

Preparation and Characterization of Modified Starch-Based Plastic Film Reinforced with Short Pulp Fiber. II. Mechanical Properties

Dae-Hyun Kim, Seong-Ki Na, Jong-Shin Park

Division of Biological Resources and Materials Engineering, Seoul National University, Suwon 441-744, Korea

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ABSTRACT: Native corn starch- and hydroxypropylated starch (HPS-) based plastic films were prepared using the short pulp fiber as the reinforcement and the glycerol as the plasticizer. The results of tensile test showed that the strain and stress at break and elastic modulus increased with pulp content. With glycerol content, the strain at break increased considerably, but the breaking stress and elastic modulus decreased. And the stress-strain curves showed that the brittleness problem of films was overcome by the pulp, glycerol, and water content. The hydroxypropyl starch films showed results similar to those of the native starch films. The results of the three-point bending test showed that maximum deflection, flexural strength, and specific work increased with pulp content, but the flexural modulus was

the highest at a pulp content of 20%. And with the glycerol content, the maximum deflection and specific work of rupture increased, but the bending elastic modulus decreased. The hydroxypropyl starch films showed results similar to those of native starch films as far as the maximum deflection and flexural strength were concerned, but the bending elastic modulus and specific work of the hydroxypropyl starch films were considerably lower than those of starch films. So it was concluded that the flexibility of films was improved by the hydroxypropylation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2108–2117, 2003

Key words: plastics; mechanical properties; strength

INTRODUCTION

Because of environmental pollution problems caused by using synthetic polymers based on petroleum chemistry, the development of environmentally friendly polymeric materials have attracted extensive interest. The development of environmental friendly polymeric materials are classified into two categories: degradable synthetic polymers (polycaprolacton, polylactide, PVA, polyesteramide, etc.) and renewable natural polymers (chitin, chitosan, pectin, starch, cellulose, etc.). Among these, starch is a biodegradable natural polymer that exists abundantly in nature and is very cheap. So, starch has been used as the replacement for synthetic polymeric plastics, as well as in food, textile, and paper industries by various modifications and processes.

Starch-based (bio)degradable plastic materials can be prepared by various methods: embedding granular or gelatinized starch in synthetic polymeric matrices^{1–5}; blending with hydrophilic polymer^{6,7}; using modified starch by substitution, copolymerization, oxidation, and hydrolysis^{8–11}; foaming of starch within

the extruder^{12,13}; and preparing the thermoplastic starch (TPS) by melting under conditions of high temperature and pressure.^{14–16} But because the starch is usually used as a auxiliary component, the synthetic polymeric components still remain in a undegraded state even after the starch is biodegraded. In the case of blending with other polymeric materials, the problem of the phase separation, which causes the reduction of the mechanical properties of the blend, exists.¹⁷ Also, when starch is used as a major component, there are disadvantages such as the inferior mechanical properties due to the brittleness and the limitation of usage due to the hydrophilicity of starch-based plastics.^{18,19}

On the other hand, it has been reported that starch-based plastics reinforced with short pulp fiber had improved mechanical properties.¹⁹ It also was reported that films made from hydroxyalkylated starch had improved clearness and flexibility, and the process could overcome the hydrophilic problem by introduction of hydrophobic groups.^{8,20,21}

So, in this study, native corn starch- and hydroxypropylated starch (HPS)-based plastic films were prepared using short pulp fiber as the reinforcement and glycerol as the plasticizer to improve the mechanical properties and overcome the hydrophilic problem, and the mechanical properties by tensile and three-point bending were investigated.

Correspondence to: J.-S. Park (jongshin@plaza.snu.ac.kr).

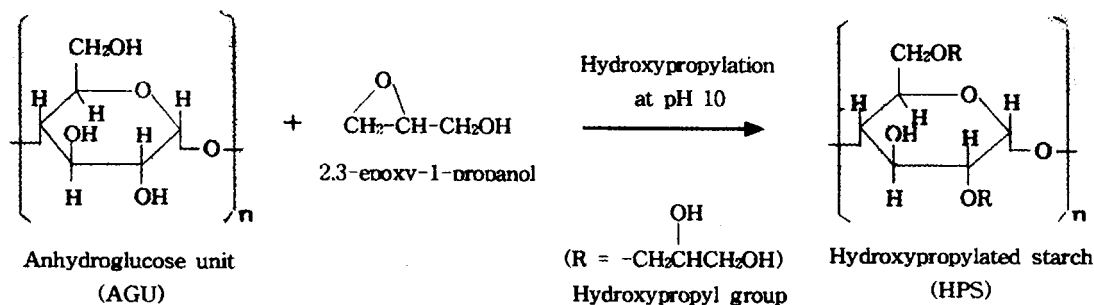


Figure 1 Mechanism of hydroxypropylation of starch with 2,3-epoxy-1-propanol.

EXPERIMENTAL

Materials

The starch was corn starch (Samyang Co., Korea) and the pulp (Hansol Co., Korea) was from a coniferous tree for papermaking, whose lignin content was less than 5%. The 2,3-epoxy-1-propanol (Wako Pure Chemical Industries, Ltd.), NaOH, and HCl were used without further purification.

Preparation of HPS

Starch (20 g) was added to distilled water (380 mL) and gelatinized at 95°C for 1 h and then cooled to 25°C. After the pH was adjusted to 10 with 1N NaOH, 2,3-epoxy-1-propanol was added to the reaction vessel and the reaction was carried out for 1 h. After the completion of the reaction, the products were washed with methanol 2~3 times and dried at 50°C in a vacuum oven. The hydroxypropylating process of starch with 2,3-epoxy-1-propanol was the same as shown in Figure 1. The results of the reaction was confirmed by ¹H-NMR (Avance 600, Bruker, Germany) and the degree of substitution of HPS was determined by the integration of each peaks. The characteristics of HPS are shown in Table I.

Preparation of films

The mixture of starch or HPS, pulp (0~40% w/w), and glycerol (0~20% w/w) was mixed with the distilled water to make a 5% slurry and gelatinized at 95°C for 1 h. Then the homogeneous dispersion was poured

into a petri dish and dried at 55°C in a vacuum oven to make the films by casting.

Mechanical properties

The tensile tests of each samples (30 × 5 × 0.3 ~ 0.5mm) were performed with MiniMat2000

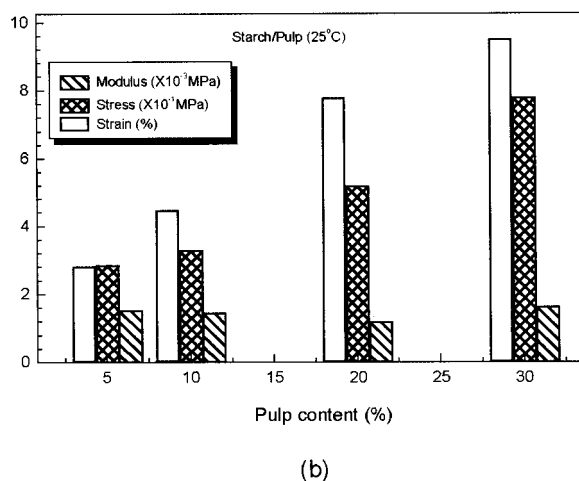
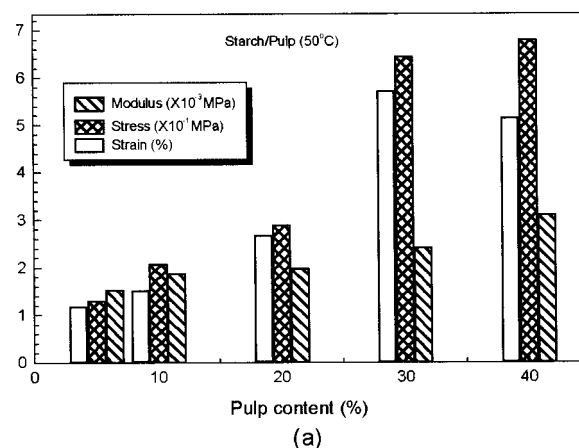


TABLE I
Characteristics of HPS

	2,3-Epoxy-1-Propanol/ AGU ^a Ratio	Degree of Substitution (DS)
HPS0.5	0.5	0.148
HPS1.0	1.0	0.166
HPS1.5	1.5	0.176

^a AGU:

Figure 2 Tensile test results of starch/pulp films as a function of pulp content (a) after being dried at 50°C in a vacuum oven for 24 h and (b) after being equilibrated at ambient temperature and humidity for 12 h.

TABLE II
Tensile Test Results of Starch/Pulp Films as A function of Pulp Contents

Pulp (%)	Thickness (mm)	Strain (%)	Stress (MPa)	Elastic Modulus (GPa)	Toughness (Nm/m ³)	Water Content (%)
After being dried in 50°C oven for 24 h						
5	0.29 ± 0.01	1.2 ± 0.12	13.2 ± 2.01	1.5 ± 0.03	47,748	1.3
10	0.32 ± 0.01	1.5 ± 0.13	20.9 ± 1.98	1.9 ± 0.02	294,650	0.4
20	0.33 ± 0.02	2.7 ± 0.09	29.0 ± 3.02	2.0 ± 0.04	369,150	1.4
30	0.30 ± 0.01	5.7 ± 0.11	64.5 ± 2.25	2.4 ± 0.02	2,155,200	0.7
40	0.26 ± 0.01	5.2 ± 0.08	68.0 ± 3.21	3.1 ± 0.05	1,973,000	1.6
After being equilibrated at ambient conditions for 12 h						
5	0.31 ± 0.01	2.8 ± 0.15	28.6 ± 1.87	1.6 ± 0.03	380,100	6.4
10	0.31 ± 0.02	4.5 ± 0.18	33.1 ± 2.02	1.5 ± 0.02	960,600	7.6
20	0.29 ± 0.01	7.8 ± 0.13	52.2 ± 3.75	1.2 ± 0.05	2,371,000	6.1
30	0.32 ± 0.01	9.5 ± 0.24	78.0 ± 2.05	1.6 ± 0.08	4,546,500	7.1

(Rheometric Scientific, Inc., USA) in the tensile mode. The strain rate was 5 mm/min. The three-point bending tests were based on ASTM D 790-91²² and performed with MiniMat2000 (Rheometric Scientific, Inc., USA) in the three-point bending mode. The testing conditions were support length (L) = 20 mm, width (b) = 5 mm, rate = 20 mm/min. And the stress (S) at maximum or break and the flexural modulus (E_b) were obtained using the following equations. The tests for each samples were performed five times.

$$S = 3PL/2bd^2[1 + 6(D/L)^2 - 4(d/L)(D/L)]$$

$$E_b = L^3m/4bd^3$$

S is the stress at maximum or break (N/m²), E_b the flexural modulus (N/m²), P is the load at maximum or

break (N), L the support length (mm), b the sample width (mm), d the sample thickness (mm), D the deflection at maximum or break (mm), and m the initial slope at load-deflection curve (N/m).

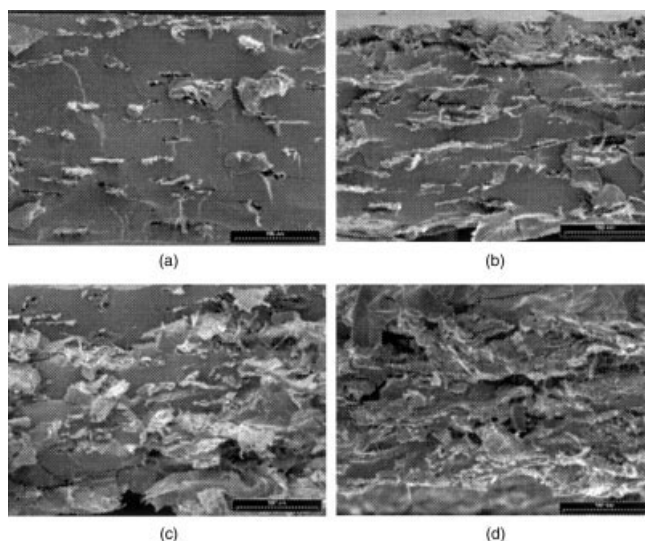


Figure 3 SEM micrographs of starch/pulp films: (a) SP10, (b) SP20, (c) SP30, and (d) SP40.

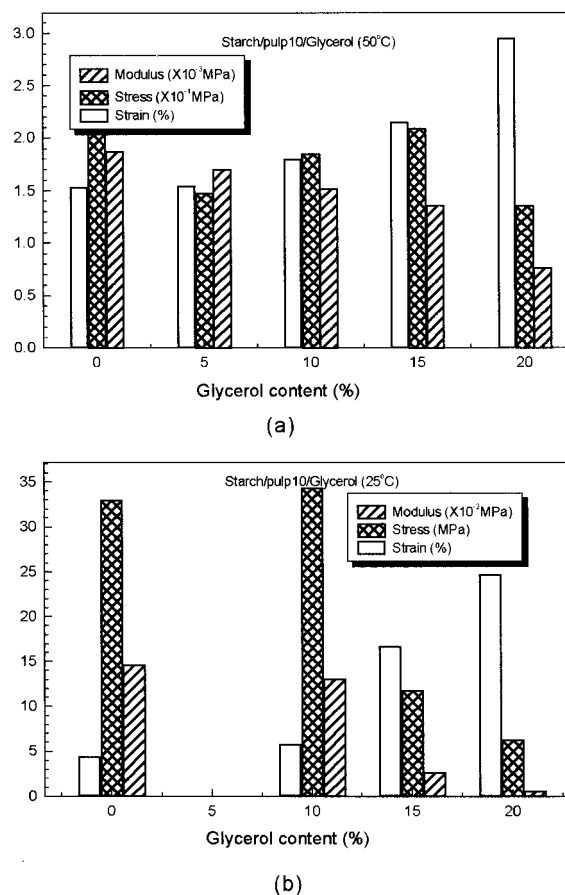


Figure 4 Tensile test results of starch/pulp10/glycerol films as a function of glycerol content (a) after being dried at 50°C in a vacuum oven for 24 h and (b) after being equilibrated at ambient temperature and humidity for 12 h.

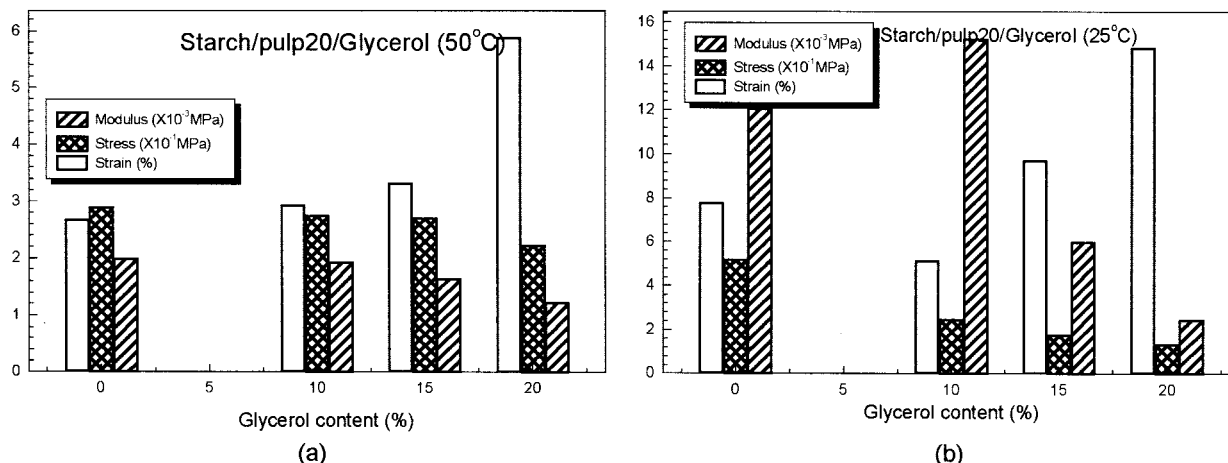


Figure 5 Tensile test results of starch/pulp20/glycerol films as a function of glycerol content (a) after being dried at 50°C in a vacuum oven for 24 h and (b) after being equilibrated at ambient temperature and humidity for 12 h.

Scanning electron microscopy

The cross-sections of samples were examined using SEM (scanning electron microscopy) JSM 5410LV, JEOL, Japan) after the fractured cross-sections of dried samples were coated with gold.

RESULTS AND DISCUSSION

Tensile properties

In Figure 2, the results of tensile tests for starch/pulp films are shown. Figure 2(a) has the results for the films sufficiently dried at 50°C vacuum oven and

TABLE III
Tensile Test Results of Starch/Pulp/Glycerol Films as a Function of Glycerol Contents

Glycerol (%)	Thickness (mm)	Strain (%)	Stress (MPa)	Elastic Modulus (GPa)	Toughness (Nm/m ³)	Water Content (%)
Starch/pulp(10%)/glycerol: After being dried in 50°C oven for 24 h						
0	0.32 ± 0.01	1.5 ± 0.13	20.9 ± 1.98	1.9 ± 0.02	294,650	0.4
5	0.30 ± 0.01	1.6 ± 0.09	14.8 ± 1.58	1.7 ± 0.04	94,330	1.4
10	0.31 ± 0.01	1.8 ± 0.18	18.6 ± 1.67	1.5 ± 0.03	112,830	0.5
15	0.31 ± 0.01	2.2 ± 0.21	21.0 ± 2.17	1.4 ± 0.06	184,960	1.5
20	0.30 ± 0.01	3.0 ± 0.19	13.6 ± 1.34	0.8 ± 0.02	170,550	1.3
After being equilibrated at ambient conditions for 12 h						
0	0.31 ± 0.02	4.5 ± 0.18	33.1 ± 2.02	1.5 ± 0.02	960,600	11.4
10	0.31 ± 0.01	5.8 ± 0.01	34.4 ± 0.01	1.3 ± 0.01	1,225,000	7.6
15	0.30 ± 0.01	16.7 ± 0.01	11.9 ± 0.01	0.3 ± 0.01	1,471,700	8.4
20	0.33 ± 0.01	24.7 ± 0.01	6.3 ± 0.01	0.07 ± 0.01	1,097,000	8.2
Starch/pulp(20%)/glycerol: After being dried in 50°C oven for 24 h						
0	0.33 ± 0.02	2.7 ± 0.09	29.0 ± 3.02	2.0 ± 0.04	369,150	1.4
10	0.31 ± 0.01	2.9 ± 0.12	27.5 ± 2.79	1.9 ± 0.03	423,900	1.5
15	0.36 ± 0.02	3.3 ± 0.21	27.2 ± 3.02	1.6 ± 0.01	510,600	1.5
20	0.40 ± 0.03	5.9 ± 0.25	22.4 ± 2.01	1.2 ± 0.03	928,800	1.3
After being equilibrated at ambient conditions for 12 h						
0	0.29 ± 0.01	7.8 ± 0.13	52.2 ± 3.75	1.2 ± 0.05	2,371,000	6.0
10	0.32 ± 0.02	5.2 ± 0.21	24.9 ± 2.38	1.5 ± 0.08	856,300	10.0
15	0.38 ± 0.02	9.7 ± 0.16	18.0 ± 1.21	0.6 ± 0.03	1,191,500	8.9
20	0.39 ± 0.03	14.9 ± 0.25	13.6 ± 1.78	0.3 ± 0.07	1,288,500	10.0

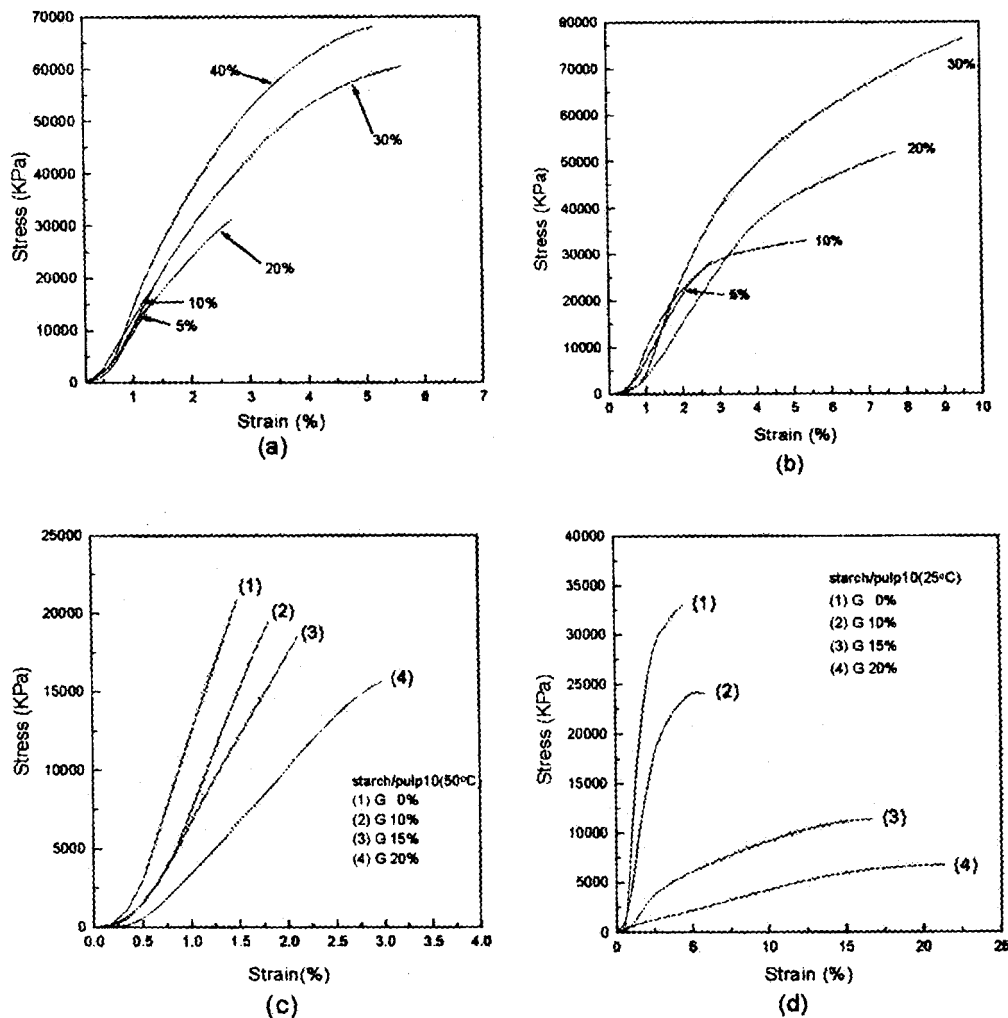


Figure 6 Stress-strain curves of starch/pulp/glycerol films as a function of (a) pulp content after being dried at 50°C in a vacuum oven for 24 h, (b) pulp content after being equilibrated at ambient temperature and humidity, (c) glycerol content after being dried at 50°C in a vacuum oven for 24 h, and (d) glycerol contents after being equilibrated at ambient temperature and humidity.

shows that the strain at break increased from 1.2 to 5.7%, the stress at break from 13.19 to 68.03 MPa, and the elastic modulus from 1.5 to 3.1 GPa with pulp content added as reinforcement. And toughness also increased significantly (Table II). But on the contrary, the strain at break of the films with 40% pulp content decreased. This is because the starch content, which functions as the matrix, was reduced so much that the integration of films was inhibited when pulp was added excessively. This result is confirmed by SEM micrographs in Figure 3. Figure 2(b) shows the results of the tensile test for the films kept at the ambient condition [25°C, 55~65% relative humidity (RH)] for 12 h and contained 7~10% water content. The strain at break increased from 2.8 to 9.5%, the stress at break from 28.6 to 77.9 MPa with the pulp content; toughness also increased. Lourdin et al. reported that the maximum elongation and stress at break of the films

made of starch at the ambient condition are 6% and 40~50 MPa, respectively.²³ From the above results, it can be concluded that the film with 20% pulp content has the most improved tensile properties.

In Figure 4 and Figure 5, the tensile test results of starch/pulp/glycerol films are shown. In the case of the films with 10% pulp content in the dried state [Fig. 4(a)], strain at break increased a little with glycerol content, but the stress at break and the toughness did not show any tendency. On the other hand, in the case of the films with 20% pulp content [Fig. 5(a)], the strain at break and the toughness increased, but the stress at break and the elastic modulus decreased with glycerol content, which acts as a plasticizer. And the films with 20% pulp content were superior to those with 10% pulp content in the strain and stress at break and in the toughness. So, it seems that the reinforcing effect by the pulp predominated over the plasticizing

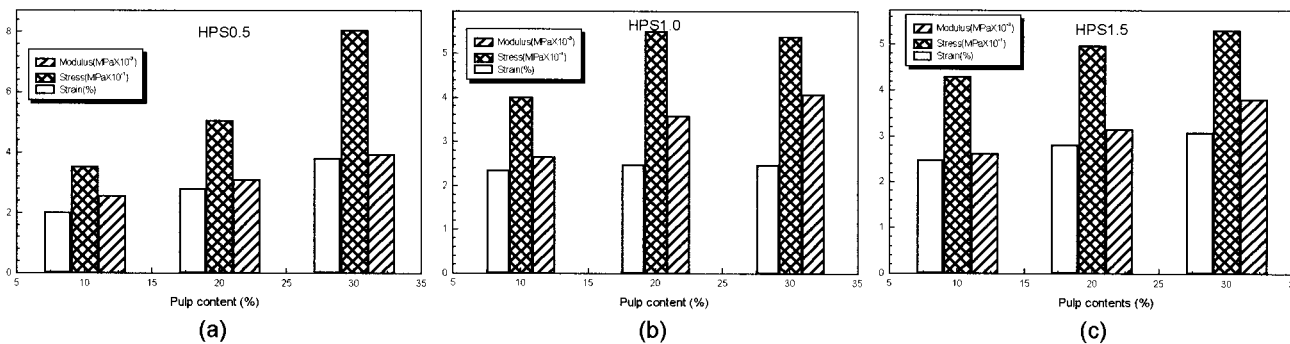


Figure 7 Tensile test results of HPS/pulp films as a function of pulp content: (a) HPS0.5, (b) HPS1.0, and (c) HPS1.5.

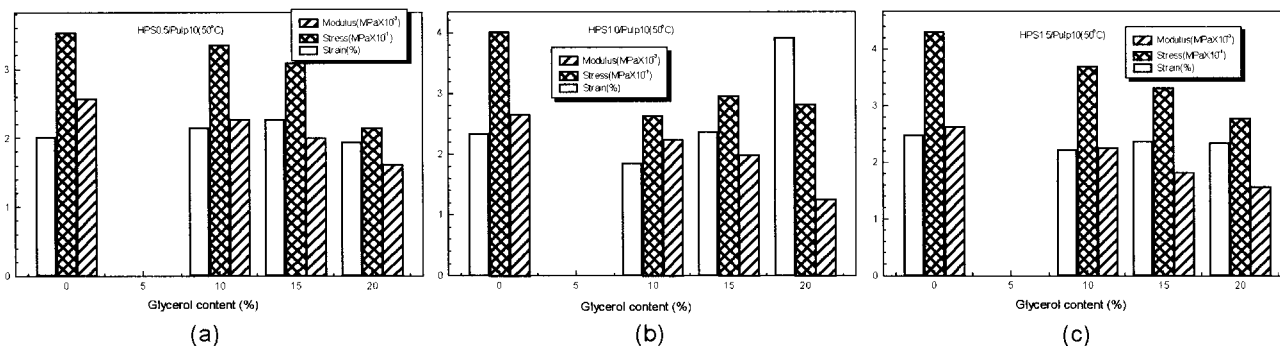


Figure 8 Tensile test results of HPS/pulp (10%)/glycerol films as a function of glycerol content after being dried at 50°C in a vacuum oven for 24 h: (a) HPS0.5, (b) HPS1.0, and (c) HPS1.5.

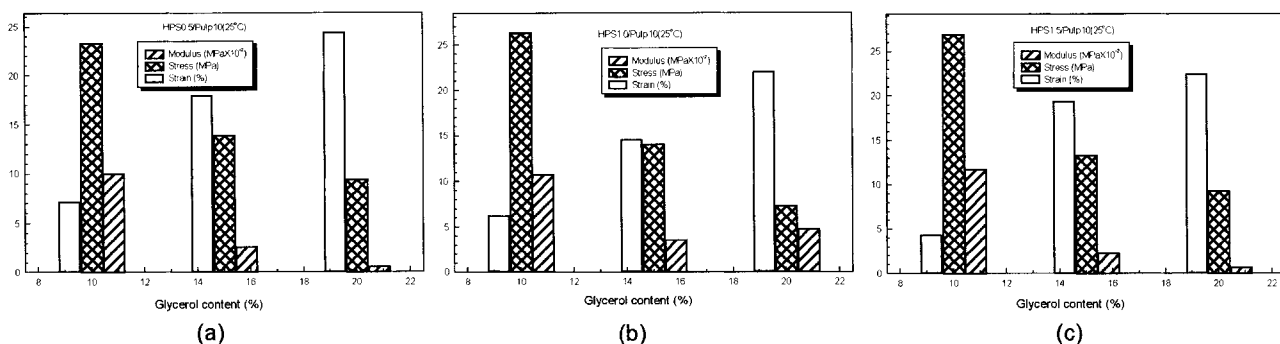


Figure 9 Tensile test results of HPS/pulp (10%)/glycerol films as a function of glycerol content after being equilibrated at ambient conditions for 12 h: (a) HPS0.5, (b) HPS1.0, and (c) HPS1.5.

effect of the glycerol in the dried state. But in the wet state, the strain at break of the films with 10% pulp content [Fig. 4(b)] increased from 4.5 to 24.7%, and those of the films with 20% pulp content [Fig. 5(b)] increased from 7.8 to 14.9%. On the other hand, the stress at break and the elastic modulus decreased largely in both cases. So, it seems that the plasticizing effect of the glycerol and water predominated over the reinforcing effect of the pulp in the wet state. (See Table III.)

In Figure 6, the stress–strain curves of starch/pulp/glycerol films are shown. Generally, it has been

known that the brittle polymer shows the S–S curve, which has the yield point when drawn in the direction parallel to the orientation of the polymer, but shows the linear type of S–S curve up to breaking when drawn in the direction perpendicular to the orientation of the polymer. On the other hand, the ductile polymer shows the S–S curve that has the yield point even when drawn in the direction perpendicular to the orientation.²⁴ The dried starch films show the linear type of S–S curve up to breaking due to the brittleness of films. But films reinforced with pulp and plasticized with glycerol and water show the S–S

TABLE IV
Tensile Test Results of HPS/Pulp/Glycerol Films

	Thickness (mm)	Strain (%)	Stress (MPa)	Elastic Modulus (GPa)	Toughness (Nm/m ³)	Water Content (%)
After being dried in 50°C oven for 24 hrs						
Pulp (%)				HPS0.5 (glycerol 0%)		
10	0.45 ± 0.03	2.0 ± 0.12	35.5 ± 3.11	2.6 ± 0.05	232,800	1.2
20	0.42 ± 0.03	2.8 ± 0.23	50.7 ± 2.42	3.1 ± 0.07	608,400	0.9
30	0.50 ± 0.02	3.8 ± 0.15	80.7 ± 2.47	4.0 ± 0.03	1,349,000	1.1
Pulp (%)				HPS1.0 (glycerol 0%)		
10	0.45 ± 0.03	2.4 ± 0.09	40.2 ± 2.75	2.7 ± 0.11	374,200	1.3
20	0.42 ± 0.02	2.5 ± 0.12	55.3 ± 1.59	3.6 ± 0.08	498,020	1.5
30	0.52 ± 0.04	2.5 ± 0.16	54.1 ± 3.25	4.1 ± 0.06	524,700	1.0
Pulp (%)				HPS1.5 (glycerol 0%)		
10	0.46 ± 0.02	2.5 ± 0.11	43.7 ± 2.63	2.6 ± 0.06	390,400	0.8
20	0.41 ± 0.03	2.8 ± 0.09	49.8 ± 3.42	3.2 ± 0.04	627,070	1.2
30	0.43 ± 0.02	3.1 ± 0.09	53.2 ± 1.21	3.8 ± 0.09	695,080	1.4
Glycerol (%)				HPS 0.5 (pulp 10%)		
0	0.45 ± 0.03	2.0 ± 0.12	35.5 ± 3.11	2.6 ± 0.05	232,800	1.2
10	0.49 ± 0.05	2.2 ± 0.13	33.6 ± 3.24	2.3 ± 0.08	224,800	1.3
15	0.49 ± 0.04	2.3 ± 0.05	31.0 ± 1.36	2.0 ± 0.11	263,660	1.2
20	0.52 ± 0.01	2.0 ± 0.07	21.6 ± 2.21	1.6 ± 0.09	164,250	1.4
Glycerol (%)				HPS1.0 (pulp 10%)		
0	0.45 ± 0.03	2.4 ± 0.09	40.2 ± 2.75	2.7 ± 0.11	374,200	1.3
10	0.56 ± 0.02	1.9 ± 0.07	26.5 ± 3.02	2.2 ± 0.08	177,896	0.9
15	0.60 ± 0.04	2.4 ± 0.10	29.7 ± 2.34	2.0 ± 0.09	268,370	1.4
20	0.47 ± 0.02	3.9 ± 0.12	28.3 ± 1.89	1.3 ± 0.05	629,930	1.2
Glycerol (%)				HPS1.5 (pulp 10%)		
0	0.46 ± 0.02	2.5 ± 0.11	43.7 ± 3.17	2.6 ± 0.06	390,400	0.8
10	0.40 ± 0.03	2.2 ± 0.08	37.1 ± 2.79	2.3 ± 0.04	319,200	1.5
15	0.45 ± 0.02	2.4 ± 0.09	33.3 ± 3.53	1.8 ± 0.03	321,700	1.2
20	0.43 ± 0.04	2.4 ± 0.12	27.9 ± 2.72	1.6 ± 0.05	269,240	1.4
After being equilibrated at ambient conditions for 24 h						
Glycerol (%)				HPS 0.5 (pulp 10%)		
10	0.49 ± 0.04	7.2 ± 0.08	23.4 ± 3.12	1.0 ± 0.08	1,194,200	11.3
20	0.51 ± 0.03	18.1 ± 0.19	14.0 ± 2.17	0.26 ± 0.04	1,808,200	7.9
30	0.53 ± 0.05	24.4 ± 0.27	9.5 ± 2.54	0.06 ± 0.09	1,575,500	8.7
Glycerol (%)				HPS1.0 (pulp 10%)		
10	0.54 ± 0.04	6.3 ± 0.07	26.4 ± 2.08	1.1 ± 0.09	1,112,800	10.8
20	0.63 ± 0.05	14.6 ± 0.13	14.1 ± 2.37	0.36 ± 0.04	1,517,750	13.4
30	0.53 ± 0.02	22.1 ± 1.09	7.4 ± 1.02	0.05 ± 0.02	1,139,400	8.2
Glycerol (%)				HPS1.5 (pulp 10%)		
10	0.41 ± 0.03	4.4 ± 0.09	27.0 ± 2.71	1.1 ± 0.09	703,650	6.6
20	0.46 ± 0.02	19.4 ± 1.53	13.4 ± 1.52	0.24 ± 0.03	1,887,000	5.6
30	0.44 ± 0.05	22.5 ± 2.17	9.3 ± 0.88	0.07 ± 0.01	1,438,000	7.5

TABLE V
Parameters of Three-Point Bending Test

Parameter	
Beam length, <i>L</i> (mm)	20
Crosshead motion rate, <i>R</i> (mm/min)	20
Specimen dimension	
Length (mm)	50
Width, <i>b</i> (mm)	5
Thickness, <i>d</i> (mm)	0.3–0.5

curves of the ductile polymers. So, from the above results, it is concluded that the brittleness problem of starch-based films could be overcome by the reinforcement with pulp and by the plasticization with glycerol and water.

In Figure 7, the tensile test results of HPS/pulp films are shown. Similar to the results shown in Figure 2, in the dried state, the strain and stress at break and the elastic modulus increased with the pulp contents. And it is shown in Figure 8 that with the glycerol

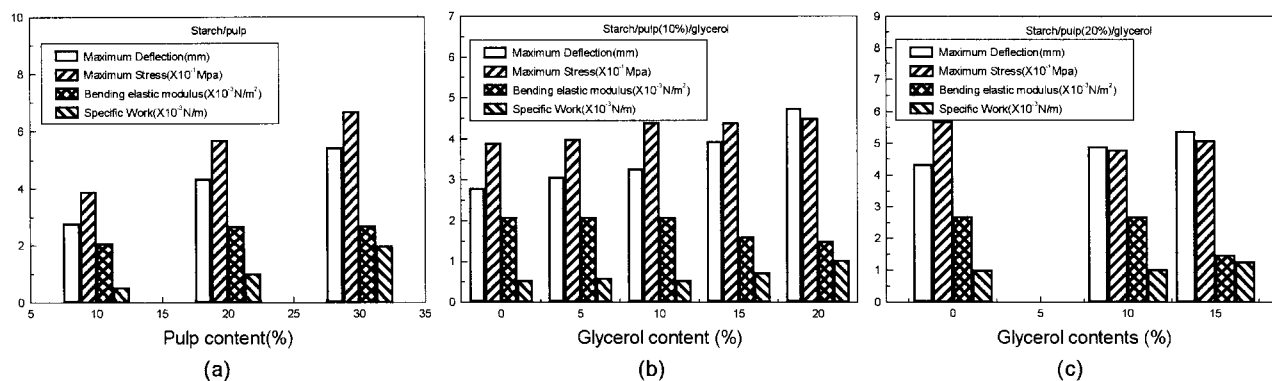


Figure 10 Three-point bending test results of starch/pulp/glycerol films as a function of (a) pulp content, and (b) and (c) glycerol contents.

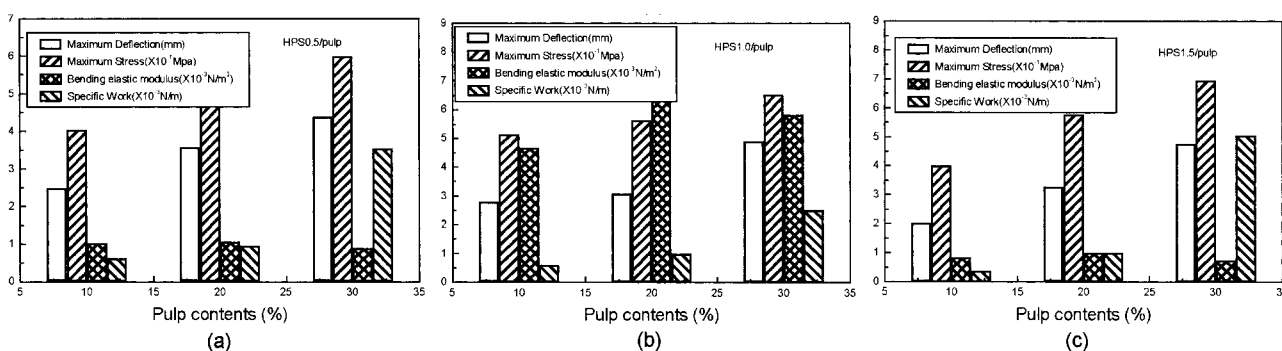


Figure 11 Three-point bending test results of HPS/pulp films as a function of pulp content: (a) HPS0.5, (b) HPS1.0, and (c) HPS1.5.

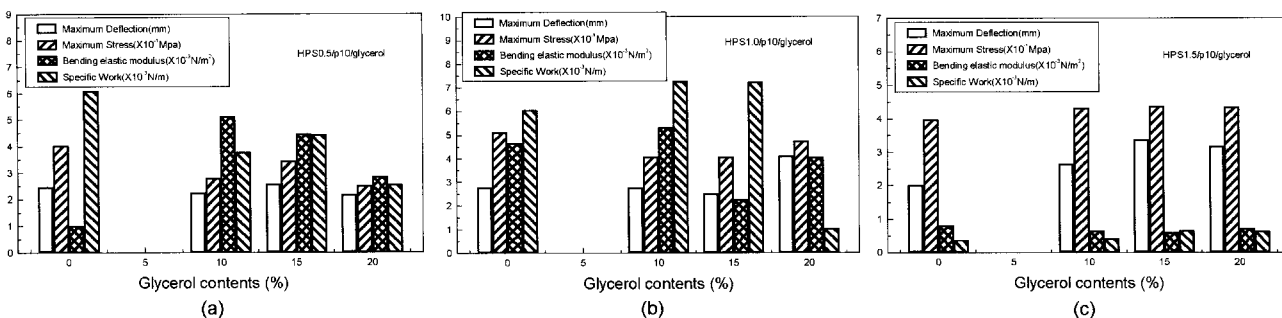


Figure 12 Three-point bending test results of HPS/pulp10/glycerol films as a function of glycerol content: (a) HPS0.5, (b) HPS1.0, and (c) HPS1.5.

content, the strain at break increased, but the stress at break and the elastic modulus decreased. In the wet state, on the contrary, the strain at break increased largely, but the stress at break and the elastic modulus decreased. The DS of HPS did not seem to affect the tensile properties of films. (See Fig. 9 and Table IV.)

Bending properties

The bending tests of films were based on ASTM D 790-91(flexural testing method) and the properties were determined by the following equations²²:

$$R = ZL^2/6d$$

R is the rate of crosshead motion (mm/min), L the support span (mm), d the depth of beam (mm), and Z the rate of straining of the outer fiber (mm/mm min).

$$D = rL^2/6d = rR/Z = Rt$$

D is the midspan deflection (mm) and r the maximum strain of the outer fiber (mm).

$$S = 3PL/2bd^2$$

TABLE VI
Three-Point Bending Test Results of Starch (or HPS)/Pulp/Glycerol Films

	Thickness (mm)	At Maximum		At Break		Bending Elastic Modulus (N/m ²)	Specific Work (N/m)
		Deflection (mm)	Stress (MPa)	Deflection (%)	Stress (MPa)		
Starch/pulp/glycerol films							
Pulp (%)				(Glycerol 0%)			
10	0.37 ± 0.03	2.79 ± 0.08	39 ± 3.52	2.79 ± 0.08	39 ± 3.52	2100	536.3
20	0.34 ± 0.02	4.35 ± 0.10	57 ± 2.78	4.35 ± 0.10	57 ± 2.78	2700	1025.8
30	0.38 ± 0.05	5.45 ± 0.12	67 ± 2.19	6.11 ± 0.15	69 ± 2.74	2200	1987.8
40	0.36 ± 0.04	5.38 ± 0.09	65 ± 1.97	—	—	—	—
Glycerol (%)				(Pulp 10%)			
5	0.30 ± 0.04	3.06 ± 0.13	40 ± 2.12	3.06 ± 0.13	40 ± 2.12	2200	585.9
10	0.38 ± 0.01	3.27 ± 0.09	44 ± 1.79	3.27 ± 0.09	44 ± 1.79	2100	548.5
15	0.32 ± 0.03	3.94 ± 0.16	44 ± 3.45	3.94 ± 0.16	44 ± 3.45	1600	737.1
20	0.35 ± 0.03	4.74 ± 0.17	45 ± 2.58	4.74 ± 0.17	45 ± 2.58	1500	1033.1
Glycerol (%)				(Pulp 20%)			
10	0.33 ± 0.03	4.91 ± 0.17	48 ± 2.53	4.91 ± 0.17	48 ± 2.53	2700	1039.4
15	0.42 ± 0.05	5.38 ± 0.21	51 ± 1.15	5.38 ± 0.21	51 ± 1.15	1500	1286.9
Hydroxypropylated starch/pulp/glycerol films							
Pulp (%)				(HPS0.5, glycerol 0%)			
10	0.45 ± 0.01	2.48 ± 0.21	40 ± 2.21	2.48 ± 0.21	40 ± 2.21	1023	612.5
20	0.46 ± 0.04	3.58 ± 0.16	47 ± 1.78	3.58 ± 0.16	47 ± 1.78	1055	947.1
30	0.52 ± 0.02	4.38 ± 0.34	60 ± 2.63	6.78 ± 0.12	63 ± 3.59	886	3544.7
Pulp (%)				(HPS1.0, glycerol 0%)			
10	0.47 ± 0.04	2.78 ± 0.18	51 ± 4.01	2.78 ± 0.18	51 ± 4.01	467	606.3
20	0.47 ± 0.01	3.08 ± 0.26	56 ± 2.53	3.08 ± 0.26	56 ± 2.53	642	994.7
30	0.53 ± 0.03	4.91 ± 0.13	65 ± 2.96	4.91 ± 0.13	65 ± 2.96	583	2517.4
Pulp (%)				(HPS1.5, glycerol 0%)			
10	0.44 ± 0.02	2.02 ± 0.13	40 ± 2.01	2.02 ± 0.13	40 ± 2.01	826	380.7
20	0.45 ± 0.01	3.28 ± 0.11	58 ± 1.24	3.28 ± 0.11	58 ± 1.24	959	1006.1
30	0.53 ± 0.02	4.78 ± 0.09	69 ± 1.16	8.25 ± 0.23	63 ± 3.08	738	5057.1
Glycerol (%)				(HPS0.5, pulp 10%)			
10	0.52 ± 0.01	2.25 ± 0.20	28 ± 1.58	2.25 ± 0.20	28 ± 1.58	513	379.4
15	0.52 ± 0.03	2.58 ± 0.09	35 ± 2.22	2.58 ± 0.09	35 ± 2.22	448	445.4
20	0.54 ± 0.02	2.18 ± 0.17	25 ± 2.46	2.18 ± 0.17	25 ± 2.46	286	255.5
Glycerol (%)				(HPS1.0, pulp 10%)			
10	0.59 ± 0.03	2.78 ± 0.06	41 ± 3.12	2.78 ± 0.06	41 ± 3.12	532	728.2
15	0.60 ± 0.02	2.52 ± 0.32	41 ± 2.67	2.52 ± 0.32	41 ± 2.67	228	723.4
20	0.48 ± 0.02	4.12 ± 0.12	47 ± 2.82	4.12 ± 0.12	47 ± 2.82	406	1061.3
Glycerol (%)				(HPS1.5, pulp 10%)			
10	0.48 ± 0.03	2.65 ± 0.15	43 ± 3.02	2.65 ± 0.15	43 ± 3.02	661	433.7
15	0.49 ± 0.01	3.38 ± 0.21	44 ± 2.71	3.38 ± 0.21	44 ± 2.71	603	672.1
20	0.45 ± 0.03	3.18 ± 0.17	44 ± 1.54	3.18 ± 0.17	44 ± 1.54	727	645.3

S is the stress in the outer fibers at midspan (N/m²), P the load at a given point on the load-deflection curve (N), and b the width of beam.

$$E_b = L^3 m / 4bd^3$$

E_b is the modulus of elasticity in bending (N/m²), and m the slope of the tangent to the initial straight-line portion of the load-deflection curve, N/m of deflection.

If the deflection is small, Z is 0.01 and if the deflection is high, Z is 0.1. In this study, the Z value of 0.1 is used and the calculated rate of the crosshead motion is

20 mm/min. And if the deflection is more than 10% of the support span length, the maximum stress is determined by the following equation:

$$S = (3PL/2bd^2)[1 + 6(D/L)^2 - 4(d/L)(D/L)]$$

The work of rupture of the films in three-point bending was determined using the load-deflection curve. To avoid the errors due to the thickness variation of the films, the work was divided by the cross-section area of the films and called the specific work (N/m).

The parameters used in three-point bending test are shown in Table V.

In Figure 10, the three-point bending test results of starch/pulp/glycerol films are shown as a function of pulp content and glycerol content. Figure 10 (a), as a function of the pulp contents, shows that the maximum deflection and stress increased from 2.79 to 5.38 mm and from 39 to 65 MPa, respectively, and the specific work increased with pulp content. But the flexural modulus was the highest in 20% pulp content. Figures 10(b) and 10(c), which contain the pulp contents 10 and 20%, respectively, show the bending test results as a function of glycerol content. The maximum deflection and specific work increased with glycerol content, but the flexural modulus decreased. Usually, the films with 20% pulp content has superior properties to that with 10% pulp content. In other words, the pulp as the reinforcement increases the maximum deflection, flexural strength, and flexural modulus, but the glycerol as the plasticizer increases the maximum deflection and reduces the flexural modulus.

In Figure 11 and Figure 12, the bending test results of HPS/pulp/glycerol films are shown. The maximum deflection and the flexural strength had similar values to those of starch/pulp/glycerol films, but the flexural modulus and the specific work were less than those of starch/pulp/glycerol films. So, it could be concluded that the flexibility was improved by the hydroxypropylation. (See also Table IV.)

CONCLUSIONS

The tensile test results of the starch- and HPS-based films showed that the strain and stress at break and elastic modulus increased with pulp contents. With the glycerol contents, the strain at break increased considerably, but the stress and elastic modulus decreased. The three-point bending test results showed that the maximum deflection, flexural strength, and specific work increased with the pulp contents, but the bending elastic modulus was the highest at the pulp content of 20%. And with glycerol content, the maximum deflection and specific work increased, but the bending elastic modulus decreased. The hydroxypropyl starch films showed results similar to those of the

native starch films as far as the maximum deflection and flexural strength were concerned, but the bending elastic modulus and specific work of the hydroxypropyl starch films were considerably lower than those of starch films. So it is concluded that the flexibility of films is improved by the hydroxypropylation.

References

1. Arvanitoyannis, I.; Biliaderis, C. G.; Ogawa, H.; Kawasaki, N. *Carbohydr Polym* 1998, 36, 89–104.
2. Shah, P. B.; Bandopadhyay, S.; Bellare, J. R. *Polym Degrad Stab* 1995, 47, 165–173.
3. Yang, Z.; Bhattacharya, M.; Vaidya, U. R. *Polymer* 1996, 37(11), 2137–2150.
4. Pierra, N. S.; Favis, B. D.; Ramsay, B. A.; Ramsay, J. A.; Verhoogt, H. *Polymer* 1997, 38(3), 647–655.
5. Zuchowska, D.; Steller, R.; Meissner, W. *Polym Degrad Stab* 1998, 60, 471–480.
6. Nwufu, B. T. *J Appl Polym Sci* 1985, 23, 2023–2031.
7. Wel, Y. C.; Hwang, M. H. *Proc 4th Asian Textile Conference*, June 24–26, 1997.
8. Wulff, G.; Steinert, A.; Holler, O. *Carbohydr Res* 1998, 307, 19–31.
9. Wurzburg, O. B. *Modified Starches: Properties and Uses*; National Starch and Chemical Corp.: Bridgewater, NJ, 1986; Chap 2, pp 23–29.
10. Autio, K.; Suortti, T.; Hamunen, A.; Poutanen, K. *Carbohydr Polym* 1996, 29, 133–161.
11. Sisi, F. F. E.; Abdel-Hafiz, S. A.; Saleh, A. R. Hebeish, A. *Polym Degrad Stab* 1998, 62, 201–210.
12. Abecassis, J.; Abbou, R.; Chaurand, M.; Morel, M. H.; Vernoux, P. *Cereal Chem* 1994, 71(3), 247–253.
13. Sokhey, A. S.; Kollengode, A. N.; Hanna, M. A. *J Food Sci* 1994, 59, 895–898.
14. Lacourse, N. L.; Altieri, P. A. U.S. Pat. 1989, 4,863,655.
15. Altieri, P. A.; Mead, N. J. B. U.S. Pat. 1992, 5,135,037.
16. Lim, D. L.; Im, S. S.; Han, J. S.; Yim, S. H.; Kim, J. S.; Lee, Y. M. *J Environ Polym Degrad* 1997, 5, 191.
17. Bikiaris, D.; Prinos, J.; Panayiotou, C. *Polym Degrad Stab* 1997, 56, 1–9.
18. Warburton, S. C.; Donald, A. M. *J Mater Sci* 1990, 25, 4001–4007.
19. Tsiapouris, A.; Dresden, L. L. *Starch* 2000, 52, 53–57.
20. Arvanitoyannis, I.; Nakayama, A.; Aiba, S. I. *Carbohydr Polym* 1998, 36, 105–119.
21. Rivard, C.; Moens, L.; Roberts, K.; Brigham, J.; Kelley, S. *Enzyme Microbial Technol* 1995, 17, 848–852.
22. Annual Book of ASTM Standards, Designation: D 790–91
23. Lourdin, D.; Coignard, L.; Bizot, H.; Colonna, P. *Polymer* 1997, 38, 5401–5406.
24. Nielsen, L. E.; Landel, R. F. *Marcel Dekker*: New York, 1994; pp 285–291.