



## CHAPTER 4

### RESULTS

The progress of photodegradation of blow moulding poly(vinyl chloride) with and without photosensitizer, benzophenone or anthraquinone, were observed both by natural weathering and accelerated irradiation test. Blow moulding poly(vinyl chloride) sheets contain the photosensitizer at concentrations of 0 %, 0.1 %, 0.5 % and 1.0 % by weight for natural exposure and 0 %, 0.05 %, 0.1 % and 0.5 % by weight for accelerated irradiation. Unsensitized and sensitized blow moulding poly(vinyl chloride) sheets were exposed under natural weathering condition for 9 months. For the accelerating tests, the sheet samples were irradiated with a medium pressure mercury lamp for 240 hours. The mechanical properties (tensile strength, elongation at rupture) and physical properties (molecular weight, optical absorption, visual inspection) of all samples before and after irradiation were used for investigating the photodegradation processes.

#### 4.1 Natural Weathering test

##### 4.1.1 Result of tensile properties

The example of load-elongation (stress-strain) traces of both irradiated unsensitized and sensitized samples is shown in Fig. 4.1a - 4.1b. The decreasing of elongation at rupture of the irradiated polymer can be seen in Fig. 4.3a and b while the load of every sample is slightly changed with irradiation time as in Fig. 4.2a and b. Thus, for this work, the elongation at rupture will be used for showing the degradation tendency of the investigation of the photodegradation process.

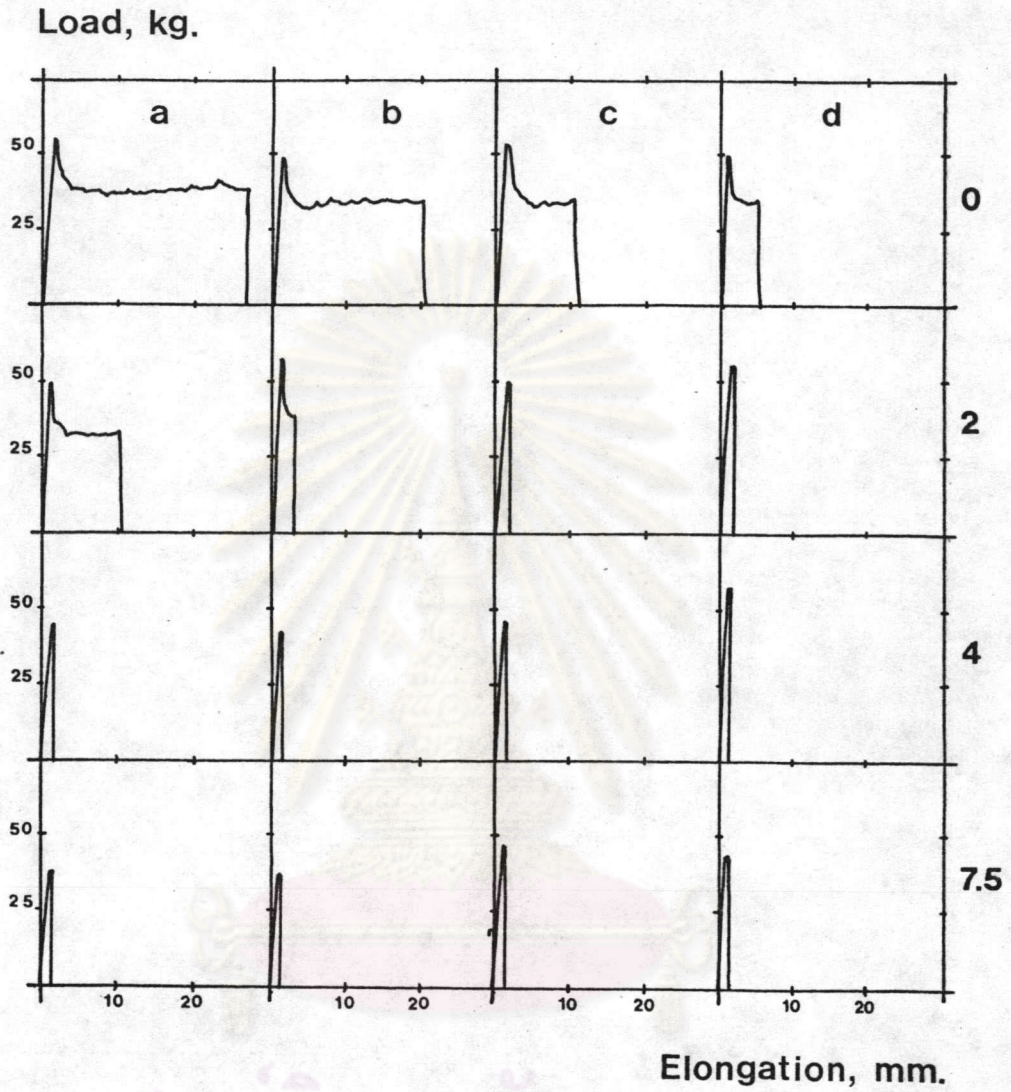


Fig. 4.1a Load-Elongation of outdoor exposure samples at various exposure time (indicated on curve in months) :

a) 0 % photosensitizer, b) 0.1 % anthraquinone, c) 0.5 % anthraquinone and d) 1.0 % anthraquinone

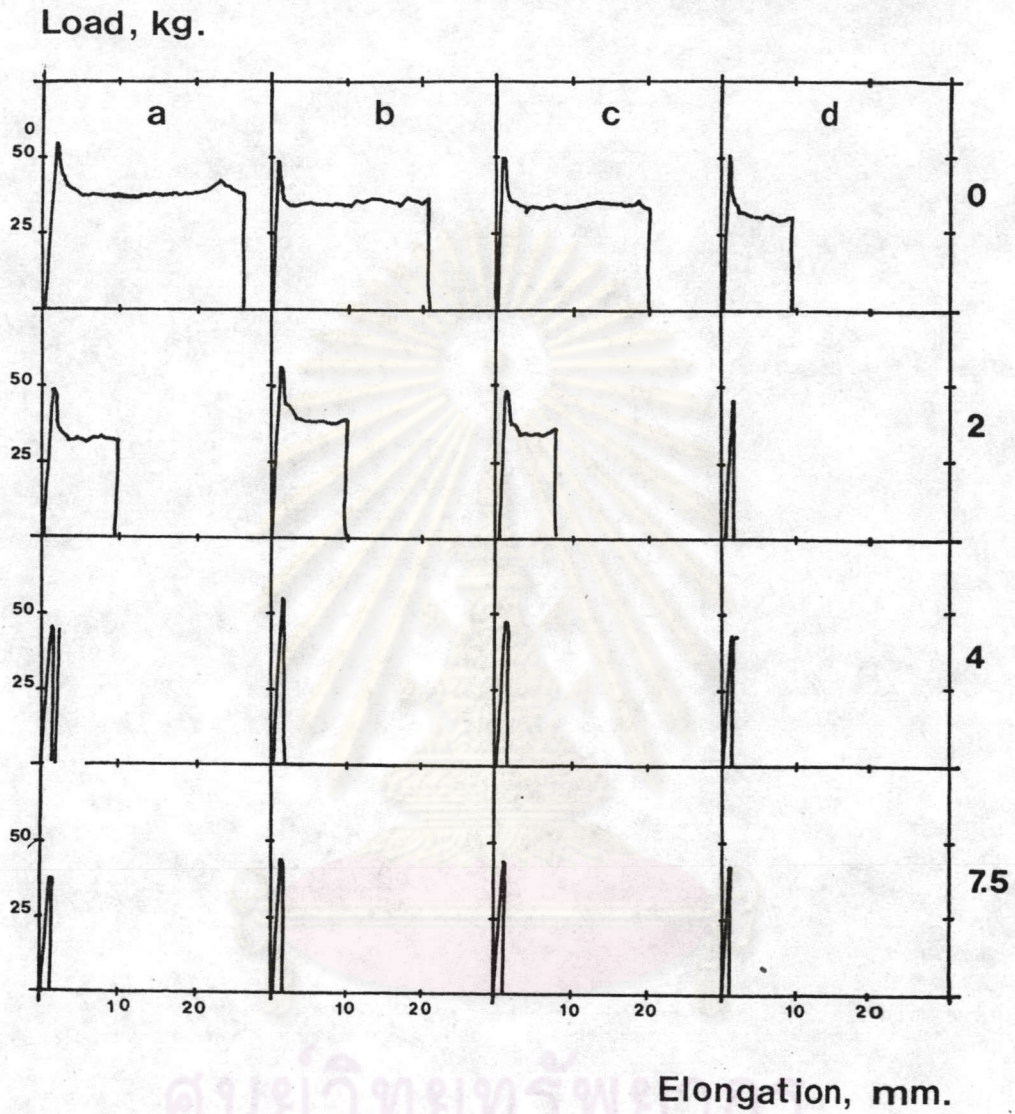


Fig. 4.1b Load-Elongation of outdoor exposure samples at various exposure time (indicated on curve in months) :

a) 0 % photosensitizer, b) 0.1 % benzophenone, c) 0.5 % benzophenone and d) 1.0 % benzophenone

TABLE 4-1a The relationship of tensile strength and the exposure time for PVC outdoor exposure samples (photosensitizer : anthraquinone)

| Exposure time (months) | Tensile strength (kg/mm <sup>2</sup> ) |          |          |          |
|------------------------|--|----------|----------|----------|
|                        | 0% ANT                                 | 0.1% ANT | 0.5% ANT | 1.0% ANT |
| original               | 5.55                                   | 5.90     | 5.85     | 6.10     |
| 1.0                    | 5.85                                   | 6.20     | 5.85     | 5.90     |
| 2.0                    | 5.90                                   | 5.85     | 5.85     | 6.20     |
| 3.0                    | 6.30                                   | 5.95     | 4.90     | 5.95     |
| 4.0                    | 6.00                                   | 5.20     | 5.40     | 5.95     |
| 5.0                    | 6.00                                   | 5.20     | 5.35     | 6.00     |
| 6.0                    | 5.65                                   | 5.15     | 5.00     | 5.35     |
| 7.5                    | 4.90                                   | 4.25     | 4.20     | 4.55     |
| 9.0                    | 3.95                                   | 3.80     | 3.80     | 3.55     |

TABLE 4-1b The relationship of tensile strength and the exposure time for PVC outdoor exposure samples (photosensitizer : benzophenone)

| Exposure time (months) | Tensile strength (kg/mm <sup>2</sup> ) |          |          |          |
|------------------------|--|----------|----------|----------|
|                        | 0% BEN                                 | 0.1% BEN | 0.5% BEN | 1.0% BEN |
| original               | 5.55                                   | 5.85     | 5.90     | 6.15     |
| 1.0                    | 5.85                                   | 5.50     | 5.95     | 6.20     |
| 2.0                    | 5.90                                   | 6.25     | 6.05     | 5.35     |
| 3.0                    | 6.30                                   | 6.55     | 6.20     | 5.60     |
| 4.0                    | 6.00                                   | 5.95     | 5.90     | 5.65     |
| 5.0                    | 6.00                                   | 5.30     | 5.40     | 5.70     |
| 6.0                    | 4.95                                   | 4.60     | 4.60     | 4.45     |
| 7.5                    | 4.10                                   | 4.25     | 4.78     | 4.90     |
| 9.0                    | 3.75                                   | 3.90     | 3.85     | 3.30     |

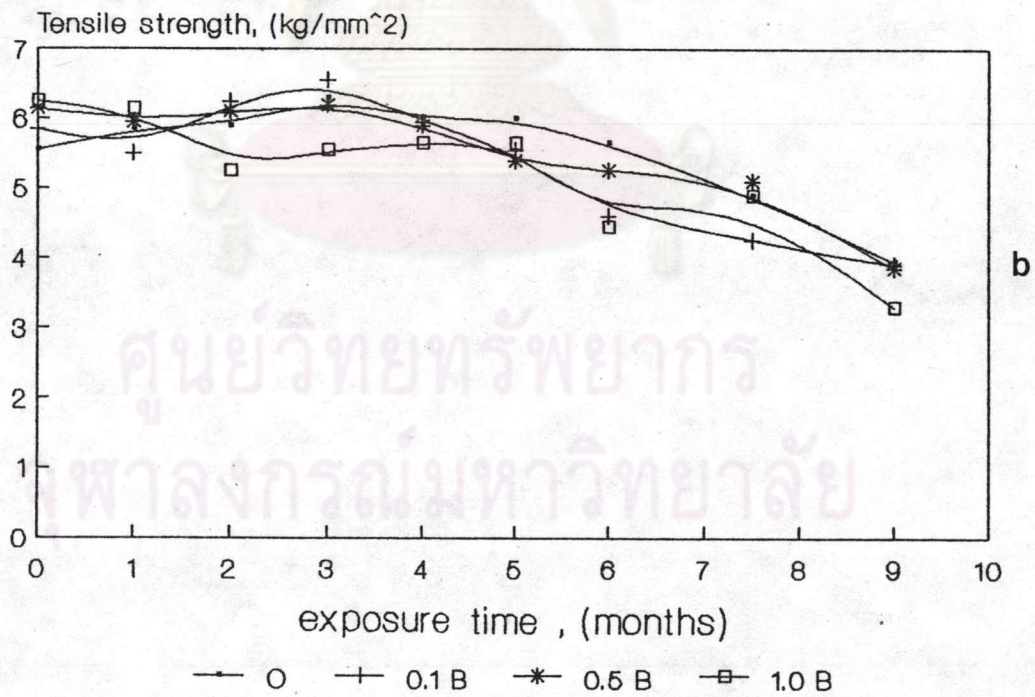
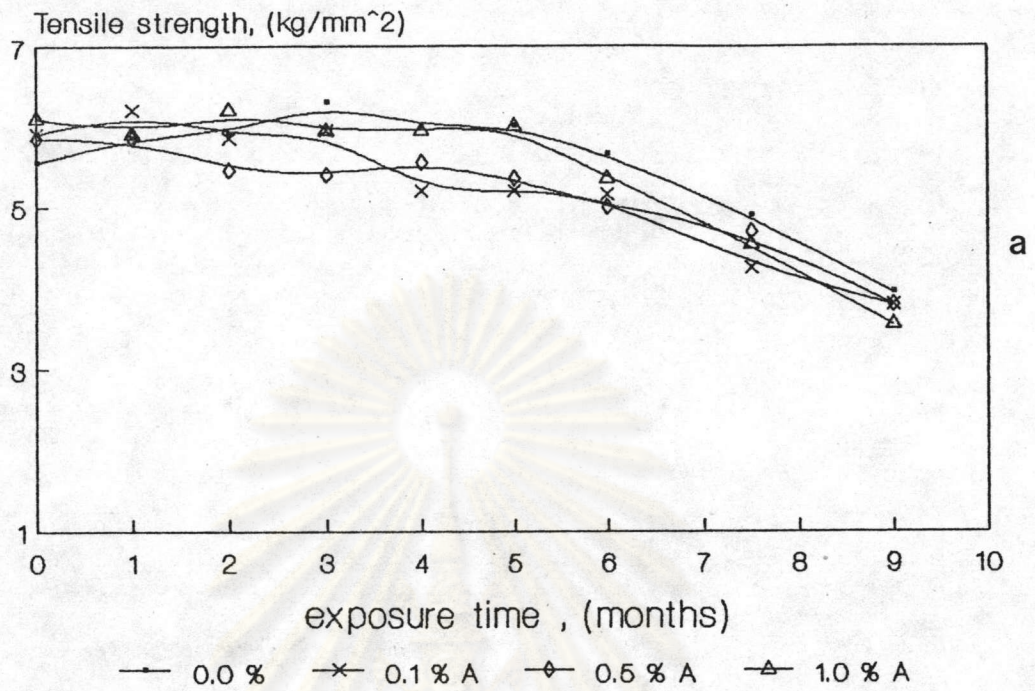


Fig. 4.2 Tensile strength of PVC samples at various concentrations of photosensitizer as a function of outdoor exposure time. : a) anthraquinone, b) benzophenone

TABLE 4-2a The relationship of % elongation and the exposure time for PVC outdoor exposure samples (photosensitizer : anthraquinone)

| Exposure time (months) | Elongation at rupture (%) |          |          |          |
|------------------------|---------------------------|----------|----------|----------|
|                        | 0% ANT                    | 0.1% ANT | 0.5% ANT | 1.0% ANT |
| original               | 87.00                     | 62.00    | 23.00    | 7.00     |
| 1.0                    | 28.00                     | 14.50    | 2.00     | 1.50     |
| 2.0                    | 23.30                     | 9.00     | 1.00     | 1.50     |
| 3.0                    | 11.00                     | 5.00     | 1.00     | 1.00     |
| 4.0                    | 5.00                      | 3.00     | 1.00     | 1.00     |
| 5.0                    | 3.00                      | 1.00     | 1.00     | 1.00     |
| 6.0                    | 1.50                      | 2.00     | 1.00     | 1.00     |
| 7.5                    | 1.50                      | 1.50     | 1.00     | 1.00     |
| 9.0                    | 1.00                      | 1.00     | 1.00     | 1.00     |

TABLE 4-2b The relationship of % elongation and the exposure time for PVC outdoor exposure samples (photosensitizer : benzopheonone)

| Exposure time (months) | Elongation at rupture (%) |          |          |          |
|------------------------|---------------------------|----------|----------|----------|
|                        | 0% BEN                    | 0.1% BEN | 0.5% BEN | 1.0% BEN |
| original               | 87.00                     | 71.00    | 65.00    | 22.00    |
| 1.0                    | 28.00                     | 28.63    | 13.00    | 5.00     |
| 2.0                    | 23.30                     | 18.50    | 13.50    | 1.50     |
| 3.0                    | 11.00                     | 9.00     | 2.00     | 2.00     |
| 4.0                    | 5.00                      | 4.00     | 1.50     | 1.80     |
| 5.0                    | 3.00                      | 3.50     | 1.00     | 1.00     |
| 6.0                    | 1.50                      | 1.50     | 1.00     | 1.00     |
| 7.5                    | 1.50                      | 1.00     | 1.00     | 1.00     |
| 9.0                    | 1.00                      | 1.00     | 1.00     | 1.00     |

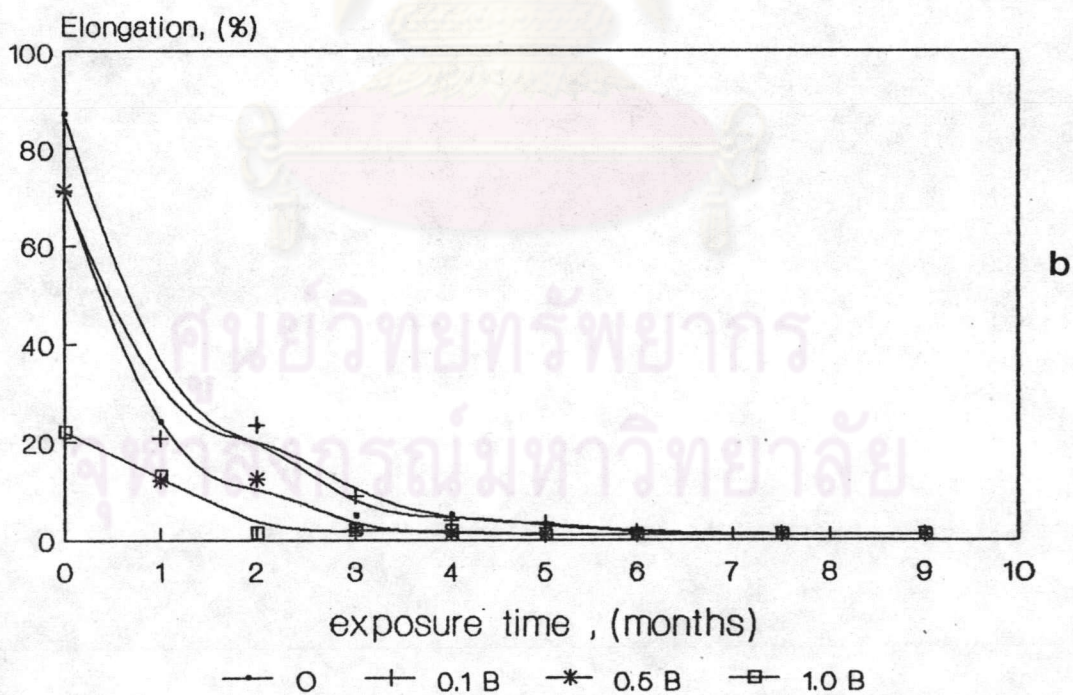
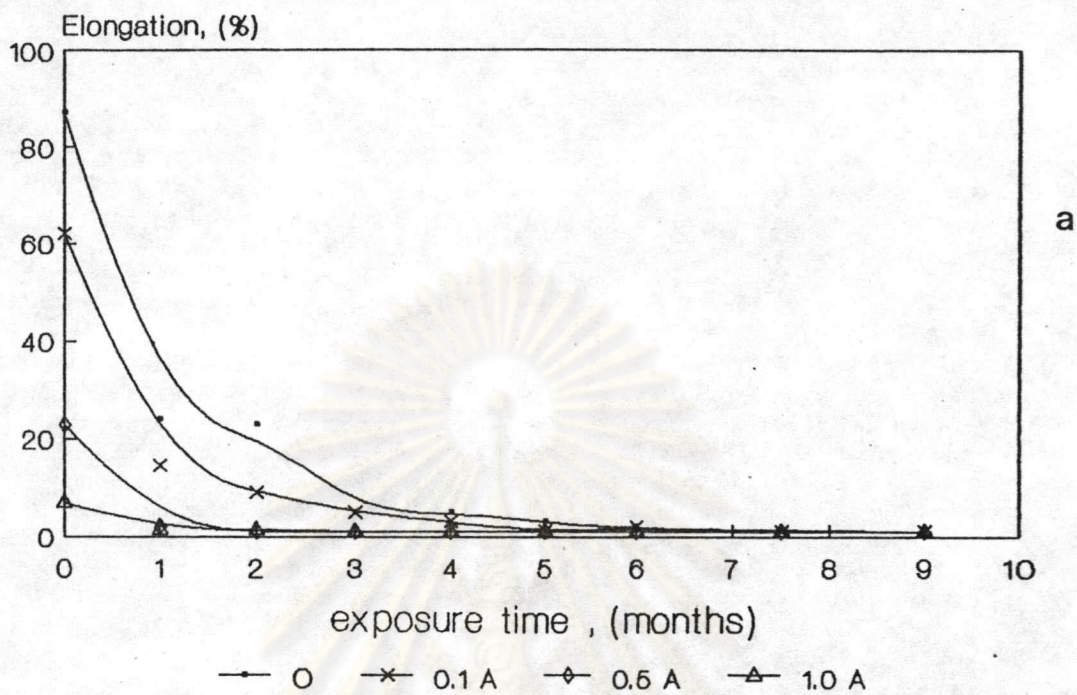


Fig. 4.3 Elongation at break of PVC samples at various concentrations of photosensitizer as a function of outdoor exposure time.  
: a) anthraquinone, b) benzophenone

#### 4.1.2 Result of molecular weight

##### (a) Unsensitized PVC samples

The molecular weight of unsensitized PVC samples decrease very slightly within the first four months of the exposure periods. After then, the molecular weight decreases gradually with exposure time.

##### (b) Sensitized PVC samples

###### - Anthraquinone sensitized PVC

The molecular weight of the PVC contained 0.1 % anthraquinone decreases slightly at the early months of exposure. While the molecular weight of PVC contained 0.5 % anthraquinone increases from the original value of the unirradiated at the first month and then decrease at the second month as well as the occurrence of the insoluble gel residues. The molecular weight of PVC contained 1.0 % anthraquinone decreased gradually since the beginning of the exposure and insoluble gel residues were observed since the first months of the exposure. The soluble fraction was separated from the insoluble part by filtration and then taken for further measurement of the molecular weight.

###### - Benzophenone sensitized PVC

The molecular weight of sensitized PVC samples decrease slightly during the early months of irradiation. The trend of decreasing in molecular weight is the same as anthraquinone sensitizer. As the polymer contains more photosensitizer, the lower molecular weight receives. The gel particles for every concentration is not noticeable except at the concentration of 1.0 % by weight after 7.5 months of exposure periods.



Table 4-3a Relation between intrinsic viscosity  $[\eta]$  and average molecular weight (MW) for PVC outdoor exposure samples (photosensitizer : anthraquinone)

| Exposure time (months)   | Intrinsic viscosity $[\eta]$ | molecular weight $\times 10^{-4}$ |
|--------------------------|------------------------------|-----------------------------------|
| PVC-0% ANT<br>original   | 0.7305                       | 5.5220                            |
| 1                        | 0.7290                       | 5.5070                            |
| 2                        | 0.7258                       | 5.4760                            |
| 3                        | 0.7200                       | 5.4190                            |
| 4                        | 0.7178                       | 5.3980                            |
| 5                        | 0.7086                       | 5.3080                            |
| 6                        | 0.6992                       | 5.2170                            |
| 7.5                      | 0.6854                       | 5.0840                            |
| 9                        | 0.6692                       | 4.9280                            |
| PVC-0.1% ANT<br>original | 0.7445                       | 5.6600                            |
| 1                        | 0.7349                       | 5.5660                            |
| 2                        | 0.7194                       | 5.4130                            |
| 3                        | 0.7081                       | 5.3030                            |
| 4                        | 0.6940                       | 5.1670                            |
| 5                        | 0.6765                       | 4.9980                            |
| 6                        | 0.6578                       | 4.8190                            |
| 7.5                      | 0.6372                       | 4.6240                            |
| 9                        | 0.6138                       | 4.4050                            |
| PVC-0.5% ANT<br>original | 0.7509                       | 5.7230                            |
| 1                        | 0.7549                       | 5.7630                            |
| 2                        | 0.7420                       | 5.6360                            |
| 3                        | 0.7261                       | 5.4790                            |
| 4                        | 0.7102                       | 5.3240                            |
| 5                        | 0.6924                       | 5.1510                            |
| 6                        | 0.6708                       | 4.9440                            |
| 7.5                      | 0.6424                       | 4.6730                            |
| 9                        | 0.6145                       | 4.4110                            |
| PVC-1.0% ANT<br>original | 0.7593                       | 5.8070                            |
| 1                        | 0.7482                       | 5.6970                            |
| 2                        | 0.7323                       | 5.5400                            |
| 3                        | 0.7141                       | 5.3620                            |
| 4                        | 0.6934                       | 5.1610                            |
| 5                        | 0.6722                       | 4.9570                            |
| 6                        | 0.6513                       | 4.7580                            |
| 7.5                      | 0.6309                       | 4.5650                            |
| 9                        | 0.6011                       | 4.2870                            |

Table 4-3b Relation between intrinsic viscosity  $[\eta]$  and average molecular weight (MW) for PVC outdoor exposure samples  
(photosensitizer : benzophenone)

| Exposure time<br>(months) | Intrinsic viscosity<br>$[\eta]$ | molecular weight<br>$\times 10^{-4}$ |
|---------------------------|---------------------------------|--------------------------------------|
| PVC-0% ANT<br>original    | 0.7305                          | 5.5220                               |
| 1                         | 0.7290                          | 5.5076                               |
| 2                         | 0.7258                          | 5.4760                               |
| 3                         | 0.7200                          | 5.4590                               |
| 4                         | 0.7178                          | 5.3980                               |
| 5                         | 0.7086                          | 5.3080                               |
| 6                         | 0.6992                          | 5.2170                               |
| 7.5                       | 0.6854                          | 5.0840                               |
| 9                         | 0.6692                          | 4.9280                               |
| PVC-0.1% BEN<br>original  | 0.7412                          | 5.6280                               |
| 1                         | 0.7365                          | 5.5810                               |
| 2                         | 0.7266                          | 5.4840                               |
| 3                         | 0.7161                          | 5.3810                               |
| 4                         | 0.7018                          | 5.2420                               |
| 5                         | 0.6851                          | 5.0810                               |
| 6                         | 0.6698                          | 4.9340                               |
| 7.5                       | 0.6490                          | 4.7360                               |
| 9                         | 0.6239                          | 4.4990                               |
| PVC-0.5% BEN<br>original  | 0.7480                          | 5.6960                               |
| 1                         | 0.7445                          | 5.6600                               |
| 2                         | 0.7367                          | 5.5830                               |
| 3                         | 0.7194                          | 5.4140                               |
| 4                         | 0.7031                          | 5.2550                               |
| 5                         | 0.6840                          | 5.0700                               |
| 6                         | 0.6654                          | 4.8920                               |
| 7.5                       | 0.6411                          | 4.6610                               |
| 9                         | 0.6163                          | 4.4280                               |
| PVC-1.0% BEN<br>original  | 0.7555                          | 5.7690                               |
| 1                         | 0.7450                          | 5.6650                               |
| 2                         | 0.7319                          | 5.5360                               |
| 3                         | 0.7175                          | 5.3950                               |
| 4                         | 0.7017                          | 5.2410                               |
| 5                         | 0.6843                          | 5.0730                               |
| 6                         | 0.6665                          | 4.9020                               |
| 7.5                       | 0.6435                          | 4.6840                               |
| 9                         | 0.6157                          | 4.4230                               |

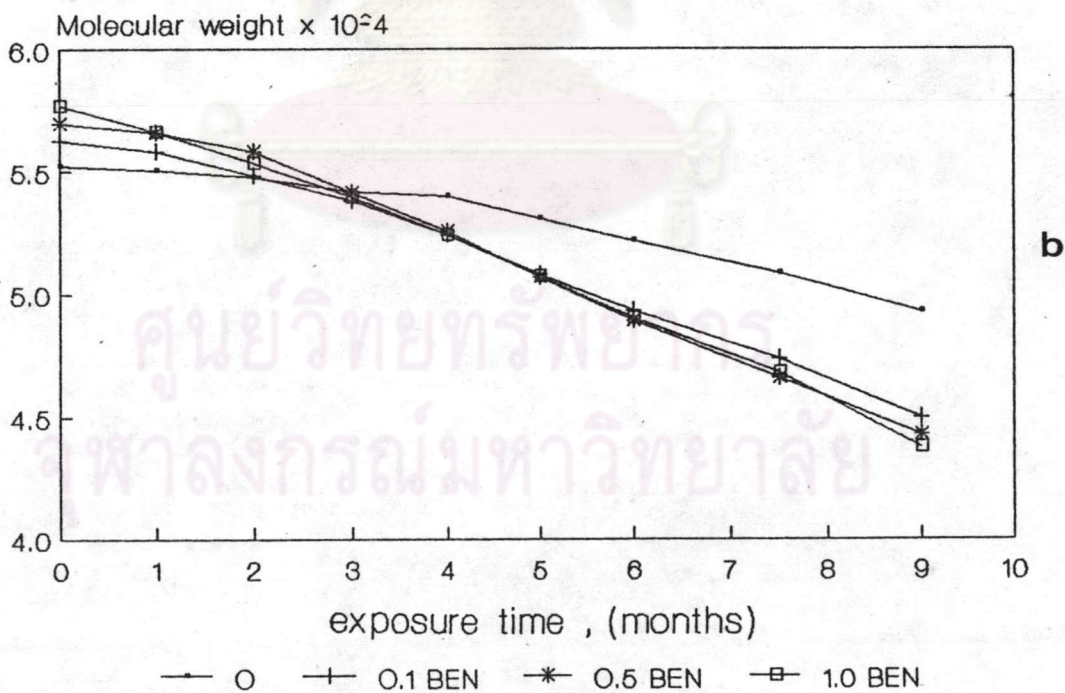
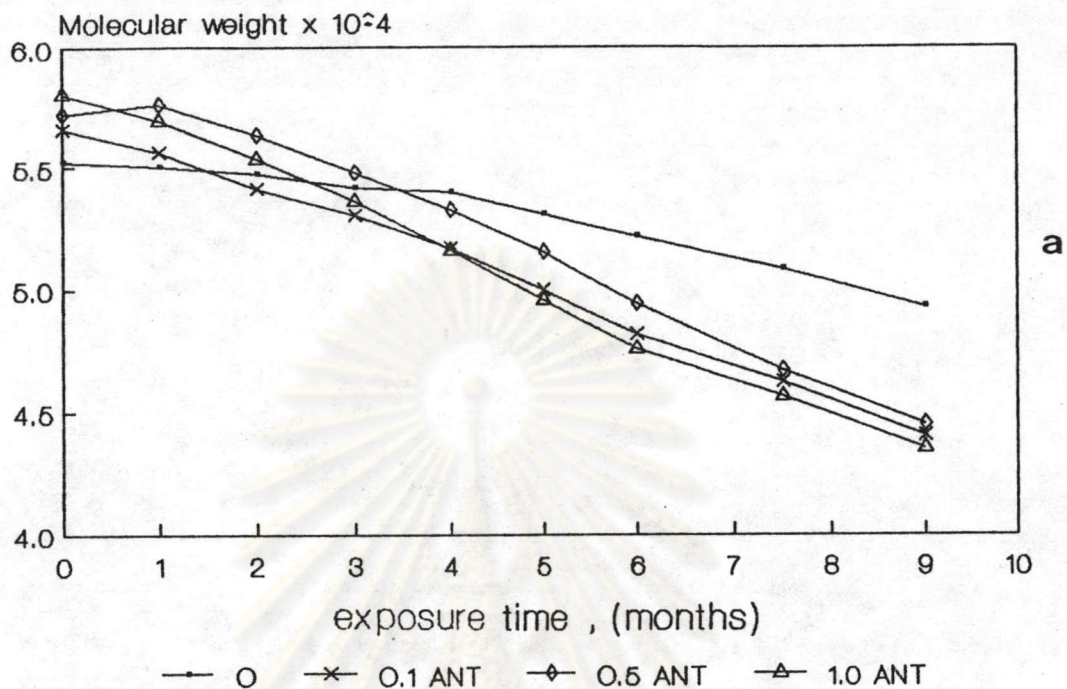


Fig. 4.4 Molecular weight traces of PVC samples at various concentrations of photosensitizer as a function of outdoor exposure time. : a) anthraquinone, b) benzophenone

#### 4.1.3 Result of Fourier Transform infrared absorption

The Fourier transform infrared absorption spectra of the exposed samples are obtained and the typical spectra are shown in Fig. 4.5. Absorption peaks are observed in

(a) the  $1735\text{ cm}^{-1}$  band corresponds to the presence of the carbonyl group in the PVC chain.

(b) the intensity of the maximum of a broad band at  $3460\text{ cm}^{-1}$ , reflects the concentration of hydroxyl group in PVC sheets.

(c) The poly(vinyl chloride) band at  $638\text{ cm}^{-1}$  serves as an internal standard to which the absorbances of the other bands that are related.

The relative absorbance of PVC carbonyl groups ( $A_{1735}$ ) is plotted in Fig. 4.6 a and b as a function of exposure time. The rate of formation of carbonyl group for the sensitized samples increases remarkably at the beginning and subsequently slows down. While the carbonyl formation of the unsensitized samples increases slowly at the beginning. The formation of carbonyl group in the anthraquinone system is higher than the benzophenone one.

Fig. 4.7 a and b show the changing intensity of the hydroxyl absorption band ( $A_{3460}$ ) with exposure time. The absorption of hydroxyl bands increases slowly at the early stage of the exposure and then increases rapidly at the exposure time that corresponds to the greatest change in the tensile properties.

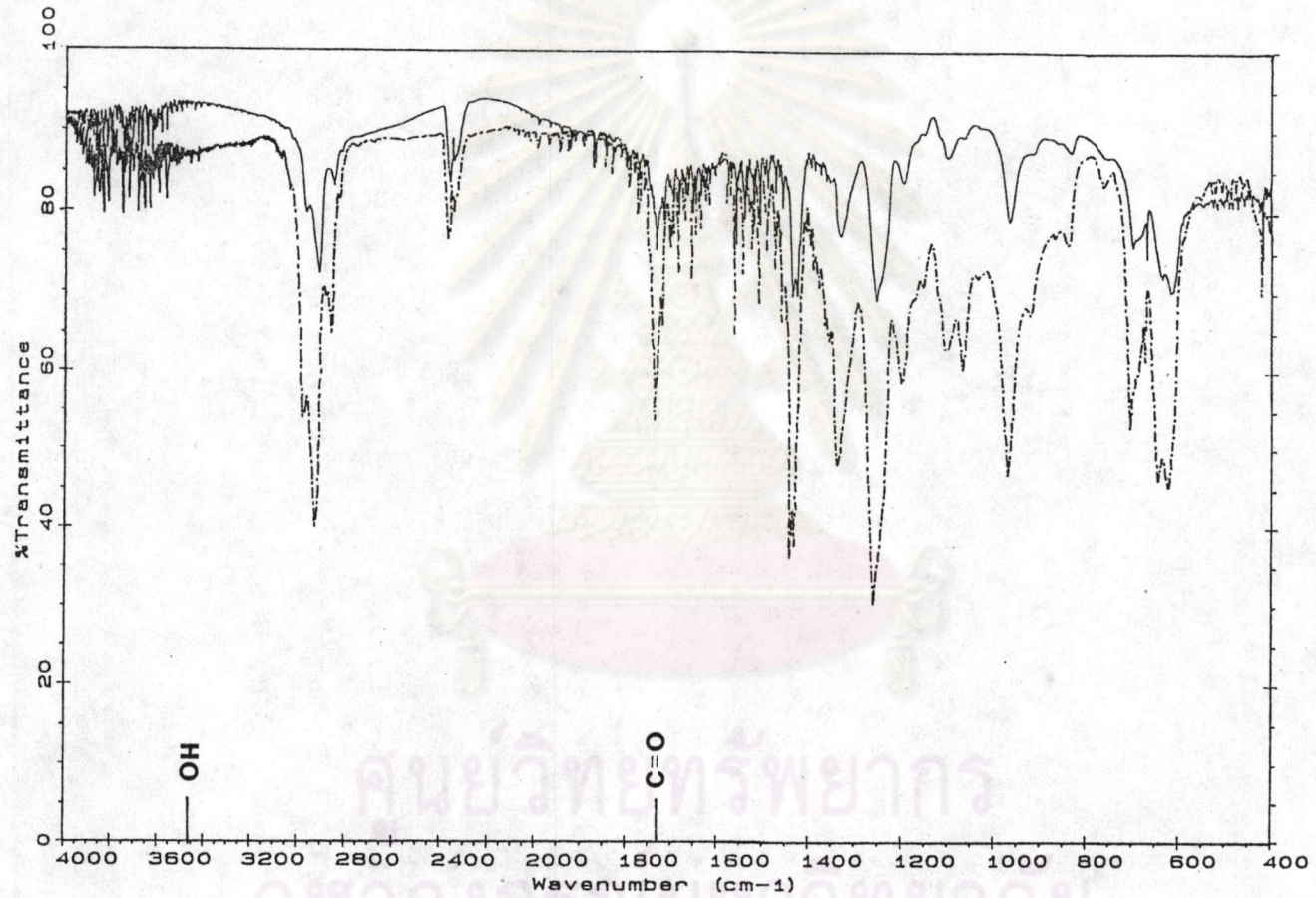


Fig. 4.5.1 FT-IR spectra of PVC outdoor exposure samples at 0 % photosensitizer  
----- unirradiated ,    - - - - - irradiated for 6 months

Table 4.4a Carbonyl Index in PVC chain of outdoor exposure samples (sensitizer : anthraquinone)

| Exposure Time | Carbonyl Index (1735 cm <sup>-1</sup> ) |        |
|---------------|---|--------|
|               | 0 %                                     | 0.1% A |
| original      | 0.280                                   | 0.561  |
| 1 month       | 0.383                                   | 0.624  |
| 2 months      | 0.548                                   | 0.674  |
| 3 months      | 0.627                                   | 0.713  |
| 4 months      | 0.675                                   | 0.745  |
| 5 months      | 0.705                                   | 0.790  |
| 6 months      | 0.761                                   | 0.807  |
| 7.5 months    | 0.775                                   | 0.918  |

Table 4.4b Carbonyl Index in PVC chain of outdoor exposure samples (sensitizer : benzophenone)

| Exposure Time | Carbonyl Index (1735 cm <sup>-1</sup> ) |        |        |        |
|---------------|---|--------|--------|--------|
|               | 0 %                                     | 0.1% B | 0.5% B | 1.0% B |
| original      | 0.280                                   | 0.410  | 0.610  | 0.659  |
| 1 month       | 0.383                                   | 0.519  | 0.670  | 0.680  |
| 2 months      | 0.548                                   | 0.542  | 0.672  | 0.705  |
| 3 months      | 0.627                                   | 0.638  | 0.734  | 0.745  |
| 4 months      | 0.675                                   | 0.686  | 0.761  | 0.797  |
| 5 months      | 0.705                                   | 0.735  | 0.810  | 0.812  |
| 6 months      | 0.761                                   | 0.768  | 0.814  | 0.896  |
| 7.5 months    | 0.775                                   | 0.867  | 0.887  | 0.965  |

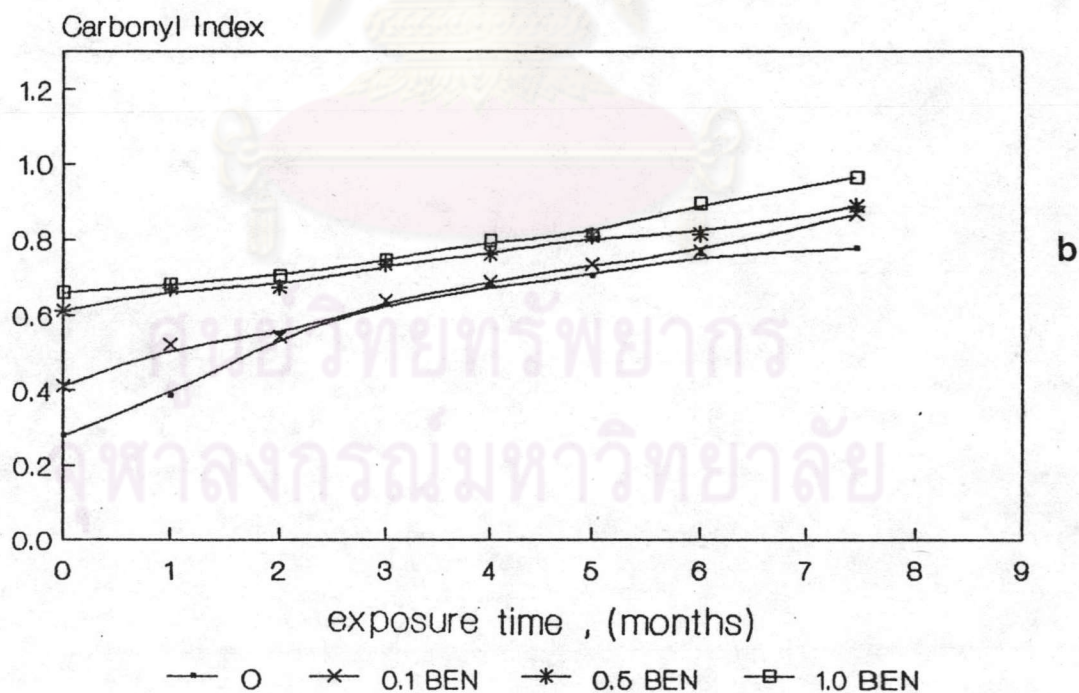
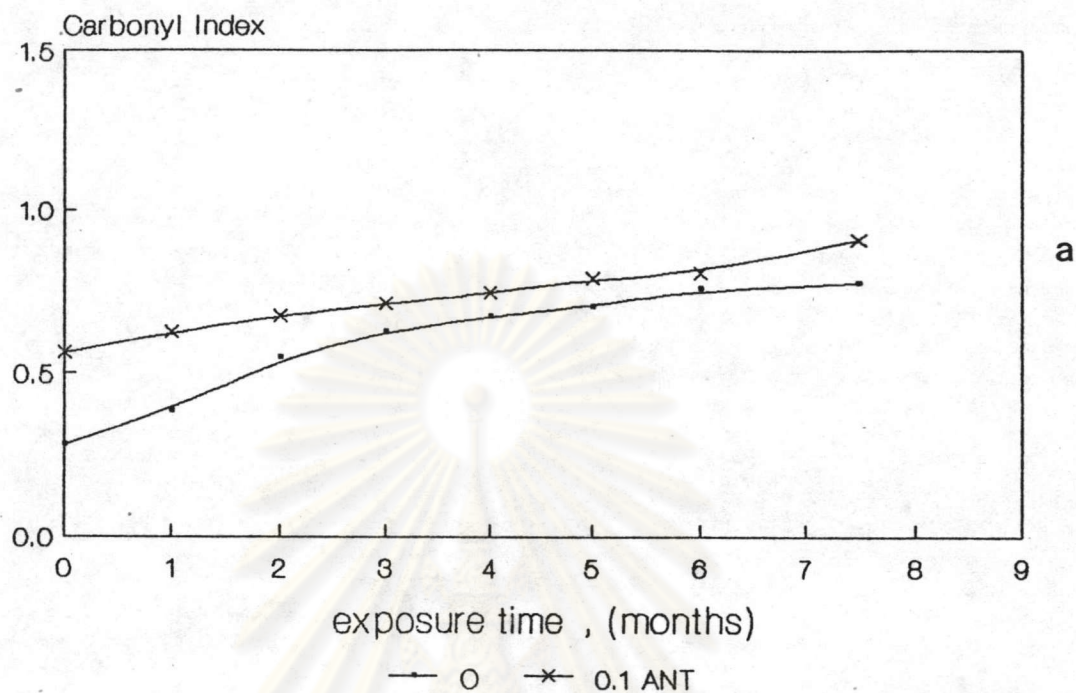


Fig. 4.6 Change of the relative FT-IR absorbance of carbonyl group in PVC chains as a function of outdoor exposure time at various concentrations of photosensitizer. :  
a) anthraquinone, b) benzophenone

Table 4.5a Hydroxyl Index in PVC chain of outdoor exposure samples  
(sensitizer : anthraquinone)

| Exposure Time | Hydroxyl Index ( $3460 \text{ cm}^{-1}$ ) |        |
|---------------|---|--------|
|               | 0 %                                       | 0.1% A |
| original      | 0.242                                     | 0.382  |
| 1 month       | 0.305                                     | 0.584  |
| 2 months      | 0.340                                     | 0.668  |
| 3 months      | 0.391                                     | 0.778  |
| 4 months      | 0.487                                     | 0.948  |
| 5 months      | 0.577                                     | 1.083  |
| 6 months      | 0.604                                     | 1.151  |
| 7.5 months    | 0.651                                     | 1.233  |

Table 4.5b Hydroxyl Index in PVC chain of outdoor exposure samples  
(sensitizer : benzophenone)

| Exposure Time | hydroxyl Index ( $3460 \text{ cm}^{-1}$ ) |        |        |        |
|---------------|---|--------|--------|--------|
|               | 0 %                                       | 0.1% B | 0.5% B | 1.0% B |
| original      | 0.242                                     | 0.273  | 0.353  | 0.406  |
| 1 month       | 0.305                                     | 0.335  | 0.435  | 0.486  |
| 2 months      | 0.340                                     | 0.372  | 0.592  | 0.653  |
| 3 months      | 0.391                                     | 0.500  | 0.748  | 0.887  |
| 4 months      | 0.487                                     | 0.623  | 0.944  | 0.982  |
| 5 months      | 0.577                                     | 0.716  | 1.040  | 1.174  |
| 6 months      | 0.604                                     | 0.874  | 1.211  | 1.231  |
| 7.5 months    | 0.651                                     | 0.923  | 1.312  | 1.335  |



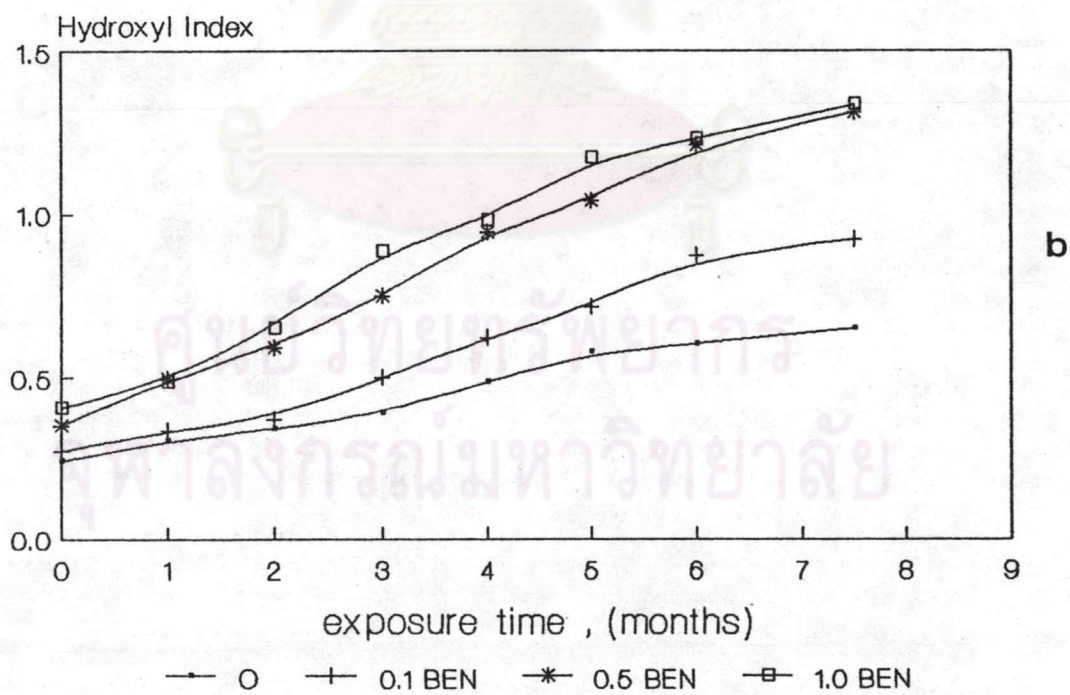
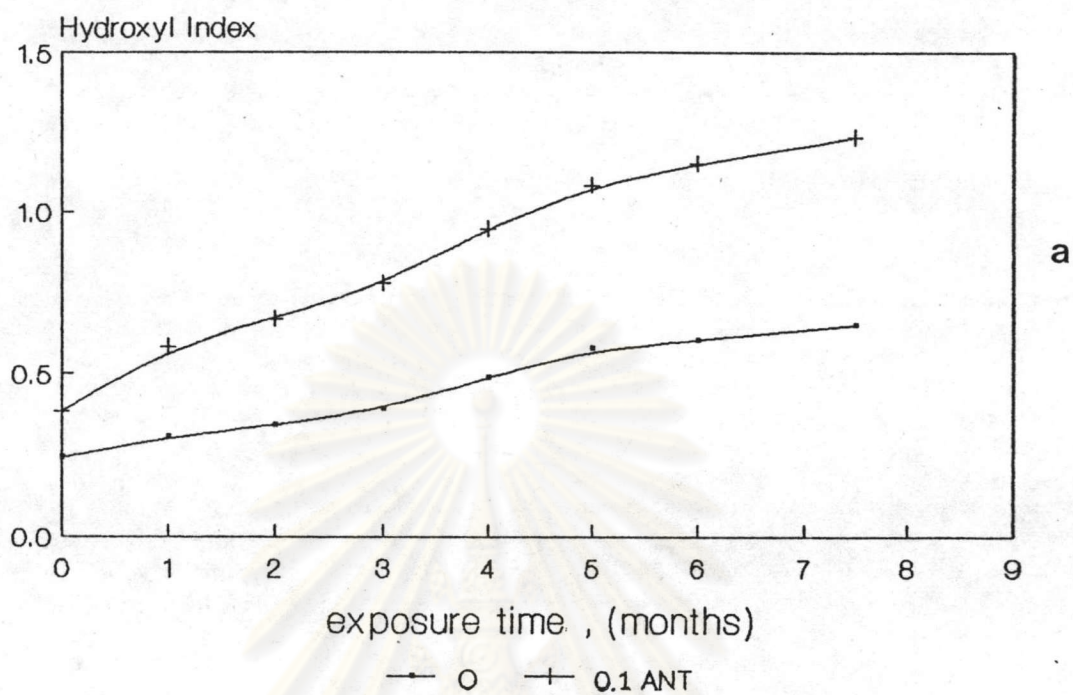


Fig. 4.7 Change of the relative FT-IR absorbance of hydroxyl group in PVC chains as a function of outdoor exposure time at various concentrations of photosensitizer. :  
 a) anthraquinone, b) benzophenone

#### 4.1.4 Result of UV absorption

The UV absorption spectra is the absorption in the range between 200 - 450 nanometres. From the absorption spectra particularly for wavelength less than 350 nanometres will correspond to polyene with  $n = 6$ . For absorbance at 307 nm. the polyene of  $n = 4$  is assigned. The absorbance at 230 and 280 nm. are due to  $n = 2$  and 3, respectively. The absorbance at 320 nm can be identified for the  $n = 5$  polyene. The absorbance at 354 nm is due mainly to polyene  $n = 6$ . And absorbance at 380 and 410 nm. are due to  $n = 7$  and 8, respectively.

##### a) Unsensitized PVC samples

The UV absorption spectra of the PVC samples were shown in Fig. 4.8. The absorbance of the irradiated PVC at the range 200 - 280 nm. decreased while the absorbance at the range 280 - 450 nm. increased from the original one. Thus, the polyene with  $n = 2$  and 3 decreased whereas the polyene with  $n > 4$  increased with exposure time.

##### b) Sensitized PVC samples

The UV - visible absorption spectra of both unirradiated and irradiated PVC contained 0.1 % anthraquinone has the absorption spectra similar to the unsensitized. But the absorbance of the exposed PVC at any wavelength are higher than the other one.

The absorbance spectra of PVC contained benzophenone has the same feature as the PVC contained anthraquinone. But the absorbance of PVC containing benzophenone at any wavelength is lower than that of anthraquinone at the same concentration.

#### 4.1.5 Result of visual inspection

The result of visual inspection are summerized in Table 4.6.

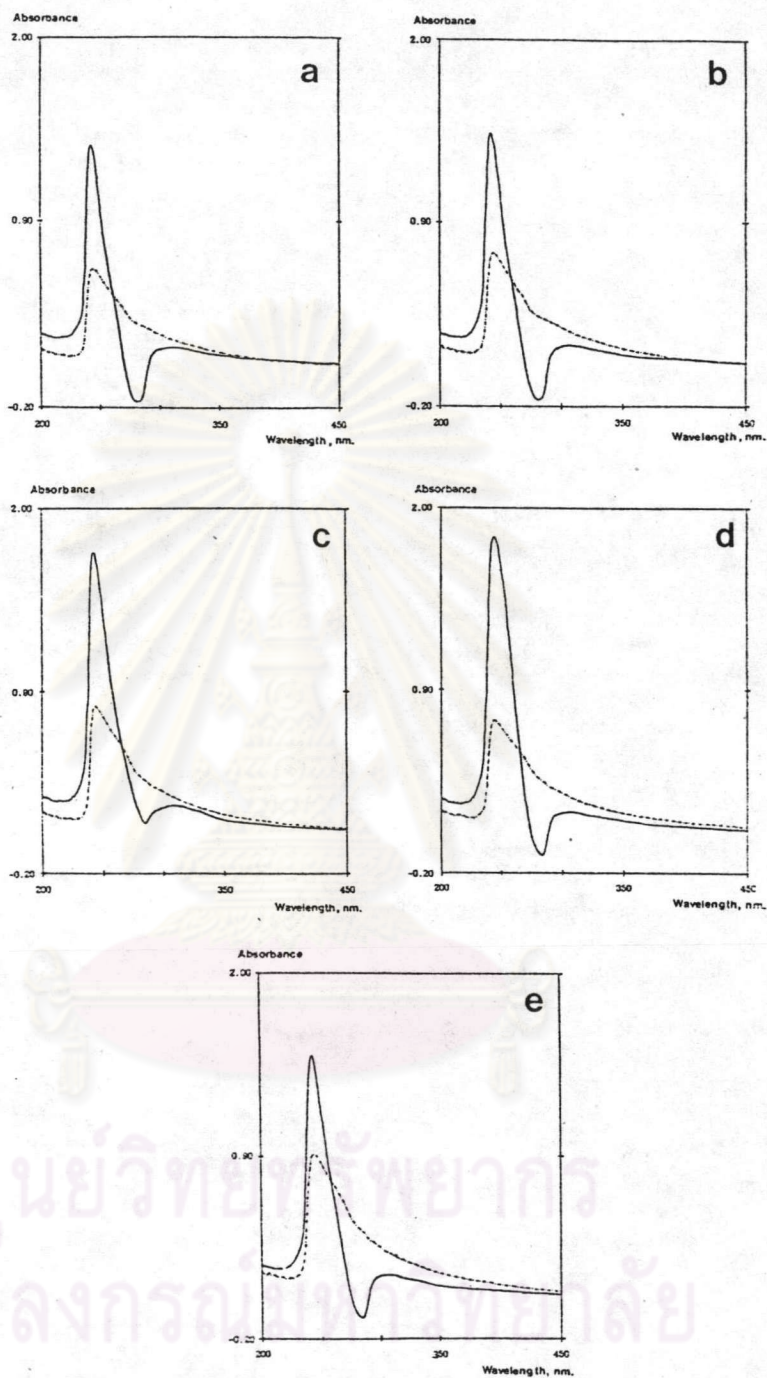


Fig. 4.8 UV spectra of PVC outdoor exposure samples at :

a) 0% photosensitizer, b) 0.1% anthraquinone, c) 0.1% benzophenone, d) 0.5% benzophenone, e) 1.0% benzophenone

----- unirradiated, - - - - irradiated for 6 months

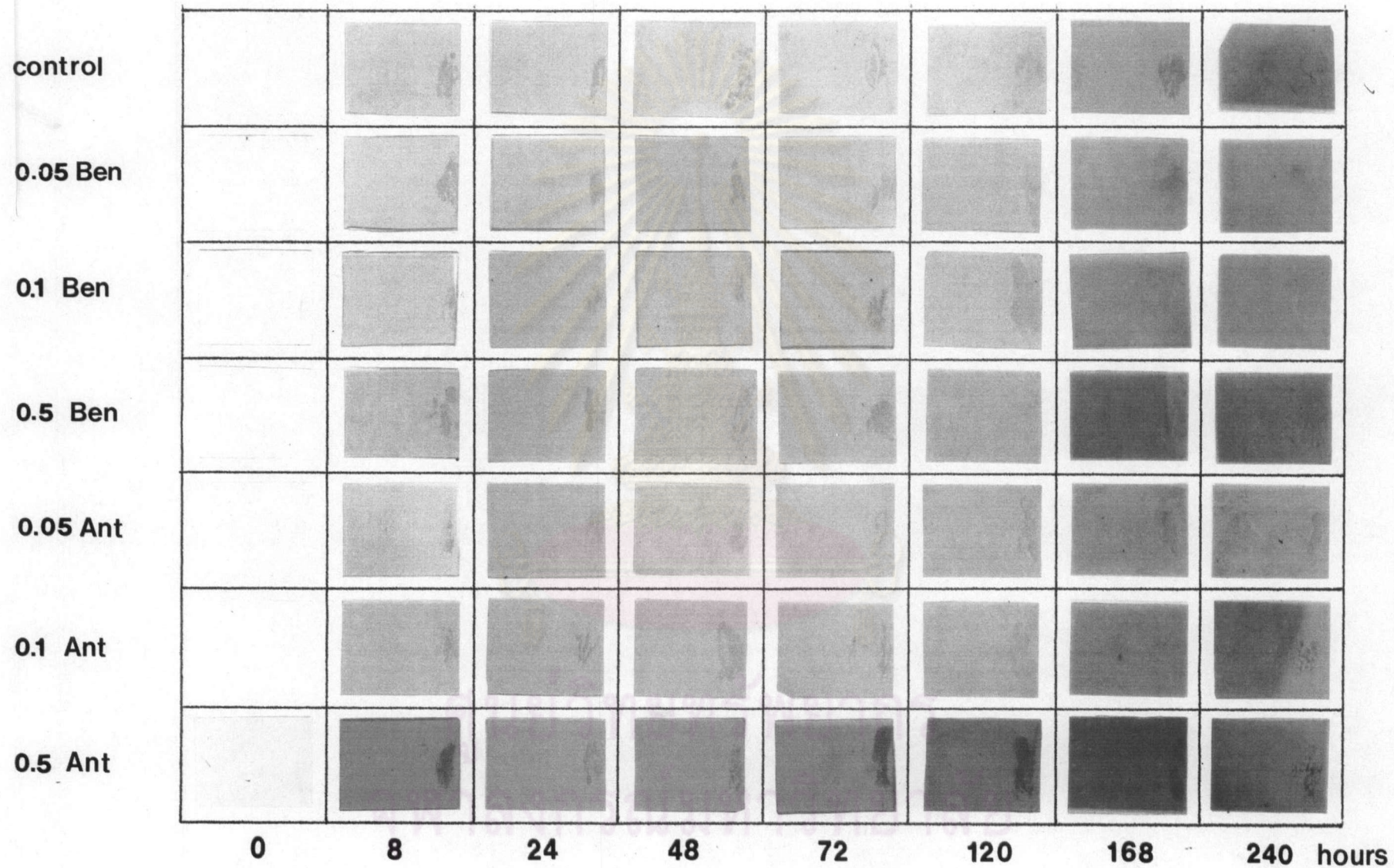


Fig. 4.9 Difference in surface changes of the accelerating exposure samples

Table 4.6 Results of visual inspection for outdoor exposure as a function of time with various concentrations of photosensitizers ( anthraquinone and benzophenone )

| Results of visual inspection            |   | Ranks of change |
|---|---|-----------------|
| CONTROL<br>colour<br>gloss<br>fragile   | Noticable change after 1 month exposure<br>No change<br>Breakable by hand after 5 months exposure   | 7               |
| 0.1 % BEN<br>colour<br>gloss<br>fragile | Noticable change after 1 month exposure<br>No change<br>Breakable by hand after 5 months exposure   | 6               |
| 0.5 % BEN<br>colour<br>gloss<br>fragile | Noticable yellowing after 1 month exposure<br>No change<br>Breakable by hand after 5 months exposure  | 5               |
| 1.0 % BEN<br>colour<br>gloss<br>fragile | Noticable yellowing after 1 month exposure<br>severly change into dark brown after 7.5<br>months exposure<br>No change<br>Breakable by hand after 3 months exposure           | 3               |
| 0.1 % ANT<br>colour<br>gloss<br>fragile | Yellowing after 1 months and become brown<br>after 9 months of exposure<br>No change<br>Breakable by hand after 3 months exposure   | 4               |
| 0.5 % ANT<br>colour<br>gloss<br>fragile | Browning after 1 month exposure and become<br>black after 6 months exposure<br>Change slightly after 5 months exposure<br>Breakable by hand after 2 months exposure           | 2               |
| 1.0 % BEN<br>colour<br>gloss<br>fragile | Becoming dark brown at 1 month and severly<br>change to black after 3 months exposure<br>Change slightly after 3 months exposure<br>Breakable by hand after 2 months exposure | 1               |

## 4.2 Accelerating weathering test

### 4.2.1 Results of Tensile properties

The load-elongation (stress-strain) diagram of PVC sheet irradiated by high pressure mercury lamp 125 W. are shown in Fig. 4.10 a and b. The behavior of each samples in this diagram is the same as the samples from outdoor exposure in Fig. 4.1 a and b.

The changes in tensile strength and elongation at break with irradiation time are shown in Fig. 4.10 a and b, Fig. 4.11 a and b. The tensile strength value of both unsensitized and sensitized samples increase from its original value and then gradually decrease after 120 hours of irradiation. But the tensile strength of every irradiated samples at 240 hours is still higher than its original value, exclude for the PVC contained 0.05 % anthraquinone and 0.1 % benzophenone. The tensile strength of these samples have tendency to decrease as increasing the irradiation time.

The result of elongation at break of PVC samples containing benzophenone decrease rapidly after 8 hours of irradiation. Whereas the elongation of PVC samples containing anthraquinone increase from its original value and then decrease rapidly after 24 hours for 0.05 % A and 48 hours for 0.1 % and 0.5 % A. After 120 hours, the elongation of PVC samples containing photosensitizers show slowly decrease and have tendency to approach zero value.

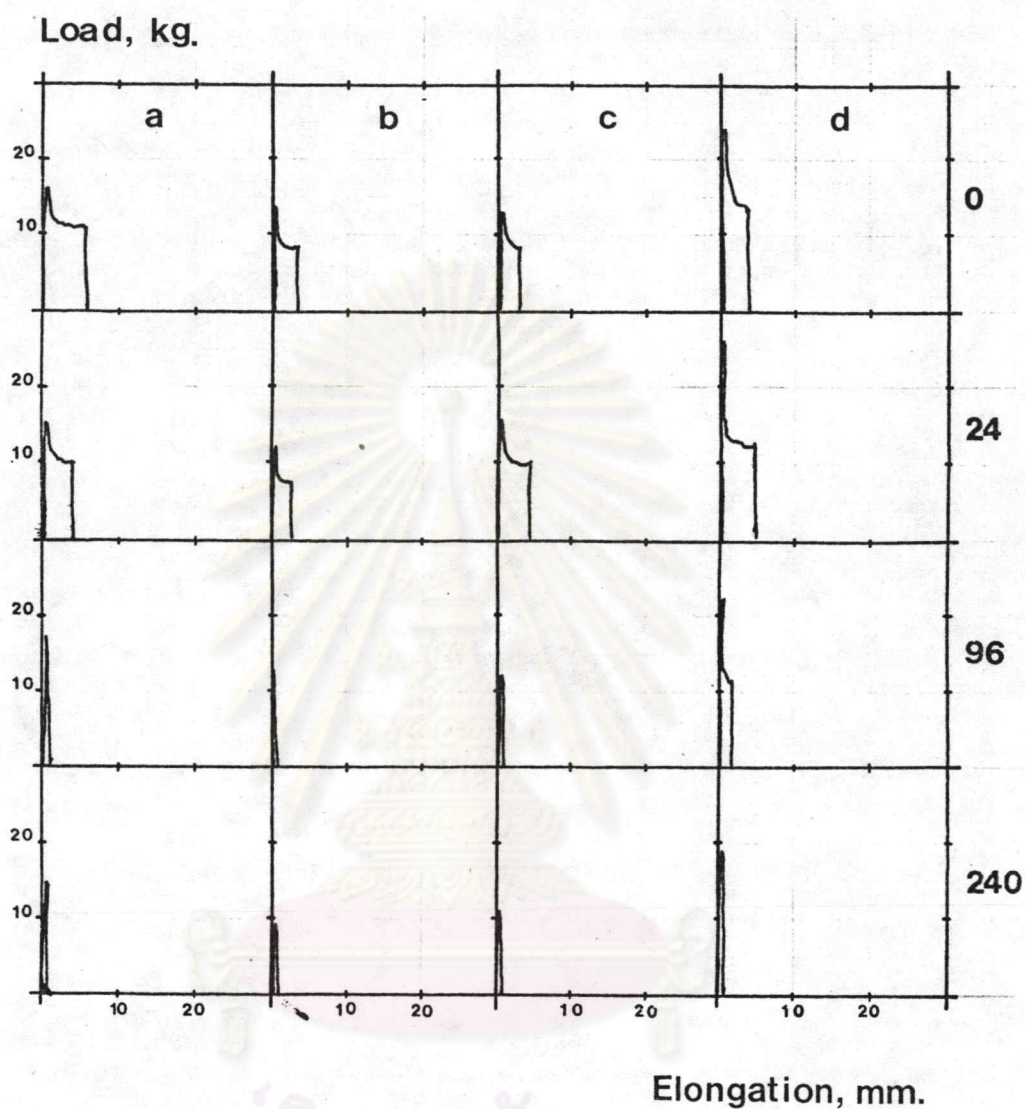


Fig. 4.10a Load-Elongation of accelerating exposure samples at various irradiation time (indicated on curve in hours) :

a) 0 % photosensitizer, b) 0.05 % anthraquinone,  
 c) 0.1 % anthraquinone and d) 0.5 % anthraquinone

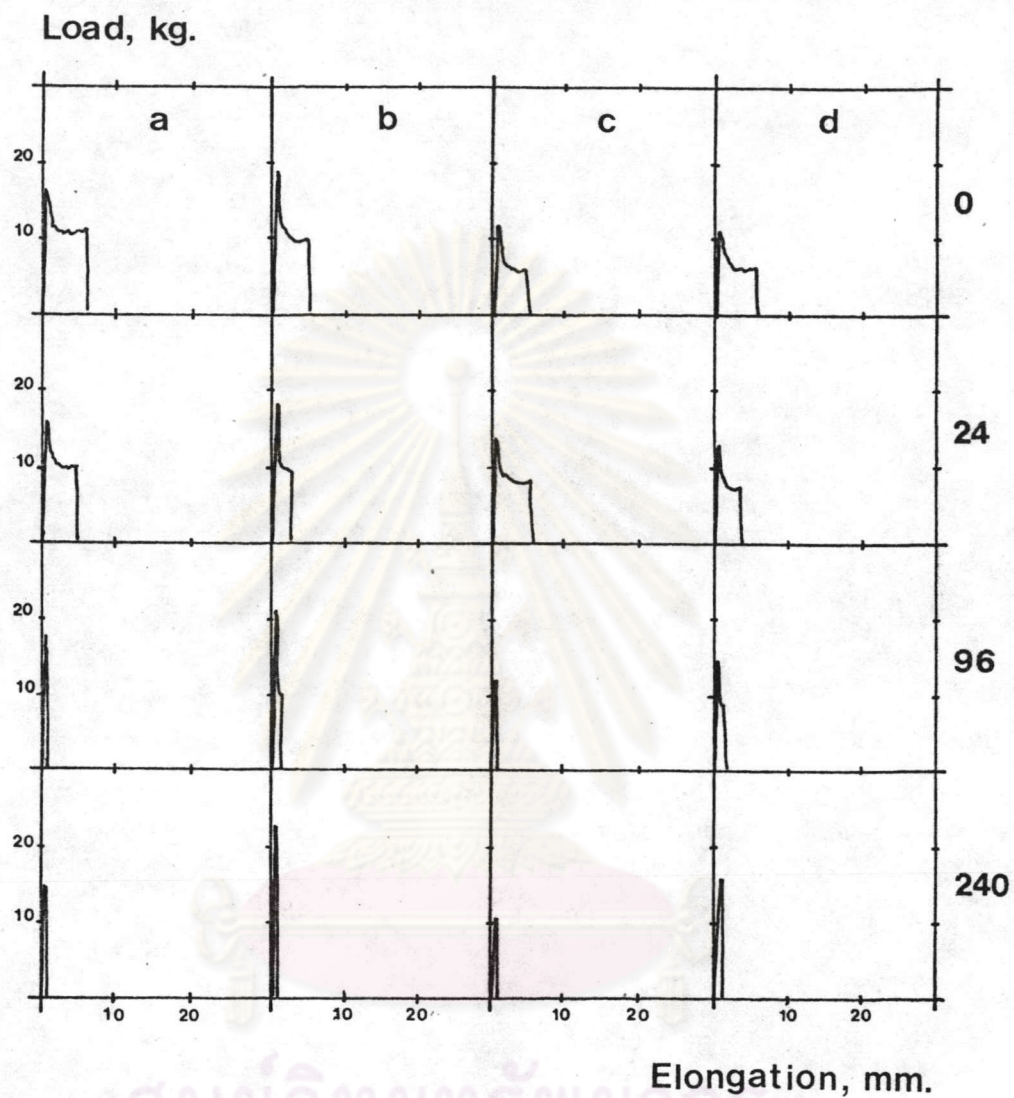


Fig. 4.10b Load-Elongation of accelerating exposure samples at various irradiation time (indicated on curve in hours) :

a) 0 % photosensitizer, b) 0.05 % benzophenone,  
 c) 0.1 % benzophenone and d) 0.5 % benzophenone



TABLE 4-7a The relationship of tensile strength and the irradiation time for PVC accelerating irradiated samples (photosensitizer : anthraquinone)

| Irradiation time (hours) | Tensile strength (kg/mm <sup>2</sup> ) |           |          |          |
|--------------------------|--|-----------|----------|----------|
|                          | 0% ANT                                 | 0.05% ANT | 0.1% ANT | 0.5% ANT |
| original                 | 6.14                                   | 6.40      | 6.13     | 6.39     |
| 8                        | 6.25                                   | 6.52      | 6.46     | 6.41     |
| 24                       | 6.63                                   | 6.50      | 6.56     | 6.69     |
| 48                       | 6.71                                   | 6.41      | 6.66     | 6.61     |
| 72                       | 6.73                                   | 6.20      | 7.42     | 6.04     |
| 120                      | 6.88                                   | 4.67      | 6.76     | 6.51     |
| 168                      | 6.52                                   | 4.58      | 6.64     | 6.40     |
| 240                      | 6.33                                   | 4.43      | 6.42     | 6.37     |

TABLE 4-7b The relationship of tensile strength and the irradiation time for PVC accelerating irradiated samples (photosensitizer : benzophenone)

| Irradiation time (hours) | Tensile strength (kg/mm <sup>2</sup> ) |           |          |          |
|--------------------------|--|-----------|----------|----------|
|                          | 0% BEN                                 | 0.05% BEN | 0.1% BEN | 0.5% BEN |
| original                 | 6.14                                   | 5.85      | 5.69     | 6.30     |
| 8                        | 6.25                                   | 5.61      | 6.36     | 6.49     |
| 24                       | 6.63                                   | 5.61      | 6.24     | 6.24     |
| 48                       | 6.71                                   | 6.55      | 6.32     | 6.32     |
| 72                       | 6.73                                   | 6.37      | 6.59     | 6.59     |
| 120                      | 6.88                                   | 3.36      | 6.71     | 6.71     |
| 168                      | 6.52                                   | 6.20      | 6.41     | 6.47     |
| 240                      | 6.33                                   | 6.14      | 6.32     | 6.03     |

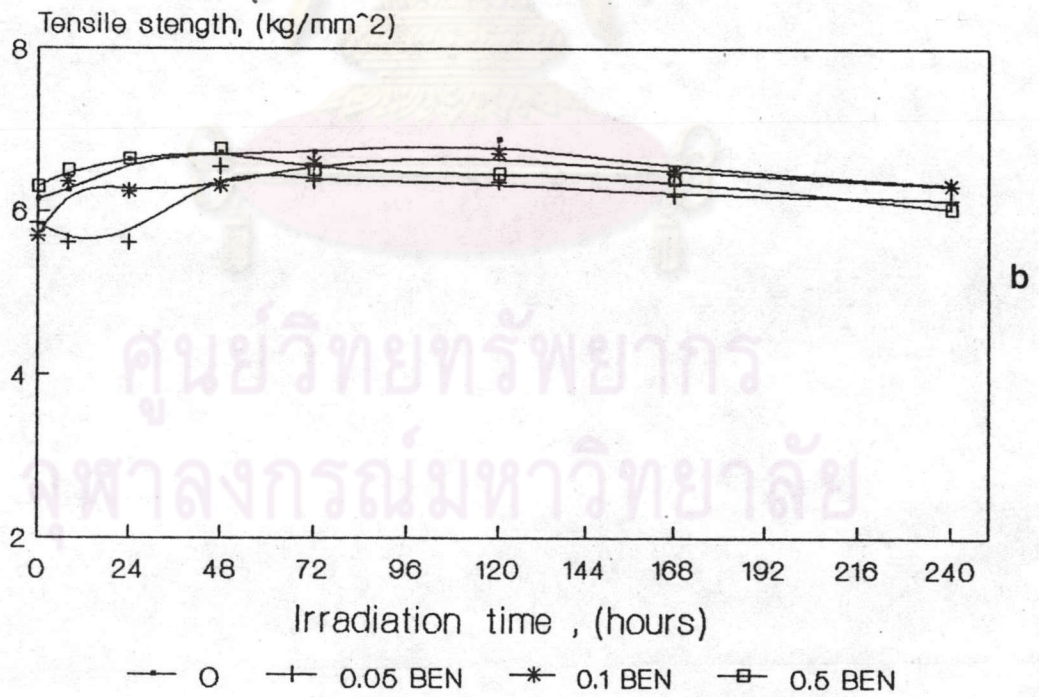
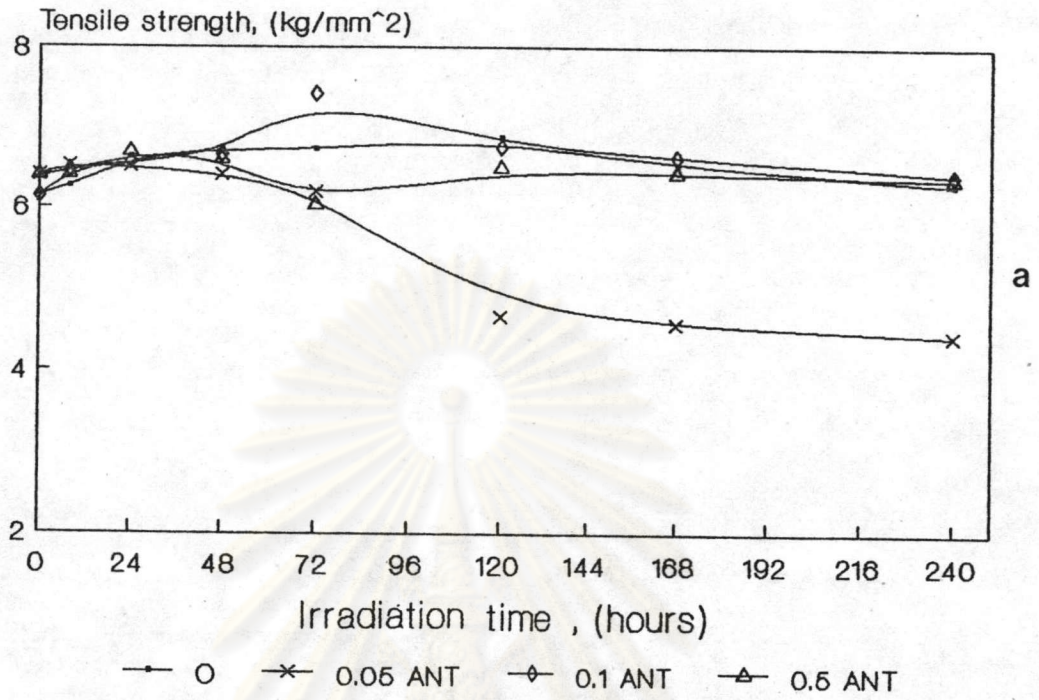


Fig. 4.11 Tensile strength of PVC samples at various concentrations of photosensitizer as a function of irradiation time. : a) anthraquinone, b) benzophenone

TABLE 4-8a The relationship of % Elongation and the irradiation time for PVC accelerating irradiated samples (photosensitizer : anthraquinone)

| Irradiation time<br>(hours) | Elongation at rupture (%) |           |          |          |
|-----------------------------|---------------------------|-----------|----------|----------|
|                             | 0% ANT                    | 0.05% ANT | 0.1% ANT | 0.5% ANT |
| original                    | 14.00                     | 7.50      | 5.63     | 8.00     |
| 8                           | 12.50                     | 8.00      | 6.00     | 8.00     |
| 24                          | 10.00                     | 10.50     | 9.50     | 8.50     |
| 48                          | 9.00                      | 5.50      | 10.00    | 12.50    |
| 72                          | 8.13                      | 3.13      | 5.50     | 8.13     |
| 120                         | 4.17                      | 2.50      | 2.50     | 5.00     |
| 168                         | 3.75                      | 1.88      | 2.00     | 3.50     |
| 240                         | 3.00                      | 1.50      | 1.88     | 1.80     |

TABLE 4-8b The relationship of % Elongation and the irradiation time for PVC accelerating irradiated samples (photosensitizer : benzophenone)

| Irradiation time<br>(hours) | Elongation at rupture (%) |           |          |          |
|-----------------------------|---------------------------|-----------|----------|----------|
|                             | 0% BEN                    | 0.05% BEN | 0.1% BEN | 0.5% BEN |
| original                    | 14.00                     | 11.50     | 10.00    | 11.67    |
| 8                           | 12.50                     | 10.00     | 8.13     | 5.50     |
| 24                          | 10.00                     | 7.50      | 7.50     | 5.00     |
| 48                          | 9.00                      | 6.75      | 8.75     | 8.00     |
| 72                          | 8.13                      | 5.63      | 4.50     | 4.60     |
| 120                         | 4.17                      | 4.00      | 3.90     | 4.00     |
| 168                         | 3.75                      | 3.13      | 2.50     | 3.13     |
| 240                         | 3.00                      | 2.85      | 2.00     | 2.00     |

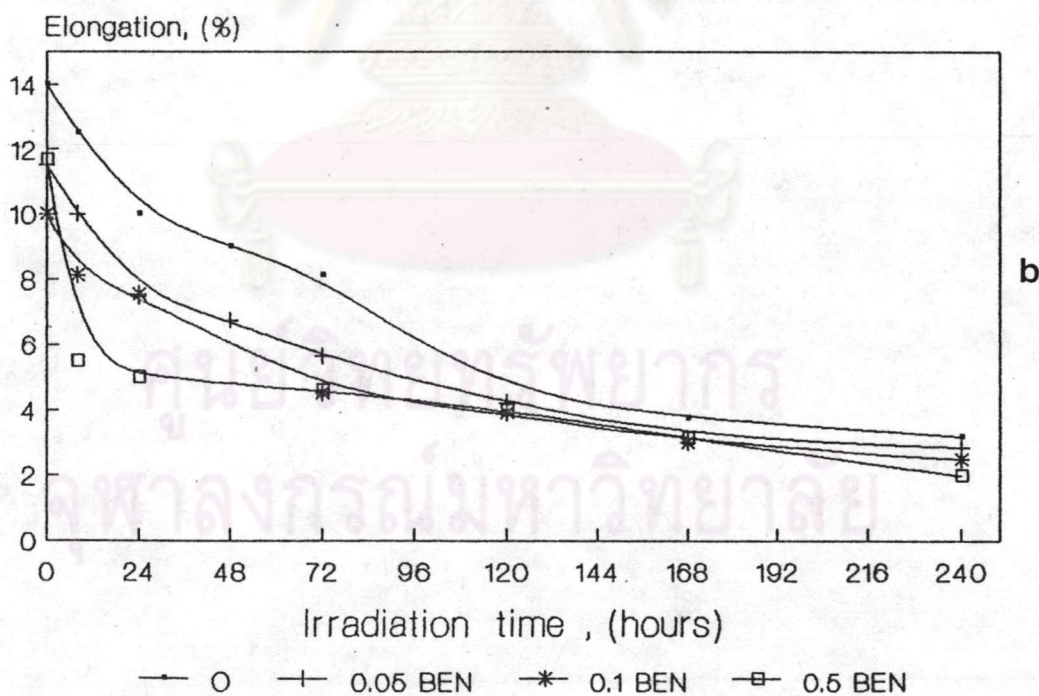
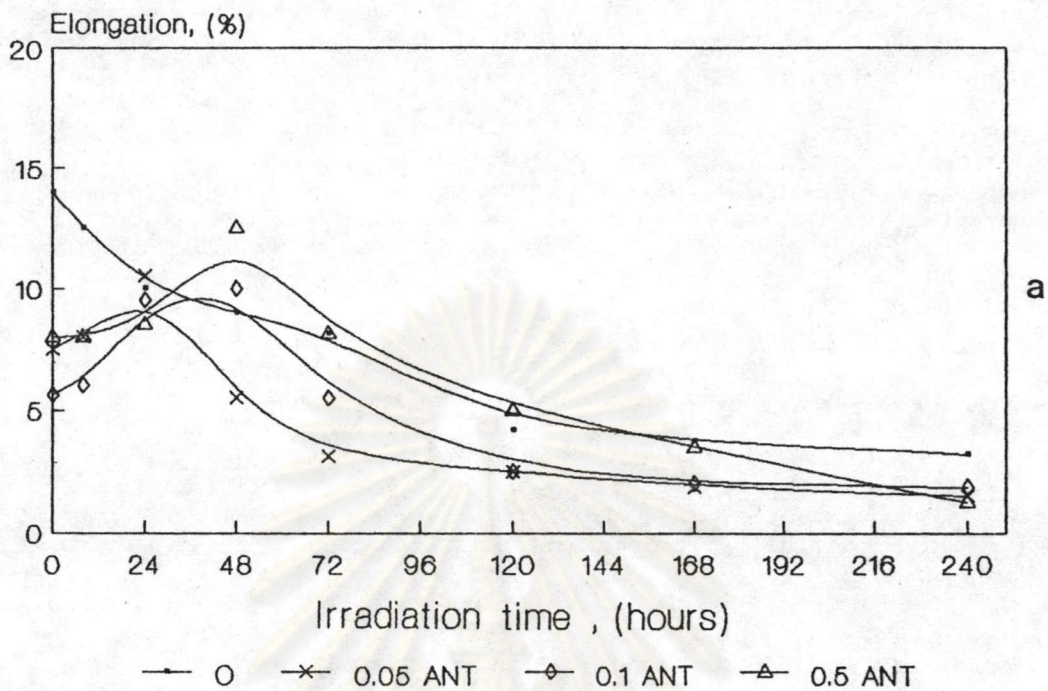



Fig. 4.12 Elongation at break of PVC samples at various concentrations of photosensitizer as a function of irradiation time. : a) anthraquinone, b) benzophenone

#### 4.2.2 Result of molecular weight

When unsensitized and sensitized PVC samples are irradiated to medium pressure mercury lamp, the gel residue are formed in every samples since the beginning of the irradiation. The molecular weight of the irradiated PVC samples both sensitized and unsensitized decreased gradually with the irradiation time as shown in Fig. 4.12.



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Table 4-9a Relation between intrinsic viscosity  $[\eta]$  and average molecular weight (MW) for PVC accelerating irradiated samples (photosensitizer : anthraquinone)

| Irradiation time (hours) | Intrinsic viscosity $[\eta]$ | molecular weight $\times 10^{-4}$ |
|--------------------------|------------------------------|-----------------------------------|
| PVC-0% ANT<br>original   | 0.7293                       | 5.5110                            |
| 8                        | 0.7225                       | 5.4440                            |
| 24                       | 0.7160                       | 5.3800                            |
| 48                       | 0.7072                       | 5.2950                            |
| 72                       | 0.6978                       | 5.2030                            |
| 120                      | 0.6864                       | 5.0930                            |
| 168                      | 0.6769                       | 5.0020                            |
| 240                      | 0.6660                       | 4.8980                            |
| PVC-0.05 ANT<br>original | 0.7344                       | 5.5610                            |
| 8                        | 0.7305                       | 5.5220                            |
| 24                       | 0.7243                       | 5.4620                            |
| 48                       | 0.7140                       | 5.3610                            |
| 72                       | 0.6980                       | 5.2050                            |
| 120                      | 0.6821                       | 5.0520                            |
| 168                      | 0.6661                       | 4.8990                            |
| 240                      | 0.6527                       | 4.7710                            |
| PVC-0.1 ANT<br>original  | 0.7411                       | 5.6270                            |
| 8                        | 0.7346                       | 5.5630                            |
| 24                       | 0.7278                       | 5.4960                            |
| 48                       | 0.7150                       | 5.3710                            |
| 72                       | 0.7021                       | 5.2450                            |
| 120                      | 0.6815                       | 5.0460                            |
| 168                      | 0.6656                       | 4.8940                            |
| 240                      | 0.6537                       | 4.7800                            |
| PVC-0.5 ANT<br>original  | 0.7840                       | 6.0530                            |
| 8                        | 0.7426                       | 5.6410                            |
| 24                       | 0.7361                       | 5.5770                            |
| 48                       | 0.7266                       | 5.4840                            |
| 72                       | 0.7091                       | 5.3130                            |
| 120                      | 0.6840                       | 5.0700                            |
| 168                      | 0.6619                       | 4.8590                            |
| 240                      | 0.6412                       | 4.6620                            |

Table 4-9b Relation between intrinsic viscosity  $[\eta]$  and average molecular weight (MW) for PVC accelerating irradiated samples (photosensitizer : benzophenone)

| Irradiation time<br>(hours) | Intrinsic viscosity<br>$[\eta]$ | molecular weight<br>$\times 10^{-4}$ |
|-----------------------------|---------------------------------|--------------------------------------|
| PVC-0% BEN<br>original      | 0.7293                          | 5.5110                               |
| 8                           | 0.7225                          | 5.4440                               |
| 24                          | 0.7160                          | 5.3800                               |
| 48                          | 0.7072                          | 5.2950                               |
| 72                          | 0.6978                          | 5.2030                               |
| 120                         | 0.6864                          | 5.0930                               |
| 168                         | 0.6769                          | 5.0020                               |
| 240                         | 0.6660                          | 4.8980                               |
| PVC-0.05 BEN<br>original    | 0.7321                          | 5.5380                               |
| 8                           | 0.7270                          | 5.4880                               |
| 24                          | 0.7203                          | 5.4220                               |
| 48                          | 0.7139                          | 5.3400                               |
| 72                          | 0.7031                          | 5.2550                               |
| 120                         | 0.6881                          | 5.1100                               |
| 168                         | 0.6768                          | 5.0010                               |
| 240                         | 0.6629                          | 4.8680                               |
| PVC-0.1 BEN<br>original     | 0.7370                          | 5.5860                               |
| 8                           | 0.7302                          | 5.5190                               |
| 24                          | 0.7236                          | 5.4550                               |
| 48                          | 0.7114                          | 5.3360                               |
| 72                          | 0.7000                          | 5.2250                               |
| 120                         | 0.6811                          | 5.0420                               |
| 168                         | 0.6740                          | 4.9740                               |
| 240                         | 0.6614                          | 4.8540                               |
| PVC-0.5 BEN<br>original     | 0.7480                          | 5.6950                               |
| 8                           | 0.7401                          | 5.6170                               |
| 24                          | 0.7308                          | 5.5250                               |
| 48                          | 0.7185                          | 5.4050                               |
| 72                          | 0.7070                          | 5.2940                               |
| 120                         | 0.6895                          | 5.1230                               |
| 168                         | 0.6700                          | 4.9360                               |
| 240                         | 0.6480                          | 4.7260                               |

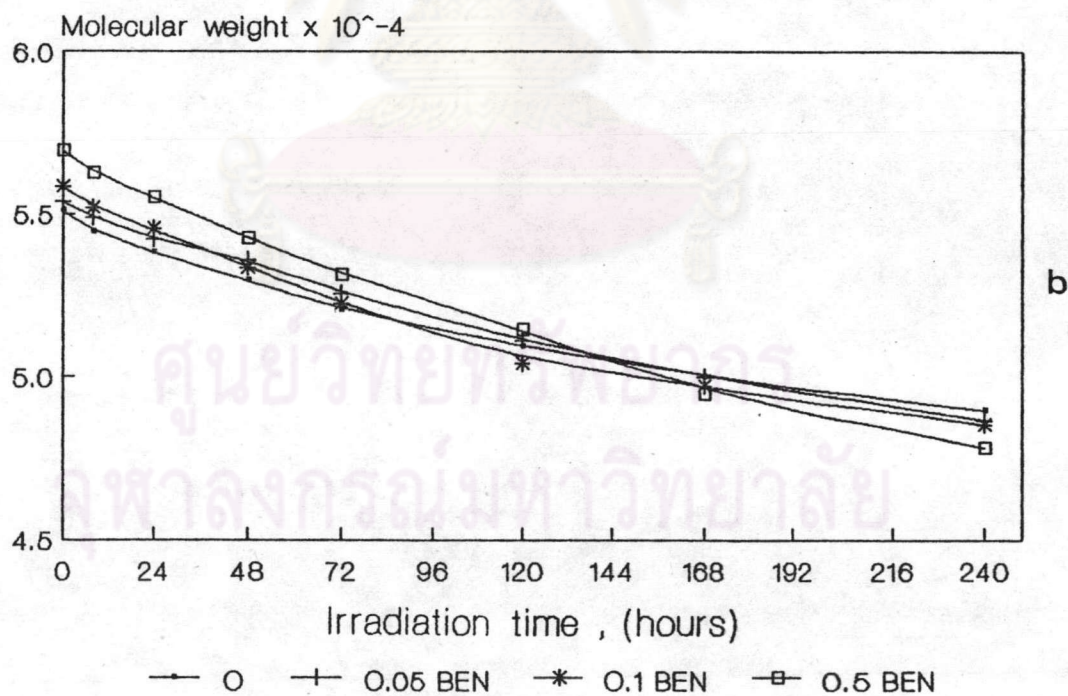
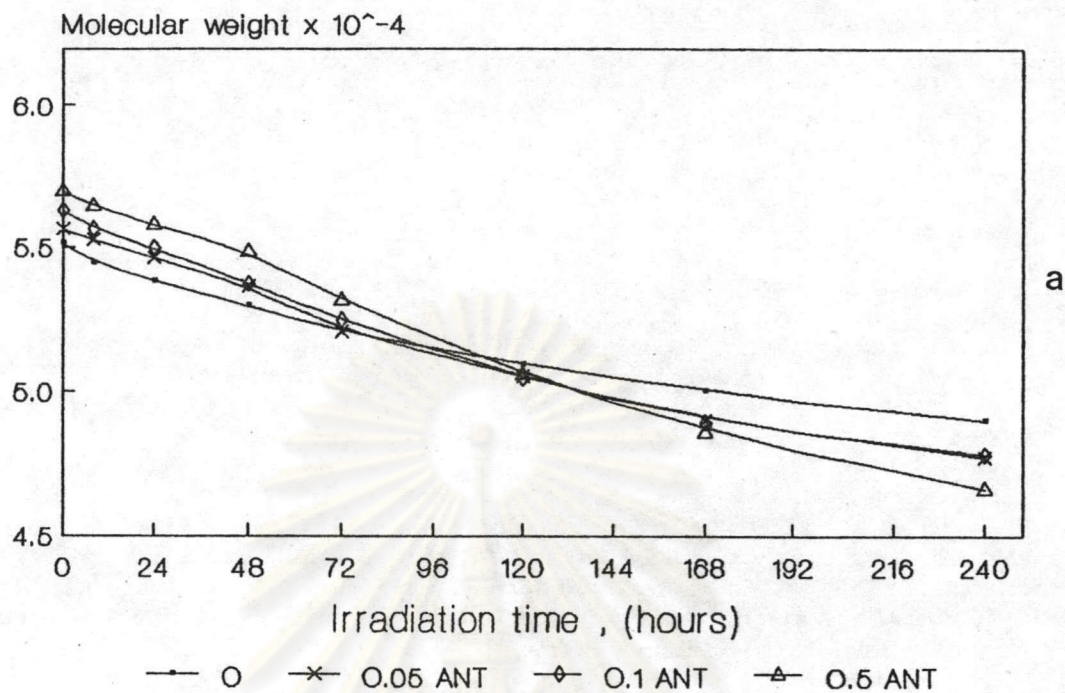


Fig. 4.13 Molecular weight traces of PVC samples at various concentrations of photosensitizer as a function of irradiation time. : a) anthraquinone, b) benzophenone



#### 4.2.3 Result of Fourier transform infrared absorption

The FT-IR spectra of unirradiated and irradiated PVC at various concentration of photosensitizers are measured and typical spectra are shown in Fig. 4.13. The absorption at  $1735\text{ cm}^{-1}$  and  $3460\text{ cm}^{-1}$  are observed with the irradiation time as shown in Fig. 4.14 - 4.15. It shown that the absorption of each interested band increase continuously with irradiation time.



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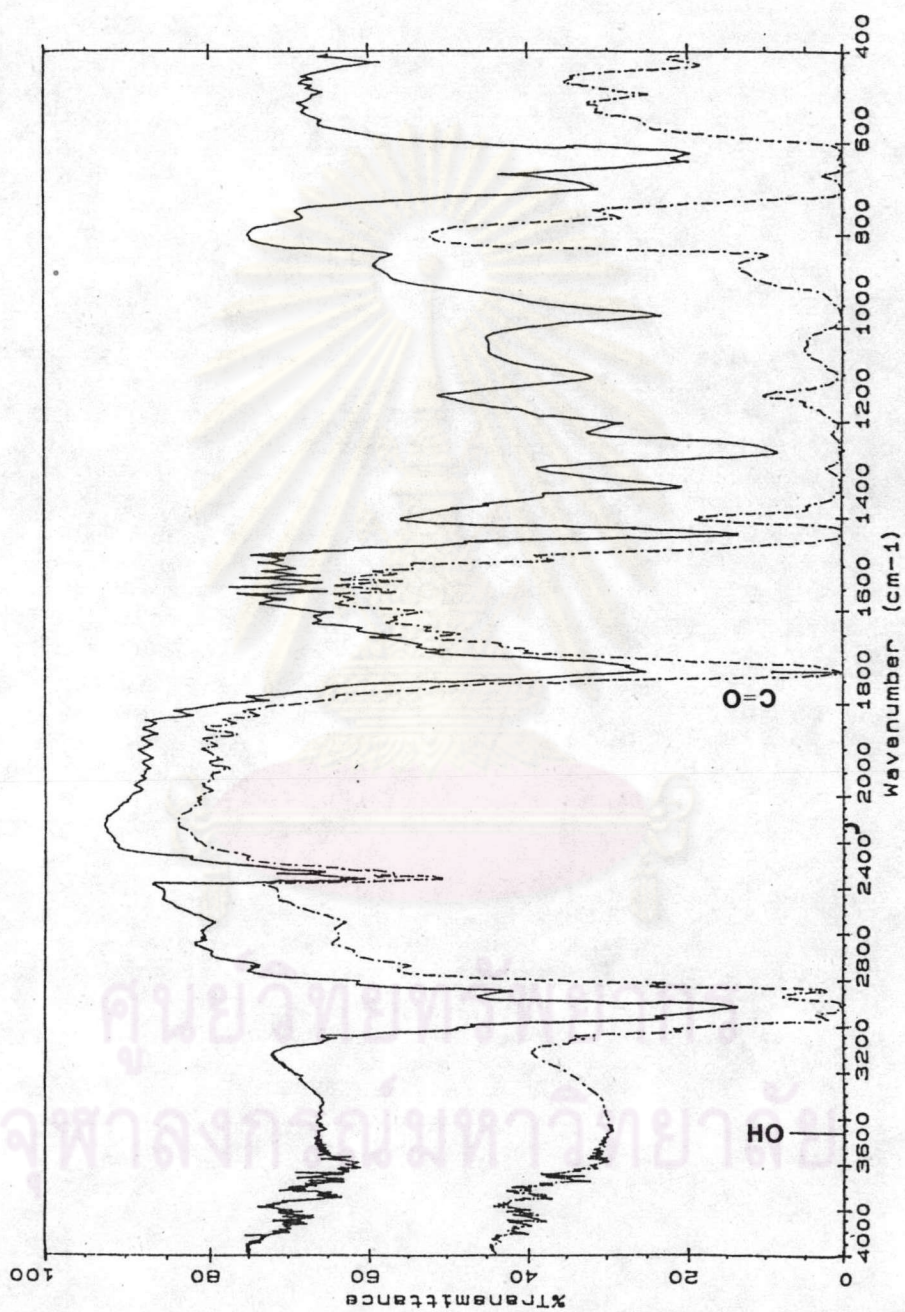


Fig. 4.13.1 FT-IR spectra of irradiated PVC samples at 0 % photosensitizer  
----- unirradiated , - - - - irradiated for 240 hours

Table 4.10a Carbonyl Index in PVC chain of accelerating irradiated samples  
(sensitizer : anthraquinone)

| Irradiation time | Carbonyl Index (1735 cm <sup>-1</sup> ) |         |        |        |
|------------------|---|---------|--------|--------|
|                  | 0% A                                    | 0.05% A | 0.1% A | 0.5% A |
| original         | 0.780                                   | 0.825   | 0.876  | 0.899  |
| 8 hours          | 0.987                                   | 0.931   | 0.987  | 1.000  |
| 24 hours         | 1.022                                   | 1.092   | 1.134  | 1.167  |
| 48 hours         | 1.167                                   | 1.396   | 1.296  | 1.301  |
| 72 hours         | 1.424                                   | 1.431   | 1.406  | 1.520  |
| 120 hours        | 1.441                                   | 1.558   | 1.557  | 1.873  |
| 168 hours        | 1.523                                   | 1.698   | 1.912  | 2.078  |
| 240 hours        | 1.579                                   | 1.963   | 2.155  | 2.450  |

Table 4.10b Carbonyl Index in PVC chain of accelerating irradiated samples  
(sensitizer : benzophenone)

| Irradiation time | Carbonyl Index (1735 cm <sup>-1</sup> ) |         |        |        |
|------------------|---|---------|--------|--------|
|                  | 0% B                                    | 0.05% B | 0.1% B | 0.5% B |
| original         | 0.780                                   | 0.790   | 0.848  | 0.931  |
| 8 hours          | 0.987                                   | 0.899   | 0.975  | 1.083  |
| 24 hours         | 1.022                                   | 1.083   | 1.167  | 1.287  |
| 48 hours         | 1.167                                   | 1.134   | 1.250  | 1.494  |
| 72 hours         | 1.424                                   | 1.395   | 1.395  | 1.523  |
| 120 hours        | 1.441                                   | 1.496   | 1.451  | 1.693  |
| 168 hours        | 1.523                                   | 1.686   | 1.645  | 1.921  |
| 240 hours        | 1.579                                   | 1.873   | 1.970  | 2.259  |

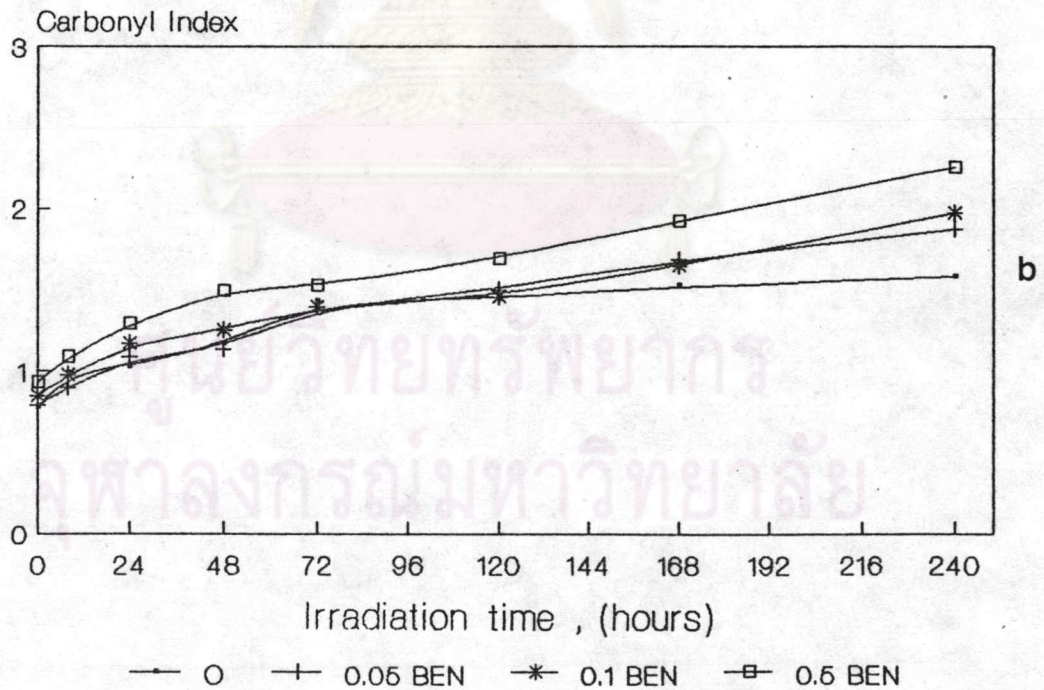
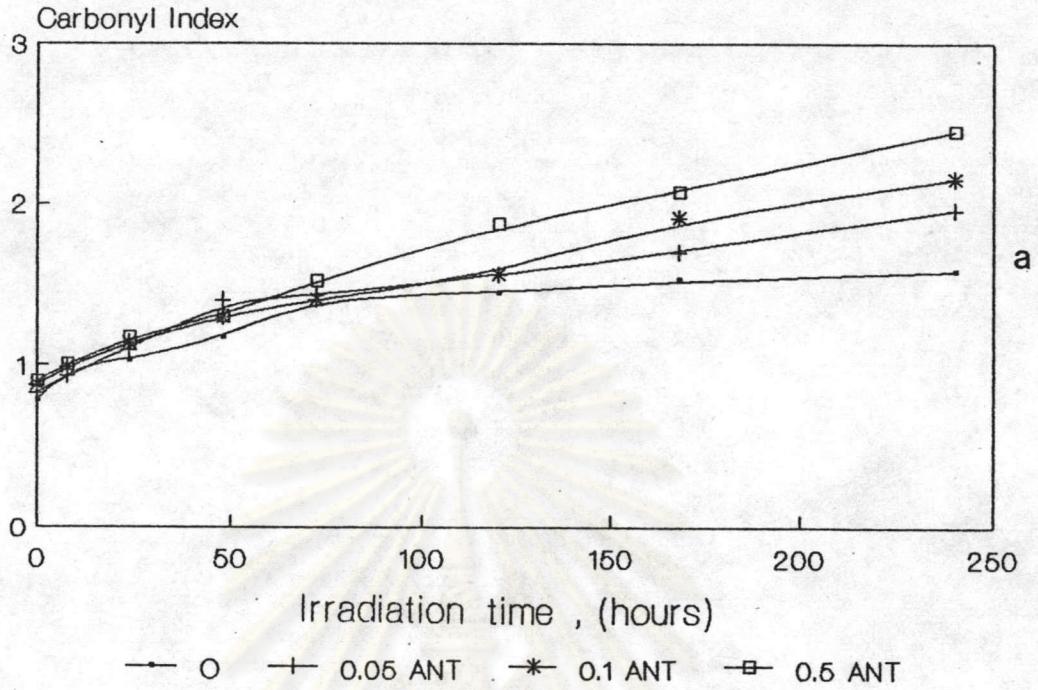


Fig. 4.15 Change of the relative FT-IR absorbance of carbonyl group in PVC chains as a function of irradiation time at various concentrations of photosensitizer. :  
a) anthraquinone, b) benzophenone

Table 4.11a Hydroxyl Index in PVC chain of accelerating irradiated samples  
(sensitizer : anthraquinone)

| Irradiation time | Hydroxyl Index ( $3460\text{ cm}^{-1}$ ) |         |        |        |
|------------------|--|---------|--------|--------|
|                  | 0% A                                     | 0.05% A | 0.1% A | 0.5% A |
| original         | 0.067                                    | 0.107   | 0.204  | 0.281  |
| 8 hours          | 0.076                                    | 0.132   | 0.238  | 0.287  |
| 24 hours         | 0.087                                    | 0.147   | 0.266  | 0.293  |
| 48 hours         | 0.101                                    | 0.164   | 0.288  | 0.354  |
| 72 hours         | 0.106                                    | 0.173   | 0.314  | 0.421  |
| 120 hours        | 0.134                                    | 0.197   | 0.336  | 0.457  |
| 168 hours        | 0.152                                    | 0.238   | 0.374  | 0.478  |
| 240 hours        | 0.179                                    | 0.289   | 0.411  | 0.538  |

Table 4.11b Hydroxyl Index in PVC chain of accelerating irradiated samples  
(sensitizer : benzophenone)

| Irradiation time | Hydroxyl Index ( $3460\text{ cm}^{-1}$ ) |         |        |        |
|------------------|--|---------|--------|--------|
|                  | 0% B                                     | 0.05% B | 0.1% B | 0.5% B |
| original         | 0.067                                    | 0.103   | 0.106  | 0.114  |
| 8 hours          | 0.076                                    | 0.124   | 0.113  | 0.139  |
| 24 hours         | 0.087                                    | 0.131   | 0.150  | 0.202  |
| 48 hours         | 0.101                                    | 0.157   | 0.218  | 0.246  |
| 72 hours         | 0.106                                    | 0.185   | 0.265  | 0.326  |
| 120 hours        | 0.134                                    | 0.231   | 0.329  | 0.384  |
| 168 hours        | 0.152                                    | 0.268   | 0.357  | 0.432  |
| 240 hours        | 0.179                                    | 0.311   | 0.378  | 0.479  |

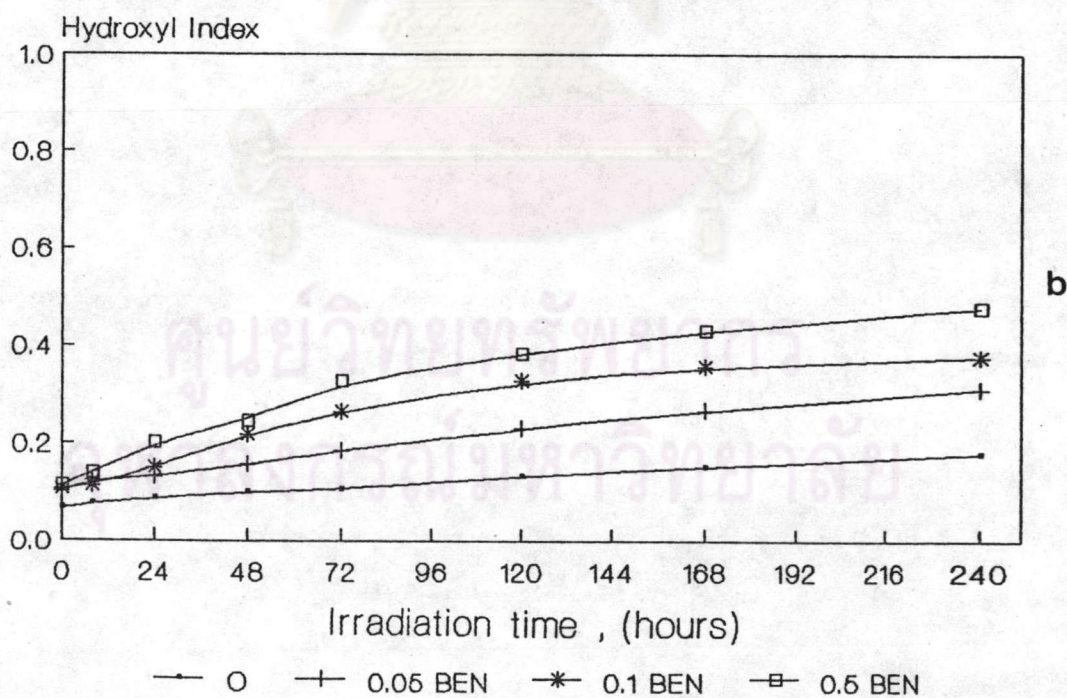
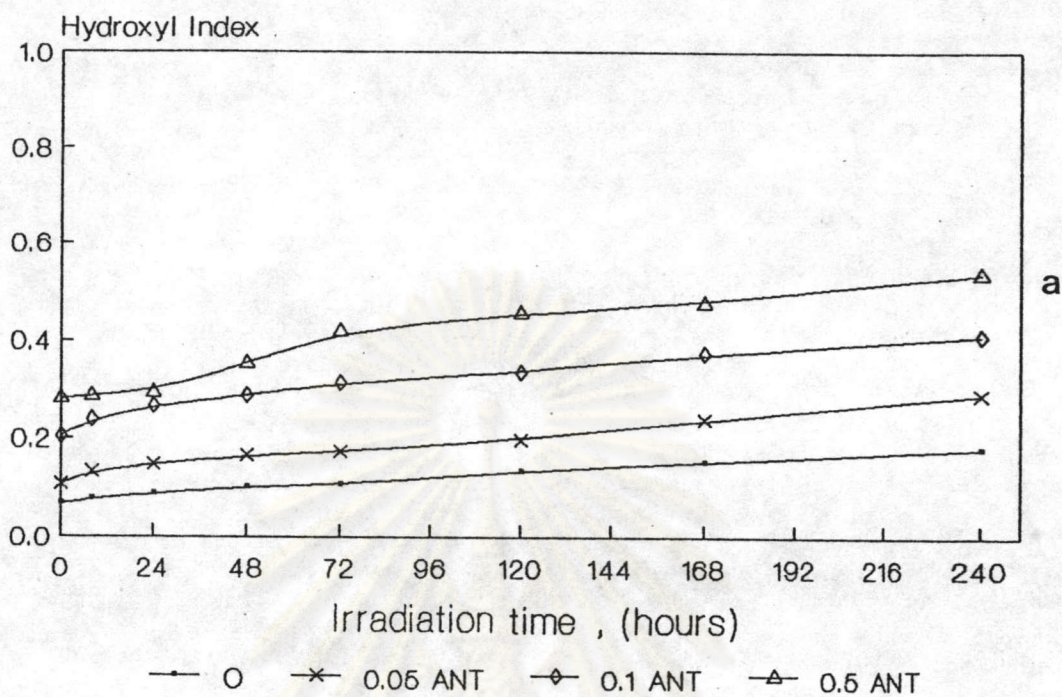


Fig. 4.16 Change of the relative FT-IR absorbance of hydroxyl group in PVC chains as a function of irradiation time at various concentrations of photosensitizer. :  
a) anthraquinone, b) benzophenone

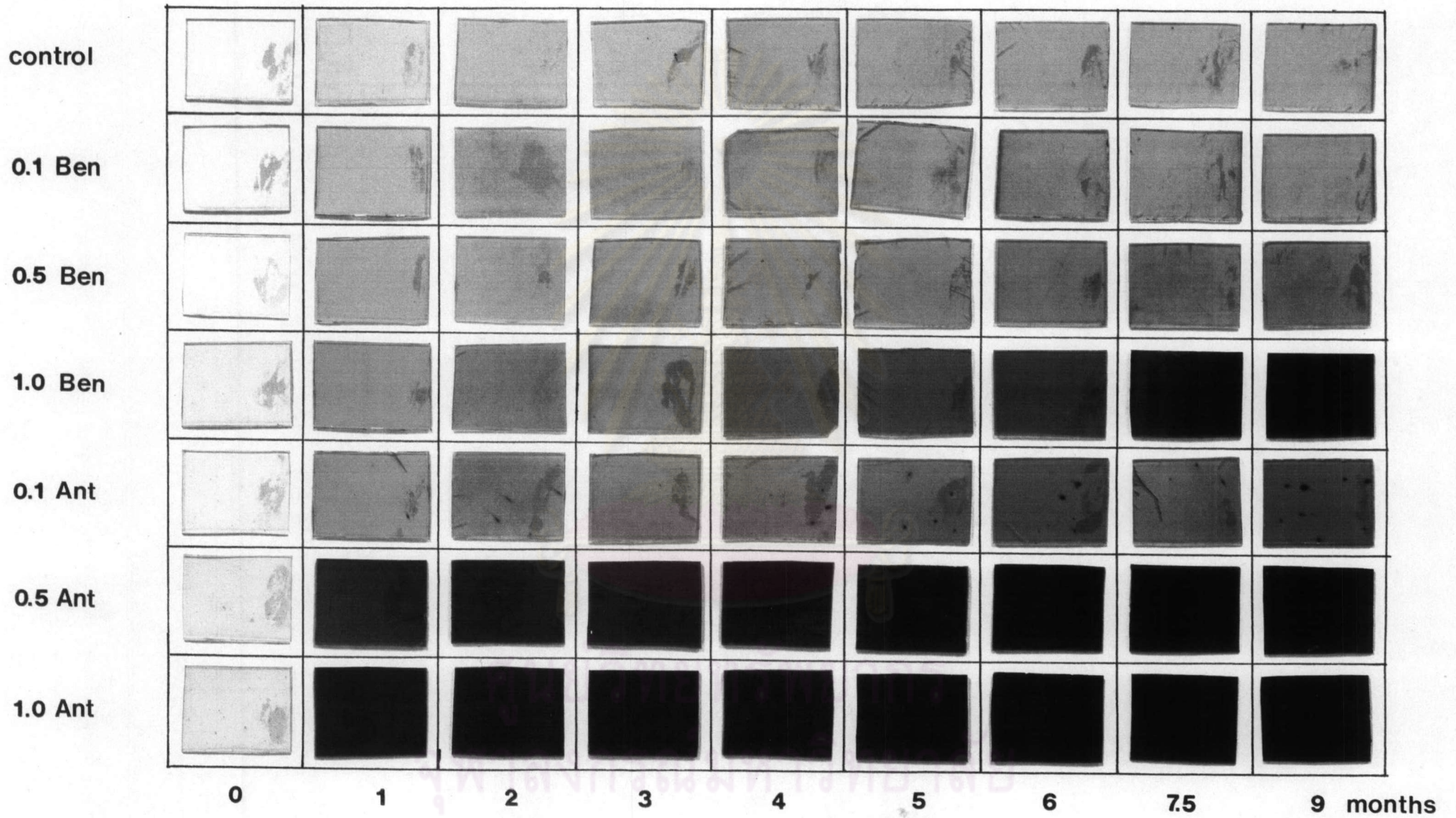


Fig. 4.17 Difference in surface changes of the outdoor exposure samples

Table 4.12 Results of visual inspection for accelerated irradiation as a function of time with various concentrations of photosensitizers ( anthraquinone and benzophenone )

| Results of visual inspection |   | Ranks of change |
|------------------------------|---|-----------------|
| CONTROL<br>colour<br>gloss   | Yellowing after 8 hours<br>Change slightly after 120 hours, no gloss<br>after 240 hours exposure  | 7               |
| 0.05% BEN<br>colour<br>gloss | Yellowing after 8 hours<br>Change slightly after 120 hours, no gloss<br>after 240 hours exposure  | 6               |
| 0.1 % BEN<br>colour<br>gloss | Yellowing after 8 hours<br>Change slightly after 120 hours, no gloss<br>after 240 hours exposure  | 5               |
| 0.5 % BEN<br>colour<br>gloss | Yellowing after 8 hours and slidely brown<br>after 168 hours of exposure<br>Change slightly after 120 hours, no gloss<br>after 168 hours exposure | 3               |
| 0.05% ANT<br>colour<br>gloss | Yellowing after 8 hours exposure<br>Change slightly after 120 hours, no gloss<br>after 168 hours exposure   | 4               |
| 0.1 % ANT<br>colour<br>gloss | Yellowing after 8 hours and become brown<br>after 168 hours exposure<br>Change slightly after 120 hours, no gloss<br>after 168 hours exposure     | 2               |
| 0.5 % ANT<br>colour<br>gloss | Yellowing after 8 hours and become brown<br>after 72 hours exposure<br>Change slightly after 120 hours, no gloss<br>after 168 hours exposure      | 1               |