Carbohydrate Polymers 50 (2002) 331–337

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Characteristics of crosslinked potato starch and starch-filled linear low-density polyethylene films

Meera Kim*, Sun-Ja Lee

*Department of Food Science and Nutrition, Kyungpook National University, Taegu 702-701, South Korea*

Received 19 March 2001; revised 4 September 2001; accepted 3 October 2001

**Abstract**

Potato starch was crosslinked with 0.1, 0.5, 1.0 and 2.0 g epichlorohydrin per 100 g of starch and some physicochemical characteristics of the starch were determined. Starch-filled linear low-density polyethylene cast films were prepared to contain 5 or 10% crosslinked starch. Mechanical properties of these films were measured and compared to those of the films containing native potato starch. Molar degree of crosslinking of the crosslinked starch increased proportionally as epichlorohydrin concentration increased. X-ray diffraction pattern and scanning electron microscopy showed that crosslinking of starch did not affect the crystallinity or granular shape of the starch. The tensile strength, percent elongation and strain energy of the films containing crosslinked starch were generally higher than those of the films containing native starch. Films containing crosslinked starch were whiter in color than native starch films. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Crosslinked starch; Potato starch; Starch–polyethylene film; Mechanical property

## 1. Introduction

Plastics are not biodegradable (Potts, Clendinning, Ackart, & Niegisch, 1973) and therefore cause environmental pollution. Since the mid-1970s, polymer–starch blends with acceptable physical properties have been developed (Wei & Nikolov, 1992). Starch has been used commercially as a biodegradable additive for polyethylene (Gage, 1990). Gelatinized starch (Otey & Westhoff, 1984; Otey, Mark, Mehltretter, & Russell, 1974; Otey, Westhoff, & Doane, 1980; Otey, Westhoff, & Doane, 1987), modified starch (Griffin, 1977), oxidized polyethylene (Kim, Pometto, Johnson, & Fratzke, 1994) and dry granular starch (Griffin, 1974) have been used as fillers to improve the biodegradability of plastics. One of the problems inherent in films prepared with dry granular starch and gelatinized starch is the reduction of mechanical properties because of the incompatibility between plastics and starch. Accordingly, starch granule has been chemically modified to overcome some of the incompatibility between hydrophobic plastics and hydrophilic starch. Chemical modification of starches could improve the interfacial contact between starch granule and polymer. Griffin (1977) proposed a process for making low-density polyethylene (LDPE) blown films containing native or modified starches. Swanson, Westhoff, and Doane (1988) examined the effect of starch modification on LDPE films and found that the mixture of LDPE and poly(ethylene-co-acrylic acid) (EAA) polymers filled with hydroxypropyl or acetyl derivatives of starch had a higher elongation and often had a higher tensile strength than native starch-filled films. Otey, Westhoff, and Russell (1977) used a mixture of polyvinylalcohol (PVA) and modified starch to develop water-soluble packaging plastics.

Crosslinking of starch reinforces the granule by chemical bonds that act as bridges between molecules. Crosslinked starch maintains a higher viscosity and shows less viscosity breakdown (Wurzburg, 1987). Crosslinking can prove to be a valuable tool for providing maximum film strength (Wurzburg, 1987). Crosslinking of the starch can also modify the paste properties of the swollen granule, altering the texture and rheology of the paste (Kim & Lee, 1996). It can also reduce the sensitivity of the swollen granule paste to acidic conditions and shear force (Rutenberg & Solarek, 1984). Crosslinking can be utilized to improve the film-forming properties of starch pastes. Thus, crosslinked starches are used in the preparation of starch xanthates for water treatment ion-exchangers, stilt materials for micro-encapsulated coatings and anti-blocking agents for film in

---

* Corresponding author. Tel.: +82-53-950-6233; fax: +82-53-950-6229.
*E-mail address:* meerak@knu.ac.kr (M. Kim).

PII: S0144-8617(02)00057-7

the food industry, textile industry and paper industry (Rutenberg & Solarek, 1984; Wurzburg, 1987).

The use of starch-filled degradable plastics has been increasing in many countries. An example is the regulatory requirement in Korea to use for household waste. Unfortunately, starch-filled plastic bags are often easily torn when garbage is put into the bag. Therefore, it is necessary to improve the mechanical properties of the degradable starch-filled plastics. There is not much research on degradable film prepared with modified starch. In this study, we examined the mechanical properties of polyethylene cast films that contained crosslinked potato starch and compared them with the properties of films prepared with native potato starch.

## 2. Materials and methods

### 2.1. Preparation of crosslinked potato starch

Potato starch was extracted by alkali precipitation (Lee, Pyun, Cho, Yu, & Lee, 1984) and crosslinked potato starch was prepared by the modified method of Jane, Radosavljevic, and Seib (1992). Potato starch (100 g) was suspended in 166 ml of distilled water with stirring for 2 h. The constant quantity of epichlorohydrin (0.1, 0.5, 1.0 or 2.0%) was added to the solution (Table 1) and pH was adjusted to 10.5 by adding 1N of NaOH solution. The mixture was stirred with a magnetic stirrer bar for 24 h at room temperature and was adjusted to pH 5.5 with acetic acid. The slurry was subsequently washed with distilled water and 95% ethanol and then filtered. The prepared starch was dried for 48 h at 40 °C and was passed through a 100-mesh sieve.

Table 1
Degree of crosslinking and reaction yield in crosslinked potato starches

| Type of starch | Applied epichlorohydrin (g/100 g of starch, dry basis) | Unreacted epichlorohydrin (g/100 g of starch, dry basis) | Reacted epichlorohydrin (g/100 g of starch, dry basis) | Reacted epichlorohydrin (mol/100 g starch) | Reaction yield (%) | AGU[a]/crosslink | Crosslink/100AGU (MDC[b]) |
|---|---|---|---|---|---|---|---|
| 0.1 EP | 0.1 | 0.02469 | 0.07531 | 0.000814 | 75.31 | 732 | 0.137 |
| 0.5 EP | 0.5 | 0.05935 | 0.44065 | 0.004760 | 88.13 | 124 | 0.807 |
| 1.0 EP | 1.0 | 0.14972 | 0.85028 | 0.009185 | 85.03 | 64 | 1.563 |
| 2.0 EP | 2.0 | 0.16439 | 1.83561 | 0.019829 | 91.78 | 30 | 3.333 |

[a] Anhydroglucose unit.
[b] Molar degree of crosslinking.

### 2.2. Determination of molar degree of crosslinking (MDC)

The degree of crosslinking and product yield were calculated by determining the amount of unreacted epichlorohydrin in the filtrates (Hamerstrand, Hofretter, & Mehltretter, 1960). That is, unreacted epichlorohydrin is oxidized with periodate, which is estimated calorimetrically using the color reaction of chromotropic acid. The absorbance was read at a wavelength of 570 nm in a spectrophotometer (Beckman DU-650, Fullerton, CA) and the MDC of the sample was calculated using absorbance and the instrumental constant.

### 2.3. X-ray diffraction

X-ray diffraction patterns of starches were recorded on an X-ray diffractometer (X'pert PW3710, Philips, Netherlands) (Cu Kα radiation, voltage: 30 kV and current: 20 mA). The range of diffraction angles $2\Theta$ was 5–40° and the scanning speed of 0.04° ($2\Theta$/s). Relative

Table 2
Composition of the starch–LLDPE films per kilogram

| Type of film[a] | Starch kind used | Crosslinked starch (g) | Pro-oxidant (g) | Polyethylene (g) |
|---|---|---|---|---|
| 50 ST/0 EP | 0 EP (native) | 50 | 50 | 900 |
| 50 ST/0.1 EP | 0.1 EP | 50 | 50 | 900 |
| 50 ST/0.5 EP | 0.5 EP | 50 | 50 | 900 |
| 50 ST/1.0 EP | 1.0 EP | 50 | 50 | 900 |
| 50 ST/2.0 EP | 2.0 EP | 50 | 50 | 900 |
| 100 ST/0 EP | 0 EP (native) | 100 | 50 | 850 |
| 100 ST/0.1 EP | 0.1 EP | 100 | 50 | 850 |
| 100 ST/0.5 EP | 0.5 EP | 100 | 50 | 850 |
| 100 ST/1.0 EP | 1.0 EP | 100 | 50 | 850 |
| 100 ST/2.0 EP | 2.0 EP | 100 | 50 | 850 |

[a] ST means crosslinked starch; EP means epichlorohydrin.

crystallinity of the starch was determined following the method of Komiya, Nara, and Tsu's (1986).

### 2.4. Scanning electron microscopy

Morphology of native potato starch and crosslinked potato starch was examined at a magnification of 700 × using a Scanning Electron Microscope (SEM, Hitachi S-4200, Japan).

### 2.5. Starch–LLDPE film preparation

Starch–LLDPE (linear low-density polyethylene) cast films were composed of LLDPE, pro-oxidant (IR1025, Novon International, Inc., New York, USA) and crosslinked potato starches with different MDCs (Table 2). Pro-oxidant contained native starch (10%), unsaturates (8.0%) and transition metal compounds (0.2%) in LLDPE. Crosslinked potato starches were dried in a vacuum oven until the moisture content was less than 0.3%. The master batch was prepared by mixing LLDPE and starch (1:1, w/w) using a kneader (Haake Pheomex 3000, Germany) at 150 °C at 50 rpm. Then, the master batch was blended with LLDPE and pro-oxidant in a Haake Rheocord 90 equipped with a single screw extruder (Rheomex 254, Germany). The extruder barrel was thermocontrolled at four consecutive heating zones of 150, 145, 150 and 150 °C. The strand of compounded mixture was extruded through the die nozzle at 20 rpm. The strands (diameter, 0.25 cm) were forced-air cooled and then pelletized into 0.5 cm chips. The chips were extruded into cast films using a extruder (Postex Haake Fisions, Germany) with barrel sequential temperatures of 120, 140, 150 and 150 °C and a screw speed of 55 rpm. LLDPE films containing native potato starch were prepared by the same process.

### 2.6. Color of starch–LLDPE film

$L$, $a$ and $b$ values of the films containing crosslinked starch and native starch were measured using a color difference meter (Model whiteness checker RF-1, Nippon Denshoku Kogyo Co., Japan). A standard white plate ($L = 92.5$, $a = 0.7$ and $b = 3.0$) was used to calibrate the color difference meter. The colors of each film were measured five times.

### 2.7. Mechanical properties of starch–LLDPE films

Film thickness was measured with a micrometer caliper (Peacock, Ozaki Mfg Co., Ltd, Tokyo, Japan) and films with a thickness of 0.12 ± 0.01 mm were chosen. Starch–LLDPE films were cut into strips (1 cm × 3 cm) in the same direction as extruded and then tensile strength, percent elongation and strain energy were determined using an Instron (AGS-500A, Shimadzu, Japan). The strips were equilibrated to 50% relative humidity for at least 40 h at 25 °C prior to testing. The mechanical properties of the films were measured immediately after the strips were taken out of the humidity chamber. The Instron was operated under the conditions of a load cell: 50 kg, load range: 5 and crosshead speed: 100 mm/min. Mechanical properties of the each film were measured with 10 replicates.

### 2.8. Data analysis

The data obtained from the experiments were analyzed by PC-SAS Program (version 6.12) (SAS, 1985) using an analysis of variance. Duncan's multiple range test was used at $p < 0.05$ to determine significant differences of the means.

## 3. Results and discussion

### 3.1. Determination of MDC of crosslinked starch

MDC and product yield in the reaction of starch with epichlorohydrin reaction were determined by the method of Hamerstrand et al. (1960). The reaction yield between epichlorohydrin and starch ranged from 75 to 91% and averaged about 85% (Table 1). This result was similar to that of Hollinger, Kuniak, and Marchessault (1974), who

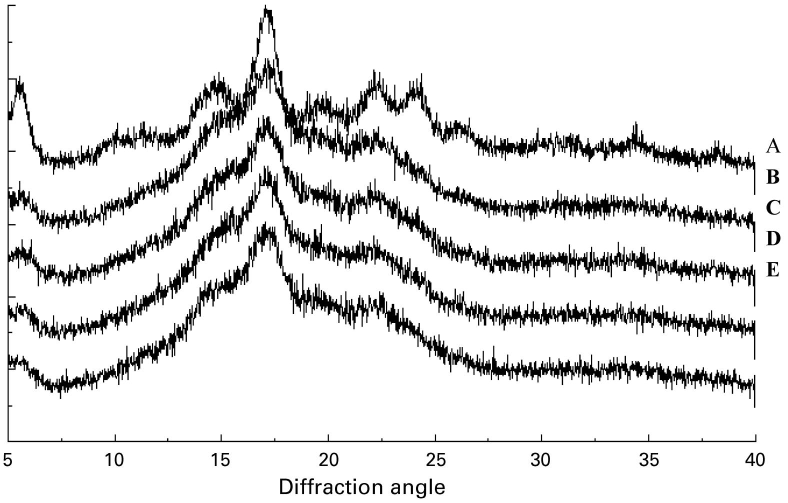

Fig. 1. X-ray diffraction patterns of crosslinked potato starches: (A) 0 EP (native); (B) 0.1 EP; (C) 0.5 EP; (D) 1.0 EP; (E) 2.0 EP.

reported that 85% of the amount of added epichlorohydrin was used in the crosslinking reaction. The value of the degree of crosslinking, in moles of epichlorohydrin, was calculated on the basis of the amount of epichlorohydrin that did not participate in crosslinking. This amount was reported to be less than 5% of the added epichlorohydrin (Hollinger et al., 1974). Reaction of epichlorohydrin with starch under alkaline condition led to the formation of glycerol mono- and diethers. The rate of reaction of epichlorohydrin with starch was slow, but the alkaline condition accelerated the reaction rate (Hamerstrand et al., 1960). It was reported that an 18 h reaction time was required to react to about 80% of the added epichlorohydrin with the starch when approximately 1% NaOH and 0.024–1.140% epichlorohydrin on the weight of dry starch were used at 25 °C. Therefore, the crosslinking reaction was conducted at pH 10.5 for 24 h because 0.1–2.0% epichlorohydrin was added in this study. MDC of potato starch increased proportionally as epichlorohydrin concentration in use increased ($r^2 = 0.9992$). This implies that the starch was successfully crosslinked.

### 3.2. X-ray diffraction

X-ray diffraction patterns of crosslinked potato starch and native potato starch are shown in Fig. 1. According to the starch classification described by Zobel (1964), both native potato starch and crosslinked potato starch belong to the B type which shows peaks at 5.59, 14.4, 7.2 and 22.1 ($2\Theta$). When compared with native starch, crosslinked starch shows weak peaks at 14.4, 17.2–17.5, 22 and 24 ($2\Theta$). However, there was no obvious difference between the X-ray diffraction patterns of crosslinked potato starches. Additionally, crystallinities between the crosslinked potato starch and native starch were not significantly different (Table 3). This means that the crystal area of the starch was not greatly affected by crosslinking.

### 3.3. Starch morphology

Granular morphology of the crosslinked and native potato starches is presented in Fig. 2. The morphology of the crosslinked potato starch was similar to that of native potato starch even when a high concentration of epichlorohydrin was used. This is consistent with the results of Kartha and Srivastava (1985), who reported that crosslinking of the starch did not affect the surface morphology of the starch granule. It may be concluded that the results obtained from X-ray diffraction and SEM indicate that the crosslinking reaction used with 2.0% epichlorohydrin did not affect the morphology of the starch surface.

### 3.4. Color of starch–LLDPE film

*L*, *a* and *b* values of the starch–LLDPE films are shown in Tables 4 and 5. In the starch–LLDPE films containing 50 g of crosslinked potato starch per kilogram of film (50 ST films), *L* and *b* values were not significantly different among

Table 3
Relative crystallinity of crosslinked potato starches

| Variety | Type of starch | | | | |
|---|---|---|---|---|---|
| | 0 EP | 0.1 EP | 0.5 EP | 1.0 EP | 2.0 EP |
| Crystallinity ($A_c/(A_c + A_a)$)[a] (%) | 39.59 | 38.15 | 39.39 | 39.68 | 38.11 |

[a] $A_c$: crystalline area; $A_a$: amorphous area.

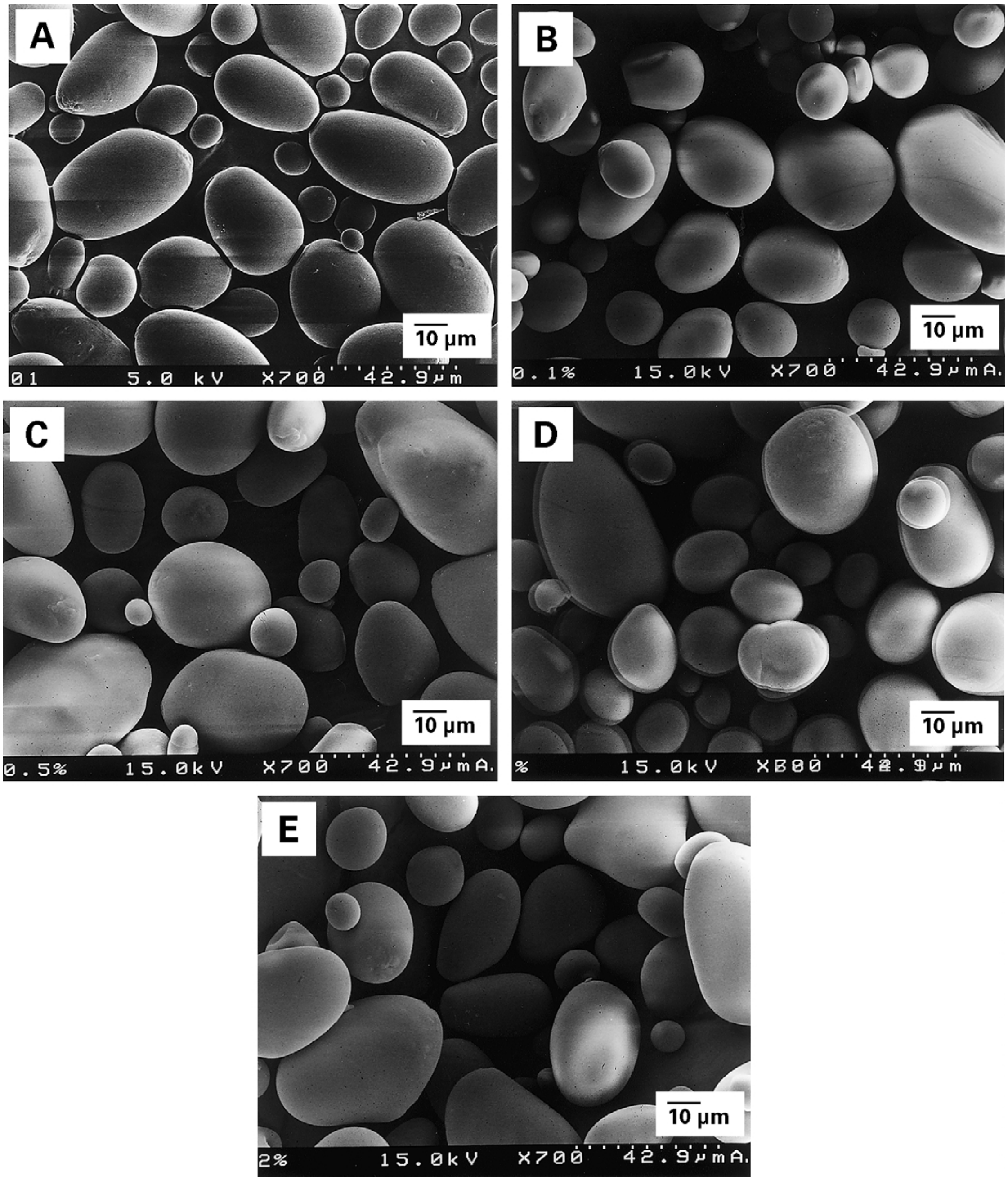

Fig. 2. Scanning electron micrographs (700 × ) of crosslinked potato starches: (A) 0 EP (native); (B) 0.1 EP; (C) 0.5 EP; (D) 1.0 EP; (E) 2.0 EP.

the films. However, the *a* value was the highest in 50 ST/2.0 EP film ($p < 0.05$) (Table 4). In the starch–LLDPE films containing 100 g of crosslinked potato starch per kilogram of film (100 ST films), *a* and *b* values were not significantly different. However, the *L* values of the films with crosslinked starch were generally higher than those of the films with native starch (Table 5). This indicates that LLDPE films containing the crosslinked starch were whiter than the LLDPE films containing the native starch. The color difference of the starch–LLDPE films, however, could not be distinguished by the naked eye.

### 3.5. Mechanical properties of starch–LLDPE film

Mechanical properties of the LLDPE films containing crosslinked or native potato starch are listed in Tables 6 and 7. Tensile strength and strain energy represent the force per unit of area required to tear the film and the work required to take the film to its breaking point, respectively (Kim et al., 1994). Percent elongation means the film’s ability to stretch (Lee, Kim, & Kim, 1999). The tensile strength of the films prepared with crosslinked starch was higher than that prepared with native

Table 4
Color properties of starch–polyethylene films containing 50 g of crosslinked starch per kilogram of film

| Type of film[a] | $L$[b] | $a$[b] | $b$[b] |
|---|---|---|---|
| 50 ST/0 EP | 23.53 ± 0.90 | −0.07 ± 0.06bc | −3.23 ± 0.38 |
| 50 ST/0.1 EP | 23.63 ± 1.42 | −1.23 ± 0.45c | −3.53 ± 0.64 |
| 50 ST/0.5 EP | 24.67 ± 0.93 | 0.73 ± 0.72ab | −4.37 ± 1.05 |
| 50 ST/1.0 EP | 26.03 ± 0.12 | −0.83 ± 0.59bc | −2.27 ± 0.75 |
| 50 ST/2.0 EP | 25.07 ± 1.20 | 2.03 ± 1.64a | −2.03 ± 2.93 |

Means with different letters (a–c) within the same column are significantly different ($p < 0.05$).

[a] ST means crosslinked starch; EP means epichlorohydrin.

[b] Means ± SEM (each value is the mean of three replicates).

Table 5
Color properties of starch–polyethylene films containing 100 g of crosslinked starch per kilogram of film

| Type of film[a] | $L$[b] | $a$[b] | $b$[b] |
|---|---|---|---|
| 100 ST/0 EP | 27.33 ± 0.38c | 0.30 ± 1.23 | −3.30 ± 0.87 |
| 100 ST/0.1 EP | 28.70 ± 1.04b | −0.20 ± 2.36 | −4.07 ± 0.74 |
| 100 ST/0.5 EP | 31.80 ± 0.53a | −2.77 ± 1.00 | −3.80 ± 0.36 |
| 100 ST/1.0 EP | 28.17 ± 0.47bc | −2.47 ± 1.78 | −3.90 ± 0.56 |
| 100 ST/2.0 EP | 29.33 ± 0.57b | 2.23 ± 2.87 | −5.33 ± 0.97 |

Means with different letters (a–c) within the same column are significantly different ($p < 0.05$).

[a] ST means crosslinked starch; EP means epichlorohydrin.

[b] Means ± SEM (each value is the mean of three replicates).

starch in the 50 ST films. In addition, the 50 ST/10 EP film had the highest tensile strength (Table 6). The percent elongation and strain energy of the films containing crosslinked potato starch were higher than those of the films containing native starch. In the crosslinking reaction, the available hydroxyl groups on starch molecules react stepwise with epichlorohydrin (Kartha & Srivastava, 1985). Monoglycerol ether starch may be produced by the competitive reaction of hydroxyl ions to open the oxirane during the reaction. As a further reaction, dimeric-crosslinked starch could form by two molecules of epichlorohydrin (Hollinger et al., 1974). The crosslinked starch has more carbon chains than native starch, which causes the crosslinked starch to be more hydrophobic. Therefore, it is believed that LLDPE films containing crosslinked starch showed higher mechanical strength than films containing native starch because the hydrophobic property of the starch promoted compatibility of starch and polyethylene in the film.

Tensile strength values of the 100 ST films containing crosslinked starch were higher than those of 100 ST films containing native starch (Table 7). The strain energy of the 100 ST films prepared with crosslinked starch was also significantly higher than that of the films with native starch. The percent elongation values of the 100 ST films were not significantly different, however, even though the films containing crosslinked starch had a relatively higher percent elongation.

As the amount of starch added increased from 50 to 100 g/kg of film, the mechanical properties of the films containing crosslinked or native starch decreased. These results support the previous observation that an increase in the starch concentrations reduces the mechanical strength of the films (Evangelista, Nikolov, Wei, Jane,

Table 6
Mechanical properties of starch–polyethylene films containing 50 g of crosslinked starch per kilogram of film

| Type of film[a] | Tensile strength[b] (MPa) | Percent elongation[b] | Strain energy[b] (kJ) |
|---|---|---|---|
| 50 ST/0 EP | 10.0479 ± 0.04b | 200.42 ± 19.71c | 617.19 ± 8.34b |
| 50 ST/0.1 EP | 12.0736 ± 0.03ab | 230.62 ± 32.78ab | 881.76 ± 14.28a |
| 50 ST/0.5 EP | 10.2822 ± 0.03b | 252.95 ± 35.78a | 853.83 ± 13.41a |
| 50 ST/1.0 EP | 15.5144 ± 0.94a | 217.11 ± 20.07bc | 858.72 ± 8.77a |
| 50 ST/2.0 EP | 12.7792 ± 0.05ab | 227.35 ± 21.55b | 895.90 ± 10.10a |

Means with different letters (a–c) within the same column are significantly different ($p < 0.05$).

[a] ST means crosslinked starch; EP means epichlorohydrin.

[b] Means ± SEM (each value is the mean of three replicates).

Table 7
Mechanical properties of starch–polyethylene films containing 100 g of crosslinked starch per kilogram of film

| Type of film[a] | Tensile strength[b] (MPa) | Percent elongation[b] | Strain energy[b] (kJ) |
|---|---|---|---|
| 100 ST/0 EP | 9.8598 ± 0.05d | 175.73 ± 16.00 | 511.59 ± 5.38c |
| 100 ST/0.1 EP | 10.2381 ± 0.04c | 183.37 ± 10.90 | 581.63 ± 5.67bc |
| 100 ST/0.5 EP | 8.9758 ± 0.03e | 191.21 ± 32.51 | 556.27 ± 10.90bc |
| 100 ST/1.0 EP | 11.9570 ± 0.04a | 185.54 ± 23.45 | 690.66 ± 10.42a |
| 100 ST/2.0 EP | 11.4297 ± 0.03b | 175.89 ± 13.22 | 626.79 ± 5.73ab |

Means with different letters (a–d) within the same column are significantly different ($p < 0.05$).

[a] ST means crosslinked starch; EP means epichlorohydrin.

[b] Means ± SEM (each value is the mean of three replicates).

& Gelina, 1991; Kim et al., 1994). This is probably due to the discontinuity created by the addition of starch granules to LLDPE film and by the poor interfacial interaction between the starch and LLDPE matrix.

## 4. Conclusions

Crosslinking by the use of less than 2% epichlorohydrin per starch gram did not greatly change the physicochemical properties of the potato starch. The surface morphology and X-ray diffraction patterns of the crosslinked starch were similar to those of the native starch. Crosslinked starch-filled LLDPE cast films had stronger mechanical properties (tensile strength and strain energy) than native starch-filled LLDPE. This result implies that the crosslinked starch-filled LLDPE is superior to the conventional native starch-filled LLDPE in terms of the mechanical properties of the films. It suggests that the crosslinked starch-filled LLDPE films have the potential to be substituted for native starch-filled LLDPE films.

## Acknowledgments

This work was supported by the Research Equipment Grant (No. 1999-220-00-002-1) of the Korea Science and Engineering Foundation.

## References

Evangelista, R. L., Nikolov, Z. L., Wei, S., Jane, J., & Gelina, R. J. (1991). Effect of compounding and starch modification on properties of starch-filled low-density polyethylene. *Industrial Engineering Chemistry and Research*, *30*, 1841–1846.

Gage, P. (1990). Degradable polyethylene film—The fact. *Tappi Journal*, *73*, 161–169.

Griffin, G. J. L. (1974). Biodegradable fillers in thermoplastic. *Advances in Chemistry Series*, *134*, 159–170.

Griffin, G. J. L (1977). Synthetic resin sheet material. US Patent 4, 021,388.

Hamerstrand, G. E., Hofretter, B. T., & Mehltretter, C. L. (1960). Determination of the extent of reaction between epichlorohydrin and starch. *Cereal Chemistry*, *37*, 519–524.

Hollinger, G., Kuniak, L., & Marchessault, R. H. (1974). Thermodynamic aspects of gelatinization and swelling of crosslinked starch. *Biopolymers*, *13*, 879–890.

Jane, T., Xu, A., Radosavljevic, M., & Seib, P. A. (1992). Location of amylose in normal starch granules. I. Susceptibility of amylose and amylopectin to cross-linking reagents. *Cereal Chemistry*, *69*, 405–409.

Kartha, K. P. R. & Srivastava, H. C. (1985). Reaction of epichlorohydrin with carbohydrate polymers. Part II. Starch reaction mechanism and physicochemical properties of modified starch. *Stärke*, *37*, 297–306.

Kim, H. S., & Lee, Y. E. (1996). Physicochemical properties of crosslinked potato starch. *Korean Journal of Food Science and Technology*, *28*, 573–579.

Kim, M., Pometto, A. L., Johnson, K. E., & Fratzke, A. R. (1994). Degradation studies of novel degradable starch–polyethylene plastics containing oxidized polyethylene and prooxidant. *Journal of Environmental Polymer Degradation*, *2*, 27–38.

Komiya, T., Nara, S., & Tsu, M. (1986). Changes in crystallinity and gelatinization phenomena of potato starch by acid treatment. *Stärke*, *38*, 9–13.

Lee, S. Y., Pyun, Y. R., Cho, H. Y., Yu, J. H., & Lee, S. K. (1984). Flow behaviors of native and gelatinized rice starch solutions. *Korean Journal of Food Science and Technology*, *16*, 29–36.

Lee, S. J., Kim, S. H., & Kim, M. (1999). Mechanical properties and thermal degradability of degradable polyethylene films prepared with oxidized potato starch. *Food Engineering Progress*, *3*, 141–151.

Otey, F. H., & Westhoff, R. P. (1984). Starch-based films. Preliminary diffusion evaluation. *Industrial Engineering Chemistry Production Research and Development*, *23*, 284–287.

Otey, F. H., Mark, A. M., Mehltretter, C. L., & Russell, C. R. (1974). Starch-based film for degradable agricultural mulch. *Industrial Engineering Chemistry Production Research and Development*, *13*, 90–92.

Otey, F. H., Westhoff, R. P., & Russell, C. R. (1977). Biodegradable films from starch and ethylene–acrylic acid copolymer. *Industrial Engineering Chemistry Production Research and Development*, *16*, 305–308.

Otey, F. H., Westhoff, R. P., & Doane, W. M. (1980). Starch-based blown films. *Industrial Engineering Chemistry Production Research and Development*, *19*, 592–595.

Otey, F. H., Westhoff, R. P., & Doane, W. M. (1987). Starch-based blown films. 2. *Industrial Engineering Chemistry and Research*, *26*, 1659–1663.

Potts, J. E., Clendinning, R. A., Ackart, W. B., & Niegisch, W. D. (1973). *Polymer and ecological problems*. New York: Plenum Press, p. 61.

Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: Production and uses. In R. L. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch Chemistry and Technology* (pp. 324–331). New York: Academic Press.

SAS (1985). *Statistical analysis system. User's guide, version 6.12*. Cary, NC: SAS Institute, Inc.

Swanson, C. L., Westhoff, R. P., & Doane, W. P. (1988). *Modified starches in plastic films. Proceedings of the Corn Utilization Conference*. Columbus, OH: National Corn Growers Association.

Wei, S., & Nikolov, Z. L. (1992). Accelerated degradation studies of starch-filled polyethylene films. *Industrial Engineering Chemistry and Research*, *31*, 2332–2339.

Wurzburg, O. B. (1987). Cross-linked starches. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 46–51). Boca Raton, FL: CRC Press.

Zobel, H. F. (1964). X-ray analysis of starch granular starches. In R. L. Whistler (Ed.), (*Vol. 4*) (pp. 109–113). *Methods in carbohydrate chemistry*, New York: Academic Press.