

## **Photocatalytic Degradation of Polyvinyl Chloride-Vinyl acetate Film Using 5-Phenylazo Salicylaldehyde Derivative**

**Safana ahmed farhan\*<sup>1</sup>**

<sup>1</sup>Polymer Research Unit, College of Science, Mustansiriyah University, Baghdad-Iraq.

\*Corresponding author: *safanachem@yahoo, safanah@uomustansiriyah.edu.iq*

**ORCID ID : 0000-0003-1599-1997**

### **Abstract**

Polymers are employed in a variety of applications that may be harmful to the environment. As a result, the purpose of the research is to dismantle the mutated polymers by inexpensive materials to preserve the environment. To do this, an azole ring in 5-phenylazo salicylaldehyde derivative was produced and put into a poly (vinyl chloride-vinyl acetate) (PVC-VA) chain by substitution process. The final product was created by adding 5-phenylazo salicylaldehyde to the priority chemical. Under ultraviolet light irradiation in accelerated settings, the films' resistance to deterioration and IOH,ICO,IC=C were examined using Fourier-transform infrared spectroscopy, viscosity tests , and weight loss to follow the changes caused by UV radiation exposure. The azo compound significantly improved the photo degradation of PVC-VC polymer. When compared to the original polymer.

**Keywords:** Azo compound; PVC-VA; photo degradation

### **Introduction**

Degradation of pollutants in existence of a photocatalyst is an important field of knowledge [1-4]. Agriculture as well as human activities have increased in accordance with population growth rate as a result of substantially increased industrialization, resulting in high consumption and production in all sectors. Many daily activities and industrial operations generate garbage, with the amount of

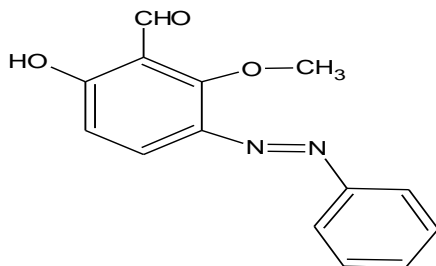
waste produced increasing proportionally to product demand. [5-7]. The issues related to resource management and garbage disposal are increasing at a faster rate. Inadequate disposal and management not just that cause severe environmental concerns, but also have a negative influence on society health [8]. Polyvinyl chloride (PVC) is one of the most versatile general-purpose polymers and very important. PVC (poly vinyl chloride) is a well-known material with unique qualities that allow it to be used in a variety of applications and it widely manufactured in both rigid and flexible forms has applications in a range of fields, including body protection and medicine, applications in sector industries; It has been used in a variety of industries, including pipelines, construction, medical appliances, doors, windows, shutters, furniture, and so on The only need for some uses is that the product be chemically and biologically pure, which is easily satisfied by highly regulated manufacture, sterilization, and storage in a sterile environment, One disadvantage of PVC is that it degrades under UV radiation to reduces its action or process in working settings. Many of that is to be added to polymer to produce modidied polymers that decompose as a solution to many environmental problems ,for example the addition of azomaterials improves the dissolution of polymers in shorter time oraccleration of fragmentation time. Pure PVC is a brittle white material that dissolves in Dimethyl sulfoxide (DMF) [9]. The photo –oxidation mechanism of polymers includes three stages: ignition, reproduction, and completion. A change occurs in the molecular structure of the material and thus leads to the disintegration of the plastic, after which it disappears completely without leaving toxic residues[10,11]. The melting point of the PVC is 128-129C°[12].

## **Experimental**

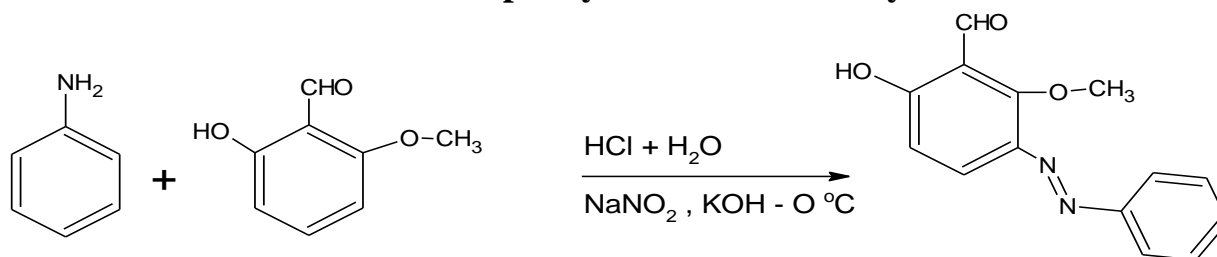
### **Preparation of 5-phenylazo salicalcaldehyde**

At 278-273 K, with quick stirring, 7 mL of 37% HCl solution was slowly added to a suitable solution of substituted aniline (0.05 mol) with little amount of water. Dropwise addition of 15 mL of 5 M aq NaNO<sub>2</sub> solution produced yellowish diazonium ions. Salicylaldehyde solution (3-methoxy salicylaldehyde, 0.05 mol) in two percent of aq KOH (100 mL) solution was then gently added over one hour.

For 30 minutes, the mixture then was mixed. The dark material was filtered and thoroughly rinsed with water. the recrystallized and purified product was from ethanol [12,13].



**Scheme 1: Structure of phenylazo salicaldehyde derivative**



**Scheme 2: Synthesis of phenylazo salicaldehyde derivative**

### Films preparation

The PVC-VA flakes were then prepared through dissolving 2.5 g of the substance in 100 mL of the tetrahydrofuran material by heating and stirring continuously. It was poured into molds of previously prepared 3cm\*3cm size. The chips were prepared at room temperature. The modified films were then dissolved 2.5 g of the polymer using 100 mL of solvent and 0.25% of phenylazo salicaldehyde derivative compound mixed with the solution, pour into glass molds and evaporate vacuum-dried at 298K for 1800 min. A German micrometer type 2610 A was used to measure the thickness of the finished PVC-VA film (25 cm thickness).

### **Irradiation experiments**

Technique for accelerated testing, Accelerated weather station For irradiation of polymer films. The chips prepared from polymer and the modified chips were irradiated with an irradiated chamber that contains a lamp of intensity 40 W a spectrum range between 250-380 nm, and distance between the source and the chip is 10 cm. The chips are placed in the device vertically and in position as parallel to the lamp in order to make sure of that the rays fall vertically on the chips continuously and homogeneously [14].

### **Methods for measuring photo degradation**

Photodegradation rate of the polymer films has been evaluated through an infrared spectrophotometer. Monitoring FTIR spectra in the 4000-400  $\text{cm}^{-1}$  range with an FTIR 8300 Shimadzu spectrophotometer was used to assess the degree of photodegradation to the polymer film samples. Carbonyl absorption is stated to be 1722  $\text{cm}^{-1}$ , polyene absorption is 1602  $\text{cm}^{-1}$ , and hydroxyl absorption is 3500  $\text{cm}^{-1}$ . The progression of photodegradation was monitored by detecting changes in carbonyl and pollen peaks over different irradiation times. All of the Carbonyl (Ico), polyene (Ipo), as well as hydroxyl (IOH) indices had been then calculated by comparing the absorption of FTIR peak at 1722, 1602, as well as 3500  $\text{cm}^{-1}$  with that of reference peak at 1328  $\text{cm}^{-1}$ , respectively. the method mentioned above, also known as band index method, involves [15].

$$I_s = A_s / A_r \dots \dots \dots (1)$$

$A_s$  = Absorbance band during irradiation

$A_r$  = Absorbance of reference band which does not change during irradiation

$I_s$  = coefficient of the group under study.

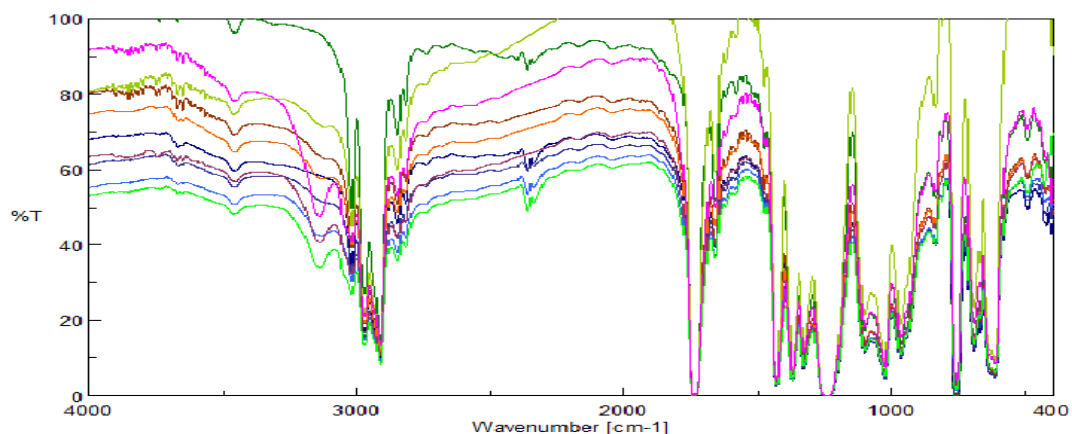
An Ostwald Viscometer method was used to measure the intrinsic viscosity value for the polymer solution. This solution was prepared through dissolving it in a solvent contain (1 gm per 100 mL), with flow times for this polymer solution and pure solvent are  $t$  and  $t_0$ , respectively. The following equation was used to calculate the relative viscosity ( $\eta_{re}$ ):

$$\eta_{re} = t/t_0 \dots \dots \dots (2)$$

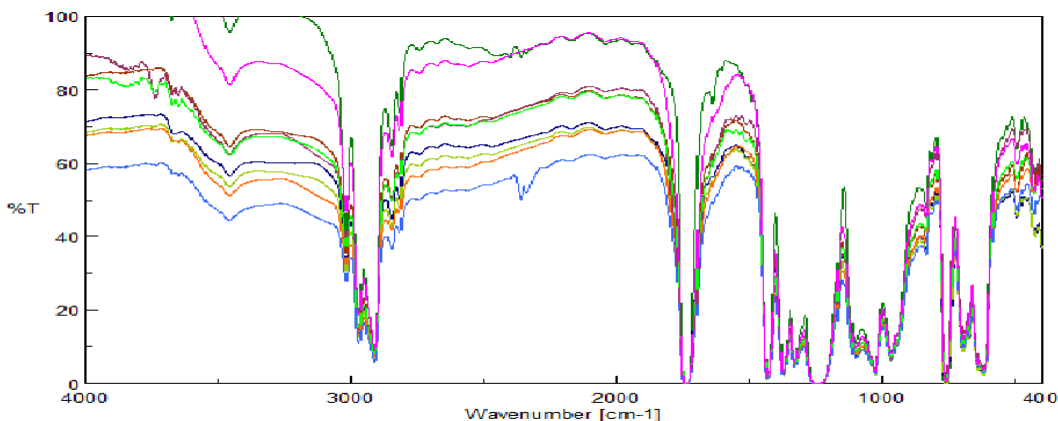
$\eta_{re}$  = Relative viscosity.

## Results and Discussion

As additives for photodegradation for PVC-VA films, 5-phenylazo salicaldehyde derivative was utilized. As shown the carbonyl, hydroxyl, and polyene indices were measured using FTIR spectrophotometry during irradiation time to evaluate the photochemical constants of these additives for the photodegradation of PVC-VA films.



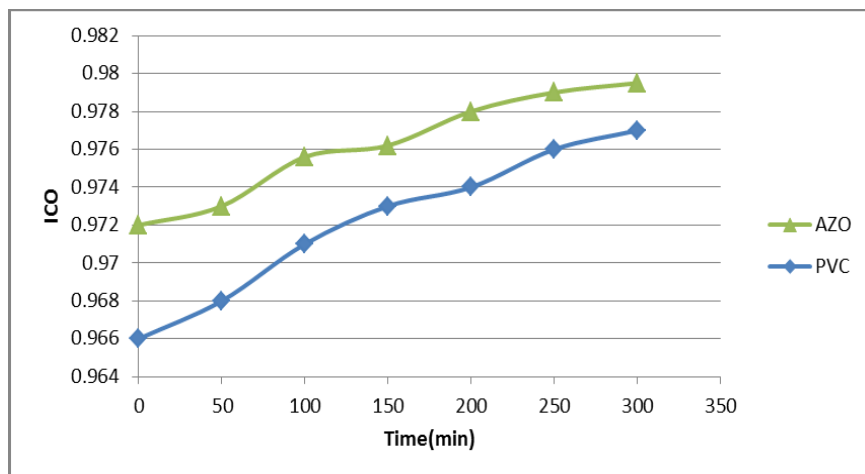
**Figure 1: FTIR spectrum for PVC-VA film in the absence of 5-phenylazo salicaldehyde**



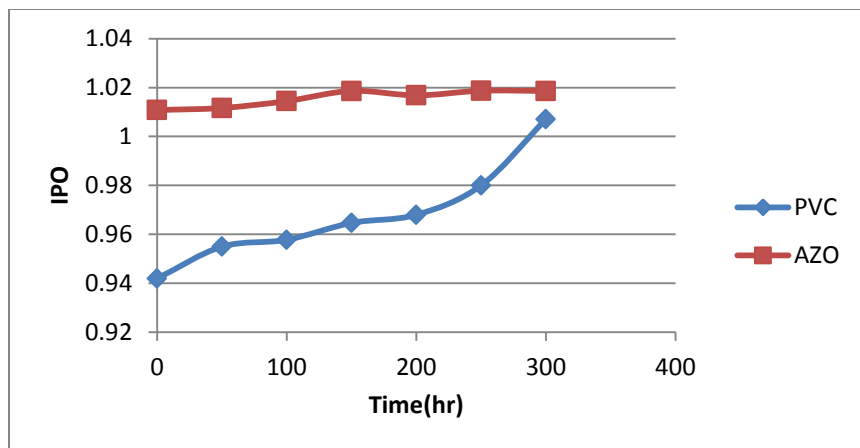
**Figure 2: FTIR spectrum for PVC-VA film in the presence of 5-phenylazo salicaldehyde**

Irradiating PVC-VC with 5-phenylazo salicaldehyde derivative film and its control film with uv light at 313 nm resulted in an exchange in spectrum of FTIR, as illustrated in Figures 1 and 2. The presence of bands at  $1772$  and  $1724\text{ cm}^{-1}$  was indicated to synthesis of the carbonyl groups associated with chloroketone as well as aliphatic ketone, respectively. Also, a third band associated with the polyene group was discovered at  $1604\text{ cm}^{-1}$ . The hydroxyl band was assigned to the OH of the hydroperoxide group at  $3500\text{ cm}^{-1}$ .

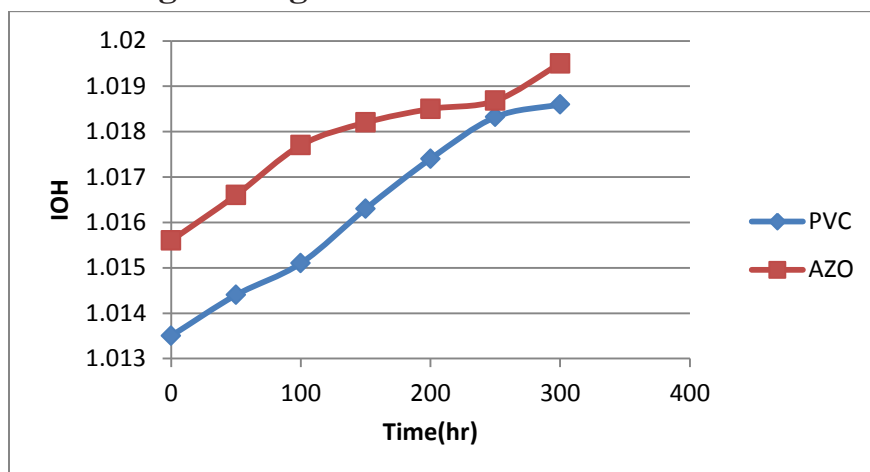
Carbonyl, polyene, and hydroxyl group absorption were used to monitor polymer degradation during irradiation. The carbonyl index (ICO), polyene index (IPO), and hydroxyl index (Ih) were used to calculate the absorption of (IOH). It is reasonable to believe that increases in ICO, IPO, and Ih are indicators of deterioration. Because these (PVC-VA and 5-phenylazo salicaldehyde derivative) indexes rise with irradiation time.



**Figure 3: The carbonyl modulus vs. irradiation time for PVC-VA films containing 0.0001g additive.**



**Figure 4: The polyene modulus vs.irradiation time for PVC-VA films containing 0.0001g additive.**

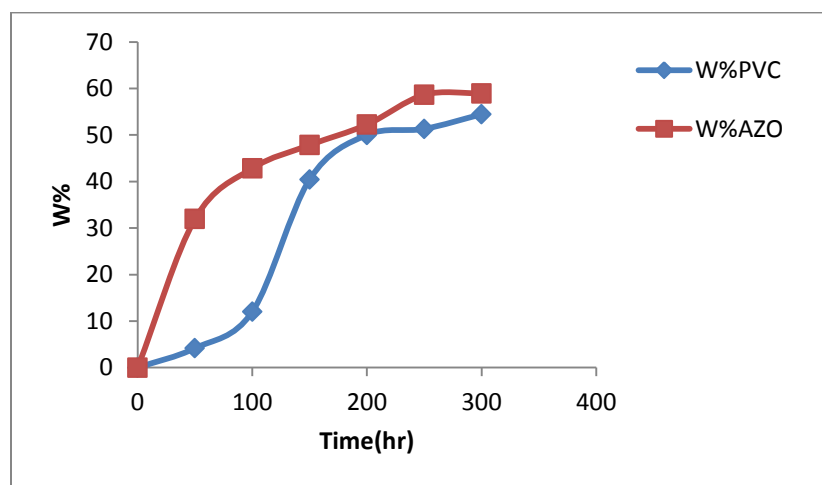


**Figure 5 : The hydroxyl modulus vs.irradiation time for (PVC-VA) films containing 0.0001gm additive.**

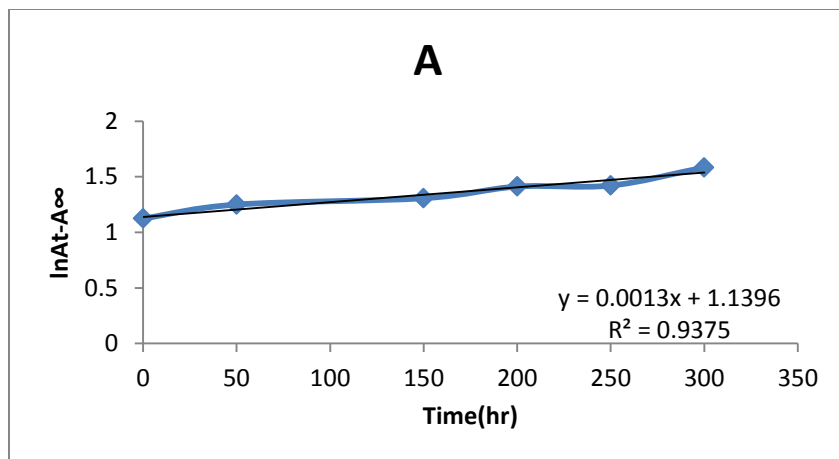
It is reasonable to have argue that the Azo additive perhaps considered as photodegradation of the (PVC-VA) polymer. A prolonged induction period is associated with efficient photodegradation.

The a values the irradiation sample are higher when Azo compounds present and lower when additives are not present. The value of a grows rapidly with time during the early phases of photo degradation of (PVC-VA), suggesting a randomly breaking of the bonds in the chain of this polymer. In Figure (6), depicts the weight change of PVC-VA with and without addition after 300 hours of UV light exposure. Our data were further studied through comparing weights of the test

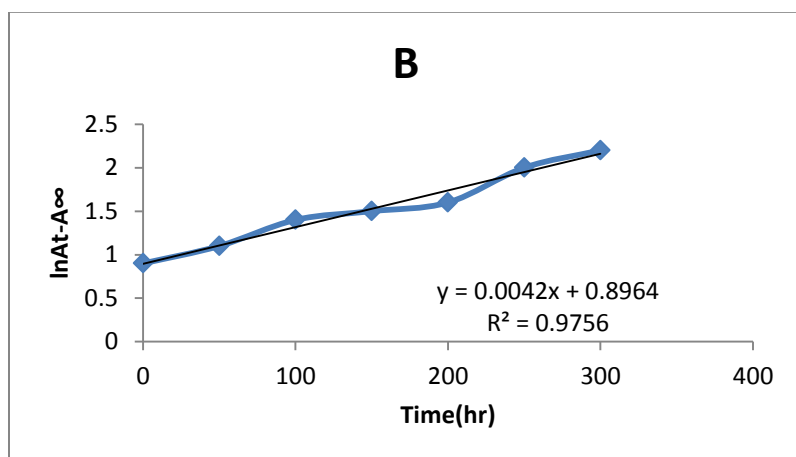
specimens before they were exposed to radiation of UV light and after that. The samples were subjected to radiation of UV light in accordance with the following parameters. These findings were further studied by comparing the weights of the specimens before they were exposure to UV light and after that. For a total of 300 hours, the samples were exposed to UV radiation under accelerated circumstances at varied time intervals. The weight differences were measured using an analytical balance. Figure (6) depicts the information. These findings revealed that PVC-VA with addition resulted in reduced weight loss. These results accord quite well with the FTIR testing results. The loss in polymer weight was clearly greater for the (CO PVC-VA) film containing 5-phenylazo salicalcaldehy derivative than for the control film.



**Figure 6: The weight loss % vs. irradiation time for PVC-VA films containing 0.0001gm additive.**



**Figure7:** The relationship between  $\ln At-A \infty$  and time (hr) for PVC-VA additive

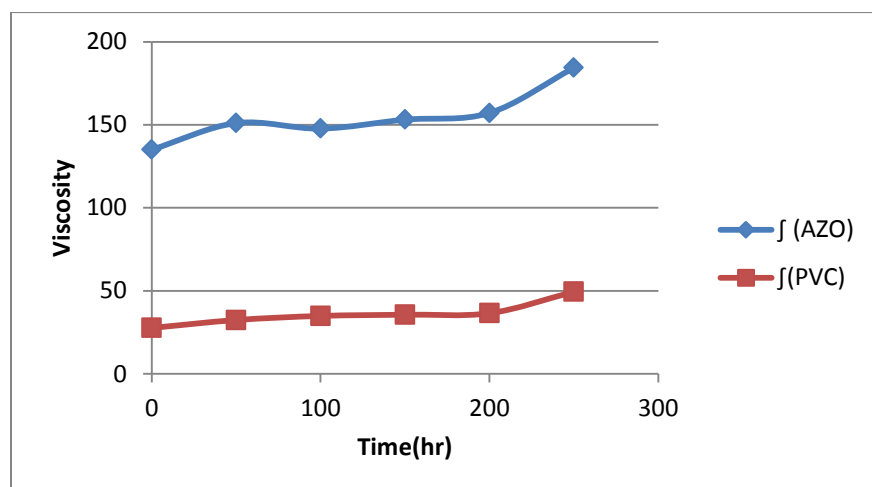


**Figure 8:** The relationship between  $\ln At-A \infty$  and time (hr) for PVC-VA-AZO additive

**Table 1:** The Photodissociation rate (kd) of the polymers

Polymers	kd(h-1 )
PVC-VA without AZO	0.0013
PVC-VA with AZO	0.0042

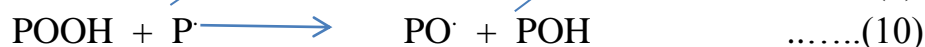
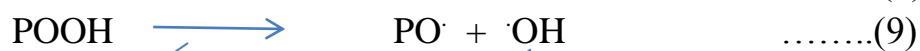
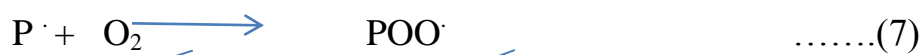
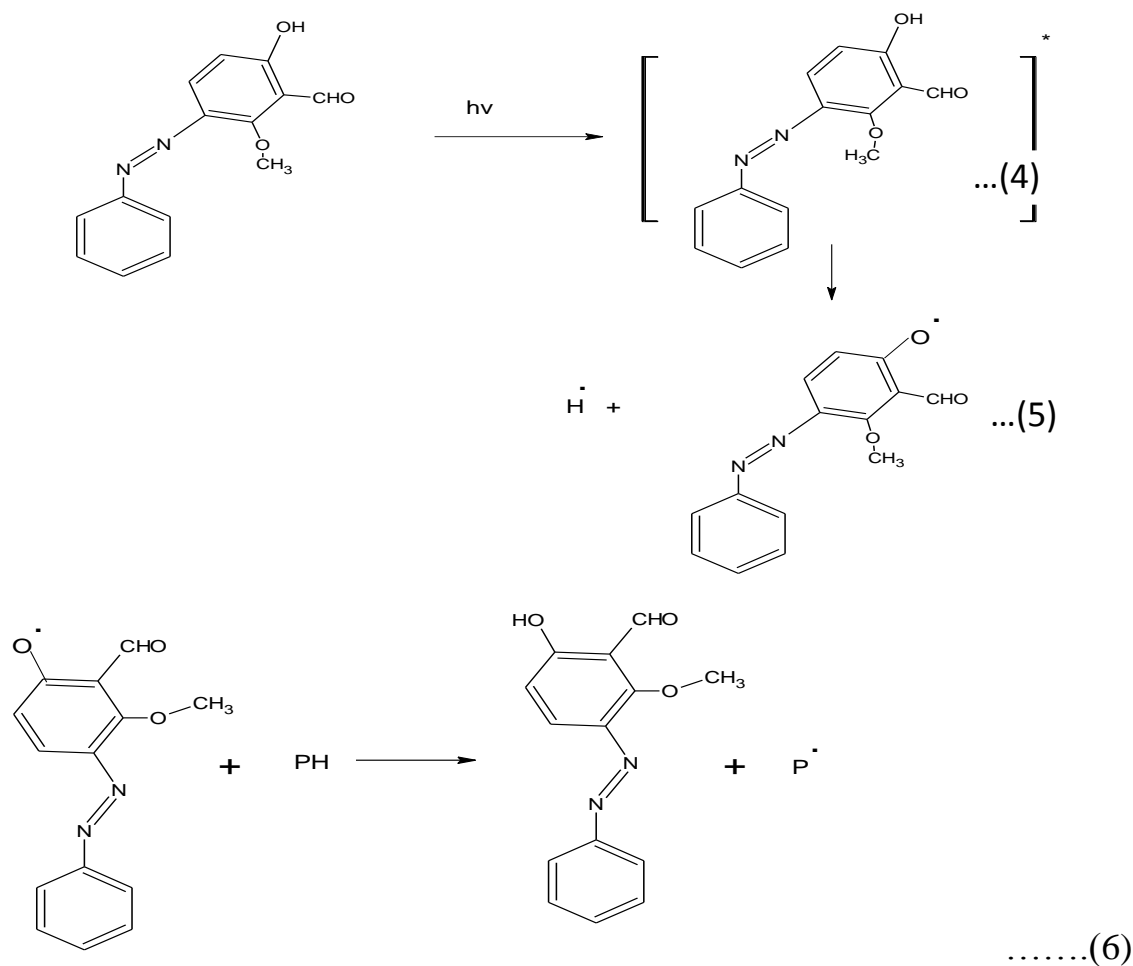
The results of irradiation of PVC-VA flakes with by weight (0.0001g) of additives. (Contracts) and thickness (80 $\mu$ m) Subject to the first order, which means that the additives (complexes) acted as optical degradation to dismantle the photo-oxidation process of the polymer makes it disintegrate against ultraviolet rays. This is consistent with the measurements Infrared for values of coefficients (IOH, ICO) and ultraviolet radiation measurements for a constant calculation. The Photodissociation rate of the added compounds (kd)[16]. It is important to note that even trace amounts of thif films containing additives are insoluble in THF. This indicates that photolysis causes cross-linking in the polymer chain or branching in the chain. As a direct consequence of this, the viscosity of (PVC-VA) containing 5-phenylazo salicaldehyde derivative increased as the amount of time that it was exposed to the irradiation as figure below.



**Figure 9: The relative viscosity vs.irradiation time for PVC-VA films containing 0.0001gm additive.**

Based on the overall results that were obtained, the effectiveness of 5-phenylazo salicaldehyde as a photodegradation regulator for PVC-VC film was evaluated according to the change in the concentrations of ICO, IOH, and IC=C [17,18], which is depicted in Figures (9). The suggested mechanism of





**Scheme 4: suggested mechanism for photodecomposition of the photosensitizers 5-phenylAzosalicylaldehyde**

### Conclusions

The photo degradation of (vinyl chloride-vinyl acetate) film employing 5-phenylazo salicylaldehyde derivative was examined in the work mentioned in this paper. Azo compound tended to promote the creation of degradation

byproducts, rise in (carbonyl, polyene, and hydroxyl indices), weight loss percent, viscosity, and surface damage polymer. This efficiency of additive in improving the pace of degradation process and generation of tiny photo degradation by-products is also measured by calculating Kd. The overall results reveal the efficacy of 5-phenylazo salicylaldehyde derivative as a photo degradation reagent for PVC-VC film based on changes in FTIR spectroscopic, UV-VIS spectra, weight loss and viscosity measurement.

### **Acknowledgment**

Author would like to thank Mustansiriyah University (www.uomustansiriyah.edu.iq) Baghdad-Iraq for its support in the present work.

### **References**

- [1] Lee W, Jeong M C, & Myoung, J M [2004]: Catalyst-free growth of ZnO nanowires by metal-organic chemical vapour deposition (MOCVD) and thermal evaporation, **Acta Mater.** 52 (13), pp. 3949–3957. <https://doi.org/10.1016/j.actamat.2004.05.010>
- [2] Xu C L, Qin D H, Li H, Guo Y, Xu T & Li H L [2004]: Low-temperature growth and optical properties of radial ZnO nanowires, **Mater. Lett.** 58 (30), pp. 3976–3979. <https://doi.org/10.1016/j.matlet.2004.08.026>
- [3] Park W I, Jun Y H, Jung S W & Yi G C [2003]: Excitonic emissions observed in ZnO single crystal nanorods, **Appl. Phys. Lett.**, 82 (6), pp. 964–967. <https://doi.org/10.1063/1.1544437>
- [4] Hussain Z, El-Hiti G A, Ahmed A, Altaee N, & Yousif E [2016]: Photocatalytic degradation of polyhydroxybutyrate films using titanium dioxide nanoparticles as a photocatalyst, **Russ J Appl Chem**, 89 (9), pp. 1536–1543. <https://doi.org/10.1134/S1070427216090238>
- [5] Abu-Bakar H, Williams L & Hallett S H [2021]: A review of household water demand management and consumption measurement, **J. Clean. Prod.**, 292, 125872. <https://doi.org/10.1016/j.jclepro.2021.125872>
- [6] Muhammad B [2019]: Energy consumption, CO<sub>2</sub> emissions and economic growth in developed, emerging and Middle East and North Africa countries. **Energy**, 179, pp. 232–245. <https://doi.org/10.1016/j.energy.2019.03.126>

- [7] Sharma S, Basu S, Shetti N P; Kamali M, Walvekar P & Aminabhavi T M [2020]: Waste-to-energy nexus: A sustainable development, **Environ. Pollut.**, 267, 115501. <https://doi.org/10.1016/j.envpol.2020.115501>
- [8] Akan O D, Udofia G E, Okeke E S, Mgbechidinma C L & Okoye C O [2021]: Zoclanclounon, Y.A.B.; Atakpa, E.O.; Adebajo, O.O. Plastic waste: Status, degradation and microbial management options for Africa. **J. Environ. Manag.**, 292, 112758. <https://doi.org/10.1016/j.jenvman.2021.112758>
- [9] Watheq B, Yousif E, Al-Mashhadani M H, Mohammed A, Ahmed D S, Kadhom M & Jawad, A H [2020]: A Surface Morphological Study, Poly (Vinyl Chloride) Photo-Stabilizers Utilizing Ibuprofen Tin Complexes against Ultraviolet Radiation. **Surfaces**, 3 (4), pp. 579–593. <https://doi.org/10.3390/surfaces3040039>
- [10] Mohammed S A, Najim L H, Al-Mashhadani M H, Ismael M, Hamad B A, Noaman R, Ibraheem H, Ahmed DS & Yousif E [2020]: Morphological and Photodecomposition Rate Constant Study of PVC Films Doped with Sulfadiazine Tin (IV) Complexes. **Science Letters**, 149(2), pp. 85-93. <https://doi.org/10.24191/sl.v14i2.9545>
- [11] Tanu S, Sanjeev A, Shyam K, Mittal V, Kalsi P & Manchanda V [2007]: Effect of gamma irradiation on the optical properties of CR-39 polymer. **J. Mater. Sci.**, 42, 1127-1130, <https://doi.org/10.1007/s10853-006-0516-7>.
- [12] Kamazani F S & Soltani S S [2016]: highly efficient synthesis of new 2h-chromene dyes using cu-sba-15, **Orient. J. Chem.**, 32 (5), pp. 2543-2548. <http://dx.doi.org/10.13005/ojc/320525>
- [13] Xia L, Cai H & Lee Y R [2015]: Microwave-assisted catalyst-free synthesis of diversely functionalized 2-amino-2H-chromene-3-carboxylates, **Tetrahedron**, 71(38), pp. 6894-6900. <https://doi.org/10.1016/j.tet.2015.07.013>
- [14] Kadhium S S , Hussen E M , Mageed Z N, Abed A H & Mohammed H H [2020]: Study the Photo-degradation of poly styrene –co-butadiene in presence of Ni complex and TiO<sub>2</sub>, The First International Conference of Pure and Engineering Sciences (ICPES2020) , IOP Conf.

Series: **Materials Science and Engineering**, 871, 012026, pp. 1-12.  
<https://doi.org/10.1088/1757-899X/871/1/012026>

- [15] Mageed Z N , Mohammed H H, Zayer T M Noori A M, Farhan S A & Dadoosh R M [2019]: Study the photodegradation and biodegradation of p-cresol novolac (poly epoxy) in presence and absence of dibenzoylperoxide, IOP Conf. Series: **Materials Science and Engineering** 571, 012088, pp. 1-10. <https://doi.org/10.1088/1757-899X/571/1/012088>
- [16] Hussain Z, Yousif E, Altaie A & Zageer D [2014]: Study the Rate Constant of Photostabilization of PVC in Presence of Schiff 's Bases of Sulphamethoxazole, **ANJS**, 17 (4), pp. 39-43. <https://doi.org/10.22401/JNUS.17.4.06>
- [17] Mageed Z N, Kadhium S S, Rodhan W F & Mohammed H H [2022]: Study of the photostabilization of polystyrene in the presence and absence of benzoxazin derivatives, **Egypt. J. Chem.**, 65(4), pp. 675-683. <https://doi.org/10.21608/EJCHEM.2021.80165.3962>
- [18] Abbas A A , Mageed Z N, Nief O A & Mohammed H H [2023]: Synthesis and Characterization of Schiff Bases Derived from 3-(4-methoxyphenyl) Acrylic Acid and 3-(Benzo[d][1,3]dioxol-5-yl) Acrylic Acid, **J. Med. Chem. Sci.**, 6 (2), pp. 205-219. <https://doi.org/10.26655/JMCHEMSCI.2023.2.4>