FTIR and UV-Visible Studies in 5(6) Carboxyfluoresceine doped PMMA

Renuka Sali, L.R.Naik*

Department of Physics, Karnatak University,Dharwad-580003, India
Corresponding Authors Email: naik_40@rediffmail.com

Abstract— The effect of 5(6) Carboxyfluoresceine dye on microstructural and optical properties of the polymer Poly (methyl methacrylate) (PMMA) is studied. The FTIR study shows the appearance of new peaks and shift in bands indicates the interaction of 5(6) Carboxyfluoresceine with PMMA. UV-Visible spectrum shows two peaks around 338nm and 458nm.The corresponding two optical energy band gaps and two activation energy band gaps are observed. These results are understood based on charge transfer complex (CTC) formation.

Keywords—5(6) Carboxyfluoresceine dye, PMMA, Optical Properties, CTC

I.   INTRODUCTION

In recent years, dye doped polymers with different optical properties have been attracted much attentions due to their wider applications in the sensors, light-emitting diodes, electronics, biotechnology, photonics[1-3]. The optical properties of these materials can be certainly modified by controlling contents of the different concentrations. Dyes have been doped in many kinds of solid hosts, such as organic modified silicates different glasses, polymethyl methacrylate (PMMA), methyl methacrylate (MMA) [4, 5] etc. PMMA has been recognized as an excellent optical polymer for use in optical fibers, optical disk and lenses it is an important thermoplastic material with admirable optical transparency and low birefringence [6, 7].

5(6) Carboxyfluoresceine (5(6) CF) is fluorescent dye, molecule with a hydroxyl group added. They are commonly used as tracer agents and also have applications in fluorescence microscopy, flow cytometry, in industrial sectors and biomedical fields etc. [8]. When dye is doped with the polymer, the dopant can modify the molecular structure as well as the microstructural property of the polymer. It is observed that doping a polymer with dye has significant effect on their physical properties including optical properties also depends on chemical nature of the dopant and the way in which they interact with the host polymer. In view of this in the present work the effect of 5(6) Carboxyfluoresceine on optical and microstructural properties of the polymer PMMA are studied.

II.   EXPERIMENTAL

The polymer PMMA used in this work is obtained in powder form from M/s. s.d. fine-Chem. Ltd, Mumbai and the 5(6) Carboxyfluorescein dye is obtained from Aldrich chemical co, USA. The 5(6) Carboxyfluorescein doped PVA films were prepared by solution casting method using DCM organic solvent [9]. The FTIR spectra of the prepared films were obtained using NICOLET FTIR-6700. UV-Vis study was performed using SHIMADZU (UV-1601) spectrometer in the wavelength range 195-700nm. Structure for PPMMA and 5(6)Carboxyfluorescein dye is given in Figure 1.
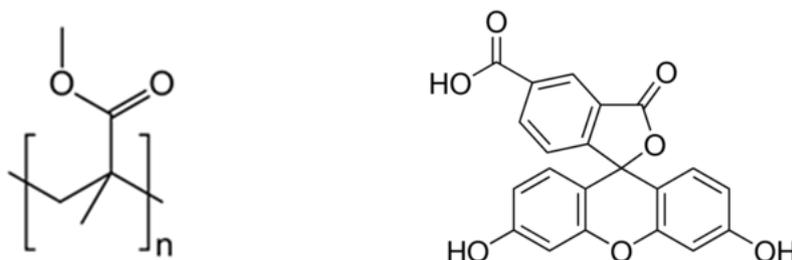
Figure1: Chemical structure of PMMA and 5(6) Carboxyfluorescein.

III. RESULT AND DISCUSSIONS

3.1. FTIR Studies

FTIR measurements were carried out to investigate the nature of chemical effect caused by doping and is used to identify the various functional groups present in the polymeric matrix. FTIR spectra of pure and 5(6)Carboxyfluorescein doped PMMA films are shown in Figure 2. and the corresponding band assignments are tabulated in Table 1.
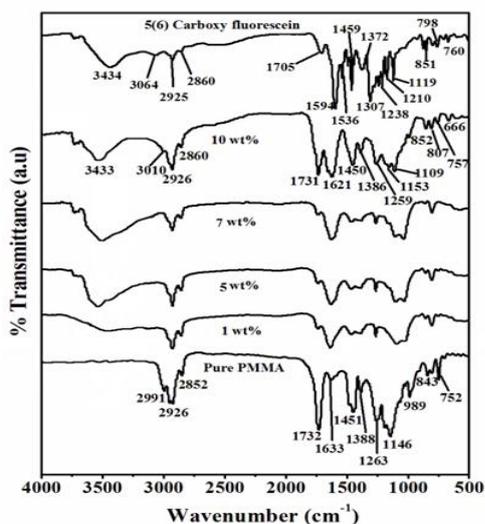

Figure 2: FTIR spectra for the pure and 5(6) Crboxyfluorescein doped PMMA

The peaks at $2991cm^{-1}$ and $2852 cm^{-1}$ observed for pure PMMA have been shifted to $3010cm^{-1}$ and $2860 cm^{-1}$ respectively , which are assigned to C-H stretching vibration and CH_2 stretching vibration of the polymeric composite. The broad peak was observed at $3433cm^{-1}$ for the composite was due to stretching vibrations of the O-H group in 5(6) CF with increasing concentration. The sharp peak at $1732cm^{-1}$ observed for pure PMMA is assigned to C=O stretching vibration, which is slightly shifted to $1723cm^{-1}$ after doping.

Table 1: FTIR peak assignments for pure 5(6) CF doped PMMA

Pure PMMA Wavenumber (cm^{-1})	Peak Assignment	5(6) CF doped PMMA Wavenumber (cm^{-1})
-----	O-H stretching vibration	3433
2991	C-H stretching vibration	3010
2926	C-H symmetric stretching	2926
2852	CH$_2$ stretching vibrations	2860
1732	C=O stretching vibration	1731
1633	C─H bending vibrations	1621
1451	C-H bending vibration	1450
1388	O-H stretching vibration	1386
1263	C-O Streching vibration	1259
1146	C-O asymmetric stretching	1153&1109
989	O-CH$_3$ – rock	980
843	CH$_2$ bending-rock	807

The peak at 1146cm^{-1} for pure PMMA splits into two peaks in the region 1153cm^{-1} and 1109 cm^{-1}. The peaks 1594 cm^{-1} and 1536 cm^{-1} for pure 5(6) CF was disappeared in 5(6) CF doped PMMA this indicates that considerable interaction between 5(6) CF and PMMA All these modifications in the FTIR spectra such as shifting in the band positions and variations in the band intensities indicates the possible interaction between PMMA and 5(6) CF, which leads to the formation of charge transfer complex (CTC) within the polymer matrix.

3.2 UV-Visible Studies

Optical absorption spectrum is one of the most important tools to understand the band structure and electronic properties of pure and dye doped polymers. The optical absorption spectra of pure and 5(6) Carboxyfluorescein doped PMMA are shown in the Figure 3. From the spectra it is clear that a band around 231nm is observed for pure PMMA which may be attributed to the n-π* transition of the carbonyl group in the polymeric macromolecules. For 5(6) CF doped PMMA films spectra shows two peaks centered at about 338nm and 458nm are due to n-π* and π- π* transitions respectively[9]. It is also observed that the peak I and peak II will shows blue shift along with the increase in the intensity of the bands upon doping which is indicates that the interaction of 5(6) CF with PMMA and presence of CTC with in the polymer matrix[10-12].
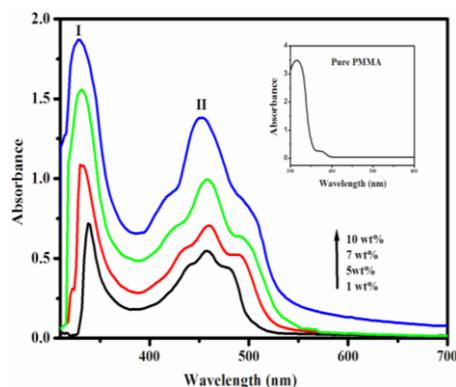

Figure 3: Optical absorption spectra of 5(6) **Carboxyfluorescein doped PMMA.**

Using UV-Visible absorption spectra, the optical energy band gap is determined by translating the spectra in to Tauc's plots. We use the frequency dependent absorption coefficient given by Mott Davis relation [13].

$$\alpha(\nu)h\nu = \beta(h\nu - E_g)^r$$

where, $\alpha(\nu) = 2.303\,A/d$ (A is the absorbance and d is the film thickness), h is Planck's constant, ν is the frequency of the incident photons, β is a constant, E_g optical energy band gap and r is an exponent which is equal to 2 for indirect allowed transition in the quantum mechanical sense responsible for optical absorption.

(a) **(b)**
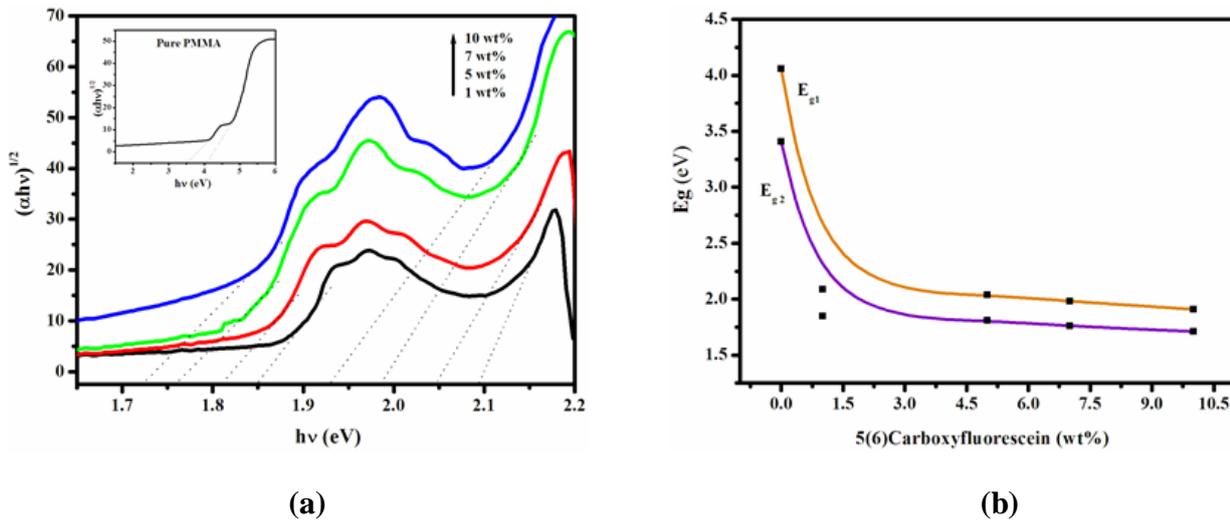
Figure 4: (a) The plots of $(\alpha h\nu)^{1/2}$ verses $h\nu$ (b) variation of optical band gaps with wt% for pure and 5(6) CF doped PMMA films.

The plot of $(\alpha h\nu)^{1/2}$ verses $h\nu$ at room temperature shows a linear behavior as shown in Figure 4(a), which is due to the indirect allowed transition. Intersection of the linear portion of the curve with the energy axis i.e. $(\alpha h\nu)^{1/2}=0$ gives the optical energy band gap E_g. The variations of E_g with the doping level are shown in Figure 4(b). The analysis of absorption coefficient reveals indirect allowed transition with one optical energy gap for pure PMMA film and two optical energy band gaps for 5(6) CF doped PMMA films [14-16]. It can be seen that optical energy band gaps E_{g1} and E_{g2} decreases with increasing concentration, the observed values are given in Table 2. These variations in optical band gap indicate the presence of additional energy states prompted by doping. From the FTIR study, the 5(6) CF is modifying the electronic structure as well as the microstructure of PMMA due to the formation of CTC or defect levels upon doping.
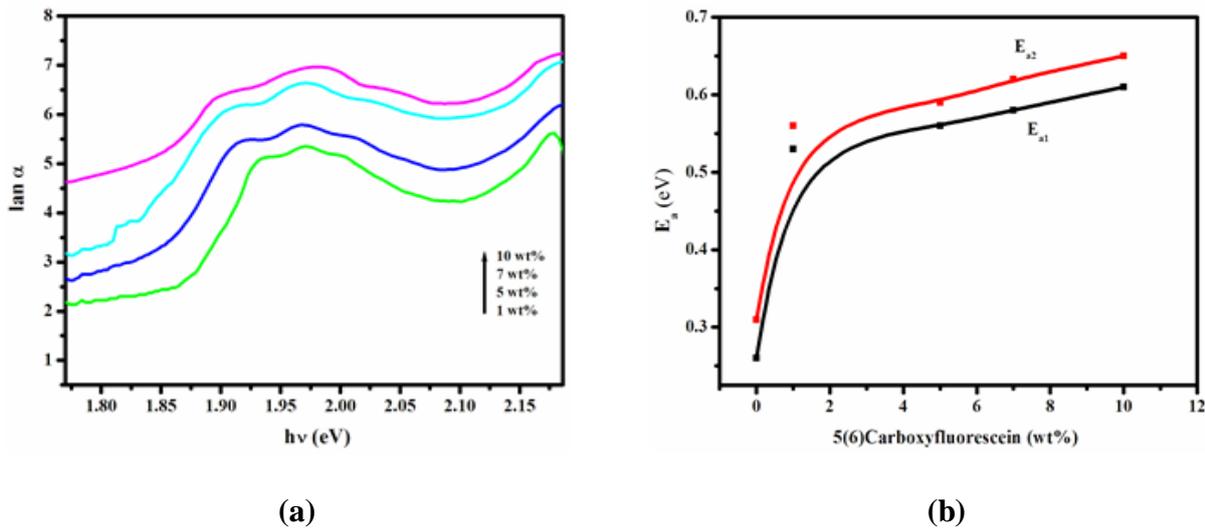
(a)   **(b)**

Figure 5: Variation of activation energy E_a for different wt% of 5(6) CF doped PMMA

To analyze the optical behavior of the composite films further, the activation energy values (widths of the Urbach tail) were determined. Figure 5, shows the linear dependence of the natural logarithm ln(α) of the absorption coefficients with the photon energy (hv) for different doping concentrations of 5(6) CF. The optical activation energy E_a values for the films were estimated from reciprocal of the slopes of the straight lines. Using the following relation the width of the activation energy has been calculated [17].

$$\alpha = \alpha_o \exp(h\nu / E_a)$$

Where α_0 is a constant and E_a is the width of the tail of localized states due to the defect levels in the forbidden gap [18]. From the Figure 5(a) shows a linear dependence of the natural logarithm of the absorption coefficient verses the photon energy for the films of pure and doped PMMA with different concentrations of 5(6) CF. From Figure 5(b) it is observed that the existence of two activation energies are increases with increasing concentration and values are given in the Table 2. Hence the variations in optical energy band gap and activation energy confirms the existence of defect levels within the 5(6) CF doped PMMA films due to the formation of charge transfer complex[19-21]

Table 2: calculated optical energy band gaps and activation energy bands of pure PMMA and 5(6) CF doped PMMA.

Doping level (wt %)	E_{g1}	E_{g2}	E_{a1}	E_{a2}
pure PMMA	3.51	4.06	0.26	0.31
1	1.84	2.08	0.53	0.56
5	1.81	2.14	0.56	0.59
7	1.76	1.98	0.57	0.63
10	1.72	1.92	0.61	0.65

IV. CONCLUSIONS

From this study it can be concluded the modifications in structural and optical properties of 5(6) Carboxyfluorescein doped PMMA. The shift in bands of FTIR spectra and change in the peak intensities indicates the possible interaction of dopant and forms the microstructural change in PMMA due to doping. It is found that the existence of two optical band gaps and two activation energies within the doped PMMA. These variations in the band gap and activation energy with doping were understood by invoking the existence of defect levels within the 5(6) Carboxyfluorescein doped PMMA films due to the formation of charge transfer complex.

REFERENCES

[1] Grazulevicius J. V., Strohriegl P., Pielichowski J., Carba-zole-containing Polymers: Synthesis, Properties and Applications. Prog. Polym. Sci, 28(9), 1297-1353 (2003)

[2] Ismayil , V. Ravindrachary , R.F. Bhajantri , S.D. Praveena , Boja Poojary , Dhanadeep Dutta , P.K. Pujari , Polymer Degradation and Stability, 95 ,1083-1091(2010)

[3] Kim D. Y., Cho H. N., Kim C. Y., Blue Light Emitting Polymers. Prog. Polym. Sci. 25(8), 1089-1139 (2000)

[4] Lo S. C., Burn P. L, Chem. Rev, 107(4), 1097-1116 (2007)

[5] Cravino A., Sariciftci N.S. J. Mater. Chem., 12, 1931-1943 (2002)

[6] Ping He ,c,n, Huili Wang, Lili Zhang , Jialing Wang, Yugang Jiang , Rongwei Fan , Deying Chen, Optics & Laser Technology, 44 ,341–343 (2012)

[7] Yariv E, Reisfeld R. Laser properties of pyrromethene dyes in sol–gel glasses. Opt Mater 13, 49-54(1999)

[8] Stephane Massou, Renaud Albigot, Michel Prats, Biochemical Education, 28, 171-173(2000)

[9] Renuka Sali, L.R. Naik, R.F. Bhajantri, C.M. Kamanavalli and S.G. Premakshi, International Journal of Luminescence and Applications 5, 1(2015)

[10] R.F. Bhajantri, V. Ravindrachary, A. Harisha, Vincent Crasta, Suresh P. Nayak, Boja Poojary, Polymer ,47,3591 (2006)

[11] S. Sreeja, S. Sreedhanya,N. Smijesh, Reji Philip and C. I. Muneer, J. Mater. Chem. C, 1, 3851(2013)

[12] L. Tutt and T. Boggess, Prog. Quantum Electron, 17,299-338(1993)

[13] Vijay K. Sharma, P.D. Sahare , Ramesh C. Rastogi , S.K. Ghoshal, Spectrochimica Acta Part A ,59, 1799-18(2003)

[14] H. M. Zidan, M. Abu -Elnader, Physica B, 355, 308(2005)

[15] AF Mansour, MG El-Shaarawy, SM El-Bashir, MK El-Mansy and M Hammam,Polym Int,51,393-397(2002)

[16] Mishra, R.; Tripathy, S. P.; Sinha, D.; Dwivedi, K. K.; Ghosh,S.; Khating, D. T.; Muller, M.; Fink, D.; Chung, W. H. Nucl Instr Meth B, 59,168(2000)

[17] Urbach F. The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. Phys Rev, 92, 1324(1953)

[18] H. M. Zidan, A. El-Khodary, I. A. El-Sayed, H. I. El-Bohy, Journal of AppliedPolymer Science,117,1416-1423 (2010)

[19] R.F Bhajantri, V.Ravindrachary, Boja Poojary, Ismayil, A,.Harisha, V Crasta Polym.Eng.Sci.49, 903-909 (2009)

[20] A. Harisha , V. Ravindrachary ,R.F. Bhajantri a, Ismayil , Ganesh Sanjeev ,Boja Poojary , Dhanadeep Dutta , P.K. Pujari ,Polymer Degradation and Stability 93,1554-1563 (2008)

[21] Zidan HM. Polym Test, 18,449–61(1999)