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Relaxation behavior of polymer thin film

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ABSTRACT
Thin films of composites PVC-PMMA doped with iodine, and cinnamic acid are prepared using the isothermal evaporation technique. Current time characteristics, by application of direct and reverse polarities in succession, were continued until the conduction current reached a steady state. The relaxation time 'ʊ' obtained from these plots is from the time required for the current to reach maximum value. Values of drift mobility 'ʊ' and density 'n' of charge carriers obtained from theoretical relations. The magnitude of time, found in the present composite system, agrees quite well with that reported in the literature. The increase in the concentration of dopants adversely affects mobility while favoring charge carrier density.

1. 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 to suit a particular purpose. Metal-filled conducting polymer composites, and carbon black/carbon fiber-reinforced conductive polymer composites [1-3] are some of the areas which attract investigations. The mechanical properties have been widely investigated. Recent past shows that electrical and optical properties of polymeric samples are those, which can open treasures of knowledge in the field of polymers. With this in view, we have been investigating such polymer bends and /or their composites using TSDC, UV-visible, FTIR, XRD, and electrical conduction mechanism techniques. The present paper narrows down the scope of studying the relaxation phenomenon in doped polymer blend systems via current time characteristics.

The samples chosen are two systems viz.

1. Polyvinyl chloride (PVC) + PMMA blend doped with iodine and

2. Polyvinyl chloride (PVC) + PMMA blend doped with cinnamic acid.

Current-time characteristics are discussed concerning mobility 'μ' and charge carrier density 'n' in the light of concentration variation of dopants and electric field intensity.

With the application of an electric field in one direction, the dipolar alignment takes place and the current reaches a particular value. Now the field is removed and the sample is short-circuited through a pico ammeter, which shows this current flowing through the sample decreases with the disalignment of 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 the field, the dipoles tend to align in opposite directions, and 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 shows 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 as [4]:

$$\tau = t_{\max} = \frac{d^2}{\mu v}$$

where, *d* is film thickness, μ is mobility of charge carriers and *v* is voltage applied.

The charge carrier density *n*, can then be calculated from the equation:

$J = nq\mu E$

where E (= v/d) being the electric field intensity, q is charge on carriers.

The dielectric materials are widely used in power electronic devices such as capacitors, sensors, etc. However, the low energy density of dielectric ceramics restricts the applications for energy storage [5].

2. Materials and methods
2.1 Materials

Preparation of sample: The polyvinyl chloride (PVC) of standard grade products supplied by Polychem Industries, Mumbai, and polymethylmethacrylate (PMMA) supplied by Dental Product of India Ltd., Mumbai were used for the study. The two polymers PVC (1.5 gm) and PMMA (0.5 gm) were taken in the ratio of 3.1 by weight. The 1.5 gm of PVC in 20 ml of tetrahydrofuran (THF) and 0.5 gems of PMMA in 10 ml of THF were dissolved separately. After allowing them to dissolve completely, the two solutions were mixed. Iodine and cinnamic acid were taken in the percentage weights 0.2%, 0.4%, 0.6%, 0.8%, and 1% respectively were dissolved in 5 ml THF to produce iodine and cinnamic acid solutions. These solutions were later mixed with a uniform solution of PVC and PMMA. The total volume of solvent was kept constant at 35 ml. The solution was heated at a constant temperature of 333 K for two hours to allow polymers to dissolve completely to yield a 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 (313 K). In this way, the films were prepared by isothermal evaporation technique [2, 3]. The film was subjected to 12 hours of heating at a constant temperature of 323 K and another 12 hours at room temperature to remove the traces of solvent. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities.

2.2 Methods

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 13 μm and 3.3 μm at the magnification of 1.10 and 1:100 respectively. The film thickness is 80 μm.

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

Electret preparation: The sample film was mounted into the sample holder and heated at constant temp (60°C) 333 K for 1 hour. After heating, an electric field was applied for 30 min between the two opposite faces of the sample so that the sample film was polarized for a definite time with the applied field. The electric fields were used were/are 0.375 kV/cm, 0.75 kV/cm, 1.12 kV/cm, 1.50 kV/cm and 1.8 kV/cm respectively.

2.3 Characterizations

Current-time measurements: After electret preparation current-time measurements are carried at fixed field strength, with different dopant concentrations of polymer blends.

1. The sample film, metalized on both sides, is charged by the application of a DC (direct) field at an elevated temperature of 600 (333 K). The field is removed the sample is short-circuited through a Pico ammeter and the discharge current is noted at regular intervals of time until the current shows almost a constant value.
2. Then the sample film is recharged with the same DC field but with reverse polarity at the same temperature 333 K for the same time. The field (reverse) is removed and the sample is short-circuited through a Pico ammeter again the discharge current is noted at regular intervals of time until the current shows an almost constant value.
3. On reversing the polarity, the current increases to a maximum value and then gradually falls until it shows an almost constant value. This time interval during which currently becomes maximum is denoted by t_{max}, which is approximately the relaxation time τ. Steps I and II above are repeated for different fields. Strengths and each time tmax (τ) for all samples are note.

3. Results and discussion

The relaxation time in the range of seconds, observed in the present case (Figure 1 and 2) can be explained based on considerations given below. The sample material namely a polyblend (mixture of two polymers) [6] doped with dopants like iodine/cinnamic acid. Thereby making up a composite [6] 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 [7] enhancing the probability of having a polar polyblend. The dopant added CA, is an unsaturated aromatic acid (C_6H_6-CH=CH-COOH). Due to the high degree of unsaturation in the side chain, CA can readily form C.T complexes when doped with PMMA [8]. The benzene ring of CA bears an 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. 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 hole, which moves and transfers electric charge. Further polymers like polyvinylchloride whose polar groups are arranged very closely along the chain have a kinetically rigid chain and this leads either to an increase in potential barrier or to steric hindrance to rotation. Polymers like PVC and PMMA have low kinetic flexibility [9].

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 interactions with neighbours and experiencing steric hindrance to rotation, hence such a value of relaxation time will not be out of expectation. The values of relaxation time 'ᴛ' for the same polymeric materials change within a range of 10^{-3} to 10^{+2} seconds as the temperature drops [10]. Abd El-Kader et. al [4], while studying the electrical and optical properties of polyvinyl alcohol thin films doped with metal salts, have observed the relaxation time to be in the range of seconds.
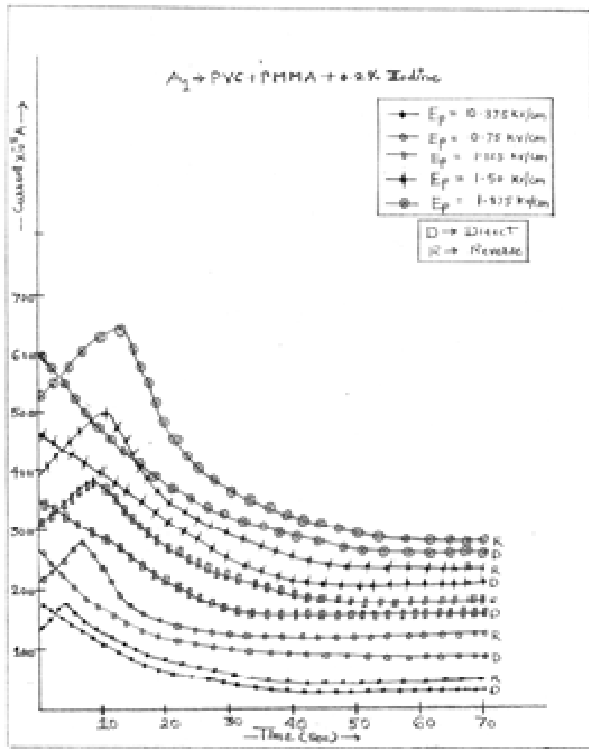
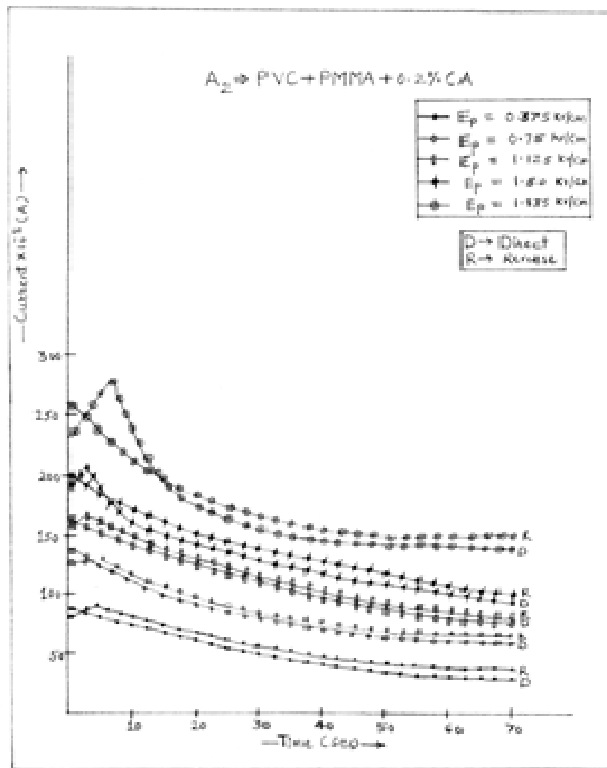**Figure 1:** Current-time curves for iodine doped samples

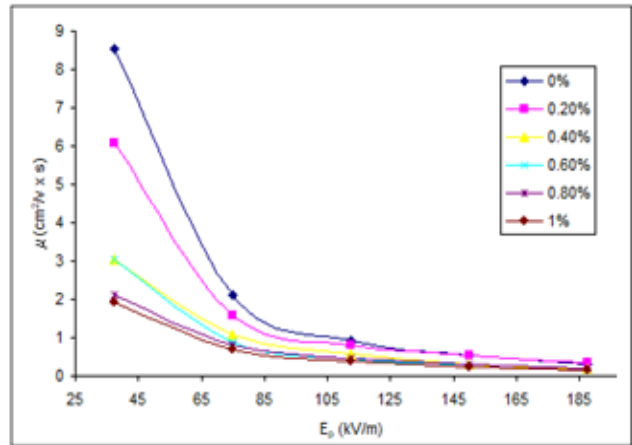**Figure 2:** Current-time curves for cinnamic acid doped samples

Figure 3: Electric field strength (E_p) versus mobility (μ) curves for iodine doped samples
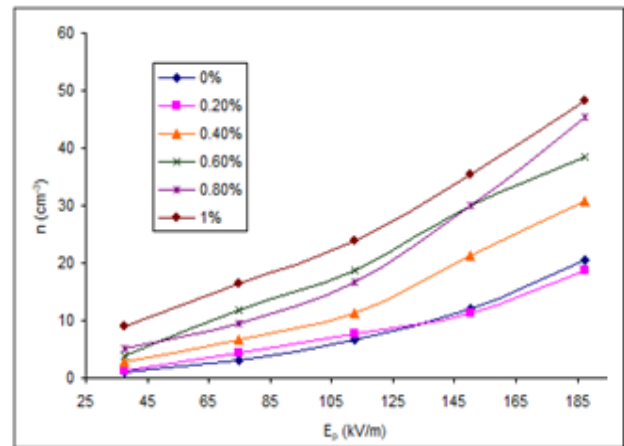

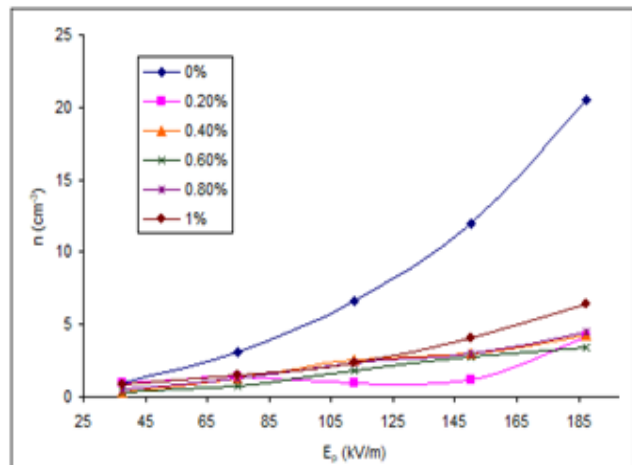**Figure 4:** Electric field strength (E_p) versus charge carrier density (n) curves for iodine doped samples

Figure 5: Electric field strength (E_p) versus mobility (μ) curves for cinnamic acid doped samples
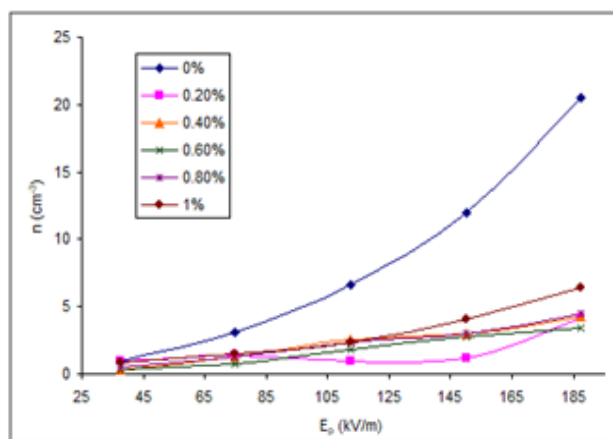
Figure 6: Electric field strength (E_p) versus charge carrier density (n) curves for cinnamic acid doped samples

The order of relaxation time arrived at here, in the case of the doped polymeric blends is in good agreement with the reported values in the literature.

In the case of iodine as a dopant, for each field intensity E, charge carrier density 'n' increases and mobility μ decreases, (Figures 3 and 4) with increasing dopant concentrations. It is evident that with increasing dopant concentration the charge carrier density should increase, at least marginally. On the contrary, the thermal motion of molecular segments and increasing dopant centers coming in the path of charge carriers obstruct their motion thereby affecting mobility adversely. Cinnamic acid used as a dopant, shows (in Figures 5 and 6) approximately a similar behavior for electric field intensity 1.125 kV/cm to 1.875 kV/cm. For lower fields of 0.375 kV/cm and 0.75 kV/cm, 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.

4. Conclusions

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 formulations should be regarded as average relaxation times. Relaxation in polymers involves a large number of simultaneous processes proceeding at different values i.e. at different relaxation times.

Acknowledgements

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