

The Effect of Environmental Conditions on Electron Beam Cross-linked Agricultural Polyethylene Films

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ABSTRACT

UV radiation of polymers causes photo-oxidation degradation which results in loss of physical and mechanical properties and limits their applications. In order to study long term stability of the radiated cross-linked polyethylene films on outdoor exposure, low density polyethylene (PE) in pure form mixed with photostabilizers and antioxidant (PE-st) was irradiated by electron beam in air at 30-300 kGy doses. The irradiated samples were exposed to the outdoor condition for 24 months. The gel content of irradiated samples demonstrated that cross-linking reaction has occurred and caused the increasing of mechanical properties. The results of FTIR measurements show that upto 200 kGy carbonyl formation is negligible. Increase of carbonyl groups and decrease of mechanical properties in irradiated and outdoor exposed samples are indication of degradation progress in cross-linked polymer structure. In addition, some of the irradiated samples were buried under the soil. Observation of unchanged chemical structure of buried samples after 24 months, proves that UV light and oxygen are the main factors of their degradation.

Key Words:

irradiation;
cross-linking;
degradation;
stabilizer;
outdoor exposure.

INTRODUCTION

The photooxidative degradation of polymers is extremely important from scientific and industrial point of views. Oxidative degradation reactions are the main limitation in the active life of synthetic polymers. This undesirable degradation may be

accelerated by exposure to UV radiation. Polyethylene is one of the extensively used plastics in outdoor applications. Its outdoor durability in modern agriculture is very important because of large scale food production. For this reason, many

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studies have been conducted over the years to investigate the natural weathering of polyethylene [1-3].

UV radiations in solar spectrum are the main cause of degradation of outdoor plastics. Thus, their light stabilization has made considerable progress since, only UV absorbers of the benzophenone and benzotriazole type were available [4]. A number of studies have been performed for improving UV stability of PE by combination of different kinds of stabilizers [5].

On the other hand, cross-linking is a broadly used method for the modification of polymer properties. This process involves the formation of tri-dimensional structures (gels) which is causing substantial changes in material properties. The cross-linking leads to an increase in viscosity of the polymer melt, and tensile strength, improvement of creep properties, and increase in the resistance against environmental stress cracking [6]. In recent years there has been a growing interest in improving UV stability of PE by combination of conventional stabilizers and radiation cross-linking [7, 8].

In this work long term stability of cross-linked polyethylene on outdoor exposure has been investigated. For this purpose, the effect of sunlight on electron beam irradiated PE films in both pure form and with UV stabilizers have been studied. Also, in order to investigate the chemical changes of irradiated samples in the absence of UV light and oxygen, they have been buried under the soil and their chemical changes have been compared with outdoor exposed ones.

EXPERIMENTAL

Materials

The materials used in this work were two kinds of commercial low density polyethylene films usually used as covering in greenhouse. The base polyethylene material for both films was Iranian petrochemical LH0075 grade. The stabilized one contained 3% Vibatan UV master (a synergic combination of photostabilizers and antioxidant) which was supplied by Viba from Italy (PE-st) and the other one was free of additives. The thickness of both films were 180 μm .

Preparation

All the samples were irradiated by a Rhodotron type electron beam accelerator at acceleration voltage of 5

MeV at doses of 30-300 kGy. A number of the irradiated films were exposed to the outdoor condition according to ASTM 1435D at 45°C towards the south for period of duration upto 24 months. The weathering test was started in July in Tehran. A number of the irradiated films were buried under the soil at a depth of 15-20 cm from the surface to study the changes in chemical structure. After the films were removed, their surfaces were wiped with water and dried at room temperature.

MEASUREMENTS

Gel Fraction

The gel content was determined by solvent extraction with xylene for 24 h. The extracted samples were dried in vacuum oven at 140°C until a constant weight was achieved.

FTIR Measurements

FTIR Measurements were done by a Bruker IFS-45 spectrophotometer. In order to minimize errors in sample thickness measuring, the 1895 cm^{-1} peak from C-H deformation mode of PE was used as an internal reference in this study.

Mechanical Properties

Mechanical properties were determined according to ASTM D-638 by using the Zwick tensile machine, model 1425. The speed of crosshead was 50 mm/min for all samples.

RESULTS AND DISCUSSION

The Changes of Chemical and Physical Properties After Irradiation

The gel content of irradiated samples was determined in order to evaluate the content of cross-linking produced by irradiation in both samples. In fact, gel content is an index of cross-linking network formed by irradiation. Figure 1 shows that gel content of both samples increase at high radiation doses upto 200 kGy, after that there is a plateau in gel formation curve. Also, it shows that in all doses the gel fraction of PE-st is lower than PE. This could be ascribed to an inhibiting

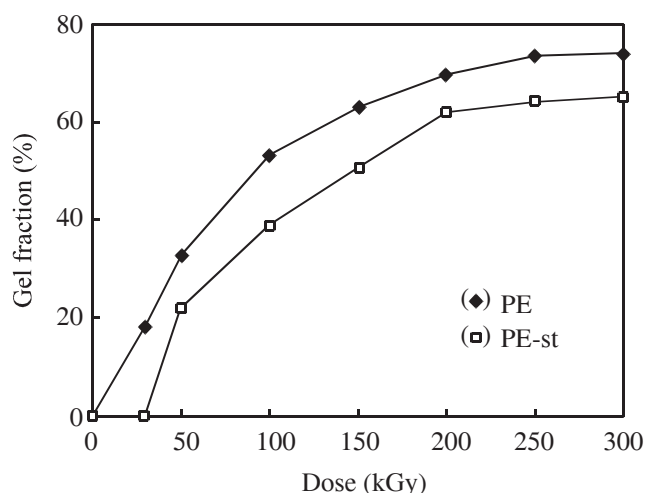


Figure 1. Effect of radiation dose on gel formation for PE and PE-st samples.

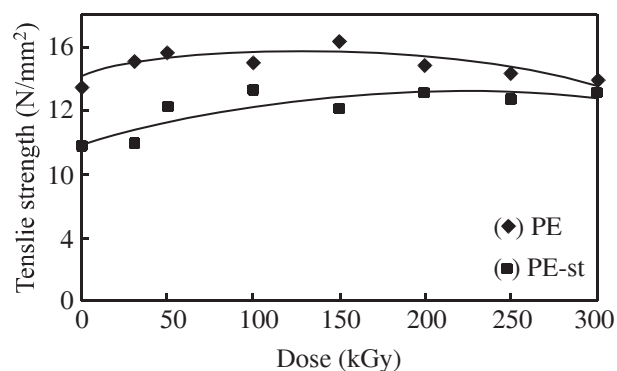
role of stabilizers in the formation of cross-linking as a consequence of the radical deactivation [9].

These results can be related to the results of tensile test in Figure 2 where it is shown that the tensile strength of both samples increases up to 150 kGy and then remains constant or decrease slightly at higher doses (Figure 2a). In PE-st due to existence of stabilizers, the major effect of radiation at very low radiation doses is an increase in the degree of branching and average molecular weight which often leading to an increase in tensile strength. However, these branches are soluble and do not show any gel fraction in PE-st up to 30 kGy (Figure 1).

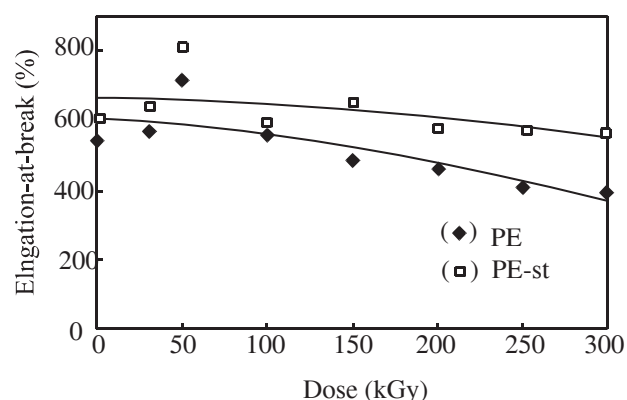
Increasing of the tensile strength at higher doses is due to the cross-linking joints among backbone chains in a net-like structure. This makes polymer matrix to attain higher tensile strength after irradiation. At higher radiation doses, more than 200kGy, competition between cross-linking and scission process leads to break down of the cross-linked structure to form small networks, consequently the tensile strength decreases slightly.

In these partially cross-linked polymers freely movement of polymer chains inhibited and elongation-at-break of both samples reduces with increasing of radiation dose (Figure 2b). As it is observed in Figure 2 at higher irradiation doses, PE sample shows rapid decrease in mechanical properties in comparison with PE-st. This is due to the lack of stabilizer in this sample which leads to more break down of cross-linked structures at higher doses.

In Figure 3 increase of carbonyl groups in both



(a)



(b)

Figure 2. Effect of radiation dose on tensile strength (a) and elongation-at-break (b) for both samples.

samples at doses upper than 150 kGy, declare that irradiation of the samples at high doses cause oxidative degradation as well as cross-linking. This is in agreement with declining of mechanical properties at the higher doses. From these results the samples which were irradiated at 150 kGy were selected to pursue the

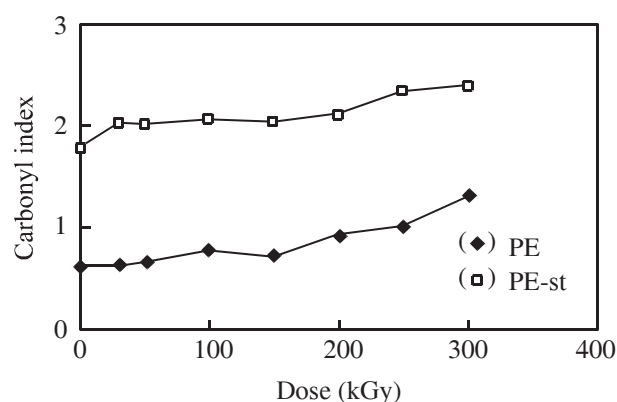


Figure 3. Effect of radiation dose on carbonyl formation for both samples.

effect of these cross-links on UV-stability of samples by the changes in chemical and mechanical properties after outdoor exposure and burying under the soil.

The Changes of Chemical and Physical Properties of Irradiated Samples After Outdoor Exposure

Figure 4 shows the development of carbonyl index during outdoor exposure for both samples, before and after irradiation. In this figure the carbonyl index of PE samples rised sharply at early months of exposure and led to complete damage of samples after 4 months. While this group in PE-st increases slowly during the outdoor exposure time. This can be attributed to the quenching of generated radicals by the antioxidants and role of the UV stabilizers which are acting by light absorption mechanism and consequently lower level of radical formation in PE-st during photo-degradation.

In addition, Figure 4 reveals that both irradiated samples have higher amount of carbonyl index when compared with unirradiated ones. In the case of PE this trend is more obvious. This is due to the fact that irradiation of the samples in the presence of air lead to produce peroxy and hydroperoxy radicals which consequently accelerate their degradation process when exposed to UV radiation.

This result is confirmed by a dramatic fall in elongation-at-break as depicted in Figure 5 for unirradiated and irradiated PE samples at the early months of outdoor exposure which lead to severe brittleness. In unirradiated PE-st the changes of elongation-at-break can be divided in three stages; In the early stage of outdoor exposure there is an induction period which is related to the existance of stabilizers. These stabilizers provide preferential absorption of the most of the incident UV

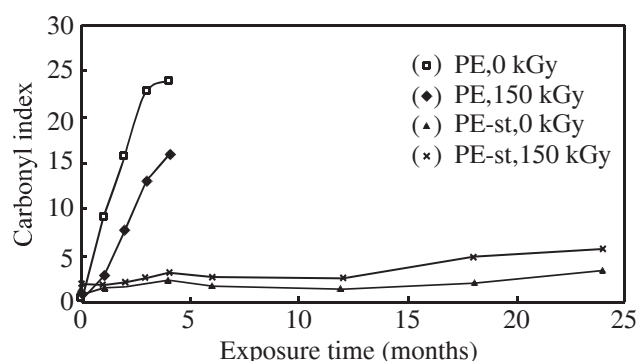


Figure 4. Development of carbonyl group during outdoor exposure for both samples before and after irradiation.

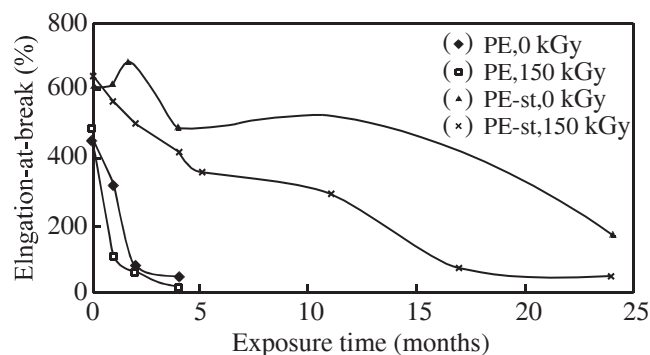


Figure 5. The changes of elongation-at-break during outdoor exposure for both samples before and after irradiation.

light and are able to dissipate the absorbed energy harmlessly. In the second step in which chain scission and cross-linking reactions are closely associated, cross-linking is predominated reaction and improves the elongation-at-break property. In the third stage, UV exposure initiates chain scission and consequently cross-link sites are broken which cause continuous reduction in elongation-at-break. While in irradiated PE-st only scission reaction is observed. Moreover, the extent of reduction in the elongation-at-break of irradiated samples is higher than the unirradiated ones.

The Changes of Chemical Properties in Irradiated Samples After Burying

In Table 1 the amount of the carbonyl index of the

Table 1. Carbonyl index of outdoor exposed and soil buried samples after 24 months.

Dose (kGy)	carbonyl index (A1720/A1895)			
	outdoor exposed		Soil buried	
	PE*	PE-st	PE	PE-st
0	16	2.1	0.58	1.53
30	20.84	3.17	0.6	1.42
50	22.08	3.35	0.61	1.47
100	23.08	4.1	0.76	1.6
150	23.97	4.92	0.89	1.64
200	24.22	4.91	1.32	1.53
250	26.01	5.83	1.28	1.61
300	33.11	5.64	1.21	1.66

(*) Data of outdoor exposed PE are related to the 4th month of exposure, before distortion of samples.

unexposed irradiated samples are compared with those which were exposed to outdoor condition and others which were buried under the soil. The results show that the amount of carbonyl index has increased rapidly after 4 months of outdoor exposure of irradiated PE samples at all doses. Also in outdoor exposed PE-st samples, the amount of carbonyl group has risen slowly after 24 months. Whereas, in the case of buried samples it can be seen that the amount of carbonyl index has decreased for both of the samples after 24 months. This is due to the fact that the termination reactions of the peroxy radicals have taken place for buried samples in the absence of oxygen and light.

CONCLUSION

Chain scission and cross-linking are two processes which occur simultaneously during irradiation of polyethylene film but cross-linking is predominated reaction. Thus, EB radiation causes partially cross-linking in both PE samples. These cross-linked polymers show higher mechanical properties than unirradiated ones.

The generated radicals in the irradiated polyethylene cause acceleration of degradation in outdoor condition and make major defects in polymer chain. This can be confirmed by rapid increase of carbonyl group in irradiated PE samples which is closely associated with changes in the mechanical properties during the early stages of photo-oxidation. Whereas the generated radicals in irradiated PE-st samples quench by stabilizers and prevent the progress of degradation in polymer chain and causes long term stability in the mechanical properties during outdoor exposure.

UV light and oxygen are the main cause of degradation process in the outdoor exposed irradiated samples. In buried samples due to the absence of them the trend of degradation process declined obviously. It can be concluded that irradiation cross-linking not only improves UV stability of PE films but also, the anti-rad additives prevent scission of polymer chain during irradiation and exposing to outdoor condition.

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