



CHAPTER 5 DISCUSSION

5.1 Natural Weathering

The tensile strength of the exposed samples were found to be higher than those of unexposed samples. Since, the tensile strength of all samples gradually increased with exposure time, until 5 months and then after that the tensile strength decreased rapidly. The increase of tensile strength was concerned with the incorporation of oxygen in atmosphere which could be elucidated in scheme 5.1. Together with the exhausting of the stabilizing agents presented in the original PVC compounds, therefore 5 months was the induction time of the PVC samples. The original and the exposed photosensitized PVC had the tensile strength value higher than values of the unphotosensitized PVC. While the elongation at rupture of the photosensitized was reduced to zero of its original value faster than the unphotosensitized PVC as shown in Fig. 4.2 and Fig. 4.3. This behavior could be explained by the effect of photosensitizer which increased the degradation processes. PVC chains passed through an efficient scission process which was considered to be one of the observed loss of the mechanical properties of PVC sheets exposed to natural weathering.

During the photooxidation of PVC, the samples degraded continuously with exposure time by the decreasing of the average molecular weight as shown in Fig. 4.4. The average molecular weight of PVC containing 0.1 %, 0.5 % and 1.0 % by weight of anthraquinone decreased approximately 2.06, 2.13, 2.43 times respectively and the benzophenone also decreased approximately 1.88, 2.07 and 2.17 times of the PVC containing 0 % photosensitizer at the ninth month of exposure.

In Fig. 4.6 and 4.7, the carbonyl and hydroxyl absorption of the sensitized PVC was higher than that of unsensitized PVC and their original value through the exposure time. The absorption at 1735 cm^{-1} and 3660 cm^{-1} increased with the increase of exposure time. The main reaction of the photosensitizers is photoreduction during the photooxidation processes by abstracting hydrogen on decompose PVC chains after excitation. This cause the initiating radicals which effects the degradation processes by increasing the content of oxidation products such as carbonyl and hydroxyl groups in the PVC chains.

The main characteristic feature of the dehydrochlorination reaction was the formation of conjugated polyene sequences with concomitant evolution of HCl. The polyene structure could be easily characterized by their UV absorption. Fig. 4.8 shows the UV absorption and the long conjugated polyene sequence $\sim(\text{CH}=\text{CH})\sim$, $n > 4$ increased with exposure time. Furthermore, the long conjugated polyene sequence, $n > 20$, in a single sequences led to a strongly coloured material. As shown in Fig. 4.9, the exposed samples increased in colour with exposure time. While the colour of the unsensitized samples changed less severely than the sensitized samples. It could be considered that PVC with photosensitizer degraded faster than PVC without photosensitizer. The contents of polyene sequences cause the changes in colour of the exposed samples as well as the changes of gloss and fragile.

5.2 Accelerated irradiation test

For accelerated irradiation test by Medium Pressure Mercury lamp, the tensile strength of the irradiated samples that containing and not containing photosensitizer were higher than its original value at the early period. After 48 hours of irradiation, the tensile strength decreased gradually with time but the samples containing photosensitizers decreased more than the unsensitized ones, as shown in Fig. 4.11. The increase in tensile properties at the early period could be explained by the formation of the crosslinking structure since the suddenly increase of the insoluble gel that observed at the first 8 hours of irradiation. Along with the incorporation of oxygen from the atmosphere which could form the different morphology structures and characterized by higher tensile strength. Meanwhile, the photodegradation proceeded continuously by the decrease of the elongation at rupture of all irradiated samples, as shown in Fig. 4.12.

The molecular weight of irradiated PVC containing 0.05% , 0.1% and 0.5% by weight of anthraquinone and benzophenone were about 1.28, 1.35 , 1.63 and 1.09, 1.18, 1.53 times less than the PVC containing 0% photosensitizer at 240 hours of irradiation respectively. This could be explained that the effect of photosensitizer increased the degradation processes as chain scission processes occurred efficiently.

Carbonyl and hydroxyl absorption values in Fig. 4.15 and 4.16 were used to study the degradation processes. The absorbance of sensitized PVC was higher than that of unsensitized PVC from its original value and increased gradually with irradiation time similar to the outdoor exposure.

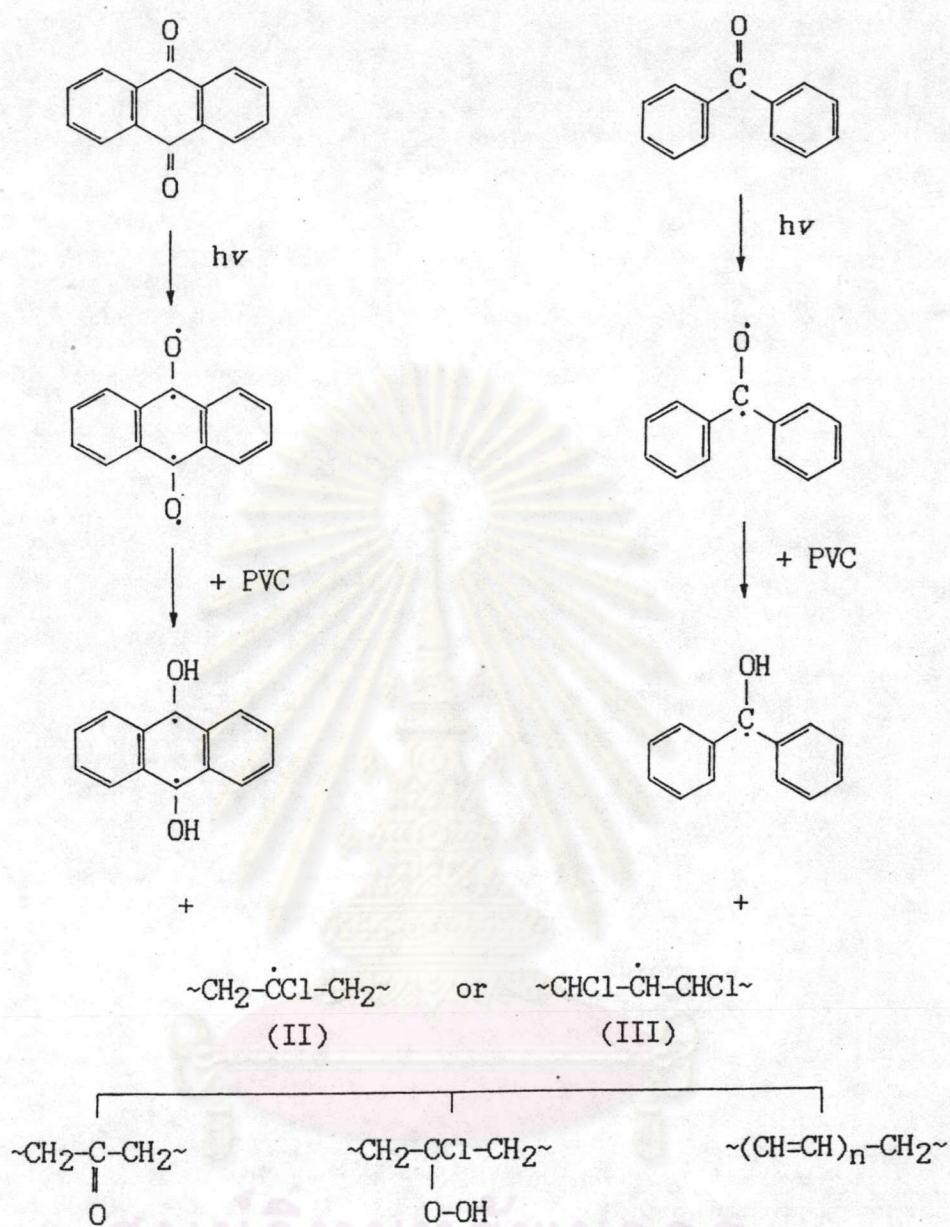
The polyene formation in the laboratory test was determined

only by observing the changes in colour of the irradiated samples. Since all these samples contained insoluble gel residues that could not dissolve in any solvent. Thus, the UV spectroscopy method could not be employed. The irradiated samples increased in colour with irradiation time. The sensitized samples changed rapidly and severely than the unsensitized one as shown in Fig. 4.17.

5.3 Mechanisms

The studies of photodegradation of PVC have been reported by many investigators. The knowledge and the available information recently obtained from the laboratory indicate that regarding the primary products such as HCl, conjugated polyene, hydroxyl and carbonyl groups and the structure changes taking place by main-chain scissions and crosslink processes, may suggest the possible reaction scheme. For the unphotosensitized PVC sample, the photodegradation processes occurring by interaction of UV light by natural weathering and accelerated irradiation can be elucidated in Scheme 5.1.

But for the photodegradation processes of sensitized PVC, the initiation stage is different from the unsensitized one. Since the photosensitizer (anthraquinone and benzophenone) has a highly absorption coefficient for UV light which is easily activated to become excited compound and then decomposed into free radicals and initiated degradation of the polymer. The mechanism of the initiation stage can be represented by Scheme 5.2.



Scheme 5.2 Photosensitized degradation reaction of PVC sheet

crosslink reaction

