

CHAPTER 4

RESULTS AND DISCUSSIONS

Experimental procedures have been described in previous chapter. Results of the experiments were discussed for each type of film, as follow:

4.1 Polypropylene (PP) films.

4.1.1 Changes in chemical structures.

The chemical properties of PP films were affected by photoreaction as result of the chemical changes in the polymer molecules. Due to the photo-oxidation, the polymer chains were broken; which can be confirmed by the increasing of carbonyl index. From FT-IR spectrum of PP before exposure and after exposure to UV light, the carbonyl group are presented at 1715 cm^{-1} . This result is shown in Figure 4.1.

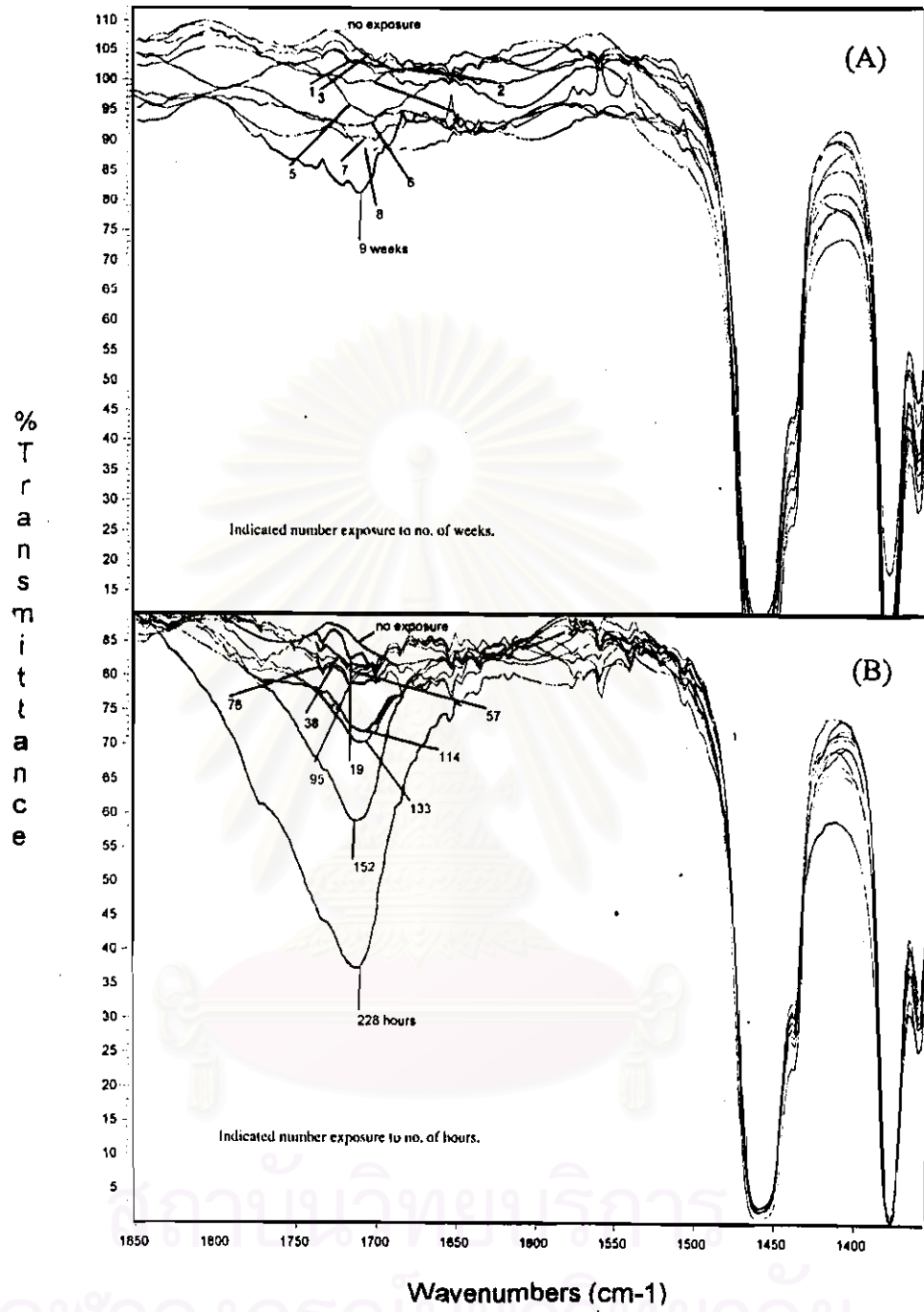


Figure 4.1 IR spectrum of carbonyl groups of PP films (A) from outdoor exposure condition and (B) from Xenotest condition.

From the carbonyl band intensity, no carbonyl peak was observed from unexposed PP, but it broadens, and shifts after several weeks of outdoor exposure and accelerated UV exposure indicating the presence of a variety of carbonyl containing degradation products. From carbonyl regions, it will be converted to carbonyl index, as shown on Table 4.1. The same data is displayed graphically in Figure 4.2. It shows the changes of carbonyl index of PP films as a function of exposure time, the values of carbonyl index increase with increasing in exposure time for both exposure conditions (outdoor exposure and in Xenotest). These can be explained that, the decomposition of polyolefins under the condition of outdoor exposure and accelerated UV exposure were caused by the photooxidation. UV light causes the formation of various free radicals which some of them combine with oxygen dissolved in the polymer to initiate chain reaction and form thermally unstable products. The oxidation process will involve peroxide radicals derived directly from the radiation reaction and also these initial peroxide radicals attack on the polymer, give hydroperoxide. Hydroperoxide is believed to slowly breakdown and produce carbonyl compound. The carbonyl compounds predominate those expected from the Norrish type I and II process.

By comparing the occurring of carbonyl index during exposure to UV light in both exposure conditions (Figure 4.2), it was found that the carbonyl index value in accelerated UV exposure showed higher amount than outdoor exposure. In the case of outdoor exposure, the uniformity of UV light intensity expose on PP films is not as good as in the case of Xenotest. Eventhough the oxygen permeability also has an important role on the rate of oxidation in outdoor exposure, but due to a tight structure of the polymer the result shows that oxygen is not easily allowed to attack the structure. Therefore, the effects of oxygen turned out to be a minor role.

The curve fittings (Figure 4.2), show the empirical model of the changing of carbonyl index as a function of exposure time. This model is analyzed by using statistical approach,

$$I = Ae^{Bt} \dots\dots\dots (4.1)$$

or

$$\ln I = \ln A + Bt \dots\dots\dots (4.2)$$

where,

I : carbonyl index

t : exposure time

A and B : constants

When substitute the values from experiments and then fitting the curve with exponential model, we can obtain Equation (4.3) for outdoor exposure and Equation (4.4) for Xenotest condition. Correlation parameter R^2 is also shown in each model.

$$\ln I_n = \ln 0.0173 + 0.1565t_n \dots\dots\dots(4.3)$$

$$R^2 = 0.83$$

$$\ln I_x = \ln 0.0272 + 0.2672t_x \dots\dots\dots(4.4)$$

$$R^2 = 0.85$$

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Table 4.1 Carbonyl Index of PP films at each exposure time in outdoor exposure and in Xenotest

Outdoor Exposure		Xenotest	
Time (weeks)	Carbonyl Index	Time (hours)	Carbonyl Index
0	0.0170	0	0.0170
1	0.0286	19	0.0270
2	0.0313	38	0.0912
3	0.0316	57	0.0958
4	0.0427	76	0.1059
5	0.0396	95	0.1349
6	0.0470	114	0.1500
7	0.0473	133	0.1620
8	0.0592	152	0.2936
9	0.1195	228	0.4798

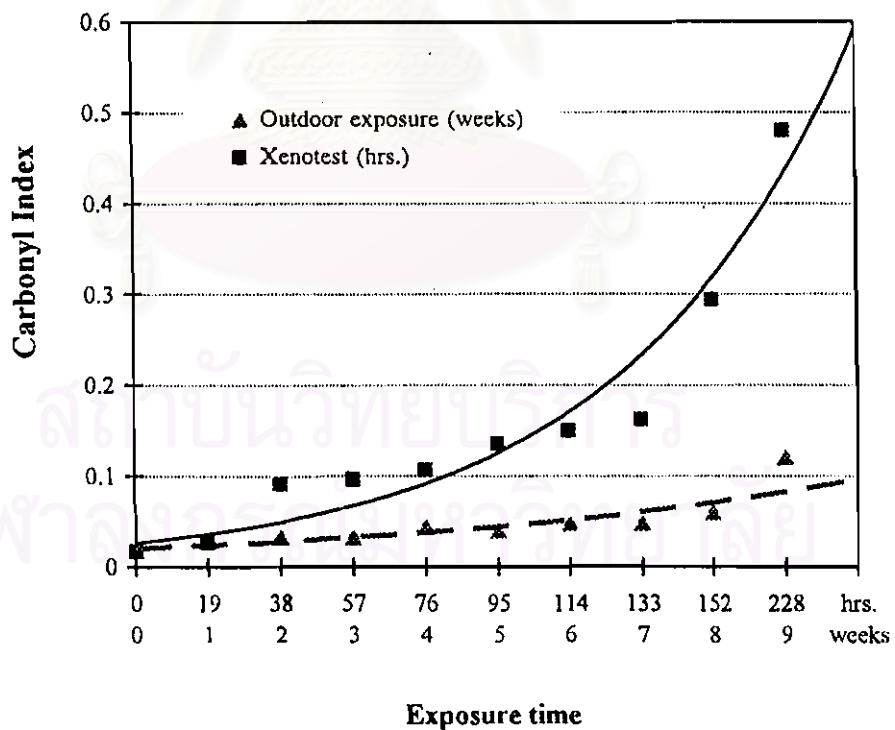


Figure 4.1 Carbonyl Index variation with to exposure times for PP films

4.1.2 Changes in mechanical properties.

The changes of mechanical properties in both outdoor exposure and accelerated UV exposure were determined by elongation at break and initial modulus.

Table 4.2 shows the influence of carbonyl index on the changes of elongation at break and initial modulus of PP films. The trend is clearly demonstrated in Figure 4.3 and Figure 4.4, displaying variation of the elongation at break versus the carbonyl index : The lost of mechanical properties of the outdoor exposure samples can be easily observed. Decreasing in elongation at break and increasing in the initial modulus are drastically occurred at the beginning stage.

While the changes in Xenotest condition appear slower. This is due to the fact that in outdoor condition washing out of additives and erosion by rain and dew play significant role on responsible for these lost of mechanical properties.

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Table 4.2 Influence of carbonyl index on mechanical properties of PP films.

Outdoor Exposure			Xenotest		
Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)	Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)
0.0170	659.40	574.22	0.0170	659.40	574.22
0.0286	229.90	694.62	0.0270	599.50	597.29
0.0313	56.74	728.76	0.0912	478.40	667.21
0.0316	30.46	627.94	0.0958	491.10	677.74
0.0427	27.00	666.33	0.1059	37.31	777.57
0.0396	26.50	718.51	0.1349	23.58	928.33
0.0470	23.64	616.00	0.1500	1.02	978.83
0.0473	23.62	781.13			
0.0592	2.80	824.45			
0.1195	1.95	874.12			

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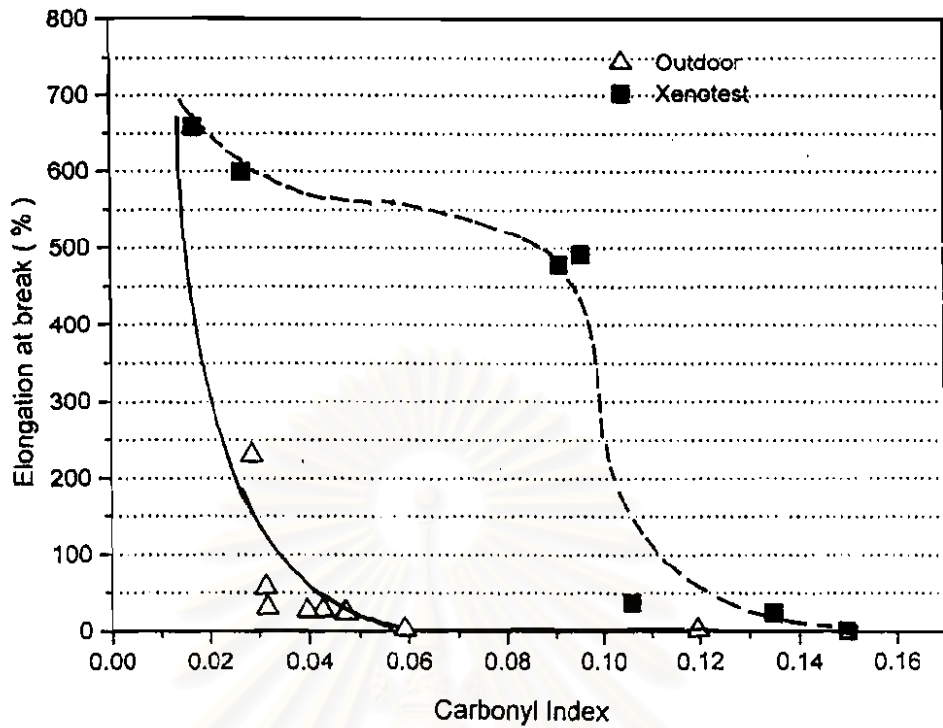


Figure 4.3 Elongation at break values in relationship to carbonyl index of PP films

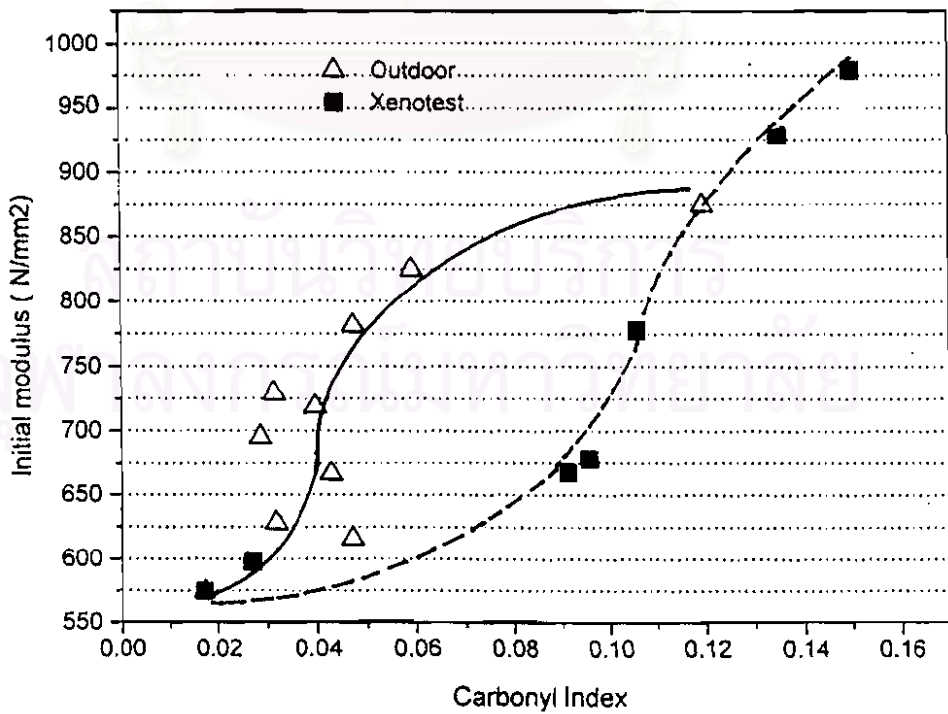


Figure 4.4 Initial modulus in relationship to carbonyl index of PP films

4.2 High Density Polyethylene (HDPE) films.

4.2.1 Changes in chemical structures.

Similar results to PP films were obtained, photooxidation causes the formation of carbonyl group. The spectrum from Figure 4.5 shows the occurrence of carbonyl groups as increasing in exposure times for both conditions. The results were then interpreted by plotting carbonyl index values against exposure time in Table 4.3 and Figure 4.6. The results show similar manner in the increasing of carbonyl index as an exponential function of exposure time.

Eventhough the results of carbonyl index of HDPE films were the same trend as PP films, the curve fitting was not exactly the same. The empirical model, showed the relationship between carbonyl index and exposure time in both exposure conditions, determined by equation (4.1 or 4.2).

The fitted curves in Figure 4.6 were represented by Equations (4.5) and (4.6) with correlation coefficients (R^2) 0.92 and 0.81 respectively.

$$\ln I_n = \ln 0.0568 + 0.0478t_n \dots\dots\dots(4.5)$$

$$R^2 = 0.92$$

$$\ln I_x = \ln 0.1118 + 0.0417t_x \dots\dots\dots(4.6)$$

$$R^2 = 0.81$$

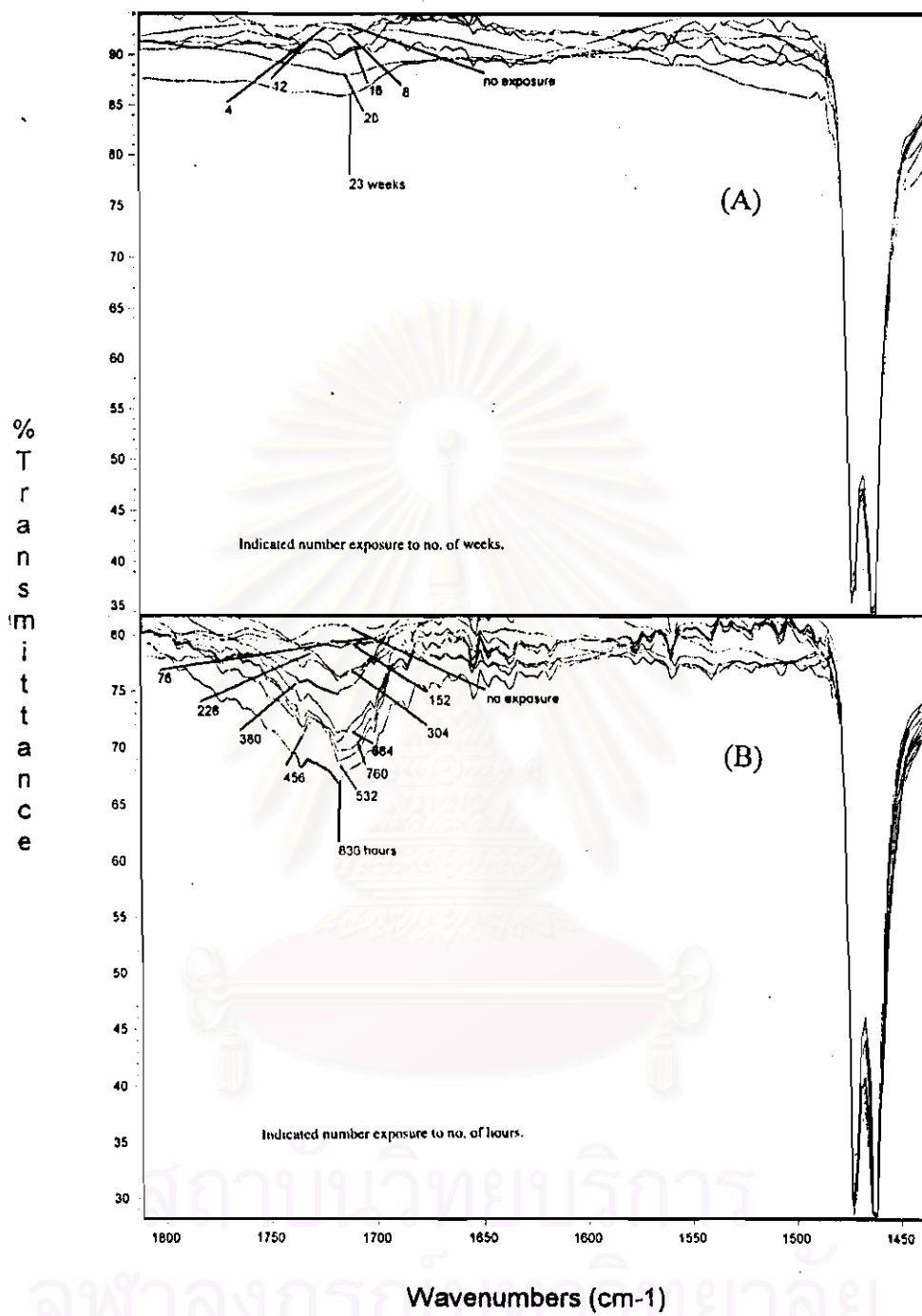


Figure 4.5 IR spectrum of carbonyl groups of HDPE films (A) from outdoor exposure condition and (B) from Xenotest condition.

Table 4.3 Carbonyl index of HDPE films at each exposure time in outdoor exposure and in Xenotest

Outdoor Exposure		Xenotest	
Time (weeks)	Carbonyl Index	Time (hours)	Carbonyl Index
0	0.0622	0	0.0622
4	0.0800	76	0.1690
8	0.1041	152	0.2520
12	0.1435	228	0.2310
16	0.1726	304	0.2810
20	0.1556	380	0.4138
24	0.2006	456	0.4508
28		532	0.6278
32		608	0.4620
36		684	0.4575
40		760	0.5967
44		836	0.6740

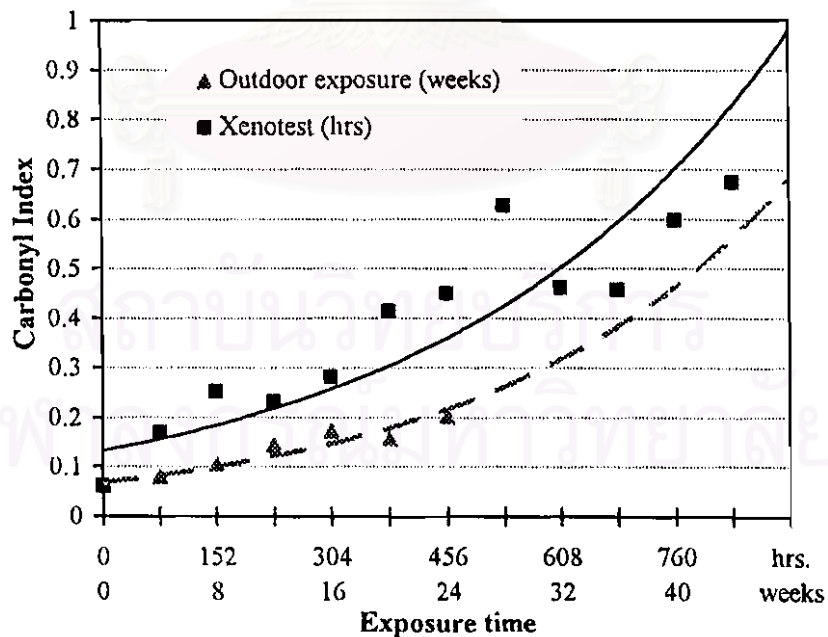
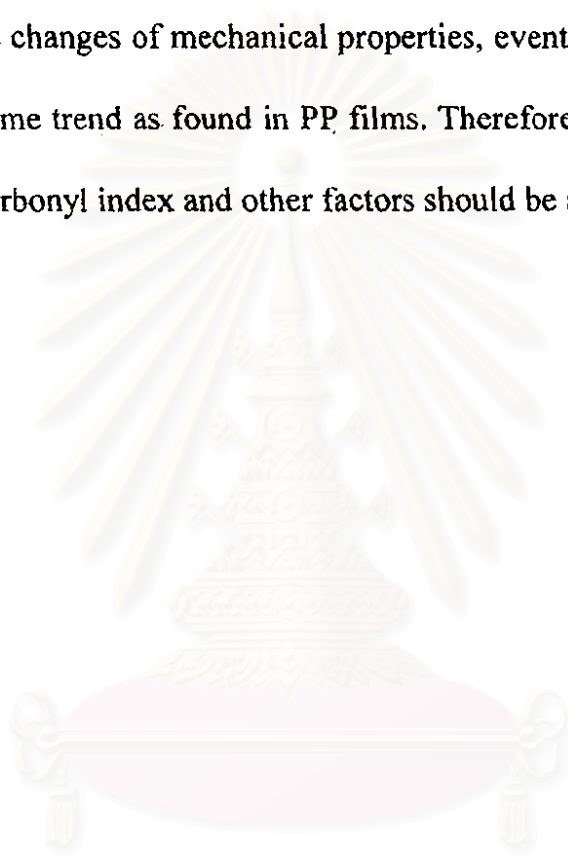


Figure 4.4 Carbonyl Index variation with exposure times for HDPE films

4.2.2 Changes in mechanical properties.

Similar fashion on the influence of carbonyl index on mechanical properties of HDPE films can be observed in Table 4.4 and plotted in Figure 4.7 and 4.8. The changes of mechanical properties, eventhough is not as fast as but are in the same trend as found in PP films. Therefore the same explanation on the role of carbonyl index and other factors should be applied.



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Table 4.4 Influence of carbonyl index on mechanical properties of HDPE films.

Outdoor Exposure			Xenotest		
Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)	Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)
0.0622	276.00	927.97	0.0622	276.00	927.97
0.0800	151.10	977.46	0.1690	221.30	806.34
0.1041	134.80	1017.41	0.2520	167.20	962.33
0.1435	98.37	1191.56	0.2310	77.32	1129.51
0.1726	64.75	1304.40	0.2810	48.30	1354.64
0.1556	42.25	1531.76	0.4138	35.91	1479.10
0.2006	5.04	1656.28	0.4508	16.59	1524.44
			0.6278	2.08	1496.33
			0.4620	1.49	1708.69
			0.4575	1.06	1789.50

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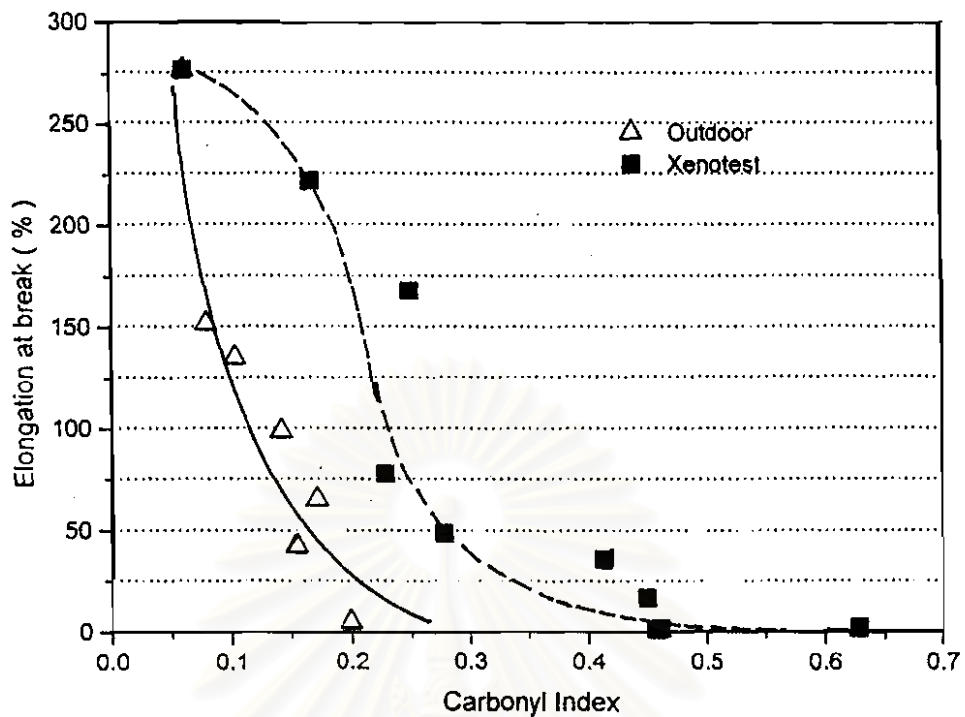


Figure 4.7 Elongation at break values in relationship to carbonyl index of HDPE films

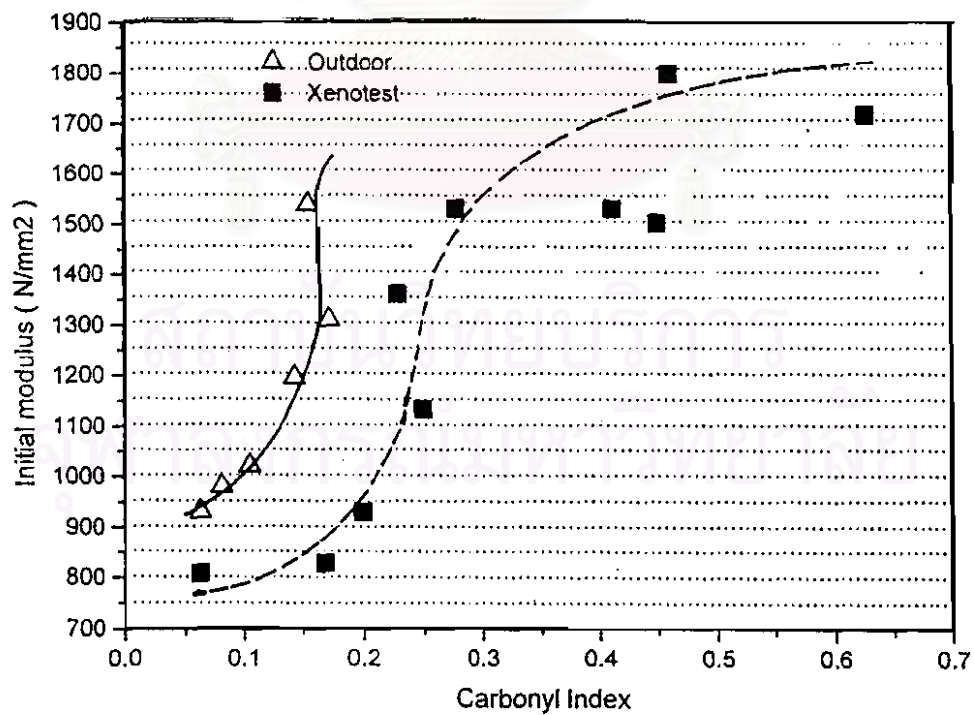


Figure 4.8 Initial modulus in relationship to carbonyl index of HDPE films

4.3 Low density polyethylene (LDPE) films.

4.3.1 Changes in chemical structures.

Figure 4.9 shows the IR spectrum of carbonyl group of LDPE films before and after exposed to UV light under outdoor exposure and accelerated UV exposure conditions. The results were converted to carbonyl index in Table 4.5, and displayed in the Figure 4.10. It can be seen that the same trend of carbonyl index increasing with increasing in exposure time as happened in PP and HDPE films is also obtained. However the carbonyl index in outdoor exposure of LDPE was higher than in accelerated UV exposure. This may be resulted from the higher disordered structure in LDPE. The attack of oxygen causing degradation is easily done. Therefore photooxidation degradation is not responsible by only UV light. Although, the intensity of UV light can be regularly controlled in Xenotest, but the effects of oxygen attacking is a major role.

Figure 4.10 represents the relationship of the variables mentioned above. Once again, an exponential models were proposed in Equations (4.7) and (4.8)

$$\ln I_n = \ln 0.0244 + 0.0736t_n \dots\dots\dots(4.7)$$

$$R^2 = 0.90$$

$$\ln I_x = \ln 0.0333 + 0.0539t_x \dots\dots\dots(4.8)$$

$$R^2 = 0.83$$



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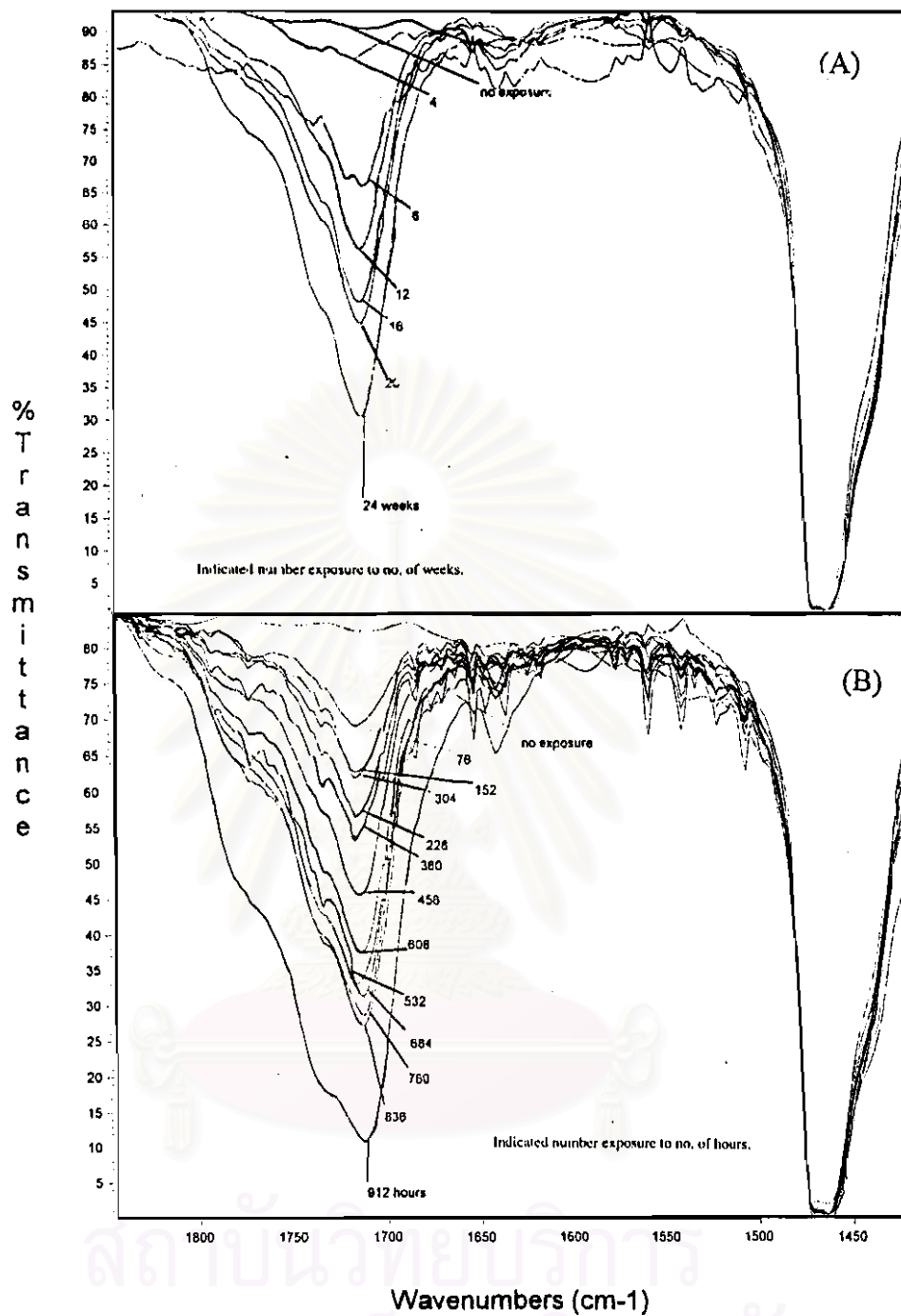


Figure 4.9 IR spectrum of carbonyl groups of LDPE films (A) from outdoor exposure condition and (B) from Xenotest condition.

Table 4.5 Carbonyl Index of LDPE films at each exposure time in outdoor exposure and in Xenotest

Outdoor Exposure		Xenotest	
Time (weeks)	Carbonyl Index	Time (hours)	Carbonyl Index
0	0.0149	0	0.0149
4	0.0484	76	0.0700
8	0.0639	152	0.0960
12	0.1161	228	0.1210
16	0.1489	304	0.1006
20	0.1789	380	0.1271
24	0.2329	456	0.1707
28		532	0.2266
30		608	0.1930
36		684	0.2733
40		760	0.2867
44		836	0.4077
48		912	0.5580

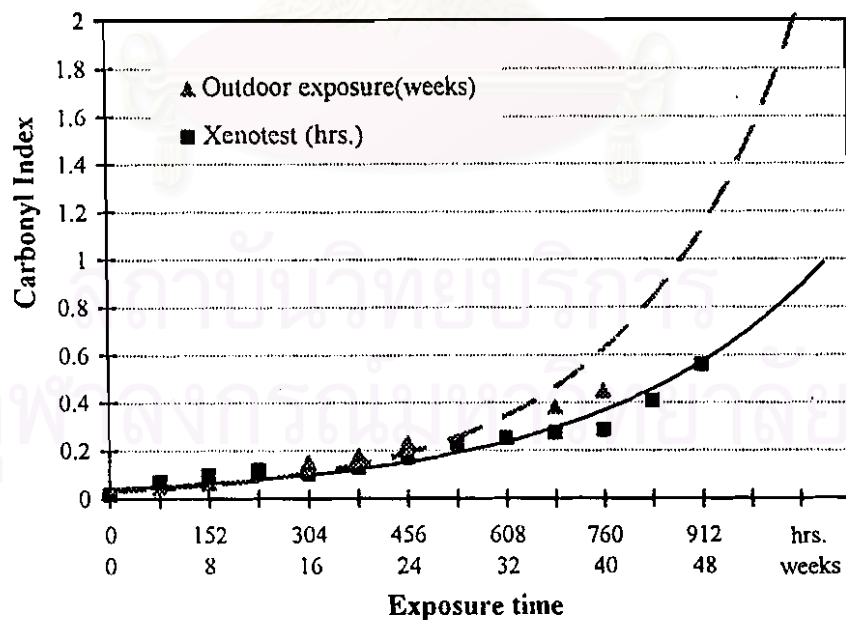
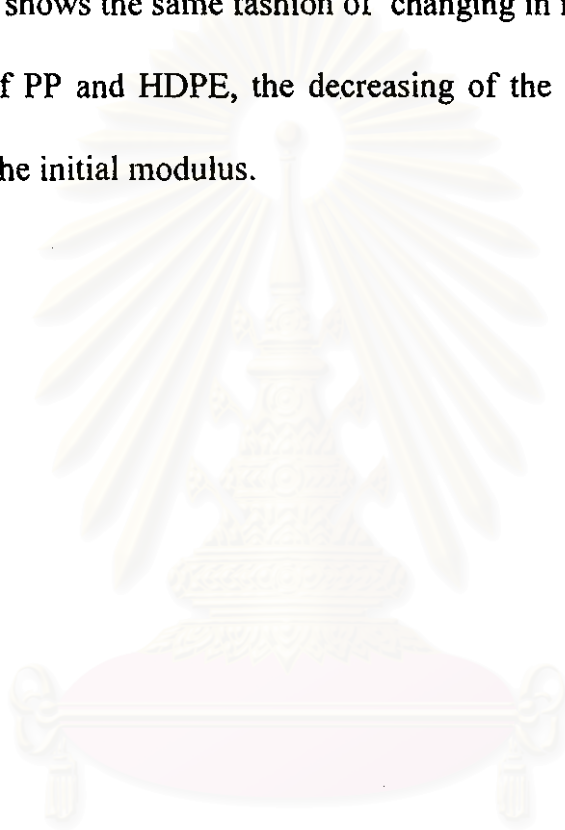


Figure 4.7 Carbonyl Index variation with exposure times for LDPE films

4.3.2 Changes in mechanical properties.

Table 4.6 shows the influence of carbonyl index on elongation at break and initial modulus of LDPE films. These data were plotted in Figure 4.11 and Figure 4.12. It shows the same fashion of changing in mechanical properties as in the cases of PP and HDPE, the decreasing of the elongation at break and increasing of the initial modulus.



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Table 4.6 Influence of carbonyl index on mechanical properties of LDPE films.

Outdoor Exposure			Xenotest		
Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)	Carbonyl Index	Elongation at break (%)	Initial Modulus (N/mm ²)
0.0149	621.50	156.20	0.0149	621.50	156.20
0.0484	480.90	168.98	0.0700	537.70	176.80
0.0639	446.10	174.79	0.0960	400.60	164.91
0.1161	109.50	178.64	0.1210	466.70	169.63
0.1489	54.04	193.18	0.1006	140.60	175.56
0.1789	27.55	184.89	0.1271	280.50	186.79
0.2329	5.94	201.48	0.1707	52.77	201.54
			0.2266	43.70	250.32
			0.1930	39.34	253.44
			0.2733	30.55	257.84
			0.2867	18.47	259.64
			0.4077	18.47	264.58
			0.558	9.06	280.55

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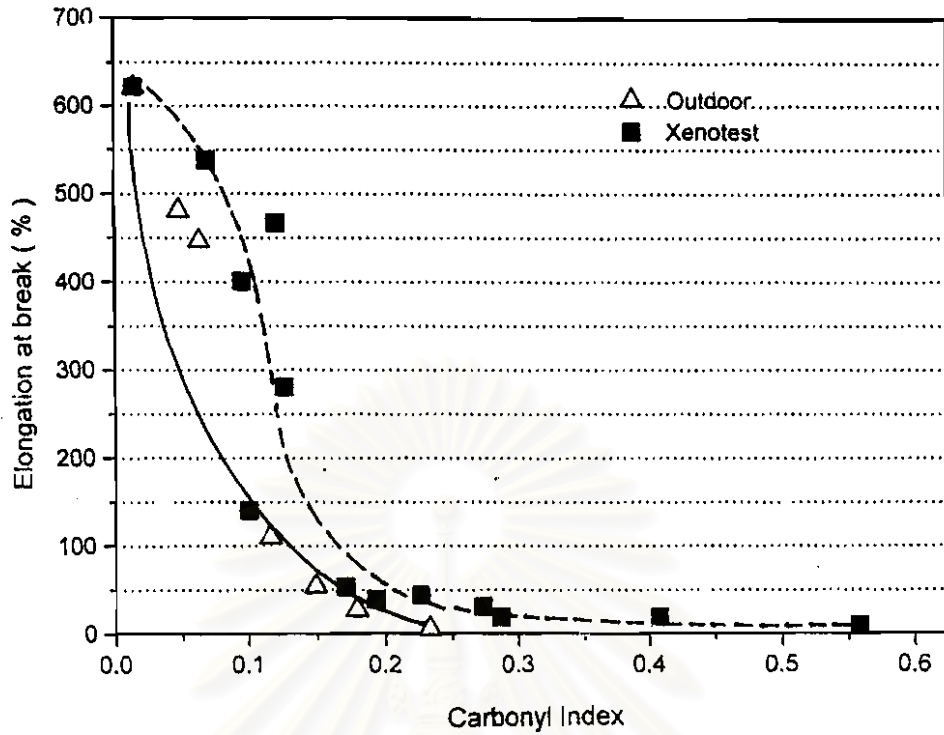


Figure 4.11 Elongation at break values in relationship to carbonyl index of LDPE films

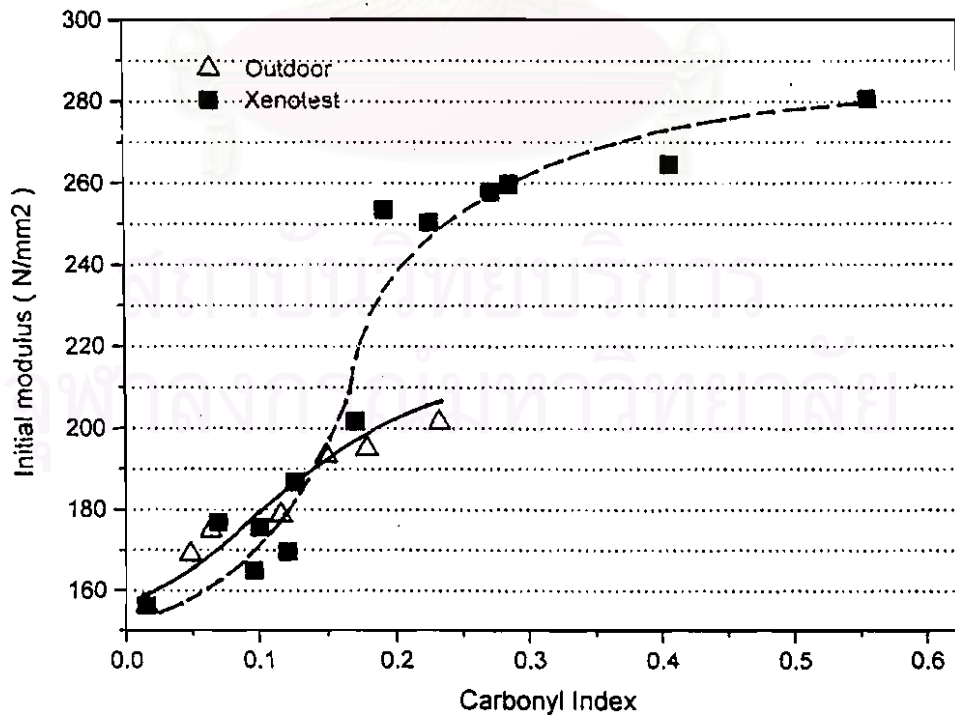


Figure 4.12 Initial modulus in relationship to carbonyl index of LDPE films

4.4 The comparative results among the three polyolefin films.

Results of the carbonyl index increases as increasing in exposure time which were proposed by exponential model in Equations (4.3), (4.4), (4.5), (4.6), (4.7) and (4.8) are summarized in Table 4.7. The coefficient of the variable exposure time represents the rate of degradation. This implies that in PP films the degradation rate is much higher than in PE films. It is believed that in PP structure containing tert-CH which is more sensitive to UV light causes the high degradation rate. In outdoor exposure, this is confirmed by the result of exposure time in PP taking only 9 weeks to become brittle. While in HDPE and LDPE, it took 23 and 24 weeks respectively to become entirely brittle. This phenomena is also happen in the condition of Xenotest. It take 114 hrs., 684 hrs. and 912 hrs. to become brittle for PP, HDPE and LDPE respectively.

In the cases of mechanical properties lost, Figure 4.13 and 4.14 show the decreasing of elongation at break and increasing of initial modulus of the three types of films. It should be noticed that, washing out of additives in the film and erosion by rain and dew also play important role on degradation of PP, HDPE and LDPE films. This can be observed by outdoor exposure test, the curves of both elongation at break and initial modulus are higher than in Xenotest.

Table 4.7 Exponential models represent changes in carbonyl index with increasing in exposure time in both conditions, outdoor exposure and Xenotest.

Outdoor Exposure		Xenotest	
Models	Exposure Time Limit* (weeks)	Models	Exposure Time Limit* (hrs.)
PP : $R^2 = 0.83$ $\ln I_n = \ln 0.0172 + 0.1565t_n$	9	PP : $R^2 = 0.85$ $\ln I_n = \ln 0.0272 + 0.2672t_n$	114
HDPE : $R^2 = 0.92$ $\ln I_n = \ln 0.0568 + 0.0487t_n$	23	HDPE : $R^2 = 0.81$ $\ln I_n = \ln 0.1118 + 0.0417t_n$	684
LDPE : $R^2 = 0.90$ $\ln I_n = \ln 0.0244 + 0.0736t_n$	24	LDPE : $R^2 = 0.83$ $\ln I_n = \ln 0.0333 + 0.0539t_n$	912

* : Exposure Time Limit represents the testing time require for the sample to become brittle.

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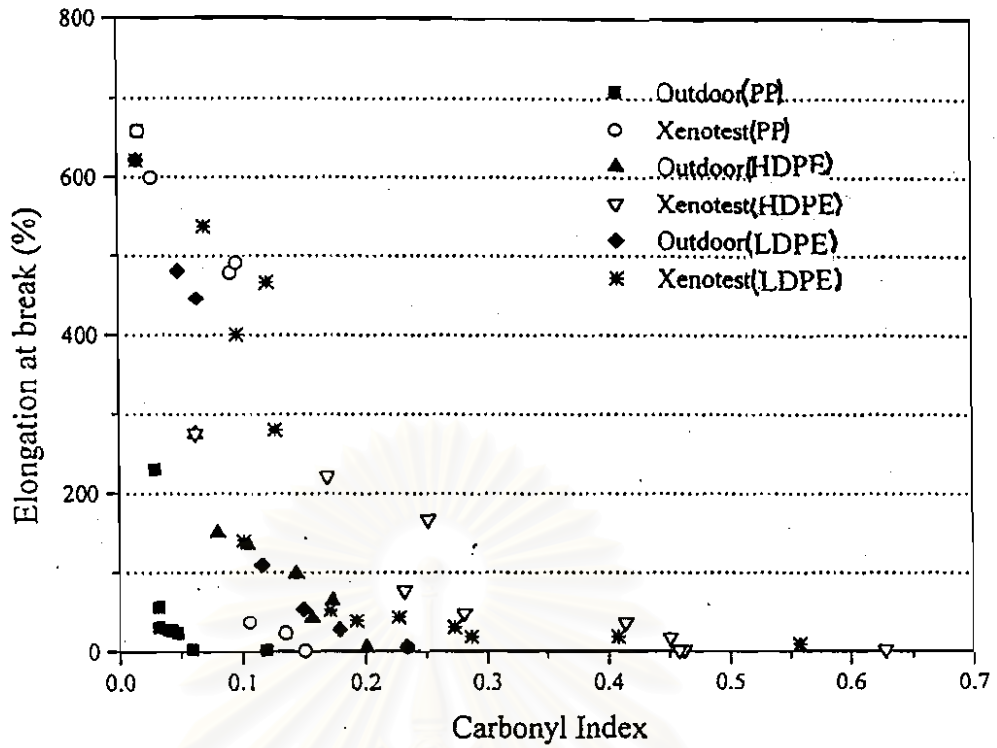


Figure 4.13 Changes of values in elongation at break versus carbonyl index of the three examined films: PP, HDPE and LDPE in both conditions : outdoor exposure and Xenotest.

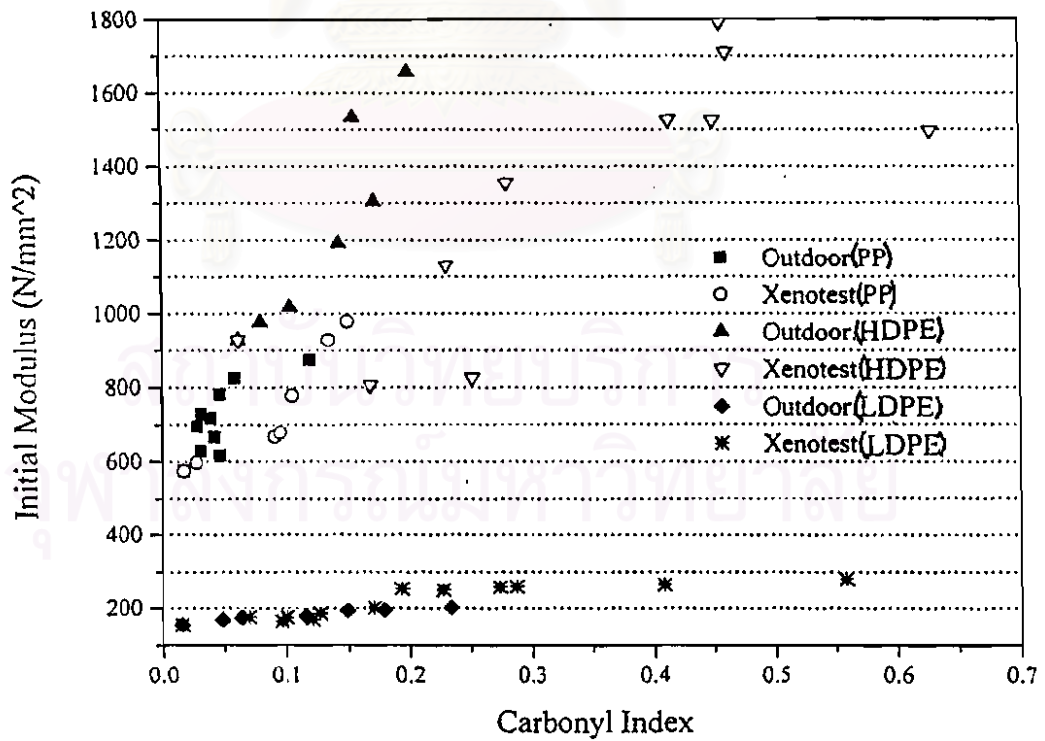


Figure 4.14 Changes of values in initial modulus versus carbonyl index of the three examined films : PP, HDPE and LDPE in both conditions : outdoor exposure and Xenotest.