Studies on the Physical Properties of Modified Starch-Filled HDPE Film

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SYNOPSIS

To improve the physical properties of starch-filled polyolefin, starch was modified into more hydrophobic material by the introduction of cholesterol unit, and the different starch-compositioned high-density polyethylene (HDPE) films were prepared with addition of either native starch or modified starch to compare their physical properties. The addition of either native starch or modified starch resulted in decreased crystallinities in all the different composite films containing starch. Interestingly, HDPE-blown films containing more than 10% native starch (HDPE/ST) showed a steeper decrease in crystallinity than correspondent HDPE containing the modified starch (HDPE/MS). Improvement of the dispersion and adhesion in HDPE/MS and HDPE/ST were also observed; but at high starch content, the HDPE/MS films showed higher tensile strength and elongation than the HDPE/ST. The degradation of HDPE/MS films in active sludge condition was much faster than that of the HDPE/ST films, although the degradation rate of HDPE/MS films in α-amylase condition were slower than the one of HDPE/ST films.

INTRODUCTION

Degradable plastics, especially polyolefins, which are widely used in disposable packing materials, have been of interest for many years due to environmental pollution. In response to this concern, the development of new biodegradable polymeric materials has focused mainly on the following four areas since the beginning of 1970s:

1. synthesis of new biodegradable polymers such as PHB (poly-β-hydroxybutyrate), PHB/PHV (polyhydroxyvalarate), and polysaccharide, like pullulan[1,2];
2. modification of natural polymers[3];
3. modification of synthetic polymers such as PL (polylactide), PG (polyglycolide), and PCL (polycaprolactone)[4]; and
4. biodegradable polymer composites.[5]

However, most of these materials, especially bulk plastic such as packing materials, have not been developed commercially for years because of failure to be cost competitive with existing resins and problems in fabrication by injection molding or melt extrusion into films.[6] Since Griffin et al.[7,8] first reported that the degradation rate of PE/ST composites films containing 6–10% of starch content was accelerated by adding an autooxidant such as unsaturated acid to the system, the use of natural fillers such as starch in a polymeric system has been studied extensively for a long time as an alternative method to solve the problem. Otey et al.[9,10] prepared composite films incorporating starch in the matrix of PE and found that the content of starch in starch-based films can be increased without affecting the physical properties of films by adding urea and polyol to the starch-poly(ethylene-*co*-acrylic acid) (EAA) system. Swanson et al.[11] also found that tensile strength and elongation of EAA/LDPE composites films were improved by using the modified starch and introducing hydroxypropyl or acetyl group in starch. In addition, Nikolov et al.[12] reported that LDPE/MS composite films improved the tensile strength and

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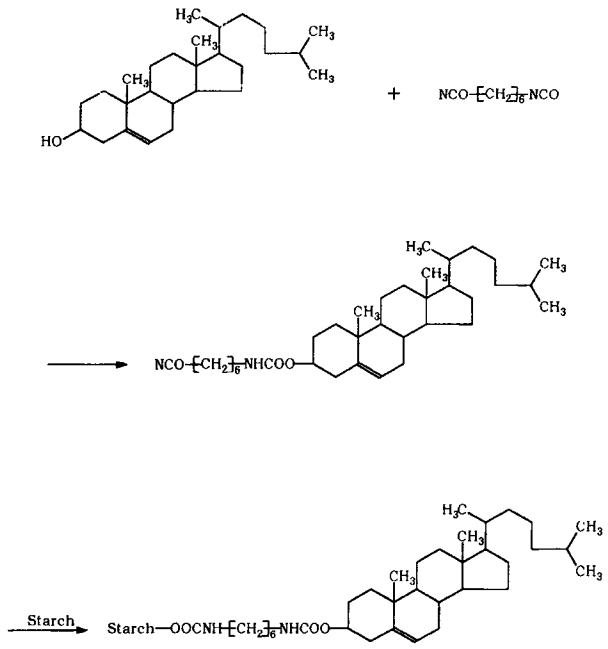


Scheme 1.

elongation in comparison with the LDPE/ST composite films, but the enzyme degradation rate of the modified starch-filled cast film was lower than the rate of the starch-filled films.

As a part of the program developing the biodegradable starch-filled HDPE films, we observed recently that PE/ST composite film containing more than 10% starch showed a sharp decline of physical property.[13] From this result, we modified starch by introducing cholesterol moiety as a hydrophobic biodegradable component for the purpose of improving the compatibility of the PE/ST composite. We prepared the modified starch-filled HDPE films and found that these systems could increase the content of starch without affecting the physical properties of the films as well as rate of composite's biodegradation. Here, we report the syntheses, the physical properties, and the biodegradabilities of the modified starch-filled HDPE films.

EXPERIMENTAL

Materials

Extra-pure grade corn starch and cholesterol were purchased from Sigma (St. Louis, MO) and Shinyo (Osaka, Japan), respectively. Both of them and the modified starch were dried in a vacuum oven (20 mmHg) at 60°C for 2 days and were stored in desiccator before use. Reagent-grade hexamethylene diisocyanate (HMDI), used as linkage material of starch and cholesterol, was purchased from Aldrich (Milwaukee, WI). HDPE (TR144) was provided by Daelim Industrial Co., Korea, and was used as base resin. Industrial-grade butyl-hydrated toluene (BHT), used as a heat stabilizer in this study, was provided by Miwon Commercial Co., Korea. α-Amylase from Bacillus was purchased from Sigma (1750 unit/mg). Igepal CO-720, used as surfactant, was purchased from Aldrich. Water was sterilizing distilled water. All of the solvents were distilled once before use. Other organic and inorganic chemicals were extra-pure grade and were used without further purification.

Synthesis of Modified Starch[14]

The mixture of cholesterol (20 g, 51.8 mmol), hexamethylenediamine (86 mL, 0.53 mmol), and 10 mL of pyridine in 750 mL of dry hexane was refluxed for 18 h. After completion of the reaction monitored by thin-layer chromatography (TLC), the solvent and unreacted hexamethylenediamine were removed in vacuum. The petroleum ether (700 mL) was added to the residue and stored at −20°C overnight. The resulting precipitate was filtered, dried, and identified as cholesteryl *N*-6-isocyanatohexyl carbamate (CIC). For the synthesis of modified starch, CIC (7.36 g, 13.3 mmol) was mixed with starch (17.2 g, 0.1 mol equiv as the glucose unit) in 1 L of Dimethylsulfoxide (DMSO), and the resulting mixture was stirred for 20 h at 40°C. After complete disappearance of CIC by checking TLC, the unreacted reactant was successively decanted with ethylacetate, and the remaining product was dried in vacuum. Scheme 1 illustrates the chemical synthesis, measured by infrared (IR) and nuclear magnetic resonance (NMR) methods.

Cholesteryl *N*-6-isocyanatohexyl carbamate (CIC).

IR (KBr, cm^{-1}):	3350 (N—H), 2980 (C—H), 2240 (—NCO); 1730 (C=O), 1540 (—NH bending), 1470 (—CH_2 bending), 1380 (—CH_2 bending), 1230 (C—O)
NMR ($CDCl_3$, ppm):	5.4 (—C=CH, 1H), 4.65–4.4 (—NH, 1H), 3.3 (OCN—CH_2—, 2H) 3.15 (CH_2—NH—CO—, 2H) 1.7–1.55 (—CH_2—, 8H) 2.4–0.69 (Cholesterol, 42H)

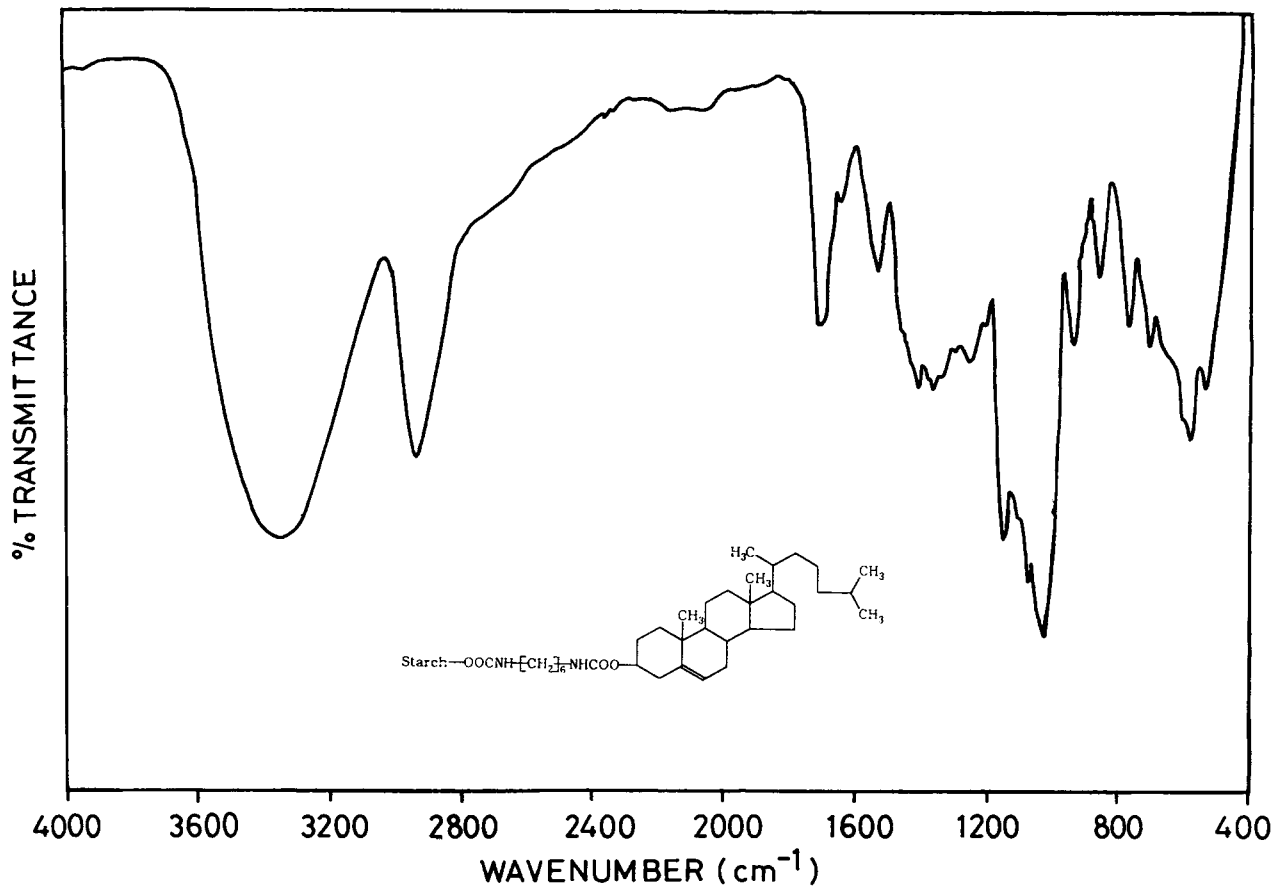


Figure 1 IR spectrum of modified starch in KBr.

Starch modified with CIC.

IR (KBr, cm^{-1}):	3700–3150 (O—H), 2980 (C—H), 1760–1680 (C=O, —OH bending), 1160–1000 (C—O—C)
NMR (DMSO-d_6, ppm):	5.6–5.4 (1'H, 4'H, 5'H Starch, 3H), 5.2–5.0 (2'H, 3'H Starch, 2H), 4.7–4.5 (6'H Starch, 2H), 1.6–0.6 (CIC, 46H) (Scheme 1)

Film Preparation

The different contents of starches (ST and MS) were mixed with HDPE containing 1000 ppm heat stabilizer (BHT) by using a Brabender two-roll mill at 160°C for 15 min; their final starch concentrations were adjusted at 5, 10, 15, and 20% (w/w). The mixed strands were pelletized by using a granulizer to provide a product that could be fed through a blown film extruder. The pelletizer batches were extruded into blown film of 50 μm in average thickness through the Brabender film blowing die assembly (Model No. 628288) which contained a Brabender plastic-corder (Type PLE-331), an extruder (type 19/25 D), and a film-blowing unit (Model No. 840805). The operating screw speed was 50 rpm, and the temperatures of four heating zones of the extruder were set at 170, 175, 180, and 185°C. The samples of all process were stored in a desiccator until needed for processing.

Compatibility and Mechanical Properties

DSC Measurement

Differential scanning calorimeter (DSC) measurements were performed with a DuPont 9900 instrument in order to investigate the variation in the crystallinity of MS-filled blown films in comparison with ST-filled blown films. The instrument was calibrated in a temperature range of 25–170°C with an indium standard sample. All of the samples were placed in an aluminum DSC pan and were run on

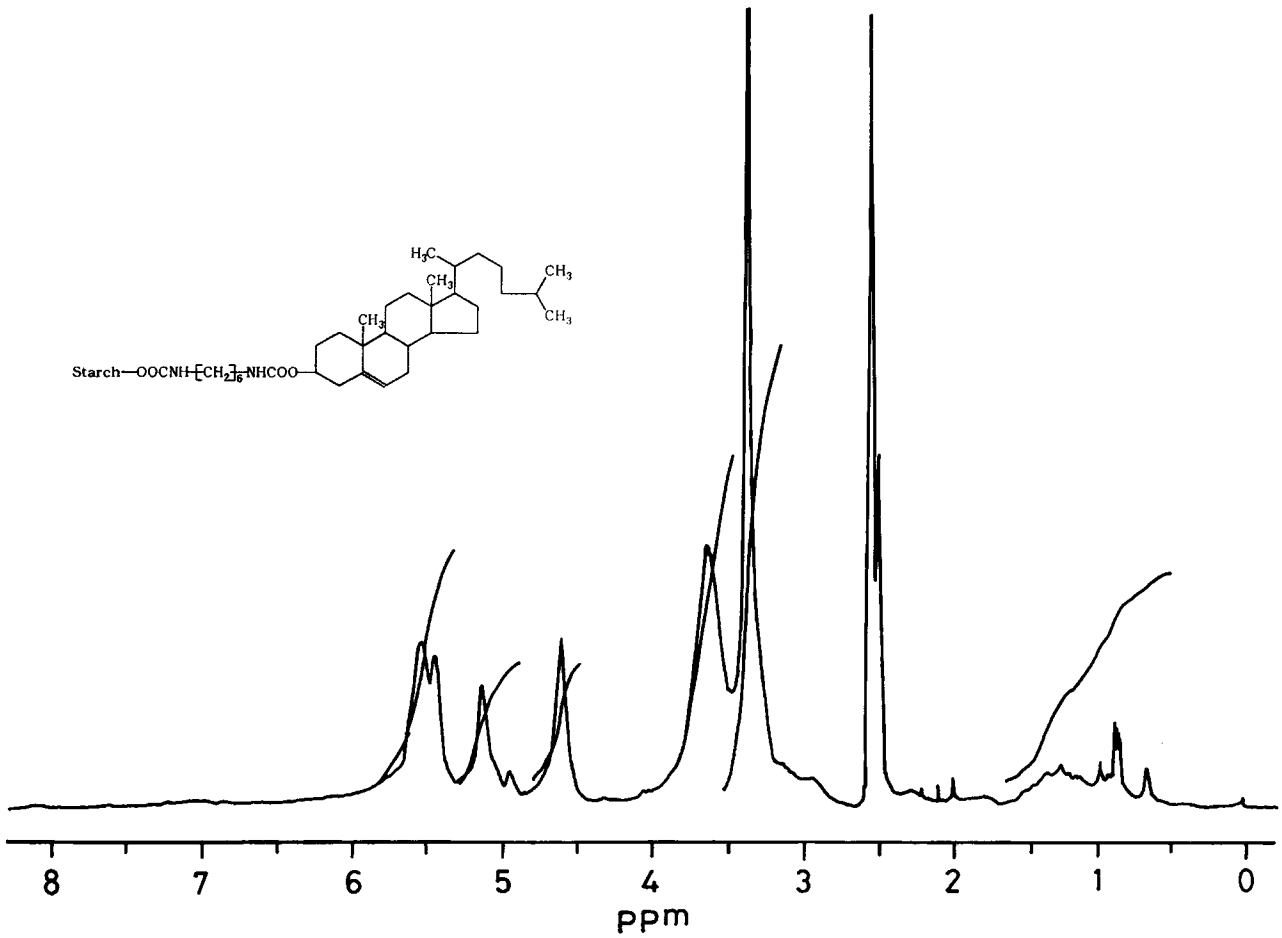


Figure 2 ^1H NMR spectrum of modified starch in $CDCl_3$.

the DSC under free flow of nitrogen between 30 and 160°C while the heating rate was 10°C/min.

Morphological Property

Scanning electron microscopy (SEM) analysis was performed with Amray 1200C instrument and observed the fractured surface of films. Blown films were fractured immediately after rapid cooling in liquid nitrogen and were sputter-coated with gold to be visualized under a scanning electron microscope.

Mechanical Properties

Tensile strength and elongation were tested by using the ASTM D882-83 method with an Instron universal testing machine (Model 4502). The samples were stored at 20°C and 60% relative humidity for 2 days before testing. The test speed was set at 500 mm/min. The ten samples per treatment were measured and evaluated on an arithmetical average.

Measurement of Degradation

Degradation by α-Amylase

Enzyme solution was prepared as concentrate containing 100 units per 1 mL of α-amylase in 8.3 mM phosphate buffer in pH 7.2 condition. To this solution, 3.0 mM sodium azide was added for inhibiting growth of fungi. The 2 × 2 cm^2 sized starch-based

Table I The Degree of Substitution of Modified Starch

Product	Reaction Rate (Starch wt/CIC wt)	Characteristic Peak Area of Starch	Characteristic Peak Area of CIC	DS
MS 15	85/15	118.3	16.9	6.8
MS 30	70/30	132.7	19.0	17.0

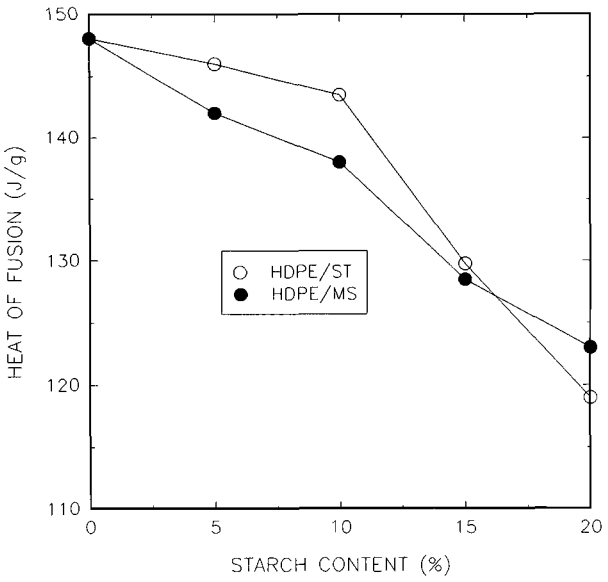


Figure 3 Heats of fusion of HDPE/ST and HDPE/MS films plotted against starch contents.

blown films were sterilized with 2% solution of sodium azide, as well as 70% (v/v) ethanol solution, dried in vacuum, and then weighed. About 0.8 g of each sample was immersed in 45 mL enzyme solution then placed in a sterile centrifugal tube of 50 mL volume. The tubes were incubated at 30°C and agitated at 150 rpm. The 1.0 mL of reaction mixture was removed at an appropriate time interval to analyze the total carbohydrate content. The biodegradability of the samples was evaluated by measurement of glucose content, which was produced from hydrolysis of starch by α-amylase. The phenol-sulfuric acid method was used for quantitative analysis of glucose content.

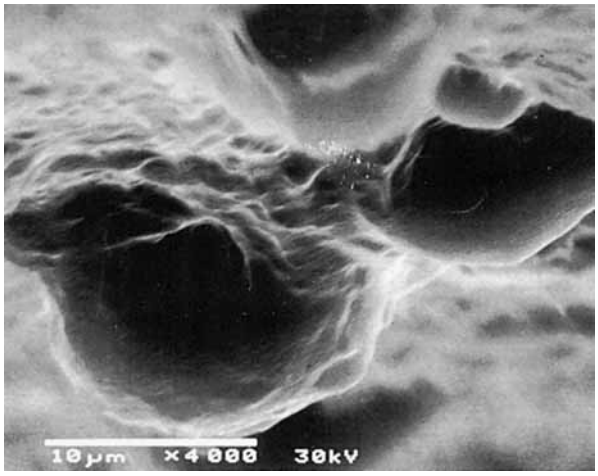
Biodegradation by Activated Sludge

Activated sludge was prepared as follows. The sludge solution, which was collected from Kwachun Sewage Treatment Plant, Kwachun, Korea, was added with nutrient salts and then incubated. After incubation, the mixed liquor volatile suspended solid (MLVSS)[15] was measured according to standard methods for examination of water and wastewater. The value of MLVSS was 4.6 g/L. The strip of the films, which was cut into the size of 2 × 6 cm, was immersed into the mixed solution of 4 L of the nutrient salt solution and 1 L of the activated sludge; then the resulting reaction mixture was incubated at room temperature at 150 rpm for 18 days. During the incubation, Igepal CO-720 was frequently added to the sludge solution as the surfactant in order to improve wetting of the samples in the wastewater, which eventually leads to the acceleration of biodegradation.[16,17] At an appropriate intervals, the degraded films were removed, sterilized, washed, and dried. Their degradability as analyzed by Fourier transform–infrared (FT–IR) equipment (Nicolet DX VS.25)[18] and calculated based on the contents of the starch removal out of the films.

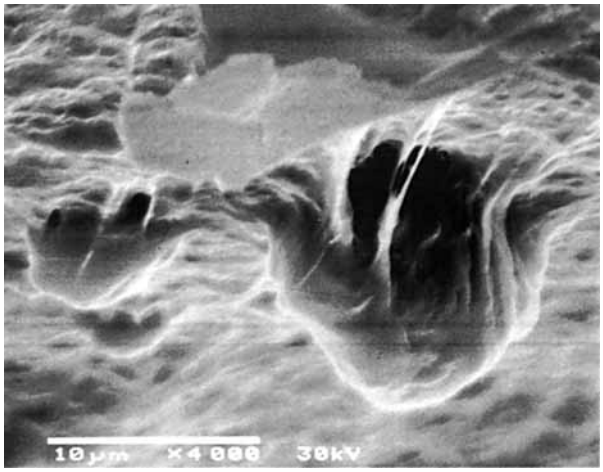
RESULTS AND DISCUSSION

Synthesis of the Modified Starch

The modified starch was synthesized as shown in Scheme 1. The cholesterol was reacted first with



(a) ST(15%)/HDPE



(b) MS(15%)/HDPE

Figure 4 SEM micrographs of fractured HDPE/ST and HDPE/MS blends: (a) ST (15%)/HDPE; (b) MS (15%)/HDPE.

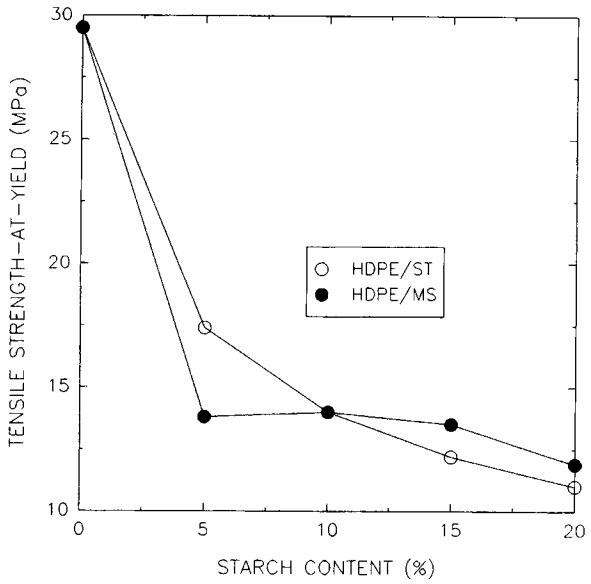


Figure 5 Tensile strength of HDPE/ST and HDPE/MS films plotted against starch contents.

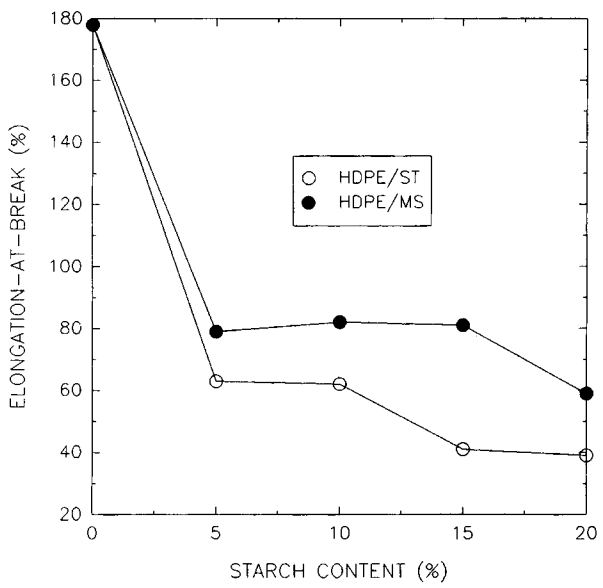


Figure 6 Elongation of HDPE/ST and HDPE/MS films plotted against starch contents.

hexamethylenediisocyanate in refluxing dry hexane condition to generate cholesteryl *N*-6-isocyanatohexyl carbamate (CIC) as a white powder that was soluble in most of organic solvents (ethylacetate, acetone, methylene chloride). The CIC was then reacted with a different ratio of starch to give the desired modified starches in good yield as a white powder that was soluble in DMSO. The structural identification of the synthesized modified starches was performed by FT-IR and ^{1}H-NMR methods (Figs. 1 and 2), and the results were satisfactory when taking into account their expected structures.

In addition, their degree of substitution (DS) by the cholesteryl unit was calculated by the following equation from the ^{1}H-NMR spectrum and revealed to be 6.8 and 17.0 for the two samples shown in Table I.

$$\mathrm{DS} = \frac{\text{Characteristic peak area of CIC} \times n^b \text{ of protons in starch (7)}}{\text{Characteristic peak area of starch} \times n^b \text{ of protons in CIC (46)}} \times 100$$

Unless otherwise stated, in this study, we used the modified starch whose degree of substitution by cholesteryl unit was fixed at a value of 17.0.

Compatibility and Physical Property

To evaluate the effects of the modified starch on the blown films' properties in comparison with the one of the natural starch, the two types of blown films of 50 μm in average thickness with different starch contents ranging from 5 to 20% were prepared. As shown in Figure 3, the heat of fusion of HDPE was 148 J/g, which is not consistent with the literature value.[19] This discrepancy might be attributed to the thermal history during its processing. The heat of fusion for the two types of samples were normalized with respect to HDPE concentrations in the compound. These values generally decreased with the increase of the starch content, although decreasing patterns were different at each cases. For example, HDPE/ST blown films showed a slow decline up to

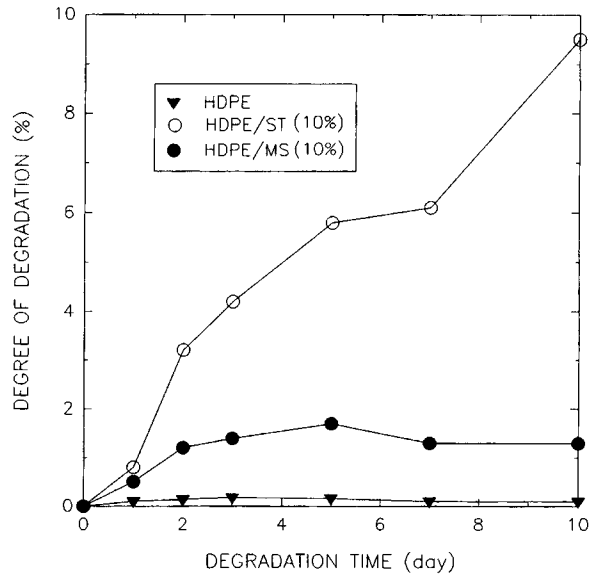


Figure 7 Biodegradation of HDPE/ST (10%), HDPE/MS (10%), and HDPE in α-amylase solution.

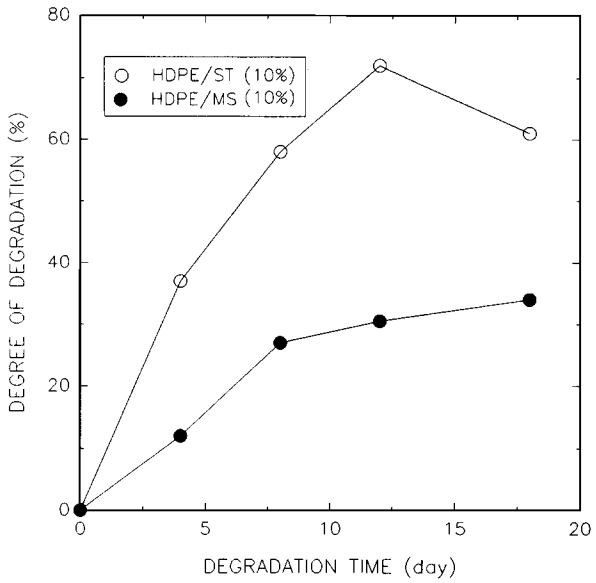


Figure 8 Biodegradation of HDPE/ST (10%) and HDPE/MS (10%) in activated sludge.

10% starch level and then a sharp decline at above 10% starch content, while HDPE/MS blown films showed the gradual decline with the increasing modified starch content. These results indicate that HDPE/MS blown films were able to prevent more decline of mechanical properties from the addition of degradable material than the HDPE/ST because of the slower decline of crystallinity at above 10% MS content. This indication was very consistent with the data of mechanical properties of HDPE/MS blown films.

Blend Morphology

Two types of films with 15% starch content were selected for the observation of the fractured surface, and their morphology was compared by using SEM (Fig. 4). In the starch-filled system, starch was dispersed in heterogeneous granular particles without interfacial adhesion to the HDPE matrix because of the hydrophobic nature of starch, which resulted in a smooth surface at the fractured region. However, the modified starch was dispersed in homogeneous minute particles in the HDPE matrix, which resulted in an adhered surface at the fractured region. These results indicate that cholesterol moiety of MS improves the compatibility with the HDPE matrix.

Mechanical Properties

The same films that were used for DSC measurement were used for this test. As shown in Figures 5 and 6, the mechanical properties of the two types of blown films revealed the sharp decline with addition of 5% starch, although the tensile strength of HDPE/MS films showed less decrease than that of HDPE/ST with an increase in the starch content. The HDPE/MS films generally showed higher tensile strength than corresponding HDPE/ST at high starch content. In an elongation test, HDPE/MS films showed higher property than HDPE/ST at all starch contents. It is of interest that the elongation of HDPE/ST film showed the considerable decline at 10–15% starch contents, while that of the HDPE/MS was preserved. These differences in mechanical properties are due mainly to adhesion of starch with the HDPE matrix. In other words, HDPE/MS films overcame the decrease of mechanical property due to interfacial adhesion with the HDPE matrix and homogeneous fine dispersion of the particles.

Biodegradability

Biodegradation by Enzyme

The following calibration equation was obtained for the quantitative analysis of carbohydrate by using the least squares method, and glucose was used to obtain this equation as standard material.

$$\text{Concentration (ppm)} = 110.91 \times A_{490\,\text{nm}} + 1.66$$

The degradability was tested with the two types of blown films containing 10% starch or modified starch, respectively, and represented the loss of starch leached from the hydrolysis by α-amylase. As seen in Figure 7, HDPE/ST and HDPE/MS films were degraded up to 10 and 2%, respectively, at a 10-day degradation period. Interestingly, HDPE/MS films were no longer degraded after 5 days. These results show that α-amylase, which selectively hydrolyzes the linkages of starch, cannot degrade the cholesterol unit because of the hinderance of bulky moiety and prevention of the attack of α-amylase. In addition, it is also suggested that the hydrolyzed starch was not possibly leached into enzyme solution because of its interfacial adhesion with HDPE matrix.

Biodegradation by Activated Sludge

Since α-amylase selectively hydrolyzes the linkages of starch, α-amylase cannot degrade the cholesterol unit. But the starch-containing mixtures would accelerate the biodegradation when placed in natural environments, such as soil microbes.[20] Accordingly, the activated sludge was used to accelerate the biodegradation of the samples within the test period

because the microbes in the activated sludge could subsist in the soil.

The starch and polyethylene were measured at 870–810 and 2087–1997 cm^{-1} in the IR spectrum region. The absorbance values of starch were rationed against the polyethylene internal reference band, and they normalized the difference in plaque thickness.

The following calibration equation was obtained from the absorbance values of the two types of blown films after biodegradation with 5, 10, and 15% as initial starch contents.

$$\text{Content (\%)} = 5.26 \times \frac{\text{absorbance value of ST}}{\text{absorbance value of HDPE}}$$

$$\text{Content (\%)} = 8.33 \times \frac{\text{absorbance value of MS}}{\text{absorbance value of HDPE}}$$

The tested films were the films that were used in the enzymatic study. As shown in Figure 8, HDPE/St and HDPE/MS were degraded up to 70 and 33%, respectively, at 18 days of degradation and were degraded well in all cases. Specifically, HDPE/MS blown films showed a remarkable improvement of degradability, which was quite different from the enzymatic method results. These results suggested that the microbes assimilate easily with the cholesterol moiety that subsists in the natural environment.

CONCLUSION

The modified starch was used to improve the mechanical property of starch-filled polyethylene films by introducing cholesterol moiety as a hydrophobic biomaterial. The MS-filled blown films showed higher dispersion and adhesion than the ST-filled films. Accordingly, its tensile strength and elongation were improved in almost all cases. Although there were many differences with the enzymatic hydrolysis tests of the two types of film, HDPE/MS films showed the improvement of biodegradability in activated sludge method due to easy attacking of the microbes to the cholesterol moiety. From the results presented, the MS-filled polyethylene films concept could increase the content of the biodegradable component without adversely affecting the physical properties of the films.

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