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Research Article

THE EFFECT OF SENSITIZATION ON POLYVINYL CHLORIDE (PVC), ESTIMATED BY THE SPECTROSCOPIC STUDY

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ABSTRACT

In the present paper, spectroscopic [*i.e.*, Ultraviolet (U.V) and Infrared (I.R.)] and transient current studies of pure Polyvinyl chloride (PVC), Malachite green (M Green) and Malachite green sensitized Polyvinyl chloride samples of 6, 7.5, 10 and 15 percent have been investigated. It is observed that in case of UV spectra no band appears for pure PVC however the addition of malachite green in PVC gives rise four absorption bands around 260,310,440 and 630 nm. In IR spectra, incorporation of sensitizer into the system induces spectroscopic changes with concentration in the system. Few absorption peaks present in the pure samples disappeared in sensitized samples. The maximum numbers of peaks disappearing were in the samples, sensitized with optimum concentration. Also there is a shift in the absorption peak towards the higher and lower wave number with the increase in concentration. In transient current study the current value is increase with sensitization. All above behavior may be due to the formation of charge transfer complex.

***Keywords**: IR Spectroscopy, UV Spectroscopy, Transient current and Charge Transfer Complexes*

INTRODUCTION

Polymers have attracted a particular attention due to their useful mechanical and optical properties, unique disordered structure and their potential applications in many technological and engineering areas. The efficiency of solid state devices has opened up yet another new field for use of polymers, which are very vast, attractive and promising, given by Febel and Henish (1971) and Muthaupt *et al.*, (1991). Extensive research is underway in many laboratories on electrical properties of pure and sensitized polymers, copolymers, polymeric blends and polymeric compositions. Electrical properties of a polymer are partly dependent on their physical as well as chemical structure. Chemical structure of polymers may be modified by sensitizing copolymerization, substitution and blend formation etc. These processes affect the electrical behavior to various extents, determined by their influence on inter and intermolecular interactions. The structural information and effects of structural modification with sensitization if any, in polymer can be investigated by using a number of techniques viz. ultraviolet and infra-red visible spectroscopy by Devis *et al.*, (1978) and Kaura *et al.*, (1991).

The ultraviolet spectrum is a spectroscopic tool, through the absorption bands, to provide an idea about the charge produced due to sensitizing in the polymer matrix. It`s throws light on the group (Rao, 1961) but does not give structural investigation of the molecules however infrared spectroscopy is appropriately suited for structural investigation to detect various functional groups because of the ideal wavelength region, it covers in the electromagnetic spectrum. Infrared spectroscopy of polymers is useful in studying structural modifications occurring during electret formations, blending or on sensitizing with impurities are given by Narula (1984) and Latoar (1977).

It has been observed from earlier studies on thermally stimulated depolarization and ultraviolet spectroscopy by Bhardwaj and Khare (2012) on pure and various malachite green (M green) sensitized samples of Polyvinyl Chloride (PVC), that the charge storage properties of this polymer are markedly affected by sensitizing. It is worthwhile to demonstrate this through spectroscopic studies, to provide an important tool to judge against pure and sensitized samples.

Therefore these two complementary tools have been used in present study, to investigate the changes brought about by the sensitizing in the polymer matrix and correlated it with transient current measurement.

MATERIALS AND METHODS

Technique of Film formation: The Polyvinyl chloride (PVC) used as material and malachite green as sensitizer in the present work. Dimethylformamide (D.M.F.) was used as the solvent. PVC 100 mg was dissolved in DMF 10 ml by stirring at 60^{o}C for 4 hours to get a homogenous and transparent solution. The solution thus, prepared was then poured onto a cleaned glass plate floating on mercury pool. The solvent was allowed to evaporate in an oven at 60^{o}C for 6 hours to yield the desired samples. The films so prepared were dried for 18 hours in a dust free chamber. For further period of time to remove by residual solvent, dried sample thus obtained was uniformly smooth and could be easily peeled. The films so prepared were approximately 30µm thick calculated by micrometer gauge method. The concentration of the sensitizer was varied from 6-15 percent of the solvent. The present studies were presented for all concentrations i.e. 6,7.5,10 and15 percent. Infrared absorption spectra of pure and sensitized samples were taken at room temperature, using i.r. spectrophotometer SIMADZU-2450. The scanning range is 4000 cm^{-1} to 400 cm^{-1} and scanning rate of absorption spectra was kept on 4 minutes per sample and for ultraviolet spectroscopy studies PARKIN ELMER UV/VS spectrophotometer Mambda-12 was used.

RESULTS AND DISCUSSION

IR spectra of PVC, Malachite green and malachite green sensitized PVC samples of 6, 7.5, 10, and 15 percents are exposed in figure 1-6. From figures peak 2924 cm-1 shifts towered lower to higher wave number i.e. 2950,2924,2931,2916 cm-1.

The various bands obtained in IR analysis are listed in table 1.The characteristic bands of PVC can broadly be classified into three regions.. The first is called C-Cl stretching region in the range 400-700 cm^{-1} .The second region is called C-C stretching in the range 900-1290 cm^{-}1.The third region is 1250-2790 cm^{-1} in the PVC (numerous modes). Vibrational bands of PVC are obtained at 2960 cm^{-1} (C-H of CHCI), 2924 cm^{-1} (C-H of CH_2), 1423 cm^{-1} (CH_2), 1300.00 cm^{-1} (C-HO$^+$ CHCI), 1249 cm^{-1} (C-H of CHCL), 1089.01 cm^{-1} (C-C), 968.60 cm^{-1} (CH_2) 846 & 703 cm^{-1} (C-Cl) and 640.00, 580 and 440 cm^{-1} (C-Cl).

The IR spectra of malachite green (Figure-2) appears at regions 3000-2900 CH stretching vibration, 2340 hydroxyl stretching,1750 ester linkage, 1580 NH bending vibration,1360 tertiory amino group or CH bending of CH_3 group ,1160 aromatic phenyl group, 725 chloro group. In the IR spectra the band position of sensitized samples is listed in table 6. In all cases incorporation of sensitizer into the system induces spectroscopic changes with concentration in the system

In addition of 6 percentage sensitization, one additional peak near 1673-1681cm^{-1}and 1180 cm^{-1} present as carry in pure sample, became clear peak in the sensitized ones. On the other hand a few absorption peaks present in the pure samples disappeared between the ranges 1673-600 nm (figures 5-6) in sensitized samples. Further with the increase in sensitized concentration the number of peaks disappearing. The maximum numbers of peaks disappearing were in the samples, sensitized with optimum concentration. Also there is a shift in the absorption peak (2924cm^{-1}) towards the higher and lower wave number with the increase in concentration of the sensitizer. it may be due to the cause of CTC. Distinct absorption peaks near 2935±16 were observed for pure, malachite green and malachite green sensitized samples. This peak could be credited to the stretching frequency of CH band during the preparation of the samples.

UV spectra of pure and sensitized samples are shown in figure 7-11 and band positions are exposed in table 2. No band appears in the spectra of pure PVC however the addition of M-green gives rise four absorption bands around 260, 310,440 and 630nm.

Transient current spectrums are represented by figure 12-15, current value of charging and discharging current is increase with sensitization.

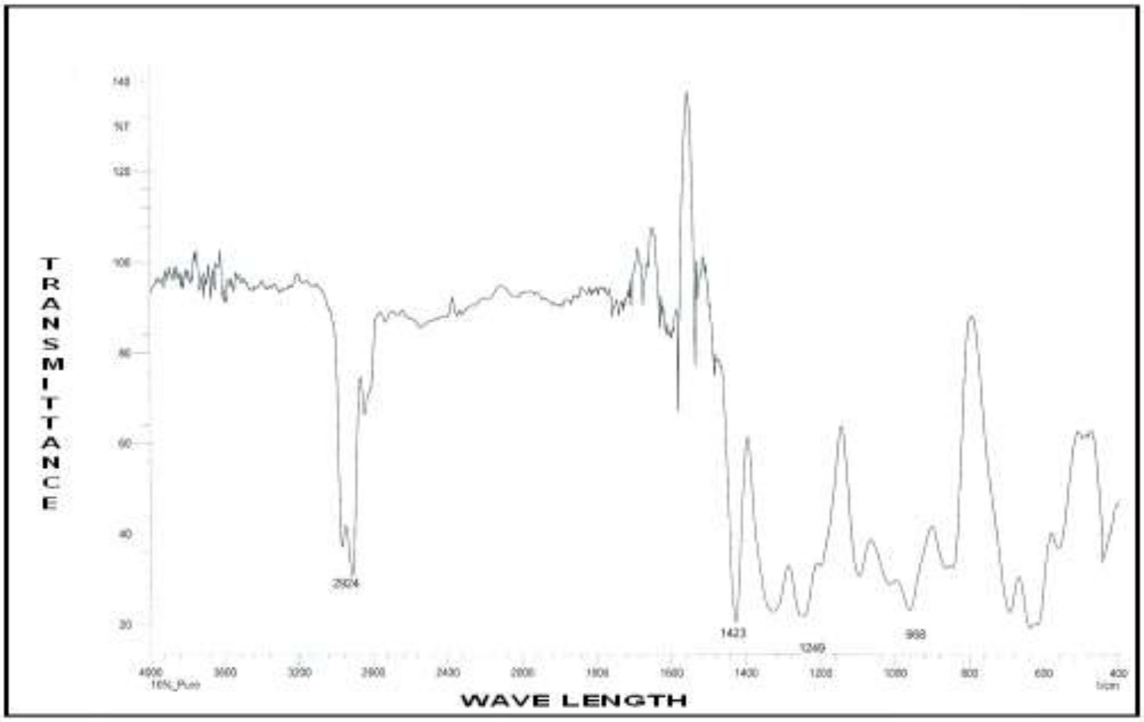

Figure 1: IR Spectra of polyvinyl chloride (PVC) sample

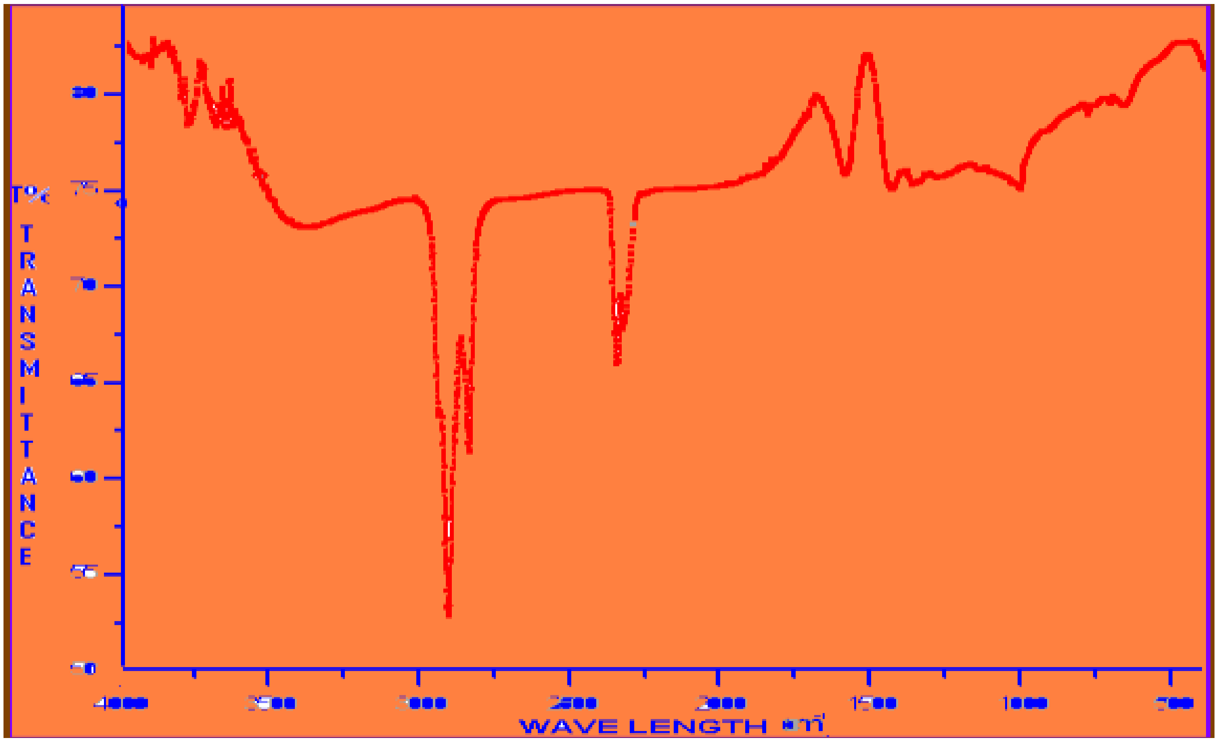

Figure 2: IR Spectra of malachite green

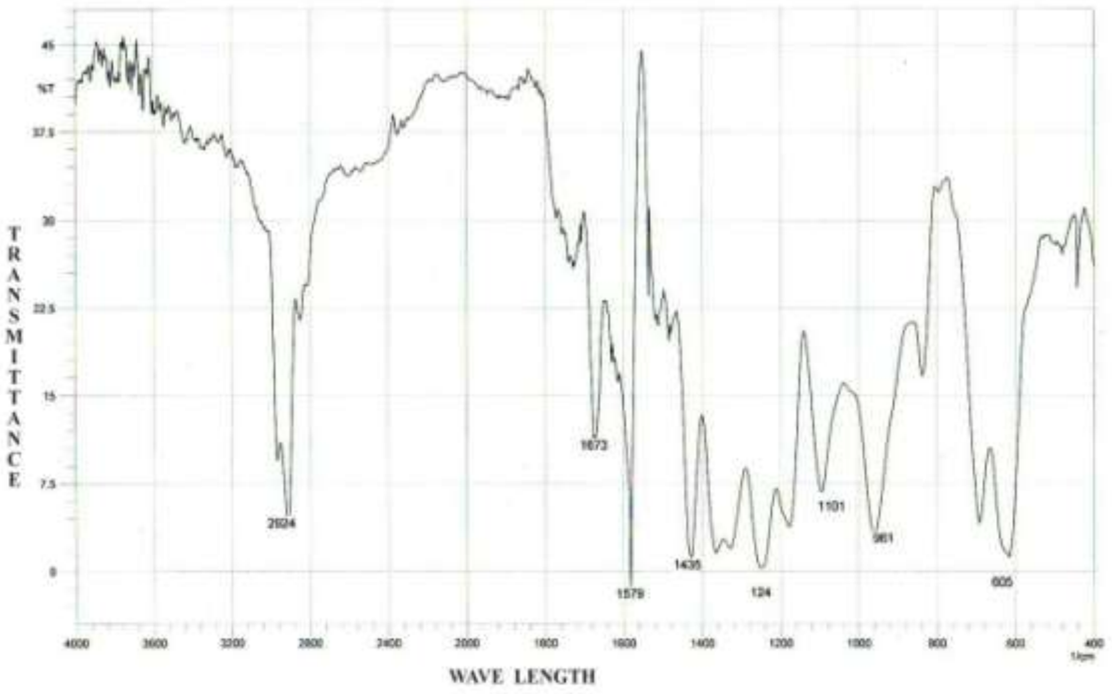

Figure 3: IR Spectra of 6 % malachite green sensitized PVC sample

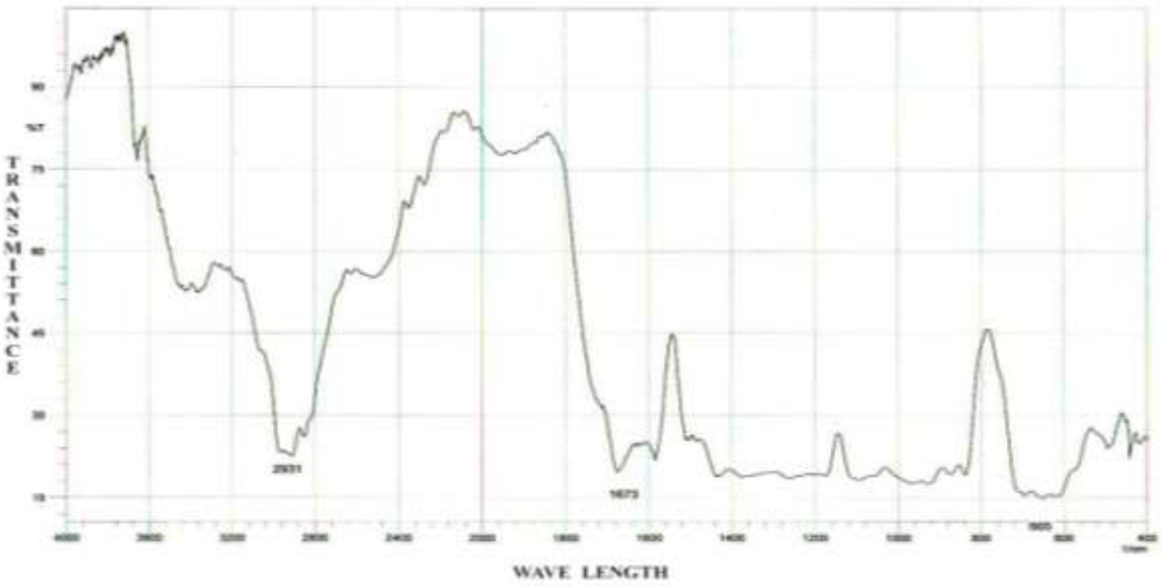

Figure 4: IR Spectra of 7.5% malachite green sensitized PVC sample

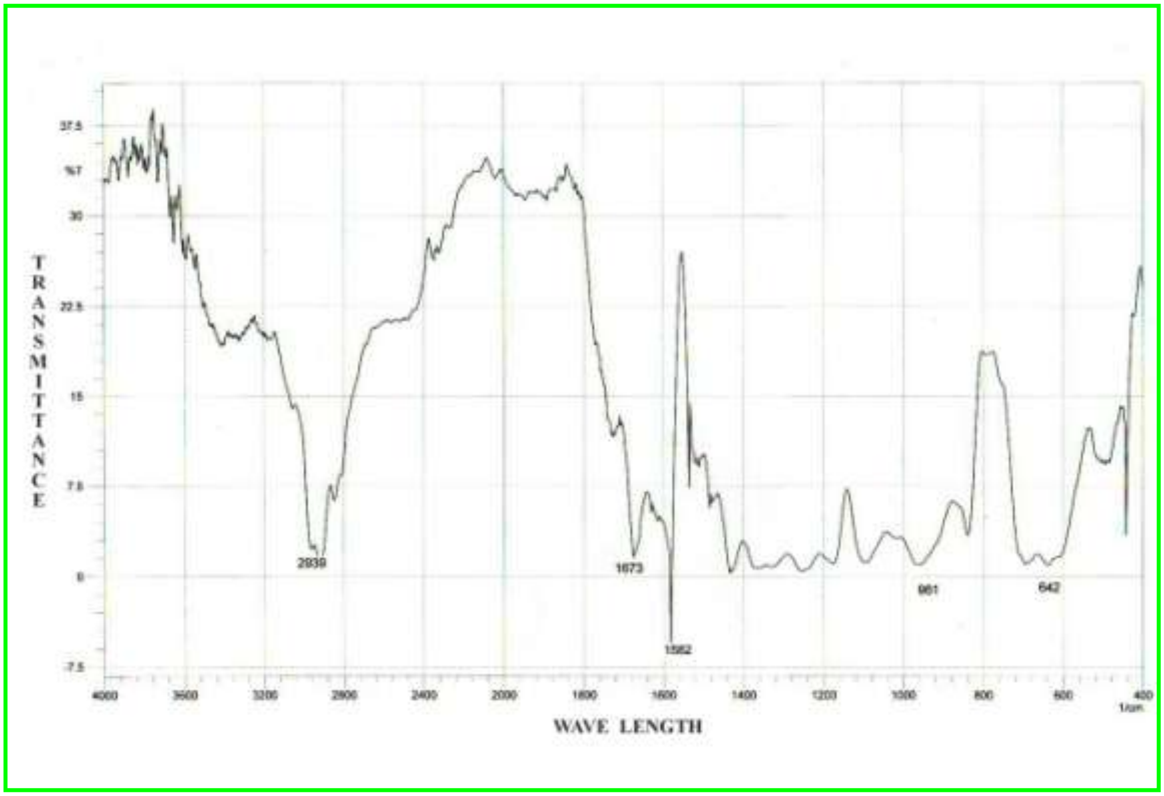

Figure 5: IR Spectra of 10 % malachite green sensitized PVC sample

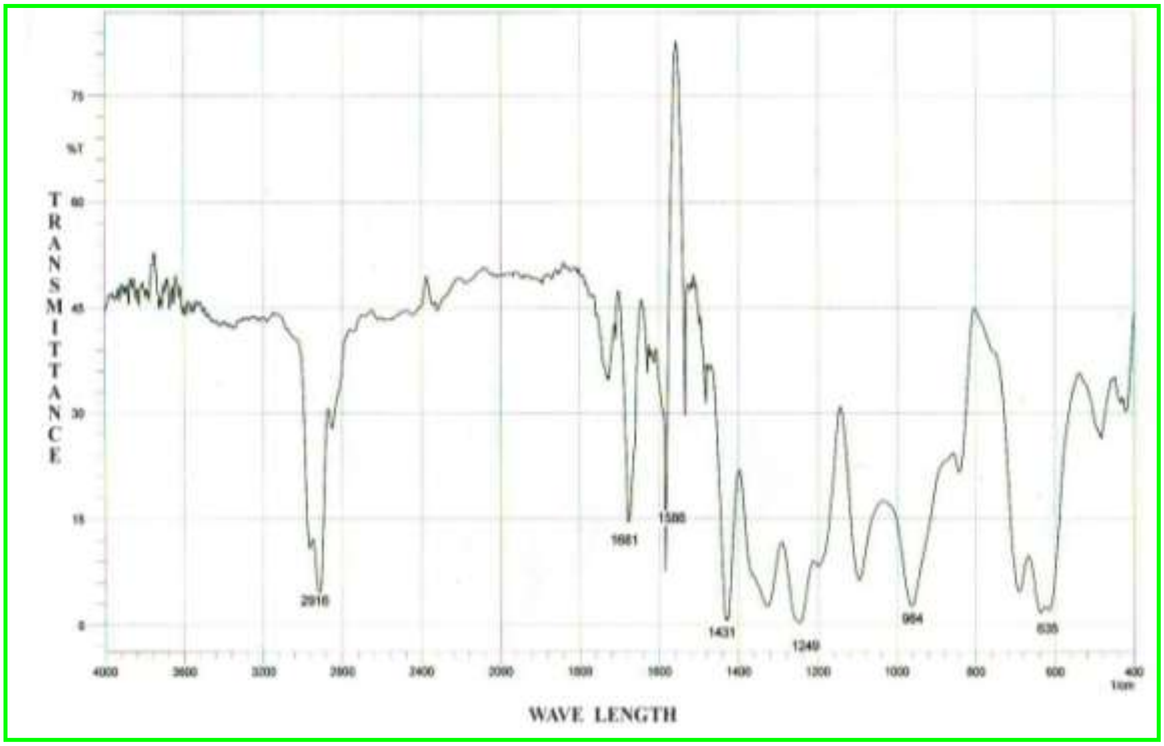

Figure 6: IR Spectra of 15% malachite green sensitized PVC samples

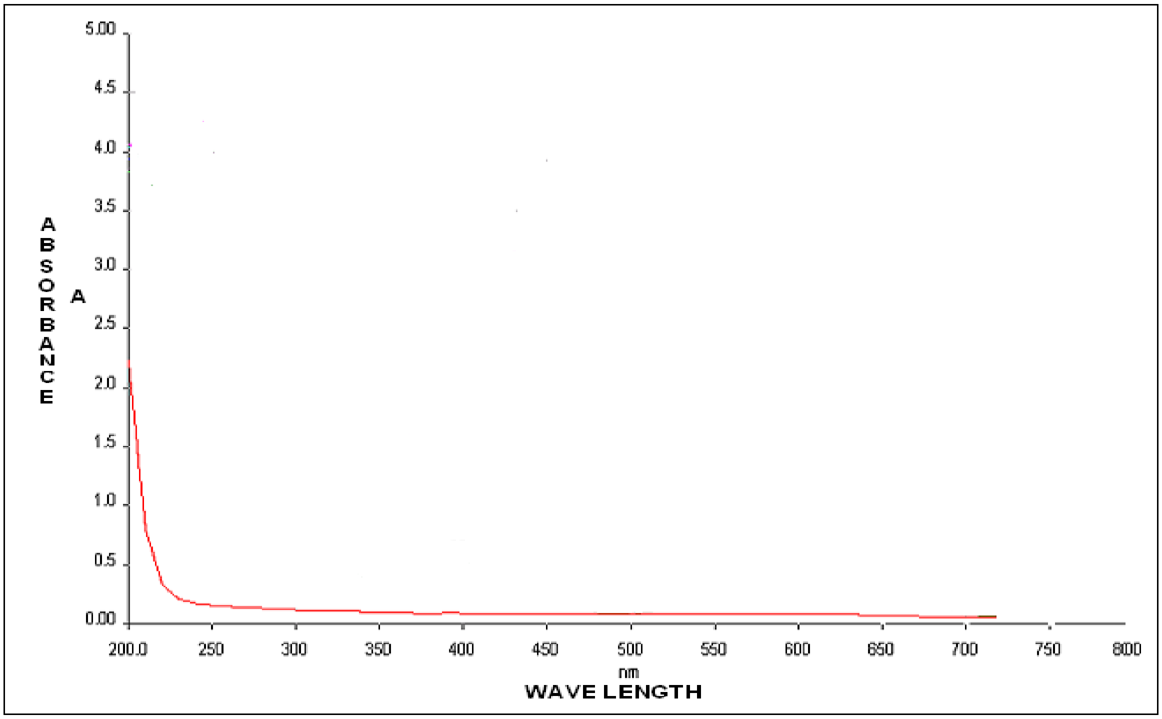

Figure 7: UV Spectra of pure polyvinyl chloride (PVC) sample

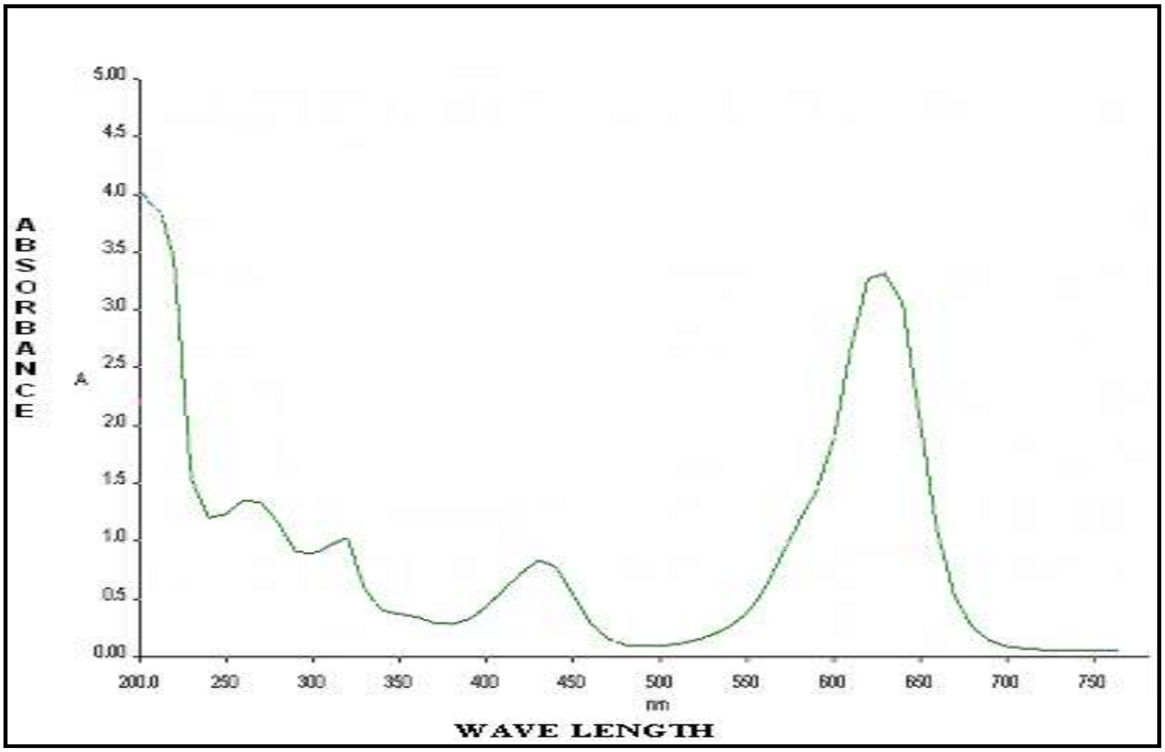

Figure 8: UV Spectra of polyvinyl chloride 6% sensitized (PVC) sample.

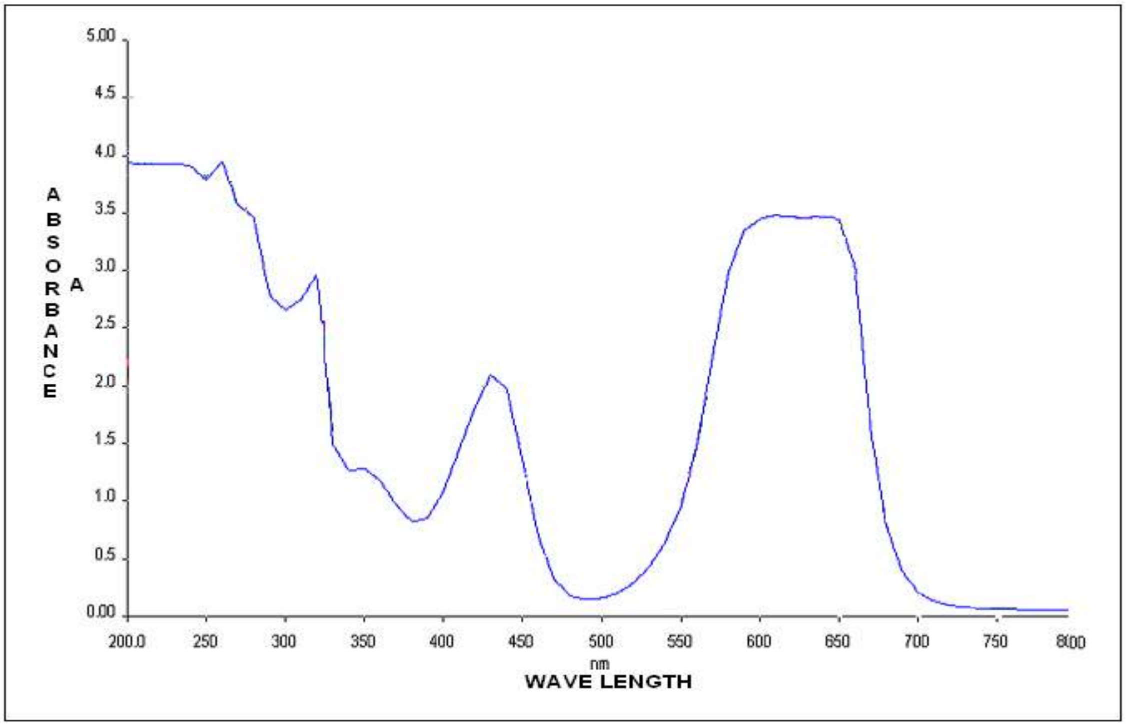

Figure 9: UV Spectra of polyvinyl chloride 7.5% sensitized (PVC) sample

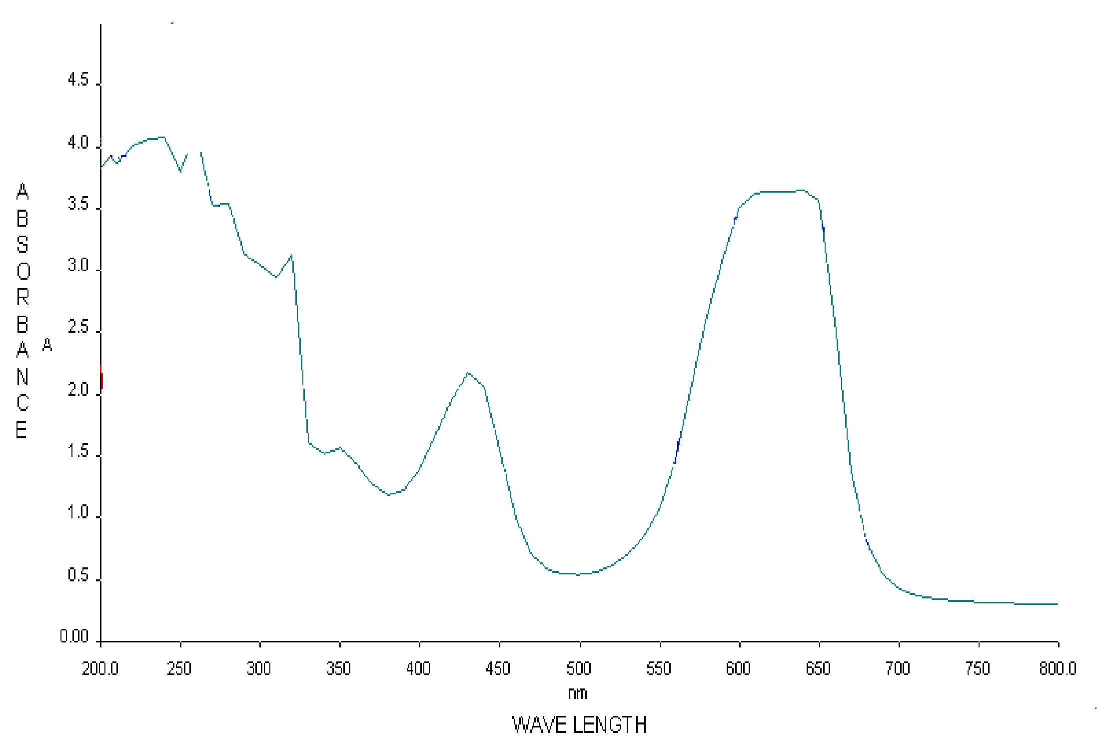

Figure 10: UV Spectra of polyvinyl chloride 10% sensitized (PVC) sample

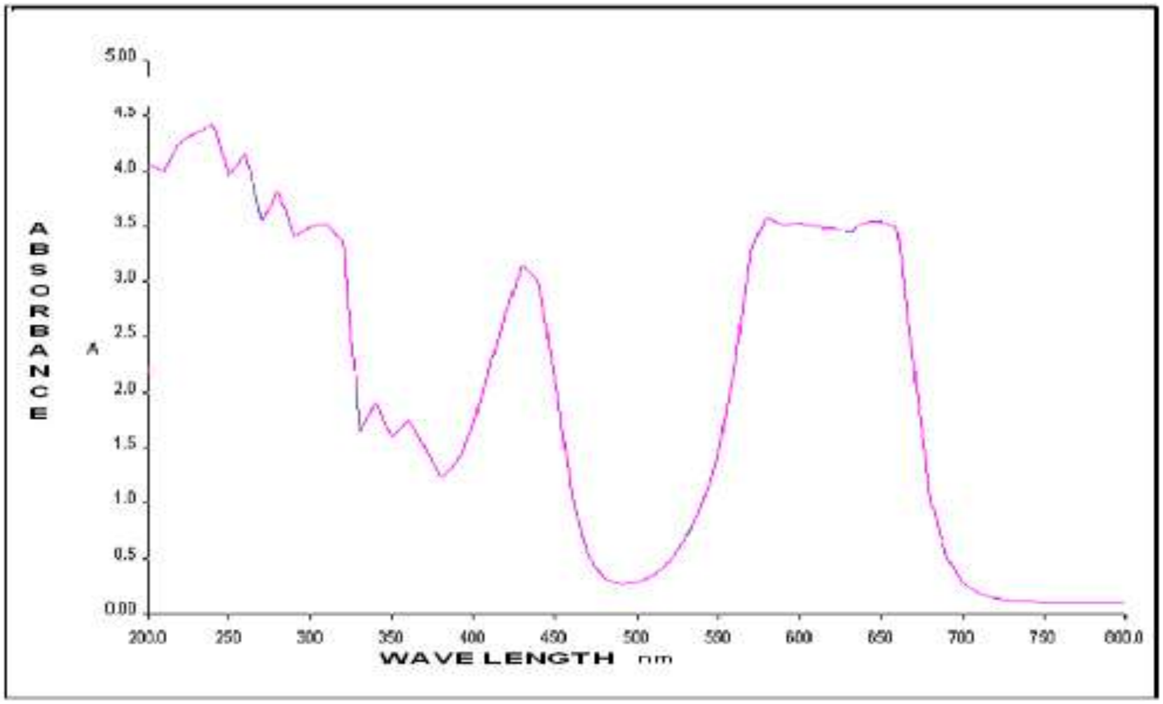

Figure 11: UV Spectra of 15 % malachite green sensitized PVC samples

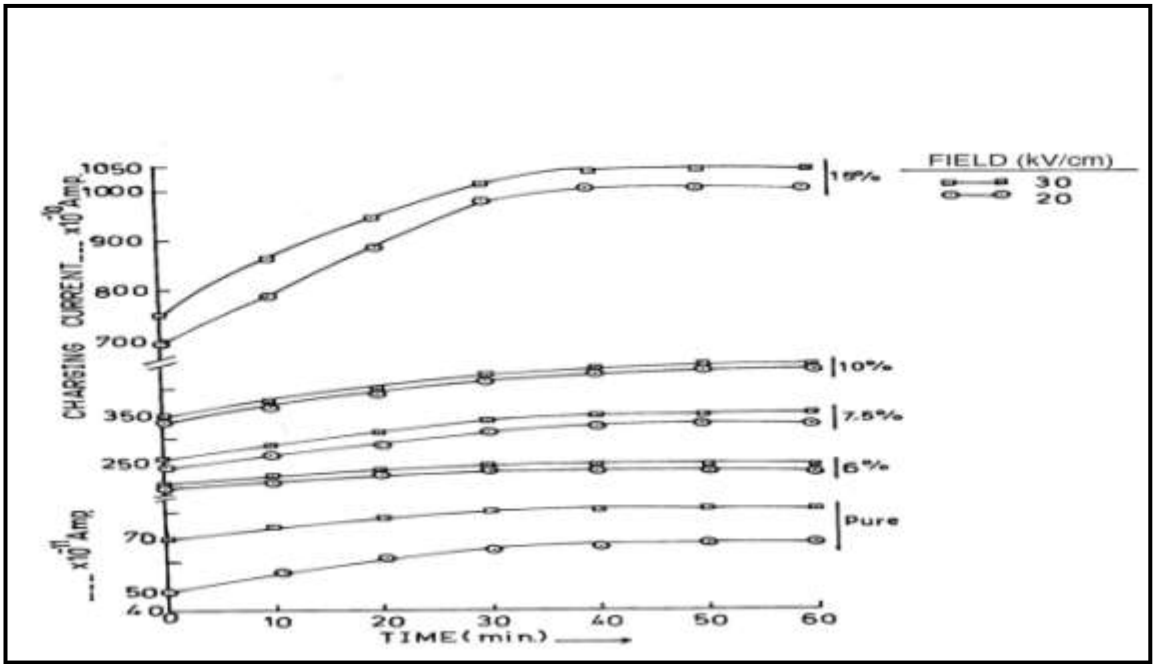

Figure 12: Time dependence of transient charging current for pure and various sensitized (i.e. 6, 7.5, 10 and 15%) polyvinyl chloride samples charged with fields Ep=20 and 30 kV/cm at temperature Tp=90°C.

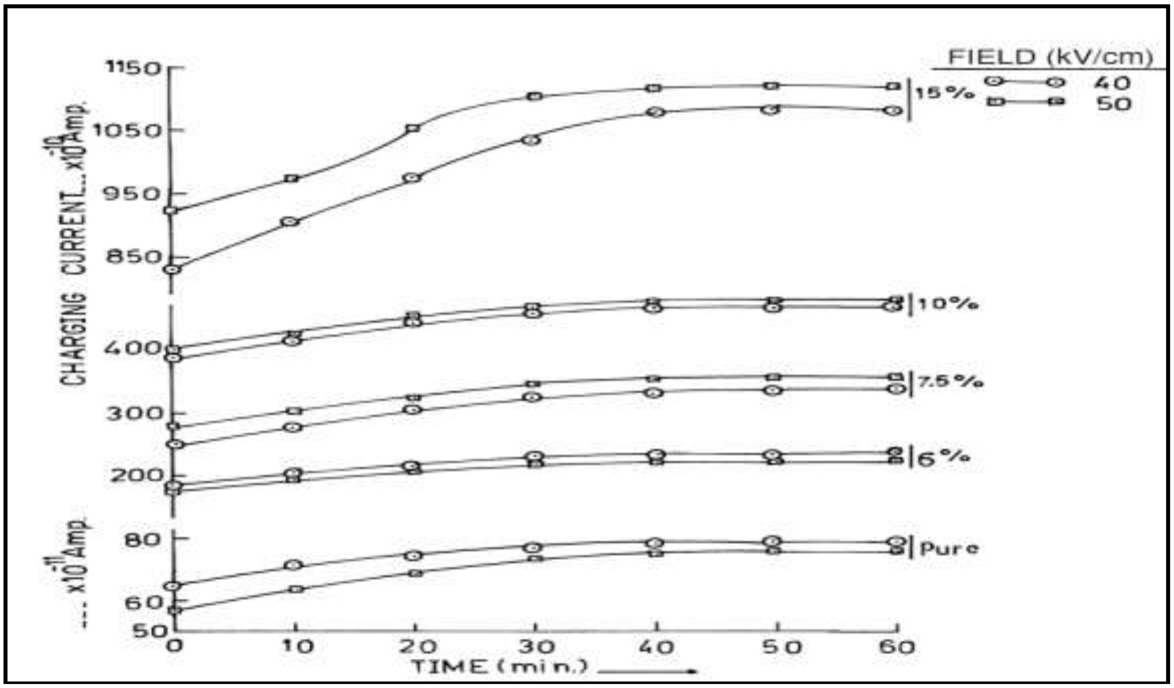

Figure 13: Time dependence of transient charging current for pure and various sensitized (i.e. 6, 7.5, 10 and 15%) polyvinyl chloride samples charged with fields Ep=40 and 50 kV/cm at temperature Tp=90°C

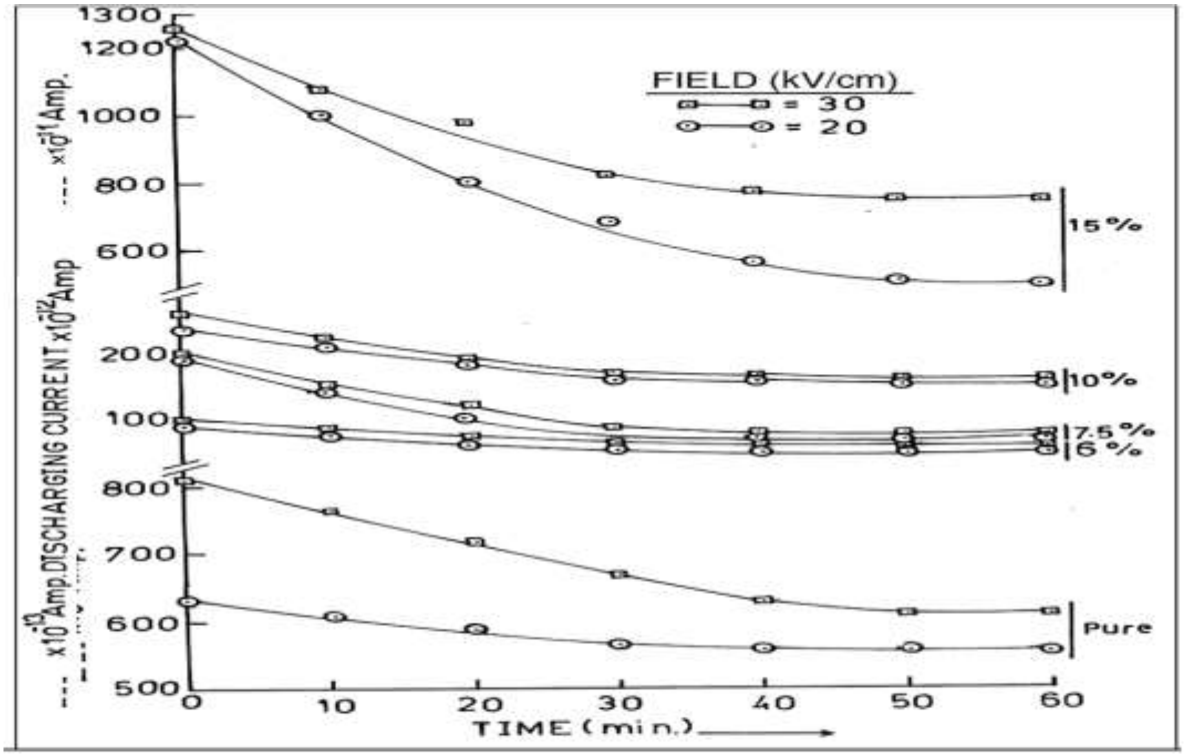

Figure 14: Time dependence of transient discharging current for pure and malachite green sensitized polyvinyl chloride samples charged with fields 20 and 30 kV/cm at temperature Tp=90°C.

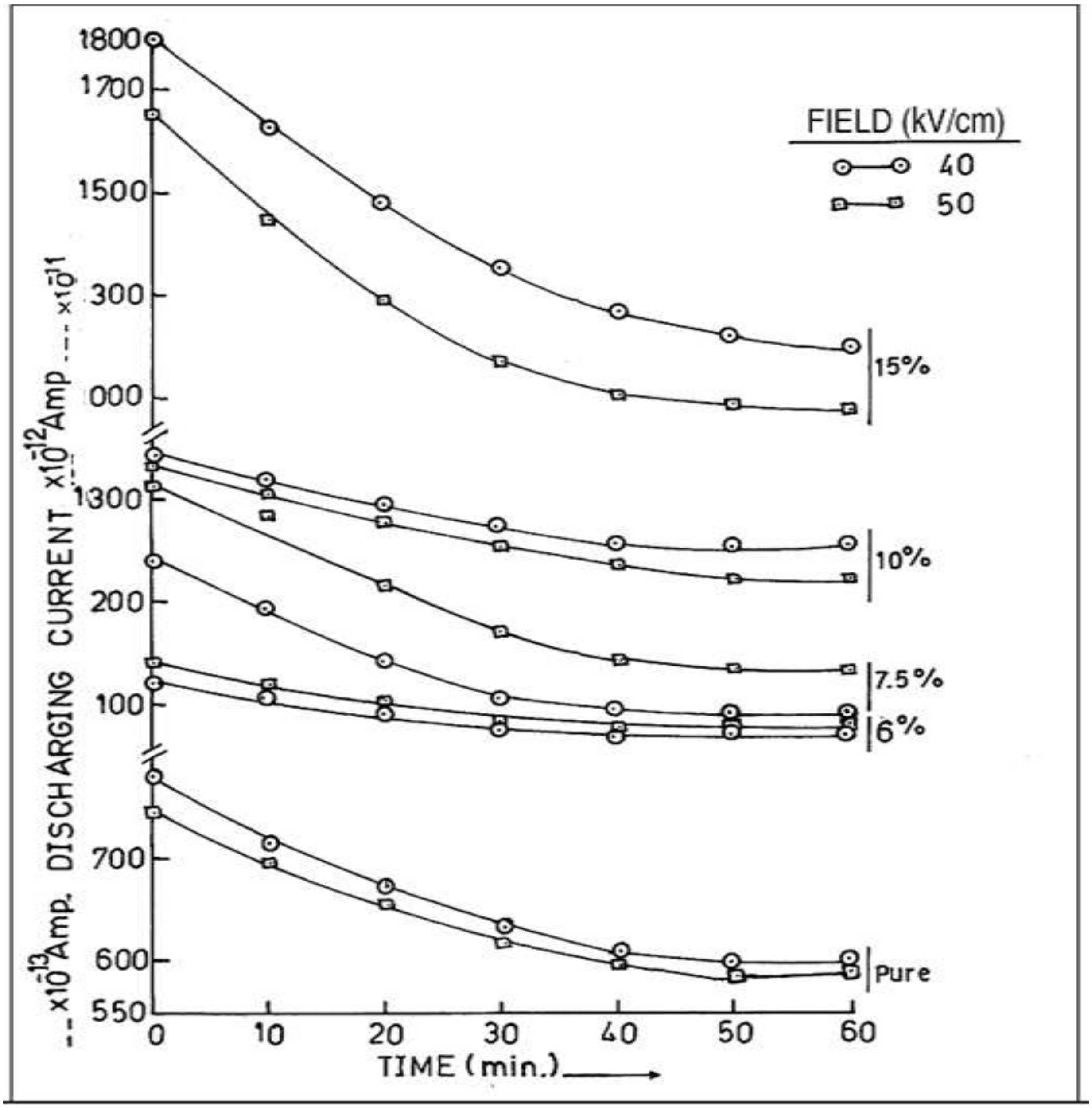

Figure 15: Time dependence of transient discharging current for pure and malachite green sensitized polyvinyl chloride samples charged with fields 40 and 50 kV/cm at temperature Tp=90°C.

Table 1: Analysis of IR spectra of pure and sensitized polyvinyl chloride samples

PURE PVC	MALACHITE GREEN	SENSITIZED PVC			
		6%	7.5%	10%	15%
WAVE LENGTH Wave number (cm^{-1})	WAVE LENGTH Wave number (cm^{-1})	WAVE LENGTH Wave number (cm^{-1})	WAVE LENGTH Wave number (cm^{-1})	WAVE LENGTH Wave number (cm^{-1})	WAVE LENGTH Wave number (cm^{-1})
2960	3895	3020	3680	3680	2970
2924	29503	2924	3440	3440	2916
------	2844	1760	2931	2939	1720
------	2350	1673	1673	1673	1681
1590	2340	1579	1586	1582	1586
1423	1750	1435	1440	------	1510
1300	1580	1346	--------	------	1431
1249	1360	1240	-------	-----	1358
------	------	1180	-------	-----	1249
-----	------	1101	-------	------	1200
1089	1160	961	-------	961	1102
968	725	839	-------	-----	964
846	-------	696	665	642	840
703	-------	605	-------	------	680
640	-------	-----	-------	------	635
580	-------	450	-------	------	500

Table 2: Analysis of UV spectra of pure and sensitized polyvinyl chloride samples

ABSORBANCE PEAKS	PURE PVC SAMPLES	SENSITIZED SAMPLES							
		6%		7.5%		10%		15%	
		PEAK POSITION (nm)	ABSORBANCE (A)	PEAK POSITION (nm)	ABSORBANCE (A)	PEAK POSITION (nm)	ABSORBANCE (A)	PEAK POSITION (nm)	ABSORBANCE (A)
FIRST	NOT FOUND	260	1.25	230	3.9	240	4.1	230	4.4
SECOND	NOT FOUND	320	1.00	310	2.9	280	3.1	270	3.5
THIRD	NOT FOUND	430	0.7	430	2.1	430	2.25	430	3.2
FOURTH	NOT FOUND	630	3.4	580	3.5	640	3.7	610	3.6

The sensitizer M-green used in the present study is a cytonic dye having triphenylmethane structure reported by Gutman and Lynos (1967) and Lalnand and Srivastava (2011)**.** The colored ion is charged positively and has one amino group retaining with an unshared pair of electron, with reference of Khare and Chandok (1995) and Khare and Srivastva (1982) which may responsible for the formation of charge transfer complexes according to Piper and Williams (1958) and Onodo *et al.*, (1979). CTC`S are new molecular complexes formed by the interaction between an electron accepting A and electron donating D molecule CTC'S may be formed as a result of partial or complete transfer of electron from D to A. Complex formation of sensitized polymer has also been explained by Pillai (1981),on the basis of a weak band formed between the electron accepting molecule and electron donating molecule. The appearance of new peaks near about 1673 and 1180cm^{-1} may be indicated of this charge transfer complex according to Talwar *et al.*, (1985).

The higher value of the transient current in the sensitized samples is expected to be due to the formation of charge transfer complexes. Malachite green when mixed in polymer may reside at various sites, it may be substituted into the polymer chains or resite at the amorphous crystalline boundaries and defuse preaprentially to the amorphous region forming charge transfer complexes or it may be exist into the form of molecular aggregates between the polymer chains. In the case of PVC the possibility of malachite green substituting into the structure is negligible because of the lower electro negativity of malachite green compared with that of the PVC macromolecule. The CTC are supposed to create localized states of various depths which we lead to trapping sites distributed over a considerably wide energy range. The formation of CTC is considered to reduce the barrier between the trapping sites providing a conducting path through the polymer matrix and would result in the enhancement of its conductivity.

The formation of the charge transfer complex between PVC and M green is also evident from the increase in the current value of these samples reported earlier in TSDC study by Khare and Bhardwaj (2011)**.**

Conclusion

All of these results lead to the conclusion that sensitizer interacts with the polymer matrix and forms charge transfer complex, effecting the spectroscopic behavior of the polymer. The CTC formation is responsible for the development of charge storage properties of the sensitized polymer samples.

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