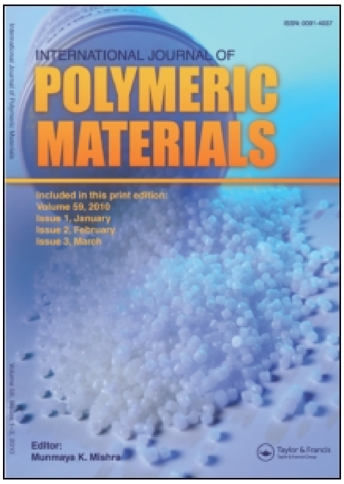


International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Durability of Polyethylene Films

A. Ram[a]; T. Meir[a]; J. Miltz[b]
[a] Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, Israel [b] Department of Food Engineering, Technion-Israel Institute of Technology, Haifa, Israel

To cite this Article Ram, A. , Meir, T. and Miltz, J.(1980) 'Durability of Polyethylene Films', International Journal of Polymeric Materials, 8: 4, 323 — 336

To link to this Article: DOI: 10.1080/00914038008077958

URL: http://dx.doi.org/10.1080/00914038008077958

Intern. J. Polymeric Mater., 1980, Vol. 8, pp. 323–336
0091-4037/80/0804-0323 $06.50/0

Printed in Great Britain

Durability of Polyethylene Films

A. RAM and T. MEIR
Department of Chemical Engineering

and J. MILTZ
Department of Food Engineering,
Technion-Israel Institute of Technology, Haifa, Israel

(*Received January 21, 1980*)

This work deals with the weather-resistance of low-density polyethylene films. The performance under controlled laboratory conditions, of well-characterized polymer grades and various combinations of stabilizers was studied. The high molecular weight and narrowly-distributed grades seemed to have a better performance. While the unstabilized films were found to fail after a relatively short period, the synergistic combinations of UV absorbers, quenchers and anti-oxidants showed a marked increase in film duration. For the protected films, increasing film thickness improved performance. The increase of crystallinity upon ageing with the resulting decrease in oxygen permeability are highlighted. The role of oxygen diffusion into the film is significant both in thermal and in photo-oxidation.

1. INTRODUCTION

It is well established that photo-oxidation has a major role in the degradation of polymeric materials exposed to natural weathering. The various aspects of polymer stability have been extensively described in the literature.[1–10] For the case of polyolefins, the photodegradations is initiated through a free-radical reaction induced by ultraviolet (UV) radiation followed by oxidation. The reaction is enhanced at higher temperatures. Thus, light, oxygen and heat cause chain scission and crosslinking. As chain scission is the predominating reaction, the net result is a degradation in the molecular weight and mechanical properties until, ultimately, the polymer becomes useless. The presence of tertiary carbon atoms in polypropylene and in branched (low-density) polyethylene (LDPE) augments their sensitivity to chemical attack. The latter can be described as follows:

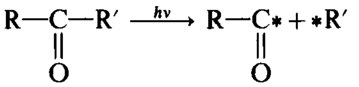
$$\text{PH (Polymer)} \rightarrow P* + H* \qquad (1)$$

$$P* + O_2 \rightarrow POO* \qquad (2)$$

$$POO* + PH \rightarrow POOH + P* \qquad (3)$$

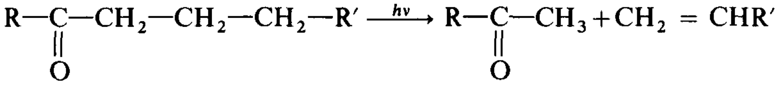
$$POOH \rightarrow PO* + *OH \qquad (4)$$

Thus, oxidation of polyolefins produce peroxide radicals which eventually decompose into carbonyl groups (ketonic) with hydroperoxides as intermediates.[8] The breakdown of the oxidized polyolefin follows two known scission mechanisms:



$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{h\nu} R-\underset{\underset{O}{\|}}{C}* + *R'$$

Norrish I (radical) (5)



$$R-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-R' \xrightarrow{h\nu} R-\underset{\underset{O}{\|}}{C}-CH_3 + CH_2 = CHR'$$

Norrish II (nonradical) (6)

Reactions (5) and (6) clarify why the increase in carbonyl concentration is a useful tool to follow photodegradation of polyethylene.

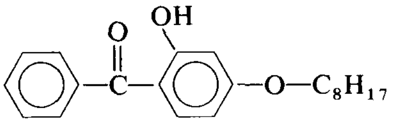
Although the branched, low-density polyethylene is one of the least weather-resistant polymers, its films and sheets are very widely used in agriculture as well as in many other applications. It therefore calls for appropriate protection in order to extend its durability. The present work deals with the performance of LDPE films differing in polymer grade, film thickness and in type and concentration of stabilizer. Photo- and thermal oxidation were followed up by chemical changes (increase in carbonyl concentration) and mechanical changes (decrease in ultimate elongation and energy to break). Morphological changes and associated transport properties (permeability to oxygen) were also studied and analyzed.

2. EXPERIMENTAL

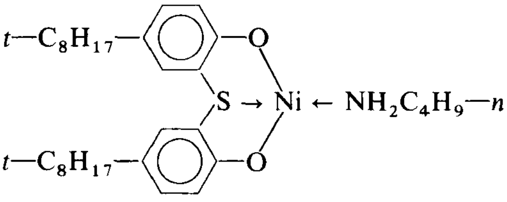
Various grades of commercial LDPE, produce of "Israel Petrochemical Enterprises, Ltd" were film-blown in two single-screw extruders: a 1.5 in Iddon and a 2.5 in Prodex extruder. The stabilizers, as master-batches, were incorporated in the polymer in a laboratory twin-screw extruder.

The polyethylenes used in the present study were previously characterized and described.[11-13] Their important features are summarized in Table I.

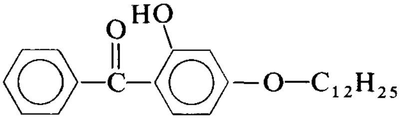
The following stabilizers (UV absorbers, quenchers, antioxidants) were used in this work.



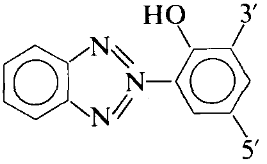
(American Cyanamid) UVA-531
2-hydroxy-4-octyloxy-
benzophenone
ultra-violet absorber.



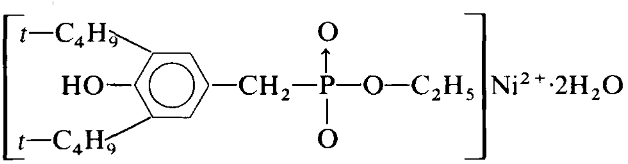
(American Cyanamid) UV-1084
Quencher.
[2,2′-thiobis
(4-t-octylphenolate)]
n-butylamine nickel (II)



(Eastman) Inhibitor DOBP
4-dodecyloxy-2-hydroxy
benzophenone
ultra-violet absorber



(Ciba-Geigy) Tinuvin 328
2-(3′,5′-dialkyl-2′-
hydroxyphenyl)benzotriazole
ultra-violet absorber



(Ciba-Geigy) Irgastab
2002
Nickel bis[o-ethyl
(3,5-di-tert-butyl-4-
hydroxybenzyl)]
phosphonate
Quencher

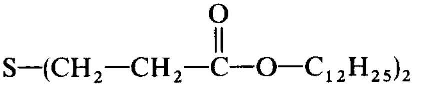
TABLE I

LDPE Characteristics

Designation	A	B	C	E
Weight-average molecular weight $\bar{M}_w$	320,000	191,000	140,000	691,000
Number-average molecular weight $\bar{M}_n$	20,600	23,800	22,100	20,100
$D_n = \bar{M}_w/\bar{M}_n$	15.6	8.06	6.34	34.4
Short-chain branching SCB/1000C	20.7	20.32	20.67	22.41
Long-chain branching LCB/1000C	2.16	2.88	4.63	5.09
MFI gr/10 min	0.3	0.7	2.0	2.0
Density gr/cm^3	0.923	0.923	0.921	0.919
Degree of crystallinity, %	45.9	43.0	47.8	38.4
Ultimate elongation, %, plates	700	600	575	550
film	490	510	520	420

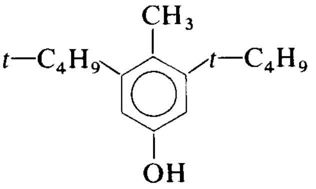
Antioxidants:

1. (American Cyanamid) 1735 Phosphates and phenolic amines
2. (American Cyanamid) LTDP dilaurylthiodipropionate



$S-(CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_{12}H_{25})_2$

3. BHT
butylated hydroxy toluene



The various compositions of the stabilized films are summarized in Table II.

Accelerated weathering experiments were carried out in two types of instruments: (a) Atlas Weather-O-Meter (WOM) with a 2.5 KW Osram Xenon lamp, (b) Sun-Lamp (SL), especially built for the present study, using mercury Ultra-Vitalux lamps as the source for UV radiation. Both systems were air or water cooled to temperatures of 44–52°C. The use of accelerated weathering provides several advantages: controlled conditions and shorter periods. An air circulated oven was utilized for studying the effect of heat on polymer degradation (up to 100°C).

Carbonyl content was measured in a Perkin-Elmer infra-red spectrophotometer and calculated from the peaks at 1712 cm^{-1} and 1835 cm^{-1} using the following equation

$$\%CO = \frac{A_{1712} - A_{1835}}{0.203l} \tag{7}$$

where l is the film thickness (in mils).

TABLE II

Composition of stabilized films (W %)

Type	UVA 531	UVA 1084	DOBP	Tinuvin 328	Irgastab 2002	AO 1735	AO LTDP
1	—	—	—	—	—	—	—
2	0.25	0.25	—	—	—	—	—
3	0.5	0.5	—	—	—	—	—
4	—	—	0.5	—	—	—	—
5	—	0.25	0.25	—	-	—	—
6	0.5	1.0	—	—	—	0.3	—
7	0.5	1.0	—	—	—	0.3	0.25
8	—	—	—	0.25	0.25	—	—

Tensile properties were measured on an Instron testing machine driven at a speed of 20 cm/min.

The degree of crystallinity was determined from x-ray diffraction, and oxygen permeability was determined from the change in its concentration with time in a standard permeation cell.[14]

3. RESULTS AND DISCUSSION

Figure 1 is a plot of the residual tensile strength and elongation as a function of irradiation time. It is clearly seen that elongation at break is more sensitive to ageing than the ultimate tensile strength as was also pointed out by Miltz and Narkis[15] for the case of crosslinked polyethylene. In Figure 2 the retained elongation is plotted as a function of carbonyl percent. It can be seen that a rough correlation between these parameters exists, which also leads to our criterion for failure: carbonyl concentration of 0.1% which seems to be equivalent to about $\frac{2}{3}$ of the retained elongation. This represents, however, an arbitrary, rather conservative, criterion. While the weathering instruments (SL and WOM) differ in their radiation spectra, our results verify quite a close resemblance in their effect on carbonyl content or residual elongation. This similarity is demonstrated in Figure 3, which also demonstrates the autoacceleration in photo-oxidation. The performance of unprotected films made of five different LDPE grades is presented in Figure 4 and Table III. It

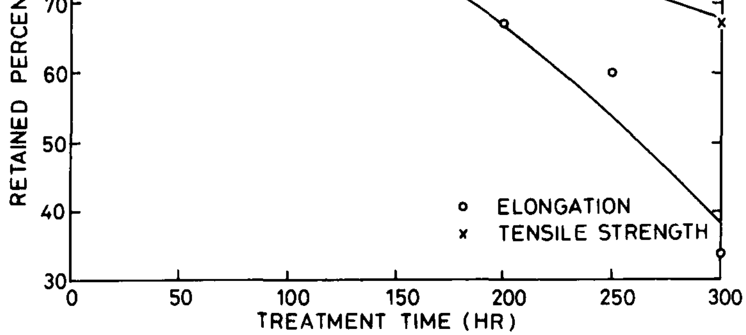


FIGURE 1 Retained tensile strength and ultimate elongation with time of accelerated ageing.

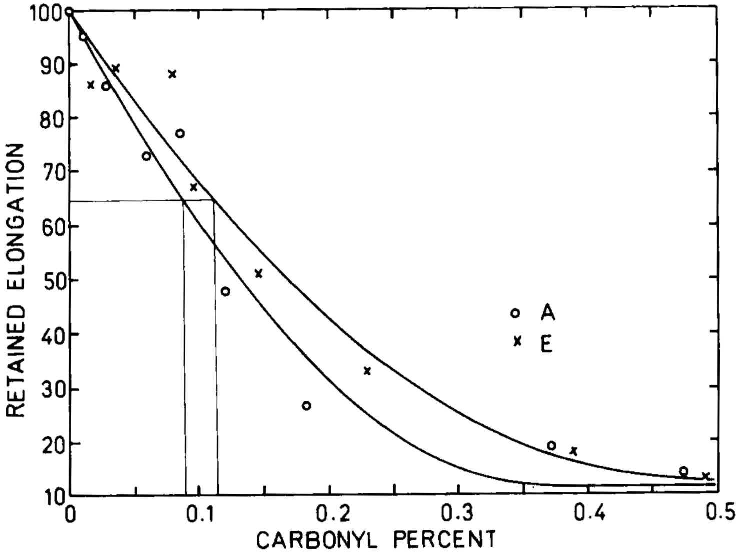


FIGURE 2 Retained elongation versus carbonyl percent in S.L.

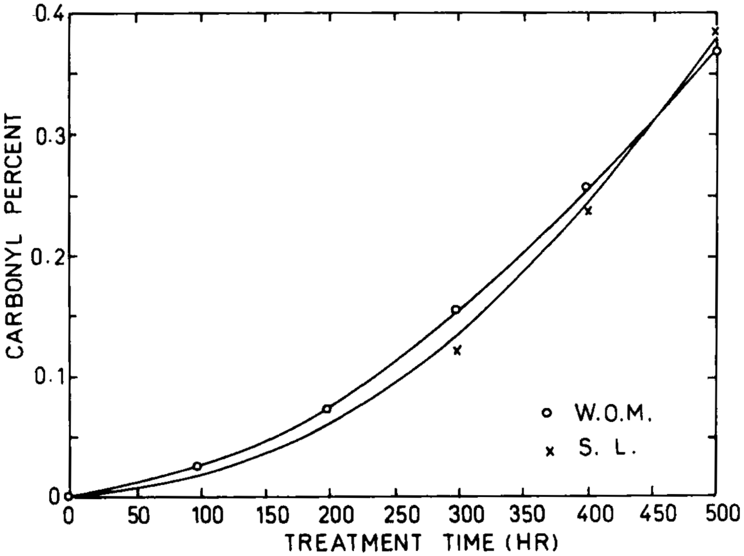


FIGURE 3 Comparative ageing in W.O.M. and S.L.

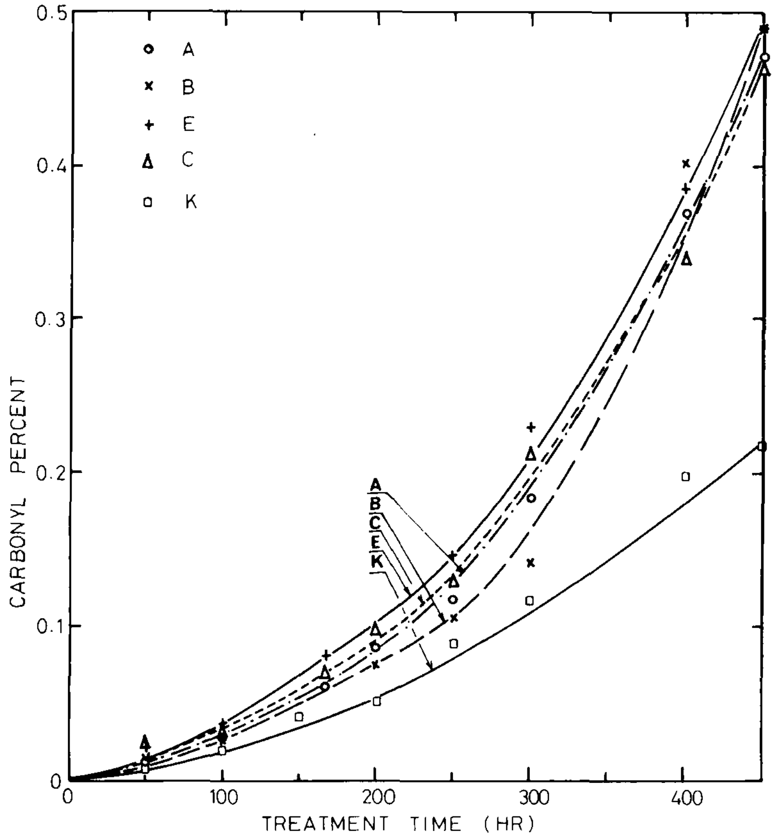


FIGURE 4 Ageing characteristics of various LDPE grades in S.L.

TABLE III

Carbonyl contents (CO) and retained elongation (% ε) of unstabilized films after exposure in SL.

Exposure hours	Grade A		Grade B		Grade C		Grade E		Grade K*
	CO %	ε %	CO %	ε %	CO %	ε %	CO %	ε %	CO %
50	0.012	95	0.013	84	0.019	89	0.017	86	0.006
100	0.029	86	0.025	90	0.033	93	0.036	89	0.019
150	0.060	73	0.060	81	0.068	95	0.080	88	0.040
200	0.086	77	0.075	76	0.096	88	0.097	67	0.050
250	0.119	48	0.106	82	0.129	80	0.146	51	0.088
300	0.183	27	0.141	86	0.211	34	0.229	33	0.115
400	0.371	19	0.402	32	0.339	15	0.389	18	0.197
450	0.473	14	0.491	15	0.463	11	0.491	13	0.217

* Grade K is an experimental one with MFI = 0.2.

is seen that the four grades described in Table I behave in a similar fashion and that the critical time for failure lies in the range of 200–250 hours of exposure. In addition to the exceptional good performance of grade $K(MFI = 0.2)$ there are some advantages to grades 100 and 110, both relatively high molecular weight ($\bar{M}_w$) and narrow-distributed polymers. These grades are typical film grade LDPE characterized by a low melt flow index (MFI) and a relatively high density. It is worthwhile to stress that all these grades are similar in $\bar{M}_n$ and in short chain branching (SCB) as well as in the ultimate elongation of the original films. Additional data will indicate, however, the deficiency of the broadly distributed, highly branched grade E. It is therefore assumed that a high $\bar{M}_w$, narrow molecular weight distribution (MWD) and low degree of branching provide a higher life expectation.[16] A recent publication[17] recommends $\bar{M}_n$ of 24,000–29,000 (MFI 0.2–0.7) and thickness of 0.150–0.180 mm. Analysis of ageing in a forced air circulated oven at 100°C indicates the deficiency of grade C (lowest $\bar{M}_w$) as compared to the others (see Figure 5). The carbonyl concentration increases faster as a result of ageing in the oven (at 100°C) than that in the weatherometer as has been also claimed by Winslow.[4] At lower oven temperatures, however, when the circulation of air was eliminated, the ageing of the LDPE films diminished significantly. The presence and diffusion of oxygen plays therefore a significant role in thermal ageing. The importance of oxygen diffusion into the film is also exhibited when films of various thickness (70, 100 and 150 microns) were

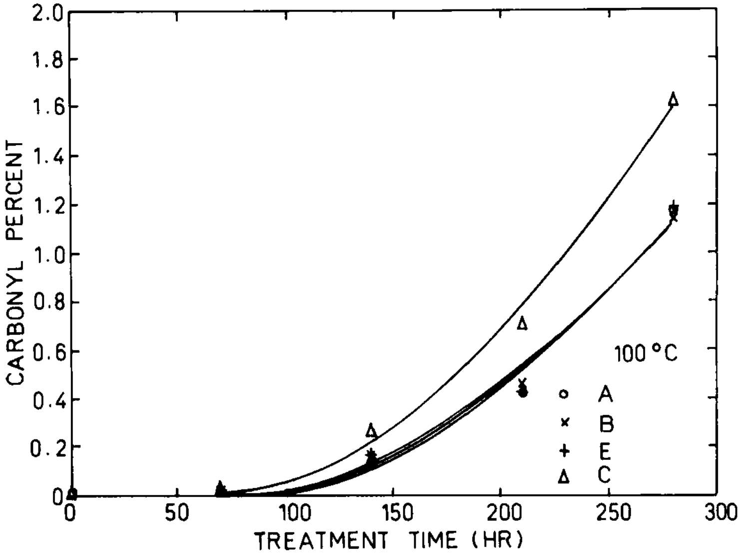


FIGURE 5 Ageing of LDPE films in oven at 100°C.

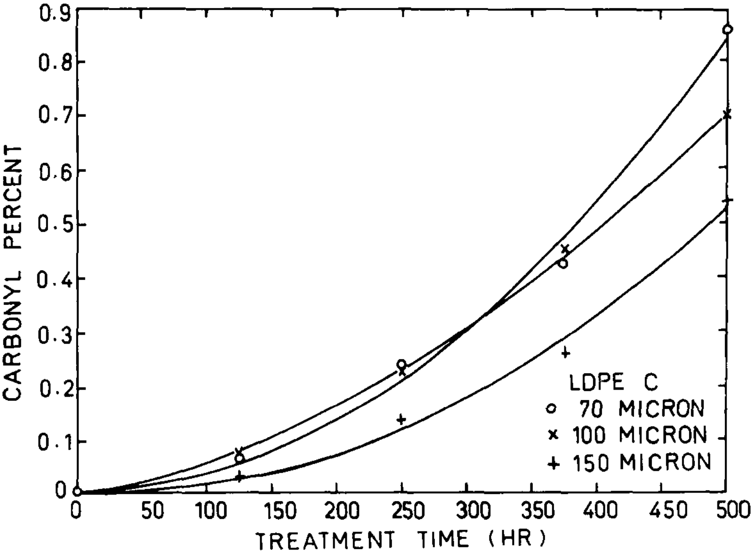


FIGURE 6 Effect of thickness on ageing of unstabilized films.

compared as shown in Table IV and Figure 6 (for unprotected films) and Figure 7 (for protected films). In the latter the increased thickness has also the effect of serving as a stabilizer reservoir for replacing depleted zones in the outer surface. The very effect of UV stabilization is seen to strongly increase the durability of the films (from around 200 to 1200 irradiation hours). Compared to this increase, the role of film thickness in the studied range does not seem to be very significant. The trend fits however the anticipated performance and there is no doubt that thicker films will verify higher resistance to ageing.[5,10,16]

The effect of various stabilizers' compositions is shown in Table V and Figures 8 and 9. Carbonyl concentration as well as retained elongation underline the excellent performance of compositions 6 and 7 which extend the

TABLE IV

Effect of thickness on weathering in SL grade C, unstabilized

Exposure hours	Thickness 0.007 cm		Thickness 0.010 cm		Thickness 0.015 cm	
	CO %	ε %	CO %	ε %	CO %	ε %
125	0.067	74	0.077	74	0.033	88
250	0.238	33	0.227	37	0.137	51
375	0.428	14	0.450	17	0.259	16
500	0.858	—	0.697	—	0.538	—

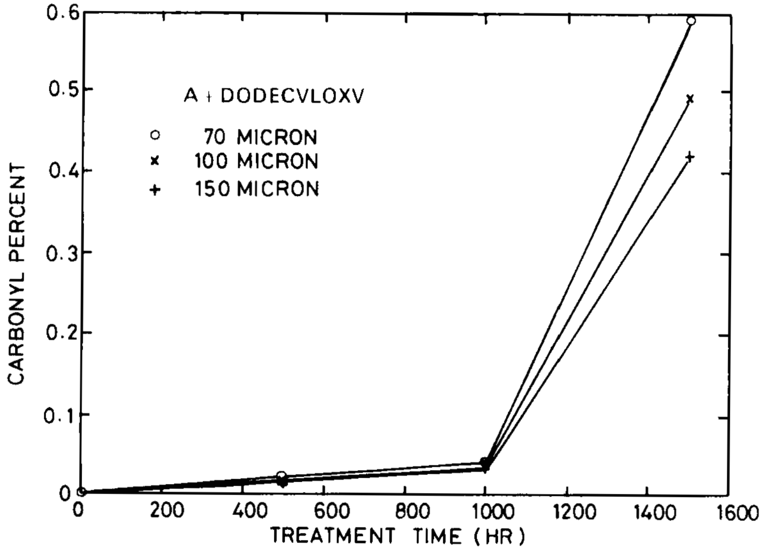


FIGURE 7 Effect of thickness on ageing of stabilized films.

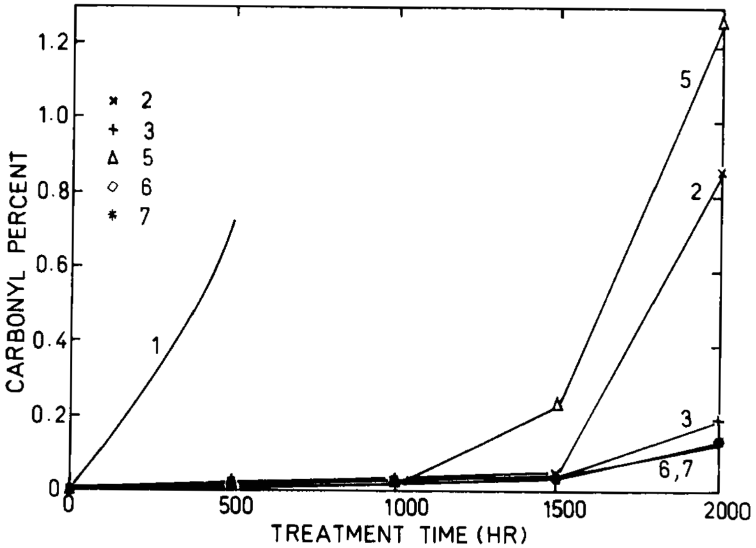


FIGURE 8 Ageing of stabilized films: carbonyl percent.

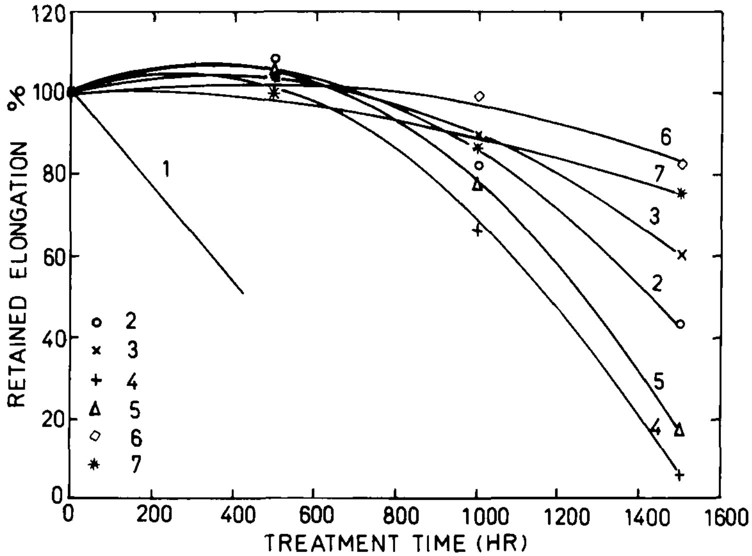


FIGURE 9 Ageing of stabilized films: retained elongation.

endurance of the films to over 2000 hours. These two compositions represent the highest concentration of a synergistic mixture of a UV absorber and quencher together with an antioxidant. A similar composition has been recently recommended by Lind.[18] On the other hand the inclusion of DOBP (a dodecyloxy side chain replacing the conventional octyloxy in hydroxy benzophenone) in compositions 4 and 5 verified early failure. It is postulated that due to enhanced compatibility of the longer side chain stabilizer, it loses effectiveness as diffusion to the surface to replace lost stabilizer is

TABLE V

Ageing of stabilized films in SL

	500 hrs		1000 hrs		1500 hrs		2000 hrs	
Type	CO %	ε %	CO %	ε %	CO %	ε %	CO %	ε %
1	0.380	5	—	—	—	—	—	—
2	0.010	109	0.023	90	0.050	44	0.866	—
3	0.007	104	0.024	83	0.034	61	0.204	21
4	0.005	104	0.051	67	0.530	7	—	—
5	0.009	106	0.019	78	0.240	18	1.267	—
6	0.011	100	0.017	84	0.041	82	0.142	73
7	0.028	100	0.026	87	0.049	76	0.136	84
8	0.01	93	0.140	62	1.500	—	—	—

reduced. It is also worthwhile to indicate that benzotriazoles are deficient when compared to benzophenones (composition 8). The possibility of enhancing durability from 200 to 2000 hours and over (with the option of increasing film thickness) elucidates the great contribution of appropriate light stabilizers (antioxidants provide insufficient protection without UVA as also claimed by others[19,20]). A conservative correlation between accelerated and natural weathering of LDPE predicts a ratio of 6–8. An endurance of 2000 hours in accelerated weathering corresponds therefore to a lifetime of 18–24 months. The initial increase in elongation at the early stages of ageing (see Figure 9) may be explained by the apparent increase in chain length due to branching and beginning of crosslinking (microgel). This assumption is based on our observation of an increase in the intrinsic viscosity at the early stages of ageing prior to its sharp decrease at the longer weathering periods. This result is also in agreement with the initial rise in $\bar{M}_w$ upon ageing reported by Winslow.[4]

An interesting aspect of morphological changes upon ageing was observed when the degree of crystallinity and permeability to oxygen were measured. The results shown in Table VI lead to the conclusion that prolonged exposure to radiation and heat promotes secondary crystallization.[10] Grade E which has the highest branching frequency verifies also the highest increase in crystallinity. It is also predicted that the creation of new intermolecular polar bonds (due to carbonyl groups) may lead to secondary crystallization.[21,22] As far as permeability is concerned, there is a general agreement in the literature that gas permeability through a semicrystalline polymer decreases as the percent crystallinity is increased. There is no agreement however on the exact correlation between these two variables and several different correlations have been reported[23–26] according to which the oxygen permeability changes with a power of 1.3–2.2 of the amorphous content in the polymer. Our results show also a decrease in permeability with the increase in crystallinity.

TABLE VI

Crystallinity (C) and permeation to oxygen (P) of LDPE films exposed to SL

	0 hrs		250 hrs	500 hrs	
Grade	C %	P	P	C %	P
A	45.9	433	413	53.4	248
B	43.0	578	544	54.7	258
C	47.8	623	—	50.5	496
E	38.4	736	674	50.6	611

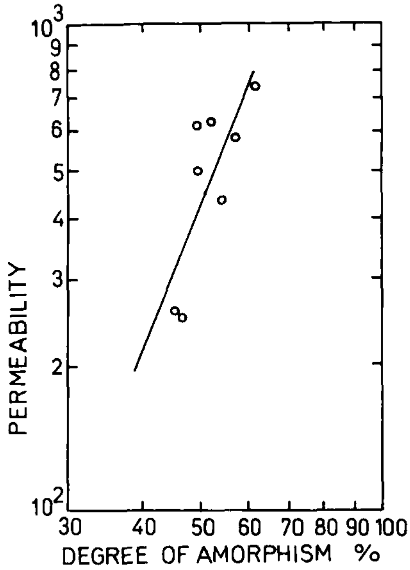


FIGURE 10 Correlation between permeability to oxygen and degree of crystallinity.

The constants in the equation (see Figure 10)

$$P = A\phi_a^x \tag{8}$$

were found to be: $A = 10^{-2.6}$; $x = 3$ where P is the permeability in units cm. mil per 100 inch^2 per 24 hours, and ϕ_a the amorphism (%). Thus in the limited range of our experiments, a very strong dependence of the oxygen permeability on degree of crystallinity was found. It is worth mentioning that although the constants of Eq. (8) were obtained for the crystallinity range of 38–55%, extrapolation predicts the permeability to drop to almost zero for very high crystallinity, which is a reasonable prediction.

4. CONCLUSIONS

1. Unprotected polyethylene films will fail to function (due to brittleness) after a relatively short exposure to weather, mainly by a process of photo-oxidation. Life expectation is 200 hrs of accelerated radiation, which corresponds to around 1200 hrs (less than two months) of natural weathering in a hot country.

2. There are slight indications that by increasing molecular weights (decreasing MFI) keeping narrow MWD, and increasing film thickness—durability will be improved.

3. A synergistic composition of stabilizers consisting of UVA (based on hydroxybenzophenone), a quencher (organo-nickel compound) and antioxidants provides a significant protection.

4. The crystallinity increases with time of exposure to photooxidation, and the permeability to gas decreases consequently.

References

1. L. W. Hawkins (ed.), *Polymer Stabilization*, (Wiley Inc., 1971).
2. H. H. G. Jellinek (ed.), *Aspects of Degradation and Stabilization of Polymers* (Elsevier, Amsterdam, 1978).
3. R. Ranby and J. F. Rabek, *Photooxidation, Photodegradation and Photostabilization of Polymers* (Interscience, 1975).
4. F. H. Winslow, *Pure and Appl. Chem.*, **49,** 495 (1977).
5. L. Reich and S. S. Stivala (eds.), *Autooxidation of Hydrocarbons and Polyolefins: Kinetics and Mechanisms* (Dekker, 1969).
6. M. R. Kamal, *Polym. Eng. & Sci.*, **10,** 108 (1970).
7. G. Scott, *Atmospheric Oxidation and Antioxidants* (Elsevier, 1965).
8. M. U. Amin, G. Scott and L. M. K. Tillekerate, *Europ. Polym. J.*, **11,** 85 (1975).
9. P. I. Plooard and S. E. Guillet, *Macromolecules*, **5,** 405 (1972).
10. F. H. Winslow, W. Matreyek and A. M. Trozzolo, *SPE J.*, **28,** 19 (1972).
11. J. Miltz and A. Ram, *Polymer*, **12,** 685 (1971).
12. A. Ram and J. Miltz, *J. Appl. Polym. Sci.*, **15,** 2639 (1971).
13. A. Ram and J. Miltz, *Intern. J. Polym. Mater.*, **2,** 39 (1972).
14. ASTM D-1434, *Gas Transmission Rate of Plastic Film and Sheeting*, (1966).
15. J. Miltz and M. Narkis, *J. Appl. Polym. Sci.*, **20,** 1627 (1976).
16. H. M. Quackenbos and H. Samuels, *Appl. Polym. Symp.*, **4,** 155 (1967).
17. J. Hanras, *PRI International Symposium on the Weathering of Plastics and Rubber*, (London, 1976), pp. F4.1.
18. H. Lind, *Kunststoffe*, **69,** 397 (1979).
19. S. L. Fitton, R. N. Haward and G. R. Williamson, *Br. Polym. J.*, **2,** 217 (1970).
20. E. W. Lovely and J. D. Hargis, *Plast. Eng.*, **35,** 32 (1979).
21. N. C. Billingham, P. Prontice and T. J. Walker, *J. Polym. Sci.*, Symposium No. **57,** 287 (1976).
22. F. H. Winslow *et al.*, *Polym. Eng. & Sci.*, **6,** 273 (1966).
23. S. W. Lasoki and W. H. Gibs, *J. Polym. Sci.*, **36,** 21 (1959).
24. C. E. Rogers, Chap. 9 in *Engineering Design for Plastics*, E. Baer (ed.) (Reinhold 1964).
25. W. R. Vieth, E. S. Matulevicus and S. P. Mitchel, *Koll. Z.*, **220,** 49 (1967).
26. H. Alter, *J. Polym. Sci.*, **57,** 925 (1962).