Thermo- and Photo- Degradation of LDPE and PP Films Using Metal Oxides as Catalysts

Sarinya Shawaphun[1,a], Thara Manangan[1,b] and Sirirat Wacharawichanant[2,c]

[1]Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, 10800 Thailand
[2]Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000 Thailand

[a]sarinya73@yahoo.com, [b]jxudel@yahoo.com, [c]iamsirirat@yahoo.com

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Abstract. In a study of photo-degradation of LDPE and PP films using the photo sensitive metal oxides or pro-oxidants (e.g. Fe_2O_3, Cu_xO, ZnO, and TiO_2 at various particle sizes) as the catalysts in both thermo- and photo-oxidation of plastic films with oxygen followed by photolytic process to give free radicals, our preliminary study in hexane solution found that the carbonyl index (CI) increased under the shortwave ultraviolet (254nm) significantly greater than under the longer wave (366nm) due to its greater energy and highly absorbed by the pro-oxidants generating more free radical concentration which could then be photolysed into carbonyl compounds. The pro-oxidant blended PE and PP films under ultraviolet (254nm) irradiation showed the carbonyl index elevation at the beginning and then reducing to a constant level similarly in most cases. This probably indicated that the carbonyl primarily formed and degraded into other free radicals. Moreover, the LDPE film containing TiO_2-200nm (1%w/w) was able to reduce the film tensile strength by 32% within 72 hours with rutile TiO_2 and by 55% with anatase TiO_2 while the PE film containing commercial TiO_2 both with and without size sieving at 63µm lowering their tensile strength only by 7-10%. However, in PP film, the tensile strength tends to increase possibly due to cross linkage.

Introduction

Not only global warming has recently become major environmental problems worldwide, but also the conventional fuel based plastic wastes have become worldwide major public concerns. Polyethylene and polypropylene are the most popular plastics in packaging industries that caused the gigantic amount of waste every year due to their useful mechnical properties and physical properties for foods and household products packaging. However, it takes upto 450 years to decompose a plastic bag, so many countries applied varous regulations, policies and managements to overcome these problems e.g. recycle reuse and reduce protocol, yet it is far from success. Biodegradable plastics such as modified starches, polylactic acids, polyhydroxyalkanoates and such were brought up to research attentions in the last 45 years. However, their production costs and limited applications have always been considerated.

In a natural pathway of auto-oxidative degradation of polyethylene and polypropylene which were normally initiated by light or heat (so called photo-oxidative degradation or thermo-oxidative degradation). This step usually is the slow process and becomes the rate determining step because plastics have to combine with oxygen in the air and react to give the unstable peroxy compounds which can then decompose to carbonyl and free radical intermediates e.g. alkyl radicals or hydroxyl radicals.[1] Moreover, the carbonyl compounds can be photolysed to more free radicals. [2] The radicals then undergo propagation step in the degradation chain reaction of polyethylene and polypropylene and give more and more of oxygenated carbon skelatons in the plastics in form of hydroxyls, aldehydes, ketones and carboxylic acids [3] which then can be further biodegraded at low molecular weight finally resulting carbondioxide and water. [4] The objective of this research is to accelerate the rate determining step by using pro-oxidants or pro-degradants which generate carbonyl compounds during the processing step and induce degradaion of plastics under solar light exposure after used and casted away. Typical pro-oxidants are metal oxides or metal salts such as Mn^{2+}/Mn^{3+}, Fe^{3+}, Zn^{2+}, Zr^{2+}, Ce^{2+} and Ti^{4+} have been used as photocatalysts. [5-9] Due to its supurb charactoristics such as inexpensiveness, non-toxicity, stability and highly photoactiveness, TiO_2 has become the excellent choice for photocatalyst.[10-11] To compare activity of TiO_2 with other metal oxides, the preliminary study was done in hexane solution. Furthermore, its photolytic reactivity with carbonyl compounds was also investigated. Effects of particle size and surface area were then also briefly looked at. Finally, TiO_2 with various particle sizes were blended into LDPE and PP, casted into a thin film, irradiated under ultraviolet light at 254nm and 366 nm to understand their catalytic degradation pathways.

Experimental

Materials

Virgin grade LDPE (IRPC) and PP (IRPC) were used for the preparation of films. Ferric oxide (Fe_2O_3, analytical grade), zinc oxide (ZnO, analytical grade), cupric oxide (CuO, analytical grade), TiO_2 (analytical grade), TiO_2 (rutile, 200nm) and hexane (HPLC grade) were purchased from Sigma Aldrich. TiO_2 (63µm) was prepared by particle size sieving and oven dry for 24 hours.

Photo-degradation of hexane

The powders of Fe_2O_3, ZnO, CuO, TiO_2 (63µm), TiO_2 (anatase, 200nm) and TiO_2 (rutile, 200nm) were separately mixed with hexane at 1, 2, 3, and 5% w/v in 10-ml Pyrex sealed tubes. After vigorously shaken, the obtained suspensions then were exposed under a 20-watt shortwave ultraviolet lamp (254nm) and a 20-watt long wave ultraviolet lamp (366nm) at 30 cm in distance. Then they were taken out daily to determine the rate of oxygenation and/or degradation *via* carbonyl index using a Perkin Elmer spectrum 2000 FTIR spectrometer. [12]

Thermo- and photo-degradation of PP and PP films

The powders of TiO_2 (63µm), TiO_2 (commercial), TiO_2 (anatase, 200nm) and TiO_2 (rutile, 200nm) were blended into both LDPE and PP at 1, 2, 3, and 5% w/w concentrations using a Twin-Screw Extruder (TSE 16 TC; Intro enterprise Co., Ltd), and then casted to 10-micron thick films using a Chill Roll Cast Film (LE 25-30/C; Labtec Engineering Co., Ltd). The plastic films then were cut to 10x10 cm size and exposed under a 20-watt shortwave UV lamp (254nm) and a 20-watt longwave UV lamp (366nm) at 30 cm in distance. The plastic films then were taken out daily to determine carbonyl index using a Perkin Elmer spectrum 2000 FTIR spectrometer, tensile strength using a Universal testing machine (Tensile H5K-T; Calserve Thailand), and % weight loss using a Sartorius BP 2105 Electric balance.

Results and Discussion

Catalysed photo-degradation of hexane:

After irradiation of the hexane suspensions containing Fe_2O_3, ZnO, CuO, TiO_2 (63µm), TiO_2 (rutile, 200nm) and TiO_2 (anatase, 200nm), the carbonyl index then was determined. Most catalytic oxygenation under UV 254nm showed higher reactivity than under UV366nm. Moreover, only ZnO and TiO_2 showed good catalytic reactivity, especially both nanocrystalline TiO_2. Furthermore, the higher concentration of commercial ZnO and TiO_2 did not show higher photolytic reactivity possibly due to their low mobility in hexane.

In PE and PP films:

During the processing period, TiO_2 with various particle sizes and concentrations showed significant increasing of carbonyl index in both LDPE and PP films as shown in Fig. 1a and 1b. However, the carbonyl formation in PP films did not increase linearly according to additives concentration possibly due to other mechanical pathways.

As shown in Fig. 1c, LDPE films blended with various types and sizes of TiO_2 showed high elevation rate of carbonyl index after 48 hours of UV 254 nm irradiation while PP films showed some increasing and then lowering back. At low TiO_2 concentration, active particle sizes are 200nm and 63µm. Furthermore, it appeared that anatase crystalline show slightly higher reactivity than rutile crystalline in PE films.

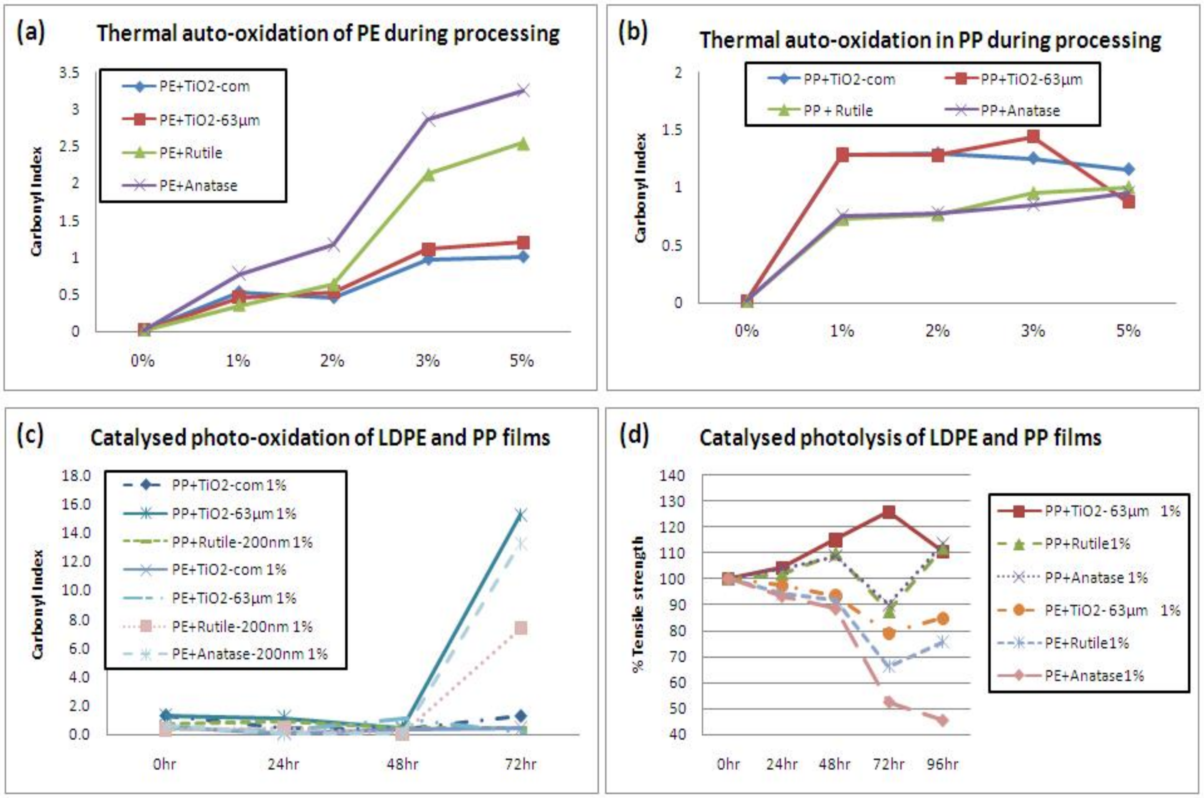

Fig. 1 The thermal and photo oxidation of LDPE and PP films during processing and under ultraviolet 254nm irradiation

As shown in Fig. 1d, LDPE films blended with various types and sizes of TiO_2 showed high elevation rate of carbonyl index after 48 hours of UV 254 nm irradiation. At low TiO_2 concentration, active particle sizes are 200nm and 63µm. Furthermore, it appeared that anatase crystalline show slightly higher reactivity than rutile crystalline in PE films. Moreover, the LDPE film containing nanocrystalline TiO_2–rutile (1%w/w) was able to reduce the film tensile strength by 32% within 72 hours and the anatase nanocrystalline TiO_2 provided greater tensile strength reduction by 55% within 96 hours. The LDPE film containing commercial TiO_2 lowered their tensile strength only by 7% while TiO_2 with size sieving at 63µm reduced the tensile strength of LDPE film up to 20 % within 72 hours. However, the tensile strength of PP films blended with TiO_2 tends to increase possibly due to cross linkage of hydrocarbon chains or recombination of free radical intermediates *via* another mechanism. This explained the carbonyl index study results. The investigation of the PP films degradation profile using weight loss technique also showed small value only 2% with the highest TiO_2 concentration at 5%, while LDPE films gave up to 4% weight loss at 1% TiO_2 concentration.

Summary

Most catalytic oxygenation under ultraviolet 254nm irradiation showed higher reactivity than under ultraviolet 366nm irradiation. Among chosen metal oxides, only ZnO and TiO_2 showed good catalytic reactivity, especially both nanocrystalline TiO_2 in both hexane and in plastic films. During the plastics processing period, TiO_2 with various particle sizes and concentrations showed significant increasing of carbonyl index in both LDPE and PP films. However, the carbonyl formation in PP films did not increase linearly according to additives concentration possibly due to cross linkage of hydrocarbon chains or recombination of free radical intermediates *via* another mechanism. Similar results also occurred in catalyzed photo-degradation of PP films. However, nanocrystalline TiO_2 showed great reactivity in both thermal oxygenation during the plastic processing and the photo-degradation during the shortwave ultraviolet irradiation.

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