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Investigation of Dc Conductivity of 4:1 PMMA PVDF Polymer Blends at Different Temperatures

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Abstract

In the present work dc conductivity of PMMA and PVDF (4:1) blend sample have been investigated at various constant temperatures ranging from (313K to 343K). The results have been presented in the form of graphs. It has been found that the DC electrical conductivity (σ) increases with increases in temperature at every applied voltage. The pure and doped samples show ohmic characteristics. And also, it shows that the increase in current density (J) with respect to the applied electric field at various temperature.

Index Terms: *'Solution cast method', percentage of amorphousness/crystallinity,4:1 (PMMA+PVDF), DC conductivity, Current density etc.*

Introduction

When two or more polymers are mixed together, polyblends or polymer alloys are obtained. This physical mixing or blending of two polymers produces alloys with quite different properties, which can be potentially useful. Two polymers are generally incompatible as they have very low combinatorial entropy of mixing for the components. This is insufficient to overcome the positive heat of mixing of polymers to make the Gibb's free energy of mixing negative. Only in the presence of specific interaction between two polymers (e.g. Hydrogen bonding, acid-base type interaction etc.), heat of mixing is negative that makes the free energy of mixing a negative quantity and then the mixing is spontaneous. Unlike the mixing of small molecules, the dictum *like likens like* does not hold good for mixing of macromolecules. However, both compatible and incompatible blends are industrially important materials. Two polymers may form the compatible blend, which exists as single phase. The incompatible blends on the other hand exist as two- phase system. Since most blends combine immiscible components and so the material that results contains tiny particles of one polymer in a matrix of the other. Controlled mixing and cooling of the blend makes it possible to form the. particles in the optimum concentration and range of sizes. Blending makes it possible to combine the good properties of several polymers. The most direct method to obtain a polyblend is to mix two component polymers in the molten state (melt mixing). In this case the extent of mixing depends on the rate of diffusion of the molecules. Since such a mixing requires high temperature, the polymer may decompose and undergo chemical changes**.**

Experimental Technique

Method of Preparation of PMMA PVDF Films using Dopant Iodine

Sample Preparation

The two polymers PMMA and PVDF were taken in the ratio 4:1 by weight and dopant iodine were taken as doping percentage are 0%,0.5%, 1%, 2% respectively.

Method of synthesis

PVDF dissolved 10ml of DMF, PMMA also dissolved 10ml of DMF and Iodine dissolved in 10ml of DMF. All these three were dissolved separately. After allowing them to dissolve completely all the three solutions were mixed together. The solution was then heated at 60°C for one hour to yield clear solution. A glass plate (15cm x15cm) cleaned with hot water and then with acetone was used as a substrate.

To achieving perfect leveling and uniformity in the thickness of the film a pool of mercury was used in the plastic tray in which the glass plate was placed. The solution was poured on the glass plate and allowed to spread uniformly in all direction on the substrate. The whole assembly was placed in a dust free chamber maintained at constant temperature. The film was subjected to 12 hr at room temperature to remove traces of solvent. Finally, the film was removed from glass plate and cut into small pieces of suitable size which were washed with acetone to remove the surface impurities. In this way the film was prepared by isothermal evaporation technique used by Sangawar (1995), Bahri and Sood (1983).

Thickness Measurement

The thickness of each sample film was measured at the four different places by using the Digital Micro meter (Mitutoyo Corporation, Japan) as shown in fig 1. The average of four readings was taken as the sample thickness.

Fig 1. Digital Micrometer

Measurement of DC Electrical Conductivity

The thin film sample prepared by using isothermal evaporation technique, was coated with the silver paint and then loaded into the sample holder (Fig.2) which was kept in thermostatically controlled oven.

Sample Holder

The sample holder (Fig.2) is used for the measurement of DC Conductivity. It was fabricated in the laboratory and has two brass electrodes of equal diameter 1.9 cm. The lower electrode remains fixed with the assembly, while the upper one can be moved vertically up or down and can be locked at any desired position with the screws provided as shown in Fig.2.

Fig. 2 Sample Holder

The DC voltage was applied (in the range 10 V-200 V) across the sample by using highly regulated DC power supply (Keithley 2400 source meter).

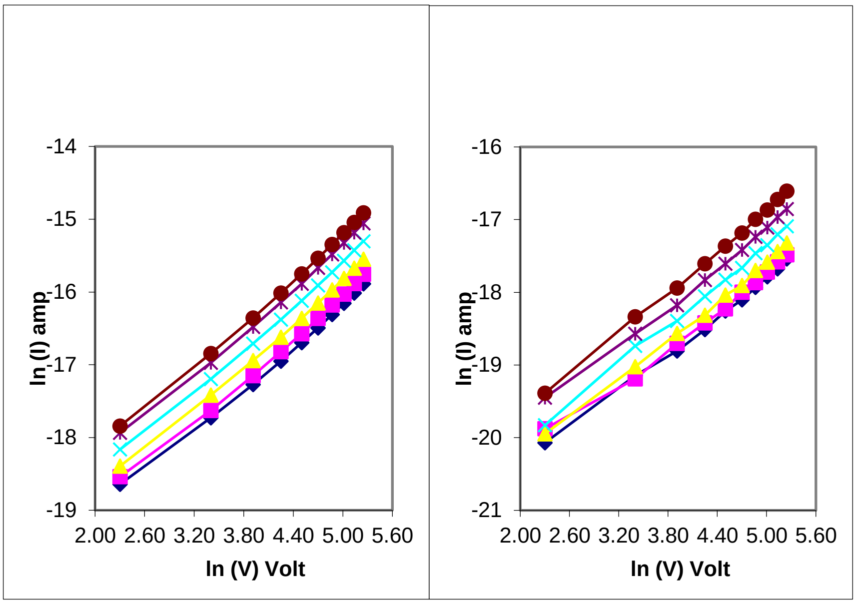
Fig. 3 DC Conductivity measurements unit

The corresponding DC current was measured by using Keithley 2400 source meter. Such current–voltage (I-V) measurements were taken at different constant temperatures (313K, 323 K, 333 K, 343 K, 353 K, 363 K.). From these measurements the DC conductivity for all the samples was calculated. Experimental setup of DC conductivity measurement is shown in Fig. 3

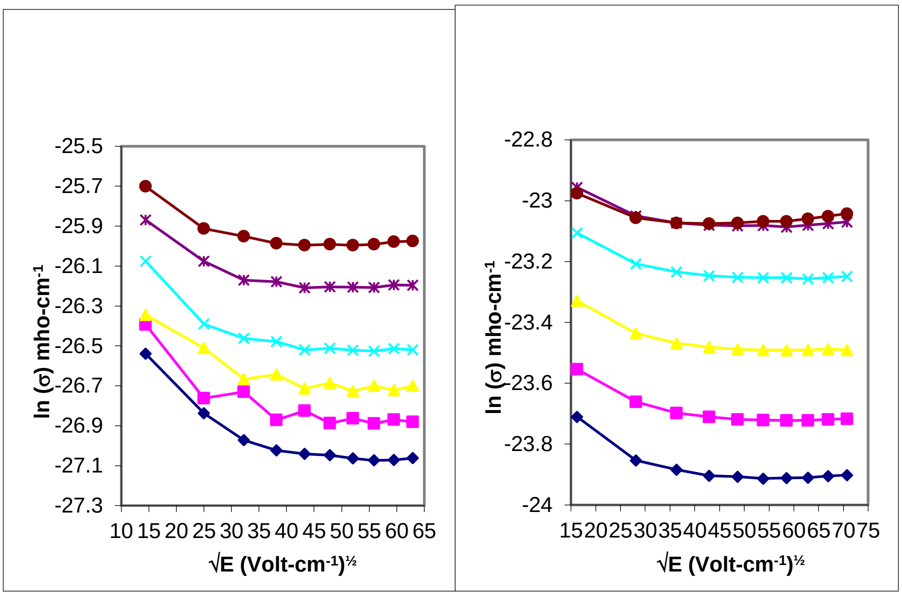
Results And Discussion

The DC conductivity study of all the blended samples of PMMA and PVDF (4:1) doped with different wt% of iodine have been carried out by traditional current voltage (I-V) measurements in the voltage range (10V-190V) at various constant temperatures such as 313K, 323K, 333K, 343K, 353K, 363K. The results have been reported in the form of graphs for all the polyblends such as,

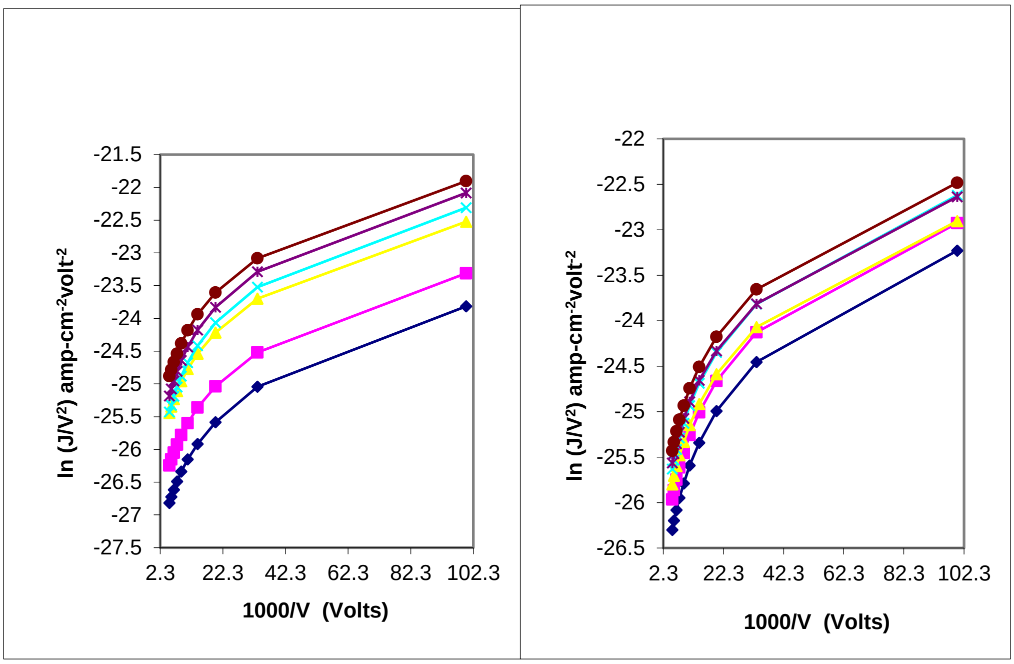
- Variation of ln (I) with ln (V) at different temperature
- Variation of ln (σ) with $E^{½}$ at different constant temperature (P-F plots)
- Variation of ln (J/V^2) with 1000/V at different temperature (F-N plots)
- Variation of ln (J) with $E^{½}$ at different temperature (Schottky plots)
- Variation of ln (J) with Temperature at different voltage
- Variation of ln (J/T^2) with 1/kT at different voltage (Richardson plots)
- Variation of ln (σ) with temperature at different voltage (Arrhenius plots)



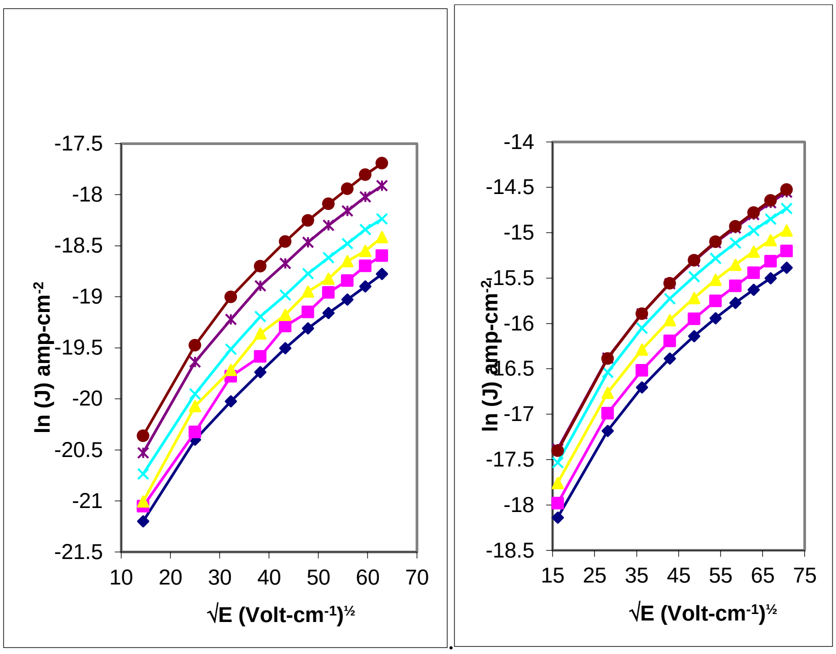
Variation of Current (I) with Voltage (V) for 4:1 PMMA PVDF doped with different wt% of 4:1 PMMA PVDF doped with Iodine



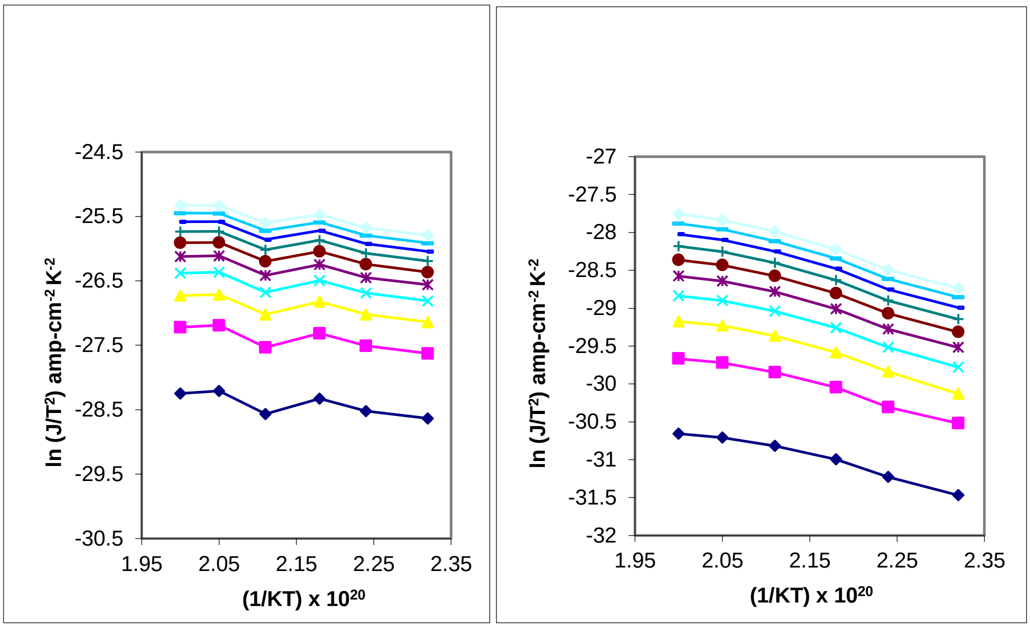
Variation of conductivity ln (σ) with Square root of Electric Field ($E^{1/2}$) at different temperatures (P-F plots) for 4:1 PMMA PVDF doped with Iodine



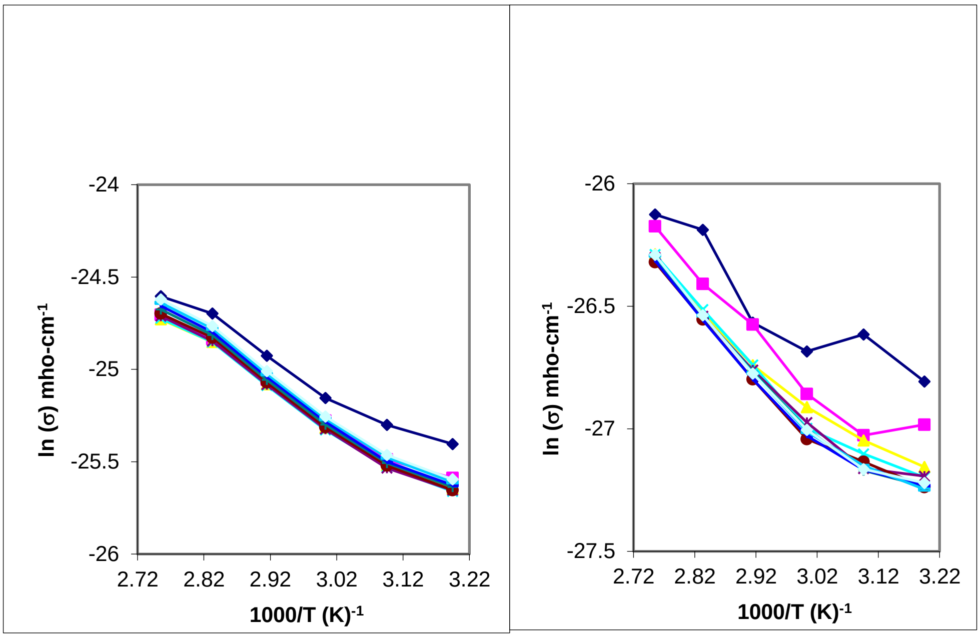
Variation of ln (J/V^2) with 1000/V at different Temperature (F-N plots) for 4:1 PMMA PVDF doped with different wt% of Iodine



Variation of Current density ln (J) with square root of Electric Field ($E^{1/2}$) at different temperature (Schottky plots) for 4:1 PVC PMMA doped with different wt% of Iodine



Variation of ln (J/T^2) with 1/kT at different voltage (Richardson plots) for 4:1 PMMA PVDF doped with different wt% of Iodine



Variation of conductivity ln (σ) with temperature at different voltages (Arrhenius plots) for 4:1 PMMA PVDF doped with different wt% of Iodine

On the basis of analysis of results the prominent findings of this part of the study as under:

- At every constant temperature (313 K, 323 K, 333 K, 343 K, 353 K and 363 K), the electrical current increases as the applied voltage increases.
- At every constant voltage (10 V to 190 V), the electrical current increases as the temperature increases.

- The current density (J) and also electrical conductivity (σ) increases with increase in temperature at every applied voltage.
- The increase in current density (J) results from increase in applied voltage.
- The order of DC Conductivity variation for the sample has been found as 10^{-11} $(\Omega cm)^{-1}$ to 10^{-12} $(\Omega cm)^{-1}$.
- The pure and doped samples show ohmic characteristics.
- The Schottky plots indicates the increase in current density (J) with respect to the applied electric field at various temperature.
- The conductivity (σ) of the sample increases with respect to the temperature as shown in Arrhenius plots.
- The values of activation energy have been found smaller than 1 eV in all samples. This shows the predominance of electronic conductivity.

Effect of Temperature (Arrhenius plots):

The dependence of DC conductivity on temperature i.e. ln (σ) vs 1/T plots are depicted at all values of applied voltage. As we raised the temperature of the sample from 40 to 90 which is very close to the values Tg of all the component polymer. So, we can expect the transition of the samples from glass to rubber state there by increasing the availability of charge carriers at higher temperature. This explains increase in the conductivity of the blend samples with the increase of temperature (Belsare and Deogaonkar1998, Gulalkari et al. 2007).

Effect of Dopant:

According to Liang–Tse Yu (1963) and Van Taut Yu (1962), the resistance of the polymer decreases (conductivity increases) when polar substances are introduced into non- polar ones. Hence in case of blended systems the value of conductivity is greater and on making the blends of PMMA and PVDF in ratio - 4:1 doped with different weight percentage of Iodine, the value of DC conductivity decreases with increasing dopant percentage.

Effect of Electric Field:

The value of conductivity increases with applied voltage for all the samples. The generation of charge carriers occur due to the emission of electrons from electrode or generation under the influence of light. Direct emission from electrode is particularly important at high fields. The surface of the polymer is complex. The surface states extend some distance into the polymer. On making the contact between the electrode and the polymer, electron transfer will take place until thermodynamic equilibrium is attained. There are two methods in which the energy is required to escape from the metal. They can be recognized as:

1) Thermal methods, in a process known as thermionic emission.

2) The application of high electric field.

In our case we have applied the electric fields in the range of 10 kV/cm to 200 kV/cm. At these fields, we can expect the injection of electron from electrodes justifying the increase of conductivity with the increase of applied electric field.

Conclusions

The activation energy (Ea) is calculated from Arrhenius plots. The value of Ea shows the predominance of electronic conductivity. Thus, the conductivity is found to increase with temperature and applied field while it decreases with increasing dopant percentage. On the basis of graph, we arrive at the conclusion that conductivity in case of PMMA and PVDF (4:1) polyblends has been found higher.

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