

Stability of PVC Films Complemented With Synthetic Bio-Lubricant

Emad Yousif^{1,†}, Ahmed A. Al-Amiery^{2,3,†}, Ahmed Yahya Issa Rubaye⁴, Abdul Amir H. Kadhum³, Abu Bakar Mohamad^{4,5}

1. Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 10072, Iraq; E-mail: emad_yousif@hotmail.com
2. Environmental Research Center, University of Technology (UOT), Baghdad 10001, Iraq; E-Mail: dr.ahmed1975@gmail.com
3. Department of Chemical & Process Engineering, University Kebangsaan Malaysia (UKM), Bangi, Selangor 43000, Malaysia; E-Mails: amir@eng.ukm.my (A.A.H.K.); drab@eng.ukm.my (A.B.M.)
4. Department of Chemistry, College of Science, University of Basrah, Basrah 61004, Iraq; E-Mail: issaay86@yahoo.co.uk
5. Fuel Cell Institute, University Kebangsaan Malaysia (UKM), Bangi, Selangor 43000, Malaysia

* Author to whom correspondence should be addressed; E-Mails: dr.ahmed1975@gmail.com (A.A.A.); emad_yousif@hotmail.com (E.Y.); Tel.: 009-964-7700-1115 (A.A.A.)

† These authors contributed equally to this work.

Abstract: Stabilization standards of PVC films are fundamentally depend on essential laws: solvation and "reverberation" Stabilization. The photo-stabilization of poly(vinyl chloride) (PVC) films by epoxidized oleic acid was investigated. Photo-stabilization activities were determined by monitoring the carbonyl, polyene and hydroxyl indices with irradiation time. The changes in viscosity average molecular weight of PVC with irradiation time were also tracked using tetrahydrofuran as a solvent. The quantum yield of the chain scission (Φ_{cs}) was evaluated and found with range 4.53'10⁻⁸ and 8.12'10⁻⁸. Postulated mechanisms were outlined depending on the structure of the additive.

Keywords: UV-light 1; Photostabilizer 2; PVC 3. oleic acid.

1. Introduction

There is an extraordinary enthusiasm at present in the photo-degradation of polymeric frameworks, and this is reflected in the huge number of research articles that seem every year in this branch of knowledge. Temperature, humidity and solar radiation are the main impacts that, cause degradation in polymers [1]. Presentation to daylight can have unfriendly consequences for the helpful awesome enthusiasm of plastic items. Ultraviolet radiation can destroy the bonds between atoms in a polymer. Photo-degradation debasement reasons splitting, chalking, shade changes and the loss of physical characteristics [2]. PVC is a polymer which is extremely delicate to the weathering activity and this limits its outside applications. This happens primarily in view of changes in mechanical characteristics and color [3]. PVC is a standout amongst the broadest thermoplastic materials on the planet because of its significant characteristics, wide range of applications, resistance and low cost [4]. In any case, PVC suffers from poor thermal and light stability. It experiences fast autocatalytic de-hydro-chlorination from presentation to high temperature and light amid its molding and utilization, individually [6, 5]. There are a few methods for avoiding UV degradation in plastics by utilizing stabilizers or blockers. Light stabilizers are utilized broadly as a part of plastics, beauty care products, and films. The principle reason for UV stabilizer is to keep polymers from photo-degradation brought on by light displayed in daylight and other light source [7]. As part of our on-going research in the photostabilization of poly(vinyl chloride), the photostabilization of PVC was studied using epoxidized oleic acid as additive..

2. Results

The epoxidized oleic acids were used as additives for the photostabilization of PVC films. In order to study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PVC films with UV light of wavelength, $\lambda = 313$ nm led to a clear change in the FTIR spectrum. Appearance of bands in 1772 cm^{-1} and 1724 cm^{-1} , were attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone, respectively. A third band was observed at 1604 cm^{-1} , related to polyene group. The hydroxyl band appeared at 3500 cm^{-1} was annotated to the hydroxyl group [13]. The absorption of the carbonyl, polyene and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (Ico), polyene index (IPO) and hydroxyl index (IOH). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure 1, the Ico of A3, A2 and A1 showed lower growth rate with irradiation time with respect to the PVC blank film without additives. Since the growth of carbonyl index with irradiation time is lower than PVC blank, as seen in Figure 2, it is suitable to conclude that these additives might be considered as photostabilizers of PVC polymer. Efficient photostabilizer shows a longer induction period. Therefore, the A1 is the most active photostabilizer, followed by A2 and A3 which is the least active. Just like carbonyl, polyene compounds are also produced during photodegradation of PVC. Therefore, polyene index (IPO) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure 2.

Fig. 1: The relationship between the carbonyl index and irradiation time for PVC films ($30\ \mu\text{m}$ thickness) containing different additives. Concentration of additives is fixed at 0.5% by weight.

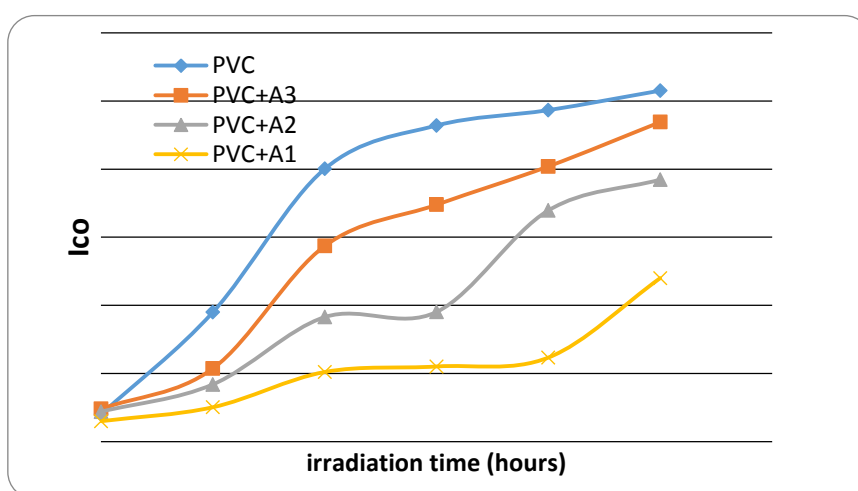
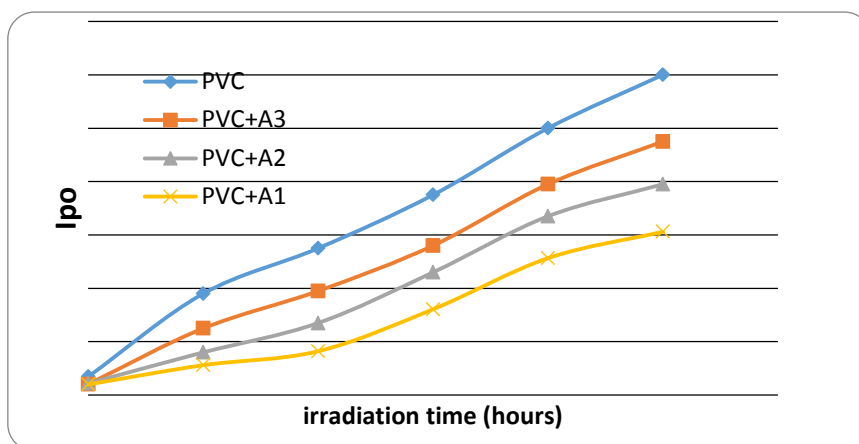
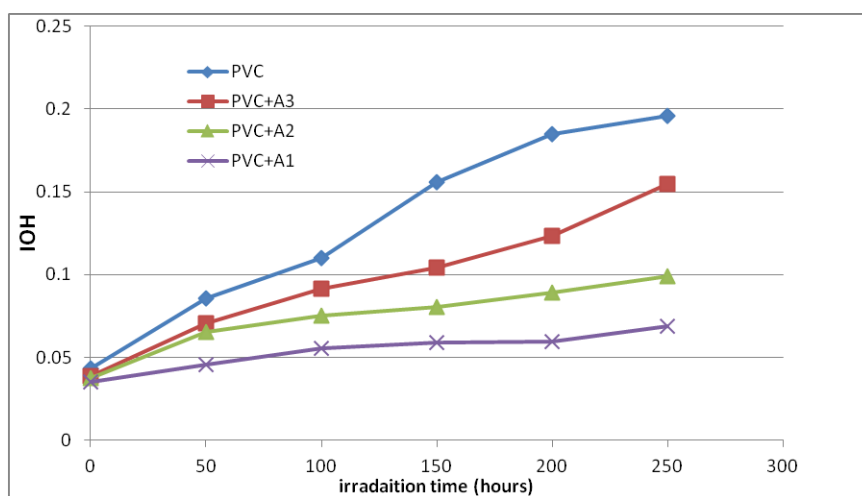


Fig. 2: The relationship between the polyene index and irradiation time for PVC films ($30\ \mu\text{m}$ thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.



Hydroxyl species were produced during photodegradation of PVC. Therefore, hydroxyl index (IOH) was monitored with irradiation time for PVC and with additives. From Figure 3, the A3, A2 and A1 showed lower growth rate of hydroxyl index with irradiation time compare to PVC film without modification.

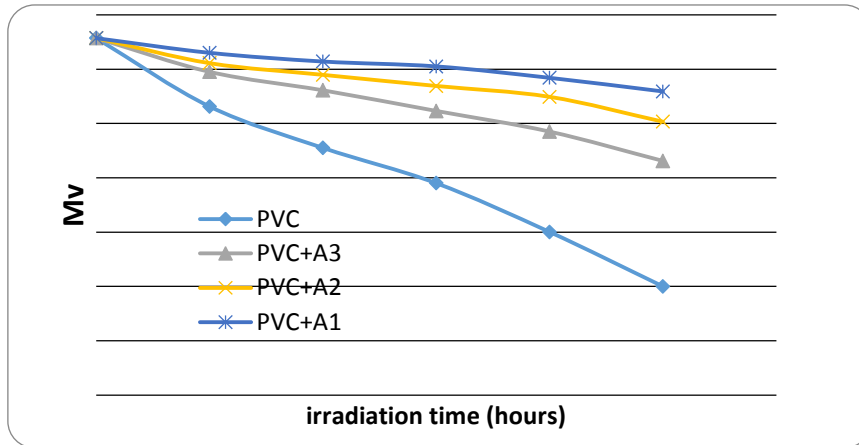
Fig. 3: The relationship between the hydroxyl index and irradiation time for PVC films (30 μm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.



Variation of PVC molecular weight during photolysis in the presence of epoxidized oleic acid as additive

Analysis of the relative changes in viscosity average molecular weight (\overline{M}_v), has been shown to provide a versatile test for random chain scission. Figure 4 shows the plot of \overline{M}_v versus irradiation time for PVC film with and without 0.5% (w/w) of the selected additives, with absorbed light intensity of $1.052 \times 10^{-8} \text{ ein. dm}^{-3} \cdot \text{s}^{-1}$. \overline{M}_v is measured using equation 4 with THF as a solvent at 25 oC.

Fig. 4: Changes in the viscosity-average molecular weight (\overline{M}_v) during irradiation of PVC films (30 μm) (blank) and with 0.5 wt% of additives.



The degradation reaction characterization used to measure of the quantum yield of the chain scission (Φ_{cs}). The quantum yield for chain scission was calculated for PVC films with and without 0.5% (wt/wt) of additive mentioned above using relation 7. The Φ_{cs} values for complexes are shown in Table 1.

Table 1: Quantum yield (Φ_{cs}) for the chain scission for PVC films (30 μ m) thickness with and without 0.5 (wt/wt) additive after 250 hrs. irradiation time.

Additive (0.5%wt)	Quantum yield of main chain scission (Φ_{cs})
PVC+A1	4.53E-08
PVC+A2	7.23E-08
PVC+A3	8.12E-08
PVC(blank)	8.33E-05

The Φ_{cs} values for PVC films in the presence of additive are less than that of additive free PVC (blank), which increase in the order:

$$\xrightarrow{\text{A1, A2, A3 and PVC}}$$

It is well established that the quantum yield (Φ_{cs}) increases with increasing temperature [14] around the glass transition temperature.

3. Materials and Methods

I) Films preparation

Commercial poly(vinyl chloride) supplied by Petkim company (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 hours. Fixed concentrations of poly(vinyl chloride) solution (5 g/100 ml) in tetrahydrofuran were used to prepare polymer films with 30 μ m thickness (measured by a micrometer type 2610 A, Germany). The prepared complexes (0.5% concentrations) were added to the films starting at 0 concentrations (blank). The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film

samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

II) Irradiation experiments

Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 Watt each. These lamps are of the type UV-B 313 giving spectrum range between 290-360 nm with a maximum at wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on the samples. The irradiated samples were rotated manually from time to time to ensure that the intensity of light incident on all samples is the same.

III) Photodegradation measuring methods

A. Measuring the photodegradation rate of polymer films using infrared spectrophotometry

The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000-400 cm^{-1} using FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified at 1722 cm^{-1} , polyene group at 1602 cm^{-1} and the hydroxyl group at 3500 cm^{-1} . The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl and polyene peaks. Then carbonyl (I_{CO}), polyene (I_{PO}) and hydroxyl (I_{OH}) indices were calculated by comparison of the FTIR absorption peak at 1722, 1602 and 3500 cm^{-1} with reference peak at 1328 cm^{-1} attributed to scissoring and bending of CH_2 group, respectively. This method is called band index method [9,10].

$$I_s = \frac{A_s}{A_r} \quad (1)$$

A_s = Absorbance of peak under study.

A_r = Absorbance of reference peak.

I_s = Index of group under study.

Actual absorbance, the difference between the absorbance of top peak and base line (a Top Peak – a base line) is calculated using the base line method.

B. Determination of average molecular weight (\bar{M}_v) using viscometry method:

The viscosity property was used to determine the average molecular weight of polymer at room temperature, using the Mark- Houwink relation [11].

$$[\eta] = K\bar{M}_v^\alpha \dots\dots(2)$$

$[\eta]$ = the intrinsic viscosity.

K, α = are constants depend upon the polymer-solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (g/100 ml) and the flow times of polymer solution and pure solvent are t and t_0 respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_0} \quad (3)$$

η_{re} = Relative viscosity .

$$\eta_{sp} = \eta_{re} - 1 \quad (4)$$

The single – point measurements were converted to intrinsic viscosities by the relation 2.

$$[\eta] = \left(\sqrt{2}/c\right) \left(\eta_{sp} - \ln \eta_{re}\right)^{1/2} \quad (5)$$

C = Concentration of polymer solution (g /100 ml).

By applying equation 5, the molecular weight of degraded and the virgin polymer can be calculated. Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution using the following equation:

$$[\eta] = 4.17 \times 10^{-4} M^{0.6} \quad (6)$$

The quantum yield of main chain scission (ϕ_{cs}) [12] was calculated from viscosity measurement using the following relation 7.

$$\phi_{cs} = (CA/\bar{M}_{v,0}) \left(\left([\eta_0]/[\eta] \right)^{1/\alpha} - 1 \right) / I_0 t \quad (7)$$

where: C = concentration; A = Avogadro's number; $(\bar{M}_{v,0})$ = the initial viscosity-average molecular weight; $[\eta_0]$ = Intrinsic viscosity of PVC before irradiation; I_0 = Incident intensity and t = Irradiation time in second.

4. Conclusions

In the work described in this paper, the photostabilization of poly(vinyl chloride) films using epoxidized oleic acid as additive were studied. These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl, polyene and hydroxyl indices for PVC films.

$$A1 > A2 > A3.$$

The epoxidized oleic acid as additive were found to be the more efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using tin complexes as stabilizer for PVC.

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Conflicts of Interest: The authors declare no conflict of interest.

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