CHAPTER 3

APPARATUS AND EXPERIMENTAL METHOD

The effect of photosensitizers on the photodegradation of blow moulding PVC was studied by incorporating photosensitizer (anthraquinone or benzophenone) into PVC samples at various concentrations. This test was divided into 2 sections: natural weathering and accelerating irradiation by using Phillips medium pressure mercury lamp. The investigating methods for following the photodegradation in degraded PVC in both natural weathering and accelerating irradiation test were the same.

3.1 Reagents and Materials

3.3.1 Blow moulding rigid PVC supplied by Thai Plastic & Chemicals Co., Ltd. The physical properties of the original sample before exposure are shown in Table 3.1

Table 3.1 Original properties of PVC resin (Type 102)

K value 1 G/100 ml	
cyclohexanone 20° C	58
Bulk density gm/ml	0.54
% volatile matter	0.5 max.
particle size	
% on 40 mesh	0 %
% under 270 mesh	3 % max
polymerization degree (P)	720

3.1.2 Photosensitizer

3.1.2.1 Anthraquinone

- yellow needle, melting point 286 º C
- ultraviolet absorption maximum between 280   and

330 nm.

3.1.2.2 Benzophenone

- white prism, melting point 47.5 º C
- ultraviolet absorption maximun between 330   and
440 nm.

3.1.3 Solvent

3.1.3.1 Tetrahydrofuran ; (Analar, GC) ; >99 %

3.1.3.2 Cyclohexanone ; (Analar, GC) ; >99 %

3.2 Apparatus and Instruments

3.2.1 Mixer

3.2.2 Two rolls mills

3.2.3 Hot Pressing

3.2.4 Punching machine

3.2.5 Exposure frame : made from steel and porcelain

size : 1.2 x 1 metres , height : 1 metre

3.2.6 Weathering cabinet

3.2.7 Lamp : Medium-pressure mercury vapour lamp (Phillip

125 W) emits a high degree of ultraviolet radiation

Fig. 3.1 Medium-pressure mercury 125 W lamp

Table 3.2 Absolute spectrum power distribution

Wavelength nm	248.2	253.7	265.3	269.9	257.3	280.4	289.4	296.7	302.5	313.0	334.1	365.5	404.7/407.8	435.8	491.6	546.1	57?
Lines W	0.5	2.5	1.1	0.2	0.2	0.5	0.3	0.9	1.4	3.1	0.4	5.1	1.8	3.5	0.2	4.4	

Region nm	240-280	280-315	315-400	400-600
Lines W	4.5	6.2	5.5	13.4
Continuum W	4.4	2.5	2.3	1.5
Total W	8.9	8.7	7.8	14.9

3.2.8 Tensile tester : Shimadzu AUTOGRAPH model S-100-C
test speed 100 mm/min , load selected 50 kg.

3.2.9 Furier Transform Infrared spectrometer :
Nicolett model 205

3.2.10 UV-Visible spectrophotometer : Ultraviolet Shimadzu
model 240

3.2.11 Viscosity analysis apparatus
- Ubbelohde viscometer
- Water bath
- Temperature control
- Transfer pipet 10 ml.
- Volumetric flask 50 ml. , 25 ml.
- Thermometer 0-100 $^{\circ}$ C
- Timer

3.2.12 Micrometer

3.3 Preparation of samples

3.3.1 Compositions of PVC compound

PVC (grade 102, rigid bottle)	100	g.
Impact modifier	6	g.
Tin stabilizer	2	g.
Internal lubricant	1	g.
External lubricant	0.3	g.
Processing aid	1.5	g.
CMBS-CLR	0.03 %	

3.3.2 Moulding method

Blending:- Compound mixer (for making PVC compound and mixing photosensitizer into PVC compound)
- heating from 60 to 120°C , speed 2000 rpm ,
- cooling from 120 to 60 °C , speed 1000 rpm

Mixing and calendering :
- Two rolls mills (for better mix of the compositions by applying higher heat)
- mixing at temperature 160 °C for 5 min.,
- set the thickness of the film , then
- curing sheet at temperature 160 °C for 3 min.

Pressing:- Hot pressing (for curing the plastic film)
- preheating at 180 °C , steam pressure 50 kg/cm^2 for 2 min.
- heating at 180 °C , steam pressure 180 kg/cm^2 for 3 min.
- cooling by cooling water, pressure 220 kg/cm^2 for 30 min.

3.4 Samples irradiation

3.4.1 Natural weathering test

The location of the exposure site is Bangkok which is located at latitude 13° 44′ N and longitude 100° 34′ E. The meteorological data for the exposure period is shown in Table 3.3 which was obtained from " The monthly report of the Climatology Division, Mateorological Department".

The dimensions of the exposed samples are 20 x 20 cm. and the thickness is approximately 1 mm. The samples were placed on

the exposure frames by having cloth adhesive tapes attached with the iron wire at the top side of the samples, as shown in Fig. 3.2 .

The samples were mounted on the exposure stages in such way the the main part of the specimen was free from the obstructions. Exposure frames are place in the horizontal. As shown in Fig. 3.3

Table 3.3 Meteorological data

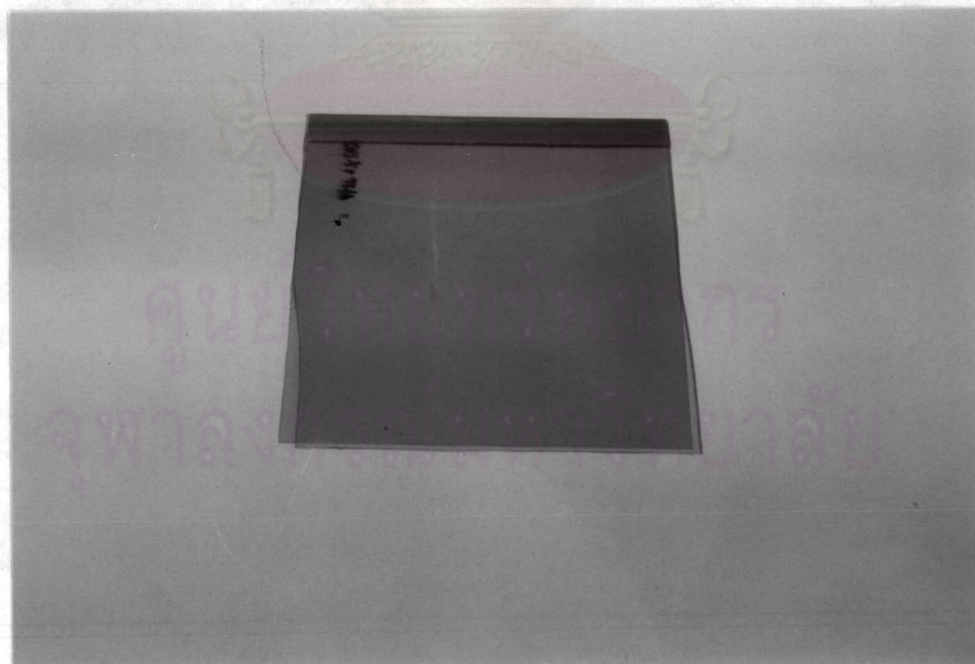| Site	Avg.temp. °C	Ann.Humid. % RH	Ann.Rainfall mm.	Ann.Solar Rad. 10^2 MJ/M^2
Bangkok	28.7	73	1496.4	1938.92

* Value for Jan. 1989 to Dec. 1989

Fig. 3.2   Exposure sample

Fig. 3.3   Exposure frame

3.4.2 Accelerating irradiation test

As an accelerating tester   the Philips medium-pressure mercury lamp was selected.   Irradiation were performed   at room temperature.   The   thickness of the specimens are approximately 0.4 mm.   and were cut into a dumbbel shape as shown in Fig. 3.4.

The cabinet is composed of the lamp (at the center of the cabinet), a round rack (for the sample holders) which is 20 cm. from the lamp and   the cooling fan placed at the bottom of the tester, as shown in Fig. 3.5.   The   irradiation specimens were set on the sample holders (four dumbbels for each holder), then placed into the tester as in Fig. 3.6 .
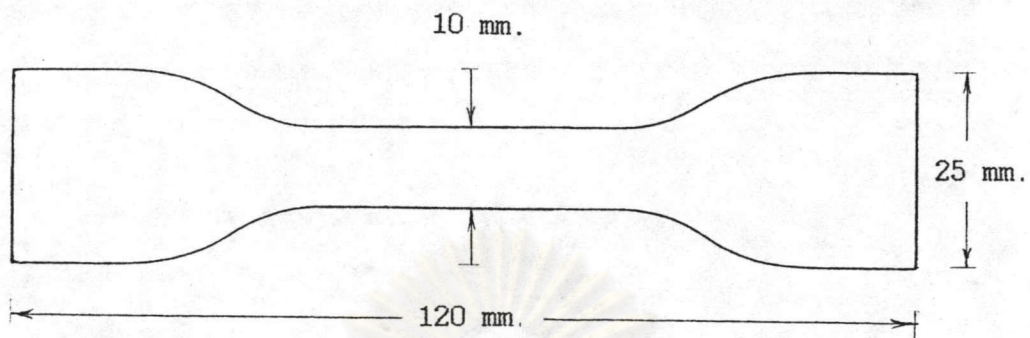
10 mm.

25 mm.

120 mm.

Fig.3.4 Exposure sample

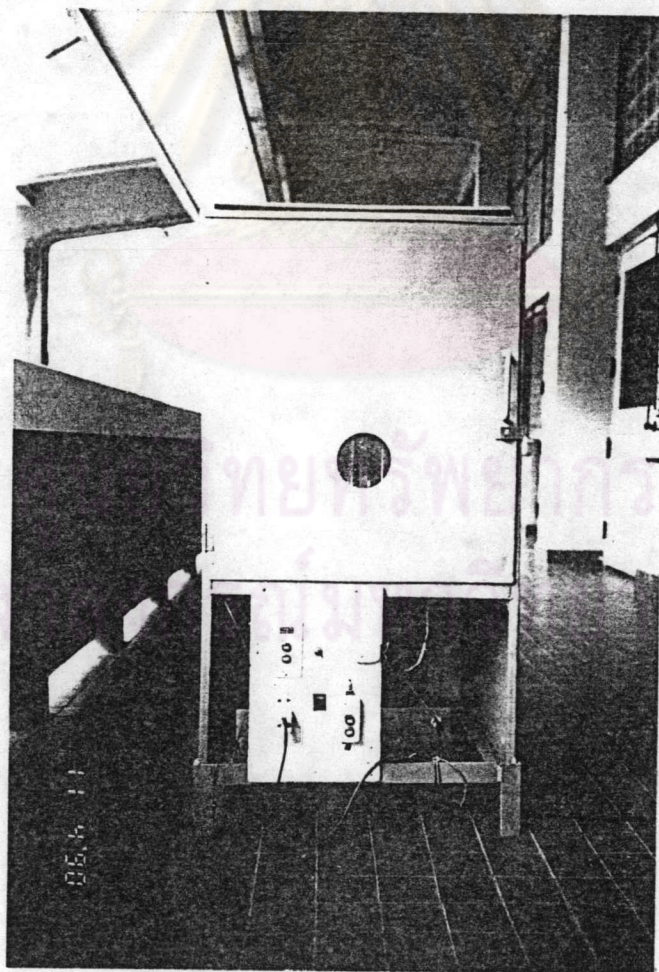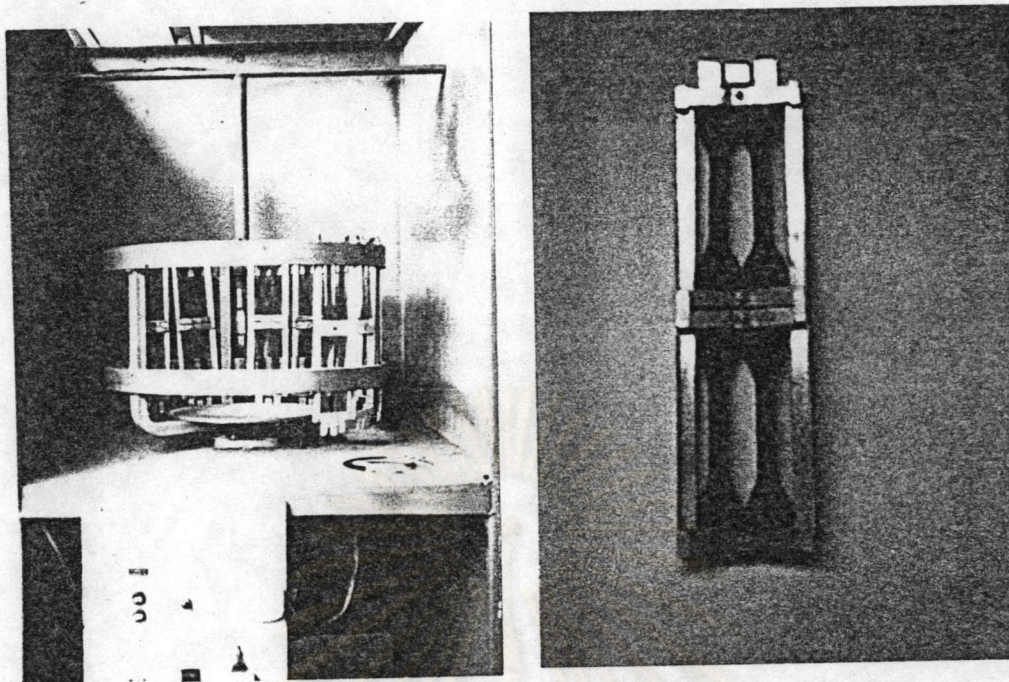Fig.3.5 Exposure cabinet

Fig.3.6 Sample holder

3.5 Studying polymer degradation

As mentioned before, the natural weathering exposed PVC films will deteriorate within the exposure time . Here are many changes in the exposed materials , such as the formation of visible colours which usually is the first evidence indication of degradation, the steady drop in the mechanical properties and loss of abrasion resistance and gloss in the physical properties, etc.

In order to investigate the effects of photosensitizers on the photodegradation of blow molded PVC , only the mechanical and physical methods were selected to examine the properties of the degradation samples .

3.5.1 Mechanical methods

To examine the influence of UV light on the PVC specimens at various sensitizer concentrations, the tensile properties were measured. Since there are several standard test methods for the

tensile test of films with various specimen shapes, dimensions and test speed specification. However in this experiment the JIS K-6734 (1968) standard which is for the rigid poly(vinyl chloride) film was selected. The details of the specimens and the conditions of the test are as follows :

- Test specimens : in dumbbel form with nominal width 10 mm. gage length 120 mm, initial gage length 40 mm and thickness of not more than 1 mm.
- Conditioning : conduct tests in laboratory atmosphere of 23 + 2 $^{\circ}$C and 50 + 5 % relative humidity
- Test speed : the speed of testing is 100 mm/min.
- Number of test specimens :
  five specimens were tested for each sample.

The received tensile strength were then determined as an average result.

3.5.2 Physical methods

Modern physical methods of analysis have been used for the scientific study of polymer degradation processes. For this experiment we will determine the changes in 3 ways :

3.5.2.1 Determination of average molecular weight by viscosity method

The average molecular weights of the samples were determined using the ASTM D. 1243 method , using a cyclohexanone solution, and can be calculated from the Mark-Houwink-Sakurada equation.

$$[\eta] = kM^a$$

where [η] = viscosity number of a solution

k = constant value = 16.3×10^{-3}

a = constant value = 0.77

M = molecular weight

Procedure in determining viscosity :

An approximate quantity of cyclohexanone (13 ml.) was introduced into the viscometer which is sufficient to fill the suspended level bulb :
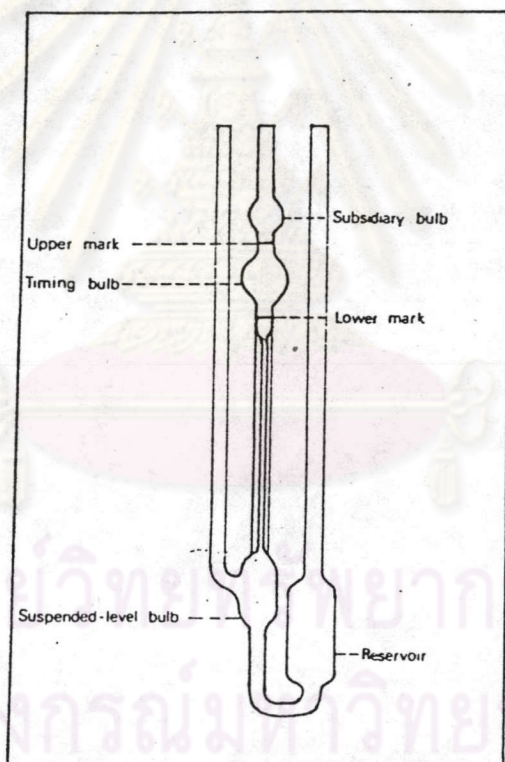

Fig. 3.7 Ubbelohde viscometer

Then, it was clamped vertically in a water bath at constant temperature (30 º C) until the solution attained thermal equilibrium (about 10 min). Consequently, cyclohexanone was drawn into the subsidiary bulb and was allowed to flow freely. The flow time was

recorded between the points at which the minicus of cyclhexanone pass the upper mark and the lower mark of the Ubbelohde viscometer. The measurement of flow time was repeated three times before removing the solvent from the viscometer.

Each sample was washed with methanol using a liquid-solid extraction for one day, then it was dried at 80 °C . The solution of washed PVC in cyclohexanone ($0.2000 + 0.0001$ g.dl^{-1}) was taken by 5 ml. ,10 ml. and 15 ml. into a 25 ml. volumetric flask and then marked up with fresh solvent to 25 ml. After that we obtained a PVC solutions of 0.04 ,0.08 , 0.12 and 0.2 g.dl^{-1}. In the same manner as pure cyclohexanone, three successive flow times of the PVC solution at every concentration was recorded. The whole procedure was repeated for all samples. The calculation method is shown in Appendix B.

3.5.2.2 Spectroscopic study

The objective of these spectroscopic studies on the samples is to determine the photooxidation products of the degraded PVC. The techniques used in this work are :

3.5.2.2.1 Ultraviolet and visible spectroscopic study

PVC specimens at selected irradiation time were dissolved in tetrahydrofuran to 1.00 g.dl^{-1}. Ultraviolet spectra of photodegraded PVC samples at various times and various concentrations were examined using a Ultraviolet 240 Shimudzu UV-Visible Spectrophotometer.

3.5.2.2.2 FT-IR spectroscopic study

Irradiated PVC samples were dissolved in tetrahydrofuran (2.0 g.dl^{-1}). Approximately 3 ml. of the solution was drawn down into a glass petri dish to give a coat glass surface. After

evaporation at room temperature, a film of PVC was obtained. This film was attached to a holder fitting directly into the sample compartment of a Nicolett FT-IR spectrophotometer. The changes in absorbance peak at 1730, 3200, 3460 cm^{-1} were estimated.

3.5.2.3 Visual Inspection

The modification of optical and surface properties of PVC sheets exposed to UV radiation are investigated and recorded such as gloss and colour.