Study of the Electronic Transitions of Polymethyl methacrylate (PMMA) doped with Red methyl

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Abstract
Thin films of pure poly(methyl methacrylate) (PMMA) and those doped with 2% red methyl dye were prepared using the spin- coating technique at room temperature. The optical properties of the films were investigated by recording their absorption and transmission spectra in the wavelength range of 300–900 nm. From the absorption spectra, the absorption coefficient was calculated to evaluate the optical transitions within the material. Detailed analysis was carried out to estimate the optical bandgap energies corresponding to indirect allowed and indirect forbidden electronic transitions. The results reveal significant modifications in the optical behavior of the PMMA matrix due to the incorporation of the red methyl dye, indicating changes in electronic structure and light interaction. These findings are essential for understanding the tunability of PMMA-based composites for potential applications in optoelectronic devices and functional coatings.

Keywords: PMMA films, Red methyl dye, Optical properties, Absorption coefficient, Optical bandgap.
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1. Introduction

Polymers have provided an alternative to industrial and scientific materials in work and laboratories, due to the unique properties of polymer molecules that have been incorporated into the optical materials industry [1]. PMMA boasts excellent chemical and physical properties [2,3]. Chemically, PMMA is resistant to acids and dilute alkaline chemicals, but it dissolves in strong and weak organic solvents such as benzene, and chloroform. Regarding its physical properties, PMMA is a thermoplastic polymer, at room temperature, it is a solid, clear material that can be cut and filed [4]. Temperature has an important effect on its formation, as the temperature increases, it becomes more malleable. Upon reaching $T_g = 102°C$, which represents the glass transition temperature of PMMA, its elasticity, stretchability, and formability begin to emerge, enabling it to be heat-formed into complex and diverse shapes. PMMA is also characterized by high transparency, as its practical light transmittance reaches 92% compared to the theoretical value of 92.3% at wavelengths 100-360 nm at a thickness of 2.54 cm. It is transparent to visible light, providing an alternative to glass for use as transparent protective panels in aircraft, factories, greenhouses, and laboratories in complex optical technologies such as lenses and prisms, due to its ease of manufacture and shaping, in addition to its low cost. Recently, it has been used in the field of smart detectors [5,6] due to its properties. Polymethyl methacrylate (PMMA) is also an important industrial material and is known commercially and industrially as organic glass (Organic Glass) or Perspex, which is widely used in the manufacture of geometric shapes, decorations, agricultural purposes, etc. [7].

To improve the industrial properties of polymers, selected materials with specific properties are added. Additives and auxiliaries enter with the polymer either as a physical mixture, dissolved in the polymer solution, or as surface layers, so that they do not affect the chemical composition of the polymer, but they affect the physical properties (mechanical, electrical, optical, etc.) by affecting the shape of the molecules and their composition (crystalline and amorphous). One or more chemicals are added to the polymer, such as a metal, a simple or complex salt, etc. [8], to obtain the desired properties. The mixture (polymer + additives) is called the polymer system [9,10].

2. Experimental part

Spin-coating method was used to prepare poly(methyl methacrylate) (PMMA) $[C_5H_9O_2]_n$, where n number of molecules, and organic dye red methyl ($C_{15}H_{15}N_3O_2$) thin films to ensure homogeneous films with a thin thickness. This method can be used to prepare samples with a relatively large area and uniform thickness depends on the area of the substrate [11].

The percentage of red methyl ($C_{15}H_{15}N_3O_2$) 2% was chosen as an impurity to give an idea of the effect of adding the organic dye, and to prevent the resulting thin films from having dark colors that affect the light transmittance, with the possibility of increasing the

percentage of the dye as an effective action on the properties of the films in the future and making films with an optical window for specific wavelengths.

The samples were prepared in the form of films composed of a mixture of pure polymer and red methyl. For polymer and dye films with a thickness of 20 microns and a weight percentage of 2%, the polymer was mixed with the dye and and then were dissolved in chloroform. The mixture was then mixed for two hours at room temperature to obtain a homogeneous viscous solution. The mixture solution was then applied to the substrate by the spin coating method.

Rapid rotation at approximately 1000 rpm yielded homogeneous thin films, for pure and doped polymer films 20 microns thick. The homogeneity of the thin film was confirmed using an optical microscope. The sample thickness was measured with a micrometer by measuring the thickness of the film with the substrate minus the thickness of the substrate. Transmittance and absorbance spectra were recorded using a UV-160A UV-VIS Recording Spectrophotometer manufactured by Shimadzu, Japan, over a wavelength range of 300-900 nm. All measurements were recorded at room temperature.

3. Results and Discussion

The absorption coefficient (α) was calculated in the primary absorption region according to the following relationship [12,13]:

$$\alpha = 2.303\ A/d \qquad (1)$$

where A is the absorbance, d is the film thickness

Figure (1) illustrates the relationship between the absorption coefficient and the incident photon energy for the pure and doped polymer film. We note from the figure that the change in the absorption coefficient at low energies is small, and therefore the probability of electronic transitions is low. However, at high energies, the change in the absorption coefficient is large, indicating a high probability of electronic transitions, which is the absorption edge region. The absorption coefficient helps infer the nature of electronic transitions.

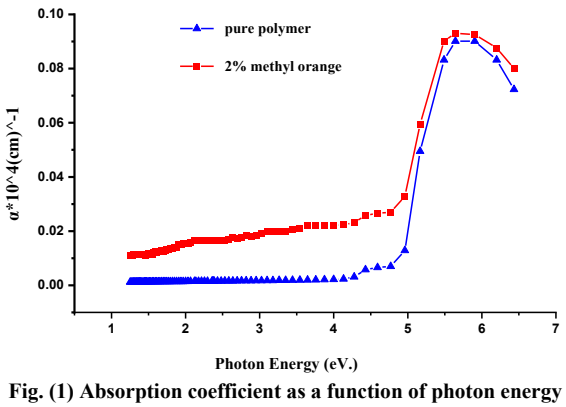


Fig. (1) Absorption coefficient as a function of photon energy

When the absorption coefficient values are high (10^4 cm^{-1} <α) at high photon energies, direct electron transitions are expected to occur, and the energy and momentum of the electron and photon are conserved. However, when the absorption coefficient values are low (10^4 cm^{-1} >α) at low photon energies, indirect electron transitions are expected to occur, in which the momentum of the electron and photon is conserved with the help of the phonon [14].

The results showed that the absorption coefficient values for the pure and doped polymers are less than 10^4 cm^{-1}, which suggests indirect electron transitions. The forbidden gap energy for indirect transition was calculated according to the permitted and forbidden types according to the equation [15,16]:

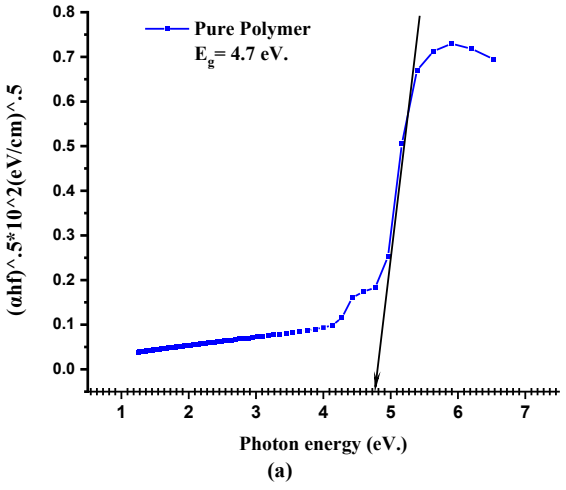
$$\alpha hf = B(hf - E_g \pm E_p)^r \qquad (2)$$

where hf represents photon energy (eV), B represents proportionality constant, E_g represents forbidden gap energy for indirect transition (eV), E_p represents associated phonon energy (eV), (+)represents phonon absorption, (-)represents phonon absorption

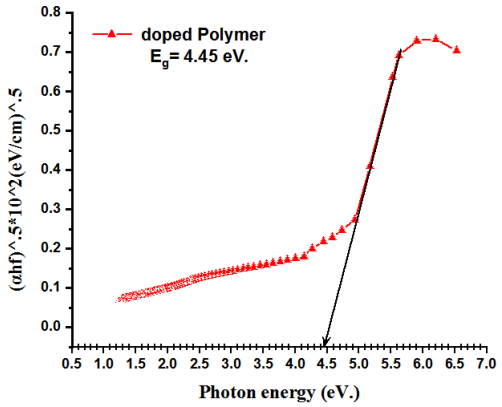
If r=2, indirect transition is permitted, then equation (2) becomes as follows: [17,18]:

$$(\alpha hf)^{1/2} = B^2 (hf - E_g \pm E_p) \qquad (3)$$

Figure (2a) represents the relationship between $(\alpha hf)^{1/2}$ and the photon energy of the pure PMMA polymer. By taking the extension of the straight part of the curve to intersect the photon energy axis at the point = 0 $(\alpha hf)^{1/2}$, we will get the value of the forbidden energy gap for the allowed indirect transition which is equal to 4.7 eV. Figure (2b) represents the same previous relationship but for the PMMA polymer doped with red methyl and in the same previous way we can get the value of the forbidden energy gap for the allowed indirect transition which is equal to 4.45 eV, where we notice that the value of the energy gap decreased after doping.



(a)



(b)

Fig. (2) The relationship between $(\alpha hf)^{1/2}$ and the photon energy of the pure and doped polymer thin films

4. Conclusions

In concluding remarks, doping increased the absorption coefficient. The results showed that the absorption coefficient was less than 10^4 cm^{-1}, indicating the occurrence of both allowed and prohibited indirect electronic transitions. Doping did not change the nature of the electronic transitions in the PMMA polymer films, but rather maintained their indirect nature. Doping reduced the energy gap.

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