

SYNTHESIS AND EVALUTION OF NEW BIS-BENZOTRIAZOLE PHOTOSTABILIZER

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Abstract

Polymers such as plastics, as well as naturally occurring polymer materials such as wood, are extensively used in building construction and in greenhouse applications where they are routinely exposed to sunlight. The UV-B content in sunlight is well known to affect adversely the mechanical properties of these materials, limiting their useful life. Presently their outdoor lifetimes depend on the use of photostabilizers in the case of plastics and on protective surface coatings in the case of wood. In the present work the 2-hydroxyphenyl benzotriazoles are typical UV absorbing compounds that can diminish the photodegradation of polymers. Here the synthesis of two benzotriazole compounds is described. Each compounds obtained are characterized by IR spectra, CHN and the melting points. The PVC films incorporated with these stabilizers where subjected to UV irradiation and then tested for any change in the carbonyl index and hydroxyl index in different temperatures to evaluate the efficiency of the new stabilizers. The PVC films incorporated with these stabilizers where subjected to UV irradiation and then tested for any change in the carbonyl index to evaluate the efficiency of the new stabilizers.

Introduction

The photodegradation of polymers can be diminished by some types of photostabilizers [١]. The five typical UV absorbing compounds that have the greatest importance in UV stabilization are salicylate esters, α -hydroxybenzophenones, α -cyano β -phenyl cinnamate esters, ϵ -aminobenzoate esters and α -hydroxyphenyl benzotriazoles [١,٢]. The choice of satisfactory photostabilizers for light exposure depends on the ultimate use for which the polymer is destined . The stabilizer concentration depends on the polymer which is to be stabilized and often, a combination of different additives is necessary to obtain a synergistic effect [٣,٤] . α -(α -Hydroxyphenyl)- α H-benzotriazoles have been indicated as powerful ultraviolet- absorbing molecules and a number of compounds with this basic structure have been synthesized and used as UV absorbers [١,٥-٧] .

Low density Polyethylene (LDPE) is a famous commercial polymer used in a many industrial applications. Electrically, it's known as insulating material. It's compatible properties, such as, good insulation together with its excellent mechanical properties (high tensile strength) make it as a candidate they're utilized in different applications as an active material replacing other materials [٨]. Polyethylene is a widely used thermoplastic found in everyday life[٩].

EXPERIMENTAL

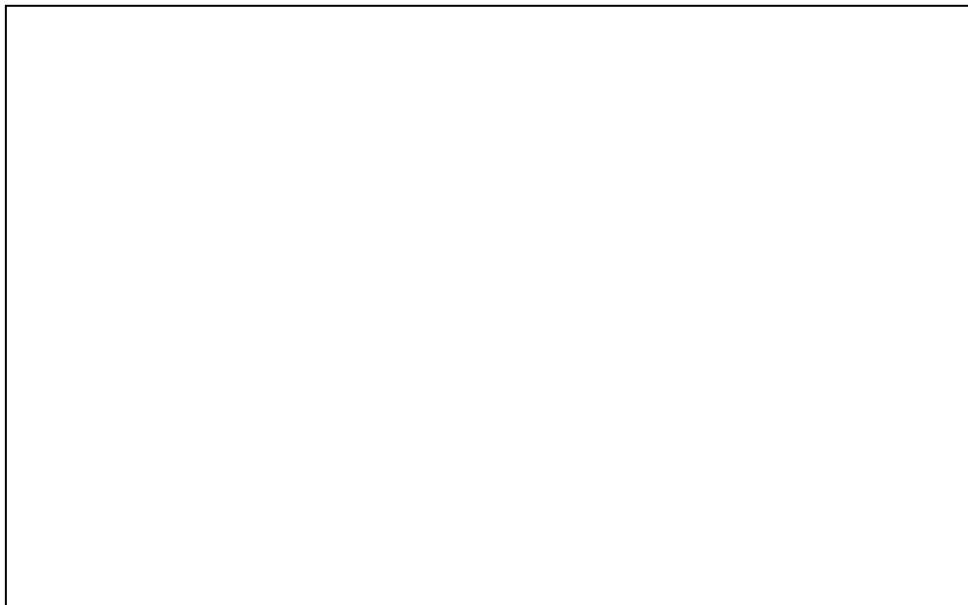
Synthesis

Synthesis of Compounds

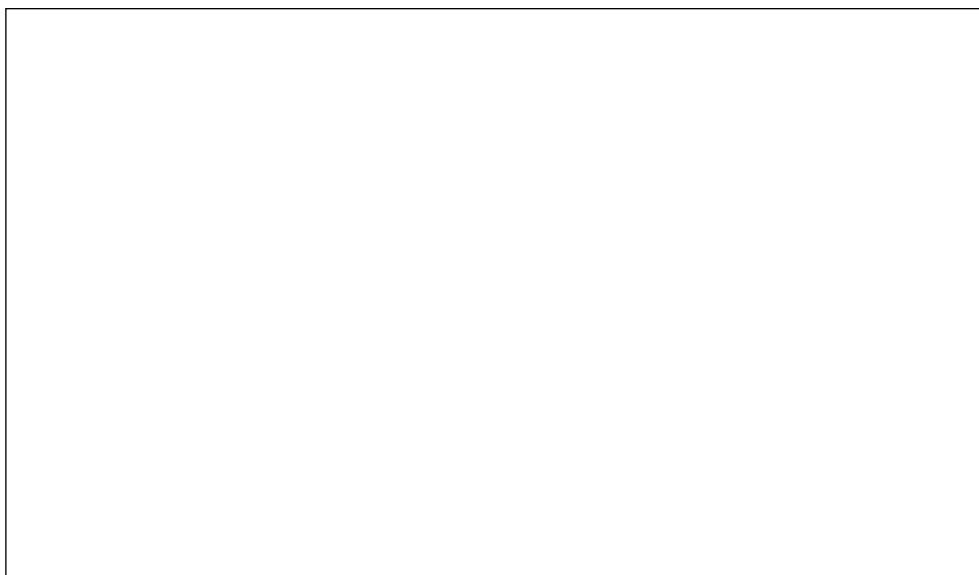
The structure of the ultraviolet absorbers are shown below **Schem. ١** to **Schem. ٤**. The synthesis of the 2H-benzotriazole derivatives discussed in this paper have been published elsewhere^[١] Using the appropriate phenols and zinc powder reductive cyclization of o-nitrophenylazophenols in alkaline solution.

The product (١) was precipitated as cream-colored solid, filtered, washed with water and dried (٦٦% yield). Recrystallization from CH_٣Cl_٣ gave yellowish powder, m.p. ١٨٧–١٨٩ °C.

The product (٢) was filtered, washed with water and dried (٧٥% yield). Recrystallization from ethanol gave yellowish needles, m.p. ٢٨٨–٢٩٠ °C.



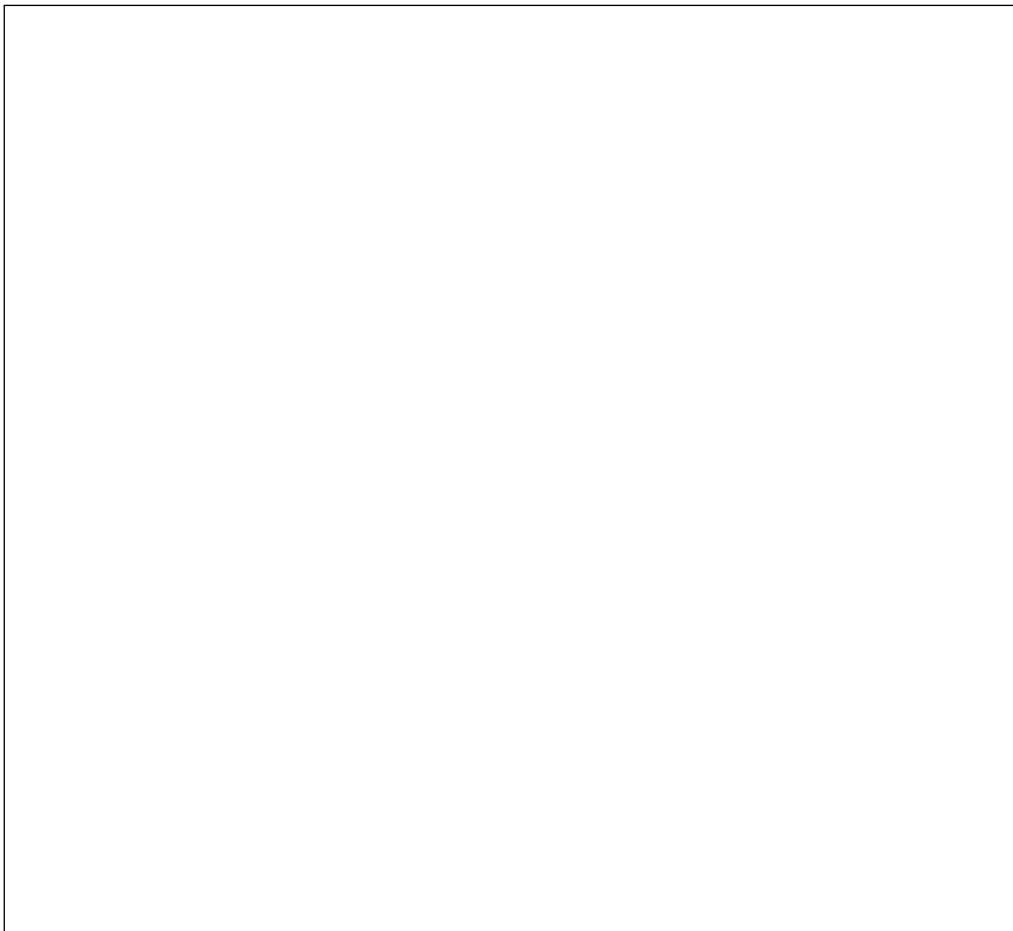
Scheme ١ .Benzotriazolic derivative synthesis : model compound (١) .



Scheme ٢ .Benzotriazolic derivative synthesis : model compound (٢) .

The product (٣) was precipitated as solid, filtered, washed with water and dried (٧١% yield) . Recrystallization from $\text{CH}_\gamma\text{Cl}_\gamma$ gave yellowish powder, m.p. ٢٠٠-٢٠١ °C.

The product (٤) was filtered, washed with water and dried (٧٥% yield). Recrystallization from ethanol gave yellowish needles, m.p. ١٨٨-١٨٦ °C.



Scheme ٣ .Benzotriazolic derivative synthesis : model compound (٣) .



Scheme ٤ .Benzotriazolic derivative synthesis : model compound (٤) .

Table.١ : Elemental Analysis for prepared compounds

Comp.	Theoretical			Experimental		
	%N	%H	%C	%N	%H	%C
١	١٣.٧٧	٤.٩٠	٧٠.٨١	١٢.٢١	٤.٧٥	٦٩.٨٤
٢	١٩.٨٩	٤.٢٩	٦٨.٢٤	١٨.١١	٤.١٢	٦٧.٣٣
٣	١٤.٧٨	٣.١٩	٦٥	١٥.٠٣	٣.٩٩	٦٧.١
٤	١٠.٢٥	٣.٣٢	٦٥.٩٣	١١.٠١	٣.٦٣	٦٦

RESULTS AND DISCUSSION

١-Structure characterization

There are many known methods for reductive cyclization of 2-nitro-azo benzene derivatives. The most commonly used method is reduction with such as sodium hydroxide solution [١٠-١٢] . A few years ago, other possible methods of reductive cyclization were also reported. For example, a ring closure reduction was reported using aluminium dust and sodium hydroxide as a reducing agent [١٣] ; cyclization reductions were also made using ammonium or alkali sulfides as reducing agents [١٤]

^[١٥] and, even, the catalytic reduction of azo dyes to benzotriazole derivatives in the presence of a transitional metal or compositions has been reported ^[١٦]. In this work, the reductive cyclization was accomplished by zinc dust in the presence of strong alkali.

We used the zinc dust in the presence of strong alkali such as sodium hydroxide solution in this work .

The benzotriazole derivatives that we obtained were characterized by IR spectra, elemental analysis and melting points . Infrared spectra of obtained compounds are shown in (Figures ١ to ٤). ^[١٧]. The most impotent peak in FT-IR spectrum is C=N triazole in $1590 - 1600 \text{ cm}^{-1}$ but this peak was in the same range of C=C for the benzene ring therefore The CHN analysis was very important to characterization . But we can recognized the (O-H) bond in ($3000 - 3200 \text{ cm}^{-1}$) , (C=O) bond for compounds ٣ and ٤ in the range ($1700 - 1720 \text{ cm}^{-1}$) .

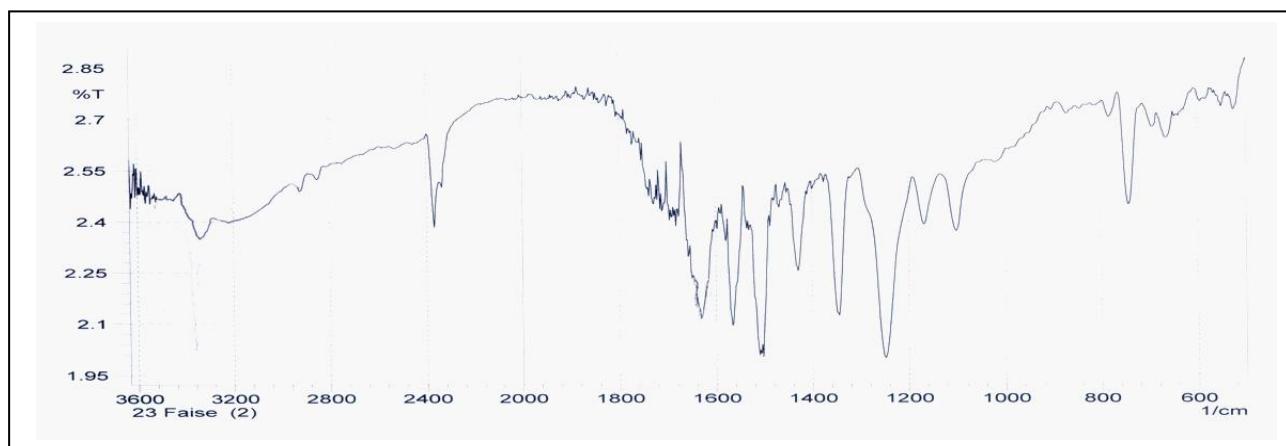


Fig. ١ : FTIR Spectra of compound (١)

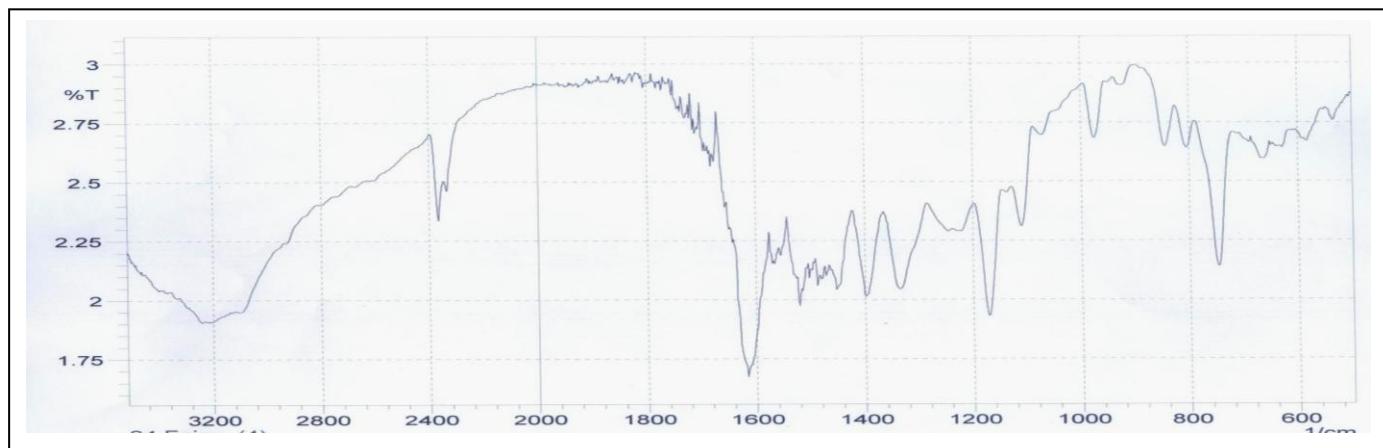


Fig. ٢ : FTIR Spectra of compound (٢)

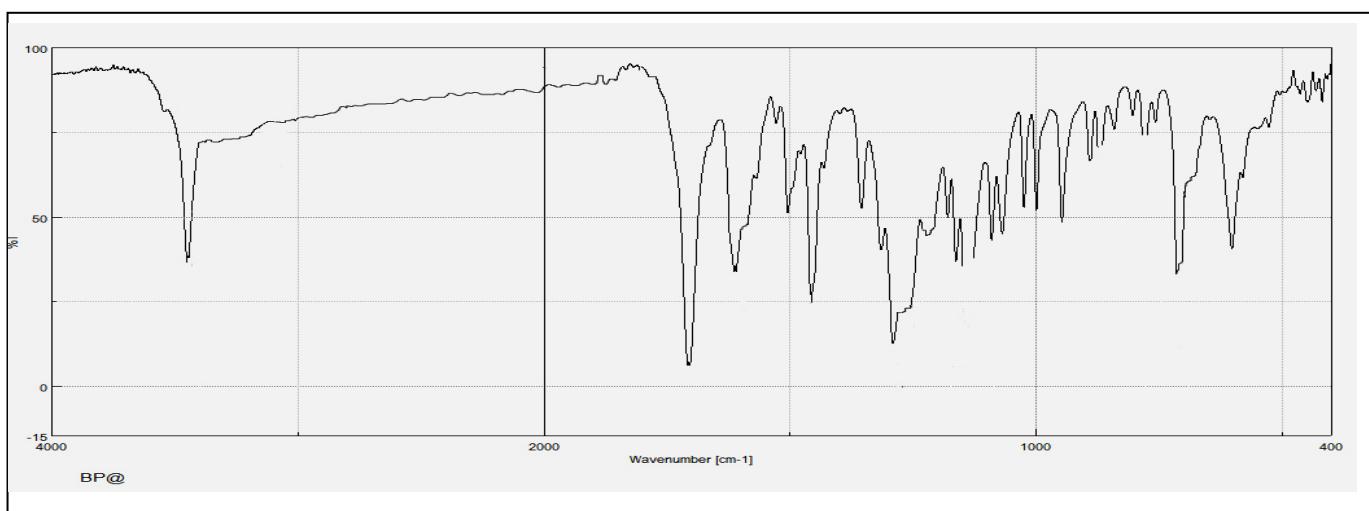


Fig. ٣ : FT-IR spectra for compound (٣)

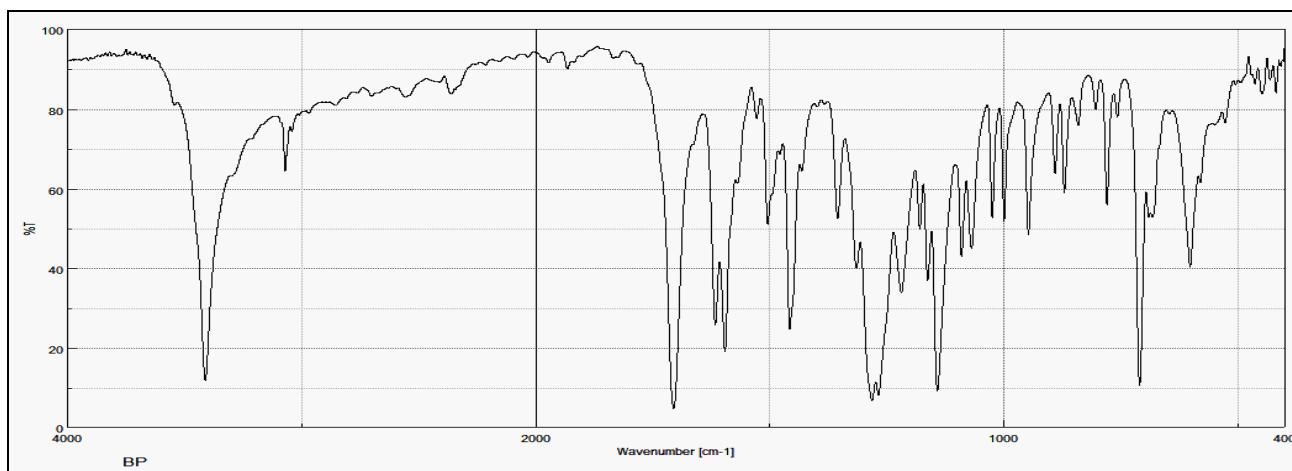


Fig. ٤ : FT-IR spectra for compound (٤)

٢- Efficiency of the prepared compounds

٢.١ Films preparation

A solution of poly (vinyl chloride) (٤.٩٨٥g of PVC + ٠.١٥g of photostabilizer) in ١٠.٠ml of tetrahydrofuran was used to prepare (٣٠ μm) thickness of polymer films. The films were prepared by evaporation technique at room temperature for ٢٤ h . To remove the possible residual tetrahydrofuran solvent , film samples were further dried at room temperature for ٣ h under reduced pressure .

٢.٢ Irradiation experiments

All films containing the above materials were treated with different temperatures and placed at the same distance away from mercury lamp and exposed at the same

period of times to the U.V. Source. The photodegradation of the samples were followed by FT-IR from measurement of the change of transmittance intensity of the carbonyl band against the time of U.V. Irradiation according to the following equation [٢٣].

$$\% \Delta CO = [T_t - T_0] / T_0 \times 100$$

Where

T_0 : Transmittance before U.V. Irradiation

T_{ot} : Transmittance of carbonyl bond over time (t) of U.V. Irradiation

Figure (٤ -٧) indicates that the prepared compound (٤) is most effective as photostabilizer for PVC. Percent of transmittance of $\% \Delta CO$ as a function of irradiated U.V. Light is more less than that of other compounds at different temperatures $٢٥^{\circ}C$, $٥٠^{\circ}C$, $٦٠^{\circ}C$ and $٧٠^{\circ}C$. This most probably because the compound behaves as a photostabilizer (two benzotriazole group) and antioxidant when exposed to U.V. light.

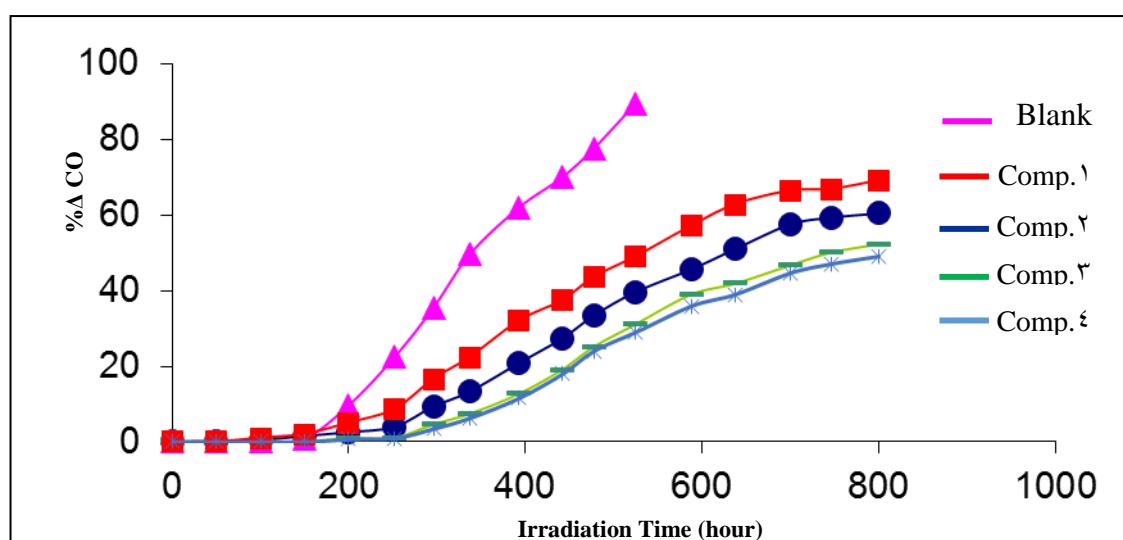


Fig. ٤ : change of transmittance intensity of carbonyl band against the time of U.V. irradiation at room temperature ($٢٥^{\circ}C$)

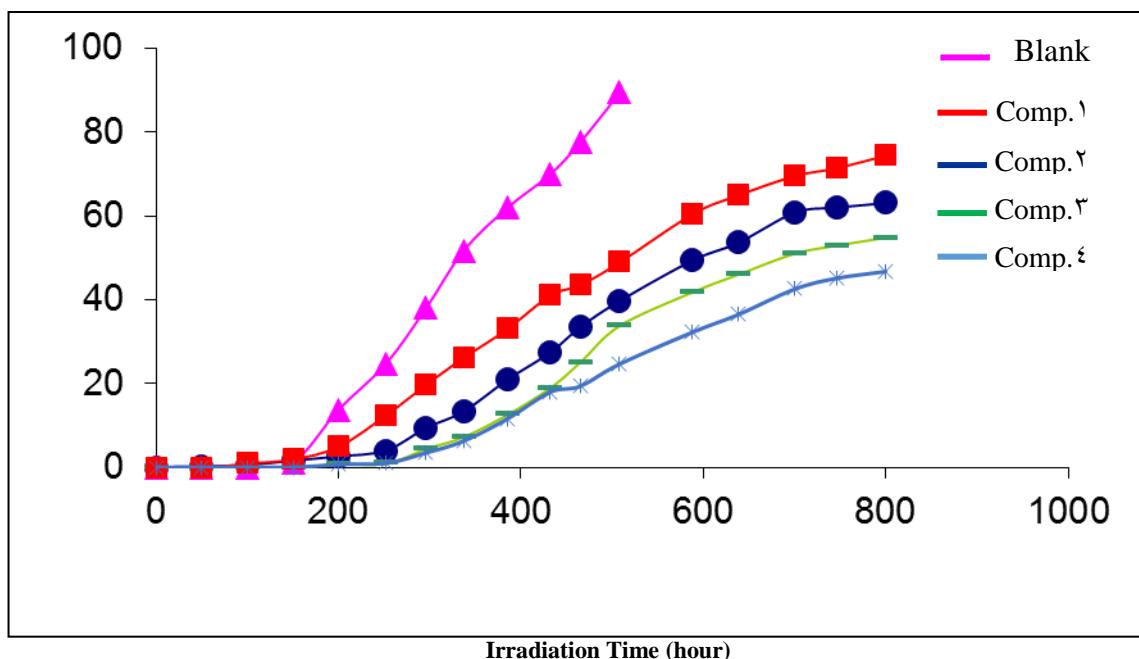


Fig. ٥ : change of transmittance intensity of carbonyl band against the time of U.V. irradiation at (50°C)

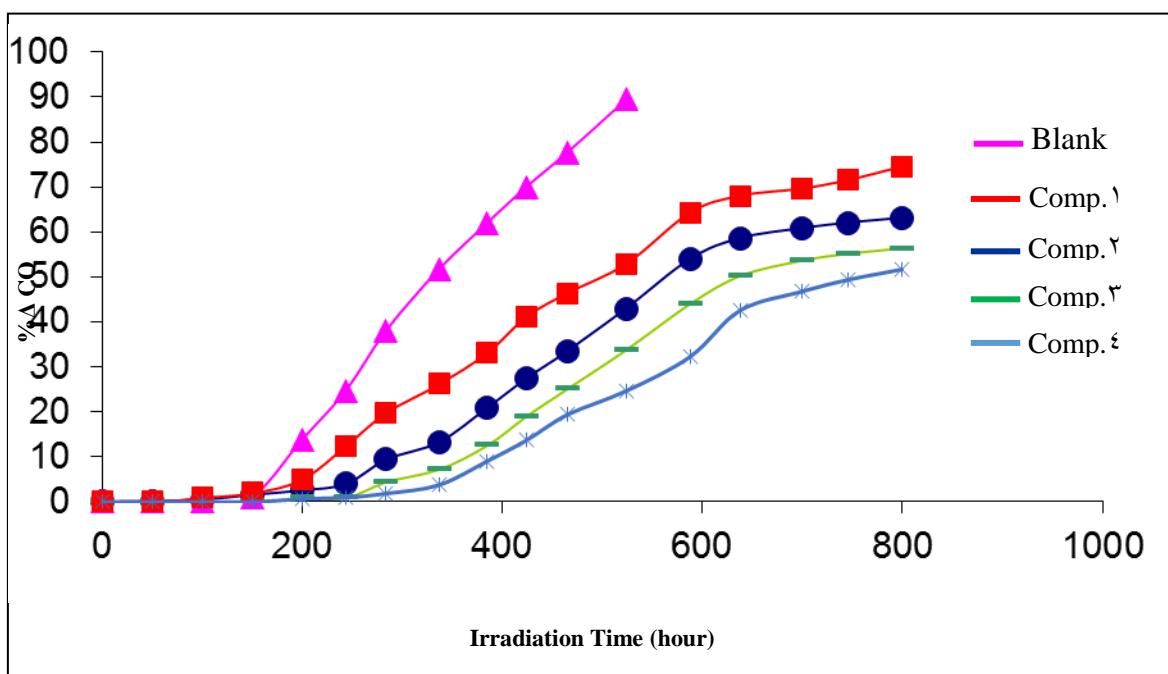


Fig. ٦ : change of transmittance intensity of carbonyl band against the time of U.V. irradiation at ($60^{\circ}\text{C}^{\circ}$)

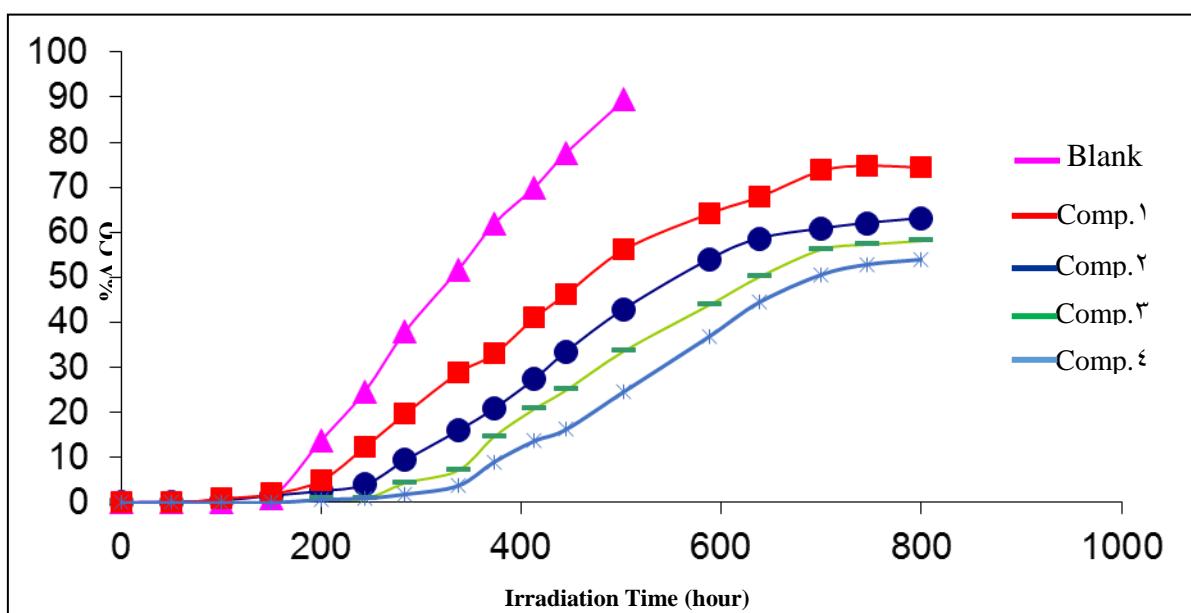


Fig. ٧ : change of transmittance intensity of carbonyl band against the time of U.V. irradiation at ($70^{\circ}\text{C}^{\circ}$)

CONCLUTION

The design of compounds (٤) and (٣) as photostabilizers for PVC is very successful since its structure may act as U.V. photostabilizers and antioxidant which together , drop the present of transmittance of carbonyl group compared with other additives .

REFERENCES

١. Emad Yousif and Raghad Haddad , SpringerPlus, ٢:٣٩٨ (٢٠١٣)
٢. Vogl O ., and Yoshida S ., Revue Roumaine de Chimie, ٢٥, ٧, ١١٢٣ (١٩٨٠).
٣. Lappin G .R ., "Encyclopedia of Polymer Science and Technology", Wiley-Interscience, NewYork, ١٤, ١٢٥ (١٩٧١).
٤. Bonino F.A. at al., Macromolecules, ٢٢, ١٠, ٢٦٦٢, (١٩٩٠).
٥. Yoshida S ., and Vogl O., Polymer Preprints ٢١, ١, ٢٠٣(١٩٨٠) .

٦. Pradeilok W., Vogl O ., et al., f. Palym. SciL, Palm. Chem. Ed., ١٩, ١٢, ٣٣٠٧, (١٩٨١).
٧. Bohringer B, Schindling G, Schon U, Hanke D, Hoffman K, Altmeyer R, Klotz M L. UV Protection by Textiles. Melliand International ١٩٩٧; ٣: ١٦٥-١٦٧.
٨. Wael A.S Abdul Ghafor and M.N. kalaf; Iraqi J. Polymers, ٧, ١, (٢٠٠٣), ١١-١٦.
٩. Guo-Bin Liu , Hong-Yun Zhao, Hong-Jie Yang, . Adv. Synth. Catal. ٣٤٩ , ١٦٣٧– ١٦٤٠ (٢٠٠٧) .
١٠. Bonino F.A. at al., Macromolecules, ٢٣, ١٠, ٢٦٦٢, (١٩٩٠).
١١. Yoshida S ., and Vogl O., Polymer Preprints ٢١, ١, ٢٠٣(١٩٨٠) .
١٢. Nir z ., Vogl O ., and Gupta A ., J. Polym. Sci., Polym. Chem. Ed, ٢٠, ١٠, ٢٧٣٥ (١٩٨٢).
١٣. Elbs, L, pr . [٢], ١٠٨, ٢١٥, Beilsteins Handbuch der Organischen Chemie ٢٦, II, p. ٢٢ (١٩٢٨).
٢١. Ger. ١, ١١٦, ٢٣٠١١٩٦١, CA. ٥٧: ٩٨٦١٣ (١٩٦١).
٢٢. Markova T.J ., et al . Jzv. Aka& Nauk. Kaz SSR, Ser. Al nm. ١, ٣٢ (١٩٨٧), C.A . : ١٠٧ : ١٧٦٩٧١j (١٩٨٧) ; Nemtseva, MP; et al ., lay. Vyssh. Uchebn. Zavat; Khim . Khim. Tekhnol. ٣٥, ١١-١٢, ٣٥ (١٩٩٢) CA. ١١٨ : ١٠٥٢٦٨b (١٩٩٣).
٢٣. Al-Assadi K.A , (٢٠١٢) , Ph.D thesis , antioxidant activity of some new dimeric nitrons , Basrah University .