Iraqi J. Polymers, Vol.4, No.1, 1-6, 2000

Study on Optical Properties of PMMA and the Effect of Graphite Addition

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ABSTRACT. Optical properties of polymethyl methacrylate were studied by recording the absorption spectrum in the wavelength range (200-900) nm at room temperature. The effect of graphite addition on the optical properties was also studied in according to the electronic transitions in polymers. The absorption behaviour with photon energy shows additional states due to wt% of graphite addition.

INTRODUCTION

The study of absorption and reflection spectra for a polymer film gives an information to determine some optical properties in different ranges of wavelenghts. The study in UV range leads to the types of bonds, orbitals, and energy bonds. In IR range, the polymer structure can be characterized and the constituent elements can be determined.

The nature of the excited states in polymer due to photon absorption depends on the nature of the upper occupied molecular orbitals and the lower unoccupied orbitals. Five types of molecular orbitals can be distinguished, σ and π bonding orbitals, σ^* and π^* antibonding orbitals, and non-bonding orbitals n. Three different transitions may occure, which are $\sigma \rightarrow \sigma^*$ (at UV region, 200 nm), $\pi \rightarrow \pi^*$ (at the common region between UV and visible regions), and $n \rightarrow \pi^*$ (at long wavelength) transitions [1]. These energy bonds closely looking with what was suggested by Frolich (1947) [2] for the bond structure of polymers. In which n-level is at depth v below the conduction band in the firbidden energy band. The type of bonding in polymer chain indicates the possible type of transition for each bond of the bonded atoms.

The electronic and the optical transitions in polymers is interesting subject to be investigated in terms of theories of non-crystalline solids. In the present work the optical properties of PMMA and the effect of graphite addition were studied in the view of absorption variation with photon energy.

EXPERIMENTAL

The commercial PMMA (atactic) was dissolved in acetone and then films were casted and kept for two days under constant temperature (15°C). The undoped films have high transparency and were homogeneous and flexible. Thin films of doped PMMA polymer were obtained by mixing the desired wt% of graphite powder in pure polymer solution followed by casting the viscous solution on dry glass sheet washed by acetone. The PMMA films doped with graphite powder of different wt% are listed in Table 1.

Table. 1

Specimen number	1	2	3
wt% graphite	0.00	7.40	28.50
Thickness	85 μm	45 μm	100 μm

The absorbance of the polymer films was recorded at room temperature using Pye-Unicam SP8-100 spectrophotometer in the wavelength range 200-900 nm.

RESULTS AND DISCUSSION

In the region of bond to bond transition, the absorption is large, so that the transmittance equation can be expressed by the relation

$$T = (1 - R)^2 e^{-\alpha d} \qquad \ldots\ldots (1)$$

where T is the transmittance through a wavelength absorbing slab of reflectivity R, d is thickness and α is the absorption coefficient in air. The absorption coefficient after correcting for reflection losses can be calculated from the relation [3]

$$\alpha(\nu) = \frac{2.303}{d} A \qquad \ldots\ldots (2)$$

where A is the absorbance (= - log T)

The absorption coefficient spectra versus photon energy for specimens listed in Table 1 are shown in Figure (1) and the transperancy in Fig.(2). The plot of log a versus hν was done to study the effect of photon energy and the effect of graphite addition on the absorption coefficient. The absorption edge for the three cases is also calculated by plotting $(\alpha h\nu)^{1/2}$ versus hν according to the theory of interband optical absorption [4] which shows that at the

absorption edge the absorption coefficient a varies with the photon energy hν according to the following expression expression, results are shown in Fig.3.

$$\alpha h\nu = C\,(h\nu - E_g)^N \qquad \ldots\ldots\ldots (3)$$

where C is constant and N is a number which characterises the transition process, being 1/2 for direct allowed and 2 for indirect allowed trnasition. This depends on the value of the absorption coefficient (α), if $\alpha > 10^3$ cm^{-1} the transition is direct, and if $\alpha < 10^3$ cm^{-1} the transition is indirect [5]. As shown from Fig. 1 $\alpha < 10^3$ cm^{-1}, so the transition is indirect and then N=2.

Fig. 1 shows the possible absorptions and transitions for the three specimens. At the range 5.3-6.3 eV is the fundamental absorption region and at 3.7 eV is the absorption edge while at the region 3.7 - 5.0 eV is the a $\sigma \rightarrow \sigma^*$ transition. At 3.3 eV is the $\pi \rightarrow \pi^*$ transition. At the range 1.5 - 3.3 eV is the additional absorption that can be attributed due to the presence of the graphite in the PMMA matrix which in due to different mechanisms of absorption. At the range 2.0-3.0 eV is the exciton absorption while 1.5 eV the absorption is due to free carriers produced by the graphite [6] in which the wt% addition of graphite is very clear which is increased with increasing the wt% addition of graphite. At the range 1.57 - 2.00 eV is the $n \rightarrow \pi^*$ transition. The additional absorption at the energy 1.5 eV have values 2, 8 and 20 cm^{-1} for pure PMMA, 7.40% and 28.57% respectively.

The absorption edges Eg shown in Fig.3 are tabulated in Table 2. which are of slight difference for different wt%. The constant C was calculated by using the slope of the linear part of Fig.2 in the followinf relation [5]:

$$C = \frac{\alpha h\nu}{(h\nu - E_g)^2} \qquad \ldots\ldots\ldots (4)$$

and the unit of C was calculated according to $cm^{-1} \cdot eV^{(1-N)}$ [7]

Table. 2

Sample	Eg (eV)	Const. C ($cm^{-1}.eV^{-1}$)	ΔE (eV)	mobility gap $E_g+\Delta E$ (eV)
Pure	3.42	625.0	0.09	3.51
7.40%	3.46	4604.6	0.07	3.53
28.57%	3.52	2640.8	0.09	3.61

The obtained results show that E_g tends to increase with the graphite filler concentration.

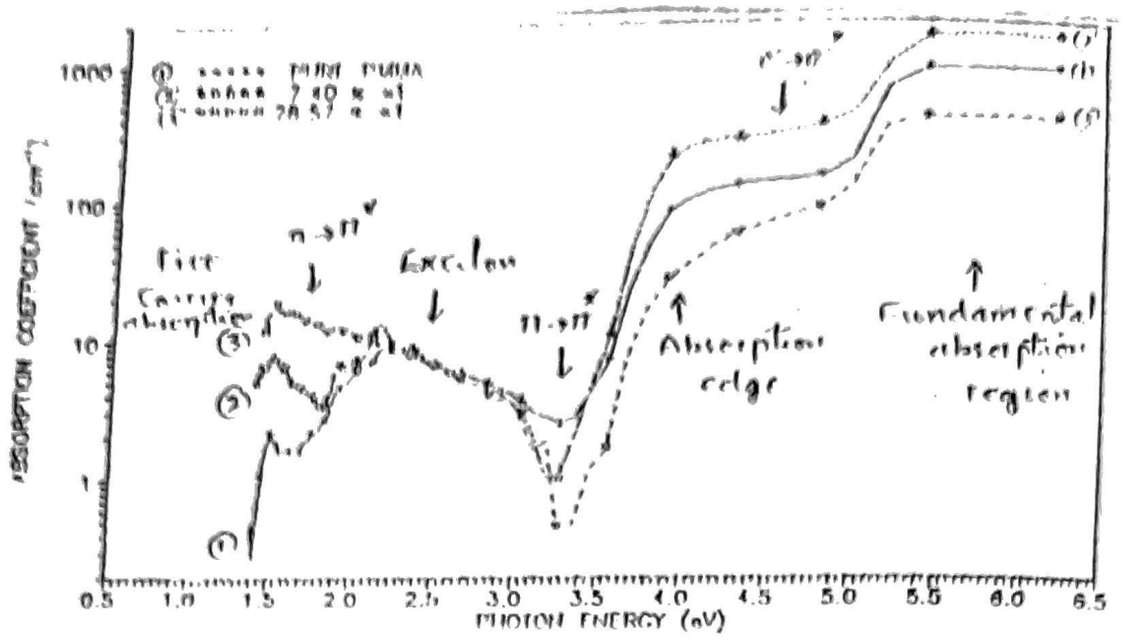
ABSORPTION COEFFICIENT (cm⁻¹)
PHOTON ENERGY (eV)
Exciton
Absorption edge
Fundamental absorption region

Fig.1

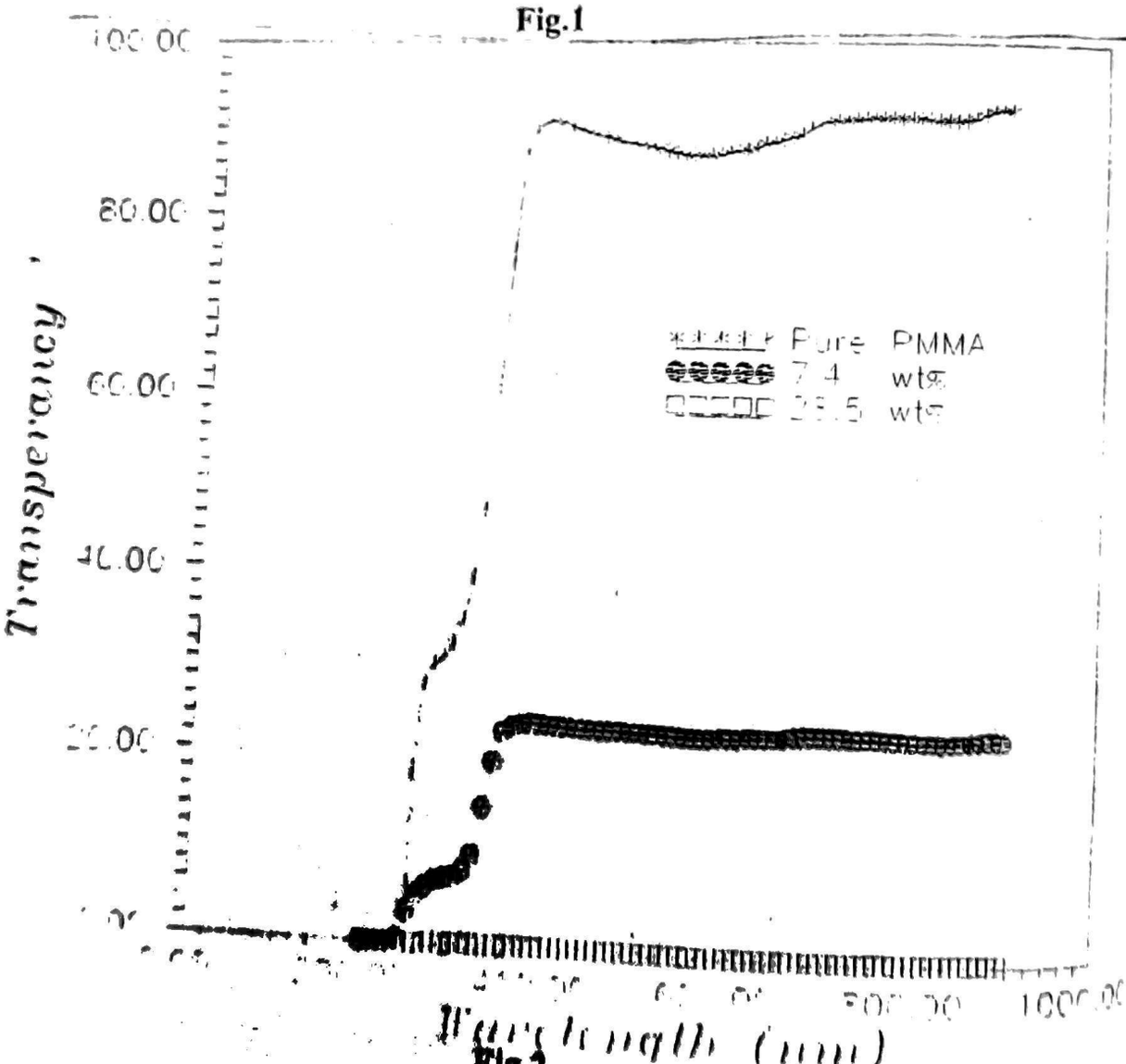
Transparency
Wavelength (nm)
Pure PMMA
7.4 wt%

Fig.2

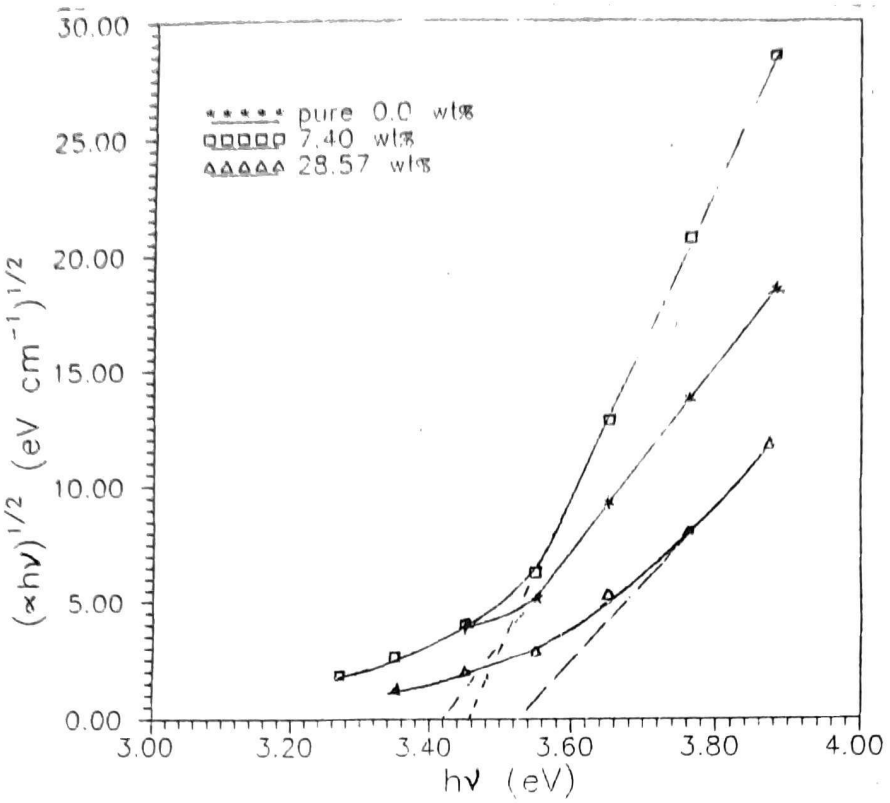
pure 0.0 wt%
7.40 wt%
28.57 wt%
$(\alpha h\nu)^{1/2}$ (eV cm^{-1})$^{1/2}$
hν (eV)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
3.00
3.20
3.40
3.60
3.80
4.00

Fig.3

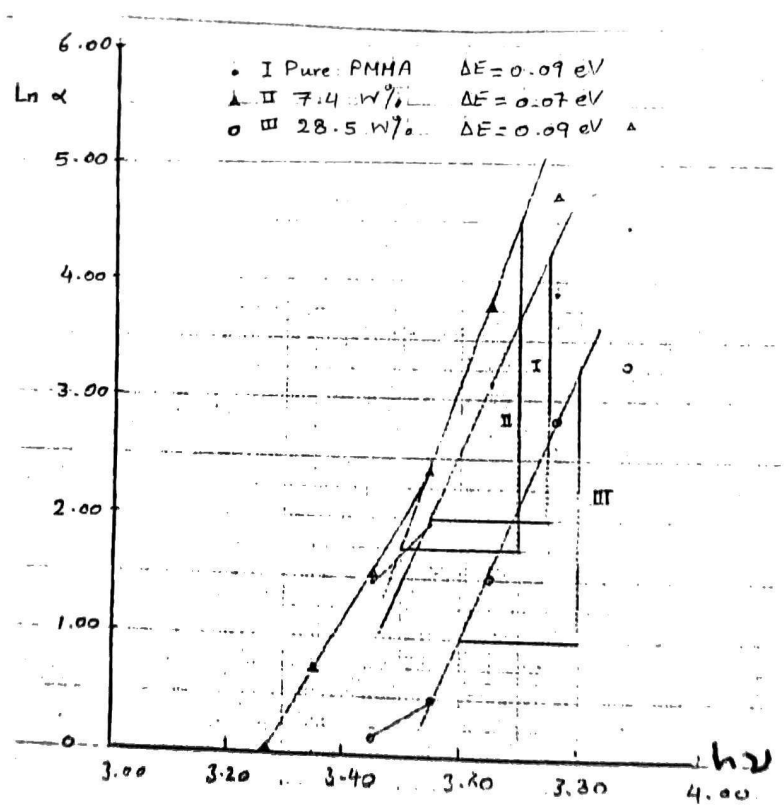
I Pure PMMA ΔE = 0.09 eV
II 7.4 W% ΔE = 0.07 eV
III 28.5 W% ΔE = 0.09 eV
Ln α
hν
6.00
5.00
4.00
3.00
2.00
1.00
0
3.00
3.20
3.40
3.60
3.80
4.00

Fig.4

To know the effect of graphite on PMMA matrix the absorption coefficient $\alpha(h\nu)$ is described by Ubrach formula [5]

$$\alpha(\nu) = \alpha_o e^{h\nu/\Delta E} \quad \ldots\ldots\ldots (4)$$

where α_o is constant and ΔE is the width of the tail of localized states in the forbidden band gap. The plot of $(\ln \alpha)$ versus $(h\nu)$ is shown in Fig.4 which represents the Ubrach rule. The term $(E_g + \Delta E)$ represents the mobility gap [5], which is increased with increasing the filler concentration. Thus, we expect the decrease in electrical conductivities with increasing the filler concentration.

Conclusion

The behaviour of the optical absorption in the UV-visible region for PMMA polymer and the effect of graphite addition is studied. Additional absorption is occurred at energy of 1.5 eV which can be attributed due to the free carriers generated by the graphite addition to the PMMA matrix. In addition to that the graphite is also affect the fundamental absorption at UV-region (3.5-6.5 eV). The graphite addition with low wt% (about 7.40%) will increase the absorption while the high wt % addition of graphite will decrease the absorption at the fundamental absorption region.

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المستخلص

درست الخواص الضوئية للبوليمر PMMA وذلك بقياس طيف الامتصاص في مدى الاطوال الموجية (200-900 nm) في درجة حرارة الغرفة. درس كذلك تاثير اضافة نسب معينة من الكرافيت على الخواص الضوئية حسب نظرية الانتقالات الالكترونية في البوليمرات. اظهر سلوك الامتصاص مع تغير طاقة ثانوية اضافية بسبب اضافة الكرافيت.