Study and Comparison the Photodegradation and Biodegradation of Poly Vinylchloride in Absence and Presence Alizarin Dye And 2- (Benzylidene) Benzothiazole Hydrazone - Pd Complex

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INTRODUCTION

Poly vinyl chloride (PVC) is the second most product and used plastic (polyethylene being the first). Its use is widespread and diverse, ranging from everyday products to highly specialized applications (1)
There are many routes that polymers encounter with metals or metallic compounds. For examples, catalyst residues\textsuperscript{2}, pigments\textsuperscript{3}, metal particles contaminated during machine processing\textsuperscript{4}, and so on can be considered. It is also well known that in a minor amount of metals or metallic compounds as well as oxygenated groups in substrates play extremely important roles either in the photodegradation or in the thermal degradation of polymers.

The role of these metals and/or metallic salts (compounds) in polymer photooxidative degradation has been reviewed and depends on\textsuperscript{5}:

1- The nature of polymer. 2- Environmental conditions to which the polymer has been exposed. 3- The nature of metal (transition or not-transition). 4- The valence of the metal. 5- The anion or ligand of the metallic compounds. 6- The spin state of the transition metal and the symmetry of its ligand field. 7- Photochemistry of a metal salt or a metal coordination compounds. External metal salts and metal compounds play an evident role in the photooxidative degradation and environmental aging of polymers\textsuperscript{5}.

Alizarin (1,2-Dihydroxyanthraquinone) is a polycyclic bio-organic molecule which occurs in plants such as Rubia tinctorium in combination with the sugars glucose and xylose. Coordination complexes of alizarin molecules with metal atoms are used as natural pigments since ancient times, one of the earliest known metal chelate is the calcium aluminum complex of alizarin (alizarin [Al]), first used as a pigment in India\textsuperscript{6}.

During UV-irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack of bacteria in natural environment. It is also well known that the efficient main chain scission in irradiated polymers causes their mechanical deterioration and breaking on to small pieces. Thus, the access of oxygen and microorganisms is facilitated to the bulk of such destroyed products. In this way polymers become biodegradable\textsuperscript{7}.

The biological degradability is defined as the degradation and deterioration of polymers solely by living organisms (including microorganisms and/or enzymes excreted by microorganisms)\textsuperscript{8}. The biochemical attack on polymers can occur at the side chain and/or directly at the backbone. In the first instance the properties are certainly altered, but basic polymeric structure may be retained and the material is not degraded. The reduction in molecular mass is an essential requirement for polymers in order to serve as nutrient for microorganisms because only low molecular substances can be transported into the cells and incorporated in internal cycles\textsuperscript{8}.

The aim
of this work is study and comparison the biodegradation of photodegraded poly vinylchloride, this type of polymers have found useful applications: in industry. Study of their either UV-light degradation or biodegradation may give an understanding of their application as degradable polymer.

**Experimental**

**The following materials were used**

a- Laboratory poly vinyl chloride powder ( B.D.H. Ltd A.R.Grade , purity 99%) was used at the test sample .

b- Laboratory alizarin dye (1,2-Dihydroxyanthraquinone) powder ( B.D.H. Ltd A.R.Grade , purity 99%) was used at the test sample .

c- 2- (benzylidine) benzothiazole hydrazone - pd complex

\[ \text{[Pd(C}_{14}\text{H}_{11}\text{N}_{3}\text{OS})_{2}]Cl_{2} \] was prepared and characterization as literature\(^9\).

**Ultraviolet visible spectrophotometry (U.V):**

The absorption spectra was recorded using the ultraviolet visible spectrophotometer using the Hitachi U-2000 and Cary 100 conc. to record the absorption spectra in the wavelength range between (200-600)nm.

**Infrared spectrophotometry (IR)**

A Pye-Unicam SP\(_3\)-100 infrared spectrophotometer was used to record the IR spectra between (600-4000) \(cm^{-1}\).

**Film preparations**

0.1% solution of alizarin dye or 2- (benzylidine) benzothiazole hydrazone - pd complex (in tetrahydofuran) was added to 1% solution of poly vinyl chloride in tetrahydofuran . A thickness of about 25\(\mu\)m was measured by a micrometer type, (2610 , Germany) , poly vinylchloride films with and without dye and complex were obtained by casting of solutions into horizontal glass plate . After solvent evaporation, samples
were dried in vacuum for 24 hrs. this was found to be adequate to completely remove of solvent from films.

**Irradiation**

The accelerated weather-o- meter, Q.U.V. tester, (Q-panel company, U.S.A), was used for irradiation of poly vinylchloride films. The films were positioned (25µm) apart from the UV.lamps (eight fluorescent lamps give essentially monochromatic light at λ=313 nm). Temperature of the tester chamber is nearly constant at 45 °C.

**Analysis**

The photodegradation of the polymer film was followed by I.R and UV-visible spectrophotometer. The absorption spectra (for I.R method) of the film samples were recorded in the wavenumber ranged from 600 to 4000 cm⁻¹. Carbonyl index were calculated by comparison of the I.R absorption peak at 1720 cm⁻¹ for (C=O) group with reference peak at 1430 cm⁻¹ for (-CH₂ ) group for poly vinyl chloride. The ultraviolet-visible spectrophotometer was used to measure the change in the U.V-Visible spectrum during irradiation.

**Biodegradation method**

Bacteria isolated from crude oil, type *Pseudomonas aeruginosa* was grown on irradiated polymers, poly vinyl chloride without and with photosensitizer (dye and complex), as a sole source of carbon and energy in order to ensure their ability to utilize them. Five milliliters of mineral salt medium (table 1) distributed in 25 ml tube. The tube was sterilized by autoclaving at 120 °C for 15 minute, the tubes were inoculated with 1% of fresh culture (18hrs.), then 1g/l of polymer was added and incubated with shaking (180 rpm) at 37°C for two weeks.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Weight(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂HPO₄</td>
<td>1.170</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.121</td>
</tr>
<tr>
<td>MgSO₄.7H₂O</td>
<td>0.121</td>
</tr>
<tr>
<td>NH₄CL</td>
<td>2.140</td>
</tr>
<tr>
<td>FeSO₄.7H₂O</td>
<td>0.28</td>
</tr>
<tr>
<td>MnSO₄.4H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.005</td>
</tr>
<tr>
<td>ZnSO₄.7H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>CuSO₄.5H₂O</td>
<td>0.061</td>
</tr>
<tr>
<td>Co(NO₃)₂.6H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>NiSO₄.7H₂O</td>
<td>0.00006</td>
</tr>
<tr>
<td>Distilled water</td>
<td>1000 ml</td>
</tr>
</tbody>
</table>
The pH was adjusted to 7.5 by buffer solution (K₂HPO₄ 1.17g and KH₂PO₄ 0.121g in 100mL). The %loss weight of polymer calculated as following:

%loss weight = weight of polymer before biodegradation - weight of polymer after biodegradation

**Bacteria strains**
The bacteria isolates used in this study is:

<table>
<thead>
<tr>
<th>Bacterial isolate</th>
<th>phenotype</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>Neo⁺, sm⁻</td>
</tr>
</tbody>
</table>

Neo⁺: neomycin resistant

sm⁻: streptomycine resistant

**RESULTS AND DISCUSSION**

The photodegradation of polymer films has been studied. The UV.-visible spectra of poly vinyl chloride films (control) irradiated with different time intervals. After 200 hrs. of irradiation, the absorbance is increase, the rate of increase is relatively much greater than in the wavelength region of (λ= 245-350)nm. The increase in absorbance is due to the formation carbonyl groups in polymer.

Figure -1: UV. –visible spectral change of PVC film without photosensitizer (25 µm in thickness)
In the present work, the photodegradation of polymer films was studied using (dye and complex) photosensitizers. The spectral changes during photolysis of polymer films, with 0.1% w/v of photosensitizers (dye and complex) are shown in figures (2) and (3) for poly vinyl chloride with dye and complex respectively.

Figure-2: UV. -visible spectral change of PVC film with dye photosensitizer (25 μm in thickness)

Figure -3: UV. –visible spectral change of PVC film with complex photosensitizer (25 μm in thickness)
From the results obtained in these figures, one can be observed that the absorbance of the polymer with dye in the wavelength 300-400 nm range increases with irradiation time but with complex the absorbance of the polymer in the wavelength 300-350 nm range decrease because the photodissociation of the Pd complex with polymer.

When the polymer film (control) samples, irradiated with wavelength ($\lambda=313$ nm), the FTIR shows the high growth of carbonyl groups absorbance in the wavenumber 1720 cm$^{-1}$, and this band intensity increases exponentially with irradiation time, which is expressed in term carbonyl index ($I_{CO}$).

The relationship between the carbonyl index ($I_{CO}$) with irradiation time is showed in figures (4).

![Figure -4: The relationship between carbonyl index and irradiation time for polyvinyl chloride films with and without (0.1% w/w) of photosensitizers](image)

It has been observed that the carbonyl index greatly increases with irradiation time for polyvinyl chloride film with dye and complex photosensitizers. The degradation of polymers and formation of carbonyl groups are similar to general mechanism in literatures$^{(11)}$. 


So these photosensitizers (i.e., dye and complex) are all considered as photodegradation inducers for poly vinyl chloride, as the growth of carbonyl index with these photosensitizers is higher than polymer without photosensitizers. Also results show that (dye) act as better-inducer of polymer photodegradation compared to other photosensitizer (complex), this is because the increased in carbonyl index ($I_{CO}$) are higher than that for polymer (control) or with photosensitizers complex and also the stability of Pd complex, these results are in agreement with literatures (12-16).

Ones therefore, might suggest the following mechanism for the photodecomposition of the photosensitizers used in this work. The UV light and free radical generated effectively initiating the photodegradation of the poly vinyl chloride as:
Scheme 2: Reaction scheme for the photodegradation of Alizarin dye

\[
[Pd(C_{14}H_{11}N_3OS)_2]Cl_2 \rightarrow [Pd(C_{14}H_{11}N_3OS)_2\cdot] + Cl_2
\]

\[
[Pd(C_{14}H_{11}N_3OS)_2]^{-} + Cl_2 \rightarrow 2 Cl^{-}
\]

Scheme (3) : Reaction scheme for the photodegradation of Pd complex

Biodegradation of polymers

The bacteria, *Pseudomonas aeruginosa*, used in this work, was isolated from crude oil is utilizing aliphatic and aromatic hydrocarbons (such as phenol and n-hexane). In order to ensure that the isolated bacteria was indeed capable to growth in procure of irradiated polymers (as the sole available carbon source), a series of experiments were carried out in which the growth in the polymer environment was compared with that in control (mineral medium free of carbon source). A typical result are shown in table (2)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bacterial growth</th>
<th>% loss weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PVC before irradiated</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2. PVC after irradiated</td>
<td>1</td>
<td>8.1</td>
</tr>
<tr>
<td>3. PVC with dye before irradiated</td>
<td>1</td>
<td>9.1</td>
</tr>
<tr>
<td>4. PVC with dye after irradiated</td>
<td>4</td>
<td>62</td>
</tr>
<tr>
<td>5. PVC with complex before irradiated</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>6. PVC with complex after irradiated</td>
<td>2</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Table 2: Growth of bacteria on polymers after 200 hours photolysis
ASTM rating: \(^{(17)}\)
(0) = no visible growth, (1) = 10\% surface growth, (2) = 10-30\% surface growth, (3) = 30-60\% surface growth, (4) = 60-100\% surface growth

It was concluded from such data that these bacteria were indeed capable of a significant amount of growth when the only carbon source present was the polymer. Color changes from colorless solution to green solution indicate to microbial growth as in figure (5).

Figure -5: The Color changes for PVC before and after irradiation, for PVA with dye or complex before and after irradiation

Where (C) : the control without any polymer or sensitizer, (1) : PVC with dye before irradiated, (2) : PVC with complex before irradiated, (7) : PVC before irradiated, (8) : PVC with dye after irradiated, (9) : PVC with complex after irradiated, (10) : PVC after irradiated

The biodegradation are followed by percentage weight loss of polymer after biodegradation, where the polymer precipitated from bacterial solution by ethanol, then dried under vacuum.

\[
\text{\%loss weight} = \frac{\text{weight of polymer before biodegradation} - \text{weight of polymer after biodegradation}}{\text{weight of polymer before biodegradation}}
\]

In general, during UV-irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack by bacteria in natural environment. It is also well-known that the efficient main chain scission in irradiated polymers causes their mechanical deterioration and breaking on to small pieces. Thus, the access of oxygen and microorganisms is facilitated to the bulk
of such destroyed products. In this way polymers become biodegradable.
From above results, the irradiation polymers contain dye and complex was biodegradaded higher than irradiation polymer without sensitizer where sensitizer increases photodegradation of polymer into small species ,then the molecular weight was reduced. This results agreement with literatures (18-21).

CONCLUSIONS
It can be concluded that addition of small amount (0.1% w/v) of low-molecular compounds such dye and complex effectively influences the photoprocesses in polymer. It has been found that photo-oxidative degradation of polymer is more efficient in the presence of these sensitizers and dye action is strongest as inducer for poly vinyl chloride and complex is less for poly vinyl chloride. These results confirm that polymer fragments produced by photodegradation of certain plastic molecules indeed attacked and metabolized by soil microorganism.
The use of biodegradation offers a cheap method for recycling nutrients efficiently and , when optimized, at a faster rate than under natural conditions. It would appear to be low in its energy requirements.

REFERENCES
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