Diamine Derivatives as Photostabilizers for Thermoplasticized Poly(Vinyl Chloride) [I]

Hussein N. salmon1 Olfat A. Nief1* Firyal W. Askar1 Marwa N. Jasim2

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Abstract:
The photostabilization of poly vinyl chloride (PVC) films has been investigated by using diamine derivatives. The (PVC) films were contained 0.5% weight of diamine derivatives which prepared by the method of casting. The photostabilization of these compounds were determined by monitoring the carbonyl index value with irradiation time. Also, the effect of concentrations of additives (range 0.1-0.5wt) on the rate of photostabilization process was studied. Therefore we found that a increased photostabilization rates was increase with increasing concentrations of compound. Besides, the influence on film thickness of photostabilization process was also studied; and the results showed that the increasing of film thickness increase the rate of photostabilization. Also, the changes in the viscosity of the average molecular weight, the degree of deterioration (α) and the average number of chain scission (s) were tracked, it was concluded that the random chain scission is always occurs in PVC film, also Quantum yield of the chain scission of these compounds was calculated. Several mechanisms have been suggested and according to experimental results obtained, these mechanisms are dependent on the structure of the additive. Among UV absorber and radical scavenger.

Keywords: UV absorber, Photostabilizer, Photochemistry, Poly vinyl chloride (PVC).

Introduction:
Polymeric materials were photodegradable when exposed to the ultraviolet radiation, leading to the breaking of polymer chains, the production of radicals, reduced the molecular weight and also caused the deterioration of mechanical properties and changed to the unfeasible materials, after an predictable time(1). Poly(vinyl chloride) is one of the world's most comprehensive plastic materials because of valuable properties, wide-ranging applications, great chemical resistance, barrier properties, low price.(2,3) Vinyl chloride monomer and its polymers occupy a unique place in the history of plastics. When synthetic resin technology was reached early, it was not displaced by newer polymers. Poly(vinyl chloride) is second only of polyethylene among the five kinds of general plastics materials, which was widely used in industries including electronic, architecture, chemical engineering, packaging and transportation(4,5).

Poly(vinyl chloride) may degrade in the presence of oxygen and during processing, storage and utilization when exposed to high temperatures, high mechanical stresses or ultraviolet radiation. Polymer degradation took place by the successive elimination of hydrogen chloride (hydrochloric acid), which is called dehydrochlorination, resulting in long polyenes, which thus caused discoloration, deterioration of mechanical properties and reduction of chemical resistance (2). The low cost and outstanding performance of poly(vinyl chloride) make it a very gorgeous and appropriate plastic for a wide range of applications(6). However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat and light during its molding and use respectively (4). As a result, conjugated polyene sequences were formed from the beginning of the reaction, and they gave rise to discoloration of the polymer and seriously changed its physical properties. Degradation also caused a strong change in the mechanical properties of the polymer, which was attended by a decrease or increase in its average molecular weight as a result.

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of either chain scission or crosslinking of the polymer molecules, respectively (7).

To avoid the ultraviolet degradation occurring in plastic materials, there are several ways, including the use of stabilizers, absorbers or blockers. For many outdoor applications the simple addition of carbon black at around a 2% level, will provide the protection for the structure by the blocking process. Other pigments such as titanium dioxide can also be effective. Organic compounds such as benzophenones and benzotriazoles are typical absorbers which selectively absorb the UV and re-emit at a less harmful wavelength, mainly as heat. The benzotriazole type is good, as it has a low color and can be used at low dose rate below 0.5%. The other main mechanism for protection is to add a stabilizer the most common being a HALS (hindered amine light stabilizer). These absorb the excited groups (hindered radicals) and stop the chemical reaction of the radicals (8). As a possible way to solve the problem of polymer stabilization, a number of different stabilizers have been successfully used (9,10).

Organic UV-stabilizers, generally with small molecular weight, include fluorescent compounds, phenyl-ester of benzoic acid, hydroxyl benzophenone, benzotriazoles, etc (11). A number of heterocyclic compounds including polydentate amines, crown ethers, bipyridines, naphthrydines, 2-amino benzothiazol and 2-mercaptopbenzothiazole have been bounded with mainly polystyrene, divinylbenzene copolymers or linked with poly(vinyl chloride) (12,13).

Lately, researchers have used substituted benzothiazole and benzimidazole ring as photostabilizers for rigid PVC. They have also used 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives as novel photostabilizers for rigid PVC and some synthesized organic compounds as N-substituted maleimides, N-phenyl pyrazolone, phenyl urea, some glucoside derivatives, and other organic compounds to be used as photostabilizers for PVC (14–18). In this study, a series of new diamine derivatives have been synthesized and studied their use as a photostabilizers for poly(vinyl chloride).

### Table 1. Symbol name and structural formula of compounds

<table>
<thead>
<tr>
<th>Symbol Compound</th>
<th>Structural Formula of Compound</th>
<th>Name of Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td><img src="image" alt="Structural Formula C1" /></td>
<td>1,1'-Bis (4-aminophenyl) -4-Phenyl Cyclohexane</td>
</tr>
<tr>
<td>C2</td>
<td><img src="image" alt="Structural Formula C2" /></td>
<td>1,1'-Bis[4-(2-hydroxy benzylidene)amino phenol]-4-phenyl cyclo hexane</td>
</tr>
<tr>
<td>C3</td>
<td><img src="image" alt="Structural Formula C3" /></td>
<td>Bis[(2-hydroxy phenyl)-N-phenyl]-4,4'(4-phenyl cyclo hexane)-2,3-dihydro[1,3]oxazepine-4,7-dione</td>
</tr>
<tr>
<td>C4</td>
<td><img src="image" alt="Structural Formula C4" /></td>
<td>Bis[(2-hydroxy phenyl)-N-phenyl]-4,4'(4-phenyl cyclo hexane)-2,3-dihydrobenz[1,2e][1,3]oxazepine-4,7-dione</td>
</tr>
</tbody>
</table>

### Materials and Methods:

**Materials:**

Three derivatives of (1,1'-Bis (4-aminophenyl) -4-Phenyl Cyclohexane) were prepared (Table 1) in the way which have already been depicted by Olfat et al (19). Poly(vinyl chloride) and tetrahydrofuran were used.

### Irradiation Experiments:

**Method of Preparation Films:**

The poly(vinyl chloride) (supplied by Petkim Company in Turkey) was dissolved in tetrahydrofuran solvent, left until dissolve then re-precipitated by adding drops of methanol. The solid material was filtered and dried under vacuum at laboratory temperature for 24 hours.

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The poly (vinyl chloride) films were prepared at (40 μm) thickness (measured by a micrometer Type 2610 A, Germany, using a stationary concentration of poly(vinyl chloride) solution (5g/100ml) in tetrahydrofuran. The evaporation technique at room temperature for 24 h was used to prepare the films. The poly (vinyl chloride) films were dried for (3 hours) at room temperature to remove any tetrahydrofuran residues. The films were fixed on stands specially used for irradiation. The stand was provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company (8,20).

Accelerated Testing Technique:
An accelerated weather-meter Q-panel Laboratory ultraviolet (QUV; Q-Panel Company, Homestead , Florida , USA) for irradiation of poly(vinyl chloride) films and provided by Q-plate company has been used. The accelerated weathering test included a stainless steel plate that has one hole in the back side and two others in the front. Each side contained lamp (type Fluorescent Ultraviolet Lights) 40 Watt each (Q-Panel Company), giving wavelength range between (250 to380 nm) and the maximum wavelength light intensity was at (6.4 x 10^-7 Ein dm^-2 S^-1). The poly vinyl chloride films were fixed parallel to the lamps and vertically to make sure that UV incident radiation is perpendicular on the samples, the irradiated films were rotated from time to time to ensure that the intensity of light incident on all samples is the same. The distance between the polymer films and the source was (10cm)(21).

Photodegradation Measuring Methods:
The photodegradation of polymer film samples were followed using FT-IR Shimadzu Spectrophotometer (model FT-8400S). The absorption spectra of poly (vinyl chloride) films were recorded in the range of (4000-400) cm^-1. The position of carbonyl absorption was specified at 1730 cm^-1 (22,23). The progresses of photodegradation through different irradiation times were followed by noting changes in carbonyl peaks. Then carbonyl (C=O) indices were calculated by comparison of the FTIR absorption peak at 1722 cm^-1 with reference peak at 1328 cm^-1, respectively. This method is called band index method which includes as equation (1):

\[ I_s = \frac{A_s}{A_r} \] ........(1)

where:  \( A_s = \) absorbance of the band under study.  
\( A_r = \) absorbance of the reference band.  
\( I_s = \) group index under study.

The actual absorbance difference between the absorbance of the highest peak and the baseline (A Top beak-base line) was calculated using the baseline method (22, 24).

Determination of Viscosity Average Molecular Weight by Using viscosity:
It is one of the most precise measurements in polymer science and also the simplest and cheapest. Intrinsic viscosity, which is measured from the flow time of a solution through a simple glass capillary, has considerable historical importance for establishing the very existence of polymer molecules. It also provides considerable physical insight. The viscosity measurement was used to determine the molecular weight of polymer, using the Mark-Houwink relation equation(2)(23):

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

.........(2)

Where \([\eta] = \) Intrinsic viscosity. \( K \) and \( \alpha \) are constant depending on polymer, solvent and temperature (in this work, \( K = 1.5x10^2 g/ml \), \( \alpha = 0.77 \)). The relative viscosity (\( \eta_{rel} \)) of polymer solution was measured with on Ostwald-U-tube viscometer solution was made by dissolving the polymer in a solvent (g / 100 ml) and the flow time of polymer solution (t) and pure solvent (t0). Relative viscosity was calculated by using equation (3):

\[ \eta_{rel} = \frac{t}{t_0} \] ........(3)

The relative viscosity (\( \eta_{rel} \)) can be used to calculate specific viscosity (\( \eta_{sp} \)) as follows in equation (4):

\[ \eta_{sp} = \eta_{rel} - 1 \] ........(4)

Using the specific viscosity and relative viscosity in the equation below (5) to calculate intrinsic viscosities \([\eta]\) (25):

\[ [\eta] = \left( \frac{\sqrt{2}}{C} \right) \left( \eta_{sp} - \ln \eta_{rel} \right)^{\frac{1}{2}} \] .......(5)

C = Concentration of polymer solution (g /100 ml). The quantum yield of main chain scission (\( \phi_{cs} \)) was calculated from viscosity measurement using the following relation(25):

\[ \Phi_{cs} = \left( \frac{C.N}{\bar{M}_{v,0}} \right) \left[ \frac{\eta_{sp}}{\eta} \right]^{\alpha - 1} \frac{1}{I_0} \] ....(6)
Where:”C = concentration, N = Avogadro’s number, (Mv,o ) = the initial viscosity average
molecular weight, [ηo] = Intrinsic viscosity of PVC polymer before irradiation , I0 = Incident
intensity (6.4 x 10-7 Ein.dm-3.s-1) and t = Irradiation time in second.”

Results and Discussion:

Photodegradation Mechanism for PVC

The PVC photochemical degradation steps are summarized as shown below (23):

1) When PVC is photolyzed in the presence of (O2), (the excited singlet polyenes occuring. Those
excited states homolytic cleavage of the (C–Cl) bonds happening, the formation of free radicals, [I] and
Cl.

2) The polyenyl radical [I] has been scavenged by (O2) to give peroxy radical [II].

3) peroxy radical [II] reacted with the (CH2) and (CH Cl) groups on chain PVC to give [III], [IV] and
radical [V] reacted with [O2] to give [VI].

4) The radical [VI] abstraction from PVC with the formation of hydroperoxide [VII] and [VIII] or it
reaction with PO2 leads to formation of Peroxide bridge[X] and alkoxy radicals [IX].

5) Tertiary alkoxy radicals [IX] are also proved to be stabilized by scission which may involve
either (C-Cl) bond cleavage to form ketone or/and (C-C) bond cleavage to form polyene (26).
Carbonyl groups in the polymer chain play a key role in the formation of acyl radicals via oxidative degradation of the main polymer chain. The carbonyl index ($I_{co}$) was monitored with irradiation time using FT-IR spectrophotometry. The irradiation of PVC films using light of wavelength ($\lambda = 313$ nm) led to new change in their FT-IR spectrum. Figure (1), (2), (3), (4), (5) show the change in IR-spectra of PVC film without additives and in the presence of (0.5 %) additives respectively.

Figure 1: FT-IR Spectra of PVC (control) at (40 µm thickness) under UV degraded for different exposure time.

![Figure 1](https://via.placeholder.com/150)

Figure 2. FT-IR Spectra of PVC samples stabilized with 0.5% (C1) at (40 µm thickness) under UV degraded for different exposure time.
Figure 3. FT-IR Spectra of PVC samples stabilized with 0.5% (C2) at (40 µm thickness) under UV degraded for different exposure time.

Figure 4: FT-IR Spectra of PVC samples stabilized with 0.5% (C3) at (40 µm thickness) under UV degraded for different exposure time.

Figure 5. FT-IR Spectra of PVC samples stabilized with 0.5% (C4) at (40 µm thickness) under UV degraded for different exposure time.
The absorption bands appearing at (1720 cm\(^{-1}\)) was attributed to the formation of the (C=O) groups. In the present work the photostabilization of poly(vinyl chloride) was examined with additive concentration which weight ranges from (0.1 to 0.5%). The thickness of the films PVC was kept constant at (40μm). Figure (5-8) show that both of carbonyl index (\(I_{\text{CO}}\)) with irradiation time for PVC films containing different concentration on additives.

The results fig. 5-8 show that the carbonyl index (\(I_{\text{CO}}\)) are decreasing with increases weight ratio concentration of additives and show that additive concentration of 0.5% by weight gave the best results (27). Such a concentration has been applied successfully for photo stabilization of PVC films with other additive(10). However in Figure (9), the (\(I_{\text{CO}}\)) of C1, C2 , C3 and C4 indicated a lower CO growth rate with irradiation time for the PVC control film in the absence of any additives. Since the growth of the carbonyl index (\(I_{\text{CO}}\)) with irradiation time was lower than the PVC control (Fig. 9), it was concluded that such additives could be considered as photostabilizers for the PVC polymer. In principle, a longer induction period is a sign of an efficient photostabilizer. Therefore, the C4 is considered to be the most efficient photostabilizer, followed by C3, C2 and C1.
Also, in the present work, the photodegradation rate of PVC films was studied in different thickness of (40, 70, 100 μm) without and with fixed concentration of (0.5%) of additive. The relationship between the carbonyl index with irradiation time are shown in fig. 9-11. The results shown in fig. 9-11 indicated that the rate of photo-oxidation (carbonyl indices) at fixed irradiation time steadily decreases with the increasing of film thickness for (0.5 wt%) additive used and so dose that of the PVC control. Therefore, one could expect that the slope of the relationship between index with film thickness fig. 12 varies with the type of additives since the interaction mechanism of these different oxygen or oxygenated polymer materials are certainly different. Figure (12) shows the relationship between the carbonyl index (I<sub>CO</sub>) with thickness film which indicates the decreases of photodegradation with the increasing of thickness of the film.

![Figure 9. The relationship between carbonyl index and irradiation time for PVC films with thickness (40 μm) and that containing 0.5 wt% of additives.](image)

![Figure 10. The relationship between carbonyl index and irradiation time for PVC films with thickness (70 μm) and that containing 0.5 wt% of additives.](image)

![Figure 11. The relationship between carbonyl index and irradiation time for PVC films with thickness (100 μm) and that containing 0.5 wt% of additives.](image)

![Figure 12. The relationship between carbonyl index and film thickness (μm) for PVC film at 250 (hrs) irradiation time containing 0.5 wt% of additives.](image)

**Determination of average molecular weight using viscometry method:**

As a consequence of photo-oxidation degradation in PVC is the reduction of the average molecular weight of the polymer which is a result of photolytic chain scission. The changes in the molecular weight 〈<i>M</i><sub>p</sub>〉, of PVC films with and without additive after irradiation with light intensity of (6.4 x 10<sup>-7</sup> Ein.dm<sup>-3</sup>.s<sup>-1</sup>) were monitored by viscosity measurement using equation (2) and THF as solvent at 25°C.The values of constant in this equation(Κ=1.5x10<sup>-2</sup>g/ml, α=0.77),when PVC films (with or without additive) were exposed to irradiation the intrinsic viscosity and viscosity average molecular weight decrease with the increase of irradiation time(22,23).

Figure (13) shows the relative changes in the viscosity average molecular weight (〈<i>M</i><sub>p</sub>〉) with irradiation time for PVC without and with 0.5 % of additives, this figure indicates a rapid decrease in (〈<i>M</i><sub>p</sub>〉) initially then it slows down suggesting that the initial rapid drop in 〈<i>M</i><sub>p</sub>〉 is due to scission of bonds at various weak links that distributed along the polymer chain.
The number average chain scission (average number cut per single chain) (S) was calculated by using the equation(7):

\[ S = \frac{M_{v0}}{M_{vt}} - 1 \]  

(M) and (Mvt) are the viscosity average molecular weights before and after irradiation respectively.

The plot of (S) versus time is shown in figure (14). The relation indicates an increasing in the degree of branching which might arise from crosslinking occur. The degree of deterioration (α) changes with time according to the following equation (8).

\[ \alpha = \frac{m}{M_{v0}} S \]  

Where (m) and (Mv0) are the molecular weights of the monomer and polymer before irradiation respectively. The plot of (S) as a function of irradiation time is shown in fig. 15. The curves indicate that the degradation is taking place by the random breaking of bonds in the polymer chain.

![Figure 13. Change in the viscosity average molecular weight (Mv) during irradiation of PVC films(40µm in thickness) (control) and with 0.5% of additives.](image)

![Figure 14. Change in the number average chain (S) during irradiation of PVC films (40µm in thickness) (control) and with 0.5% of additives.](image)

Figure 15. The change in the degree of deterioration (α) during irradiation of PVC films (40µm in thickness) (control) and with 0.5% of additives.

Another way in measuring the extent of the degradation reaction characterization is the measurements of the quantum yield of the chain scission (Φcs) (28) The quantum yield of chain scission (Φcs) was calculated and tabulated as shown in Table (2) for PVC film without additive and PVC films with (0.5% wt/wt) of additive mentioned above using the equation (6).

![Table 2. Quantum yield (Φcs) for the chain scission for PVC films (40 µm) thickness with and without 0.5% (wt/wt) additive after 250 hrs. irradiation time.](image)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Quantum yield of main chain scission (Φcs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>9.24</td>
</tr>
<tr>
<td>C1</td>
<td>4.24</td>
</tr>
<tr>
<td>C2</td>
<td>1.538</td>
</tr>
<tr>
<td>C3</td>
<td>0.892</td>
</tr>
<tr>
<td>C4</td>
<td>0.357</td>
</tr>
</tbody>
</table>

The (Φcs) values for PVC films in the presence of additive are less than that of PVC without additives, which decrease in the order : PVC > C1 > C2 > C3 > C4

Suggested mechanisms of photostabilization of PVC by diamine derivatives:

The action of (1,1 -Bis (4-aminophenyl) -4-Phenyl Cyclohexane ) derivatives [Schiff base ,1, 3-Oxazepine] as photostabilizers in PVC films might be attributed to absorption by this additive and dissipation on this energy to harmless heat energy. The rings of additives in these compounds play role in the mechanism of the stabilizer process by acting as UV absorber schemes (1, 2).
Scheme 1. The suggested mechanism of photostabilization of PVC Schiff bases compound as UV absorber.

Scheme 2. Suggested mechanism of photostabilization of PVC by 1,3-oxazepine ring as UV absorber.

The explaining of other mechanism to use compound (C1) as photostabilizer was through the elimination by radical scavenger, which led to the formation of intermediate radical stabilized in the delocalization of odd electrons along in the nucleus of the phenyl to as indicated in the scheme (3).

Scheme 3. The suggested mechanism of photostabilization of PVC by [C2] as radical scavenger.

Conclusions:
The work in manuscript, the photostabilization of PVC films using (1,1-Bis (4-aminophenyl) -4-Phenyl Cyclohexane) derivatives were studied. These additives behave as photostabilizers for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl index for PVC films: C4 > C3 > C2 > C1 > PVC.

These additives stabilize the PVC films through UV absorption or screening, peroxide decompose and radical scavenger mechanisms. The derivatives were found to be the most efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the indication of using (1,1-Bis (4-aminophenyl) -4-Phenyl Cyclohexane) derivatives as commercial stabilizers for PVC.

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Conflicts of Interest: None.

Reference:


مشتقات ثنائي أمين كمثبتات ضوئية للدوبليمرات الحرارية (بولي فينايل كلورايد) [I]

حسين ناصر سلمان1
فريال ولي عسكر2
اليفة عبد نايف1
مروة ولي عسكر1

1 الجامعة المستنصرية، كلية العلوم، قسم الكيمياء، العراق، بغداد.
2 الجامعة المستنصرية، كلية التربية، قسم الفيزياء، العراق، بغداد.

الخلاصة:
التثبيت الضوئي لافلام بولي فينايل كلورايد قد تحققت باستخدام مشتقات ثنائي امين. كانت الأفلام (PVC) تحتوي على وزن 0.5% من مشتقات ثنائي امين التي خضعت بواسطة طريقة الصب. درس التثبيت الضوئي للمركبات عن طريق الكشف عن نمو مجموعة الكاربونيل مع وقت التشعيع. وكذلك تم دراسة تأثير تركيز المضافات في المدى بين (0.1-0.5% wt/wt) على سرعة التثبيت الضوئي لافلام البولي فينايل. وهكذا وجدنا أن سرعة التثبيت الضوئي تزداد بزيادة تركيز المضافات. إلى جانب ذلك، تم دراسة تأثير سماكة الفيلم لعملية تثبيت الضوئي، وأظهرت النتائج زيادة سماكة الفيلم تزداد من معدل التثبيت الضوئي. أيضا، تم تتبع التغيرات في معدل الوزن الجزيئي الحجمي (Mn) والمعدل العددي لقطع السلسلة (Mw) ودرجة التجزئة (PDI) بعد أن قطع السلاسل البوليمرية يحدث. تم قياس منتج كم قطع السلسلة (Φ) لبولي فينايل كلورايد. وقد أقترح عدة ميكانيكدات، ووفقا للنتائج التجريبية التي تم الحصول عليها، تعمد هذه الميكانيكدات على ترتيب المضافات: ممتصات أو حاجبات الأشعة فوق البنفسجية، المثبتات الضوئية، الكيمياء الضوئية، متعدد فينايل كلورايد.

الكلمات المفتاحية: ممتصات الأشعة فوق البنفسجية، المثبتات الضوئية، الكيمياء الضوئية، متعدد فينايل كلورايد.