



## CHAPTER 5

### DISCUSSION

#### 5.1 Environmental degradation of polyethylene

The environmental degradation of unsensitized and sensitized LDPE films was studied up to 6 months of outdoor exposure. The degradation of sensitized HDPE films was investigated up to 3 months because the sensitized HDPE ones were very brittle under outdoor exposure.

The tensile properties of unsensitized and sensitized polyethylene, both LDPE and HDPE, films are shown in Fig.4.3 and 4.4, respectively. From these figures, the tensile strength of sensitized polyethylene films decreases more rapidly than that of unsensitized ones. But the tensile strength of the material does not vary in a well-defined manner, possibly due to extensive crosslinking which accompanies the weathering process. The value of elongation at break of sensitized LDPE samples decreases drastically in the first month and then decreases linearly with time. But that of sensitized HDPE ones decreases drastically in the first 15 days and then approach zero within 2 months. The rapid drop in elongation at break of HDPE films and the slow drop in that of LDPE ones can be seen as reflecting on their densities.

Figures 4.7 and 4.8 show the presence of large quantities of insoluble material for outdoor exposure. It can be seen that unsensitized and sensitized LDPE samples contain about 30 % of and 40-60 % insoluble material, respectively. From Fig. 4.8, the unsensitized HDPE films contain 20-25 % of insoluble material and 30-55 % of insoluble material for sensitized ones. These are caused by the formation of crosslinking into polyethylene chain

which improves its heat stability, solvent resistance and mechanical properties. Figures 4.9 and 4.10 show the decrease of molecular weight of polyethylene sample with exposure time. The greatest decrease in molecular weight of sensitized LDPE films takes place in the first month (decreasing about 50-60 % of the beginning value) and then molecular weight of sensitized ones decreases continuously with exposure time. For sensitized HDPE films, the decrease of molecular weight takes place in the first 15 days about 20-30 % of the initial value, and then molecular weight decreases slowly with exposure time. Table 5.1 summarizes the physical-mechanical characteristics of polyethylene exposed outdoor for 6 months.

The increase of formation of carbonyl and vinyl groups are shown in Fig. 4.13 and 4.14. It is also found that the carbonyl and vinyl intensity of sensitized samples is higher than that of unsensitized ones. These figures also show the increase of carbonyl and vinyl groups with the exposure time.

From these experimental results, the reaction mechanism of unsensitized polyethylene (Fig. 5.1) can explain reasonably radical formation and the reaction pathways to final products during outdoor exposure. The mechanism of sensitized polyethylene (Fig. 5.2) can describe reasonably the action of photosensitizer in polyethylene films during natural exposure.

It can be said that the action of photosensitizer is concentrated mainly in the first stage of the degradation process. The content of the carbonyl group in the molecule of photosensitizer drops very rapidly, indicating a depletion of the photosensitizer system [15]. This depletion is a consequence of the photo-reduction of photosensitizer during the sensitized polyethylene oxidation. Thus, in the presence of sensitizers, the critical conditions necessary to affect mechanical behavior are reached very rapidly after the beginning of exposure and no

Table 5.1 Changes in tensile properties, molecular weight and relative absorbance  $I_{CO}$  and  $I_{vinyl}$  for outdoor exposure  
(a) LDPE films

Sensitizer	Exposure time(month)	$\sigma$ (MPa)	$\epsilon$ (%)	M.W. $\times 10^{-3}$	$I_{CO}$	$I_{vinyl}$
No additive	0	12.6	288	39.80	0.00	0.68
	3	10.4	92	21.00	2.20	2.08
	6	10.1	59	14.20	2.51	1.45
Benzophenone	0	13.2	290	34.20	1.00	1.45
	3	14.1	79	17.70	NA	NA
	6	10.2	45	9.07	5.07	1.91
4-Methoxy- benzophenone	0	15.2	273	39.40	0.99	1.37
	3	12.8	70	13.40	2.96	1.41
	6	9.8	30	6.64	6.64	3.02
Thioxanthone	0	14.0	285	36.40	0.99	1.22
	3	14.5	47	13.90	3.02	1.84
	6	9.2	12	5.39	4.49	2.40
Anthraquinone	0	13.0	281	33.70	0.90	1.13
	3	13.8	54	18.70	NA	NA
	6	10.6	22	6.69	6.13	2.43
2-Methyl- anthraquinone	0	15.9	280	36.40	0.00	0.78
	3	11.2	50	10.10	5.17	1.32
	6	9.4	8	4.08	9.51	5.47
2-tert-Butyl anthraquinone	0	15.9	279	37.70	0.68	1.01
	3	14.4	51	12.30	4.47	1.17
	6	9.0	10	5.40	11.30	5.48

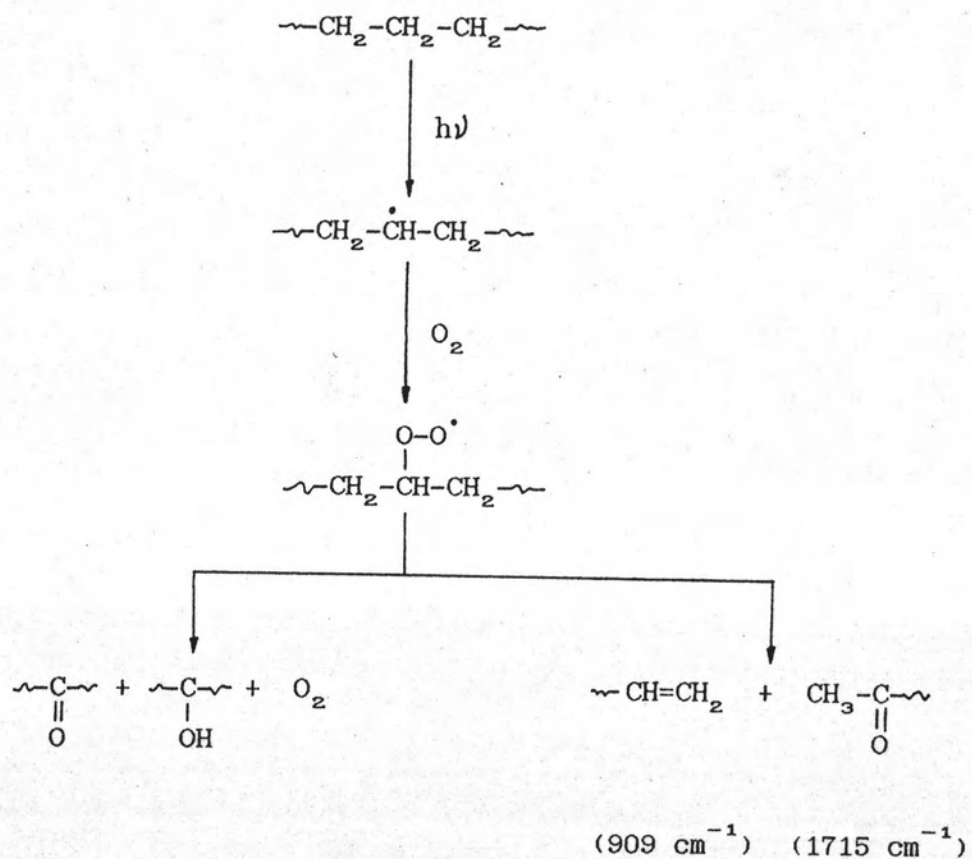
Note NA = Not available

## (b) HDPE films

Sensitizer	Exposure time(month)	$\sigma$ (MPa)	$\epsilon$ (%)	M.W. $\times 10^{-3}$	$I_{co}$	$I_{viny1}$
No additive	0	32.7	573	118.00	0.00	0.22
	1	24.0	435	94.90	0.00	0.23
	2	27.8	118	38.60	0.95	0.52
	4	23.2	12	17.20	NA	NA
	6	11.9	1	12.00	NA	NA
Benzophenone	0	36.7	594	155.00	0.00	0.24
	1	23.8	71	33.10	NA	NA
	2	11.4	2	17.60	1.19	0.52
4-Methoxy- benzophenone	0	32.5	526	150.00	0.00	0.22
	1	26.9	34	27.50	1.08	0.30
	2	7.1	1	17.80	1.28	0.63
Thioxanthone	0	32.2	520	123.00	0.00	0.28
	1	12.6	3	16.30	1.50	0.41
	2	0.0	0	12.80	1.69	0.73
Anthraquinone	0	28.9	519	120.00	0.00	0.36
	1	25.0	13	23.30	NA	NA
	2	0.0	0	17.60	1.31	0.38
2-Methyl- anthraquinone	0	27.4	510	113.00	0.00	0.26
	1	23.0	4	14.80	1.17	0.29
	2	0.0	0	10.90	1.37	0.59
2-tert-Butyl anthraquinone	0	30.1	524	150.00	0.00	0.31
	1	32.5	7	17.30	1.45	0.60
	2	0.0	0	11.30	2.05	0.68

Note NA = Not available

In the presence of air :



Crosslinked reaction

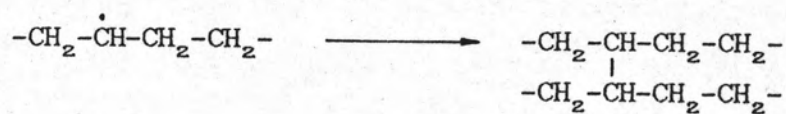
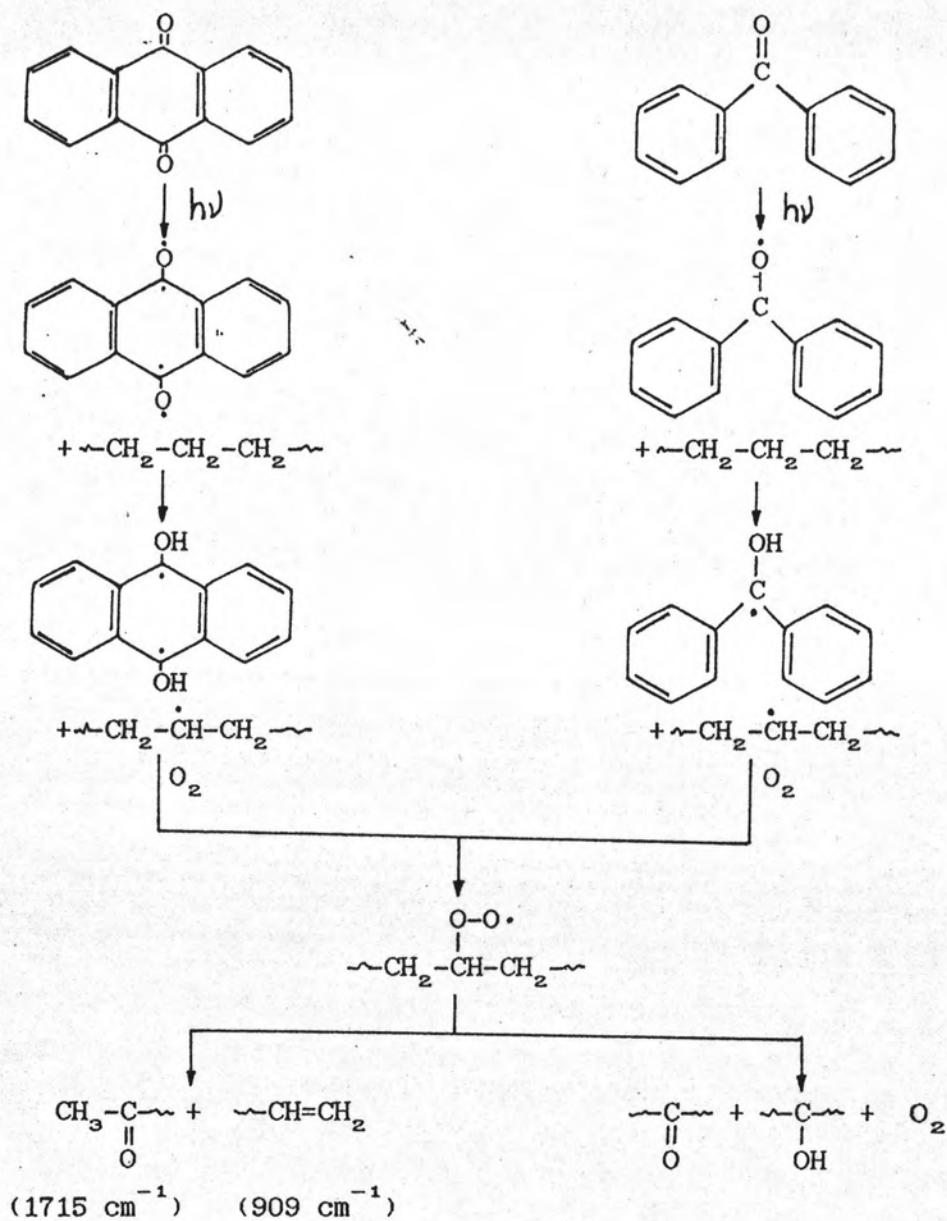


Figure 5.1 Scheme of degradation reaction of polyethylene films

For example of anthraquinones and benzophenones



Crosslinked reaction

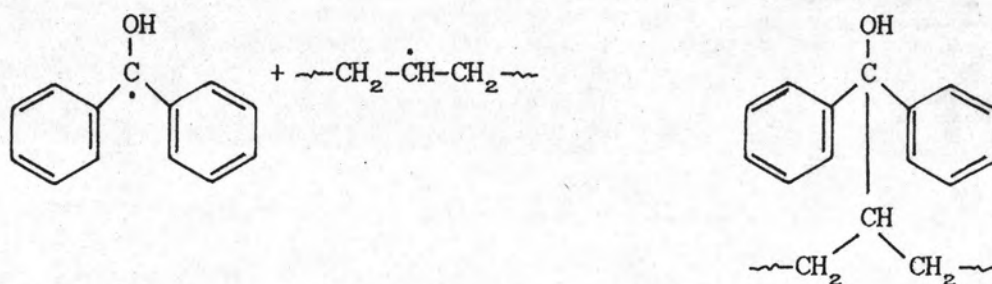


Figure 5.2 Scheme of degradation reaction of sensitized PE films

induction period in the evolution of tensile properties is observed.

For polyethylene films containing different sensitizers it is found that thioxanthone, 4-methoxybenzophenone, 2-methylanthraquinone, 2-tert-butylanthraquinone appear to be more effective as degradation-promoting additives than benzophenone and anthraquinone. This observation is tentatively attributed to the higher dispersion of substituted benzophenone and anthraquinones in the polymer.

## 5.2 Irradiation using medium pressure mercury lamp

The degradation of polyethylene films irradiated with medium pressure mercury lamp was studied up to 30 hours for LDPE ones and 8 hours for HDPE ones. The tensile properties of unsensitized and sensitized polyethylene, LDPE and HDPE, films are shown in Fig. 4.17 and 4.18, respectively. The irradiation of sensitized LDPE films results in an average decrease of tensile strength 75 % of the beginning values and that of elongation at break 5 % of the beginning values after 30 hours. The irradiation of sensitized HDPE films results in an average decrease of tensile strength 60 % of the beginning values and that of elongation at break 1 % of the beginning values after 8 hours.

Tables 4.13 and 4.14 give the gel content formed during irradiation for polyethylene samples. The initially existing gel in sensitized HDPE ones also increases with irradiation time. This means that the crosslinking of polyethylene takes place during irradiation. The changes of molecular weight of polyethylene, LDPE and HDPE, films irradiated with a mercury lamp are presented in Tables 4.15 and 4.16. For LDPE films, it is found that the molecular weight of sensitized ones decreases, reaches 50% of the beginning value after 30 hours of irradiation, respectively. For HDPE films, it is found that the molecular

weight of sensitized ones decreases, reaches 13% of the beginning value after 8 hours of irradiation. The characteristics of the polyethylene, which was irradiated with medium pressure mercury lamp are summarized in Table 5.2.

Changes of carbonyl and vinyl group in polyethylene chain as a function of irradiation time are presented in Tables 4.17 and 4.18. It can be seen that the carbonyl and vinyl group increase with their relative absorbance. All absorption intensity of sensitized samples is higher than that of unsensitized ones.

From the experimental results, it is found that the degradation rate of sensitized polyethylene films is higher than that of unsensitized ones. From the tensile and absorbance properties, polyethylene films sensitized with thioxanthone, derivatives of benzophenone and of anthraquinone enhance higher degradation rate than ones sensitized with benzophenone and anthraquinone.

### 5.3 Indoor test of sensitized polyethylene films

For indoor test of LDPE and HDPE films, there is a little or no change of tensile properties in sensitized samples, as shown in Fig. 4.5 and 4.6. Therefore, it will take a long time for the degradation of indoor exposed polyethylene films.



Table 5.2. Changes in tensile properties, molecular weight and relative absorbance  $I_{Co}$  and  $I_{viny1}$  for irradiation with HPK 125 W

(a) LDPE films

Sensitizer	Irradiation time(hour)	$\sigma$ (MPa)	$\epsilon$ (%)	M.W. $\times 10^{-3}$	$I_{Co}$	$I_{viny1}$
No additive	0	12.6	288	39.80	0.00	0.68
	15	12.0	118	-	-	-
	30	11.1	75	23.60	1.31	1.67
Benzophenone	0	13.2	290	34.20	1.00	1.46
	15	12.7	101	-	-	-
	30	11.0	58	19.10	1.48	2.01
4-Methoxy-benzophenone	0	15.2	273	39.40	0.99	1.37
	15	13.1	80	-	-	-
	30	11.2	25	18.90	2.03	2.27
Thioxanthone	0	14.0	285	36.40	0.99	1.22
	15	14.1	73	-	-	-
	30	10.7	23	16.00	5.16	3.44
Anthraquinone	0	13.0	281	33.70	0.90	1.13
	15	13.4	85	-	-	-
	30	9.3	23	19.50	3.27	2.24
2-Methyl-anthraquinone	0	15.9	280	36.40	0.00	0.78
	15	13.0	78	-	-	-
	30	10.4	6	17.10	2.51	2.12
2-tert-Butyl anthraquinone	0	15.9	279	37.70	0.68	1.01
	15	13.8	71	-	-	-
	30	12.4	27	17.90	2.03	1.40

## (b) HDPE films

Sensitizer	Irradiation time(hour)	$\sigma$ (MPa)	$\epsilon$ (%)	M.W. $\times 10^{-3}$	$I_{co}$	$I_{viny l}$
No additive	0	32.7	573	118.00	0.00	0.22
	4	28.4	442	-	-	-
	8	25.4	22	44.50	0.61	1.30
Benzophenone	0	36.7	594	155.00	0.00	0.24
	4	28.5	17	-	-	-
	8	22.3	4	20.30	1.54	1.32
4-Methoxy- benzophenone	0	32.5	526	150.00	0.00	0.22
	4	30.5	11	-	-	-
	8	28.5	6	17.60	2.18	1.07
Thioxanthone	0	32.2	520	123.00	0.00	0.28
	4	28.3	10	-	-	-
	8	27.3	5	15.00	2.90	1.40
Anthraquinone	0	28.9	519	120.00	0.00	0.36
	4	27.1	37	-	-	-
	8	21.6	5	18.90	2.85	1.22
2-Methyl- anthraquinone	0	27.4	510	113.00	0.00	0.26
	4	27.7	12	-	-	-
	8	25.1	6	18.60	2.18	1.18
2-tert-Butyl anthraquinone	0	30.1	524	150.00	0.00	0.31
	4	30.0	12	-	-	-
	8	25.5	5	15.80	2.74	1.24

#### 5.4 Comparison of the degradation tendencies between outdoor exposure and irradiation using medium pressure mercury lamp

For comparison of the degradation rate between outdoor exposure and irradiation, the values of exposure period when elongation at break reduced by half are summerized in Table 5.3. For unsensitized polyethylene films, the degradation degree of LDPE (1519 hours) and HDPE (1189 hours) ones of outdoor exposure was equal to 12.7 and 5.4 hours of irradiation by medium pressure mercury lamp.

Kubota, H., et al. [19] reported that the elongation at break was suitably used to evaluate the weatherability of plastics. The same idea was applied to evaluate the relationship between unsensitized and sensitized polyethylene films and then the accelerating factor,  $A_1$ , was obtained.

$$A_1 = \frac{t_{1/2}(0)}{t_{1/2}(i)}$$

where  $t_{1/2}(0)$  = the period for character to decrease by half of original unsensitized PE sample  
 $t_{1/2}(i)$  = the period for character to decrease by half of sensitized PE sample

The result of accelerating factors of polyethylene films is shown in Table 5.4.

Table 5.3 Time period when the failure criterion of 50 % loss of elongation is reached

Photosensitizer	Outdoor exposure (hour)		Irradiation (hour)	
	LDPE	HDPE	LDPE	HDPE
No additive	1519	1188	12.7	5.4
Benzophenone	1087	435	10.5	2.8
4-Methoxybenzophenone	821	402	9.3	2.2
Thioxanthone	687	151	7.6	2.1
Anthraquinone	871	352	9.4	2.7
2-Methylanthraquinone	720	151	8.1	2.1
2-tert-Butylanthraquinone	670	285	6.9	1.8

Table 5.4 Accelerating factors of outdoor exposure and irradiation PE films

Photosensitizer	Outdoor exposure		Irradiation	
	LDPE	HDPE	LDPE	HDPE
No additive	1.0	1.0	1.0	1.0
Benzophenone	1.4	2.7	1.2	1.9
4-Methoxybenzophenone	1.9	3.0	1.4	2.5
Thioxanthone	2.2	7.9	1.7	2.6
Anthraquinone	1.7	3.4	1.4	2.0
2-Methylanthraquinone	2.1	7.9	1.6	2.6
2-tert-Butylanthraquinone	2.3	4.2	1.9	3.0