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UV and FTIR Studies of Pure PMMA and V_2O_5 Doped Films

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Abstract: In this work, poly (methyl methacrylate) (PMMA) thin films with doped V_2O_5 have been synthesized using solvent-casting method with various concentrations of dopant (V_2O_5; 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05 and 0.1 wt%). The structure of the obtained films were characterized using Fourier transform infra-red spectroscopy (FTIR) and UV-Vis (ultra violet- visible spectroscopy). In FTIR studies, after doping, one extra peak at 1036 cm^{-1} shows terminal oxygen bonds (V=O) are vibrating in stretching manner. the direct band gap energy of the composites decreases in small amount at concentration (0.001 wt%) of V_2O_5 increases.

Keywords **- V_2O_5 doped PMMA ;FTIR; UV-Vis; Band Gap.**

I. INTRODUCTION

In the recent years, the use of polymer has received great attention due to variety of new technology applications like molecular electronics[1], optics, sensors[2] ,electromagnetic shields[3], microwave absorbing materials[4-6], supercapacitors[7,8] and batteries[9]. Polymethylmethacrylate (PMMA) has unique chemical and mechanical properties[10], optical, amorphous nature, transparency, low cost[11] due to which PMMA has wide range of applications. Polymethylmethacrylate(PMMA) is also well tested group of lightweight insulating organic material.

The most common metal which has several valances is vanadium , its oxidation states form (2+ to 5+) different number of compounds such as vanadium monoxide(VO), vanadium dioxide (VO_2), vanadium trioxide (V_2O3), vanadium pentoxide(V_2O_5). Among this, V_2O_5 is most stable form with high energy, density, good reversibility and ability to exist in different oxidation states , due to which , widely used as catalysts, switching devices, gas sensors etc[12-15].

Here, an attempt has been made to investigate the doping effect of polymer undergoing a significant improvement especially Polymethylmethacrylate(PMMA) because of its excellent optical, electrical, and structural properties[16]. The undoped PMMA thin films usually are not stable , insufficient UV- light filters and possess a thermal sensitivity[17]. To overcome this problem, doping strategy were used which is an effectively tune the surface state and improve the properties. The characteristics of Polymethylmethacrylate(PMMA) has been significant interest after modification ,producing conducting PMMA , reduce thermal sensitivity and ion- induced disorder, increase crystallinity[18,19].

On the other hand, Redha A. Alkhadry et. al.[18] have reported that ,the presence of V_2O_5 nanoparticles significantly enhanced the photocatalytic efficiency of PMMA for organic pollutant MB (methylene blue) degradation, beneficial applications in the field of water treatment, addressing the critical issue of pollutant degradation, G A Niklasson et al.[20] proves the potential applications in energy efficient window technology of vanadium dioxide. The aim of most of these researches modified the structural , optical and electrical properties because after doping , complex is formed due to the dopant molecules.

In this paper, after doping the vanadium pentoxide (V_2O_5) , synthesis and characterization of PMMA and PMMA/ V_2O_5 thin films is studied using FT-IR and UV-Vis with a view to evaluate their possible use such that it can be used in various application including industrial catalysts , energy storage devices and supercapacitor electrodes in organic solar cell[21-22].

II. Experimental procedure

Pure PMMA and PMMA/ V_2O_5 (PMMA doped V_2O_5) samples with different concentration (V_2O_5; 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05 and 0.1 wt%) of thickness 80-100 microns were prepared using solvent casting technique. Pure PMMA and PMMA/ V_2O_5 thin films in this method were prepared by stoichiometric amount of PMMA and V_2O_5 dissolved in benzene using a magnetic stirrer at a temperature slightly below 50ºC , mixture was pour on a glass slab and left in dry atmosphere for 24 hour.

The Fourier transform infrared (FTIR) instrument used was a (Bruker Tensor 27) spectrophotometer with a wave number range 250-4000 cm^{-1} .Ultra violet and visible absorption spectra using (Shimadzu UV-3600) Spectrophotometer were measured in the wavelength 200-400 nm.

III. Result and Discussion

3.1 Fourier Transform Infrared analysis

Fig. 2(a) shows FTIR spectra of pure PMMA film and PMMA/V_2O_5 composite thin films where the interactions between dopant and pure PMMA polymer matrix are clearly seen. The FTIR spectrum of pure PMMA with transmittance bands at 754 cm^{-1}, 977 cm^{-1}, 1728 cm^{-1} , 2954 cm^{-1} and 3441 cm^{-1} are assigned to the characteristic due to CH_2 rocking vibration mode , C-CH_3 bending , ester carbonyl group stretching vibration , C-H stretching and C=O stretching vibration. The transmittance peak appeared in doped thin films in this region at 1480 cm^{-1} was related to C-H stretching vibration[18,24]. An obvious absorption band and PMMA/V_2O_5 composite thin films, existence of peak at 1388 cm^{-1} due to lower intensity for V_2O_5 .After doping results showed that some modifications occurred in the samples chemical structure ,shape and shift in position of the ester carbonyl group(C=O) stretching vibration assigned to 1728 cm^{-1}. Pronounced variation in the shape of the peak (slight increase in width) in the wavenumber range 1500-1650 cm^{-1} which agree with the amorphous nature of the films after doping[18]. The peak at 1038 cm^{-1} can be attributed to the stretching vibration of C-O (ester bond)[19]. FTIR absorption spectra shows the various interactions within the V_2O_5 , peaks around 842 cm^{-1}, 1038 cm^{-1} is due to the stretching vibration of terminal oxygen bonds, V=O(842 cm^{-1}) and the vibration of doubly coordinated oxygen (bridge oxygen) bonds V-O-V (1038 cm^{-1}) respectively[25]. In the wave number range 600-1020 cm^{-1} exhibits the three vibration modes because of V_2O_5[26]. In the spectrum the sharp peaks between 3300 cm^{-1} and 3500 cm^{-1} which can be associated with -NH_2 vibration. The peaks between 500-1000 cm^{-1} and 3200-3600 cm^{-1} due to the vibration V-O type and spread O-H vibrations respectively[27].

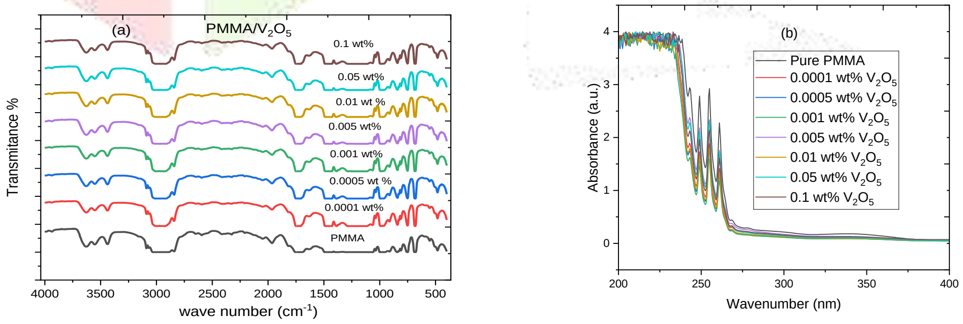

Fig.2 (a) FTIR and (b) UV spectra for pure PMMA and PMMA doped with different wt% of V_2O_5

3.2 Optical characterization

Fig.2(b) presents the absorbance spectra for undoped and doped PMMA polymer thin films with V_2O_5 via Ultraviolet visible (UV-Vis) spectroscopy. At lower wavelengths (λ>300 nm) absorption increases with increasing V_2O_5 doping ratios, due to the metal oxide which easily scatter the photons incident on the sample and continuously increase with higher level of doping showing absorption of light from the samples and absorption is nearly constant for higher wavelengths (250< λ 800 nm).The absorption coefficient (α) of the PMMA / V_2O_5 samples with different ratios of V_2O_5(0.0001 , 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1 wt %)were calculated in the following equation[5] :

$$\alpha = 1/d \ln [(1-R^2)/T] + \sqrt{[R^2 + (1-R^2)/4T^2]}$$

The band gap was calculated using the Tauc's formula. The frequency dependent absorption coefficient according to Tauc's formula[6] :

$$\alpha h\upsilon = A(h\upsilon - Eg)^n$$

Where α is the absorption coefficient , A is constant and n depends on the type of transition having values ½, 2, 3/2 and 3 corresponding to the allowed direct ,allowed indirect, forbidden direct and forbidden indirect respectively[19]. Tauc's method which represents the relation between $(\alpha h v)^2$ values and hv incident photon energy values can be used to find the transitions to determine the band edges, $(\alpha h\upsilon)^2$ against $h\upsilon$ to zero absorption value plots of the pure PMMA and V_2O_5 /PMMA films respectively shown in fig.3(a) and (b).

To observe the width of the band tail of the localized states at the optical bandgap , the Urbach energy E_u can be determined by the relationship

$$\alpha (h) = \alpha_0 \exp(h/ E_u)$$

As shown fig.4 , the value of Urbach energy may be determined by the variation of ln(α) with the photon energy ($h\upsilon$) and the reciprocal slope of the straight line yields E_u.fig.4(a) & (b) shows the Urbach energy of pure PMMA and 0.1 wt% V_2O_5 /PMMA films, the value of Urbach energy increase with increases the doped amount of V_2O_5.

Calculated energy band gap values of pure PMMA and 0.001 wt% V_2O_5 /PMMA films have been revealed in fig 3. In the table 1 the variation of direct band gap energy and the Urbach energy of pure PMMA and doped amount of V_2O_5 /PMMA for different wt % are represented. The value of bandgap energy of pure PMMA is 4.66 eV, as PMMA doped with V_2O_5 the energy gap changed. As the amount of V_2O_5 in these PMMA films increases, the energy band gap value decreases and Urbach energy increases due to the formation of chemical bonds between PMMA chains (functional groups) and doped V_2O_5 responsible for the creation of localized states (charge transfer complexes) between the HOMO and LUMO energy bands allows for the lower energy transfers which relies on the defects inside the material[24].

Energy band gap of others samples decreases from 4.66 eV to 4.54 eV for the PMMA doped with V_2O_5 , for the doping level (0.001 wt%) energy band gap is lower (Eg=4.54eV) than the pure PMMA thin films this is due the fact of oxidation of the samples from the V_2O_5 in the PMMA. It means conductivity of samples increases with the amount of V_2O_5 increases to the PMMA films. As the optical conductivity increases[6,7] , the insulating behavior decreases and refractive index of samples increases[28]. The bandgap energies decreases sharply with adding the dopants of V_2O_5 up to 0.001 % V_2O_5 doping , then becomes nearly constant for higher doping levels (higher than 0.001 %) which surely shows a conversion from insulating state of PMMA to metallic state with V_2O_5 doping , where the 0.001 % V_2O_5 doped PMMA sample is the optimum sample.

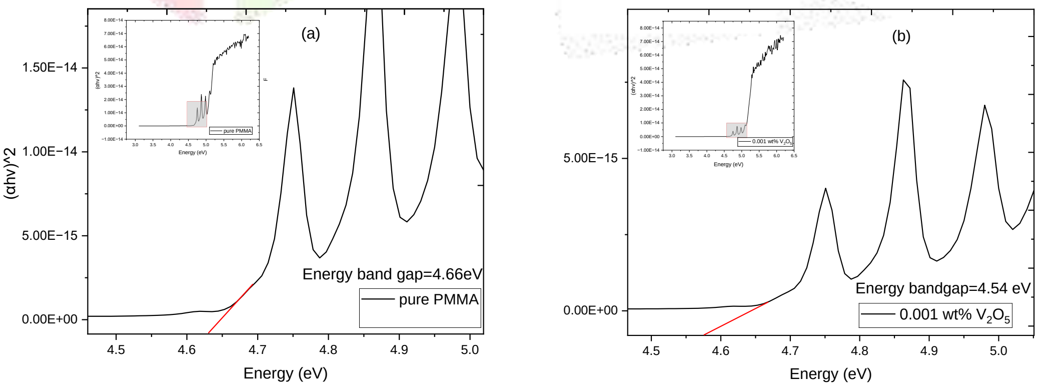

Fig.3 Energy bandgap of (a) PMMA and (b) 0.001 wt% of V_2O_5.

Table 1

Band gap energy and Urbach energy for pure PMMA and V_2O_5 doped PMMA at different wt%

Doping percentage(wt%)	Band gap energy Eg (eV)	Urbach energy E_u (eV)
Pure PMMA	4.66	0.2906
0.0001	4.59	0.5208
0.0005	4.59	0.4629
0.001	4.54	0.4651
0.005	4.64	0.4926
0.01	4.62	0.5291
0.05	4.64	0.4784
0.1	4.61	0.5988

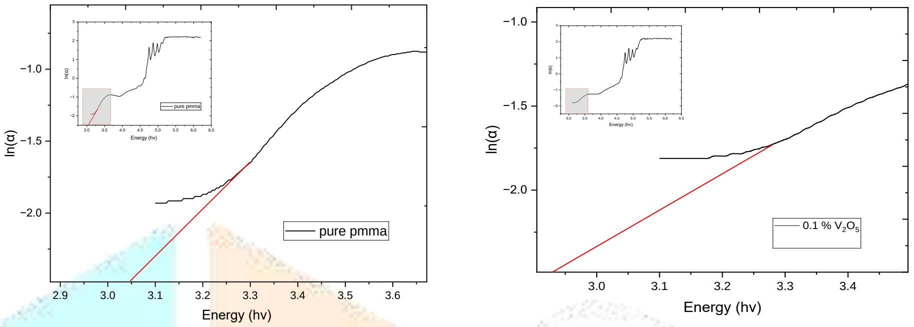

Fig.4 Determination of Urbach energy plots between ln(α) against hv for (a) pure PMMA and (b) 0.1 wt % doped V_2O_5

IV. CONCLUSION:

This work presents the synthesis of thin films of V_2O_5 doped into a Poly (methyl methacrylate) (PMMA). These films, with an average thickness of 80 microns, were prepared using a solvent casting method. The characterization of these thin films has been observed using UV-Vis absorbance, and FTIR spectroscopy. Five distinctive peaks at 754 cm^{-1}, 977 cm^{-1}, 1728 cm^{-1} , 2954 cm^{-1} and 3441 cm^{-1} in the IR spectra of PMMA , significant changes in the shape of the IR spectra can be observed for higher level (0.1 wt%) doping of V_2O_5. Doped thin films were seen at UV-Vis spectra confirmed that the addition of V_2O_5 , the band gap energy value decreased from 4.66 eV to 4.54 eV for the sample with doping level (0.001 wt %) of V_2O_5 and the Urbach energy increased from 0.2906 eV to 0.5988 eV for the sample with higher doping level (0.1 wt%).

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