Effect of Propylation of Starch with Different Degrees of Substitution on the Properties and Characteristics of Starch-Low Density Polyethylene Blend Films

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ABSTRACT: Corn starch was modified by propylation and degree of substitution (DS) of four starch modifications were 0.61, 1.56, 2.27, and 2.51. Different films were prepared by blending native and propylated starch with low-density polyethylene (LDPE). The mechanical properties, thermal properties, water absorption capacity, and biodegradability of the blend films varied with the quantity of starch as well as DS. Tensile strength, elongation, and melt flow index of propylated starch blend films were higher compared to the corresponding native starch blend film. These properties improved with increase in DS from 1.56 to 2.51. Propylated starch blend films were found thermally stable than native starch blend films. There was a decrease in water absorption capacity for the films containing propylated starch at high DS. Enzymatic and soil burial degradation results showed that biodegradability of starch-LDPE films increased with the increase in the starch concentration but it decreased with increase in the DS. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2197–2208, 2011

Key words: propylated starch; starch-LDPE blend films; mechanical properties; water absorption capacity

INTRODUCTION

The environmental impact of synthetic plastic wastes is of global concern as these are inert to the immediate attack of microorganisms.[1] These persistent polymers are a significant source of environmental pollution and harm wild life when these are dispersed in nature.[2] Therefore, the use of partially or fully biodegradable polymers provides a promising solution to this problem and has been an area of work for many researchers.[3–5]

Starch due to its abundance, biodegradability, and low cost has been considered as a partial substituent for synthetic polymers in packaging, agricultural mulch, and other low-cost applications.[6–8] However strong hydrophilicity of starch results in poor starch-polymer interfacial interaction in starch filled blends with a resultant loss of mechanical properties.[9] The researchers have adopted different ways of modifying starch in starch based films to resolve the problem. Various modifications such as plasticized starch in low-density polyethylene (LDPE),[10] hydroxypropylated starch in polyethylene,[11] crosslinked starch in LDPE,[12] crosslinked and plasticized starch in LDPE[13] etc. have been reported in different studies.

Among these modification methods, acylation of starch has received significant attention in recent years for its different properties arising from the introduction of acyl groups. The introduction of acyl groups interrupts the ordered structure of the native starch and interferes with the reassociation of amylose and amylopectin in gelatinized starch; leading to change in morphological and crystalline properties. Acetylated starch with high degree of substitution, DS (2.0–3.0) has been used for a number of nonfood applications such as excipients in tablets, hot melt adhesives, cigarette filters, and coating materials.[14,15] Acylation could be an effective way for hydrophobic transformation of starch and to improve compatibility of starch based plastic materials. The length of the acyl group can also be one of the factors that contribute to the properties of acylated starch. Recently the present authors has studied the transformation of physico-chemical properties of modified starch by propylation in details.[16] The objective of this study was to prepare propylated starch -LDPE blend films and to examine the effect of DS and starch concentration on the mechanical properties, morphology, and water absorption capacity of blend films. Biodegradability of the blend films were also conducted in enzyme solution and in the soil.

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EXPERIMENTAL

Materials

Low density polyethylene (LDPE) was obtained from Indian Petrochemical (Baroda, India). Corn starch was made by Sukhjit Starch and Chemicals Limited (Phagwara, India). The characteristic composition of starch was: carbohydrates 98% (amylose: 23.6%), protein 0.4–0.5%, fiber < 1%, moisture < 13%, ash < 0.3%. Propionic anhydride was purchased from High Media Chemicals (India). Pyridine, ethanol, potassium hydroxide (KOH), hydrochloric acid (HCl), and phenolphthalein indicator used were reagent grade chemicals obtained from s.d. Fine Chemicals Limited (Mumbai, India).

Propylation of starch

Propylation of starch was done by propionic anhydride and pyridine as catalyst. Twenty gram of dried starch sample was taken in reaction flask followed by 100 mL of pyridine. The flask was then heated to 90°C for 2 h to preactivate the starch. A reflux-condenser was used to prevent the loss of organic liquid. After the pre activation for 2 h, the reaction mixture was cooled to 75°C. Propionic anhydride was

added drop-wise and the reaction continued for 22 h to ensure reaction equilibrium. The content of the reaction mixture was coagulated by adding 100 mL of isopropanol. The product was filtered and washed with methanol three times. Finally, product was dried in an oven at 70°C for 24 h.

Propyl content and DS

Propyl content and DS were determined by titration method. Propylated starch (1.0 g) was taken in a 250 mL flask and 75% ethanol (50 mL) was added. The solution was stirred at 50°C for 30 min at 40 rpm in a shaker cum incubator and cooled to room temperature and 0.5M KOH (40 mL) was added with swirling. The flask was stoppered and allowed to stand for 72 h with stirring at 40 rpm for 10 min after every 2 h interval for complete saponification. The excess of alkali was back titrated with 0.5M HCl using phenolphthalein indicator. The solution was allowed to stand for 2 h and additional alkali, which leached from the sample was titrated. A blank was titrated in parallel. The propyl content and DS were calculated by

$$\% \, \text{propyl content} = \frac{[(\text{blank, ml} - \text{sample, ml}) \times \text{molarity of HCL} \times 0.057 \times 100]}{\text{sample weight, g}}$$

$$\text{DS} = \frac{(162 \times \text{propyl} \, \%)}{[57 \times 100 - ((57-1) \times \text{propyl} \, \%)]}$$

where 162 is molecular weight of glucose units and 57 is the formula weight of propyl group.

Fourier transform infrared (FT-IR) spectra

The native and propylated starch were equilibrated at 50°C for 24 h and FT-IR spectra of native and propylated starch were recorded by FT-IR instrument (Perkin–Elmer, Model RX-1) using potassium bromide (KBr) pellets (Sigma Aldrich). FT-IR spectra were recorded at a resolution of 4 cm^{-1} and wave number ranged between 400 and 4000 cm^{-1}.

X-ray diffraction studies

X - ray diffraction of native and propylated starch was recorded by X - ray diffractometer (XPERT-PRO PW 3064, Philips, Japan). Tube Anode was Cu, tube voltage was 40 kV and generator current was 35 mA. The range of diffraction angle was 5 to 40° (2θ). Intensity ratio and wavelength were 0.50 and

1.54060 Å. Minimum and maximum peak widths were 0° and 1° (2θ), respectively.

Starch-LDPE blend film

Different films were prepared by incorporating native and propylated starch with different DS in LDPE. Essential quantities of glycerol were added. The blend mixture was prepared by taking the different components in appropriate ratios in tumbler mixture for 15 min with 30 rpm speed. The blend was propelled continuously through the single screw extruder (Haake Polydrive, Model 5578300, Germany) to be melted, compacted, and finally forced through the die. Single screw extruder had a screw length to screw diameter ratio of 25 and a diameter of 19.05 mm. The temperature of the extruder was fixed at 135°C at the feed end after some trials. The extruder barrel was thermocontrolled at 135°C at the feed end and increased in the direction of extrusion to 152°C. After extrusion, films were made by an integrated blow film plant (Konark Instruments, Ahmedabad, Gujarat, India). Tubular die was used in the blow film plant, from which a hollow tube of

the product was extruded vertically upward like a film tower. The tube was blown into a thin cylindrical film by air blown through the die and trapped in the film bubble. At the top of the tower, the blown film was squeezed through two chilled rolls of diameter 76 mm and width 250 mm. The produced films after the squeeze rolls were collected in an integrated winder with take off speed 8 m/min. The film thickness was controlled by air flow rate and the speed of the rollers. The thicknesses of the films were 0.1 ± 0.01 mm. Then the films were kept for conditioning for 48 h at room temperature 25°C, 70% R.H.

Tensile strength, percent elongation and melt flow index (MFI)

Tensile strength and percent elongation of the films were determined by Instron Universal Testing Machine (Lloyd instruments, Bognor Regis, West Sussex, UK) at load cell 100N, load range 5 and cross-head speed 100 mm/min. Samples were cut into strips of 3×1 cm^2 according to standard ISO-527 in the longitudinal direction of extrusion and were conditioned to equilibrium moisture content in the room at 70% R.H. for 24 h at 25°C prior to testing. Measurements were done in five replicates. MFI was measured by using Melt Flow Index Tester (Lloyd instruments, UK) at temperature 199°C and 2.16 kg load. Preheat time was set to 5 min. Extrudate cut timer was set to 30 s. The first extrudate was rejected and next five extrudates were collected for calculation of MFI

$$\text{MFI} = \frac{\text{Average weight of extrudate (g)}}{\text{Cut off time (10 min)}}$$

Thermal analysis

Thermal analysis of blend films was performed in TG-DTA apparatus (Perkin–Elmer, Pyris Dimond). Change in weight of sample against temperature (thermogravimetric analysis, TG), rate of change of weight against temperature (derivative thermogravimetric analysis, DTG) and heat evolved or absorbed in the sample because of exothermic or endothermic activity in the sample (differential thermal analysis, DTA) were measured. Film samples (8–10 mg) were heated from 50 to 650°C with a heating rate of 20°C/min. Nitrogen was used as purge gas at flow rate of 200 mL/min.

Scanning electron microscopy (SEM) of films

Scanning electron microscopy of the films was done by scanning electron microscope (JEOL JSM -6100 Jeol, Tokyo, Japan). The range of accelerating voltage

was 0.3–30 kV. The samples were first sputter coated with a thin layer of gold and then observed at magnification of 100× and 2000×.

Water absorption test

The water absorption capacity of the films was measured using 25×25 mm plastic film according to standard ASTM D570-98. The test specimens were first dried in vacuum oven for 24 h at 50°C and then cooled in a desiccator and immediately weighed. The conditioned specimens were entirely immersed in a container filled with distilled water. Each sample was removed from the water container at a specified interval, wiped with a clean cloth, and consequently weighed. The samples were placed back in water after each measurement. The result of each sample represents the average of three tests. The water absorption capacity was calculated as

$$\text{Water absorption capacity (\%)} = \frac{(W_A - W_1)}{W_1} \times 100$$

where W_A is the weight of the wet sample and W_1 is the initial dry weight of the sample.

Enzymatic and soil burial degradation test

The dried film samples were cut into 4×4 cm square specimens, weighed and immersed in conical flasks containing 20 mL buffer solution containing mixture of α-amylase and β-amylase. The enzymes were manufactured by NOVO industry (Denmark). Activities were measured by standard procedure.[17] The initial activities of the enzyme were 300 U/mL for α- amylase and 0.5 U/mL for β-amylase. The flasks were placed in a shaking incubator with a rate of 120 rpm for 96 h at 37°C. The samples were removed after every 24 h interval, rinsed with distilled water, and dried in a desiccator under vacuum for 24 h until achieving constant weight. The % weight loss was calculated as

$$\% \text{ weight loss} = \frac{(W_1 - W_H)}{W_1} \times 100$$

where W_H is the dry weight of the specimen after enzymatic treatment and W_1 is the initial dry weight of the specimen.

Soil burial degradation was performed as described by Thakore et al.[2] The garden pots with approximate capacity of 10 L were filled with the soil, taken from sewerage sludge in Jalandhar City (India). The blend film samples were cut into 30×100 mm pieces and buried in soil at the depth of 10 cm. The soil was kept moist by sprinkling water at regular time interval to maintain 60–80% humidity.

TABLE I
Percentage of Propyl Content and DS of Native Starch and Modified Starches

Starch/ pyridine (g/mL)	Propionic Anhydride (%)	Propyl content (%)	DS (sites/ glucose unit)
1 : 5	0.0	0.0	0.0
1 : 5	1.5	17.67	0.61
1 : 5	2.5	35.63	1.56
1 : 5	3.5	44.71	2.27
1 : 5	5.5	47.31	2.51
1 : 5	6.5	47.31	2.51

The excess water was drained through hole at the bottom of the pot. The degradation of the specimen was determined at a regular time interval (15 days) by taking the specimen carefully from the soil and washing it gently with distilled water to remove the soil. The specimen was then dried at 50°C for 24 h in a vacuum oven. Weight loss of the specimen with time was used to measure degradation rate in the soil burial test. The surface morphology of the films before and after biodegradation was recorded by SEM.
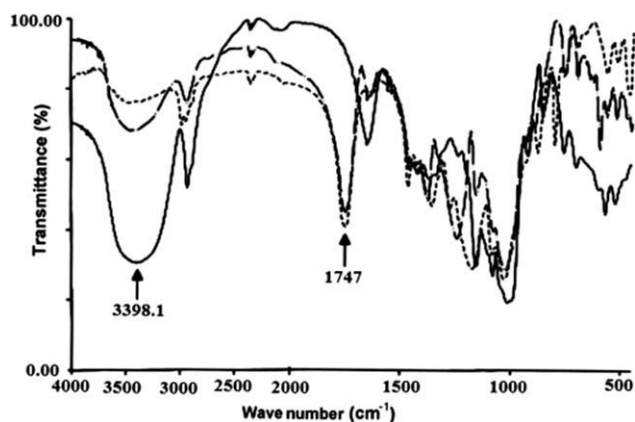
RESULTS AND DISCUSSION

Degree of substitution (DS)

Propylated starch samples were prepared with different DS. Table I shows the variation of DS and propyl content at different propionic anhydride concentrations. It was observed that DS and propyl content of starch increased with the increase in concentration of propionic anhydride in reaction medium. With increase in concentration of propionic anhydride from 0 to 5.5%, DS and propyl content of starch increased from 0 to 2.51% and 0 to 47.31%, respectively. Increase in concentration of propionic anhydride beyond 5.5% did not have any effect on DS.

The reaction equation of propylation of starch is given in Scheme 1. The acylation of starch takes place by an addition-elimination mechanism.[18] The three free OH groups of the starch have different reactivities. The primary C (6) OH is more reactive and is acylated more readily than the secondary ones on C (2) and C (3) due to steric hindrance. Of the two secondary OH groups, the C (2) OH is more reactive

Figure 1 FT-IR spectra of native starch (DS 0.0) and propylated starch (DS 1.56 and 2.51). DS 0.0(—), DS 1.56 (— · —), DS 2.51 (-----).

than the C, (3) mainly because the former is closer to the hemi-acetal and more acidic than the later.[19]

At low concentration of propionic anhydride, the numbers of propyl groups were not sufficient to convert the hydroxyl groups. But at high concentration of propionic anhydride, the propyl groups were sufficient to associate at the hydroxyl sites. As the reaction was not homogeneous one, it was likely that some glucose units were completely inaccessible to the propionic anhydride and so had unacylated C (2) OH and C (6) OH groups as well. As a result DS was less than 3.0.

FT-IR spectra

FT-IR spectroscopy was used to verify the change in chemical structure of starch molecules after acylation. Spectra of native starch, propylated starch with different DS are shown in Figure 1. In the spectra of native starch (DS 0.0), there were bands at 1158.1, 1081, 1014 cm^{-1}, which were attributed to C—O band stretching. Additional characteristic absorption bands appeared at 928.8, 860.7, 764.6, 575.1 cm^{-1}, which were due to anhydroglucose ring stretching vibrations. A broad band due to hydrogen bonded —OH groups appeared at 3398.1 cm^{-1}. FT-IR spectra of propylated starch showed new band at 1747 cm^{-1} assigned to carbonyl C=O vibration. The new

Scheme 1 Reaction equation of propylation of starch.
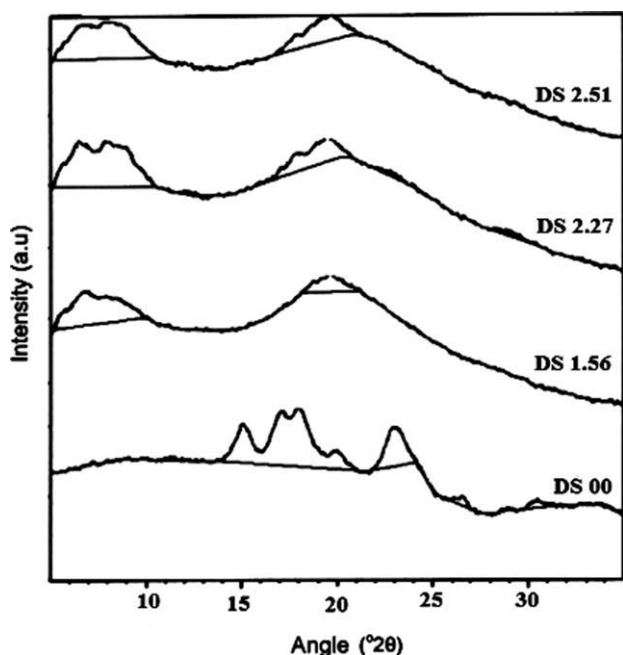
Figure 2 X-Ray diffraction patterns of native (DS 0.0) and propylated starch samples (DS 1.56, DS 2.27, and DS 2.51).

absorption band suggested that propylated starch products were formed due to acylation. With the increase in DS of propylated starch from 1.56 to 2.51, the intensity of the peak at 3398.1 cm^{-1} weakened and almost disappeared at DS 2.51, indicating that hydroxyl groups participated in the reaction.

X-ray diffraction

X - ray diffraction patterns of native and propylated starch are shown in Figure 2. Variation in intensity of light with angle (2θ) was recorded in the diffractograms. Diffractogram of native starch (DS 0.0) showed five sharp peaks at 15.02°, 17.04°, 17.89°, 19.77°, and 23.12° (2θ) indicating the crystalline structure.

Starch is a mixture of linear amylose and branched amylopectin. Linear amylose composed of α-1, 4-glucopyranose was responsible for the amorphous region, while large amylopectin contributed to crystalline region. The intramolecular and intermolecular hydrogen bonds were responsible for the highly ordered crystalline structure. Starch could adopt different types of crystalline structures (A, B, C, and V).[20,21] The A, B, and C structures consisted of packed double helix. The V-type structure was a single helix structure. The A type is largely present in cereal starches and B type in potato, amylomaize, and in retrograded starches. Each type of structure give typical characteristic peaks described by various researchers.[22,23] Chi et al.[22] described that A pattern of cereal starch exhibited sharp peaks at 15°, 17°, 18°, and 23°. Xu et al.[23] reported that peak at 5.68° was the characteristic peak of B type structure and

TABLE II
Composition of Starch–LDPE Blend Films

Film	Starch sample	Composition (% w/w)		
		Starch	LDPE	Glycerol
LDPE	–	–	100	–
LDPE-5 DS 0.0	DS 0.0	5	92.5	2.5
LDPE-5 DS 0.61	DS 0.61	5	92.5	2.5
LDPE-5 DS 1.56	DS 1.56	5	92.5	2.5
LDPE-5 DS 2.27	DS 2.27	5	92.5	2.5
LDPE-5 DS 2.51	DS 2.51	5	92.5	2.5
LDPE-10 DS 0.0	DS 0.0	10	85	5
LDPE-10 DS 0.61	DS 0.61	10	85	5
LDPE-10 DS 1.56	DS 1.56	10	85	5
LDPE-10 DS 2.27	DS 2.27	10	85	5
LDPE-10 DS 2.51	DS 2.51	10	85	5

peak at 27.01° was indicative of A type structure. C type was a mixture of A and B type structures. The peaks observed in this study showed that the native corn starch has A-type of structure.

It was observed from the diffractograms of propylated starch that the peaks at 15.02°, 17.04°, 23.12° (2θ) disappeared after modification and peak intensities at 17.89° and 19.77° were nearly nonexistent indicating the disappearance of typical A type pattern. It was also observed that a new type of crystal structure formed by amylose containing starches, namely, the V type as indicated by the new peaks developed at 6.5° and 7.9°. This might be due to crystallization of amylose in single helices during esterification reactions.[24,25] The propyl groups in
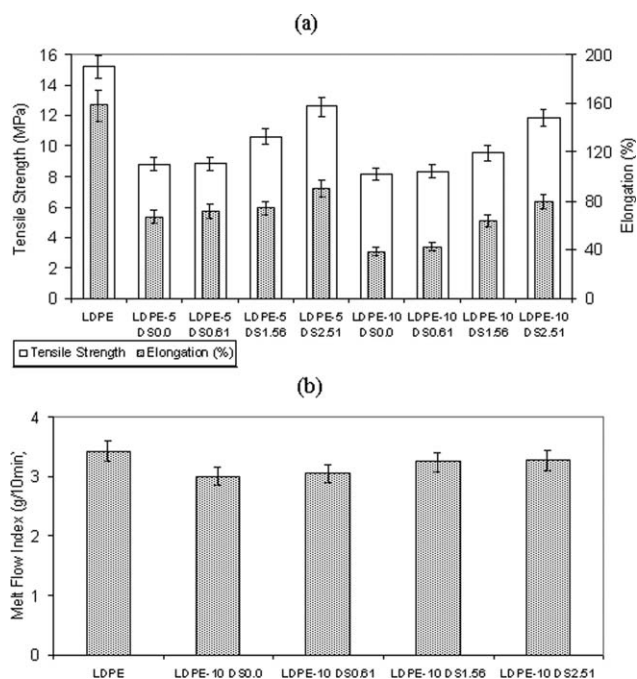
Figure 3 (a) Tensile strength and % elongation of starch-LDPE blend films and (b) melt flow index of starch-LDPE films.

TABLE III
Mechanical Properties of the Blend Films and Variations Relative to LDPE Film

Film	Tensile strength		Elongation		Melt flow index	
	MPa	Relative to LDPE (%)	(%)	Relative to LDPE (%)	g/10 min	Relative to LDPE (%)
LDPE	15.18 ± 0.76	100	158.17 ± 12.65	100	3.44 ± 0.17	100
LDPE-5 DS0.0	8.78 ± 0.44	57.85	66.69 ± 5.34	42.18	–	–
LDPE-5 DS0.61	8.82 ± 0.44	58.03	71.40 ± 5.45	45.16	–	–
LDPE-5 DS1.56	10.63 ± 0.45	70.02	73.67 ± 5.95	46.48	–	–
LDPE-5 DS2.51	12.59 ± 0.56	82.93	89.97 ± 7.24	56.85	–	–
LDPE-10 DS0.0	8.15 ± 0.41	53.68	38.26 ± 3.06	24.19	3.00 ± 0.18	87.46
LDPE-10DS0.61	8.32 ± 0.44	54.81	42.23 ±3.50	26.67	3.05 ± 0.17	88.66
LDPE-10DS1.56	9.53 ± 0.47	62.78	62.82 ± 5.04	39.57	3.25 ± 0.15	94.48
LDPE-10DS2.51	11.85 ± 0.65	78.06	79.12 ± 6.40	50.12	3.27 ± 0.14	95.06

modified starch samples replaced most of the hydroxyl groups on starch, which was responsible for different type of ordered structure.

Blend film

Films were prepared by incorporating native starch (DS 0.0) and propylated starch of different DS in LDPE. The composition of various films prepared is summarized in Table II.

It was observed that the surface of the film containing 5% native starch in the blend (LDPE-5 DS0.0) was rough as compared to LDPE film under similar die, pressure and temperature conditions. Starch particles could be viewed separately in the matrix of the blend film. Films containing 5% propylated starch were smoother than the native starch blend film and smoothness improved with the increase in DS of propylated starch.

Films containing 10% starch had air gaps. This entrainment of the air was because of the higher moisture in the blend due to increase in starch content. Another reason could be nonuniformity of flow through the die at higher starch concentrations. Depending upon the size of the bubbles, the films were perforated at some points.

MECHANICAL PROPERTIES

Tensile strength, % elongation, and MFI

Tensile strength is the capacity of the film to take the load and percent elongation is its ability to stretch. MFI is used to grade the material in extrusion, injection or blow molding processes. Tensile strength, percent elongation and MFI of the films were measured and the results are shown in Figure 3. To isolate the effect in individual blend and for comparison, a comprehensive result of the properties and their changes relative to control sample LDPE has been shown in Table III. The tensile strength of LDPE film was 15.18 MPa. With addition of 5% native starch, the tensile strength of the blend film (LDPE-5 DS0.0) reduced to almost 58%. However, tensile strength of the propylated starch blend films was higher than native starch blend film. With increase in DS from 1.56 to 2.51, tensile strength of the films increased. Tensile strength of the blend film containing propylated starch of high DS (LDPE-5 DS2.51) was much higher and was almost 78% of the LDPE film. With the increase in starch content to 10% in blend (LDPE-10 DS0.0), tensile strength decreased. However, it increased considerably with the addition of propylated starch (LDPE-10 DS2.51).

Percent elongation of the LDPE film was 158.17. With the addition of native starch (LDPE-5 DS0.0) in

TABLE IV
TG-DTA Studies of Native Starch Film and Modified Starch Films

	TG							
	First stage		Second stage		DTA		DTG	
Sample	T_D (°C)	Weight loss (%)	T_D (°C)	Weight loss (%)	T_E (°C)	Energy absorbed (mJ/mg)	T_D (°C)	Rate of weight loss (mg/min)
LDPE-10 DS 0.0	50–125	6	349–440	89%	103, 381	91.5, 215	372	6.2
LDPE-10 DS 0.61	25–98	2.4	367–478	95%	432	198	426	4.8
LDPE-10 DS 1.56	20–100	2.0	375–480	98%	454	207	438	4.1
LDPE-10 DS 2.51	–	–	384–492	94%	472	220	454	4.2
LDPE	–	–	399–509	100%	486	223	480	3.7

T_D, Decomposition temperature; T_E, Endothermic peak temperature.

the blend, the percent elongation of the film was reduced to 43% of LDPE film. However, it increased to 50% with the blending of propylated starch of high DS (LDPE-5 DS2.51).

MFI of the films is shown in Figure 3(b). MFI of the LDPE films was 3.44 g/10 min. With the addition of 10% native starch (LDPE-10 DS0.0), the MFI decreased to 87% of LDPE film. But there was an increase in MFI due to addition of propylated starch in the blend. MFI of the film containing propylated starch of high DS (LDPE-10 DS2.51) was close to LDPE film.

The above results clearly showed that the addition of native starch and propylated starch reduced the tensile strength and percent elongation of the blend films. The extent of decrease depended on the properties and the concentration of starch in the blend. Figure 3(a) clearly showed that at the same concentration of starch, the tensile strength, and percent elongation increased to a large extent due to an increase in DS of the propylated starch.

Chemically, starch is a polymer of glucose having α-1, 4 and α-1, 6 linkages as amylose and amylopectin. Native starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to hydroxyl groups on the granule surface. In case of propylated starch at high DS, the propyl groups replaced most of the hydroxyl groups on starch molecules. The introduction of acyl groups into starch molecules altered its properties and alterations relied upon the DS and nature of starch.[26] After propylation the hydrophilic nature of starch decreased. The homogeneity, inter phase adhesion, and compatibility of starch-LDPE blend improved. The improvement in starch-LDPE blend due to inter phase adhesion was confirmed from subsequent SEM images of films and discussed in the section of SEM.

Results showed that with the addition of starch in the blend film, the melt flow index decreased. The addition of starch contributed to the increase in viscosity of the melt and poor miscibility of the starch and LDPE. In case of propylated starch, miscibility of starch, and LDPE improved, and shifted towards a single phase behavior. So flow ability improved resulting in increase in MFI. Garg and Jana[16] observed that propylated starch at low DS exhibited higher solubility and viscosity at 95°C as compared to native starch, which was due to the weakening of the associated forces in the amorphous area of the granules. However at high DS, there were sufficient propyl groups to inhibit the swelling power and solubility of starch and there was decrease in viscosity.

Thermal analysis

Thermo gravimetric analysis (TG), differential thermal analysis (DTA) and derivative thermal analysis (DTG) of blend films were studied and results are
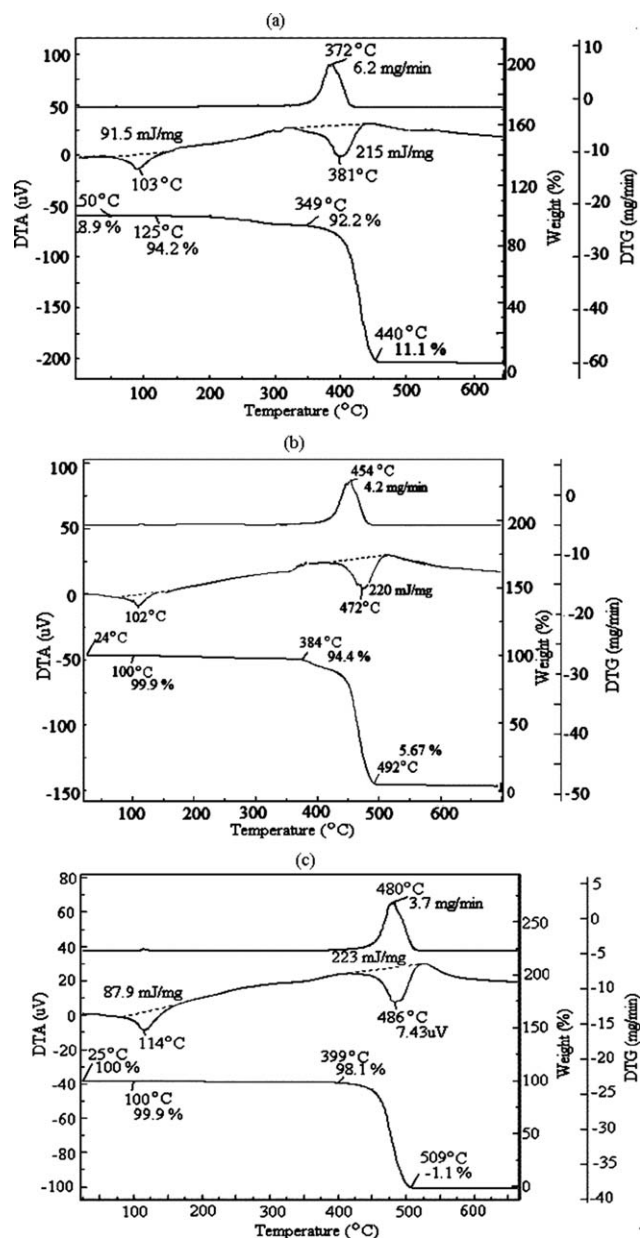
Figure 4 (a) TG, DTA, and DTG curves of native starch blend film (LDPE-10 DS 0.0), (b) propylated starch blend film (LDPE-10 DS 2.51), and (c) LDPE film.

shown in Table IV. Characteristic TG/DTA/DTG curves of native starch blend film (LDPE-10 DS0.0), propylated starch blend film (LDPE-10 DS2.51), and LDPE film, are shown in Figure 4(a–c). TG results of native starch blend film (LDPE-10 DS0.0) showed two-stage decomposition with the first one corresponding to loss of water from 50 to 125°C with a weight loss of 6% and second from 349 to 440°C with a weight loss of 89% due to depolymerization process [Fig. 4(a)]. Blend films containing propylated starch (LDPE-10 DS0.61, LDPE-10 DS1.56) also showed two-stage decomposition but the first stage weight loss due to dehydration of starch was less compared to native starch blend film. Second stage
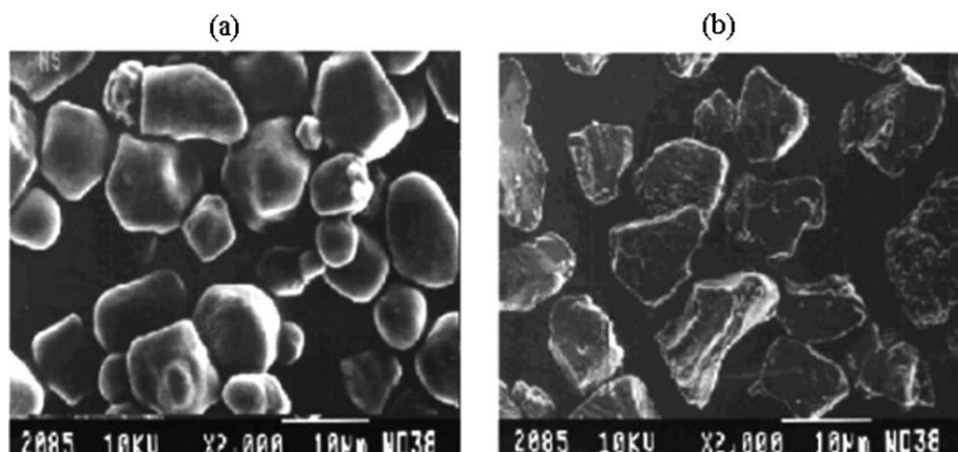
Figure 5 (a) SEM micrographs (×2000) of native starch (DS 0.0) and (b) propylated starch (DS 2.51).

decomposition temperature was 367–478°C and 375–480°C with a weight loss of 95 and 98%, respectively. Film containing high DS propylated starch (LDPE-10 DS2.51) and LDPE film showed second stage decomposition at temperature range 384–492°C and 399–509°C with a weight loss of 94 and 100%, respectively, [Fig. 4(b,c)]. Thus, it was evident from TG data that propylated starch blend films were thermally more stable than native starch blend film and decomposition temperature increased with the increase in DS. LDPE film has the maximum thermal stability.

DTA results of native starch blend film (LDPE-10 DS 0.0) exhibited two endothermic peaks with first one corresponding to loss of water at 103°C with energy absorbed 91.5 mJ/mg followed by second stage of decomposition at 381°C with energy absorbed 215 mJ/mg [Fig. 4(a)]. Films containing propylated starch (LDPE-10 DS0.61, LDPE-10 DS1.56, LDPE-10 DS2.51) and LDPE film had endothermic decomposition at higher temperature 432, 454, 472, and 486°C with energy absorbed 198, 207, 220, and 223 mJ/mg, respectively.

DTG analysis of blend films was studied as a function of rate of weight loss (mg/min) versus temperature. In native starch, blend film (LDPE-10 DS 0.0) decomposition took place at 372°C with a rate of weight loss 6.2 mg/min. However, in propylated starch blend films and LDPE film decomposition was observed at higher temperatures with lower rate of weight loss. DTG results revealed that the rate of thermal decomposition of native starch blend film was higher in comparison to that of acylated starch blend film and LDPE film.

The propylated starch blend film samples were thermally more stable than native starch blend film. The increase in thermal stability with increase in DS was due to low amount of remaining hydroxyl groups in starch molecule after propylation. The increase in molecular weight and covalent bonding

due to the acylation of hydroxyl groups were also responsible for the increased thermal stability.[27,28]

Scanning electron microscopy (SEM)

Surface scanning of the films was done to examine morphology of the blend films. SEM micrographs of native (DS 0.0) and propylated starch (DS 2.51) are shown in Figure 5(a,b). It was observed from micrographs that the surface of the starch became rough and eroded after propylation which was attributed to substitution of propyl groups in starch. Increase in roughness of starch surface may improve the adhesion of the starch with synthetic polymers due to increased surface area for bonding and mechanical interlocking.

Surface morphology of LDPE film, and starch-LDPE blend films are shown in Figure 6(a–f). LDPE film did not show any specific morphology due to smooth surface of the film, whereas the micrographs of film containing 5% native starch (LDPE-5 DS0.0) in blend had surface cracks and starch particles were separately visible in LDPE matrix. Films containing propylated starch of low DS (LDPE-5 DS0.61) showed less cracks although starch particles were visible on the surface. Micrograph of propylated starch blend film at high DS (LDPE-5 DS2.51) showed well-dispersed starch particles and appeared smoother than the native starch blend film. Starch particles seemed to be embedded in the matrix.

Cracks and surface roughness in the starch blend films appeared due to incompatible blend of starch and LDPE. The phase separation between starch and LDPE in the blend was overcome by propylation of starch and led to smoother film. Smoothness of the film increased with the increase in DS of propylated starch due to improvement in surface adhesion between starch and LDPE. Average size of the starch particles in films containing native, low DS and high DS starch was 1.13, 1.11, and 0.94 μm, respectively. Due to better surface adhesion and compatibility of
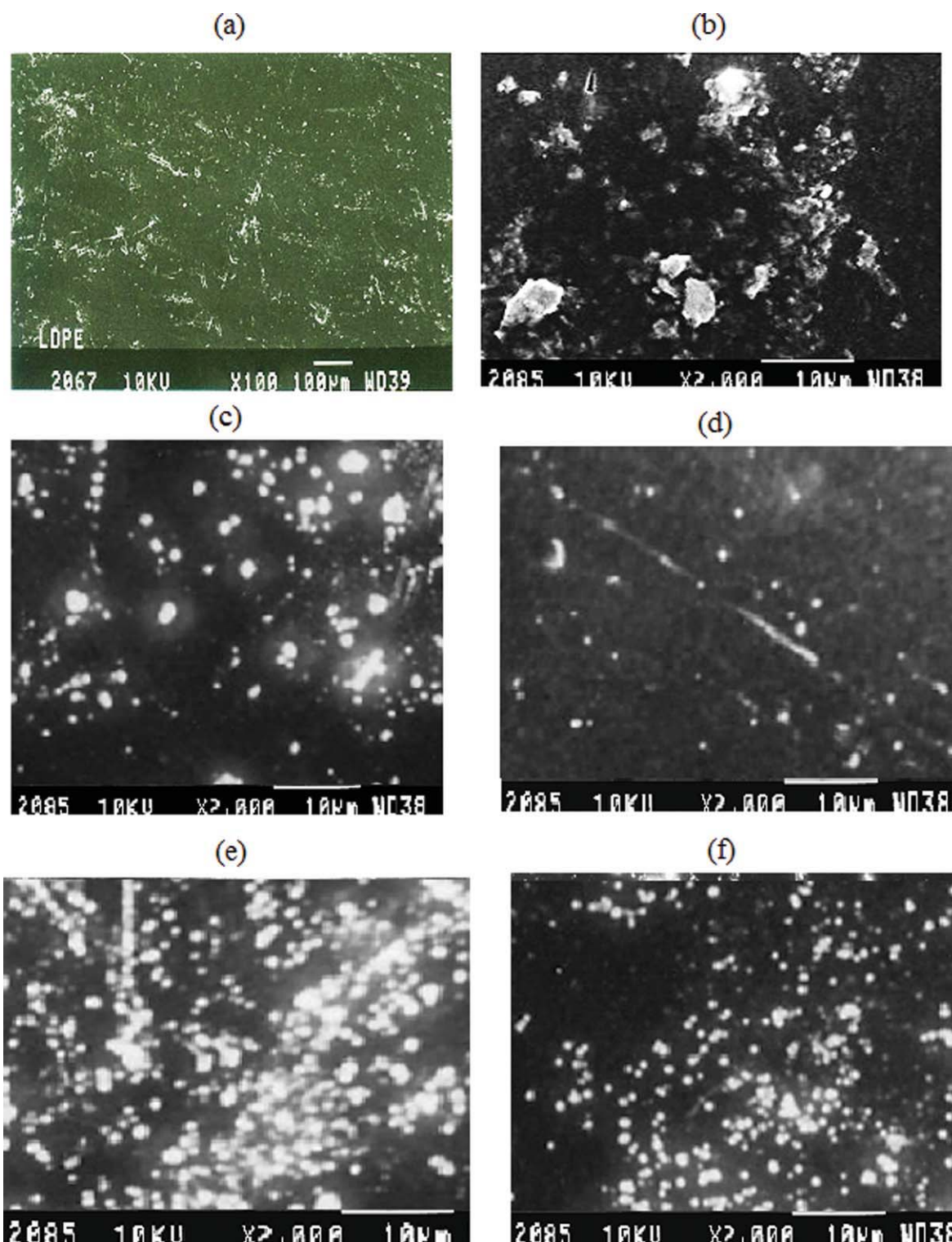
Figure 6 (a) SEM micrographs of starch-LDPE blend films [LDPE, (b) LDPE-5 DS0.0, (c) LDPE-5 DS0.61, (d) LDPE-5 DS2.51, (e) LDPE-10 DS0.0, and (f) LDPE-10 DS2.51]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the starch particles at high DS, it dispersed more uniformly and size of the starch particles decreased in the blend film.

With the increase in starch to 10%, both the native starch and propylated starch blend films exhibited a coarse structure [Fig. 6(e,f)]. Surface cracks and air gaps were visible in the film. This could be due to higher moisture content at high starch concentrations. The evaporation of moisture created air gap in the film. The micrograph of film containing 10%
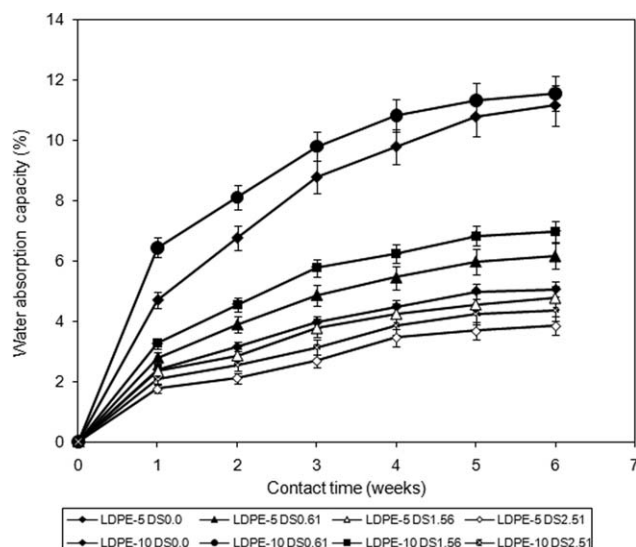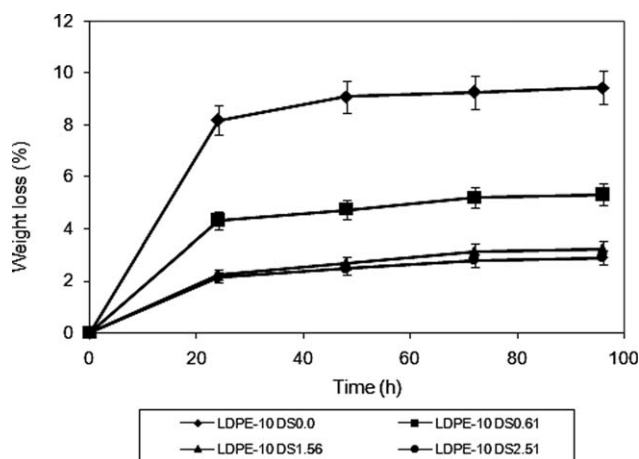
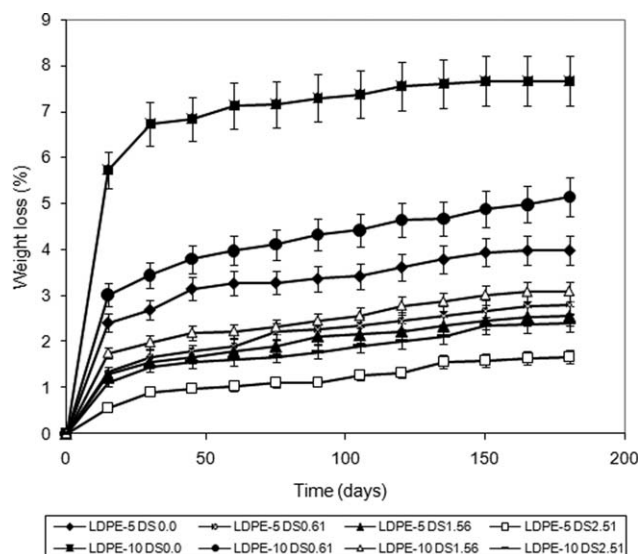**Figure 7** Water absorption capacity of starch-LDPE films.

propylated starch (LDPE-10 DS2.51) was comparatively smoother and the air gaps and surface cracks were also less.

Water absorption capacity

Water barrier property is one of the most important properties of biodegradable packing materials.[29,30] Figure 7 shows the results of water absorption capacity of the films containing native starch and propylated starch as a function of time. Results showed that with the increase in starch content in the blend, water absorption capacity of the blend films increased. Water absorption capacity of the blend films containing 5% native starch (LDPE-5 DS0.0) was 2.41% after 1 week and that of film containing propylated starch of low DS (LDPE-5 DS0.61) in the blend was 3.15%, which was higher than native starch blend film. With the increase in

**Figure 8** Weight loss of starch-LDPE films during enzymatic treatment.

Figure 9 Weight loss of starch-LDPE films during soil burial test.

DS from 1.56 to 2.51, water absorption capacity of the blend films decreased. At high DS, the water absorption capacity of the propylated starch blend film was lower than the native starch blend film.

Water absorption capacity of the film containing propylated starch of low DS was higher than native starch blend film as acyl groups were not sufficient to change the behavior of hydroxyl groups at low DS. There was weakening of intermolecular hydrogen bonds in starch with the introduction of propyl groups. At high DS, water absorption capacity of the films decreased to below that of native starch blend film as propyl groups replaced most of the hydroxyl groups on starch and interaction with water decreased.[16]

Enzymatic and soil burial degradation test

Degradability of polymers is a critical parameter for their application. Figure 8 shows the % weight loss of starch-LDPE blend films containing 10% starch after 96 h of incubation in enzyme at 37°C. β-amylase and α-amylase function in different ways to hydrolyze the acetal bonds of starch. β-amylase hydrolyzes the main chain acetal bonds, and does not affect the branch points. α-amylase can cleave the bonds either in main chain or in branch.[31–33] Results showed that blend film containing propylated starch had slower degradation rate compared to native starch blend film. With the substitution of hydroxyl groups with propyl groups in starch molecule, weight loss decreased. Weight loss in the propylated starch blend film of high DS (LDPE-10 DS1.75) was minimum. This was because the presence of propyl groups in starch molecules inhibited the catalytic reaction of amylases. The dispersion of starch
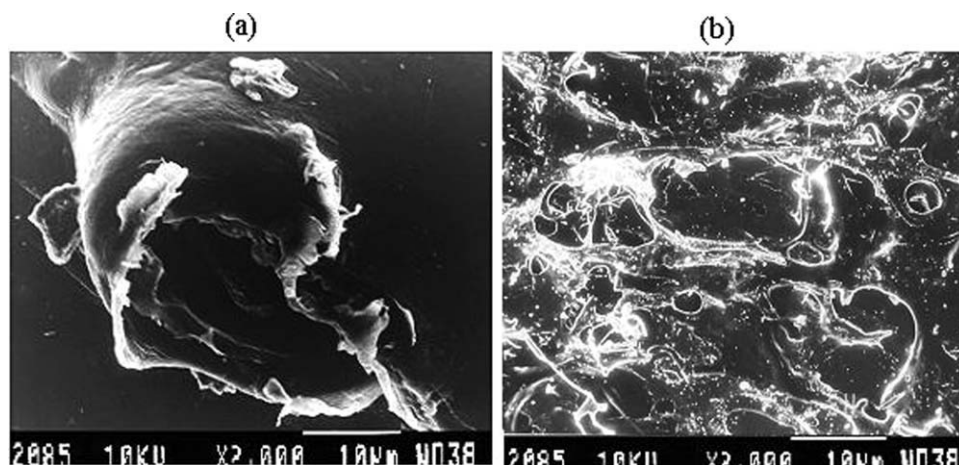
Figure 10 SEM micrographs of starch-LDPE blend films after soil burial degradation test [(a) LDPE-10 DS0.0 and (b) LDPE-10 DS2.51].

molecules within the LDPE increased the difficulty for enzymes to reach to the starch molecules.

Soil burial test was carried out to evaluate the degradation of starch in natural environment. Soil burial test is an outdoor experiment, where soil humidity, temperature, and amount of microorganisms are in less control and change with season. Biodegradability of the samples in soil was studied by evaluating weight loss of films over a period of 180 days and shown in Figure 9. The diffusion of water into films resulted in swelling of the film and allowed the growth of microorganisms. Enzymatic and other secreted degradation caused a weight loss and disruption of the film samples. The starch-LDPE films degraded rapidly up to 45 days and after that, the degradation rate decreased. The films containing propylated starch showed lower weight loss compared to native starch blend films indicating that modification of the starch reduced biodegradability. Weight loss of the films increased with the increase in starch content in the blend.

The surface morphology of films containing 10% native starch (LDPE-10 DS 0.0) and propylated starch (LDPE-10 DS 2.51) in the blend after soil burial test was obtained by SEM (Fig. 10). Micrographs of blend films showed that the surface of the film broke up after 180 days of treatment in soil.

CONCLUSIONS

Propylated starch samples were prepared with different DS. X-ray diffraction studies showed that crystalline structure of starch was destroyed during propylation. The characteristics of starch-LDPE blend films improved with propylation of starch at high DS. Mechanical strength of the films containing propylated starch of high DS (LDPE-5 DS2.51) was significantly higher than native starch blend film.

Propylated starch blend films were found thermally stable than the native starch blend film due to low amount of remaining hydroxyl groups. SEM studies showed that the films containing propylated starch were smoother than the native starch blend film because of improved blend characteristics. The starch content and DS of the propylated starch governed the water absorption capacity and biodegradability of the starch-LDPE films. Water absorption capacity of the film containing propylated starch of low DS (LDPE-5 DS 0.61) was higher than native starch blend film. At high DS, water absorption capacity of the propylated starch blend films decreased to below that of native starch blend film.

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