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Study on The Effect of Ultraviolet (UV) Radiation on Polyvinyl Chloride Polymer

Jasim Mohammed Dahir^{*1}

1. Ministry of Education – Salah Al-Din Directorate of Education

* Correspondence: jasimaljanaby@gmail.com

Abstract: This study investigates the effect of ultraviolet (UV) radiation on a number of polymers by incorporating specific chemical compounds. The main findings are summarized as follows: A series of oxazepine compounds were synthesized from the hydrazone compound (KH1), which was prepared using the Schiff base method. These included oxazepine derivatives designated as KH2, KH3, KH4, and KH5. Polyvinyl chloride (PVC) was exposed to UV radiation, and UV-VIS spectra were recorded. Subsequently, the oxazepine compounds were added to the PVC polymer, and measurements were repeated at different exposure intervals (100, 200, , 300 hours). The results showed that UV radiation induced degradation in the polymer. However, the addition of these compounds (KH6, KH7, KH8, KH9) improved the photostability of the polymers when incorporated at a concentration of 0.5% by weight. All experiments were conducted at room temperature. Another method involved exposing several polymers to natural sunlight. Slight changes were observed in some polymers through absorbance measurements at varying wavelengths. However, the effect was more significant in polymer films. These findings suggest that adding certain compounds to polymers can enhance their resistance to UV radiation.

Keywords: Polymers, Polyvinyl Chloride, Ultraviolet Radiation

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1. Introduction

Polyvinyl Chloride (PVC)

Plastic possesses unique chemical and physical properties, along with low production costs, leading to its mass production and widespread application in various industries [1]. However, the chemical industry has recently faced significant pressure to address issues arising from the use of plastics, such as the volume and nature of plastic waste and its harmful impact on the environment. Moreover, a key challenge lies in improving the properties of plastic materials for long-term use [2].

Polyvinyl chloride (commonly abbreviated as PVC) is one of the most versatile types of plastic [3]. It is the second most widely produced synthetic resin globally [4]. Among the five general-purpose plastics, polyvinyl chloride ranks second only to polyethylene. PVC is extensively used across a wide range of industries, including architecture, electronics, chemical engineering, packaging, and transportation [5][6][7], see Figure 1.

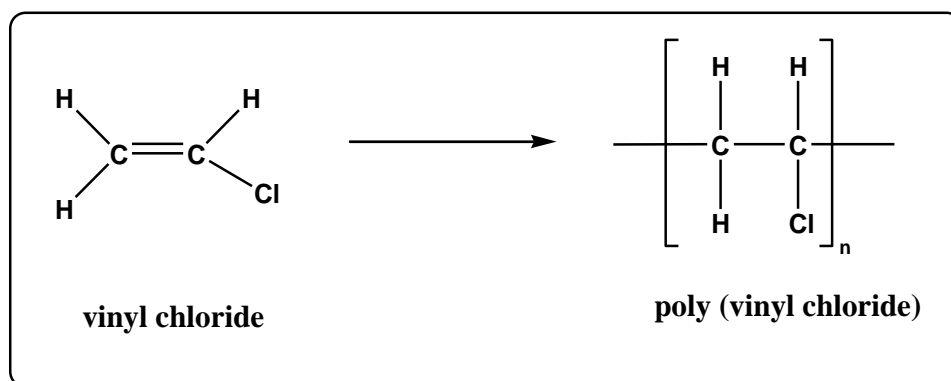


Figure 1. Monomer of Polyvinyl Chloride and PVC Polymer.

Origin and Development of Polyvinyl Chloride

Since 1872, vinyl chloride monomer (VCM) polymerization has been understood. Baumann was the first to inadvertently create polyvinyl chloride (PVC), revealing that when VCM was exposed to sunlight, a solid white material that could withstand temperatures of up to 130°C without breaking down was produced [8].

The polymerization of VCM involves a free-radical addition process that consists of three main steps: initiation, propagation, and chain transfer (which marks the termination of the monomer chain reaction) [9].

Properties of Polyvinyl Chloride

Pure PVC has a fine granular texture and is a bright white powder. It is chemically inert, non-toxic, and stiff. Many industrial and environmental organizations generally agree that polyvinyl chloride is not a serious hazard to the environment or human health because it is non-toxic. PVC has a variety of useful qualities, and certain chemical additives can be added during production to give the finished product the following qualities:

1. Increased flexibility of the product.
2. Enhanced heat and flame resistance.
3. Improved stability and extended service life.
4. Resistance to impact, with the ability to achieve desired color or texture.

By integrating into the polymer matrix, these additives change the plastic's physical characteristics even if they don't chemically change the PVC molecular structure. PVC-based products can be processed and applied in a vast array of ways thanks to the large variety of additives that can be mixed in different ratios. However, there are environmental and public health concerns regarding these chemicals' prevalence in PVC goods [10].

The Changes That Occur in Polyvinyl Chloride

PVC is appropriate for a variety of applications because of its low cost and superior performance. But when PVC is molded and used in environments with heat and light, it quickly dehydrochlorinates. Conjugated polyene sequences are thus created from the very beginning of the reaction [11][12][13].

Degradation of Polyvinyl Chloride (PVC)

Degradation of polymers is caused by a number of causes, including heat, humidity, and sunlight. Plastics deteriorate over time when exposed to sunshine, losing their mechanical and physical qualities. Outdoor applications of polyvinyl chloride (PVC) are limited due to its high sensitivity to external conditions [14][15].

2. Materials and Methods

This study has used aggregic method in the synthesis of oxazepine derivatives and also to assess their ability to promote the photostability of polyvinyl chloride (PVC) films under the influence of ultraviolet (UV) radiation. After the development, there were three

phases to the study. In the first step, KH1, a hydrazone precursor, was prepared by condensing 2-pyrimidin-2-yl acetohydrazide with 4-hydroxybenzaldehyde in ethanol with 5-6 hours of refluxing in an atmosphere of glacial acetic acid as a catalyst. Recrystallization and drying of the crude product was done at 50 o C. The second-phase reactions involved reactions of KH1 with maleic anhydride, phthalic anhydride and the respective di-ester derivatives under reflux conditions in benzene that was completely dry to give a series of 1,3-oxazepine-4, 7-dione derivatives KH2, KH3, KH4, and KH5. The oxazepines that were produced were recrystallized and analyzed in terms of its melting point as well as the calculated yield. Preparation of the PVC films was done in the third step. A solution of PVC in tetrahydrofuran (THF) with the percentage of 5 was made, and the compounds synthesized were added to this solution with the percentage of 0.5. The mixtures of polymer with additives were cast in glass molds and left to evaporate at room temperature, so thin film of polymer could be obtained. These movies were aged via accelerated UV levels in a Q.U.V. Weathering Tester that had UVB313 nm fluorescent lamps. The exposure cycle was divided into a sequence of 3 time intervals 100, 200 and 300 hours after which UV-Vis spectra lined up 200-400 nm would be determined to observe photodegradation. The values of absorption and shifts of the peaks were read to determine the stability of the films of the polymers as well as the protective capacity of the additives of oxazepine. Considerations of the ambient temperature were made in all the experimental procedures so as to ensure consistency of the experiment.

3. Results and Discussion

Photostabilization of Polyvinyl Chloride

One of the main problems with thermoplastic manufacturing is the deterioration of PVC under ultraviolet (UV) light, which is a natural feature of the polymer. Dehydrochlorination, auto-oxidation, mechanical-chemical cleavage, crosslinking reactions, and condensation are all examples of this degradation. Stabilizing additives are necessary to control this degradation because they must prevent the dehydrochlorination reaction, which is the main process that causes degradation [16].

Ultraviolet (UV) Radiation

An electromagnetic wave with a wavelength longer than X-rays but shorter than visible light is known as ultraviolet radiation. This type of light is known as "ultraviolet" because it has the shortest wavelength in the visible spectrum. UV radiation is a component of the solar electromagnetic spectrum, which is the range of electromagnetic waves with different wavelengths and energies that the sun emits and that reach Earth. These include radio frequencies, thermal infrared, and high-energy gamma rays. In particular, wavelengths shorter than 400 nanometers are referred to as ultraviolet radiation [17], see Figure 2.

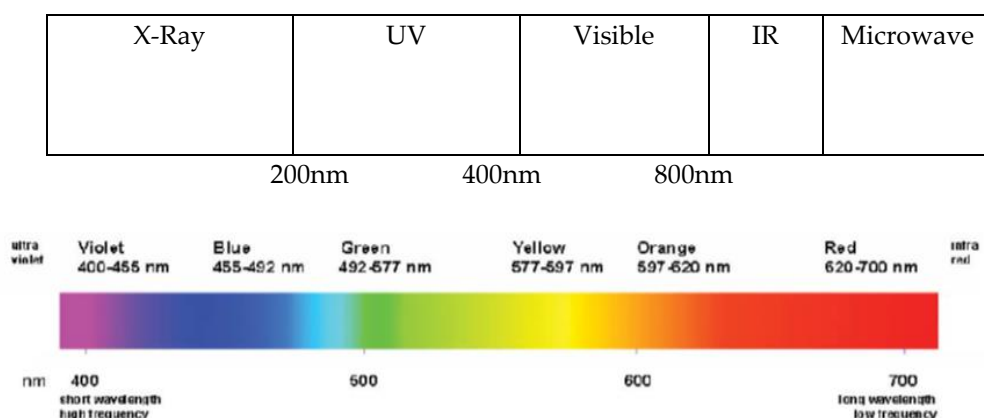


Figure 2. Regions of the Spectrum Including Ultraviolet and Visible Light

Mechanism of UV Absorption

Degradation of plastics and organic coatings used outdoors is frequently caused by exposure to ultraviolet (UV) radiation with wavelengths ranging from 295 to 400 nanometers. In these applications, ultraviolet absorbers (UVAs) are frequently used to stop UV rays from entering the polymer's bulk or piercing the coating to reach UV-sensitive areas. Early research on UVAs showed that their performance was subpar and that exposure might cause them to be depleted [18].

UV Damage to Polymers

Polymers exposed to UV light undergo a multitude of simultaneous chemical reactions that cause distinct kinds of damage, each of which advances at a different pace. The product's usable service life is usually determined by the first visible indication of damage. For instance, window frames made of polyvinyl chloride (PVC) that are exposed to sunshine experience a variety of chemical changes, including staining, a reduction in tensile strength, and a loss of impact strength. The service life of window frames is typically determined by uneven yellowing [19]. Customers may use this criterion alone to demand replacement. Despite obvious damage, these products are frequently still in use in many underdeveloped nations. Continued use may cause more damage, such as discoloration, a reduction in impact resistance, and finally cracking, which would make the product unusable.

How to Avoid UV Degradation

There are several ways to stop UV deterioration in plastics by employing inhibitors, stabilizers, or absorbers. By inhibiting UV rays, the straightforward addition of 2% carbon black offers protection for a variety of outdoor applications. Titanium dioxide and other pigments may also work well. Typical absorbers that selectively absorb UV light and re-emit it at less hazardous wavelengths, particularly heat, include organic molecules like benzo-phenones and benzotriazoles. Because they work so well, benzotriazoles can be utilized at concentrations as low as 0.5%. The inclusion of stabilizers, the most popular of which are hindered amine light stabilizers (HALS), is another important protective mechanism. These substances prevent radical chemical reactions and absorb excited species. To create grades especially made for UV protection, several additives are added to or accumulated inside the base polymer [20].

Organic Compounds Used in the Study: Oxazepines

Oxazepines are heterocyclic compounds with seven members that have two atoms in the ring besides carbon: nitrogen and oxygen. The compound oxepine, which has seven members and one oxygen atom, is the source of the name "oxazepine." Oxazepines are classified into three isomers, 2,1-, 3,1-, and 4,1-oxazepine, according to the locations of the nitrogen and oxygen atoms in the seven-membered ring [21], see Figure 3.

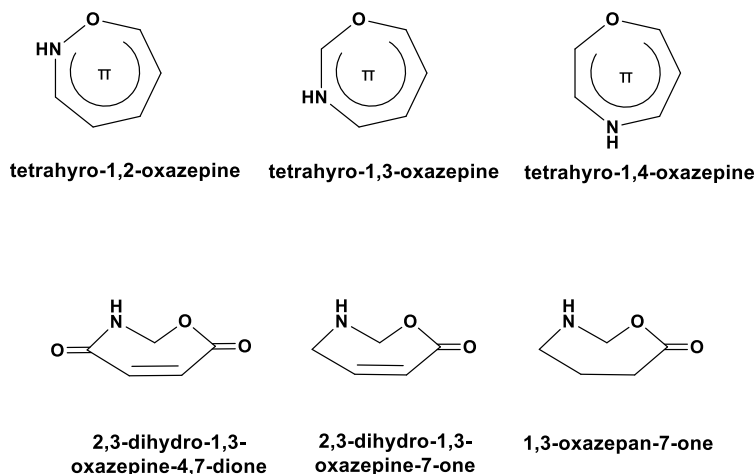


Figure 3. Structural Isomers and Derivatives of 1,3-Oxazepine Compounds.

Instruments Used

1. Automatic Melting Point Apparatus, model SMP40, for measuring melting points.
2. UV-Visible Spectrophotometer, model GARY-100 Conc., for measuring UV-Visible spectra.
3. Device for irradiating materials with ultraviolet light (UV): Spectrophotometer used for irradiation and measurement of materials.

Methods of Preparation

1. Preparation of the Hydrazone Compound [KH1]:

After dissolving 2 grams of 2-pyrimidin-2-yl acetohydrazide in 15 milliliters of 100% ethanol, 2.71 milligrams of 4-hydroxybenzaldehyde were added. Glacial acetic acid was added in four drops, and the mixture was refluxed for six hours. The resultant mixture was filtered, allowed to cool gradually, and the precipitate was gathered. After being recrystallized from 100% ethanol, the precipitate was dried at 50°C. With a melting point of 189–191°C, the yield was 88%. The prepared hydrazone [KH1] is consistent with the suggested chemical formula for the brown molecule [22].

The preparation of hydrazone is illustrated by the following reaction, see Figure 4.

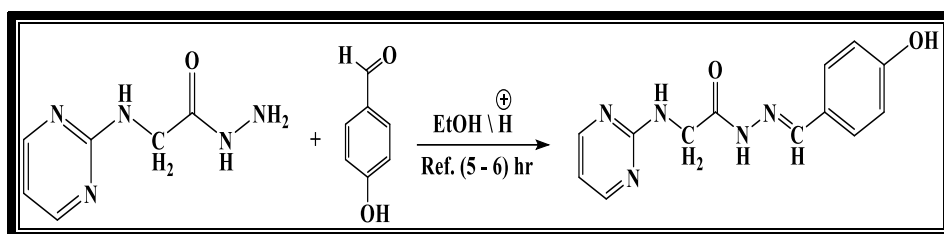


Figure 4. Synthesis Reaction of Hydrazone Compound (KH1).

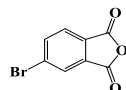
2. Preparation of 1,3-Oxazepine-4,7-dione-2-pyrimidinylacetamide Compounds [KH2-KH5]

Maleic anhydride, 3,4-dimethylmaleic anhydride, phthalic anhydride, and 5-bromophthalic anhydride (0.0069 mol) were dissolved in 5 ml of the same solvent after 1.87 g of the produced hydrazone [KH1] was dissolved in 10 ml of dry benzene. After 8 to 9 hours of refluxing, the mixture was cooled, filtered, cleaned with cold water, recrystallized from 100% ethanol, and dried at 23 to 50 degrees Celsius, see Table 1.

Table 1. Some Physical Properties and Percentage Yield of 3,1-Oxazepine-4,7-dione Derivatives [KH2-KH5].

Comp. No.	Ar	Molecular Formula/ M.Wt g/mol	M.P. (°C)	Yield (%)
KH2		C ₁₇ H ₁₅ N ₅ O ₅ 369,34	210-212	78
KH3		C ₁₉ H ₁₉ N ₅ O ₅ 397,39	198-200	70
KH4		C ₂₁ H ₁₇ N ₅ O ₅ 419,40	232-236	82

KH5



$C_{21}H_{16}N_5O_5Br$ 251-253 93
498,29

3. Preparation of Poly(vinyl chloride) (PVC) Films

Organic chemicals were added to PVC to create poly(vinyl chloride) films. Tetrahydrofuran (THF) was mixed with a fixed concentration of 5% PVC to create a solution for making 40 micrometer-thick polymer films. The solvent was then allowed to evaporate at room temperature for 24 hours in order to eliminate any remaining THF solvent. Beginning at zero concentration, the synthesized compounds were applied to the films at a concentration of 0.5%. To ensure minimal turbidity and acceptable optical quality during casting, the solvent's evaporation rate and humidity level have to be regulated. The resultant solution was poured into a glass frame and allowed to sit overnight once it had completely dissolved.

The glass frame was glued onto a regular glass plate to form a small trough with a volume of 4 ml.

Accelerated Testing Technique

The Q-Panel company's Q.U.V. Accelerated Weathering Tester was used to irradiate the samples. The apparatus is made out of a chamber made of stainless steel that has apertures on the front and back. Four 40-watt fluorescent ultraviolet lamps of the 313 nm UVB type, which emit light in the 290–360 nm range with the highest intensity at 313 nm, are located on each side. In addition to the lights, the gadget has an irradiation time meter and a humidity controller. To guarantee perpendicular UV exposure, the samples to be irradiated were positioned parallel to the lamps and vertically. The apparatus was turned on to begin irradiation, and the temperature was kept at 25°C. To guarantee consistent light intensity on every sample within the irradiation chamber, the samples' positions were alternated on a regular basis [23][24].

UV-Vis Spectra for Organic Compounds Added to PVC Polymer Before Irradiation [KH6-KH9]

Ethanol (95%) was used as a solvent to study the UV-visible spectra (UV-Vis) of the produced compounds at concentrations ranging from 10⁻⁴ to 10⁻⁵ M. The spectrum revealed extended wavelength bands at 331–334 nm, which were ascribed to $n \rightarrow \pi^*$ electronic transitions, and short wavelength maxima (λ_{max}) between 221 and 277 nm, which were ascribed to $\pi \rightarrow \pi^*$ transitions. The spectral bands matched those found in previous research [25], see Figure 5, 6, 7, 8.

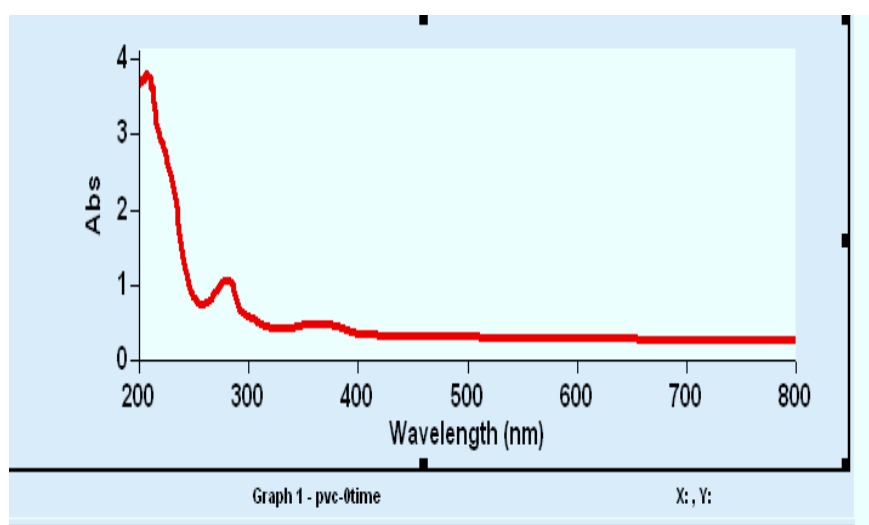


Figure 5. UV-Visible Spectrum of the Compound KH6 + PVC before Irradiation.

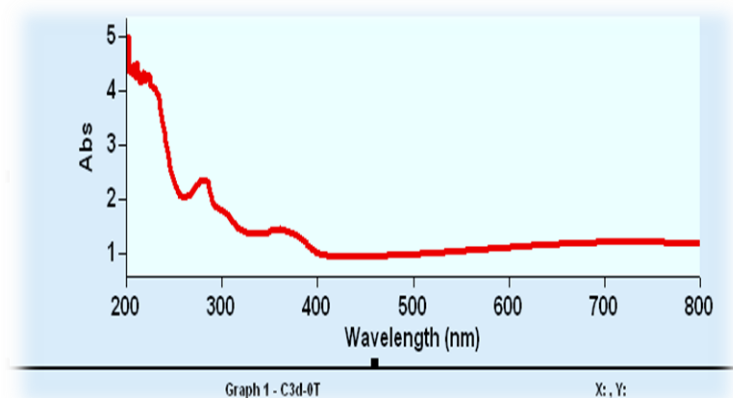


Figure 6. UV-Visible Spectrum of the Compound KH7 + PVC before Irradiation.

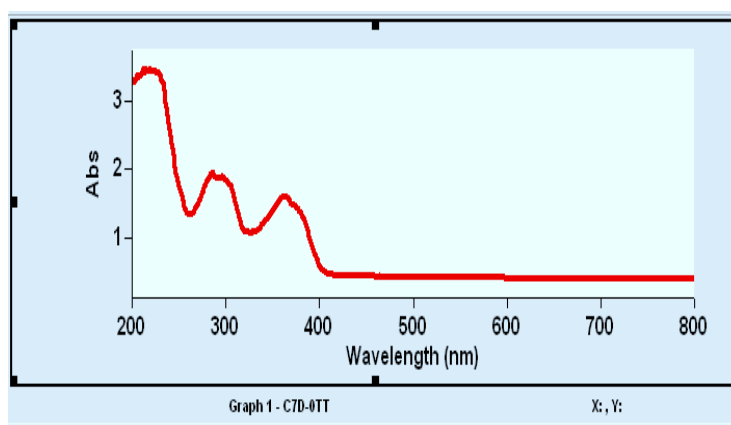


Figure 7. UV Spectrum Before Irradiation of the Compound KH8 + PVC.

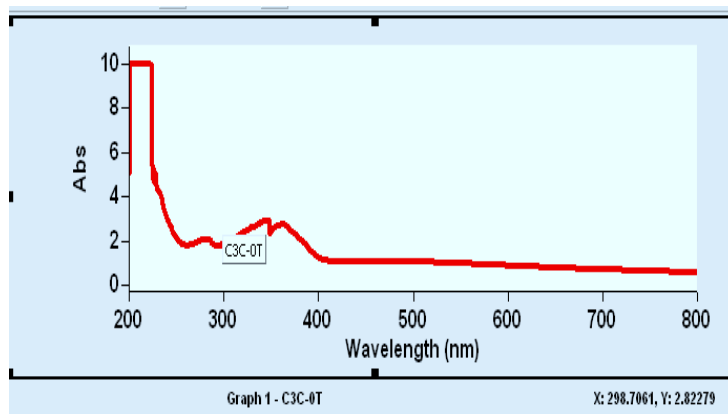


Figure 8. UV Spectrum Before Irradiation of the Compound KH9 + PVC.

Exposure of PVC Polymer Films [KH9-KH6] to (Vis-UV) Radiation for Time Periods of (100-200-300) Hours

The UV-Visible (Vis-UV) spectra of the prepared polymer films [KH9-KH6] were studied using ethanol as a solvent at concentrations ranging from $(10^{-5}$ to 10^{-4}) Molar. Short wavelengths ($\max \lambda$) appeared in the range of (200–267) nm, attributed to $(\pi^* \leftarrow \pi)$ transitions, along with long wavelengths ($\max \lambda$) in the range of (333–389) nm corresponding to electronic transitions of the type $(\pi^* \leftarrow n)$. Peaks also appeared at various other positions.

Table 2 shows the absorption values in the UV spectrum for the PVC films [KH9-KH6], and these results were consistent with those reported in the literature [26].

The figures 9-15 below illustrate the UV spectra for the compounds [KH7-KH2].

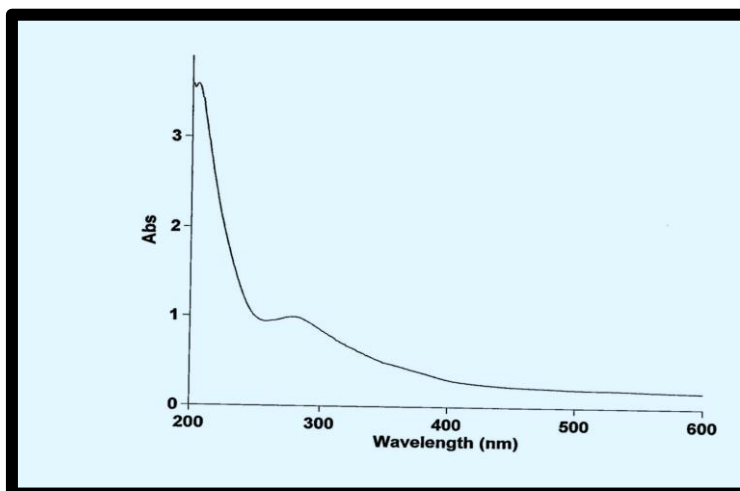


Figure 9. UV Spectrum of the Compound [KH6] = [KH2 + PVC] after 100 hours.

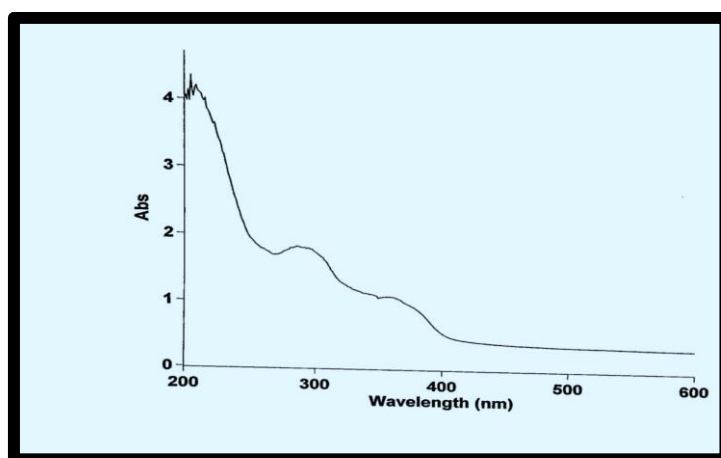


Figure 10. UV Spectrum of the Compound [KH7] = [KH3 + PVC] after 100 hours.

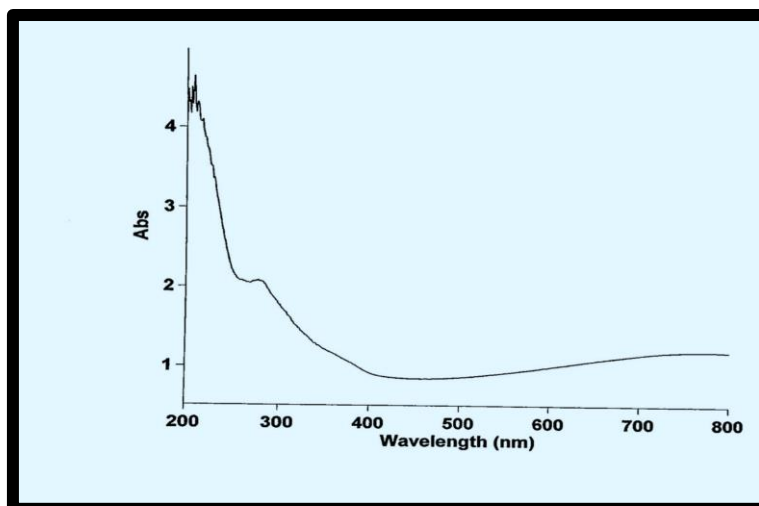


Figure 11. UV Spectrum of the Compound [KH8] = [KH4 + PVC] after 100 hours.

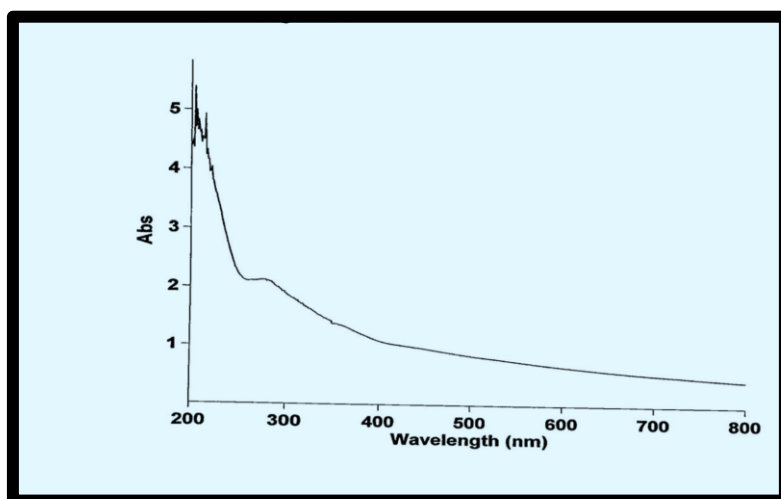


Figure 12. UV Spectrum of the Compound [KH9] = [KH5 + PVC] after 100 hours.

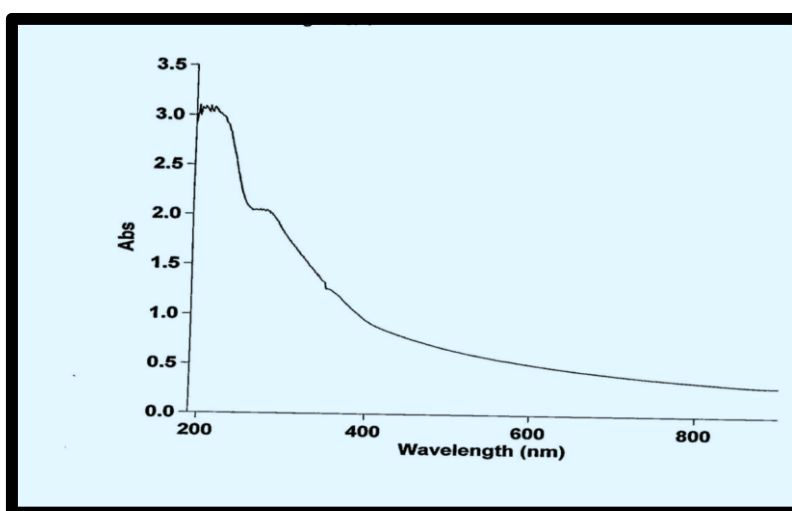


Figure 13. UV Spectrum of the Compound [KH6] = [KH2 + PVC] after 200 hours.

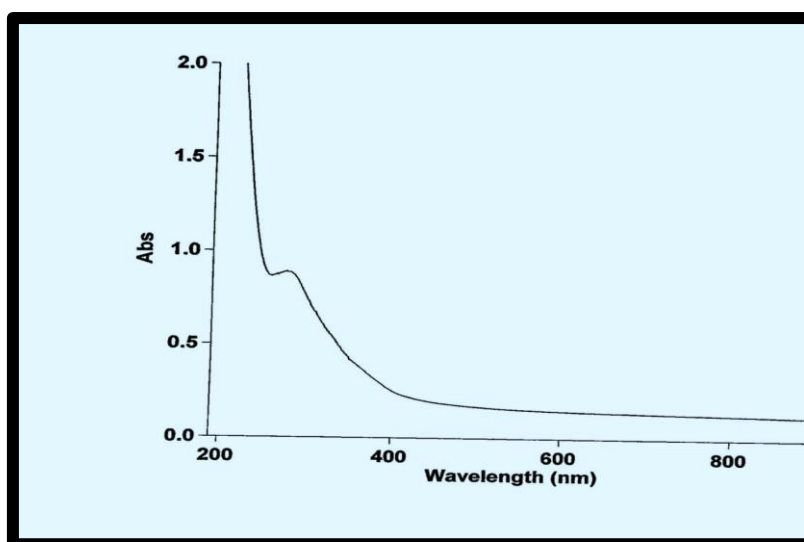


Figure 14. UV Spectrum of the Compound [KH7] = [KH3 + PVC] after 200 hours.

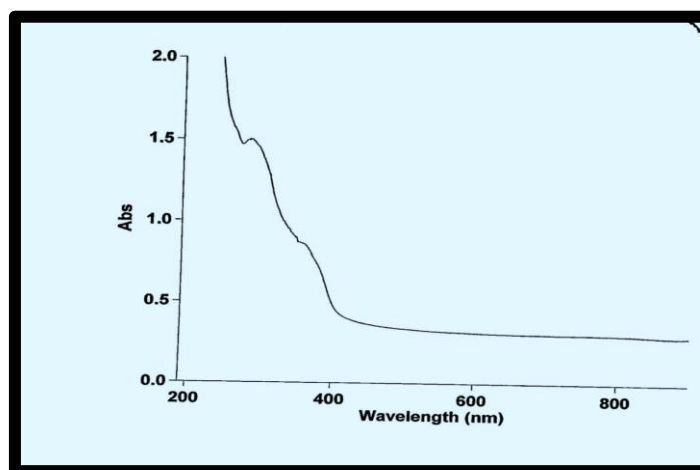


Figure 15. UV Spectrum of the Compound [KH8] = [KH4 + PVC] after 200 hours.

Table 2. Comparison between Absorbance and Wavelength Before and After Irradiation in the UV Spectrum:

"UV spectrum at 100 and 200 hours"				"UV spectrum before irradiation"		
Comp NO.	Max λ 100hrs	Abs	max 200hrs	Abs	Maxλ	Abs
KH6+PVC	280,00	1,002	340,00	1,407	361,00	0,484
	205,00	3,590	276,00	2,054	282,00	1,048
	201,00	3,587	194,00	3,102	201,00	3,740
KH7+PVC	358,00	1,110	274,00	0,895	223,00	4,300
	223,00	3,655	210,00	3,464	211,00	4,533
	201,00	4,057	197,00	3,429	202,00	5,013
KH8+PVC	278,00	2,087	281,00	1,507	286,00	2,891
	230,00	3,378	198,00	3,776	224,00	2,652
	201,00	4,473	195,00	3,715	201,00	10,000
KH9+PVC	278,00	2,140	190,00	3,755	341,00	2,891
	208,00	4,834	202,00	4,211	331,00	2,652
	202,00	4,496	313,00	1,545	223,00	10,000

Comparison of UV Spectra of the Four Compounds Before Irradiation (KH6, KH7, KH8, KH9)

For example, in Figure 5, a clear band appears at the wavelength of 282 nm, showing an absorbance of 1.048. From the table, it is observed that the highest wavelength is 361 nm with an absorbance of 0.48, corresponding to an ($\pi \leftarrow n$) electronic transition, and the lowest wavelength is 201 nm with an absorbance of 3.740, corresponding to an ($\pi \leftarrow \pi$) transition.

In Figure 6, the spectrum shows a clear band at a wavelength of 223 nm with an absorbance of 4.300, representing the highest wavelength and corresponding to the ($\pi \leftarrow n$) transition. The lowest wavelength is 202 nm with an absorbance of 5.013, which corresponds to the ($\pi \leftarrow \pi$) transition.

When comparing the previous two spectra with Figure 7, two distinct peaks appear at wavelengths 286 nm and 260 nm. At 286 nm, an absorbance of 1.960 is observed, representing the highest wavelength corresponding to the ($\pi \leftarrow n$) transition, while the lowest wavelength is 201 nm, corresponding to the ($\pi \leftarrow \pi$) transition.

In Figure 8, there is no distinct peak. The highest wavelength for compound KH9 is 341 nm with an absorbance of 2.891, corresponding to the ($\pi \leftarrow n$) transition, and the lowest wavelength is 223 nm with an absorbance of 10, corresponding to the ($\pi \leftarrow \pi$) transition.

From Figures 9-11 at 100 hours, the highest wavelength is 280 nm with an absorbance of 1.002, and the lowest wavelength is 201 nm with an absorbance of 3.587 for compound KH6. The last compound, KH9, showed the highest wavelength at 278 nm with an absorbance of 2.140 and the lowest wavelength at 202 nm with an absorbance of 4.496. A slight shift in peak positions was also observed.

At 200 hours, compound KH6 gave the highest wavelength at 340 nm with an absorbance of 1.407 and the lowest wavelength at 194 nm with an absorbance of 3.102. Comparing this with the last compound, which had the longest wavelength at 281 nm and the shortest at 194 nm at the same time point, also shows some slight differences in the peaks.

Comparing the wavelengths and absorbance values of the compounds before and after irradiation shows clear differences in the values and variations in the resulting peaks. This indicates the decomposition or fragmentation of the polymer as well as the presence of surface cracks due to the high energy of the radiation. The results show that the wavelength correlates with the irradiation exposure time.

Monitoring these changes precisely provides insight into the photodegradation mechanism. Also, observing the external appearance and color change of the irradiated samples along with surface cracks due to the release of gases produced by photooxidation is important. The absorption spectra increase with longer irradiation times, with a relatively high increase initially that gradually decreases.

The changes in the UV spectrum after irradiation indicate the formation of carbonyl and hydroxyl groups. The poor stability of polyvinyl chloride (PVC) is due to structural defects that exist to varying degrees in different commercial polymer samples, such as oxidized structures like carbonyl and hydroxyl groups [27].

4. Conclusion

Since photodegradation reactions are essentially oxidation reactions, fragmentation can be monitored spectroscopically (UV spectroscopy) by tracking the formation of new groups such as carbonyl (C=O) and hydroxyl (OH), which provides insight into the photodegradation mechanism. Monitoring changes in the external appearance and color of the irradiated sample along with surface cracks and bubbles resulting from the release of gases during photodegradation. The changes occurring in the polymer due to UV exposure include surface cracks caused by the high energy of UV radiation, indicating that

wavelength correlates with the film's exposure duration. The study showed that irradiation of polymer films produced satisfactory results.

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