Optical properties of crystal violet doped PMMA films

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ABSTRACT

Optical properties of crystal violet doped polymethyl methacrylate (PMMA) films were studied. Absorption and transmission spectra were measured from UV-Visible spectrophotometer. Reflection spectra was calculated for all samples. CV- PMMA samples were prepared by casting method. CV solution was 0.5×10^{-4}mol/liter, and different amount of this solution as (2, 5, 10, 15, 25, 35, and 40) ml were added to get CV- PMMA films. Energy band gap was calculated for CV dye equal to 2eV and for PMMA 5eV and calculated for all CV-PMMA films which about (1.92- 1.98)eV. Also, all optical constants (absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constant) were measured for all samples. Morphology behavior and FTIR spectrum and X-ray diffraction were illustrated and compared with other researchers.   © 2013 Trade Science Inc. - INDIA

INTRODUCTION

In recent years, one of the most important and useful laser dye is crystal violet that have received much attention in physical chemistry from both fundamental and applied researches[1]. Also, crystal violet is a triphenyltmethane dye. It is antimicrobial, mutagenic, and used to prevent fungal growth in poultry feed[2-5]. It is used as a bacteriostatic agent in medical solution[6,7], so this property benefit to treat skin infection by staphylococcus aurous[7,8]. Crystal violet is one of the dyes that alters in many studies concerning molecular structures[1,9], electronic state, so that there are many applications for it in the sensors[10], light emitting diodes[11,12].

The optical properties of this dye can be easily tuned by controlling contents of different concentrations of dye solution and different weight of poly-

mers[13]. Several efforts to develop components based on solid –state matrices with embedded dye are concentrated in pure polymers, the thermoplastic PMMA is considered as one of the most efficient dye matrices with excellent optical properties[14]. One of very important applications in polymer film doped dye; it used in humidity measurement and control in industry and other fields require an accurate and reproducible determination of the water vapor concentration in moist air[15].

In present work, we aim to synthesis the optical constants such as refractive index, extinction coefficient, real and imaginary part of dielectric constant and calculate energy band gap for crystal violet doped poly (methylmethacrylate) films in different doping ratio of CV solution. Also, the microstructure and FTIR spectrum were studied for all films and show the effect of change of doping ratio of CV solution on it.

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EXPERIMENTAL WORK

The host material is a hard and rigid polymer with outstanding clarity and good outdoor weathering[14]. Polymer present some important advantages as they usually show good compatibility with organic dyes and excellent optical homogeneity[16]. Then polymer PMMA will obviously induce structural absorption changes and good transparency and good solubility with this dye. Crystal violet (CV) or called methyl violet (2B), has chemical formula $C_{24}H_{27}N_3HCl$ with molecular weight $M_w=393.95$ gm/mol[17]. Both dye and polymer are soluble by the solvent chloroform ($CHCl_3$).

The dye solution with concentration 0.5×10^{-4} mol/liter is prepared according to the method mentioned in ref. [18]. The dye doped polymer films are prepared by casting method. Certain amounts of polymer PMMA powder (0.5gm) were dissolved in (10ml) of solvent chloroform. Then, different ratio of dye solution (2, 5, 10, 15, 25, 35, 40)ml were added to polymer solution and mixed very well. The mixture poured in glass petri dish with (10cm) diameter and left to dry for 24hr at room temperature about (25 C) to get homogeneous films. The thickness of films was measured by digital micrometer and it about (0.55)mm.

The absorption, transmission spectra of dye solution and dye doped polymer films were achieved by the UV-Visible spectrophotometer type (Cary 100 Conc, UV-Visible, Spectrophotometer Varian, EL04113001).

The microstructure behavior was achieved by optical microscope type (Bel Etaly Photonics) with digital camera (X10). FTIR spectra were performed by FTIR spectrophotometer type (Shimadzu- 8400). Also, X-ray diffraction was be taken for all samples.

RESULTS AND DISCUSSION

(Figures 1 and 2) illustrate the absorption A and transmittance T spectra of CV-PMMA films with different doping ratio of dye solution (2, 5, 10, 15, 25, 35, and 40) ml which measured by UV- spectrophotometer. Reflectance R was calculated from the relation[19]:
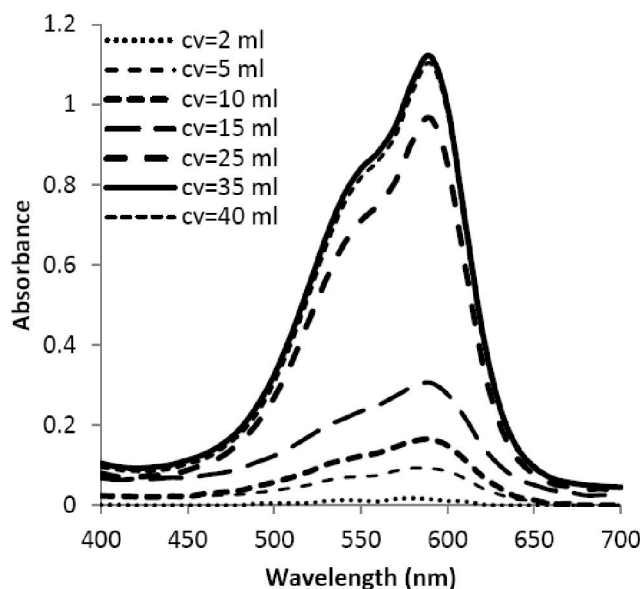
$$A + T + R = 1 \tag{1}$$

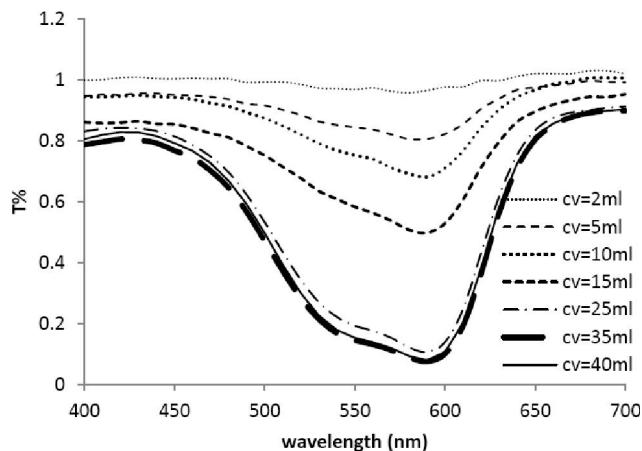**Figure 1 : Absorption spectrum of CV- PMMA films in different doping ratio of CV solution**

Figure 2 : Transmittance spectrum of CV- PMMA films in different doping ratio of CV solution

Reflection spectra for different doping ratio of CV in CV-PS films was shown in Figure 3.
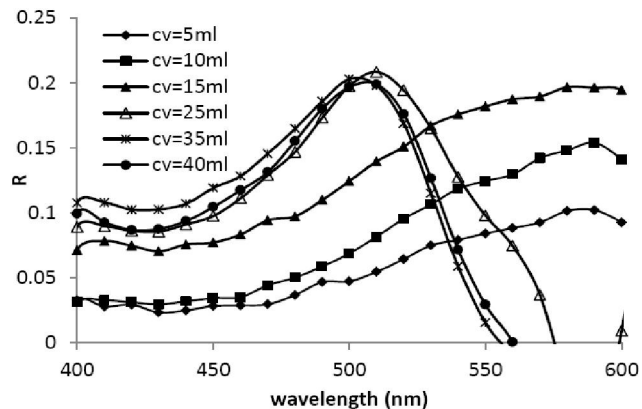

Figure 3 : Reflection spectrum of CV- PMMA films in different doping ratio of CV solution

It is clear that the transmittance Figure 2 declare reduction in its value; i.e. increase absorbance Figure 1, with increasing the doping ratio of CV solution. Moreover, T decreases from 1 to 0.07 for 5ml to 40ml doping ratio, respectively. This indicate that films become more opaque or less transparent with increasing doping ratio, this behavior reflects as an increment in refractive index (n) and extinction coefficient (k) values as a result of increasing doping ratio (see TABLE 1, and as shown in (Figures 4 and 5), respectively.

TABLE 1 : The value of energy band gap

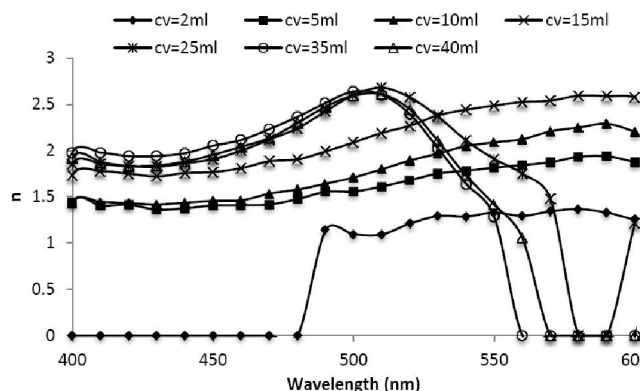| Doping ratio of (CV)	Pure PMMA	Pure CV	2ml	5ml	10ml	15ml	25ml	35ml	40ml
Energy gap of CV-PMMA (eV)	5	2	1.92	1.92	1.95	1.96	1.98	1.98	1.96

Figure 4 : Refractive index of CV-PMMA films for different doping ratio of CV solution.
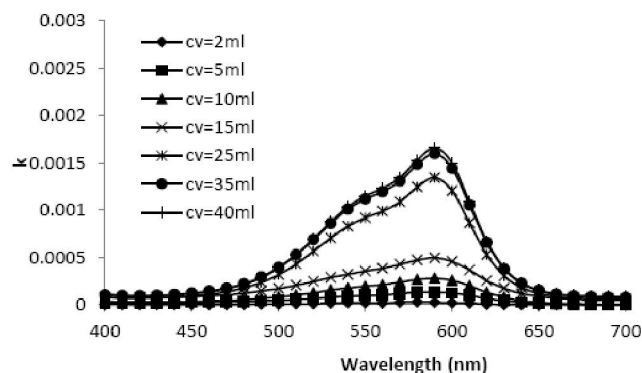

Figure 5 : Extinction coefficient of CV-PMMA films for different doping ratio of CV solution

These optical constants; refractive index (n) and the extinction coefficient k were computed from these relations[20,21]

$$n = (1 + R^{1/2}) / (1 - R^{1/2}) \qquad (2)$$

$$K_0 = \alpha \lambda / 4\pi \qquad (3)$$

Where α is absorption coefficient, which was calculated

$$\alpha = 2.303 \, A/t \qquad (4)$$

λ: wavelength of incident light (in nm).

The increase of n values with increasing doping ratio ascribes to increase the number of CV molecules into CV-PMMA films that led to increase absorbance and make the films more dense which in turn decreases propagation velocity of light through them that resulting to increase (n) values. While, (n) represent the ratio of light velocity through vacuum to velocity through any material. Then, the material become more opaque to the incident light thus the velocity of light decreases and consequently n and k increases[22].

Also, the complex dielectric constant that characterizes the optical properties of the solid material can be calculated as follows[19-21]

$$\varepsilon = \varepsilon_r + i\varepsilon_j \qquad (5)$$

The ε_r and ε_i describe the real and imaginary parts of dielectric constant, respectively and determined by the following relations.

$$\varepsilon_r = n^2 - \kappa^2 \text{ (realpart)} \qquad (6)$$

$$\varepsilon_i = 2n\kappa \text{ (imaginarypart)} \qquad (7)$$

Figures 6 and 7 show the real and imaginary part of dielectric constant for CV-PS films and for all doping ratio of CV solution, respectively. It is concluded that the variation of ε_r mainly depend on the value of (n^2) because the smaller value of (k) comparison with (n^2), while the (ε_i) mainly depend on (k) values which are related to the variation of (α).

The determination of band gap energy (E_g) is often necessary to develop the electronic band structure of film material. Absorption coefficient (α) is related to the energy (E) of the incident photons by the relation[21].

$$\alpha h\nu = B \, (h\nu - E_g^{opt})^r \qquad (8)$$

Where B : constant depended on type of material; ν: frequency of incident photon; r : exponential constant, its value depended on type of transition; where r =1/2 for allowed direct transition; r =3/2 for the forbidden

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direct transition; r =2 for allowed indirect transition; r =3 for the forbidden indirect transition.

So that, the energy gap can be obtained by plotting $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ in the high absorption range followed by extrapolating the linear region of the plots to $(\alpha h\nu)^{1/2}=0$.

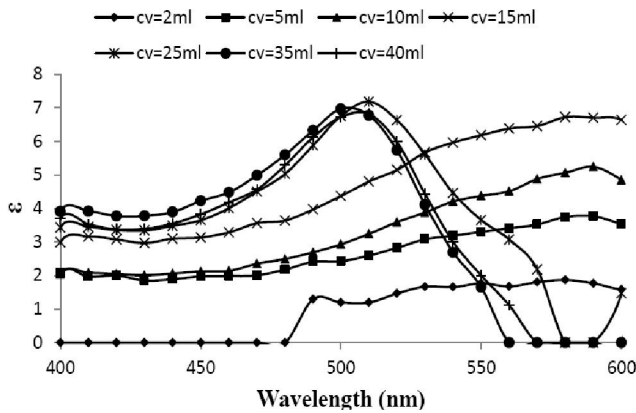Figure 8 shows the relation between $(\alpha h\nu)^2$ and photon energy for pure PMMA film and calculate the en-

Figure 6 : Real part of dielectric constant of CV-PMMA films for different doping ratio of CV solution.
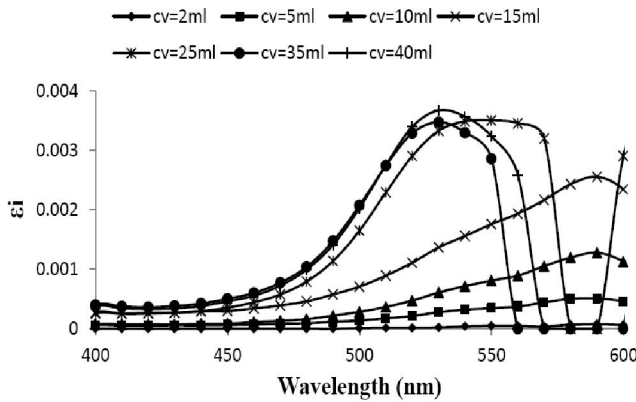

Figure 7: Imaginary part of dielectric constant of CV-PMMA films for different doping ratio of CV solution

ergy gap to be $(E_g=5ev)$ that is satisfied with the result obtained by Svorcik et al[23]. While, (Figures 9-11) illustrated the relation between $(\alpha h\nu)^{1/2}$ and photon energy for CV solution, CV-PMMA with different doping ratio 5ml and 40 ml, respectively. The energy gap for all films was calculated and mentioned in TABLE 1. The energy gap for CV solution is 2ev as match with Abbas and Zahraa[24], and decreased for doping with polymer PMMA to be from 1.92ev to 1.96ev (see TABLE 1).

Also, the microstructure behavior of PMMA polymer film was demonstrated in Figure 11. Homogeneous
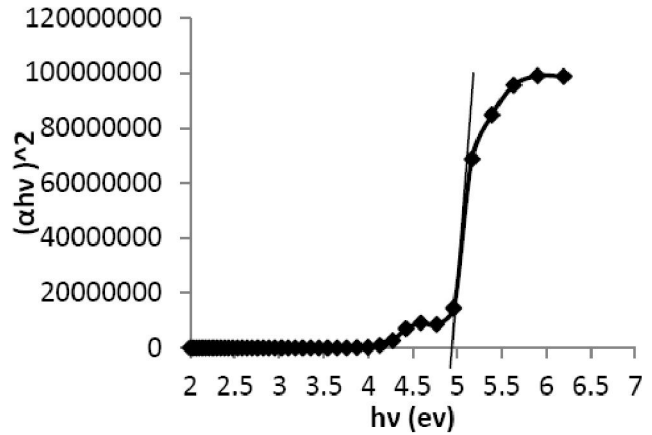

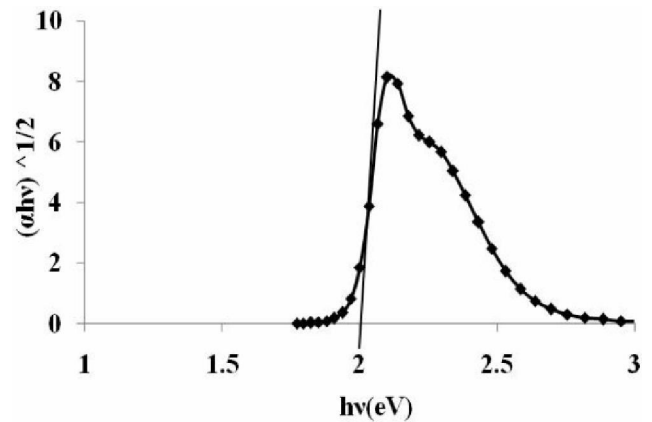Figure 8 : Energy band gap of pure PMMA film
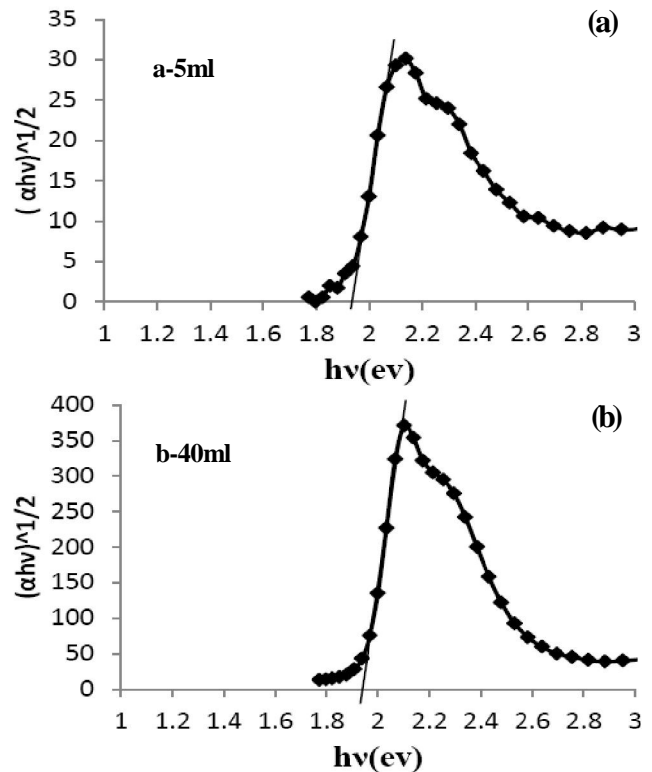

Figure 9 : Energy band gap of CV solution

Figure 10 : Energy band gap for CV-PMMA with doping ratio

structure was shown in these films and this behavior similar to studies of Dubey et. al.[25], and Al- Kadhemy et.al.[26]

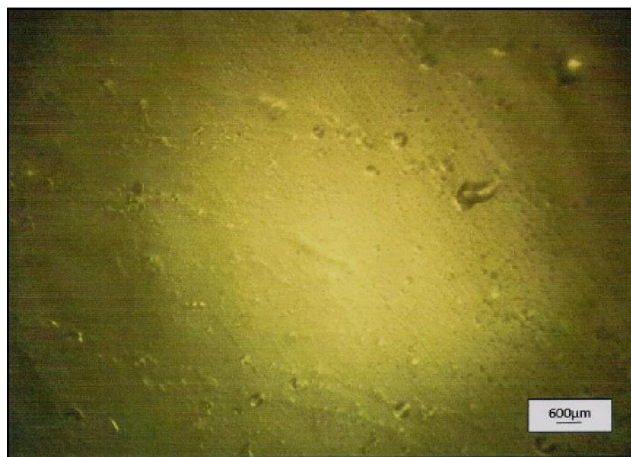The X-ray diffraction pattern for pure PMMA and CV-PMMA films show the amorphous structure for all

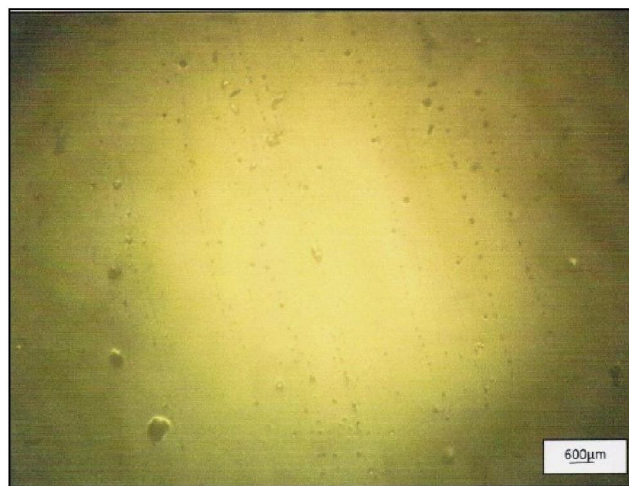**Figure 11 : Microstructure of pure PMMA film**

Figure 12 : Microstructure of CV- PMMA film with doping ratio

films, this will be match with work of Sava et al.[27]. The role of crystal violet dye clear to increase the amorphous of polymer by increasing the intensity of X-ray spectrum.

The most importance of (FTIR) spectroscopy is to identify the main characteristics peaks of crystal violet dye, PMMA, and CV- PMMA with different doping ratio of CV dye. All (FTIR) spectra are taken in transmission mode. Figure (14) shows the FTIR spectrum of (CV) dye and compared with chemical formula of this dye, as in Figure 1. There have more than one peak obtained in region of the C–H bending vibrations (900–600 cm^{-1}) can support the presence of an aromatic

structure. In region (1200-1000 cm^{-1}), there is a peak at 1062 cm^{-1} refers to C–H bending vibrations, and a peak at 1168.90 cm^{-1} corresponds to the C-N stretching vibrations. The benzene rings very clear which is supportive to the peak at 1583.61 cm^{-1} that acts the C= C stretching of the benzene ring, and a peak at 2917.14cm^{-1} for C–H stretching with asymmetric CH_3 group. FTIR spectra of this dye shows the presence of two bands (3219.3and 3093.92cm^{-1}) allot to N–H stretching vibrations of primary amines[28].

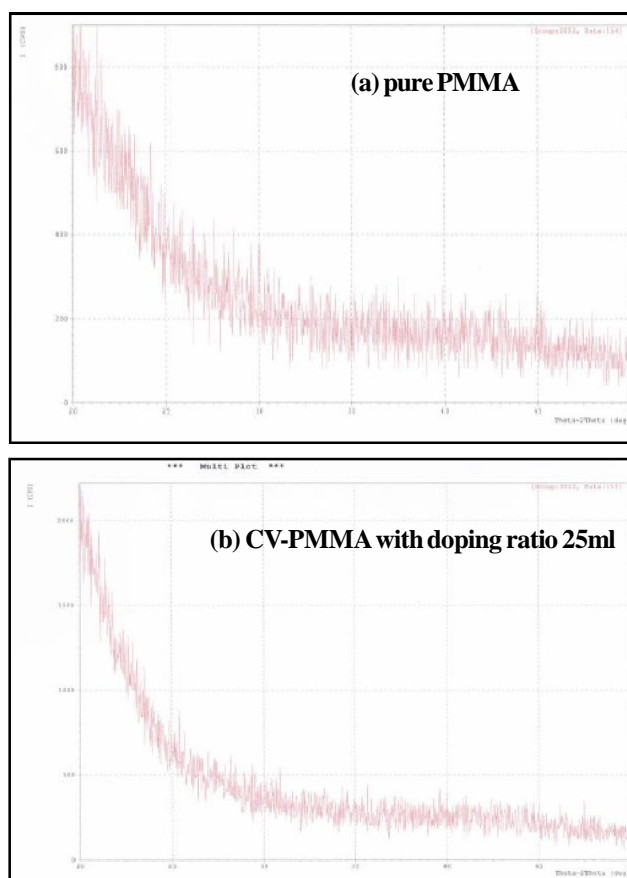The FTIR spectrum of pure PMMA polymer was shown in Figure 15 and as acompared with a chemical

(a) pure PMMA

(b) CV-PMMA with doping ratio 25ml

Figure 13 : X-ray of films

formula of this polymer as in Figure 2. The transmission bands corresponding to CH_2 twisting, wagging and rocking modes of PMMA are appeared at 989 and 763 cm^{-1}. The peaks (1246 and 1274 cm^{-1}) correspond to the C- O stretching vibrations of δ ester groups. The characteristic peak at 1386.86 cm^{-1} is appeared due to O-CH_3 deformation of PMMA. The transimission around 1435 and 1487cm^{-1} characterize the asymmetric bending vibrations of (C- CH_3) and (C- CH_2) bonds,

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respectively; the C-O stretching vibration of ester group appears around 1730 cm^{-1}, and the,and –CH$_3$ asymmetric stretching at 2951.19 cm^{-1} due. In addation three bands at 3473.26 cm^{-1}, 3551.07 cm^{-1}, and 3632.08 cm^{-1} refers to amine group that is useful to keeping the polymer from humidity. All peaks are compared with the results of other researchs[28], and showed a good matched with them.

The effect of addition (CV) dye to PMMA polymer on FTIR spectrum is shown in Figures (16 and 17)
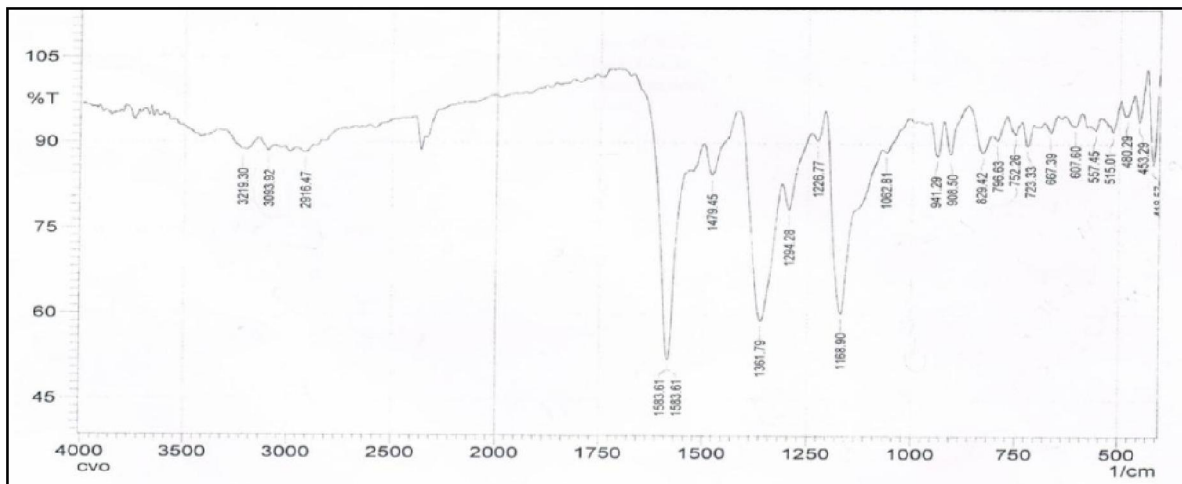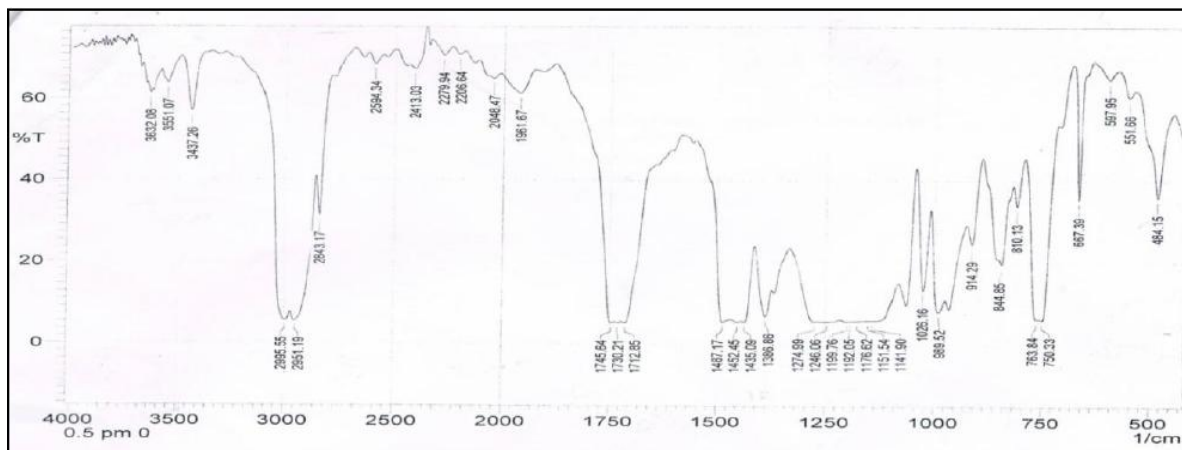

Figure 14 : FTIR spectrum of CV dye

Figure 15 : FTIR spectrum of PMMA polymer
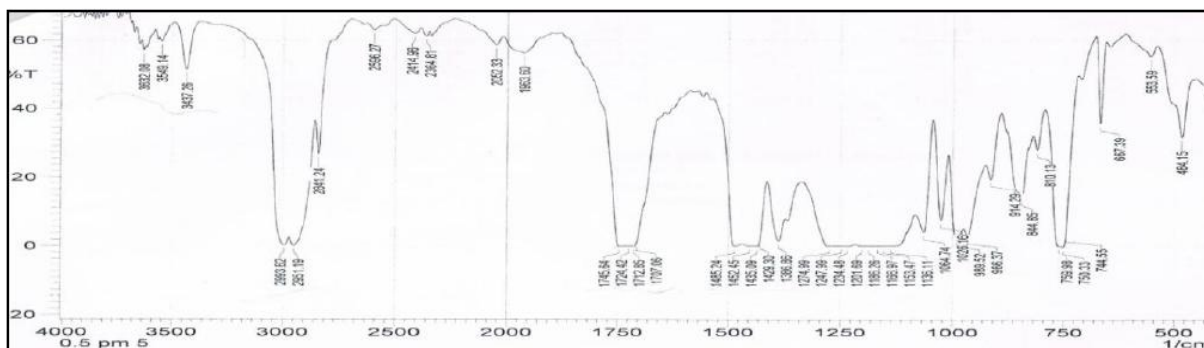

Figure 16 : FTIR spectrum of 5ml CV- PMMA polymer

for different doping ratio (5, and 40 ml), respectively. There is one peak (3010.98) cm^{-1} refers to (CV) dye appeared in all doping ratio, and all other peaks as the same for pure PMMA polymer.
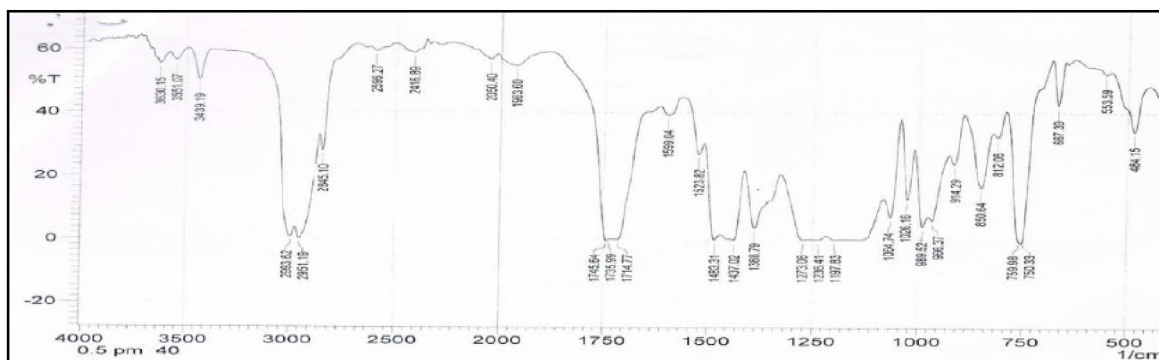
Figure 17 : FTIR spectrum of 40ml CV- PMMA polymer

CONCLUSIONS

Optical properties of crystal violet doped polymethyl methacrylate (PMMA) films were studied. Energy band gap for CV was 2eV and for PMMA 5eV and CV-PMMA about (1.92- 1.98) eV. Absorption coefficient, extinction constant, real and imaginary dielectric constant, and refractive index for all samples were synthesized. XRD measurements showed the amorphous structure for both PMMA and CV-PMMA films. Microstructure behavior of PMMA film was flat and CV-PMMA become more homogenous. FTIR spectra of CV, PMMA, and CV-PMMA films were illustrated and showed that the effect of doping ratio of CV solution didn't affect on FTIR spectrum of PMMA.

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