Effect of UV irradiation on the structural and optical properties of polymethylmethacrylate (PMMA) doped with chromium nitrate

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Abstract. Chromium nitrate ($CrNo_3$) doped PMMA films with concentration range of 0.5, 1.5, 2.5, and 3% mass fraction were prepared by the solution casting technique.Optical properties of these filmswere estimated by measuring absorption, transmission spectra in UV and visible range. From the absorption edge studies the values of optical band gap (E_{opt}) were calculated. It was found that such values decrease by increasing Cr content where as the values of the absorption edges were decreased.Moreover, the thermal characterization of prepared sample was studied under non-isothermal conditions. The procedure was applied to the experimental data obtained by differential scanning calorimetry (DSC), using heating rate 15K/min. In addition, from the heating rate of the prepared samples, the glass transition, T_g, melting point, T_m and decomposed temperature were estimated. It was found that the glass temperature increased from the 147 to 169^{0}C with increasing $CrNO_3$ ions from 0.5 to 3 mass %.

*Keywords***:** Polymer films, absorption coefficient, Optical gap, UV-Irradiations, DSC.

1. Introduction:

In recent years, studies on the optical and electrical properties of polymer films have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarization properties [1–5]. The optical properties of polymer films can be suitably modified by the addition of dopants depending on their reactivity with the host polymer matrix. It is also well known that the physical and chemical properties of a polymer needed for specific application may be obtained by adding or doping metal like salts, which has significant effect on their optical, thermal and electrical properties [6]. Optical properties justify importance in fabrication of optical sensors, LEDs, antireflective coatings etc. The systematic analysis of the optical absorption spectra is one of the most productive tools for understanding the energy band diagram of both crystalline and amorphous materials. Among the optical polymers, Polymethylmethacrylate (PMMA) is one of the most important polymers used for different applications due to its high transparency and low birefringence [7-8]. PMMA as a polymeric waveguide has attracted much attention for use as optical components and in optoelectronics devices due to their low cost and volume productivity. Polymeric composites of PMMA are known, for its importance in technical applications. Studies of doping transition metal salts into PMMA are important for determining and controlling the operational characteristic of the different PMMA composites. The addition of these salts to the PMMA network will cause a remarkable change in their properties.

2. Experimental

Polymethylmethacrylate[-$CH_2C(CH_3)(CO_2CH_3)$-]$_n$(PMMA) polymer (powder) of average molecular weight 550000supplied from Alfa Aeaser united kingdumused as polymeric material and Chromium(III) nitrate (99.9%) supplied from Sigma Aldrich as doping material in sample preparation.Pure (undoped) and $CrNo_3$-doped PMMA films with concentration range of 0.5, 1.5, 2.5, and 3% mass fraction were prepared by the solution casting technique. Pure PMMA films were prepared by dissolving of PMMA powder in chloroform, thoroughly stirred using magnetic stirring at room temperature for about 8 hours till a transparent homogeneous solution is obtained. The mixture left for about 24 hours in room temperature to attain a homogenous and bubble free solution. The solution is simply effused into a Petri-dish that is a perfectly flat bottom. Subsequently, the solvent is allowed to evaporate for 3 days at room temperature. The film thickness can be controlled by the area of the dish that is used and by the volume and the concentration of the solution. $CrNo_3$-doped PMMA samples were prepared by the same technique, with mixing the solutions of the desired concentrations of $CrNo_3$ to the polymer solutions. The desired solutions are also poured on a leveled petridishes. The prepared films are then gently separated from the Petri dishes. Thickness of the prepared samples was measured using a micrometer.Some pieces of the prepared samples were subjected to UV irradiation

for 2 hours using Camag UV lamp ($\lambda = 254$ nm). The distance between the lamp and sample was 5 cm. Optical transmission and absorption measurements have performed for all samples by using a JASCO V-570 spectrophotometer. The Absorption coefficients for all samples were calculated from absorption data by using the following relation [9]:

$$\alpha = 2.303(A/d) \tag{1}$$

Where A is absorption and d is thickness of samples in (cm). The calorimetric measurements were carried out by using Setaram (DSC 131 Evo) with an accuracy of $+ 0.1$ ^{0}C. Temperature and energy calibrations of the instrument were performed using the well- known melting temperatures and melting enthalpies of high purity indium and zinc supplied with the instrument. For non-isothermal experiments the prepared samples weighing about 10 mg were sealed in an aluminum pans and it tempered at 15 K/min from 30 to 500 ^{0}C. An empty aluminum pan was used as reference and in all cases a constant 60 ml/min flow of nitrogen was maintained in order to extract the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC 131 Evo furnace.

3. Results and Discussions

3. 1. Optical absorption Spectra

Figure (1). represents the relation between the transmittance and wavelength for both pure and Cr-doped PMMA. It is clear from such figure that there is no clear pronounced change for the transmission value for pure and low (0.5 and 1.5%) Cr-content (where the average transmission value exceeds 85% which agree very well with the data of polymer were reported in Ref. [10]. Here there is also no clear absorption band in this range 200- 300 nm but an absorption shoulder at about 247 nm. The corresponding values of transmittance for 2.5 and 3% Cr-content are slightly decreases by increases the Cr-content. In addition to that clear absorption bands at about 423 and 591 nm are observed. The intensity of such bands may increase by increasing Cr-content. Such results are attributed to the increasing of the polymer density as a result of transition element doping.
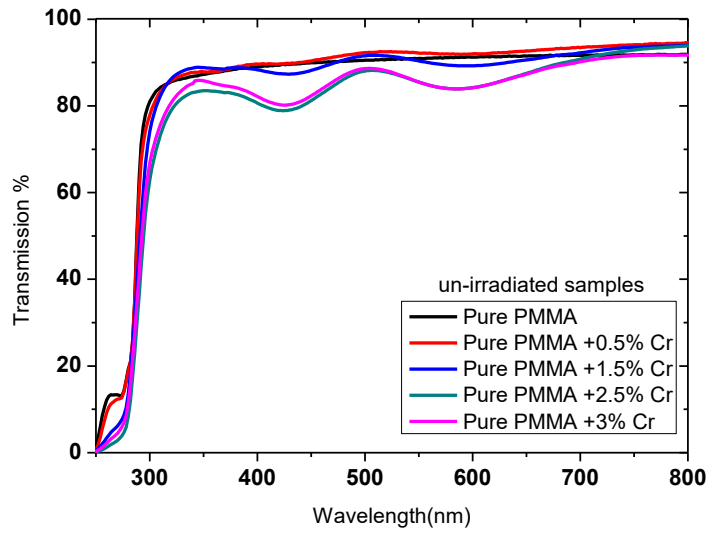
Figure (1). Represents the relation between the transmittance and wavelength for both pure and Cr-doped PMMA.

The optical transmission spectra of samples subjected to UV-irradiation for four hours are shown in figure 2. Form this figure one can observe that the observed absorption peak (at 247 nm) shifts to longer wavelength (red shift). Such result may be attributed to the photodegradation of the irradiated samples also there is no linear relationship between the height of this peak and the concentration of Cr. Figure 3 and 4 shows a relation between the absorption coefficient α and wavelength for both unirradiated and UV irradiated samples. It is obvious from those figures that the behaviors are opposite to that of the transmission spectra, the observed shoulders are observed in the same positions and the spectra of the UV-irradiated samples confirms the red shifts of the observed peaks.
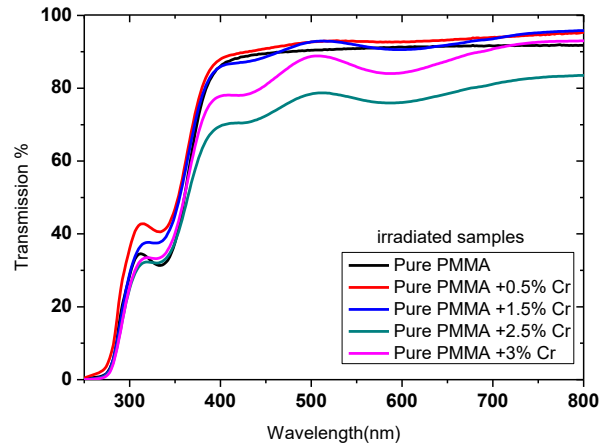
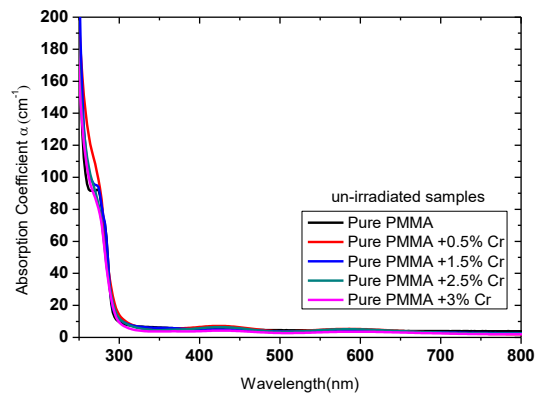**Figure (2). The optical transmission spectra of samples subjected to UV-irradiation for 4hr.**

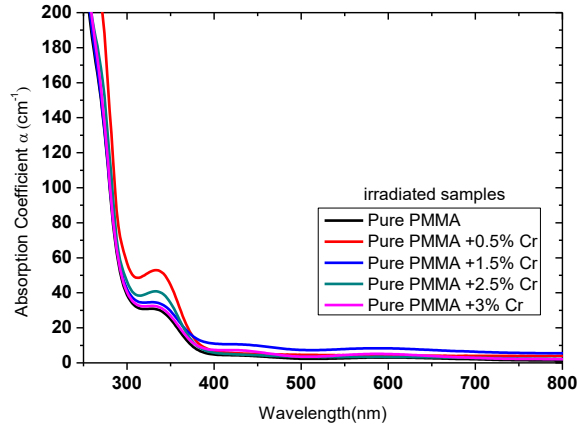**Figure (3). shows a relation between the absorption coefficient α and wavelength for unirradiated samples.**

Figure (4). shows a relation between the absorption coefficient α and wavelength for UV irradiated samples

3.2. The fundamental absorption edge

The fundamental absorption edge can be determined by plotting a relation between the photon energy *hv* and absorption coefficient *α* for all samples under consideration Figure 3 and 4. The position of the absorption edge was determined by extrapolating of the linear portion of the *hv* to zero absorption value. For pure film, the absorption edge lie at about 4.25 eV while for 0.5, 1.5, 2.5 and 3 wt. % Cr-doped films, the positions of the absorption edge was located

between 4.24, 4.22 eV. It is clear from the calculated values of the Absorption edges for samples that absorption edge decrease alittle (not significant) as a result of increasing Cr doping. The calculated values for the irradiated samples shows a significant decreas of the corresponding values of the absorption edge and the observed values depends also on the Cr-content. The calculated values given in Table 1. Such strong variations of the fundamental edge confirm the UV irradiation creats a free carries distributed in the polymer matrix which can be affects the transmission properties of the Cr-doped PMMA films.

3.3 The Optical energy gap

For amorphous materials in the high absorption region, Tauc and Davis-Mott [10] independently derived an expression relating the absorption coefficient *α* to the photon energy E as: $\alpha E = B(E - E_g^{opt})^m$. Where $E=hv$, *B* is an energy independent constant, E_g^{opt} the optical band gap, *m* an index which characterizes the optical absorption process and *α* the absorption coefficient on photon energy in the

high absorption region. Consider the function F of energy defined as:$F(E) = (\alpha E)^{\frac{1}{m}} = \beta(E - E_g^{opt})$.The first derivative of the function F with respect to E is:$F'(E) = \frac{dF(E)}{dE} = \beta$. The slope of the linear portion to the curve of F(E) versus the energy E in the high absorption region can be calculated β and evaluate the energy band gap value. The plot of both $(\alpha v)^{1/2}$ and $(\alpha v)^2$ versus the photon energy ,hv , at room temperature for pure and Cr-doped PMMA samples are shown in figures 5 and 6. As shown in these figures, clear difference between the corresponding curves for the unirradiated and irradiated samples are observed which can be considered as an evidence for the photodegradation of the irradiated samples. The calculated data for direct and indirect energy gaps are shown in table 1.

Table (1) summarize the calculated optical properties of the investigated samples.

Cr-content (%)	UV	$E_{g\text{-ind}}$(eV)	$E_{g\text{-dir}}$(eV)	E_u(eV)	Abs-edge(eV)
0	0H	4.17409	4.29635	0.0961	4.25216
0.5	0H	4.15772	4.29431	0.11512	4.24191
1.5	0H	4.06539	4.32094	0.14394	4.22890
2.5	0H	4.05527	4.32514	0.1575	4.22879
3	0H	4.04984	4.32266	0.15346	4.22548
0	2H	3.03689	3.35867	0.18139	3.24451
0.5	2H	3.01885	3.35191	0.18921	3.23361
1.5	2H	2.99292	3.34957	0.21913	3.20935
2.5	2H	2.82163	3.30288	0.31504	3.13817
3	2H	2.93061	3.33236	0.23082	3.18389

The relations between $(\alpha v)^2$ and hv for the investigated samples before and after UV irradiation are shown in figure 7 and 8 respectively.
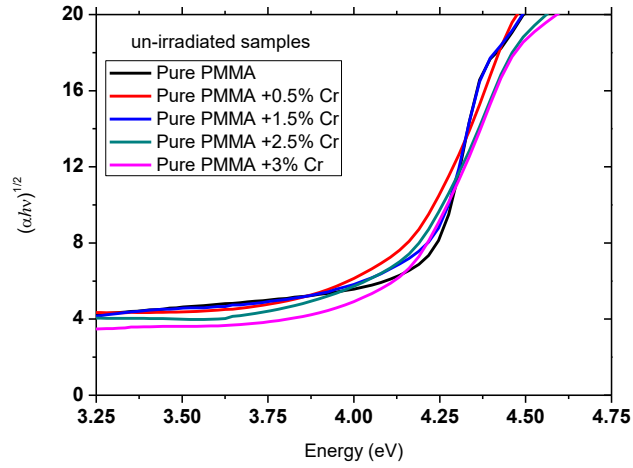
Figure 5: shows a relation between, $(\alpha h\upsilon)^{1/2}$, and and, $h\upsilon$, for unirradiated samples.
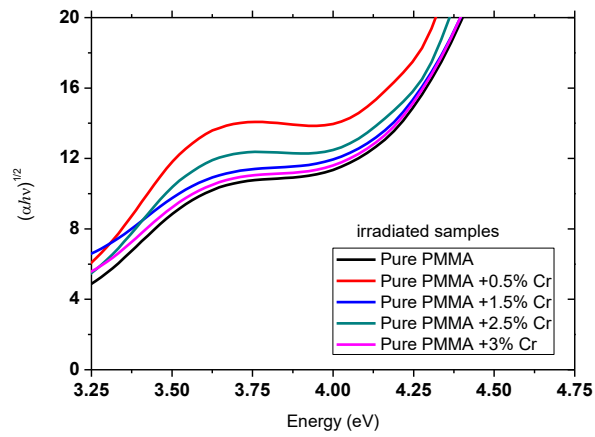

Figure 6: the relation between $(\alpha h\upsilon)^{1/2}$ and, $h\upsilon$, after UV-irradiation
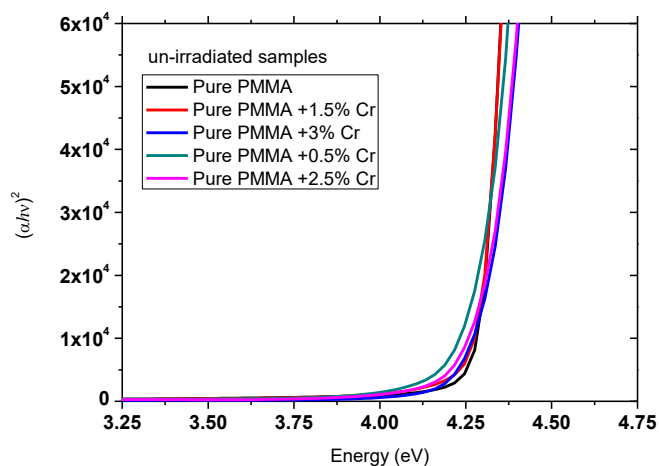
Figure 7. The relations between $(\alpha h\upsilon)^2$ and hυ for the investigated samples before UV-irradiation
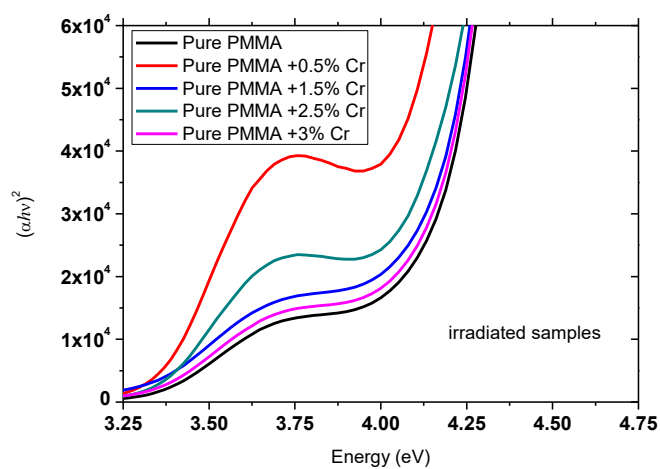

Figure 8: The relations between $(\alpha h\upsilon)^2$ and hυ for the investigated samples after UV-irradiation

From such data one can observe that both direct and indirect energy gaps decrease by increasing the Cr-content whereas the band tail increase. Such observed data may be due to the trapping levels which are produced in the energy gap as a result of Cr-doping. By comparing the corresponding data for the UV irradiated

samples one can observe that a strong difference in energy gap by about 1 eV less than that of the unirradiated samples in addition to that the observed values are also decrease by increasing Cr-content. Such observed results may represent an evidence of the photodegradation of the polymer films which may leads to breaking of the covalent bonds and additional electrons becomes free which can be easily move in polymer matrix leads to decrease the optical energy gap to a pronounced values.Table (1) summarizes the calculated optical properties of the investigated samples.

3.4 Thermalcharacterization:

DSC is one the most convenient method to determine the miscibility and thermal properties of the material. Figures 9 show the DSC profiles of pure and $CrNo_3$-doped PMMA films with concentration range of 0.5, 1.5, 2.5, and 3% mass fraction. From the DSC curves, characteristic temperatures such as the glass transition temperature, T_g, melting temperature, T_m, and decomposition temperature, T_d. The data of T_g, T_m and T_d were summarized in Table 2. The glass transition temperature, T_g, increase from 147 to 169 ℃ with increasing $CrNo_3$ from 0.5 to 3 mass %. Thus the increase in T_g usually means a rigid network composite, hence $CrNO_3$ leads to strong interactions between the polymer and the dopant particles. The second endothermic peak melting temperature point, Tm, that shows a increase from 299 to 310 ℃ with increasing in the rigidity of samples. Our prepared samples have a higher thermal stability
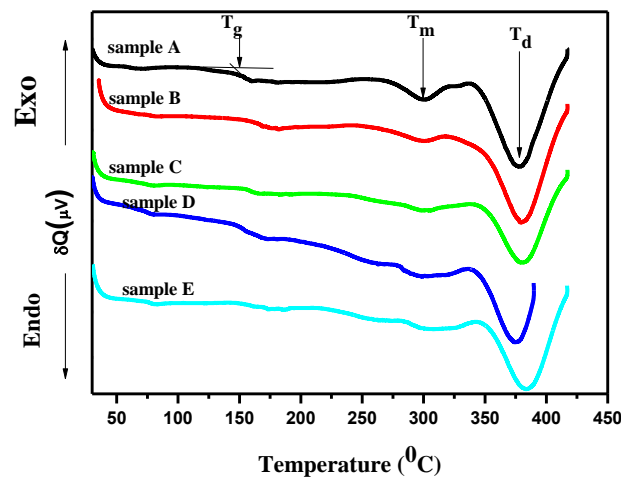

Figure 9: DSC profiles of the prepared sampleusing heating rates at (β=15 K s⁻¹).

Table (2). Polymer composition, glass transition temperature T_g, melting point, T_m , and decomposition temperature, T_d, of prepared samples.

Sample name	polymer composition	Tg in (^{0}C)	T_m in (^{0}C)	T_d in (^{0}C)
Sample A	[-CH$_2$C(CH$_3$)(CO$_2$CH$_3$)-]$_n$ (pure)	147	299	377
Sample B	[-CH$_2$C(CH$_3$)(CO$_2$CH$_3$)-]$_n$ -$_0$.5 CrNo$_3$ %	160	300	399
Sample C	[-CH$_2$C(CH$_3$)(CO$_2$CH$_3$)-]n-1.5 CrNo$_3$ %	162	303	380
Sample D	[-CH$_2$C(CH$_3$)(CO$_2$CH$_3$)-]$_n$ -2.5 CrNo$_3$ %	165	307	376
Sample E	[-CH$_2$C(CH$_3$)(CO$_2$CH$_3$)-]$_n$ -3 CrNo$_3$ %	169	310	385

compared with PMMA doped with CrCl$_3$[12]. These results suggest that the decrease in the crystallinity of PMMA doped with CrNO$_3$. Last endotheramic peak denotes by decomposition temperature, T_d. It increase from 377 to 385 ^{0}C with increasing CrNO$_3$ from 0.5 to 3 mass %.We can suggest that, the cross link density of the network for prepared samples increased with increasing CrNO$_3$. Therefore the increase in T_d indicates that the network structure is becoming stronger due to the interstitial of CrNO$_3$ ions.

Conclusions

Undoped and Cr-doped PMMA were successfully synthesized by casting technique. The samples were subjected to UV-irradiation for 4 hours. Optical transmission and absorption spectra showed that UV irradiation of the investigated samples play a very important role in the observed absorption band as well as varying optical energy gap values for both direct and indirect transitions compared to the un-irradiated samples. DSC measurements were performed for the un-irradiatedsamples showsthat the glass transition temperature increase by increasing Cr-content and the network structure becomes stronger via increasing the decomposition temperature of the samples.

Acknowledgements

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" تأثير الأشعة الفوق بنفسجية على الخصائص التركيبية والضوئية لأفلام البولى ميثيل ميثاكريلات المطعمة بنترات الكروم"

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ملخص البحث. حضرت أفلام من بوليمر البولي ميثيل ميثاكريلات النقية وأخرى مطعمة بنترات الكروم بتركيزات مختلفة وتم دراسة الخصائص الضوئية لتلك الأفلام وذلك لغرض تحديد التغير الممكن حدوثه بسبب التطعيم حيث سجلت قيم النفاذية والامتصاص في مدى الأشعة الفوق بنفسجية والمرئية ومن ثم حساب قيم طاقة الفجوة الضوئية (Eopt) والتي بينت الحسابات أنها تقل كلما ازدادت نسبة تركيز الكروم كما يظهر نفس السلوك بالنسبة لحافة الامتصاص. كما تم أيضا دراسة الخصائص الحرارية للأفلام المحضرة وذلك باستخدام الماسح الحرارى التفاضلي (Differential Scanning Calorimetry DSC) بمعدل تسخين 15K/min حيث تم تعيين قيم درجة حرارة التحول الزجاجي (glass transition temperature Tg) ودرجة الانصهار(melting temperature Tm) بالإضافة إلى درجة التفكك الحرارى (decomposition temperature Tm) وقد تبين أن درجة حرارة الانتقال الزجاجي تزداد من 147oC إلى 169oC مع زيادة نسبة تركيز الكروم من 0.5% إلى 3% .