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AGING OF LOW DENSITY POLYETHYLENE FILMS FOR AGRICULTURAL USE IN THAILAND

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ABSTRACT

The aging behaviour of low density polyethylene (LDPE) films for the construction of green houses and shelters for agricultural uses in Thailand were studied. Plastic films were exposed to sunlight as well as in an accelerated weathering tester. The effectiveness of a few ultraviolet stabilizers in preventing photo-degradation of LDPE films were studied. Changes of physical properties, e.g. tensile strength, elongation at break, were followed and used as a criteria of failure. Spectroscopic methods were used to investigate any change in molecular structure of polymers. Under accelerated condition, it was found that addition of 0.2% of UV-stabilizer could extend the life time of LDPE films to about 4-5 times longer than those without light-stabilizer. Plastic films under accelerated test condition was found to degrade 7-9 times faster than when exposed to natural condition.

INTRODUCTION

It is well known that plastics have long been employed in agriculture.[1] This is because of the following properties of plastics (compared to glass), namely, unbreakability, low price, transparency, flexibility, ease of forming into various shapes and light weight. Plastics are used to protect plants, for examples: for the construction of greenhouses in order to create micro-climate that are suitable for plant growth, for making shelters to protect plants from bad weather and reduction of light intensity, for making low tunnels for protection of early crop-production, for mulching in order to save water and suppression of weed growth, etc. Plastics are also widely used for water management.

All applications of plastics in agriculture are used to improve the quality as well as the quantity of agricultural products. Furthermore, plastics also make possible the cultivation of out-of season fruits, vegetables and flowers. Packaging using plastics give rise to well-protected and thus improved transportation and distribution of the agricultural products to all parts of the world.

An important problem faced in the outdoor use of plastics is its lifetime. Research concerning the use of plastic materials in agriculture at different geographical locations in the

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Dedicated to Professor Dr. Ing. Bernhard Schrader on the occasion of his 60th birthday world should be carried out because of the differences in local climate which affect the physical properties and thus the lifetime of these materials. In Thailand, except for packaging, the use of plastics in agriculture is not yet widely practised. There is no systematic study to find the most suitable polymer materials and additives appropriate to tropical climate in Thailand.[2]

This work presents the study of the aging behaviour of low density polyethylene films for the construction of greenhouse and shelters.[3] For comparison, exposure of plastic films to sunlight as well as accelerated weathering tester with fluorescent lamps were investigated. The changes of tensile properties are taken as the criteria of failure[4] and any change in infrared and ultraviolet spectra are observed to follow the change in molecular structure of polymer.[5, 6]

MATERIALS AND METHODS

Materials

1. Low density polyethylene (Thai Petrochemical Industry): type CS2425 density 0.924 g/cm^3, melt flow index (190° C/2.16 kg.) 2-3 g/10 min, and LDPE type D2024 density 0.922 g/cm^3, melt flow index (190°C/2.16 kg) 0.65-0.75 g/10 min.
2. UV-stabilizers: hindered amine type, Chimassorp 944 LD and Tinuvin 622 and benzothiazole type, Tinuvin 326 from Ciba-Geigy Corp.
3. Antioxidant: Irganox 1076 from Ciba-Geigy Corp.

The chemical structures of the additives of LDPE are shown in Table 1.

Instruments

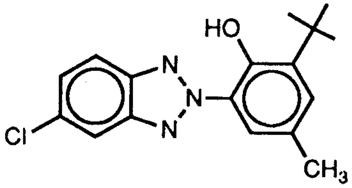
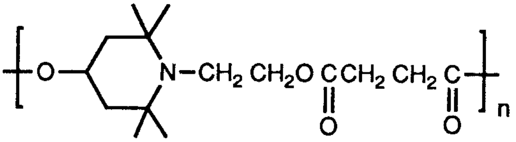
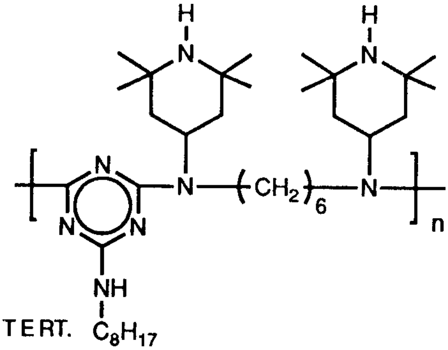
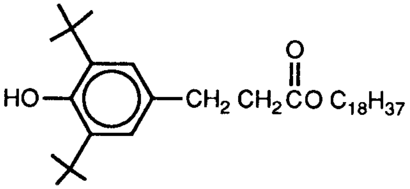
1. Film blowing machine Model HDPE-45-AW from Siam Plastic Machinary Co., Ltd.
2. Accelerated weathering Tester Q-UV from Q-Panel company using fluorescent lamps with maximum energy at 340 nm.
3. Tensile tester Instron model 1026
4. Infrared spectrophotometer Perkin Elmer model PE683 equipped with data station model 3600
5. UV-visible spectrophotometer Jasco model UVIDEC-650

Methods

The following steps were carried out.

1. LDPE films were blown at different thickness with and without UV-stabilizer masterbatches (containing 10% UV-stabilizer and 1% antioxidant)
2. Tested films were exposed (no backing) to sunlight on the roof of the Faculty of Science, Mahidol University, Bangkok, mounted at an angle of 14 degree south, average light energy approximately 143 kLy/year.[7]
3. Tested films were exposed in the accelerated weathering tester (with aluminium backing) under testing condition with 4 hours UV-light at 60°C and 4 hours condensation at 50°C (ASTM G53-84)

TABLE 1. LDPE additives.

Compound	**Chemical Structure**
Tinuvin 326	
Tinuvin 622	
Chimassorb 944 LD	
Irganox 1076	

4. Films were taken at different exposure time for tensile testing. Reduction of elongation at break to 2/3 of initial values were taken as the criterion of failure.

5. Infrared and UV-visible spectra of exposed films were recorded. Any change in intensity of absorption bands or appearance of new peaks were followed.

RESULTS AND DISCUSSION

1. Tensile Properties

Tensile strengths and elongations at break of plastic films exposed to sunlight and under accelerated condition are shown in Fig. 1 and 3 respectively. The tested films (thickness 70 μm) were blown from LDPE type CS2425 without UV-stabilizer. Since the ultimate mechanical properties, particularly elongation at break of various polymer systems, were found to be more sensitive to photo-oxidation degradation than other analytic methods,[8] thus this value is used in the present work as an indicator of degradation. It can be seen from Fig. 1 and 2 that the exposure time for the reduction to 2/3 of the initial value of elongation at break, $t_{2/3}$ (EB), of tested films under accelerated condition was about 9 days whereas for those exposed to sunlight took about 65 days. This means that the accelerated test method was about 7 times faster than natural exposure in Bangkok (April-June)

Tensile strength and elongation at break are shown in Fig. 3 and 4, respectively, for plastic films type D2024 (thickness 50 μm), containing no UV-stabilizer, exposed to sunlight and under accelerated condition. In this case, $t_{2/3}$ (EB) of the tested films exposed to natural light is approximately 60 days and those exposed in accelerated condition is about 7 days, i.e. about 9 times faster.

Tensile strength and elongation at break of LDPE films type D2024 (thickness 50 μm) without UV-stabilizer and with 0.2% Chimassorp 944 LD, exposed to UV-light in the accelerated tester, are shown in Fig. 5 and 6, respectively. LDPE films without UV-stabilizer took about 10 days to reach 2/3 of the initial value of elongation at break, while those with 0.2% Chimassorp 944 LD, required about 60 days. Thus the life of the films stabilized with 0.2% Chimassorp 944 is approximately 6 times that of the unstabilized films. Films containing 0.2% Chimassorp 944 LD, but with thickness of 100 μm were also investigated under accelerated condition. Its $t_{2/3}$ value was found to be about 90 days. The results showed that life of LDPE films increased with their thickness. In this case 100 μm thick films lasted almost one and a half time longer than the 40 μm thick films. This is understandable since degradation occurs from surface into the bulk of the materials.

LDPE blown films containing 0.2% Chimassorp 944 and 0.02% thermal stabilizer, Irganox 1076 were also investigated. Its $t_{2/3}$ (EB) value was found to be about 32 days. This means that the effectiveness of Chimassorp 944 is reduced to about one-half in the presence of the phenolic antioxidant Irganox 1076.

Tensile strength and elongation at break of LDPE films type D2024 (thickness 50 μm) containing UV-stabilizer, 0.2% Tinuvin 326 and 0.02% Irganox 1076, exposed in accelerated tester is shown in Fig. 7. The value of $t_{2/3}$ (EB) of these specimens was 15 days. Thus LDPE films stabilized with 0.2% Tinuvin 326 and 0.02% Irganox are only twice as durable as the unstabilized films.

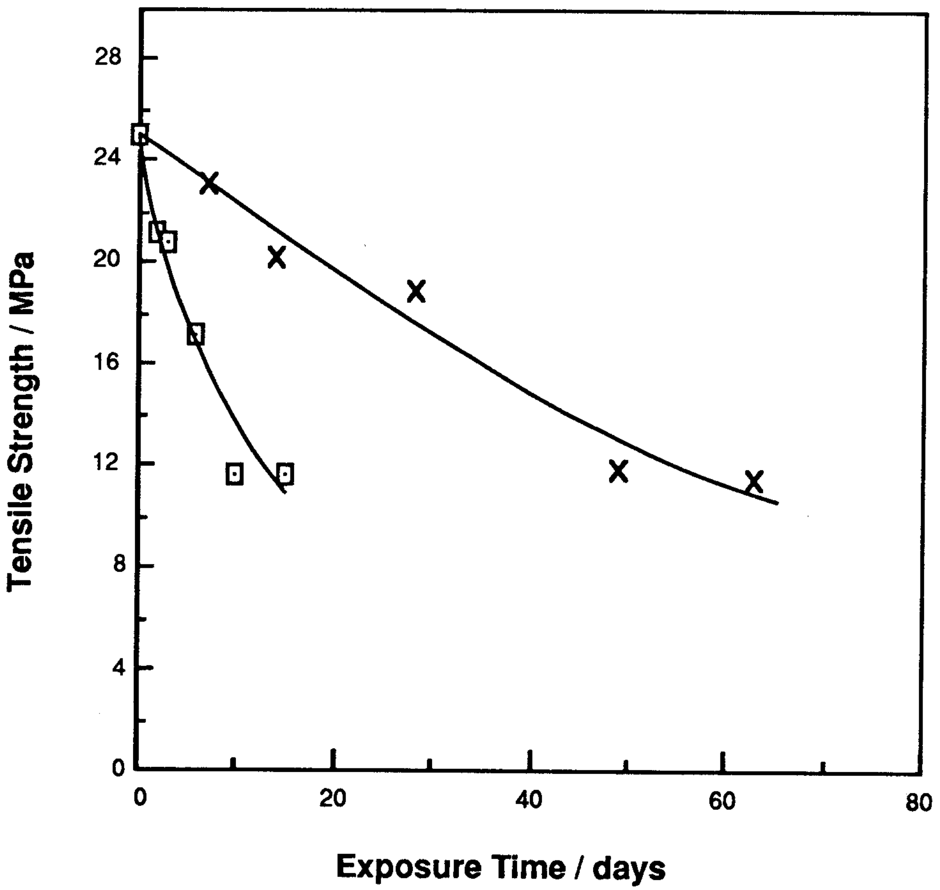


Fig. 1. Tensile strength as a function of exposure time of LDPE (CS2425) films (70 μm thick), no uv-stabilizer, under accelerated test (□) and natural light (x)

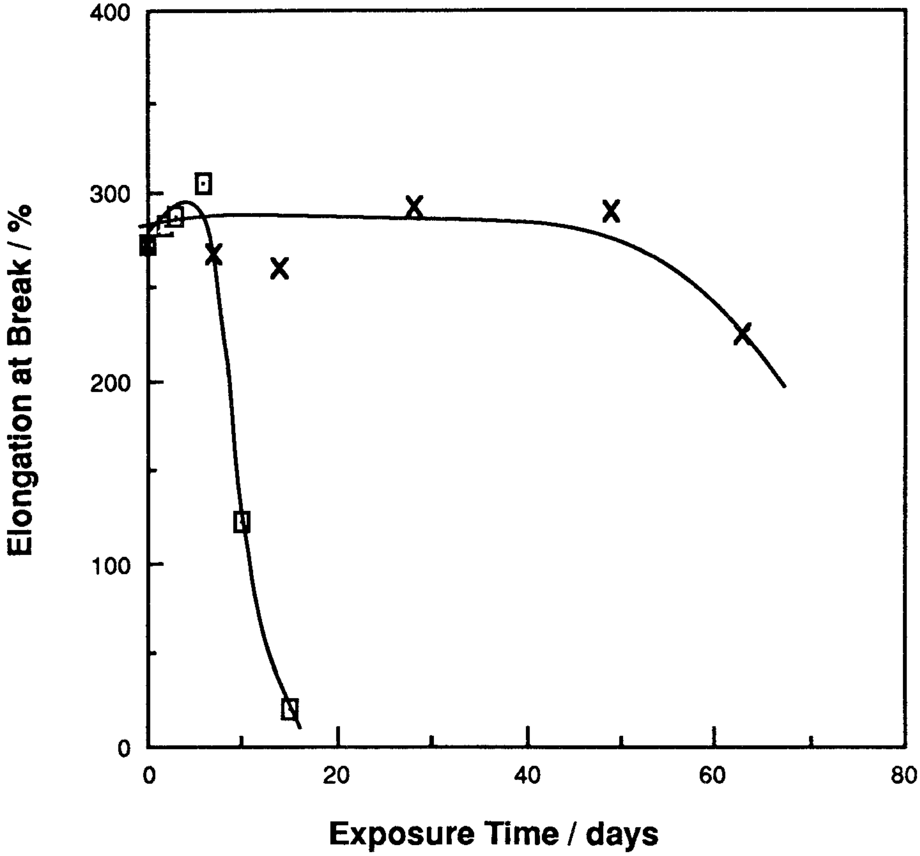


Fig. 2. Elongation at break as a function of exposure time of LDPE (CS2425) films (70 μm thick), no uv-stabilizer, under accelerated test (☐) and natural light (x).

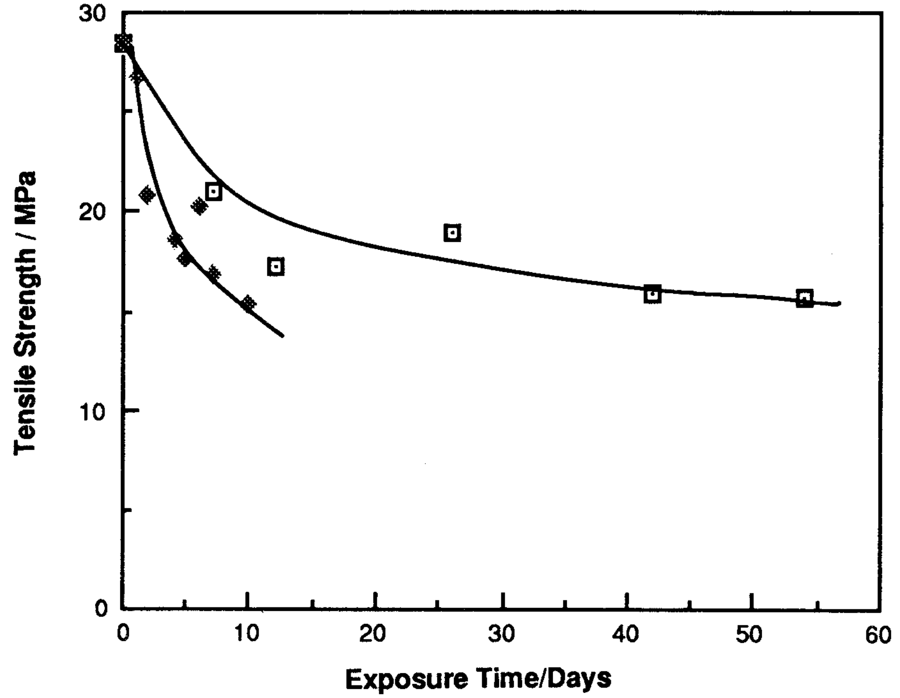


Fig. 3. Tensile strength as a function of exposure time of LDPE (D2024) films (50 μm thick), no uv-stabilizer, under accelerated test (■) and natural light (□).

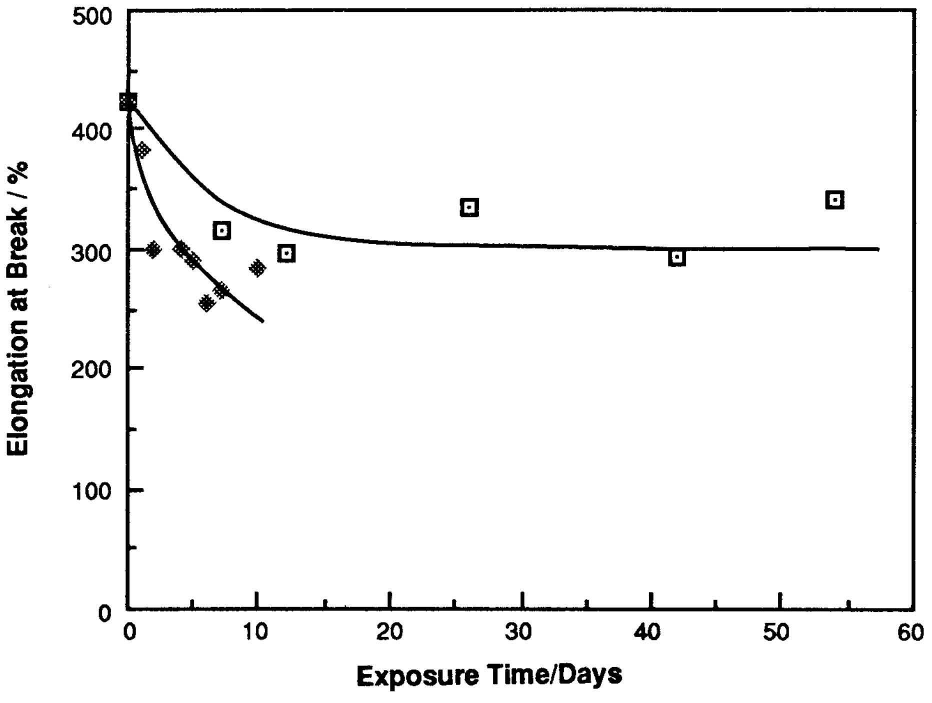


Fig. 4. Elongation at break as a function of exposure time of LDPE (D2024) films (50 μm thick), no uv-stabilizer, under accelerated test (■) and natural light (□).

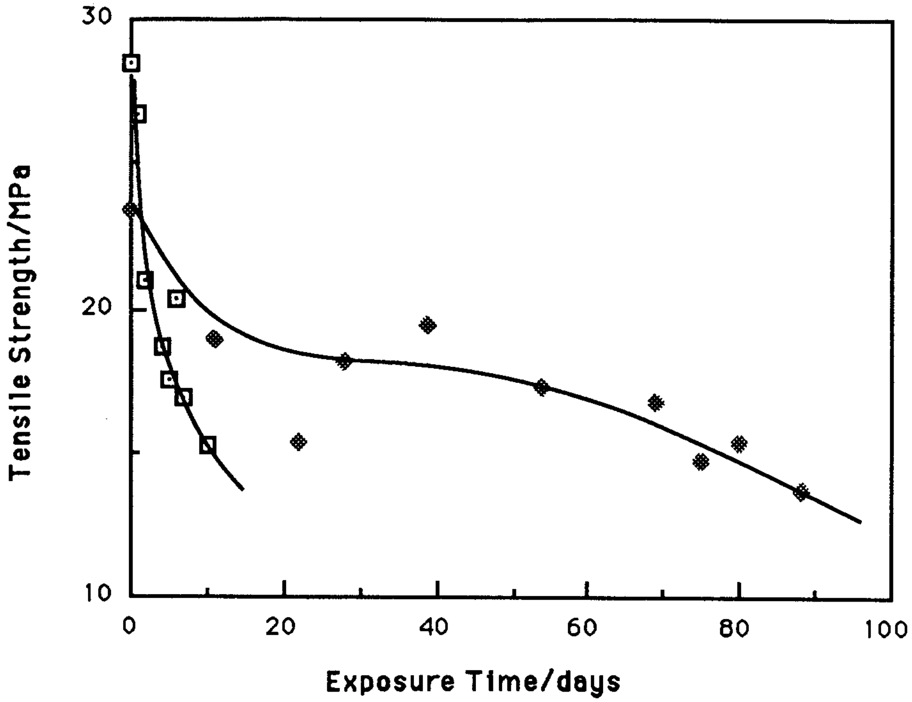


Fig. 5. Tensile strength as a function of exposure time of LDPE (D2024) films (50 μm thick), no uv-stabilizer (□) and containing 0.2% Chimassorp 944 (■), under accelerated condition.

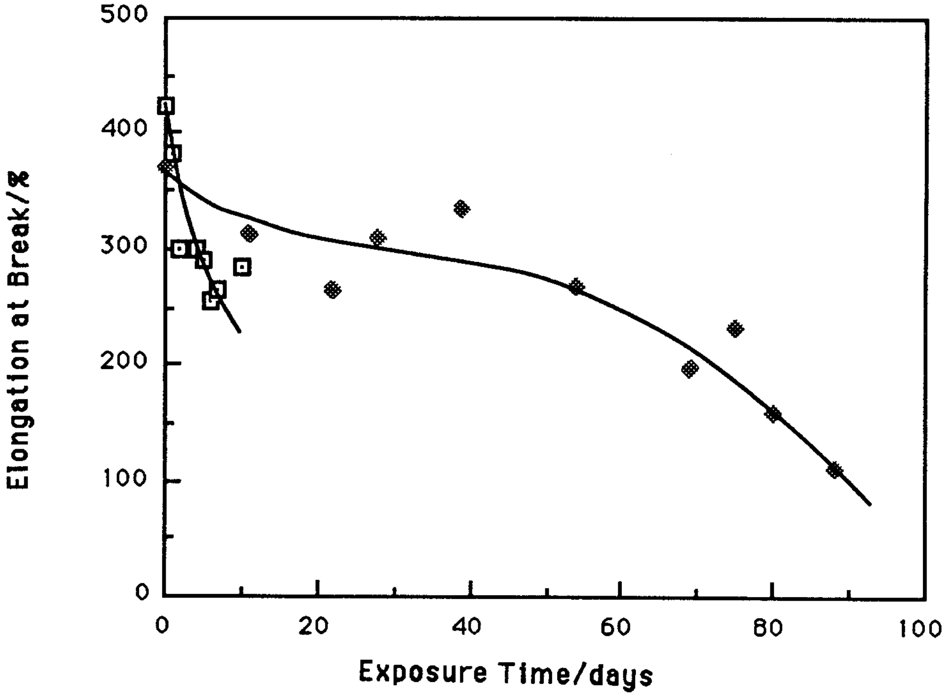


Fig. 6. Elongation at break as a function of exposure time of LDPE (D2024) films (50 μm thick), no uv-stabilizer (□) and containing 0.2% Chimassorp 944 (■), under accelerated condition.

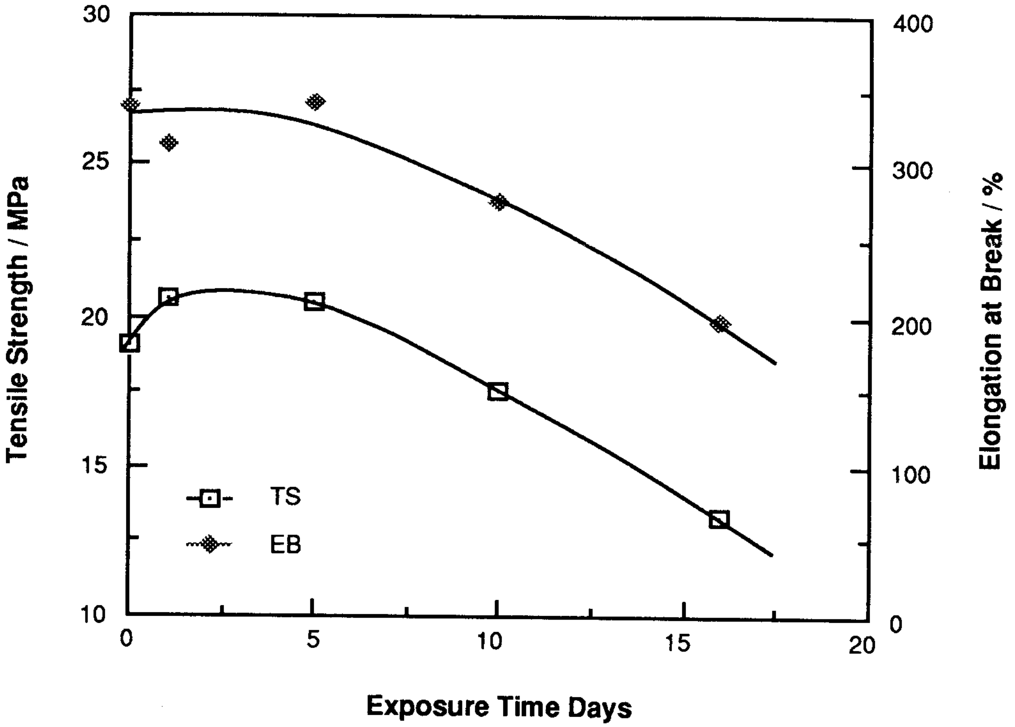


Fig. 7. Tensile strength (TS) (□) and elongtion at break (EB) (■) as a function of exposure time under accelerated test of LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 326 and 0.02% Irganox 1076.

Tensile strength and elongation at break of LDPE films type D2024 (thickness 50 μm) contained UV-stabilizer, 0.2% Tinuvin 622, and 0.02% Irganox 1076, exposed in an accelerated tester is shown in Fig. 8. $t_{2/3}$ (EB) of this specimen is about 28 days. That is approximately 4 times longer than the control containing no stabilizer (cf. Fig. 4). Therefore, Tinuvin 622 is a more effective UV-stabilizer than Tinuvin 326. And Chimassorp 944 is in turn more effective than Tinuvin 622. From the chemical structures of these UV-stabilizers showed in Table 1, Tinuvin 622 and Chimassorp 944 are oligomers (molecular weight) $>$ 2500), therefore the loss of these compounds by migration to the surface and then evaporated or washed out by rain or condensation in the accelerated test are less probable than Tinuvin 326. Similar ranks of effectiveness of these stabilizers were also observed in the case of high density polyethylene films.[9]

2. Measurement of Infrared Spectra

Infrared spectra of samples of type D2024 films taken at different time interval during accelerated test condition were recorded. The results are shown for unstabilized film (Fig. 9), with 0.2% Chimassorp 944 (Fig. 10), with 0.2% Tinuvin 326 (Fig. 11), and with 0.2% Tinuvin 622 (Fig. 12).

From Fig. 9, it is seen that eleven-day exposed film showed a large peak at 1716 cm^{-1} which corresponds to the formation of C=O group as the degradation product, whereas in Fig. 10, there is no appearance of C=O absorption band. This means that the Chimassorp 944 could hinder photo-oxidation of LDPE. In the case of Tinuvin 326 (Fig. 11), a large peak of C=O group appeared at 1716 cm^{-1} whereas the Tinuvin 622 sample exhibited a smaller C=O peak. Therefore it can be concluded from the results obtained that Chimassorp 944 is more effective in inhibiting photo-oxidation of LDPE than Tinuvin 622 which is in turn more effective than and Tinuvin 326.

3. Measurement of Ultraviolet-visible Spectra

UV-visible spectra of LDPE films at different exposure times were recorded from 500 to 200 nm. Typical results are shown for films without UV-stabilizer (Fig. 13), with 0.2% Chimassorp 944 LD (Fig. 14), with 0.2% Tinuvin 326 (Fig. 15), and with 0.2% Tinuvin 622 (Fig. 16). After irradiation, UV-spectrum of polyethylene film without UV-stabilizer (Fig. 13), showed a small shoulder at about 220-240 nm and the base line is somewhat higher than those of the unexposed film. This might be due to the absorption of unsaturation from polymer chain scission and the higher baseline resulted from light scattering caused by loss of gloss of the degraded films. The UV-spectrum of LDPE film with light-stabilizer, Chimassorp 944 (Fig. 14), showed a small reduction of intensity of the stabilizer at about 225 nm. Fig. 15 shows that the absorption bands due to Tinuvin 326 disappeared after 38 days of exposure to UV-light. Furthermore, the specimens containing Tinuvin 622 showed a small shoulder at about 220-240 nm after irradiated by artificial UV-light. Since there is no absorption band of Tinuvin 622 in this region, the small shoulder is probably due to unsaturation occurring in degraded product.

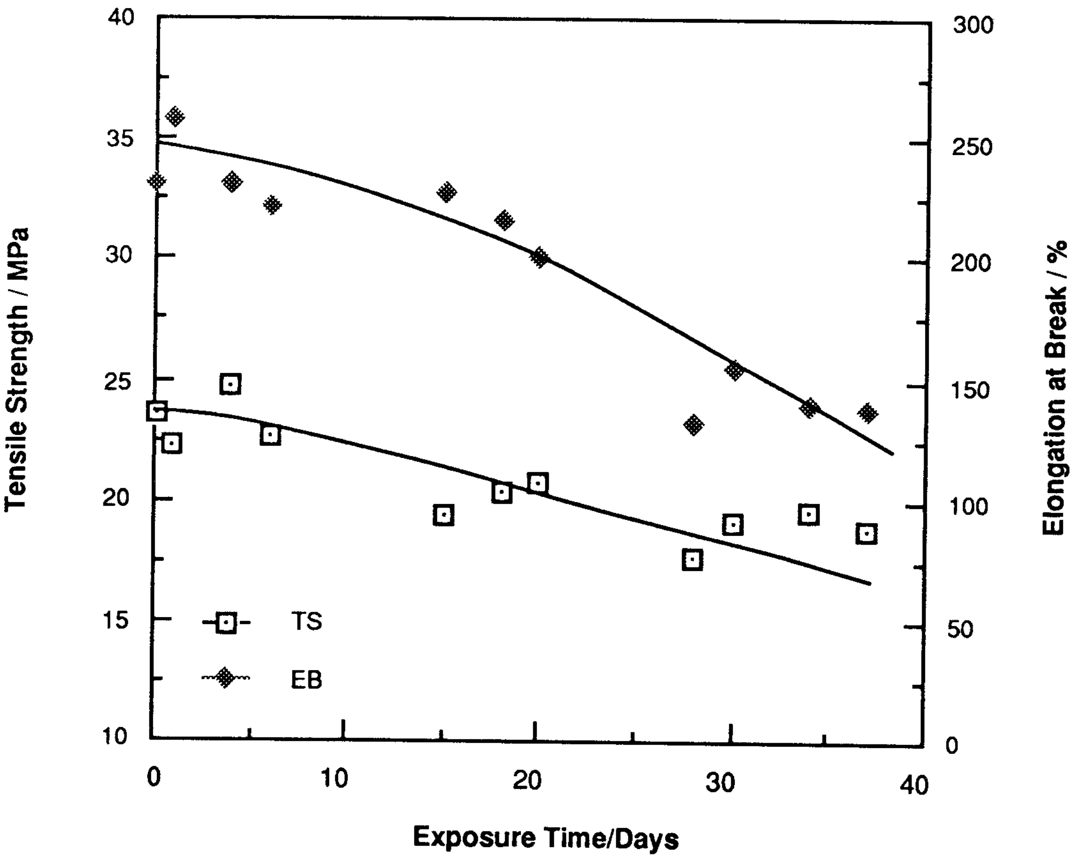


Fig. 8. Tensile strength (TS) (□) and elongtion at break (EB) (■) as a function of exposure time under accelerated test of LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 326 and 0.02% Irganox 1076.

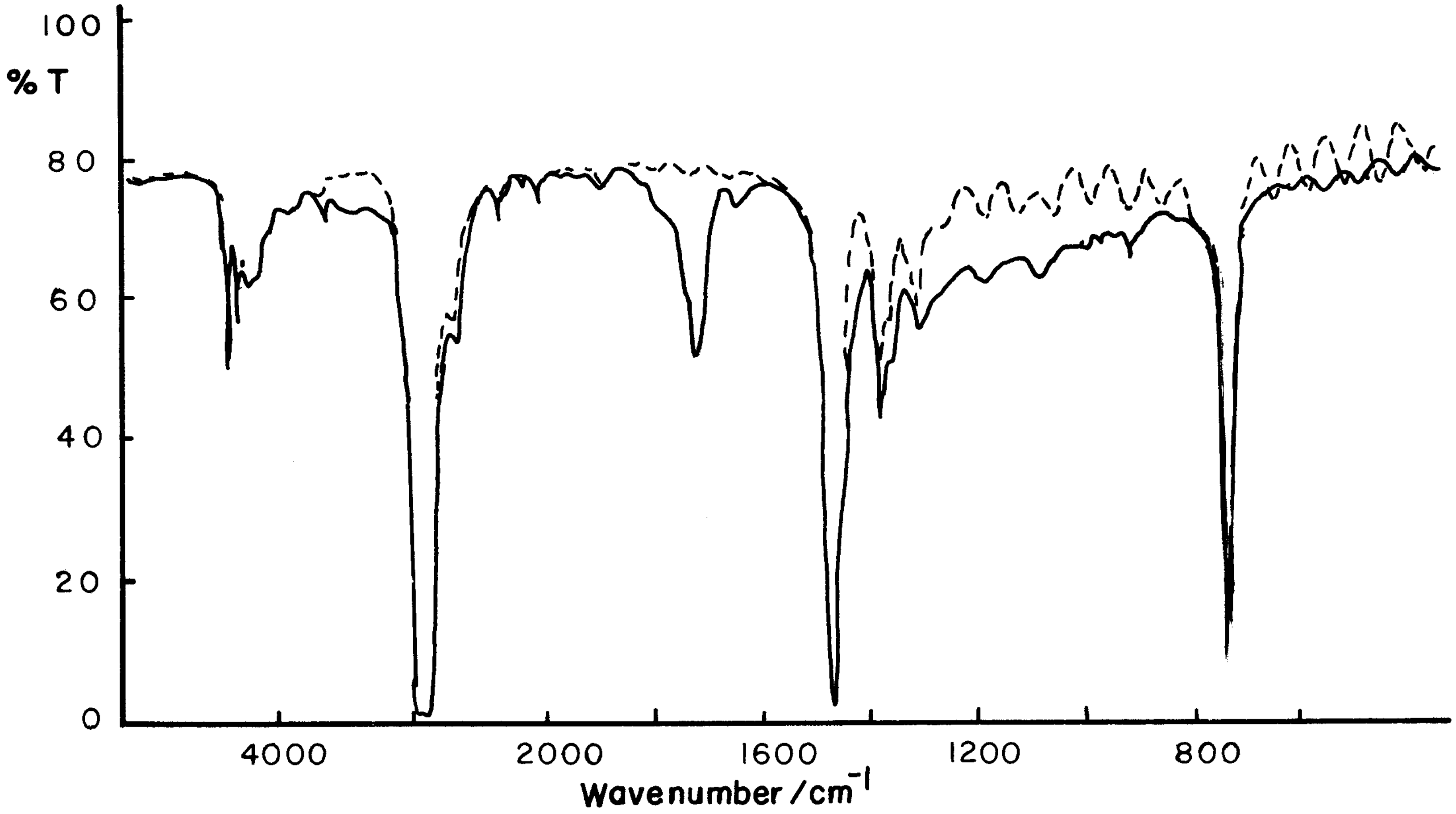


Fig. 9. Infrared spectra of unexposed (---) and 11 days exposed (________) LDPE (D2024) films (50 μm thick), no uv-stabilizer under accelerated test.

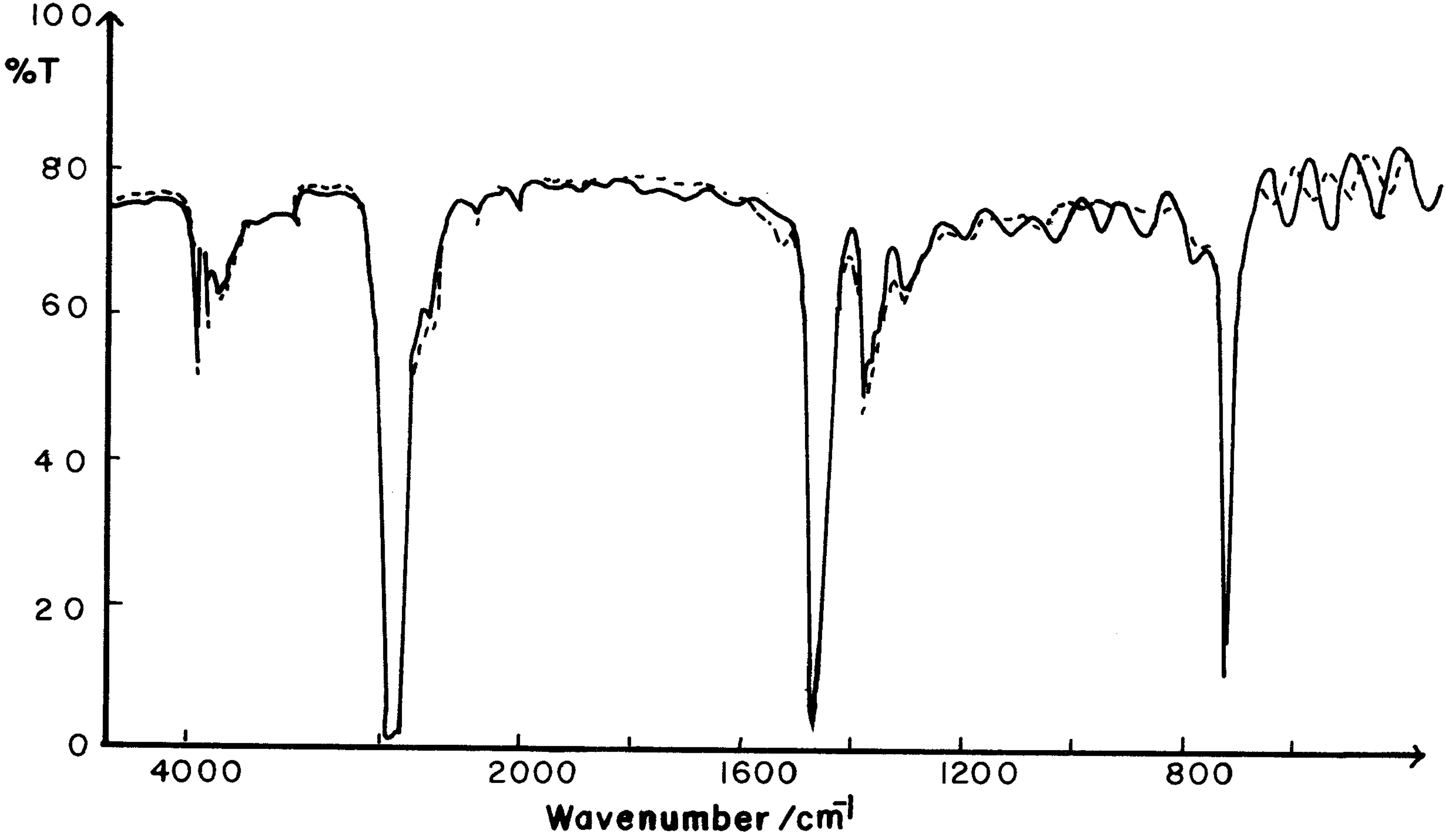


Fig. 10. Infrared spectra of unexposed (----) and 88 days exposed (________) LDPE (D2024) films (50 μm thick), containing 0.2% Chimassorp 944, under accelerated test.

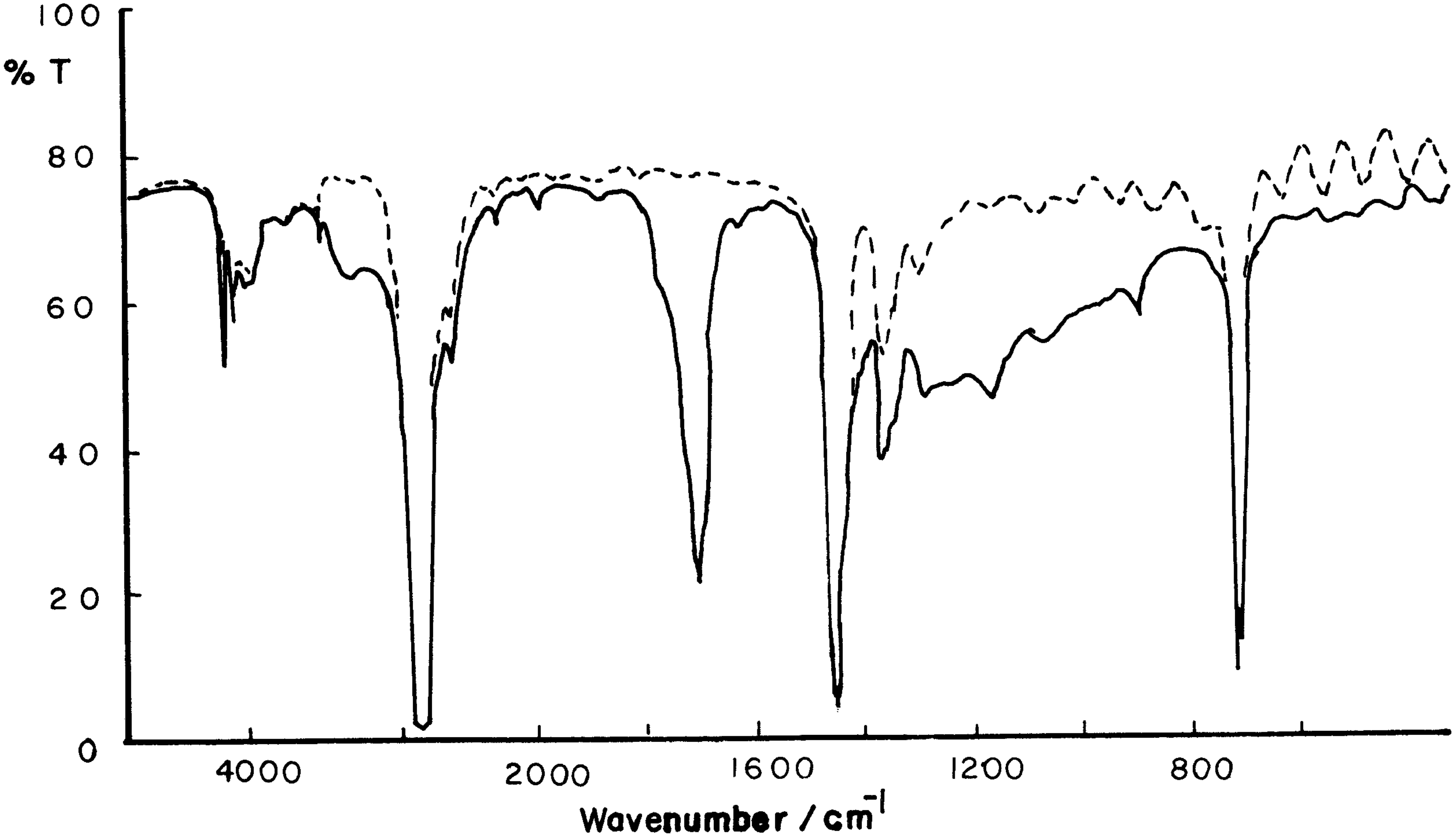


Fig. 11. Infrared spectra of unexposed (----) and 38 days exposed (________) LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 326 and 0.02% Irganox 1076, under accelerated test.

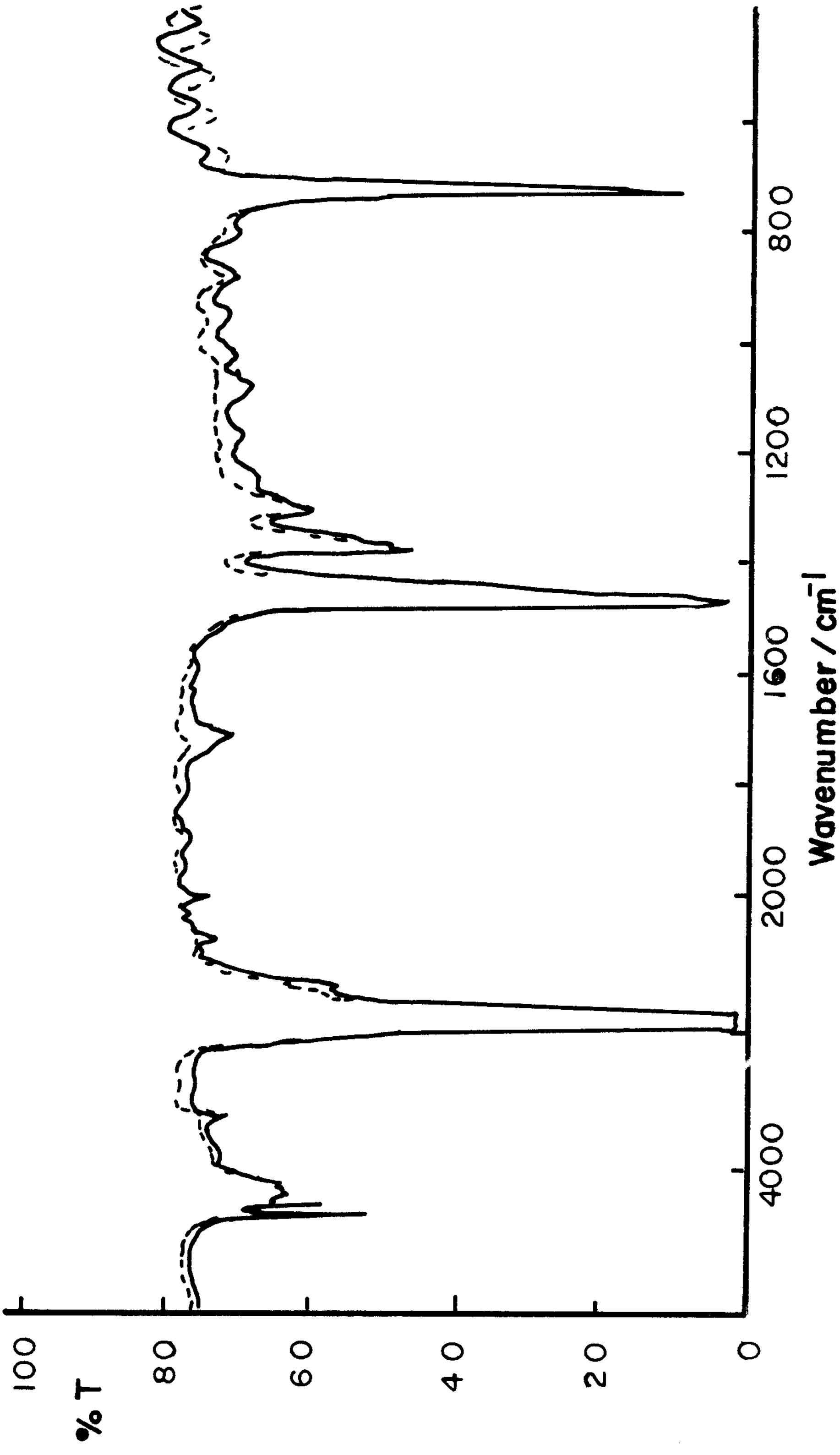


Fig. 12. Infrared spectra of unexposed (---) and 38 days exposed (———) LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 622 and 0.02% Irganox 1076, under accelerated test.

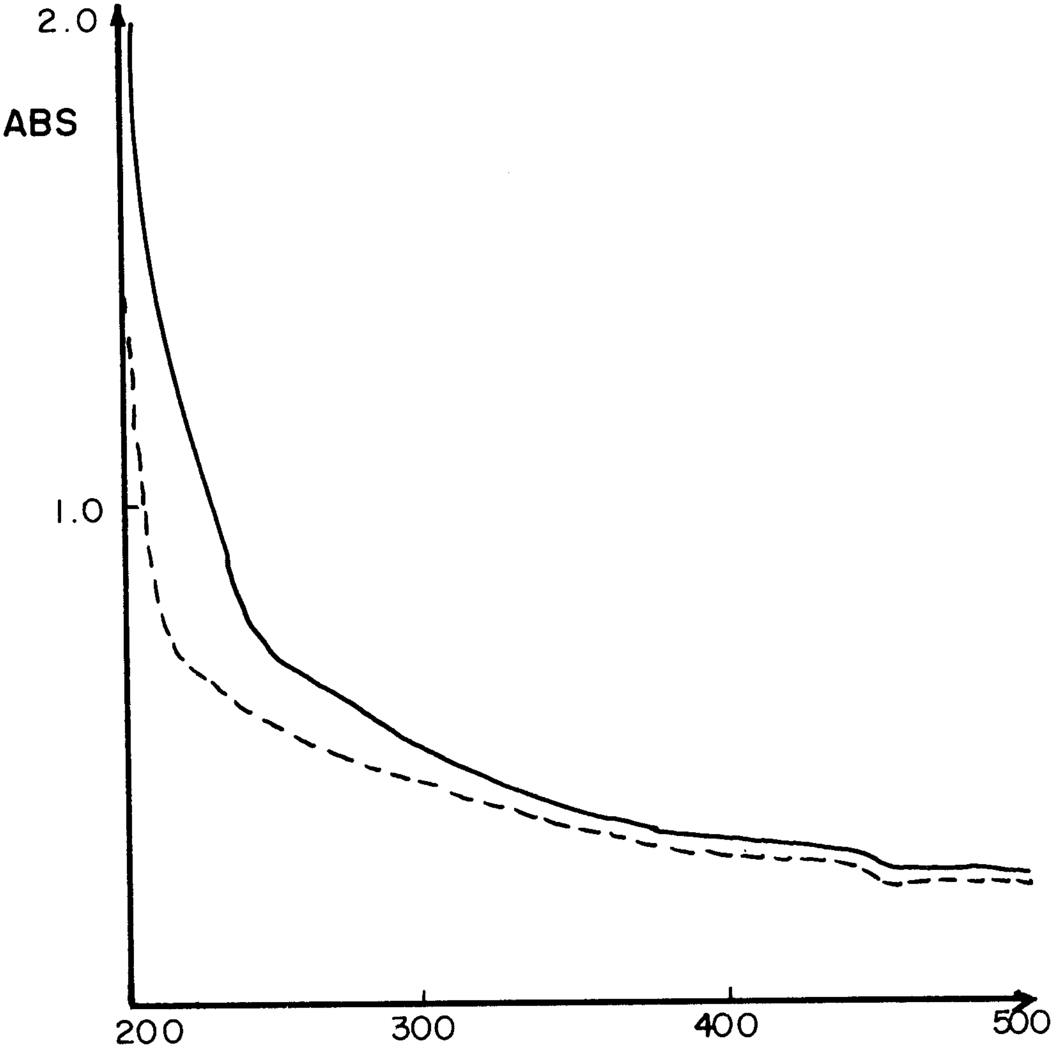


Fig. 13. UV-spectra of unexposed (----) and 11 days exposed (________) LDPE (D2024) films (40 μm thick) no uv-stabilizer, under accelerated test.

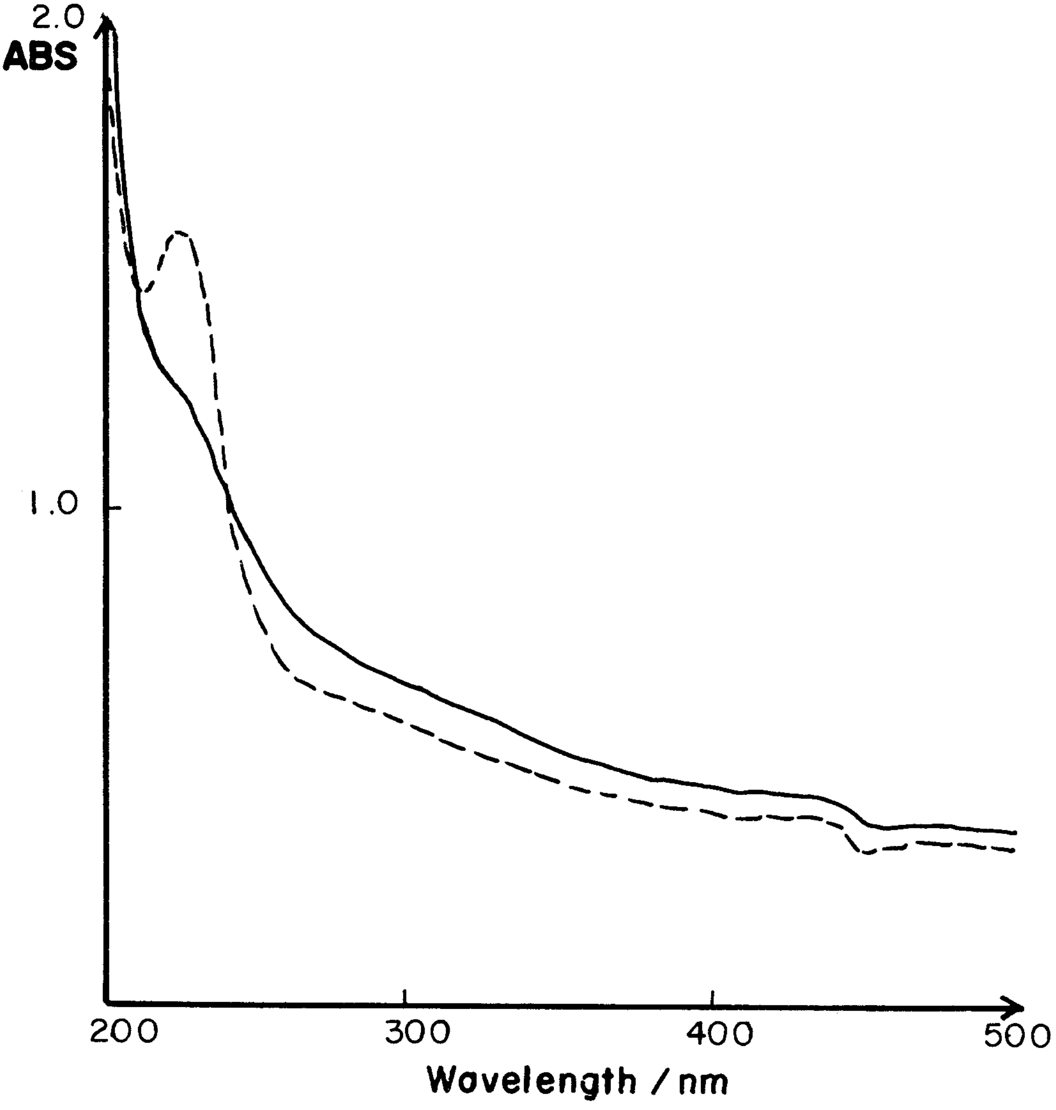


Fig. 14. UV-spectra of unexposed (----) and 88 days exposed (________) LDPE (D2024) films (50 μm thick), containing 0.2% Chimassorp 944, under accelerated test.

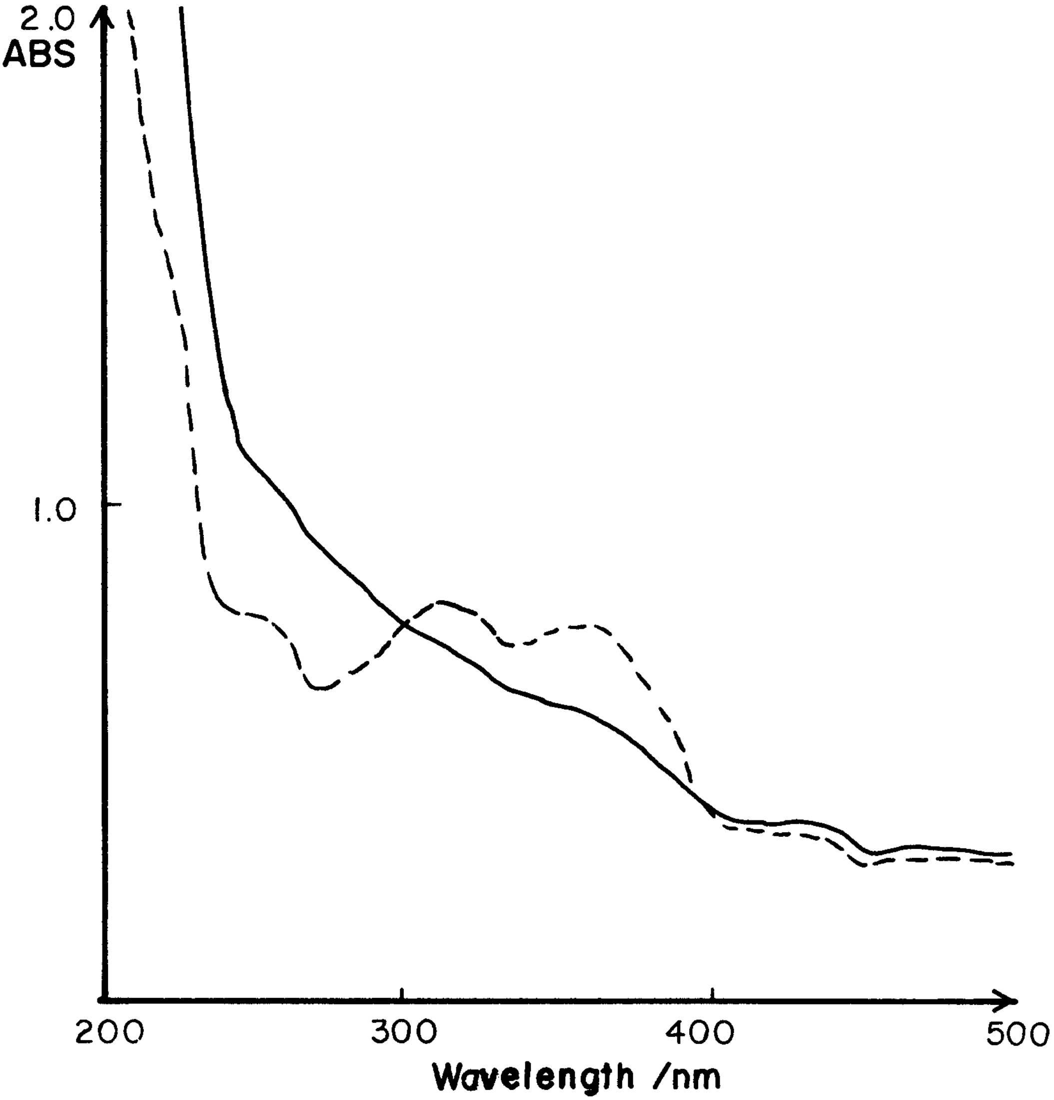


Fig. 15. UV spectra of unexposed (----) and 38 days exposed (________) LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 326 and 0.02% Irganox 1076, under accelerated test.

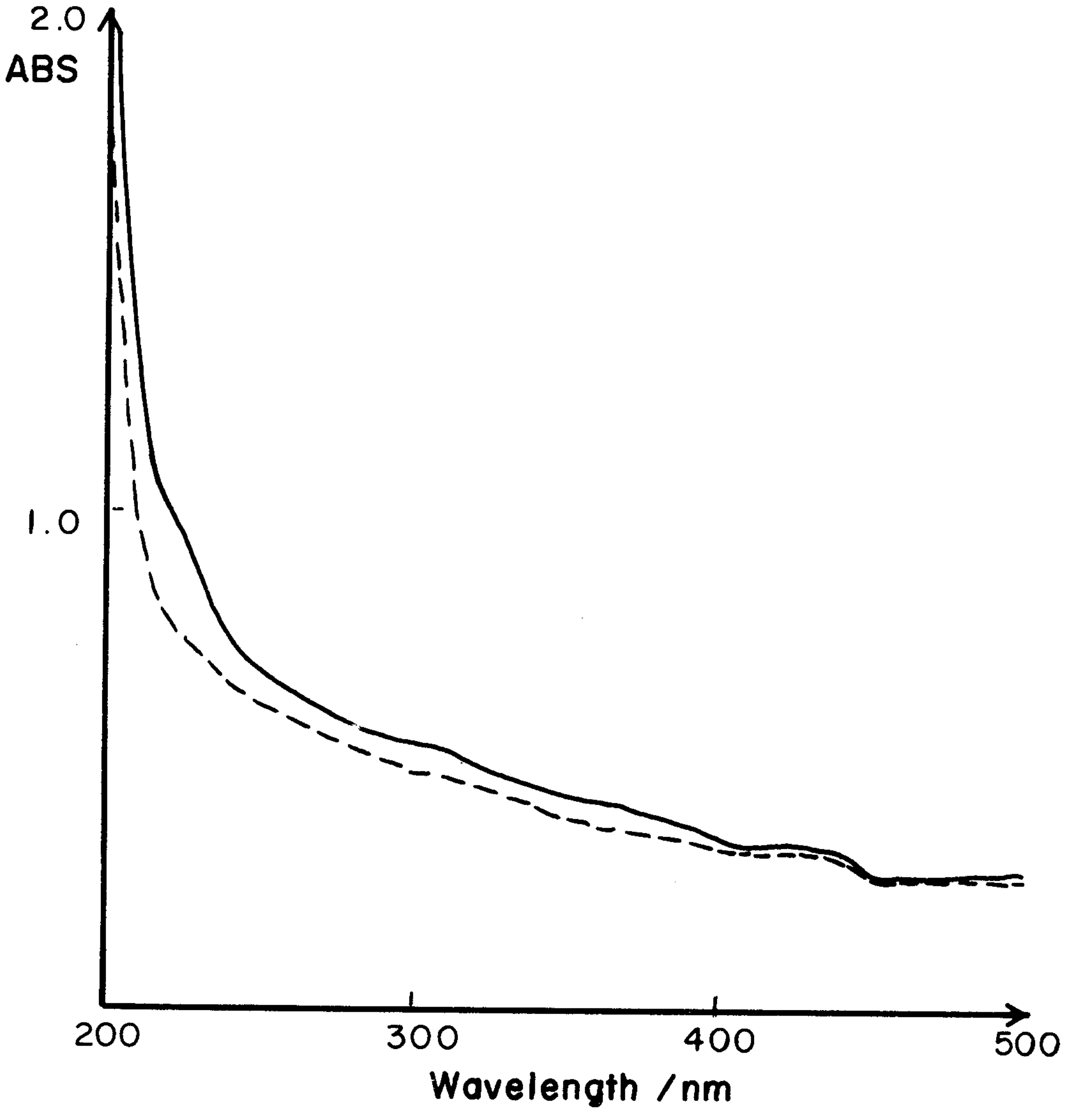


Fig. 16. UV spectra of unexposed (----) and 38 days exposed (________) LDPE (D2024) films (50 μm thick), containing 0.2% Tinuvin 622 and 0.02% Irganox 1076, under accelerated test.

The following statements can be made from the present study.

1. LDPE films aged under accelerated condition degrade 7 to 9 times faster than when exposed to natural condition in Bangkok.
2. For the UV-stabilizers studied. Chimassorp 944 is more effective than Tinuvin 622 which is in turn better than Tinuvin 326.
3. LDPE films stabilized with 0.2% of Chimassorp 944 can withstand degradation under the accelerated test condition 6 times longer than the films without stabilizer.
4. Carbonyl group is formed when unstabilized film degrades but no such group can be observed during the degradation of the UV-stabilized (Chimassorp 944) films, indicating the efficiency of Chimassorp 944 in suppressing photo-oxidation of LDPE films.
5. Life of LDPE films exposed to UV-radiation increased with thickness of the films.

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บทคัดย่อ

ศึกษาอายุการใช้งานของฟิล์มโพลีเอทธิลีนสำหรับใช้สร้างโรงและเพิงปลูกพืชโดยการตากแสงอาทิตย์และตากแสงอุลตราไวโอเล็ตในเครื่องเร่งอายุเปรียบเทียบกัน และได้ศึกษาผลของการใช้สารช่วยให้เสถียรต่อแสงอุลตราไวโอเล็ตสามชนิดเพื่อป้องกันการเสื่อมสภาพ โดยติดตามการเปลี่ยนแปลงสมบัติทางกายภาพของฟิล์ม เช่นการทนต่อแรงดึงและความยาวเมื่อดึงขาดพอดี และติดตามการเปลี่ยนแปลงของโครงสร้างโมเลกุลโดยการวัดอินฟราเรดและอุลตราไวโอเล็ตสเปคตรัม พบว่าเมื่อเติมสารช่วยให้เสถียรต่อแสง 0.2% จะช่วยให้อายุการใช้งานของฟิล์มยาวขึ้น 4 ถึง 5 เท่าของฟิล์มที่ไม่ใส่สารช่วยให้เสถียร และพบว่าการทดลองในเครื่องเร่งอายุทำให้ฟิล์มเสื่อมสภาพเร็วกว่าการตากแสงอาทิตย์ในกรุงเทพฯ 7-9 เท่า