Dielectric Characteristic and Ac Studies of Pure and 1% Iodine Doped Polystyrene Films

K.Maragatham
Research Scholar
Department of Physics
karpagam university

S.Muruganand
Assistant professor
Department of Electronics and instrumentation
Bharathiar University

N.Manikandan
Research scholar
Department of Electronics and Instrumentation
Bharathiar university
Coimbatore

Abstract

The Polystyrene thin films are prepared by solution growth technique using glass substrates. Polystyrene solution is prepared by dissolving of polystyrene in the 100cc of benzene.PS is not water resistance and high dimensional stability. it is tougher and stronger at low temperature and than most other plastics. it is valued as an electrical insulating material and has a low dielectric loss factor at moderate frequencies and it has tensile strength of 8000psi.the present investigation is focused on the preparation of PS and iodine doped PS film by solution growth and on the study of their physical properties viz., electric conduction properties at different frequencies and temperatures

Keywords: Polystyrene, AC Conduction ,Temperatures ,FTIR.

I. INTRODUCTION

Dielectric studies are of special interest in relation to polymer since they provide vital information on the molecular configuration of system. Through the dielectric properties of number of polymer have been investigated in the last decade [1,4],the molecular orientation behavior and associated relaxation mechanism are not fully understood. Only very limited work has been carried out on polystyrene (PS) films, which are polymers of great utility in the field of electrical insulation.
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II. THEORY OF DIELECTRICS

Complex dielectric constant (Ɛ*) and dielectric loss(tan δ)
The capacitance C (Farads) of a parallel plate capacitor, neglecting edge effects is given by
C = Ɛ' Ɛ0A/d
Where 'A' is the area of electrodes (m2),
'd' is the thickness (nm),
Ɛ' is the relative permittivity and Ɛ0 is the permittivity of free space(8.85x10-12 Fm-1)
the displacement or dielectric flux density D is related to the field E as,D=ƐE
Where Ɛ is the permittivity of the medium.therfore under as AC field, displacement can be written as

D1=D0 cos (wt -) =D1 cos wt =d2 sin wt

For the most dielectrics, d0 is proportional to E0,but the ratio D0/E0 is generally frequency dependent. Hence we introduce two frequency dependent component w and w' , real and imaginary parts of the dielectric permittivity ,which are given by

Ɛ'(w) = D1/E0 = (D0/E0) cos S

It is convenient to combine these two into a single complex dielectric permittivity as

Ɛ* = Ɛ' - jƐ''

Where j Ɛ is the component with resistive vector.
tan δ =Ɛ''/Ɛ'(w),0≤δ≤π/2
tan δ is called as the loss factor .
Temperature coefficient of capacitance and permittivity
Dielectrics are used at all temperatures and the temperature variation of capacitance is hence crucial. An important parameter used to indicate the carination of capacitance with temperature is the temperature coefficient of capacitance (TCC) that is defined by

TCC=1dc/C dT

Where T Is the temperature and C is the capacitance.

The temperature coefficient of permittivity a factor used to estimate change in the permittivity of a material with change in its temperature I defined as

TCP=1 dƐ/Ɛ dT

TCP is an important practical figure foe assessing the expected behaviors of thin film circuits. The relation between TCC and TCP has the form.TCC=TCP + α. Where 'α' is the linear expansion coefficient of the material used as the dielectric in the capacitor. The TCC and TCP are usually expressed in parts per million(ppm) Per kelvin. Neglecting changes in the linear dimensions of specimen with temperature changes, TCC and TCP of the specimen may be equal in magnitude.

III. AC CONDUCTION

The steady interest in the conduction properties of dielectric polymer in the last few decades reflects their technical importance. Thin film of polymeric materials are being condisdered for technical application for insulation, isolation and passivation in microelectronics .In such application the polymer material have to function in contacts with semiconductor or metal films. The charge transport measurement in disordered insulators are of much interest because they provide information regarding the electronics structure of the material. The study of a.c. conductivity also give information about the type of conduction mechanism in the film.

A. Theory

The ac conductivity of amorphous material gives an idea about the conduction mechanism in such materials. Ina parallel plate capacitor, if C0 is it's capacitance value in air and Ɛr is the permittivity of the medium that fills the condenser, then neglecting the fringing effects, th capacitance can be expressed as

C = Ɛr C0

When an alternating e.m.f 'V' angular frequency ϾϿ=(2πf) is applied across this condenser, the alternating current is given by

I=jϾϿƐrC0V

The value of C0=A/d, where 'A' is the common area of the plates, d the separation between then and the

Ɛangular frequency.

I = jϾϿ(Ɛ'-jƐ ')(A/d) Ɛ0V

By definition the field strength is E=V/d where 'V' is the voltage applied and the current density is J=i/A, therefore

J=JϾϿƐ0Ɛ'E +ϾϿƐ0Ɛ'' E

The conductivity (σ=J/E)

σ = JϾϿƐ0Ɛ'+ϾϿƐ0Ɛ''

The conductivity ,σD represent the sum of all the loss mechanisms in the material and is measure of the performance of the dielectric as an insulator.

The frequency dependence of conductivity of different materials has been widely investigated by many researchers [8-12] because they can given information about the electronic structure of these material. In all these cases the conductivity was found to be non-decreasing function of frequency. Such behaviors is suggestive of hopping conducting[13],either by electrons or ions. This their is in line with Anderson's theory[14],according to which, the localized states generally exist in disordered system, and with Mott's[15] model of pseudo gap in amorphous solids. Pollack and gabble[16]interpretation of the frequency dependence of the electrical conduction in amorphous solids. The a.c. conductivity should increase with frequency of the applied field and saturate at frequencies high enough to be comparatable to the natural frequency of hopping between the centers. It has been pointed out that it is necessary to average conductivity over all hopping distance ahd activation energies for all pairs of occupied and

IV. EXPERIMENTAL

A. Solution Growth Technique

The technique used for deposition of thin films in the present study is solution growth, which involves the isothermal immersion of the substrate into the polymer solution of suitable concentration held at a constant temperature for a certain time. The rate of growth and the thickness of the film depend on the nature of the substrate, the concentration, and temperature of the solution and also on the time for which the substrate is left immersed in the solution. The experimental arrangement of solution growth technique is shown in Fig.3.1. Pure polystyrene (99.99%) supplied by the Kemphasol, Mumbai is used for the study. Polystyrene (PS) films were deposited from a polystyrene solution. The polystyrene solution was prepared by dissolving 3.4 g of PS in 100 cc of benzene. The solution was continuously stirred by means of a magnetic stirrer to ensure a homogeneous mixing. In the same way 1% iodine doped PS films were prepared from 1% iodine concentrated homogeneous solution of 3.4 g PS dissolved in 100 cc of benzene. Films were grown on pre deposited aluminium electrodes on a glass substrate. The substrates with film were withdrawn from the solution and dried in a hot air oven for 7 hours at a constant temperature of 333 K to remove the solvent effect.

B. Thickness Measurement

The commonly used thickness measurement methods are (i)mechanical method (ii) ionization method (iii) microbalance method (iv)radiation method (v) optical method and (vi) capacitance method [27-33]. The optical method that employs the interference technique has been found to be the most suitable method for the measurement of film thicknesses of the order of the wavelength of light. thicknesses of the electrode films used in this study have been measured using this optical (multiple beam interlard meter) method. Since the thicknesses of the polymer films in the present study are very high, other methods of thickness measurements like, mechanical, capacitance and microbalance methods have been used. In the present work the mechanical method is used to measure the thickness of the film.

V. SAMPLE PREPARATION

A. Substrates

The substrates serve as a mechanical support for the film and in electronic applications; it also serves as an insulator. The need for long term stability makes it imperative that no chemical reactions occur which would change the properties of the film. The substrates should have mechanical strength and there must be a good adhesion between the film and the substrate at room temperature as well as at very high temperature. The substrate should also have an appropriate heat conductivity to ensure constant temperature of the surface and sufficient heat removal during the operation of electronic devices. The surf}ace of the substrates should be flat and smooth to form the films with well defined and reproducible electrical and other parameters.

A number of materials like glasses, ceramics, quartz are available for use as thin film substrates. Of all these materials, glass has the maximum surface smoothness and is also optically plane [34]. It is easily and cheaply available and has a Iow cost. Hence in the present study, glasi micro slides halve been employed as the substrates. '1

B. MPM Structure

MetaI-Polymer-Metal (MPM) sandwich structures were formed onto well cleaned glass substrates with the insulating layer in between the two metal electrodes by making use of suitable masks as' shown ill fig 3.2. The electrode material should be such that it does not react with the dielectric film and should have good adhesion with the substrate and also a low electrical resistance. Metals like gold, silver, copper and aluminium are used as electrode materials. Of these, aluminium bas been observed to possess all the desirable properties while the other materials are blend to be lacking in one or the other. Hence aluminium has been used as the electrode material in the present study. The vacuum coating unit was employed for the deposition of the electrodes. Pure aluminium (99.99% Balzers) was evaporated at a pressure of 1.33 x 103 Pa from a helical tungsten filament, by resistive heating onto well-cleaned glass substrates through suitable masks to form the base electrode. The source to substrate distance was maintained at 0.18m. Prior to evaporation the aluminium was degassed under the Sheller for two minutes. After evaporating aluminium to form the base electrode, the dielectric material was deposited by solution growth (details are given in section 3.3). FinaIly the top electrode was formed by again evaporating auminium, thus completing the MPM structure.

VI. DIELECTRIC MESUREMENTS

Measurements of series capacitance and the loss factor (tanb) in the frequency range I 0 kHz-10 MHz were carried out at various temperatures in the range of 302 to 450 K in a rotary vacuum (1.33 mpa). The experimental setup is shown in the block diagram 3.3. Studies in the frequency range of 10 kHz-10 MHz were carried out using a multi frequency LCR meter (HEWLETT-PACKARD). The temperature of the samples during the study was measured with a digital thermometer.

VII. STRUCTURE

A. FT- IR STUDIES

The FT - IR spectra of pure and 1% iodine doped Polystyrene films are recorded (using a PERKIN ELMER - Spectrophotometer) in the wave number range of (4000 - 500 cm -l).

VIII. RESELTS AND DISCUSSION

A. FTIR

By comparing the FTIR spectra of(Figure 4.2a &4.2b) pure and iodine doped PS films, the following observations are made, (al on doping, no prominent additional absorption peaks are observed. (b) Doping results with a slight shift in the absorption peaks by the order of 1 to 20 cm -f. The table 4.1 shows the presence of different molecular groups in the pure and iodine doped PS samples.

B. DIELECTRIC STUDIES

1) *Annealing*

Freshly prepared films were subjected to annealing studies. Application of mild heat treatment would anneal out the defects present in the film. Stabilization of these films could be achieved by repeated annealing cycles (slow heating and cooling).Two cycles of annealing at about at 350K in air for 7 hrs are required for pure PS and iodine doped PS films. Figs 4.3(a&b) show the changes in capacitance with frequency for different annealing cycles for pure PS and l%iodine doped PS films of thicknesses 2.1 to 3.8 [tm. The capacitance value was found to decrease with the repeated annealing cycles for a particular frequency. An almost stable value of capacitance was obtained after two cycles of annealing of all these films.Freshly deposited films have many defects and impurities such as voids, grain boundaries, dislocations, stresses, inhomogeneity etc. The annealing process reduces many of the above defects and fhrther improves the dielectric properties. This is because annealing is a process related with stress relief and local structural rearrangements Ill of polymer chains. Cycle after cycle, the defects are reduced gradually and each atom occupies a stable position in the interior of the film until the dielectric parameters attain a stable value. Similar annealing effects have been observed in pure and iodine doped PVA and PMMA films [2].

2) *Variation of capacitance with temperature*

The variation of capacitance with temperature at various frequencies (l 0 klqz, 100 kHz, 500 kHz &l MHz) for films of pure PS and 1% iodine doped concentration are studied systematically. Fig.4.4a shows a plot of capacitance as a function of temperature for pure polystyrene film at various constant frequencies. For a constant f?equency the capacitance increases with temperature and above 353K it becomes almost constant. Fig.4.4b shows the variation of capacitance with temperature for 1% iodine doped PS film for various constant fYequencies. The capacitance steadily increases with temperature and reaches a maximum at 353 K.

From the figs 4.4(a&b) it is observed that 1. for both the pure and iodine doped PS films, capacitance increases with increase in temperature for a constant frequency.2. The increase of capacitance with temperature is more in the low frequency range increase of temperature. The increase of ~' with temperature is due to the enhancement of polarization in the material and also as the temperature grows, the chaotic thermal oscillations of molecules are intensified [7].

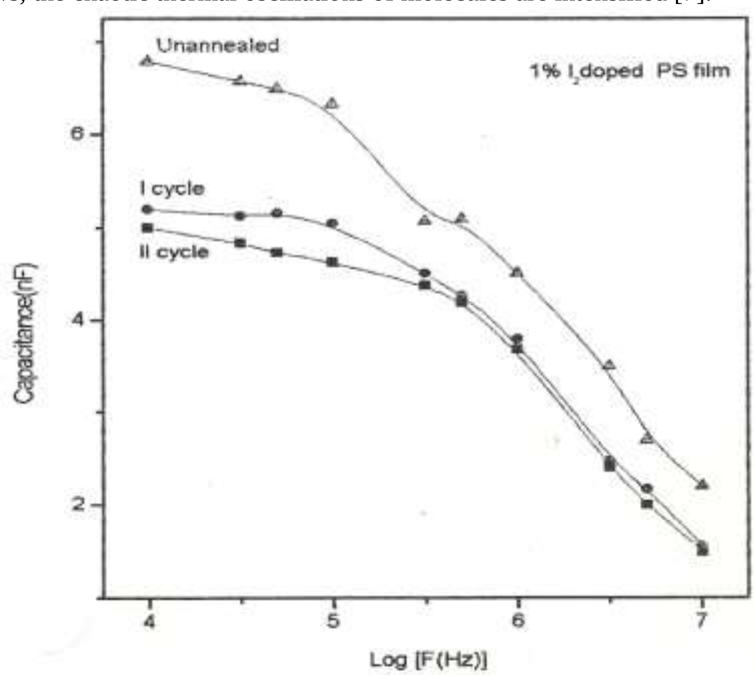

Fig.4.3b Annealing behaviour of 1% iodine doped PS film

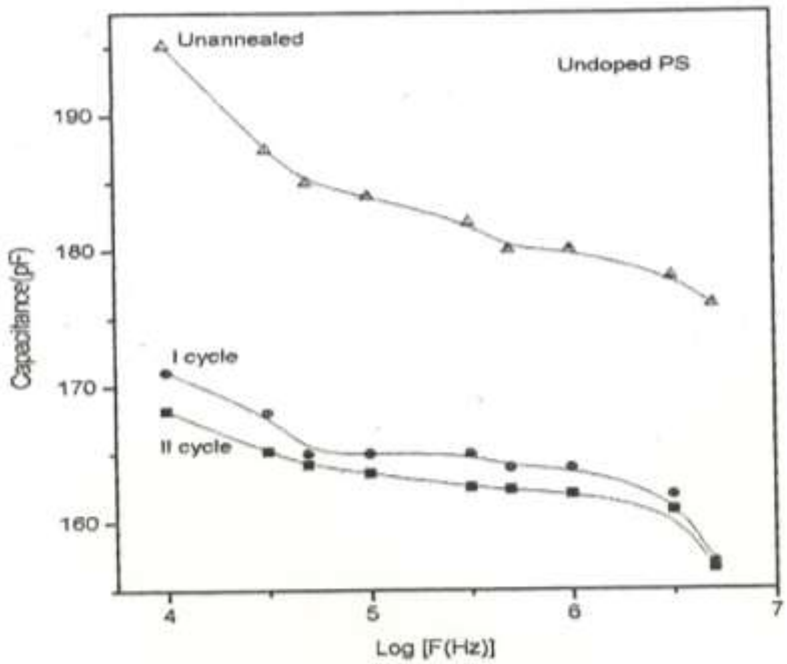

Fig.4.3a Annealing behaviour of undoped PS film

C. *Temperature Coefficient of Capacitance and Permittivity*

The dependence of capacitance and dielectric constant on temperature are expressed by the quantities, Temperature coefficient of capacitance (TCC) and Temperature coefficient of pennittivity (TCP) respectively. Both these parameters are of high practical importance in assessing the expected behaviour of the thin film circuits. The temperature dependence of capacitance and dielectric constant for pure PS and 1% iodine doped PS films for various constant frequency ranges are shown in Figs. 4.4 (a&b) and Fig. 4.6 TCC and TCP values are calculated from the slopes of the curves of above figures at different temperatures by adopting the procedure [8&9]. The values of TCC and TCP of pure and iodine doped PS films are presented.

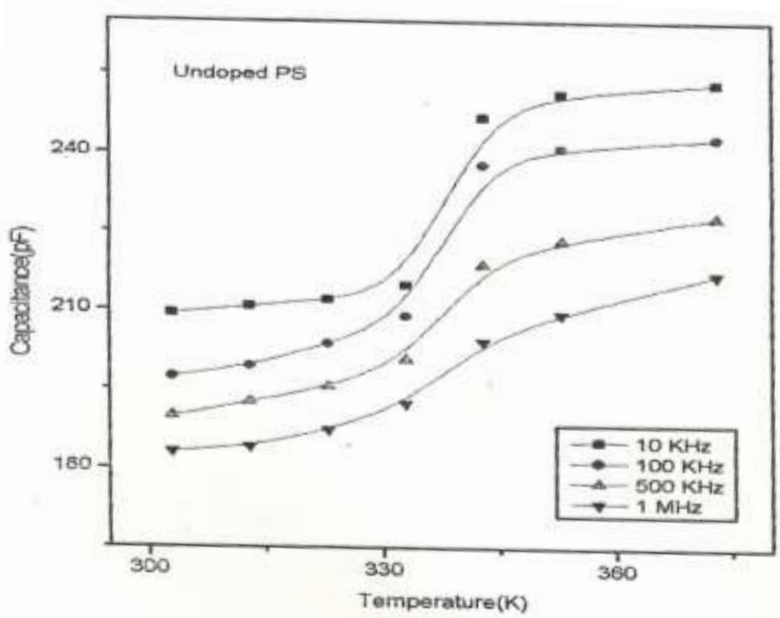

Fig. 4.4a Temperature versus Capacitance of undoped PS film

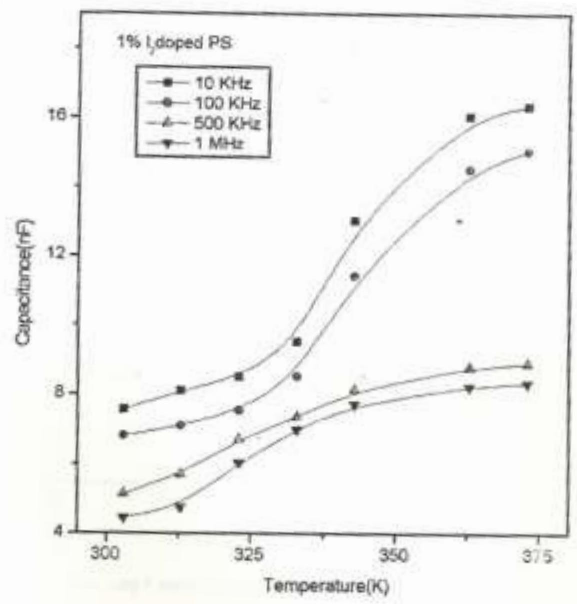

Fig 4.4b Temperature versus Capacitance of 1 % I2doped PS film

– Variation of dielectric loss (tan(5) with temperature

Figures 4.7(a&b) indicate the variation of dielectric loss with temperature fbr various constant frequencies (30 kHz ,100 kHz &l MHz) of pure and iodine doped polystyrene films. Fig.4.7a represents the dielectric loss with temperature for a pure polystyrene film at constant frequencies. The dielectric loss initially increases, showing a peak at 343K for 1 MHz. For other frequency range peaks are not found. But a sharp increase is found initially up to 343 K and above that the dielectric loss remains almost constant. Fig.4.7b shows the variation of dielectric loss with temperature for 1% iodine doped polystyrene film for various constant frequencies. In this case also dielectric loss increases with temperature, peaks are present at 333 K (13-peak) at 1 MHz and 100 kHz relaxation by Okauo [18], Large -amplitude rotational vibrations of the back bone segments become incoherent among neighboring chains. When the polymer is strained the distance between the chains is changed and the distribution of the rotational displacement goes to a new equilibrium with a corresponding relaxation time. Therefore, the [3-relaxation may be caused by the an harmonic character of the interaction potential for the rotational chain motion. Incorporation of iodine in PS reduces the viscosity of the system and the system resulting in the maxima shifting towards lower temperature region.

IX. CONCLUSION

In the present study the structure, dielectric and ac conduction properties of solution grown pure polystyrene (PS) and 1% iodine doped polystyrene films have been investigated. The structures of the pure PS and 1% iodine doped PS films have been found to be amorphous. FT-IR studies reveal the possible formation of charge transfer complex and / or molecular aggregates by dopant impurity in the polymer matrix. The studies on the dielectric properties have been carried out at different frequencies and temperature. With a view to study their effects on capacitance, dielectric loss and dielectric constant, annealing sample. Stabilizing effect on the dielectric properties of these films, Capacitance increases with increasing temperature and decreases with increase of frequency in pure and doped films. The temperature co-efficient of capacitance, and relative permittivity values of pure PS and 1% iodine doped PS films have been estimated. Low temperature peak (peak) is found in doping with 1% iodine doped PS film.

The AC. conduction study has given an idea of the conduction mechanism in pure PS and iodine doped PS films. The A.c. conductivity is found to follow a σ_{ac} α ω^n relation in pure and doped films. The increase in conductivity at high temperature is due to the increase of crystallite in the film. The hopping mechanism is found to be responsible for a.c conduction. Doping resulted with higher value of conductivity, which is attributed to the formation of Charge Transfer Complex (CTC) between iodine and PS polymer matrix.

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