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SYNTHESIS AND CHARACTERIZATION THE OPTICAL PROPERTIES AND FT-IR SPECTROSCOPY OF PMMA/CR_2O_3 BLEND FILMS

Rushdi. I. Jasim, Athraa N. Jameel, Tariq J. Alwan

Al-Mustansiriyah University, College of Education, Physics Department, Iraq.
E-mail: tariqjaffer2000@yahoo.com

Abstract
The PMMA and PMMA doped with Cr_2O_3 films with different concentration (1%, 3%,5%), were prepared using the casting technique in order to study the effect of doping in the optical properties of this films. The optical properties of the films were examined by UV-VIS spectrophotometer in wavelengths ranging 250 - 900 nm. The optical transmittance and absorption were utilized to compute the optical constant of the films; refractive index, extinction coefficient and the real and imaginary parts of dielectric constant, were found to very effect by increasing the concentration of Cr_2O_3 in films. The FTIR was carried out of PMMA and PMMA/Cr_2O_3 with range 400–4000 cm^{-1} to study the functional groups of PMMA and PMMA/Cr_2O_3 films.

Key words: *PMMA, PMMA/Cr_2O_3, optical properties*

1. Introduction

Poly-methyl Methacrylate (PMMA) is an important and interesting polymer because of its attractive physical and optical properties. PMMA contains both hydrophobic (methylene) and hydrophilic (carbonyl) groups in each unit. As a polymer waveguide, PMMA has attracted much attention for use as optical components in optoelectronic devices due to its low cost and volume productivity. In addition, it is found that it can produce a large refractive index difference with acryl amide-based photopolymer [1].

Polymeric substances make up the most important class of organic materials, technically and economically. The familiar plastics, fibers, elastomers and biological materials that surround us attest to this importance. Such substances, which are composed of great many identical groups or repeating units, are known as (high polymers). Polymers composed of more than one kind of repeating units are termed copolymers [2]. It is well known that polar polymers in solution are divided into two groups according to their dielectric behavior. The first group exhibits a dielectric absorption in low frequency region [10^1-10^6 Hz], the second group exhibits a dielectric absorption in the high frequency region [10^6-10^{12} Hz] [3]. Some researchers reported PMMA optical components such as an optical switch, a coupler, a splitter, and a transceiver [4, 5]. Poly methyl methacylatc have been widely used due to attractive physical and optical properties decisive about its broad applications. This is the thermoplastic material with a good tensile strength and hardness, high rigidity, transparency, good insulation properties and thermal stability dependent on toxicity [6, 7].

In recent years, the doped polymers have been the subject of interest for both theoretical and experimental studies, because of the physical and chemical properties needed for specific application may be obtained by adding or doping with some dopant. Many studies reveal that the optical properties of PMMA is affected by using different dopants or by increasing the doping concentrations [1, 8].

Chromium (III) oxide is the inorganic compound of the formula Cr_2O_3. It is one of principal oxides of chromium and is used as a pigment.Chromium (III) oxide is formed by the decomposition of chromium salts such as chromium nitrate or by the exothermic decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

The reaction has a low ignition temperature of less than 200°C and is frequently used in "volcano" Demonstrations. Because of its considerable stability, chromia is a commonly used pigment and was originally called viridian. It is used in paints, inks, and glasses. It is the colourant in "chrome green" and "institutional green." Chromium (III) oxide is a precursor to the magnetic pigment chromium dioxide, according to the following reaction.[9,10]:

$$Cr_2O_3 + 3CrO_3 \rightarrow 5CrO_2 + O2$$

Table 1

Properties of Cr_2O_3 [11-13].

Chemical formula	Cr_2O_3
Molar mass	151.9904 g/mol
Appearance	light to dark green, fine crystals
Density	5.22 g/cm^3
Melting point	2,435 °C (4,415 °F; 2,708 K)
Boiling point	4,000 °C (7,230 °F; 4,270 K)
Solubility in water	Insoluble
Solubility in alcohol	insoluble in alcohol, acetone, acids
Refractive index (n_D)	2.551
Crystal structure	Hexagonal

The aim of the present work is to prepare Polymethyle methacrylate doped with varying concentration of chrome oxide films by a simple and inexpensive method. Moreover, investigate the effect of doping on the optical properties of films.

2. Experimental

The casting method is used to prepare films of pure Poly methyl methacrylate and doped by Cr_2O_3 at different concentration (1%, 3%, %5). PMMA solution was prepared by dissolving PMMA in Chloroform ($ChCl_3$), the Cr_2O_3 used as a dopant. The solution was stirred, using a magnetic stirrer for 3h until the polymer completely dissolved. The solution was poured into flat glass plate dishes. Homogeneous films were obtained after drying in air for 48 h at room temperature. The thicknesses of the produced films 88 $\pm$10 µm were measured using a digital micrometer.

The optical properties of the samples were carried out by using a double beam UV/VIS spectrometer Shimadzu Japan UV-160A in the wavelength range (250-900) nm. The functional groups of PMMA and PMMA/Cr_2O_3 films have been carried out using Shimadzu FTIR-8400S Fourier Transform infrared spectrophotometer with range 400–4000 cm^{-1}.

3. Results and Discussion

The relationship between incident intensity I and penetrating light intensity I_o is given by[14]

$$I=I_o e^{-\alpha t} \qquad (1)$$

Where t is the thicknesses of matter (cm) and α is the absorption coefficient $(cm)^{-1}$.

$$\alpha t = 2.303 log \frac{I}{I_{\circ}} \qquad (2)$$

Where the amount of $log \frac{I}{I_{\circ}}$ represents the absorbance (A).

Fig. 1 shows the absorbance spectra as function to the wavelength of the incident light for PMMA and PMMA/Cr_2O_3 film with different concentration of Cr_2O_3. It is clear that the increasing of Cr_2O_3 concentration in the polymer matrix leads to increasing the peak intensity, from another hand the absorbance is rapidly decreased with increasing wavelength. This behavior may be attributed to perfection and stoichiometry of the films [4], and the increment in the absorption is attributed to the increment of the concentration of Cr_2O_3 which is the absorbing component.

The relation between absorbance, transmittance and reflectivity can be seen by the following Equation [15]:

$$R = A - T - 1 \qquad (3)$$

Where T is transmittance.

Fig. 2 shows the optical transmittance spectra as function to wavelength of incident light for several Cr_2O_3 concentration, the polymer transmittance decrease with the increasing the concentration of Cr_2O_3, this is due to the added Cr_2O_3 molecules that contains in it is outer orbits, these electrons absorb the electromagnetic energy of the incident light ,then, as a result electrons excited to higher energy levels, this process is not accompanied by emission of radiation because the electron that moved to higher levels have occupied vacant positions of energy bands ,thus part of the incident light is absorbed by the substance and does not penetrate through it ,on the other hand the pure Poly (Methyl Methacrylate) has high transmittance because there are no free electron (i.e .electrons are strongly linked to them atoms through covalent bonds)[14].

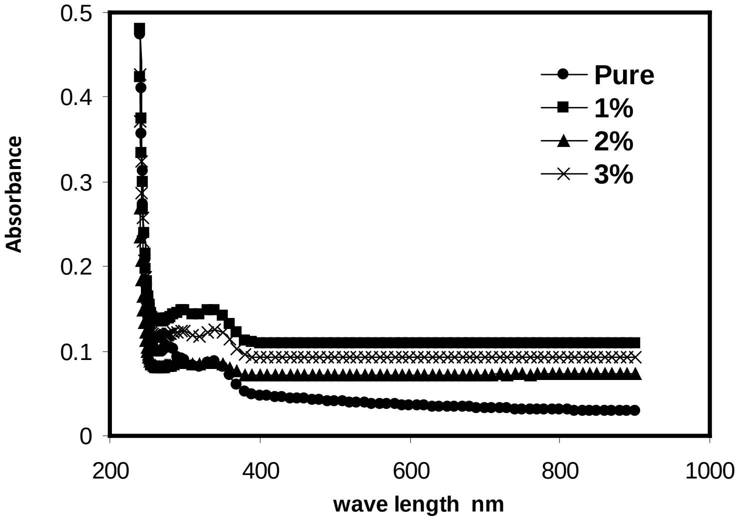

Fig. 1 Absorbance as a function to wavelength for pure PMMA and PMMA/Cr_2O_3 with different Cr_2O_3 concentration.

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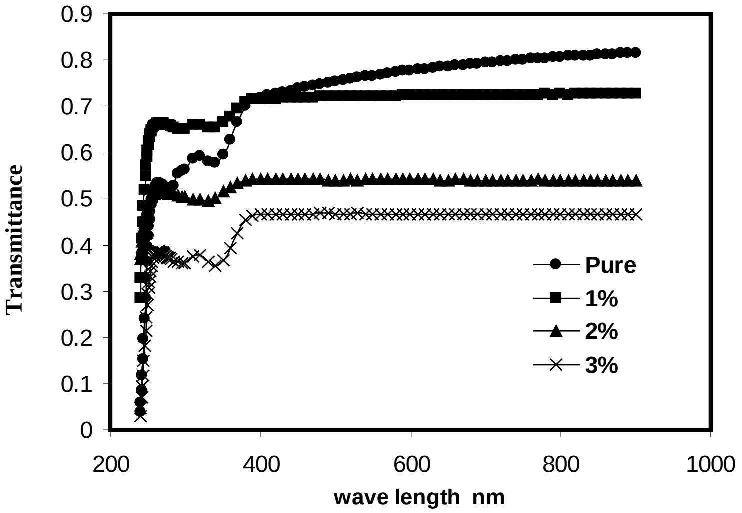

Fig. 2 Transmittance as a function to wavelength for pure PMMA and PMMA/C r_2O_3 with different Cr_2O_3 concentration.

The refraction index consists of real and imaginary parts ($N = n - ik$)[2].
The refractive index can be expressed by [16]:

$$n = \left[\left(\frac{1+R}{1-R} \right)^2 - \left(K^2 + 1 \right) \right]^{1/2} + \frac{1+R}{1-R} \qquad (4)$$

Where K is the extinction coefficient, R is reflectivity and n is refraction index.
The extinction coefficient can be calculated by [11, 15]:

$$K = \frac{\alpha \lambda}{4\pi} \qquad (5)$$

Where λ is the wavelength of the incident ray.
The absorption coefficient α can be calculated by [17,11]

$$\alpha = 2.303(A/t) \qquad (6)$$

Fig. 3 Shows the variation of n as a function to energy of photon, the value of the refractive index increase as the doping percentage increased and it has a peak at (4.8eV), the refraction index

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decreases at the greatest wavelengths and increases at greatest dopant concentration. The behavior of the refraction index is same the reflectivity because the refraction index dependent on the reflectivity.

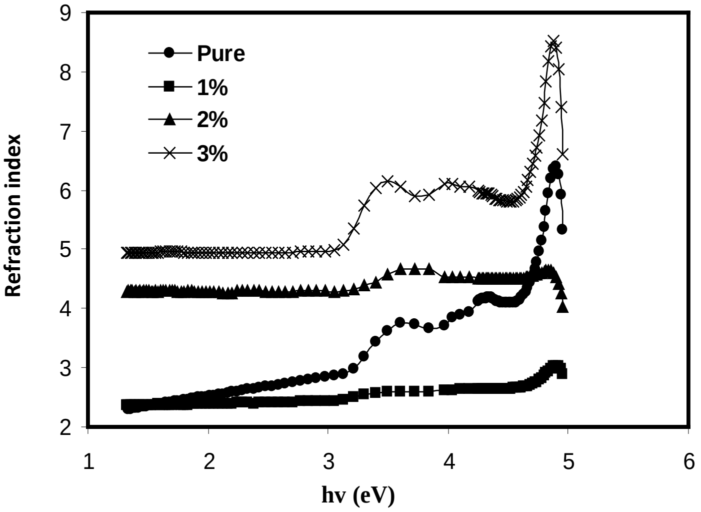

Fig. 3 The refraction index versus photon energy for pure PMMA and PMMA/C r_2O_3 with different Cr_2O_3 concentration.

The change of extinction coefficient as a function to wavelength is shown in Fig. 4. The behavior of the pure PMMA is different in comparison with doping films this result indicates that the dopant atoms of Cr_2O_3 will modify the structure of the host polymer. An interesting result is Cr_2O_3 dopant increases the absorbance in the visible region.

The relation between the complex dielectric constant and the complex refractive index N is expressed by:

$$\varepsilon = N^2 \qquad (7)$$

It can be concluded that:

$$(n - ik)^2 = \varepsilon_1 - i\varepsilon_2 \qquad (8)$$

The real and imaginary complex dielectric constant can be expressed by equation [4,14]:

$$\varepsilon_r = n^2 - k^2 \qquad (9)$$

$$\varepsilon_i = 2nk \qquad (10)$$

The dependence of ε_r and ε_i on photon energy are shown in Figs. (5 and 6). The ε_r values are higher than ε_i values because of the ε_r they are dependent on n while ε_i dependent on k values. Where the values of real part undergoes rising and falling and this behavior is similar to the behavior of refractive index according to equation (9), also from Figs. (5 and 6) it is seen that the ε_r and ε_i values increase with increasing photon energy and decrease with the doping concentration of Cr_2O_3. It is concluded that the variation of ε_r mainly depends on n^2 because of small values of k^2, while ε_i mainly depends on the k values which are related to the variation of absorption coefficients [2].

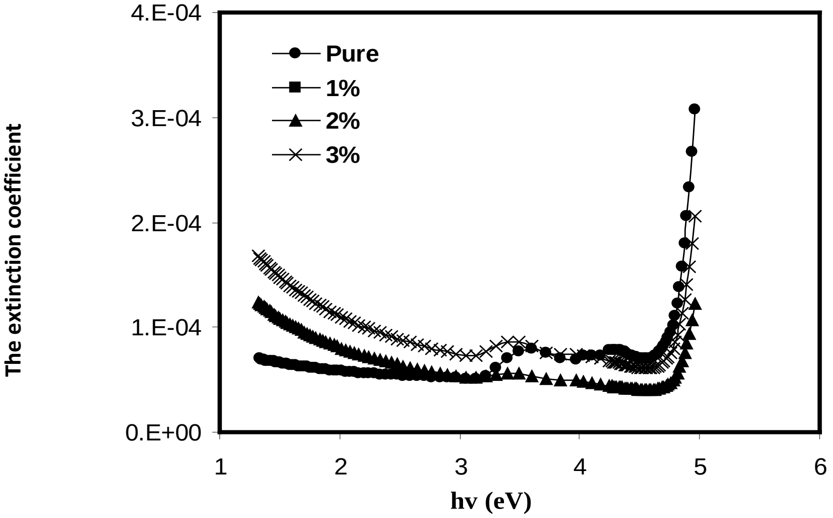

Fig. 4 The extinction coefficient versus photon energy for pure PMMA and PMMA/Cr_2O_3 with different Cr_2O_3 concentration.

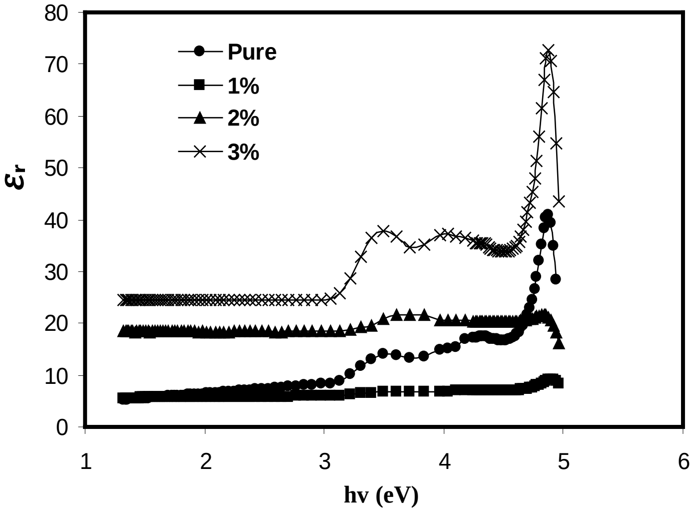

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Fig. 5- The real part of dielectric constant versus photon energy for pure PMMA and PMMA/Cr_2O_3 with different of Cr_2O_3 concentration.

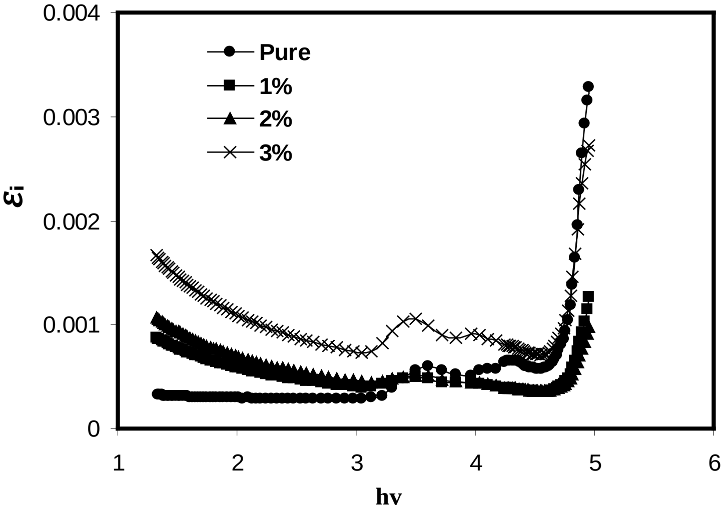

Fig. 6- The imaginary part of dielectric constant versus photon energy for pure PMMA and PMMA/Cr_2O_3 with different Cr_2 O_3concentration.

The FTIR spectra of PMMA and PMMA/Cr_2O_3 films are shown in Fig.7. The FTIR spectrum of PMMA show in Fig. 7(a) indicates the details of functional groups present in the PMMA. A intense peak appeared at 2999 and 2954 cm^{-1} due to the presence the CH stretching vibration. The peak ranging from 1737-1710 cm^{-1} can be refer to the C-O double bond stretching vibration. The peak ranging at 1433-1483 cm^{-1} is attributed to the presence of CH_3 and CH_2 deformation vibration. The peak ranging at 1134-1272 cm^{-1} and the peak at 966 cm^{-1} are assigned to C-O-C cm^{-1} single bond stretching vibrations [18,19,20]. Fig.7(b) shows the FTIR spectra of PMMA/Cr_2O_3 films. The new peak at 441 cm^{-1} may be refer to Cr_2O_3.

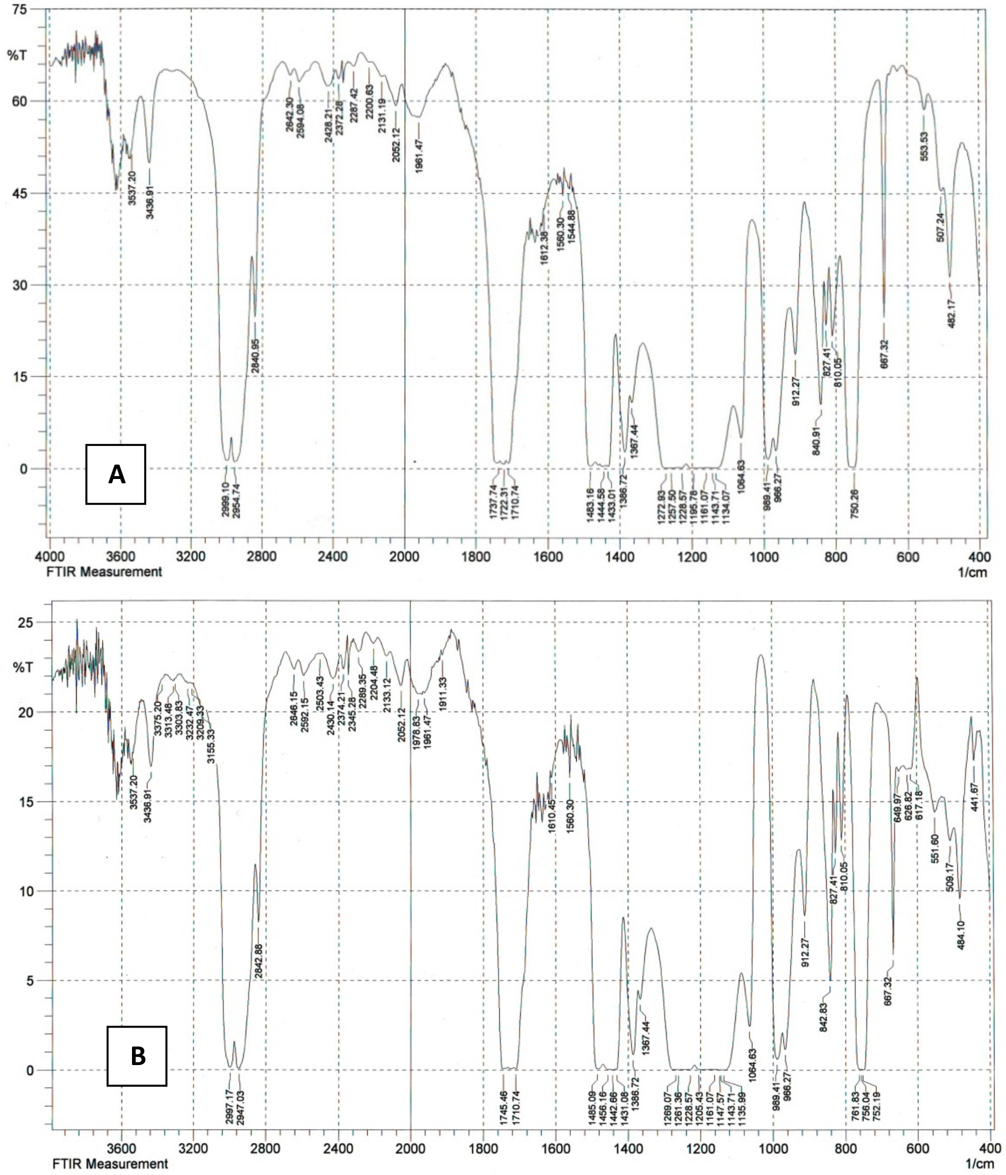

Fig.(7) The FTIR spectra for A) pure PMMA and B) PMMA/Cr_2O_3 at 3% films.

4. Conclusion

The pure PMMA and PMMA/Cr_2O_3 films with the different concentration have been prepared successfully by casting method, the Cr_2O_3 are effectively modifying the optical properties of PMMA films. The refractive index in the optical region has been found to be increases with the increasing doped content and photon energy of incident light. Also noticed that the extinction coefficient has unsystematic behavior with increasing Cr_2O_3 concentration in PMMA films.

The FTIR spectra appearance show a new peak at 441 cm^{-1} may be refer to formation bond between Cr_2O_3 and PMMA.

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