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Research Article

The effect of dye on conductivity of Polymer (PVC) observed by spectroscopic studies

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Abstract

The conducting behaviour of Pure and Malachite green mixed Polyvinyl Chloride (PVC) samples prepared using the solution cast method in various ratios, was investigated using Ultraviolet (UV)transmittance, UV absorbance, Infrared (IR) transmittance, and X-ray Diffraction (XRD). The results show that UV transmittance decreases with sensitizer concentration in PVC. UV absorbance shows an increasing trend with the degree of sensitization. The formation of a charge transfer complex in a polymer matrix was inferred from these studies. Reduction in electronic bandgap and hence change in conductive behaviour is reported.

Keywords: Sensitization, UV Spectroscopy, ATR spectroscopy, Intermolecular Interaction, Optical energy band gap, Charge transfer complexes, Polymer semiconductor

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1. INTRODUCTION

It is possible with polymers to acclimate the instrument factors and construction of the solar cells purposefully. In colour-acclimatized solar cells, polymers might be utilized as flexible substrates, severance and samples forming agents of photo-anode flicks, without -platinum counter electrodes, and the materials of partly solid-state electrolytes. In solar cells of perovskite, polymers could be utilized as accessories to acclimate the crystallization and nucleation processes in perovskite flicks. Polymers could also be utilized as hole transfer accoutrements, electron transfer accoutrements, and partner sub-casters to improve the carrier separation efficiency and diminish recombination

The translucency, good sample-forming parcels, low processing temperature and high work function of some polymers allow it to help as an effective Hole Transporting Layer[1,2], particularly in stretchy Perovskite Solar Cells. Chen et al. made up the gadget with a blend of materials and attained the effectiveness of blends[3]. L. B. et al. differentiate the performances of Perovskite Solar Cells grounded on various dissimilar hole Transporting Layers. The results demonstrate that the Polystyrene Sulphonate: Ethylene dioxythiophenes grounded gadget attained lesser effectiveness than others, which could be explained by the impressive work function of PEDOT: PSS than ground counterparts [4]. The semiconducting polymer samples are also used in organic Solar Cells [5].

Research on Electrical conductivity in polymers was started by Heeger, Mac Diarmid, and Shirakawa in 1976 and it made a bridge between chemistry and physics[6,7]. These polymeric materials have the optical and electrical properties of a conductor or semiconductor and research was focussed on determining a new set of mechanical and electrical properties of a mixed or doped polymer. With the emergence of conducting polymers a new technology emerged which is called plastic electronics[8]. Structurally, polymers are normally characterised by a carbon-rich backbone, which is responsible for their flexibility. The electrical property of the polymer ranging from insulator to semiconductor or conductor depends on the molecular structure of the used polymer, doped material, doping conditions, and concentration[9].

The nature of electro-optical properties, easy availability, easy-to-grow solution, cheap, lightweight, flexible, and used in various organic devices such as LED displays, bio-sensors, transistors, solar cells etc., has attracted the attention of researchers in this area [10,11,12,13,14,15,16,17].

2. MATERIALS AND METHOD

For the preparation of sensitized samples solution cast technique is used [18,19,20]. PVC (60 mg) and sensitizer malachite green were taken in different ratios, i.e. 60:2, 60:4, 60:6, 60:8, and 60:10 were dissolved in solvent DMF at 60 degrees by continuously stirring. After getting the clear solution, the solution was poured on a clean glass plate floating on a mercury pool and then the plate was put in dust dust-free oven kept at 60 degrees. After 24 hours, the glass plate was taken out and the prepared samples were peeled out. For drying samples were again kept for another 24 hours. In this way, pure dried samples were obtained for characterization.

3. EXPERIMENTAL WORK

The UV, Attenuated Total Reflectance (ATR), and Powder X-ray diffraction (PXRD) studies were done at Central Instrumentation Laboratory, Government Science College Jabalpur, using UV 1700 Pharma Space UV-VIS spectrophotometer SHIMADAZU and a Rigaku Mini-flex X-ray diffractometer equipped with Cu Kβ radiation at 40 kV and 15 mA in the range 2θ = 2-40˚, at a speed rate of 4˚/min.

Table 1: - UV Absorbance data of Pure and sensitized PVC

Pure PVC		PVC 60:2		PVC 60:4		PVC 60:6		PVC 60:8		PVC 60:10	
Wave length (nm)	Abs.	Wave length (nm)	Abs.	Wave length (nm)	Abs.	Wav length (nm)	Abs.	Wave length (nm)	Abs.	Wave length (nm)	Abs
787 773 759 745 732 720 708	0.041 0.041 0.041 0.041 0.041 0.041 0.040	640 433 319	3.436 2.189 2.034	640 433 319	3.436 1.374 2.290	636 433 314	3.612 1.548 2.459	643 433	3.436 1.890	642 431	3.612 3.436

Table 2: -Calculated optical energy bandgap by formula and by online Insta nano application

PVC 60:2 optical energy bandgap (eV)		PVC 60:4 optical energy bandgap (eV)		PVC 60:6 optical energy bandgap (eV)		PVC 60:8 optical energy bandgap (eV)		PVC60:10 optical energy bandgap (eV)		Average bandgap Energy (eV)
Calcu.	Online	Calcu.	Online	Calcu.	Online	Calcu.	Online	Calcu.	Online	
2.12	1.95	2.119	1.948	2.116	1.943	2.11	1.94	2.09	1.939	2.025

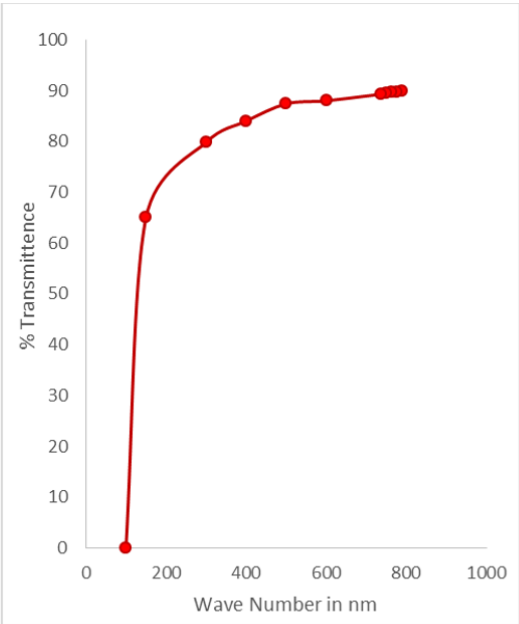

Figure 1. UV Transmittance plot of PVC

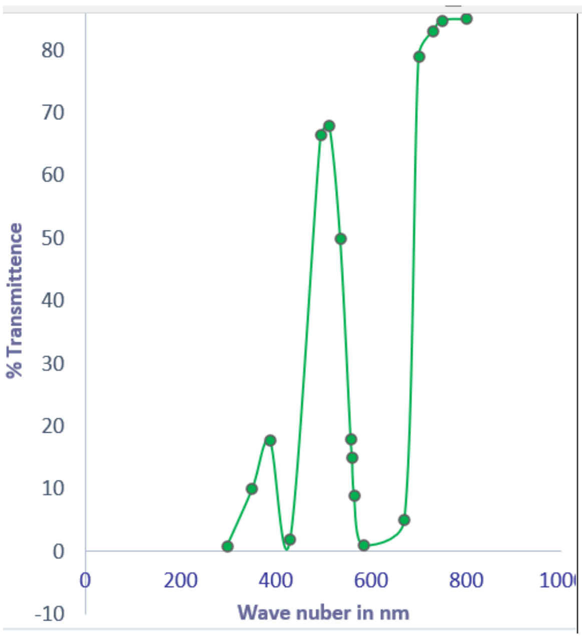

Figure 2. UV transmittance plot of PVC sample 60:2

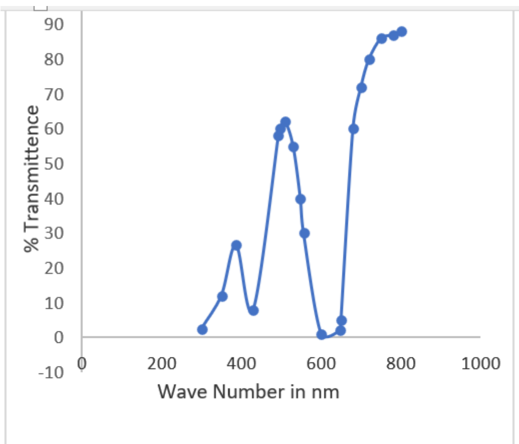

Figure 3. UV Transmittance plot of PVC sample 60:4

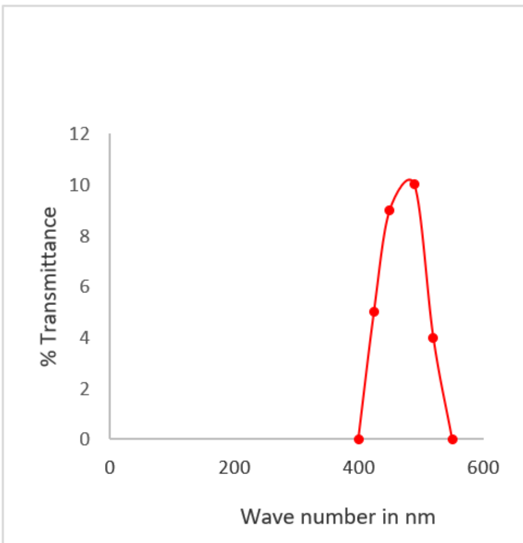

Figure 4. UV Transmittance plot of PVC sample 60:6

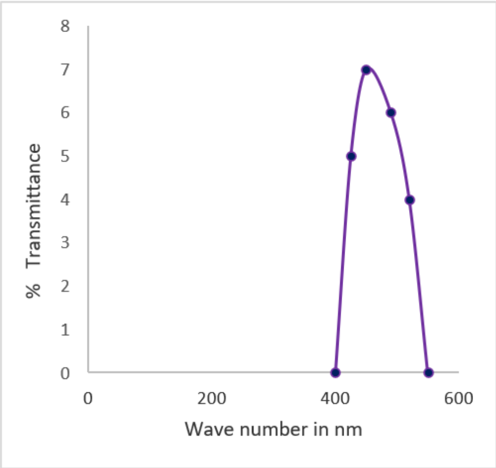

Figure 5. UV Transmittance plot of PVC sample 60:8

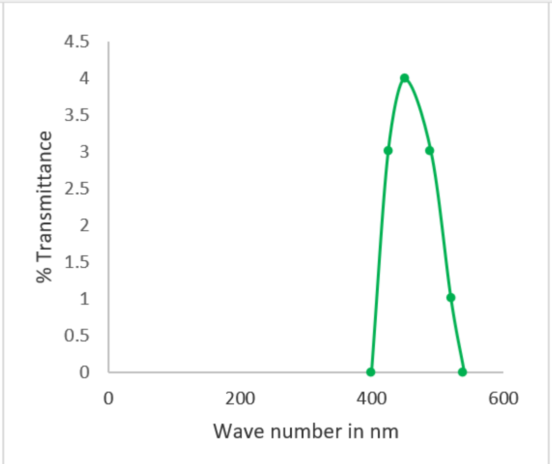

Figure 6. Transmittance plot of PVC sample 60:10

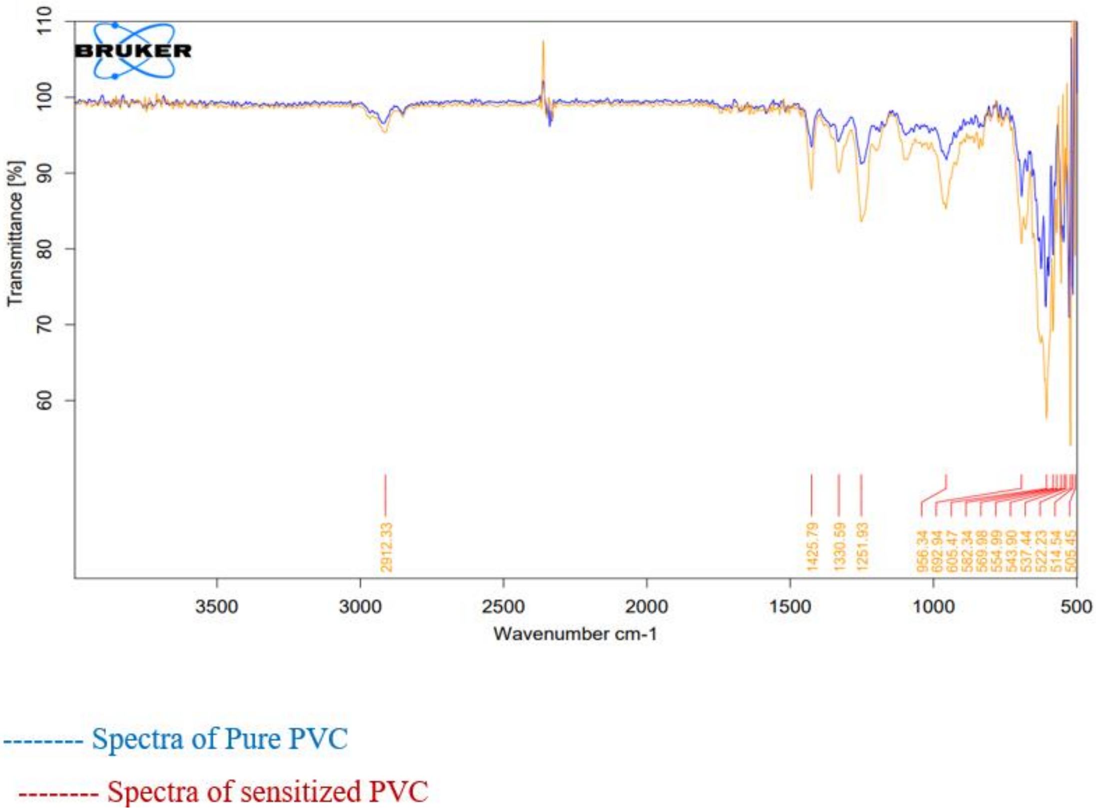

Figure 7. ATR Transmittance spectra of pure PVC and sensitized PVC.

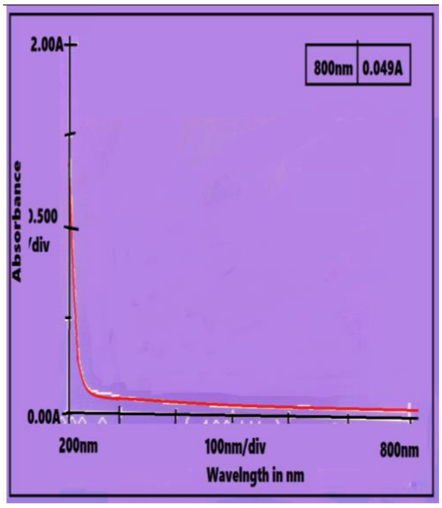

Figure 8. UV Absorbance spectrum of pure PVC

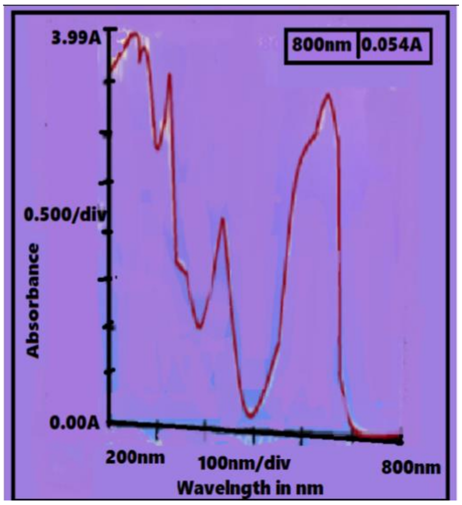

Figure 9. UV Absorbance spectrum of 60:2 sensitized PVC

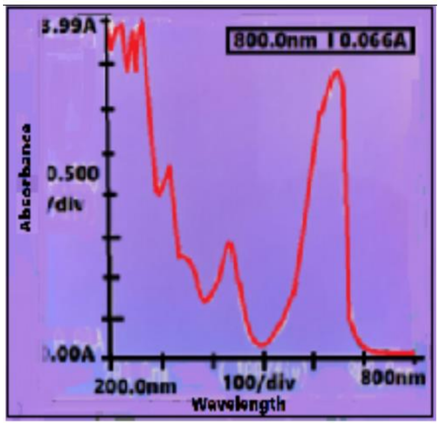

Figure 10. UV Absorbance spectrum of 60:4 sensitized PVC

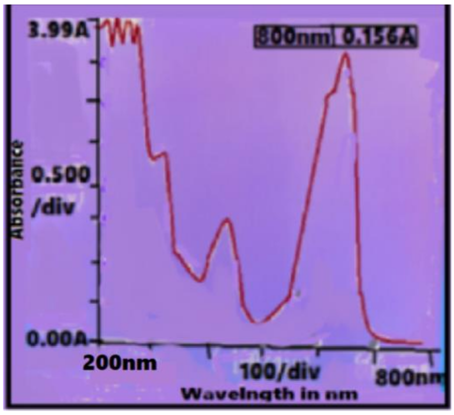

Figure 11. UV Absorbance spectrum of 60:6 sensitized PVC

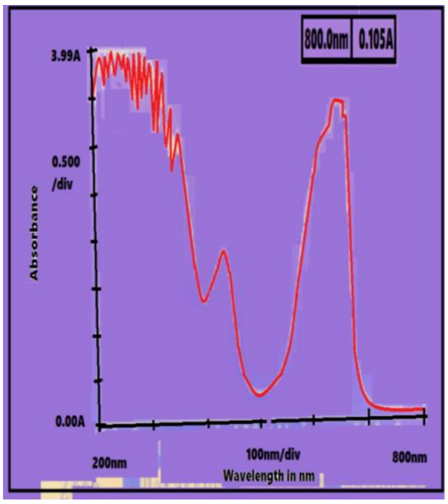

Figure 12. UV Absorbance spectrum of 60:8 sensitized PVC

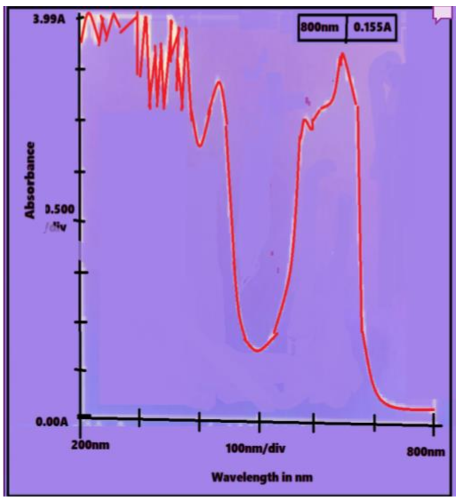

Figure 13. UV Absorbance spectrum of 60:10 sensitized PVC

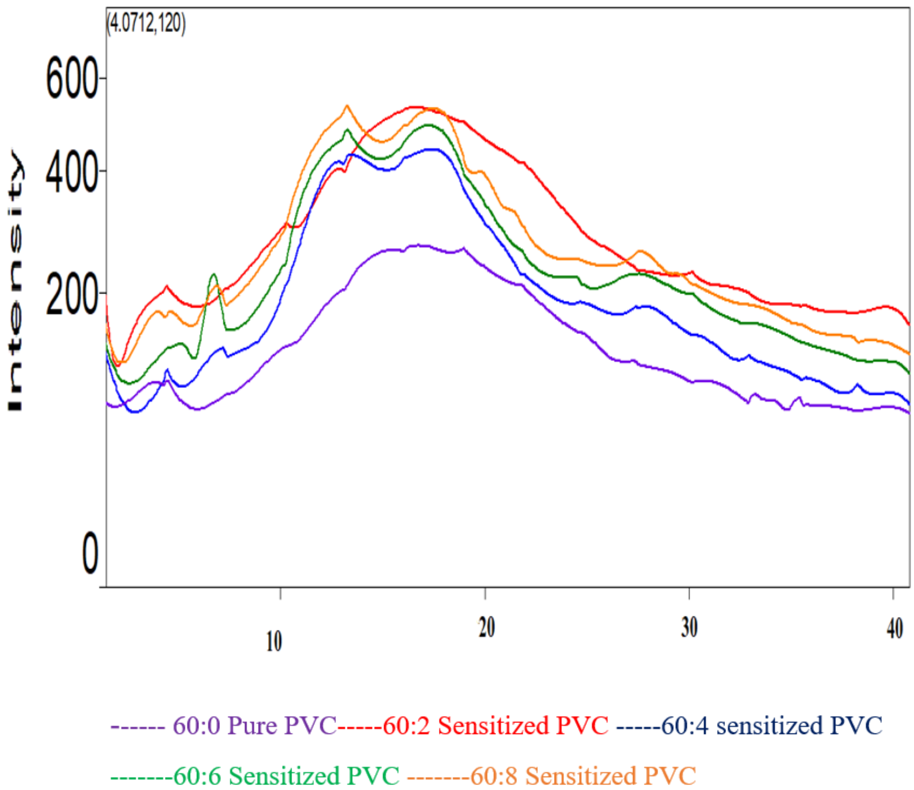

Figure 14. XRD of pure and sensitized PVC.

4. RESULTS AND DISCUSSION

Figures No. 1 to 6, depict the UV transmittance plots of pure and sensitized polyvinyl chloride samples. Figure 1 expresses that the maximum percentage transmittance observed is 89.9 % at 790 nm wavelengths. Figures 2 and 3 show the percentage transmittance of 62.5% and 66.3% respectively. It is therefore evident that T% (transmittance%) decreases with an increase in the concentration of malachite green in sensitized PVC samples up to 4% afterwards with an increase in malachite green concentration transmittance shows a decreasing trend. Figure 7 represents the ATR transmittance spectra. This spectrum strengthens the previous result that for particular concentration range of malachite green in sensitized samples, percentage transmittance decreases, while absorption peaks of sensitized PVC are higher than that of pure PVC. Higher area of absorption peak clearly infers strengthening of intermolecular interactions that are the formation of a charge transfer complex. From both studies, it is clear that decreased transmittance and increased absorbance in doped PVC are due to the formation of a charge transfer complex because of the interaction of the sensitizer with the polymer matrix and thereby it effects the spectroscopic behaviour of the polymer [18].

Figures 8,9,10,11,12,13 show the UV absorbance spectrum of pure PVC as well as sensitized samples. It is evident from Fig.8 that for pure PVC, the spectrum is almost flat, below 80nm there is some absorbance, later on almost no absorption is seen; this result is identical to what we got from the UV transmittance plot. From the figures and observed data there are no peaks seen in pure PVC. Absorbance spectra for sensitized PVC samples show the number of broad and narrow bands. It is evident that bandwidth and absorbance increase with level of sensitization. Absorption in various bands clearly indicates that malachite green leads to the formation of a charge transfer complex because of the interaction between polymer and die[21].

From the absorption spectra of sensitized samples, λmax lies between the frequency band 640-642 nm with absorption in the range 3.43-3.61 Angstrom. From absorbance spectra, the optical energy band gap was calculated by:

$$Eg = \frac{\mathrm{hc}}{\lambda}$$

Where λ is the wavelength of peak absorption obtained from the UV absorption spectra, h is Planck’s constant and c is the velocity of light[22].

The calculated average optical energy band gap by a formula is 2.11 eV and the calculated optical energy band gap by online software is≈1.95 eV[23]. From both ways of calculation, it is clear that the average optical energy band gap of sensitized PVC is ≈2 eV. It has been reported by other studies that the activation energy decreases with M green concentration [24,25,26]. Therefore, one can infer that by incorporation of sensitizer, the band gap between the valance band and conduction band decreases hence decreasing excitation energy; like ways binding energy as well as activation energy also decreases resulting in increased conductivity. The sensitization of PVC may results in changing it to a semiconductor. The Optical energy band gap of sensitized PVC is ≈2 eV, which is near the observed band gap of known semiconductors. The absorption spectrum of pure PVC is flat, which means that the optical energy band gap of pure PVC is higher than 3 eV.

The Electrical Band Gap is the combination of an Optical Band Gap and Exciton Binding Energy[27]. The calculated optical energy band gap decreases from pure to sensitized PVC observed by the UV graph. The activation energy calculated by thermally stimulated depolarization current (TSDC) and transient current shows that it decreases with an increase in sensitization and the energy band gap decreases with an increase in the degree of sensitization. The increasing conductivity and decrease in the activation energy with sensitization were also reported earlier. The decrease in indirect optical energy gap and Urbach energy with M green content was reported elsewhere [27,28]. As malachite green acts as a plasticizer, therefore by addition of plasticizer in a polymer, an increase in ionic conductivity results [19,29,30,31,32].

Figure 14 shows the XRD pattern of pure and various malachite green-sensitized Polyvinyl chloride. The XRD pattern shows that the width and height of the hump increases with malachite green concentration. It means that the amorphous nature of PVC increases due to the formation of charge transfer complex within the polymer matrix which results in a change in conducting behaviour of the polymer [20,33,34].

5. CONCLUSION

From these results, it is clear that for pure PVC having an optical energy band gap greater than 3 eV, when sensitized with malachite green its optical energy band gap reduces near to value 2 eV. The decrease in transmittance with sensitizer is due to molecular interaction; the miscibility of malachite green in PVC causes interaction between PVC and the M green component chain [35]**.** Thus, we can say that PVC which has insulating behaviour when it is sensitized it changes from insulator to semiconductor. This nature of doped polymer needs further investigation and correlation with other future studies for future fruitful applications in various fields.

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