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# EFFECT OF PRO-OXIDANT ADDITIVES ON DEGRADATION OF MULCH FILM BASED ON RECYCLED POLYETHYLENE

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## ABSTRACT

The effect of pro-oxidant additives (Iron, Cobalt and Manganese stearates) on the biodegradation of recycle polyethelene mulching films was studied in both accelerated weather and natural exposure conditions. The degradation degree of film was determined by measuring mechanical properties and scanning electronic microscope (SEM). The results showed that the mechanical properties of film samples with pro-oxirant additives decreased rapidly, and that surface film with additives was degraded clearly compared to the films without additives after 30 cycles of accelerated weather. Reliability in terms of acceleration are 28 - 30 cycles of exposure and in the natural conditions reached 10-12 months.

*Keywords*: pro-oxidant additives; photodegradable mulching films, polyethylene with pro-oxidants.

## 1. INTRODUCTION

Polyolefin film (plastic bags, mulch ....) has become familiar in everyday life activities. With the advantages of durable, convenient and low cost, polyolefin film was present in almost all field of daily life activities. However, these products are often very persistent when released into the environment, which is negative impact on the environment and human health. Plastic waste causes serious impact to soil and water because it would prevent oxygen ingress through the soil that causing soil erosion and making the soil not porous, less nutrients support, which makes plants grow slowly. More seriously, soil and water contaminated by polyolefin film will affect directly and indirectly to human health. When burned they produced emissions dioxin and furan toxicity, endocrine influence, caused cancer, reduced immunity, digestive disorders and birth defects in infants. Therefore, the research on the manufacture of the potentially degradable polyolefin films to replace the persistent products is now an urgent request to solve the current [1 - 3].

There are a number of methods to minimize the impact on the environment of polyolefin films as collected and recycled, biodegradable increase of film material by adding some additives to promote the degradation of the films after disposal, blend of polyolefin with natural

or synthetic polymer as polylactic acid, polycaprolactam, or the research of environmentally friendly products.

Currently, the biodegradable film based on PE or PP with pro-oxidant additives has been interested. Pro-oxidant additives will make the path to self-destruct polyolefin catalysts to break the chain length of the polyolefin into shorter chain molecules and the incorporation of oxygen into these molecules as organic functional groups (i.e.: carboxylic or hydrocarboxilic acids, esters as well as aldehydes and alcohols). The molecules of low molecular weight are easily degraded by microorganisms, temperature and humidity in the environment, making the biomass, $CO_2$ and $H_2O$ [1 - 5].

In this report, biodegradable films with and without pro-oxidant additives were prepared based on recycle PE resin. The biodegradation was determined in accelerated weather and natural exposure. Film characteristics were determined by measuring the mechanical properties (tensile strength and tensile elongation at break and SEM image.

## 2. EXPERIMENTAL

### 2.1. Materials

Low-density Polyethylene (LDPE) (Malaysia); recycled polyethylene (PE) (Vietnam); pro-oxidant additives: Iron (II) stearate $Fe(C_{17}H_{35}COO)_2$, cobalt(II) stearate $Co(C_{17}H_{35}COO)_2$, manganese (II) stearate $Mn(C_{17}H_{35}COO)_2$, (Merck), containing by weight 99 % was made under masterbatch form at polymeric Lab - Institute of Chemistry, additive process palmowax (Malaysia).

### 2.2. Method

The process of film blowing was done using plastic mixture (including mLDPE 4%, recycle polyetylene plastic 67,2 % and polyetylene plastic 22,8 %). The plastic mixture was mixed with the amount of masterbatch containing additives such that each type of additive concetration in the film is 1 % w/w.

- Film blowing: thin films (50 µm) were blowed from recycled polyethylene and masterbatch as mentioned above so that the concentration of additive in the film is 1 % w/w.

- The film samples were noted as follows: film without additive (PE), film with Iron (II) stearate (PE-Fe), film with manganese (II) stearate (PE-Mn), film with cobalt(II) stearate (PE-Co).

- The film samples with or without pro-oxidant additives were tested in accelerated weather and natural exporuse after that mechanical properties and surface morphology of the films were determined.

- *Accelerated weathering*: PE films with and without additives were accelerated weather tested on equipment UVCON (Ultra Violet / Condensation Screening Device) Model UC-327-2. Samples were cut into rectangular dimensions of 7 × 14 (cm × cm) and mounted on aluminum panels. 30 cycles accelerated weather (UV 8-hour day, 4 hour stop / 1 cycle) were performed to evaluate weather durability and longevity. Samples were taken periodically and after every 4 cycles samples were undertaken to measure the durability and longevity (ASTM G154).

- *Natural exposure:* Samples were cut into rectangular dimensions of 10 × 14 (cm × cm), hanging on the rack model. Film samples were exposed in period from July 2013 to July 2014. In that period, the samples were taken periodically to determine the properties.

*2.3. Methods of analysis and testing*

- Testing of critical mechanical properties: Samples of the films were tested accordingly to determine the tensile properties. Tensile tests were performed at room controlled conditions (25 $^0$C and 50 % humidity) and at 5 mm/min rate by AGS-J 10 kN (Shimadzu) equipment. Each sample was measured 5 times and then taking the average of the measurements.

- Morphology of the film surface is determined on the scanning electron microscope Hitachi S4800 FESEM at Institute of Materials Science - Academy of Science and Technology Vietnam).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of additives on the properties of film in accelerated weathering

Tensile strength and elongation at break of the film samples with and without pro-oxidant additives were measured. The results are presented in Figure 1 and Figure 2.

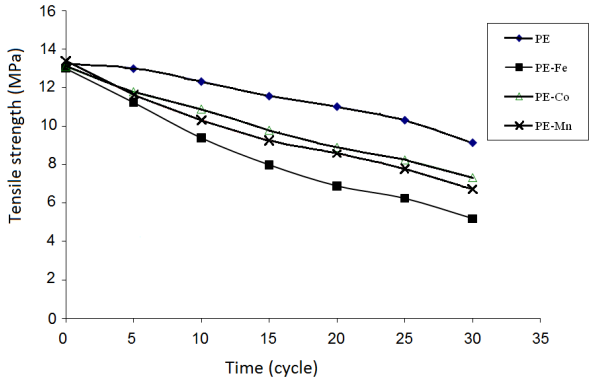



*Figure 1.* Decrease in the tensile strength due to accelerated weather testing.

The results showed that the value of $t_{1/2}$TS (the time at which the tensile strength decrease by 50 % compared to the initial value, when the $t_{1/2}$TS < 50 % of the initial value, the film as broken and film containing additives decreases faster than that without additives. The PE-Fe film has the fastest decreases, the value of $t_{1/2}$TS is about 24 cycles. Value $t_{1/2}$TS of the PE-Mn film is about 27 cycles, 3 cycles higher than that of PE-Fe; while the value of PE-Co film is of about 29 cycles, which is of 5 cycles more than that of additive iron stearate. On the other hand, PE films containing pro-oxidants exhibited a significant decrease in tensile strength.

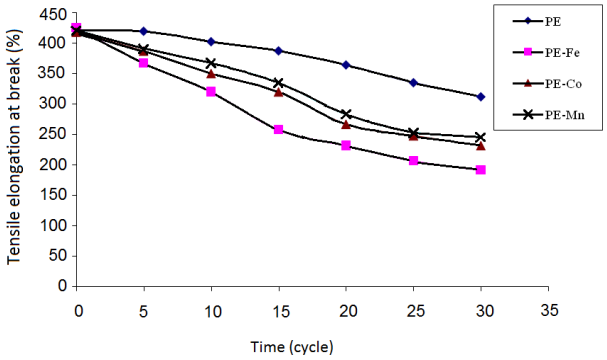
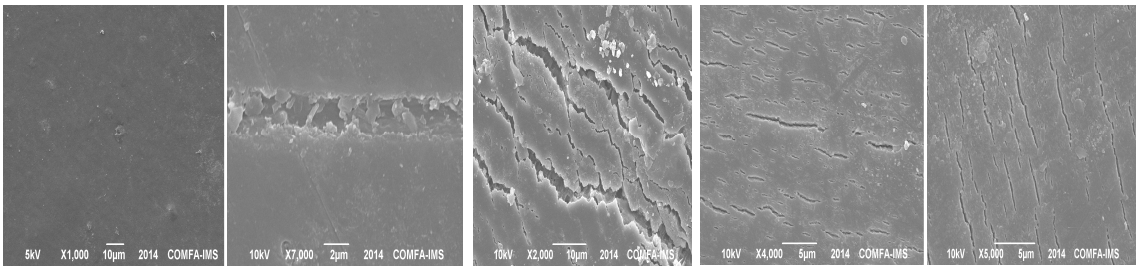



*Figure 2.* Decrease in tensile elongation at break due to accelerated weather testing.

Similarly to broken tensile, the tensile elongation at break of PE-Fe film occurs much faster than that of the film without additives and it is the fastest of the PE-Mn and PE-Co films. Value t1/2EB (time at which the elongation at break decrease by 50 % compared to the initial values) of PE-Fe is about 26 cycles. Thus it suggests that the effective degradation of the PE-Fe film is higher compared with the manganese and cobalt based PE films. This may be due to differences in chemical structure of pro-oxidant additives.

- The surface morphology of the film samples before and after accelerated weather is presented in Figure 3.



| Original | PE film after 30 cycles | PE-Fe film after 30 cycles | PE-Mn film after 30 cycles | PE-Co film after 30 cycles |
|---|---|---|---|---|

*Figure 3.* The surface morphology of the film samples before and after accelerated weather.

The surface morphology investigation of the films showed that after weather acceleration the films with additives exhibited cracks appearing on the surface. The cracks density on the surface of the PE film is reduced in comparison with those in the other additives added samples. This indicates an important role of pro-oxidant additives, namely under the impact of high energy radiation, the additive is capable of promoting the disconnected chain macromolecules into shorter chain molecules and the incorporation of oxygen into these molecules as organic functional groups (i.e: carboxylic or hydro-carboxilic acids, esters as well as aldehydes and alcohols). The photo-oxidative behavior was found to depend upon the type of metal present in the matrix and follows the order: Fe>Co>Mn.

### 3.2. Effect of pro-oxidant additives on the properties of film in natural exposure

Tensile strength and elongation at break of the film samples with and without pro-oxidant additives were determined. The results are presented in Figure 4 and Figure 5.

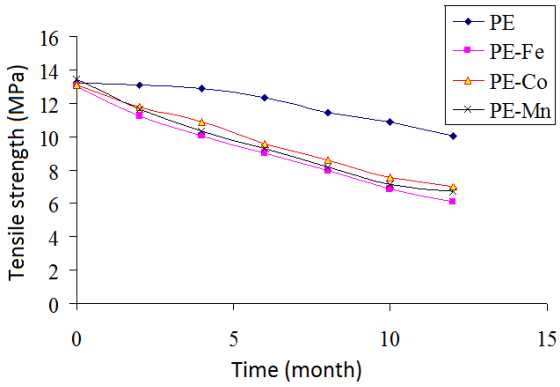



*Figure 4*. Decrease in the tensile strength due to natural weather testing.

It can be noted that tensile strength of PE film mitigated after 12 months of outdoor weather exposure. Conversely, tensile strength of PE films containing additives significantly decreased after 12 months of outdoor weather exposure. This is due to that the ability of the metal stearate in catalyzing the degradation process has been reported to arise from its ability to intra-molecularly cleave into radicals, which can abstract hydrogen from the polymer chain, thereby generating free radicals. Products are hydrophilic oligomer, the double bond and the ester group susceptible to hydrolysis to form smaller molecules, a source of food for microorganisms and bacteria. After about 10-12 months of exposure, tensile strength of the film samples containing additives are reduced to less than 50% of the initial value.

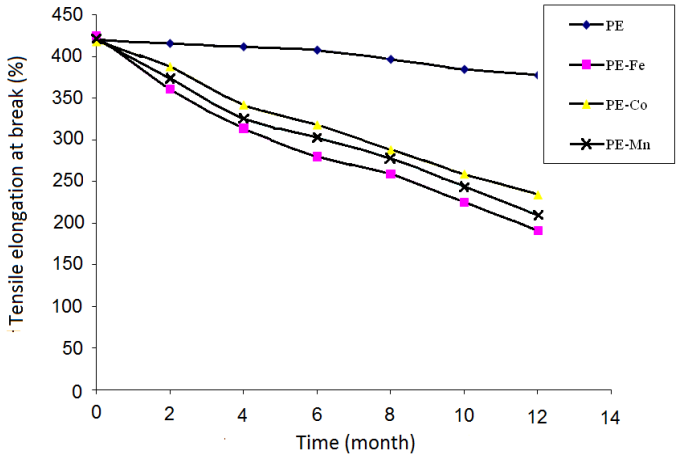



*Figure 5***.** Decrease in tensile elongation at break due to natural weather testing.

Tensile elongation at break of the film sample containing additives in samples exposed to natural conditions also decreased over time. The combined influence of such factors as temperature, UV radiation, humidity etc plays a role of an agent to promote the process of free radicals, and cause hydrocarbons disconections in the molecular structure of polyethylene. The interruption and oxidation of macromolecules circuit result in forming hydrophilic molecules such as esters, ketones, alcohol, which in turn, lead to deterioration of physical properties,

especially elongation at break. Meanwhile the elongation at break of PE samples decreased slightly.

## 4. CONCLUSIONS

This study attempted to investigate the effects of pro-oxidant additives on mechanical strength and the surface morphology of films in two conditions, accelerated weather and natural weather. The results showed that for the film samples containing pro-oxidant additives, tensile strength and elongation at break decreased significantly during the trial period. Besides, tensile strength of the film samples containing additives was reduced to less than 50% after 12 months exposed under natural weather condition. Analysis results by morphological surface SEM images showed that after 30 cycles accelerated weather, the surface film containing additives were degraded compared with films containing no additives.

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## REFERENCES

1. Abrusci C., Pablos J. L., Marín I., Espí E., Corrales T., Catalina F. - Comparative effect of metal stearates as pro-oxidant additives on bacterial biodegradation of thermal- and photo-degraded low density polyethylene mulching films, International Biodeterioration & Biodegradation **83** (2013) 25-32.
2. Abrusci C., Pablos J. L., Marín I., Espi E., Corrales T., Catalina F. - Photodegradation and biodegradation by bacteria of mulching films based on ethylene-vinyl acetate copolymer: effect of pro-oxidant additives, Journal of Applied Polymer Science **126** (2012) 1664-1675.
3. Chiellini E., Corti A., Swift G. - Biodegradation of thermallyoxidized, fragmented low-density polyethylenes, Polymer Degradation and Stability **81** (2003) 341-351.
4. Ioanna Kyrikou, Demetres Briassoulis, Miltiadis Hiskakis, Epifaneia Babou - Analysis of photo-chemical degradation behaviour of polyethylene mulching film with pro-oxidants, Polymer Degradation and Stability **96** (2011) 2237-2252.
5. Roy P. K., Titus S., Surekha P., Tulsi E., Deshmukh C., Rajagopal C. - Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium, Polym Degrad Stab **93** (2008) 1917-22.

## TÓM TẮT

### ẢNH HƯỞNG CỦA PHỤ GIA XÚC TIẾN OXI HÓA ĐẾN KHẢ NĂNG TỰ HỦY CỦA MÀNG PHỦ TRÊN CƠ SỞ NHỰA POLYETYLEN PHẾ THẢI

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Ảnh hưởng của phụ gia xúc tiến oxi hóa (muối stearat của Fe, Mn, Co) đến khả năng phân hủy của màng phủ trên cơ sở nhựa polyetylen phế thải đã đươc đánh giá trong điều kiện gia tốc thời tiết và phơi mẫu tự nhiên. Mức độ phân hủy của màng được xác định bằng cách đo tính chất cơ lí và ảnh SEM chụp bề mặt màng sau khi gia tốc thời tiết. kết quả cho thấy tính chất cơ lí của màng chứa phụ gia giảm nhanh so với màng không chứa phụ gia. Cụ thể, độ bền kéo của màng chứa phụ gia giảm xuống còn dưới 50 % giá trị ban đầu sau 12 tháng phơi mẫu tự nhiên và 30 chu kì gia tốc thời tiết. Kết quả chụp ảnh SEM cho thấy bề mặt các mẫu màng chứa phụ gia bị phá hủy so với mẫu màng không chứa phụ gia sau 30 chu kì gia tốc thời tiết.

*Từ khóa:* màng phủ tự hủy; màng phủ nông nghiệp.