Dielectric Investigation of Doped Poly (methyl acrylate) (PMA) Conducting Polymer Films

Vikram S. Yadav *Member, IAENG*, Devendra K. Sahu

Abstract— **Dielectric behavior of doped poly (methyl acrylate) (PMA) Conducting polymer has been investigated in electret state. The permittivity and loss factor have been obtained at varying temperatures from 30 to 230^{0}C and different frequencies 05,10,25 and 50 kHz for different electrode configurations of doped poly (methyl acrylate) (PMA) conducting polymer films of 25µm thickness. The capacitances are found to increase with the increase in temperature for similar electrode Al-Al system, however, in case of dissimilar electrode Al-Cu combinations, a shoulder peak is found at 110±10°C and remaining variations are the same, as found in case of similar electrode system. The variation of permittivity with temperature is attributed to thermal expansion in the lower temperature region and to the orientation of dipolar molecules in the neighborhood of glass tuber transition temperature Tg (180^{0}C) of doped poly (methyl acrylate) (PMA) conducting polymer. The variation of loss factor with temperature at different constant frequencies show two loss maxima, first at 90±10^{0}C and second at 108±10^{0}C, below and near Tg of PMA, corresponding to α and β relaxations of the polymer which shift to lower temperatures as frequency is decreased. The increase in losses with the decreases of frequency is ascribed to the increase in conductivity of the polymer.**

Index Terms—**Dielectric relaxation, PMA, isothermal immersion technique, dipole orientations**

I. INTRODUCTION

Dielectric behavior of Electret state prepared from various substances has been studied by different workers [1-6] (both at audio and radio frequencies). The dielectric constant and permittivity are the crucial quantities in the design of devices. The study of these parameters as a function of temperature and frequency reveal much information on the chemical and physical state of a conducting polymer. The dielectric properties of polymeric films are of direct interest to both the basic studies of electrical conduction through such films, and their application in capacitors for microelectronics. [7]. To obtain high values of capacitance, the dielectric constant should be high and the thickness be small. Due to the difficulty of

obtaining structurally continuous and stable ultra thin films, capacitor applications are generally limited to thick films. Extensive observations have been the molecular motion and the charge-carrier migration in a variety of polar / nonpolar linear polymers containing one, or more than one, active groups in the same monomer unit [8]. Although the dielectric properties of a number of polymers have been investigated [9], the molecular orientation behavior and the associated relaxation mechanisms of the polymers are not fully understood. Considerable attention has been devoted to the problems of the change in the dielectric properties in polymers due to intentional doping with low-molecular-weight compounds (Sasabe et al) [10]. Depending on their chemical structure and the way in which they react with the macromolecular matrix, doping substances decrease the resistivity of the polymer to varying degrees.

The present paper reports the investigations intended to get an insight into various molecular relaxation processes which occur in doped poly(methyl acrylate) (PMA) under the influence of alternating field and describes the capacity and loss factor of doped PMA film, as a function of frequency and temperature. Field is also one of the important parameters, particularly in case of conducting polymers. Many researchers have observed isotropic increase in capacity and loss factor with field but no satisfactory interpretation has been given for this effect. In the present investigation, attention has been paid to audio frequencies and temperature range 30-210^{0}C. Frequency range selected is from 5 to 50 Hz.

II. EXPERIMENTAL DETAILS

Dielectric studies were carried out on the entire sample to study the dielectric and loss variation of doped Poly methyl acrylate (PMA) films as a function of frequency and temperature because field is also one of the impotent function. The instrument used was HP 4192A impedance analyzer which gives a direct display of capacitance and tan δ in the frequency range 10 Hz to 13 MHz.

The sample of doped Poly methyl acrylate (PMA) was placed inside the temperature controlled measurement cell and the test leads of the impedance analyzer were connected to it. The isothermal immersion technique was utilized for preparing the films of doped Poly methyl acrylate (PMA). The sample capacitance and loss Factor of the samples were measured at fixed temperature and the frequency was varied from 5 Hz to 50 kHz in steps. These observations were repeated for different temperatures ranging from 30 to

Vikram S Yadav **Ph.D**. is Associate Professor with the Bundelkhand Institute of Engineering and Technology, Jhansi, INDIA and also is Additional Controller of Examination, Gautam Buddh Technical University, Lucknow, INDIA (corresponding author to provide phone: +91-9415903189; fax: +91-522-2732188; e-mail: vikramyad@gmail.com).

Devendra K Sahu Ph.D. with Department of Physics, R.S. Government Degree College, Lalitpur (U.P), INDIA

210^0C.

The dielectric constant and losses were calculated from capacitance and tan δ using the equation valid for parallel plate capacitor.

$$\in' = \frac{C_x\,d}{\in_0\,A} \;\; and \;\; \in'' = \in' \tan \delta$$

where C_x is the sample capacitance in Farad, A is the area of the sample, d is the thickness of the sample and $\in_0$ is a constant representing permittivity of free space.

III. RESULT AND DISCUSSION

Dielectric properties of conducting doped Poly (methyl acrylate) (PMA) is investigated by measuring simultaneously the capacitance and the loss factor at regularly varying temperatures and frequencies. Figures no. 1 & 2 shows, the capacitance versus temperature fixed at frequencies of 05,10,25,50 Hz for similar (Al-Al) and dissimilar (Al-Cu) electrode configurations of doped poly (methyl acrylate) with 25 μm thicknesses. As the temperature increases, the capacitance of doping film increases. This increase in capacitance is less in the temperature range 30-90^{0}C corresponding one in the temperature range 90-210^{0}C. Thus, it may be inferred that increase in capacitance is more above its glass transition temperature Tg (-100^{0}C).
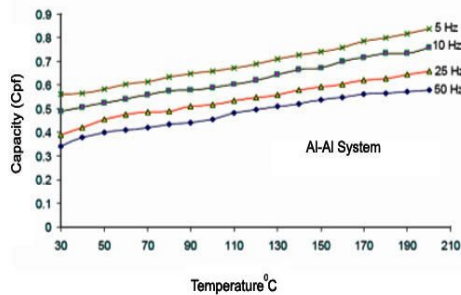

Fig 1: Variation of Capacity with temperature at different constant frequency i.e. 05, 10, 25 and 50 Hz for doped poly (methyl acrylate) (PMA) at Al-Al System
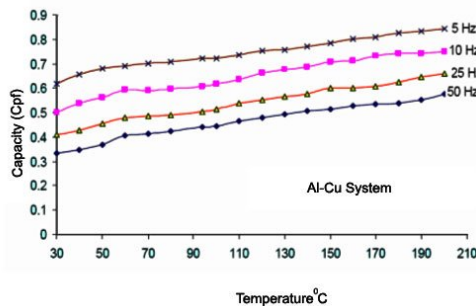

Fig 2: Variation of Capacity with temperature at different constant frequency i.e. 05, 10, 25 and 50 Hz for doped poly (methyl acrylate) (PMA) at Al-Cu System

This behavior is found to be same for Al-Al electrodes configurations. However, in case of Al-Cu electrode combinations, in general, a peak is found at 105±5^{0}C and remaining variations are the same, as found in case of similar electrode systems. The capacitance is found to be maximum at lowest frequency and found minimum at the highest frequency at all the temperatures. The largest rate of fall of capacitance with frequency is found at the highest temperature.

Figures no. 3 & 4 exhibit the variation of loss factor with temperature at different fixed frequencies 05,10,25, and 50 Hz for similar (Al-Al) and dissimilar (Al-Cu) electrode configurations for Poly(methyl acrylate) (PMA) of same thickness. All the curves show two loss maxima, one below the glass transition temperature Tg (-100^{0}C) while higher temperature loss maxima occur at 120+10^{0}C, and are designated as α and β peaks, respectively. Both the loss maxima shift to lower temperature as the frequency is decreased. Both the maxima show nearly same amount of shift. Beyond 140^{0}C, the decrease in loss factor with temperatures for the doped PMA is more pronounced. All thermograms also show an increase in magnitude of both loss maxima, with the decrease in frequency. However, magnitude of β loss maxima is more than that for α loss maxima.
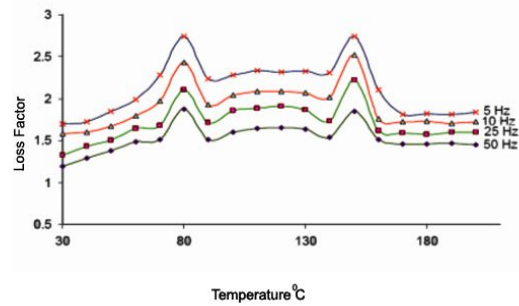

Fig 3: Variation of loss factor with temperature at different constant frequency i.e. 05, 10, 25 and 50 Hz for doped poly (methyl acrylate) (PMA) for Al-Al System

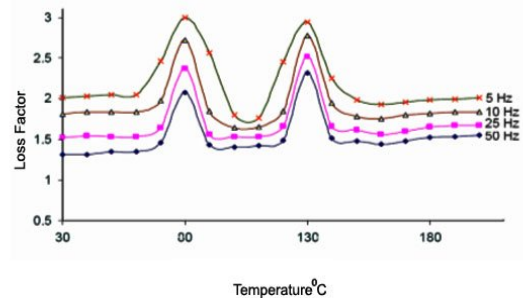Fig 4: Variation of loss factor with temperature at different constant frequency i.e. 05, 10, 25 and 50Hz for doped poly (methyl acrylate) (PMA) for Al-Cu System

Permittivity is the basic parameter of a dielectric describing its properties from the point of view of the processes of its polarization or propagation of electromagnetic waves in it, or more generally from the point of views of the processes of its interaction with an electric field. Permittivity is a microscopic parameter of a dielectric which reflects the properties of a given substance in a sufficiently large volume but not the properties of the separate atoms and molecules in the substance. There are three well known types of polarizations: electronic, ionic and

dipole polarization.

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, precisely displacement under the action of an external field of the orbits in which negatively charged electrons move around a positively charged nucleus. This type of polarization occurs in all atoms or ions and can be observed in all dielectrics irrespective of whether other types of polarization are displaced in the dielectric.

Ionic polarization is the mutual displacement of ions forming a heteropolar (ionic) molecule. A shorter time is required for the process of ionic polarization to set in, but it is longer than that for electronic polarization, i.e., 10-12 s. On the whole, the process of electronic and ionic polarization is much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of charge with respect to each other, in the direction of the field. Apart from a very high velocity mentioned above, with which the state of polarization sets in, it is important to bear in mind that the process of deformational polarization is practically unaffected by the temperature of the dielectric. The electric energy required to polarize a molecule is completely returned to the energy sources after voltage is removed. For this reason, deformational polarization does not entail any dielectric losses.

Polar dielectrics [11, 12] exhibit a tendency towards dipole or orientation polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye, to the rotation of the molecules of a polar dielectric having a constant dipole moment in the direction of a field. If orientation polarization is considered more strictly, it must be understood as the introduction by an electric field of certain orderliness in the position of polar molecules being in uninterrupted chaotic 'thermal' motion, and not as a direct rotation of polar molecules under the action of a field. For this reason, dipole polarization is connected by its nature with the thermal motion of molecule, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

After a dielectric is energized, the process establishing a dipole depolarization requires a relatively long time as compares with that of practically almost intertialess phenomena of deformational polarization. As distinct from deformational polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which transforms into heat in a dielectric, i.e. this energy causes dielectric losses corresponding one in the temperature range 90-210^{0}C. Thus, it may be inferred that increase in capacitance is more that its glass transition temperature Tg (-100^{0}C). This behavior is found to be same for Al-Al electrodes configurations. However, in case of Al-Cu electrode combinations, in general, a peak is found 105±5^{0}C and remaining variations are the same, as found in case of similar electrode systems. The capacitance is found to be maximum for lowest frequency and assumes a minimum value at the highest frequency at all the temperatures. The rate of fall of capacitance with frequency is largest at the highest temperature and as temperature is decreased.

Figures 3 & 4 exhibit the variation of loss factor with temperature at different fixed frequencies 05,10,25, and 50 Hz for similar (Al-Al) and dissimilar (Al-Cu) electrode configurations for Poly (methyl acrylate) (PMA) of same thickness. All the curves show two loss maxima, one below the glass transition temperature Tg (-100^{0}C) while higher temperature loss maxima occur at 120±10^{0}C, and are designated as α and β peaks, respectively. Both the loss maxima shift to lower temperature as the frequency is decreased. Both the maxima show nearly same amount of shift. Beyond 140^{0}C, the decrease in loss factor with temperatures for the doped PMA is more pronounced. All thermograms, also show an increase in magnitude of both loss maxima, with the decrease in frequency. However, magnitude of β loss maxima is more than for α loss maxima.

A. Frequency Dependence of Capacitance:

The capacitance and hence the dielectric constant of film decreases with the increase in frequency (Figure 1 to 4). This is so because the polarization settles itself during a very short period of time. Dielectric constant of non-polar polymers remains invariable with frequency. In case of conducting polymers PMA the dielectric constant begins to drop at a certain critical frequency and at very high frequencies it approaches the values typical of non-polar polymers. In amorphous polymers, structural polarization is also possible. For this type of polarization, the capacitance falls with the increase in frequency [13]. However, this behavior can also be explained in the following manner.

Decrease of capacitance with frequency may be due to the failure of dipoles to settle them completely during the short time of one half period of applied voltage. This sort of polarization like orientation component, atomic component, etc. further drops the value of capacitance. In our present investigation, we have observed a considerable change in capacitance value as expected in polar polymers. The dependence of capacitance on frequency is given by:

$$C = C_g + \frac{S\tau}{1 + \omega^2 \tau^2}$$

where Cg is the geometrical capacitance.

It is obvious from the above equation that capacitance reaches its maximum width ω = 0 (direct voltage) and is minimum when ω=∞.

B. Temperature Dependence of Capacitance:

Whenever a dielectric is heated or energy is supplied in the form of heat, there is expansion of lattice. The ratio of the number of molecules to the effective length of dielectric diminishes when the temperature increases. As a result of this, the capacitance and hence dielectric constants should decrease but because of presence of dipoles in case of conducting polymer PMA permittivity changes its behavior. At the lower temperatures, the dipoles remain almost frozen in and are unable to orient themselves [14]. When the temperature is raised, the orientation of dipoles gets facilitated, which increases the permittivity. The increase in capacitance and dielectric constant with temperature may be partly due to ionic mechanism of polarization.

C. Electrode Material Dependence of Capacitance:

Electrode material show marked dependence of permittivity (capacity). It is found that with Al-Al, Al-Cu combinations, permittivity is enhanced in lower temperature region at all frequencies, as compared to Al-Al, Al-Cu system. Rise of permittivity at a particular temperature may be due to maximum orientation of dipoles and then fall in permittivity value is because of loss of oriented dipoles as temperature further increases

D. Variation in loss factors:

In case of polar conductivity polymers of PMA loss values depend strongly on temperature [15]. Two loss maxima are observed (Fig. 3 & 4). The first type of dielectric loss called dipole-segmental, is associated with orientation/rotation of the polar units of the macromolecule under conditions where segmental movement is possible i.e., in the rubber-like state (> Tg) of the polymer. The second type called dipole group is due to orientation of the polar groups themselves. Losses of this kind may also occur below the Tg, i.e., in the glassy state and above Tg, i.e., rubbers like state. First loss maxima occur at 80 ± 10^0C and the second loss maxima at 120 ± 10^0C.

Therefore, two loss maxima have been anticipated in the dielectric thermograms of PMA, since the dielectric properties are associated with the molecular relaxation modes of a system because conducting polymer is supposed to be a mixture of crystalline and amorphous phase. In crystalline region, the molecules (dipoles) are bound with equilibrium position to the other. In the amorphous region the dipoles associated with one equilibrium position to another equilibrium position, can orient rather easily. The conducting polymer film grown by solution technique is a mixture of crystalline and amorphous regions. Due to amorphous nature, Vander Wall's force is weak and binding force is less. This facilitates the movements of segments. In the present investigation, β maxima occur at 120 ± 10^0C, which is slightly above Tg of PMA. Andrews and Kimmel [16, 17] have discussed a high temperature transition in poly acrylonitrile which lies above its Tg. Therefore, β relaxation process in PMA may be attributed to the motion of the more mobile molecular chains in which the intermolecular forces between the crystalline regions are weakened due to thermally activated process. This weakening of forces causes the motion of the entire molecular chain and hence, the occurrence of β-relaxation.

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