

Enhancement of Pro-Degradant Performance in Polyethylene/Starch Blends as a Function of Distribution

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ABSTRACT: The effect of pro-degradant distribution in polyethylene (PE)/starch blends on ultraviolet (UV) photo-oxidative degradation was investigated. Two kinds of pro-degradants, Fe and Co-based, were used in this study. The distribution of pro-degradants in the different phases was varied by a dual step process using a side-feed on a reactive extruder. The variation in mechanical properties and evaluation of carbonyl groups by FTIR were conducted to investigate the effect of degradation following exposure to UV photo-oxidative degradation. It was found that the variation in mechanical properties was higher when the pro-degradants were distributed in the PE phase. The concentration of carbonyl groups increased as a function of UV exposure, and the concentration of carbonyl groups was higher when the pro-degradants were distributed in the PE phase. Micro-cracking was observed on the interface between starch and PE after adding the pro-degradants. When the pro-degradants were distributed in high-density polyethylene (HDPE) phase, the micro-cracks mainly appeared in HDPE matrix, and the density of micro-crack was higher. In general, the function of the pro-degradants in PE/starch blends was enhanced when their distribution was varied within HDPE phase. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: degradation; polymer blends; polyethylene (PE); processing; spectroscopy

Received 5 February 2012; accepted 21 June 2012; published online

DOI: 10.1002/app.38229

INTRODUCTION

Development of degradable polyolefins has attracted huge interest owing to their low price, useful properties, broad suppliers, and mature processing facilities and techniques. It has been generally realized that the full degradation of polyolefin involves two stages^{1–4}: oxidative degradation (oxo-degradation) and biodegradation. Oxo-degradation incorporates oxygen into the carbon chain and results in the formation of functional groups such as carboxylic or hydro-carboxylic acids, esters as well as aldehydes and alcohols. This process can be accelerated by ultraviolet (UV) light or heating. When the molecular weight of a polymer is reduced to a certain level through oxo-degradation, the oxidation products can then be biodegraded by microorganisms that consume the oxidized carbon backbone fragments to form CO₂, H₂O, and biomass.^{5,6}

Various pro-degradants have been developed to accelerate the oxidation of polyolefin under UV light.^{1,4} Generally, the pro-

degradant can be divided into two groups: (1) transition metal systems^{4,7–13}: such as transition metal salts, ferrocene, metal oxides; (2) metal-free systems^{4,14–16}: such as ketone copolymers, chemicals containing oxo-hydroxy groups, peroxides, and unsaturated alcohols or esters, etc. Transition metal salts are the most extensively studied pro-degradants and among the transition metal salts, the most commonly used pro-degradants, especially in commercial products, are Fe- and Co-based chemicals.

It has been reported that to achieve significant biodegradation in a reasonable time period, the average molecular weight of oxidized polyolefin should be under 5000.^{5,6,8,9,16–21} To accelerate biodegradation, starch has been added into the polyolefin as microorganisms (bacteria, fungi, and algae) initial home.^{1,22–25} However, the added starch generally has limited effect on the biodegradation of polyolefin if the polymer has not undergone predegradation by UV or thermal treatment. Practically, pro-degradants and starch are often used together to develop degradable polyolefin.^{26–29}

Table I. Sample List Used for Evaluation

Sample code	Formulation	Comments
Pure HDPE	Pure HDPE	Passed extruder under same conditions as compounding
HDPE/Co	HDPE 99.8/Co 0.2	
HDPE/Fe	HDPE 99.68/Fe 0.32	
HDPE/Co/Starch	HDPE 79.8/Co 0.2/Starch 20	0.2% Fe-based pro-degradant was added into HDPE/Starch blend
(HDPE/Co)/Starch	(HDPE 99.75/Co 0.25) 80/Starch 20	0.2% Co-based pro-degradant was controlled in HDPE phase
HDPE/Fe/Starch	HDPE 79.68/Fe 0.32/Starch 20	0.32% Fe-based pro-degradant was added into HDPE/Starch blend
(HDPE/Fe)/Starch	(HDPE 99.6/Fe 0.4) 80/Starch 20	0.32% Fe-based pro-degradant was controlled in HDPE phase

It is expected that only when the pro-degradant is distributed in polyolefin phase, it can be functional and active. Based on our knowledge, there is no report about how pro-degradant distribution affect on the oxo-degradation. The aim of this study is to develop a processing technique to enhance the function of pro-degradant in the hybrid blends as a function of distribution. In this study, the effect of pro-degradant distribution in high-density polyethylene (HDPE)/starch blends on their UV degradation was studied. This is done based on the variation in mechanical properties and the level of carbonyl groups detected by FTIR after UV photo-oxidative degradation exposure. Two types of pro-degradants, Fe and Co-based, were used as model materials in this study.

EXPERIMENTAL

Materials and Sample Preparation

Commercially available HDPE (Etilinas HD5301) with MFI of 9 g/10 min (21.6 kg load, 190°C) from Petronas, Malaysia was used in this study. Commercially available starch (cornstarch) was supplied by Penforld (Australia). Two commercially available pro-degradants were used in this study: Co-based pro-degradant was supplied by Petronas, Malaysia, and Fe-based pro-degradant was kindly supplied by Research Institute of Fujian Plastic (China). The materials were compounded using a Theysohn twin-screw extruder ($\phi = 30$ mm, $L/D = 40$) with the highest temperature of 200°C.

Pro-degradant was added into the HDPE/starch blends at different stages to vary its distribution. The pro-degradant was added to the blend in two ways: (1) adding pro-degradant into the blends of HDPE/starch during premixing starch and HDPE, labeled as HDPE/pro-degradant/starch; (2) adding pro-degradant to the HDPE phase by compounding the HDPE with the pro-degradant first, then compounding the HDPE-containing pro-degradant with starch, labeled (HDPE/pro-degradant)/starch. An additional set of samples was produced whereby premixed HDPE and pro-degradants were delivered to the extruder through the main hopper, whereas starch was added via a side-feeder attachment. The results from this set of samples were used to support those blends prepared with pro-degradants distributed in the HDPE phase prior to blending with starch. In this study, 0.2 wt % of Co-based pro-degradant and 0.32% of Fe-based pro-degradant were used in the experimental according to the suggestions by the material suppliers. The film was extruded using a Haake single-screw extruder ($\phi = 19$ mm, L/D

= 19) with a sheet die (13 cm wide). The film with 0.1 mm thickness was extruded and used for various characterizations. The highest temperature of the extruder and die temperature was 200°C. All blends were subjected to the same extrusion conditions. Pure HDE was also extruded under the same conditions for reference. Table I lists the blends containing the pro-degradant distributed in different phases.

UV Degradation

Film samples were exposed to accelerated UV exposure using a QUV-A weatherometer (Q-Panel, 340 nm lamps) with a 20 h UV/4 h condensation exposure in cycle in accordance with ASTM D5208. The film samples were collected and evaluated after different UV exposure times.

Testing of Mechanical Properties

Tensile properties of dumb-bell-shaped specimens were cut from extruded films parallelized extrusion direction, and measured in accordance with ASTM D638 using an Instron mechanical testing apparatus (model 3366). Tensile strength and elongation were measured at a crosshead speed of 5 mm/min. An external extensometer was used for independent modulus measurement at a crosshead speed of 5 mm/min.

Thermal Properties

A PerkinElmer 8500 DSC with a LN coolant (LCN2) and nitrogen purge gas was used in the experimental work to investigate the endothermic behaviors. Melting temperature and enthalpy of indium were used for temperature and heat capacity calibrations. Specimen with about 2 mg was sealed in an aluminum pan (PE No. 0219-0041). Samples were heated from 30 to 200°C at the rate of 20°C/min, then cooled from 200 to 30°C at the rate of 20°C/min. The peak temperature in differential scanning calorimetry (DSC) curve during heating was used to present the melting temperature of HDPE, whereas the peak temperature in DSC curve during cooling was used to present the crystallization temperature of HDPE. The enthalpy (ΔH) of the crystallization peak was used to indicate the crystallinity of HDPE, where the calculation was based on pure HDPE.

Morphological Studies

A Phillips XL-30 FEGSEM scanning electronic microscope (SEM) was used to investigate the morphological variation of the film with and without UV treatment, in particular the surface of the film samples. The specimens were coated with

Table II. Effect of Pro-Degradants on Thermal Properties of HDPE Measured by DSC^a

Sample code	T_c (onset) (°C)	T_c (peak) (°C)	ΔH_c (J/g)	T_m (onset) (°C)	T_m (peak) (°C)	ΔH (J/g)
Pure PE	116.0	114.4	131.0	121.3	130.1	153.3
PE + Co	116.7	114.5	151.9	121.9	130.3	172.6
PE + Fe	116.5	114.9	160.2	121.9	130.9	180.4
(PE + Co)/Starch	117.6	114.9	170.9	121.0	130.4	178.3
PE/Co/Starch	117.4	114.7	170.2	120.8	130.3	176.2
(PE + Fe)/Starch	116.9	114.3	166.7	121.2	130.3	178.8
PE/Fe/Starch	117.1	114.4	156.9	120.3	130.2	177.2

^aHeating and cooling rate: 20°C/min.

iridium in a vacuum evaporator and viewed in the SEM at an accelerating voltage of 2 kV.

Fourier Transform Infrared Spectroscopy

A Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) was used to detect the carbonyl group on the surface of the specimen. A Nicolet Nexus-670 FTIR equipped with a DTGS detector was employed in this

study. A smart orbit diamond ATR sampling accessory was employed for FTIR-ATR experiments. Each spectrum represents 128 coadded scans measured at a spectral resolution of 4 cm⁻¹ in the range of 4000–800 cm⁻¹. Spectral data were acquired and analyzed with Omnic software version 8.0. The concentration of functional groups (carbonyl group) was determined from the peak absorption area index (the ratios of integral from 1731 to 1693 cm⁻¹ to integral 1500–1417 cm⁻¹).

Table III. Mechanical Properties of Samples After Different UV Exposure Times

Materials and formulations	UV time (h)	Tensile strength (MPa)	Tensile modulus (MPa)	Break elongation (%)
Pure HDPE	0	16.07 ± 1.90	202.12 ± 59.05	>200
	100	15.19 ± 6.68	245.17 ± 53.11	>200
	200	14.41 ± 5.78	251.42 ± 81.89	>200
	340	16.34 ± 2.75	435.93 ± 111.36	7.63 ± 4.40
HDPE/Co 99.8/0.2	0	15.14 ± 1.69	219.88 ± 75.18	>200
	100	14.51 ± 7.01	304.85 ± 19.28	>200
	200	13.34 ± 5.65	345.92 ± 72.43	185.72 ± 8.86
HDPE/Fe 99.68/0.32	0	2.58 ± 0.65	381.29 ± 156.11	1.21 ± 0.52
	100	14.84 ± 0.68	221.48 ± 36.58	>200
	100	13.90 ± 3.84	266.19 ± 61.14	>200
HDPE/Co/Starch 79.8/0.2/20	200	13.04 ± 2.89	245.92 ± 62.84	145.72 ± 7.82
	340	8.69 ± 1.39	394.60 ± 57.37	1.64 ± 0.78
	0	9.23 ± 0.96	341.37 ± 79.34	124.70 ± 28.19
	100	10.09 ± 2.72	355.23 ± 40.18	27.97 ± 18.39
(HDPE/Co)/Starch (99.75/0.25) 80/20	200	14.95 ± 0.28	479.73 ± 83.51	6.65 ± 2.00
	340	7.19 ± 1.70	577.61 ± 122.13	1.58 ± 0.63
	0	10.44 ± 0.68	379.48 ± 36.58	149.32 ± 8.84
	100	13.90 ± 3.84	466.19 ± 64.00	10.99 ± 9.82
HDPE/Fe/Starch 79.68/0.32/20	200	13.04 ± 2.89	547.90 ± 68.84	3.52 ± 1.45
	340	8.69 ± 1.39	624.60 ± 157.97	1.64 ± 0.77
	0	7.29 ± 1.03	309.44 ± 53.06	136.88 ± 83.40
	100	13.77 ± 1.93	420.72 ± 78.38	16.83 ± 2.80
(HDPE/Fe)/Starch (99.6/0.4) 80/20	200	10.33 ± 3.87	443.50 ± 100.02	3.59 ± 1.76
	340	5.21 ± 1.79	651.67 ± 68.67	0.93 ± 0.47
	0	6.56 ± 0.92	305.74 ± 60.18	144.29 ± 15.39
	100	11.13 ± 2.38	476.31 ± 54.81	6.81 ± 3.09
	200	10.52 ± 3.67	515.16 ± 91.82	2.69 ± 0.91
	340	-	-	-

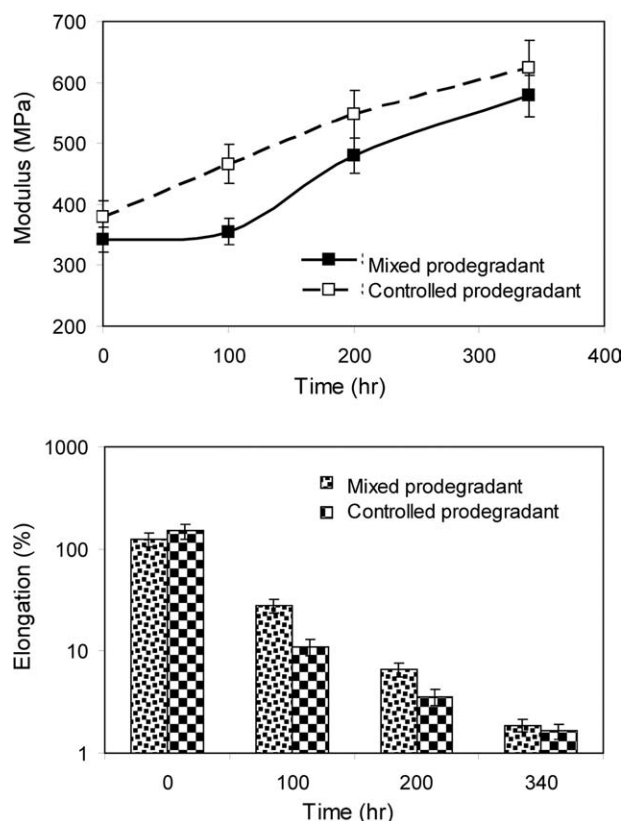


Figure 1. Effect of distribution of Co-based pro-degradant on the mechanical properties of HDPE/starch blend after different UV exposure times.

RESULTS AND DISCUSSION

Table II lists the effect of pro-degradants on the thermal properties of polyethylene (PE) measured by DSC. It was observed that both Fe- and Co-based pro-degradants acted as nucleation agents that increased crystallinity (ΔH) of the HDPE. There was no observable difference for the crystallization and melting temperatures of the HDPE after adding the pro-degradants. The crystallization and melting temperatures of the HDPE before and after exposure to UV were relatively unchanged.

Table III lists the mechanical properties of samples before and after UV photo-oxidative degradation for different times. It is seen that elongation of all specimen decreased, which indicated the materials became brittle after UV treatment. The tensile strength generally decreased with UV treatment time. Previous studies^{1,30} have shown that the mechanism of PE degradation is chain scission and recrystallization, which results in brittleness. It has been noted that decrease ratios of both elongation and tensile strength were higher after adding the pro-degradants, which is expected.

It is important to point out that the distribution of the pro-degradants clearly affects the mechanical properties of the blends. Figures 1 and 2 show the effect of UV on the mechanical properties of HDPE/starch blends containing Co- and Fe-based pro-degradant distributed in different phases, respectively. It can be observed from the results that the materials became

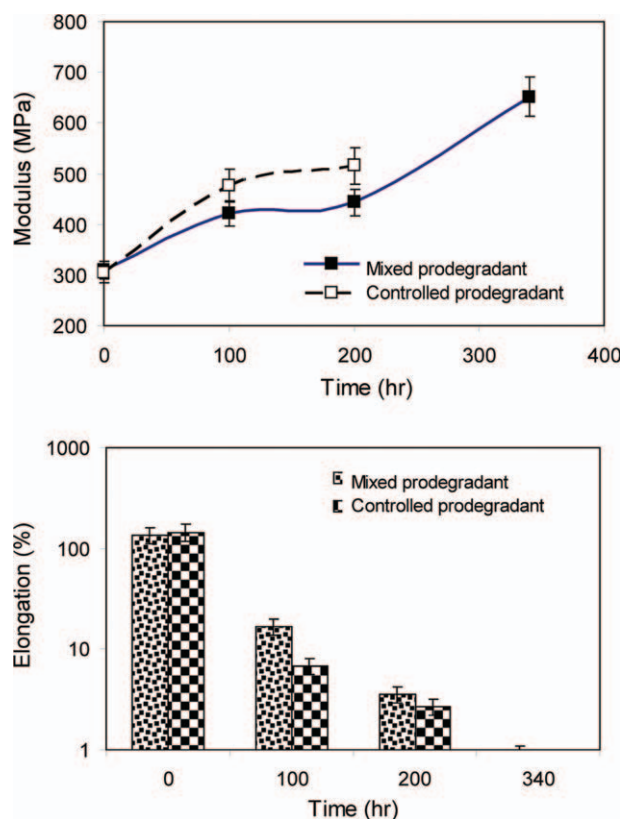


Figure 2. Effect of distribution of Fe-based pro-degradant on the mechanical properties of HDPE/starch blends after different UV exposure times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more brittle when the pro-degradants were distributed in the HDPE phase, which is indicated by higher modulus and lower elongation. The results also proved that the pro-degradants have been distributed in different phases. The tensile strength generally decreased with UV treatment time, and the decrease ratios are generally higher when the pro-degradants were distributed in the HDPE phase (Table III).

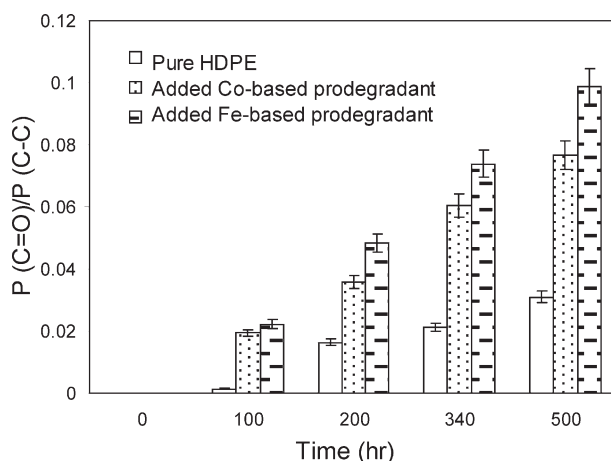


Figure 3. Effect of pro-degradants (Co and Fe based) on the C=O index measured by FTIR-ATR for the HDPE after different UV exposure times (mixed samples).

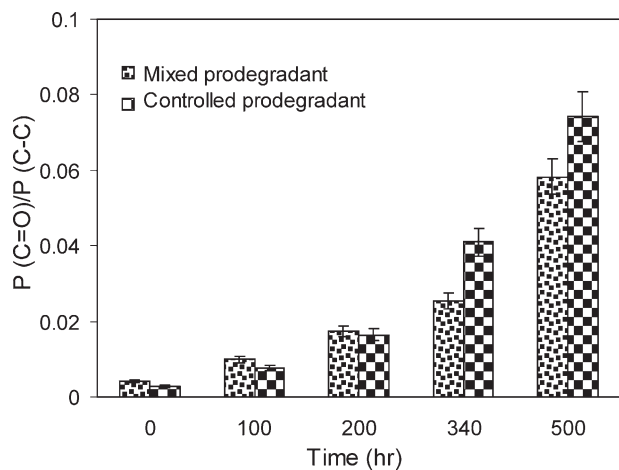


Figure 4. Effect of distribution of Co-based pro-degradant on the C=O index measured by FTIR-ATR for the HDPE/starch blend after different UV exposure times.

A well-accepted method to study the degree of UV photo-oxidative degradation of PE is to measure the carbonyl group by IR at the absorption peak $1731\text{--}1693\text{ cm}^{-1}$.^{2,6,30} Figure 3 shows the effect of pro-degradants (Co and Fe based) on the carbonyl group measured by FTIR-ATR for the HDPE which was exposed to UV for a different period of time. It is seen that the area index of carbonyl group is increased with UV treatment time. It was observed that the addition of both pro-degradants has increased the intensity of carbonyl group, which is expected.

Figure 4 shows the effect of distribution of Co-based pro-degradant on the carbonyl group measured by FTIR-ATR for the HDPE/starch blend after different times of UV photo-oxidative degradation. It was observed that the area index of carbonyl group was higher when the pro-degradant was distributed in HDPE phase. This observation is expected as the pro-degradant function can be released and active only when they are distributed in polyolefin phase. Similar results were also observed for the blends containing Fe-based pro-degradant (Figure 5). The

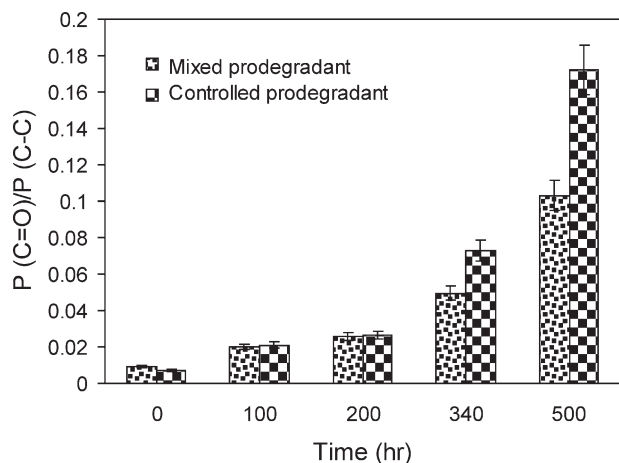


Figure 5. Effect of distribution of Fe-based pro-degradant on the C=O index measured by FTIR-ATR for the HDPE/starch blend after different UV exposure times.

results support that the pro-degradants were distributed in different phases and distribution affects the degradation of PE. The FTIR results also correspond with the mechanical properties and can be used to explain the variation of the mechanical properties. The larger area index of carbonyl group indicates acceleration of the LDPE degradation, and results in higher decrease ratio of toughness.

Figure 6 shows the film surfaces observed by SEM before and after 500-h UV exposure. There is no observable difference for the pure HDPE film after exposure to UV for 500 h. It can be seen from the SEM images that there were micro-cracks observed on the surface of the HDPE/starch blends containing pro-degradants after UV degradation. The micro-cracks have been observed for PE samples after UV degradation previously.³¹ It has been noted that the micro-cracks mainly

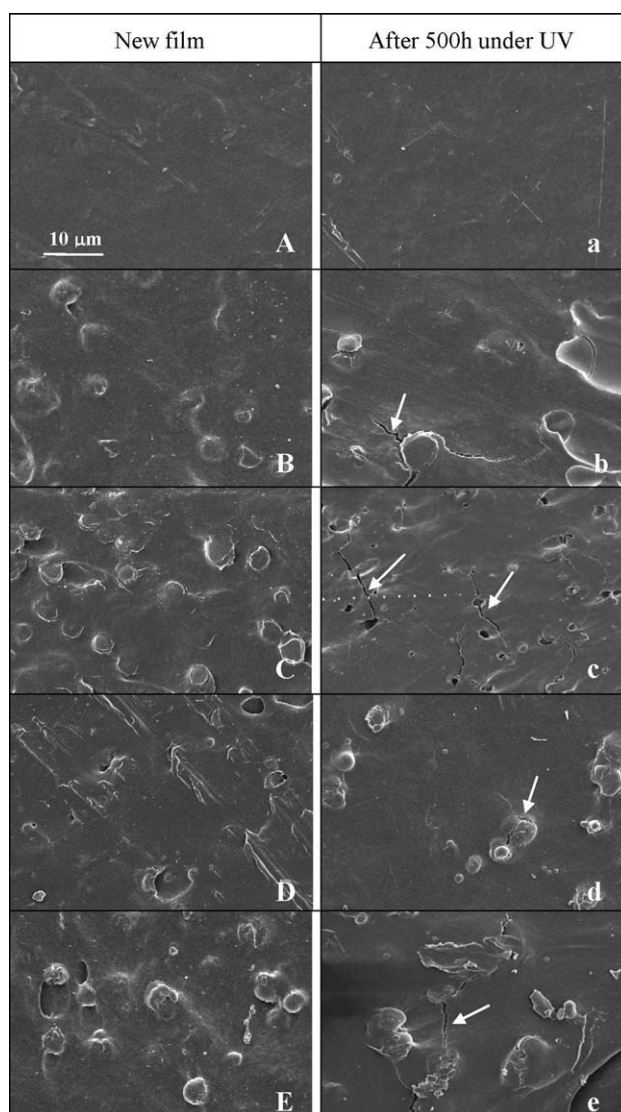


Figure 6. SEM macrographs of the film surfaces before and after 500-h UV exposure: A, (a): pure PE film; B, (b): HDPE/Co/Starch; C, (c): (HDPE/Co)/Starch; D, (d): HDPE/Fe/Starch; E, (e): (HDPE/Fe)/Starch (under same scale).

appeared on the interface between starch and HDPE after adding the pro-degradants. As the starch was added into HDPE in the form of dried granules, the pro-degradants cannot be diffused into starch phase. However, the pro-degradants prefer to stay with starch as they both have polar surfaces. The pro-degradants appear on the interface, which enhanced the UV photo-oxidative degradation of HDPE in this region. When the pro-degradants were distributed in HDPE phase, the micro-cracks mainly appeared in HDPE matrix and the density of micro-crack was higher. These micro-cracks can cause stress concentration and detrimentally affected the mechanical properties. This is one of the reasons why the pro-degradants have caused variation in mechanical properties of samples after UV exposure, in particular the decrease of toughness. The mechanism of degradation corresponded with the results of FTIR detection. Both SEM and FTIR indicated that the distribution of pro-degradants had been distributed into different phases.

CONCLUSIONS

The distribution of Fe-based and Co-based pro-degradants in HDPE or interface phase was varied through processing as supported by SEM observation and FTIR detection. The distribution effect of pro-degradants was studied based on mechanical properties variation and carbonyl index group detection. The change in mechanical properties was more pronounced, as indicated by a higher modulus and lower elongation when the pro-degradants were distributed in HDPE phase. Based on the FTIR study, it was found that the peak of the carbonyl group was higher particularly when the distribution of pro-degradants was distributed in HDPE phase. Some micro-cracks were observed at the interface between starch and HDPE after adding the pro-degradants in the blends. When the pro-degradants were distributed in HDPE phase, the micro-cracks mainly appeared at HDPE matrix and the density of micro-crack was higher. There is a significant correlation between results from FTIR analysis and SEM observations to mechanical properties of the blends. In general, the function of the pro-degradants in PE/starch blends was enhanced when their distribution is controlled within HDPE phase.

ACKNOWLEDGMENTS

Authors acknowledge the research fund from Petronas to support this work. X. Liu acknowledges the financial assistance (State Scholarship Fund) provided by China Scholarship Council for his study in Australia.

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