

Preparation of LDPE-Acetylated/Butyrylated Starch Blend Blow Films and Characterization

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Abstract Development of modified plastics has been studied through the LDPE-acetylated starch blend films to examine the effect of different acyl groups and degrees of substitution (DS) on properties of films. Corn starch was modified with acetyl and butyryl groups and films were prepared by blending acylated starch with low density polyethylene (LDPE). Systematic studies were done to observe the effect of acyl groups, DS and starch concentration on the properties and biodegradability of the blend films. It was observed that blend films containing 5% acetylated and butyrylated starches of high DS (2.5, 1.7) maintained 75% and 83% of tensile strength of LDPE films. Thermal analysis results indicated that acetylated and butyrylated starch blend films decomposed at 370 °C and 389 °C which were higher than the decomposition temperature of native starch film (349 °C). Scanning electron micrographs of blend films containing high DS acylated starch showed well dispersed starch particles due to improvement in dispersion between starch and LDPE. Water absorption capacity of high DS acetylated and butyrylated starch blend films (4.18% and 3.76%, respectively) was lower than that of native starch films (5%). This study has an advantage because of blown films prepared can be integrated with the present manufacturing systems without any other requirement.

Keywords: Acylated starch; LDPE-starch blend films; Mechanical properties; Water absorption capacity; Biodegradability.

INTRODUCTION

Plastics are one of the largest groups of polymeric materials of petrochemical-based organic origin, which may be formed into useful shapes by application of heat and pressure^[1]. But, at the same time these polymers are contributing to an ever increasing amount of plastic waste^[2]. Therefore, in past two decades, development of modified plastics or substitutes has been paid attention, to enhance the biodegradability and to lessen the dependency on the depleted petroleum resources^[3, 4]. Blending of starch with plastics has been one of most attractive choice because of its low cost, easy availability and biodegradability^[5–7]. However, the low water resistance, high brittleness and incompatibility with hydrophobic polymers have limited the extensive use of starch based products. Therefore improvement in properties of starch is utmost necessity for quality products.

Different ways for modification of starch in starch based films have been adopted by researchers to incorporate the desired properties and to solve the problem^[8–11]. Starch was crosslinked with epichlorohydrin, and mechanical properties of LDPE-crosslinked starch blend films were reported^[12, 13]. Results indicated that mechanical strength of the films containing modified starch was higher as compared to native starch films due to crosslinking of starch which reinforced the granule by chemical bonds that acted as bridges between molecules and increased the hydrophobicity of the molecules of starch. Formulation and characterization of the biodegradable packing film derived from potato starch and LDPE grafted with maleic anhydride were

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investigated^[14]. It was observed that the films prepared with starch and LDPE grafted with maleic anhydride had higher flexibility with respect to LDPE and hence the films were more suitable for packing applications as compared to LDPE.

Acetylated starch of high DS (2.0–3.0) has been used recently because of specific properties attained with the introduction of substitution groups such as hydrophobicity, melt processibility and non food applications^[15, 16]. Xu *et al.*^[17] studied the morphology, crystalline structure and thermal properties of yam starch acetates and found that structural modification resulted in significant changes of the physico-chemical properties of starch. Selected morphological and functional properties of extruded acetylated starch-cellulose foams were evaluated by Guan *et al.*^[18] They reported that both glass transition temperature (T_g) and melting temperature (T_m) of the extruded foams increased with the increase in DS of the acetylated starch. Bikiaris *et al.*^[19] examined the biodegradation of octanoated starch and its blends with LDPE. It was concluded that modified starch could be used for film production as it exhibited high elongation at break.

The effect of acylation of starch using different acyl groups on physico-chemical properties has been reported recently by the present authors^[20]. The hydrophobic transformation of starch was significant at high degrees of substitution. It is expected that the hydrophobic transformation of starch can improve the compatibility of starch with LDPE in the blend. The objective of this work was to prepare LDPE-acetylated/butyrylated starch blend blow films. The effects of different acylations (acetylation and butyrylation) and DS on mechanical properties and water absorption capacity of blend films were evaluated.

EXPERIMENTAL

Materials

Commercial grade low density polyethylene (LDPE) was manufactured by Indian Petrochemical Baroda, (India). Corn starch obtained from Sukhjit Starch and Chemicals Limited, Phagwara (India) contained 24% amylose content, moisture < 13% and ash < 0.3%. All other analytical grade chemicals were obtained from s.d. Fine Chemicals Limited, Mumbai, India.

Modification of Starch by Acylation and Analysis

Acylation of starch was done using acetic and butyric anhydride separately as described earlier^[20]. The native and acylated starch samples were equilibrated at 50 °C for 24 h. Fourier transform infrared (FTIR) spectra of starch samples were acquired by FTIR instrument (Perkin Elmer, Model RX-1, USA) prepared from powdered samples mixed with dry KBr in the ratio 1:100. X-ray patterns of native starch and acylated starch with different DS was conducted between 5° to 40° (2 θ) using X-ray diffractometer (XPRT-PRO PW 3064, Philips, Japan) with CuK α radiation at a voltage of 40 kV and 35 mA.

Blend Films and Analysis

LDPE and starch blends were prepared by using a single screw extruder (Haake Polydrive, Model 5578300, Germany). The temperature of the extruder barrel was maintained from 135 °C to 152 °C in the direction of extrusion. After extrusion, films were made by a blow film plant (Konark Instruments Ltd., 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 takeoff speed 8 m/min. The films were kept for conditioning for 48 h at room temperature (25 °C), 70% R.H. The average thicknesses of the films were 0.1 ± 0.01 mm. Measurements of mechanical properties on films were performed on an Instron universal mechanical tester (Lloyd instruments, UK) according to standard ISO-527. Measurements were done in five replicates. MFI was measured at temperature 199 °C and 2.16 kg load by using a Melt Flow Index Tester (Lloyd instruments, UK).

$$\text{MFI} = \frac{\text{Average weight of extrudate}}{\text{Cut off time}}$$

Thermal analysis of blend films was done using a TG-DTA apparatus (Perkin Elmer, Pyris Dimond). Each sample was heated up to 650 °C at a rate of 20 K/min. Nitrogen was used as purge gas at flow rate of 200 mL/min.

Effect of acylation on the morphological properties of the films was conducted by using a JEOL JSM-6100 scanning electron microscope (SEM) (Jeol Ltd, Tokyo, Japan). All specimens were coated with gold and then observed at magnification of 100 X to 2000 X.

Water absorption capacity of the films was determined according to ASTM D570-98 by soaking the samples in distilled water at room temperature. At regular time intervals samples were removed from the water, dried by wiping with tissue paper, weighed, and then placed back into the water container.

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

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

The dried films (4 cm × 4 cm) were weighed and immersed in 20 mL buffer solution containing mixture of α -amylase and β -amylase. The samples were removed after every 24 h interval, rinsed with distilled water and dried in a desiccator for 24 h until 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 by burying the film samples (30 mm × 100 mm) in sewerage sludge soil^[22]. The humidity of the soil was maintained up to 60%. 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

Characterization of Acylated Starch

The acyl (%) and degree of substitution of starch samples are shown in Table 1. FTIR spectra of native starch (NS 0.0), acetylated and butyrylated starch (Ac 1.45, Bu 1.41) are shown in Fig. 1. In the spectra of native starch, three characteristic peaks appeared at 1158.1, 1081 and 1014 cm^{-1} attributed to C—O band stretching. A strong absorption band at 1652.9 cm^{-1} was also observed. This band was believed to be the absorption of tightly bound water in the starch^[23,24]. The absorption band at 2929 cm^{-1} was characteristic of C—H stretches associated with the ring methine hydrogen atoms. A broad band due to hydrogen bonded —OH groups also appeared. FTIR spectra of acetylated and butyrylated starch showed a new band at 1749 cm^{-1} , assigned to carbonyl C=O vibration. The new absorption band confirmed the acyl moiety in the starch. It appeared that the intensity of C—H and O—H absorption bands decreased simultaneously but the intensity of O—H band decreased significantly.

Table 1. DS of native starch and modified starch

Acetylated starch			Butyrylated starch		
Acetyl (%)	DS	Sample	Butyryl (%)	DS	Sample
—	—	NS 0.0	—	—	NS 0.0
13.76	0.60	Ac 0.60	12.78	0.34	Bu 0.34
27.95	1.45	Ac 1.45	28.76	0.92	Bu 0.92
36.41	2.13	Ac 2.13	38.34	1.41	Bu 1.41
40.75	2.55	Ac 2.55	43.67	1.75	Bu 1.75

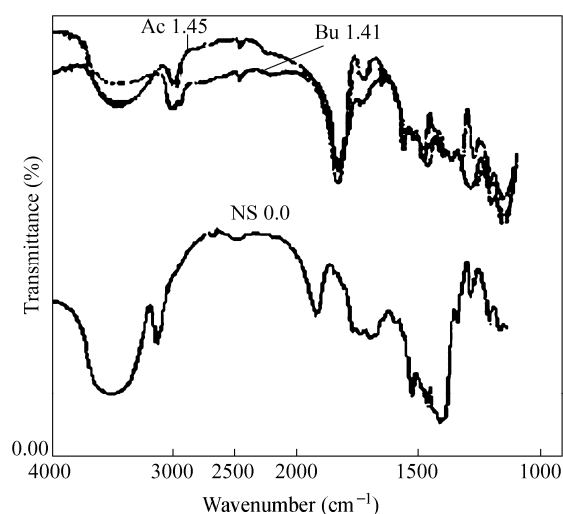


Fig. 1 FTIR spectra of native starch (NS 0.0), acetylated and butyrylated starches (Ac 1.45 and Bu 1.41)

The X-ray diffraction patterns of native and acylated starch samples are shown in Fig. 2. The native starch (NS 0.0) diffractogram showed crystalline structure with five sharp peaks. However, in the diffractograms of acetylated and butyrylated starch (DS *ca.* 1.45), the crystalline peaks disappeared and a new V type of crystal structure was formed, indicated by the new peaks near 6° to 8° (2θ). This might be due to crystallization of amylose in single helices during esterification reactions^[25]. The broad band at 20° might be the sign of amorphous nature of the modified starch.

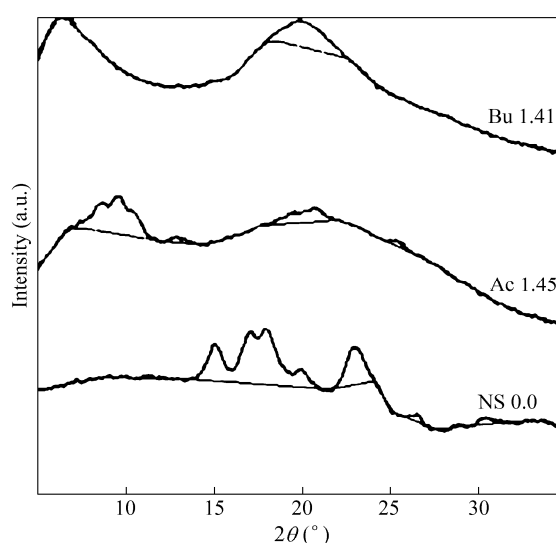


Fig. 2 X-Ray diffraction patterns of native starch (NS 0.0), acetylated and butyrylated starches (Ac 1.45 and Bu 1.41)

Blend Films and Analysis

The composition of the blend films is shown in Table 2. The starch in the films varied in (i) concentration, (ii) modification of starch and (iii) degrees of substitution (DS). It was observed that the films containing 5% acylated starch at high DS were smoother than the native starch blend film and smoothness improved with the increase in DS of acylated starch.

Table 2. Composition of LDPE-starch blend films

Film	Starch sample	Composition (wt%)		
		Starch	LDPE	Glycerol
LDPE	—	—	100	—
LDPE-5 NS0.0	NS 0.0	5	92.5	2.5
LDPE-10 NS0.0	NS 0.0	10	85	5
LDPE-5 Ac0.60	Ac 0.60	5	92.5	2.5
LDPE-5 Ac2.55	Ac 2.55	5	92.5	2.5
LDPE-10 Ac0.60	Ac 0.60	10	85	5
LDPE-10 Ac2.55	Ac 2.55	10	85	5
LDPE-5 Bu0.33	Bu 0.33	5	92.5	2.5
LDPE-5 Bu1.75	Bu 1.75	5	92.5	2.5
LDPE-10 Bu0.33	Bu 0.33	10	85	5
LDPE-10 Bu1.75	Bu 1.75	10	85	5

Tensile strength, elongation and melt flow index results of the LDPE-starch blend films are shown in Table 3. Results showed that with addition of 5% native starch, the tensile strength of the blend film (LDPE-5 NS0.0) reduced to 58% of that of the LDPE film. However, tensile strength of the acylated starch blend films was higher than that of native starch blend film. With increase in DS of acetylated and butyrylated starch from 0.60 to 2.55 and 0.33 to 1.75, tensile strength of the blend films increased from 8.9 MPa to 11.4 MPa, and 9.0 MPa to 12.6 MPa, respectively. Tensile strength of the blend films (LDPE-5 Ac2.55; LDPE-5 Bu1.75) containing acetylated and butyrylated starch of high DS was almost 75% and 83% of that of the LDPE film. With the increase in starch content to 10% in the blend film (LDPE-10 NS0.0), tensile strength decreased considerably. However, it increased with the addition of acylated starch in the blend films (LDPE-10 Ac2.55; LDPE-10 Bu1.75).

Table 3. Mechanical properties of the blend films

Film	Tensile strength (MPa)	Elongation (%)	Melt flow index (g/10 min)
LDPE	15.2 ± 0.76	158 ± 12.6	3.4 ± 0.17
LDPE-5 NS0.0	8.8 ± 0.44	67 ± 5.3	—
LDPE-10 NS0.0	8.1 ± 0.41	38 ± 3.1	2.3 ± 0.12
LDPE-5 Ac0.60	8.9 ± 0.45	68 ± 5.4	—
LDPE-5 Ac2.55	11.4 ± 0.57	87 ± 6.9	—
LDPE-10 Ac0.60	8.2 ± 0.41	41 ± 3.3	2.4 ± 0.12
LDPE-10 Ac2.55	10.2 ± 0.51	79 ± 6.3	2.8 ± 0.14
LDPE-5 Bu0.33	9.0 ± 0.45	68 ± 5.5	—
LDPE-5 Bu1.75	12.6 ± 0.63	91 ± 7.2	—
LDPE-10 Bu0.33	8.6 ± 0.43	44 ± 3.5	2.6 ± 0.13
LDPE-10 Bu1.75	12.1 ± 0.60	80 ± 6.4	3.2 ± 0.17

Elongation of the LDPE film was 158%. With the addition of native starch in the blend film (LDPE-5 NS0.0), the elongation reduced to 42% of that of the LDPE film. However, in the blend films (LDPE-5 Ac2.55; LDPE-5 Bu1.75) containing high DS acetylated and butyrylated starch, it increased to 55% and 58% of that of the LDPE film.

MFI of the blend films is shown in Table 3. It was observed that the melt flow index of LDPE film was 3.44 g/10 min. With addition of 10% native starch in the blend, the MFI of the blend film (LDPE-10 NS0.0) decreased to 68% of that of the LDPE film. But there was an increase in MFI due to addition of acylated starch in the blend. MFI of the blend films (LDPE-10 Ac2.55) containing acetylated starch of high DS, increased to 81% of that of the LDPE film. However, melt flow index of the blend film (LDPE-10 Bu1.75) containing butyrylated starch of high DS was close to that of LDPE film. Table 3 shows that the tensile strength and elongation of blend films increased due to increase in DS of the acylated starch. It was also observed that

increase in chain length from acetyl to butyryl group had considerable effect on tensile strength and elongation of blend films. The acylation of starch molecules has considerable effect on properties of the blend films depending upon the DS and nature of starch^[26–28]. After acylation the homogeneity and compatibility of LDPE-starch blend improved. The better compatibility of LDPE-starch blend films was also shown by SEM images of films.

Reduction in MFI values with the addition of starch in the blend films was due to increase in viscosity of the melt and poor miscibility of the starch and LDPE as the starch granules retained their shape and acted as rigid particulate filler in the matrix during processing. When starch content increased in blend, the interaction among granules increased and spaces between particles became small. Under this situation, the particle-particle interactions may be larger than particle-matrix interactions resulting in agglomeration of starch particles. In case of acylated starch, compatibility of starch and LDPE increased and the blends showed a single phase behavior. So flow ability improved resulting in increase in MFI.

Thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA) curves of LDPE film, native starch blend film (LDPE-10 NS0.0), and acylated starch blend films (LDPE-10 Ac2.55 and LDPE-10 Bu1.75) are shown in Fig. 3(a–d). TG results of LDPE film showed thermal degradation from 399 °C to 509 °C with a weight loss of 100%, whereas the blend film (LDPE-10 NS0.0) containing 10% native starch showed two-stage decomposition. First was because of loss of water from 50 °C to 125 °C and second was from 349 °C to 440 °C with a weight loss of 89% (Fig. 3b). With the addition of starch in LDPE, decomposition temperature of the blend film shifted towards a low temperature indicating that the degradation at 349 °C was due to decomposition of starch, however LDPE started to degrade at about 400 °C.

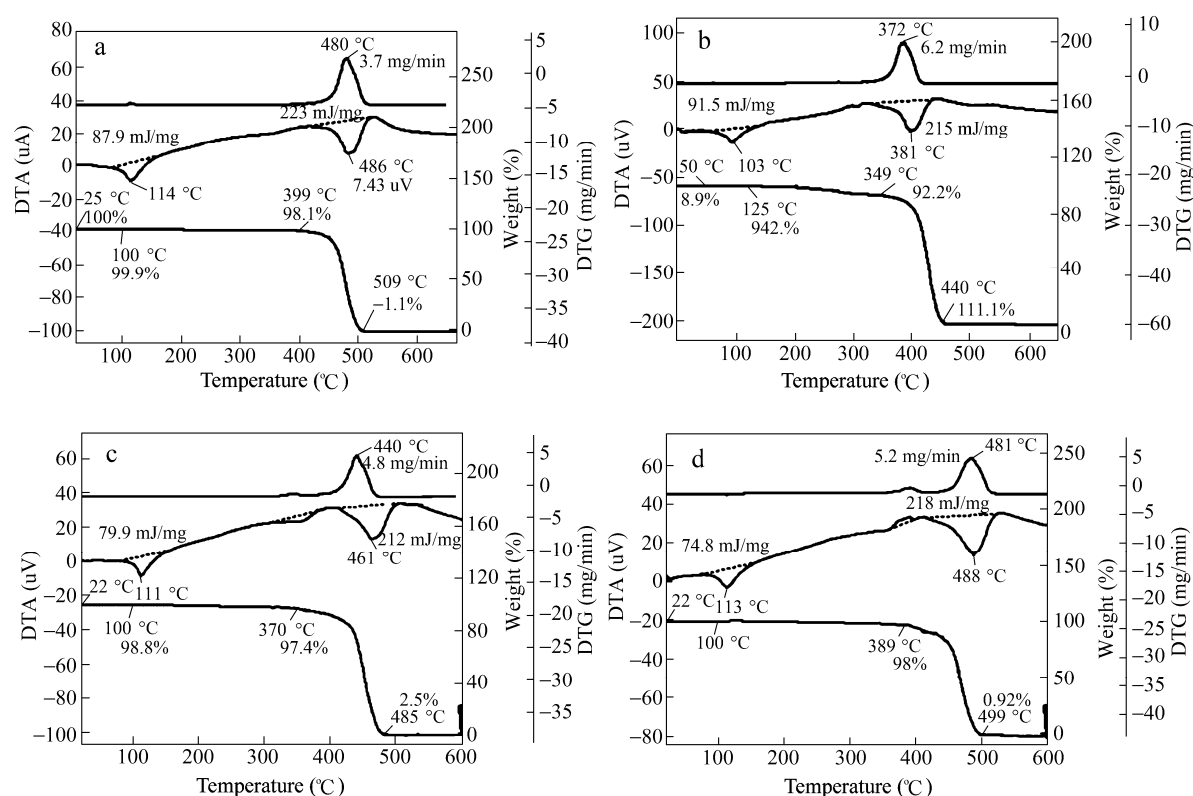


Fig. 3 TG-DTA studies of LDPE and LDPE-starch blend films: (a) LDPE film, (b) LDPE-native starch (LDPE-10 NS0.0), (c) LDPE-acetylated starch (LDPE-10 Ac2.55) and (d) LDPE-butyrylated starch (LDPE-10 Bu1.75) blend films

Certainly, the starch content affected the amount of weight loss of the blend films. Garg and Jana^[20] also observed that with increase in temperature from 250 °C to 350 °C, the thermal decomposition of starch took place with a weight loss of 83%. The main product of decomposition below 300 °C was formation of water by intermolecular or intra-molecular condensation of starch hydroxyls. At higher temperatures aromatic and even crosslinked structures were also formed^[29].

Blend films containing acylated starch also showed two-stage decomposition but the first stage weight loss due to dehydration of starch was less as compared to that of the native starch film. Films (LDPE-10 Ac2.55 and LDPE-10 Bu1.75) containing high DS acylated starch and LDPE film showed second stage decomposition at temperature ranges of 370–485 °C, 389–499 °C and 399–509 °C with a weight loss of 97%, 99% and 100%, respectively. Thus, TG data showed that acylated starch films decomposed at higher temperatures than native starch films.

DTA results of native starch blend film (LDPE-10 NS 0.0) exhibited two endothermic peaks with first one corresponding to loss of water at 103 °C, followed by second stage of decomposition at 381 °C (Fig. 3b). Acylated starch blend films (LDPE-10 Ac2.55; LDPE-10 Bu1.75) and LDPE film had endothermic decomposition at higher temperatures 461 °C, 488 °C and 486 °C, respectively.

DTG analysis of blend films showed that native starch blend film (LDPE-10 NS0.0) had decomposition at 372 °C with a rate of weight loss 6.2 mg/min. However, in acylated starch films and LDPE film decomposition was observed at higher temperatures with lower rate of weight loss. The acylated starch blend film samples were thermally more stable than native starch blend films. The increase in thermal stability with increase in DS was due to low amount of remaining hydroxyl groups in starch molecules after acylation. The increase in molecular weight and covalent bonding due to the acylation of hydroxyl groups were also responsible for the increased thermal stability^[30, 31].

Effects of acylation on the morphological properties of starch and blend films were analyzed by SEM. It was observed that the surface of the starch was eroded during acylation. This may be due to substitution of acyl groups in starch or may be due to swelling in pyridine. Increased roughness of starch increased the surface area for bonding and mechanical interlocking of starch and LDPE in blend films.

Surface morphology of LDPE film, and LDPE-starch blend films are shown in Fig. 4(a–f). LDPE film did not show any specific morphology, whereas 5% native starch blend film (LDPE-5 NS0.0) had surface cracks.

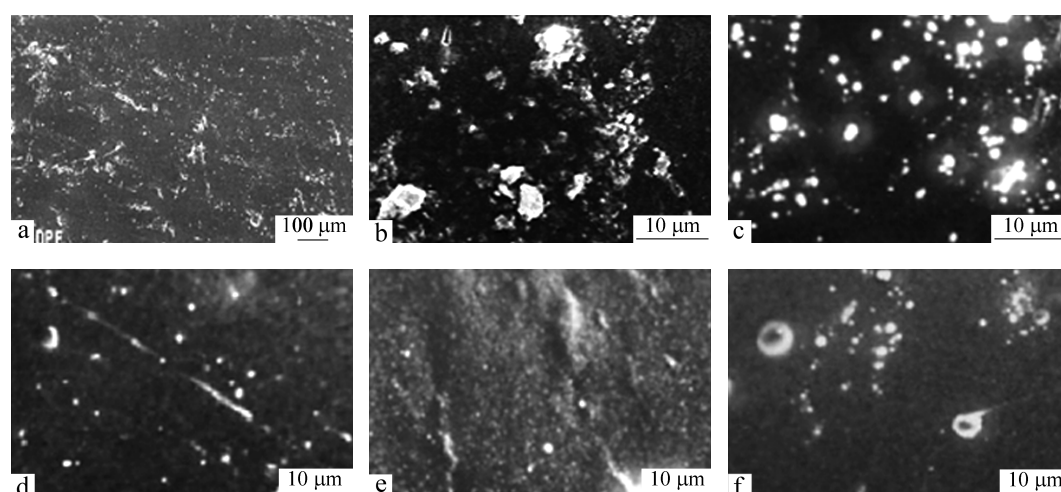


Fig. 4 SEM images of LDPE and LDPE-starch blend films: (a) LDPE, (b) LDPE-native starch (LDPE-5 NS0.0), (c) LDPE-acetylated starch (LDPE-5 Ac0.60), (d) LDPE-butyrylated starch (LDPE-5 Bu0.33), (e) LDPE-acetylated starch (LDPE-5 Ac2.55) and (f) LDPE-butyrylated starch (LDPE-5 Bu1.75) blend films

Surface roughness was because of poor compatibility between starch and LDPE matrix. However, blend films (LDPE-5 Ac0.60 and LDPE-5 Bu0.33) having low DS acetylated and butyrylated starches were smoother than the native starch blend film. Micrographs of blend films (LDPE-5 Ac2.55 and LDPE-5 Bu1.75) containing high DS acylated starch showed good dispersion of starch particles as compared to native starch blend film due to improvement in surface adhesion between starch and LDPE. Distribution of starch particles was uniform in the high DS blend film due to increased surface adhesion and reduction in size of the particles.

Water Absorption Capacity

Results of water absorption capacity of the blend films as a function of time are shown in Table 4. It was observed that water absorption capacity of 5% native starch blend films (LDPE-5 NS0.0) was 2.41% after one week and increased to 5% after six weeks. Water absorption capacity of low DS acetylated and butyrylated starch blend films (LDPE-5 Ac0.60 and LDPE-5 Bu0.33), was 7.92%, and 7.13%, respectively and was higher than that of the native starch film. With the increase in DS of acylated starch, water absorption capacity of the blend films decreased. For high DS acetylated and butyrylated starch blend films (LDPE-5 Ac2.55 and LDPE-5 Bu1.75), water absorption capacity decreased to 4.18% and 3.35%, respectively, and was lower than that of native starch blend film. Blend film (LDPE-5 Bu1.75) containing butyrylated starch of high DS had lower water absorption capacity of 3.35% as compared to acetylated starch blend films (LDPE-5 Ac2.55) because of enhanced hydrophobic transformation of starch^[32–34]. Water absorption capacity of low DS acetylated and butyrylated starch films (LDPE-5 Ac0.60 and LDPE-5 Bu0.33) was higher than that of the native starch 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 acyl groups. At high DS, water absorption capacity of the films decreased to below that of native starch blend film as acyl groups replaced most of the hydroxyl groups on starch and the interaction with water decreased.

Table 4. Water absorption capacity of LDPE-starch blend films

Contact time (weeks)	Water absorption capacity (%)				
	LDPE-5 NS0.0	LDPE-5 Ac0.60	LDPE-5 Bu0.33	LDPE-5 Ac2.55	LDPE-5 Bu1.75
0	0	0	0	0	0
1	2.41 ± 0.54	3.98 ± 0.34	3.14 ± 0.12	1.56 ± 0.62	1.13 ± 0.14
2	3.15 ± 0.46	5.47 ± 0.32	4.38 ± 0.23	2.24 ± 0.71	1.72 ± 0.22
3	3.96 ± 0.52	6.45 ± 0.67	5.8 ± 0.34	2.76 ± 0.32	2.13 ± 0.45
4	4.48 ± 0.34	7.34 ± 0.72	6.54 ± 0.24	3.35 ± 0.25	2.46 ± 0.52
5	5.0 ± 0.41	7.86 ± 0.54	7.01 ± 0.36	3.98 ± 0.53	3.15 ± 0.24
6	5.06 ± 0.44	7.92 ± 0.22	7.13 ± 0.56	4.18 ± 0.41	3.35 ± 0.42

Enzymatic and Soil Burial Degradation

Degradation of blend films was studied by weight loss due to enzyme mixture, weight loss due to soil burial, SEM and mechanical strength.

Weight loss of LDPE-starch blend films after 96 h of incubation in enzyme mixture at 37 °C was measured. It was observed that weight loss of native starch blend film (LDPE-10 NS0.0) was 8.18% after 24 h of incubation in enzyme and increased to 9.45% after 96 h. The degradation rate was maximum for starch as starch substrates were easily available to the enzyme. Starch particles which were at the surface of the film degraded at a faster rate as compared to other particles due to pore diffusion limitation of enzyme into film^[35]. Weight loss in the high DS acylated starch blend films (LDPE-10 Ac2.55 and LDPE-10 Bu1.75) was 1.76% and 2.56% after 24 h and increased to 2.28% and 3.11% after 96 h of incubation. The degradation of acylated starch in the blend film was lower as compared to native starch because of substitution of hydroxyl groups with acyl groups in starch and increased dispersion of starch molecules within the LDPE matrix.

Biodegradability of the samples in soil was studied by evaluating weight loss of films over a period of 180 days, and results are shown in Fig. 5. Results showed that of LDPE-starch blend films degraded at fast rate up to 45 days and after that the degradation rate decreased indicating that microorganism present in the soil

degraded the starch and caused a weight loss of the film samples^[36]. It was observed that the blend films containing acylated starch had lower weight loss compared to native starch blend films which showed that modification of the starch reduced biodegradability.

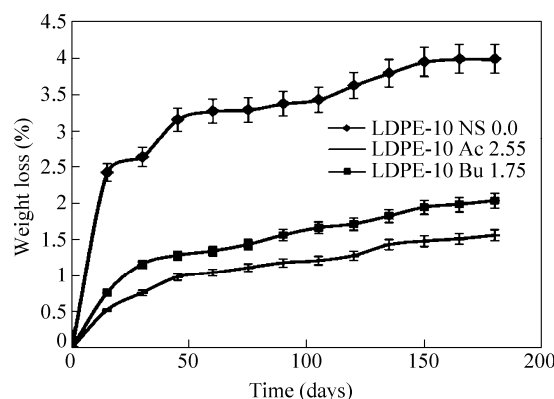


Fig. 5 Weight losses of LDPE-starch blend films during soil burial test

Scanning electron microscopy of the blend films was done to observe the change in surface structure of the film after biodegradation. The surface morphology of blend films containing 10% native, acetylated, and butyrylated starch (LDPE-10 NS0.0, LDPE-10 Ac2.55 and LDPE-10 Bu1.75) before and after soil burial test for 180 days is shown in Fig. 6. SEM micrographs showed holes appeared in the film indicating the degradation of starch by the microorganisms present in the soil.

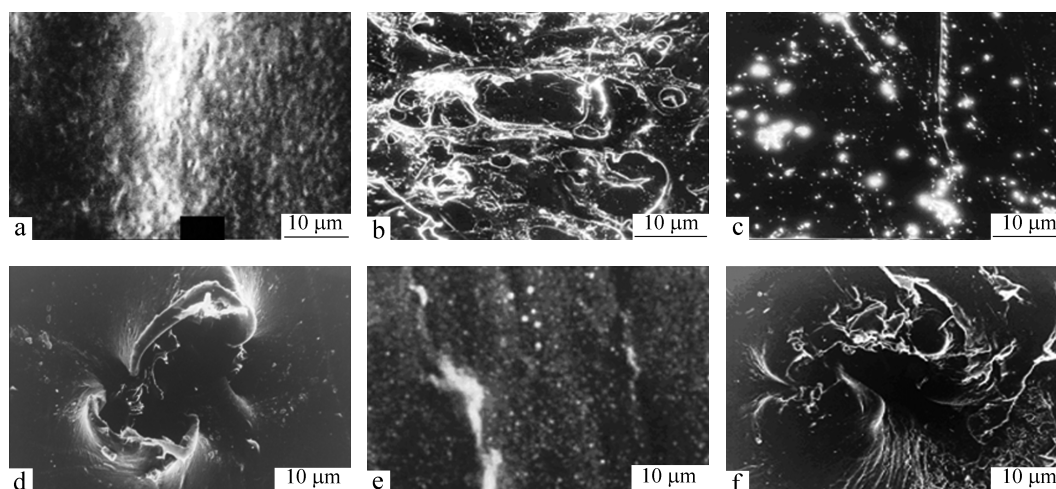


Fig. 6 SEM images of LDPE-starch blend films before (a, c, e) and after biodegradation (b, d, f): (a–b) LDPE-native starch (LDPE-10 NS0.0), (c–d) LDPE-acetylated starch (LDPE-10 Ac2.55) and (e–f) LDPE-butyrylated starch (LDPE-10 Bu1.75) blend films

The stress-strain curves of blend films containing 10% native, acetylated and butyrylated starch (LDPE-10 NS0.0, LDPE-10 Ac2.55 and LDPE-10 Bu1.75) before and after degradation are shown in Fig. 7. Results clearly showed that the mechanical strength of the blend films decreased after degradation in soil.

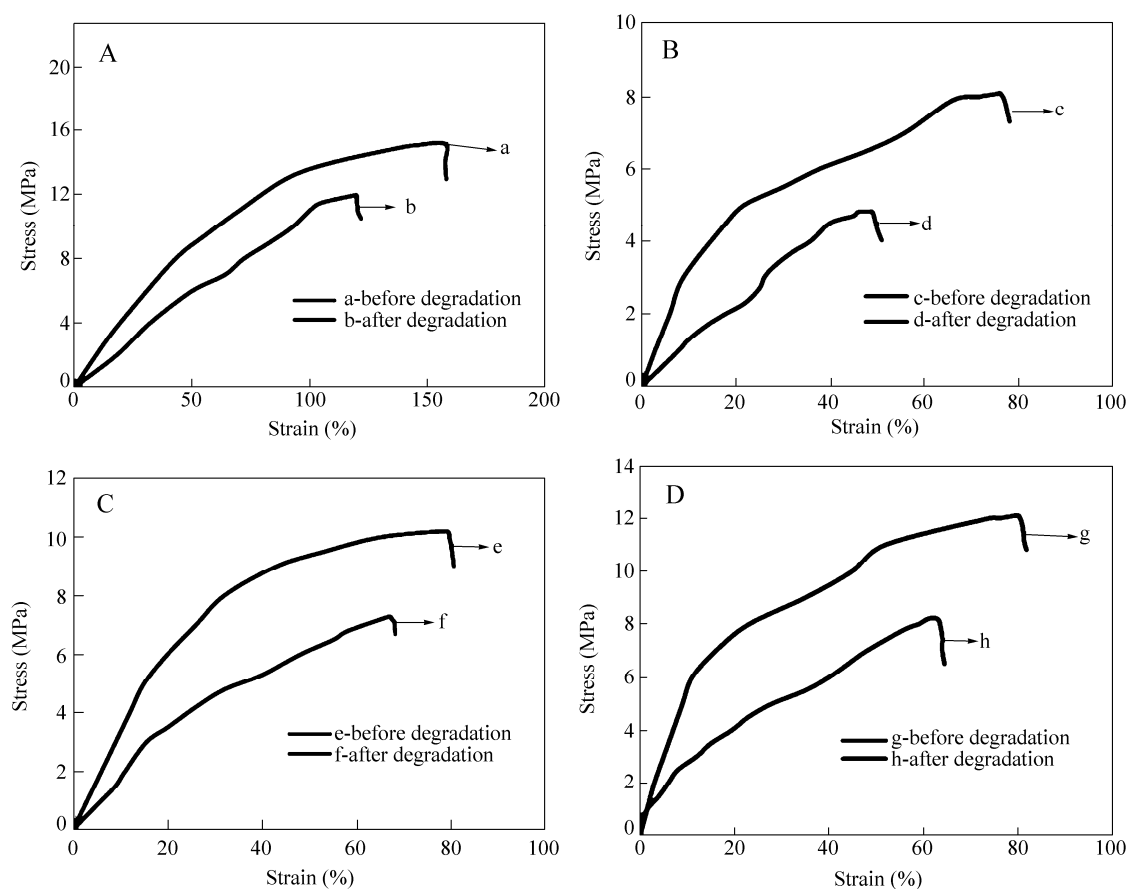


Fig. 7 Stress-strain curves of LDPE, LDPE-starch blend films before and after biodegradation: (A) LDPE, (B) LDPE-native starch (LDPE-10 NS0.0), (C) LDPE-acetylated starch (LDPE-10 Ac2.55) and (D) LDPE-butyrylated starch (LDPE-10 Bu1.75) blend films

Table 5. Properties of polymer-starch blends/films

Reference	Polymer-starch modification/composition of starch	Tensile strength (MPa)	Elongation (%)
Rodrigue <i>et al.</i> ^[1]	Low density polyethylene/thermoplastic starch/0–50% (blends)	11.8–9.8	482–400
Kiatkamjornwong <i>et al.</i> ^[2]	Low density polyethylene/cassava starch-g-poly (acrylic acid)/0–20% (blends)	8–8.2	–
Nakamura <i>et al.</i> ^[5]	Low density polyethylene/adipate starch/0–20% (blends)	13–11	132–33.7
Guohua <i>et al.</i> ^[6]	Poly(vinyl alcohol)/methylated starch/0–100% (blend films)	32–12	380–40
Thakore <i>et al.</i> ^[22]	Low density polyethylene/phthalic anhydride modified starch/0–30% (blends)	7.2–4.5	70–25
Aburto <i>et al.</i> ^[9]	Low density polyethylene/octanoated starch/0–30% (blends)	9.6–5.3	760–180
This study	Low density polyethylene/acetylated starch/0–10% (blown films)	15.2–10.2	158.2–78.9
This study	Low density polyethylene/butyrylated starch/0–10% (blown films)	15.2–12.1	158.2–80

Comparison with Earlier Studies

The comparison of properties of polymer-modified starch blends/films reported earlier with properties of blend films in present study is shown in Table 5. It has been observed that the most of the previous studies were done with the polymer-starch blends only. Very few studies have been reported with the blend films similar to our studies. Moreover, the results of the mechanical properties of the blend films reported earlier in the literature were based on preparation of cast films, where the starch concentration could be increased to large extent. But in our case we have prepared the blown films by using conventional commercial technique which has a potential to be integrated with the present manufacturing systems without any other requirement.

CONCLUSIONS

The LDPE-starch blend films containing acylated starch at high DS showed better properties than the native starch blend film. With the increase in chain length from acetyl to butyryl group, tensile strength, elongation and melt flow index increased by 11%, 4% and 14%, respectively at 5% starch in the blend. In films containing high DS ($DS > 2.5$ for acetylated, $DS > 1.7$ for butyrylated) acylated starches, water absorption capacity decreased to below that of the native starch blend film. This study has commercial significance because blend films were prepared by the conventional blow film technique.

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