



CHAPTER 5

DISCUSSIONS

5.1 Undoped high density polyethylene

The tensile strength and molecular weight of the samples exposed for one month are higher (2.8 kg/mm^2 and 5.26×10^4) than the values of the starting HDPE (2.78 kg/mm^2 and 5.08×10^4). The observed increase cannot be attributed to the formation of cross-linking structures because of the complete solubility of the sample. However, this increase may take place through incorporation of oxygen which can be seen from scheme 1. Figures 4.2 and 4.3 show that degradation is proceeding continuously with exposure time. There is a rapid increase in the rate of formation of carbonyl, vinyl and hydroxy groups after 3 month exposure as shown in figure 4.6-4.9. This increase is most probably associated with the exhaustion of the stabilizing agents present in the original material.

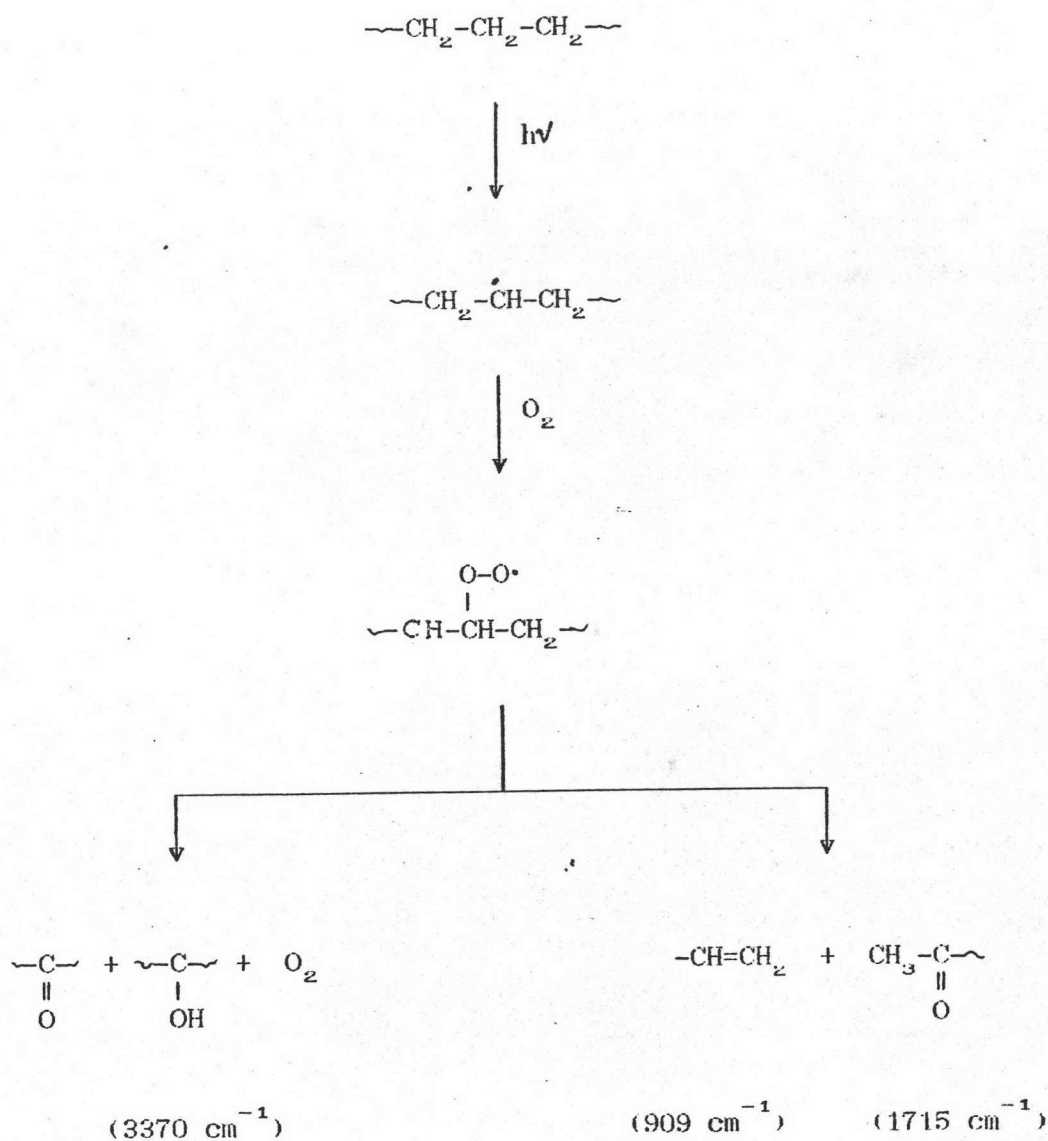
For the samples irradiated with 4-fluorescent lamps, the degradation tendencies is the same as that of outdoor exposure in the first 30 days. With further photo-irradiation, the degradation tendencies could not be different from that of outdoor exposure.

The changes in HDPE irradiated with medium pressure mercury lamp also have the same degradation tendencies. From figure 4.19, it was clarified that medium pressure mercury lamp show higher acceleration with regards to the tensile properties with irradiation time. Comparison between effect of fluorescent lamp and medium pressure mercury lamp indicated that the samples irradiated with 4-fluorescents have a lower degradation rate than those irradiated with medium pressure mercury lamp. The lower

degradation rate may be due to the low intensity of the light source (about 260 watts/mm² for fluorescent lamps and 760 watts/mm² for medium pressure mercury lamp).

From this experimental results, the following reaction mechanism (scheme 1) should be able to explain the radical formation and the reaction pathways to final products during irradiation.

In the presence of air :

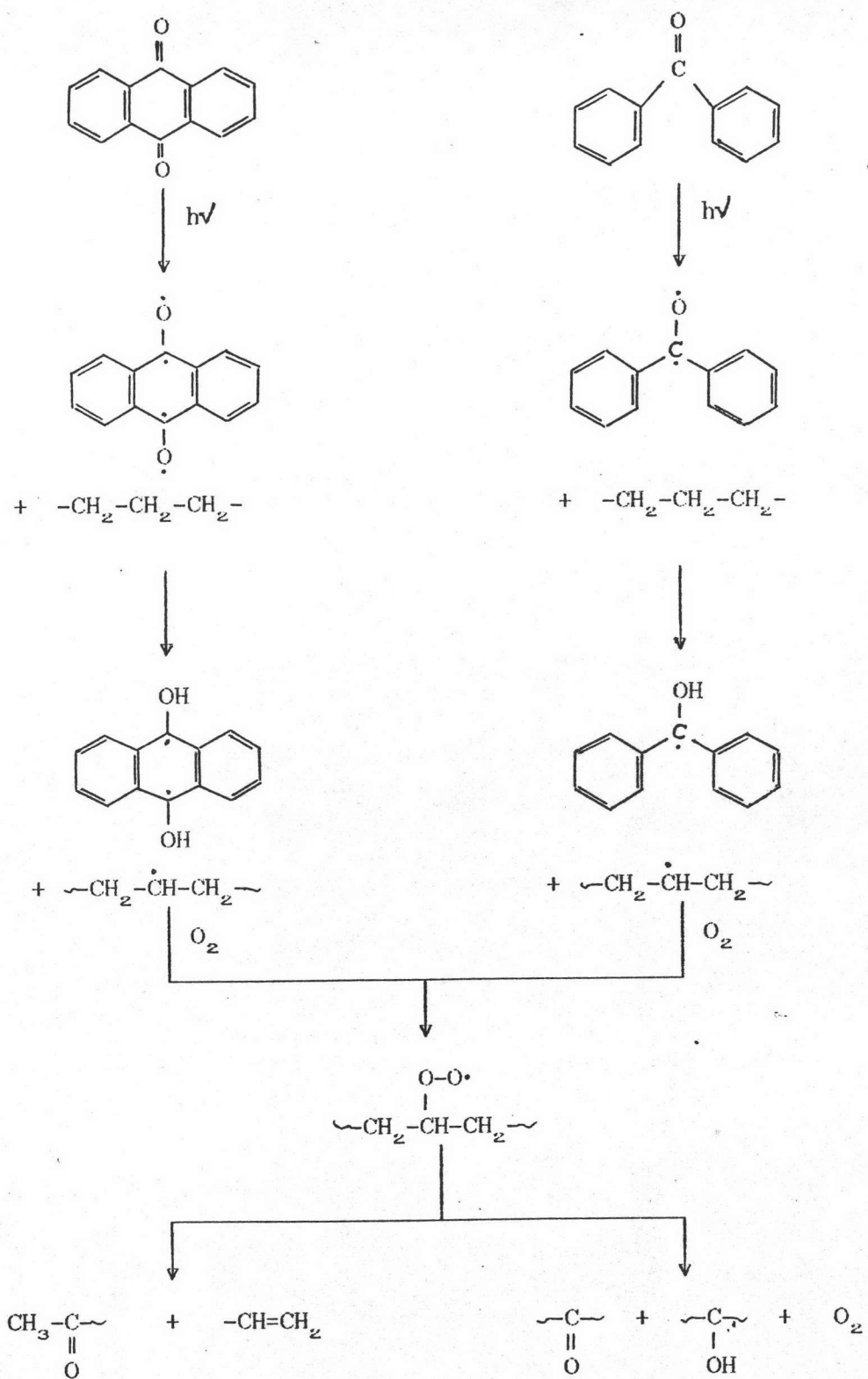


Scheme 1 Photo-oxidative degradation reaction of HDPE sheet.

5.2 Doped high density polyethylene

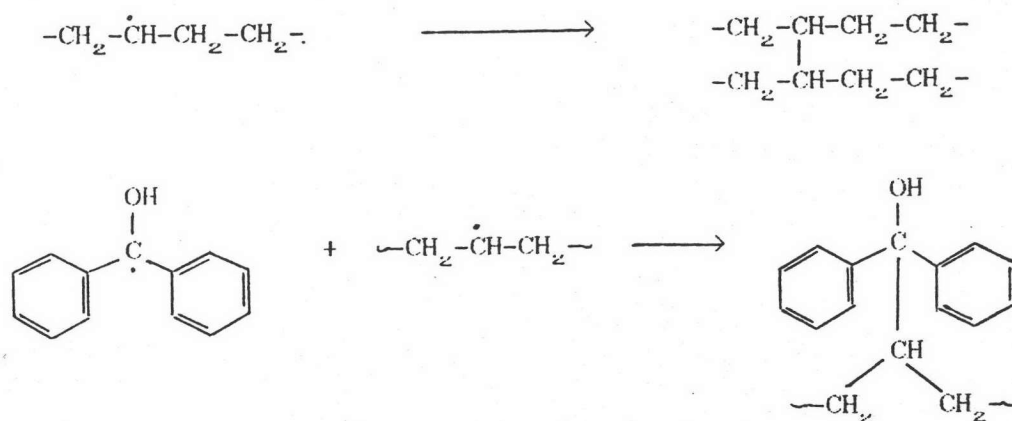
The effect of the photosensitizers on the ease of photodegradation is also of interest, since in most cases it is desired to incorporate the photosensitizer into the polymer prior to the fabrication of a film, sheet or molded article by convention melt processing technology. The effect of time and photosensitizer concentration on the extent of photodegradation were determined by tensile strength, elongation at break and fourier transform infrared absorption. The outdoor exposure resulted in an average decrease of molecular weight of doped HDPE containing 1.0 %, 1.5 % and 2.0 % by weight of 2-photosensitizers on about 4.43, 4.73, 5.20 times and for the tensile strength about 79.9 %, 82.2 % and 90.5 %, respectively, in comparison with nonexposed sheets (figure 4.4). The greatest changes of the sheet properties occurred during the first 2 months of outdoor exposure. Especially for elongation at break which decreased almost 100 %. The influence of the shorter chain molecules, present in the degraded product, might result in the formation of a structure with different morphology characterized by higher tensile strengths. The sample exposed for 30 days show cross-linked structures and tensile strength values still higher than those of the starting sheet. After 30 days decay of the tensile strength starts and proceeds regularly with time. This behavior takes place in the early stage for all doped samples irradiated under both natural and accelerated weathering.

The mechanisms of chain scission and cross-linking which occurs when doped HDPE is irradiated are shown as follows



Scheme 2 Photo-sensitized degradation reaction of HDPE sheet.

Cross-linked reaction



As shown in figures 4.15-4.18, the action of anthraquinone and benzophenone photosensitizers is concentrated mainly in the first stage of the process. The content of the carbonyl group in the molecule of photosensitizers drops very rapidly, indicating a depletion of the photosensitizer system. This depletion is a consequence of the photo-reduction of photosensitizers during the photosensitized polyethylene oxidation. After depletion of photosensitizer carbonyls, the sensitizing function of aliphatic carbonyls and of hydroperoxides forms via polyethylene photo-oxidation begins to be important. Thus, in the presence of sensitizers the critical conditions necessary to affect mechanical behavior are reached very rapidly after the beginning of irradiation and no induction period in the evolution of tensile properties is observed.

With regards to the concentration of 2-photosensitizers, anthraquinone and benzophenone, the degradation tendencies are the same but HDPE sheets containing the highest quantity of photosensitizers have the most rapid degradation rates. However, the difference in photodegradation rate is slight.

5.3 Comparison of the degradation tendencies between outdoor exposure and accelerating test

For comparison of the degradation rate between outdoor exposure to accelerating weathering, the values on the point that the curves were cut by the line showing a half of the originals are taken from figures 4.25-4.26. The values are collected in table 5.1. From this table, for example, the result obtained was that the degradation degree of undoped HDPE sheets are equal in 612 hours of outdoor exposure starting in september to 397.8 hours of irradiation by fluorescent lamp.

Table 5.1 Exposure period when elongation at break is reduced by half

Photosensitizer content (%)	Outdoor exposure (hour)	Fluorescent irradiation (hour)
0.0	612	397.8
1.0	168	33.1
1.5	156	32.4
2.0	144	28.8

It has been reported in other reports [13] is that the elongation at break is suitable to use to evaluate the weatherability of plastics. The same idea must be applicable in evaluating the correlation between undoped and doped HDPE at various concentrations of photosensitizers and then the accelerating factor, A_1 , was obtained.

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

where

$t_{1/2} (0)$ is the exposure period for a character to decrease by half at 0 % photosensitizer

$t_{1/2} (i)$ is the exposure period for a character to decrease by half at i % photosensitizer

For outdoor exposure , the following accelerating factors were obtained : 1.0 , 3.6 , 3.9 and 4.3 for 0 , 1.0 , 1.5 , 2.0 % photosensitizers , respectively. Accelerating factors for irradiation with fluorescent lamps were 1.0 , 12 , 12.3 and 13.8 for 0 , 1.0 , 1.5 and 2.0 % photosensitizers , respectively. The result are shown in table 4.2.

Table 5.2 Accelerating factors of outdoor exposure and accelerated weathering test.

Photosensitizer content (%)	Outdoor exposure hours	Fluorescent irradiation hours
0.0	1.0	1.0
1.0	3.6	12.0
1.5	3.9	12.3
2.0	4.3	13.8

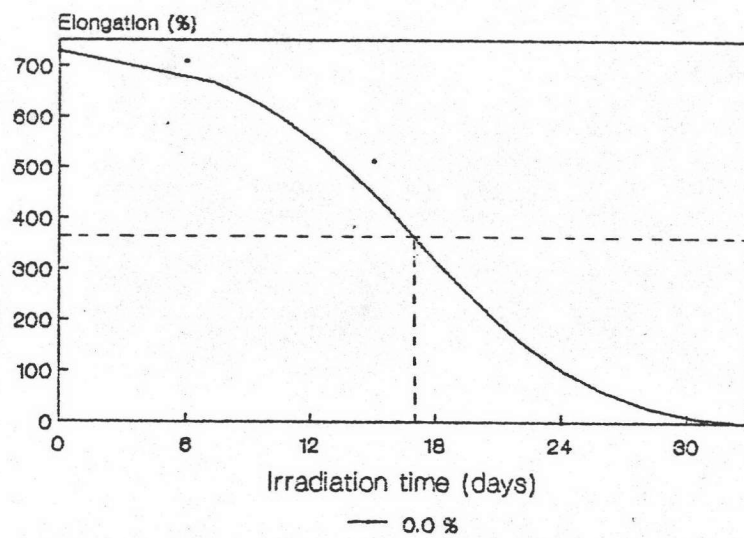
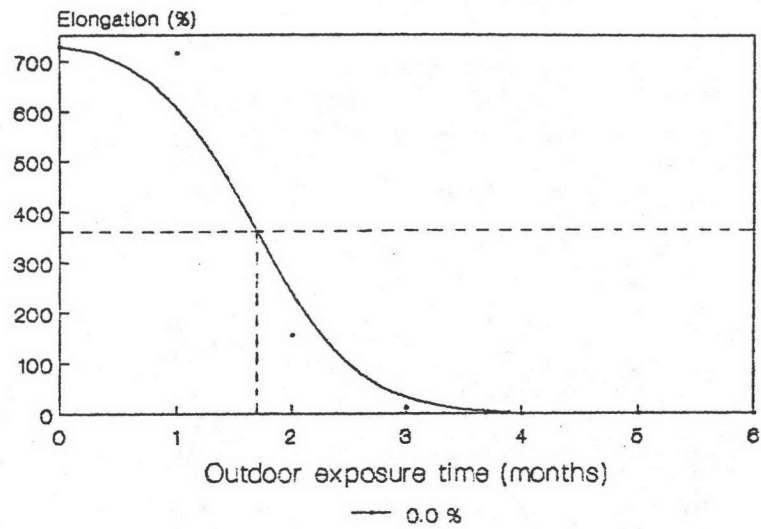


Figure 4.25 Comparisons of degradation rate of undoped HDPE in outdoor exposure test, and 4-fluorescent lamps test.

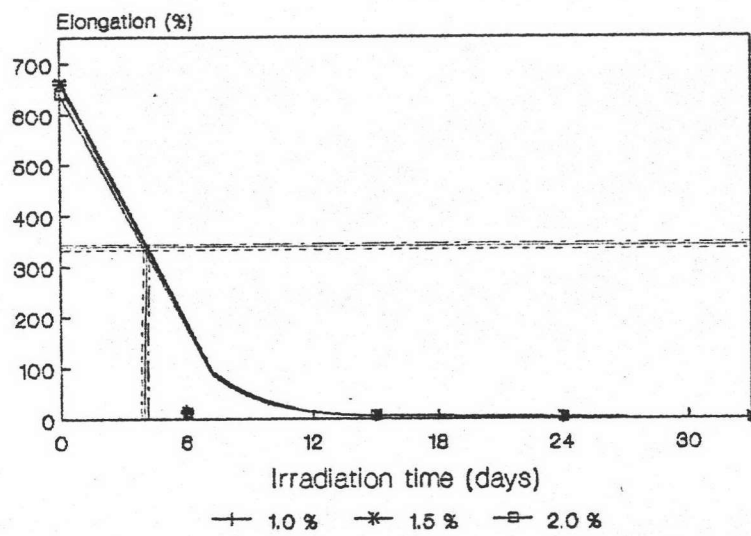
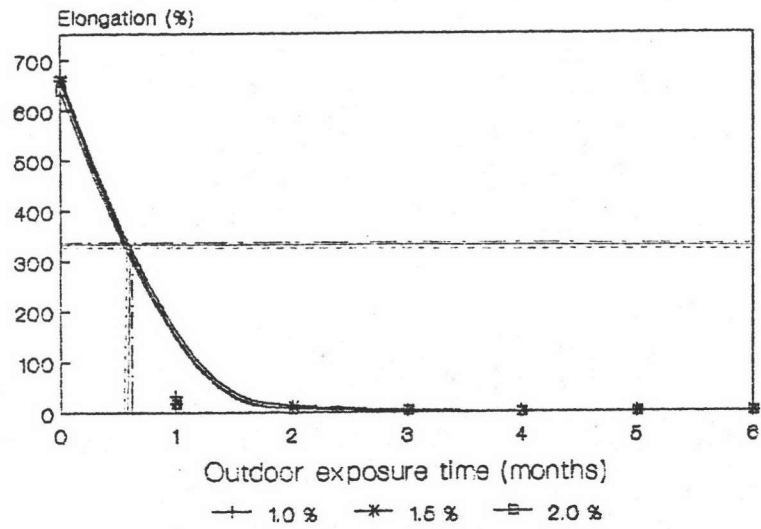


Figure 4.26 Comparisons of degradation rate of doped HDPE in outdoor exposure test and 4-fluorescent lamps test.