web. <http://www.astm.org>. Accessed 23 November 2011
- ASTM Standard. E96-00 (2000). Standard test methods for water vapor transmission of materials. ASTM International Web. <http://www.astm.org>. Accessed 17 June 2012
- Behera AK, Avancha S, Basak RK, Sen R, Adhikari B (2012) Fabrication and characterizations of biodegradable jute reinforced soy based green composites. *Carbohydr Polym* 88:329–335
- Brandenburg AH, Weller CL, Testin RF (1993) Edible films and coatings from soy protein. *J Food Sci* 58:1086–1089
- Denavi GA, Perez-Mateos M, Anon MC, Montero P, Mauri AN, Gomez-Guillen MC (2009) Structural and functional properties of soy protein isolate and cod gelatin blend films. *Food Hydrocoll* 23:2094–2101
- Dutta PK, Tripathi S, Mehrotra GK, Dutta J (2009) Perspectives for chitosan based antimicrobial films in food applications. *Food Chem* 114:1173–1182
- Ezrin M (2013) Environmental Recycling and health aspects of plastics failure. *Plastic Failure Guide* 779–809
- Galus S, Lenart A, Voilley A, Debeaufort F (2013) Effect of oxidized potato starch on the physicochemical properties of soy protein isolate based edible films. *Food Technol Biotechnol* 51:403–409
- González A, Strumia MC, Igarzabal CIA (2011) Cross-linked soy protein as material for biodegradable films: Synthesis, characterization and biodegradation. *J Food Eng* 106:331–338
- Huang XS, Netravali A (2007) Characterization of flax fiber reinforced soy protein resin based green composites modified with nano-clay particles. *Compos Sci Technol* 67:2005–2014
- Huang XS, Netravali W (2009) Biodegradable green composites made using bamboo micro/nano-fibrils and chemically modified soy protein resin. *Compos Sci Technol* 69:1009–1015
- Kumar R, Zhang LN (2009) Aligned ramie fiber reinforced arylated soy protein composites with improved properties. *Compos Sci Technol* 69:555–560
- Lithner D, Larsson A, Dave G (2011) Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Sci Total Environ* 409:3309–3324
- Lodha P, Netravali AN (2005) Characterization of stearic acid modified soy protein isolate resin and ramie fiber reinforced greencomposites. *Compos Sci Technol* 65:1211–1225
- Mesquita JP, Donnici CL, Pereira FV (2010) Biobased nanocomposites from layer-by-layer assembly of cellulose nanowhiskers with chitosan. *Biomacromolecules* 11:473–480
- Monedero FM, Fabra MJ, Talens P, Chiralt A (2010) Effect of calcium and sodium caseinates on physical characteristics of soy protein isolate–lipid films. *J Food Eng* 97:228–234
- Park SK, Rhee CO, Bae DH, Hettiarachchy NS (2001) Mechanical properties and water-vapor permeability of soy-protein films affected by calcium salts and glucono-delta-lactone. *J Agric Food Chem* 49:2308–2312
- Ratti RA, Vespignani JL (2013) Why are crude oil prices high when global activity is weak? *Econ Lett* 121:133–136
- Rhim JW, Gennadios A, Weller CL, Hanna MA (2002) Sodium dodecyl sulfate treatment improves properties of cast films from soy protein isolate. *Ind Crop Prod* 15:199–205
- Rhim JW, Mohanty KA, Singh SP, Ng PKW (2006) Preparation and properties of biodegradable multilayer films based on soy protein isolate and poly(lactide). *Ind Eng Chem Res* 45:3059–3066
- Sothornvit R, Hong SI, An DJ, Rhim JW (2010) Effect of clay content on the physical and antimicrobial properties of whey protein isolate/organo-clay composite films. *LWT-Food Sci Technol* 43:279–284
- Su JF, Huang Z, Yuan XY, Wang XY, Li M (2010) Structure and properties of carboxymethyl cellulose/soy protein isolate blend edible films crosslinked by Maillard reactions. *Carbohydr Polym* 79:145–153
- Silva SS, Goodfellow BJ, Benesc J, Rocha J, Mano JF, Reis RL (2007) Morphology and miscibility of chitosan/soy protein blended membranes. *Carbohydr Polym* 70:25–31
- Tian HF, Wang XY, Zhang LN, Quan CY, Zhang XZ (2010) Improved flexibility and water resistance of soy protein thermoplastics containing waterborne polyurethane. *Ind Crop Prod* 32:13–20
- Tian HF, Xu GZ, Yang B, Guo GP (2011) Microstructure and mechanical properties of soy protein/agar blend films: Effect of composition and processing methods. *J Food Eng* 107:21–26
- Wang NG, Zhang LN, Gu JM (2005) Mechanical Properties and Biodegradability of Crosslinked Soy Protein Isolate/Waterborne Polyurethane Composites. *J Appl Polym Sci* 95:465–473
- Wu QX, Zhang LN (2001) Preparation and characterization of thermoplastic starch mixed with waterborne polyurethane. *Ind Eng Chem Res* 40:558–564
- Wu RL, Wang XL, Wang YZ, Bian XC, Li F (2009) Cellulose/Soy Protein Isolate Blend Films Prepared via Room-Temperature Ionic Liquid. *Ind Eng Chem Res* 48:7132–7136
- Zhang M, Song F, Wang XL, Wang YZ (2012) Development of soy protein isolate/waterborne polyurethane blend films with improved properties. *Colloids Surface B* 100:16–21