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Titanium dioxide-benzophenone hybrid as an effective catalyst for enhanced photochemical degradation of low density polyethylene

<https://doi.org/10.1515/epoly-2018-0078>

Received April 11, 2018; accepted May 5, 2018; previously published online August 20, 2018

Abstract: In this study, a hybrid of titanium dioxide, benzophenone and ethylene vinyl acetate (TiO₂-BP-EVA) was used as a novel catalyst to accelerate photo-oxidization reaction of low-density polyethylene (LDPE) film under ambient conditions. The degradation of the LDPE films (thickness of ~25 µm) containing different catalyst concentrations were successfully investigated by different techniques, such as Fourier-transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and mechanical tests. The results showed that the use of catalyst in which TiO₂-BP content (1/3 w/w) is 0.5 phr (parts per hundred resin) and EVA content is 4.5 phr in a LDPE film provided the best degradation rate. The carbonyl index of the polymer film achieved the highest value without an equilibrium stage. Besides, the carbon-carbon backbone of the polymer was completely broken down consistent with the deformation of the surface. In addition, the mechanical properties impressively dropped after 3 months' exposure. The obtained results imply that the TiO₂-BP-EVA compound

can be considered as an efficient catalyst for the photodegradation of LDPE polymer.

Keywords: benzophenone; catalyst; photodegradation; polyethylene film; titanium dioxide.

1 Introduction

Nowadays, polymer-based materials have been widely applied in various applications due to useful properties, including toughness, high strength/modulus, transparency, light weight, resilience, corrosion resistance, low thermal and electrical conductivity, color, processing and cost effectiveness (1–7). Among the diverse polymers, low-density polyethylene (LDPE) has been widely used in industrial packaging because of its unique advantages, such as good flexibility, high mechanical properties and being a good air barrier. Nowadays, large amounts of post-consumer LDPE products are discarded every year, causing major problems for economies and pollution due to its non-biodegradability. Regarding the degradability of LDPE, LDPE film has been demonstrated to lose about 0.2% weight after 10 years (8) and white spots appeared on its surface after being buried in soil for 32 years (9). Therefore, specific approaches have been developed to efficiently accelerate the degradation of LDPE (10–15). In this regard, LDPE should be depolymerized to low molecular size of about 500 Da (Daltons) which can possibly be consumed by several kinds of microorganisms through passing through the semi-permeable outer bacterial membranes; then it can be used as carbon and energy sources (16). Recently, it was found that the degradable mechanism of LDPE critically depends on the creation of the radicals on the C-C backbone, followed by completely breaking down into small chains through photochemical reaction under ultraviolet-visible (UV) light. Therefore, the initial photooxidization for the creation of hydrophilic functional groups such as ketone, carboxylic acid, vinyl, alcohol and ester, plays an important role in supporting the approach of bacteria on polymer chains, then promoting for subsequent biodegradable stages. In order to promote the chain scission of LDPE, the transition metal complexes and metal oxides,

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such as Co (17, 18), Fe-Ca (19), Mn-Fe-Co (20) and TiO_2 (21) have been widely applied. In addition, montmorillonite modified by alkyl ammonium supporting the degradation of PE was also recently reported (22). It was demonstrated that the addition of 20 wt% of titania nanoparticles (NPs) under a humid environment caused weight loss of 60% for PE film after exposure for 90 days under visible light (23). The improved degradability of the LDPE was also further informed by a catalytic hybrid of titania and starch (24). Recently, TiO_2 has emerged as a potential photocatalyst for PE degradation due to its high catalytic activity, nontoxicity and it being an excellent initiator for photochemical reactions (25, 26). To further improve the performance of TiO_2 catalyst, the hybridization of TiO_2 with some other agents, such as sulfate (27), calcium phosphate (28) and polyvinyl acetate (PVAc) (21) has been successfully established. In particular, the use of some hydrophilic polymers, including poly (ethylene oxide) and PVAc can greatly promote the photo-oxidized initial ability of TiO_2 during PE degradation (29, 30). Impressively, the activity of TiO_2 was impressively enhanced 5 times higher than pure TiO_2 or pure benzophenone (BP) by incorporating TiO_2 with BP at a 1/3 (w/w) ratio of TiO_2 /BP (31).

Although numerous reports focusing on the PE degradation using transitional metal ions have been discussed, to the best of our knowledge, there is no available report which thoroughly investigated the effect of a novel hybrid based on TiO_2 , BP and ethylene vinyl acetate (EVA) towards the photodegradation of LDPE. Therefore, in this study, we developed an effective catalyst via a combination of TiO_2 , BP and EVA with an optimized weight ratio to investigate the degradation of LDPE films. The obtained results showed that such catalyst exhibited a superior effect on the degradability of LDPE in which the polymer film is completely broken down into small species after 3 months, as compared to pure TiO_2 or its BP counterpart.

2 Materials and methods

2.1 Materials

The low-density polyethylene (LDPE, code 2426H) was purchased from Eastern Petrochemical Co. Ltd (Jubail city, Saudi Arabia). TiO_2 (code Ti-Pure®R902+) and polyvinyl acetate copolymer (EVA 18) was supplied by DuPont Co. (Wilmington city, NC, USA). Benzophenone with a molecular weight of 182.22 g/mol, density of 1.11 g/cm³ and melting temperature of 47–49°C, was purchased from Sigma-Aldrich Co. (Missouri city, TX, USA).

2.2 Preparation of LDPE/ TiO_2 -BP-EVA catalysts

The masterbatches of TiO_2 -BP-EVA were firstly prepared using a mixing process in a Polydrive Haake mixer (Germany) at rotation rate of 80 rpm (rpm: the number of rotations in 1 min) and 120°C for 10 min. The obtained TiO_2 -BP-EVA material was cut into small pieces with the size of 1 cm² and was then mixed with the LDPE matrix. The LDPE/ TiO_2 -BP-EVA films with the thickness of ~25 µm were prepared using a laboratory-scale twin-screw extruder Haake Rheomex OS PTW16 with L/D ratio of 25:1 and a diameter of 19 mm. The synthesis conditions on the Haake Rheomex were controlled with four zone temperature profiles, including a feed zone with 150°C, a compression zone with 165°C, a metering zone with 175°C and a die zone with 190°C. The components for preparing the LDPE/ TiO_2 -BP-EVA films are listed in Table 1.

2.3 Evaluation of the photodegradation of polymer film

The degradation of LDPE films was investigated according to ASTM D1435-99 standard. The specimens were cut at 10 × 15 cm² size, fixed on the plank and turned to a southwestern site with 45° angle to the ground. The specimens were continually exposed to the natural weather for 3 months. The weather conditions during this test were measured in a range of 60–80% relative humidity using a moisture meter and the temperature in a range of 25 and 38°C using a thermometer. The samples were then collected, washed with distilled water and dried at 50°C to evaluate the carbonyl index every 2 weeks and for measuring the mechanical properties every 4 weeks.

2.4 Determination of the carbonyl index (ICO)

The samples investigated the carbonyl index using the band index method through the use of Fourier-transform infrared (FT-IR) spectroscopy on an IR Affinity-1 (Shimadzu) spectrophotometer. The ICO value was defined as the ratio

Table 1: The composition of LDPE/ TiO_2 -BP-EVA films.

Sample name	LDPE (g)	EVA (g)	TiO_2 (g)	BP (g)	TiO_2 : BP (1:3)
LDPE	100	–	–	–	–
ET	100	4.5	0.5	–	–
EB	100	4.5	–	0.5	–
4.5ET1	100	4.5	–	–	0.5
4ET1	100	4	–	–	1
3.5ET1	100	3.5	–	–	1.5

between the carbonyl vibrational band at 1717 cm^{-1} and $\text{-CH}_2\text{-}$ strength vibrational band at 1464 cm^{-1} (32).

ICO =

$$\frac{\text{Absorption at } 1717\text{ cm}^{-1} \text{ (the maximum of carbonyl peak)}}{\text{Absorption at } 1464\text{ cm}^{-1} \text{ (internal thickness band)}}$$

2.5 Mechanical tests

The mechanical properties of LDPE films containing catalysts before and after the photodegradation were measured according to the ASTM D882 standard by means of the AG-X plus Series Precision Universal Tester (Shimadzu Inc., Japan). All the test samples were conditioned at 25°C for 24 h before any measurement. The average values of the average Young's modulus, strength and elongation at break were calculated from five measurements for each sample.

2.6 Morphology characterization

The surface morphology of the LDPE films after photodegradation was characterized using a Field Emission Scanning Electron Microscopy Hitachi S-4800 (Hitachi Co., Japan).

2.7 Thermal analysis

Differential scanning calorimeter (DSC) measurements of LDPE films were performed using the PT1000 DSC (Mettler Toledo Co., Switzerland), under the nitrogen flow rate of 30 ml/min and a heating rate of $10^\circ\text{C}/\text{min}$. The samples

were heated from 25°C to 140°C , then cooled to -50°C before being reheated to 140°C again. The melting temperature (T_m), enthalpy of fusion (ΔH) and crystallize temperature (T_c) were determined from DSC thermographs. The crystallinity (X_c) of polymer was calculated according to the following equation:

$$\%X_c = \frac{\Delta H}{w \times \Delta H_{f0}} \times 100$$

where ΔH is the enthalpy of fusion obtained from the DSC curve, ΔH_{f0} is the enthalpy heat of a 100% crystalline polymer (289 J/g) (33), and w is the weight fraction of the LDPE.

Thermal stability of the films before and after photodegradation was performed using a TGA Q500 (TA Instruments Co., USA) under the nitrogen flow rate of 50 ml/min. The samples were heated from room temperature to 600°C at the heating rate of $10^\circ\text{C}/\text{min}$ in order to investigate the thermal degradation of the samples.

3 Results and discussion

3.1 Influence of TiO_2 -BP-EVA on the photodegradation of LDPE film

The FT-IR method is basic technique to evaluate the effect of photocatalyst on the degradation of polymers through the carbonyl index and functional groups created during exposure (16, 18, 21, 34–39). Figure 1 indicates the FT-IR spectrum of pure LDPE film after 3 months' exposure, which

Figure 1: FT-IR spectra of LDPE, 4.5ET1, 4ET1 and 3.5ET1 films after degradation for 3 months.

includes strong intensity of the C-H stretch vibrational band in wavenumber range of 2800 cm^{-1} and 2900 cm^{-1} , the blade of the $-\text{CH}_2-$ scissor vibrational band at 1464 cm^{-1} , and the $-\text{CH}_2-$ strings vibrational band at 722 cm^{-1} . Meanwhile, the FT-IR spectra of the LDPE films containing different ratios of the TiO_2 -BP-EVA catalyst after 3 months' degradation involve the existence of additional bands, such as the $\text{C}=\text{O}$ vibrational band from ketone or aldehyde at 1717 cm^{-1} and the lower intensity peak of the $\text{C}=\text{O}$ stretching vibrational band from an ester at 1740 cm^{-1} . In addition, there was the symmetric stretching oscillations of the C-O-C vibration at 1242 cm^{-1} and the fluctuating asymmetry stretching of the C-O-C vibration at 1021 cm^{-1} . It can be seen that the 4.5ET1 film containing 5 phr (parts per hundred resin) of the TiO_2 -BP-EVA catalyst with 0.125:0.375:4.5 ratio in LDPE achieves the higher intensity of $\text{C}=\text{O}$ vibrational bands which originated from the aldehyde or carboxylic acid, as compared with the LDPE 4ET1 and 3.5ET1 films. Similar characteristics were also confirmed by previous reports with the formation of ester, ketone, aldehyde and carboxylic groups after the photodegradation of the polymer (21).

In order to evaluate the initialization of photooxidization by the catalyst in the LDPE film, the gradient of the ICO value was continually recognized during the 3 months' exposure under sunlight. As revealed in the results in Figure 2, the ICO value of the LDPE film containing BP is higher than that of the film that contains TiO_2 at the same exposure time. This result implies that the initialization of photooxidization caused by BP is more prominent than TiO_2 in LDPE films. Meanwhile, the hybrid catalyst based on TiO_2 -BP-EVA shows the best effect which is associated with the impressive ICO value, being much higher than the other samples at the same exposure time. In addition, the ICO values of all the samples show the increasing tendency

at different speeds over the 3 months. The ICO value of pure LDPE film increases very slowly. The ICO values of the ET and EB films increase fast but are still lower than that of the 4ET1 and 3.5ET1 films. The impressive increase in the ICO value was observed for the 4.5ET1 film with a high ICO value of 0.59 after 3 months, much higher than that of ET (0.261), EB (0.286), 4ET1 (0.464) and 3.5ET1 (0.508). This was due to the fact that the use of EVA can enhance the compatibility between the LDPE matrix and the catalyst, thereby facilitating the good dispersion of the catalyst in LDPE, then uniformly catalyzing the degradation at the carbon chain scale of LDPE. In addition, the EVA could be degraded to form ketone functional groups through the Norrish III reaction under UV light (40, 41) for increasing water absorption. Therefore, the subsequent reaction between TiO_2 and water under UV light will accelerate to create more radicals on the carbon backbone of the LDPE polymer, then for promoting photodegradation.

The mechanisms of photodegradation of an LDPE film caused by the TiO_2 -BP-EVA catalyst is described in Figure 3. TiO_2 is well known as a strong oxidizing agent based on the absorption of energy under sunlight. The first free radicals such as $\text{OH}^\cdot$ and $\text{HOO}^\cdot$ were created by photooxidization when TiO_2 directly reacted with H_2O molecules under the irradiation of sunlight (26, 42). In the similar way, the BP molecule absorbs sunlight energy in the steady state to transfer to the excited state that is so durable on BP and easily transfers to other BP molecules in order to create the radicals and continue initiating for carbon molecules on polymer (18, 43). Afterward, the radical products will continually react with H atoms on the carbon chains to create new free radicals on the main carbon chains. By adsorbing strong energy from sunlight, the new free radicals can react with oxygen atoms in order to form peroxide and hydroperoxide products which are immediately dehydrated to form ketone (44).

For the next stage, derivatives of ketone will interact with UV light to form carboxylic acid by the Norrish I mechanism or aldehyde or vinyl are formed by the Norrish II reaction (21). In addition, ketones and aldehydes are also formed from the ester by the III Norrish reaction (41). Therefore, the final products of the LDPE photodegradation include ketones, esters, carboxylic acid, vinyl and alcohol groups which are potential candidates to accelerate the biodegradation of polyethylene in the soil.

3.2 Morphology of LDPE films during photo-degradation

Figure 4 shows the optical images and scanning electron microscopy (SEM) images of the LDPE films containing

Figure 2: ICO values of different samples during photochemical degradation for 3 months.

Figure 3: Photooxidation mechanisms of on LDPE film caused by TiO_2 -BP-EVA catalyst.

different ratios of catalyst after 3 months' exposure. From optical images, the pure LDPE sample exhibits a smooth and homogeneous surface without observation of the degradation phenomenon (Figure 4A). The 4ET1 and 3.5ET1 films showed the rough, embrittlement and brittle surfaces (Figure 4E and G), meanwhile the 4.5ET1 film exhibited being completely damaged into small pieces (Figure 4C). At micro observation, SEM images of pure LDPE still display smooth and homogeneous surfaces, which further confirmed no photodegradation of the LDPE film after 3 months (Figure 4B). Whereas, the microstructure of the 4.5ET1 film becomes scabrous, deformed and has more numerous large holes, which is evidence of the photodegradation caused by the optimized TiO_2 -BP-EVA catalyst (Figure 4D). In this regard, the enhanced fragmentation of the LDPE film was due to the depolymerization of the LDPE chains to the low molecular size of 500 Da (Daltons), which can be consumed by several microorganisms in a further stage (9, 16). The 4ET1 film containing a high TiO_2 /BP content of 1 phr also shows the decomposition with some small holes, but less than that of 4.5ET1 surface (Figure 4F). This implies that increasing the amount of photocatalyst would reduce the triggered performance during photodegradation leading to less deformed surface films. In the case of the 3.5ET1, which

contains the highest amount of TiO_2 -BP-EVA (about 1.5% phr), was recognized by the presence of 3–5 μm size particles of catalyst without the formation of holes on the surface of the film (Figure 4H). This result may be due to the accumulation of the catalyst, which cannot homogeneously disperse in the matrix film; therefore, it cannot promote photodegradation by increasing the triggered area when the films are exposed under sunlight.

3.3 Thermal analysis of films after the photo-degradation test

The thermal properties of samples before and after degradation were investigated by DSC equipment from 25°C to 140°C. LDPE and EVA are well known as semi-crystalline polymers, they are compatible in the amorphous region and incompatible in the crystalline phase (41). The amorphous regions of the LDPE/EVA blend had an influence on the photochemical stabilization and also affected their crystallization behavior (21). As presented in Table 2, the melting temperatures of all the initial samples containing different ratios of catalyst show almost the same values after the degradation process, implying that the presence of catalyst causes a minor influence on the crystallinity

Figure 4: The photos and surface morphology of films after 3 months' photochemical degradation.

(A) Optical photo and (B) SEM image of LDPE; (C) optical photo and (D) SEM image of 4.5ET1; (E) optical photo and (F) SEM image of 4ET1; and (G) optical photo and (H) SEM image of 3.5ET1 material.

Table 2: The melt temperature and crystallinity (χ_c) of the films before and after 3 months' exposure.

Sample	Aging time (days)	1st heating			2nd heating		Crystallinity χ_c (%)
		T_{on} (°C)	T_{peak} (°C)	χ_c (%)	T_{on} (°C)	T_{peak} (°C)	
LDPE	0	104	111	23.56	104	110	24.90
	90	106	111	27.26	105	112	25.04
4.5ET1	0	106	109	36.62	104	111	37.85
	90	106	113	49.54	105	112	43.52
4ET1	0	106	109	31.51	104	111	33.38
	90	105	111	46.56	104	111	40.23
3.5ET1	0	106	109	33.96	104	110	35.51
	90	105	112	46.46	104	111	41.18

of LDPE. The melting temperatures of the samples after degradation are slightly increased by about 1–3°C, as compared to the initial samples. This is due to the increase of crystallinity degree (χ_c) in which the TiO_2 acts as a nucleating agent for the crystallization of LDPE (45, 46). Besides, the reorganization of the fractured chains after aging also influences on the increase of χ_c . In this regard, the long carbon chains of the polymer matrix are decomposed to shorter chains by photooxidization with CO functional group at the last circuit. The carbon backbone chains significantly improved the mobility that promotes the rearrangements of them to form perfect crystalline areas, leading to increasing the crystallinity compared to samples that do not age (21, 47).

3.4 The mechanical properties of LDPE films

The tensile properties of various samples were investigated to evaluate the influence of the catalyst on the degradability of LDPE after 3 months. Figure 5 shows the mechanical properties of LDPE films before and after 3 months'

storage without exposure to sunlight. The results imply that the LDPE films containing TiO_2 -BP cannot be photo-degraded if they do not have contact with sunlight.

Figure 6 shows the tensile strength and elongation of samples before and after 3 months' storage under sunlight. The pure LDPE film possesses tensile strength of 23.7 MPa and elongation of 323%. Other initial samples containing different amounts of TiO_2 , BP and TiO_2 -BP showed nearly the same values of tensile strength and elongation as compared to pure LDPE. The tensile strength of ET (26 MPa) is higher than that of other samples due to reinforcement of TiO_2 fillers in PE matrix. The tensile properties of all samples during exposure to natural weather conditions are significantly decreased after 1 month. The decrease in tensile properties is basically due to the increase in the embrittlement by increasing the cross-linking of the samples after aging (18). All samples became completely brittle after 2 months' and could not be collected for testing after 3 months, due to the fragmentation under photodegradation. The decrease of the elongation rate for samples containing the TiO_2 -BP catalyst was more rapid than others.

Figure 5: The tensile strength and elongation of different films after 3 months' storage without sunlight.

Figure 6: The tensile strength and elongation of different films during the photodegradable test.

3.5 Thermal stability

Figure 7 shows the influence of the catalyst on the thermal stability of the LDPE film before and after photochemical degradation. In the case of a pure LDPE film, the thermal decomposition of the PE film has only one shift which begins around 435°C with strong weight loss at 478°C, the total weight loss is 100% (w/w) at 500°C. Regarding the 4.5ET1 film, the thermal decomposition begins at 423°C (T_{on}), 13°C lower than that of a pure LDPE film due to the first step of thermal degradation of EVA, consistent with the deacylation of the vinyl acetate groups between 300°C and 400°C. The strongest decomposition (T_{peak}) happened at 483°C, 5°C higher than that of a pure LDPE film, due to the high thermal stability of TiO_2 (48, 49). The total weight loss of 4.5ET1 sample reaches about 98.8 % (w/w) at 520°C. The residual weight about 1.2% (w/w) may be due to the presence of metal oxide in the sample. After aging for 3 months, the heat decomposition of 4.5ET1 samples shifted to the lower temperature region with T_{on} at 396°C and T_{peak} at 463°C. The total weight loss of the 4.5ET1 sample reached

about 100% (w/w) at 500°C, resulting from that the carbon chains of the LDPE being decomposed into shorter chains with reduced molecular weight, leading to a decrease of thermal stability. In addition, the formation of abundant unstable groups on the LDPE structure during the degradation process also promoted the thermal decomposition of LDPE at high temperatures (18, 21).

4 Conclusion

The ICO analysis, morphological structure, mechanical properties and thermal stabilization of the pure LDPE film and LDPE film containing photocatalysts indicated that the use of the TiO_2 -BP-EVA spurred the decomposition of LDPE film after 3 months under natural exposure. The LDPE films containing 4.5 phr EVA and 0.5 phr TiO_2 -BP (1/3 w/w) resulted in the highest CO indicators, promoting the decomposition efficiency of LDPE. This study may open up a new direction for the manufacture of packaging with oxodegradable polymers.

Figure 7: Influence of the catalyst on the thermal stability of the LDPE film. TGA (A) and DTG (B) curves of 4.5ET1 and 4.5ET1-AGE after 3 months' degradation.

Acknowledgment: The authors would like to acknowledge support from the Basic Science Research Program (2017R1D1A1B03028413) and (2016R1A6A1A03012069) through the National Research Foundation (NRF) funded by the Ministry of Education of Korea. This study was also supported by the Faculty of Material Sciences, Ho Chi Minh University of Science HCMC, and VNU-HCMC. We would like to thank our colleagues for their enthusiasm and cooperation in the study.

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