CHAPTER 4

RESULTS

The activity of photosensitizers, aromatic ketones and aromatic diketones, in PE degradation was studied by outdoor exposure and irradiation using medium pressure mercury lamp.

4.1 Outdoor exposure test

4.1.1 Tensile properties measurements

A characteristic feature of the ultimate mechanical properties is their sensitivity to the presence of flaws in the bulk of the material, which facilitates the use of ultimate properties in the detection of processes that occur at localized sites. Stress-strain tests are a simple but very sensitive detection method. A typical example of the effect of UV exposure on the stress-strain traces of unsensitized and sensitized PE films, both LDPE and HDPE, is shown in Figures 4.1-4.2. It can be seen that the curve shifts horizontally as outdoor exposure time proceeds. So from this observation, the elongation at break is a key material property which decreases as the exposure time increases. It depends markedly on the specimen geometry and is therefore a sensitive measure of the heterogeneity of the material.

(a) Unsensitized LDPE

Tensile strength (σ) and percent elongation at break (ε) are shown in Table 4.1 and Figure 4.3, respectively. It can be seen that tensile strength of unsensitized sample shows a slow decrease after outdoor exposure and elongation at break exhibits a linear drop. Within

2 months of exposure time, almost 50 % of the starting value was lost. Tensile strength and percent elongation at break continue to decrease with time until a point is reached at which the curve flattened and continue monotonously with exposure time.

(b) Sensitized LDPE

From Figure 4.3, The behavior of samples containing sensitizers differs from that of unsensitized ones (Figure 4.3). Tensile strength of sensitized samples decreases in the early period, then increases slightly and follows by a slow decrease. For elongation at break, it decreases almost 50 % of the starting value within 1 month. It is found that aromatic ketone sensitized LDPE films show a loss of their properties as well as aromatic diketone sensitized ones. LDPE films sensitized with thioxanthone, 4-methoxybenzophenone, 2-methylanthraquinone and 2-tert-butylanthraquinone give a sharper drop of elongation at break than ones sensitized with benzophenone and anthraquinone.

(c) Unsensitized HDPE

In Figure 4.2, the stress-strain curves of unexposed samples of HDPE show a very sharp force maximum at low strain. Beyond this point, there is a decrease in force with further increase in elongation. The curves flatten out and the force remains almost constant. The load then increases before the specimen ruptures. This behavior is typical of molecular-weight linear polymer. The effect of natural weathering on tensile strength and elongation at break of HDPE films is shown in Figure 4.4 and Table 4.2. It can be seen that all mechanical characteristics of an unsensitized sample show a clear induction period of about 15 days. After outdoor exposure, tensile strength decreases slowly, then increases slightly and follows by a slow decrease. For elongation at break, it reaches 50% of the original value within 6 weeks.

(d) Sensitized HDPE

From Figure 4.4, there is a sudden loss in both these properties of sensitized samples soon after outdoor exposure. Tensile strength decreases, then increases slightly and finally decreases. Elongation at break losses over 95 % of their original value in the first month. At this stage, the sensitized samples were embrittled and crumbled on handling and so their tensile test was discontinued. In the same as LDPE films, thioxanthone, derivatives of benzophenone and of anthraquinone sensitized samples show faster losing tensile properties than benzophenone and anthraquinone sensitized ones.

(e) Indoor test of sensitized LDPE and HDPE

The indoor test of sensitized LDPE and HDPE films was also conducted as blank samples for comparison with the outdoor test of ones. Stress-strain curves of sensitized LDPE and HDPE samples during indoor exposure are shown in Tables 4.3-4.4 and Figures 4.5-4.6. It can be seen that the tensile properties of sensitized LDPE and HDPE films change slightly or have no changes.

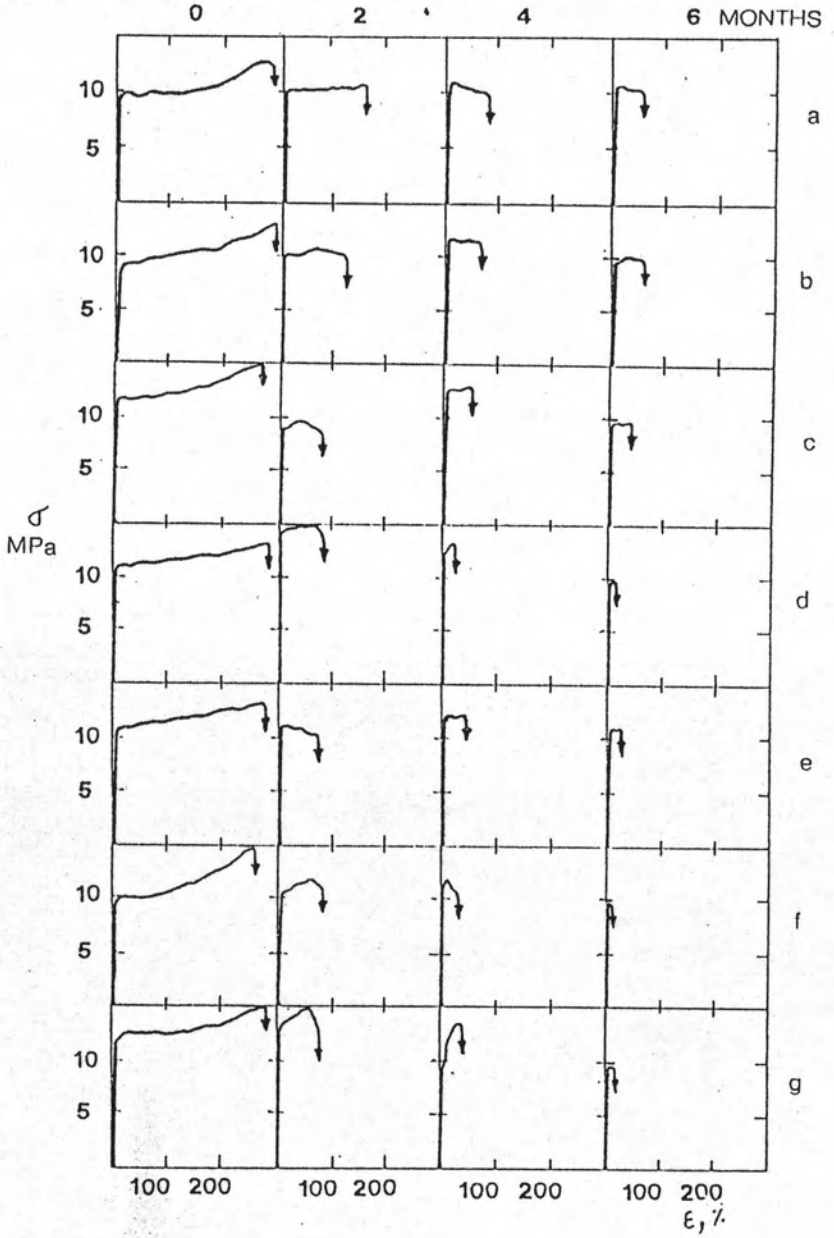


Figure 4.1 Stress-strain traces for LDPE samples at various exposure times (indicates on curves in months): unsensitized (a) and sensitized with benzophenone (b), 4-methoxybenzophenone (c), thioxanthone (d), anthraquinone (e), 2-methylanthraquinone (f) and 2-tert-butylanthraquinone (g)

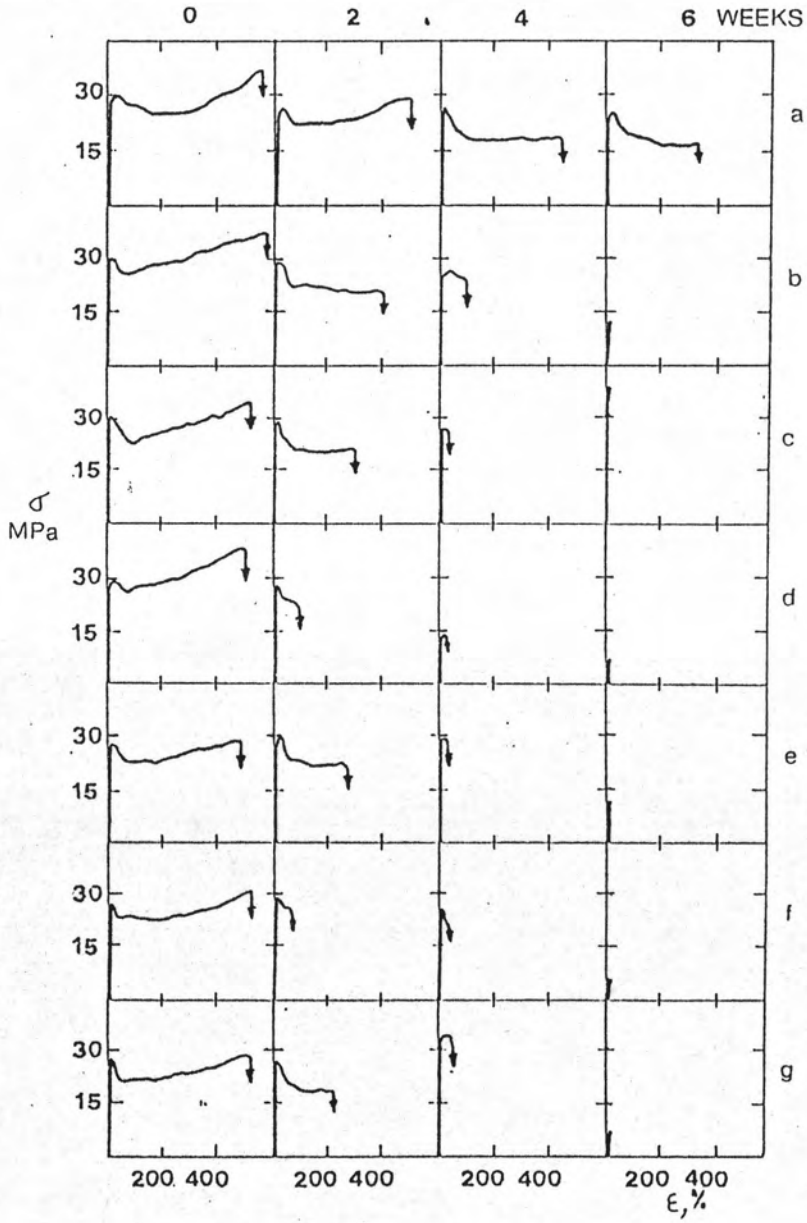


Figure 4.2 Stress-strain traces for HDPE samples at various exposure times (indicates on curves in weeks): unsensitized (a) and sensitized with benzophenone (b), 4-methoxybenzophenone (c), thioxanthone (d), anthraquinone (e), 2-methylanthraquinone (f) and 2-tert-butylanthraquinone (g)

Table 4.1 Tensile properties of outdoor exposure LDPE films

(a) Tensile strength

Sensitizer / Exposure time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	12.6	13.2	15.2	14.0	13.0	16.0	16.0
2 weeks	11.2	12.4	14.8	10.9	12.6	11.1	13.8
1 month	11.1	10.6	10.2	11.6	12.6	9.7	14.1
2 months	10.9	11.1	9.7	15.6	10.5	12.7	15.4
3 months	10.4	14.1	12.8	14.5	13.8	11.2	14.4
4 months	10.6	12.7	12.6	11.9	12.5	11.1	13.2
5 months	11.0	11.3	10.4	10.6	11.1	10.0	10.9
6 months	10.1	10.2	9.8	9.2	10.6	9.4	9.0

(b) Elongation at break

Sensitizer / Exposure time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	288	290	273	285	281	280	279
2 weeks	259	225	219	217	224	205	210
1 month	223	170	132	121	154	122	111
2 months	153	124	80	73	83	76	78
3 months	92	78	70	47	54	50	51
4 months	76	63	60	26	33	21	38
5 months	70	60	52	21	30	12	20
6 months	59	45	30	12	23	8	11

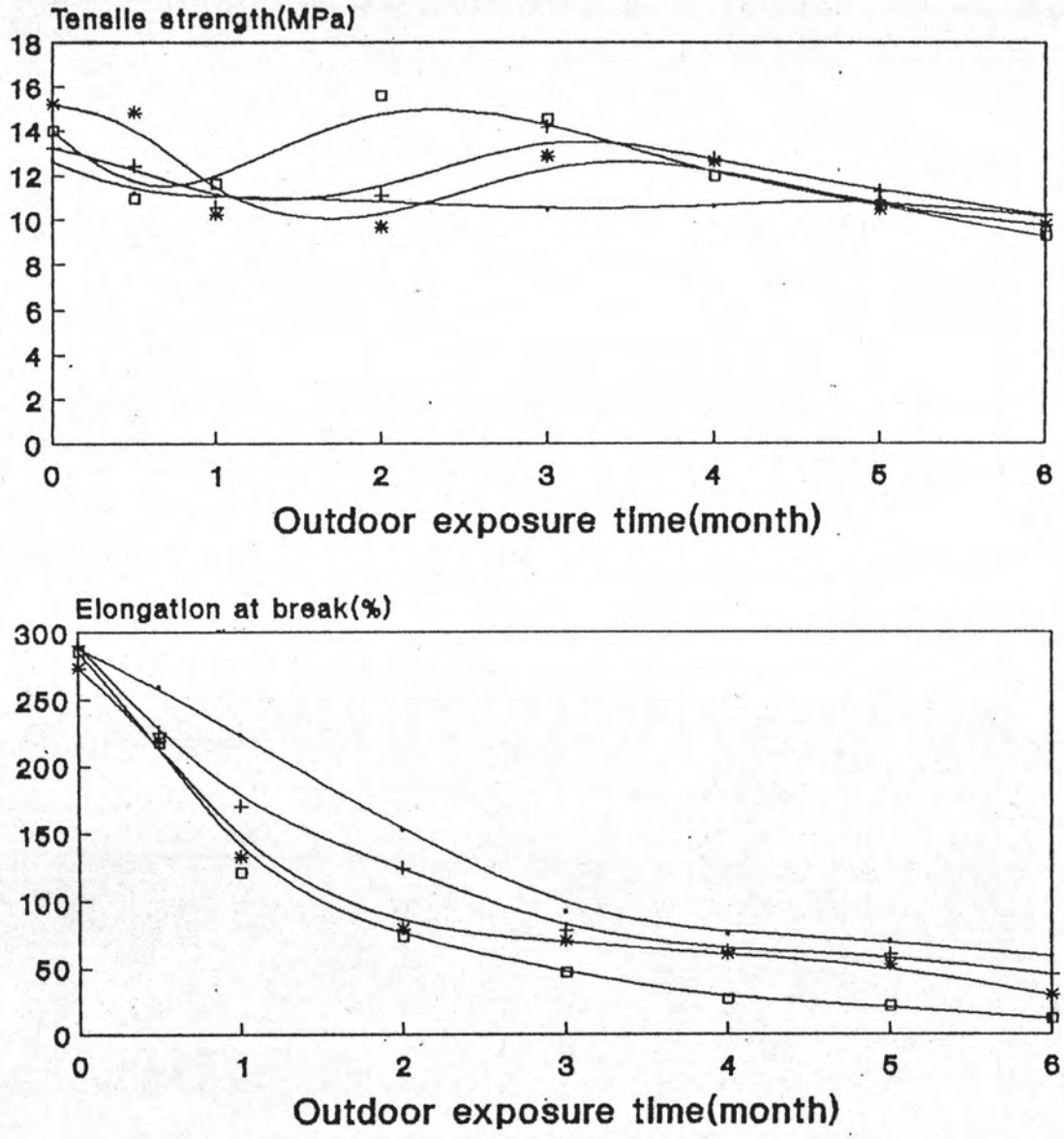


Figure 4.3 (a) Changes in tensile strength and elongation at break of LDPE film (·) and LDPE sensitized with (+) benzophenone, (*) 4-methoxybenzophenone and (□) thioxanthone during natural weathering

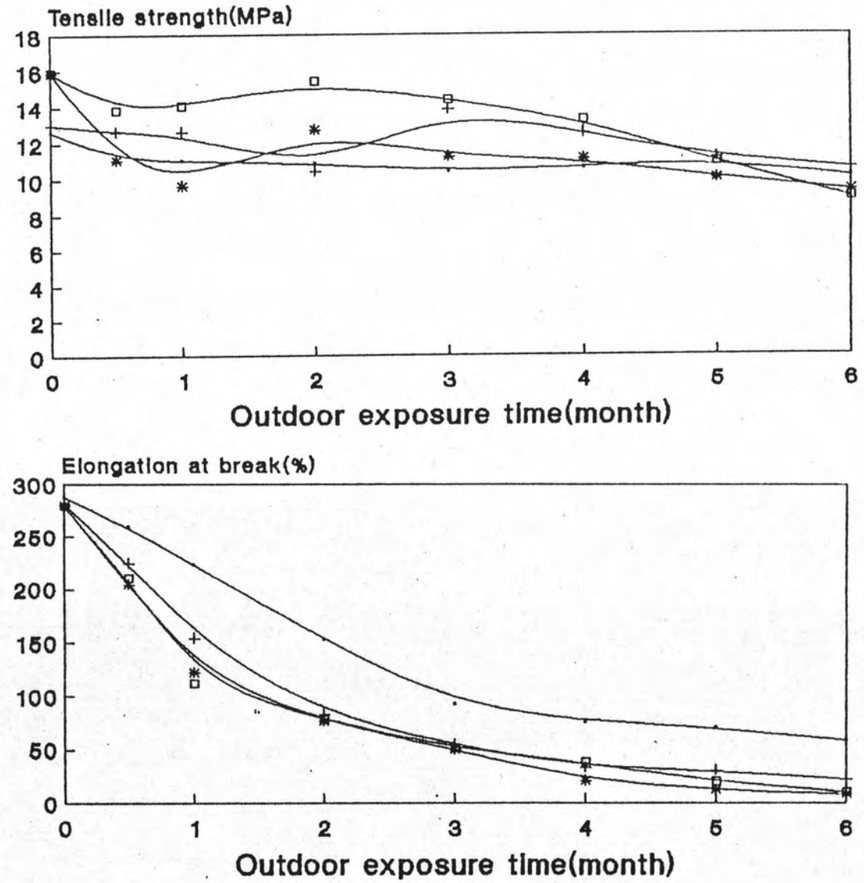


Figure 4.3 (b) Changes in tensile strength and elongation at break of LDPE film (•) and LDPE sensitized with (+) anthraquinone, (✳) 2-methylanthraquinone and (□) 2-tert-butylanthraquinone during natural weathering

Table 4.2 Tensile properties of outdoor exposure HDPE films

(a) Tensile strength

Sensitizer / Exposure time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	32.7	36.7	32.5	32.2	29.0	27.4	30.1
1 week	29.5	29.5	25.6	31.5	23.2	23.3	23.1
2 weeks	28.9	30.4	25.5	24.3	29.9	29.7	26.3
3 weeks	25.9	25.1	25.3	33.8	33.8	26.9	34.8
1 month	24.0	23.8	26.9	12.6	25.0	23.0	32.5
5 weeks	22.1	23.5	35.7	9.0	15.5	5.6	22.4
6 weeks	29.4	21.3	34.0	2.9	5.7	2.6	3.8
7 weeks	28.8	12.0	29.1	1.8	0.0	0.0	0.0
2 months	27.8	11.4	7.1	0.0	0.0	0.0	0.0
3 months	26.9	-	-	-	-	-	-
4 months	23.2	-	-	-	-	-	-
5 months	12.3	-	-	-	-	-	-
6 months	11.8	-	-	-	-	-	-

(b) Elongation at break

Sensitizer / Exposure time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	580	594	526	520	519	510	524
1 week	551	467	439	141	366	182	319
2 weeks	515	402	335	84	274	74	229
3 weeks	449	180	131	15	40	8	27
1 month	435	71	34	3	13	4	7
5 weeks	380	5	5	2	3	2	2
6 weeks	331	4	2	1	2	1	2
7 weeks	251	3	2	1	0	0	0
2 months	118	2	1	0	0	0	0
3 months	67	-	-	-	-	-	-
4 months	12	-	-	-	-	-	-
5 months	4	-	-	-	-	-	-
6 months	1	-	-	-	-	-	-

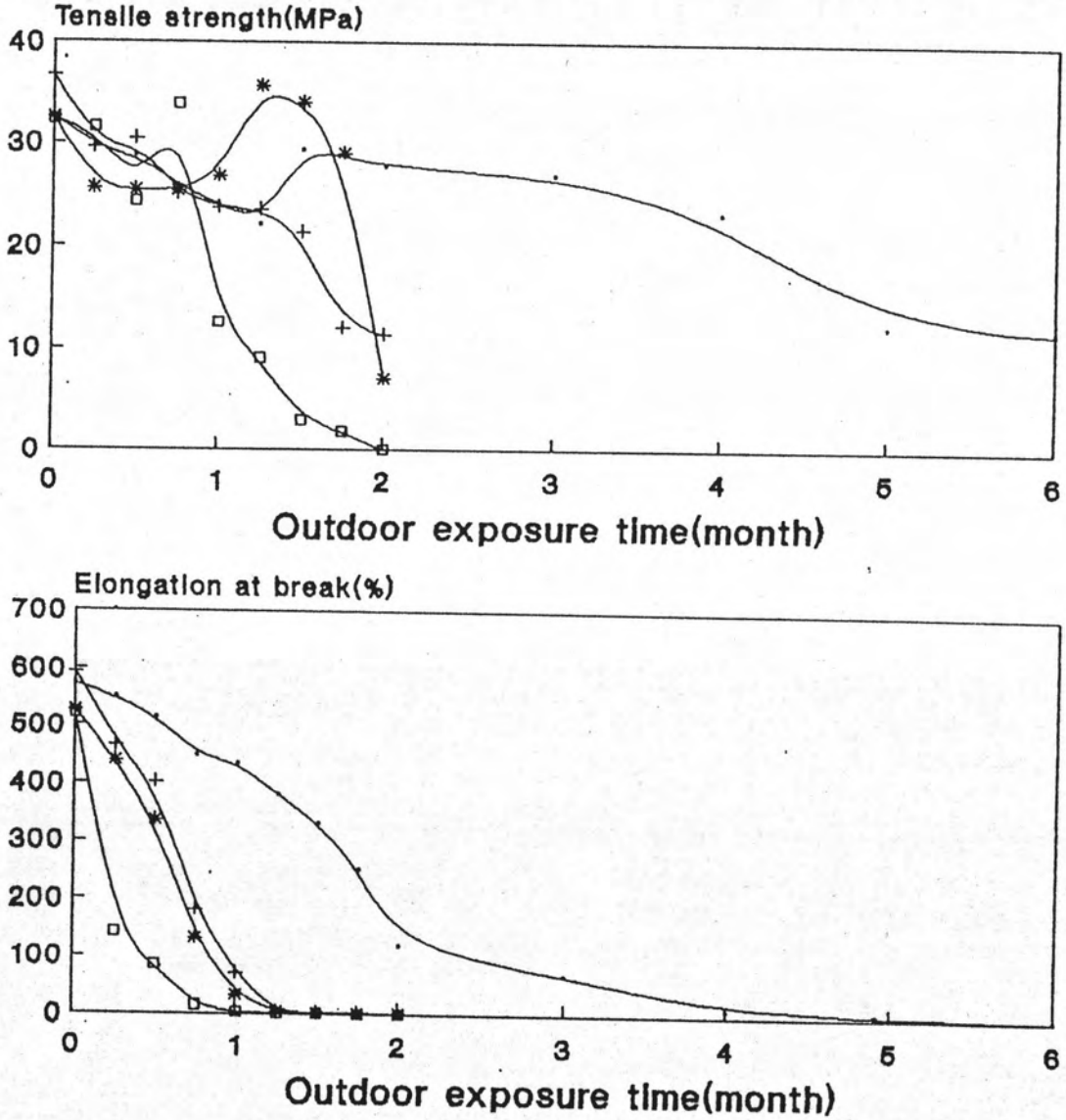


Figure 4.4 (a) Changes in tensile strength and elongation at break of HDPE film (·) and HDPE sensitized with (+) benzophenone, (*) 4-methoxybenzophenone and (□) thioxanthone during natural weathering

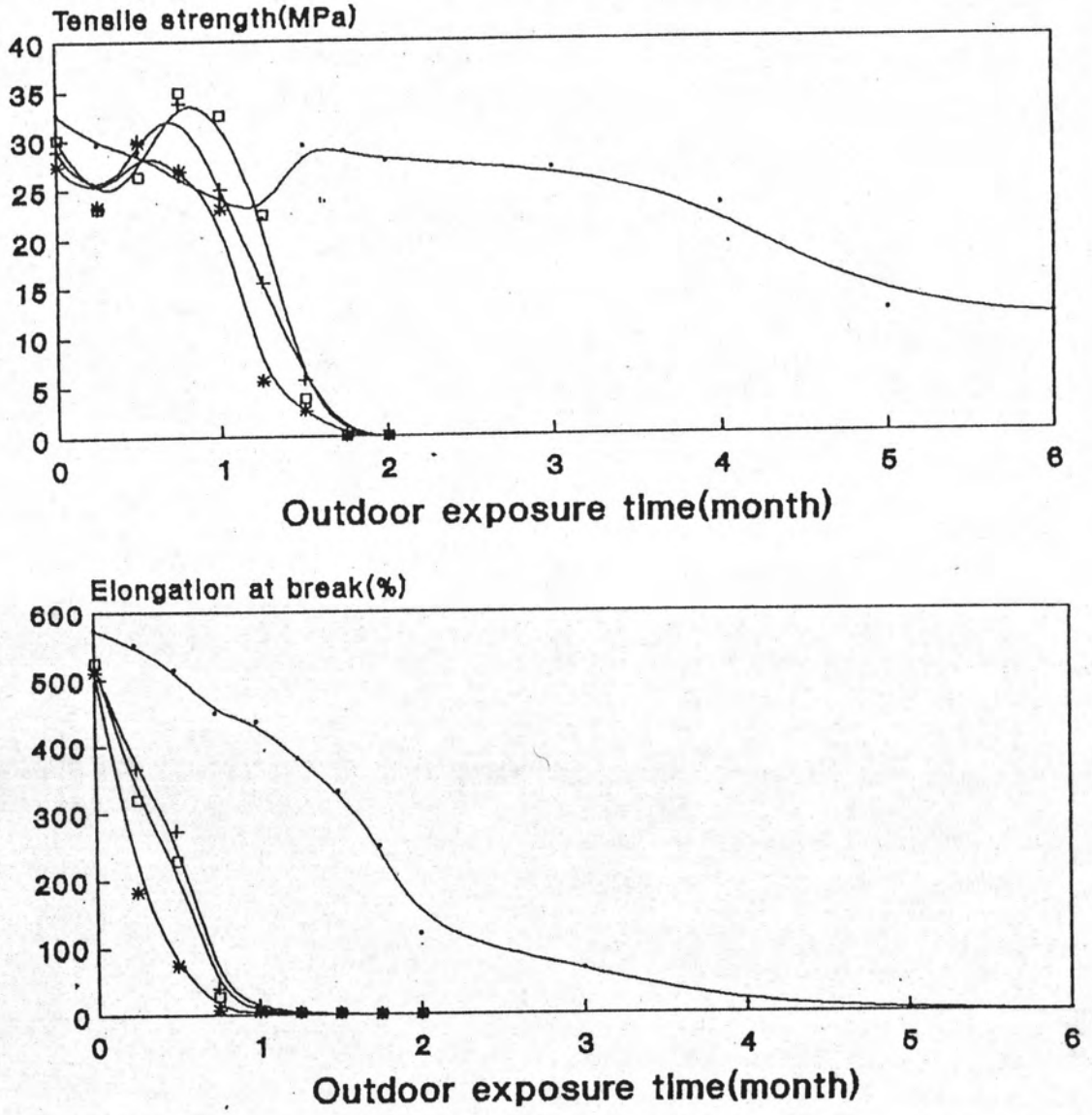


Figure 4.4 (b) Changes in tensile strength and elongation at break of HDPE film (·) and HDPE sensitized with (+) anthraquinone, (*) 2-methylanthraquinone and (□) 2-tert-butylanthraquinone during natural weathering

Table 4.3 Tensile properties of indoor exposure LDPE films

(a) Tensile strength

Sensitizer / Exposure time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	12.6	13.2	15.9	14.0	13.0	15.9	15.9
2 months	11.7	14.1	13.5	13.0	13.8	11.5	13.6
4 months	11.9	15.9	13.6	15.0	14.7	13.2	16.0
6 months	11.5	13.9	12.7	12.9	14.2	11.7	14.4

(b) Elongation at break

Sensitizer / Exposure time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	288	290	273	285	281	280	279
2 months	254	244	251	239	236	244	245
4 months	254	238	219	229	235	248	240
6 months	258	240	234	236	241	239	238

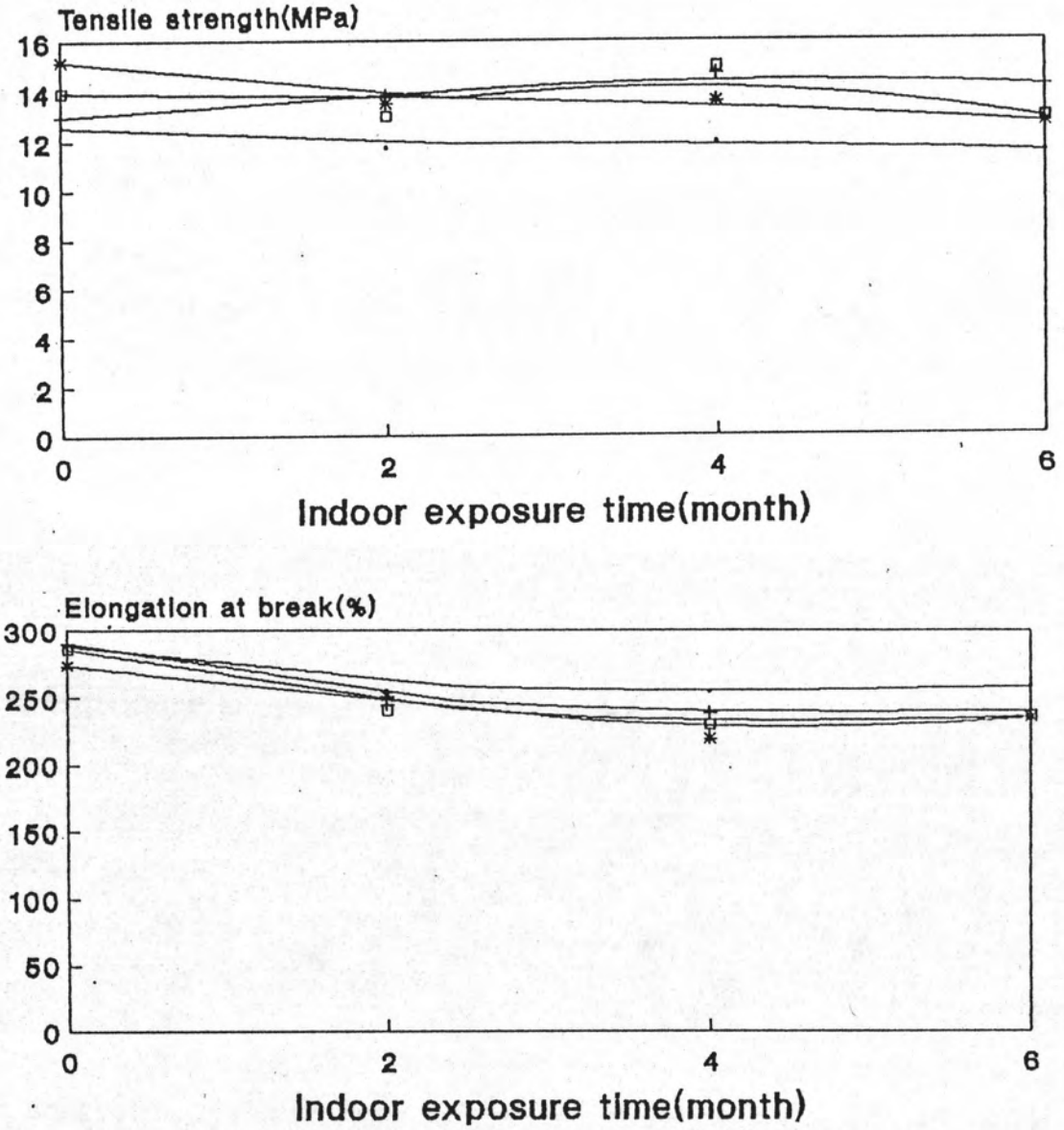


Figure 4.5 (a) Changes in tensile strength and elongation at break of LDPE film (·) and LDPE sensitized with (+) benzophenone, (*) 4-methoxybenzophenone and (¤) thioxanthone during indoor exposure

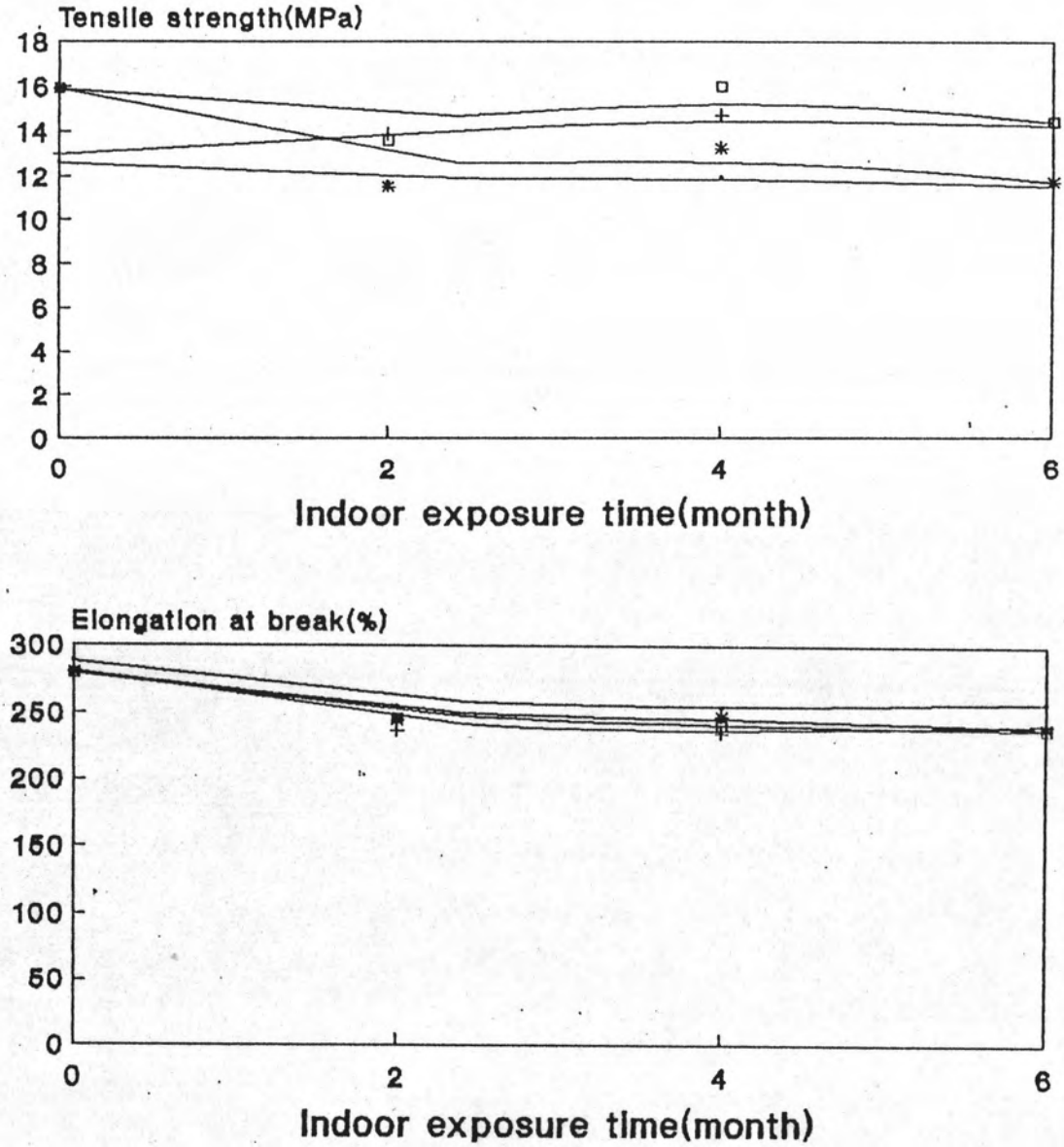


Figure 4.5 (b) Changes in tensile strength and elongation at break of LDPE film (·) and LDPE sensitized with (+) anthraquinone, (*) 2-methylanthraquinone and (□) 2-tert-butylanthraquinone during indoor exposure

Table 4.4 Tensile properties of indoor exposure HDPE films

(a) Tensile strength

Sensitizer / Exposure time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	32.7	36.7	32.5	32.2	28.9	27.4	30.1
2 months	29.0	28.8	29.7	31.6	30.7	29.3	30.9
4 months	32.2	30.0	37.6	34.9	35.9	33.8	35.9
6 months	30.7	29.0	35.0	32.3	33.7	31.3	30.3

(b) Elongation at break

Sensitizer / Exposure time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	580	594	526	520	519	510	524
2 months	481	444	483	492	427	445	485
4 months	451	438	431	480	422	434	450
6 months	449	435	441	475	431	436	442

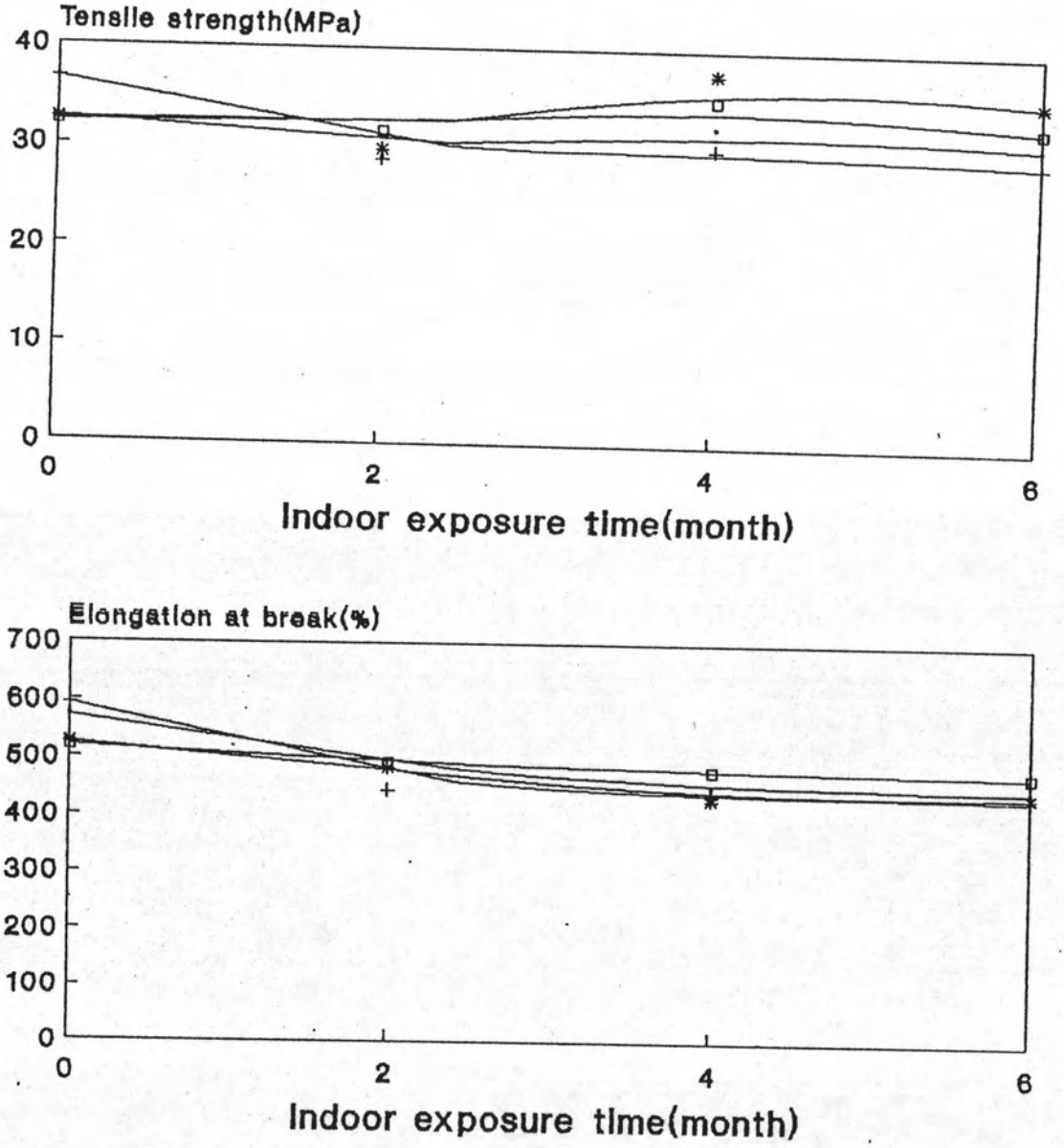


Figure 4.6 (a) Changes in tensile strength and elongation at break of HDPE film (·) and HDPE sensitized with (+)benzophenone, (*) 4-methoxybenzophenone and (□) thioxanthone during indoor exposure

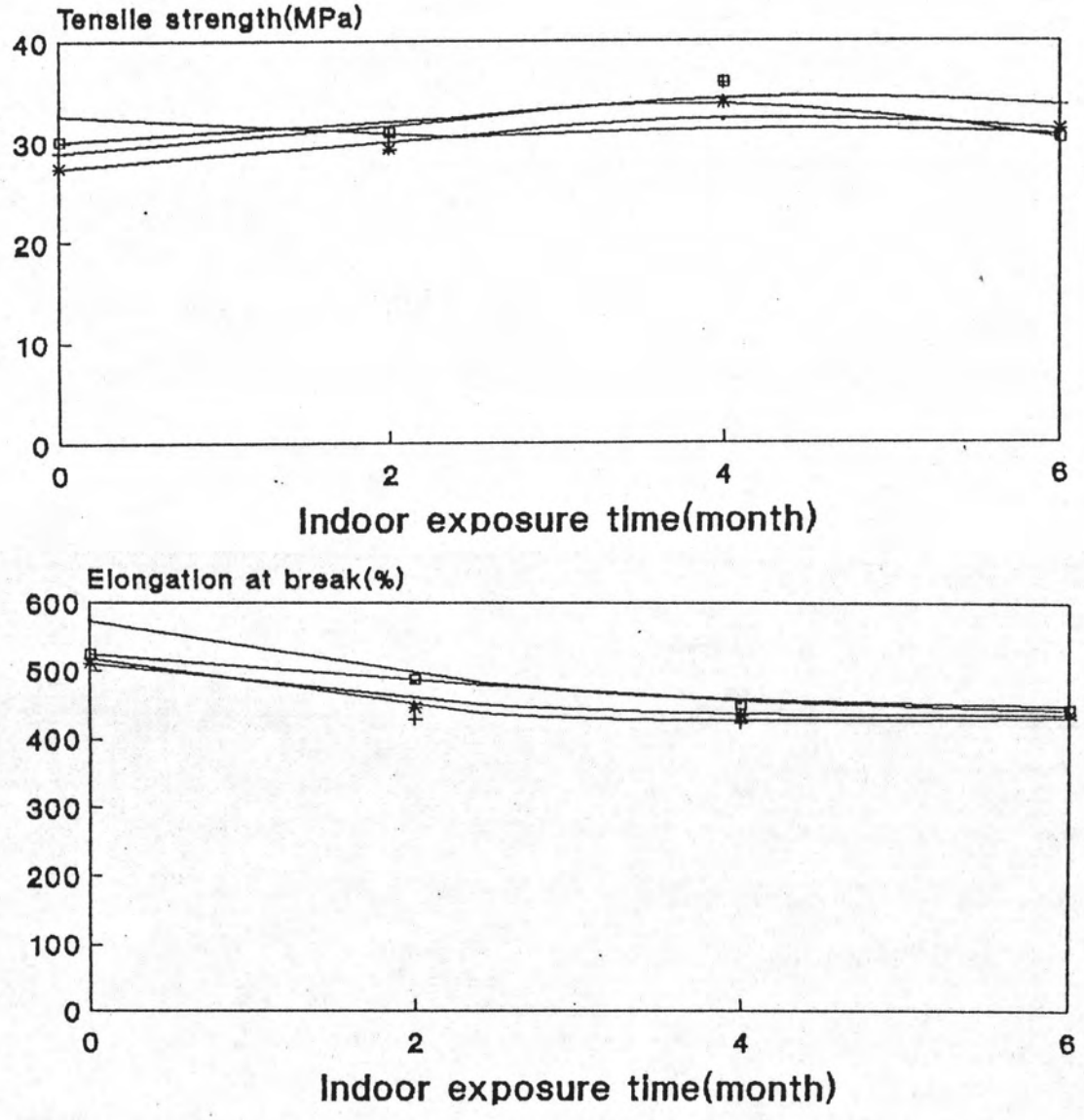


Figure 4.6 (b) Changes in tensile strength and elongation at break of HDPE film (·) and HDPE sensitized with (+) anthraquinone, (*) 2-methylanthraquinone and (□) 2-tert-butylanthraquinone during indoor exposure

4.1.2 Gel measurements

Gel contents were taken as a measure of crosslinking.

(a) LDPE

Gel contents of unsensitized and sensitized LDPE samples are presented in Table 4.5 and plotted against exposure time in Figure 4.7. It is clear that unexposed samples can completely dissolve in solvent. When exposure proceeds, the gel content increases up to a maximum value and then attains an almost constant level or a little drop. Sensitized samples had more insoluble material than unsensitized ones.

(b) HDPE

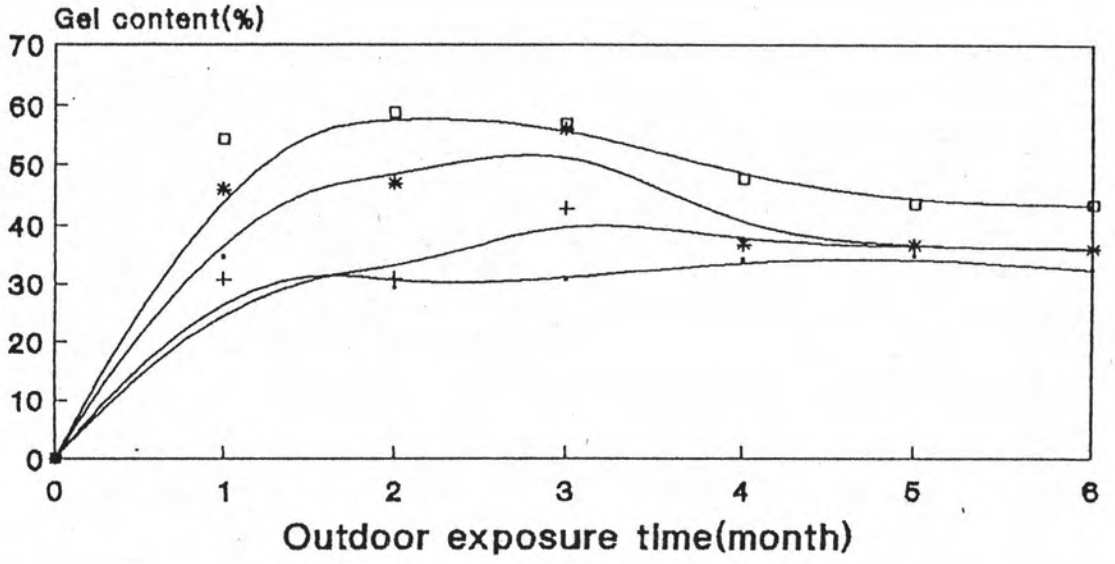
From Table 4.6 and Figure 4.8, the HDPE samples show the same manner as LDPE ones. After natural exposure, LDPE films produced more insoluble material than HDPE ones. Before exposure, unsensitized sample did not present insoluble material while sensitized samples presented insoluble material.

Table 4.5 Gel content of outdoor exposure LDPE films

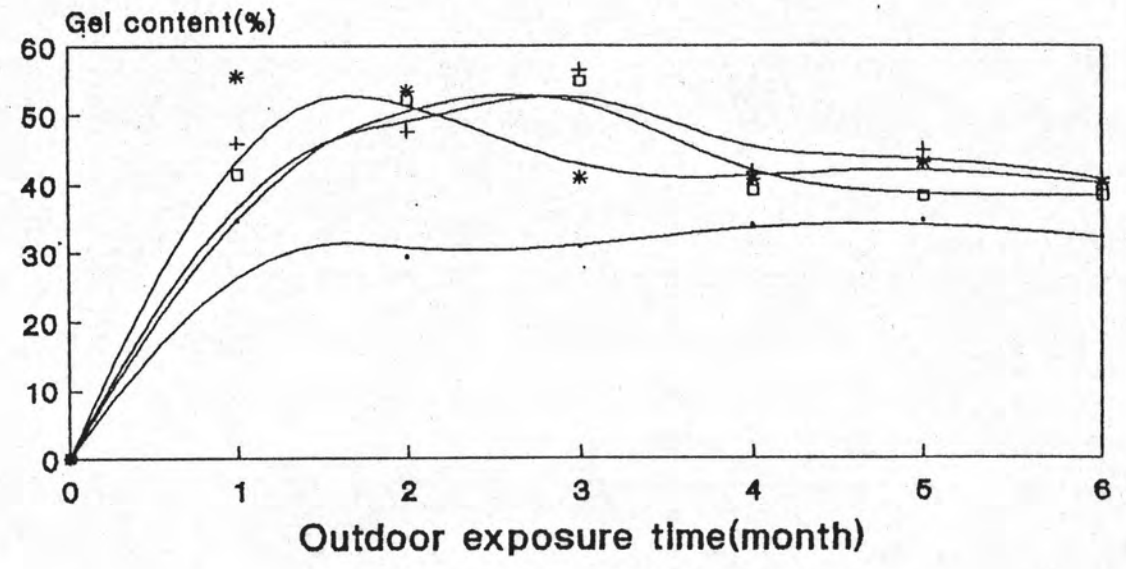
Sensitizer / Exposure time	Gel content(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1 month	34.7	30.7	45.8	54.3	45.8	55.5	41.4
2 months	29.3	30.8	46.9	58.9	47.4	53.3	51.9
3 months	30.8	42.7	55.9	56.8	56.4	40.7	54.7
4 months	34.1	36.7	36.9	47.7	41.7	40.6	38.9
5 months	34.7	36.4	36.5	43.5	44.8	42.9	38.2
6 months	32.3	36.1	36.0	43.4	40.7	40.0	38.3

Table 4.6 Gel content of outdoor exposure HDPE films

Sensitizer / Exposure time	Gel content(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.0	4.7	1.3	15.8	2.4	20.2	22.5
2 weeks	23.7	47.4	46.7	49.1	49.2	47.7	55.6
1 month	25.7	37.7	41.5	40.3	47.4	38.7	46.1
6 weeks	26.0	35.7	39.6	32.4	45.6	36.5	36.4
2 months	23.5	29.0	38.5	35.1	40.2	30.6	35.5
3 months	23.8	29.5	36.8	33.6	35.7	31.0	35.0
4 months	18.7	-	-	-	-	-	-
5 months	18.2	-	-	-	-	-	-
6 months	19.1	-	-	-	-	-	-

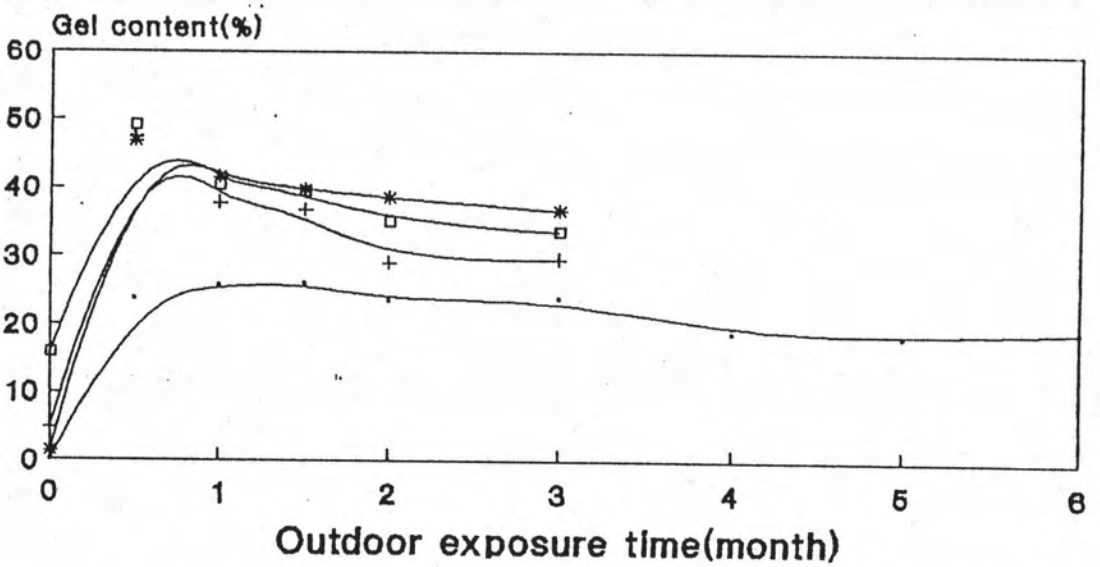


(a) LDPE film(·) and LDPE sensitized with (+)benzophenone, (*)4-methoxybenzophenone and (□)thioxanthone

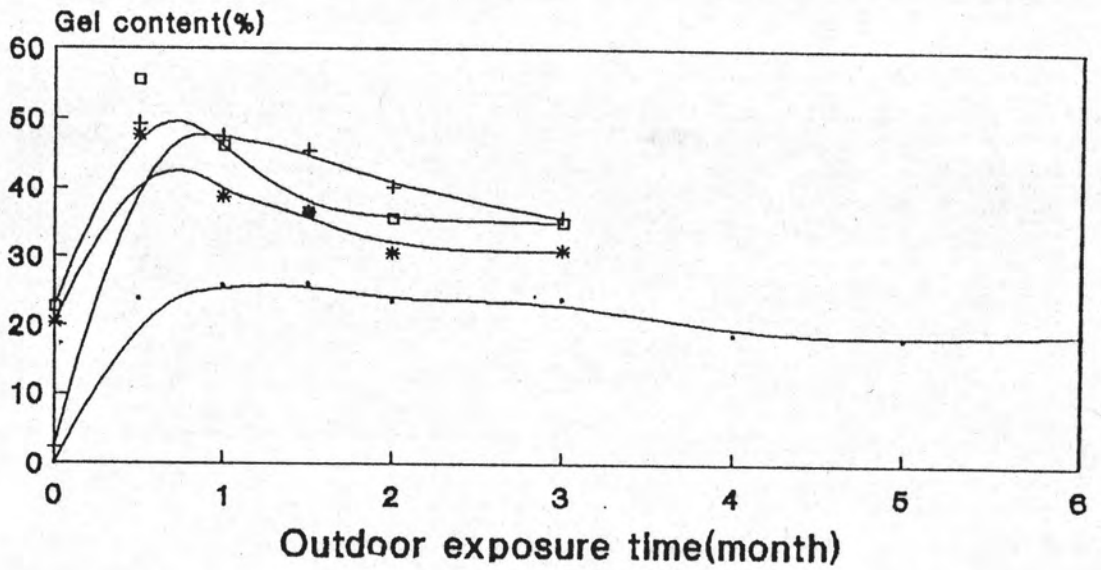


(b) LDPE film(·) and LDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (□)2-tert-butylanthraquinone

Figure 4.7 Changes in the gel content of unsensitized and sensitized LDPE films during natural weathering



(a) HDPE film(·) and HDPE sensitized with (+)benzophenone, (*)4-methoxybenzophenone and (□)thioxanthone



(b) HDPE film(·) and HDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (□)2-tert-butylanthraquinone

Figure 4.8 Changes in the gel content of unsensitized and sensitized HDPE films during natural weathering

4.1.3 Molecular weight measurements

Figures 4.9-4.10 show the molecular weight traces of unsensitized and sensitized LDPE and HDPE samples as a function of outdoor exposure time. Molecular weight data are presented in Tables 4.7-4.8.

(a) LDPE

From Figure 4.9, when exposure proceeds, the molecular weight of unsensitized sample shows an induction period about 1 month and then decreases linearly to a lower molecular weight. It can be seen that molecular weight of benzophenone and anthraquinone sensitized films decrease slower than that of thioxanthone, derivatives of benzophenone and of anthraquinone sensitized ones in the early exposure, corresponding to a sharp drop of elongation at break. Molecular weight of unsensitized and sensitized films decrease linearly with exposure time. The outdoor exposure resulted in an average decrease of LDPE molecular weight about 5-10 times in comparison with unexposed LDPE films.

(b) HDPE

From Figure 4.10, the behavior of molecular weight of unsensitized HDPE sample is similar to that of LDPE one. It shows an induction period about 15 days. It is clear that molecular weight of sensitized samples decreases suddenly, when the greatest reduction in the elongation at break is occured during 1 month, and finally almost flatten during 1-3 months. Molecular weight of thioxanthone, derivatives of benzophenone and of anthraquinone sensitized samples decreases faster than that of benzophenone and anthraquinone sensitized ones. The outdoor exposure resulted in an average decrease of HDPE molecular weight about 10-15 times in comparison with unexposed HDPE films.

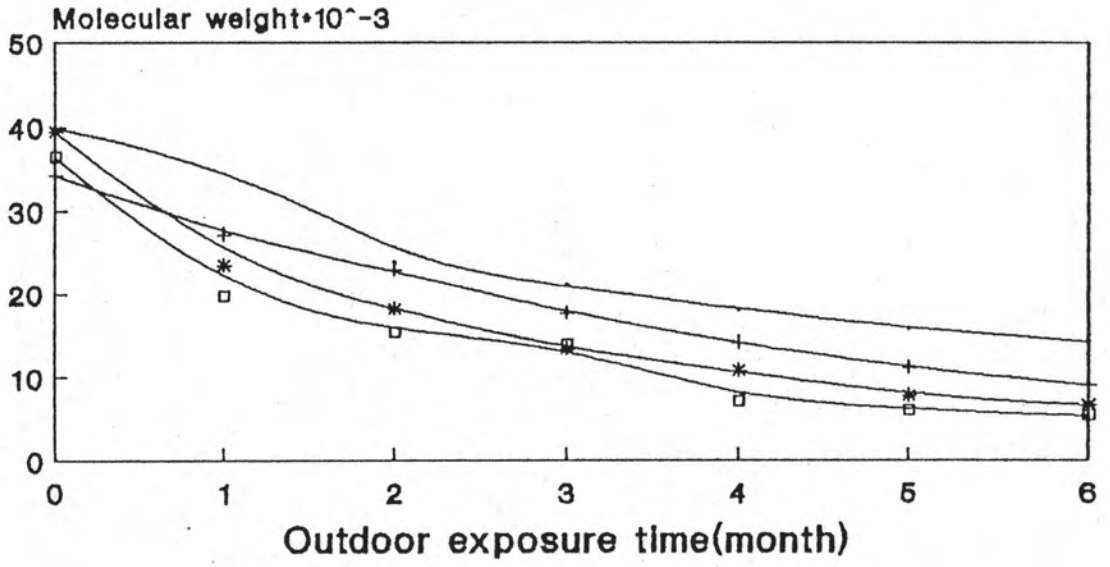
Table 4.7 Intrinsic viscosity and molecular weight of outdoor exposure LDPE films

(a) Intrinsic viscosity

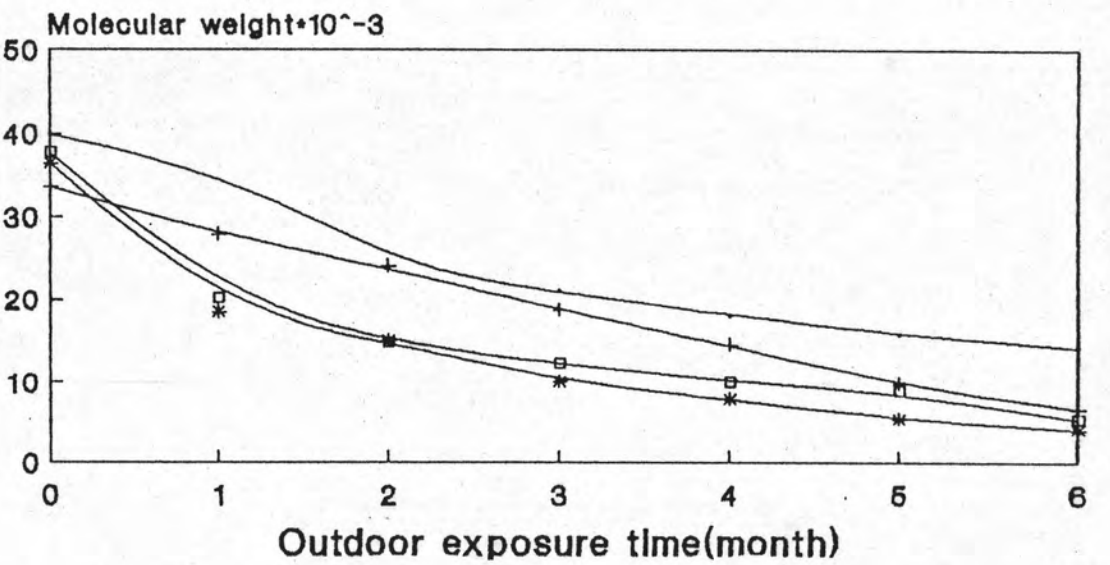
Sensitizer / Exposure time	Intrinsic viscosity						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.96	0.86	0.95	0.90	0.85	0.90	0.92
1 month	0.90	0.73	0.65	0.57	0.74	0.55	0.58
2 months	0.66	0.64	0.54	0.48	0.66	0.47	0.46
3 months	0.60	0.53	0.43	0.44	0.55	0.35	0.40
4 months	0.54	0.45	0.36	0.27	0.46	0.29	0.35
5 months	0.49	0.37	0.29	0.24	0.34	0.22	0.32
6 months	0.45	0.32	0.26	0.22	0.26	0.18	0.22

(b) Molecular weight

Sensitizer / Exposure time	Molecular weight$\times 10^{-3}$						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	39.80	34.20	39.40	36.40	33.70	36.40	39.40
1 month	36.20	27.20	23.50	19.80	27.80	18.50	20.20
2 months	23.80	23.00	18.20	15.40	24.00	15.00	14.80
3 months	21.00	17.70	13.40	13.90	18.70	10.10	12.30
4 months	18.10	14.00	10.70	7.12	14.50	7.88	10.00
5 months	15.80	11.10	7.79	6.07	9.74	5.41	8.92
6 months	14.20	9.07	6.64	5.39	6.69	4.08	5.40



(a) LDPE film(·) and LDPE sensitized with (+)benzophenone, (*)4-methoxybenzophenone and (□)thioxanthone



(b) LDPE film(·) and LDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (□)2-tert-butylanthraquinone

Figure 4.9 Changes in the molecular weight of unsensitized and sensitized LDPE films during natural weathering

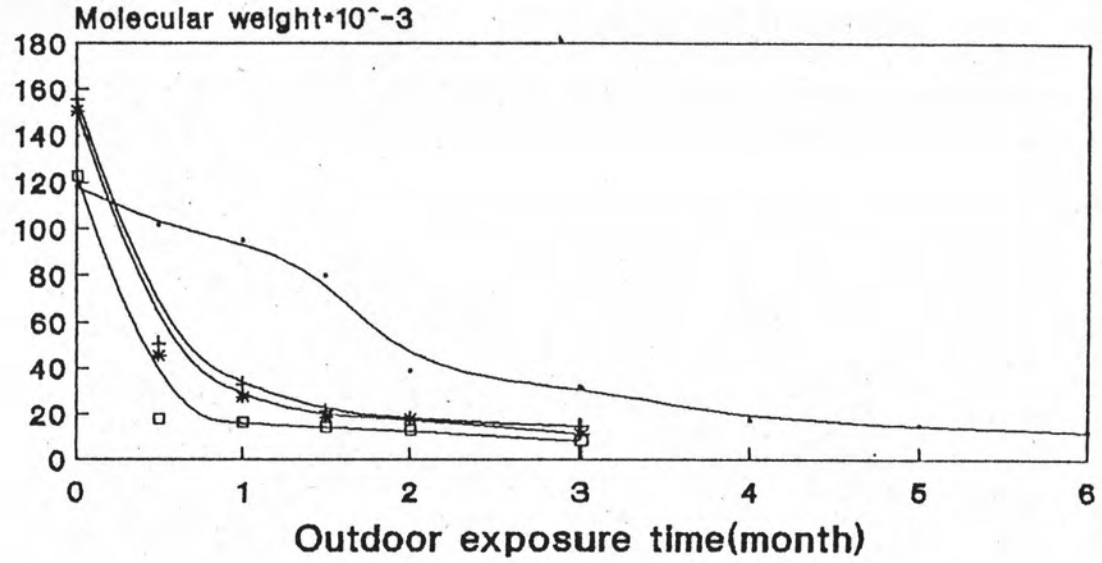
Table 4.8 Intrinsic viscosity and molecular weight of outdoor exposure HDPE films

(a) Intrinsic viscosity

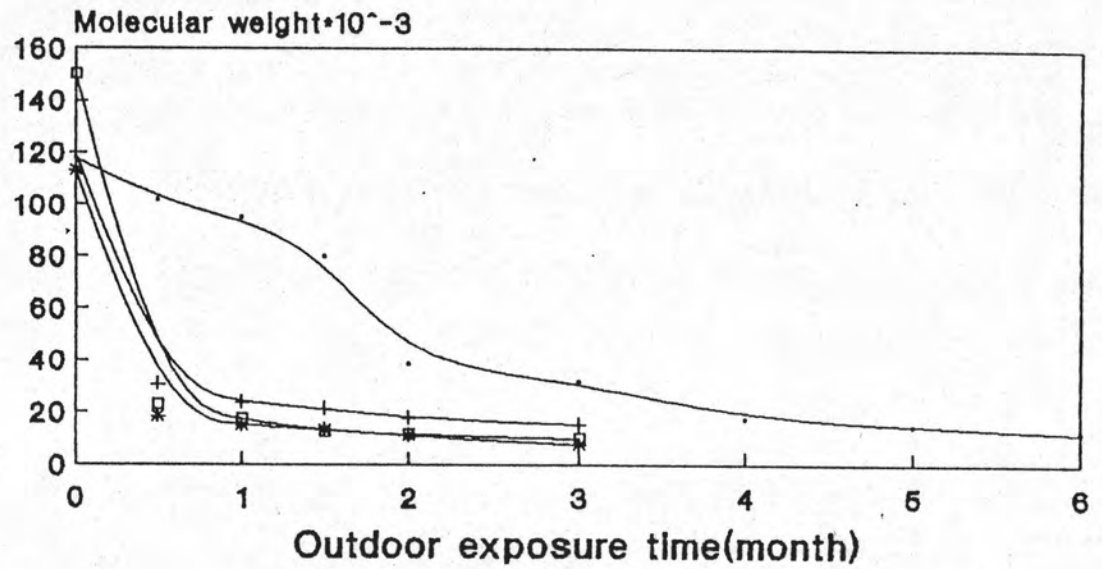
Sensitizer / Exposure time	Intrinsic viscosity						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	2.20	2.67	2.61	2.26	2.23	2.14	2.61
2 weeks	1.98	1.22	1.13	0.59	0.86	0.60	0.69
1 month	1.89	0.90	0.79	0.55	0.71	0.52	0.57
6 weeks	1.67	0.66	0.61	0.49	0.66	0.48	0.45
2 months	1.01	0.58	0.59	0.46	0.58	0.42	0.43
3 months	0.88	0.51	0.43	0.33	0.53	0.32	0.39
4 months	0.57	-	-	-	-	-	-
5 months	0.51	-	-	-	-	-	-
6 months	0.44	-	-	-	-	-	-

(b) Molecular weight

Sensitizer / Exposure time	Molecular weight$\times 10^{-3}$						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	118.00	155.00	150.00	123.00	120.00	113.00	150.00
2 weeks	102.00	50.80	45.30	17.90	30.80	18.40	22.60
1 month	94.90	33.10	27.50	16.30	23.30	14.80	17.30
6 weeks	79.70	21.30	18.70	13.80	21.20	13.20	12.40
2 months	38.60	17.60	17.80	12.80	17.60	10.90	11.30
3 months	31.80	14.60	11.40	7.99	15.30	7.57	9.99
4 months	17.20	-	-	-	-	-	-
5 months	14.60	-	-	-	-	-	-
6 months	12.00	-	-	-	-	-	-



(a) HDPE film(·) and HDPE sensitized with (+)benzophenone, (*)4-methoxybenzophenone and (□)thioxanthone



(b) HDPE film(·) and HDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (□)2-tert-butylanthraquinone

Figure 4.10 Changes in the molecular weight of unsensitized and sensitized HDPE films during natural weathering

4.1.4 Fourier transform infrared absorption measurements

The FTIR method offers valuable information concerning chemical changes produced in polyethylene samples. The FTIR spectra of all samples are measured and typical spectra are shown in Figures 4.11-4.12. Absorption peaks are followed :

(1) The 909 cm^{-1} band corresponding to the presence of vinyl groups in the polyethylene chains

(2) The 1715 cm^{-1} band corresponding to the presence of the carbonyl group in the polyethylene chain

(3) The polyethylene band at 2019 cm^{-1} served as an internal standard to which the absorbances of the other bands were related

(a) LDPE

Carbonyl and vinyl index of LDPE samples are presented in Table 4.9 and plotted against exposure time in Figure 4.13. For both unsensitized and sensitized films, the carbonyl indexes increase linearly with increasing exposure time. Particularly the carbonyl indexes of sensitized samples are higher than those of unsensitized ones. No induction period was observed. The rate of formation of vinyl groups increases linearly with time. However, a quantitative increase of vinyl index is not clearly distinguished from the beginning of outdoor exposure.

(b) HDPE

Carbonyl and vinyl index of HDPE samples are presented in Table 4.10 and plotted against exposure time in Figure 4.14. It can be seen that the rate of formation of

carbonyl and vinyl group of HDPE samples are similar to that of LDPE ones. But carbonyl index of unsensitized HDPE films shows induction period about 1 month.

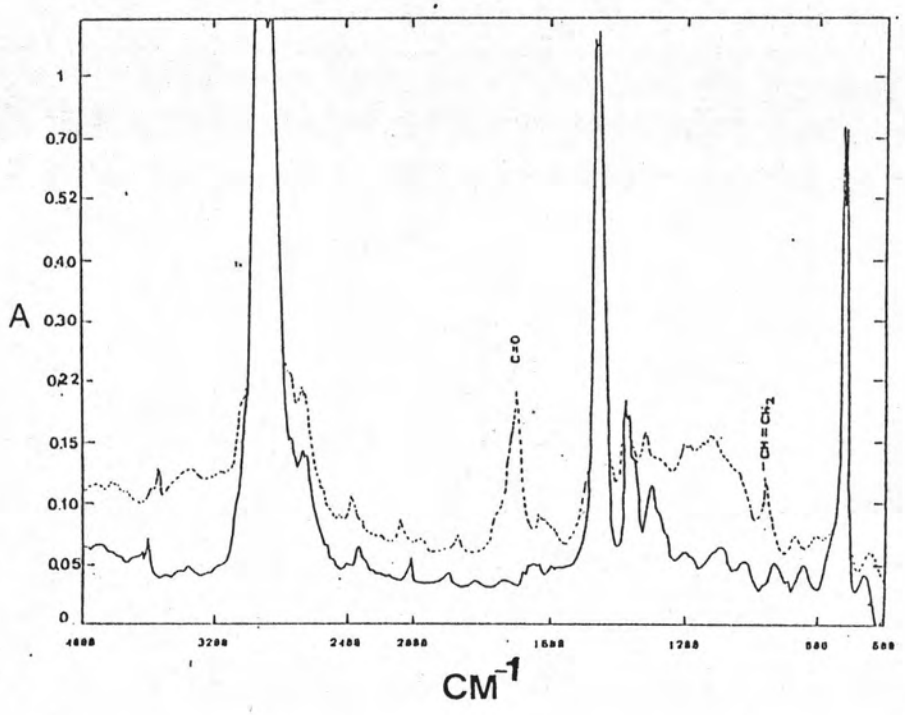


Figure 4.11 (a) FT-IR spectra of outdoor exposure LDPE samples
—— unexposed ; - - - exposed for 6 months

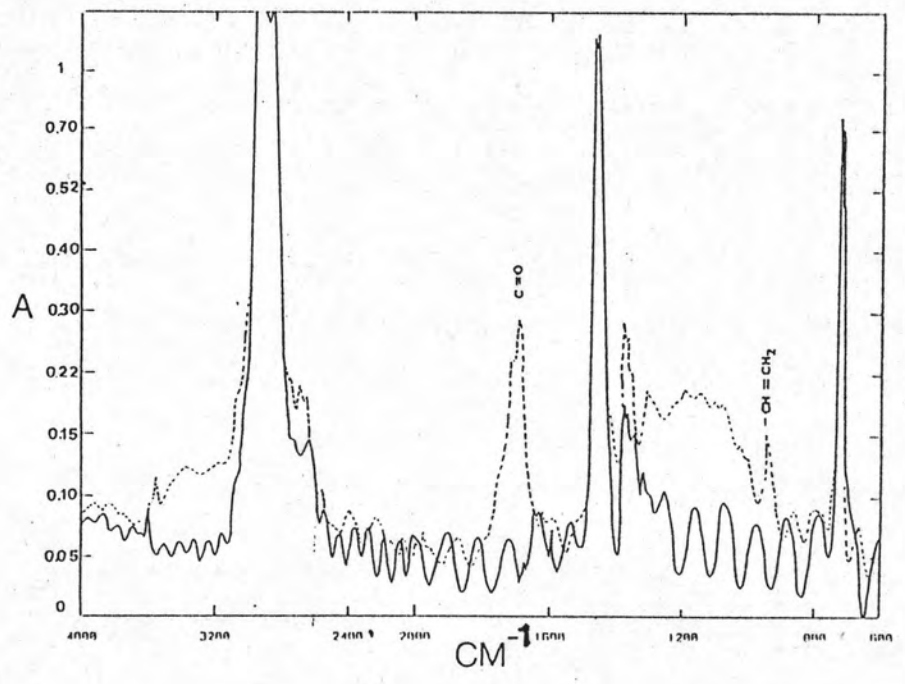


Figure 4.11 (b) FT-IR spectra of outdoor exposure LDPE samples sensitized with thioxanthone
—— unexposed ; - - - exposed for 6 months

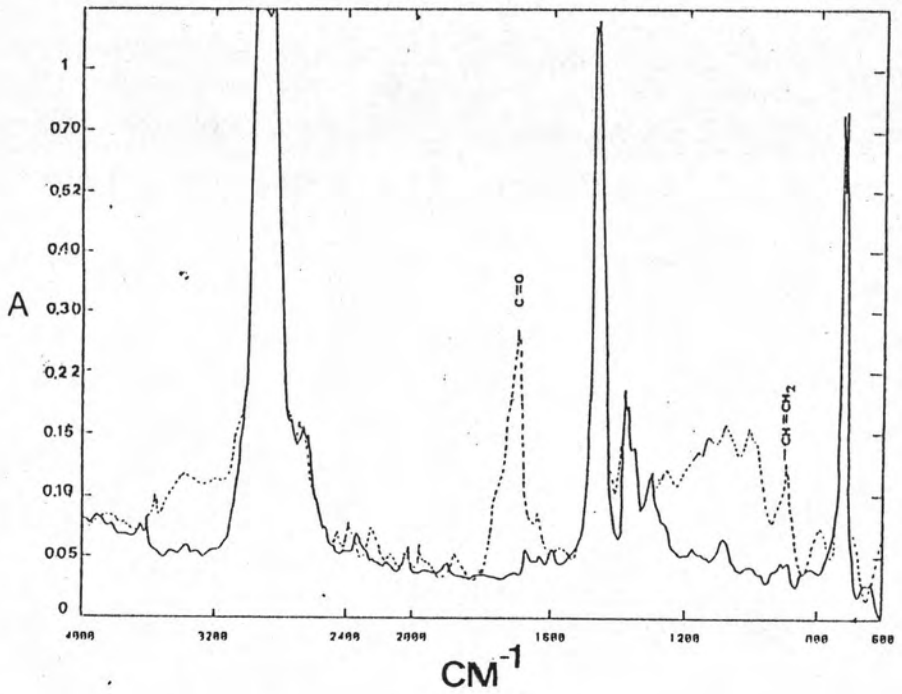


Figure 4.11 (c) FT-IR spectra of outdoor exposure LDPE samples sensitized with 2-methylanthraquinone
——— unexposed ; - - - exposed for 6 months

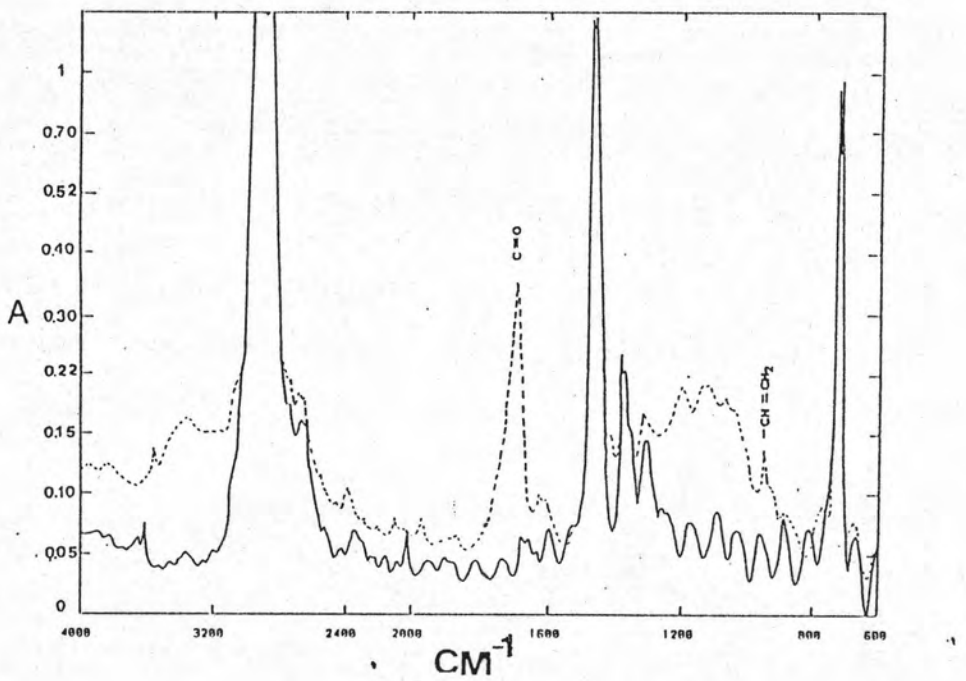


Figure 4.11 (d) FT-IR spectra of outdoor exposure LDPE samples sensitized with 2-tert-butylanthraquinone
——— unexposed ; - - - exposed for 6 months

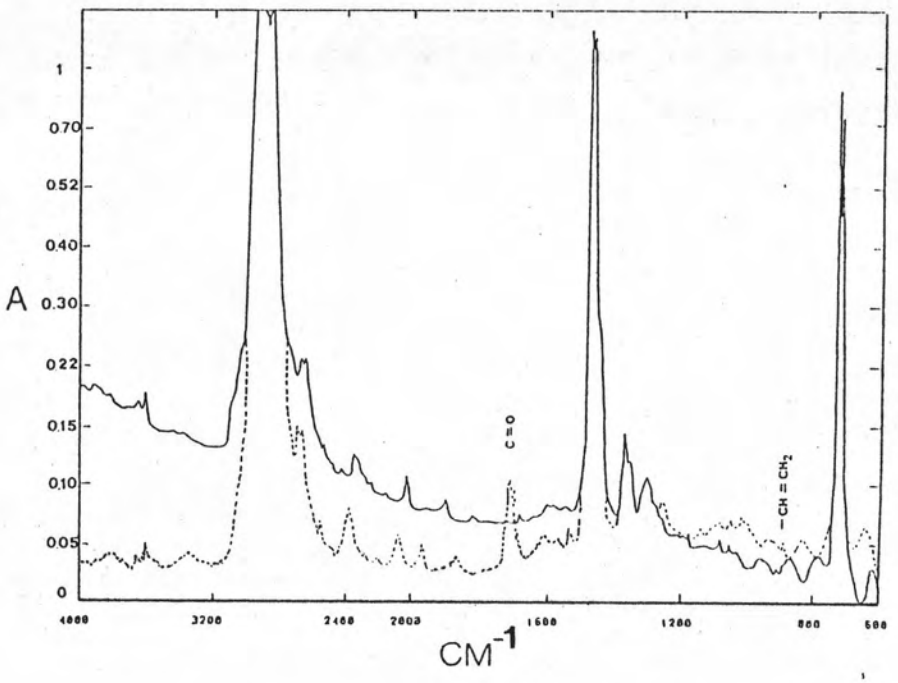


Figure 4.12 (a) FT-IR spectra of outdoor exposure HDPE samples
—— unexposed ; - - - exposed for 3 months

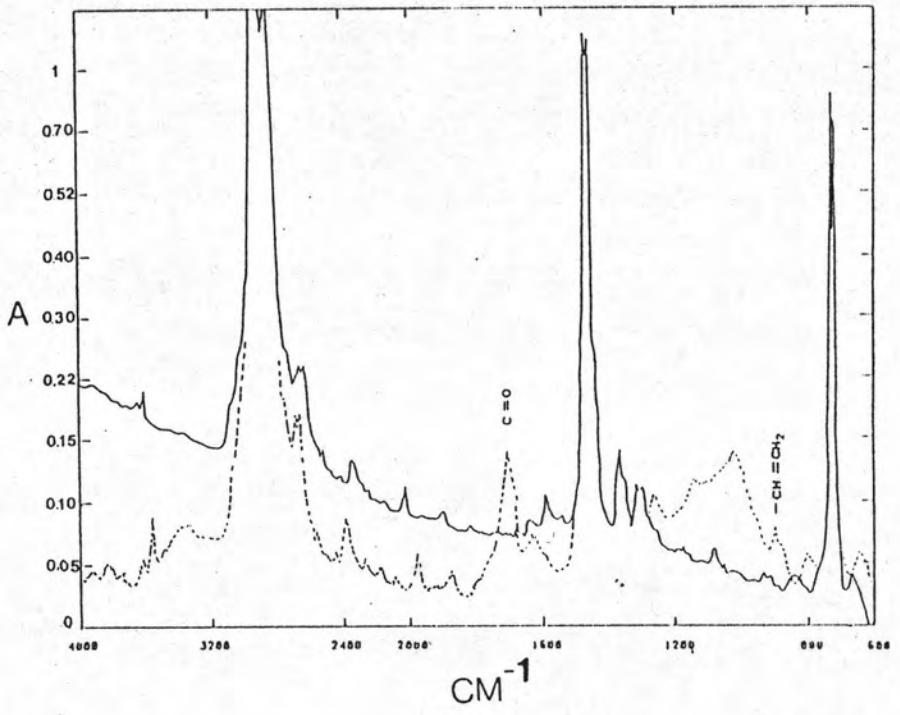


Figure 4.12 (b) FT-IR spectra of outdoor exposure HDPE samples sensitized with thioxanthone
—— unexposed ; - - - exposed for 3 months

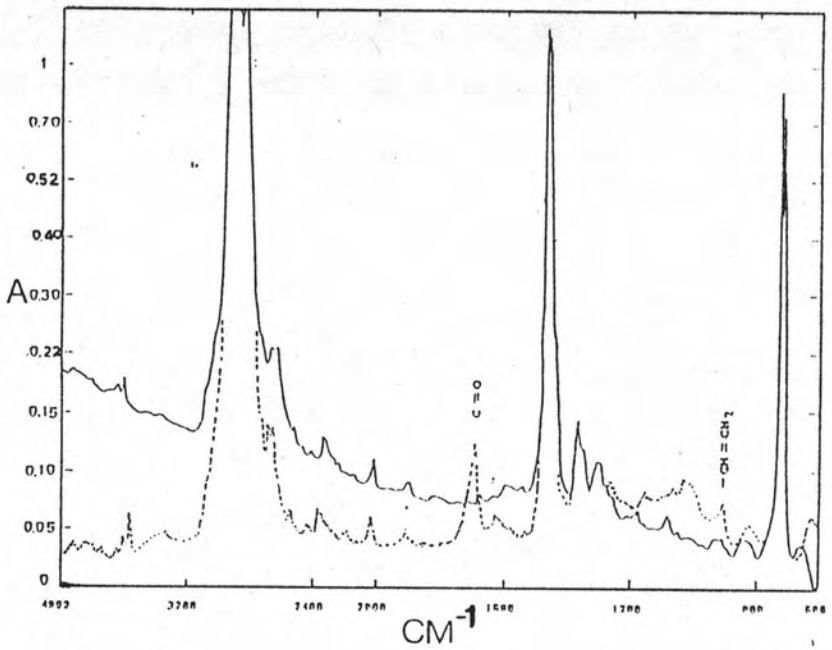


Figure 4.12 (c) FT-IR spectra of outdoor exposure HDPE samples sensitized with 2-methylanthraquinone
——— unexposed ; - - - exposed for 3 months

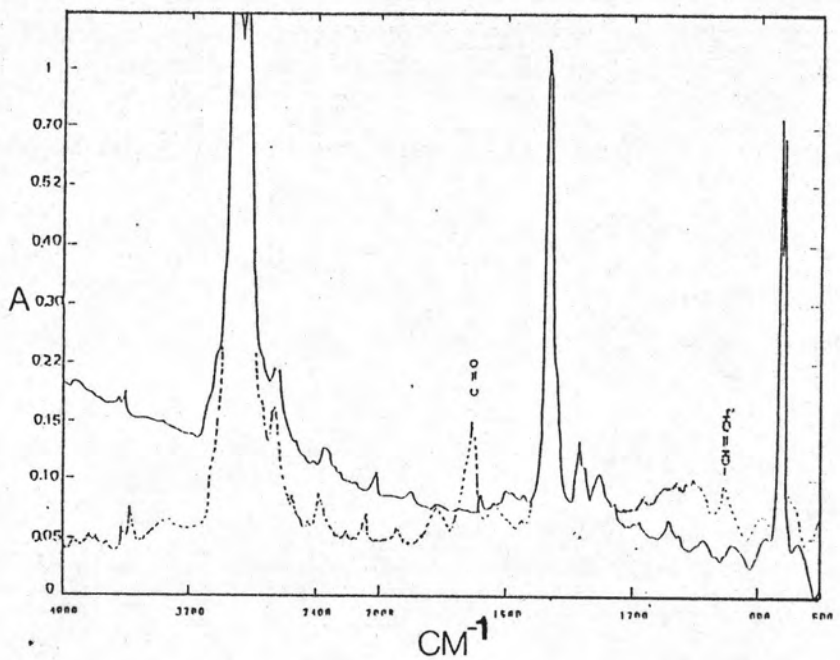


Figure 4.12 (d) FT-IR spectra of outdoor exposure HDPE samples sensitized with 2-tert-butylanthraquinone
——— unexposed ; - - - exposed for 3 months

Table 4.9 Changes in carbonyl and vinyl index of outdoor exposure LDPE films

(a) Carbonyl index

Sensitizer / Exposure time	Carbonyl index (I_{co})						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.00	1.00	0.99	0.99	0.90	0.00	0.68
2 weeks	0.57	NA	2.05	2.51	NA	0.87	1.37
1 month	1.11	NA	2.10	2.80	NA	5.02	3.67
3 months	2.20	NA	2.96	3.02	NA	5.17	4.47
6 months	2.51	5.07	6.64	4.49	6.13	9.51	11.30

(b) Vinyl index

Sensitizer / Exposure time	Vinyl index (I_{vinyl})						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.68	1.45	1.37	1.22	1.13	0.78	1.01
2 weeks	0.99	NA	1.69	1.18	NA	1.07	1.22
1 month	0.80	NA	1.87	2.43	NA	1.59	1.75
3 months	2.08	NA	1.41	1.84	NA	1.32	1.17
6 months	1.45	1.91	3.02	2.40	2.43	5.47	5.48

Note NA = Not available

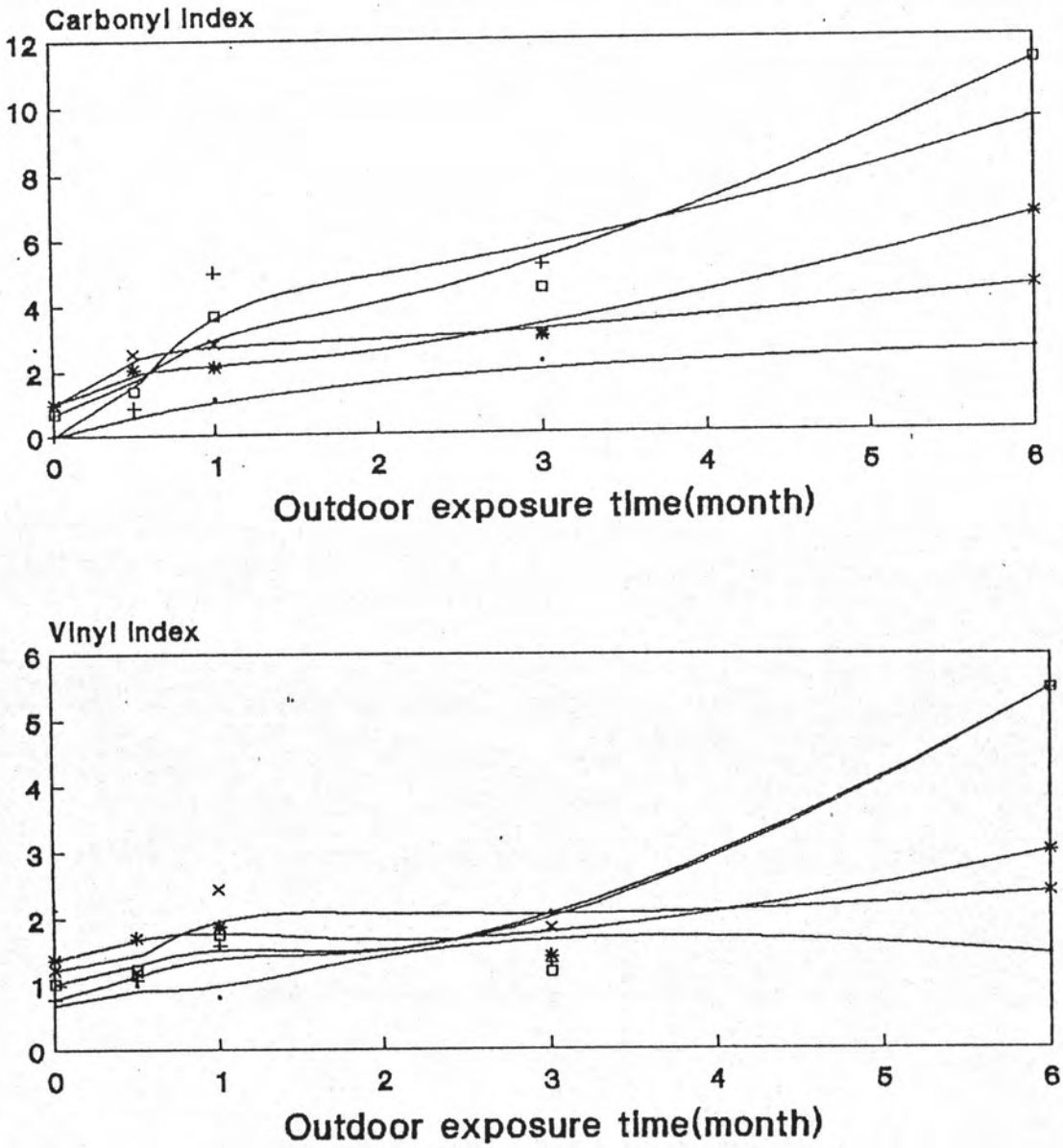


Figure 4.13 Changes in carbonyl and vinyl index of LDPE film(·) and LDPE sensitized with (+)2-methylanthraquinone, (*)4-methoxybenzophenone, (□)2-tert-butylanthraquinone and (x)thioxanthone during natural weathering

Table 4.10 Changes in carbonyl and vinyl index of outdoor exposure HDPE films

(a) Carbonyl index

Sensitizer / Exposure time	Carbonyl index (I_{co})						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2 weeks	0.00	NA	1.02	1.34	NA	1.01	1.15
1 month	0.00	NA	1.08	1.50	NA	1.17	1.45
2 months	0.95	1.19	1.28	1.69	1.31	1.37	2.05
3 months	0.97	2.54	1.95	3.37	3.40	3.22	2.98

(b) Vinyl index

Sensitizer / Exposure time	Vinyl index (I_{vinyl})						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	0.22	0.24	0.22	0.28	0.36	0.26	0.31
2 weeks	0.27	NA	0.29	0.32	NA	0.38	0.42
1 month	0.23	NA	0.30	0.41	NA	0.29	0.60
2 months	0.52	0.52	0.63	0.73	0.38	0.59	0.68
3 months	3.80	1.72	2.48	2.57	1.98	5.54	1.87

Note NA = Not available

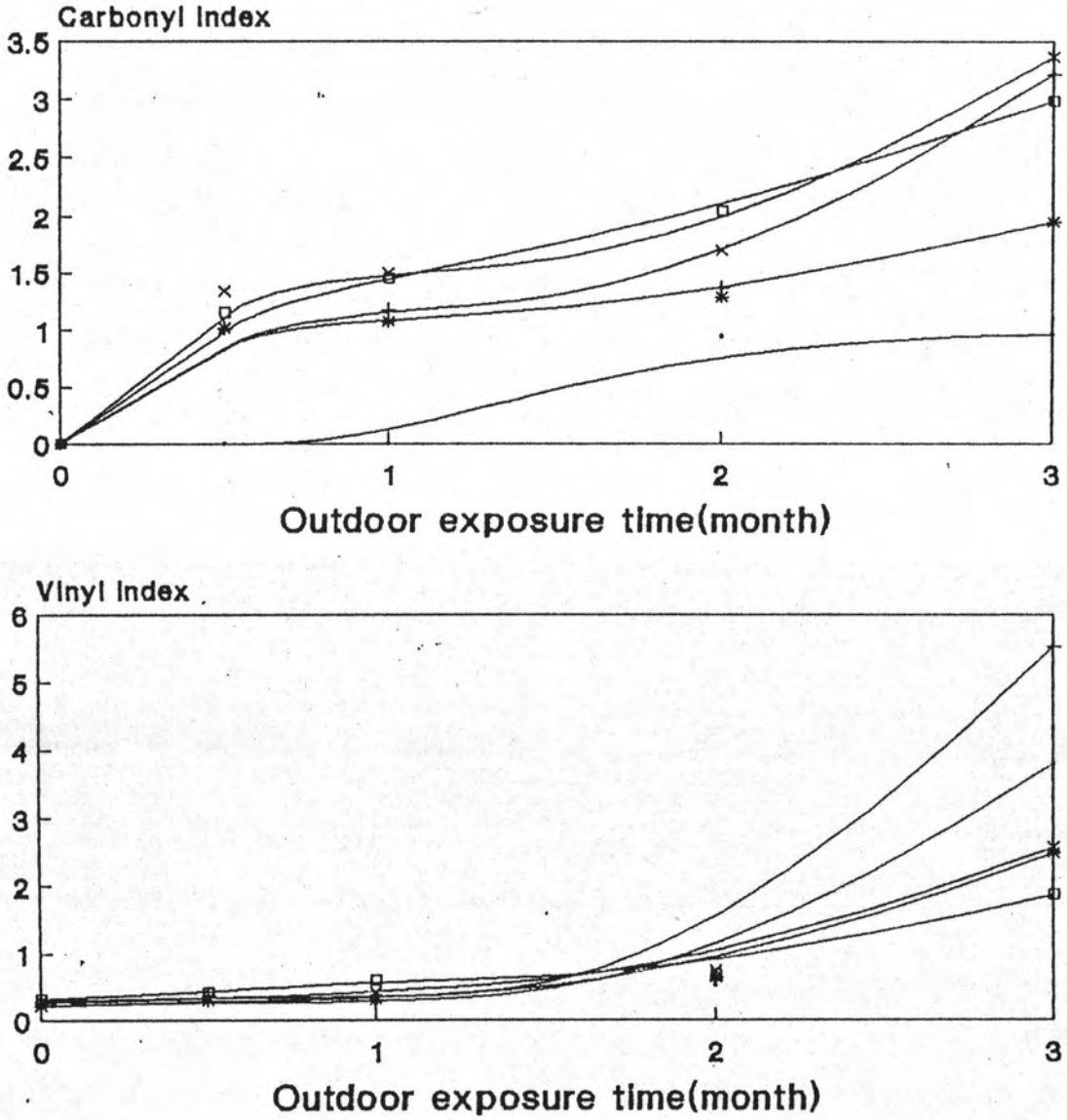


Figure 4.14 Changes in carbonyl and vinyl index of HDPE film(·) and HDPE sensitized with (+)2-methylanthraquinone, (*)4-methoxybenzophenone, (□)2-tert-butylanthraquinone and (x)thioxanthone during natural weathering

4.2 Irradiation using medium pressure mercury lamp

4.2.1 Tensile properties measurements

A typical example of the effect of UV irradiation exposure on the stress-strain traces of both unsensitized and sensitized LDPE and HDPE films is shown in Figures 4.15-4.16.

(a) LDPE

The changes of tensile strength and elongation at break of unsensitized and sensitized samples by irradiation are presented in Table 4.11 and shown in Figure 4.17 as a function of irradiation time. The tensile strength decreases from the beginning of irradiation, then increase slightly and follows by a slow decrease. The elongation at break drops sharply in the early irradiation and then decreases linearly. The tensile properties of sensitized samples have a higher decrease than those of unsensitized ones. Thioxanthone, derivatives of benzophenone and of anthraquinone sensitized LDPE samples give a higher decrease of elongation at break than benzophenone and anthraquinone sensitized ones.

(b) HDPE

The behavior of tensile properties of HDPE samples by irradiation is presented in Table 4.12 and Figure 4.18. The changes of tensile strength and elongation at break of HDPE films are similar to those of LDPE ones. The elongation at break of HDPE samples decreases more rapidly than that of LDPE ones.

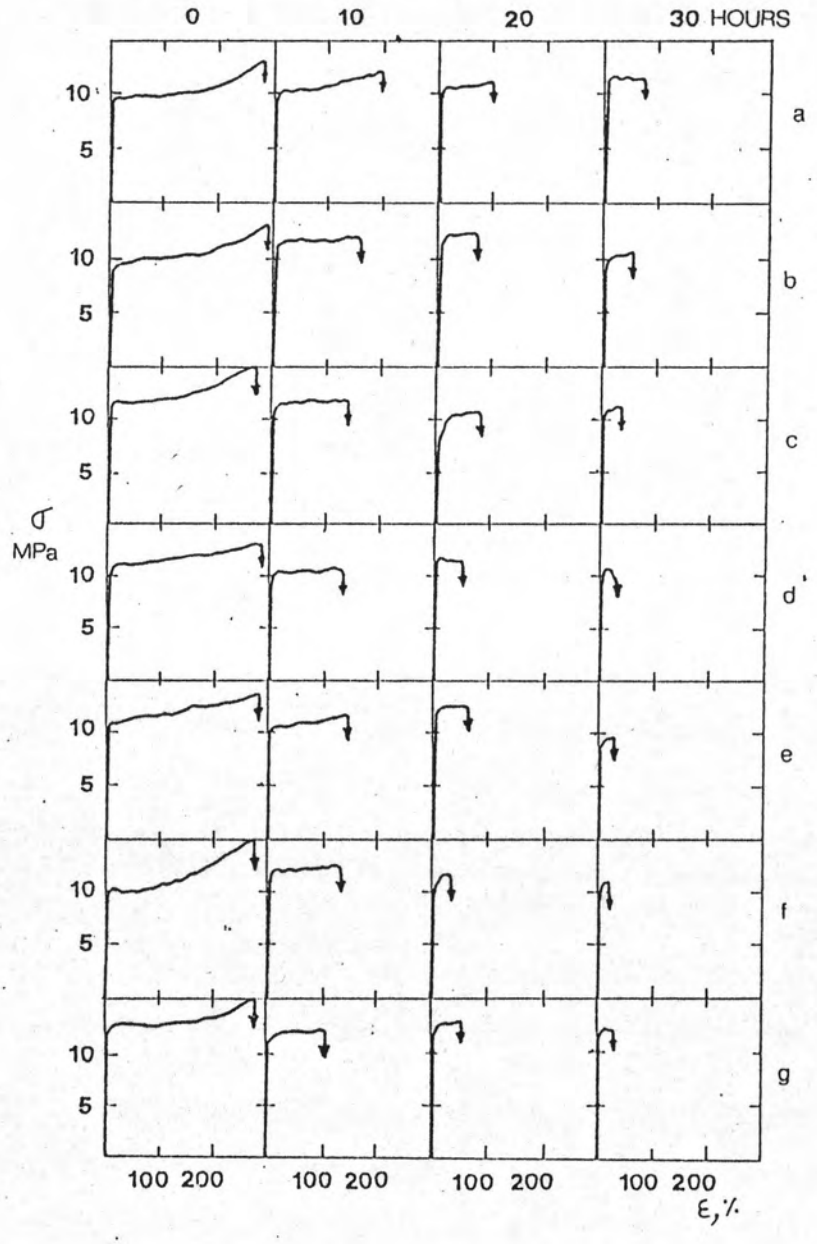


Figure 4.15 Stress-strain traces for LDPE samples at various irradiation times (indicates on curves in hours): unsensitized (a) and sensitized with benzophenone (b), 4-methoxybenzophenone (c), thioxanthone (d), anthraquinone (e), 2-methylanthraquinone (f) and 2-tert-butylanthraquinone (g)

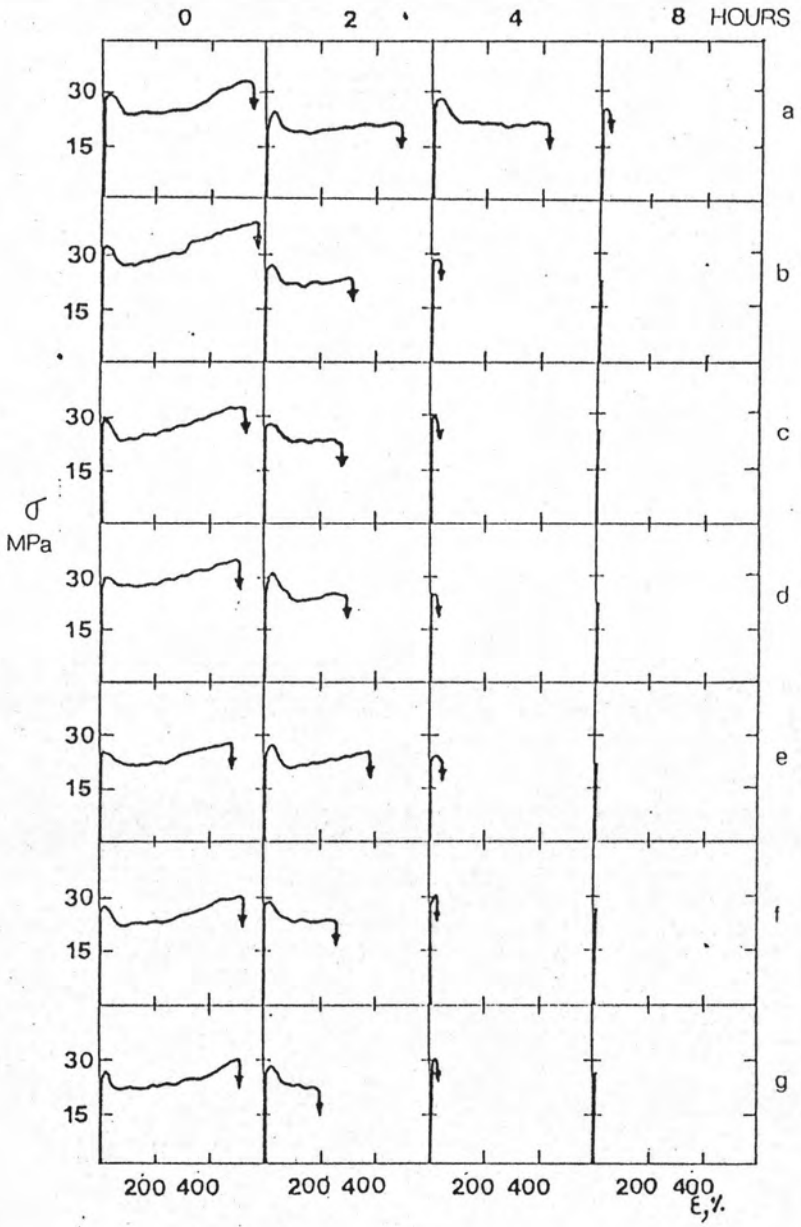


Figure 4.16 Stress-strain traces for HDPE samples at various irradiation times (indicates on curves in hours): unsensitized (a) and sensitized with benzophenone (b), 4-methoxybenzophenone (c), thioxanthone (d), anthraquinone (e), 2-methylanthraquinone (f) and 2-tert-butylanthraquinone (g)

Table 4.11 Tensile properties of irradiated LDPE films

(a) Tensile strength

Sensitizer / Irradiation time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	12.6	13.2	15.2	14.0	13.0	15.9	15.9
5 hours	11.5	13.0	12.2	13.8	13.0	14.5	14.5
10 hours	11.2	12.3	12.0	10.7	11.9	13.2	12.1
15 hours	12.0	12.7	13.1	14.1	13.4	13.0	13.8
20 hours	12.7	13.0	10.7	12.6	12.8	12.9	12.6
25 hours	11.5	11.6	10.5	12.5	10.9	12.1	12.4
30 hours	11.08	10.98	11.23	10.72	9.28	10.37	12.35

(b) Elongation at break

Sensitizer / Irradiation time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	288	290	273	285	281	280	279
5 hours	181	175	173	169	180	170	152
10 hours	173	151	132	112	137	122	109
15 hours	118	101	80	73	85	78	71
20 hours	92	73	47	30	49	27	36
25 hours	82	65	31	28	30	18	29
30 hours	75	58	25	23	23	6	27

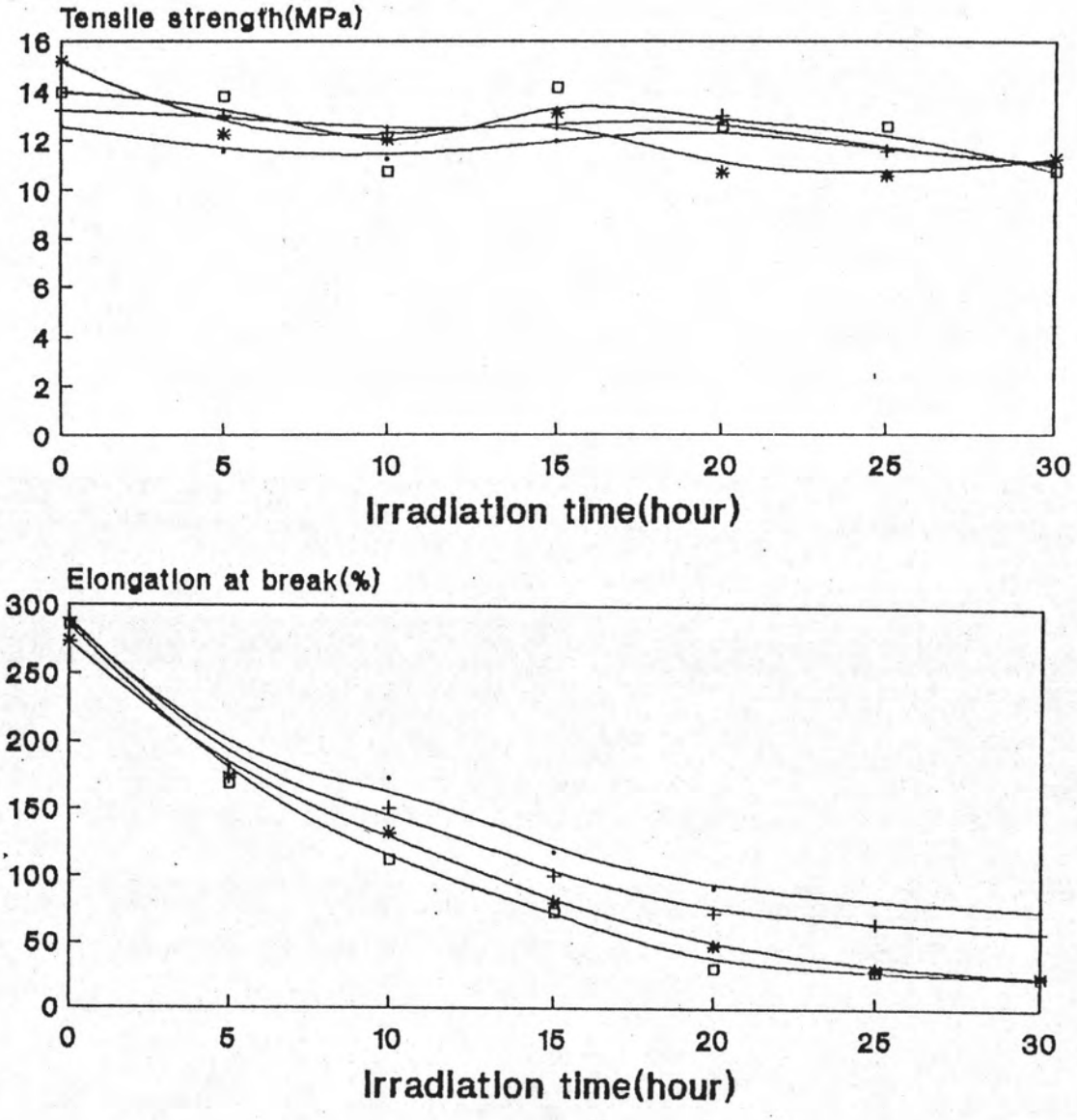


Figure 4.17(a) Changes in tensile strength and elongation at break of LDPE film(·) and LDPE sensitized with (+)benzophenone, (*)4-methoxybenzophenone and (□)thioxanthone during irradiation with HPK 125 W

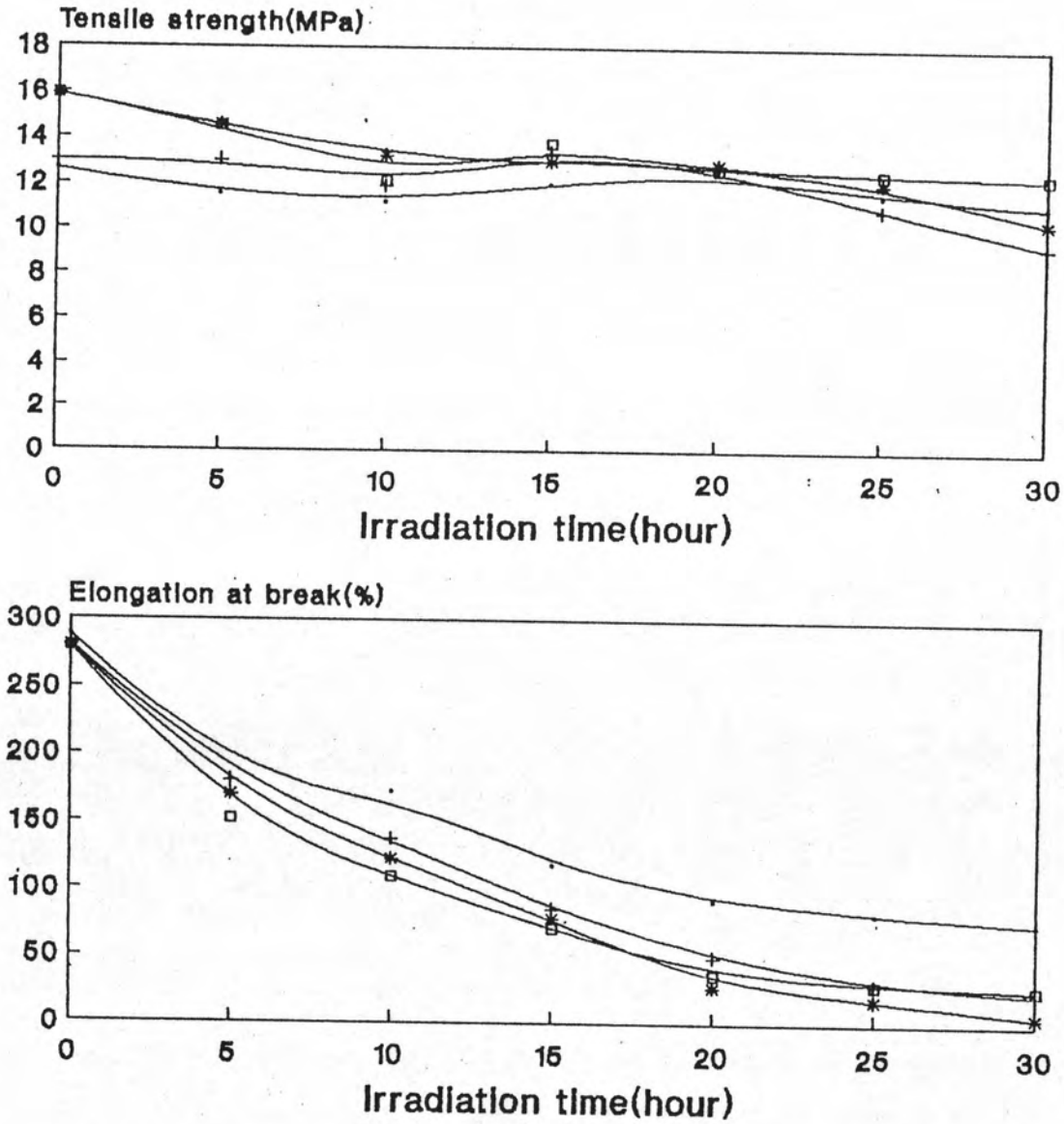


Figure 4.17(b) Changes in tensile strength and elongation at break of LDPE film(·) and LDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (□)2-tert-butylanthraquinone during irradiation with HPK 125 W

Table 4.12 Tensile properties of irradiated HDPE films

(a) Tensile strength

Sensitizer / Irradiation time	Tensile strength(MPa)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	32.7	36.7	32.5	32.2	28.9	27.4	30.1
2 hours	25.8	24.2	27.3	30.1	27.6	27.9	27.1
4 hours	28.4	28.5	30.5	28.3	27.1	27.7	30.0
6 hours	31.1	25.4	29.6	27.3	30.3	26.1	27.9
8 hours	25.4	22.3	28.5	25.2	21.6	25.1	25.6

(b) Elongation at break

Sensitizer / Irradiation time	Elongation at break(%)						
	no additive	benzo-phenone	4-methoxy benzo-phenone	thioxan-thone	anthra-quinone	2-methyl anthra-quinone	2-tert-butylanthra quinone
original	580	594	526	520	519	510	524
2 hours	479	312	285	297	389	269	202
4 hours	442	17	11	10	37	12	12
6 hours	223	10	6	6	10	6	5
8 hours	22	4	6	5	5	6	5

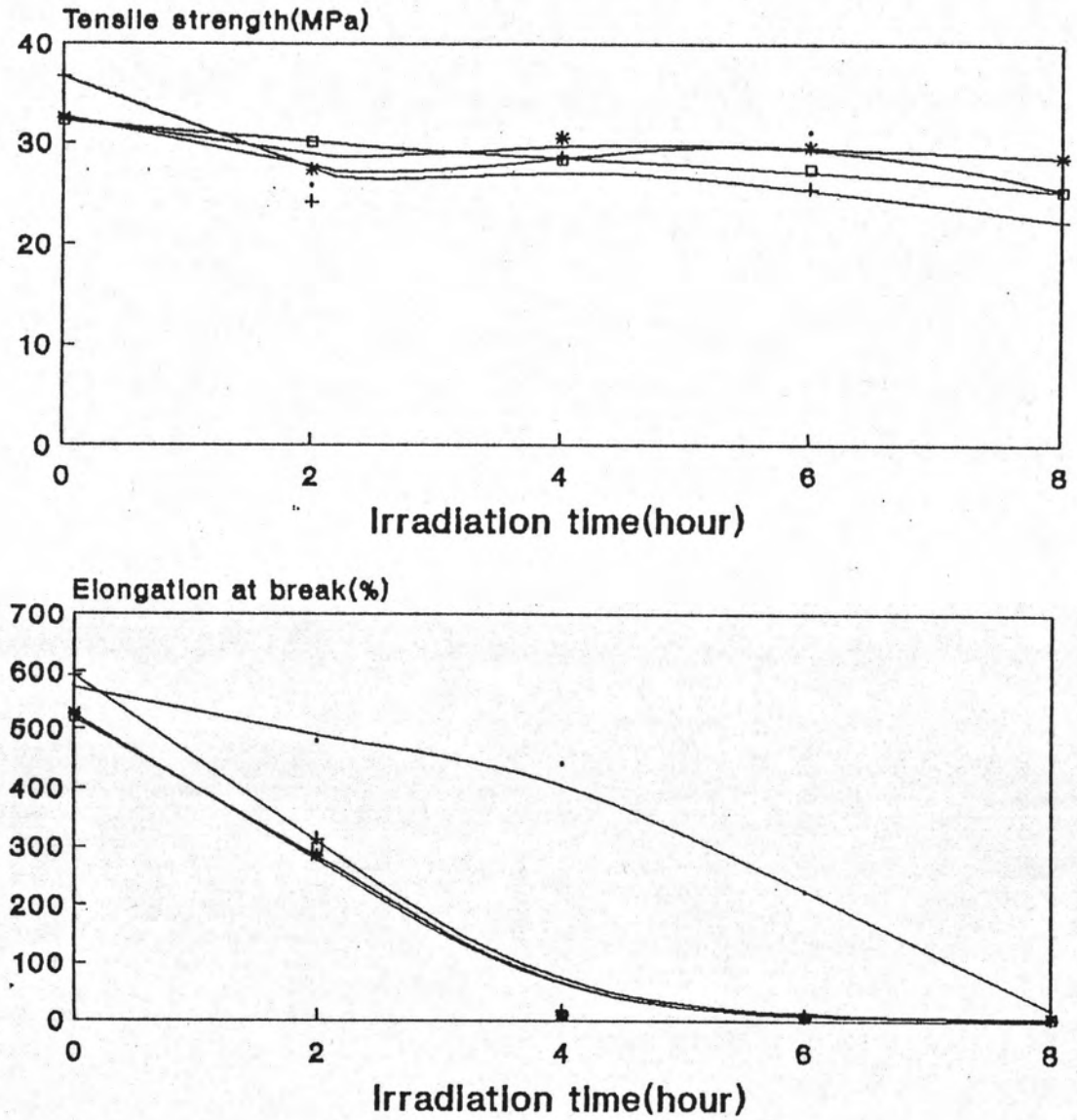


Figure 4.18(a) Changes in tensile strength and elongation at break of HDPE film(·) and HDPE sensitized with (+)benzophenone, (✱)4-methoxybenzophenone and (□)thioxanthone during irradiation with HPK 125 W

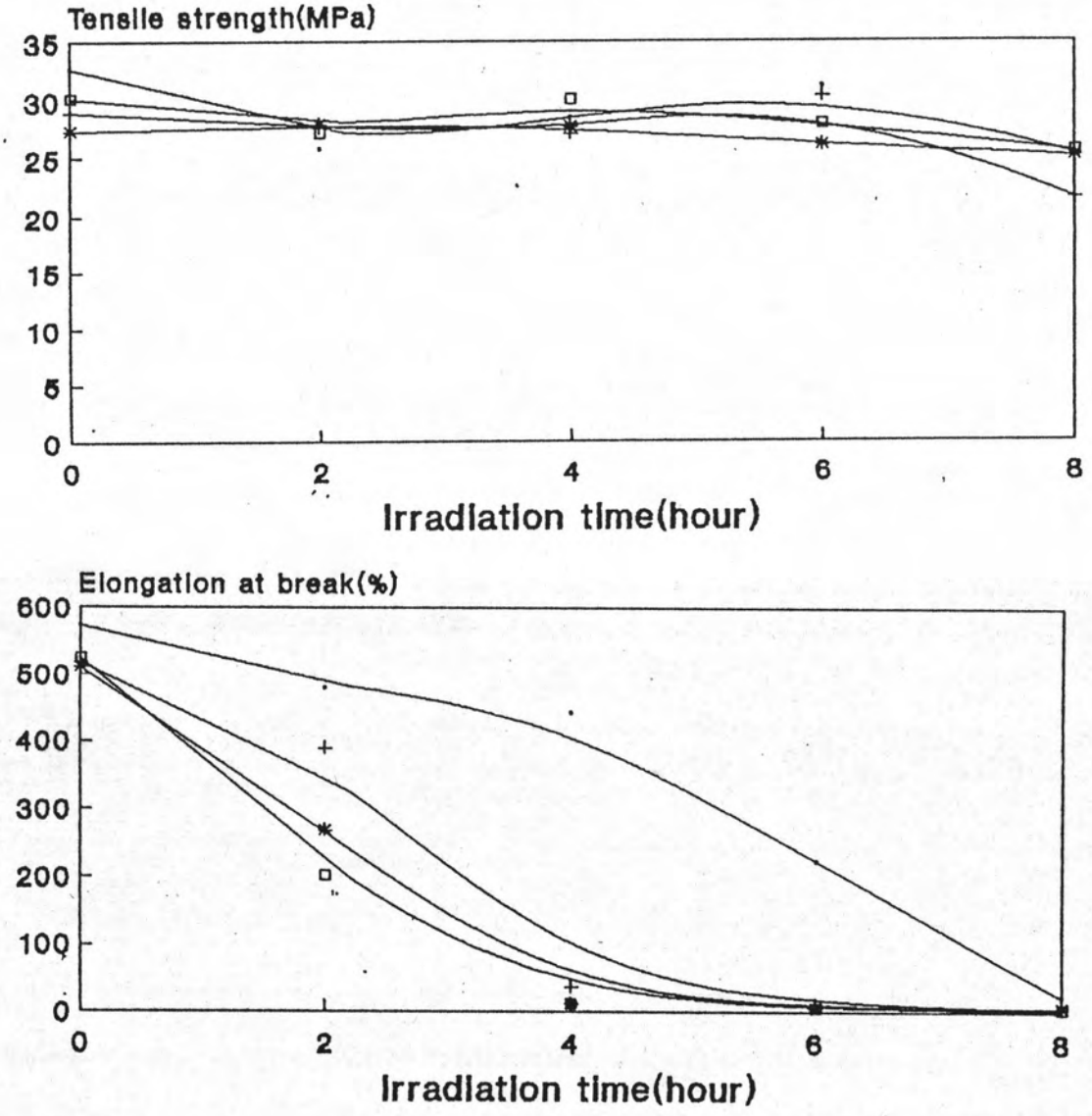


Figure 4.18(b) Changes in tensile strength and elongation at break of HDPE film(·) and HDPE sensitized with (+)anthraquinone, (*)2-methylanthraquinone and (▫)2-tert-butylanthraquinone during irradiation with HPK 125 W

4.2.2 Gel measurements

(a) LDPE

The unirradiated samples, both unsensitized and sensitized, do not contain insoluble material, while the 30 hour final product is characterized by the presence of quantities of insoluble material. The gel contents are presented in Table 4.13.

(b) HDPE

The unsensitized sample can completely dissolve in solvent before irradiation with medium pressure mercury lamp but sensitized samples can partially dissolve by presence of small quantities of insoluble material. The samples which was irradiated for 8 hours contain quantities of insoluble material. So the gel contents are shown in Table 4.14.

Table 4.13 Gel content of irradiated LDPE films

Photosensitizer	Gel content(%)	
	original	30 hours
No additive	0.0	21.7
Benzophenone	0.0	33.3
4-Methoxybenzophenone	0.0	41.3
Thioxanthone	0.0	27.6
Anthraquinone	0.0	37.1
2-Methylanthraquinone	0.0	34.9
2-tert-Butylanthraquinone	0.0	32.5

Table 4.14 Gel content of irradiated HDPE films

Photosensitizer	Gel content(%)	
	original	8 hours
No additive	0.0	16.8
Benzophenone	4.7	33.9
4-Methoxybenzophenone	1.3	35.3
Thioxanthone	15.8	39.9
Anthraquinone	2.4	32.2
2-Methylanthraquinone	20.2	37.7
2-tert-Butylanthraquinone	22.5	37.4

4.2.3 Molecular weight measurements

The final products of LDPE (30 hours) and HDPE (8 hours), both unsensitized and sensitized are examined and show a decrease from the original value. The results are listed in Tables 4.15-4.16, respectively.

(a) LDPE

From Table 4.15, it can be seen that molecular weight of sensitized samples decreases more rapidly than that of unsensitized ones, reaching 50 % of the beginning value after 30 hours of irradiation. Thioxanthone, derivatives of benzophenone and of anthraquinone sensitized films show a greater decrease of molecular weight than benzophenone and anthraquinone sensitized ones.

(b) HDPE

From Table 4.16, molecular weight of HDPE films is the same as that of LDPE ones. After 8 hours of irradiation, it reaches about 10-15 % of the initial value.

Table 4.15 Viscosity and molecular weight of irradiated LDPE films

Photosensitizer	Intrinsic viscosity		Molecular weight$x10^{-3}$	
	original	30 hours	original	30 hours
No additive	0.96	0.65	39.80	23.60
Benzophenone	0.86	0.56	34.20	19.10
4-Methoxybenzophenone	0.95	0.45	39.40	18.90
Thioxanthone	0.90	0.49	36.40	16.00
Anthraquinone	0.85	0.59	33.70	19.50
2-Methylanthraquinone	0.90	0.42	36.40	17.10
2-tert-Butylanthraquinone	0.92	0.48	37.70	17.90

Table 4.16 Viscosity and molecular weight of irradiated HDPE films

Photosensitizer	Intrinsic viscosity		Molecular weight$x10^{-3}$	
	original	8 hours	original	8 hours
No additive	2.20	1.11	118.00	44.50
Benzophenone	2.67	0.64	155.00	20.30
4-Methoxybenzophenone	2.61	0.58	150.00	17.60
Thioxanthone	2.26	0.52	123.00	15.00
Anthraquinone	2.23	0.61	120.00	18.90
2-Methylanthraquinone	2.14	0.51	113.00	14.60
2-tert-Butylanthraquinone	2.61	0.54	150.00	15.80

4.2.4 Fourier transform infrared absorption measurements

The FTIR spectra of irradiated samples, LDPE and HDPE, are shown in Figures 4.19-4.20, respectively. Observed absorption peaks of irradiation are the same as those of outdoor exposure. Carbonyl and vinyl index of polyethylene samples are presented in Tables 4.17-4.18.

(a) LDPE

From Table 4.17, carbonyl and vinyl index of sensitized samples increase higher than those of unsensitized ones, after 30 hours of irradiation.

(b) HDPE

From Table 4.18, changes in carbonyl and vinyl index of HDPE films are the same as those of LDPE films, after 8 hours of irradiation.

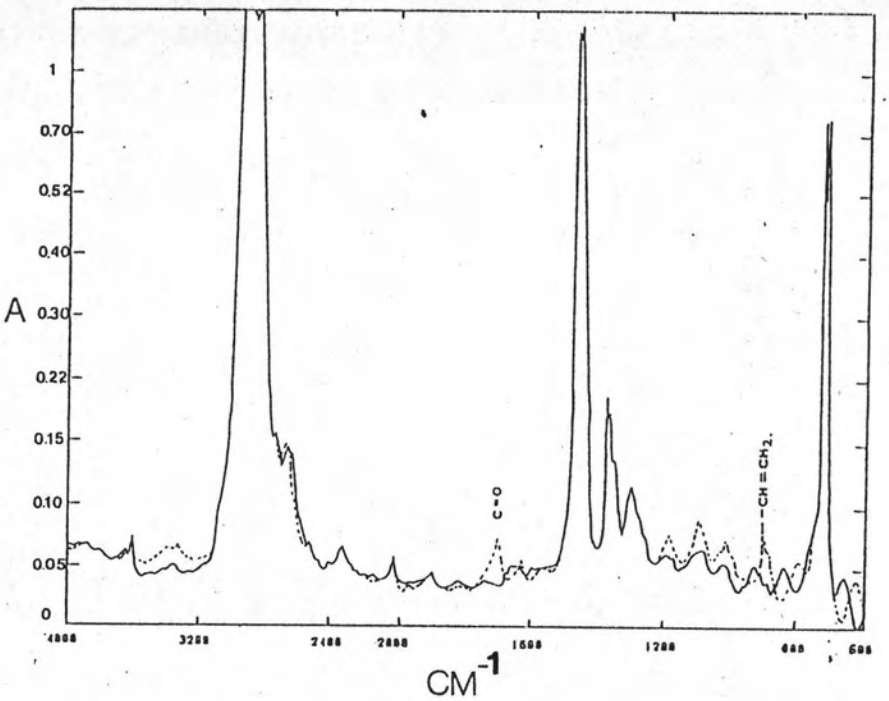


Figure 4.19 (a) FT-IR spectra of irradiated LDPE samples
——— unirradiated ; - - - irradiated for 30 hours

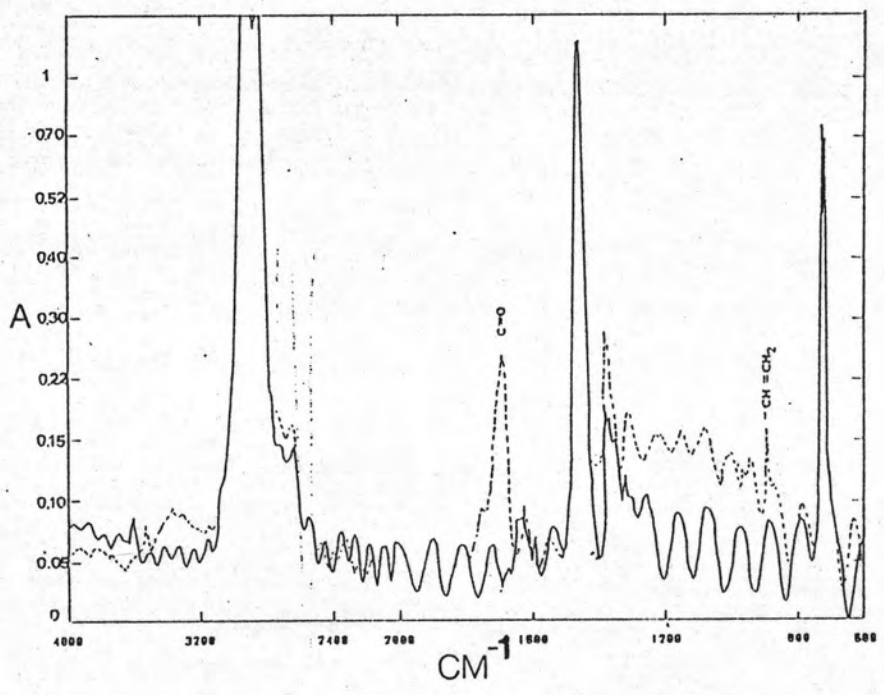


Figure 4.19 (b) FT-IR spectra of irradiated LDPE samples sensitized with thioxanthone
——— unirradiated ; - - - irradiated for 30 hours

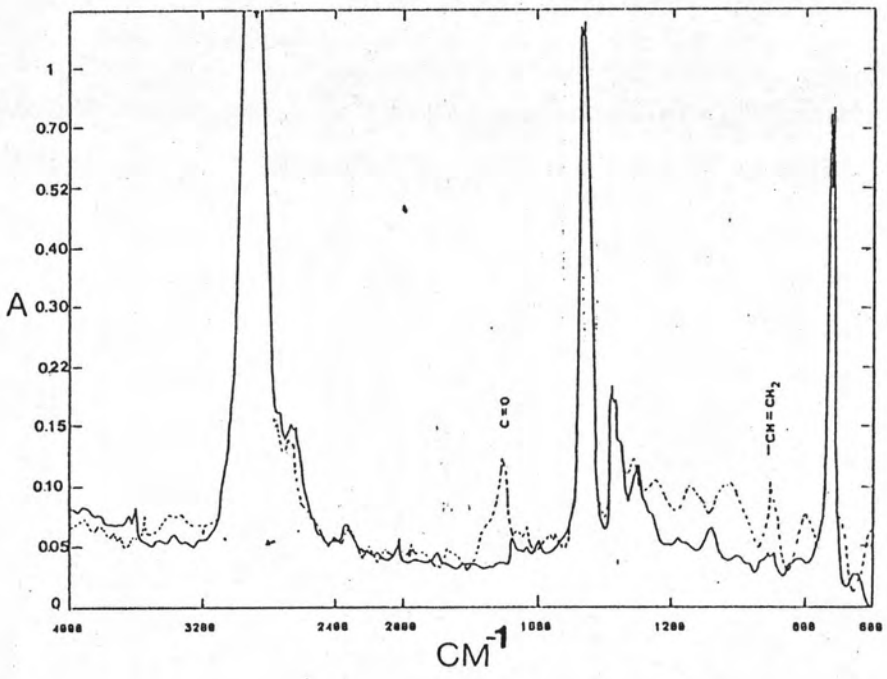


Figure 4.19 (c) FT-IR spectra of irradiated LDPE samples sensitized with 2-methylanthraquinone
—— unirradiated ; - - - irradiated for 30 hours

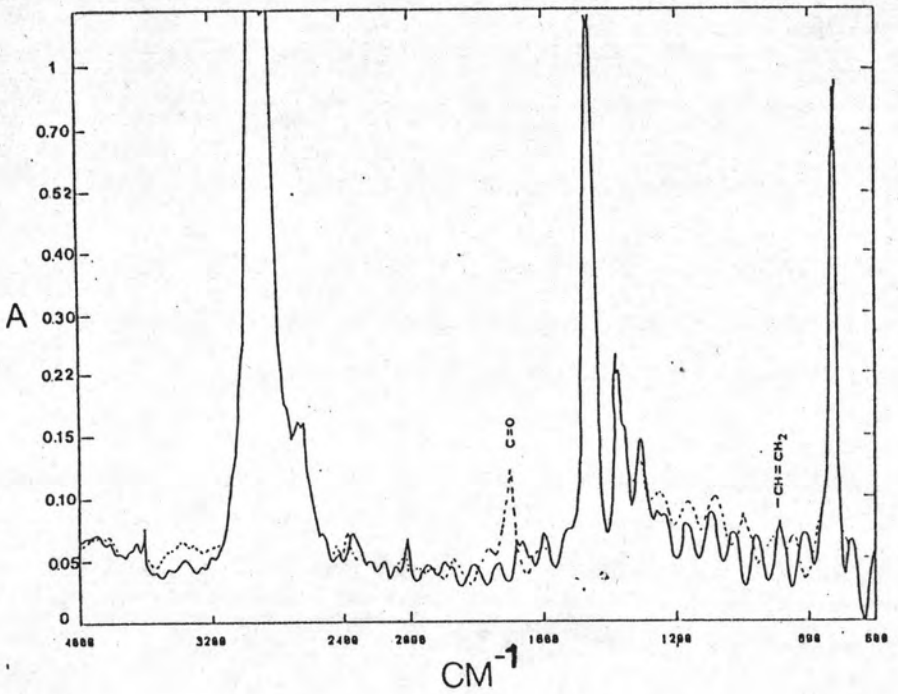


Figure 4.19 (d) FT-IR spectra of irradiated LDPE samples sensitized with 2-tert-butylanthraquinone
—— unirradiated ; - - - irradiated for 30 hours

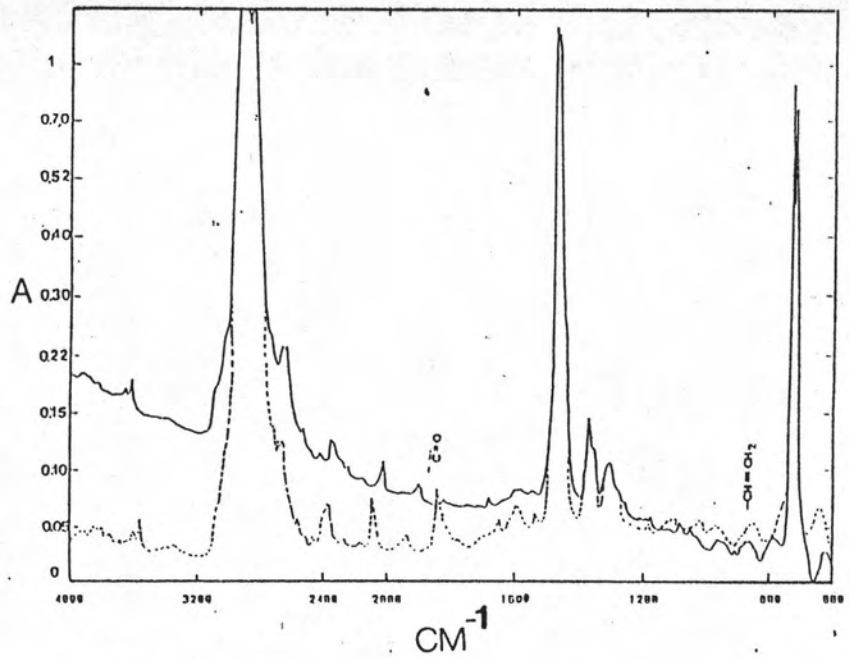


Figure 4.20 (a) FT-IR spectra of irradiated HDPE samples
—— unirradiated ; - - - irradiated for 8 hours

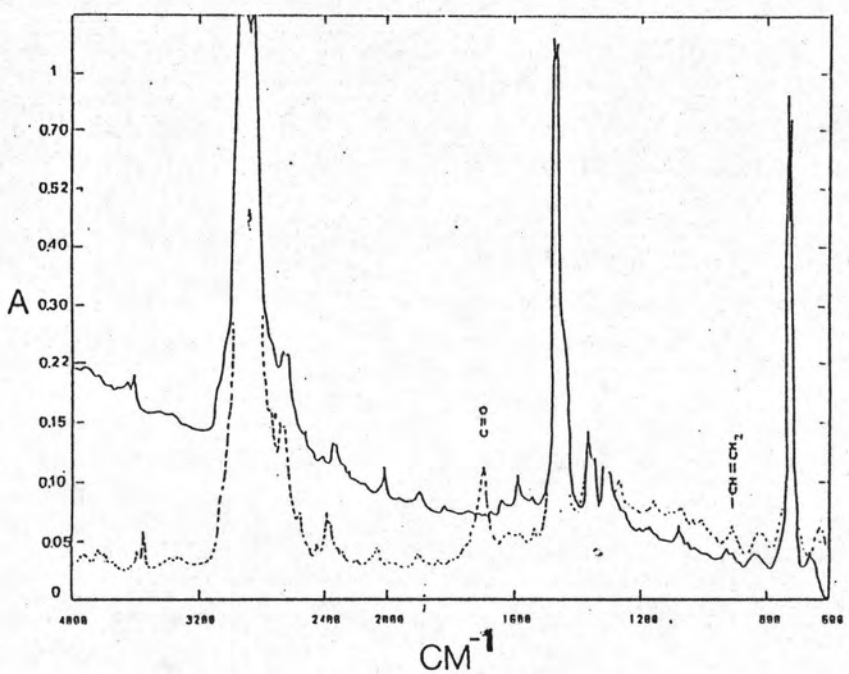


Figure 4.20 (b) FT-IR spectra of irradiated HDPE samples sensitized with thioxanthone
—— unirradiated ; - - - irradiated for 8 hours

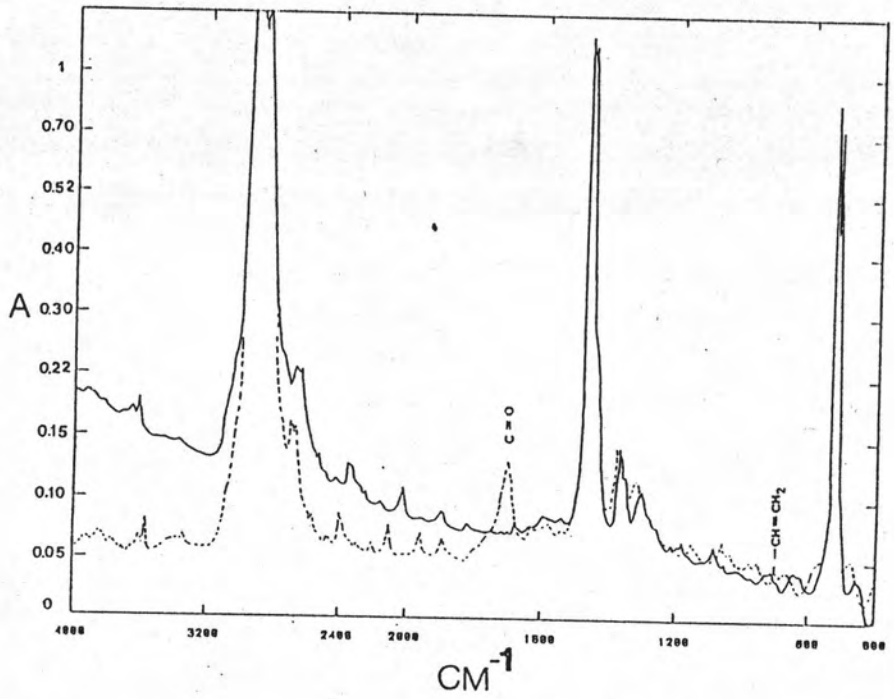


Figure 4.20 (c) FT-IR spectra of irradiated HDPE samples sensitized with 2-methylanthraquinone
——— unirradiated ; - - - irradiated for 8 hours

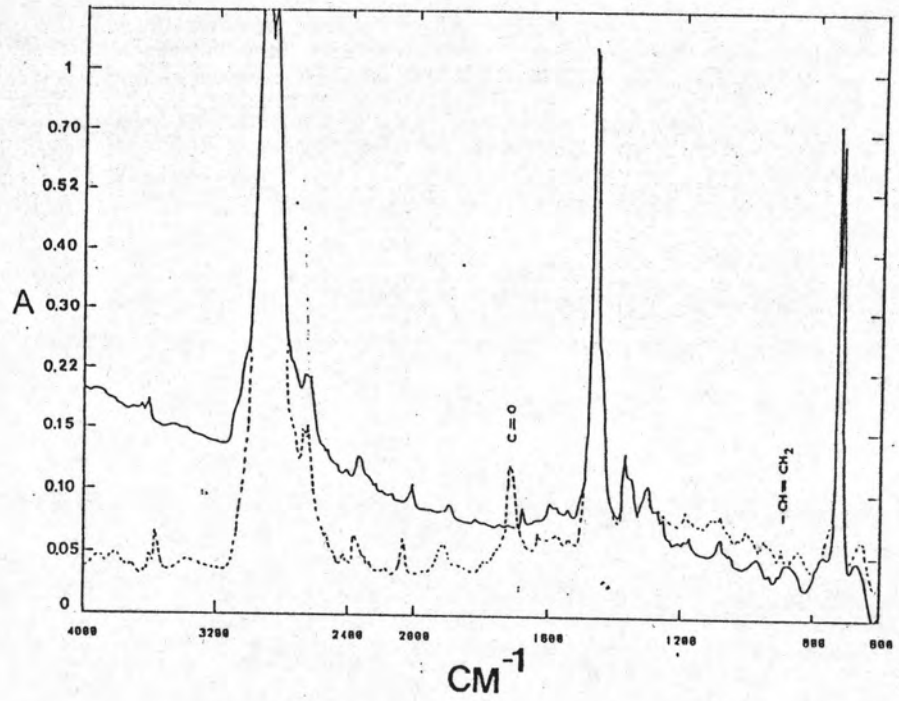


Figure 4.20 (d) FT-IR spectra of irradiated HDPE samples sensitized with 2-tert-butylanthraquinone
——— unirradiated ; - - - irradiated for 8 hours

Table 4.17 Changes in carbonyl and vinyl index of irradiated LDPE films

(a) Carbonyl index

Photosensitizer	Carbonyl index (I_{co})	
	original	30 hours
No additive	0.00	1.31
Benzophenone	1.00	1.48
4-Methoxybenzophenone	0.99	2.03
Thioxanthone	0.98	5.16
Anthraquinone	0.90	3.27
2-Methylanthraquinone	0.00	2.51
2-tert-Butylanthraquinone	0.68	2.49

(b) Vinyl index

Photosensitizer	Vinyl index (I_{vinyl})	
	original	30 hours
No additive	0.68	1.67
Benzophenone	1.46	2.01
4-Methoxybenzophenone	1.37	2.27
Thioxanthone	1.22	3.44
Anthraquinone	1.13	2.24
2-Methylanthraquinone	0.78	2.12
2-tert-Butylanthraquinone	1.01	1.40

Table 4.18 Changes in carbonyl and vinyl index of irradiated HDPE films

(a) Carbonyl index

Photosensitizer	Carbonyl index (I_{co})	
	original	8 hours
No additive	0.00	0.61
Benzophenone	0.00	1.54
4-Methoxybenzophenone	0.00	1.68
Thioxanthone	0.00	2.90
Anthraquinone	0.00	2.85
2-Methylanthraquinone	0.00	2.18
2-tert-Butylanthraquinone	0.00	2.74

(b) Vinyl index

Photosensitizer	Vinyl index (I_{vinyl})	
	original	8 hours
No additive	0.22	1.30
Benzophenone	0.24	1.32
4-Methoxybenzophenone	0.22	1.07
Thioxanthone	0.28	1.40
Anthraquinone	0.36	1.22
2-Methylanthraquinone	0.26	1.18
2-tert-Butylanthraquinone	0.31	1.24

4.3 Results of visual inspection for outdoor exposure polyethylene films

(a) Unsensitized LDPE film

(b) Sensitized LDPE film

Figure 4.21 Photographs of exposed LDPE film after 6 months

(a) Unsensitized HDPE film

(b) Sensitized HDPE film

Figure 4.22 Photographs of exposed HDPE film after 3 months