

Effect of Pro-Degradant Additive on Photo-Oxidative Aging of Polypropylene Film (Pengaruh Aditif Pro-degradasi pada Penuaan Foto-Oksidatif Filem Polipropilina)

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ABSTRACT

This paper describes the effect of pro-degradant additives (PDA) on photo-oxidative aging of polypropylene (PP) films after being time accelerated in UV-weathering chamber. Thin films (0.12 mm) containing these additives were prepared by sheeting process. The effect of UV on PP films in the presence of these additives was investigated. Changes in the PP films appearance, tensile properties and carbonyl index (CI) were used to investigate the degradation behavior. The films became completely pulverised after 100 h of photo-oxidative treatment and could not be tested further. Films containing PDA showed rapid loss in tensile properties within 100 h of photo-oxidative aging. In addition, the CI results of photo-oxidative films increased with increasing PDA amount within the time interval of aging and the activity was due to the mechanism reaction of PP with PDA particles. During the aging process the material becomes denser due to tighter packing and incorporation of oxygen into the amorphous regions of the polymer. The results indicated that the presence of PDA contributed to the photo degradation and the activity was very much influenced by the amount PDA.

Keywords: Degradable polypropylene; photo-oxidative aging; pro-degradant additives

ABSTRAK

Makalah ini menghuraikan tentang pengaruh aditif pro-degradasi (PDA) terhadap penuaan filem foto-oksidatif polipropilina (PP) selepas dipercepat penuaannya dalam kebuk cuaca-UV. Filem nipis (0.12 mm) yang mengandungi aditif ini disediakan melalui proses penipisan helaian. Pengaruh UV pada filem polipropilina dengan kehadiran aditif tersebut telah diselidiki. Perubahan terhadap rupa polipropilina filem, sifat-sifat terikan dan indeks karbonil (CI) telah digunakan untuk mengkaji perilaku degradasi. Filem-filem ini menjadi serbuk secara keseluruhan selepas 100 jam perawatan foto-oksidatif dan tidak boleh diuji dengan lebih lanjut lagi. Filem yang mengandungi PDA telah menunjukkan kemerosotan ketara dalam 100 jam penuaan foto-oksidatif. Selain daripada itu, keputusan CI filem foto-oksidatif telah meningkat dengan bertambahnya jumlah PDA dalam tempoh waktu penuaan dan aktiviti itu berlaku kerana reaksi mekanisme PP dengan partikel PDA. Semasa proses penuaan, bahan menjadi lebih tumpat kerana pembungkusan lebih ketat dan gandingan oksigen ke dalam kawasan amorfus polimer. Keputusan kajian menunjukkan bahawa PDA menyumbang kepada degradasi foto-oksidatif dan aktiviti sangat dipengaruhi oleh jumlah PDA.

Kata kunci: Aditif pro-degradasi; penuaan foto-oksidatif; polipropilina terdegradasi

INTRODUCTION

Dating back to the second half of the 20th century, many researchers attempted to produce environmentally degradable and low cost plastic materials from polyolefin. The potential degradability and ultimate biodegradability started to be considered in the early 1970s (Chiellini et al. 2003) as specific attributes for applications in packaging and agricultural market segments. General features of plastics that makes them attractive for many of the common uses including packaging, are strength and toughness, durability and long life, light weight, excellent barrier properties for water and gases, resistance to most chemical agents, excellent process ability and low cost. However, it has been a target of much criticism due to its lack of degradability (Guillet et al. 1995). Recently, recycling becomes a popular method to clean up the waste and reduce the usage of natural sources like petroleum or other material. However, this

method can only reduce in a small quantities and the piling of the plastic at the landfill is still in critical status (Nils & Kleppe 2009). The plastic waste can be discarded by burning it at the landfill but this technology is costly. For this reason, biodegradable plastic becomes an alternative method to prevent this problem and friendlier to the ecosystem. Besides that, the mechanical properties of biodegradable plastics are still similar with the traditional plastics (Anon. 2010).

In recent years, the race for producing biodegradable plastics has increased tremendously. There are many technologies for producing the degradable products. One technology uses petrochemical for example polyolefin with prodegrading additives, biodegradable polyesters and polyvinyl-alcohol (PVOH) derivatives. Other technologies use a renewable resource like cellulose, starch and vegetable oil. One of the examples is the shopping plastic bag which is widely used in the hyper-market. These plastics bags

will disintegrate in the presence of sunlight and heat, and degrade completely in the presence of oxygen, soil, moisture and microbes. However degradable polymer with starch content has higher impacts upon greenhouse due to methane emissions during landfill degradation. However oxo-degradable plastic do not produce methane as they degrade. Methane is 23 times more potent for global warming than carbon dioxide (CO₂) (Guillet et al. 1995). The use of pro-oxidant additives makes polyolefin oxo-biodegradable (Guillet et al. 1995) via catalyzing the breakdown the long chain of polyolefin and produce lower molecular weight product. In this project, cobalt stearate was chose as a pro-degradant additive. Cobalt stearate is a transition metal ion complexes which posses a remarkable ability to decompose the hydro peroxide formed during the oxidation of polymers. They are used as pro-oxidant additives in most of commercials photo degradable composition (Mohamed Islam et al. 2010)

Polypropylene is a polyolefin where the high molecular weight can be broken into small molecule by heat. The polyolefin usually has long intertwined and cross linked chains of simple hydrocarbons. These chains have very high molecular weights of hundreds of thousands versus molecular weights of 18 for water (H₂O) and 44 for carbon dioxide (CO₂). By breaking down into a small molecular weight, the pro-degradant additives can completely degrade the polymer (Doty 2005).

In this work, we examined the effect of PDA on photo-oxidative aging of polypropylene film based on the changes in tensile properties and carbonyl index. On top of that, we observed the changes in the appearance of PP and monitored the degradation of the PP films using FTIR

EXPERIMENTAL METHOD

MATERIALS

Commercial polypropylene (PP, Mw =24) PM255 was used for the film preparation supplied by Titan Petchem (Malaysia). The crystalline melting point is 170°C, density at amorphous is 0.90 g/cm³ and density at crystalline is 0.95 g/cm³. The pro-degradant additives (PDA) used was cobalt stearate (Mw 625.88) with melting points between 109 and 112°C and density 1.7 g/cm³ was purchased from Mitco Group (Malaysia).

PREPARATION OF FILMS

PP granules were dry mixed with varying amounts of PDA ranging from 1.0-5.0% w/w in a tumbler and then fed into the Brabender plasticorder Labstation single screw extruder with speed of 5 rpm and 30 bar pressure (Alaudin et al. 1995). The temperatures in the feed zone was 170°C; compression zone, 175°C; metering zone, 185°C and die zone 190°C were used for extrusion. At concentrations higher than 3.0% w/w of PDA, the compounds exhibited a blooming effect. After being extruded, the continuous compound was cut into a small pellet. After pelletized,

the compounds were dried in a vacuum oven at 80°C for 4 h to remove all the moisture content in the sample. Then sheeting process was carried out using a hot press machine at 180°C followed by cooling for 3 min.

PHOTO-DEGRADATION PROCEDURE

PP films were subjected to an accelerated test in a QUV basic chamber (Q-Panel Co.). The chamber was equipped with UVB-313 fluorescent lamps with maximum peak at 313 nm. The samples were irradiated with UVB fluorescent lamps generating energy between for 280 and 300 nm at 50°C (with radiation level 0.63 W/m²) for about 100 h. The samples were removed every 24 h in order to evaluate their properties.

EVALUATION OF DEGRADATION

Changes in tensile strength and elongation at break were monitored using Instron machine. Samples with dumbbell shape with 0.1-0.2 mm thickness were cut from the films for tensile strength measurements as per ASTM 638 (Avella et al. 2001). The cross head speed was 1.3 mm/min. The tests were undertaken in an air-conditioned environment at 25°C and a relative humidity of 65%. Five samples were tested for each experiment and the average value was determined.

Structural changes upon exposure were investigated using FTIR spectroscopy. The test was performed on the film using IR band between 4000 cm⁻¹ and 450 cm⁻¹ and at transmittance 16 cm⁻¹. CI was used to characterize the degree of photo-oxidation of polypropylene. It is defined as a ratio of an absorbance carbonyl around 1870-1650 cm⁻¹ to an internal constant band at 1375 cm⁻¹. These have been calculated by the baseline method (Avella et al. 2001):

$$\text{Carbonyl index (CI)} = \frac{\text{Absorption at the maximum of carbonyl peak}}{\text{Absorption at 1375 cm}^{-1}}$$

RESULTS AND DISCUSSION

PHOTO-OXIDATIVE STUDIES

Figure 1 shows the effect of photo-oxidative aging on appearance of PP films for PDA1PP and PDA5PP after 100 h keeping the sample in the UV chamber. The film was labeled as PDA1PP for PP with 1 wt% of PDA, PDA5PP for PP with 5 wt% of PDA and followed by exposure time from day 1 until day 4 (D#), respectively.

After 3 days, the PDA3PP, PDA4PP and PDA5PP start to degrade (Osawa et al. 1979) and could not be tested further. Based on the observation, after 100 h the samples for 3, 4 and 5 wt% of PDA was totally pulverized. The catalytic degradation in the presence of transition metal in PP has been attributed to its ability to generate free radical on the PP surface, which later reacts with oxygen to generate carbonyl groups (Roy et al. 2008). PDA requires the presence of oxygen and some form of activation energy like light (UV) or heat for the initial oxidative degradation of the polymer

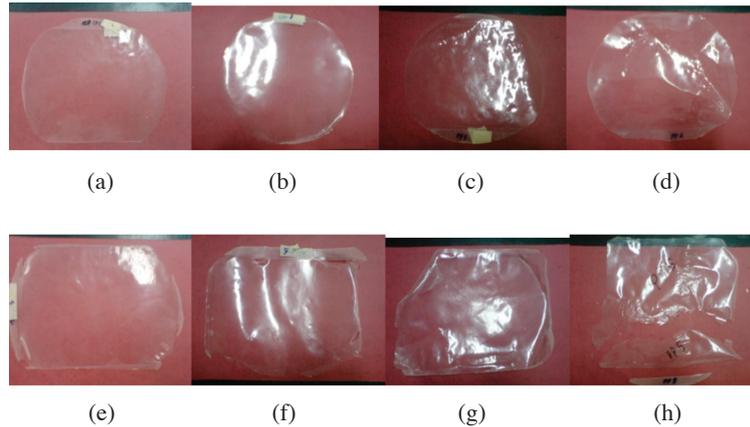


FIGURE 1 Effect of photo-oxidative aging on appearance of PP films; PDA1PP (a) day 1, (b) day 2, (c) day 3, (d) day 4, and PDA5PP of (e) day 1, (f) day 2, (g) day 3 and (h) day 4

back-bone (Nils & Kleppe 2009). According to Roy et al. (2006) during exposure the amorphous regions are effected as oxygen diffuses into the amorphous phase leading to chain scission thereby weakening the intermolecular forces further and finally the films disintegrated to pieces.

Figure 2 represents the effect of exposure time in UV chamber on tensile strength and elongation break of PP films in the presence of additives. Both properties decreased with increase in the percent of PDA with 100 h of photo-oxidative aging. The reduction in tensile strength of the film can

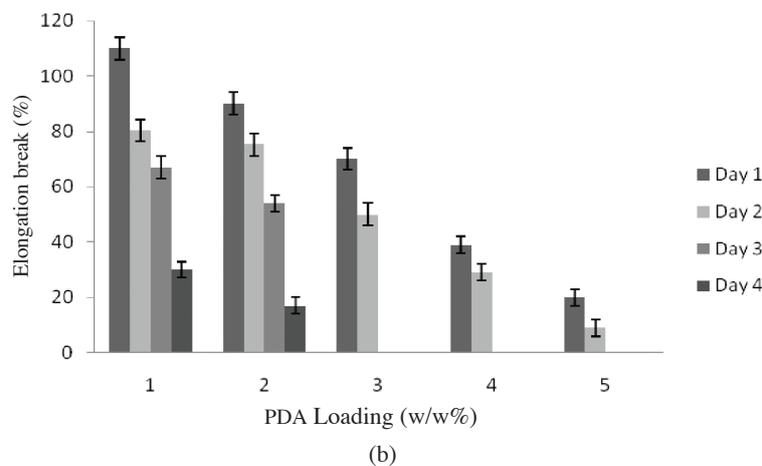
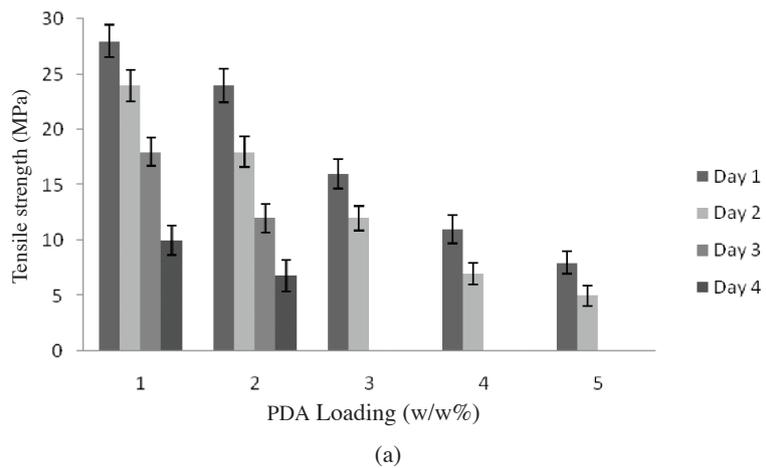


FIGURE 2. Effect of PDA loading on (a) tensile strength and (b) elongation at break of PP film after 100 h photo-oxidative aging

be attributed to chain scission due to the PDA with aging, which finally led to the embrittlement of the sample. The PP chains take up oxygen and led to the formation of hydro peroxide which breakdown to give oxygenated products (Roy et al. 2006; Sudhakar et al. 2007). The reduction in elongation at break with increasing PDA loading may be attributed to the fact that PDA particles do not elongate coherently with PP. Therefore less strain is required to cause the sample to fail. Poor interaction between PP and PDA particles permits easier break propagation (Sudhakar et al. 2007). Films containing 1.0% PDA retained high level of tensile strength and elongation break for entire exposure time period. After 100 h photo-oxidative aging, PDA3PP, PDA4PP and PDA5PP films became completely pulverised and could not be tested further. The results indicated that the presence of PDA in PP film takes part in the degradation and the activity is proportional to the amount of PDA (Osawa et al. 1979)

The degree of degradation upon exposure to UV in the UV chamber was monitored by changes in the structure (FTIR). Photo-degradation led to generation of carbonyl groups in the polymer surface. Figure 3 shows the change in FTIR spectra of polymer containing 1% of PDA due to the photo-oxidative treatment at 100 h.

FTIR spectra of PP film containing mixture of PDA are shown in Figure 3. Significant changes in the carbonyl (1785–1700 cm^{-1}), hydroxyl region (3400 cm^{-1}) and amorphous (1300 cm^{-1}) were observed upon aging. The absorption band around 1714 cm^{-1} , which can be assigned to be at the C=O stretch of a ketones, grew in intensity and the same time a band broadening was

observed which indicated the presence of more than one oxidation product. The carbonyl band can be assigned to C=O stretching vibrations in aldehydes and/or esters (1733 cm^{-1}), carboxylic acid groups (1700 cm^{-1}) and γ lactones (1780 cm^{-1}). After thermo-oxidative aging, slight changes were observed in the carbonyl peak C=O from 1601 cm^{-1} of PDA1PP when added PDA to 1643 cm^{-1} (day 1), 1644 cm^{-1} (day 2), 1738.48 cm^{-1} (day 3), and 1767 cm^{-1} (day 4). PDA5PP changes the carbonyl peak from 1637 cm^{-1} to 1678 cm^{-1} (day 1), 1778 cm^{-1} (day 2), 1788 cm^{-1} (day 3) and 1795.12 cm^{-1} (day 4). The carbonyl index (CI) was calculated by taking ratio of absorption bands at maximum peak of carbonyl index and 1375 cm^{-1} .

Figure 4 shows the carbonyl index of PP film with 100 h of photo-oxidative aging. The increase in CI is proportional to the amount of PDA in the film with aging time. PDA3PP, PDA4PP and PDA5PP films were completely pulverised after 100 h of photo-oxidative aging. This was due to the mechanism of the transition metal catalyzed degradation of polyolefin is a free radical chain mechanism (Bikaris et al. 1997; Grant 1991; Osawa et al. 1998). When polymer containing PDA absorbs energy, electron transfer occurs in the 3d subshell of the cobalt atom leading to the production of carboxylic acid free radical ($\text{R}'\text{COO}^\bullet$). Then, it is further decarboxylates to form R'^\bullet which transforms polyolefin films (RH) into free radical R^\bullet . In the presence of heat and oxygen, hydro peroxides ROOH are formed which further decomposed to radicals in the presence of metal salts. The reactions are shown as below;

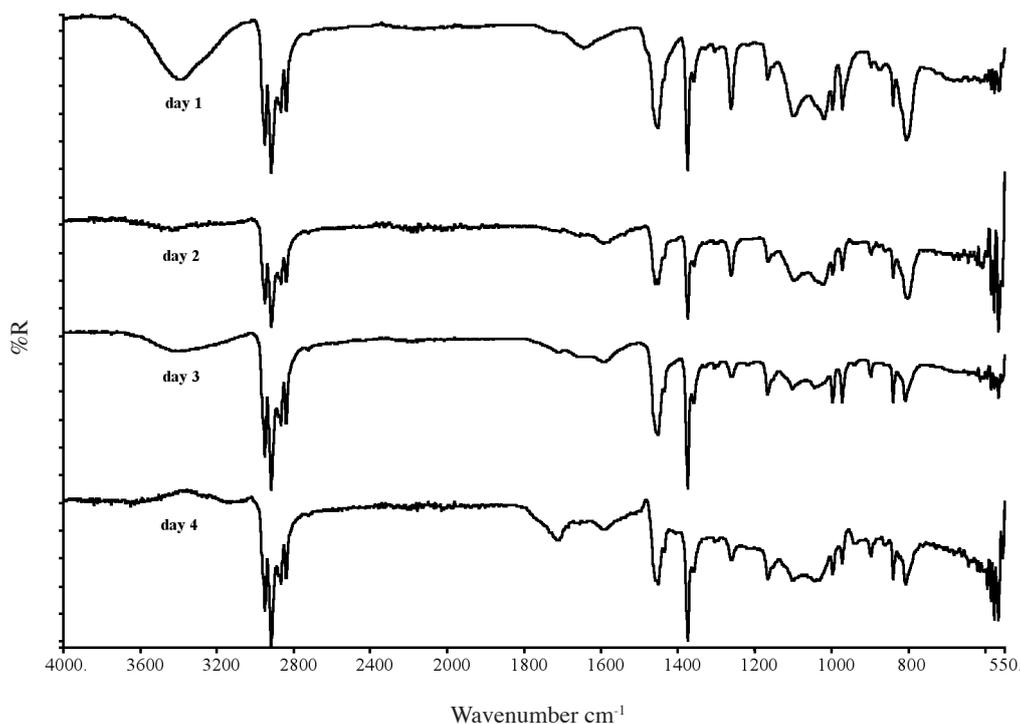


FIGURE 3. Spectrum of PDA1PP within 100 h of photo-oxidative aging

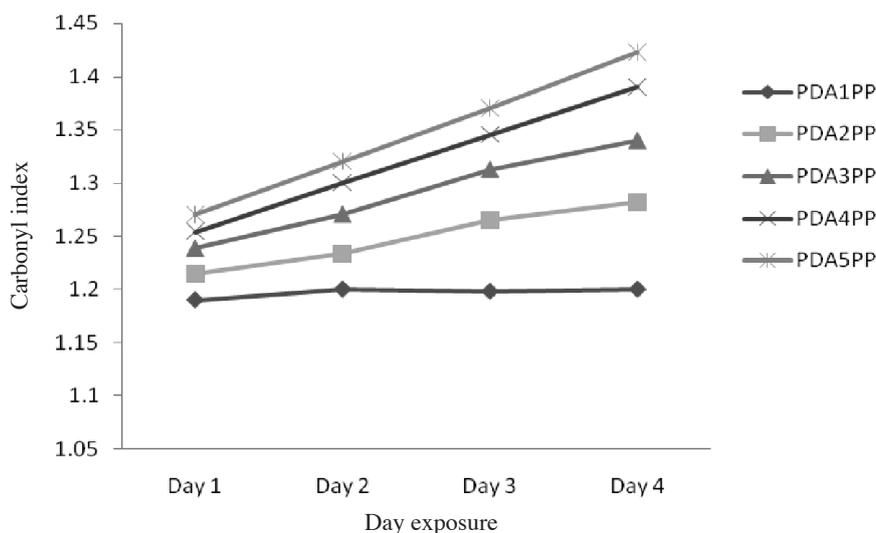


FIGURE 4. Carbonyl index of PP films within 100 h of photo-oxidative aging



where, M and RH represent a cobalt salts and PP molecule, respectively. It is known that these redox reactions amount to a lowering of the activation energy of bimolecular peroxide decomposition. This decomposition by a redox couple (a transition metal in two oxidation states) will be a factor in both heat and light-induced oxidation.

CONCLUSIONS

Based on these results it can be concluded that PDA promoted the degradation of polypropylene within photo-oxidative aging. The rate of degradation was enhanced and found to be dependent on the amount of cobalt stearate. In the presence of UV, the pro-degradant additives can contribute to the degradation process.

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