Study of Degradation Effect on Physical Properties of Methyl Orange Doped PMMA

Nahida J.Hameed Al-Mashhadan* & Mohamad S*

Abstract

The samples were cast as thin film from homopolymer (PMMA) before and after doping with methyl orange at different concentration. The samples were exposed to UV-radiation for exposure time within (10-50hr) range. These polymer systems were evaluated spectrophotometrically for using the UV-detector. The absorption spectra of UV-irradiated samples showed radiation induced absorption changes in the wavelength range, which depends on the polymer type and polymer composites. The increment depends dopant concentration, especially in ultra violet region in exposed PMMA doped with methyl orange at 6.7×10-2wt/wt concentration. Decreasing in absorption was found for the cases in which, photo degradation caused surface damage, i.e. crazes or cracks formation, especially at ultraviolet region. Calibration curves were drawn at peaks, selected wavelength in the absorption spectra. The linear regions from the calibration curves were selected, and dosimeter range was determined from the UV-irradiation sample response. It was found that PMMA doped with methyl orange at 6.7×10 -2wt/wt concentration can be use the UV-detector within range (10-40hr) at the wavelength of (300nm) for its linear response at this range of irradiation.

Morphological investigations for the surface damages caused by thermal and photo degradation are detected by optical microscope. It is found that the photo degradation could easily lead to some mechanical surface degradation i. e (crazes and cracks) formation.

Keywords: PMMA UV Degradation, Optical Properties.

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دراسة تأثير التفكك الخواص البصرية للبولي مثيل ميثاأكلريت المطعم بالمثيل البرتقالي

الخلاصة

تمت قولبة النماذج البوليمرية (البولي مثيل ميثا اكرليت) بشكل اغشية رقيقة قبل وبعد التطعيم بالمثيل البرتقال بتراكيزمختلفة.شععت النماذج الى الاشعة الفوق البنفسجيةوبازمان مختلفة تتراوح بين(10-50ساعة). درست النماذج طيفيا لاستخدامها كاشف للاشعة الفوق البنفسجية. اظهرت اطياف الامتصاص للنماذج المتعرضة تغيرات في طيف الامتصاصية وضمن اطوال موجية تعتمد على نوع البوليمر وتركيز التشويب. ان عملية التفكك الضوئي قد ادى الى زيادة في الامتصاصية. ان الزيادة في الامتصاصية تعتمد على تركيز التشويب ,وبشكل خاص في المنطقة الفوق البنفسجية بالنسبة للبولي مثيل ميثا اكرليت المشوب بالمثيل البرتقالي عند التركيز6,7 x10^2. ان التناقص في الامتصاصية قد اعزي الى ان التفكك الضوئي قد يحدث اتلاف في سطح العينة مثل التصدعات والكسور.رسمت منحنيات المعايرة عند قمم بالنسبة لاطوال موجية مختارة في طيف الامتصاصراختيرت المناطق الخطية من منحيات المعايرة كونها تحدد مدى الكاشف في منحنيات الاستجابة وكما وجد بان البولي مثيل ميثا اكرليت المشوب بالمثيل البرتقالي عند

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التركيز 6,7 x 10⁻ ² عند المدى (40-10) ساعة عند الطول الموجي (300 نانومتر) لاستجابته الخطية عند هذا المدى من التعرض. أظهرت نتائج الفحص المجهر الضوئي حدوث اتلاف سطحي للعينات المتعرضة للاشعة فوق البنفسجية الناتجة عن التفكك الضوئي.

Introduction

The reactions introduced by high-energy radiation can be specific as most chemical reactions, because the initial energy is rapidly degraded in matter, and much of chemical changes produced by radiation is consequence of the action of electrons [1, 2]. Further, the transient species produced by such electrons do not give final products immediately, but take part in various transfer process in such a way that the molecules finally altered are not necessarily the only which are effected in the first instance. One of the commonest reactions is called cross-linking. It can occur in solution, although there are quantitative differences when both hydrogen atoms are formed from the same molecule, an instauration double bond can be formed instead of cross-linking. Instauration and cross-linking are often formed together. Another important reaction is degradation e.g., C-C scission. This is especially important with certain polymers, e.g., poly (methylmethacrylate), cellulose acetate, and in fact many of the physical and chemical effects on such substance as polymers can be explained in terms of two reactions cross-linking and degradation. Geetha, et al reported that unlike γ-ray and photo irradiation mainly affected the polymer surface. But the penetration power of photon is much less compared to γ-rays [3]. Deshmukh, et al, recorded the optical transmission and UV/VIS absorption spectra in the wavelength range of (450-1000nm) for different compositions of polyanline doped PVC/PMMA thin films. The absorption coefficient (α), optical energy gap (E_{opt}), refractive index (n), and optical dielectric constant had been evaluated. The effects of doping percentage of polyanilne had been discussed and nonlinear behavior for all the parameters were investigated [4]. Ahmed, prepared transparent films of (PMMA/PVAc) blend with different concentrations by using solution cast techniques. FTIR transmission spectra were carried out for the samples to detect the influence of UV radiation. In addition, optical absorption measurement was carried out for samples at room temperature across the 190-900nm wavelength region before and after exposure to UV and filtered radiation using Xenon arc lamp. The result showed no minimum was cased by absorption in the visible wavelength region, which points to the fact that all the samples are colorless. In addition, the increasing in the values of refractive index after exposure to UV radiation for 24hours could be attributed to localized density increase arising form photo induced cross linking [5]. The aim of the present work is concerned with the effect of the UV-Irradiation on the methyl orang doped PMMA to use as a UV detector.

Material and Method:

PMMA of BDH Chemicals (Ltd) in the form of granules was used as a matrix. Methyl orange doping was carried out by using methylene chloride, methanol solvents supplied

by (GCC) company. The main characteristics of these solvents and dopant are listed in the Table (1).

The homopolymers were used to cast films of different thicknesses from different concentration solutions. The polymers were dissolved in methylene chloride and handly shaked untill got a homogenous solution, the solution was transferred to clean glass petri dish of (5cm)in diameter placed on plate form. The dried film was then removed easily by using tweezer clamp. Adopting such drying cycles comes from several trying experiments to ensure no bubbling in the casted film is formed at different concentrations (6-10%wt/vol). The best concentration which gives for film production, which was cast without bubbling and can be dismounted easily from the petri dish, was found to be 7%.

The procedure of preparing polymer stated above was repeated again before doping with methyl orange taking place. Solutions of 0.005%, 0.01%, and 0.015% wt/vol concentrations were prepared by dissolving methyl orange in ethanol solvent.

The concentrations of dopant to matrix were ($6.7X10^{-2}$), ($12.5X10^{-2}$), and ($17.7X10^{-2}$) wt/wt for methyl orange doped (PMMA) respectively were prepared ,casting processes were carried out following the foregoing procedures to investigate the effect of dopant concentration.

The samples involved were irradiated by UV / radiation using the system XENOTEST 150 of xenon lamp of (320nm wavelength) for exposure time within (10, 20, 30, 40 and 50hr) range to study the UV-irradiation effect on the optical properties of the samples under test. UV/VIS spectroscopic measurements were carried out by using computerized UV/1601 Shimadzu spectrophotometer, which operates in the wavelength range of 200nm to 900nm.

1- Charactristic curves were generated by means of spectroscophotometric reading of change of optical absorbance or optical density (optical density difference (ΔA) at selected wavelengths as a function of (temperature and irradiation time for sample under study.

2- Selecting the linear region from the above curves to plot the response curves for samples involved. The response curves were drawn between ($\Delta A/t$) as a function of irradiation time.

Results and discussion:

Reprehensive ultraviolet spectrum for PMMA, before and after doping with methyl orange at different concentration is shown in Figure (1). There is increase in the absorption values according to methyl orange concentration, which is attributed to the localized state of doping material in the energy gap. The localized state causes decrease in energy gap, then increasing in absorption value [6].

The UV/VIS spectra of homopolymer (PMMA) and doped homopolymer samples exposed to intense UV/ irradiation were shown in Figures .(2) to (5) .For each set, the spectrum of un-irradiated samples are presented together with those of samples irradiated in air for exposure time of (10hr,20hr,30hr,40hr and 50hr) range. The effect of photo-oxidation degradation was illustrated within the subsidiary frames of each part of the figures,

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which occurred on the surface of the polymer, but after longer time interval, oxidation extends through the bulk with a rate limited by oxygen diffusion in the polymer phase [4, 6, 7].

In the visible region PMMA is transparent, as observed by Almashhadani, and a similar trend has been observed [8]. During irradiation, photolysis of PMMA occurred, which results in chain scission of the polymer chain back bone by a radical process. Three major reactions are reported to occur at the same time [4, 9]:

i) **Random Hemolytic Scission of Main-Chain Carbon-Carbon Bonds [4].**
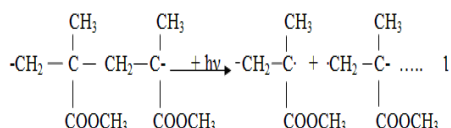
ii) **Photolysis of the Ester Side-Groups:**
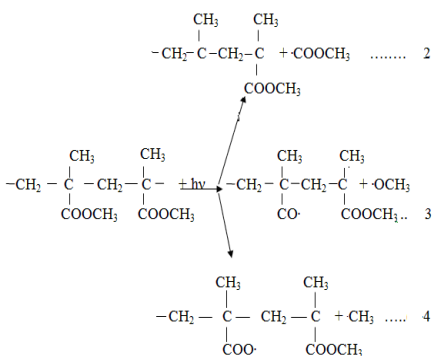
iii) **Photo-Dissociation of Methyl Side Groups:**
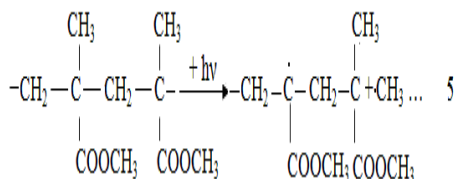
Chain scission. The main products of photo degradation of PMMA in air are methane, hydrogen, carbon monoxide, and carbon dioxide, formed in addition. Therefore, when PMMA is exposed to UV light, degradation products are formed and, electron hole trapping takes place causing change in optical absorbance as seen in Figure (2) where Figure (3) show the bubble and cracks and as reported by Deshmuskh ,et al[4]. The exposed PMMA exhibits a marked absorption below 290, other peaks may shift according to the exposure time [10].

With methyl orange the variation in UV /VIS spectrum is shown in Figures (4), (6), and (8).The variation includes shift towards higher wavelength. The absorption spectrum of exposed methyl orange doped PMMA within exposure time (10-50 hr)shows radiation induced absorption change in the wavelength (240-590 nm) range. Dyes contribute in the sensitizing of photo-oxidative degradation of polymers. By using dyes; two spectral ranges for photo degradation of polymer extend to visible region. In Figure (4) there is unsystematic change in absorption spectra for exposed samples for (10- 50 hr), and systematic change in absorption spectrum for exposed samples at 300, 340 nm wavelengths, within exposure time (30-50hr) range, which is induced by systematic photo degradation [11,12]. In Figure (4), there is unsystematic change in absorption spectrum, but systematic changes in absorption spectrum for exposed samples for exposure time (20-40hr) at 420nm wavelength and, (10-30hr) range at (300 and 340 nm wavelength). Figure (5) shows cracks and clustering in exposed samples by photo degradation.

In Figure (6), there is a systematic change in absorption spectra for

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samples exposed for exposure time (20-40 hr). Fig (7) shows cracks and clustering in exposed methyl orange doped PMMA sample. In Figure (8), there is unsystematic change in absorption spectra for exposed samples within range (10-50hr). Figure (9) shows clustering in methyl orange and bubble.

The calibration curves of PMMA shown in Figure (10) explain unsystematic changes in optical density with exposure time. At 300 nm, there is systematic decrease in optical density with exposure time within (30-50) hr range. It is attributed to the irradiation, which induced absorption change in this plastic [10-13].

By selecting the linear region from the above curve, the response is calculated for the linear part as mentioned. Response curve has been drawn as shown in Figure (11):

Fig (12) shows the calibration curves for methyl orange doped PMMA at 6.7×10^{-2} wt/wt, and at 300,340, and 420 nm wavelengths. As shown, the most interesting feature is that the exposure time is from (10-40hr) corresponding with suitable change in optical density. The dependence is linear with exposure time at 300, 420nm wavelengths. There is systematic increase in optical density with exposure time of (10-40hr) range. At 340 nm wavelength, there is systematic change in optical density with exposure time within (10-30 hr) range.

There are three linear regions in the Figure (12), at 340 nm wavelength within exposure time of (10-30hr) range, and (10-40 hr) range at 300 and 420 nm wavelengths. The response is calculated Figure (13) to (15).

In case of PMMA doped with methyl orange at 12.5 $\times 10^{-2}$ wt/wt concentration, there is systematic changes with exposure time within (20-40 hr) range at 420 nm wavelength Figures (16), and (17).

Figure (18) shows unsystematic changes in optical density with exposure time. In general, the linearity is somewhere, and non-linearity in the others in calibration curve are attributed to two general types of polymer degradation process, corresponding roughly to the two types of polymerization.

- Random degradation is analogous to stepwise polymerization. Here chain, leaving fragments, which are usually large compared to a monomer unit.
- Chain depolymerization involved the successive release of monomer unit from a chain end in a depropagation reaction, which is essentially the reverse of chain polymerization.

These two types of degradation may occur separately or in combination, they may be initiated thermally or by ultraviolet light, oxygen, ozone, or other foreign agent, and may occur entirely at random or preferentially at chain ends or at weak links in the chain [3.10, 13].

General Conclusions:

- Photo degradation increases the absorption of degraded sample. The increment at change depends dopent concentration.
- Reduction in absorption is also found in samples that had undergone photo degradation, causing surface damage, i.e. crazes or cracks formation.

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Table(3-1): The main characteristics of materials used in this work[6]:

Material	Chemical formula of repeative unit	Purity %	Density gm/cm^3
PMMA	CH_3 $-CH_2-C-$ $COOCH_3 \quad n$	-	1.2
Methyl orange	$(CH_3)N.C_6H_4N=NC_6H_4-SO_3N_3$	99.99	-
Methylene Chloride	CH_2Cl_2	99.99	1.323
Methanol	CH_3OH	99.99	0.79
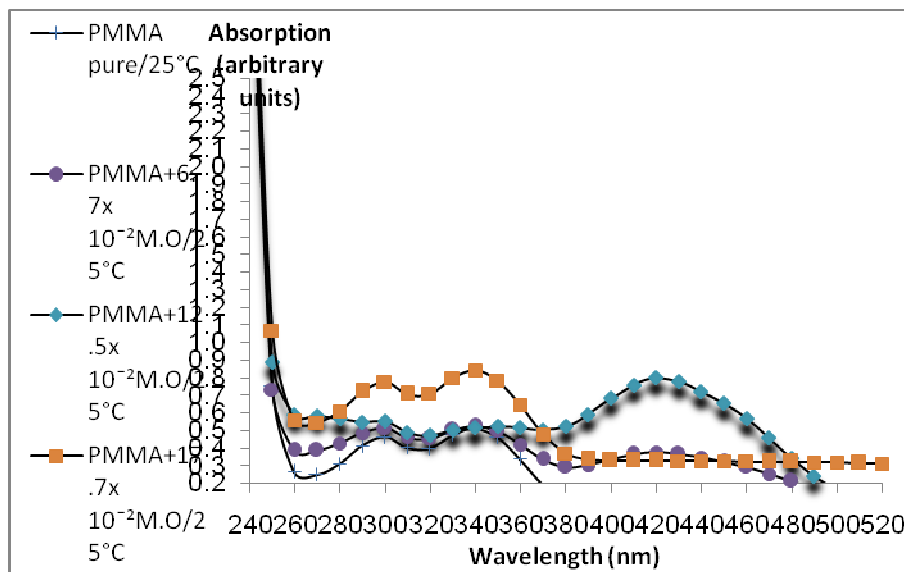
Figure (1): UV absorption spectrum of PMMA before and after doping with methyl orange at different concentration.

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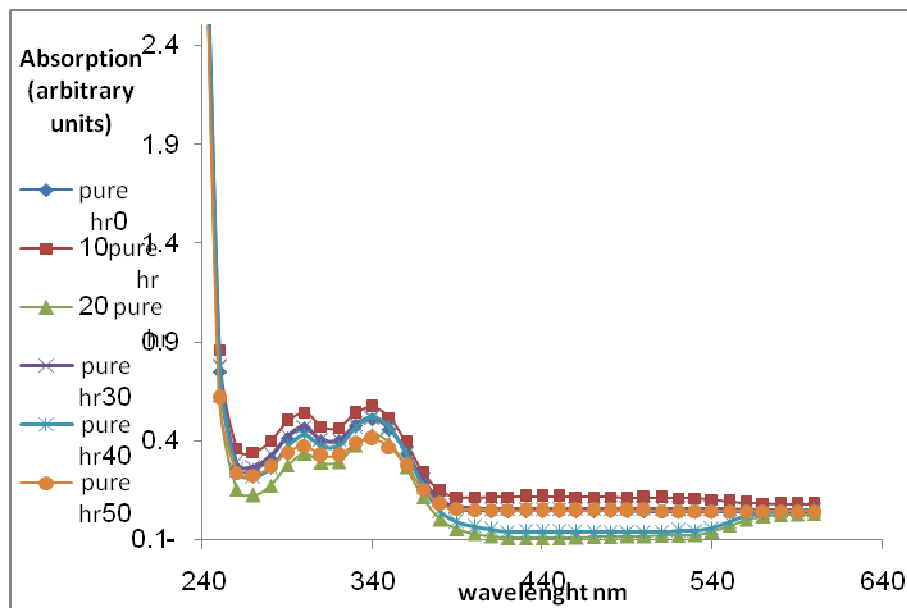
Figure (2): UV/VIS absorption spectrum of PMMA samples .exposed in air to (1500W) xenon lamp for (10 -50 hr) compared with unexposed samples.

A): Unexposed   B): Exposed
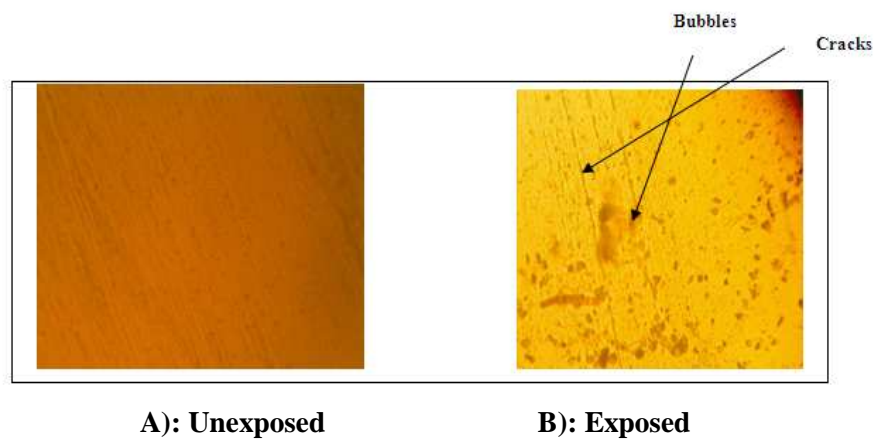
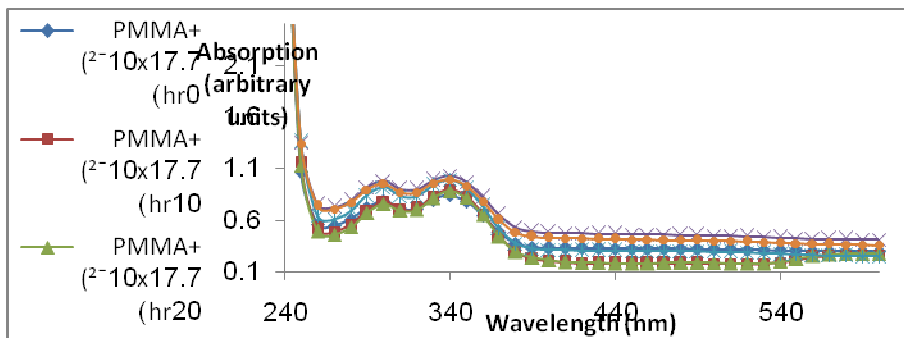**Figure (3): Optical micrographs of   PMMA samples A) unexposed B) exposed to UV- irradiation with (75x).**
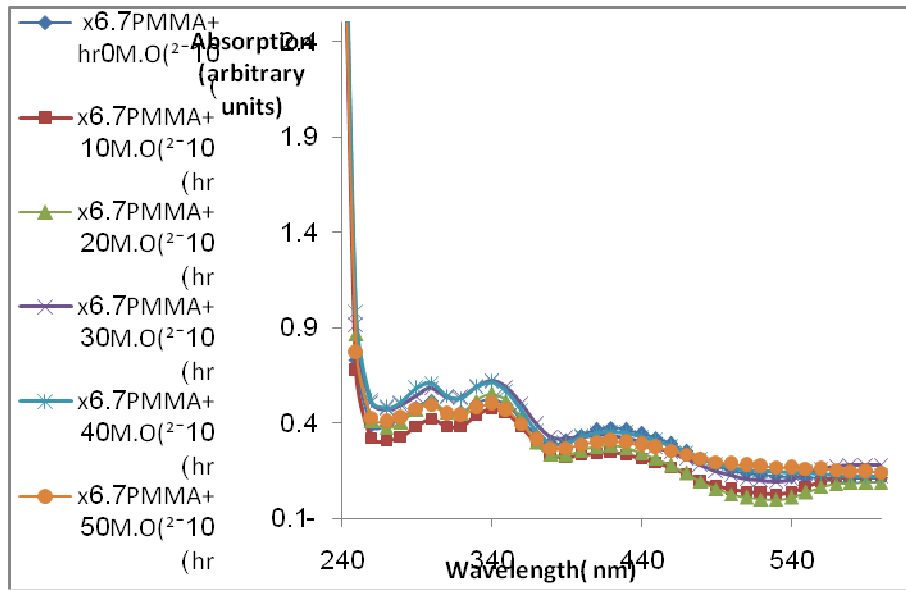
Figure (4): UV/VIS absorption spectrum of PMMA doped with methyl orange at 6.7 x 10^{-2} wt/wt concentration samples .exposed in air to (1500W) xenon lamp for (10 -50 hr)compared with unexposed samples.
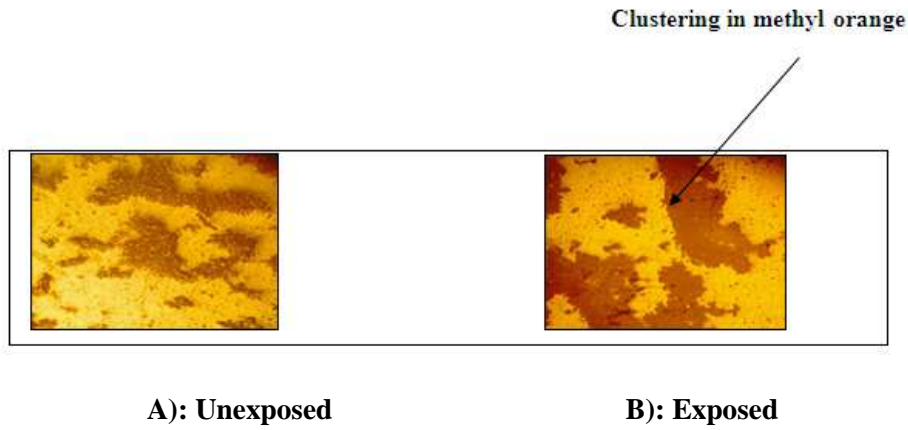

          A): Unexposed   **B): Exposed**

Figure (5): Optical micrographs of   PMMA doped methyl orange at 6.7x10^{-2} concentration samples A) unexposed, B) exposed to UV- irradiation (75x).

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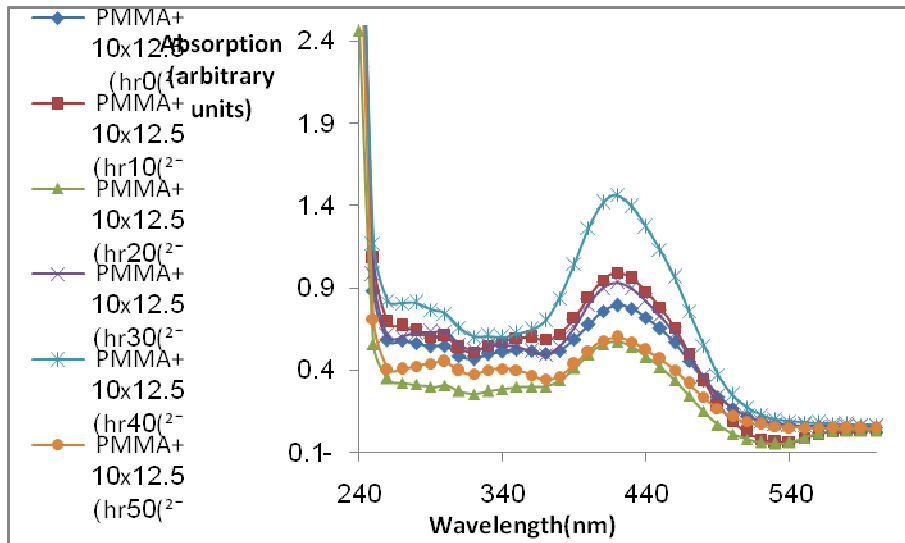
Figure (6): UV/VIS absorption spectrum PMMA doped with methyl orange at 12.5 x 10^{-2} wt/wt concentration samples .exposed in air to (1500W) xenon lamp for (10 -50 hr)compared with unexposed samples

Figure (7): Optical micrographs of PMMA doped methyl orange at 12.5x10^{-2} wt/wt concentration samples A) unexposed, B) exposed to UV- irradiation with (75x).

Figure (8): UV/VIS absorption spectrum of PMMA doped with methyl orange at 17.7 x 10^{-2} wt/wt concentration samples .exposed in air to (1500W) xenon lamp for (10 -50 hr) compared with un exposed

Clustering in methyl orange

A): Unexposed   B): Exposed

**Figure (9):Optical micrographs of PMMA doped methyl orange at
17.7 x10^{-2}wt/wt concentration samples A) unexposed, B) exposed to UV-
irradiation (75x).**
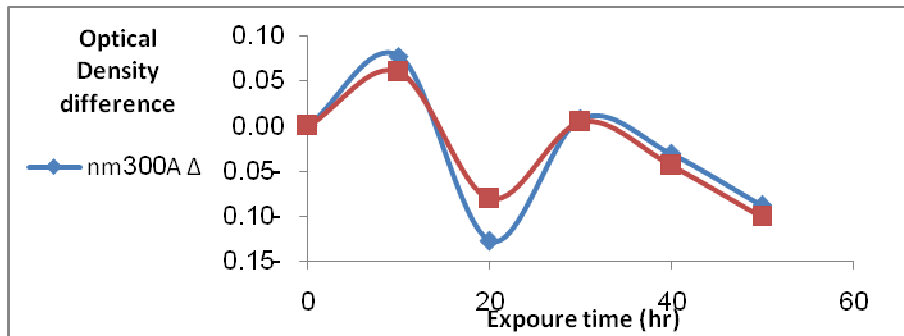
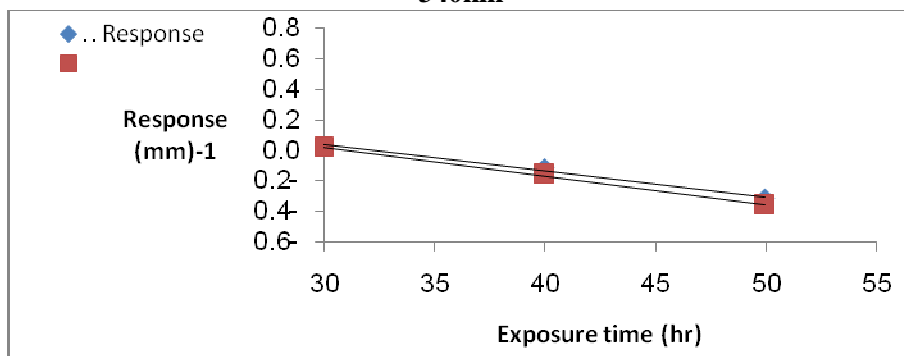**Figure (10): Calibration curve of PMMA sample at 300nm and
340nm**

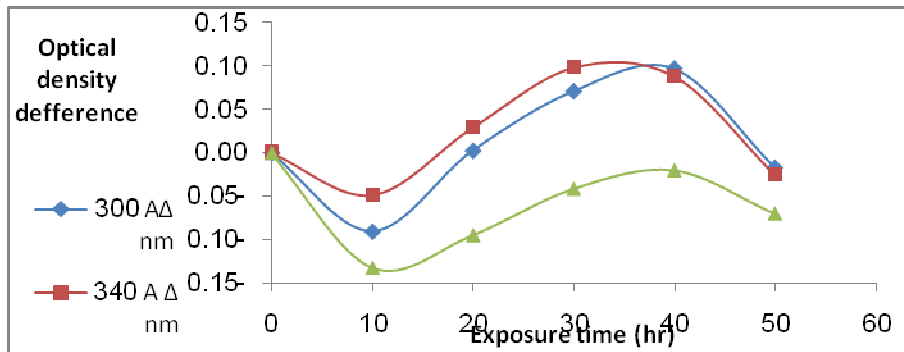**Figure (11): Response curve at 300 nm, and 340nm in PMMA samples**

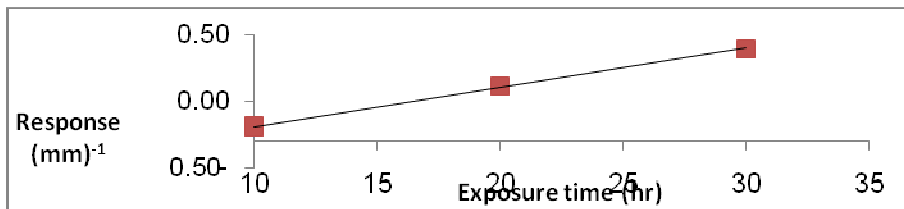**Figure (12) Calibration curves of PMMA doped with methyl orange at 6.7 x10^{-2} wt/wt, and at 300,340,420 nm**

Figure (13): Response curve of PMMA doped with methyl orange at 6.7 x10^{-2} wt/wt, and wavelength at 340 nm.
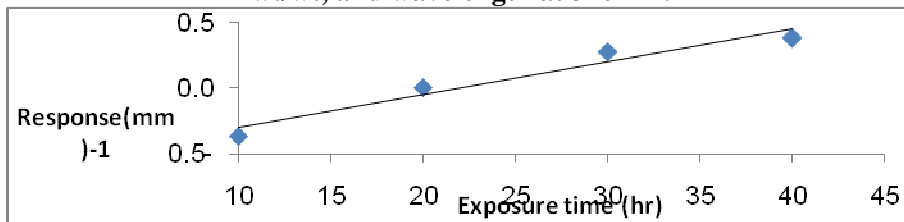

Figure (14): Response curve of PMMA doped with methyl orange at 6.7 x 10^{-2} wt/wt, and wavelength at 300 nm.
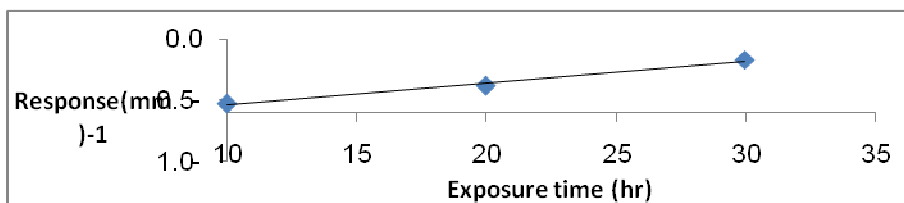

Figure (15): Response curve of PMMA doped with methyl orange at 6.7 x 10^{-2} wt/wt, and wavelength at 420 nm.
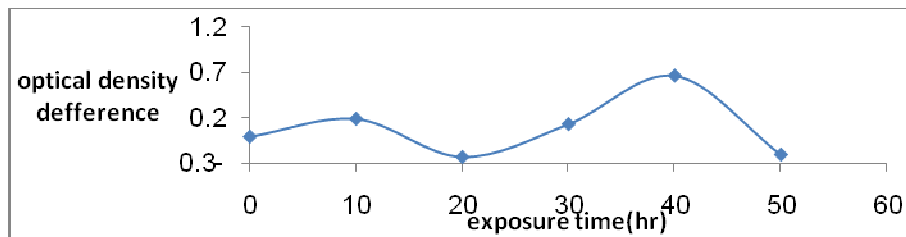
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Figure (16) Calibration curve of PMMA doped with methyl orange at
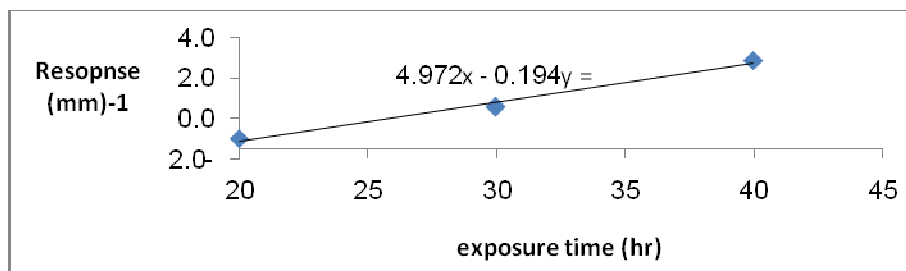**12.5 x 10^{-2} wt/wt, and at 420 nm.**

Figure (17) Response curve of PMMA doped with methyl orange at
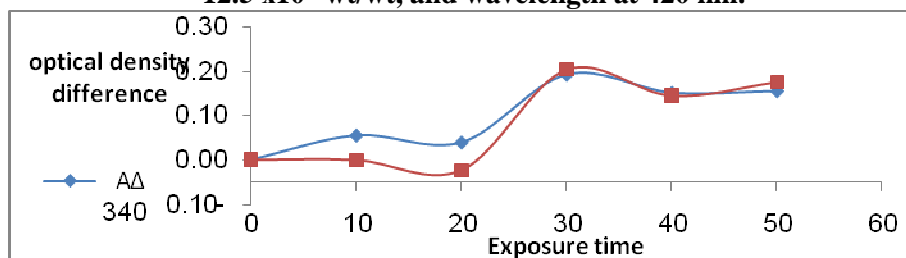**12.5 x10^{-2} wt/wt, and wavelength at 420 nm.**

Figure (18) Calibration curve of PMMA doped with methyl orange at
17.7 x10^{-2} wt/wt, and at 300, and340 nm wavelength.