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Comparative Study of Relaxation in Polymer Blends Film

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Abstract: *Thin films of micro composit polymer PVC-PMMA doped with and cinnamic acid are prepared using isothermal evaporation techanique. Current time characteristics, by application of direct and reverse polarities in succession was continued until conduction current reached stady state. Therelaxation time τ obtained from these plots. The Values of drift mobility 'μ'and density 'n' of change carriers obtained from theoretical relations. The magnitude of time, found in the present micro composites system, agrees quite well with that reported in a literature. Increase of concentration of dopants adversely affects mobility while favours charge carrier density.*

Keywords: *Polyvinyl chloride (PVC) ; Polymethyl methacrylate (PMMA);Micro – Composites ; Relaxation time.*

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I. Introduction

The polymer blends (mixture of two or more polymers), and doped polymeric blends also known as composites (consisting of polymer with some non-polymeric material) are presently the samples, which are providing a wide scope for investigation. This is on account of the various ways by which their properties can be tailored so as to suit a particular purpose. Metal filled conducting polymer composites, carbon black/carbon fiber reinforced conductive polymer composites [1] are some of the ares which attract investigations. The mechanical properties have been widely the investigated. Recent past shows that electrical and optical properties of polymeric sample are those, which can open treasures of knowledge in the field of polymer, with this in view we have been investigating such polymer blends and /or their composites using TSDC, UV-Visible, FTIR. XRD and electrical conduction mechanism techniques. The present paper narrows down the scope in studying the relaxation phenonmenon in doped polymer blend system via current time characteristics.

The sample chosen are two system viz.

1. Polyvinyl chloride (PVC) + PMMA blend doped with iodine and
2. Polyvinyl chloride (PVC) + PMMA blend doped with cinnamic acid. current – time characteristic are discussed with reference to mobility 'μ' and charge carrier density 'n' in the light of concentration variation of dopants and electric field intensity.

II. Theory :

With the application of electric field in one direction, the dipolar alignment takes place and current reaches a particular value. Now the field is removed and sample short circuited through a picoammeter, which shows this current flowing through the sample which decreases with disalignmentof dipoles as the charging field is removed, and time is advancing. Initially the fall in current is steeper which settles down to a constant value. (as is evident from the graph). Now with reverse polarity of field, the dipoles tending to align in opposite direction. The distribution of dipoles passes through a random phase showing current. Which grows to a maximum value corresponding to an alignment in the opposite direction. This instant of time denoted by tmax at which the current show a maximum value can be very approximately taken as the time interval between disoriented and oriented dipolar arrangement i.e. the relaxation time. The relaxation time τ is given by equation [4] as

$$T = tmax = \overline{}$$

Where. d - film thickness

μ - mobility of charge carriers

v - voltage applied

The charge carriers density n. can then be calculated from equation.

$J = nq\mu E$

E – being the electric field intensity v/d Q – charge on carriers

III. Experimental details :

3.1 Preparation of sample :

The polyvinyl chloride (PVC) of standard grade product supplied by Polychem Industries. Mumbai and polymethylmathacrylate (PMMA) supplied by Dental Product of India Ltd. Mumbai were used for the study. The two polymers PVC (1.5gm) and PMMA (0.5gm) were taken in the ratio of 3.1 by weight 1.5gm of PVC in 20ml of tetrehydrofuran (THF) and 0.5gms of PMMA in 10ml of THF were dissolved separately. Afterallowing them to dissolve completely the two solution were mixed together. Iodine and cinnamic acid were taken in the percentage weight (0.2 %) was dissolved 15ml THF to produce iodine and cinnamic acid solution were later mixed with uniform solution of PVC and PMMA. The total volume of solvent was kept constant at 35ml. The solution was heated at constant temperature 333K for two hours to allow polymers to dissolve completely to yield as homogenous solution.

The films were prepared by pouring this solution on a thoroughly cleaned optically plane glass plate kept floating in a pool of mercury at a constant temperature (313K). In this way films was prepared by isothermal evaporation technique [2.3]. The film was subjected to 12hrs heating at constant temperature 323K and another 12 hours at room temperature to remove the traces of solvent. Finally the film was removed from glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alchol to remove the surface impurities.

3.2 Thickness measurement :

The thickness of the sample film was measured at the edge, by a compound microscope with an acculometer with a least count of 13μm and 3.3μm at the magnification of 1:10 and 1:100 respectively. The film thickness is 80μm

3.3 Electrode coating :

Electrode coating on the film was done with quick drying silver paste using a mask of circular aperture of diameter 2.4cm.

3.4 Electret Preparation :

The sample was mounted into the sample holder. The polarising field Ep was maintained for 30 min between two faces at temp 333K. The electric field across the sample was removed & the sample was short circuited for 15 min to remove the stray charges by wapping the sample in a conducting aluminium foil. The electrets were prepared at differentpolarizing field i.e. Ep = 37.5kv/m, 75 kv /m, 112kv/m 150kv/m & 180kvm respectively at temp 333k

IV. Current – time measurements :

After electrets preparation current – time measurement are carried out at a fixed field strength, with different dopant concentrations of the polymer blends.

I] The sample film, metalized on both sides, is charged by application of dc (direct) field at an elevated temperature of 60 °C (333K). The field is removed and the sample is short circuited through a Picoammeter and the discharge current is noted at regular intervals of time, unit the current show almost a consatant value.

II) Then the sample film is recharged with same dc field but with reverse polarity at same temperature 333k for same time. The field (with reverse polarity) is removed and sample is short circuited through picoammeter and again the discharge current is noted to regular interval of time until the current shows almost constant value .

On reversing the polarity the current increases to a maximum value and then gradually falls until is shows almost constant value. This time interval during which current become maximum is denoted by tmax is approximately the relaxation time τ.

Step I and II are repeated for different field, Strengths and for each field strength time tmax (τ) is noted.

V. Result an discussion :

The relaxation time in the range of seconds, observed in the present case figure (1 & 2) can be explained on the basis of consideration given below.

The sample material namely a polyblend (mixture of two polymers) [5] doped with dopant like iodine/cinnamic acid. There by making up a composite [5] consisting of a polymer with some non-polymeric material. Here the polyblend is a mixture of PVC and PMMA.

It is well known that both these polymers are polar molecules with dipole moments of 1.73D and 1.33D [6] enhancing the probability of having a polar polyblend. The dopant added CA. is an unsaturated aromatic acid (C6H6 - CH=CH-COOH). Due to high degree of unsaturation in the side chain, CA can readily from C.T complexes when doped with PMMA [7]. The benzene ring of CA bears and unsaturated carboxylic group (- COOH) in the side chain. The carboxyl carbon in the carboxylic group due to its high electronegativity makes the entire molecule partially polar one.

The other dopant namely iodine. Due to its strong electron withdrawing nature, pulls out electronic charge from the conjugated chain rendering a resultant positive charge stabilized by its delocalization over a section of (-CH = CH-)n chain. This positive charge can be considered as the mobile positive whole, which moves and transfers electric charge.

Further polymers like polyvinylchloride whose polar group are arranged very closely along the chain have kinetically rigid chain and this leads either to increase in potential barrier or to steric hindrance to rotation. Polymers like PVC and PMMA have low kinetic flexibility [8].

Thus the blend sample PVC-PMMA doped with CA/I is expected to be of a long chain molecule embedded in the surrounding sea of molecules, will be experiencing interaction with neighbours and experiencing steric hindrance to rotation, hence such a value of relaxation time not be out of expectation. The values of relaxation time τ for same polymeric materials change within a rang of to seconds as temperature drops [9] Abd E1-Kadar et al [4], while studying the electrical and optical properties of polyvinyl alcohol thin films dopedwith metal salts, have observed the relaxation time to be in the range of seconds. The order of relaxation time arrived at here, in case of the doped polymeric blends is in good agreement with the preported values in the literature.

In case of iodine as dopant, for each field intensity E, charge carrier density ‘n’ increases and mobility μ decreases which is shown in figure (3 &4) with increasing dopant concentration. It is evident that with increasing dopant concentration the charge carrier density should obviously increase, at least marginally.On the contradrary the thermal motion of moleculer segment and increasing dopant centers coming in the path of charge carriers creates of struction to there motion there by affecting mobility adversely.

Cinnamic acid used as dopant. Shows (in figures 5 & 6) approximately a similar behavior for electric field intensity 112kV/m to 180kV/cm. For lower field of 37kV/m and 75kV/m the mobility is found to increase to a maximum value at 0.6% concentration and then falls as concentration further increases to 1% at lower fields the dopant centers do not cause much hindrance to the motion of slower moving charge carriers, thereby allowing the mobility to shows a marginal rise.

Since polymers have a wide set of relaxation times, that conform to the regroupings of chain units and chain regions (consisting of different units), the relaxation times determined from empirical formulation should be regarded as average relaxation times. Relaxation in polymers involves a larg number of simultaneous processes proceeding at different value i.e. at different relaxation times.

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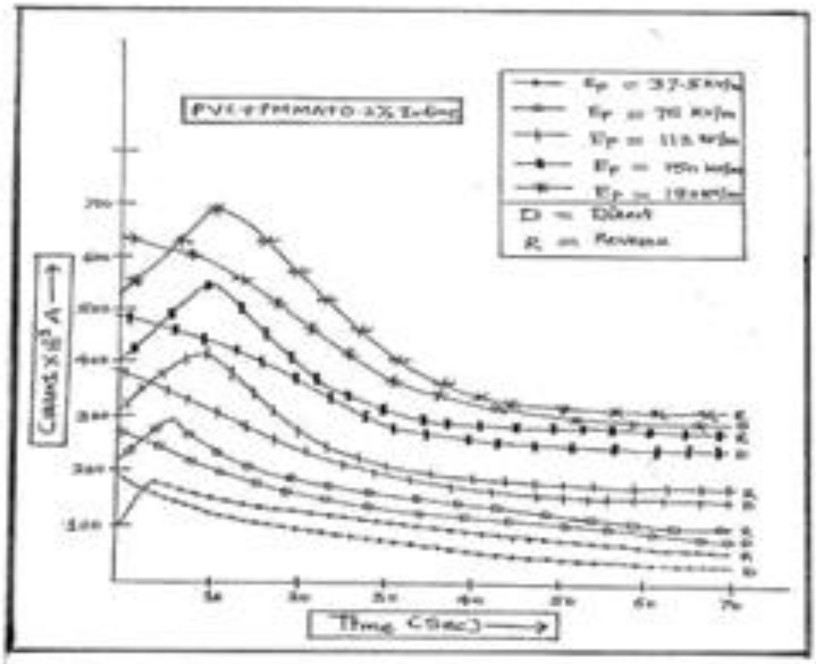

Figure 1: Current- time curves for Iodine doped samples

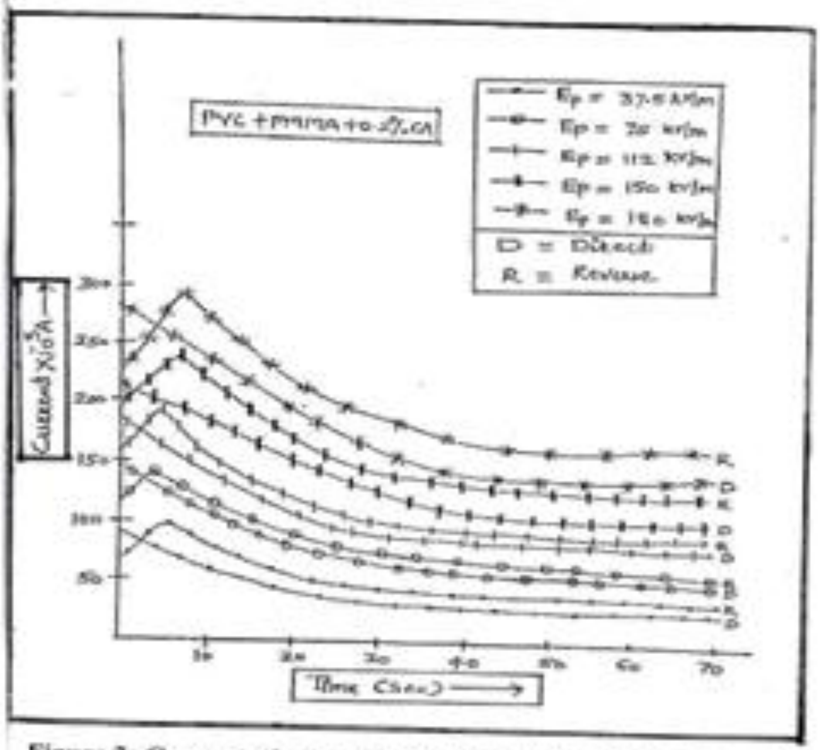

Figure 2: Current- time curves for Cinnamic acid doped samples

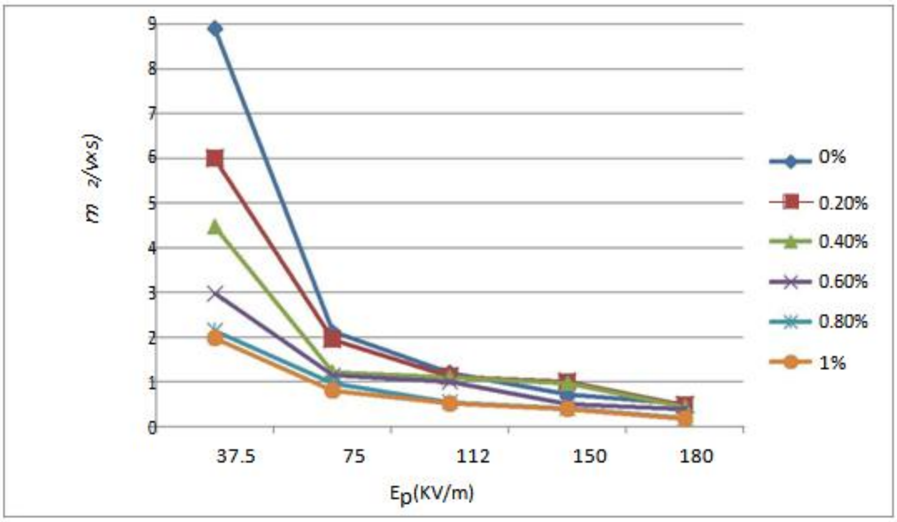

Figure 3: Electrical field strength (E_p) versus mobility (μ) curves for Iodine doped Samples

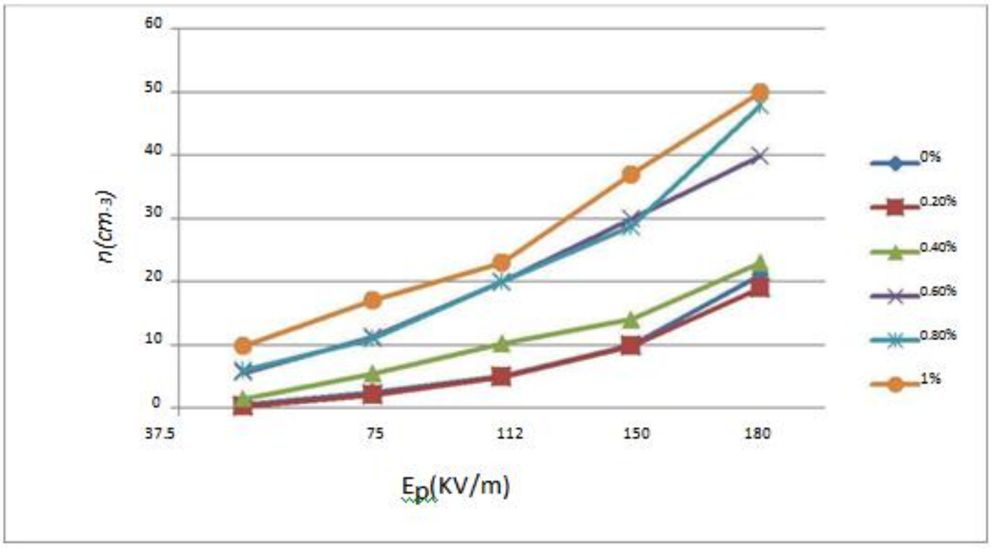

Figure 4: Electric field strength (Ep) versus charge carrier density (n) curves for Iodine doped Samples

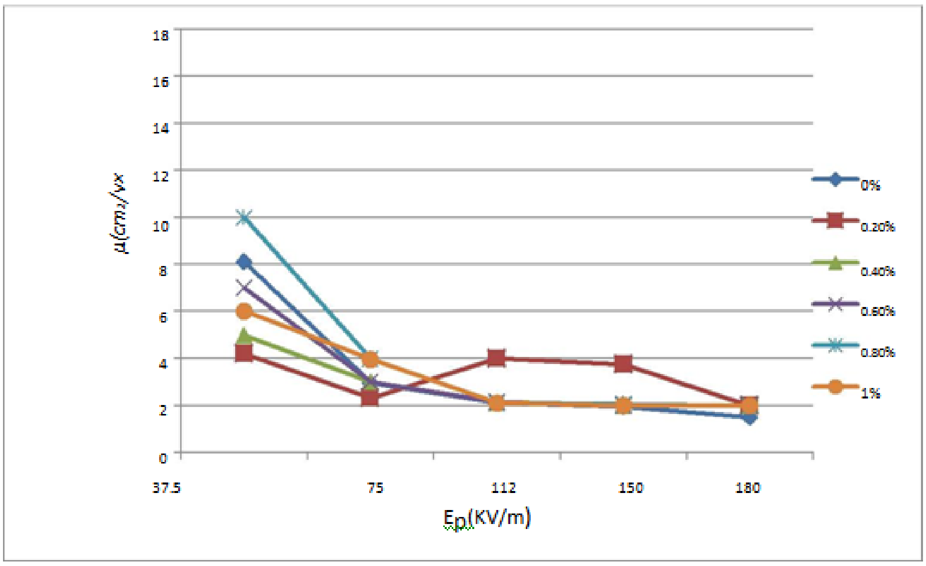

Figure 5: Electrical field strength (Ep) versus mobility (μ) curves for Cinnamic Acid doped Samples

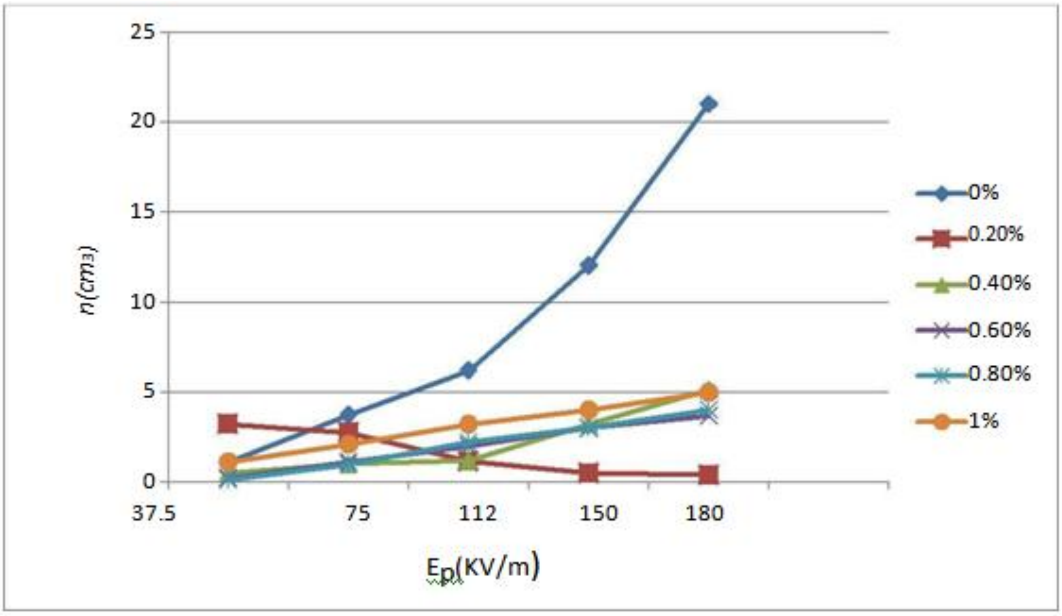

Figure 6: Electric field strength (Ep) versus charge carrier density (n) curves for Cinnamic Acid doped Samples

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