

Natural Weather Ageing of the Low-Density Polyethylene: Effect of Polystarch N

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ABSTRACT: Blends of low-density polyethylene (LDPE) with Polystarch N were prepared by extrusion. Tensile properties, thermal behavior, and natural weathering of these blends were investigated as a function of blend composition. The addition of Polystarch N to the matrix decreased the tensile properties and the degree of crystallinity of LDPE when the proportion of Polystarch N increased in the blend, as revealed by differential scanning calorimetric studies. Scanning electron microscope analysis of the blends retrieved after being exposed to natural weathering showed that natural degradation increased with increase in the amount of Polystarch N in the LDPE and is ascribed to higher extent of chain scission as revealed by Fourier transform infrared spectroscopy analysis. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Low production cost, excellent mechanical properties, chemical, weather, and biodegradation resistance of polyolefin have resulted in a continuous increase in the production of commodity plastic products over the last several decades.¹ Service life of the plastic materials varies widely depending on the application areas and in the post-service stage the plastic materials are considered as waste. The current increase in the disposal of waste plastics demands for solutions to reduce the negative impact of the plastic wastages on the environment. Natural weather ageing of low-density polyethylene (LDPE) films under various climatic conditions has been reported earlier.^{2–4}

The degradation of polyethylene can be increased by adding carbonyl groups within the backbone or *in situ* generation of the carbonyl groups by pro-oxidants. Prodegradants included additives such as polyunsaturated compounds, transition metal ions and metal complexes, which rendered polyethylene susceptible to hydroperoxidation.⁵ Alternative way to enhance its degradation nature is the incorporation of biodegradable polymers such as starch to make it more susceptible to bacterial attacks.^{6–9} Shah et al.¹⁰ reported that the starch filled LDPE becomes brittle when it undergoes thermal oxidation.

The present communication reports the results of the natural weather ageing studies on blends of LDPE and Polystarch N, which consists of 45% linear low-density polyethylene (LLDPE) and 55% starch masterbatch. The mechanical, thermal, and degradability characteristics of LDPE have been studied as a function of Polystarch N loading. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to analyze the degradation characteristics of the blends.

EXPERIMENTAL

Materials

LDPE of film grade having density 0.92 g/cm³ obtained from SABIC, Saudi Arabia was used as received. Its tensile strength, Young's modulus, and elongation at break were reported as 27 MPa, 143 MPa, and 693%, respectively. Polystarch N used in this study was provided by Willow Ridge Company, Erlanger, Kentucky. It is a blend of 55% corn starch master batch and 45% LLDPE. The corn starch master batch includes processing aids and a desiccant, the exact proportions of which not being revealed.

Preparation of LDPE Blends

Film grade polyethylene pellets were premixed with varying amount of Polystarch N as given in Table I. The mixture was

Table I. Composition of the Prepared Polymer Samples

Sample code	LDPE (% w/w)	Polystarch N (% w/w)
LDPE	100	0
PN10	90	10
PN20	80	20
PN30	70	30
PN40	60	40
Polystarch N	0	100

then extruded using a Brabender single screw extruder (model 125-25HC) consisting of three heating sections and a die plate. The temperature of the three heating zones of the barrel was kept at 160°C, whereas the die section was set at 120°C. During the process, the screw speed was kept at 2.92 Hz. The extrudates obtained were compressed in a Carver press at 130°C for 5 min to obtain the films of 1 mm thickness.

Tensile Properties

The tensile properties of the dumbbell-shaped samples having thickness of 1 mm were measured at 25°C as per the ASTM D638 procedure using Instron UTM (Model 5560) at a cross-head speed of 20 mm/min. Five samples were tested in each experiment and the average value with standard deviation has been reported.

Differential Scanning Calorimetric (DSC) Analysis

The melting and crystallization behavior of the blends were determined by using differential scanning calorimeter, DSC-Q1000, Universal V4.2E TA Instruments. The first heating was done from a temperature of 20°C to 200°C at a rate of 10°C/min, in nitrogen atmosphere followed by isothermal heating for 5 min. First cooling and second heating were performed at 10°C/min in nitrogen atmosphere. Calibrations in DSC were done by measuring the temperature and the enthalpy of melting of indium. The crystallinity of the blends was calculated using the expression



Figure 1. Experimental set up for exposing the polymer samples in natural weathering condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Mechanical Properties of LDPE/Polystarch N Blends

Materials	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
LDPE	27.0 ± 0.6	143 ± 1.2	693 ± 7
PN10	22.3 ± 0.8	167 ± 2.8	594 ± 12
PN20	22.3 ± 1.0	165 ± 1.5	593 ± 9
PN30	23.0 ± 0.9	161 ± 2.3	587 ± 15
PN40	17.0 ± 1.2	187 ± 2.1	405 ± 18
Polystarch N	6.3 ± 0.6	98 ± 1.4	27 ± 2

$$\% \text{ of crystallinity} = \left(\frac{\Delta H_{fus}}{\Delta H_{fus}^0} \right) \times 100 \quad (1)$$

where ΔH_{fus} is the enthalpy of fusion of the LDPE-polystarch blend and ΔH_{fus}^0 is the enthalpy of fusion of the 100% crystalline LDPE. ΔH_{fus}^0 of LDPE was taken as 287.6 J/g.¹¹

Natural Weather Ageing

For the natural weather ageing studies, the blends were exposed to outdoor environment at the exposure site located in Dhahran, Saudi Arabia. The experimental set up used for this study is given in Figure 1. Films were fixed on plexiglass and oriented in a steel rack at 45° with respect to the base of the rack and facing to east to have the maximum amount of sunlight fall on the film at all time. The samples were withdrawn at regular intervals of time (i.e., 50, 95, and 120 days) and were tested.

Scanning Electron Microscopy

The surface of the LDPE and its blends were retrieved from outdoor sunlight exposure and the surface image examined under SEM JEOL (Model JSM 5800LV). Samples were coated with a thin layer of carbon using a carbon evaporator to avoid sample charging during imaging.

FTIR Analysis

The IR spectra were obtained using a NICOLET 6700 FTIR Spectrometer. The samples were ground with KBr and made into a pellet form and analyzed. Data were collected by averaging 32 scans, at a resolution of 4 cm⁻¹. IR spectra are presented in absorbance from 500 to 4500 cm⁻¹.

Table III. DSC Parameters for the LDPE/Polystarch N Blends

Materials	T_{cry} (°C)	ΔH_{cry} (J/g)	T_m (°C)	ΔH_{fus} (J/g)	% of crystallinity
LDPE	108	99	124	87	30
PN10	111	93	124	85	30
PN20	111	91	124	82	29
PN30	110	84	124	81	28
PN40	110	85	124	80	28
Polystarch N	109	48	122	41	14

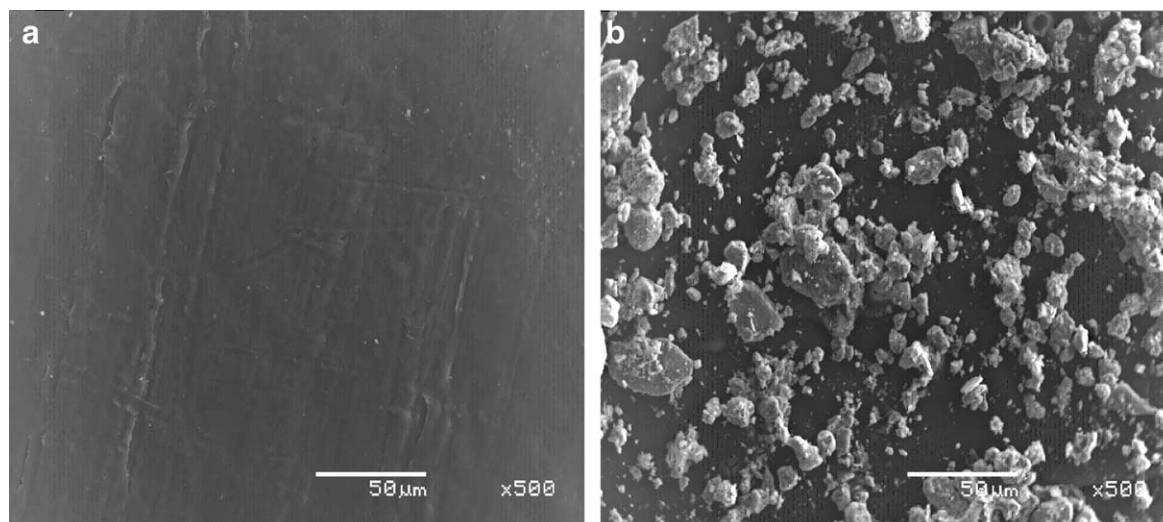


Figure 2. SEM micrographs of (a) LDPE after 50 days and (b) PN30 after 50 days.

RESULTS AND DISCUSSION

Blend Properties

Tensile Properties. Results of stress–strain measurements are given in Table II. It can be seen that incorporation of Polystarch N to the LDPE matrix increases the Young's modulus, but decreases the tensile strength and the elongation at break. The effect is pronounced in the case of blend PN40 showing fall in ductility at high loading of Polystarch N. This is believed to be due to incompatibility of the additives present in Polystarch N with LDPE. Nakamura et al.⁹ also observed fall in tensile strength in the case of LDPE/cassava starch blend. The increase in the modulus is due to the stiffening effect of the starch which is present in the Polystarch N.¹²

Differential Scanning Calorimeter (DSC). Table III summarizes the melting temperature (T_m), crystallization temperature (T_{cry}), heat of fusion (ΔH_{fus}), and heat of crystallization (ΔH_{cry}) of LDPE and its blends with Polystarch N. It is evident that the incorporation of Polystarch N does not influence the crystalliza-

tion and melting temperature of LDPE. Because the T_{cry} (109°C) and T_m (122°C) of Polystarch N are very close to that of LDPE, there is minor variation in the T_{cry} and T_m for the blends. However, the addition of the Polystarch N to the LDPE decreases its heat of fusion and crystallization. Polystarch N registers ΔH_{cry} as 48 J/g and ΔH_{fus} (41 J/g), which are lower than that of LDPE. The crystallinity was calculated per total amount of the sample. The proportion of LDPE in the blend decreases, as Polystarch N content increases in the blend, which results in gradual drop in crystallinity with increase of Polystarch N. Polystarch N alone registers crystallinity of 14%, which is expected since it consists of 45% LDPE and 55% corn starch master batch.

Natural Weather Ageing

SEM Analysis. The SEM images for the LDPE–Polystarch N blend (PN30) taken after exposure of 50, 95, and 120 days are presented in Figures 2–4, respectively. It is evident that LDPE can withstand the severe climatic conditions in Saudi Arabia

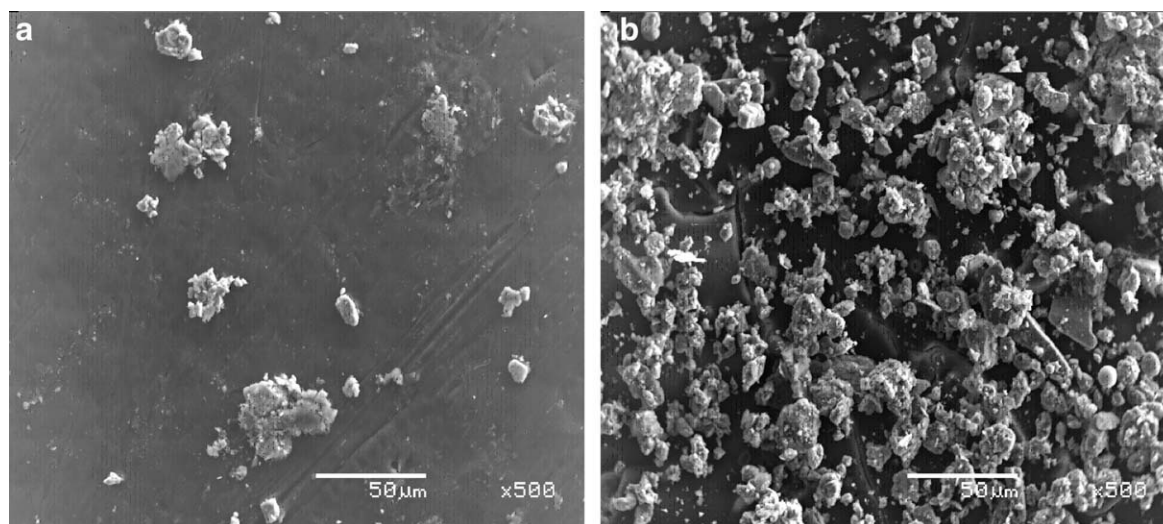


Figure 3. SEM micrographs of (a) LDPE after 95 days and (b) PN30 after 95 days.

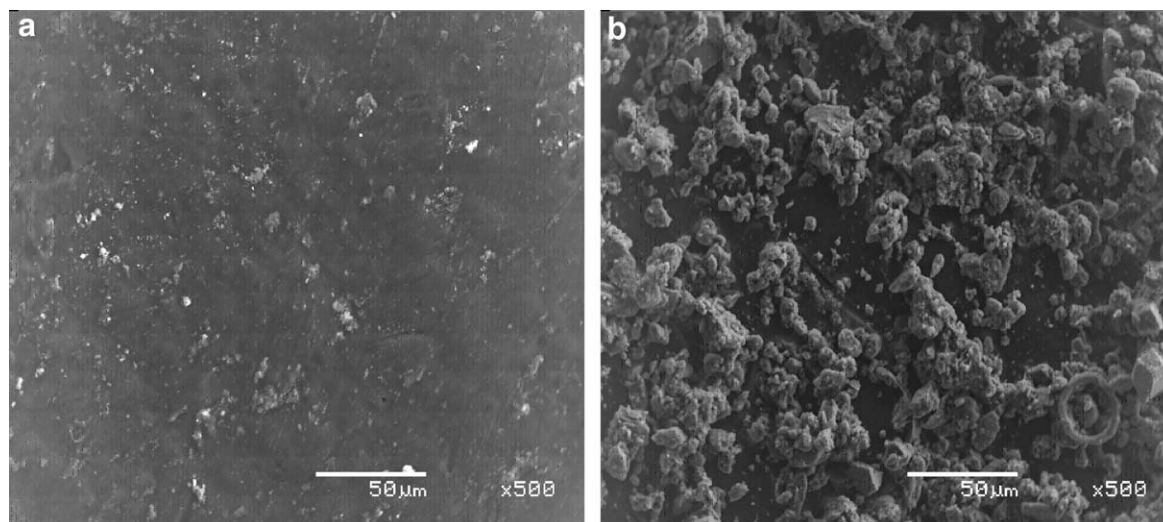


Figure 4. SEM micrograph of (a) LDPE after 120 days and (b) PN30 after 120 days.

which includes sand wind, high temperature, and humidity for more than 120 days. SEM photomicrographs of neat LDPE indicate minor changes on the surface topography. Natural weather ageing of polyethylene, such as exposure to sun, causes surface cracks without any surface debris as was seen in the case of control LDPE sample after 50 days of ageing. In the case of exposure of 95 days, small amount of debris found on the surface is due to the dust particles on to the polyethylene surfaces and this amount increases further at the exposure time of 120 days. The surface debris in the case of blends are proportional to both the ageing period and polystarch N content and are believed to be the additives present in Polystarch N, which leached out onto the LDPE surface. It is to be noted that Polystarch N is a 45/55 blend of LLDPE/corn starch masterbatch. The corn starch masterbatch contains undisclosed processing aids and desiccants and thereby letting down the corn starch level to about 25%.¹³ It is believed that the processing aids and desiccants in such proportions are not compatible with the

polymer matrix, which results in drop of the failure properties. Furthermore, the additives are likely to leach out from the LDPE matrix on prolonged ageing conditions. There are reports on migration of additives in polymers from the interior to the surface on prolong ageing.^{14,15} For short-term usage like trash bags, the leaching effect is unlikely to occur under ambient conditions. The effect of Polystarch N content in the blends with LDPE at fixed ageing period of 120 days is shown in Figure 5(a,b). It is evident that as the Polystarch N concentration increases, the surface debris also increases. In the case of PN40, the matrix becomes weak enough to become distorted on prolonged ageing along with the large amount of leached additives.

FTIR Analysis. FTIR spectra for the LDPE and PN30 before and after ageing of 95 days are given in Figure 6. Table IV summarizes the functional groups present in the LDPE and PN30 before and after ageing. For LDPE, before ageing the peaks were observed at 2917, 2843 cm^{-1} corresponding to the vibration

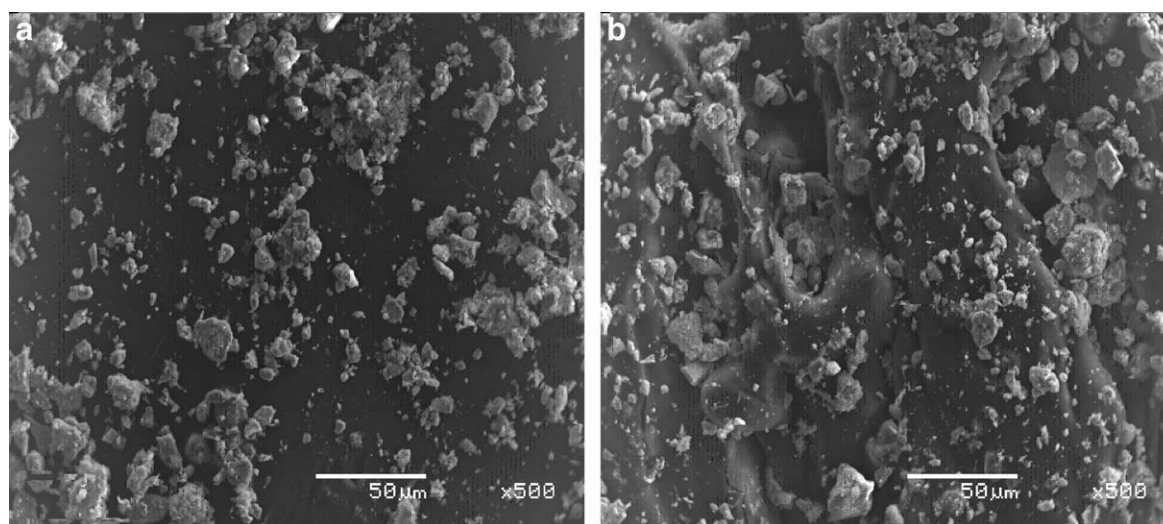


Figure 5. SEM micrograph of (a) PN10 after 50 days and (b) PN40 after 50 days.

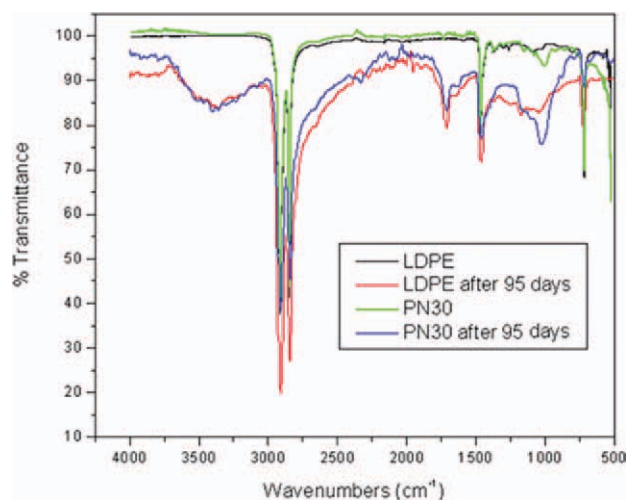


Figure 6. FTIR spectra for the LDPE and PN30 before and after ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mode of $-\text{CH}_2$ group. The peak at 1463 cm^{-1} corresponds to the scissoring vibration of CH_2 group.^{16,17} Peaks at 1031 and 729 cm^{-1} appear because of the $\text{C}-\text{C}$ stretching vibration due to the skeletal vibration of CH_2 groups. In the case of LDPE, after the degradation, prominent peaks were observed at 1715 cm^{-1} and 2276 cm^{-1} which represent the band vibration of the $\text{C}=\text{O}$ group and $\text{C}=\text{C}$, respectively. It is believed that exposure to the UV radiation causes reduction of the chain size and forms groups such as carbonyl, carboxyl, and hydroxyl. The intermediate products such as hydroperoxides, peroxides, alcohols, ketones, and some aldehydes resulting from the partial oxidation of LDPE are present in small amounts. The relative amount of some of these intermediate products varies depending on whether the oxidation has been initiated by UV radiation.^{18,19}

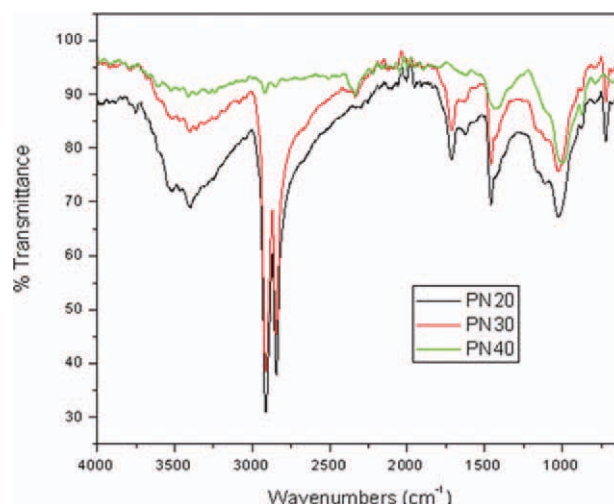


Figure 7. FTIR spectra for the PN20, PN30, and PN40 after 120 days of ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the blend PN30, a small peak was observed at 3600 cm^{-1} due to $-\text{OH}$ functional group. Peaks were also present at 1715 , 1463 , 1367 , 1150 , 1031 , and 997 cm^{-1} which correspond to the $\text{C}=\text{O}$, scissoring and skeletal vibration of $-\text{CH}_2$ group, $\text{C}-\text{O}-\text{C}$ vibration, $\text{C}-\text{C}$ and $\text{C}-\text{O}$ stretching vibrations, respectively. On comparison of the LDPE (exposed to 95 days) with the PN30 (also exposed to 95 days), it can be seen that the intensity for the peak appearing at 1031 cm^{-1} becomes broader and stronger indicating preponderance of $\text{C}-\text{C}$ stretching. The UV radiation from sunlight can lead to reactions with oxygen in air and scission of chains.⁴ As the amount of Polystarch N increases, the degradation of the blend increases. This is also evident from Figure 7, which displays the FTIR of blends after 120 days of ageing. Here, the prominent decrease was observed

Table IV. Summary of the Functional Groups Present in the LDPE and PN30 Before and After Ageing

Wave number (cm^{-1})	LDPE		PN30	
	Before ageing	After ageing of 95 days	Before ageing	After ageing of 95 days
3600-300	NA ^a	$-\text{OH}$ stretching vibrations	$-\text{OH}$ stretching vibrations	$-\text{OH}$ stretching vibrations
2915, 2842	$-\text{CH}_2$ vibrations	$-\text{CH}_2$ vibrations	$-\text{CH}_2$ vibrations	$-\text{CH}_2$ vibrations
2276	NA	$\text{C}=\text{C}$ stretching vibrations	NA	$\text{C}=\text{C}$ stretching vibrations
1715	NA	Prominent peak due to $\text{C}=\text{O}$ stretching vibrations	Prominent peak due to $\text{C}=\text{O}$ stretching vibrations	Prominent peak due to $\text{C}=\text{O}$ stretching vibrations
1463	Scissoring vibration of CH_2 group	Scissoring vibration of CH_2 group	Scissoring vibration of CH_2 group	Scissoring vibration of CH_2 group
1367, 729	Skeletal vibration of $-\text{CH}_2$	Skeletal vibration of $-\text{CH}_2$	Skeletal vibration of $-\text{CH}_2$	Skeletal vibration of $-\text{CH}_2$
1150	NA	$\text{C}-\text{O}-\text{C}$ vibrations in esters	$\text{C}-\text{O}-\text{C}$ vibrations in esters	$\text{C}-\text{O}-\text{C}$ vibrations in esters
1031	$\text{C}-\text{C}$ stretching	$\text{C}-\text{C}$ stretching	$\text{C}-\text{C}$ stretching	$\text{C}-\text{C}$ stretching
997	NA	NA	$\text{C}-\text{O}$ stretching vibrations	$\text{C}-\text{O}$ stretching vibrations

^aNot available/not applicable.

for the peak at 3600–3300 cm^{-1} which represents the —OH stretching vibrations. Moreover, for the blend PN40, the intensity of the peak at 2915, 2842, 1715, and 1463 cm^{-1} decreases, whereas there is an increase at peak 1031 cm^{-1} .

CONCLUSIONS

Higher proportion of Polystarch N in 90/10, 80/20, 70/30, and 60/40 w/w LDPE/Polystarch N blends causes drastic fall in mechanical properties. During ageing under natural weathering conditions, neat LDPE film shows no change after 50 days. Surface debris, as observed in the SEM photomicrographs on aged neat LDPE at longer ageing periods, are believed to be due to embedded sand particles. In the case of 70/30 LDPE/Polystarch N blend, the additives and starch present in the Polystarch N masterbatch, leach out from the interior and appear as surface debris along with the embedded sand particles. It was also observed that the surface debris content at a fixed ageing period is proportional to the Polystarch N content in the blend. Furthermore, at a fixed Polystarch N content, the proportion of surface debris increases with ageing period. The incompatibility between Polystarch N and LDPE and leaching out of both additives and starch in Polystarch N on the film surface makes the LDPE more accessible to sunlight and photo-oxidative degradation.

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