



CHAPTER 4

RESULTS

The effects of photosensitizers , anthraquinone and benzophenone , on injection high density polyethylene degradation by natural weathering and accelerated weathering were studied. High Density Polyethylene (HDPE) containing 2-photosensitizers (ratio of 1:1) in a concentration of 0 % , 1.0 % , 1.5 % and 2.0 % by weight were used as the sheetsamples. HDPE sheets were put under outdoor exposure for six months. In the accelerating test , the sheet samples were irradiated with 4 fluorescent lamps for 33 days and irradiated with a medium pressure mercury lamp for 240 hours. The changes of molecular weight , tensile strength , elongation at break and fourier transform infrared absorption of all samples before and after irradiation were used to study the photodegradation prrocess.

4.1 Natural weathering test

4.1.1 Result of tensile properties test

A typical example of the effect of UV light on the load-elongation (stress-strain) traces of both undoped and doped samples is shown in figure 4.1. It can be seen that the load of all samples is slightly different while the elongation decreases clearly as outdoor exposure time proceeds. So from this observation , the elongation at break is a key material property in studying the photodegradation process.

The effect off natural weathering on tensile strength and elongation at break of all samples is shown in figure 4.2-4.3 and table 4.1-4.2.

(a) Undoped HDPE

It can be seen from figure 4.2 that all mechanical characteristics of an undoped sample show a clear induction period of about 15 days. Upon further irradiation both tensile strength and molecular weight slightly increase followed by a slow decrease, while elongation at break exhibits a marked drop, it reaches 50 % of the starting value only after about 25 days, then this is followed by a slower decrease.

(b) Anthraquinone and Benzophenone doped HDPE

The behavior of samples containing photosensitizers at a concentration of 1.0 %, 1.5 % and 2.0 % by weight differed from that of undoped HDPE. The elongation at break value decreased drastically in the first 15 days, it almost decreased to 100 % of the starting value. However, the elongation at break values of doped samples approached the values of undoped sample in the thirteenth month. With regards to the concentration of the photosensitizers, the higher the concentration, the lower the tensile properties value: but the values are only slightly different.

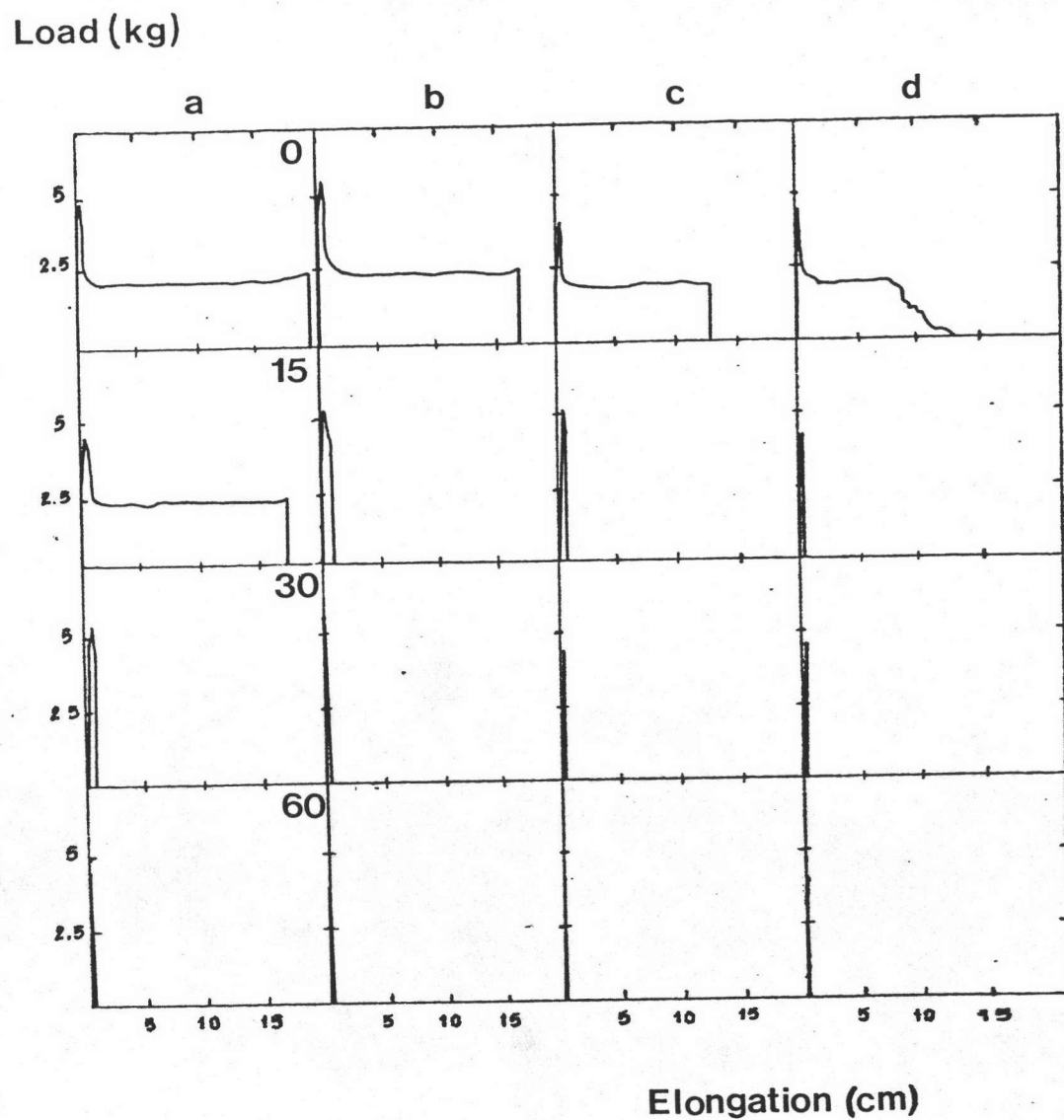


Figure 4.1 Load-elongation (stress-strain) curves of outdoor exposure sheets at various exposure times (indicates on curves in days) : a. 0 % photosensitizer ; b. 1.0 % photosensitizers ; c. 1.5 % photosensitizers ; d. 2.0 % photosensitizers as a function of exposure time

Table 4.1 Tensile Strength of outdoor exposure sheets

Photosensitizer Content (%)	Tensile Strength (kg/mm ²)			
	0	1.0	1.5	2.0
Exposure Time				
Original	2.78	2.66	2.60	2.56
15 days	2.83	2.81	2.81	2.78
1 month	2.80	2.74	2.76	2.72
2 months	2.76	2.39	2.10	1.97
3 months	2.65	2.37	2.01	1.92
4 months	2.56	2.29	1.90	1.86
5 months	2.10	1.96	1.85	1.76
6 months	1.91	1.54	1.50	1.42

Table 4.2 Elongation of outdoor exposure sheets

Photosensitizer Content (%)	Elongation (%) <i>at break</i>			
	0	1.0	1.5	2.0
Exposure Time				
Original	729	668	660	640
15 days	716	33	18.4	18
1 month	154	13.33	11.33	7
2 months	10.67	4	4	4
3 months	<1	<1	<1	<1
4 months	<1	<1	<1	<1
5 months	<1	<1	<1	<1
6 months	<1	<1	<1	<1

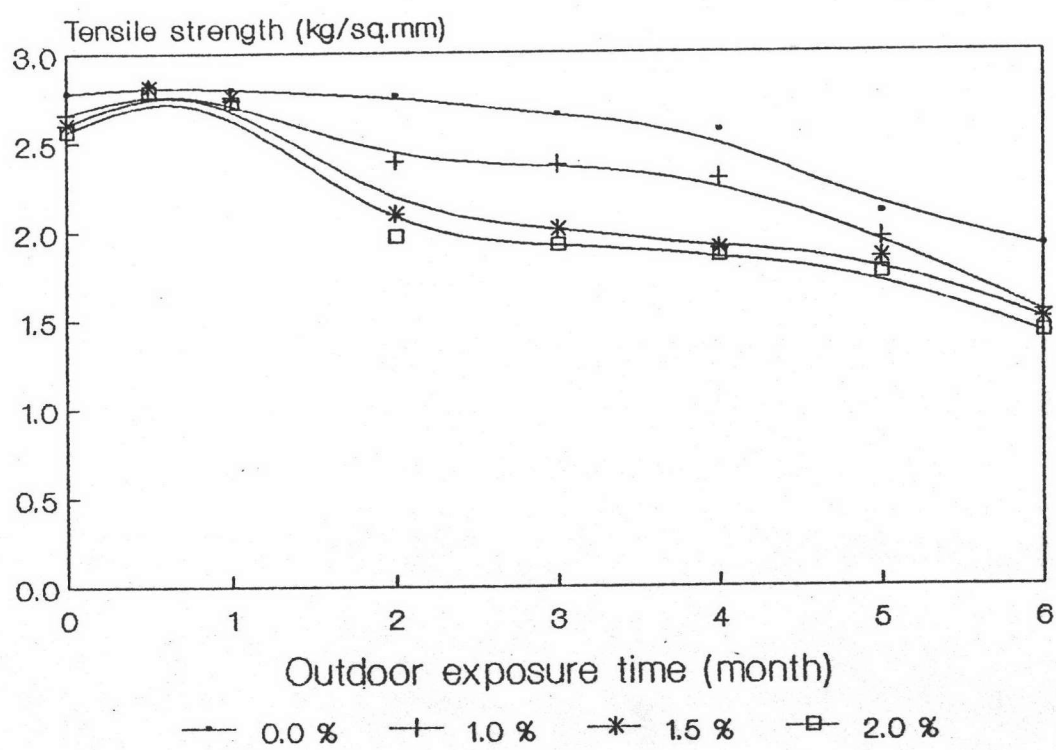


Figure 4.2 Tensile strength as a function of outdoor exposure time for HDPE sheets at various concentration of photosensitizers

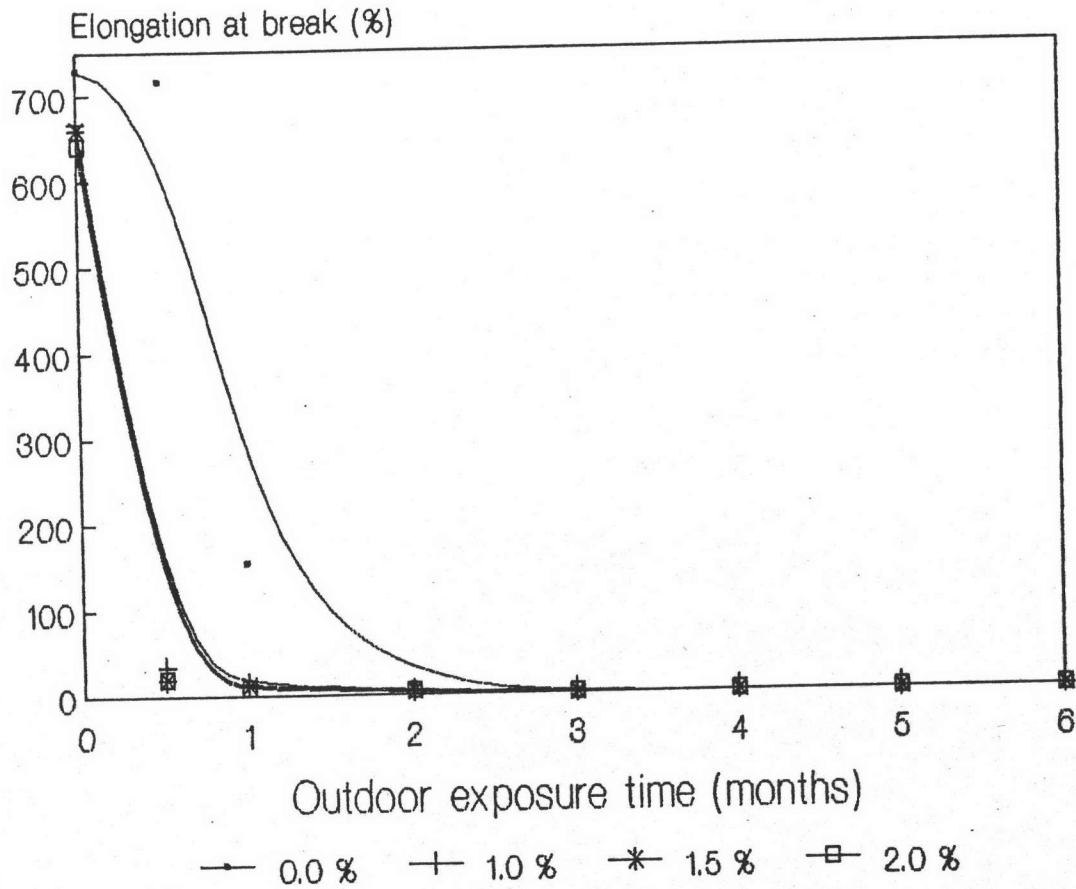


Figure 4.3 Elongation at break as a function of outdoor exposure time for HDPE sheets at various concentration of photosensitizers

4.1.2 Result of molecular weight test

Figure 4.4 show the molecular weight traces of undoped and doped HDPE samples as a function of outdoor exposure time. Molecular weight datas are shown in table 4.3.

(a) Undoped HDPE

The molecular weight of undoped HDPE sheets increases from the starting value of UV exposure to a maximum value in the first month and decreases to a lower molecular weight than the value before exposure in the second month , afterward , it decreases gradually with exposure time.

(b) Anthraquinone and Benzophenone doped HDPE

The samples exposed only for 15 days were characterized by the presence of large quantities of insoluble materials. Even if the molecular weight obtained from the samples including insoluble materials must be considered inaccurate , a progressive decay of molecular weight is observed. The greatest reduction in molecular weight of doped HDPE sheets takes place in the 15 days from the beginning of exposure time , it decreases about 44 % to 76 % as the concentration value and then decreases continuously with exposure time. Similarity as tensile property , the higher the concentration , the lower the molecular weight values.

Table 4.3 Viscosity and Molecular Weight of outdoor exposure sheets

Photosensitizer Content (%)	Viscosity				Molecular Weight. x 10 ⁻⁴			
	0	1.0	1.5	2.0	0	1.0	1.5	2.0
Exposure Time								
Original	1.22	1.35	1.39	1.55	5.08	5.87	6.22	7.15
15 days	1.23	0.89	0.67	0.57	5.14	3.24	2.16	1.71
1 month	1.25	0.60	0.52	0.43	5.26	1.84	1.50	1.14
2 months	1.00	0.58	0.50	0.41	3.82	1.76	1.42	1.07
3 months	0.98	0.54	0.44	0.36	3.71	1.58	1.18	0.89
4 months	0.68	0.45	0.35	0.33	2.20	1.22	0.85	0.78
5 months	0.63	0.44	0.33	0.30	1.98	1.18	0.85	0.68
6 months	0.55	0.35	0.30	0.24	1.63	0.85	0.68	0.50

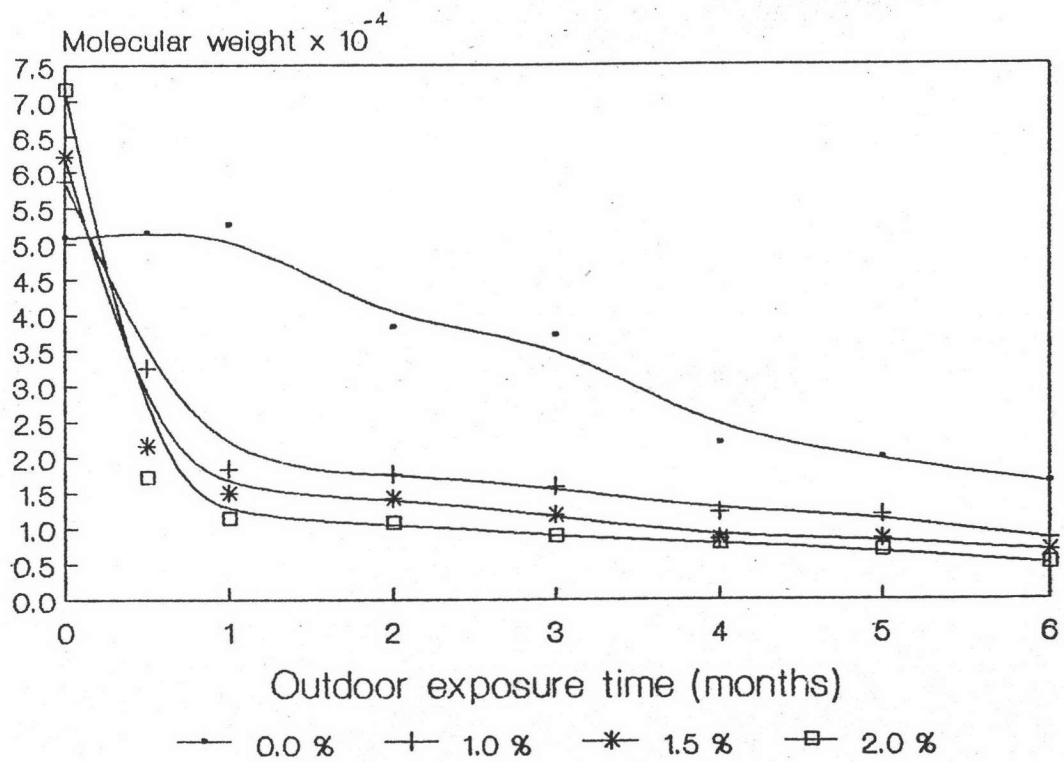


Figure 4.4 Molecular weight traces as a function of outdoor exposure time at various concentration of photosensitizers.

4.1.3 Result of Fourier Transform Infrared Absorption test

The FTIR spectra of all samples exposed in natural weathering were obtained and typical spectra are shown in figure 4.5. Absorption peaks were observed in

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

(b) the 1617 cm^{-1} band corresponding to the carbonyl group in the molecule of photosensitizers, Anthraquinone and Benzophenone

(c) the intensity of a maximum of a broad band at 3370 cm^{-1} , reflecting the concentration of hydroxyl groups in the HDPE sheets.

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

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

The relative absorbance of HDPE carbonyl groups (A_{1715}) is plotted in figure 4.6 from data in table 4.4 as a function of the exposure time. The rate of formation of carbonyl compound for doped samples is highest at the beginning of outdoor exposure and subsequently slows down. The carbonyl intensity of doped samples is substantially higher than that of undoped ones.

In figure 4.7 the carbonyl group of the band at 1677 cm^{-1} is plotted as a function of the exposure time and the data is shown in table 4.5. The rapid decrease in the concentration of carbonyl groups corresponding to photosensitizers is clearly visible. The results show that the photosensitizing additives are consumed at a surprisingly early stage of the photosensitized oxidation: the corresponding absorbance disappears completely after about one month of outdoor exposure with all doped samples.

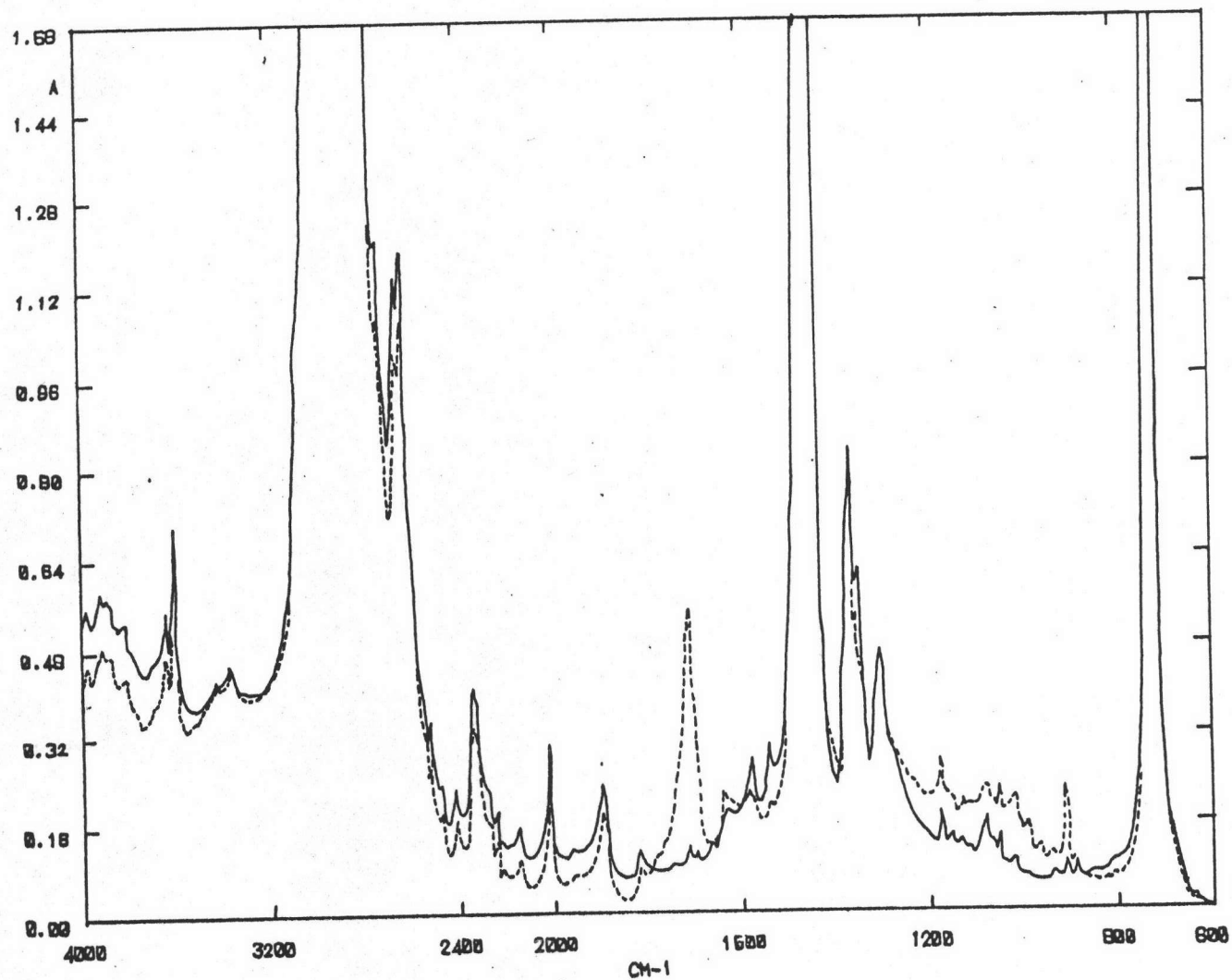


Figure 4.5 a FT-IR spectra of outdoor exposure HDPE samples at 0 % photosensitizer
 ----- nonirradiated ; - - - - - irradiated for 3 months.

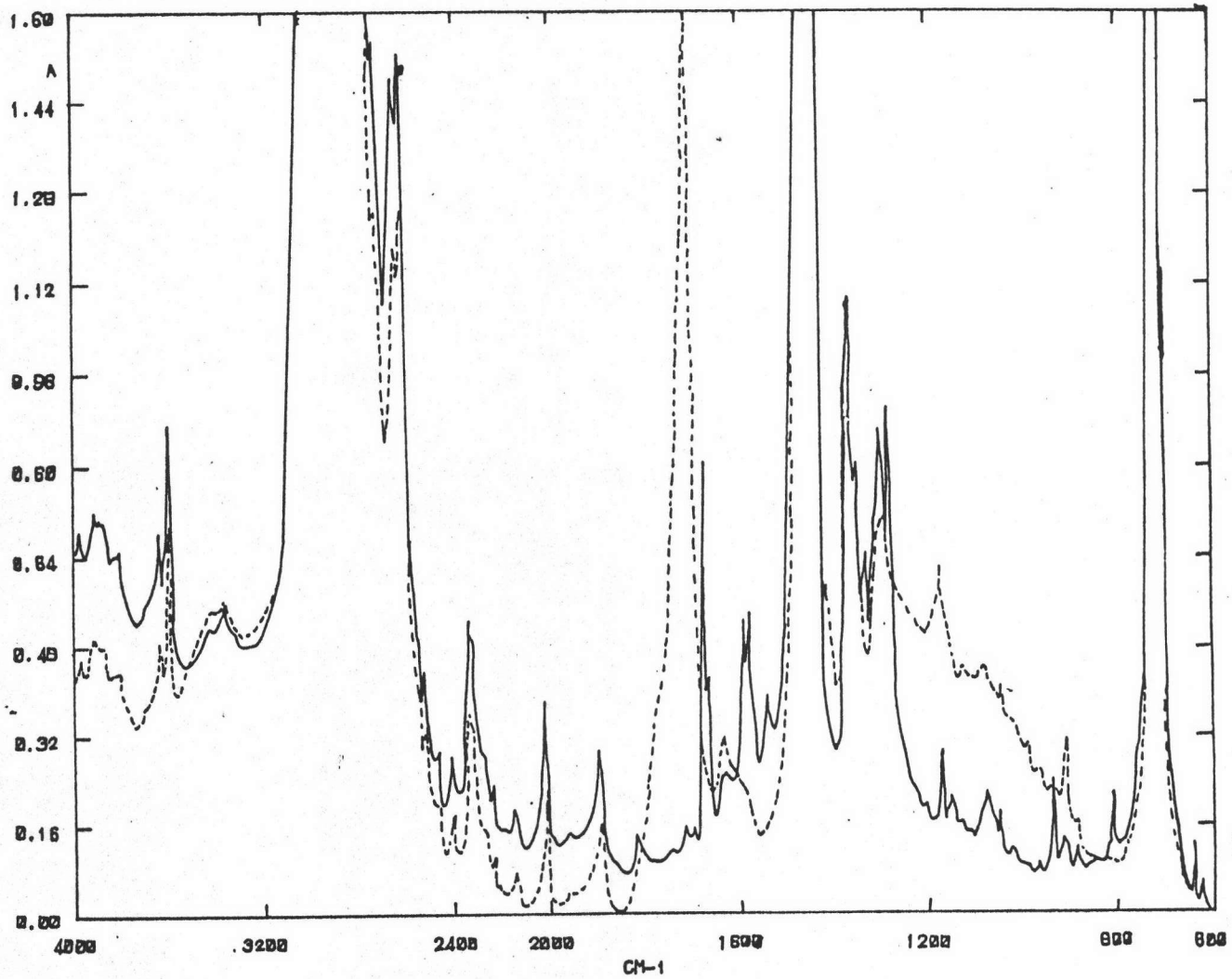


Figure 4.5 b FT-IR spectra of outdoor exposure HDPE samples at 1.0 % photosensitizer
 ----- nonirradiated ; - - - - - irradiated for 3 months.

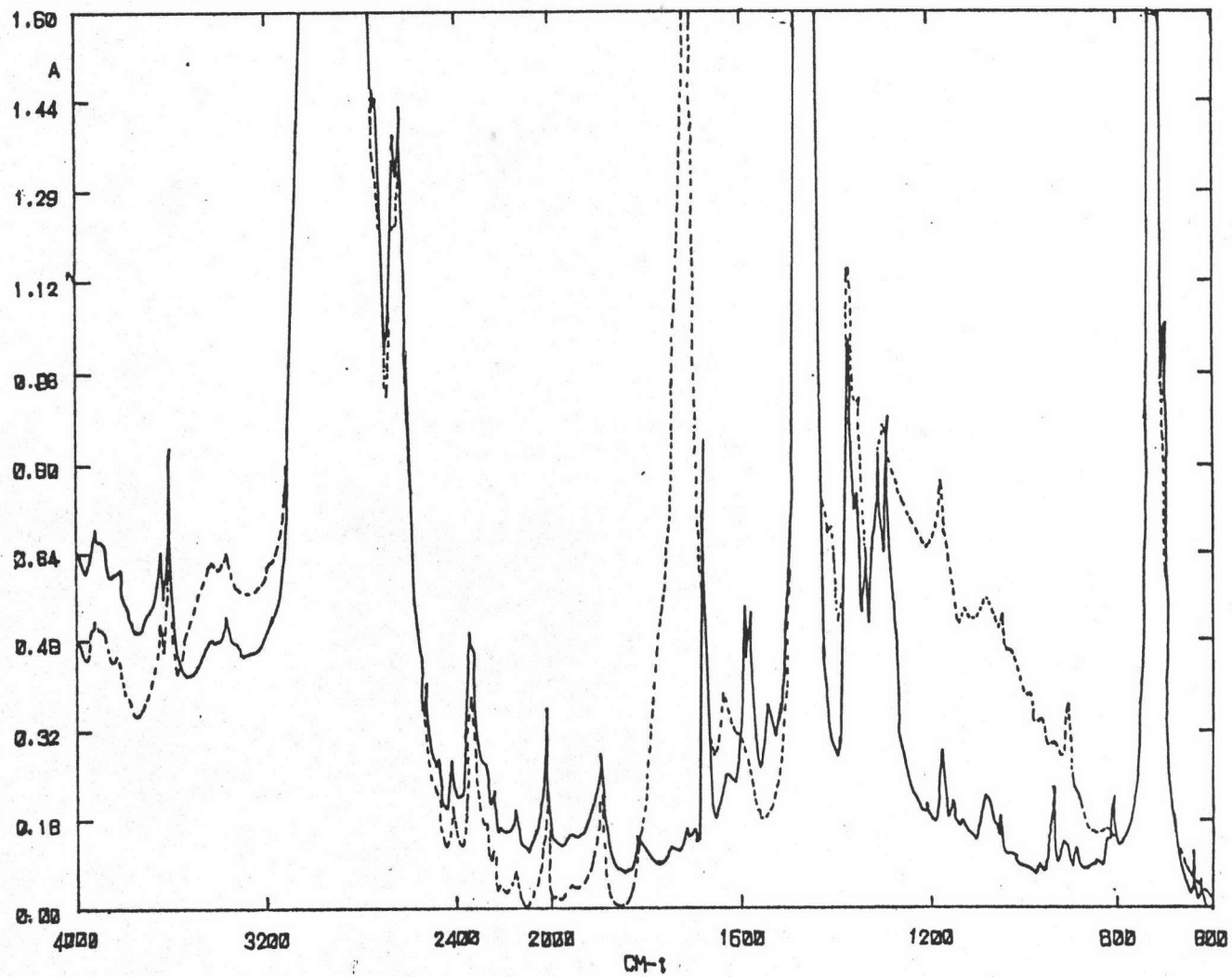


Figure 4.5 c FT-IR spectra of outdoor exposure HDPE samples at 1.5 % photosensitizer
 ----- nonirradiated ; - - - - - irradiated for 3 months.

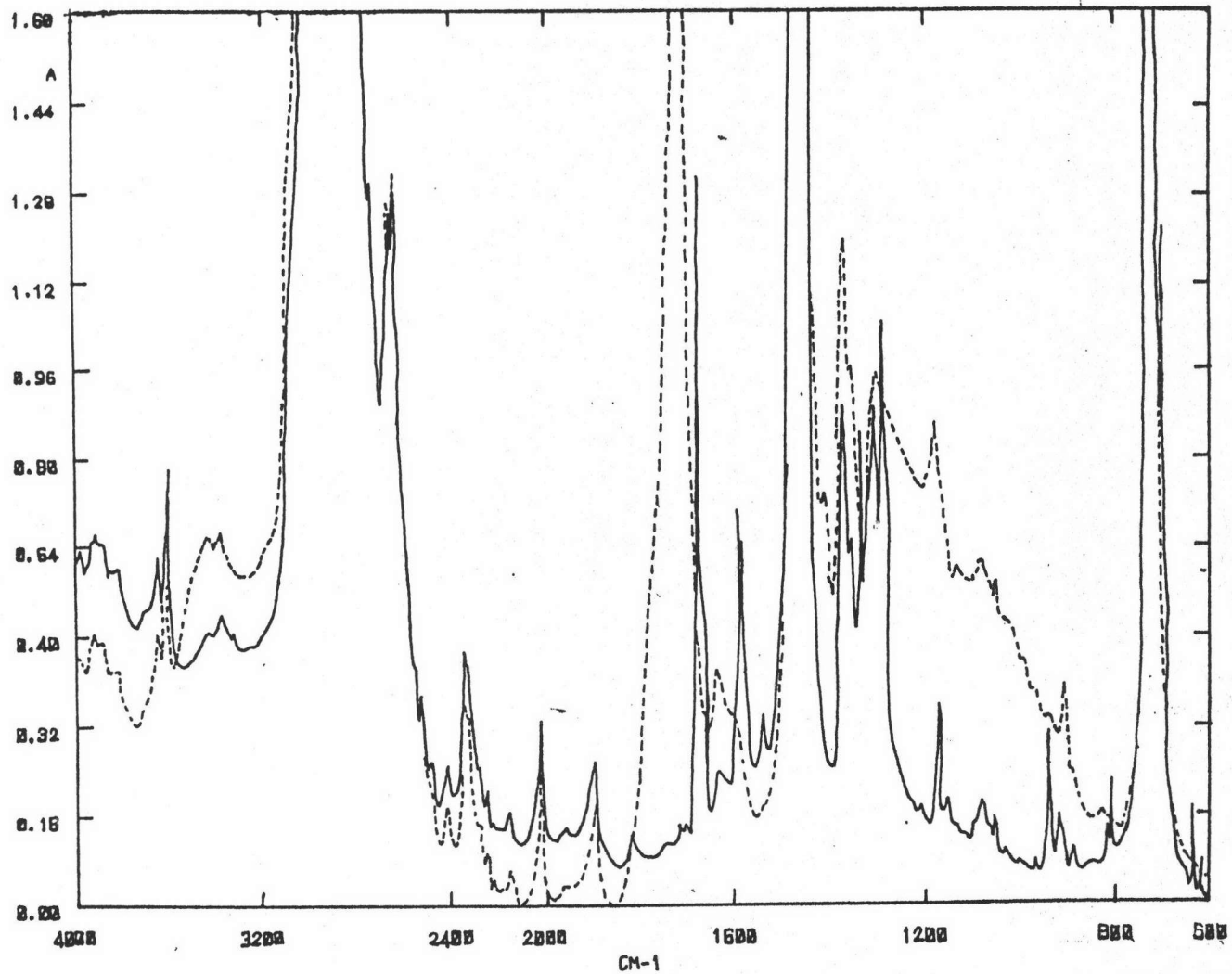


Figure 4.5 d FT-IR spectra of outdoor exposure HDPE samples at 2.0 % photosensitizer
 ----- nonirradiated ; - - - - - irradiated for 3 months.

Table 4.4 Carbonyl Index in PE chain of outdoor exposure sheets

Photosensitizer Content (%)	Carbonyl Index (1715 cm^{-1})			
	0	1.0	1.5	2.0
Exposure Time				
Original	0.3846	0.4022	0.4139	0.4366
15 days	0.5077	2.3830	2.8793	3.0780
1 month	0.6506	3.5571	3.6035	4.7734
2 months	0.9980	5.7444	7.1845	7.7701
3 months	2.2992	7.0911	8.7868	11.1190
4 months	2.4383	9.6764	11.3715	12.0054
5 months	7.4484	11.7886	13.0474	15.1283
6 months	7.2482	13.2890	13.7656	14.2840

Table 4.5 Carbonyl index in photosensitizer of outdoor exposure sheets

Photosensitizer Content (%)	Carbonyl index in photosensitizer			
	0	1.0	1.5	2.0
Exposure Time				
Original	0	1.4719	2.4333	2.8379
15 days	0	0	0	0.3740
1 month	0	0	0	0
2 months	0	0	0	0
3 months	0	0	0	0
4 months	0	0	0	0
5 months	0	0	0	0
6 months	0	0	0	0

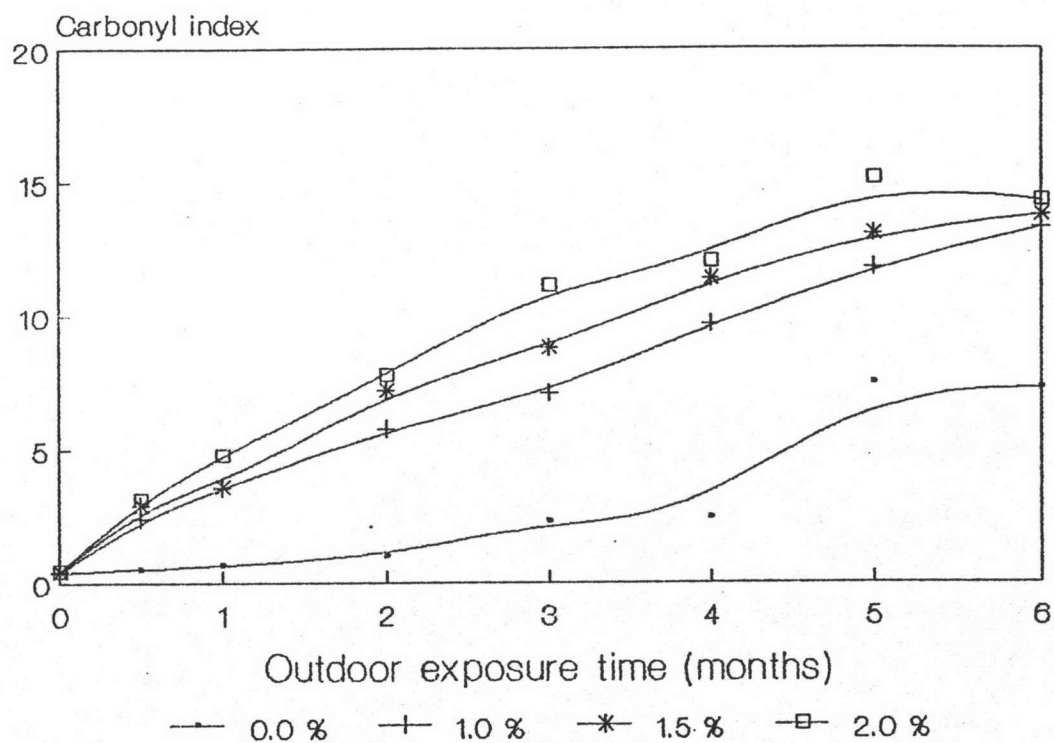


Figure 4.6 Changes of the relative FT-IR absorbance of carbonyl groups in PE chain as a function of outdoor exposure time at various concentration of photosensitizers.

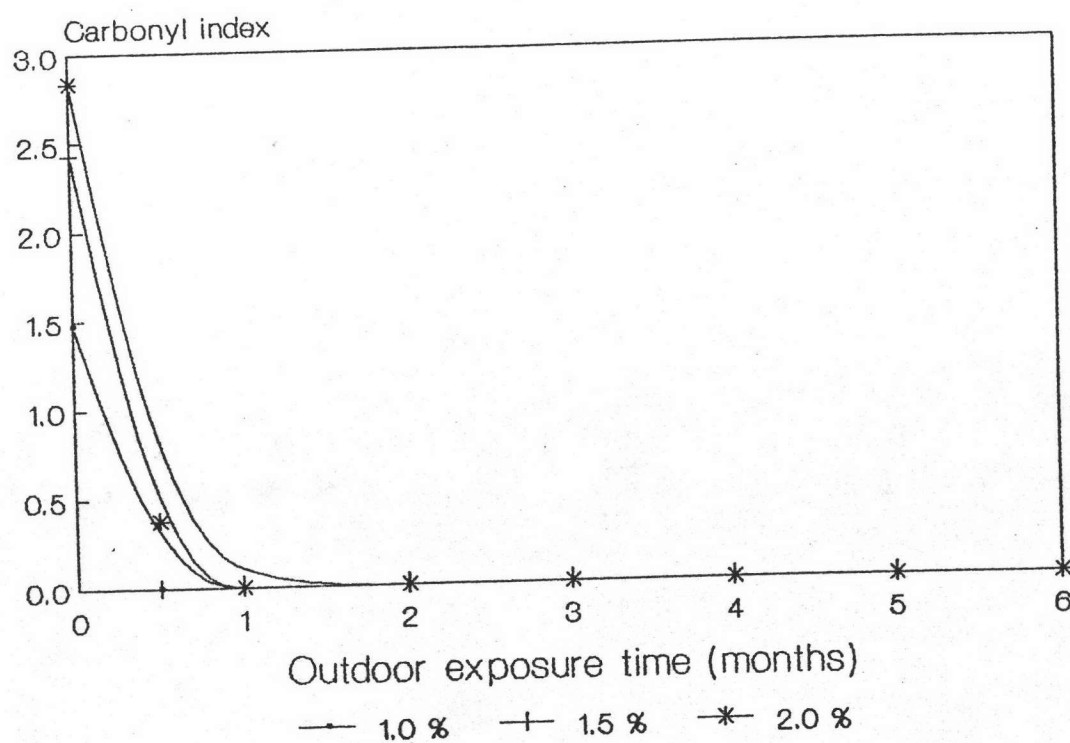


Figure 4.7 Changes of the relative FT-IR absorbance of carbonyl groups in photosensitizers as a function of outdoor exposure time at various concentration of photosensitizers.

Table 4.6 Hydroxyl Index of outdoor exposure sheets

Exposure Time \ Photosensitizer Content (%)	Hydroxyl Index (3371 cm^{-1})			
	0	1.0	1.5	2.0
Original	1.5102	1.4856	1.6103	1.5812
15 days	1.4399	2.0254	2.1971	2.1429
1 month	1.5052	2.1892	2.1879	2.4476
2 months	1.5703	2.3688	2.5727	2.7677
3 months	1.8306	2.4678	2.6268	2.9075
4 months	1.7884	2.9916	2.8030	3.0828
5 months	2.6050	3.2095	3.1636	3.1540
6 months	2.6971	3.4678	3.3203	3.4171

Table 4.7 Vinyl Index of outdoor exposure sheets

Exposure Time \ Photosensitizer Content (%)	Vinyl Index (909 cm^{-1})			
	0	1.0	1.5	2.0
Original	0.2903	0.3807	0.3101	0.4714
15 days	0.3294	0.5615	0.6264	0.6917
1 month	0.3965	0.7462	0.7454	0.9078
2 months	0.5560	1.0924	1.2417	1.3452
3 months	0.9275	1.3789	1.5221	1.7004
4 months	0.8947	1.8009	1.6255	1.7217
5 months	1.8611	1.9625	1.8419	2.1567
6 months	2.1068	2.5503	2.3215	2.5491

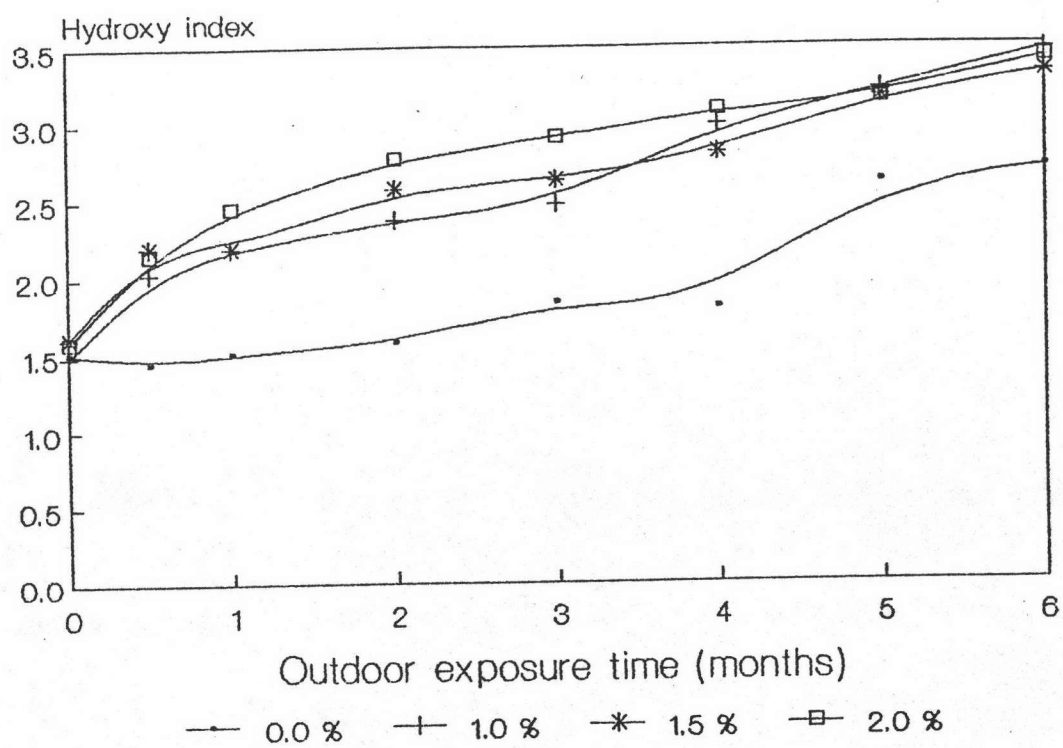


Figure 4.8 Changes of the relative FT-IR absorbance of hydroxy groups as a function of outdoor exposure time at various concentration of photosensitizers.

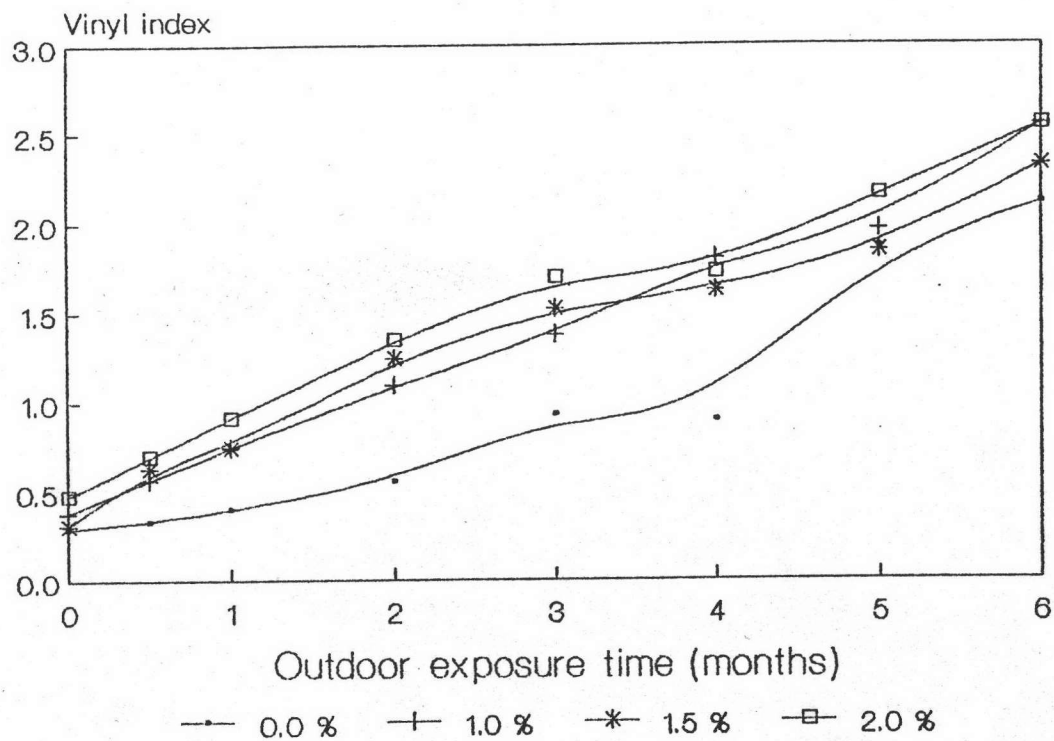


Figure 4.9 Changes of the relative FT-IR absorbance of vinyl groups as a function of outdoor exposure time at various concentration of photosensitizers

Figure 4.8 shows the changing intensity of the hydroxy band during outdoor exposure : it increases from the beginning of outdoor exposure , without induction period , with a maximum slope in the first month. An approximately linear increase of vinyl group at 909 cm^{-1} corresponding to the vinyl band can be observed for all samples as shown in figure 4.9. The greatest increase of the carbonyl and vinyl groups takes place in the exposure range corresponding to the greatest diminution of the tensile properties.

4.2 Accelerated weathering test by four fluorescent lamps

In parallel with the outdoor exposure test , accelerated test using 4-fluorescent lamps were carried out. The following results were found.

4.2.1 Result of tensile properties test

The load-elongation (stress-strain) diagrams of HDPE sheet irradiated with 4-fluorescent lamps are shown in figure 4.10. It can be seen that the load passes through a maximum and then reaches a plateau value : this behavior is the same as that of outdoor exposure sheets.

The change in tensile strength and elongation at break with irradiation time is shown in figure 4.11-4.12. Tensile properties data is shown in table 4.8-4.9.

The tensile strength of both undoped and doped HDPE samples increases from the start of irradiation time and gradually decreases when the irradiation time proceeds but the tensile strength value of samples irradiated for 33 days is still higher than that of the original samples value. The change of elongation at break of undoped samples before and after UV irradiation decreases linearly and approaches zero after

irradiation for 24 days. Elongation at break of doped samples decreases rapidly after 3 day of irradiation and a similar correlation exists for the change of molecular weight. The elongation at break approaches a zero value within 12 days. So it can be seen clearly that the elongation at break is more sensitive to degradation than is the tensile strength.

4.2.2 Result of molecular weight test

When undoped and doped HDPE sheets are degraded by irradiated with 4-fluorescent lamps, the molecular weight of undoped samples slightly decreases after some increases in about 20 days but the molecular weight of doped samples suddenly decreases in six days. Figure 4.13 shows molecular weight traces of HDPE samples irradiated with 4-fluorescent lamps as a function of irradiation time and table 4.10 shows molecular weight data of all samples.

4.2.3 Result of fourier transform infrared absorption test

The FTIR spectra of unirradiated and photoirradiated HDPE sheets at various concentrations of photosensitizers were measured and typical spectra are shown in figure 4.14. Changes in the 3370, 1715, 1677 and 909 cm^{-1} region have been detected and shown in figure 4.15-4.18 as a function of irradiation time, respectively. A continuous increase is observed in the band at 3370 cm^{-1} and 909 cm^{-1} . The band at 1715 cm^{-1} increases with irradiation time and effects the peak at 1677 cm^{-1} which decrease suddenly from the beginning of irradiation time.

Load (kg)

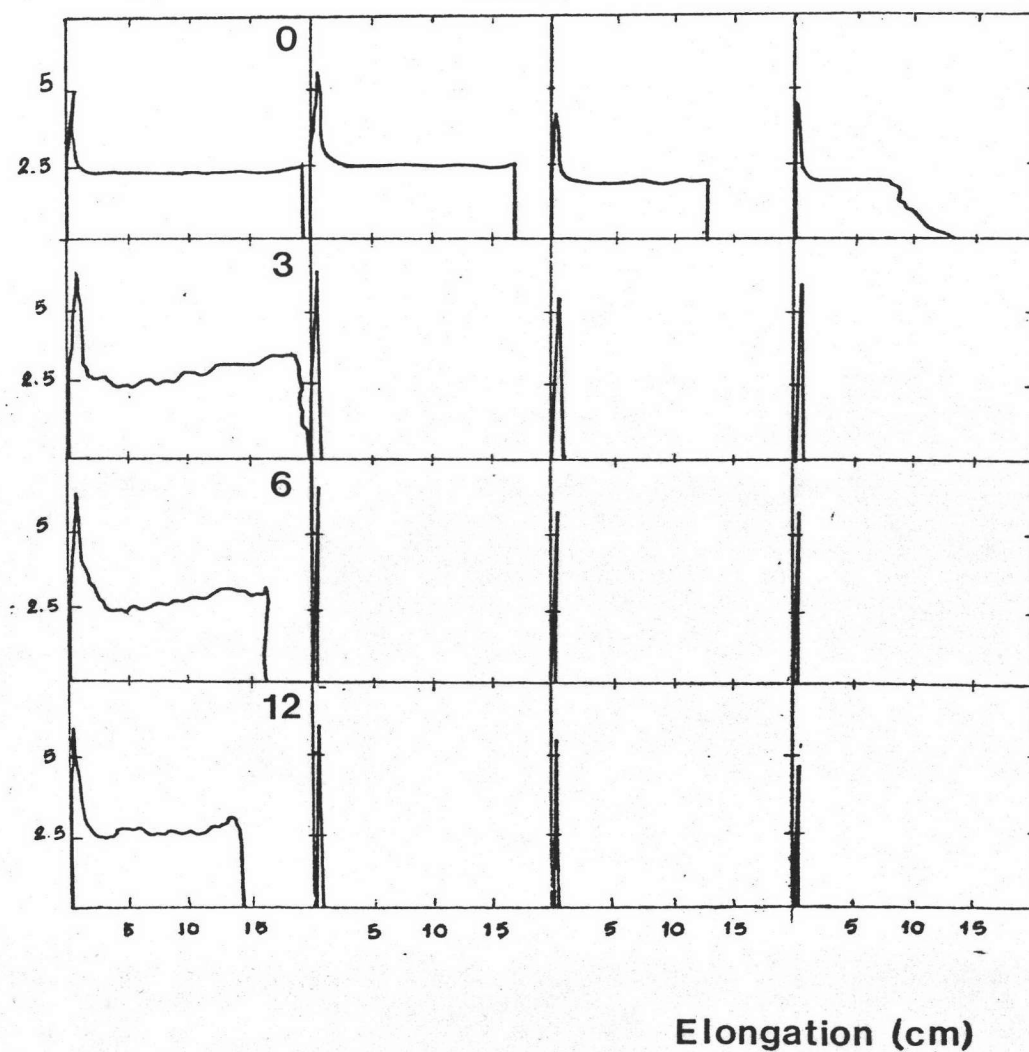


Figure 4.10 Load-elongation (stress-strain) curves for HDPE sheets at irradiation times (indicated on curves in days) : a. 0 % photosensitizer ; b. 1.0 % photosensitizers ; c. 1.5 % photosensitizers ; d. 2.0 % photosensitizers.

Table 4.8 Tensile Strength of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Tensile Strength (kg/mm ²)			
	0	1.0	1.5	2.0
Exposure Time(days)				
Original	2.78	2.66	2.60	2.56
6	3.54	3.43	3.48	3.51
15	3.37	3.25	3.46	3.47
24	3.26	3.10	3.11	2.91
33	3.12	2.91	2.90	2.80

Table 4.9 Elongation of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Elongation (%)			
	0	1.0	1.5	2.0
Exposure Time(days)				
Original	729	668	660	640
6	710	6	6	6
15	512	<1	<1	<1
24	<1	<1	<1	<1
33	<1	<1	<1	<1

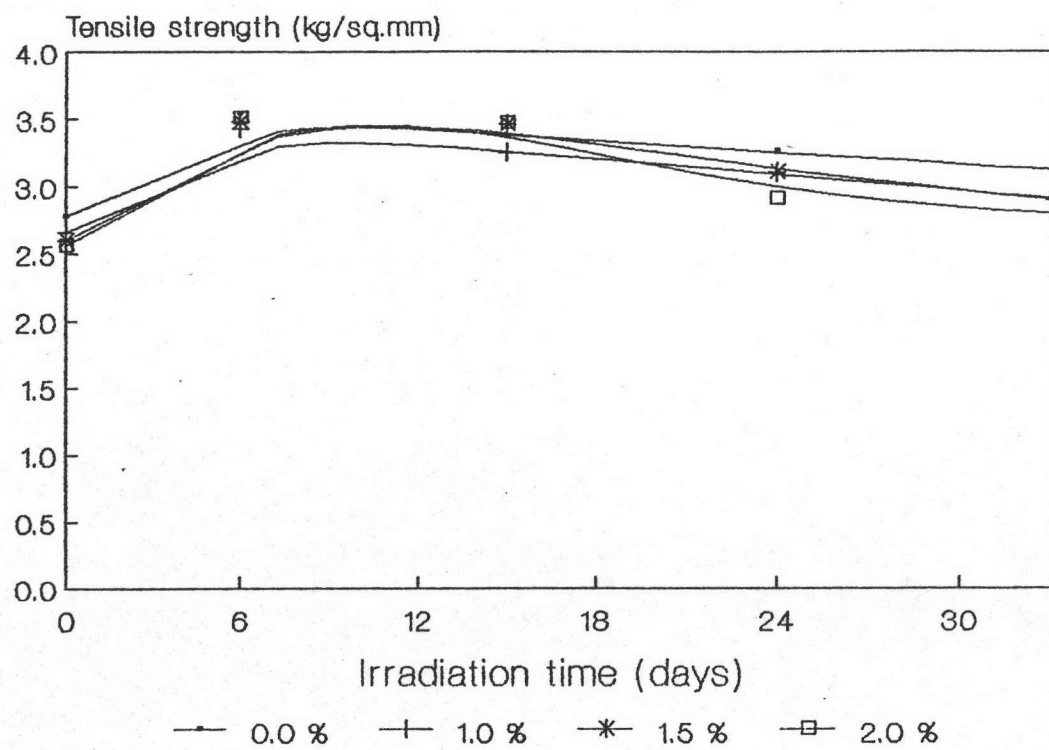


Figure 4.11 Tensile strength as a function of irradiation time for HDPE sheets at various concentration of photosensitizers.

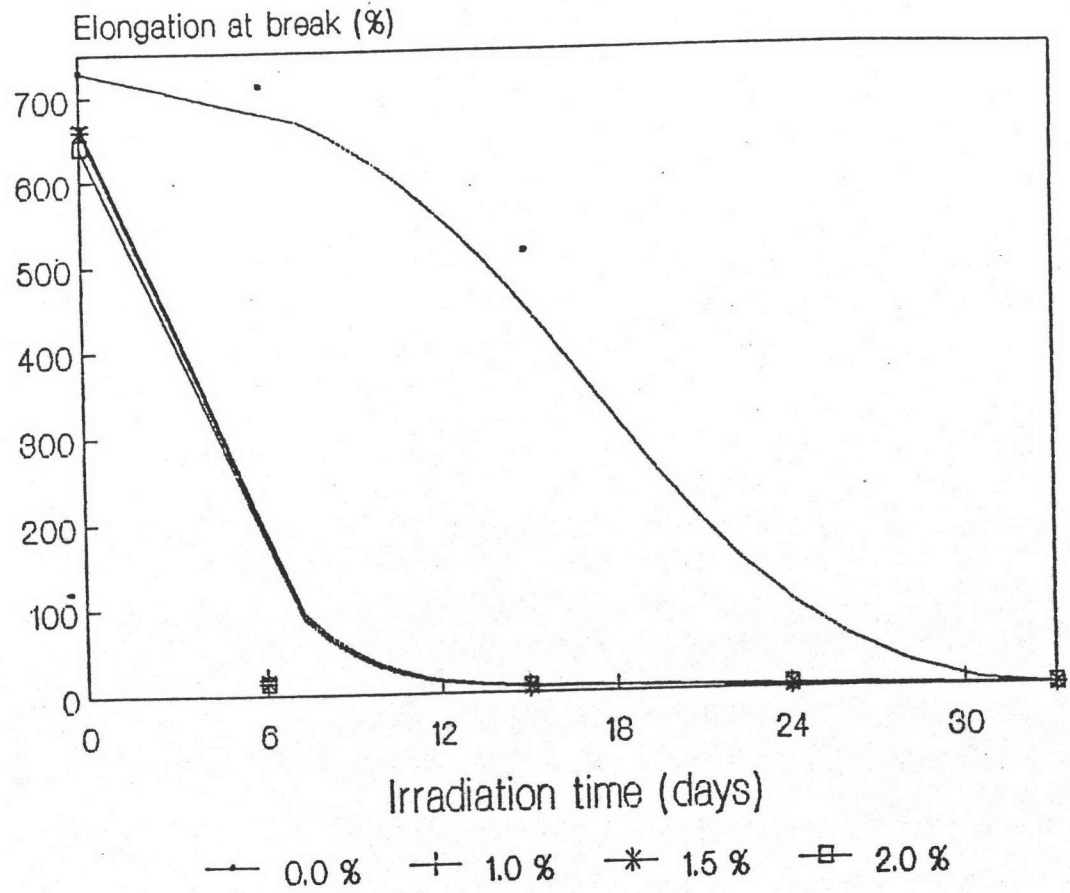


Figure 4.12 Elongation at break as a function of irradiation time for HDPE sheets at various concentration of photosensitizers.

Table 4.10 Viscosity and Molecular Weight of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Viscosity				Molecular Weight $\times 10^{-4}$			
	0	1.0	1.5	2.0	0	1.0	1.5	2.0
Original	1.22	1.35	1.39	1.55	5.08	5.87	6.22	7.15
6	1.21	1.00	0.78	0.55	5.02	3.82	2.66	1.58
15	1.15	0.57	0.50	0.47	4.67	1.71	1.42	1.30
24	1.00	0.46	0.41	0.34	3.82	1.26	1.07	0.82
33	0.85	0.44	0.38	0.32	3.03	1.18	0.96	0.75

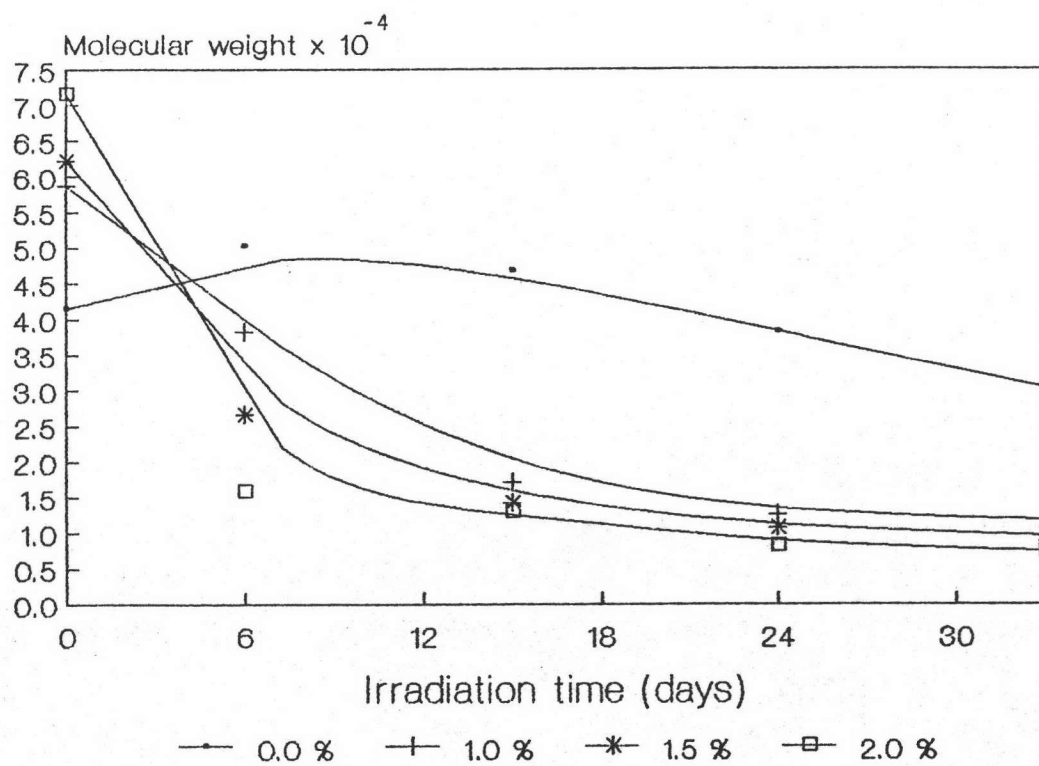


Figure 4.13 Molecular weight traces of HDPE sheets as a function of irradiation time at various concentration of photosensitizers

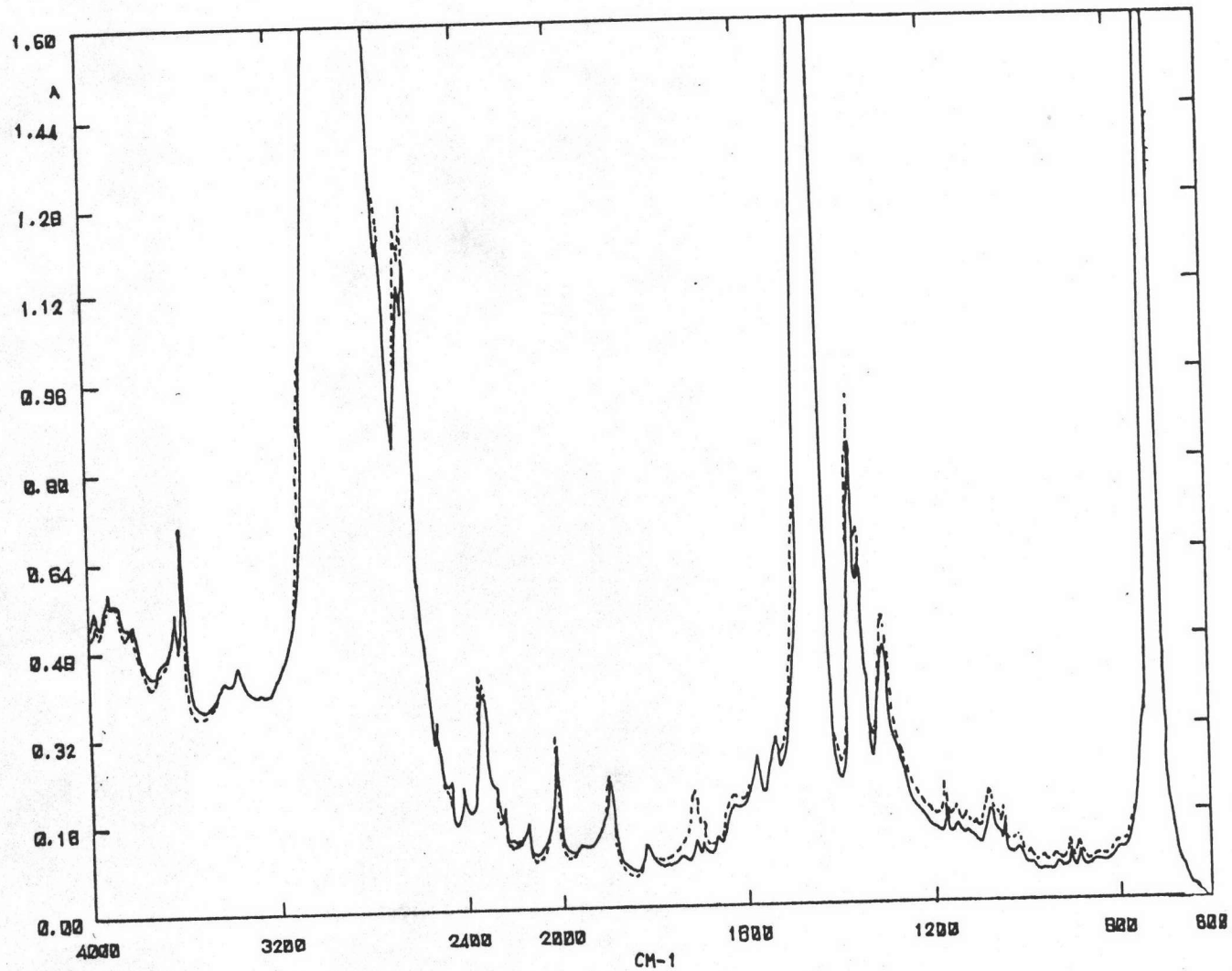


Figure 4.14 a FT-IR spectra of irradiated HDPE samples at 0 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 15 days.

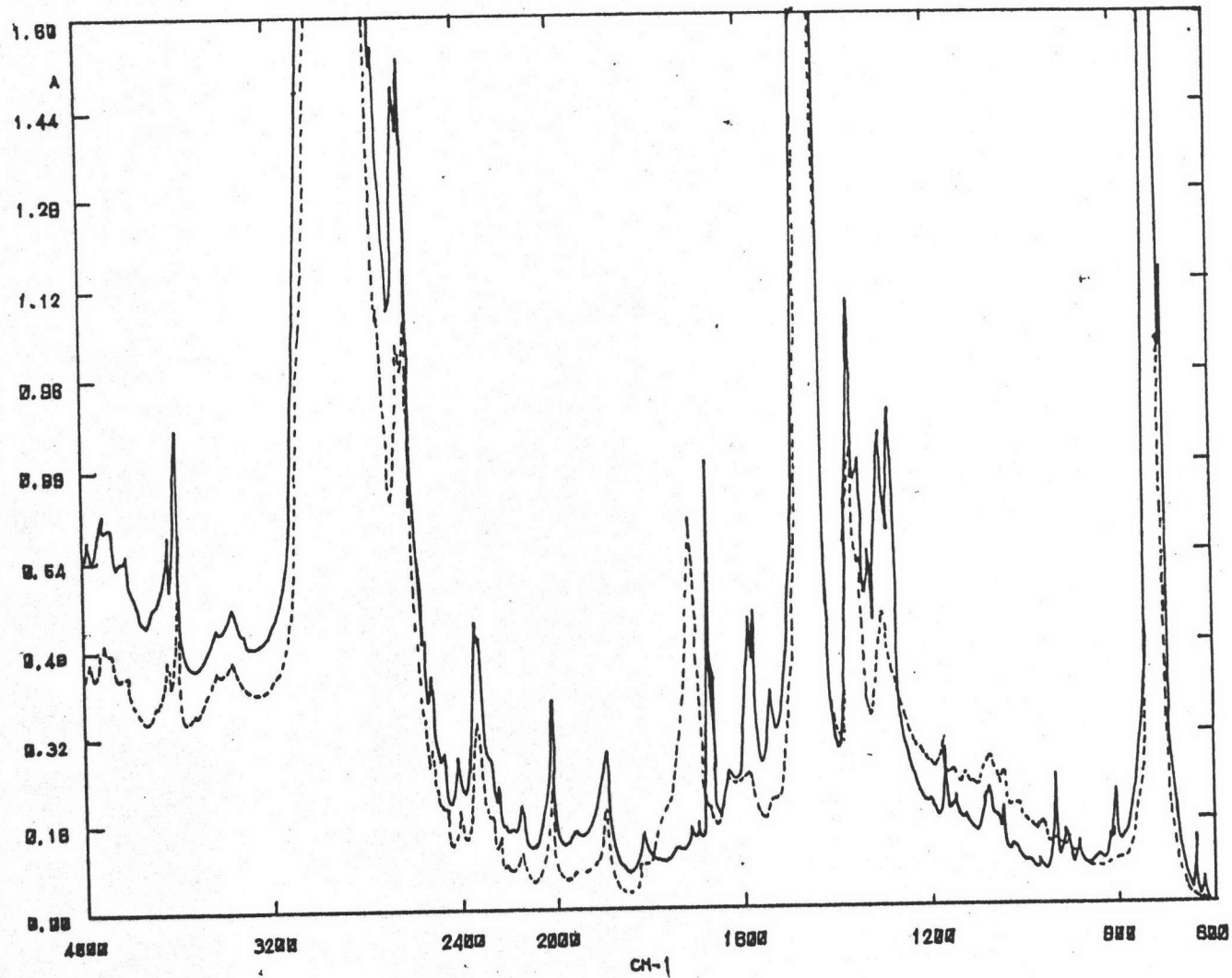


Figure 4.14 b FT-IR spectra of irradiated HDPE samples at 1.0 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 15 days.

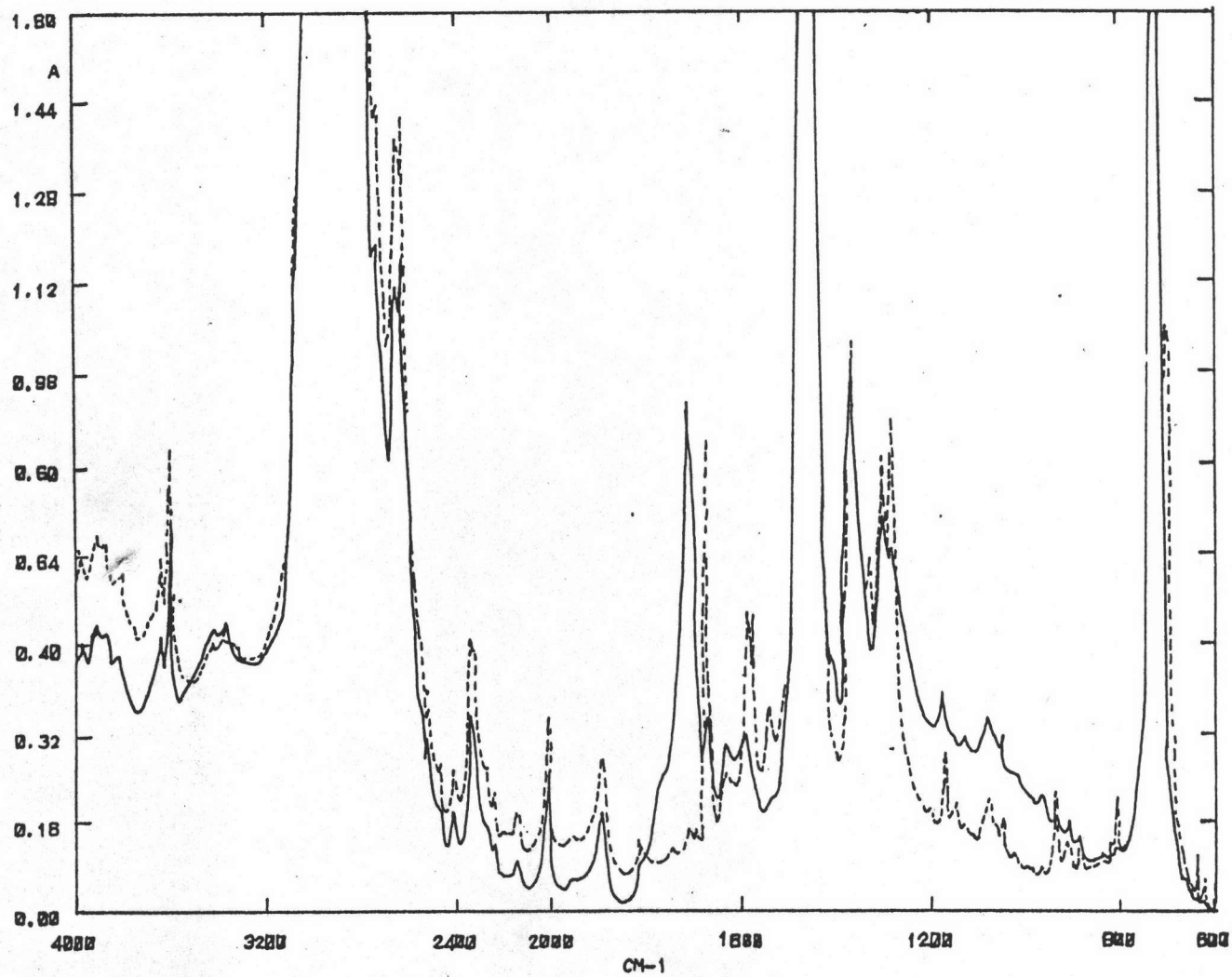


Figure 4.14 c FT-IR spectra of irradiated HDPE samples at 1.5 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 15 days.

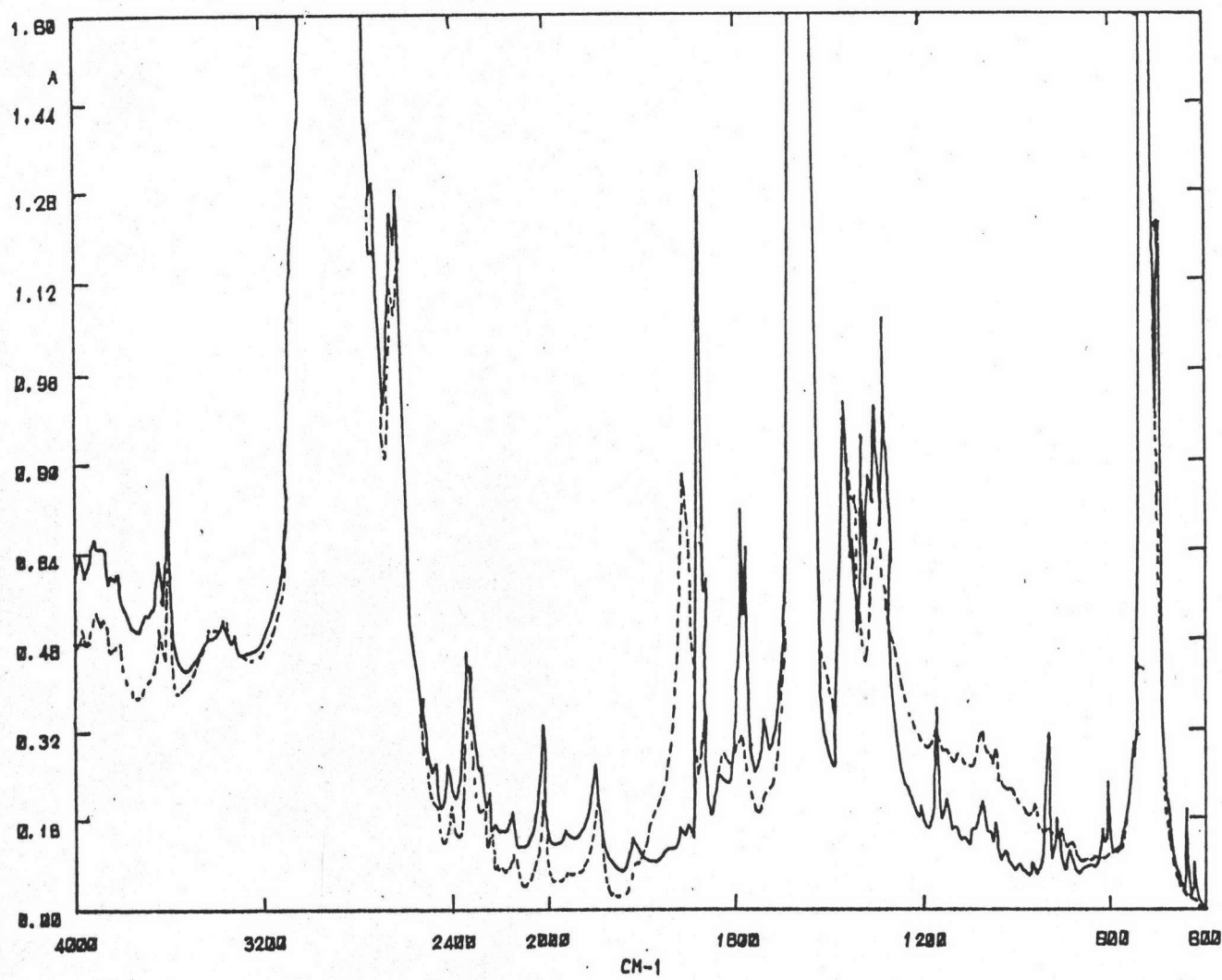


Figure 4.14 d FT-IR spectra of irradiated HDPE samples at 2.0 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 15 days.

Table 4.11 Carbonyl Index in PE chain of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Carbonyl Index (1715 cm^{-1})			
	0	1.0	1.5	2.0
Exposure Time(days)				
Original	0.3846	0.4022	0.4139	0.4366
6	0.4533	1.8071	1.4742	2.1289
15	0.6544	2.9637	3.1165	3.8261
24	1.0247	3.4346	4.1613	5.1499
33	1.4754	5.5017	6.0580	6.1044

Table 4.12 Carbonyl index in photosensitizer of HDPE sheets irradiated with 4 fluorescent lamps

Photosensitizer Content (%)	Carbonyl index in photosensitizer			
	0	1.0	1.5	2.0
Exposure Time(days)				
Original	0	1.4719	2.4333	2.8379
6	0	1.0073	2.9268	1.8541
15	0	0.6625	1.3142	1.4045
24	0	0	1.2549	1.2186
33	0	0	0	0

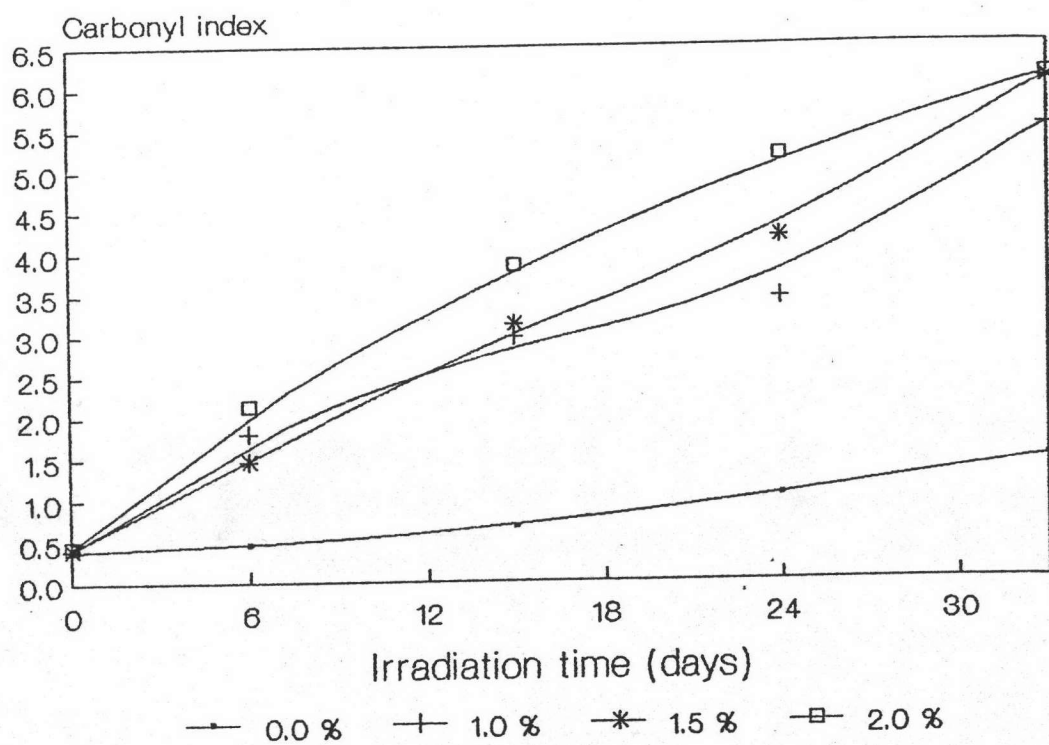


Figure 4.15 Changes of the relative FT-IR absorbance of carbonyl groups in PE chain as a function of irradiation time at various concentration of photosensitizers.

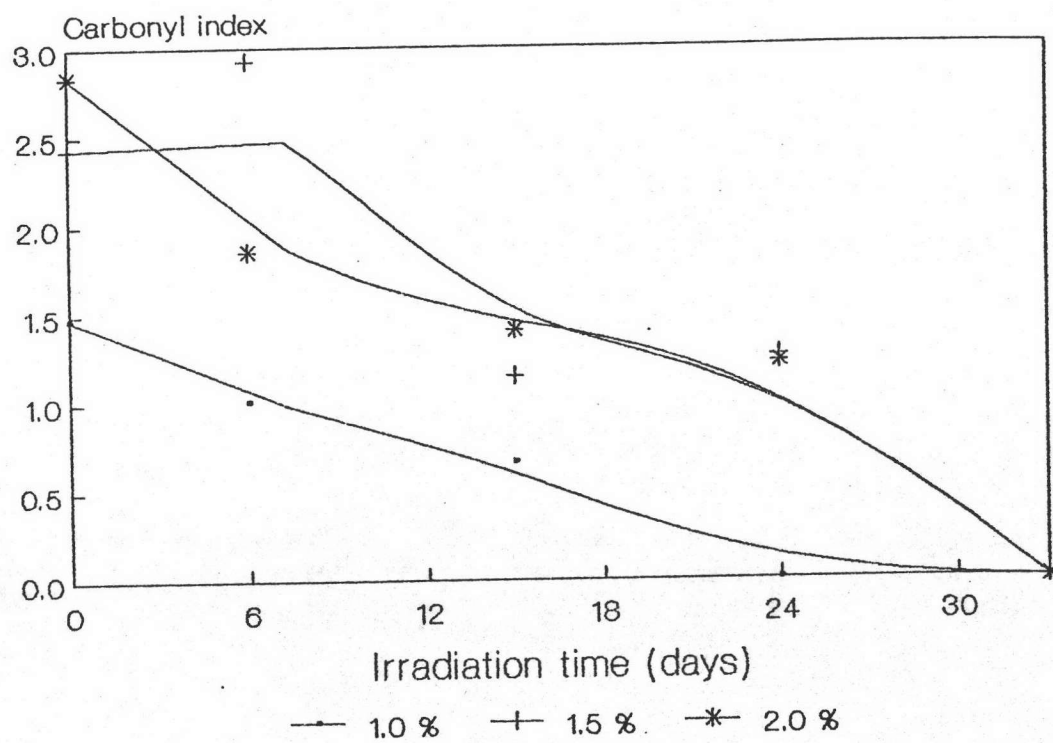


Figure 4.16 Changes of the relative FT-IR absorbance of carbonyl groups in photosensitizers as a function of irradiation time at various concentration of photosensitizers

Table 4.13 Hydroxyl Index of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Hydroxyl Index (3371 cm^{-1})			
	0	1.0	1.5	2.0
Original	1.5102	1.4856	1.6103	1.5812
6	1.3871	1.8193	1.7708	1.9842
15	1.4426	1.9095	2.1081	2.1694
24	1.5224	1.9494	2.2198	2.3771
33	1.6113	2.23361	2.4544	2.5108

Table 4.14 Vinyl Index of HDPE sheets irradiated with four fluorescent lamps

Photosensitizer Content (%)	Vinyl Index (909 cm^{-1})			
	0	1.0	1.5	2.0
Original	0.2903	0.3807	0.3101	0.4714
6	0.3057	0.4517	0.4399	0.4822
15	0.3350	0.5440	0.5731	0.6708
24	0.4080	0.6266	0.7064	0.7980
33	0.4784	0.7968	0.8671	0.8855

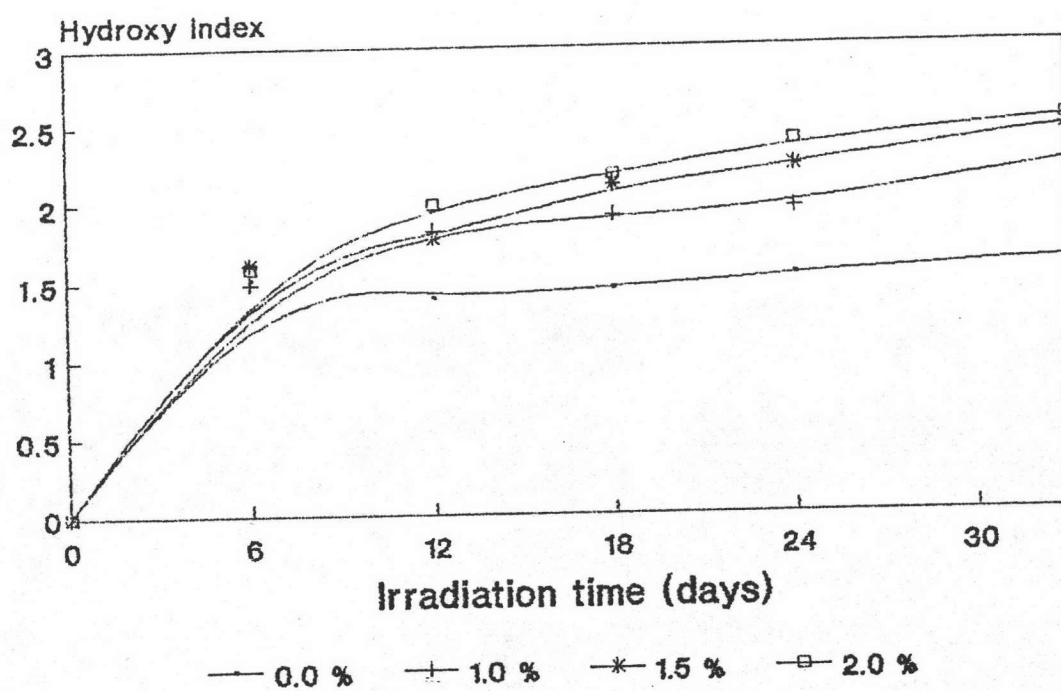


Figure 4.17 Changes of the relative FT-IR absorbance of hydroxy groups as a function of irradiation time at various concentration of photosensitizers.

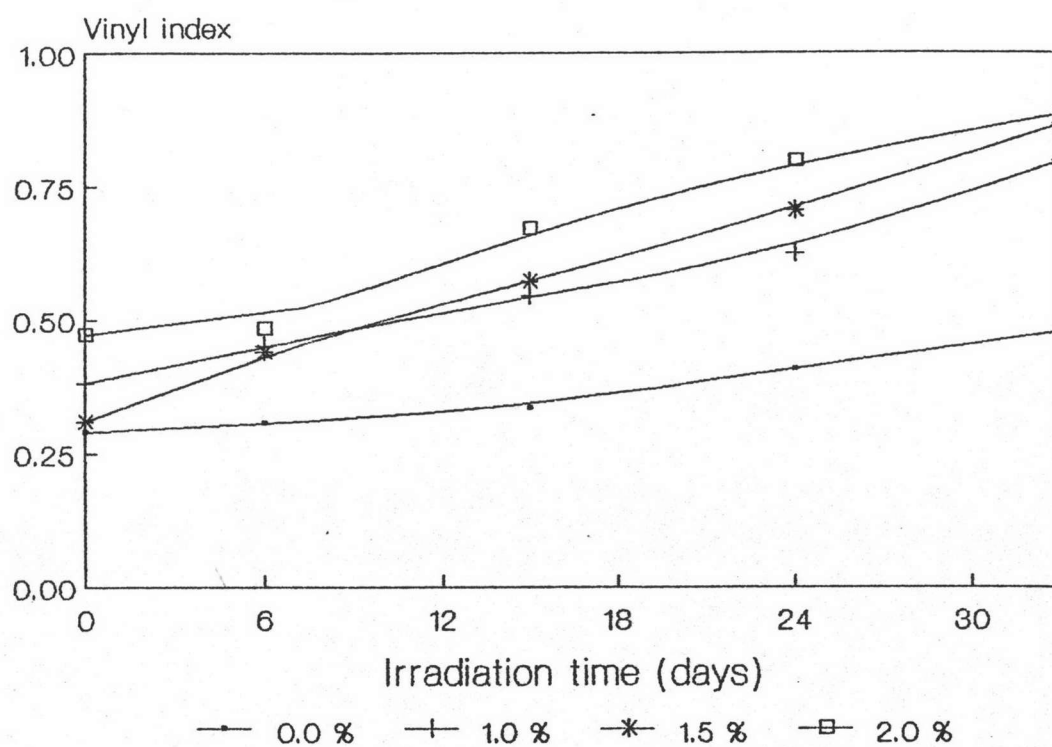


Figure 4.18 Changes of the relative FT-IR absorbance of vinyl groups as a function of irradiation time at various concentration of photosensitizers.

4.3 Accelerated weathering test by medium pressure mercury lamp

In other to compare the UV light source , a medium pressure mercury lamp source was used. The HDPE samples containing 0 % and 1.5 % by weight of 2-photosensitizers in a ratio of 1:1 were used for this test, The tensile strength , elongation at break and fourier transform infrarea absorption were measured and the degradation tendencies were compared.

4.3.1 Result of tensile properties test

The changes of tensile strength by irradiation with a medium pressure mercury lamp are shown in figure 4.19 as a function of irradiation time. It can be seen from figure 4.19 that tensile strength increases in the first 48 hours period , decreasing rapidly afterward. The rate of the decrease slows down after approximately 192 hours of irradiation. The 2-photosensitizers doped HDPE samples have a higher decrease than undoped HDPE samples. The rate of photodegradation by irradiation with a medium pressure mercury lamp is very much higher than that obtained through irradiation with 4-fluorescent lamps. The changes in elongation at break only after 24 hours irradiation could not be measured.

Table 4.15 Tensile Strength of HDPE sheets irradiated with
HPK 125 W

Photosensitizer Content. (%)	Tensile Strength (kg/mm ²)	
	0	1.5
Original	2.78	2.60
48	3.20	2.64
93	2.03	2.00
140	1.37	1.31
187	0.57	0.56
244	0.48	0.46

-All Samples irradiated with HPK 125 W have no elongation

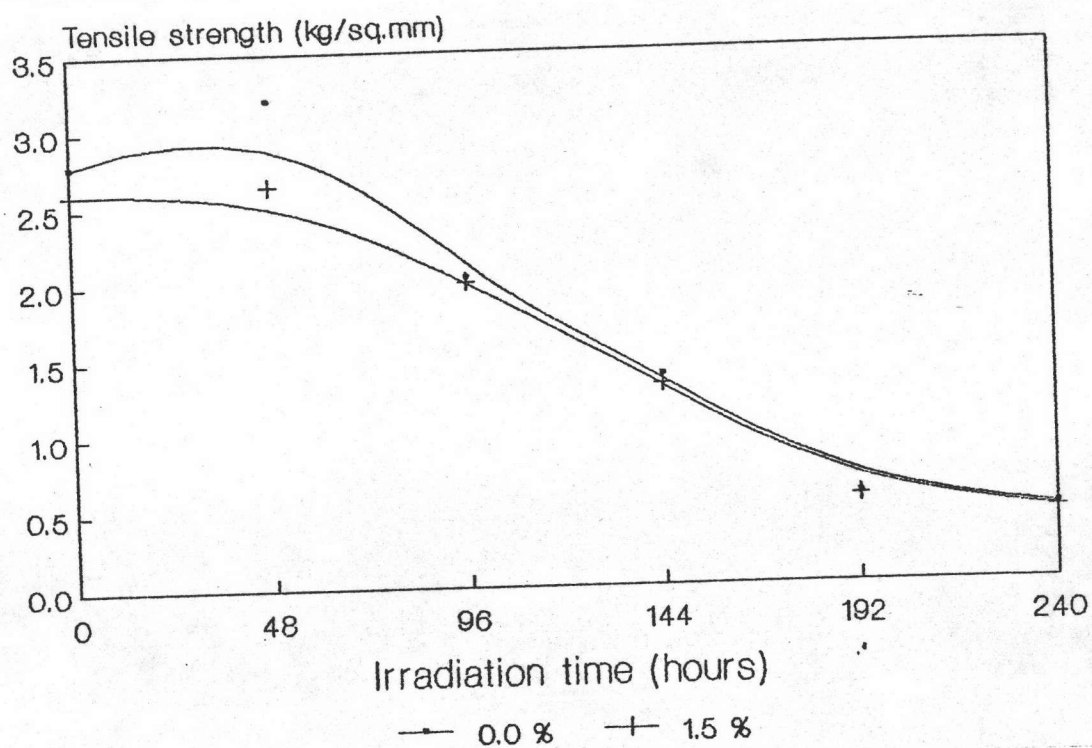


Figure 2.19 Tensile strength as a function of irradiation
time for HDPE sheets at various concentration
of photosensitizers.

4.3.2 Result of fourier transform infrared absorption test

The FTIR spectra of all samples irradiated by the medium pressure mercury lamp and typical spectra is shown in figure 4.20. Absorption peaks were observed in the regions of 3370 , 1715 , 1677 and 909 cm^{-1} and similar spectra changes were found in all samples with increasing irradiation time. Changes of carbonyl groups in PE chain and carbonyl groups in photosensitizers as a function of irradiation time are shown in figures 4.21 and 4.22 , respectively. Carbonyl groups in PE chain increase regularly in the whole period of irradiation time while carbonyl groups in photosensitizers of doped sample decrease from the starting values and disappear completely after about 144 hours of irradiation. This indicates that the initial structure of added photosensitizers are totally depleted during HDPE photo-oxidation. In figures 4.23 and 4.24 the relative absorption of the band at 3371 and 909 cm^{-1} is also plotted as a function of irradiation time , respectively. They generally increase with time of photo-oxidation. All absorption intensity of doped samples is substantially higher than that of undoped ones.

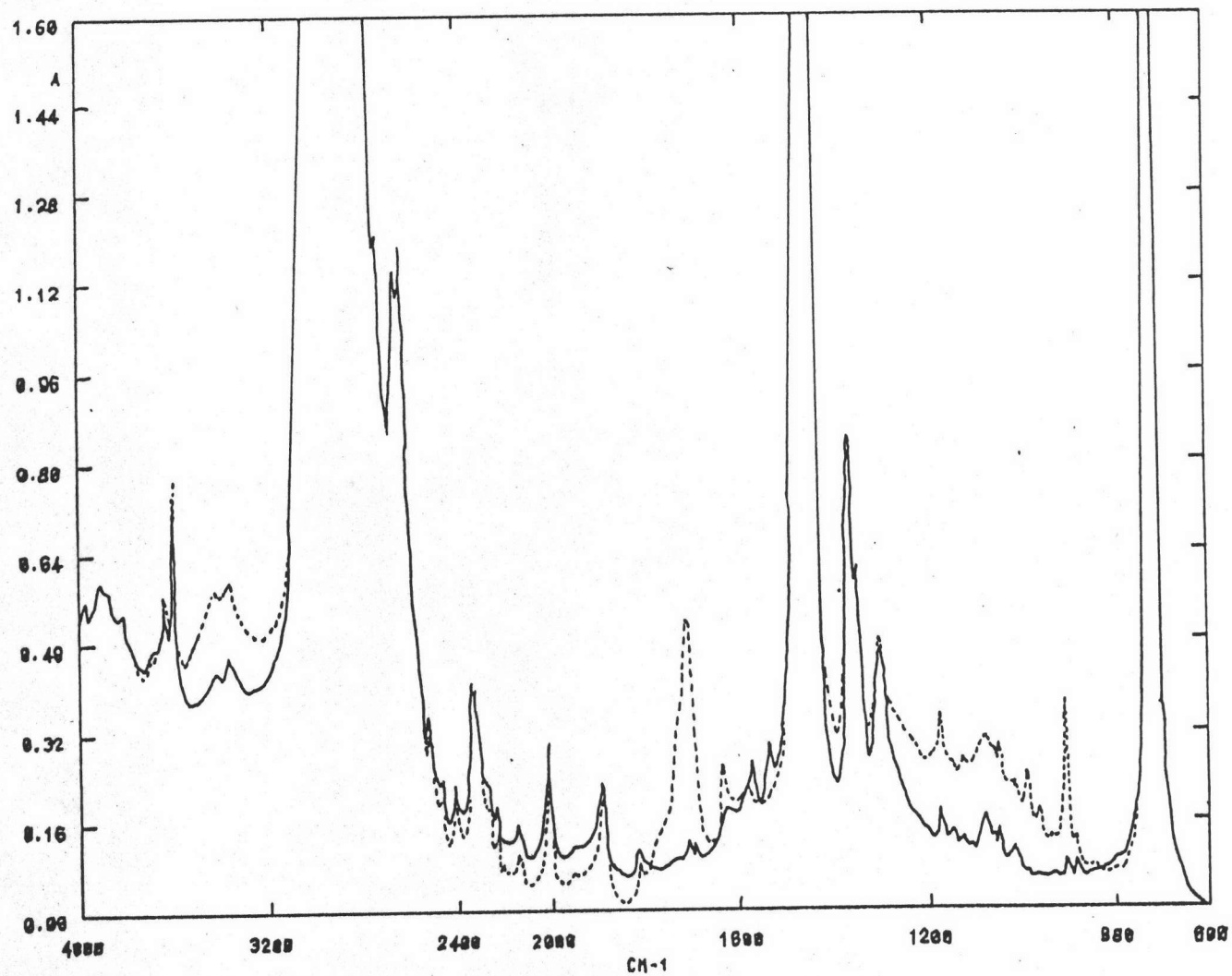


Figure 4.20 a FT-IR spectra of irradiated HDPE samples at 0 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 240 hours.

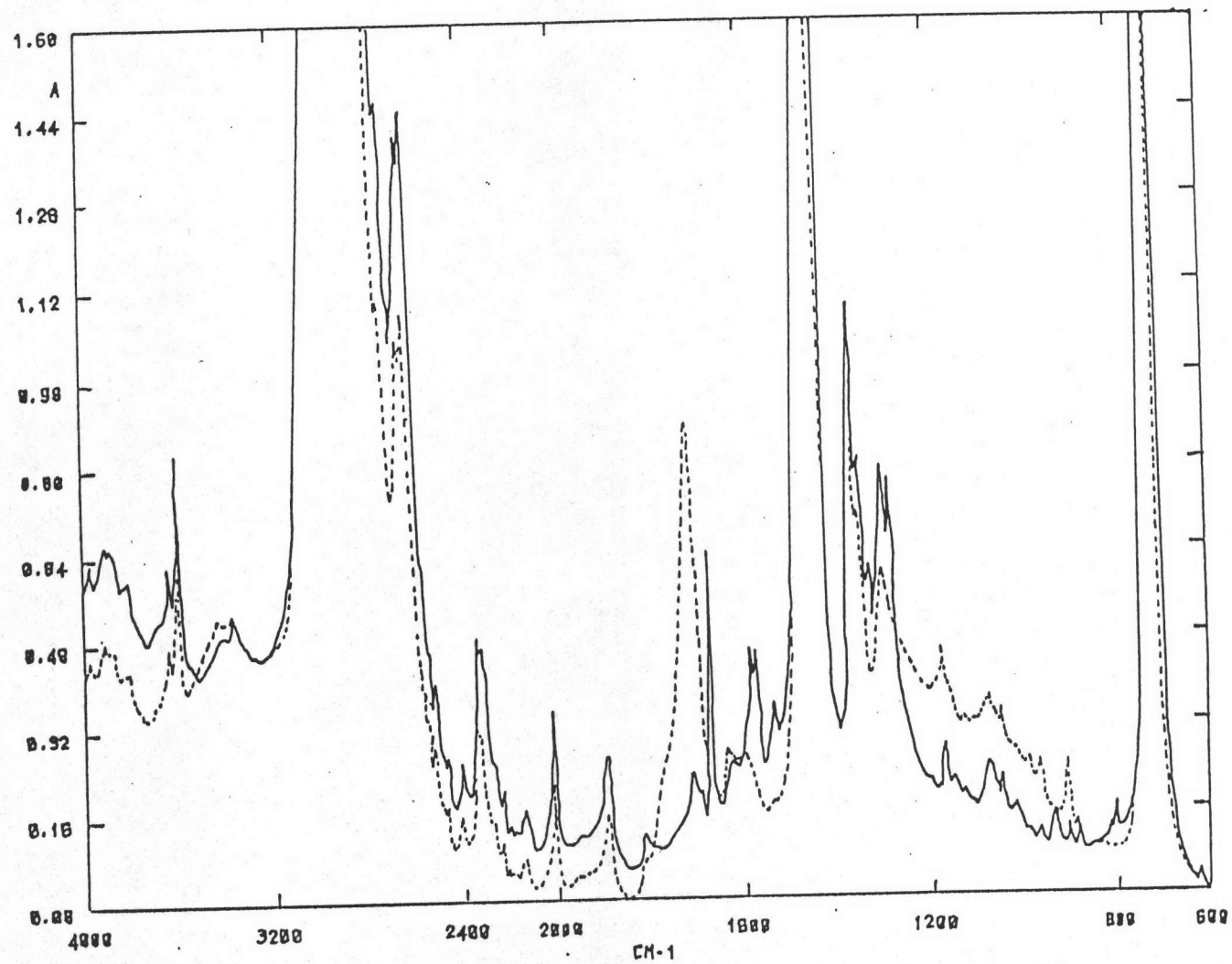


Figure 4.20 b FT-IR spectra of irradiated HDPE samples at 1.5 % photosensitizers
 ----- nonirradiated ; - - - - - irradiated for 240 hours.

Table 4.16 Carbonyl Index in PE chain of HDPE sheets irradiated with HPK 125 W

Photosensitizer Content (%)	Carbonyl Index (1715 cm^{-1})	
	0	1.5
Original	0.3846	0.4139
48	0.6515	3.0532
96	0.8220	3.4483
144	1.0409	3.1640
192	1.1754	3.3394
240	1.9065	4.0635

Table 4.17 Carbonyl index in photosensitizer of HDPE sheets irradiated with HPK 125 W

Photosensitizer Content (%)	Carbonyl Index in photo	
	0	1.5
Original	0	2.4333
48	0	1.9249
96	0	2.2154
144	0	0
192	0	0
240	0	0

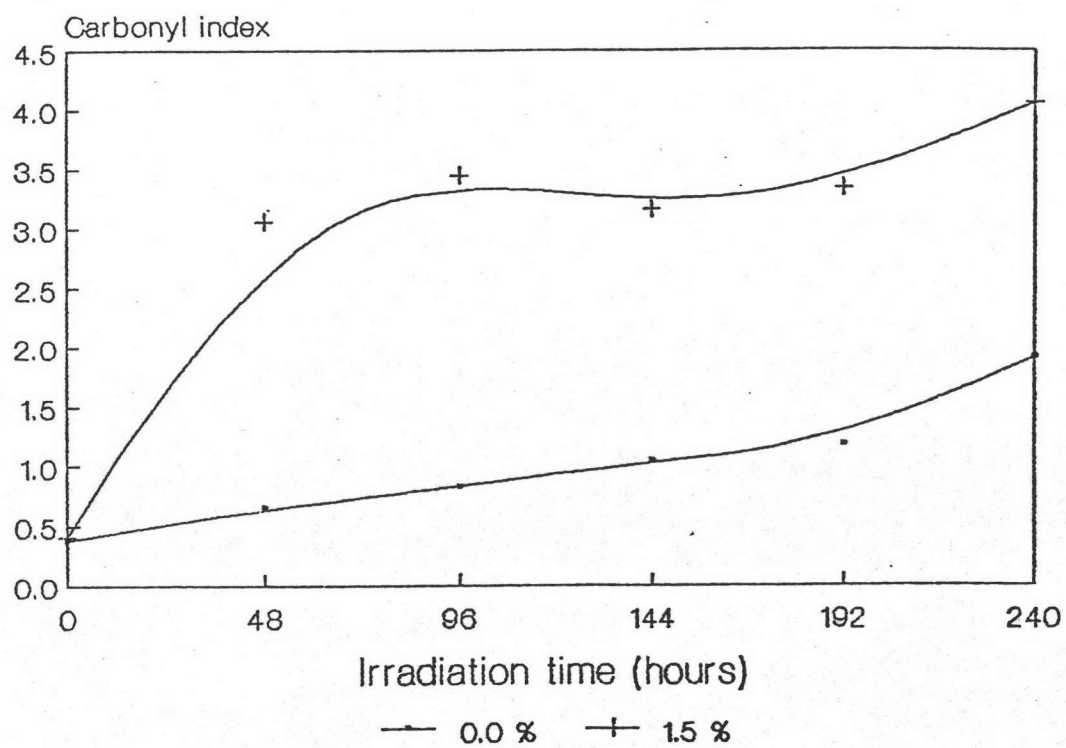


Figure 4.21 Changes of the relative FT-IR absorbance of carbonyl groups in PE chain as a function of irradiation time at various concentration of photosensitizers.

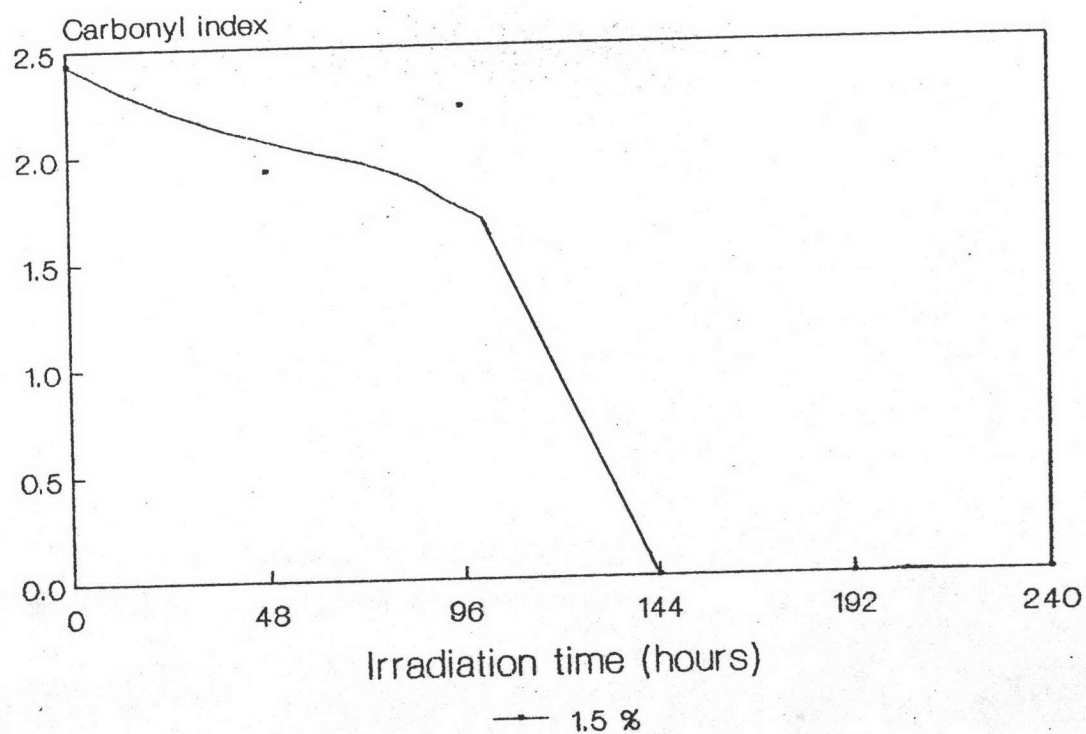


Figure 4.22 Changes of the relative FT-IR absorbance of carbonyl groups in photosensitizers as a function of irradiation time at various concentration of photosensitizers.

Table 4.18 Hydroxyl Index of HDPE sheets irradiated with
HPK 125 W

Photosensitizer Content (%)	Hydroxyl Index (3371 cm^{-1})	
	0	1.5
Original	1.5102	1.6103
48	1.4740	2.1806
96	1.5844	2.2505
144	1.6883	2.3135
192	1.7859	2.1914
240	2.1753	2.4650

Table 4.19 Vinyl Index of HDPE sheets irradiated with
HPK 125 W

Photosensitizer Content (%)	Vinyl Index (909 cm^{-1})	
	0	1.5
Original	0.2903	0.3101
48	0.5706	0.8033
96	0.8450	0.9060
144	1.0595	0.9627
192	1.1480	1.0821
240	1.3969	1.1491

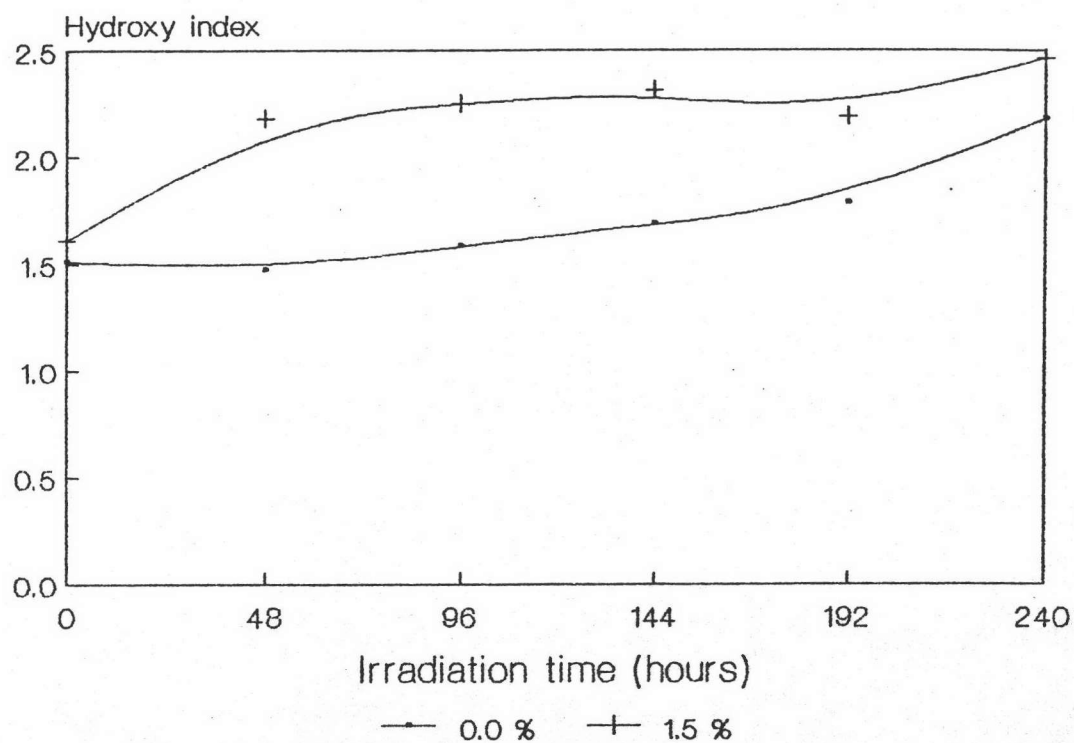


Figure 4.23 Changes of the relative FT-IR absorbance of hydroxy groups in photosensitizers as a function of irradiation time at various concentration of photosensitizers.

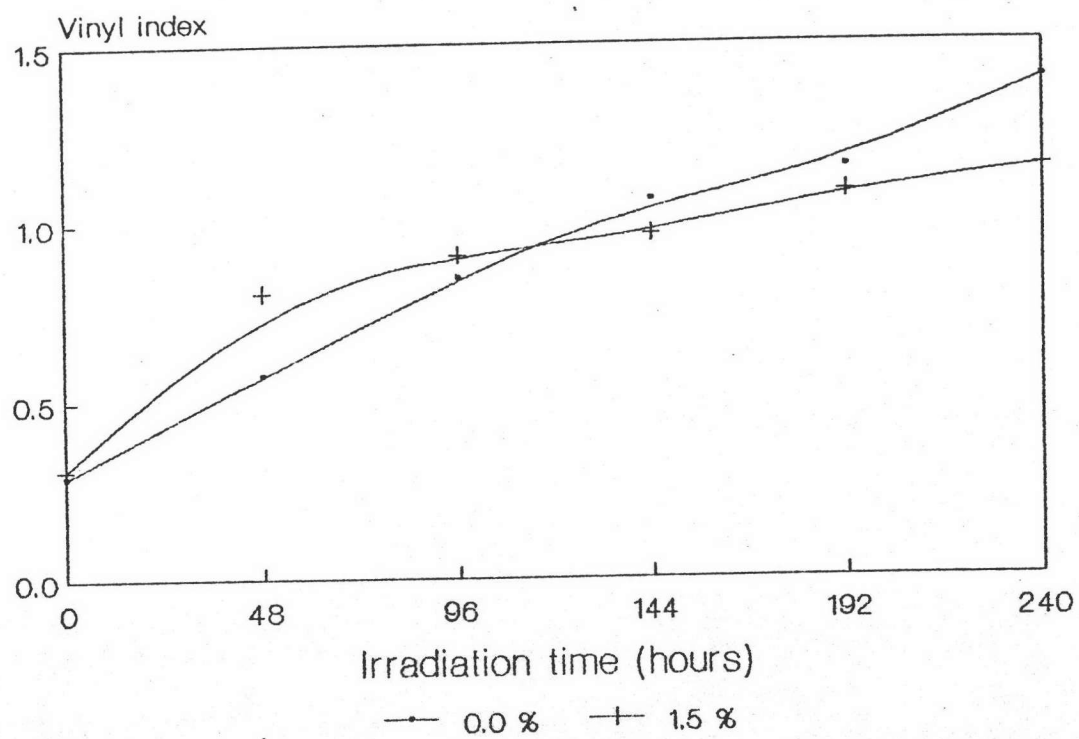


Figure 4.24 Changes of the relative FT-IR absorbance of vinyl groups in photosensitizers as a function of irradiation time at various concentration of photosensitizers.