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Food Compatibility and Degradation Properties of Pro-oxidant-loaded LLDPE Film

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ABSTRACT: To avoid environmental hazards, packaging industries are aiming to produce biodegradable films for food contact safety and its degradation. LLDPE film containing 1% pro-oxidant additive was studied for food compatibility in different simulants, at room temperature conditions as per Bureau of Indian Standards (BIS), code of federal regulations (CFR), food and drug administration USA (USFDA), and European Economic Commission directives (EEC) specifications. Overall migration values were well within the specified limits for food contact applications at room temperature filling and storing. The pro-oxidant loaded LLDPE film was also studied for its degradation behavior with the changes in physical and mechanical properties along with thermal behavior, morphology and infrared spectroscopy. The molecular oxidations of pro-oxidant-loaded LLDPE films are severed which increases hydrophilicity. Evidently, the oxidation renders the material much more vulnerable to microbial attack. The combined effect of both photo and bio degradation is most effective for complete degradation of film. The results obtained from these studies revealed that the fine balance (1%) of pro-oxidant contents in the film guarantees food contact safety and its degradation. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: biodegradable; packaging; films

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INTRODUCTION

Today urban civilization requires a continuous and reliable supply of safe and high quality food, as unprotected food is liable to deteriorate rapidly, hence it is necessary to provide appropriate protection to food by packaging. Apart from being economical, plastic packages also fulfill all the different functions necessary for packaging, protection and distribution of foods. Plastics enhances the shelf life of packaged foods due to their inherent properties like good moisture and gas barrier and retain the original properties of food. Along with basic polymers, the plastics contain additional chemical components, called additives, which are added in small amounts to alter the properties of polymers in the desired way as processing aids. Only fillers and softener (plasticizers) are used in high concentrations to increase volume and/ or weight to improve softening flexibility, elasticity, malleability, and processibility. Other additives mostly are low molecular weight components like stabilizers, antioxidants, antistatic agents, light stabilizers (UV absorbers), lubricants, optical brighteners, and pro-oxidants such as transition metal ions, aromatic ketones, dithiocarbamates, acetyl acetonates which acts as thermal and/or photo-oxidant for the degradation of polymer.

As these additives are homogenized in the polymerization there is possibility that some component may migrate into food on direct contact with the consequent risk of health hazard to the consumer. In general, the plastics are evaluated for their food safety in contact with foods by migration studies using different food simulants under conditions of time and temperature simulating the use conditions as per the specifications laid down by different countries such as BIS by India, USFDA by USA and EEC directives from Europe. These recommendations are based on the toxicology data of additives used and have been placed in positive list/gras list of the specification.[1–6] Apart from this the plastic should not leach out additives in the packed food beyond their safety limits prescribed by the standards.

Simultaneously, a very visible portion of municipal and industrial waste consists of plastic films utilized on a massive scale. A typical example for the end consumer is shopping bags. The other adverse environmental effects of disposed polyethylene films are swallowed by pet animals and encapsulation of material on landfills and in the soil, thus altering microbial processes towards anerobiosis. Increasing waste disposal problems from polymer packaging materials have resulted in constant endeavors to replace inert and nonbiodegradable materials by biodegradable alternatives. The use of plastic materials that can re-enter the biological life cycle, appear to be one of the most promising solution to this problem.[7]

Table I. Specified Food Simulants and Test Conditions for Overall Migration at Room Temperature Condition Filled and Stored (No Thermal Treatment in Container) and also in Refrigerated and Frozen Condition as per BIS, USFDA, and EEC Standards

	Simulants and test conditions		
Description of food	BIS	USFDA	EEC
1. Aqueous, nonacidic foods (pH > 5) without fat	Dist. water (40°C/10 days)	Dist. water (49°C/24 h)	10% Ethanol (40°C/10 days)
2. Aqueous, acidic foods (pH < 5) without fat	3% Acetic acid (40°C/10 days)	Dist. water (49°C/24 h)	3% Acetic acid (40°C/10 days)
3. Alcoholic beverages			
a. Alcohol % below 10 (or up to 15% in case of EEC) (beer and pharmaceutical syrups)	10% Ethanol (40°C/10 days)	8% Ethanol (49°C/24 h)	20% Ethanol (40°C/10 days)
b. Alcohol % above 10 (wine, brandy, whisky, arrack, and other alcoholic drinks)	50% Ethanol (40°C/10 days)	50% Ethanol (49°C/24 h)	50% Ethanol (40°C/10 days)
4. Oils, fats and processed dry food with surface fat or volatile oil.	*n*-Heptane (38°C/0.5 h)	*n*-Heptane (21°C/0.5 h)	Vegetable oil (40°C/10 days)

One of the most common techniques used to render a degradable polyolefin is to add pro-oxidants at the processing stage. The pro-oxidants promote chain scission reactions during the degradation and accelerate the process of degradation. The pro-oxidants normally used for the initiation of degradation are aromatic ketones, dithiocarbamates, acetyl acetonates, and organosoluble transition metal ions like Mn, Fe, Co, Ni etc. which act as thermal and/or photo-oxidant for the polymer.[8]

In general the durability of plastic exposed to the outdoor environment, is determined to a large extent by the solar radiation.[9,10] While exposing the pro-oxidant loaded plastic to outdoor environment, the volume occupied by the pro-oxidant particles in the film present a discontinuous space for polymer crystallization. It was mentioned above that the surface of the pro-oxidant particles can act as a nucleation site for crystallization. The difference between the polymer and pro-oxidants thermal expansion coefficients will result in uneven stresses in the polymer matrix, surrounding the pro-oxidants. It is well known that the presence of pro-oxidants also substantially affects the morphological structure of the matrix polymer.[11] Erosion of the surface can be observed followed by prolific bacterial growth in areas of the film well away from the fissures.[12] Thus photo degraded films are more susceptible to a microbial attack. In continuation of our research work[13–15] in the current study LLDPE film containing 1% pro-oxidant additive (metal salts of Mn, Fe, Co, and Ni- non heavy metals and non eco toxic) was studied for food compatibility in different food simulants, at room temperature condition. The material was also studied for the changes in physico-mechanical properties by photo and bio degradation.

EXPERIMENT

Materials

Film Sample. The sample was white colored opaque 1% pro-oxidant loaded LLDPE film (d2w) with thickness of 60 μm procured from Luibeg Environmental Technology, Kolkata.

Chemicals. Acetic acid, *n*-heptane, and KBr of AR grade were purchased from Merck (Darmstadt, Germany). Water, ethanol, and *n*-heptane were freshly distilled before use.

Equipments. Differential scanning calorimeter (model DSC 2010, Dupont) with a thermal analyst 2100 system (TA instruments, USA), Fourier Transform Infrared Spectroscopy (FTIR-RAMAN Nicolet 5700 USA), Scanning Electron Microscope (LEO 435, VP LEO Electronic microscopy, UK), Mechanical properties Measurement LLOYD,S (LLOYD,S-50KN U.K).

Method

The overall migration studies were carried out as per BIS, USFDA, and EEC specifications, by exposing plastic material with contact surface area of about 1000 cm^2 (two side exposure) to different preconditioned food simulants like distilled water, 8, 10, 20, and 50% ethanol, 3% acetic acid and *n*-heptane at room temperature storage conditions[1–6] (Table I). Extracted simulants was concentrated on a hot plate under low heat and finally evaporating concentrate to dryness in a tarred stainless steel dish at 100°C ± 5°C in a hot air oven. The amount of extractive was quantified gravimetrically, expressed mg in^{-2} and ppm as per USFDA and mg dm^{-2} and ppm as per BIS and EEC. Blanks were run without samples simultaneously and corrected migration values were calculated for each simulants. Experiments were performed in triplicates as per BIS, EEC, and quadruplicates as per US-FDA. Final migration value was the mean of these determinations.

Degradation Studies

Photodegradation (PD). Pro-oxidant loaded LLDPE film (10 × 10 cm^2) was exposed to sunlight for various time intervals during April to June for 2 month (PD1) and 3 month (PD2) in outdoor conditions on stationary racks located in CSIR-CFTRI, Mysore (Karnataka). During this season, Mysore experiences a moderately hot climate. There was a wide variation in temperature between days and nights. Average day temperature was 30°C, though some days were as hot as 39°C. The average night temperature was 20°C.

The Biotic Treatment

In general biotic treatment means chemical dissolution of materials by bacteria or other biological means. In our studies biotic

Table II. Overall Migration Values of Pro-oxidant Loaded LLDPE Film at Room Temperature Filled and Stored Conditions of Time and Temperature as per BIS, USFDA, and EEC Standards

		BIS		USFDA		EEC	
Sl. no	Simulant and test conditions	mg dm^{-2}	ppm	mg dm^{-2} (mg in^{-2})	ppm	mg dm^{-2}	ppm
1.	Distilled water (40°C/10 days-BIS) 10% ethanol (40°C/10 days-EEC) Distilled water (49°C/24 h-USFDA)	0.63	6.3	0.48 (0.03)	4.8	0.43	4.3
2.	3% Acetic acid (40°C/10 days-BIS and EEC)	1.04	10.4	NA	NA	1.04	10.4
3.	8% Ethanol (49°C/24 h-USFDA)	NA	NA	0.40 (0.026)	4.00	NA	NA
4.	20% Ethanol (40°C/10 days-EEC)	NA	NA	NA	NA	0.48	4.8
5.	50% Ethanol (40°C/10 days-BIS and EEC) (49°C/24 h-USFDA)	0.67	6.7	0.76 (0.048)	7.6	0.67	6.7
6.	*n*-Heptane (38°C/0.5 h-BIS) (21°C/0.5 h-USFDA)	0.34	3.4	0.26 (0.016)	2.6	NA	NA

Limits: 10 mg dm^{-2} and 60 ppm as per BIS, EEC, and 0.5 mg in^{-2} and 50 ppm as per USFDA.
NA: not applied.
Note: Expressed USFDA values 0.5 mg/in2 ≈7.75 mg dm^{-2}.

treatment means photo degraded films are buried in the soil for further degradation by micro organisms.

Photodegradation Followed by Biodegradation (PBD). After photo degradation for 1 and 2 month, the film samples were buried in organic manure rich soil for 1 month (PBD1 & PBD2).

Biodegradation (BD). Fresh film (10 × 10 cm^2) was buried in the soil containing organic manure for 2 month (BD1) and 3 months (BD2).

Analytical Characterization

Differential Scanning Calorimeter (DSC). All the above exposed samples along with fresh samples were analyzed by DSC for their degradation. The DSC measurements were carried out under nitrogen atmosphere using Differential scanning calorimeter (model DSC 2010, Dupont)with a thermal analyst 2100 system (TA instruments, USA). All the experiments were carried out with sealed empty pan as the reference, with N_2 gas flushing. Sealed pans with samples (5–10 mg) were first cooled to −50°C, held isothermally for 1 min and then ramped 10°C min^{-1} till it reached 200°C to obtain the heat flow curves.

Fourier Transform Infrared (FTIR) Spectroscopy. Degradation of the film sample is generally detected by its oxidation. The oxidation in test samples was measured by FTIR-RAMAN Nicolet 5700. All measurements were carried out at 20°C in anhydrous conditions with KBr as background. For each sample, 32 scans at a 2 cm^{-1} resolution were collected in the range of 4000–400 cm^{-1} wave number.

Scanning Electron Microscopy (SEM). Surface morphology of the degraded sample of pro-oxidant loaded polyethylene film samples retrieved from the degradation experiments was performed using scanning electron microscope (LEO 435, VP LEO Electronic microscopy, UK) at 15 kV and magnification of 1000×, 5000×, and 10,000×.

Mechanical Properties Measurement

Mechanical properties were studied by its changes in tensile strength. Tensile tests were carried out under the condition of tensile rate of 100 mm min^{-1}, at 27° C temperature and 65% relative humidity, using Universal Texture Machine LLOYD,S (LLOYD,S-50KN U.K) instrument. For the tensile measurements, the sample specimen with 100-mm length and 20-mm width were used. Stress–strain curves were procured five times in a set.

RESULTS AND DISCUSSION

Compatibility for Food Contact Application

In general, the plastics are evaluated for their food safety in contact with foods by migration studies using different food simulants under conditions of time and temperature simulating the use conditions as per the specifications laid down by different countries. In the current study overall migration studies were carried out on 1% pro-oxidant loaded LLDPE film simulating room temperature, filling and storing condition as per BIS, EEC directives and USFDA as shown in Table I. In general, mass transfer of additives from polymer into food depends on several factors such as storage time and temperature, concentration of additives in the polymer, type and nature of the additives and its solubility in food.[16] The migration rate depends on polymer's properties, such as density, crystallinity and degree of cross linking and branching. As per BIS specification, the overall migration values ranged from minimum of 0.34 mg dm^{-2} (3.4 ppm) in *n*-Heptane for 38°C/0.5 h, to maximum of 1.04 mg dm^{-2} (10.4 ppm) in 3% Acetic

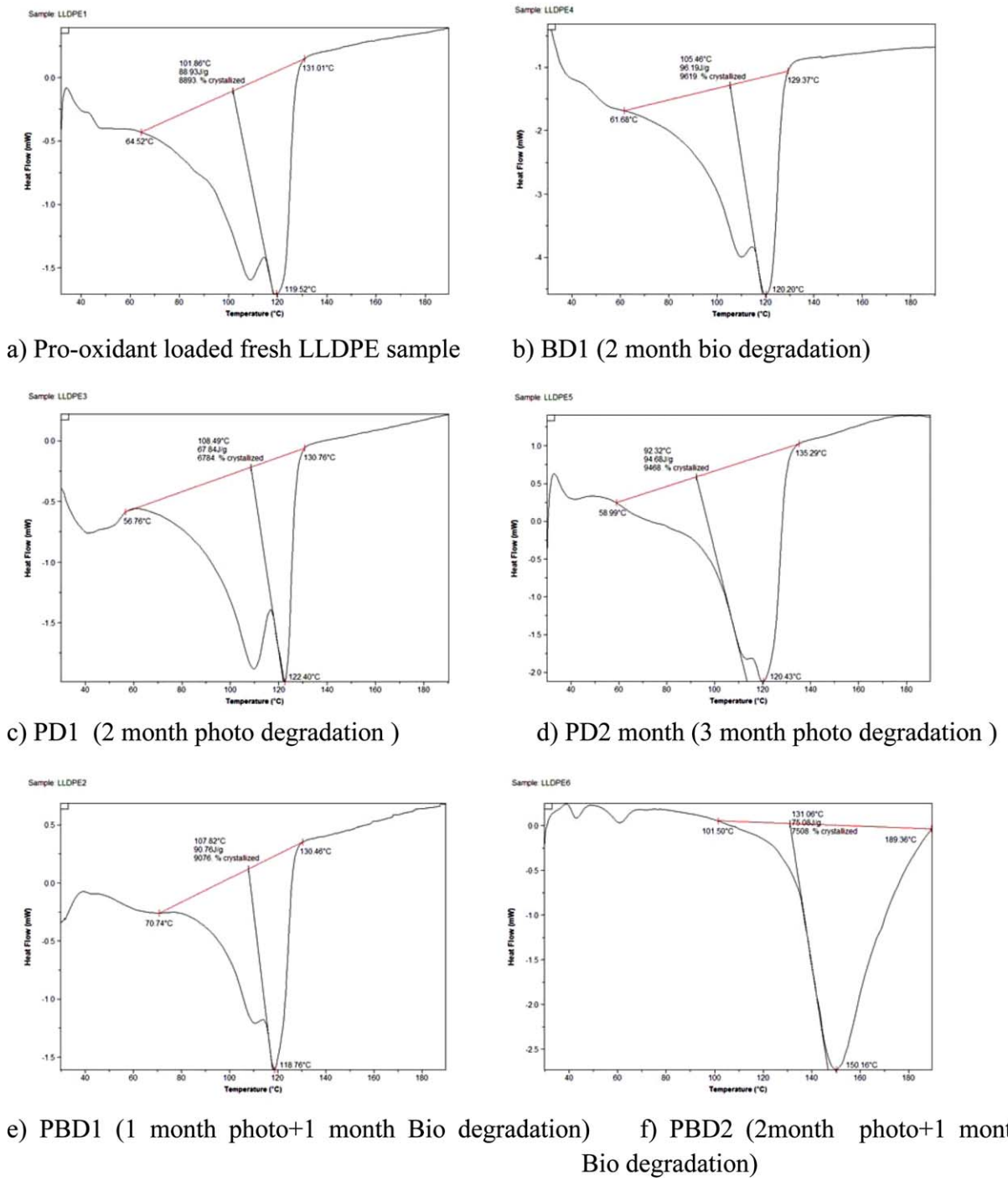


Figure 1. DSC heat flow curves of fresh and degraded prooxidant-loaded LLDPE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acid for 40°C/10 days, as mentioned in Table II. The values in acetic acid were more compared to other food simulants, which indicates greater interaction of LLDPE with acid and more solubility of additives in acid medium. Previously reported, the overall migration values for PET bottles in acetic acid were more compared to the water.[17] As per USFDA specification, the values ranged from minimum of 0.016 mg in^{-2} (2.6 ppm) in *n*-heptane for 21°C/0.5 h, to maximum of 0.048 mg in^{-2} (7.6 ppm) in 50% ethanol for 49°C/24 h shown in Table II. Whereas in case of EEC directive, the values ranged from minimum of 0.43 mg dm^{-2} (4.3 ppm) in 10% ethanol for 40°C/10 days, to maximum of 1.04 mg dm^{-2} (10.4 ppm) in 3% acetic acid for 40°C/10 days as in Table II. For all different specified conditions, the overall migration values ranged from a minimum of 0.016 mg in^{-2} (2.6 ppm) in *n*-heptane for 21°C/0.5 h, maximum of 1.04 mg dm^{-2} (10.4 ppm) in 3%

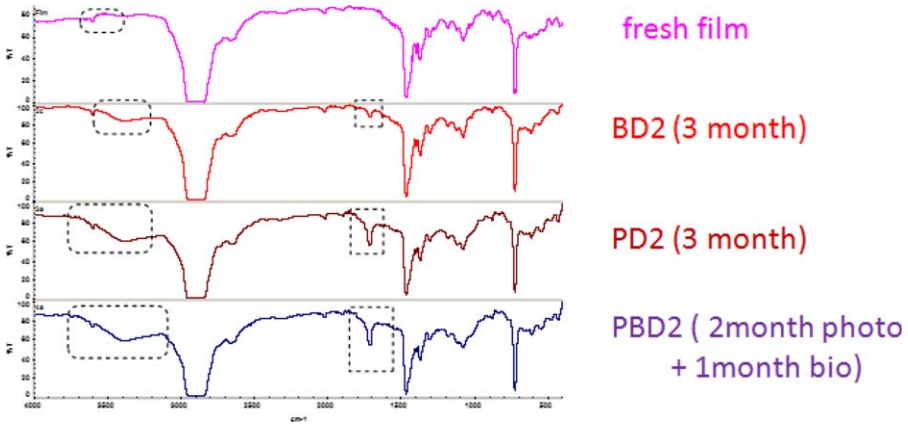


Figure 2. FT IR spectra of fresh and degraded prooxidant-loaded LLDPE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acetic acid for 40°C/10 days. All the above values were well within the specified limit of (0.5 mg in^{-2} or 7.75 mg dm^{-2} and 50 ppm) as per USFDA and as per EEC and BIS (10 mg dm^{-2} and 60 ppm). However, in our studies migration of additives from LLDPE shows a low migration tendency of its constituents in all food simulant. Hence, the pro-oxidant loaded LLDPE film confirms as per different standards for packaging of aqueous (acidic and nonacidic, pH > 5), pharmaceutical, alcoholic and fatty foods at room temperature filling and storing condition.

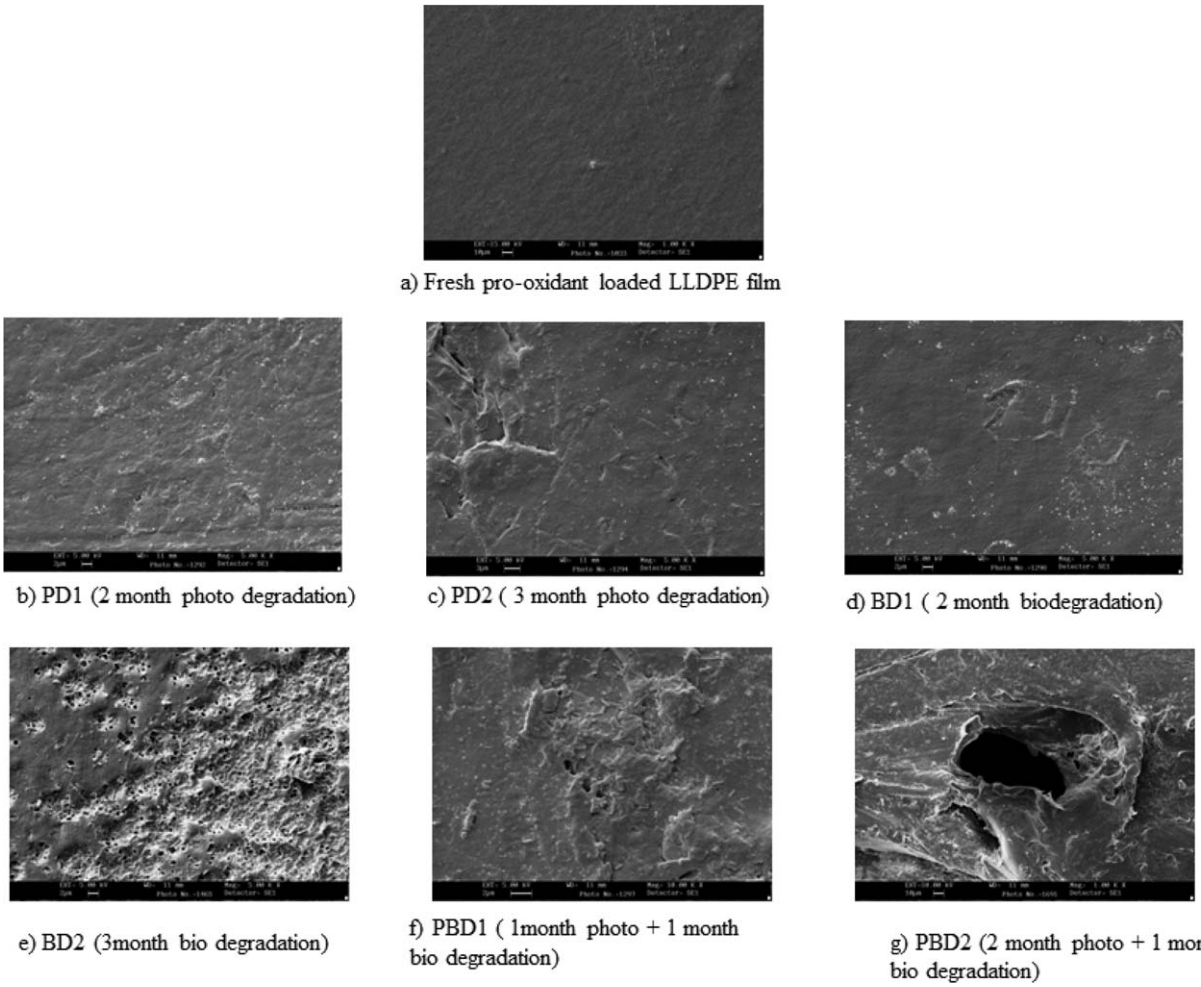
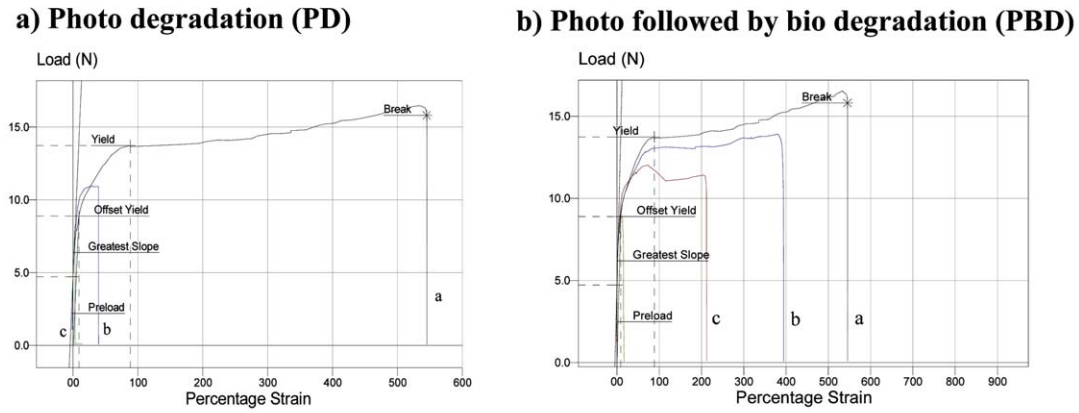
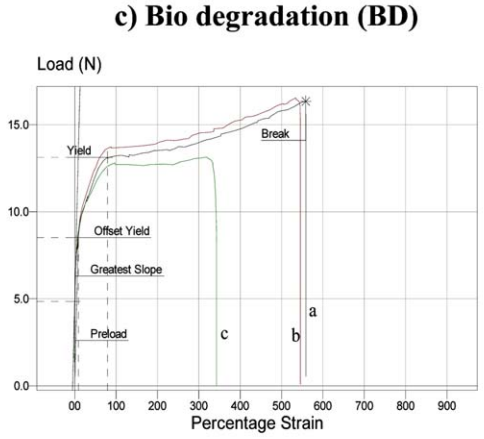


Figure 3. SEM images of fresh and degraded prooxidant-loaded LLDPE films.



a) = (a = fresh sample, b = 2 month photo degradation, c = 3 month photo degradation)

b) = (a = fresh sample, b = 1 month photo + 1 month bio degradation, c = 2 month photo + 1 month bio degradation)



c) = (a = fresh sample, b = 2 month bio degradation, c = 3 month bio degradation)

Figure 4. Overlaped stress strain cuves for fresh and degraded prooxidant-loaded LLDPE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Differential Scanning Calorimeter (DSC)

DSC measurements were used to record the changes in the crystallinity of degraded films. Figure 1 shows the heating scans of fresh and degraded samples. The mere exposure to photo oxidation led to a considerably increase of glass transition temperature (T_g) on the onset of degradation. T_g value for fresh sample was 101°C [Figure 1(a)]. Where as in PBD2 sample was 131°C [Figure 1(f)] T_g values of PBD2 is higher compared to fresh sample. This change may due to the changes in chemical structure associated with oxidation and the formation of photo products. There was a significant difference in the melting temperature range of fresh and degraded sample. As degradation proceeds melting temperature increases. In PD2 sample slight increase in melting temperature range but the increase was much more pronounced in PBD2 sample [Figure 1(f)] 101.5–189.36°C but in fresh LLDPE sample [Figure 1(a)] it was 64.52–131.01°C. However, in our studies there is an increase in melting temperature range between fresh and PBD2 sample. Perhaps this could be due to increase in crystallinity. There is increase of crystallinity and melting temperature range with the increasing exposure time. This increment of the crystallinity could be attributed to the preferential polymeric chain oxidation, that conforms the amorphous phase, as well to the formation of new crystallites induced by the chain scission reactions. The chain scission allows the resulting low molecular weight segments to crystallize or act as nucleating agents for enhancing the rate of crystallization. The creation of new intermolecular polar bonds, due to carbonyl may also lead to this effect. The increase in crystallinity also contributes to the embrittlement of the films apart from other factors like reduced molecular weight and/or photo-crosslinking of the polyethylene chains. It is known that chain scission gives rise to sufficient chain mobility to produce secondary crystallization that resulted in crack initiation. Evidently, sunlight-induced aging oxidized these films, producing low molecular weight products which readily degraded further in subsequent sunlight exposure. Because oxidation is primarily confined to the amorphous portion of the polymer matrix,

Table III. Tensile Strength of LLDPE, Fresh and Degraded Prooxidant Loaded LLDPE Films

Sl. no.	Sample		Thickness (Gauze)	Tensile stress (*N*)	Tensile strength (*N*) for 100 gauze {% decrease}
1	LLDPE		190	9.98	5.25
2	Pro-oxidant-loaded LLDPE fresh sample		240	18.08	7.53
3	Photo degradation	2 month (PD1)	230	11.40	4.95 {34.26}
		3 month (PD2)	207.4	7.95	3.83 {49.13}
4	Photo followed by bio degradation	1 month photo + 1 month bio (PBD1)	240	13.40	5.58 {25.89}
		2 month photo + 1 month bio (PBD2)	210.5	9.82	4.30 {42.89}
5	Biodegradation	2 month (BD1)	235	15.64	6.65 {11.68}
		3 month (BD2)	228.0	13.52	5.92 {21.38}

the remainder of the polymer is more susceptible to molecular reorganization which may explain the increase in crystallinity of the pro-oxidant containing photo-oxidized films.[18] Change in crystallinity was noticeable in PBD2.

Oxidation Conformation by FT-IR Studies

Chemical changes by photo oxidation were investigated by FT-IR spectra of films[19] with various period of degradation. Figure 2 shows the IR spectra of fresh and degraded film. The growth of typical peaks corresponding to carbonyl (1713 cm^{-1}) and hydroxyl groups (3370 cm^{-1}) were observed in spectras of degraded samples which were not there in fresh sample. The intensity of peak areas representing carbonyl and hydroxyl groups was less for BD2 samples where as in PBD2 and PD2, the intensity increases which are attributed to chain scission and cross linking. This indicates that a change in chemical structure is associated with oxidation and the formation of photo products due to degradation by oxidation. The molecular level oxidation results in drastic reduction in molecular weight, introduction of polar groups and increased hydrophilicity. Evidently, the oxidation renders the material much more vulnerable to microbial attack.

Scanning Electron Microscopy (SEM)

Surface morphology of pro-oxidant loaded LLDPE films, which are subjected to degradation are shown in Figure 3. In general when samples are exposed to solar radiations the outer surface responds quickly, while its inner portion is still at the original temperature. Thermal shock can thus lead to surface cracking, if the exterior contracts rapidly, while the interior is expanded or to interior cracking under the reverse conditions. Besides, the temperature level changes the rate of the chemical reactions.[20] Film which was exposed to 2 month solar radiations PD1 [Figure 3(b)] show clear two phase morphology, whitened parts with small cavities. This whitening is brought about by surface erosion due to the degradation of polyethylene. Examination of the surface of PD2 [Figure 3(c)] indicates that crack initiation at many different locations along the film. After crack initiation, brittle fracture was observed. With increasing photo exposure time brittle behavior increases, followed by tearing. Whitened spots are also detected in BD1 sample [Figure 3(d)] but in BD2 sample [Figure 3(e)] minute holes and erosion of the surface was found. Interestingly, there was prolific bacterial growth in areas of the film was noticed. PBD1 samples [Figure 3(f)] are more susceptible to a microbial attack. Microorganisms form bio film and fissures on the film. In PBD2 [Figure 3(g)] film was brittle and large cavities are noticed and it has ruptured completely. This indicates that microorganisms easily utilized the low molecular weight photo products and oxidized side products formed by the degradation initiated by the pro-oxidant when film was exposed to solar radiations.[21] From these data we can elucidate that, combined effect of both photo and biodegradation is most effective for complete degradation of pro-oxidant loaded LLDPE film.

Mechanical Properties Measurement

Tensile strength was performed to observe any change due to degradation. Figure 4(a–c) shows the stress strain curves for PD, PBD and BD films. In each figure the curves for the fresh and degraded films for different exposure time are shown. It is clear from Figure 4(a,b), that the percentage strain at breaks, is decreased with increasing exposure time. Particularly there is abrupt decrease of about 10 folds observed for 2 month PD sample [Figure 4(a)]. The percentage strain for 3 month PD sample has come almost zero. Whereas, in PBD samples [Figure 4(b)] there was a noticeable decrease in percentage strain of about 3.5 folds in PBD2 (2 month photo followed by 1 month bio) and 1.5 folds in PBD1 (1 month photo followed by 1 month bio). However in case of 2 month BD film [Figure 4(c)] there was no appreciable change in percentage strain but it was reduced up to 2 folds for 3 month BD sample. This indicates that photo exposure is essential initiating factor for degradation of pro-oxidant loaded LLDPE film. Tensile strength values of fresh and degraded films are shown in Table III. The stress of photo exposed film decreases with photo exposure time, suggesting that the molecular scission of pro-oxidant loaded film are severed by photo-irradiation that is, the chain scission may bring the change.[22] The pro-oxidants promote chain scission reactions

during the degradation and accelerate this process. The strength of the PD2 sample decreased to about 49.13% compare to original, PBD2 sample is about 42.89% whereas BD2 21.38%.

CONCLUSION

The present study was aimed to provide information regarding food compatibility and degradation of pro-oxidant loaded LLDPE film. Overall migration values are well within specified limits as per BIS, USFDA and EEC specifications for food contact applications at room temperature filling and storing. The degradation process was accompanied by a drastic change in structural characteristics, physical and chemical properties were detected using FT-IR, DSC, mechanical properties, and SEM. The increase in the T_g and melting temperature range of degraded films and appearance of ketonic and hydroxyl peaks indicate the change in chemical structure is associated with oxidation and the formation of photo products. Tensile strength and percentage strain at break decreases with increasing photo exposure time. Whitened parts, fissures and surface erosion was observed in surface micrographs of PBD2 sample. The results from degradation study envisaged that photo exposure is essential initiating factor for degradation of pro-oxidant loaded LLDPE film and in organic compost rich soil, highly preoxidized pro-oxidant loaded LLDPE film was degraded to a substantial extent.

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