

Comparison of the degradability of various polyethylene films containing pro-oxidant additive

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Abstract

This study aims to compare the effect of the type of polyethylene matrix (HDPE, LLDPE) and evaluate the role of pro-oxidant additive on the degradation of PE film samples. The degradability of HDPE, LLDPE films without and with pro-oxidant (0, 1 and 3% w/w) was studied. Thermo-oxidative degradation of PE films was carried out in an oven at 80 °C for a maximum period of 7 days. The progress of thermo-oxidative degradation was measured by monitoring physical and chemical changes of films such as mechanical properties, FTIR and SEM. The results showed that, whatever the pro-oxidant used, the HDPE matrix is less efficiently oxidized than LLDPE matrix. Tensile strength and elongation at break decreased during treatment. FTIR traces exhibited that carbonyl group's peak in the region 1700-1800 cm⁻¹ arises during thermal treatment as a result of oxidation. The degradation rate of PE films increased by increasing the amount of pro-oxidant additive incorporated.

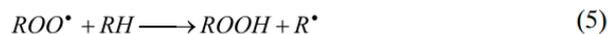
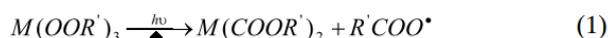
Keywords. Pro-oxidant, thermo-oxidation, polyethylene, degradation.

1. INTRODUCTION

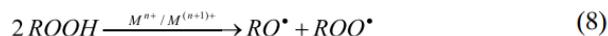
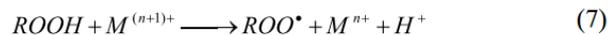
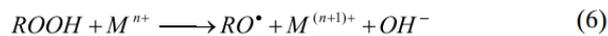
Plastics are a major contributor to the waste problem facing all societies. This has led to the development of different types of environmentally friendly polymeric materials. In particular, the use of biodegradable polymers has greatly increased in several applications. Polyethylene (PE) films containing pro-oxidant additives in their formulations have been introduced in outdoor plastics markets as new promising biodegradable materials. Primary applications of these degradable materials are mainly in the mulching and packaging film applications as well as other products of limited lifetimes, e.g. carry bags. These oxo-biodegradable materials are intended to be mineralized in soil in the case of agricultural films or during composting in the case of packaging applications. An excellent way to make polyolefin materials degradable is to include in the formulation pro-oxidant additives, which can effectively enhance the degradability of these materials [1].

In the last decade several research works supported the possibility of the biodegradability of these materials. Transition metals complexes, especially iron, cobalt and manganese stearate, have the ability to decompose the hydroperoxides formed during oxidative degradation of polymers and therefore, they are sometime used in commercial

photodegradable formulations. Abiotic agents such as solar ultraviolet radiation (UV), heat or mechanical stresses could initiate the first stage of degradation: an oxidation process promoted by the additives. Once oxidized, polyethylene should exhibit a significant reduction of its molecular weight, and thus low molecular weight compounds could be easily assimilated by the microorganisms in the ecosystem where the films were disposed (biotic mechanism) [2-4]. The mechanism of action of pro-oxidant additives is described in scheme 1.



(RH = Polyethylene R' = alkyl group)



Scheme 1 Initiation of degradation process by pro-oxidant additives

Degradation of polyethylene under thermal condition has been widely studied. Moreover, most

studies on degradation have focused on LDPE. Therefore, the objective of the study was to compare the degradability of various films (HDPE, LLDPE) with and without pro-oxidant.

2. MATERIALS AND METHODS

2.1. Materials

HDPE F00952 with a melt flow index of 0.05 g/10 min, LLDPE FV149M with a melt flow index of 2.0 g/10 min, SABIC (Saudi Arabia). Cobalt, ferric and manganese stearate, Jingjiang Hangsun Plastic Additives Co., Ltd (China). These additives were introduced into the PE matrix in the form of a masterbatch (manganese/ferric/cobalt stearate weight ratio of 18:4:1).

2.2. Sample preparation

HDPE and LLDPE films with a thickness of 30 μm were used in this study. These films were made by extrusion blowing using a SJ 45 extruder with a 45 mm screw of L/D 28:1. The pro-oxidants were incorporated into the film formulation at a concentration of 1 and 3 %, films without pro-oxidant were used as a control. Film samples were cut into dumb-bell specimens according to ASTM D638 and were used for all tests.

Table 1: Sample labeling

No	Sample label	Amount
1	HD0	100 HDPE
2	HD1	100 HDPE + 1 Additive
3	HD3	100 HDPE + 3 Additive
4	LLD0	100 LLDPE
5	LLD1	100 LLDPE + 1 Additive
6	LLD3	100 LLDPE + 3 Additive

2.3. Tensile tests

Tensile testing was carried out on an Instron 550 according to ASTM D638 at a cross-head speed of 50 mm/min. All the test samples were conditioned at room temperature and relative humidity (RH) for 24 h before testing. Three samples were tested under each batch and the average value was reported.

2.4. Thermo-oxidative tests

Thermo-oxidative testing was carried out by

placing the dumb-bell specimen in an air oven at 80 $^{\circ}\text{C}$ for 7 days of exposure based on ASTM D5510 (Heat Aging of Oxidatively Degradable Plastic). The extent of degradation after 1, 3, 5 and 7 days was monitored by measuring the tensile properties of the specimen. Degradation is to be evaluated using this standard and subsequent testing for embrittlement (< 5 % elongation).

2.5. Morphological studies

A scanning electron microscope JEOL 6390 model was used to study the morphology of the samples. Samples were sputter-coated with gold before scanning.

2.6. FTIR studies

A Fourier transform infra-red (FTIR) spectrometer (Shimadzu IR prestige 21) was used to obtain the IR spectra. The equipment was operated with a resolution of 4 cm^{-1} and scanning range from 4000 to 400 cm^{-1} . Carbonyl index was defined as the ratio of area around band of 1718 cm^{-1} , attributed to carbonyl groups, and area of band at 1375 cm^{-1} , attributed to CH_3 . All measurements were performed with three samples.

3. RESULTS AND DISCUSSION

3.1. Changes in mechanical properties

The changes in tensile strength and elongation at break for films are shown in figures 1 and 2, respectively.

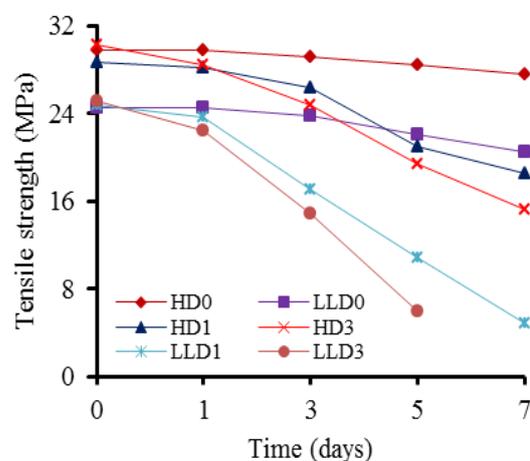


Figure 1: Changes of tensile strength of films

It can be seen from figure 1 that the tensile strength of unoxidised PE films with and without

pro-oxidant are almost similar. This suggests that there is almost negligible amount of degradation during the blend processing stage. As shown in figure 1, the additive-free HDPE and LLDPE polymer films were slowly oxidized to a low extent, LLD0 films lost about 15.6% of their tensile strength or even remained completely non-oxidized after 7 days as in the case of HDPE. In the presence of pro-oxidant additive, the HDPE matrix was the less sensitive to oxidation. The changes in the tensile strength of PE containing pro-oxidant is quiet significant. After 7 days of thermo-treatment, the tensile of HD1, HD2 and LLD1 is 18.52, 15.24 and 4.58 MPa, respectively.

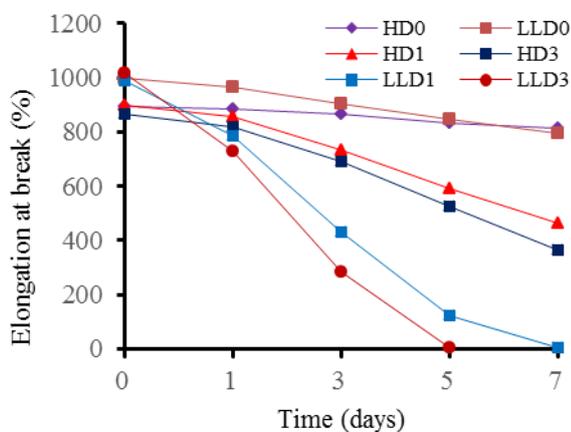


Figure 2: Changes of elongation at break of films

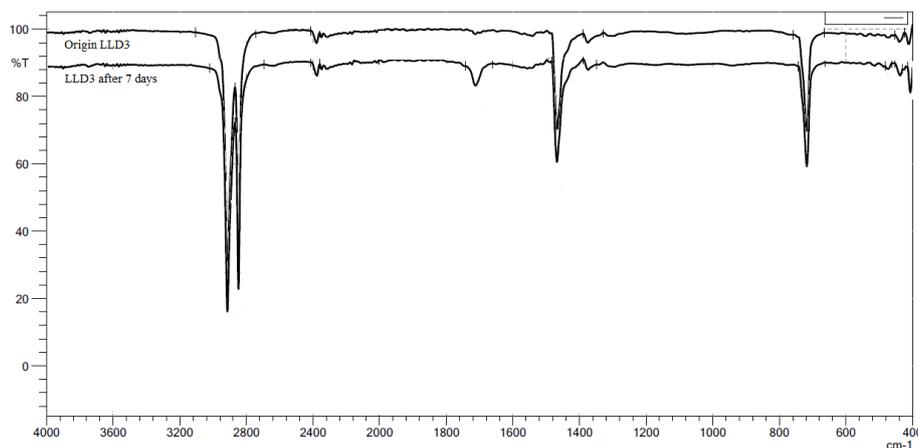


Figure 3: FTIR spectra of LLD3 films, before and after thermal treatment

An increase in absorption in the carbonyl region was recorded with time in the samples thermally aged containing pro-oxidants (Fig. 3). The plot of 1640-1850 cm^{-1} range of carbonyl groups, as determined by the overlapping bands corresponding to acids (1710-1715 cm^{-1}), ketones (1714 cm^{-1}), aldehydes (1725 cm^{-1}), ethers (1735 cm^{-1}) and lactones (1780 cm^{-1}) was observed, thus indicating the presence of different oxidized

The tensile strength of LLD3 films (LLDPE with 3% pro-oxidant) decreases drastically after 1 days of ageing and it becomes nearly zero after 7 days making them very fragile.

Elongation at break is commonly used to monitor degradation process rather than other mechanical properties. Figure 2 reveals the changes of elongation at break of various films during treatment. Similar trends are observed in the elongation at break can be seen in Figure 2. HD0, and LLD0 exhibit only about 9.4 %, 20.1 % loss while HD1, HD3 films lost about 48.4 %, 52.8 % of their elongation at break in 7 days, respectively. On the other hand LLD1, LLD3 experiences almost 100 % loss in 7 days.

These results show clearly that the pro-oxidant in PE has played a significant role in inducing oxidation in PE leading to their embrittlement. It can be also expected that oxidation of PE samples containing pro-oxidant will increase their crystallinity leading to a lack of a plastic matrix between crystalline hard domains.

3.2. FTIR

The oxidation of polyethylene resulting products with carbonyl groups was monitored by measuring the existence of carbonyl peaks. Fig. 3 shows the FTIR spectra of treated and untreated LLD3 films.

products. The absorption maxima can be assigned to carboxylic acid and ketones as the major components followed by esters in agreement with the results obtained by other authors [5].

3.3. Carbonyl index (CI)

Oxidation of PE films leads to the accumulation of carbonyl groups. Figure 4 shows

the carbonyl index (CI) of samples during treatment.

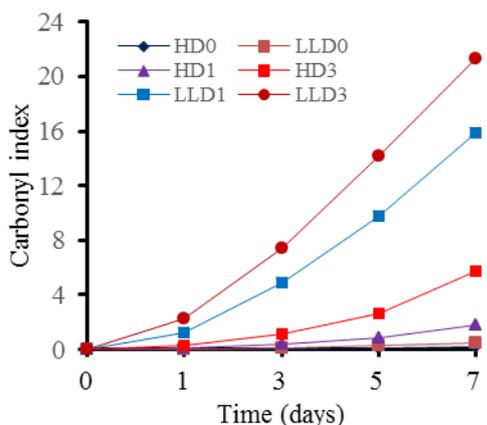


Figure 4: Carbonyl index of PE film samples during thermal treatment

In the early periods of treatment, CI slightly

increased. The results obtained assumed that the thermo-oxidation of PE is characterized by an induction period in which oxygen uptake, that is responsible for the intermediate products formation includes hydroperoxides, peroxydes, alcohols, ketones, occur at a very low rate. After 1 day of treatment, the CI increased more significantly. Samples containing pro-oxidant (HD1, HD3, LLD1, LLD3) much more increase of CI than pure samples (HD0, LLD0) during treatment as the result of higher degradation level. This trend is also earlier reported in our results [6].

3.4. Surface morphology (SEM)

The degradation of PE films containing pro-oxidant produced changes in the surface morphology. To illustrate these changes, in Fig. 5 the SEM photographs of PE films, original and thermally degraded after 7 days at 80 °C are shown.

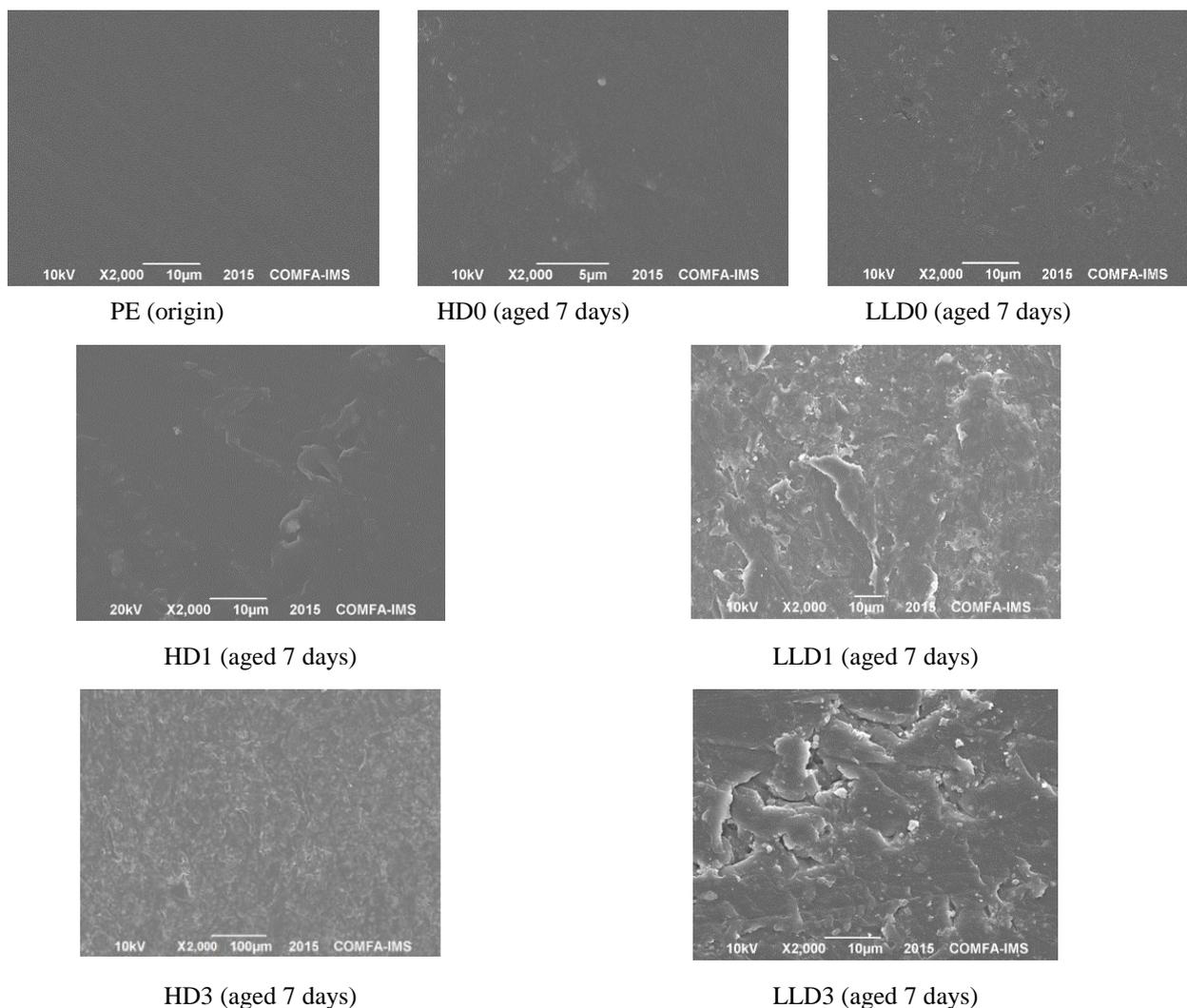


Figure 5: SEM micrographs of PE films

As seen from the figure 4, original HD0, LLD0 films and degraded these films present a smooth surface free of defects. In contrast, the surfaces of PE films with pro-oxidant after thermal aging showed a pronounced roughness with craters/grooves. The extent of the damage was much more pronounced in the LLD1, LLD3 films. The surface damage produced also favoured swelling and relaxation of the whole material structure and facilitated the diffusion of water and low soluble compounds inside therefore, substantially accelerating abiotic oxidation and the second step of biotic degradation.

4. CONCLUSION

The effect of pro-oxidant additive on enhancing degradation of HDPE during thermal treatment has been investigated. The mechanical properties were found to be decreased with increasing amount of pro-oxidant loading. LLDPE films with 3 % of pro-oxidant (LLD3) lost 100 % of their initial mechanical properties, whereas pure films lost less than 20 % of their initial mechanical properties after 7 days of thermal treatment. The very important result is that, whatever the pro-oxidant used, the HDPE matrix is less efficiently oxidized than LLDPE matrix. FTIR study also showed that carbonyl groups, as the result of oxidation, grew faster in the films with pro-oxidant than pure films. The results indicate that pro-oxidant accelerates the degradation of PE films under thermal treatment. It was found that the extent of degradation depended on the amount of additive which was added.

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