

Natural Weather, Soil Burial and Sea Water Ageing of Low-Density Polyethylene: Effect of Starch/Linear Low-Density Polyethylene Masterbatch

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ABSTRACT: Degradation of the blends of low-density polyethylene (LDPE) with a starch-based additive namely, polystarch N was studied under various environmental conditions such as natural weather, soil and sea water in Saudi Arabia. Stress-strain properties and thermal behavior were investigated for the LDPE and LDPE/polystarch N blend having 40% (w/w) of polystarch N. Environmental ageing resulted in the reduction of percentage of elongation and crystallinity for the blend. Rheological studies and scanning electron microscope photomicrographs of the polymer samples retrieved after ageing showed that addition of polystarch N enhanced the degradation of LDPE. This is ascribed to high extent of chain scission and leaching out of starch present in polystarch N, which was corroborated by the results of morphology and Fourier transform infrared spectroscopy analyses. In the case of underground soil ageing, microbes present in the soil consume the starch in the blend, thus accelerating the degradation process. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

In the last few decades, the usage of plastics for packaging applications increased many-fold because of its easy processability, light weight, low cost, good resistance to chemicals and microorganisms, and high mechanical properties.¹ Careless dumping of plastics in land-fills and sea water has long term adverse effects on the environment, human beings and marine life. There are reports on the modification of plastics especially polyolefin to make it more susceptible to degradation.^{2–5}

Since natural polymers such as starch are susceptible to bacterial attack, blending of polyethylene with starch makes polyethylene prone to natural degradation.^{6–15} Majid et al.¹⁰ studied the effect of natural weathering on LDPE/thermoplastic sago starch blends with and without polyethylene grafted maleic anhydride (PE-g-MA) as compatibilizer. They observed that both tensile strength and elongation at break decreased with weathering time for both compatibilized and uncompatibilized blends.

Garg et al.¹² showed that enzymatic and soil burial degradation of starch/low-density polyethylene (LDPE) blend increased with increase in the starch content but decreased with increase in the amount of modified starch. Gupta et al.¹³ studied the biodegradation of the blends of LDPE and a natural gum (baheda gum, *terminalia bellirica*). They found decrease in tensile properties in these LDPE blends on soil burial test. Scanning electron microscope (SEM) analysis showed the formation of fungus colony during the biodegradation of the blends. Danjaji et al.¹⁴ studied the degradation of starch filled polyethylene under soil and natural weathering conditions. Natural weathering resulted in an increase in the brittleness and dimensional changes. Oxidative degradation of the blend of oxo-degradable LDPE with thermoplastic starch under UV radiation was studied by Raquez et al.¹⁵ They reported an initial increase in the crystallinity of the LDPE till 13 weeks, beyond which it decreases. Shah et al.¹⁶ conducted accelerated degradation of starch filled LDPE under various laboratory conditions. Kyrikou et al.¹⁷ studied the

photochemical degradation of linear low-density polyethylene (LLDPE) film with Ciba Envirocare AG100 as pro-oxidant. They reported chain scission as well as crosslinking in the polymer matrix. They also observed increase in crystallinity in the polymer during photodegradation. While studying outdoor weathering of LDPE films, Al-Madfa et al.¹⁸ observed degradation by oxidation and crosslinking, depending on the exposure time. Baum and White¹⁹ proposed that initial formation of hydroperoxide is followed by chain splitting and recombination of free radicals leading to crosslinking in polyethylene during ageing.

Khoramnejadian²⁰ studied the water absorption and biodegradation of blends of polyethylene and potato starch. They observed that as the content of potato starch increased, the rate of water absorption as well as the biodegradation increased. Derraik²¹ reviewed the pollution of the marine environment by plastics debris and urged for further research in the area. Andrady et al.²² reported that the lower extent of degradation in marine exposure as compared to outdoor weathering is believed to be due to lower sea water temperature and lower extent of solar radiation reaching the polymer surface. Andrady²³ emphasized the importance of plastic pollution of the oceans with special reference to the ecological impacts of plastics debris and microplastics, formed by weathering-induced fracturing and surface embrittlement of plastics in the ocean beach.

Literature survey shows that there are scanty reports on the ageing behavior of LDPE under natural weathering, soil burial and sea water environments. The present investigation was undertaken to fill in the gap. The article reports the results of studies on the effect of a starch-based additive, namely polystarch N on LDPE, under natural weathering, soil burial and sea water ageing. Polystarch N is a masterbatch of corn starch and LLDPE in the ratio 45/55 and was obtained from Willow Ridge Plastics, KY.²⁴ The investigations include the mechanical and thermal properties along with Fourier transform infrared spectroscopic (FTIR) and SEM studies.

EXPERIMENTAL

Materials

LDPE ($M_w = 92,740$; MFI = 2 g/10 min), having a density of 0.92 g/cm³, was obtained from Exxon Mobil Chemicals, Belgium. Polystarch N is a masterbatch of corn starch and LLDPE in the ratio 45/55 and was obtained from Willow Ridge Plastics, Kentucky, USA. The masterbatch also includes undisclosed processing aid and 3–10% levels of a desiccant.²⁴ It was observed that high loading of starch in polystarch N makes it difficult to process and mould the samples for mechanical and other tests.

Blend Preparation

LDPE was blended with polystarch N in a Brabender Plasticorder (Mixer 50E) at 140°C for 10 min. Mixing speed was set at 60 rpm. The extrudates were taken out from the mixer and compressed in a Carver press at 140°C for 5 min to get a sheet having thickness of 2 mm. The amount of polystarch N in its blend with LDPE was 40% (w/w).

The loading of 40% (w/w) was chosen on the basis of suggestions made by the supplier.²⁴ The designations used in this study, PSN,

NA, SB, and SW stand for polystarch N, natural weather ageing, soil burial ageing, and sea water ageing, respectively.

Ageing Studies

For the natural weather ageing studies, the blends were exposed to outdoor environments at the exposure site located in Dhahran, Saudi Arabia. LDPE and LDPE/polystarch N sheets were fixed on a steel rack at 45° with respect to the base of the rack fixed on the roof top of a seven storeyed building at King Fahd University of Petroleum and Minerals campus (KFUPM), Dhahran and facing to east to have the maximum exposure to sunlight. For the soil burial test, the samples were buried under soil in a vegetable garden at KFUPM at a depth of 0.5 m. For the ageing in sea water, the samples were immersed at a depth of 1 m from the surface. In the Arabian Gulf, Dhahran, Saudi Arabia (Latitude: 26° 17' 0" N, Longitude: 50° 12' 0" E), the polymer sheets were exposed for 4 months from October 2011 onward and the temperature and humidity during these periods varied from 42 to 10°C and 70 to 54%, respectively. After 120 days of ageing, the samples were taken out, cleaned with distilled water and dried in an air oven at a temperature of 30°C.

Tensile Properties

The tensile properties of the dumbbell-shaped samples were measured at 25°C as per the ASTM D638 procedure using Instron UTM (Model 5560) at a crosshead speed of 50 mm/min. Five samples were tested in each experiment and the average value has been reported.

DSC Analysis

The melting and crystallization behavior of LDPE and LDPE/polystarch N blend were determined by using DSC-Q1000, Universal V4.2E TA Instruments. Heating and cooling for both first and second cycles were done in nitrogen atmosphere at the rate of 10°C/min from 20°C to 180°C. The crystallinity of LDPE and the blends was calculated using the expression

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

where ΔH_{fus} is the enthalpy of fusion of the LDPE-polystarch N 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.²⁵

Rheological Analysis

Dynamic viscosity of LDPE and LDPE/polystarch N blend were determined by using an advanced rheometrics expansion system (ARES). The measurements were carried out at 10 Hz, using cone and plate geometry (25-mm diameter and 0.1 rad cone angle) at 150°C in nitrogen atmosphere. Frequency sweeps with an angular velocity of 0.1–100 rad/s were performed in the linear viscoelastic regime at a strain of 10%. The samples were left to equilibrate for 5 min prior to each measurement.

FTIR Analysis

The IR spectra were obtained using a NICOLET 6700 FT-IR Spectrometer. Data were collected by averaging 32 scans, at a resolution of 4 cm⁻¹. FTIR spectra were presented in absorbance from 500 to 4500 cm⁻¹.

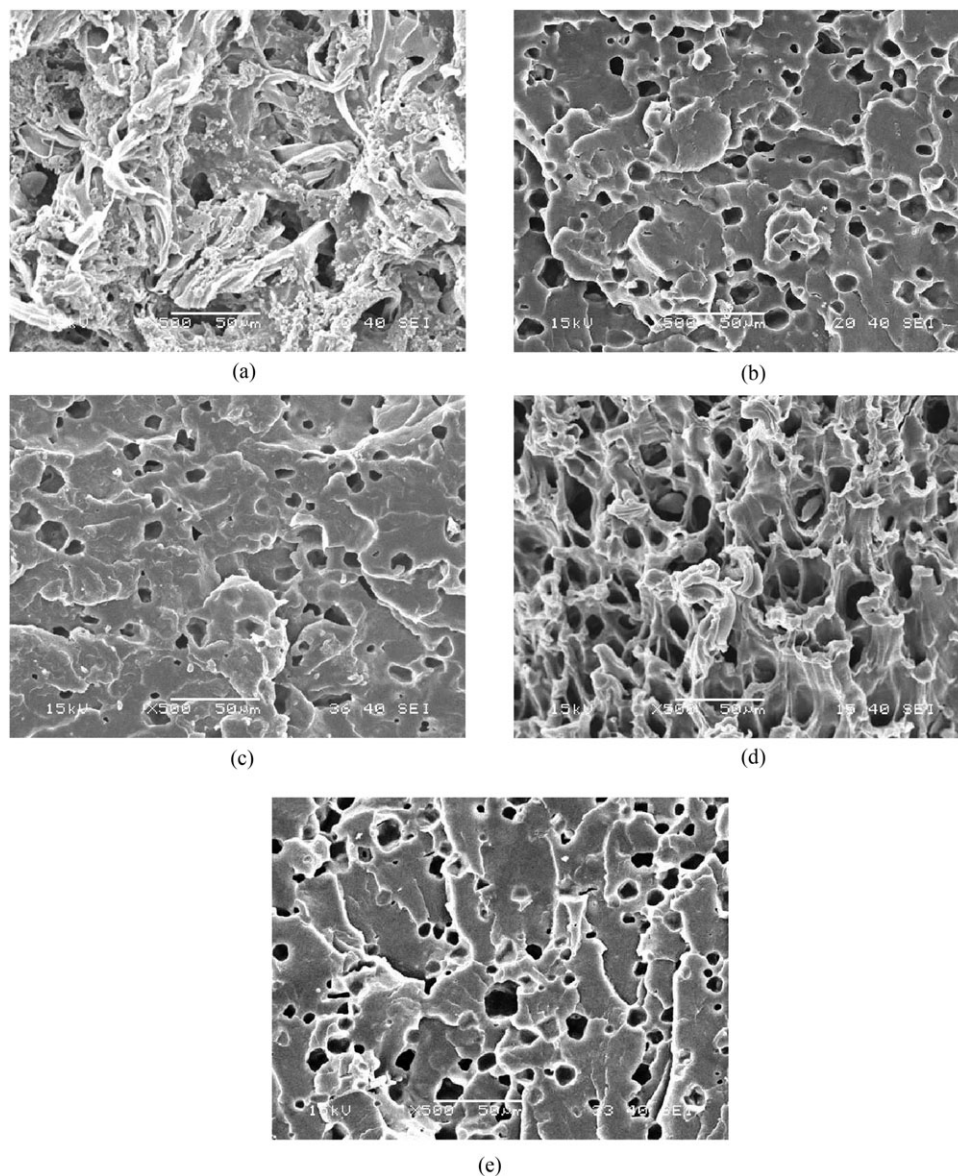


Figure 1. (a–e) Cryo-fracture SEM of PSN, before ageing (a), LDPE/PSN blends before and after ageing, (b) unaged, (c) natural weather, (d) soil burial, and (e) sea water.

Scanning Electron Microscopy

The surfaces of the LDPE and its blend with polystarch N, both before ageing and retrieved after ageing, were examined under SEM JEOL (Model JSM 5800LV).

Blend Morphology

To study the morphology of polystarch N and LDPE/polystarch N blends, the samples were subjected to cryogenic fracture followed by treatment in hot water at 80°C for 6 h to etch out the starch phase. Samples were coated with a thin layer of gold to avoid sample charging during imaging and then examined under SEM.

RESULTS AND DISCUSSION

The SEM photomicrographs of the cryo-fractured hot-water-etched polystarch N, and LDPE/polystarch N blend, namely

PSN40 are shown in Figure 1(a–e). Figure 1(a) displays the morphology of the polystarch N alone. Because of the removal of starch on hot water etching, the morphology looks porous along with extensive vacant sites, previously occupied by starch. Figure 1(b) shows the morphology of the unaged LDPE/polystarch N blend sample. The holes show the portion occupied by starch prior to hot water etching indicating uniform distribution of polystarch N in LDPE. Figure 1(c) stands for the morphology of the blend after the natural weather ageing indicating no change in the morphology. Figure 1(d) shows the morphology of the blend after soil burial and it is apparent that the number of holes has increased and they are interconnected in some regions, signifying that the microorganisms in the soil have consumed the starch present in polystarch N, thus increasing the degradation of the polymer after soil burial.²⁶ Huang et al.²⁷ reported that during soil burial, the starch phase

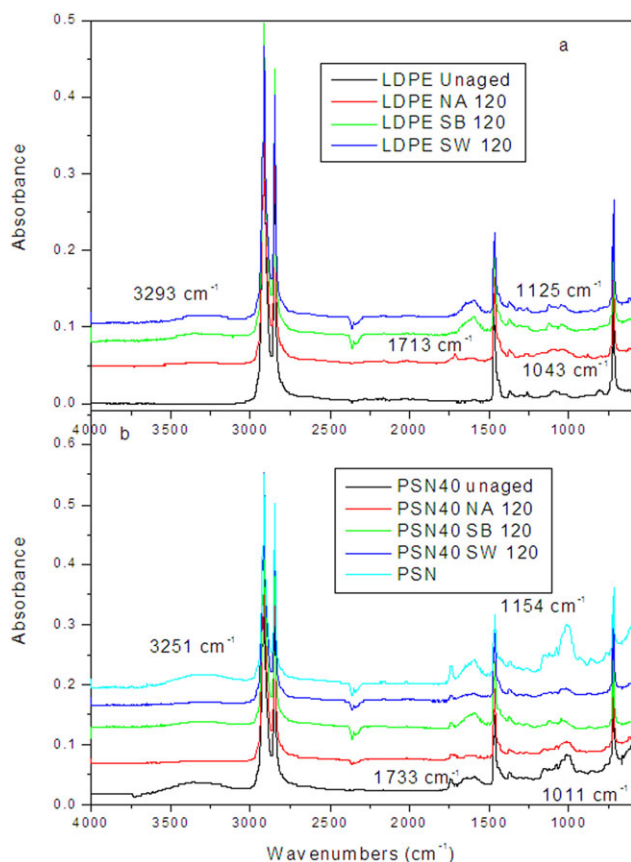


Figure 2. FTIR spectra of LDPE (a) and LDPE/PSN blends (b) before and after natural, soil burial, and sea water ageing (NA, SB, and SW stand for natural weather aged, soil burial aged, and sea water aged). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the blend undergoes degradation very fast. Figure 1(e) stands for the morphology of sea water aged blend samples. Figure 1(e) is similar to Figure 1(b), indicating no changes in morphology of the blend on sea water ageing.

Figure 2 shows the FTIR spectra of LDPE and the blend PSN40 before and after ageing for 120 days under various environmental conditions and the results are summarized in Table I. The table also shows the FTIR results of polystarch N alone. It is apparent that the most of the peaks of polystarch N are also observed in the spectra of LDPE and in the blend. For LDPE, before ageing the peaks were observed at 2917, 2843 cm^{-1} corresponding to the vibration mode of $-\text{CH}_2-$ group. The peak at 1460–1470 cm^{-1} corresponds to the $-\text{CH}_2$ bending deformation. Peaks in the region 730–715 cm^{-1} represent the C–H rocking in LDPE. After natural weather ageing new peaks were observed at 1715, 1125, and 1043 cm^{-1} due to the presence of carbonyl group, $-\text{C}-\text{O}-\text{C}-$ and vibration of CH_2-O group,²⁸ thus indicating the presence of oxidized products.²⁹ However, after soil burial and sea water ageing, the peak in the region 3000–3300 cm^{-1} which corresponds to $-\text{OH}$ appears and the carbonyl peak merges with the peak (1594 cm^{-1}) representing the adsorbed water and a new peak can be seen at 1043 cm^{-1} . These results suggest that LDPE when kept under natural

weather ageing had undergone higher degradation as compared to soil burial and sea water ageing. For the blend PSN40, peaks were observed at 3000–3400 cm^{-1} due to $-\text{OH}$ functional group. The peaks corresponding to the vibration mode of $-\text{CH}_2$ group (2915 and 2847 cm^{-1}), $\text{C}=\text{O}$ (1739 cm^{-1}), adsorbed water (1591 cm^{-1}), $-\text{CH}_2$ bending deformation (1471, 1461 cm^{-1}), skeletal vibration of $-\text{CH}_2$ group (1377 cm^{-1}), $\text{C}-\text{O}-\text{C}$ vibration (1151 cm^{-1}), $\text{C}-\text{O}-\text{H}$ stretching vibration (1077 cm^{-1}) $\text{C}-\text{C}$ (1016 cm^{-1}) and $\text{C}-\text{H}$ rocking vibrations (730–715 cm^{-1}) can be seen in the LDPE/polystarch N blend. After ageing, the intensity of the peaks at 3000–3400 cm^{-1} region, 1590 cm^{-1} and 1017 cm^{-1} which are the characteristics of polystarch N decrease due to the leaching out of polystarch N from the blend.

Figure 3 represents the DSC heating curves for LDPE and the blend (PSN40) before and after ageing of 120 days under various environmental conditions. The DSC heating curve for polystarch alone is also shown in the Figure 3. The melting peak occurring at 120°C is due to the LLDPE component in polystarch N. For the blends two peaks can be seen. The first peak at 106°C corresponds to the melting of LDPE while the minor second peak occurring at 115°C is due to melting of LLDPE present in polystarch N. The T_m values are not affected by the presence of polystarch N as well as the degradation environments. However, significant variation can be seen in the ΔH_{fus} and percentage of crystallinity of LDPE and its blend with polystarch N after ageing, as summarized in Table II. The crystallinity of LDPE remains unchanged under natural weather ageing, but increased from 38 to 43% after soil burial and sea water ageing, the reasons for which are not understood.¹⁷ Martelli et al.³⁰ reported an increase in the % crystallinity of LDPE after soil burial of 120 days. The presence of polystarch N in the LDPE decreases the crystallinity of the LDPE especially after natural weather ageing. This indicates that during natural weather ageing the chain scission is higher as compared to soil burial and sea water ageing due to the formation of oxidized products.³¹ Andrady et al.²² have observed lower extent of degradation in marine exposure as compared to outdoor weathering and attributed the changes to lower sea water temperature and to shielding from light-induced surface fouling in samples exposed to floating in sea water. Torikai et al.³² also reported that small amount of oxidation products in polyethylene which is generated during ageing can increase the chain scission resulting in a decrease of crystallinity.

Figure 4(a,b) shows the stress–strain plots for the LDPE and its blend with polystarch N before and after ageing of 120 days under various environmental conditions. After ageing there are no significant changes in the stress–strain curves of the LDPE. However, in the case of the blend, ageing changed the nature of the stress–strain curves. For the blend, on ageing no yielding was observed and the strain decreased abruptly especially after natural weather ageing. This decrease is attributed to the formation of free radicals due to the presence of light and oxygen which increases the crosslinking and chain scission.^{18,33} In natural weather ageing, the presence of sand wind also causes erosion of the polystarch N from the surface of the blend thus exposing LDPE bulk towards natural weather ageing.

Table 1. FTIR Results of Polystarch N, Polyethylene, LDPE/PSN Blends Before and After Ageing of 120 Days

Wave number (cm ⁻¹)	Unaged		Natural weather ageing		Soil burial		Sea water ageing		
	LDPE	PSN40 ^a	LDPE	PSN40	LDPE	PSN40	LDPE	PSN40	
-OH stretching vibrations	NA ^b	3000-3300 (s)	3000-3350 (w)	3000-3300 (w)	3000-3400 (w)	3000-3300 (w)	3000-3400 (w)	3000-3300 (w)	3000-3400 (m)
-CH ₂ vibrations	2915, 2847 (s)	2915, 2847 (s)	2909, 2847 (s)	2915, 2847 (s)	2911, 2847 (s)	2915, 2847 (s)	2913, 2847 (s)	2915, 2847 (s)	2915, 2847 (s)
-C=O Stretching Vibrations	NA ^b	1739 (m)	1713 (m)	1733 (m)	NA ^b	1738 (m)	NA ^b	1738 (m)	1738 (m)
Adsorbed -OH	NA ^b	1590 (m)	NA ^b	NA ^b	1598 (m)	1594 (m)	1594 (m)	1594 (m)	1594 (m)
-CH ₂ bending deformation	1471, 1462 (s)	1471, 1462 (s)	1471, 1462 (s)	1471, 1461 (s)	1471, 1462 (s)	1471, 1461 (s)	1471, 1462 (s)	1471, 1465 (s)	1471, 1462 (s)
Symmetrical bending -CH ₃	1376 (w)	1377 (w)	1376 (w)	1376 (w)	1376 (w)	1378 (w)	1376 (w)	1376 (w)	1377 (w)
C-O-C Stretching	NA ^b	1151 (w)	1125 (m)	1154 (w)	1122 (m)	1151 (w)	1123 (m)	1153 (w)	1151 (m)
C-O-H stretching	NA ^b	1077 (w)	NA ^b	NA ^b	NA ^b	1077 (w)	NA ^b	NA ^b	1077
C-C stretching	NA ^b	1016 (m)	1043 (w)	1011 (w)	1043 (w)	1016 (w)	1043 (w)	1017 (w)	1017 (w)
C-H rocking, crystalline in -CH ₂	729 (s)	729 (s)	729 (s)	729 (s)	729 (s)	729 (s)	729 (s)	729 (s)	729 (s)
C-H rocking, amorphous -CH ₂	718 (s)	718 (s)	718 (s)	716 (s)	718 (s)	716 (s)	718 (s)	716 (s)	719 (s)

^a'w', 'm', and 's' represents weak, medium, and strong, respectively.

^bContains 40% w/w of polystarch N in LDPE. ^cNot available/not applicable.

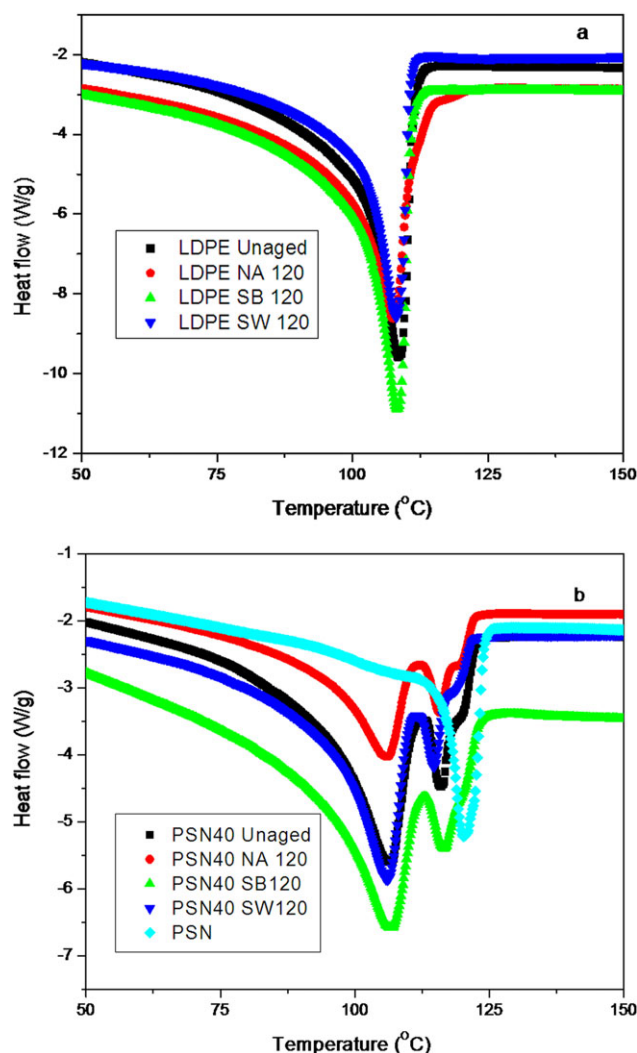


Figure 3. DSC heating curves of LDPE (a) and LDPE/PSN blends (b) before and after natural, soil burial, and sea water ageing (NA, SB, and SW stand for natural weather aged, soil burial aged, and sea water aged). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Al-Madfa¹⁸ reported occurrence of both oxidation and cross-linking during outdoor exposure of polyethylene films. They also reported that the ductility decreased as the extent of cross-linking increased. Danjaji et al.¹⁴ observed a decrease in the percentage of elongation for the starch filled polyethylene, when kept in natural weathering and soil burial.

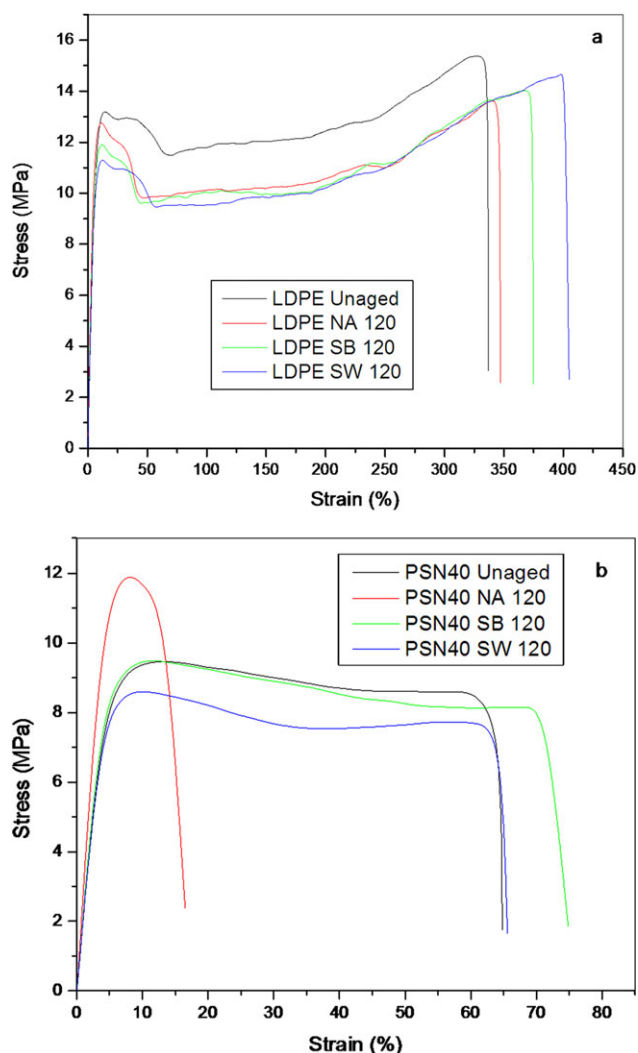


Figure 4. (a, b) Stress–strain plots of LDPE and LDPE/PSN blends before and after ageing (NA, SB, and SW stand for natural weather aged, soil burial aged, and sea water aged). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the case of sea water ageing, the degradation depends upon the temperature, salinity, pH, microbial population, and the dissolved amount of oxygen.³⁴ Exposure of the samples to oxygen and sunlight is less in sea water than that in natural weather ageing condition. The deficiency of oxygen at the reaction site can lead to the formation of peroxide crosslinks due to the presence of free radicals produced during ageing.³⁵ Absorbance of

Table II. DSC Parameters of LDPE and PSN40 Blends Before and After Natural, Soil Burial, and Sea Water Ageing for 120 Days

Materials	T_m (°C)								ΔH_{fus} (J/g)				Crystallinity (%)			
	Unaged		Natural ageing		Soil burial		Sea water		Unaged	Natural ageing	Soil burial	Sea water	Unaged	Natural ageing	Soil burial	Sea water
	T_{m1}	T_{m2}	T_{m1}	T_{m2}	T_{m1}	T_{m2}	T_{m1}	T_{m2}								
LDPE	108	-	107	-	108	-	108	-	110	108	123	123	38	38	43	43
PSN40	106	115	106	115	106	115	106	115	94	65	77	97	33	23	27	34

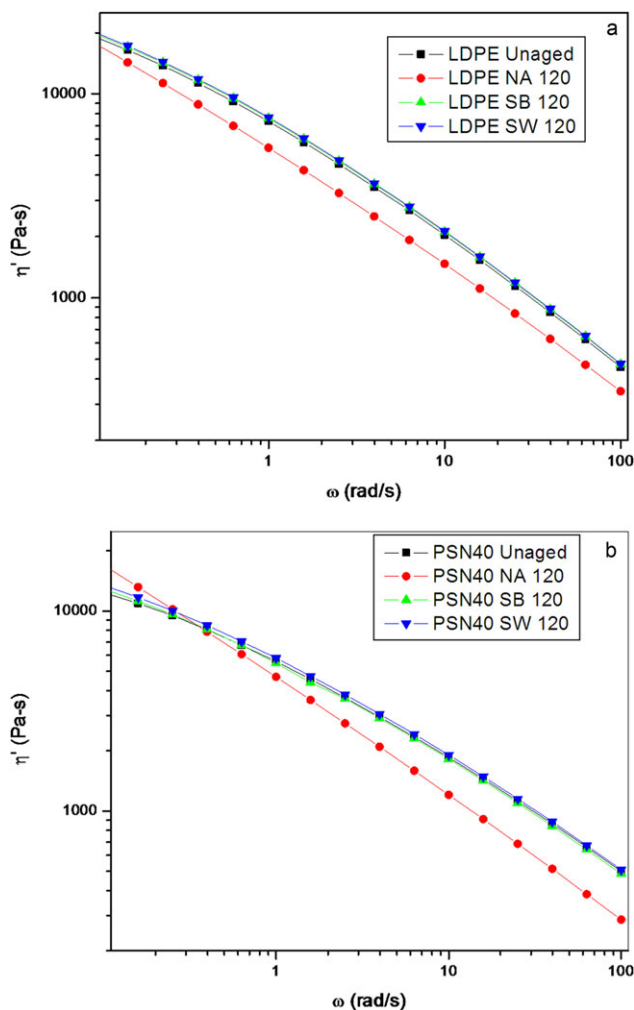


Figure 5. Variation on the dynamic viscosity of LDPE and LDPE/PSN blends before and after natural, soil burial, and sea water ageing for 120 days (NA, SB, and SW stand for natural weather aged, soil burial aged, and sea water aged). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

moisture by polystarch N from the sea water results in the removal of starch component in polystarch N/LDPE blends.¹⁰ For soil burial, the presence of moisture as well as microorganisms can influence the degradation of the blends. As discussed earlier, the microorganisms can consume the starch present in the polystarch N resulting thereby in an increase the surface to volume ratio of polyethylene available for degradation.³⁶ However, the degradation is less for the blend kept in soil compared to natural weather ageing due to the absence of light. Muthukumar et al.⁹ reported that variation in the ageing conditions can vary the degradation rate and higher degradation is observed for the samples kept in natural weathering condition compared to the soil burial and marine ageing conditions. The above results are corroborated with the finding from FTIR and SEM studies.

Figure 5 shows the variation in the dynamic viscosity of LDPE and LDPE/polystarch N blend before and after ageing of 120 days. It is apparent that after natural weather ageing, the dynamic viscosity of LDPE decreases compared to soil burial

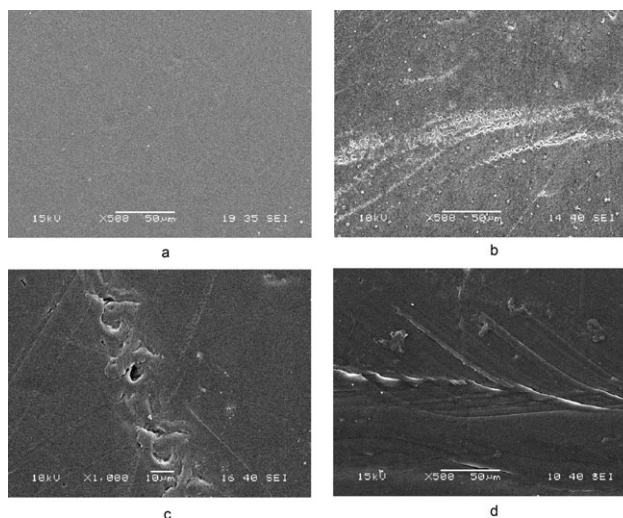


Figure 6. (a–d) SEM micrographs of LDPE: (a) unaged, (b) natural ageing, (c) soil burial, and (d) sea water ageing of 120 days.

and sea water ageing in the entire frequency region. This is ascribed to the chain scission in LDPE after natural weather ageing.³⁷ Similarly, in the case of natural weather ageing of LDPE/polystarch N blend, the dynamic viscosity decreases in the entire frequency region and the decrease is pronounced for the blend kept in natural weather ageing. Al-Madfa et al.¹⁸ reported that outdoor weathering of LDPE caused degradation by both oxidation and crosslinking. They also observed drop in ductility with increase in crosslinking. Shah et al.¹⁶ reported that after thermal ageing, a decrease in the molecular weight of starch filled polyethylene by using melt flow index values.

Figures 6(a–d) and 7(a–d) represent the SEM of the surface of LDPE and LDPE/polystarch N blend before and after ageing. The surface of the unaged sample of LDPE is smooth and free from any cracks and tear lines [Figure 6(a)]. After natural weather ageing, crazing can be seen throughout the surface of LDPE [Figure 6(b)]. Soil and sea water ageing causes micro cracks and holes indicating degradation to LDPE on ageing [Figure 6(c,d)]. In the case of LDPE/polystarch N blend, the surface shows micro-crazing and holes after ageing, presumably due to the de-bonding between LDPE and polystarch N particles, thereby leaching out of starch from polystarch N present in the blend [Figure 7(a–d)]. Rehim et al.³⁸ reported that microbes present in the soil can degrade the starch and accelerates the oxidation of the amorphous portion of LDPE which helps in the increase in the surface area of polymer blend susceptible to degradation.

CONCLUSIONS

Addition of polystarch N decreased the ductility of the LDPE after natural weather ageing compared to soil burial and sea water ageing. The T_m of LDPE and LDPE/polystarch N blend were not affected by the ageing, while a decrease in the degree of crystallinity occurred. As compared to soil burial and sea water ageing, natural weather ageing caused reduction in the dynamic viscosity of the blend presumably due to the chain scission of the polymer. SEM photomicrographs of the surface

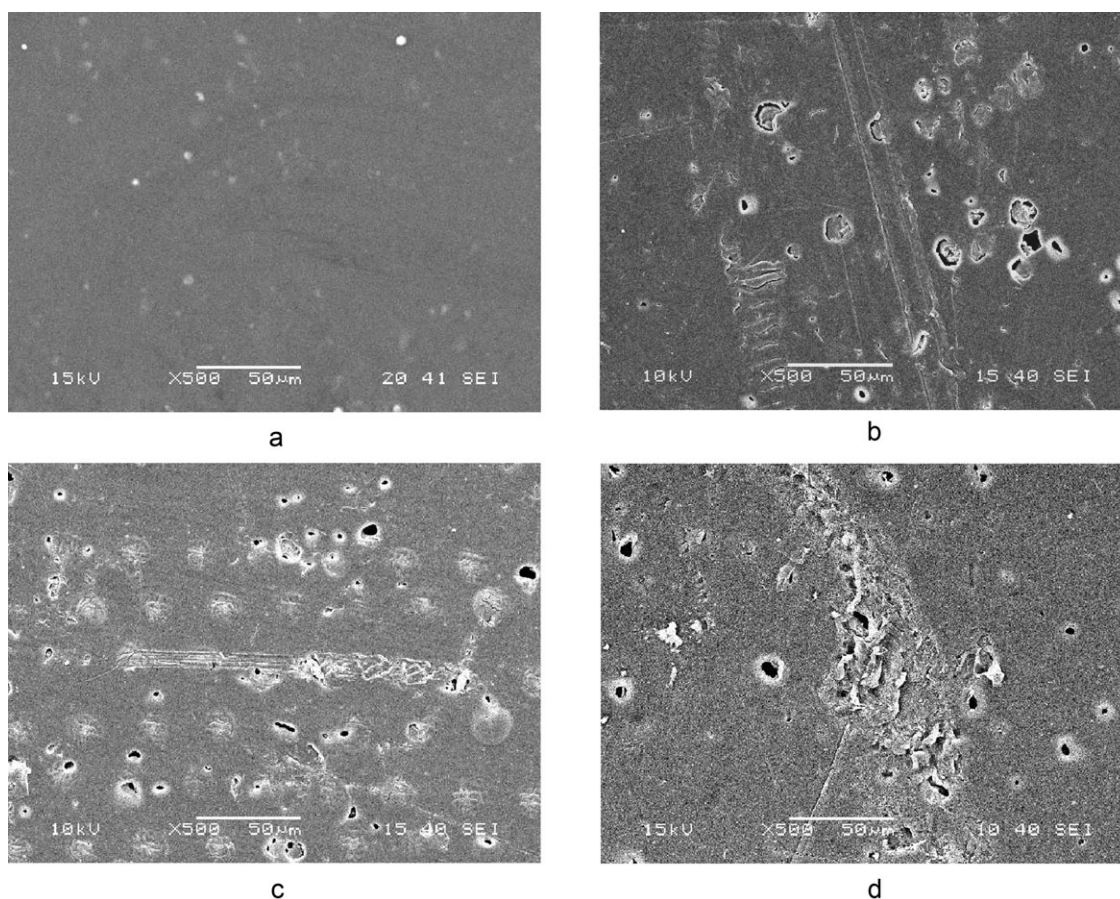


Figure 7. (a–d) SEM micrographs of LDPE/PSN blends: (a) unaged, (b) natural ageing, (c) soil burial, and (d) sea water ageing of 120 days.

indicated that ageing caused micro cracks and crazes in LDPE, while holes on the surface in the case of blends exposed to soil and sea water ageing is due to the leaching out of starch from polystarch N. The morphology studies further indicated that microbes present in the soil consumes the starch present in the blends, increasing the surface area of the soil aged polyolefin available for further degradation to occur. It is apparent that polystarch N, when present in LDPE, helps in degradation through chain scission when exposed to natural weather without affecting the morphology of the blend. In the case of soil burial and sea water ageing, the degradation through chain scission is absent due to lack of sufficient oxygen and corrosive weather conditions such as wind, sand and high temperature.

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