

Preparation and Characterization of Soy Protein Isolate–Carboxymethylated Konjac Glucomannan Blend Films

Rupei Tang, Yumin Du, Hua Zheng, Lihong Fan

Department of Environmental Science, Wuhua University, Wuhan 430072, China

Received 10 December 2001; revised 9 May 2002; accepted 9 May 2002

Published online 18 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11703

ABSTRACT: To improve the mechanical and water vapor barrier properties of soy protein films, the transparent films were prepared by blending 5 wt % soy protein isolate (SPI) alkaline water solution with 2 wt % carboxymethylated konjac glucomannan (CMKGM) aqueous solution and drying at 30 °C. The structure and properties of the blend films were studied by infrared spectroscopy, wide-angle X-ray diffraction spectroscopy, scanning electron microscopy, thermogravimetric analysis, differential thermal analysis, and measurements of mechanical properties and water vapor transmission. The results demonstrated a strong interaction and good miscibility between SPI and CMKGM due to intermolecular hydrogen bonding. The thermostability and mechanical and water vapor barrier properties of blend films were greatly enhanced due to the strong intermolecular hydrogen

bonding between SPI and CMKGM. The tensile strength and breaking elongation of blend films increased with the increase of CMKGM content: the maximum values achieved were 54.6 MPa and 37%, respectively, when the CMKGM content was 70 wt %. The water vapor transmission of blend films decreased with the increase of CMKGM content: the lowest value achieved was $74.8 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ when the CMKGM content was 70 wt %. The SPI–CMKGM blend films provide promising applications to fresh food packaging. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1095–1099, 2003

Key words: proteins; blending; miscibility; thermal properties; mechanical properties

INTRODUCTION

Petroleum-based films dominate today's food packaging and other industrial applications because of their high strength, light weight, low cost, easy processibility, etc. However, most synthetic polymers are not biodegradable. With the increasing concerns of environmental pollution caused by nonbiodegradable materials, much research has been done to utilize natural polymers from agricultural products.

Soy protein is extracted from soybean, which is one of the major agricultural products in the world. In recent years, researchers have paid increasing attention to soy protein, which is biodegradable, environmentally friendly, and from an abundant renewable resource. Recent studies demonstrated that soy protein films are effective barriers to aroma compounds and light gases, such as oxygen and carbon dioxide.^{1,2} Unfortunately, compared with synthetic films, the major limitation of soy protein films in food packaging is their relatively poorer mechanical and water vapor barrier properties. So, studies on how to improve their mechanical perfor-

mance and water vapor barrier are urgently needed and of great significance.

Previous experimental results showed that the properties of soy protein can be modified by physical, chemical, or enzymatic treatments; for examples, enzymatic treatment with horseradish peroxidase,³ acylation with acetic and succinic acids,⁴ cross-linking with formaldehyde,⁵ and compression molding.⁶ In addition, blending is an effective and convenient method to improve the performance of polymeric materials. The properties of soy protein films may also be improved by blending with other natural polysaccharides, such as starch⁷ and sodium alginate.⁸

The purpose of this research was to promote the mechanical and water vapor barrier properties of soy protein isolate (SPI) by blending with a natural polysaccharide, carboxymethylated konjac glucomannan (CMKGM), which is derived from the abundant agricultural source konjac glucomannan. The morphological structure, miscibility, thermal stability, mechanical properties, and water vapor transmission of the blend films were studied by infrared spectroscopy (IR), wide angle X-ray diffraction spectroscopy (WAXD), scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of the mechanical properties and water vapor transmission (WVTR). The relationship be-

Correspondence to: Y. Du (duyumin@whu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29977014.

tween the structure and the physicochemical properties of the blend films is discussed.

EXPERIMENTAL

Materials

Soy flour was supplied by Yunmeng Protein Technology Company (Hubei, China). Soy protein isolate (SPI) was prepared as follows: Soy flour was suspended in a 100 mM Tris-HCl buffer of pH 10 in a 1:10 ratio (w/v) and stirred for 2 h at room temperature. After removal of the insoluble parts by centrifugation, the supernatant was brought to pH 4.5 with 2M HCL to induce precipitation of soy proteins. After 2 h at 4°C, the dispersion was centrifuged. The precipitate obtained was washed twice with a 10 mM sodium acetate buffer at pH 4.5 and then freeze-dried. This material had a protein content of >97% and is referred to as SPI. The weight-average molecular weight (M_w) was calculated as 1.9×10^6 with the Mark-Houwink equation ($[\eta] = 5.8 \times 10^{-2} M_w^{0.44}$).⁹

Konjac glucomannan was extracted and purified from the tuber of *amorphophallus konjac* (supplied by Fangxian Konjac Institute, Hubei, China) according to a published procedure.¹⁰ Carboxymethylated konjac glucomannan (CMKGM) was prepared by the following method: Konjac glucomannan was suspended in alcohol solution in a 1:5 ratio(w/v) and stirred for 1 h. Then, chloroacetic acid aqueous solution, with a very small amount of KI, was slowly added to the solution and allowed to react as a catalytic agent for 6 h at room temperature. This solution was then neutralized with 10 wt % acetic acid. Next, the product was washed several times with anhydrous alcohol and then vacuum dried. The degree of carboxymethylation was calculated as 61.8% by the colloid titration method.¹¹

Preparation of blend films

SPI was suspended in water for 30 min at room temperature, and the pH was adjusted to 10 with 1M NaOH to obtain a 5 wt % solution. CMKGM was dissolved in water to obtain a 2 wt % solution. Chosen volumes of CMKGM were added to the required amount of SPI solution. The resulting solution was stirred energetically and degassed, and then was spread over a glass plate. Blend films with different ratios were obtained after drying at 30°C. A series of blend films with CMKGM/SPI weight ratios of 9:1, 7:3, 5:5, 3:7, and 1:9 were coded CKS-1, CKS-2, CKS-3, CKS-4, and CKS-5, respectively. The films obtained from pure CMKGM and SPI were coded as CMKGM and SPI, respectively. The thicknesses of the films were $40 \pm 5 \mu\text{m}$.

Characterization of films

Infrared (IR) spectra of the pure and blend films were measured with a Fourier transform infrared (FTIR) spectrometer (Nicolet 170SX FTIR;), using KBr pellets. Wide-angle X-ray diffraction (WAXD) spectra of the films were measured with a Rigaku Dmax-II X-ray diffractometer, using a $\text{CuK}\alpha$ target at 40 kV and 50 mA. The diffraction angle ranged from 6 to 40°. The crystallinities of the films were calculated by the following equation:¹²

$$X_c = F_c / (F_c + F_a) \times 100\% \quad (1)$$

where F_c and F_a are the areas of crystal and noncrystalline regions, respectively. The surface morphology of blend film samples was studied with a Hitachi SX-650 scanning electron microscope. Samples were coated with gold at 0.1 τ vacuum degree, and photos were taken. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the film samples were performed with a DT-30B thermal analyzer; the conditions were a nitrogen atmosphere, a flow capacity of 30 mL/min, a heating range of 0 to 500°C, and a heating rate of 15°C/min. The tensile strength and breaking elongation of the films were measured on an electron tensile tester (AG-A) at a tensile rate of 10 mm/min and at a gauge length of 90 mm. The temperature and relative humidity were 25°C and 60%, respectively. Water vapor transmission (WVTR) of films was measured in accordance with ASTM(1993) E96-93. Special cups, with an average diameter of 3.9 cm and a depth of 1 cm, were used. After placing 3 g of anhydrous CaCl_2 in each cup, the cups were covered with the blend films. The cups with their content were weighed and placed in a desiccator that contained saturated KCl solution in a small beaker at the bottom. Saturated KCl solution in the desiccator provides a constant relative humidity medium of 84% at 25°C. The desiccator was kept in an incubator at $25.0 \pm 0.1^\circ\text{C}$. Cups were weighed every 24 h until a steady increase in weight was achieved.

RESULTS AND DISCUSSION

Miscibility

Pure and blend films were transparent and optically clear to the naked eye. The CMKGM film was easily dissolved in the distilled water at room temperature.

The IR spectra of the pure and blend films are shown in Figure 1. The pure CMKGM film spectrum has the following characteristic absorption bands: $\sim 3300 \text{ cm}^{-1}$, revealing the stretching vibration of the O—H group; 1615 cm^{-1} , which can be ascribed to the stretching vibration of the carbonyl group, C=O, suggesting CMKGM exists as a carboxylate; and 1148 cm^{-1} , reflecting the bending vibration of C—O—C

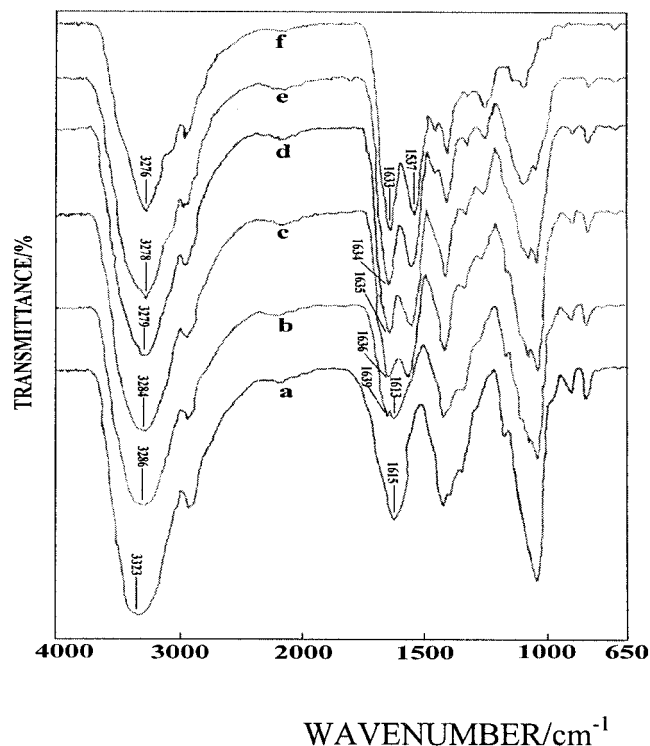


Figure 1 IR spectra of pure and blend films: (a) CMKGM; (b) CKS-1; (c) CKS-2; (d) CKS-3; (e) CKS-4; (f) SPI.

group. The pure SPI film spectrum has the following characteristic bands: $\sim 3300\text{ cm}^{-1}$, revealing the stretching vibration of the N—H group; 1633 cm^{-1} , which can be attributed to the amide I (stretching vibration of carbonyl group, C=O), and 1537 cm^{-1} , which can be attributed to the amide II (bending vibration of secondary carbonyl group, N—H). Comparing the spectra of pure SPI and CMKGM films with those of the blend films reveals the following major differences: (1) The absorption bands at $\sim 3300\text{ cm}^{-1}$, corresponding to O—H and N—H stretching vibrations, shifted in an obvious manner to a lower wave number with the increase of SPI content in blend films. This result suggests the formation of strong intermolecular hydrogen bonding between CMKGM and SPI. (2) The absorption band of the carbonyl group of CMKGM at 1615 cm^{-1} shifted to a lower wave number, 1613 cm^{-1} , and greatly weakened when the SPI content was 10 wt %. This band disappeared completely with the increase of the SPI content in the blend films, suggesting the formation of the hydrogen bonding between the C=O group in CMKGM and N—H group in SPI. (3) The absorption band of amide I in SPI at 1633 cm^{-1} also weakened and shifted gradually to a higher band at 1639 cm^{-1} with the increase of CMKGM content. This result suggests that the CMKGM molecule disturbed the intramolecular strong hydrogen bonding of SPI, which further supports the presence of interaction between O—H and

C=O groups in CMKGM and N—H and C=O groups in SPI by intermolecular hydrogen bonding. The IR results show that there was no formation of a polyelectrolyte complex between CMKGM and SPI, mainly because of the solution condition (pH 10), which is in agreement with the results in the literature.¹³ The IR results also indicate that the blend between the two kinds of molecules was miscible due to the strong intermolecular hydrogen bonding.

The X-ray patterns of the pure and blend films are shown in Figure 2. The degree of crystallinity (X_c) of the films is of the order CMKGM < CKS-4 < CKS-5 < SPI < CKS-3 < CKS-2 < CKS-1, with values of 19, 23, 25, 30, 31, 32, and 36%, respectively. It is clear that the X_c values of the blend films decreased with increasing CMKGM content, with the minimum X_c of 23% at 30 wt % CMKGM content. This result suggests that the intermolecular interaction between CMKGM and SPI disturbed the crystallization of SPI in a blend state. The results also suggest a certain lever of miscibility for the blend films.

The surface morphology of the blend films determined by SEM are shown in Figure 3. The micrographs of CKS-2 and CKS-4 indicate a smooth and homogeneous surface morphology, suggesting high miscibility and blend homogeneity between SPI and CMKGM.

In view of IR, WAXD, and SEM analyses of SPI-CMKGM blend films, it can be concluded that good

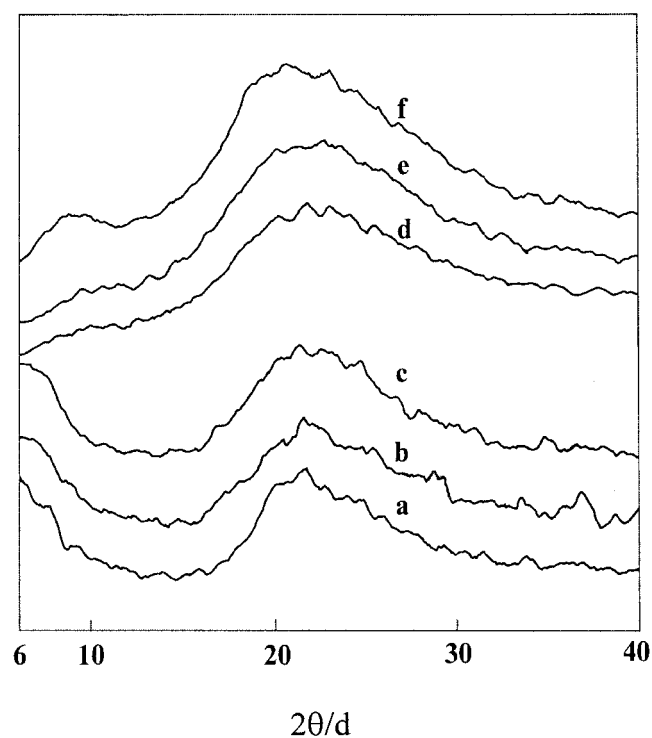


Figure 2 The X-ray patterns of the pure and blend films: (a) CMKGM; (b) CKS-1; (c) CKS-2; (d) CKS-3; (e) CKS-4; (f) SPI.

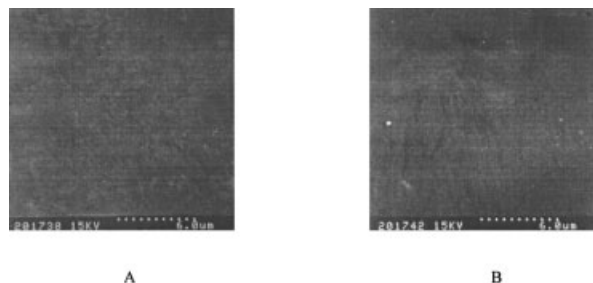


Figure 3 SEM photographs of the blend films (A) CKS-2 and (B) CKS-4.

miscibility was sustained because of the intermolecular hydrogen bonding between SPI and CMKGM.

Thermal stability

The DTA thermograms of the pure and blend films are shown in Figure 4. The films all show endothermic peaks in the range 80–110°C, corresponding to dehydration in the films. All the films show endothermic peaks at ~240–270°C, which resulted from the greatest thermal degradation of the films. With the increase of SPI content in the blend, the greatest thermal degradation peak shifted in an obvious manner to a higher temperature, which indicates the strong interaction between the two kinds of molecules.

The results of the TGA measurements of the pure and blend films are shown in Figure 5. The starting temperature of the greatest degradation of the blends shifted to higher temperature with the increase of SPI content. The thermal stability of the blend films is of

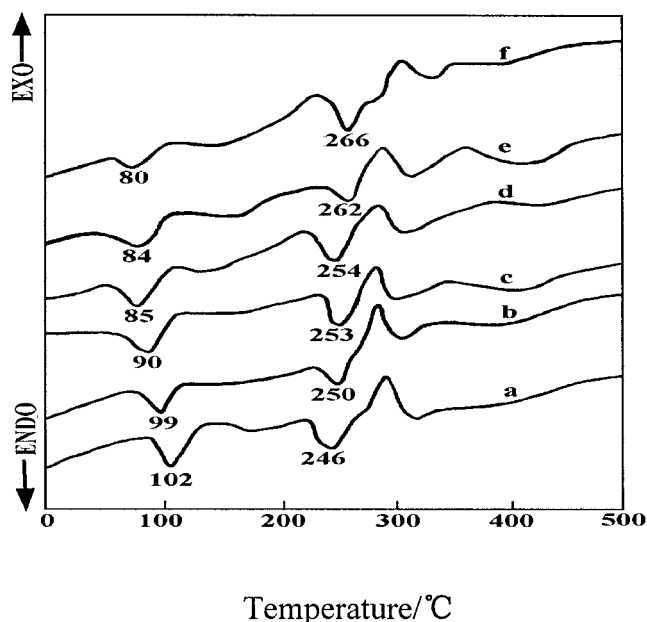


Figure 4 DTA thermograms of the pure and blend films: (a) CMKGM; (b) CKS-1; (c) CKS-2; (d) CKS-3; (e) CKS-4; (f) SPI.

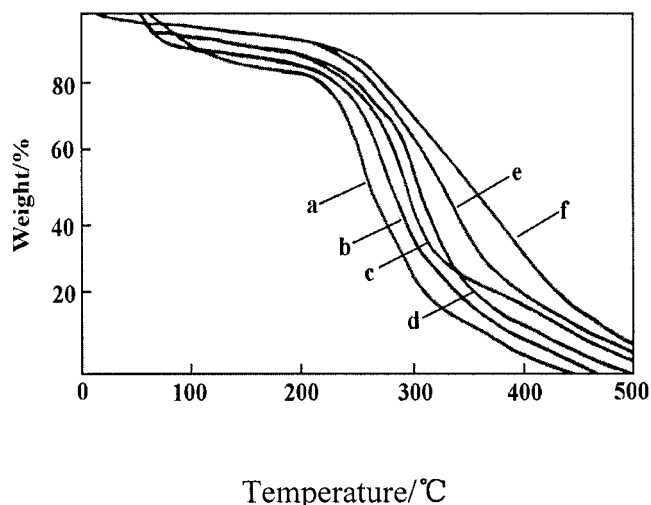


Figure 5 TGA thermograms of the pure and blend films: (a) CMKGM; (b) CKS-1; (c) CKS-2; (d) CKS-3; (e) CKS-4; (f) SPI.

the following order: CMKGM (222°C) < CKS-1 (223°C) < CKS-2 (224°C) < CKS-3 (228°C) < CKS-4 (232°C) < SPI (236°). This result implies that the thermostability of the blend films is obviously enhanced due to the hydrogen bonding between SPI and CMKGM molecules.

Mechanical properties

The effects of CMKGM content on the tensile strength and breaking elongation of the films are shown in Figure 6 and 7, respectively. The tensile strength of the blend films increased with increasing CMKGM content, and the maximum value of 54.6 MPa was achieved when the CMKGM content was 70 wt %. However, the tensile strength of the blend films decreased rapidly when the CMKGM content was >70 wt %. The alteration of breaking elongation expressed

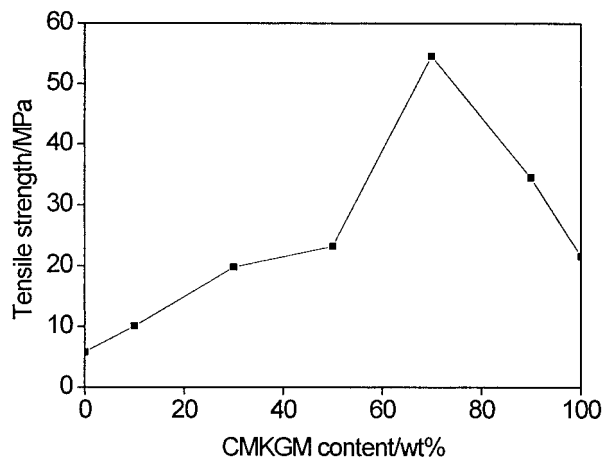


Figure 6 The effect of CMKGM content (wt %) on tensile strength of the films.

a tendency similar to that of the tensile strength, and the maximum value of 37% was achieved when the CMKGM content was 70 wt %.

The conclusion can be drawn that compared with SPI or CMKGM pure films, blend films of SPI and CMKGM have considerably enhanced mechanical properties in the dry state because of the hydrogen bonding between SPI and CMKGM. The better mechanical properties of the blend films makes these films more promising than the pure soy protein films used in food packaging and renewable applications.

Water vapor transmittance

The effect of CMKGM content on the WVTR of the films is shown in Figure 8. WVTR values of the blend films decreased in an obvious manner with the increase of CMKGM content, and the minimum of $74 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ was achieved when the CMKGM content was 70 wt %. However, WVTR values of the blend films rapidly increased when the CMKGM content was >70 wt %. The results indicate that the blend of SPI with CMKGM has considerably improved water barrier properties compared with those of pure soy protein films because of the formation of a compact molecular structure as a result of the strong hydrogen bonding between SPI and CMKGM. The SPI-CMKGM blend films were more effective than the pure SPI film in reducing the moisture loss when used for fresh food packaging.

CONCLUSION

A series of transparent films were prepared by blending 5 wt % SPI alkaline water solution with 2 wt % CMKGM aqueous solution in predetermined ratios and drying at 30°C . The mechanical properties in the dry state, thermostability, and water vapor barrier

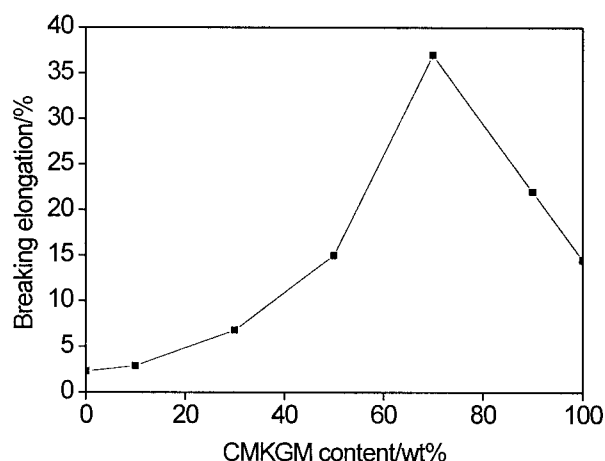


Figure 7 The effect of CMKGM content (wt %) on breaking elongation of the films.

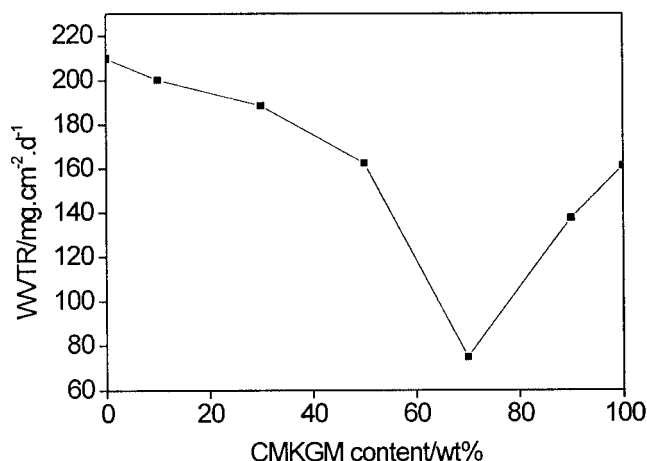


Figure 8 The effect of CMKGM content (wt %) on WVTR of the films.

properties of the blend films were obviously improved. The best values of the tensile strength, breaking elongation, and water vapor transmission, achieved when the CMKGM content was 70 wt %, were 54.6 MPa, 37%, and $74.8 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$, respectively. The good miscibility between SPI and CMKGM was confirmed by the results of IR, SEM, and WAXD analyses. The interaction due to the strong intermolecular hydrogen bonding resulted in the enhancement of the thermostability and the mechanical and water vapor barrier properties of SPI-CMKGM blend films. The high tensile strength in the dry state and the good water vapor barrier properties of the SPI-CMKGM blend films make them promising packaging materials and provide a niche and a value-added industrial outlet for two abundant agricultural feedstock.

References

1. Cavallaro, J. F.; Kemp, P. D.; Kraus, K. H. *Biotechnol Bioeng* 1994, 43, 781.
2. Debeaufort, F.; Voilley, A.; Meares, P. J. *J Membr Sci* 1994, 91, 125.
3. Stuchell, Y.M.; Krochta, J.M. *J Food Sci* 1994, 59, 1332.
4. Ghorpade, V.M.; Gennadios, H.; Hanna, M.A. *Trans ASAE* 1995, 38, 1805.
5. Feeney, R.E.; Blankenhorn, G.; Dixon, H.B.F. *Adv Protein Chem* 1975, 29, 135.
6. Qiangxia, Wu; Lina, Zhang. *Ind Eng Chem Res* 2001, 40, 1879.
7. Otaigbe, J.U.; Goel, H.; Bab, T.; Jane, J. *J Elast Plast* 1999, 31, 56.
8. Brandenburg, A.H.; Weller, C.L.; Testin, R.F. *J Food Sci* 1993, 58, 1086.
9. Qiangxian, Wu; Lina, Zhang. *J Appl Polym Sci* 2001, 82, 3373.
10. Chaobo, Xiao; Shanjun, Gao; Hen, Wang; Lina, Zhang. *J Appl Polym Sci* 2000, 76, 509.
11. Okimasu, S. *Bull Agr Chem Soc Japan* 1956, 20, 29.
12. Rabek, J.F. *Experimental Methods in Polymer Chemistry: Applications of Wide Angle X-ray Diffraction(WAXD) to the Study of the Structure of Polymers*; Wiley-Interscience: Chichester, UK, 1980; p. 505.
13. Dickinson, E. *Trends Food Sci Technol* 1998, 9, 347.