Natural Weathering, Artificial Photo-Oxidation, and Thermal Aging of Low Density Polyethylene: Grafting of Acrylic Acid onto Aged Polyethylene Films

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ABSTRACT: The photo-oxidation and thermal initiation changes of commercial low density polyethylene (LDPE) films used in greenhouse covering, in the presence or absence of ultraviolet (UV) stabilizer, were monitored by infrared (IR) spectroscopy, by mechanical tests and by applying the grafting of acrylic acid onto the aged films. It was found that the resistance of PE films to UV irradiation and heat initiation as proved by tensile strength and elongation at break % was better for stabilized PE films compared with the unstabilized ones. A simple correlation was not observed between the fall in mechanical properties and the rate of film oxidation. On the other hand, an almost linear relation was obviously noticed between the degree of PE oxidation (C=O) measured by IR spectroscopy and the grafting level. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2365–2371, 2003

INTRODUCTION

When polyethylene (PE) films for greenhouse covering are exposed to ultraviolet (UV) light and thermal initiation in the presence of oxygen, they become brittle,[1] and visual signs of degradation are apparent. The oxidation of PE film has the common feature of an attack of free radicals on the polymer chain followed by reaction of the alkyl radicals with oxygen to lead to the buildup of the vinyl group and of a variety of oxygen-containing groups such as carbonyl functions.[2,3]

PE is a semicrystalline polymer.[4] Its structure can be considered as alternating crystalline and amorphous layers (two-phase system). Both kinds of layers are connected to each other by tie molecules passing through the amorphous[5] interlamellar regions. Oxidation damage at the amorphous and tie molecule regions can be responsible for significant changes in the physical, chemical, and mechanical properties of the polymer.[6]

The aim of this work was the study of the durability of PE films used in greenhouse covering in the presence and absence of UV stabilizer by tests under thermal initiation, natural weathering, and accelerated UV irradiation. The relations between the mechanical properties, infrared (IR) spectra and grafting of acrylic acid and the evolution of the chemical structure of PE films were also studied and evaluated.

MATERIALS AND EXPERIMENTAL METHODS

Materials

- LDPE films (stabilized and unstablized) with thickness of about 200 μ, commercially available from Hemaplast Co., Cairo, Egypt, were used in exposure experiments.
- Acrylic acid 99% purity (BDH chemicals) was used as received. Other chemicals were reagent grade and thus used without further purification.

Exposures

- The natural exposure tests were carried out at Alexandria, Egypt. The samples were mounted on a wooden panel, facing south and inclined at 45° according to the standards.
- The accelerated UV photo-irradiation exposures tests were performed by using a Tera Light Fastness Tester[7] having a MBTF lamp. Exposure was conducted for different periods varying from 250 to 1500 h at a temperature of 25 ± 2°C and relative humidity of 60 ± 5%.
- The thermal aging tests were carried out in a 70 ± 1°C in a regular drying oven.

Instrumental

- The mechanical test data for both exposed and unexposed films were measured using a Zwick Electronic Universal Testing Machine model 1425.
- The IR spectra were carried out using Jasco FT/IR 300 E Spectrophotometer.

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In the following ΔOD% (difference in OD%) is the difference of the intensity values between the exposed sample and the starting one.

The intensity was measured at the maximum absorption band of carbonyl groups.

Grafting procedure

LDPE-*g*-polyacrylic acid was prepared by direct (mutual) radiation grafting of 25% aqueous acrylic acid solution containing 2.5 wt % Mohr's salt (a homopolymerization inhibitor) for acrylic acid onto LDPE films and irradiated at a dose of 3 Mrad from γ-ray of Co^{60} source, at a dose rate of 0.02 Mrad /h. After thoroughly cleaning in warm water, the films were dried under reduced pressure at 60°C for 24 h. The degree of grafting was calculated from the weight increase of the original PE films.

RESULTS AND DISCUSSION

Thermal aging

The effect of thermal initiation on tensile strength and elongation at break (*E*%) at various exposure times is represented in Figure 1. As shown from the figure, the tensile strength and *E*% of unstabilized polyethylene (unst. PE) films [Fig. 1(A)] are increased with increasing the exposure time up to 300 h; thereafter they decrease. In case of stabilized polyethylene (st. PE.) film [Fig. 1(B)], the tensile strength is also found to increase with time but up to 500 h, while *E*% exhibits a gradual decrease if compared with that of unst. film. This probably results from the combined effect of crosslinking and the bonds formed between the UV stabilizer[8] and the polymer matrix, especially in the amorphous regions. The overall effect is a decrease in *E*%, with a limited increase in tensile strength.

The IR spectra of the exposed PE films to thermal aging were examined. Careful inspection of their spectra showed a negligible or very slight change in the polymer structure. This behavior confirms the suggestion that aging of PE at 70°C ± 1 is practically insufficient to cause a detectable change in the polymer structure.

Under ionizing irradiation of acrylic acid and polyethylene in air, three types of radicals are formed in the amorphous regions[9] of the polymer: alkyl, allyl, and peroxy. Among these, peroxy radicals are unreactive and do not participate in grafting reactions. The alkyl radicals disappear rapidly as the grafting reactions proceed. Most of the allyl radicals occurred on the surfaces of the PE crystallites, and only 10% of the radicals are trapped in the crystallites.[10] In the atmosphere of a grafting monomer, allyl radicals occurring on the surfaces of the crystalline regions meet the surrounding diffused monomer, then react with it to
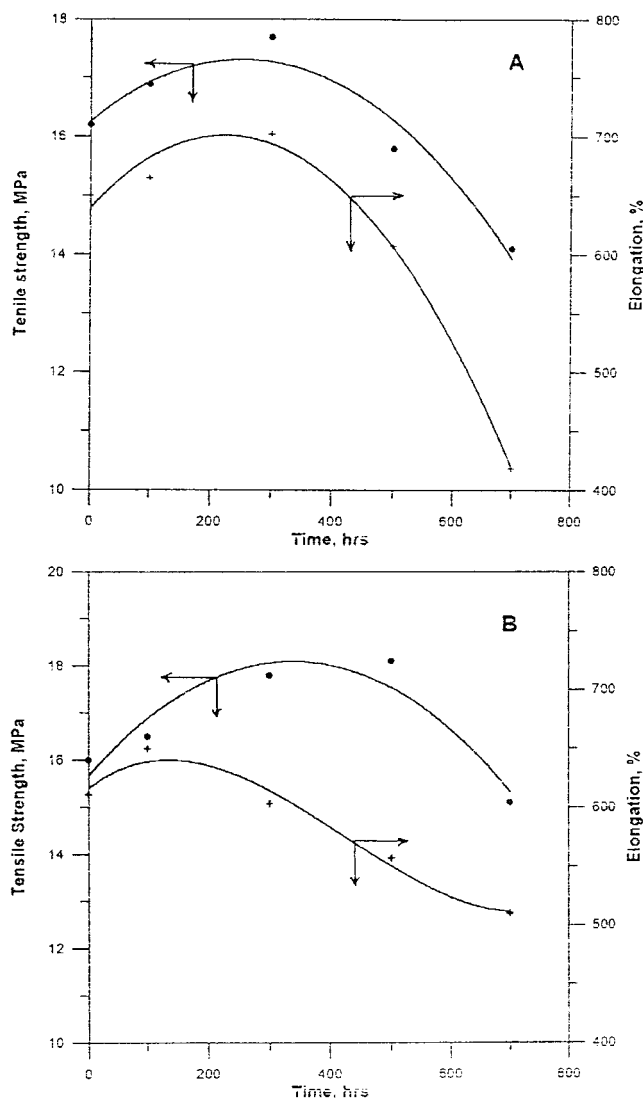

Figure 1 Changes in tensile strength and *E*% at break with thermal aging time (●: tensile strength; +: *E*%); (A) unst. PE and (B) st. PE.

produce propagating radicals. In the case of thermally aged PE films, as shown in Figure 2, the st. polymer shows, in general, some resistance to grafting that the unst. one does not. Besides, all values observed (except those recorded at 700°C in both films) are relatively lower than the values of the nonaged films (control) regardless of the increase in exposure time. Also, in all cases, the differences in grafting levels between unst. and st. polymers are about 20% on the average. Such behaviour can be explained in terms of the predominance of crosslinking reaction in amorphous regions of the polymer and the absence of chain scission reactions. These reactions result in a decrease in the interamollecular spaces, thus forming a relatively densed films. The films under these conditions may act as a diffusion barrier not only to the monomer but also to the mobility of allyl radicals trapped in the
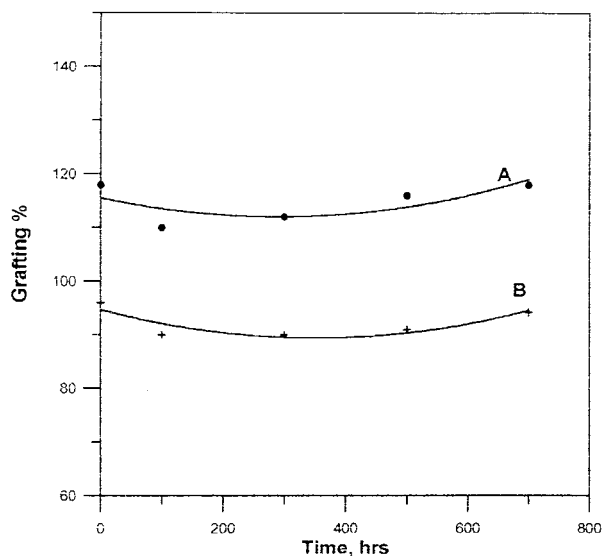
Figure 2 Changes in grafting % with thermal aging time; (A) unst. PE and (B) st. PE.

amorphous regious, thus reducing the coupling reactions, and consequently the grafting levels.

Accelerated photo-irradiation

The PE films were exposed to artificial UV irradiation at different time intervals up to 1500 h. Visual observation of the aged films showed no cracking defects and all films were still flexible.

The tensile strength and $E\%$ for both films had been plotted against photo-irradiation time in Figure 3. It is evident that the tensile strength of the unst. polymer [Fig. 3(A)] is found to increase slightly with increasing time up to 250 h; then the values are steeply decreased. With the st. polymer, the tensile strength shows a gradual decrease with increasing time up to the end of the experiment. In other words, about a 70% decrease in the tensile strength was reached after 750 h of exposure for the unst. sample, whereas it reached 30% in the same period for the st. one. Such differences may be explained in terms of oxidation degrees at the tie molecules, which join PE crystalline lamellae together.[6]

Photo-irradiation on PE at room temperature in air produces carbonyl and hydroperoxide compounds as oxidation products.[3,11] The latter is monitored by the growth of 1720–1740 cm^{-1} (C=O) and 3450 cm^{-1} (ROOH) in the Fourier transform irfrared (FTIR) spectra. The carbonyl band (a complex range of carbonyl species) is due to one or more of the overlapping chemical functions containing ester, carboxylic groups, ketons, aldhydes, and γ-lactones. In this work, measurements of the extent of the carbonyl band were taken from the peak heights (maximum absorption) at 1720 cm^{-1}. The changes in intensity of the carbonyl band at this region before and after photo-irradiation

of st. and unst. polymers as represented by their $\Delta OD\%$ (difference in OD%), with irradiation time, are shown in Figure 4. It is clear that the $\Delta OD\%$ is found to increase linearly in the unst. polymer with an increase in irradiation time, but for st. polymer, no significant change is detected in the polymer structure up to 1000 h—then the growth of carbonyl band starts to appear. During such an induction period (1000 h), the UV stabilizer absorbs UV light with a high extinction coefficient and the absorbed energy with an overwhelming degree is converted to heat.[12]

In the atmosphere of a grafting monomer, the allyl radicals trapped in the amorphous regions of the polymer migrate to reach the surrounding monomer then react with it to produce propagating radicals. Figure 5 exhibits the variation in grafting yield of PE samples vs $\Delta OD\%$ of carbonyl band of the aged PE films. It can
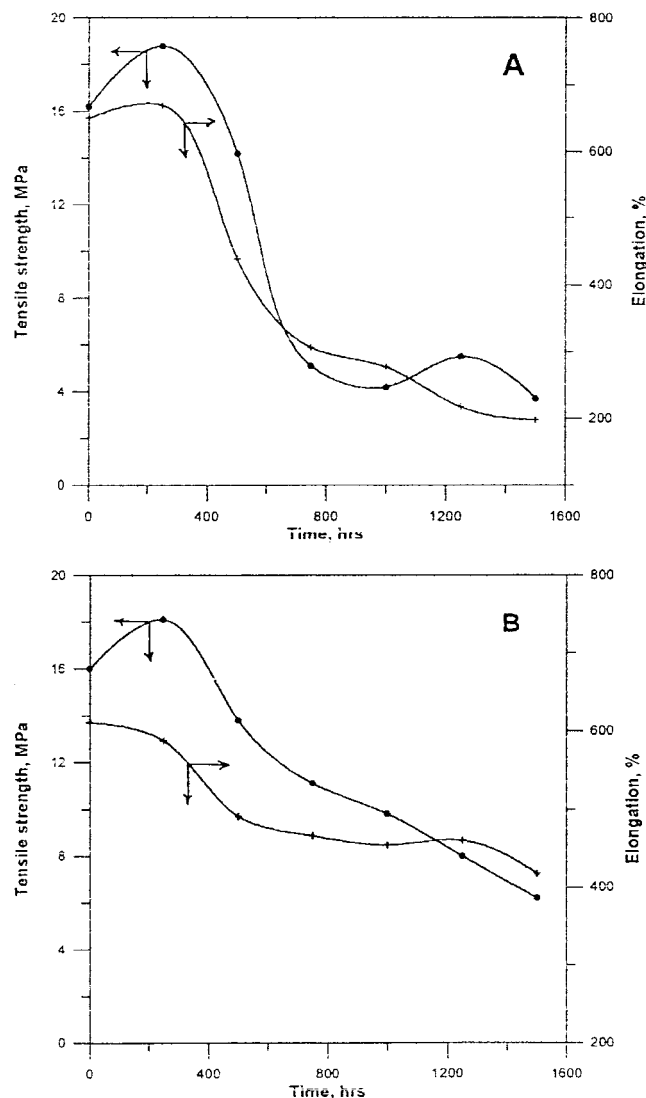

Figure 3 Variation of the tensile strength and $E\%$ at break with the photo-oxidation time at room temperature (●: tensile strength; +: $E\%$); (A) unst. PE and (B) st. PE.
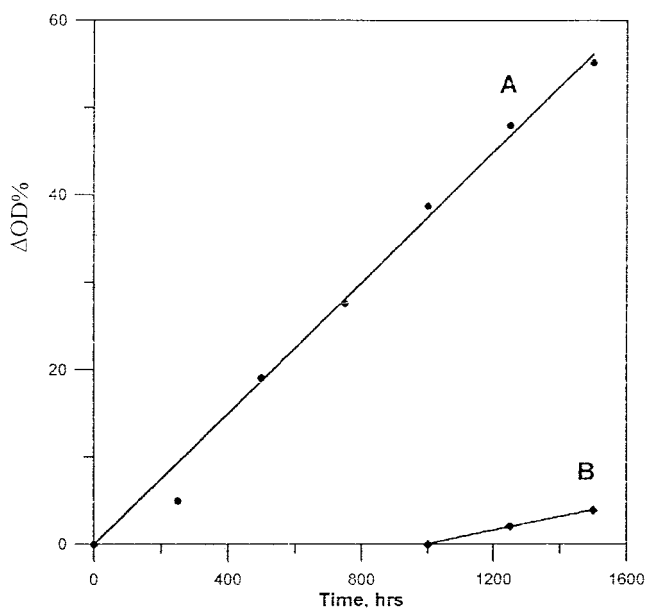
Figure 4 Changes in FTIR spectra of carbonyl group ΔOD% (difference in OD%) with UV irradiation time; (A) unst. PE and (B) st. PE.

be seen that the grafting yield is increased linearly with increasing the ΔOD% for unst. polymer [Fig. 5(A)], whereas for the st. polymer [Fig. 5(B)] the grafting yield shows a slight increase with increasing the exposure time up to the end of experiments with fluctuation not exceeding 20%. This simple correlation reflects to large extent the intimate relation between grafting yield and oxidation degree of the exposed film to UV radiation.

Natural weathering

Natural weathering experiments were extented 30 months at Alexandria, Egypt. Visual observation of the aged films showed that the exposure of unst. films to natural weather conditions had a rapid, marked effect on the physicomechanical properties of the film. A sample will snap in two when flexed after only 9 months of exposure.

Changes in tensile strength and $E\%$ with exposure time are shown in Figure 6. It can be seen that the tensile strength and $E\%$ of unst. polymer [Fig. 6(A)] are found to increase slightly with increasing exposure time up to the third month; thereafter they fall off rapidly. For elongation at break, which is more sensitive to the degradation process than tensile strength,[13] the values were found to decrease sharply with time, and almost 90% of the value of this property was lost after an exposure time of 9 months. In comparison with the unst. polymer, the tensile strength and $E\%$ of the st. polymer practically remained steady along the first 10 months of exposure, then they gradually decrease with time up to the end of experiments. During

the early stages of weathering, there was an increase in crosslinking (increase in gel formation)[14] due to the high rate of radical termination in the bulk of the polymer where O_2 cannot gain access. Thus, there was an observed increase in the elongation at break, but this eventually decreased due to the predominance in chain scission.

The IR spectra of the aged films were also investigated and the results are represented in Figure 7. As shown from the figure, there is no change in the IR spectra for the st. PE films during the first 12 months of exposure; afterward the growth of carbonyl bands start to develop but slowly. During the induction period (12 months), the harmful hydroperoxide radicals are simultaneously photolyzed to give hydroxy and alkoxy radicals, which then attack the UV stabilizer and reduce its effectiveness.[12,15] With the unst. PE film, the polymer has been observed to undergo changes similar to those observed in acceler-
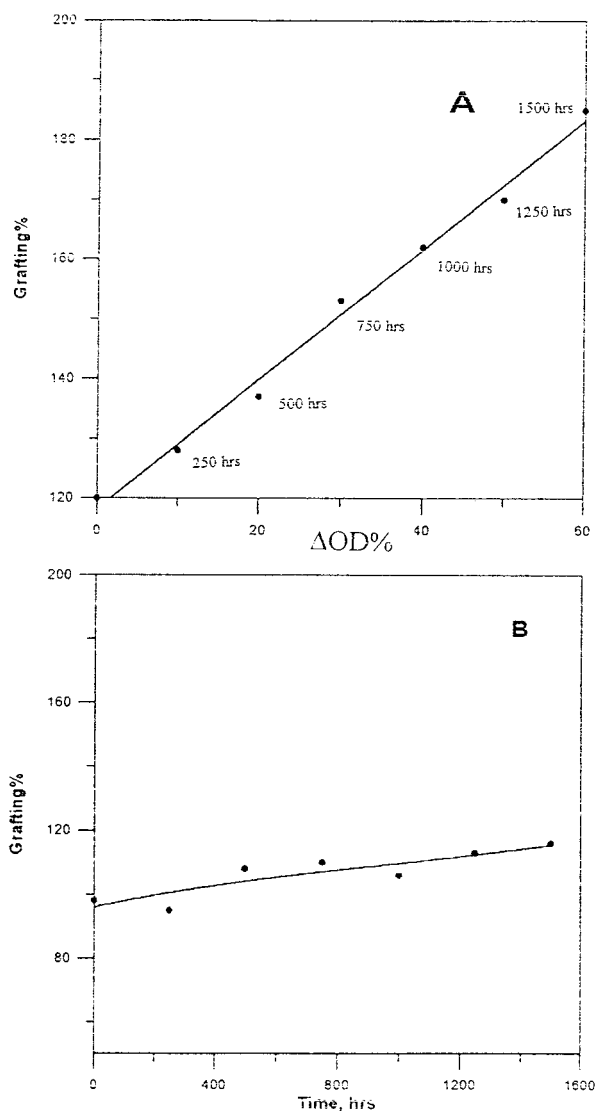

Figure 5 Changes of grafting % with UV irradiation time; (A) unst. PE and (B) st. PE.
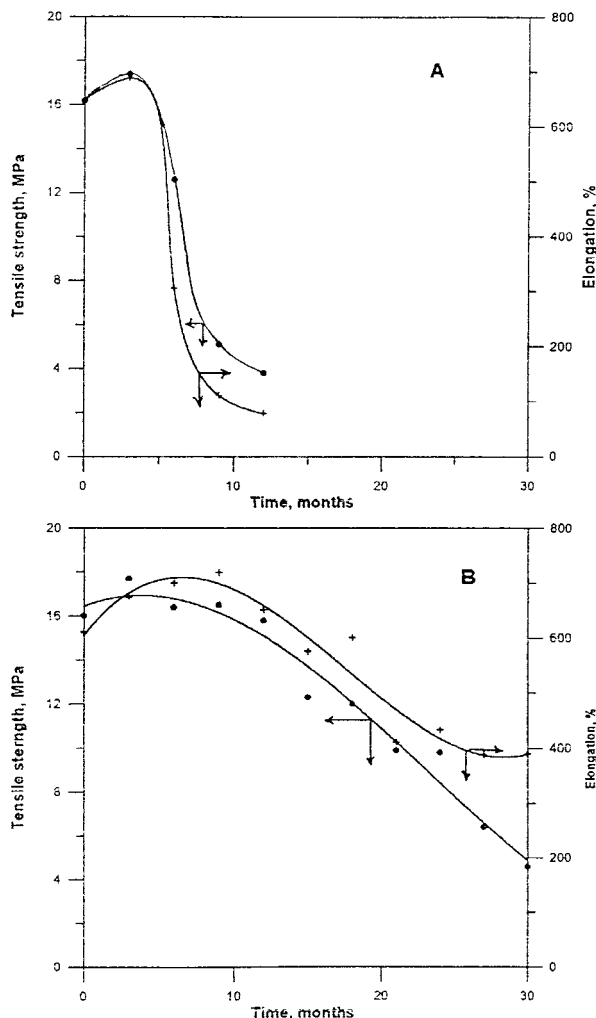
Figure 6 Changes in mechanical properties of PE films with outdoor exposure time (●: tensile strength; +: E%); (A) unst. PE and (B) st. PE

ated test. However, in natural weathering, the carbonyl bands of unst. polymer start to develop, without an apparent induction period, to reach their maximum intensity after few months. It is worth noting that the carbonyl bands of the polymer photo-oxidized by sunlight form more carboxylic groups, but less ester and vinyl alkene.[16] Thus, the enrichment of the aged films with carboxylic groups may themselves accelerate further the degradation process,[17] producing an autocatalytic effect. Furthermore, there is some evidence that the carboxylic groupsmay promote microbiological growth within the system. When this takes place, the fungal metabolites may further increase the rate of oxidation[8] of PE film.

The effect of outdoor weathering on the degree of grafting, obtained upon grafting acrylic acid onto aged PE films, is depicted in Figure 8. For the unst. PE film, the degree of grafting is found to increase rapidly with increasing exposure time to reach a maximum value of 260% after 12 months. With the aged st. PE film, the
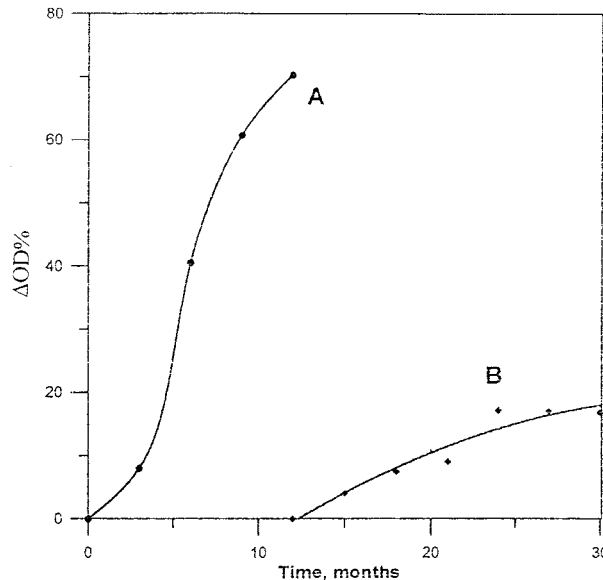

Figure 7 Chagnes of ΔOD% (difference in OD%) vs exposure time; (A) unst. PE and (B) st. PE.

variation is slightly influenced with times up to 9 months of exposure, where it reaches an average value of 105%. Afterward, it increases but slowly, to reach the maximum value of 158% after exposure time extending 30 months. Such differences reflect to a large extent the role of the UV stabilizer in the polymer matrix in reducing the chain scission reactions and the rate of chain propagation by scavenging[18] radicals $RO_2^{\bullet}$ or $R^{\bullet}$, etc., and consequently the grafting yield . In the absence of UV stabilizer, the increased property of permeability[14] in the photo-oxidized films in addition to the presence of a maze of tinny fissures as a result of natural contractions of the surface layer,
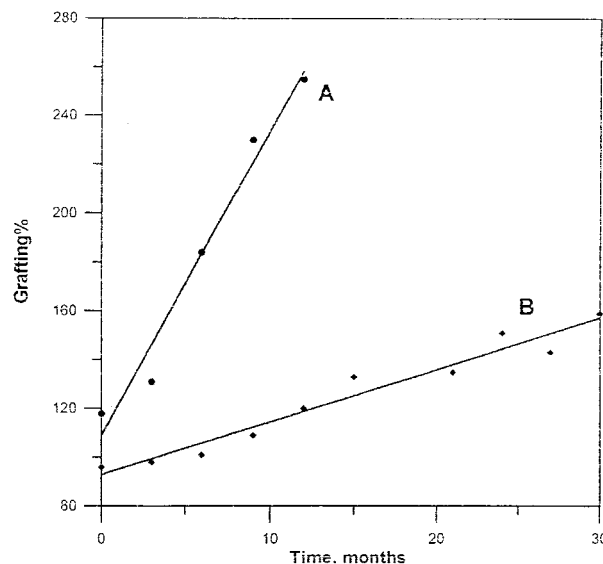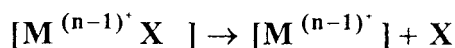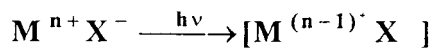

Figure 8 Changes in grafting % with outdoor exposure time; (A) unst. PE and (B) st. PE.

$$M^{n+}X^- \xrightarrow{h\nu} [M^{(n-1)^\cdot}X\ ]$$

$$[M^{(n-1)^\cdot}X\ ] \rightarrow [M^{(n-1)^\cdot}] + X$$

Scheme 1

which formed by the virtue of crosslinking reactions and/or by loss of volatile products,[16,19] will certainly contribute to improving grafting process through the rapid diffusion of the monomer into the film surface. This is the explanation of why the unst. PE film is characterized by a remarkable increase in grafting level, reaching more than 250% in comparison with the grafting level (150%) of st. PE film.

The predominance of heavy rainfalls and windy atmosphere in the city of Alexandria may play an important role in accelerating the weathering process. The rainfall duration extends 6 months per year. During this period, the films are subject several times to washing by rainwater. This factor may contribute to the following effects:

1. Continuous washing of the thin layer of dust coating the film surface. Dust, however, can have a protective effect on polymer. It can also absorb a significant amount of solar radiation and thus have the dual effect of decreasing the temperature attained by the specimen and of decreasing the extent of photolytic degradation; i.e., in both cases, it can offer some protection but is less effective than the UV stabilizer.[12]
2. Leaching the unreacted UV stabilizer concentrated in the amorphous phase at defective places of crystallites and their boundaries.[12]
3. Increasing the effect of long and intensive sunny periods per day and incident of solar energy prevailing in Egyptian regions,[20,21], which ranges from 275 to 425 Langley in winter and 675 to 740 Langley in summer.
4. Continuous exposure to atmospheric humidity can promote the biodegradation process of the film.[12,18]
5. Continuous contact with harmful pesticides and the other pollutants associated generally with hu-

man industrial and domestic activities as well as the automobile exhausts, for example, of transition metals such as Fe, Cu, Ni, Cr, and Ti are almost invariably present in atmospheric pollutants. On light absorption the compounds of these metals in contact with the polymer surface can produce free radicals by an electron transfer[18,22] process such as that shown in Scheme 1. The hydroxyl radical ($x^\bullet$) may then abstract a hydrogen atom from the polymer.

Table I shows the changes in the induction periods, ΔOD%, grafting levels, and mechanical properties of st. PE films exposed to outdoor exposure for about 20 months at two sites of rainy (Alexandria) and dry (Cairo).

It is evident from this table that the lifetime of the films exposed under dry conditions is expected to be relatively longer than that of the films exposed in the rainy region. This can be explained in terms of one or more of the factors mentioned above.

From the results given in this study certain features are worthy of comment:

1. It is possible to apply the graftability technique as a qualitative means for evaluating the degree of photo-oxidation or thermal aging of PE films used in greenhouse covering. The data have proved the existence of an intimate correlation between the grafting level and the concentration of C=O functional groups.
2. The data indicated that the effect of UV radiation is the decisive factor. The thermal effect at 70°C ± 1 had practically a very limited role in the degradation process. However, the thermal effect under the studied conditions may lead to some improvement in mechanical properties, particularly at the early stages of exposure.
3. There is no direct correlation between mechanical properties (tensile strength and $E\%$) of the photodegraded polymer and the rate of buildup of oxidation product in the polymer.
4. The effect of dry and rainy regions may play a non-negligible role on the mechanical, chemical, and physical properties of the film exposed to

TABLE I
Test Results of Outdoor Exposures of st. PE Films After 20 Months of Exposure in Alexandria and Cairo Regions

	Tensile Strength (Mpa)	$E\%$	ΔOD%	Grafting %	Induction period[a] (months)
Before outdoor exposure (Control)	15.8	640	—	98	—
After outdoor exposure					
Alexandria (rainy region)	11.2	478	10.6	140	12
Cairo (dry region)	13.	521	8.9	122.8	14

* The time is extracted from the IR spectroscopy measurements.

solar radiation, a phenomenon often neglected in the studies of photo-oxidation of PE films used in greenhouse covering.

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