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The Study of Mechanisms of Charge Production in Pure and Sensitized Polymer Films

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Abstract

The mechanisms of charge production in pure and malachite green sensitized Polyvinyl chloride (PVC) samples have been studied by short circuit thermally stimulated depolarization current (TSDC) measurement and ultraviolet spectroscopy (U.V.) studies. The samples were prepared by the casting from solution technique whose thickness measured around 30µm. The samples were sandwiched between similar aluminum electrodes and polarized at temperature 105°C with polarizing fields 20, 30, 40 and 50kV/cm. Two peaks current maximum found around at 63±8 and138±7°C for pure, 06 and 7.5% sensitized PVC samples, while for higher concentration (i.e.10 and 15%) one peak was measured around ≈65°C in positive direction and the other peak around ≈140°C in the negative direction. The TSDC spectra have been used to calculate activation energy by initial rise method .The calculated activation energies are 0.389-0.719ev for pure PVC and 0.298-1.09ev for sensitized PVC samples. The magnitude of peak current increases with polarizing field and temperature, dipolar, space charge and charge transfer complexes mechanisms may be responsible for this nature. In the case of UV spectra no band appears in pure PVC however the addition of malachite green, gives rise four absorption bands around 260, 310, 440, and 630nm.The average effect has been observed in the intensity of third (400-450nm) and fourth bands (550-700nm). The formation of charge transfer complexes is evidenced in the UV-visible absorption spectra by the appearance and change in the intensity of absorption bands.

Keywords: Thermally stimulated depolarization current (TSDC), ultraviolet spectroscopy, pure and sensitized polyvinyl chloride, casting from solution technique, thermo electrets, dipolar, space charge and CTC`S mechanisms.

Introduction

The thermally stimulated depolarization current (TSDC) is an effective tool for extracting information about internal structure and molecular relaxation as well as the establishment and decay of the space charge due to trapping of charge carriers and their subsequent thermal release from trap in polymer[1-4]. The total charge stored in a polymeric electrets and the different mechanisms which contributed to these charge are sensitive to the structure of the forming material .Charge storage may be due to either dipolar orientation or space charge, there must be free equilibrium charges in the electrets which are responsible for its intrinsic ohmic conductivity. The reorientation of all aligned dipoles at random due to the thermal agitation, the motion of excess charges origination from space limited drift and diffusion and ohmic conduction result in the decay of the net charge of an electrets during TSDC. The TSDC of polar dielectrets usually shows different peaks indicating thereby the depolarization of thermo-electrets are realized by several processes two of these are the relaxation of aligned impurity point defect complex[5] and relaxation of the space charge caused by mobile defects accumulated at the electrodes[6,7].

It is known that a dielectric medium takes a long time to relax to the steady state at low temperature. Therefore it is useful to stimulated the discharge of the polarized dielectric at a higher temperature**.** If the temperature of the dielectric is increased at a constant rate glow peaks will be obtained at a particular temperature which are related to the activation energy of the relaxation process. The carrier mobility in polymer is extremely small because the carrier are predominantly located in trap[8] increased the mobility in the polymer by impregnating the material with impurity[9]. Basically three kinds of phenomena can occur in thermal charging[10,11].

We have studied the depolarization behaviour of pure and sensitized PVC samples using the short circuit thermally stimulated discharge current technique and formation of charge transfer complex by Ultraviolet Spectroscopy.

Material and Methods

The polyvinyl chloride (PVC) and malachite green used in the present work were procured from M/s Robert Jonson, England. Dimethyl formamide (D.M.F.) was used as the solvent. PVC 100 mg was dissolved in DMF 10 ml by stirring at 60°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°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 samples approximately 30μm in thickness were sandwiched between the two aluminum electrodes. The sample holder was placed in a furnace and heated up to the poling temperature of 105°C. The sample was allowed to remain at that temperature for about 60 minute. Then electric field of desired strength was applied for 60 minute at fixed poling temperature. The sample was allowed to cool down at room temperature in the presence of applied field. Total time of polarization was adjusted to be 180 minutes in each case.

The thermo electret was then short-circuited at room temperature for 5 minutes to remove the frictional and stray surface charges. The voltage was applied by high voltage unit (EC–HV 4800 D). The sample temperature was raised at a liner heating rate of 5°C/minute, while the current was recorded by means of a Keithley 610 C electrometer. For ultraviolet study PARKIN ELMER UV/VS spectrophotometer Mambda-12 was used.

Results and Discussion

The TSDC spectra of pure PVC and sensitized samples (i.e.6 and7.5%) consist of two peaks, located around 63±8 and 138±7°C respectively, represented by figures 1-3. However on increasing sensitization, the first peak shifts towards higher temperature side and second peak shifts towards lower temperature side and current starts appearing in the negative direction. For the higher concentration (i.e.10 and15%) both the peaks merge into one and the corresponding thermograms are characterized by peaks opposite in polarity observed around 65 and 140 °C respectively are shown in figures.4-5. This shows the negative effect of malachite green[12]. The peak current increases with the increase in polarizing field. The activation energy is calculated by the initial rise method listed in table -1 (results not shown). PVC is known to exhibit three relaxation processes β, α and α'[13]. The β peak occurs in the glassy state of the polymer usually below room temperature and is due to the local reorientation of the polar side groups while the α peak is found at the glass rubber transition temperature $T_{g,}$ where either the segment motion of the main chain, or the disorientation of the polar side group carrying a net dipole-dipole moment sets in.

The third process is α' which is observed at temperature higher than those for α process probably due to the charge accumulation (space charge) near the electrodes. In the present investigation, we have observed two peaks. The first peak observed just near the glass transition temperature of PVC corresponds to α relaxation process and the activation energy associated with this discharge process is 0.3 eV. The observed activation energy is comparable to that associated with the molecular motion or the phase transition process in PVC[14,] it must correspond to a molecular motion or dipole disorientation process rather than a trap depth.

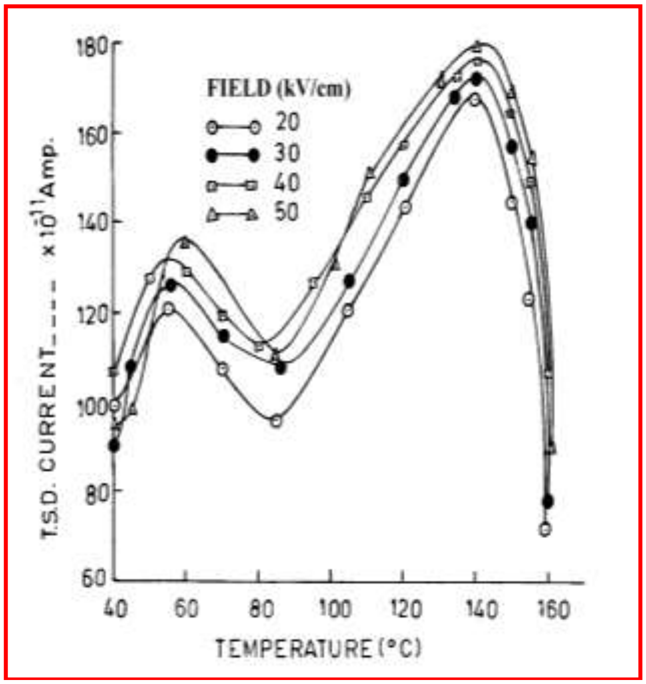

Figure-1
TSDC Thermograms of pure polyvinyl chloride (PVC) samples polarized with various fields at polarizing temperature Tp=105°C

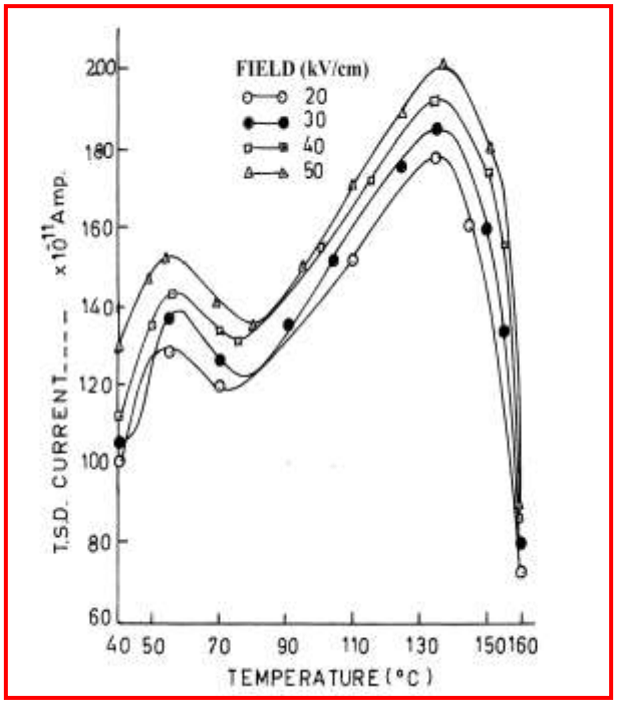

Figure- 2
TSDC Thermograms of 6% malachite green sensitized (PVC) samples polarized with various fields at polarizing temperature Tp=105°C

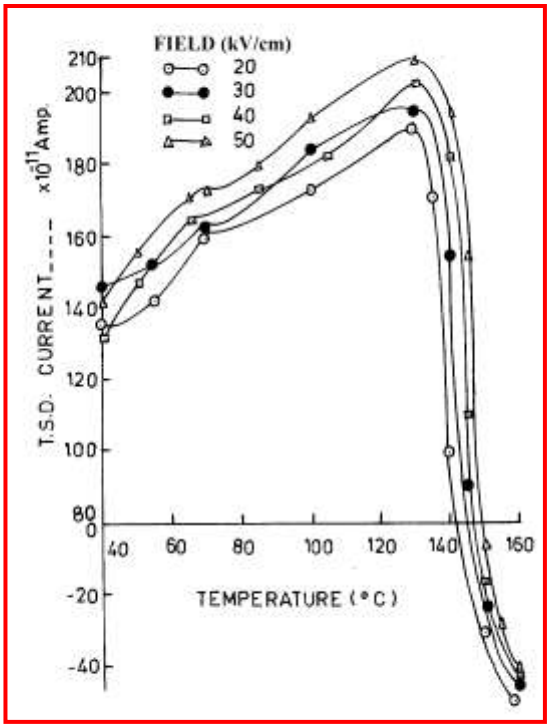

Figure-3
TSDC Thermograms of 7.5% malachite green sensitized (PVC) samples polarized with various fields at polarizing temperature Tp=105°C

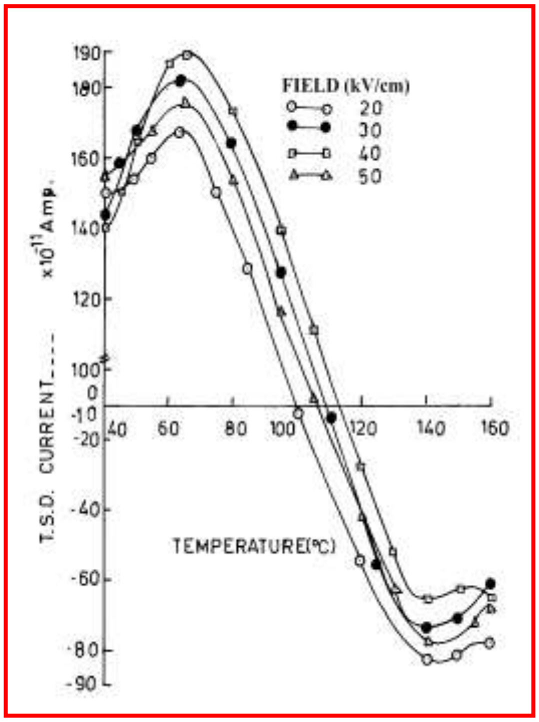

Figure-4

TSDC Thermograms of 10% malachite green sensitized (PVC) samples polarized with various fields at polarizing temperature Tp=105°C

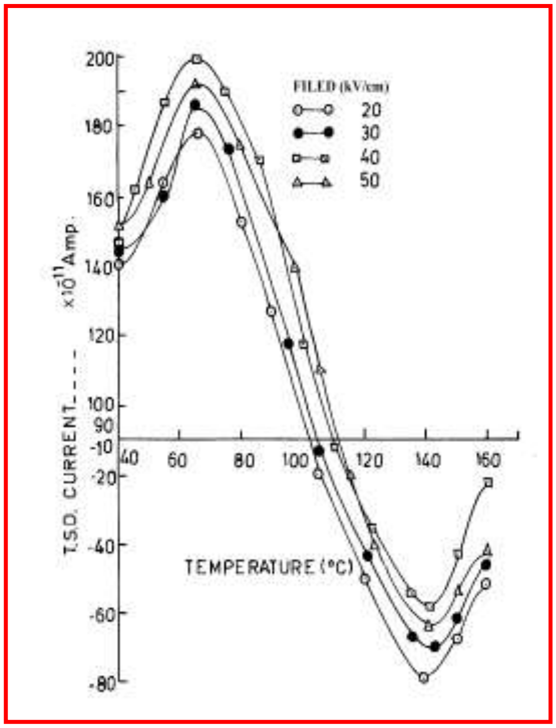

Figure-5
TSDC Thermograms of 15% malachite green sensitized (PVC) samples polarized with various fields at polarizing temperature Tp=105°C

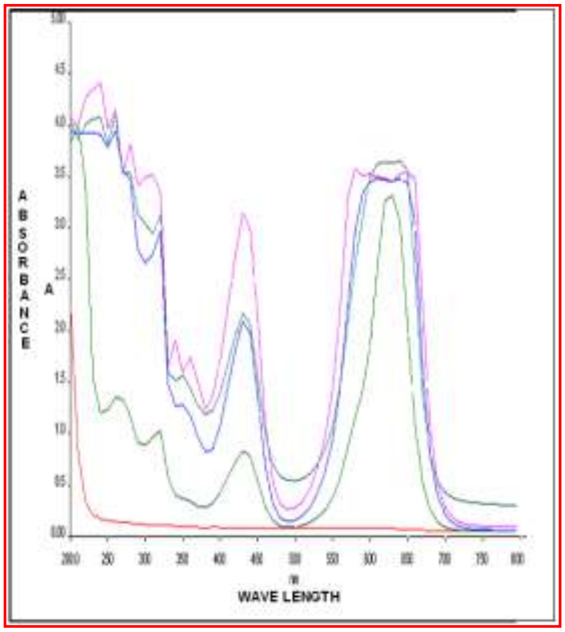

Figure- 6
UV Spectra of pure and sensitized PVC Samples

— Spectrum of pure Polyvinyl chloride sample
— Spectrum of 6% sensitized PVC sample
— Spectrum of 7.5% sensitized PVC sample
— Spectrum of 10% sensitized PVC sample
— Spectrum of 15% sensitized PVC sample

Further the observed peak must be related to the depolarization of the aligned dipoles connected with the chain of the polymer rather than to the charge released during the glass transition temperature. Because the magnitude of the charge corresponding to this peak increases linearly with an increase of E_p suggesting a dipolar mechanism is involved during the depolarization process of peak first. The activation energy of 1.07 eV for the higher temperature peak α' is large and associated with an ionic mechanism rather that with a dipolar mechanism or some dipolar mechanism of some dipolar rotation.

For this peak released charge show a saturation trend with increase in E_p. The mechanism of ionic conduction in PVC, found by several workers[15,16] and they confirm the existence of excessive ions in the bulk of the polymer. These ions must have come either from the dissociation of some of the molecules or from the thermal degradation of PVC.

The appearance of a peak with polarity opposite to that of the dipoles suggests that, in addition to the normal mechanism of polarization some other mechanism must be operative. Malachite green is a cationic dye having triphenylmethane structure [25,2] .The colored ion is charged positively[19], the dye having triphenylmethane structure can easily form charge transfer complexes (CTC) with the substrate[1,20]. Malachite green has one amino group containing an unshared pair of electrons[21,22] which may be responsible for CTC formation. Also in view of such consideration, malachite green is supposed to interact strongly with polymer matrices to form CTC[23.]

The shift of 140°C peak towards lower temperatures with increasing concentration of malachite green may be due to the increase in the mobility of charge carriers. The CTC are supposed to create localized states of various depths which will lead to trapping sites and distribute over a considerably wide energy range. This may be the cause of the merging of first and second peaks. Thus, we found not only that the original trapping levels corresponding to the TSC peaks at 63±8 and 138±7°C are quantitatively affected by the addition of malachite green but also that new peaks appear which depend upon the amount of doping used. The low temperature peaks may be attributed to the shallow trapping of mobile charge carriers, while the high temperature peak is due to the re-orientation of dipoles. On further sensitization, these carriers are bound to the impurity sites, and this result the disappearance of these peaks[24.]

It appears that because of increased intermolecular interaction on sensitizing, dipoles are entangled in such a way that the contribution of orientation of dipoles towards the polarization of the sample in the presence of an applied field becomes insignificant. It has been stated earlier, the observed peaks exhibit characteristics of both dipolar as well as space charge behavior[25,26].

The space charges consisting of charges within the samples which become mobile above the glass transition temperature is expected to be responsible for the intensity of polarization. Moreover, since the second observed peak is above the glass transition temperature, it will definitely have partial contribution from the Maxwell-Wagner type space charge at the crystalline amorphous phase boundaries.

It is interesting to note that the TSDC behaviour of PVC is modified considerably on sensitization. Ascertaining the existence of a charge transfer complex in polymeric systems is often a difficult task. Many charge transfer complexes are highly colored and therefore spectral studies are more useful. The formation of charge transfer complexes is evidenced in the UV-visible absorption spectra by the appearance and change in the intensity of absorption bands.

Absorption spectra of pure and sensitized PVC (with different percentage of malachite green i.e. 6, 7.5, 10, and 15%) are shown in figure 6. No bands appears in the spectra of pure sample however, the addition of malachite green in PVC gives rise four absorption bands around 260,310,440 and 630 nm. It is clear that an average effect has been observed in the intensity of third (400-450 nm) and fourth bands (550-700 nm).

Table-1
Depolarization kinetic data i.e. Activation Energy for pure and various malachite green sensitized PVC samples

Field (kV/cm)	Temperature °C	Pure PVC (eV)		6% M green sensitized PVC (eV)		7.5% M green sensitized PVC (eV)		10% M green sensitized PVC (eV)		15% M green sensitized PVC (eV)	
20	105	0.389	0.700	0.359	0.685	0.341	0.671	0.339	1.09	0.317	0.991
30		0.387	0.719	0.351	0.678	0.339	0.669	0.336	1.07	0.307	0.989
40		0.383	0.714	0.349	0.667	0.337	0.660	0.329	1.00	0.301	0.981
50		0.373	0.704	0.340	0.635	0.340	0.650	0.326	1.00	0.298	0.979

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 intensity of the bands appears in the range of 200-400 nm found to increase with the increases in malachite green concentration. It is evident from all the figures that width of the fourth band increases and intensity of the band is found to decrease with optimum concentration, listed in table 2. The formation of charge transfer complexes[27] is evidenced in the UV-visible absorption spectra by the appearance and change in the intensity of absorption bands.

Conclusion

Thermally stimulkated discharge current of pure polyvinyl chloride (PVC) revel a strong dependence on the sensitization. Which is the source of charge carrier responsible for conduction and observed polarization of the polymer. Space charge, ionic conduction, dipolar and charge transfer complexes mechanisms are operated by these studies.

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