Degradability of Expanded Starch/PVA Blends Prepared Using Calcium Carbonate as the Expanding Inhibitor

Jong-Shin Park,[1] June-Ho Yang,[1] Dae-Hyun Kim,[1] Dae-Hoon Lee[2]

[1]*Department of Natural Fiber Science, Seoul National University, Seoul, 151-742 Korea*
[2]*Korea Institute of Industrial Technology, Choongchungnam-do, 330-820 Korea*

ABSTRACT: In this study, expanded starch/poly(vinyl alcohol) (PVA) blends for packing material were prepared by using calcium carbonate as the expansion inhibitor to investigate the degradability and the structural and mechanical properties of expanded starch/PVA/calcium carbonate blends (ESPCs). The structure of ESPCs became more compact with increasing $CaCO_3$ content and at least 2 parts of $CaCO_3$ were required to obtain the sufficient inhibiting effect on the expansion. As $CaCO_3$ content increased from 1 to 4 parts, tensile strength more than doubled from 70 to 180 KPa, while elongation at break increased about 1.5-fold. The moduli of ESPCs also increased with increasing $CaCO_3$ content, but they decreased continuously with exposure to UV radiation over all periods of exposure and remained in the range of 10–15 KPa after exposure for 7 weeks. The weight loss of ESPCs due to exposure to soil environment increased with exposure time and the final weight loss after the 5-week exposure was about 25–30%. Specifically, the degradability of ESPC with 20 parts of PVA was 5% higher than that of ESPC with 30 parts of PVA. The water solubility of ESPC with 30 parts of PVA was somewhat higher than that of ESPC with 20 parts of PVA. Furthermore, most of ESPCs began to be degraded thermally at 292°C. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 911–919, 2004

Key words: extrusion; starch, poly(vinyl alcohol); blends; calcium carbonate; degradation

INTRODUCTION

Recently, with the increasing concern about the environmental pollution resulting from nondegradable plastic materials, numerous research to develop environment-friendly biodegradable plastic materials as replacements for synthetic polymeric materials was carried out. The developments of environment-friendly polymeric materials are classified into two categories based on their raw materials: degradable synthetic polymers and renewable natural polymers. Among these, starch, a biodegradable natural polymer that exists abundantly in nature and is very cheap, was used as a replacement for synthetic polymeric plastics as well as in the food, textile, and paper industries following various modifications and processes.[1]

Starch-based biodegradable plastic materials were prepared by various methods, as follows: embedding the starch in synthetic polymer matrices,[2–5] blending with hydrophilic polymers,[6] using modified starch,[7] foaming of starch within the extruder,[8–11] and preparing thermoplastic starch.[12,13] However, blending with synthetic polymer introduces problems such as poor mechanical properties due to phase-separation and nondegradable residues. So, research into expanded or thermoplastic starch in which starch is the major ingredient was carried out. In these cases, however, poor mechanical properties make them inappropriate for a packing material. Lacourse and Altiere[12] reported that the loose-fill type of expanded starch, suitable for commercial uses such as packing material, could be made from starch with an amylose content of more than 70%. Another patent insisted that starch must contain more than 45% amylose to produce an expanded starch with excellent physical properties, which is useful for packing material.[13] However Lim et al.[14] reported that the loose-fill type of an expanded starch could be made from ordinary starch under various conditions and that its physical properties were similar to those of expanded starch made from high-amylose-content starch.

PVA, which is a water-soluble and biodegradable crystalline polymer, has often been used in blending with other polymeric materials for improved mechanical and expanding properties, biodegradability, and biocompatibility.[15–17]

In this study, starch was blended with PVA during the extrusion process to improve the flexibility of the expanded starch. To overcome the excessive expansion resulting from PVA, calcium carbonate ($CaCO_3$) was used as the expanding inhibitor. Then, the de-

TABLE I
Composition of ESPCs

Sample number	Notation of sample	Ingredient contents (part[a])			Screw speed (rpm)
		Starch	PVA	CaCO$_3$	
1	ESP20C1-150	100	20	1	150
2	ESP20C2-150	100	20	2	150
3	ESP20C3-150	100	20	3	150
4	ESP20C4-150	100	20	4	150
5	ESP30C1-150	100	30	1	150
6	ESP30C2-150	100	30	2	150
7	ESP30C3-150	100	30	3	150
8	ESP30C4-150	100	30	4	150
9	ESP20C1-300	100	20	1	300
10	ESP20C2-300	100	20	2	300
11	ESP20C3-300	100	20	3	300
12	ESP20C4-300	100	20	4	300
13	ESP30C1-300	100	30	1	300
14	ESP30C2-300	100	30	2	300
15	ESP30C3-300	100	30	3	300
16	ESP30C4-300	100	30	4	300

[a] Part: relative quantity of ingredients to that of starch.

gradability and the structural and mechanical properties of the expanded starch/PVA/CaCO$_3$ blend (ESPC) were investigated.

EXPERIMENTAL

Materials

Native corn starch (Samyang Inc., Daejeon, Korea) was used after being dried in a vacuum oven at 60°C for 20 h. Poly(vinyl alcohol) (PVA, Dugsan Chemical Inc., Ansan-si, Korea; degree of polymerization (DP) = 1500) and CaCO$_3$ (Aldrich, Milwaukee, WI; 99+% A.C.S. reagent grade) were used without further purification.

Preparation of expanded starch/PVA/CaCO$_3$ blends (ESPCs)

ESPCs were prepared by using the pilot system composed of a supermixer and a twin-screw extruder (TSK-48, Sinsung Ltd., Korea). The diameter and L/D ratio of the extruder were 48 and 32 mm, respectively.

The length of corotating screws was 1340 mm. The heating zones of the twin-screw extruder were fixed at 215–210-90–50°C in sequence. Starch, PVA, and CaCO$_3$ were mixed in the supermixer and the resulting compositions are shown in Table I. After being fed to the extruder, along with a predetermined amount of water feed, the ingredient mixture was extruded to make ESPC under the condition of high pressure and temperature. The supply rates of the mixture and water were fixed at 500 g/min and 100 mL/min, respectively. The overall process is shown in Figure 1.

Scanning electron microscopy (SEM)

After being dried at 80°C in a vacuum oven for 24 h, each ESPC was fractured by manually bending normal to the long axis and then fragments were dried at 80°C in a vacuum oven for 24 h. Dried fragments were mounted on aluminum stubs by using double-sided tape and vacuum-coated with gold-palladium by DC sputtering. The cross sections of ESPCs were examined by using a SEM (JSM 5410LV, JEOL, Japan) at an accelerating voltage of 5 kV.

Mechanical properties

ESPC of the diameter of about 15 mm was carefully cut into a specimen (width × thickness × length = 15 × 5 × 50 mm) by using a sharp razor. The mechanical properties of the specimen were measured by using a MiniMat (Rheometric Scientific Inc.) with a loading rate of 20 mm/min. Five specimens per sample were tested.

Exposure to UV radiation

To investigate the degradation due to exposure to UV radiation, ESPC specimens were exposed to UV radiation in a UV lamp chamber (HK-IBO72U, Korean General Instruments, Korea) for 7 weeks. A 10 W germicidal lamp with the maximum intensity at 254 nm was used at a distance of 25 cm from the ESPC specimens. The internal temperature of the chamber was fixed at 25°C and the tensile test for specimens exposed to UV radiation was performed every week.
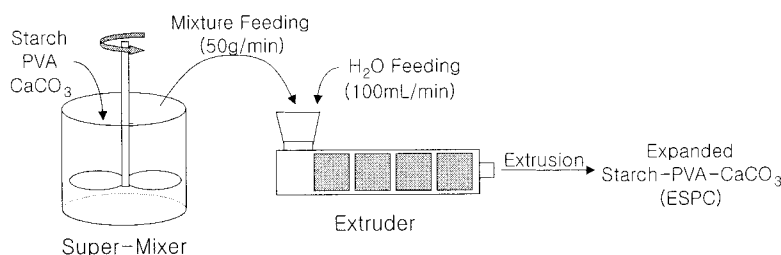

Figure 1   Preparation process of ESPCs using twin-screw extruder.

Exposure to soil environment

ESPC of the diameter of about 15 mm was cut in lengths of 5 cm and the weight of each specimen was approximately 0.3 g. Thirty specimens per ESPC were dried at 80°C in a vacuum oven for 24 h. After being weighed exactly, the dried specimens were buried in alluvial-type soil. The thicknesses of the upper and lower soil layers were 10 and 15 cm, respectively. Exposure to the soil environment continued for 5 weeks during which time five specimens were taken out, washed with distilled water, dried, and weighed exactly every week. The degradability was evaluated from the weight loss, which was calculated by

$$W_{soil} \ (\%) = \frac{W_a - W_b}{W_a} \times 100 \qquad (1)$$

where W_{soil} is the weight loss of dried ESPC by exposure to the soil environment; W_a is the weight of dried ESPC before exposure to the soil environment; and W_b is the weight of dried ESPC after exposure to the soil environment.

Solubility of ESPC

ESPC of the same dimensions and weight as used for exposure to the soil environment was used. After being weighed exactly, three specimens cut in lengths of 5 cm were soaked in distilled water of 200 mL contained in a 250-mL flask. Five flasks per ESPC were shaken in a thermostatic water bath fixed at 25°C for 5 h. After being shaken, ESPCs were filtered, dried, and weighed every hour. Solubility of ESPCs was evaluated from the weight loss, which was calculated by

$$W_{water} \ (\%) = \frac{W_c - W_d}{W_c} \times 100 \qquad (2)$$

where W_{water} is the weight loss of dried ESPC by shaking in water; W_c is the weight of dried ESPC before being shaken; and W_d is the weight of dried ESPC after being shaken.

Thermal analysis

Thermal decomposition behavior of ESPC was measured by using thermogravimetric analysis (TGA 1000, Rheometric Scientific, UK). Samples of 1–1.2 mg were exactly weighed and heated from 20 to 800°C at a heating rate of 20°C/min under N_2 atmosphere.

RESULTS AND DISCUSSION

Structural and mechanical properties of ESPC

The expansion of starch using the extruder can be summarized as the following. At first, starch and wa-

ter were fed into the barrel of the extruder. Then, the mixture of water and starch goes through the barrel at high temperature and pressure by the operation of a screw. When the mixture is extruded at the die face, it expands due to the difference between the external and internal pressures of the extruder. At that time, water plays a significant role as an expansion agent through its vaporization. After that, the expanded starch stiffens and maintains its expanded form. The expanded starch had poor mechanical properties. So, in this study, PVA, which also has flexible and expanding properties, was blended with starch during the extrusion to improve the flexibility of the expanded starch, and $CaCO_3$ was used as the expansion inhibitor to restrict excessive expanding supplemented by the expansion of PVA.

The experimental parameters which could affect the structural and mechanical properties of ESPC were a combination of the raw material mixture, screw speed, supply rates of water, and sectional temperatures and pressures of the extruder. To obtain a flexible expanded starch/PVA blend using the extruder, the difference between the internal and external pressures of the extruder must be kept very high. So, the supply rates of the mixture and water, which was added to improve the fluidity of the mixture in the extruder, were fixed at 500 g/min and 100 mL/min, respectively. The optimum sectional temperatures of the extruder were fixed at 215–210-90–50°C in sequence. Under the above-mentioned conditions, we could obtain a loose-fill type of ESPCs with various compositions of ingredients extruded at different screw speeds.

Figure 2 shows the cross-sectional SEM micrographs of ESPCs extruded at a screw speed of 150 rpm. All ESPCs had the interconnecting open-cell structure, which became more compact with increasing $CaCO_3$ content. The pore size of ESPCs decreased with increasing $CaCO_3$ content. The cross-sectional SEM micrographs of other ESPCs extruded at different conditions, which were not seen here, showed the same trend with increasing $CaCO_3$ content.

The results of the tensile test are shown in Table II and Figure 3. The stress–strain curves of all ESPCs were linear and therefore the moduli of ESPCs could be calculated as the slope of the stress–strain curves. As shown in Table II, both tensile strength and elongation at break increased with increasing $CaCO_3$ content. Particularly, as $CaCO_3$ content increased from 1 to 4 parts, tensile strength increased 2.6-fold from 70 to 180 KPa, while elongation at break increased about 1.5-fold. So, the moduli of ESPCs calculated from the slope of the stress–strain curves also increased with increasing $CaCO_3$ content except for ESPCs with one part of $CaCO_3$, as shown in Figure 3. In fact, the inhibiting effect of $CaCO_3$ on the expansion was trivial at the low $CaCO_3$ content of 1 part and ESPCs with
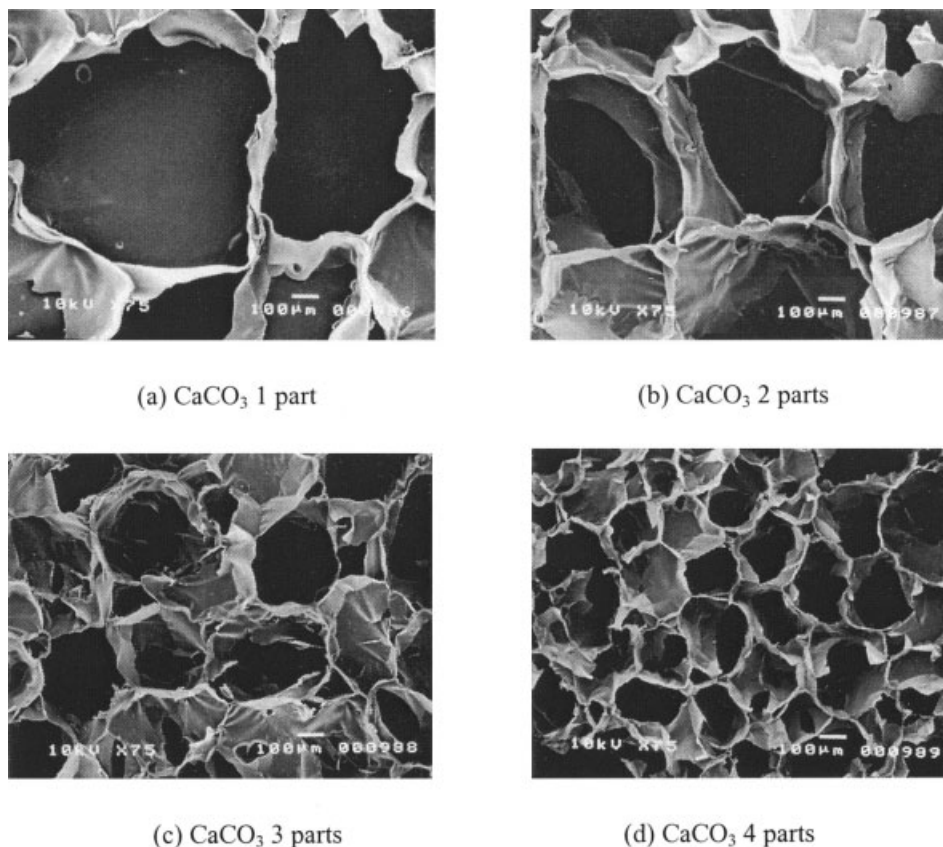
Figure 2 SEM micrographs of ESPCs extruded at a screw speed of 150 rpm (PVA = 30 parts, ×75): (a) $CaCO_3$ 1 part; (b) $CaCO_3$ 2 parts; (c) $CaCO_3$ 3 parts; and (d) $CaCO_3$ 4 parts.

this $CaCO_3$ content were rigid and brittle. In addition, their elongations at break were even lower when compared with the low values of tensile strength. The specific work of rupture of ESPCs, defined as the work of rupture divided by the cross-sectional area of each

ESPC specimen, increased with increasing $CaCO_3$ content about fourfold. Therefore, it could be concluded that the mechanical properties of ESPCs were improved by the addition of $CaCO_3$ as the expanding inhibitor. In point of PVA contents, on the whole,

TABLE II
Tensile Properties of ESPCs

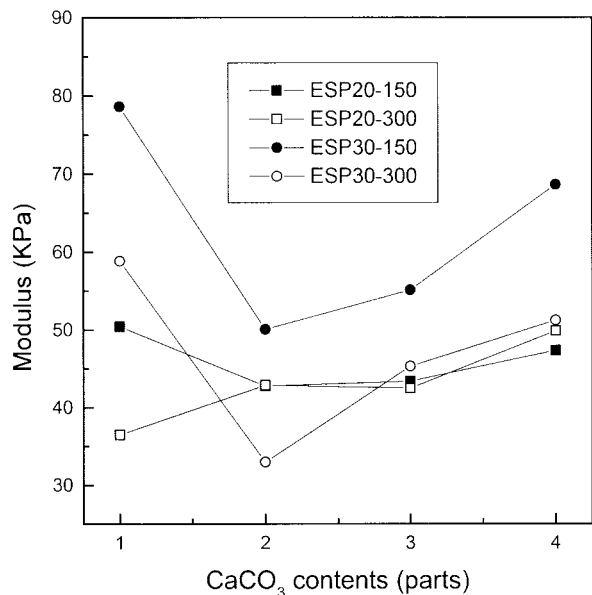| Samples	Tensile strength (KPa)	Elongation at break (%)	Modulus (KPa)	Specific work of rupture (N/m)
ESP20C1-150	73.57	1.50	50.43	16.55
ESP20C2-150	83.73	1.96	42.76	24.62
ESP20C3-150	103.90	2.29	43.35	35.69
ESP20C4-150	140.00	2.96	47.33	62.16
ESP30C1-150	75.36	0.96	78.62	10.85
ESP30C2-150	86.22	1.72	50.07	22.24
ESP30C3-150	126.25	2.29	55.11	43.37
ESP30C4-150	134.40	1.96	68.64	39.51
ESP20C1-300	71.50	1.96	36.48	21.02
ESP20C2-300	98.12	2.29	42.85	33.70
ESP20C3-300	125.60	2.96	42.46	55.77
ESP20C4-300	180.70	3.62	49.86	98.12
ESP30C1-300	70.08	1.19	58.84	12.51
ESP30C2-300	95.59	2.29	32.96	32.84
ESP30C3-300	134.05	2.96	45.29	59.52
ESP30C4-300	168.50	3.29	51.22	83.15

Figure 3 Moduli of ESPCs as a function of CaCO₃ content.

tensile strength and modulus of ESPCs with 30 parts of PVA were somewhat higher than those of ESPCs with 20 parts of PVA, but elongation at break and work of rupture were lower. Tensile strength, elongation at break, and work of rupture of ESPCs extruded at 300 rpm were somewhat higher than those of ESPCs extruded at 150 rpm, but modulus was lower.

Degradation by exposure to UV radiation

As exposure to UV radiation proceeded, a white powdery residue appeared on the surface of ESPC and the amount of chalking increased with longer exposure time. Generally, UV radiation of wavelength ranging from 200 to 400 nm has the energy of 142.9–71.5 kcal/mol. UV radiated in this study has the energy of 112.6 kcal/mol by the following equation because a UV lamp with maximum intensity at 254 nm wavelength was used. Therefore, it can be thought that ESPCs were embrittled due to the breakage of their C—H and C—O—C bonds due to exposure to UV radiation with the energy of 112.6 kcal/mol over a long period:

$$E = h\nu = h\frac{c}{\lambda} \qquad (3)$$

where λ is the wavelength of radiation; h is the Planck's constant (6.6261×10^{-34} J s); and c is the velocity of light (3.0×10^8 m/s).

In this study, the difference between the mechanical properties of ESPC before and after exposure to UV radiation was compared to investigate the degradation of ESPCs by exposure to UV radiation. In Figure 4, the moduli of ESPCs exposed to UV radiation as a function of the exposure time are shown. The moduli of all ESPCs decreased continuously by exposure to UV radiation over all exposure periods and had the
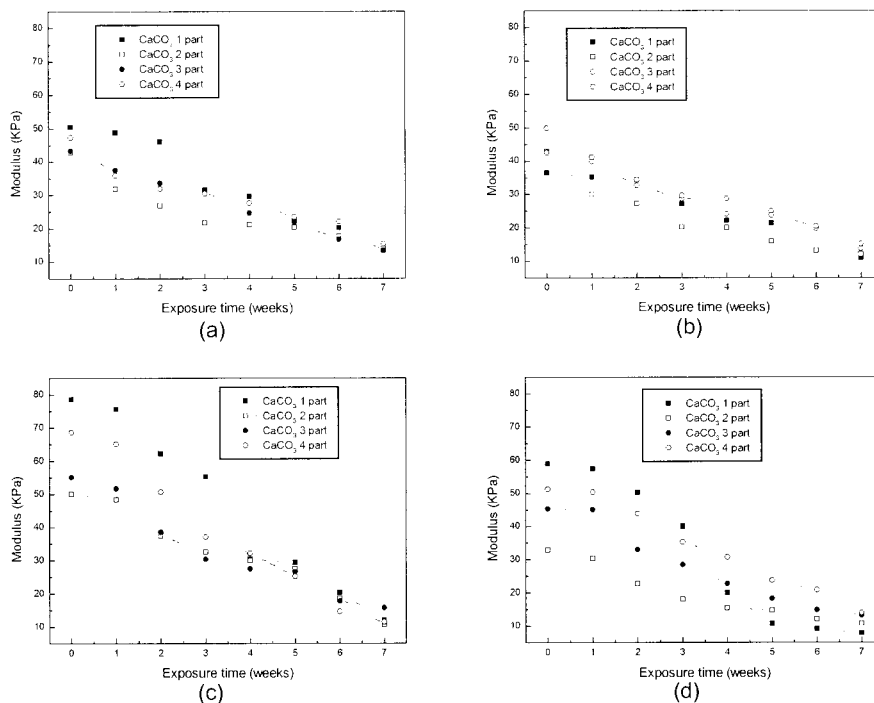

Figure 4 Moduli of ESPC as a function of the exposure time: (a) ESP20-150; (b) ESP20-300; (c) ESP30-150; and (d) ESP30-300.
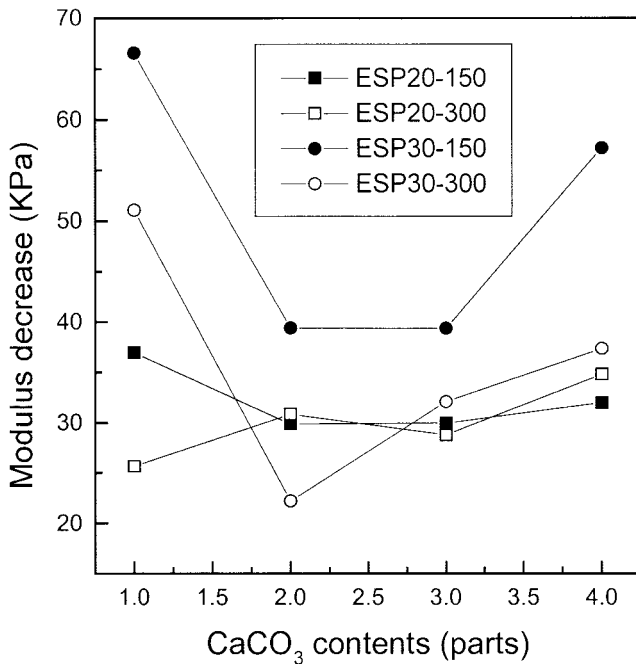
Figure 5 Modulus decreases of ESPCs as a function of CaCO$_3$ contents after exposure to UV radiation for 7 weeks.

similar modulus of 10–15 KPa after exposure for 7 weeks. The decreases were fairly constant over the entire 7-week period. Figure 5 presents the modulus

decreases of ESPCs by exposure to UV radiation, which was defined as the difference between the moduli of ESPCs nonexposed and exposed to UV radiation for 7 weeks. The moduli of ESPCs with high modulus in the nonexposed state decreased more.

Degradation by exposure to soil environment

To investigate the degradability by exposure to soil environment, ESPCs were buried in alluvial soil type put in a wooden box at ambient temperature of 22–26°C. The degradability was indirectly evaluated from the weight loss of ESPCs during the burial period and the results are shown in Figure 6. The weight loss of ESPCs increased with increasing exposure time and the maximum weight loss after exposure for 5 weeks was about 25–30%. As shown in Figure 6, the weight loss of ESPCs with 20 parts of PVA was somewhat higher than that of ESPCs with 30 parts of PVA. This tendency is clearly shown in Figure 7, where the weight loss of ESPCs after exposure for 5 weeks is presented as a function of CaCO$_3$ content. The effect of CaCO$_3$ content on the degradability of ESPC was trivial but the degradability of ESPC with 20 parts of PVA was about 5% higher than that of ESPC with 30 parts of PVA. This is thought to be because the difference in PVA content is less sensitive to biodegradation than starch.
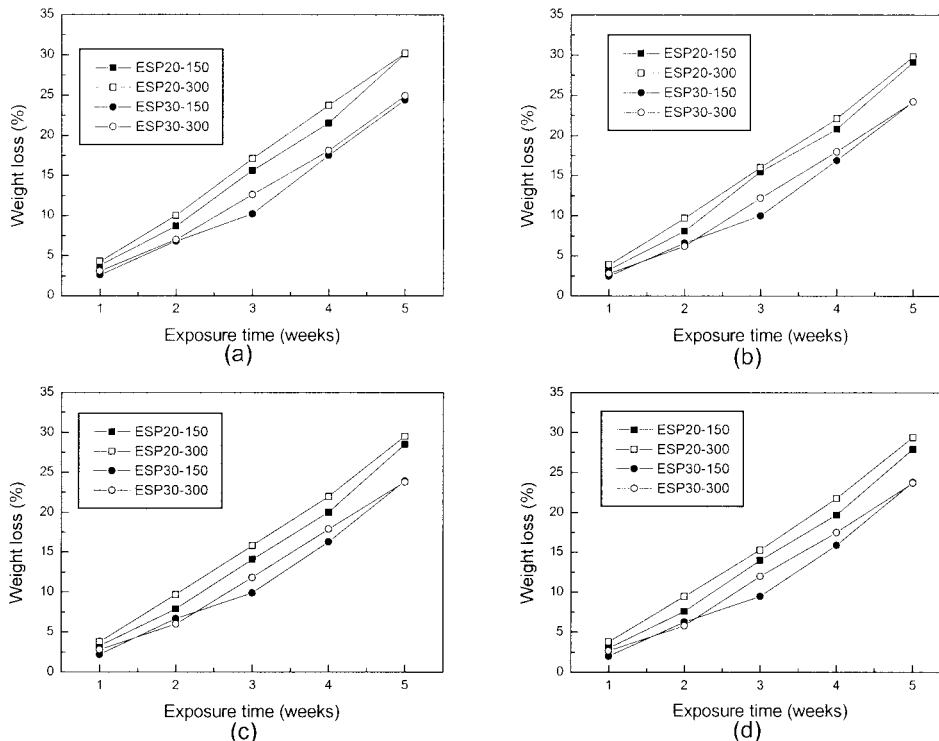

Figure 6 Weight loss of ESPC exposed to soil environment as a function of the exposure time: (a) CaCO$_3$ 1 part; (b) CaCO$_3$ 2 parts; (c) CaCO$_3$ 3 parts; and (d) CaCO$_3$ 4 parts.
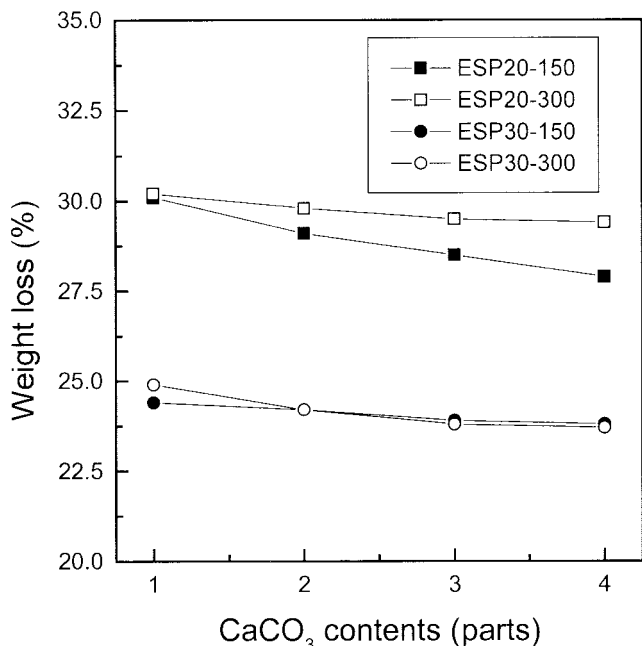
Figure 7 Weight loss of ESPCs as a function of $CaCO_3$ contents after exposure to soil environment for 5 weeks.

Solubility of ESPCs

To investigate the solubility of ESPCs in water, the ESPC specimens were soaked in distilled water contained in a flask, which was shaken in a thermostatic water bath fixed at 25°C. The weight loss of ESPCs as a function of shaking time is shown in Figure 8. Almost all weight loss of ESPCs occurred within the first hour and then increased a little more with the shaking time. On the whole, the weight loss of ESPCs extruded at a screw speed of 300 rpm was a bit higher than that of ESPCs extruded at 150 rpm. In ESPCs of the same ingredient composition, ESPCs extruded at 300 rpm had a less compact structure than those extruded at 150 rpm because the internal pressure of the extruder was higher at 300 rpm. So, it can be supposed that the weight loss of ESPCs extruded at 300 rpm was somewhat higher. However, the effect of $CaCO_3$ content on the solubility of ESPCs was not distinct except for ESPCs with 1 part of $CaCO_3$, which had the lowest weight loss.

Thermal degradation of ESPCs

To investigate the thermal degradation of ESPCs, thermogravimetric analysis was performed; the results are shown in Figures 9 and 10. As shown in Figure 9, thermal degradation of most ESPCs started at ~ 292°C and ended at ~ 358°C. The method to determine the starting and ending points of the degradation was described in the picture inset of Figure 9. The initial weight loss of 3–9% up to 100°C was thought to be due to the vaporization of water absorbed by hydrophilic starch and PVA. However, as shown in Figure 10, the
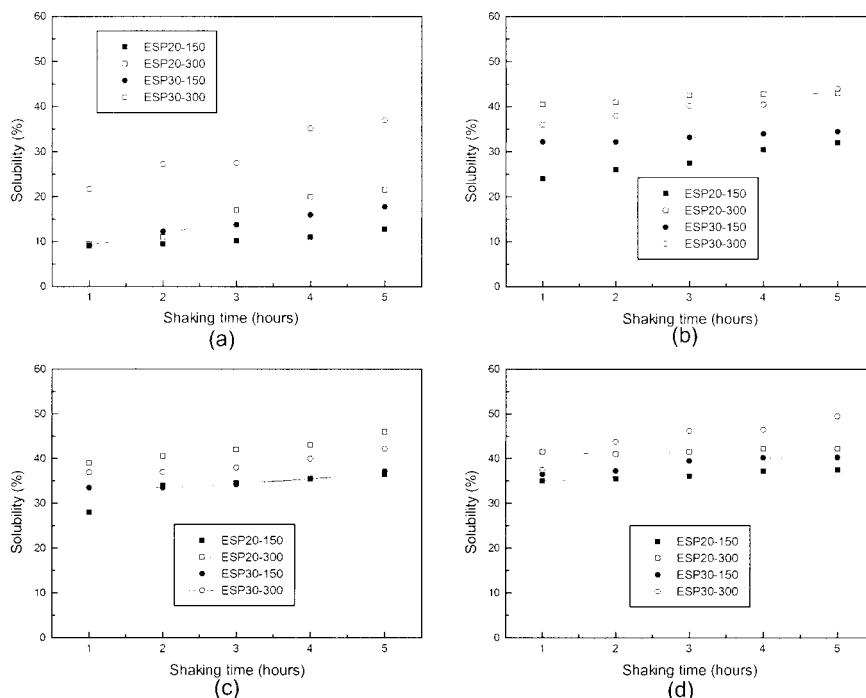

Figure 8 Weight loss of ESPCs as a function of shaking time: (a) $CaCO_3$ 1 part; (b) $CaCO_3$ 2 parts; (c) $CaCO_3$ 3 parts; and (d) $CaCO_3$ 4 parts.
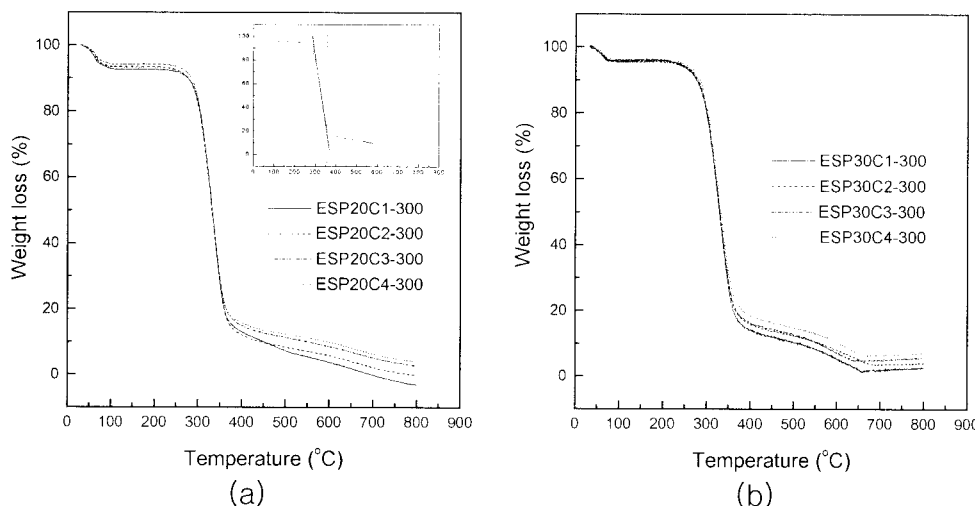
Figure 9 TGA thermograms of ESPCs extruded at 300 rpm: (a) PVA 20 parts and (b) PVA 30 parts.

weight loss of ESPCs with 20 parts of PVA was higher than that of ESPCs with 30 parts of PVA. This was thought to be due to the higher content of starch, which has a greater water-absorbing ability than PVA. After the ending temperature of degradation, the weight loss of ESPCs decreased with increasing CaCO$_3$ content. Previously, it was mentioned that CaCO$_3$ degraded into calcium oxide and carbon dioxide during the extrusion process within the extruder at high temperature and pressure, and that calcium oxide was supposed to function as the expanding inhibitor, capturing the water by converting it to calcium hydroxide. Generally, calcium hydroxide starts to degrade and release water at temperatures higher than 100°C, with complete conversion to calcium oxide occurring over 580°C. The melting temperature of calcium oxide is known to be 825°C. So, it can be supposed that CaCO$_3$ exists in the form of calcium oxide

even at higher temperature and, therefore, the weight loss of ESPCs with higher CaCO$_3$ content decreased with increasing CaCO$_3$ content over about 400°C.

CONCLUSION

In this study, expanded starch/PVA blends were prepared by using CaCO$_3$ as the expansion inhibitor. The degradability and structural and mechanical properties of ESPCs were investigated. As CaCO$_3$ content increased, the structure of ESPC became more compact and the mechanical properties such as tensile strength, elongation at break, and modulus were all improved. However, these mechanical properties deteriorated because of the degradation which occurred with exposure to UV radiation. Furthermore, the biodegradability of ESPCs was confirmed by exposure to a soil environment.
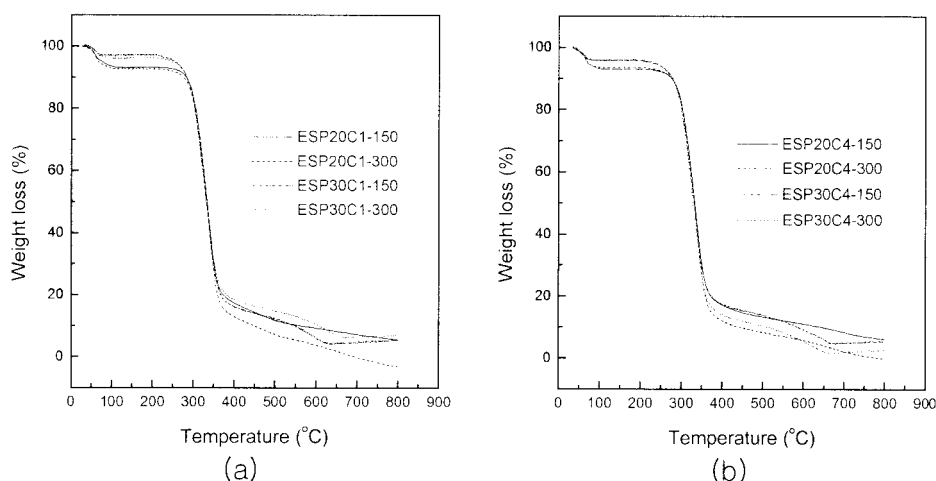

Figure 10 TGA thermograms of ESPCs: (a) CaCO$_3$ 1 part and (b) CaCO$_3$ 4 parts.

References

1. Ellis, R. P.; Cochrane, M. P.; Dale, M. F. P.; Duffus, C. M.; Lynn, A.; Morrison, I. M.; Prentice, R. D. M.; Swanston, J. S.; Tiller, S. A. J Sci Food Agric 1998, 77, 289.
2. Arvanitoyannis, I.; Biliaderis, C. G.; Ogawa, H.; Kawasaki, N. Carbohydr Polym 1998, 36, 89.
3. Shah, P. B.; Bandopadhyay, S.; Bellare, J. R. Polym Degrad Stab 1995, 47, 165.
4. Yang, Z.; Bhattacharya, M.; Vaidya, U. R. Polymer 1996, 37, 2137.
5. Pierra, N. S.; Favis, B. D.; Ramsay, B. A.; Ramsay, J. A.; Verhoogt, H. Polymer 1997, 38, 647.
6. Nwufo, B. T.; Griffin, G. J. L. J Polym Sci: Polym Chem Ed 1985, 23, 2023.
7. Abbott, T. P.; James, C.; Otey, F. H. J Appl Polym Sci 1979, 23, 1223.
8. Abecassis, J.; Abbou, R.; Chaurand, M.; Morel, M. H.; Vernoux, P. Cereal Chem 1994, 71, 247.
9. Tang, J.; Ding, X. L. Cereal Chem 1994, 71, 364.
10. Fishman, M. L.; Coffin, D. R.; Konstance, R. P.; Onwulata, C. J. Carbohydr Polym 2000, 41, 317.
11. Cunningham, R. L.; Care, M. E.; Bagley, E. B.; Gordon, S. H.; Greene, R. V. J Appl Polym Sci 1994, 51, 1311.
12. Lacourse, N. L.; Altiere, P. A. U.S. Pat. 4,863,655, 1989.
13. Altiere, P. A.; Mead, N. J. B. U.S. Pat. 5,135,037, 1992.
14. Lim, D. L.; Im, S. S.; Lee, Y. M. J Environ Polym Degrad 1998, 6, 1.
15. Chandy, T.; Sharma, C. P. J Appl Polym Sci 1992, 44 (12), 2145–2156.
16. Um, I. C.; Park, Y. H. Korean J Sericultural Sci 1998, 40, 169.
17. Kim, D. H.; Na, S. K.; Park, J. S.; Yoon, K. J.; Ihm, D. W. Eur Polym J 2002, 38, 1199.