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

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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. Starch (or HPS) films showed different X-ray diffraction patterns with the A-type of native corn starch powder. The crystallinity of films increased with pulp content, but decreased with glycerol content and degree of substitution by hydroxypropylation. Also, the intensity of peaks at $2\theta = 15.3$ and $17.3°$ decreased with glycerol content and degree of substitution. The water uptake of films as a function of the relative humidity decreased with pulp content and degree of substitution by hydroxypropylation, but increased with glycerol content. Differential scanning calorimetry (DSC) thermograms showed that the glass transition temperature of films decreased and the endothermic peaks at the melting temperature broadened due to the plasticizing effect and the decrease of the crystallinity, which were caused by the addition of glycerol and the hydroxypropylation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2100–2107, 2003

Key words: starch/pulp/glycerol film; plastics; hydroxypropylation; water uptake; crystallinity; glass transition; melting point; X-ray

INTRODUCTION

The problems of environmental pollutants caused by using synthetic polymers based on petroleum chemistry have become increasingly serious. Because of this, legal restrictions on the uses of synthetic polymeric materials have intensified worldwide. To solve these problems, various methods such as the restriction of the excess uses of commodities and packaging materials made from the synthetic polymeric plastics, burial and combustion of the plastic wastes, and recycling of renewable materials have been used. But the problems of secondary pollution and the high cost still remain. So, as another solution, environmental friendly biodegradable plastic materials have been developed recently.

The developments of environmentally friendly polymeric materials are classified into two categories: the degradable synthetic polymers (polycaprolacton, polylactide, PVA, and polyesteramide, etc.) and the renewable natural polymers (chitin, chitosan, pectin, starch, and 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 the food, textile, and paper industries by the various modifications and processes.

Starch-based (bio)degradable plastic materials can be prepared by various methods: embedding the granular or gelatinized starch in synthetic polymeric matrices such as polyethylene, polypropylene, polystyrene, and poly(vinyl chloride), etc.[1–5]; blending with the hydrophilic polymer such as poly(vinyl alcohol)[6,7]; using the modified starch by substitution, copolymerization, oxidation, and hydrolysis[8–12]; foaming of starch within the extruder[13]; and preparing thermoplastic starch (TPS) by melting under the 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 that 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 inferior mechanical properties due to brittleness and limitation of usage due to the hydrophilicity of starch-based plastics.[18,19]

On the other hand, it was reported that the starch-based plastics, which were reinforced with short pulp

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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, anhydroglucose unit.

fiber, had improved mechanical properties.[20,21] It also was reported that films made from hydroxyalkylated starch had improved clearness and flexibility, and the process could overcome the hydrophilic problem by the introduction of the hydrophobic groups.[8,21,22]

So in this study, native corn starch- and hydroxypropylated starch (HPS)-based plastic films were prepared using short pulp fiber as reinforcement and glycerol as plasticizer to improve the mechanical properties and to overcome the hydrophilic problem. And for the films prepared, the structural analysis by Fourier transform infrared (FTIR) and X-ray scattering was performed and and water-uptake behavior was investigated.

EXPERIMENTAL

Materials

The starch used 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 the 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 vacuum oven. The results of the reaction was confirmed by ^{1}H-NMR (Avance 600, Bruker, Germany) and the de-
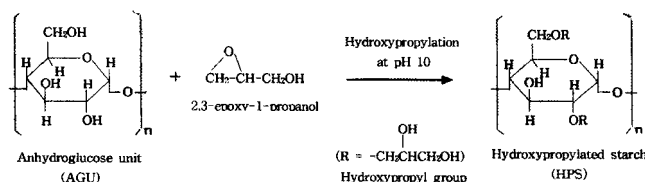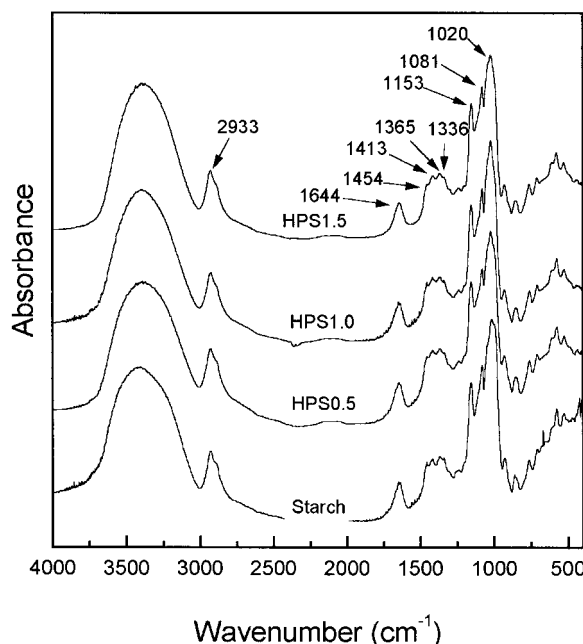

Figure 2 FTIR spectra of starch and hydroxypropylated starch between 400 and 4000 cm^{-1}.

gree of substitution of HPS was determined by integration of each peaks. The characteristics of HPS were 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 distilled water to make a 5% slurry and gelatinized at 95°C for 1 h. Then the homogeneous dispersion was poured
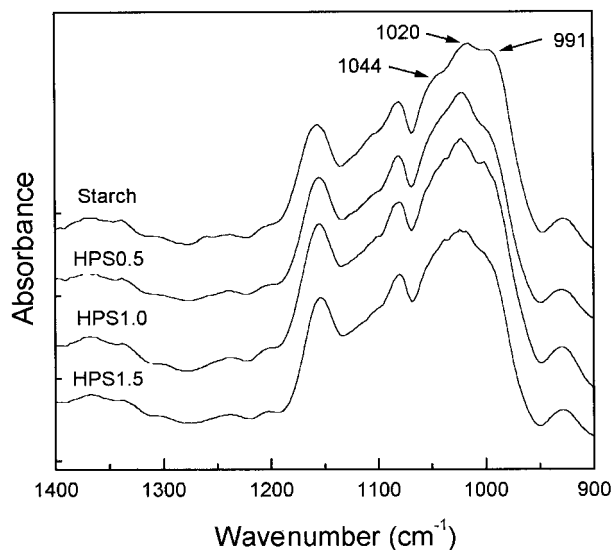

Figure 1 Mechanism of hydroxypropylation of starch with 2,3-epoxy-1-propanol.

Figure 3 FTIR spectra of starch and hydroxypropylated starch between 900 and 1400 cm^{-1}.

TABLE II
Assignment of FTIR Spectra of Native and
Hydroxypropylated Starch[7]

Frequencies (Wavenumber, cm^{-1})	Assignment
3401	OH stretching of water and glucose
2928	CH$_2$ asymmetric and symmetric stretching
1644	OH bending of water
1454	CH$_2$ bending
1413	CH bending
1365	CH bending
1336	C—OH bending
1155	C—O + C—C stretching
1079	CH bending
1021	C—O stretching + C—OH bending

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

FTIR Spectroscopy

FTIR spectroscopy (FT-IR, M series, Midac Co., USA) was used to observe the structural changes of HPS by hydroxypropylation. After HPS was dried in the vacuum oven at 60°C for 12 h, samples were prepared in the form of KBr pellets. FTIR spectra were obtained between 400 and 4000 cm^{-1}, operating with a 4 cm^{-1} resolution.
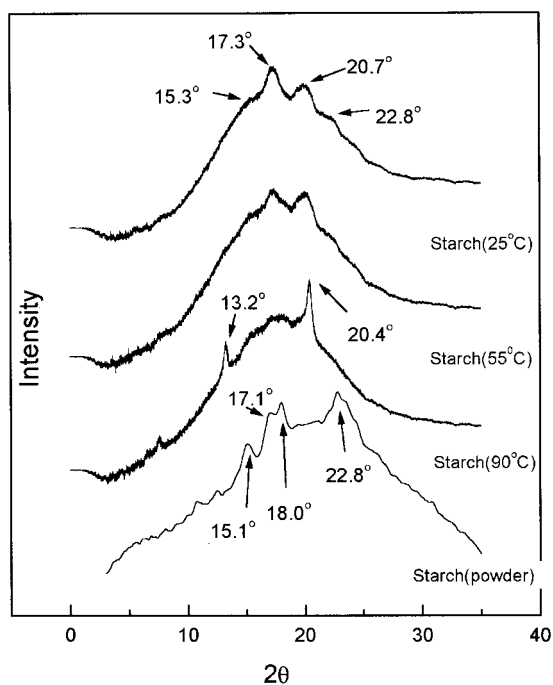
Figure 4 X-ray diffractograms of starch powder and films dried at various temperatures.
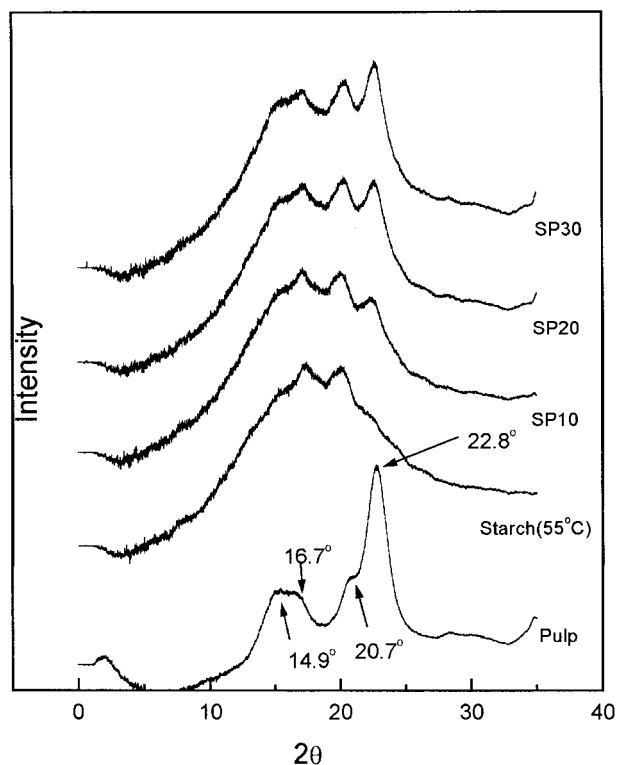
Figure 5 X-ray diffractograms of starch/pulp films at various values of pulp content.

X-ray scattering

X-ray diffractograms of each samples were obtained by DIP 2030 (MAC Science, Japan) using Cu-Kα radiation (λ = 1.5405 Å) between 5° and 40° of 2θ. The conditions were 40 kV, 30 mA, 100 mm of distance, and 120 s of beamtime. The samples were used after sufficiently dried in the vacuum oven at 60°C. The crystallinity was determined by Hermans's method and d spacing of each peak was determined by Bragg's equation:

$$n\lambda = 2d\sin\theta \text{ (Cu-K}\alpha \text{ radiation: } \lambda = 1.5405 \text{ Å)}$$

Water uptake isotherms

Water uptake isotherms were obtained using the thermohygrostat (JS/THC/1500, Johnsam) and the moisture balance (Denver Mark II-HP, USA). At first, the dried weight of each samples was measured using the moisture balance. And then samples were kept in the thermohygrostat for 12 h at 25°C and 40 ~ 90% relative humidity (RH). The water uptake were obtained by the following equation:

Water uptake(%)

$$= \frac{\text{The weight including water (g)} - \text{the dried weight (g)}}{\text{The dried weight (g)}} \times 100$$

TABLE III
Results of X-Ray Diffraction of Starch (or HPS)/Pulp(P)/Glycerol(G) Films

Composition	Crystallinity	2θ (d spacing)			
Pulp	61.84	14.9 (5.94)–16.7 (5.31)		20.7 (4.29)	22.8 (3.90)
Starch (powder)	47.9	15.1 (5.86)	17.1 (5.18)	18.0 (4.92)	22.8 (3.90)
Starch (25°C)	52.57	15.3 (5.79)	17.3 (5.12)	20.1 (4.41)	22.6 (3.93)
Starch (55°C)	49.86	15.3 (5.79)	17.3 (5.12)	20.1 (4.41)	22.6 (3.93)
Starch (90°C)	49.44	13.2 (6.70)	15.3 (5.79)	17.3 (5.12)	20.4 (4.25)
SP10	55.06	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
SP20	58.4	15.3 (5.79)	17.3 (5.12)	20.3 (4.37)	22.6 (3.93)
SP30	63.07	15.3 (5.79)	17.3 (5.12)	20.5 (4.42)	22.6 (3.93)
SP10G10	53.6	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
SP10G15	53.0	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
SP10G20	49.3	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
HPS0.5	48.6	15.3 (5.79)	17.3 (5.12)	20.1 (4.41)	22.6 (3.93)
HPS1.0	48.2	15.3 (5.79)	17.3 (5.12)	20.1 (4.41)	22.6 (3.93)
HPS1.5	49.86	15.3 (5.79)	17.3 (5.12)	20.1 (4.41)	22.6 (3.93)
HPS0.5P10	54.2	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
HPS1.0P10	53.8	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)
HPS1.5P10	52.85	15.3 (5.79)	17.3 (5.12)	20.0 (4.44)	22.3 (3.98)

Thermal behavior

The thermal behaviors of the above samples were investigated by differential scanning calorimetry (DSC) (TA 2910, TA Instruments, USA). An hermetic aluminum pan was used and heating rate was 10°C/min.

RESULTS AND DISCUSSION

Structures of HPS

The hydroxypropylating process of starch with 2,3-epoxy-1-propanol is described in Figure 1. The reaction of hydroxypropylation was ensured with ^{1}H-NMR using DMSO as the solvent and the degrees of the substitution of each HPS obtained by the integration of peaks are shown in Table I.
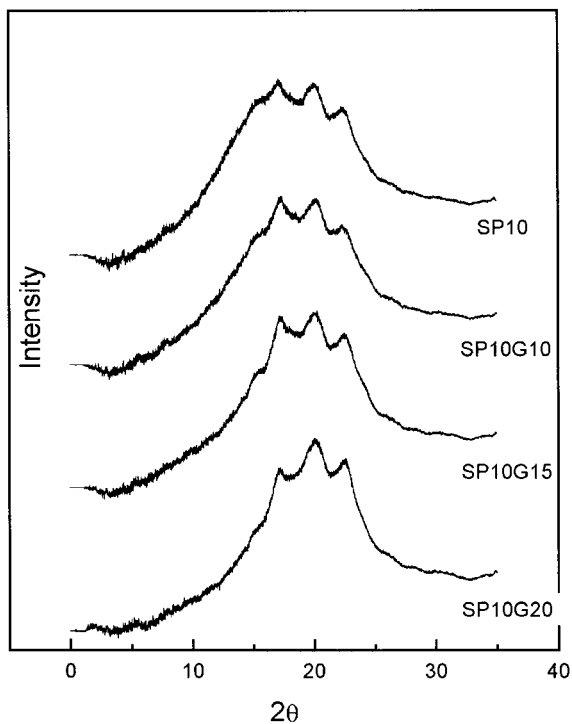

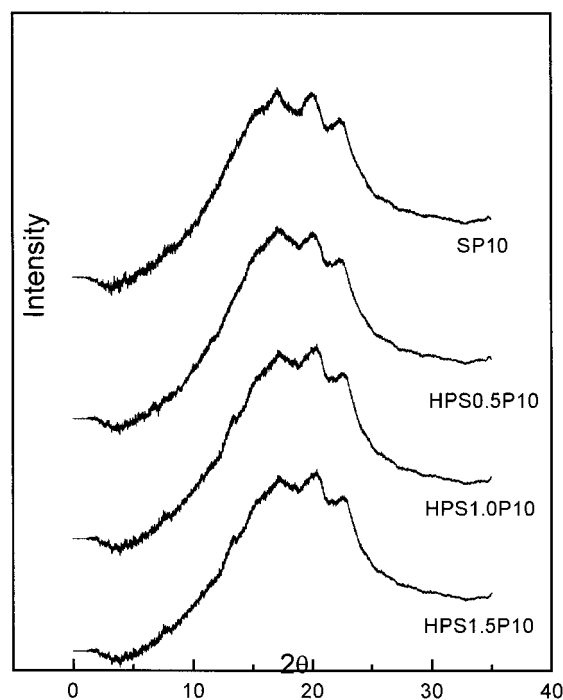**Figure 6** X-ray diffractograms of starch/pulp/glycerol films at various values of glycerol content.

Figure 7 X-ray diffractograms of HPS/pulp films at various degrees of substitution.
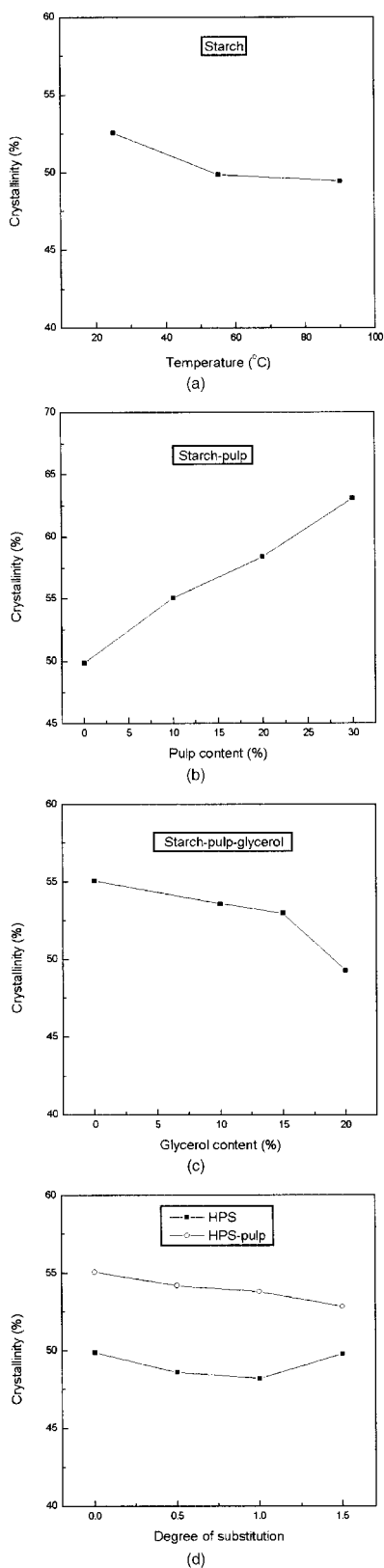
Figure 8 Crystallinity of starch/pulp/glycerol films as a function of (a) drying temperature, (b) pulp content, (c) glycerol content, and (d) degree of substitution.
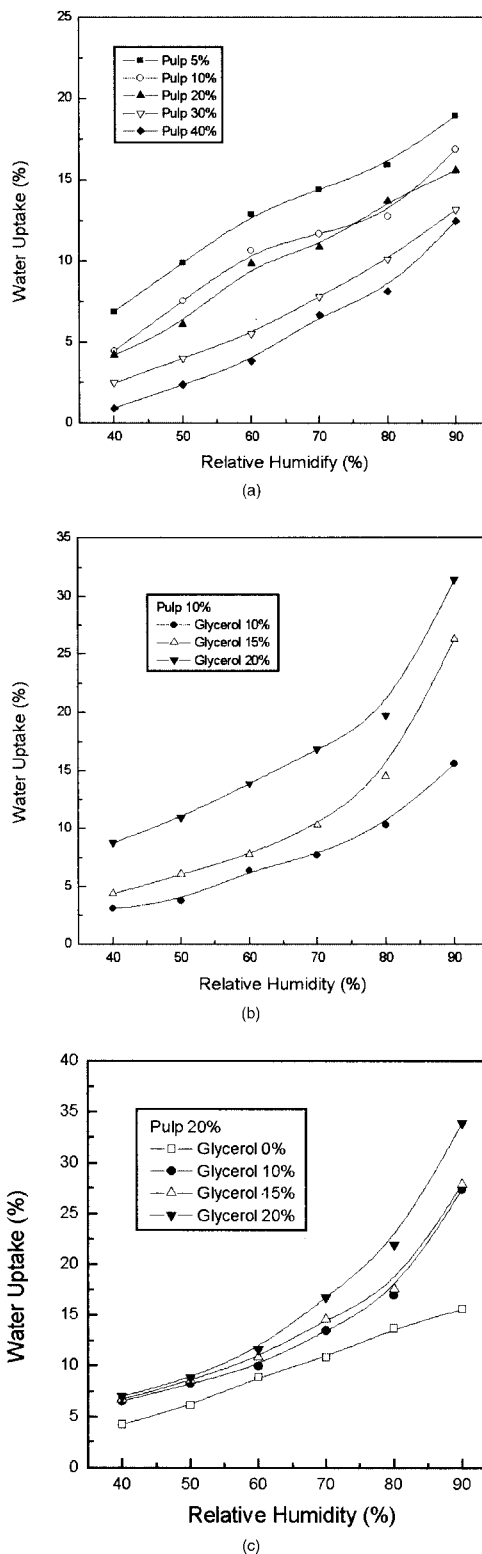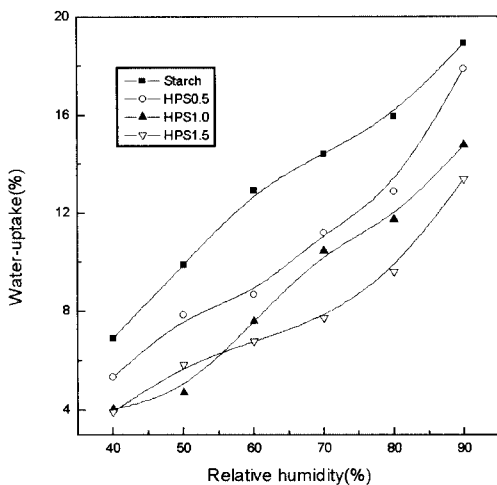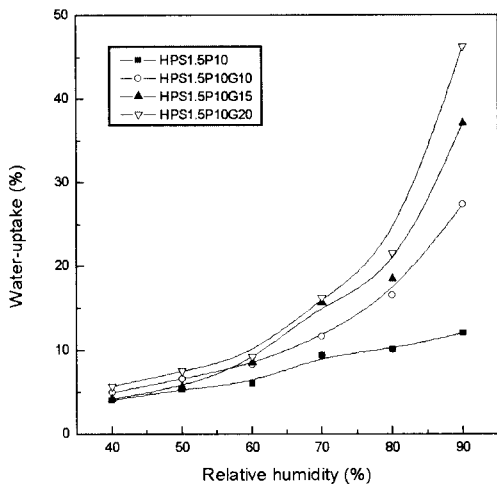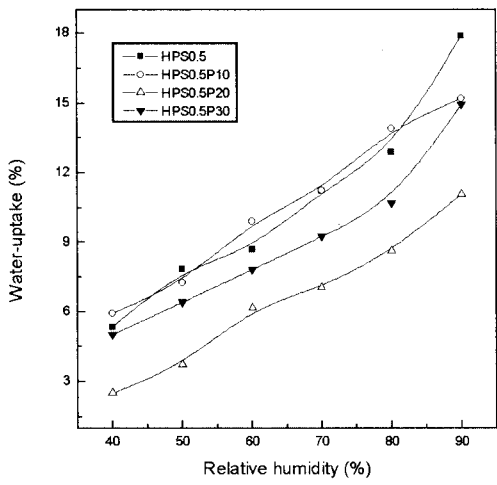

Figure 9 Water-uptake isotherms of starch/pulp/glycerol films as a function of relative humidity at various conditions: (a) pulp content (glycerol 0%), (b) glycerol content (pulp 0%), and (c) glycerol content (pulp 20%).

Figure 2 shows the FTIR spectra of starch and HPS between 400 and 4000 cm^{-1}, but distinct differences between them were not found. This is because the functional groups newly formed by the hydroxypropylation of starch have a —C—O—C— ether linkage, as shown in Figure 1, and the anhydroglucose unit of a native starch is linked by the glycosidic linkage and contains hemiacetal group in itself. But it is confirmed in Figure 3 that the intensity of peaks in 1044 and 991 cm^{-1} decreased with DS of HPS. Smits et al. have reported that the peaks in 1047 and 1022 cm^{-1} are related to the crystalline and amorphous region, respectively, and the peak in 995 cm^{-1} is sensitive to the moisture.[23] As DS increased, the hydrophilicity of HPS decreased because the hydrophobic groups were introduced by the hydroxypropylation. So the intensity of peaks in 991 cm^{-1} decreased. And the intensity of peaks in 1044 cm^{-1} decreased because the side chains formed within the anhydroglucose units inhibited the crystallization by hydrogen bonding. The assignments of FTIR spectra of starch and hydroxypropylated starch are shown in Table II.

X-ray scattering

Figure 4. shows the X-ray diffractograms of starch powder and films dried at 25, 55, and 90°C, respectively, after the gelatinization. It can be seen that the native corn starch powder has the typical A-type crystalline structure, which has major peaks at 2θ = 15.1°, 17.1°, 18.0°, and 22.8°, but films made of the gelatinized starch have a different structure from

Figure 10 Water-uptake isotherms of HPS/pulp/glycerol films as a function of relative humidity at various conditions: (a) degree of substitution (pulp and glycerol 0%), (b) glycerol content (pulp 10%), and (c) pulp content (glycerol 0%).
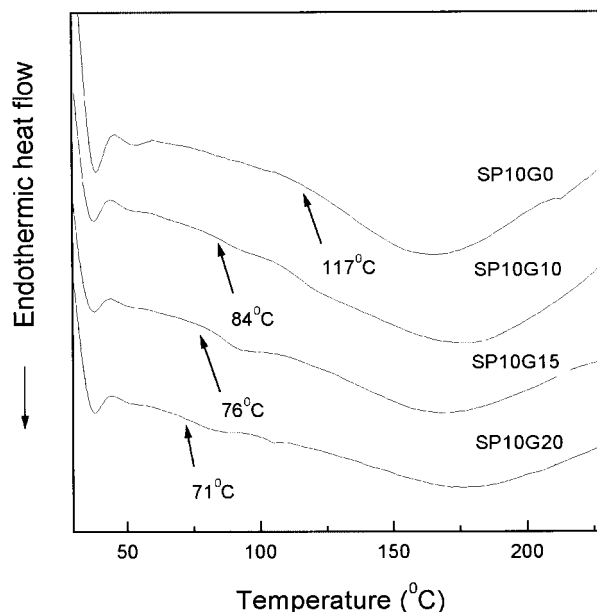

Figure 11 DSC thermograms of starch/pulp/glycerol films as a function of glycerol content.
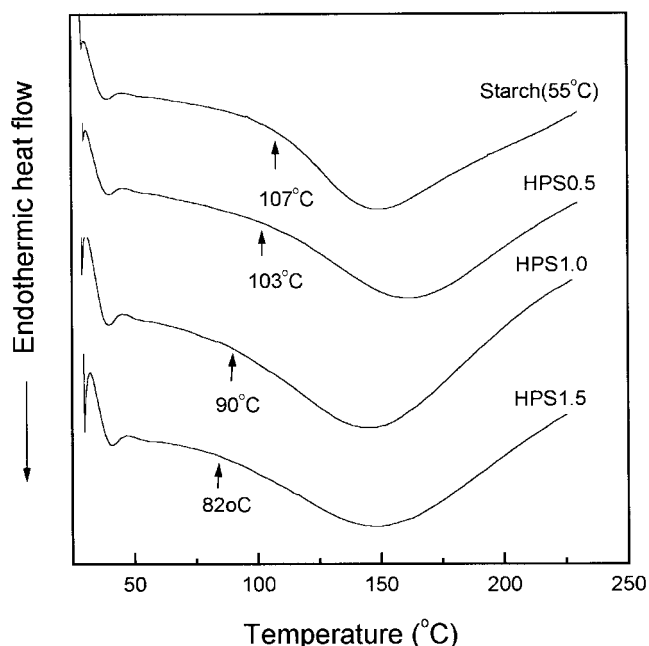
Figure 12 DSC thermograms of HPS/pulp/glycerol films as a function of degree of substitution.

the corn starch powder, which has major peaks at 2θ = 15.3°, 17.3°, 20.1°, and 22.6°. Generally, the starch begins to swell in the amorphous region by absorbing water and during this swelling process the amylose is extracted. This extracted amylose functions as the matrix in the drying process for the formation of film. And the water is absorbed into the crystalline region and then the granular structure of starch is finally destroyed. It seems that the amylose and amylopectin within the starch slurry are crystallized to form the different crystal structure. Starch films have the similar peaks in 2θ values as a function of the drying temperature. But as the drying temperature increased, the intensity of the peaks at 2θ = 15.3 and 17.3° decreased, and the crystallinity of the films also decreased [Table III, Fig. 8(a)].

In Figure 5, the X-ray diffractograms of starch/pulp films are shown at various pulp contents. Pulp shows one broad peak value extending from 14.9 to 16.7°2θ values and two sharp peaks at 20.7° and 22.8°. As seen in Figure 5, the intensities of peaks at 14.9, 20.7, and 22.8° increased with the pulp content and the crystallinity also increased with the pulp content [Table III, Figure 8(b)].

In Figure 6, the X-ray diffractograms of starch/pulp/glycerol films are shown at various glycerol contents. No distinct differences between films were found in 2θ values, but the intensity of peaks at 15.3° and 17.3° decreased with the glycerol content and the crystallinity also decreased with glycerol content [Table III, Fig. 8(c)]. It has been known that

glycerol has the ability to form a complex with amylopectin.[24] So it seems that the formation of the double-helix conformation of amylopectin is inhibited by the complex formation of amylopectin with glycerol.

In Figure 7, the X-ray diffractograms of starch (or HPS)/pulp films are shown at various DS values. There is no distinct difference in the intensity of peaks and in the crystallinity between films made of HPS of various DS values, but films containing pulp showed the peaks attributed to pulp [Table III, Fig. 8(d)].

Water-uptake isotherms

In Figure 9, the water-uptake isotherms of starch/pulp/glycerol films as a function of the RH are shown. The water uptake of films increased with RH. On the other hand, the water uptake of films as a function of pulp content [Fig. 9(a)] decreased with pulp content. Tsiapouris et al. investigated the water absorption behavior of porous starch materials containing the cellulosic fibril and reported that the water uptake of starch materials containing cellulose fibril was less than those without cellulose fibril.[22] At first, the water is adsorbed onto the surface of film, and then the water penetrates the amorphous region of film. Then, the water inhibits the hydrogen bonding to weaken the bonding force in the crystalline region and to reduce the crystallinity of film. On the other hand, the pulp used as the reinforcement exists in the state of a fiber, and crystallinity of pulp (61.84%) is higher than that of starch film (49.85%). In addition, since the pulp was embedded in the starch film matrix, it seems that the water uptake decreases with pulp content.

In (b) and (c) of Figure 9, the water-uptake isotherms of starch/pulp/glycerol films containing 10 and 20% pulp content, respectively, are shown. In both cases, the water uptake increases with glycerol content. Dufresne et al. investigated the effect of glycerol used as a plasticizer on the water uptake of starch films reinforced with cellulose microfibril, and reported that the cellulose reduced the sensitivity of films on the moisture but the glycerol increased the sensitivity.[20] In addtion, it has been known that glycerol has a higher affinity to water than starch. And because the crystallinity of films decreased with glycerol content, the water uptake of films increased with glycerol content. On the other hand, films [Fig. 9(b)] containing 10% pulp have higher water uptake than films [Figure 9(c)] containing 20% pulp.

In Figure 10, the water uptake of HPS/pulp/glycerol films increased with RH, which is similar to Figure 9. In Figure 10(a), the water uptake decreased with

DS of films. This may be because the hydrophobicity of films is increased due to the introduction of hydrophobic groups by the hydroxypropylation. And the water-uptake isotherms at various glycerol content (b), and pulp content (c) show trends similar to ones shown in Figure 9.

Thermal behaviors

Figure 11 and Figure 12 show the thermal behaviors of starch (or HPS)/pulp/glycerol films by DSC. In Figure 11, the T_g of films decreased and the temperature range related to T_m broadened with glycerol content used as a plsticizer. It is generally known that the crystalline polymer has a sharp T_m peak but the amorphous polymer has one broad peak between T_g and T_m. As shown in Table III and Figure 8, these results are attributed to the fact that crystallinity of films decreased with glycerol content. In Figure 12, the T_g of films decreased and the temperature range related to T_m broadened with DS of films, and these results are also attributed to the decrease of the crystallinity with DS.

CONCLUSIONS

Starch (or HPS) films made of A-type native corn starch powder showed different X-ray diffraction patterns reveal that the crystallinity of films increased with pulp content, but decreased with glycerol content and degree of substitution by hydroxypropylation. The water uptake of films as a function of the relative humidity decreased with pulp content and degree of substitution by hydroxypropylation, but increased with glycerol content. DSC thermograms showed that with the increase of glycerol content, the glass transition temperature of films decreased and the endothermic peaks at the melting temperature broadened due to the plasticizing effect, and that the crystallinity decreased due to the hydroxypropylation.

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