Journal of Applied Polymer Science

Composition Optimization of Polyvinyl Alcohol/Rice Starch/Silk Fibroin-Blended Films for Improving Its Eco-Friendly Packaging Properties

Pusita Kuchaiyaphum,[1,2] Winita Punyodom,[1,2] Surasak Watanesk,[1,2] Ruangsri Watanesk[1,2]

[1]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

[2]Department of Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Correspondence to: R. Watanesk (E-mail: ruangsri@gmail.com)

ABSTRACT: Biopolymers obtained from renewable sources have been exploited in developing biomaterials with eco-friendly properties. Most biopolymers have some limitations because of their poor mechanical properties, high water solubility, or low transparencies. In this study, some biopolymers, that is, silk fibroin (SF) and rice starch (RS) were used as starting materials together with polyvinyl alcohol (PVA) as a film-former for preparing novel eco-friendly films. The film preparations were done by solution casting with two different sequences of blending and the film compositions were optimized. Results from UV, SEM, and film properties testing on mechanical properties, degree of swelling, water solubility, and also oxygen permeability indicated that all film properties depended on their compositions and order of blending. The PVA/RS film obtained is transparent with good mechanical properties and low water solubility. The addition of SF increases the permeability of oxygen and also the degradability of the films. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2614–2620, 2013

Received 21 July 2012; accepted 31 December 2012; published online 30 January 2013
DOI: 10.1002/app.38977

INTRODUCTION

In recent years, biopolymers obtained from renewable sources have gained increasing attention and utilization in various areas including food packaging.[1] However, plastics currently used for food packaging such as low-density polyethylene (LDPE) and polypropylene are synthesized from petroleum-based chemicals and they are nondegradable. The wastes of material produced from petroleum-based polymer have brought negative impact not only for human being, but also generate serious environmental problems.[2] Therefore, several biopolymers have been exploited in developing materials used in making eco-friendly food packaging[3] such as the renewable or sustainable materials with enhanced barrier and also mechanical properties[4] and the innovations in food packaging based on nanotechnology.[5] Silk fibroin (SF) is a type of protein, a natural polymer produced by *Bombyx mori* silkworms, which have many good properties including biocompatibility, water absorbability, microbial resistance, and good oxygen permeability (OP). It has a potential to be used in such an application. Even though many researchers have reported various applications of SF,[6–9] such as in medical, pharmaceutical, cosmetic, and agricultural areas but not many are found in food packaging. Rice starch (RS), another renewable and biodegradable biopolymer, has been increasingly utilized in many applications, primarily because of its low cost and ease of availability. Packaging films composed entirely of SF or RS, however, lack strength and rigidity to withstand the stress to which many packaging materials are subjected.[10] Therefore, in order to improve such properties, the incorporation of SF and RS and another appropriate stronger based polymer is a logical attempt. Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer, made from the hydrolysis of polyvinyl acetate, which has the advantages of excellent film-forming and adhesive properties, together with high thermal stability. Because of such good properties, it was blended with different natural polymers[11–14] such as chitosan, chitosan/pectin, cashew gum polysaccharide, and also starch, in order to develop the antimicrobial materials that their shelf-life can be extended for using in food packaging applications. The addition of PVA may help overcome some limitations associated with SF- and RS-based polymer blends in the same fashion as it did with other natural polymers because both SF and RS contain amide and hydroxyl groups, which are potentially miscible with PVA through the formation of hydrogen bonds.[15] Therefore, PVA, RS, and SF are the alternative starting materials for blending as the packaging films depend on the different packaging applications.

In this study, PVA/RS/SF-blended films were prepared by solution casting with two different sequences of blending. The

Additional Supporting Information may be found in the online version of this article.

optimal compositions of the films were determined, considering from their properties characterization. The obtained films are expected to contain more biopolymer content and still have high strength and good flexibility. Moreover, these films should be transparent and have low water solubility (WS) with higher OP and degradability.

EXPERIMENTAL

Blended Films were prepared by solution casting with two different sequences of blending.*Sequence I*, PVA/SF solutions were mixed at various weight ratios (90 : 10–60 : 40), followed by the addition of 0.1–5% w/v of RS.*Sequence II*, the PVA/RS solutions with 80 : 20–40 : 60 in weight ratios were mixed, then the 0.5–6% w/v of SF was added. Properties of the blended films, including transparency, mechanical properties, water swelling and solubility, as well as cross-sectional morphology were determined. Furthermore, OP through the blended films and biodegradability of the films was also measured.

Materials

Silk waste was purchased from Jun Thai Silk Group Co., Thailand. SF powder was prepared from the silk waste by the method of Moonsri *et al.*,[16] without further characterization. RS (Era–Tab, Lot # T510405, Anal. # T0405, loss on drying 11.22%, residue on ignition 0.26% and pH 5.49) was obtained from Erawan Pharmaceutical Research and Laboratory Company Co., Ltd., Bangkok, Thailand. PVA (99% hydrolyzed with a molecular weight average of 85,000–124,000) was purchased from Aldrich Chemical Co. Inc. (St. Louis, MO). All other chemicals were analytical grade. Distilled water was used throughout.

Preparation of the Blended Films

Aqueous solutions of 3% w/v PVA, 0.1–6% w/v RS, and 0.5–6% w/v SF were firstly prepared at 95°C, 80°C, and room temperature, respectively. Then, solution casting of the blended films were carried out as follows:

Sequence I: The PVA and SF solutions were mixed together at various weight ratios ranging from 90 : 10–60 : 40. Fifteen milliliter each of PVA/SF mixture was stirred for 15 min at room temperature. Then, 5 mL of RS solutions at different concentrations (0.1–5% w/v) were added into the PVA/SF mixture separately and stirred for 50 min.

Sequence II: Fifteen milliliter each of PVA/RS mixture (80 : 20–40 : 60 in weight ratios) was stirred for 15 min at 80°C before adding 5 mL of SF solutions with various concentrations (0.5–6% w/v) separately at room temperature and stirred for 50 min.

The above mixtures were casted in the moulds (10 cm diameter) and the solvent was evaporated at room temperature in the laminar flow hood for 2 days. Then, the films were peeled off and kept in desiccators for further characterization.

Characterization of the Blended Films

The PVA/SF/RS (*Sequence I*)- and PVA/RS/SF (*Sequence II*)-blended films were characterized by various methods in order to find the optimal conditions for film preparation.

Film Transparency. Each film sample was cut into pieces with a size of 1 × 4 cm^2 and placed in the quartz cell. Then, % transmittance at 500 nm was recorded using a UV-VIS spectrometer (Lambda 25, Perkin-Elmer, Waltham, MA).

Mechanical Properties. Mechanical properties of the films prepared through a series of different weight ratios of PVA/SF and PVA/RS were investigated. Each film was cut into **1** × **5** cm^2 pieces. The film thickness was about 0.060 ± 0.010 mm. The tensile strength and % elongation at break of five selected pieces of the samples were measured using a universal mechanical testing machine (LRX, Lloyds Instruments, St. Clair Shores, MI) according to the ASTM D882-91 (ASTM, 1992), with a crosshead speed of 50 mm/min. The results were reported as the average values.

Degree of Swelling and WS. The dried films were weighed and then immersed in distilled water at room temperature for 24 h. After blotting out the excess water on the surface, the swollen films were weighed. Then, each swollen film was oven-dried for 24 h at 60°C and reweighed. The degree of swelling (DS) and the WS of the films were calculated using the eqs. (1) and (2), respectively, as stated by Park et al.:[17]

$$DS = \frac{W_2 - W_1}{W_1}. \quad (1)$$

$$WS = \frac{W_1 - W_3}{W_1} \quad (2)$$

where, W_1, W_2, and W_3 are weights of the initial dried film, the water saturated film, and the dried swollen film, respectively.

Film Morphology. The film samples were broken into small pieces (0.2 × 0.1 cm^2) in liquid nitrogen to avoid the scratches on the cross-section surface of films from cutting. The selected piece was mounted on a metal stub with double-sided adhesive carbon tape and coated with gold. Then morphological structures of the films were investigated using a scanning electron microscope (JSM-**5910** LV, JEOL).

Oxygen Permeability. Many kinds of foods require specific atmospheric conditions to retain their freshness and overall quality during storage.[18] Thus, in order to monitor the gas diffusion through the film, the oxygen gas was selected for testing.

OP of the films was measured at room temperature using the OP set-up as shown in Figure 1. After passing the oxygen gas through the exposed testing film (10 cm^2 size) in the sample chamber, we measured pressure of the penetrated oxygen gas in terms of $\triangle h$. The %OP of each film was then calculated by the following equation:

$$\%\mathrm{OP} = \frac{\Delta h_t}{\Delta h_o} \times 100 \quad (3)$$

where $\triangle h_o$ and $\triangle h_t$ are the height differences measured by the U-tube water manometer, without and with a film in the sample chamber, respectively. Moreover, the oxygen gas transmission rate (OTR) of the blended films were also measured by the standard method using an oxygen permeation tester (Illinois model 8000) according to the ASTM D3985-05, with a temperature of 23°C and 0% RH. The results were reported as the average values.

Applied Polymer SCIENCE

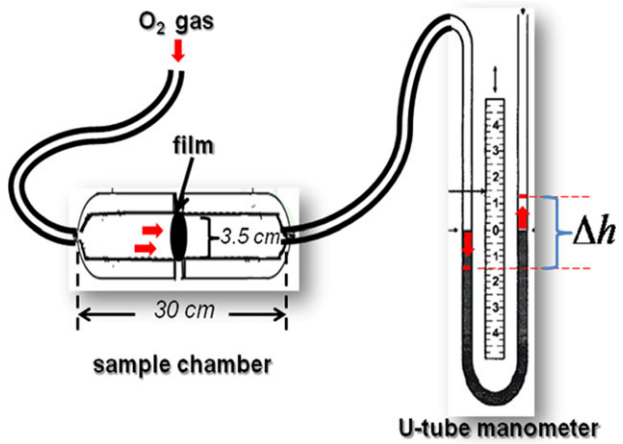

Figure 1. Apparatus for oxygen permeability measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

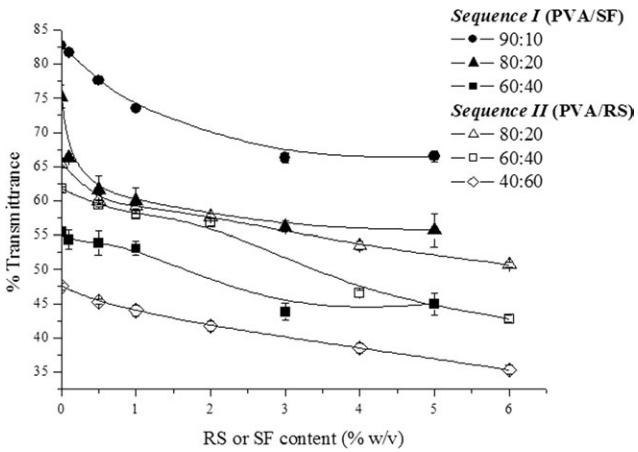

Figure 2. Percent transparencies of the blended films of PVA/SF/RS (*Sequence I*) and PVA/RS/SF (*Sequence II*) after the addition of RS and SF at various concentrations, respectively.

Films Degradation. The biodegradability of the optimized PVA/RS/SF-blended films was determined by the soil burial degradation testing using the method of Devi and coworkers[19] with some modifications. Two selected pieces of the film samples (3×3 cm^2) were weighed and then buried in the tray that filled with 45 g of soil. The trays were buried in the ground (about 30 cm depth, 20–40% humidity and pH about 6.34). The degradability of each film was determined at a weekly interval of 3 months by taking the films out of the ground, washing with distilled water to remove the soil, and drying until the a constant weight was obtained. Percent degradation of the film was calculated using the eq. (4):[20]

$$\%Degradation = \frac{W_4 - W_5}{W_4} \times 100 \quad (4)$$

where W_4 and W_5 are the weights of the film at the beginning and the degraded film, respectively.

RESULTS AND DISCUSSION

Film Transparency

Results of percent transparency of the blended films in Figure 2 clarify that the clarity of the blended films depends on PVA content. The film from *Sequence I* at 90 : 10 in weight ratio of PVA and SF exhibits the highest transparency compared with other compositions. Besides, the more RS or SF is added in each sequence, the lower the transparency of the film. However, the transparency of all films is higher than that of the conventional LDPE films (20–30% transparency).[21] In addition, at the same weight ratio of 60 : 40, percent transparency of the PVA/RS films from *Sequence II* is higher than the PVA/SF films from *Sequence I*. This indicates that the interaction between PVA and RS molecules is stronger than that of PVA and SF because of the aggregation of hydrophobic part of the amino acids in the SF molecules. Thus, the SF molecules become entangled in the solution by hydrophobic interactions.[12]

To reduce the use of synthetic polymer (PVA), the films with 60 : 40 in weight ratio of PVA from *Sequence I* and *II* were selected for further study. However, by considering the film clarity, the PVA/SF films from *Sequence I* at weight ratios of 90 : 10 and 80 : 20 still have good clarity. Therefore, they were also selected for further study as well.

Mechanical Properties

Considering the properties of stress at break and elongation of the blended films, Figures 3 and 4 demonstrate that the tensile property of all blended films also depends on their compositions. Once the content of PVA is decreased from 90 to 80 of its weight ratio, the strength of the films from *Sequence I* decreases. But as the PVA content decreases to 60 weight ratio, the strength of the films turns out to increase and is higher than that of the PVA/SF/RS film with 90 weight ratio. However, the flexibility of all PVA/SF/RS films decreases with the decrease of PVA content. These results reveal that when PVA combines directly with SF, the —NH_2/—C(O)— groups of the SF molecules could aggregate and entangle among themselves at higher

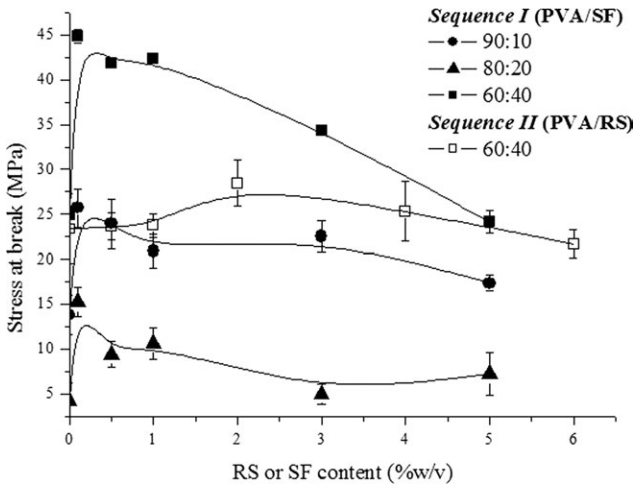

Figure 3. Stress at break of the blended films of PVA/SF/RS (*Sequence I*) and PVA/RS/SF (*Sequence II*) after the addition of RS and SF at various concentrations, respectively.

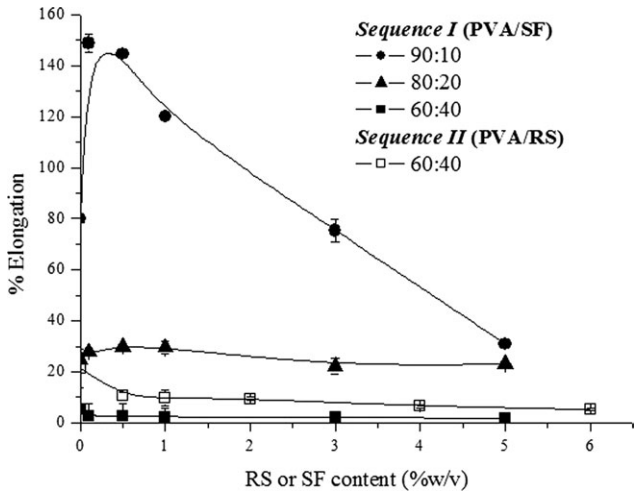

Figure 4. Elongation of the blended films of PVA/SF/RS (Sequence *I*) and PVA/RS/SF (*Sequence II*) after the addition of RS and SF at various concentrations, respectively.

SF content, thus making the interaction between PVA and SF become less. In addition, both the strength and flexibility of those films tend to decrease with the increase of added RS or SF. Only the film prepared through *Sequence I* (90 : 10 in weight ratio of PVA/SF with 0.1% w/v RS) provided the highest strength and flexibility.

Comparing the strength of PVA/SF/RS film (*Sequence I*) and PVA/RS/SF film (*Sequence II*) prepared at the same weight ratio of 60 : 40, it can be seen that the *Sequence I* film has a higher strength than the *Sequence II* film, but its elongation is the lowest. This result confirms a better flexibility of the films from *Sequence II* because of the compatibility between PVA and RS within the films.

DS and WS

Figures 5 and 6 reveal that both DS and WS of all blended films from *Sequence I* at all weight ratios are higher than those films from *Sequence II*. Moreover, in *Sequence I*, it can be seen that

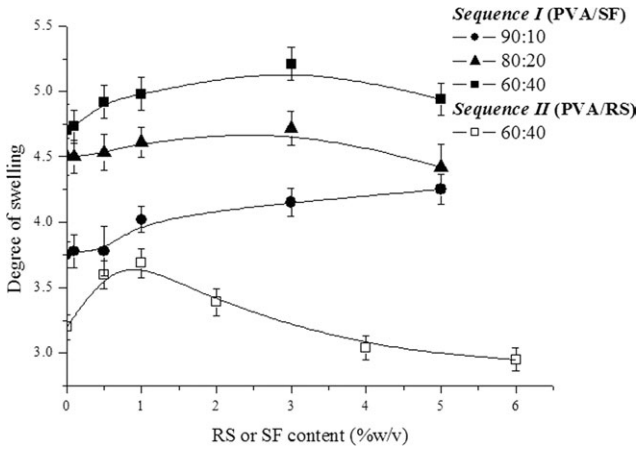

Figure 5. Degree of swelling of the blended films of PVA/SF/RS (*Sequence I*) and PVA/RS/SF (*Sequence II*) after the addition of RS and SF at various concentrations, respectively.

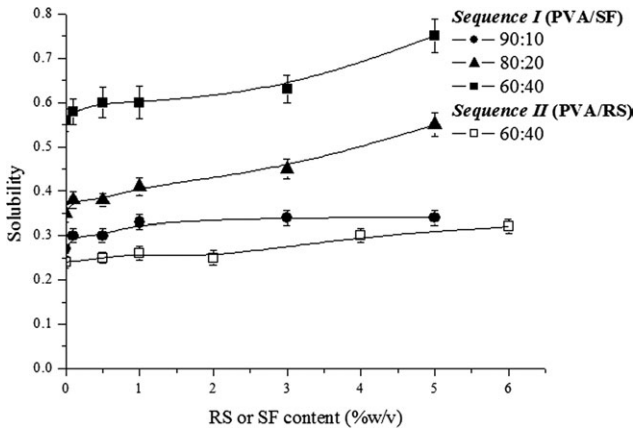

Figure 6. Water solubility of the blended films of PVA/SF/RS (*Sequence I*) and PVA/RS/SF (*Sequence II*) after the addition of RS and SF at various concentrations, respectively.

the blended films with higher SF content showed higher DS and WS compared to the lower SF content-blended films. Thus, this indicates the higher hydrophilicity of the PVA/SF films because of the WS of SF that causes the increase in water-uptake of PVA and PVA/RS after blending with SF through the increase of the number of hydrophilic groups (—NH_2/—C(O)—) in the blends.

Film Morphology

The SEM images in Figure 7 demonstrate continuous dispersion of the SF and RS particles in PVA moiety. With the decrease of PVA content in the PVA/SF films from *Sequence I* (Figures 7a,c and e), phase separation within the blends apparently increases. Although the addition of 0.1% w/v RS does not reduce the phase separation between PVA and SF (Figures 7b,d and f). At the weight ratio of 60 : 40 in *Sequence II* (Figure 7g), the blending is still compatible and the addition of 2% w/v SF (Figure 7h) does not pose much effect.

Because the phase separation is an essential factor that affects film properties,[22,23] the absence of phase separation in the SEM images of PVA/RS film at 60 : 40 in weight ratio with 2% w/v RS from *Sequence II* supports the observed mechanical properties of the films as in Figures 3 and 4, and also other properties as in Figures 5 and 6.

Oxygen Permeability

Results from the aforementioned experiment indicate that the optimal composition for film preparation is at 60 : 40 in weight ratio of PVA/RS with 2% w/v of SF from *Sequence II*. These blended films were selected as samples for determining the OP measured by the homemade set-up compared with the OTR using the standard method.

From Figure 8, the OP of the blended film measured by the homemade set-up was compared with the standard OTR method. By comparing the PVA/RS films without and with SF (2% w/v), it can be seen that each comparing test method provides agreeable result. That is, as the SF content increases, the OP also increases, whereas the results of OTR measurement by the standard method confirm the increase of OP as % SF increases as well.

Applied Polymer SCIENCE

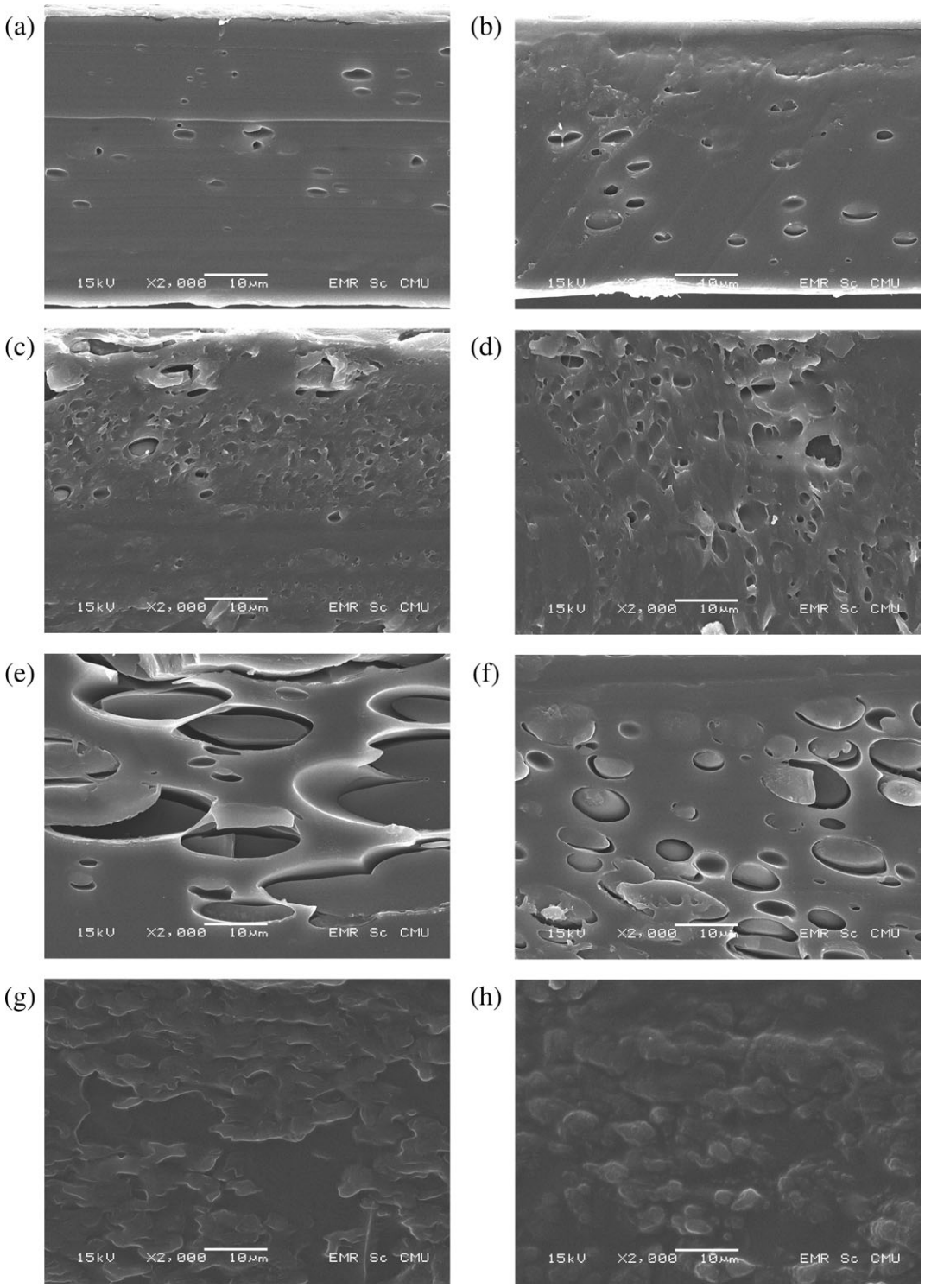

Figure 7. Cross-sectional SEM images of the films prepared by two different sequences of blending.

Film Degradation

As the soil burial test provides a realistic environmental condition, all the tested films had the same shape and size to avoid any other effects on its biodegradability. Biodegradability of the samples was studied through the evaluation of the weight loss of the films over a period of time.

It was found that a rapid degradation of both PVA/RS films with and without SF occurred within 2 weeks (Figure 9). After that a slow degradation occurred until the end of the experiment. Moreover, the films with 2% w/v SF exhibited more degradation than the films without SF.

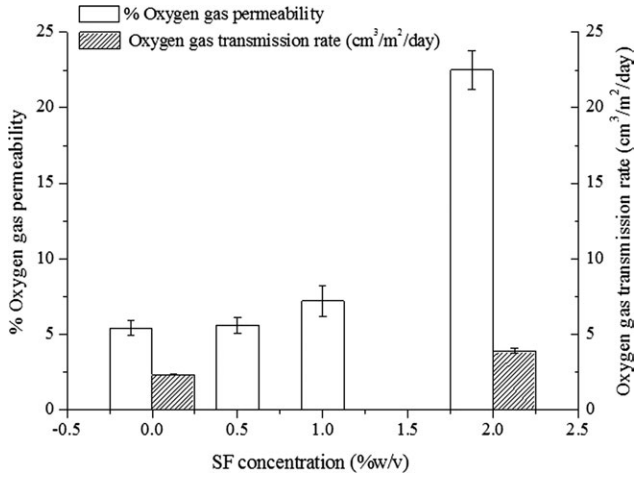

Figure 8. % Oxygen permeability and oxygen gas transmission rate of the PVA/RS films with a weight ratio of 60 : 40 (*Sequence II*) after the addition of SF at various concentrations.

Data in Table 1 reveal that the addition of SF increases the strength, OP, and degradation rate of the blended films. Although other properties, that is, the DS and also WS are quite constant, the flexibility of the film decreases.

CONCLUSION

Preparation of PVA/RS/SF-blended films was carried out by solution casting with two different sequences of blending. Results from film characterization indicated that the compatibility and phase segregation of the components in the blends affected the film properties. The optimal condition for film preparation was 60 : 40 in the weight ratio of PVA/RS with 2% w/v of SF. At this condition, the film had a high content of biopolymer and still had high strength, high flexibility and transparency, low water swelling, and solubility. The addition of SF tended to increase the OP of the film. Moreover, the film with 60 : 40 in weight ratio of PVA/RS and 2% w/v of SF can degrade with percent degradation of about 50% within 3 months.

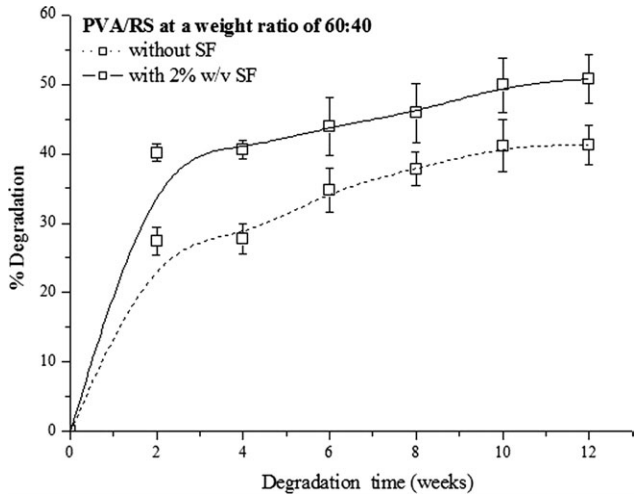

Figure 9. Percent degradation of the PVA/RS film at a weight ratio of 60 : 40 with the addition of 2% w/v SF after burying in the soil for 12 weeks.

Table I. The Properties of PVA/RS-Blended Film (60 : 40 weight ratio) with and without 2% w/v of SF

Film properties	The values of film properties	
	without SF	with 2% w/v SF
% Transmittance	61.7 ± 0.4	56.8 ± 0.5
Stress at break (MPa)	23.37 ± 3.91	28.46 ± 2.59
% Elongation	21.43 ± 7.57	9.47 ± 0.60
Degree of swelling	3.23 ± 0.09	3.39 ± 0.10
Water solubility	0.24 ± 0.01	0.25 ± 0.01
Oxygen permeability		
%OP (homemade set-up)	5.4 ± 0.5	22.5 ± 1.2
OTR (standard method, (cm^3/cm^2/day))	2.32 ± 0.01	3.90 ± 0.14
% Degradation	41.31 ± 2.82	50.82 ± 3.46

ACKNOWLEDGMENTS

Financial support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education, Thailand, is gratefully acknowledged. Thanks to the National Research University Project under Thailand's Office of the Commission on Higher Education (CHE) and also the Graduate School, Chiang Mai University, for a partial financial support.

REFERENCES

1. Long, Y.; Katherine, D.; Lin, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
2. Sahari, J.; Sapuan, S. M.; Zainudin, E. S.; Maleque, M. A. *Procedia Chem.* **2012**, *4*, 254.
3. Azeredo, H. M. C. *Food Res. Int.* **2009**, *42*, 1240.
4. Majeed, K.; Jawaid, M.; Hassan, A.; Abu Bakar, A.; Abdul Khalil, H. P. S.; Salema, A. A.; Inuwa, I. *Mater. Design.* **2013**, *46*, 391.
5. Silvestre, C.; Duraccio, D.; Cimmino, S. *Prog. Polym. Sci.* **2011**, *36*, 1766.
6. Vepari, C.; Kaplan, D. L. *Prog. Polym. Sci.* **2007**, *32*, 991.
7. Okhawilaia, M.; Rangkupanb, R.; Kanokpanonta, S.; Damrongsakkula, S. *Int. J. Biol. Macromol.* **2010**, *46*, 544.
8. Yan, L. P.; Oliveira, J. M.; Oliveira, A. L.; Caridade, S. G.; Mano, J. F.; Reis, R. L. *Acta Biomater.* **2012**, *8*, 289.
9. Wenk, E.; Merkle, H. P.; Meinel, L. *J. Control. Release.* **2011**, *150*, 128.
10. Eleni, P.; Ioannis, A.; Costas, G. B.; Hiromasa, O.; Norioki, K. *Carbohydr. Polym.* **1997**, *33*, 227.
11. Tripathi, S.; Mehrotra, G. K.; Dutta, P. K. *Int. J. Biol. Macromol.* **2009**, *45*, 372.
12. Tripathi, S.; Mehrotra, G. K.; Dutta, P. K. *Carbohydr. Polym.* **2010**, *79*, 711.

13. Silva, B. D. S.; Ulhoa, C. J.; Batista, K. A.; Medeiros, M. C. D.; Filho, R. R. S.; Yamashita, F.; Fernandes, K. F. *Carbohydr. Polym.* **2012**, *89*, 964.
14. Yoon, S. D.; Park, M. H.; Byun, H. S. *Carbohydr. Polym.* **2012**, *87*, 676.
15. Chuang, W. Y.; Young, T. H.; Yao, C. H.; Chiu, W. Y. *Biomaterials.* **1999**, *20*, 1479.
16. Moonsri, P.; Watanesk, R.; Watanesk, S.; Niamsup, H.; Deming, R. L. *J. Appl. Polym. Sci.* **2008**, *108*, 1402.
17. Park, H. R.; Chough, S. H.; Yun, Y. H.; Yoon, S. D. *J. Polym. Environ.* **2005**, *13*, 375.
18. Sothornvit, R.; Pitak, N. *Food Res. Int.* **2007**, *4*, 365.
19. Thakore, I. M.; Desai, S.; Sarawade, B. D.; Devi, S. *Eur. Polym. J.* **2001**, *37*, 151.
20. Yun, Y. H.; Yoon, S. D. *Polym. Bull.* **2010**, *64*, 553.
21. Salleh, E.; Muhamad, I.; Khairuddin, N. *Eng. Technol.* **2009**, *55*, 432.
22. Um, I. C.; Park, Y. H. *Fibers Polym.* **2007**, *8*, 579.
23. Lee, K. H.; Baek, D. H.; Ki, C. S.; Park, Y. H. *Int. J. Biol. Macromol.* **2007**, *41*, 168.