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Thermally Stimulated Depolarisation Studies of Methyl Acrylic Acid (MAA) Doped Ethyl Cellulose (EC)

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Abstract: *Thermally stimulated depolarisation current (TSDC) of polarised samples of methyl acrylic acid (MAA) doped ethyl cellulose (EC) films of about 25 µm thickness has been recorded as a function of temperature, electric field, heating rates and storage times. Two current maxima in positive direction and found around 60 and 110°C for doped sample with ethyl cellulose. FTIR of doped EC are represented the different phenomena of TSDC. Thermal sampling technique showed that the relaxation is distributed. Differentia thermal analysis gave a second-order transition at bout 345K because of good correlation between both thermal techniques it is concluded that the TSD peak is associated with glass transition of the polymer, and therefore it involves the motion of large parts of the polymer chains.*

Keywords: Thermally stimulated depolarisation current;

I. Introduction

Technology and science are placing increasing importance on the study and application of very small systems. As technological trends towards systems of micrometer size, it becomes imperative to gain a complete understanding of how the properties of such small systems might differ from those of bulk systems [1-3]. Electrets effect in polymers can be produced by the orientation of dipoles and/or trapping of charge carriers injected from the electrodes as well as generated in the bulk of the polymers. It has been show by thermally stimulated depolarization current (TSDC) technique that the characteristics of the electrets are very sensitive to structure of electrets forming material. In this respect TSDC study of composite is likely to yield information about the extent of mixing between the components [4, 5].Electrets prepared from the composite have better charge storage properties than the individual polymers and their study enables one to understand charge carrier mechanism involved in the electrets formation. This technique can be readily utilized characterize doped polymeric films because TSD current thermograms are sufficiently sensitive to additives.

In order understand the electrets forming characteristics of ethyl cellulose (EC), in present work in the present work it was doped with MAA the TSD current was investigated as a function of the doping concentration, the forming field, polarizing temperature and electrode metals.

II. Experimental Details

Commercial ethyl cellulose (EC) used in the present study having a glass transition temperature (T_g) (130°C) and molecular weight 40,000 was obtained from Sigma Aldrich. The polymer for the preparation of the films was used as such, without any further purification/recrystallization. Dopant methyl acrylic acid (MAA) used was of Johnson make. The isothermal immersion technique was applied for preparing films of pure and methyl acrylic acid (MMA) dope ethyl cellulose. The solution was prepared in a glass beaker by first dissolving 2.1 g EC in 25 ml chemically pure chloroform at room temperature and this was continuously stirred with a teflon – coated magnetic stirrer for 30 min. Tereafter,it was stirred and heated to 50°C to yield a homogeneous solution. The solution was then immersed in a constant temperature oil bath. Ultrasonically cleaned vacuum aluminized microscopic glass slides were immersed vertically into the solution for about 10 min. After the deposition of the film, the glass slide was taken out and dried in

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an oven at 40°C for 24h.This was followed by room-temperature out gassing at ~10^5 torr for a further period of 24h.The upper electrode was also vacuum deposited on the upper surface of the film to obtain a sandwich configuration. The MAA doped EC films were also prepared by the same technique under identical conditions of taking 2.1 g of EC into well stirred 1 ml of MAA that had been thoroughly mixed with 30ml of chloroform. The doping concentration was changed by varying the amount of MAA to be added in different volume of the solvent such that the total volume of solvent and MAA remains to be constant. The thickness of the sample was of the order of 20µm and used in form of square sets (1.0cm^2). The assembly was held in a thermostat and the temperature was measured using calibrated copper thermocouple. Thickness of film were measured by the dogmatic calliper (Model CD-8P) made by Mititoyo Corporation. The current was measured with an electrometer (Keithley 641).

III. Results and Discussion

Figure 1 shows the effect of various polarizing fields on TSDC characteristics of Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC) samples polarized at polarizing temperature 40°C with 05, 10 and 15MV/cm polarizing fields. It characteristics consist of two current maxima one at lower temperature (β-peak) and the other centred at higher temperature (α-peak). The magnitude of peak currents has been found to increase with increase in polarizing fields. The activation energy for all β-peaks is almost the same for field dependent TSDC thermograms (Table1). However, for high field values sometimes the current is decreased in magnitude. The α-peak is shifted towards lower temperature side with increasing values of polarizing field. Figure 2 shows TSDC spectra's Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC) samples poled at given temperature of 40°C, 60°C, 80°C and 90°C at constant electric field 10MV/m. The peak current for all samples of doped MAA is found to be poling temperature dependent .α-peak is shifted towards higher temperature side with increasing values of poling temperature. The electrification of polymers takes place due to one or more of the following mechanisms operative simultaneously when it is subjected to dynamical, mechanical or thermal treatment with or without the static electric fields. Broad peaks represent the presence of multiplicity of relaxation mechanism. The multiplicity of relaxation in doped PMA may be because of the presence of trapping levels of different depths. Two peaks were reported for MAA. The first peak reported at 40ºC (related to the charging temperature) and at 60ºC due to the release of the charges trapped at crystalline/ amorphous boundaries. PMA is a polar polymer; contribution to the polarization may be due to the alignment of dipoles and formation of space charge/injection of charge carriers from metal electrode under the effect of the electric field. β-Peak in polar polymers like PMA mainly arises from localized rotational fluctuations of the dipoles and therefore, it is also referred to as dipolar relaxation process [6-7]. The molecular mechanism of β-relaxation has been discussed by many groups [8]. In doped MAA β-relaxation can be associated to the dipole orientation of the polar side group. The occurrence of β-relaxation can be observed from certain characteristics of β-peak such as: (i) activation energy associated with this peak (Table 2) is very close to theoretically predicted value of E (i.e., ~0.20-0.50eV) and (ii) the peak position and activation energy do not change with poling field, but it strongly depends upon poling temperature. The high temperature peak (α-peak) is due to the significant injection of charge carriers from the electrodes to the surface of the dielectric, which are frozen-in during the polarization of the specimen. It is also possible that doped MAA contains a high number of impurity molecules prior to the field treatment and these molecules are dissociated into various ionic species. Therefore, it is reasonable to attribute the peaks appearing in high temperature region to space charge relaxation process (i.e., α-relaxation). α- relaxation process occurs due to the injection of charge carriers from the electrodes at the metal polymer interface. The origin of α-relaxation process of this peak is confirmed by the facts: (i) peak current varies linearly with $E^{½}$ (Figure 3) and (ii) the activation energy for this peak (i.e., 0.5-0.9 eV) does not differ much for activation energy values reported for α-relaxation in many polymers [9-12]. The charge trapping in a polymer takes place at the molecular chain, the side chain and at the interface of the crystalline and amorphous regions of the polymer [13-15]. The high field applied during electret formation may also produce some additional trapping sites. The charge release from these traps occurs because of thermal excitation and motion of the molecular chain that cause the lowering of trap's depth. The released charge can recombine, retrapped in trapping sites, or may become discharged at the electrodes. The high values of activation energies observed can only be associated

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with the ionic and electronic trapping [16]. The linear dependence of peak currents of β-peak and α-peak versus poling field (Figure 4) indicates that low temperature peak (β-peak) possesses dipolar nature and high temperature peak (α-peak) possesses the space charge phenomena [17]. In present study, at higher temperatures the charge carrier injection increases, resulting in an increase in space charge and, hence, a rise in the current and since the polarizing field is kept constant the charge released from the impurity centres present in the sample does not neutralize the space charges thus yields increasing linear nature for peak currents of α-peak [18]. As shown in Figure 5 linear relationship between T_m and T_p in the temperature region of the α-peak, suggests that the peak is due to the bulk effects [19].

Figure No. 6 shows the thermally stimulated discharge conductivity (TSDC) thermogram (log σ v/s 10^3/T) plot for Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC) at polarizing field i.e. 100kv/cm. When we plot log σ versus 1/T, a straight line with a negative slope was obtained which indicates that as temperature increases conductivity increases.As the temperature increases polymer becomes soft and mobility of the main chain segments as well as the rotation of side groups become easier. Figure no. 7 show the Monitoring of polymerization process of Methyl Acrylic Acid (MMA) doped Ethyl Cellulose (EC).Thus, at higher temperature more and more dipoles are oriented resulting in the higher equivalent surface charge density i.e as temperature increases conductivity increases. The values of activation energy have been calculated from the Arrhenius plot using the above relation (Table 3) & find that activation energy is different for different temperatures i.e for lower temperature activation energy is high while for higher temperature activation energy is low. Conduction in lower temperature region takes place by thermal activation of carrier from one disordered state to another. At higher temperature, the trap is immobilized because of segmental chain motion or entire chain motion and agrees well with that reported [20]. This could only be explained if we assume that dopant molecules when present in sufficient quantity form a link between trapping centres because of increased orbital overlaps. These experimental findings lead one to understand that satiric effects in polymeric charge transfer complex play an important role. In polymer system, the acceptor cannot get close to the donor [21]. Polymerization percentage increases in value with increasing the reaction time first. However, the prolonged reaction time does not improve them after 1.5 hour. The reason can be attributed to the following fact that the reaction is carried out in alkali medium, the amount of the hydrolysis of carbonyl group increases with the prolonged time and leads to the decrease of pH. So, prolonging the reaction time obtains the similar results in contrast with the reaction temperature. Figure 8 demonstrated the SEM micrograph of Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC). It can be seen that the atomic spacing for doped PMA is 100 micrometer which shows a broadening of the dielectric a relaxation spectrum with increasing cross-linking density, rationalized in terms of large and small-scale movements. The FT-IR spectra obtained for Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC) is shown in figure 8. From the TGA thermograms, two measured weight losses were seen for bulk MAA in which gamma and BPO were used as initiator. The thermograms are typical for acrylate polymers that thermal degradation is in the form of depolymerisation. The small peak at 402 °C for polymerization by radical initiator and a similar broad peak for polymer obtained by γ-radiation show the degradation of oligomers and/or residual monomer that may exist in cross linked polymer. This peak is not observed for polymer obtained by solution polymerization. The main decomposition peak is much sharper and appears at lower temperature for the polymer obtained in solution. The broad peaks and higher temperature in first two figures show higher molecular weights and cross linking or larger dispersive index of polymers. It is be concluded from the earlier result & discussion that the Methyl Acrylic Acid (MAA) addition to ethyl glycol increase the covalence of bonds, the density & particle size which led to increase of electrical conductivity and polymerization of TSD currents. Shape & Size of TSDC Thermograms strongly dependent upon poling temp as well as poling fields [22-23]. Commercially available polymer used in the present work is amorphous and the dopant used viz. tri substituted ethylene glycol, has an electron donating hydrocarbon group which may act as a trapping centre for charge carriers. Finally, the individual TSDC relaxation peaks can also be used to obtain various numerical estimates of relaxation parameters. In conclusion it would be appear from our work that TSDC is excellent complementary technique for investigating the electrical properties and is to be in agreement with the α-relaxation mechanism observed in MAA.

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IV. CONCLUSION

Typical TSDC spectra of EC thermoelectret formed under the appropriate polarizing conditions have two peaks which are to be attributed to the disorientation of strongly attached ethyle groups in the side chains and space charge polarization, whereas on mixing Acrylic Acid (MAA) and ethyle cellulose has been observed which might be due to contribution of included and injected charges. Increase in current in samples seems to be due to formation of charge transfer complexes and creation of new trapping levels. Pronounced effects of electrode variation on TSD currents also observed.

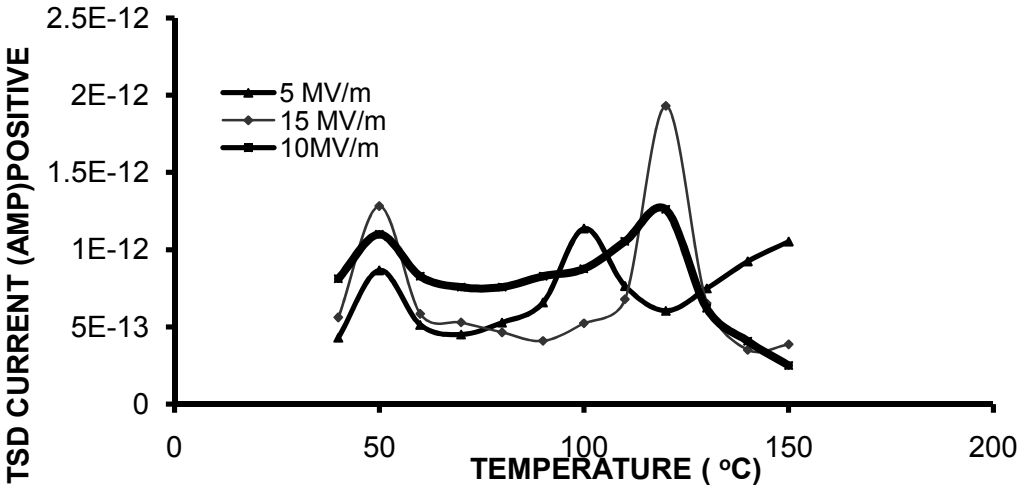

Fig 1- Effect of various polarizing fields on TSDC thermograms of Methyl Acrylic Acid (MAA) doped Ethyl Cellulose (EC) samples (25 μm) poled at temprature (Tp=50^{0}C) with Al-Al system

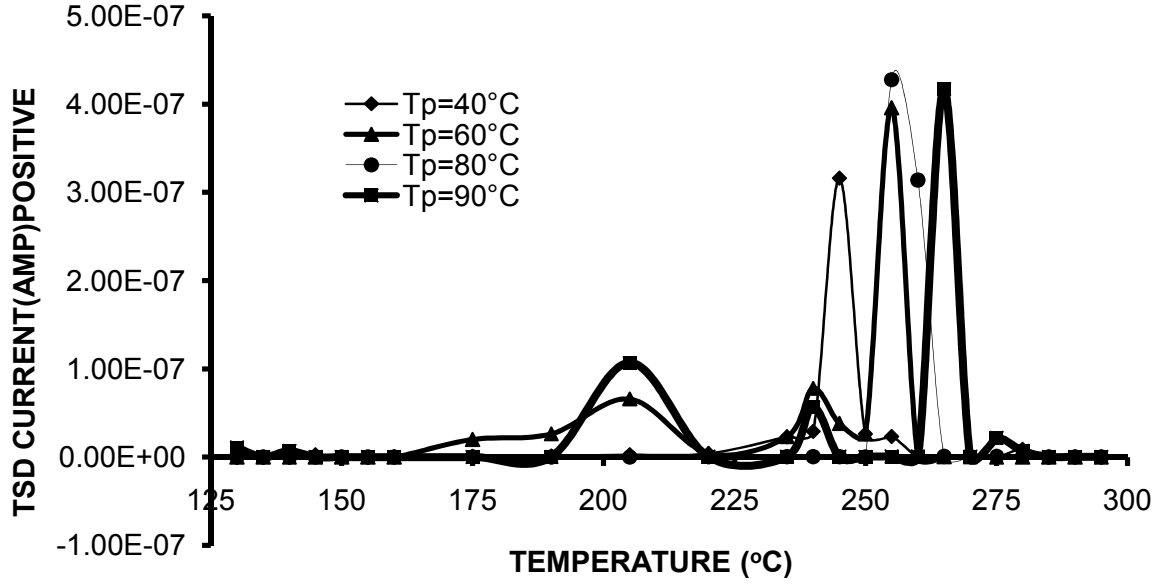

Fig. no. 2: Depolarization vs. Temprature at constant polarization temprature(40,60,80 and 90°C) of doped Methyl Acrylic Acid (MMA) doped Ethyl Cellulose (EC)

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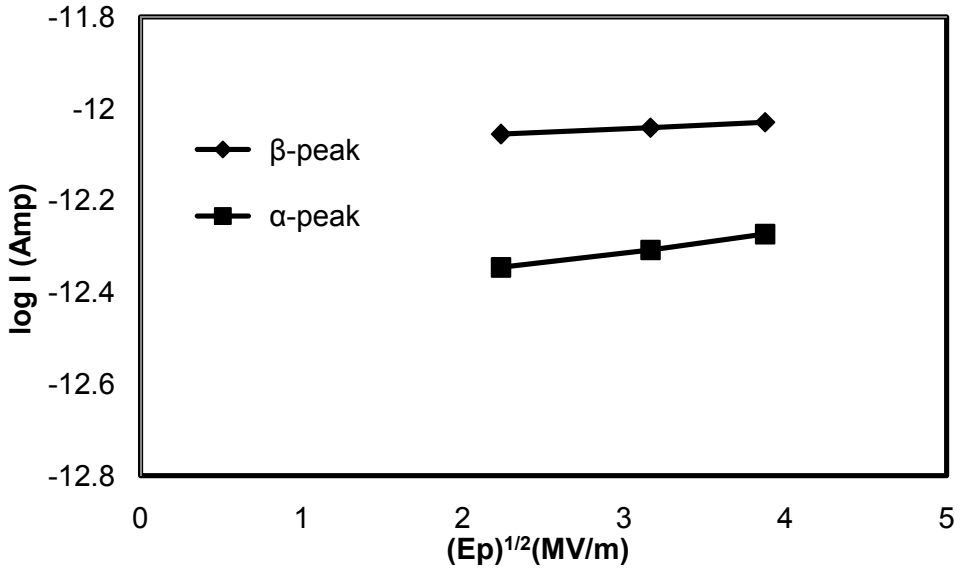

Fig no.3: log I versus $(Ep)^{1/2}$ at constant polarising temp Tp=60°C

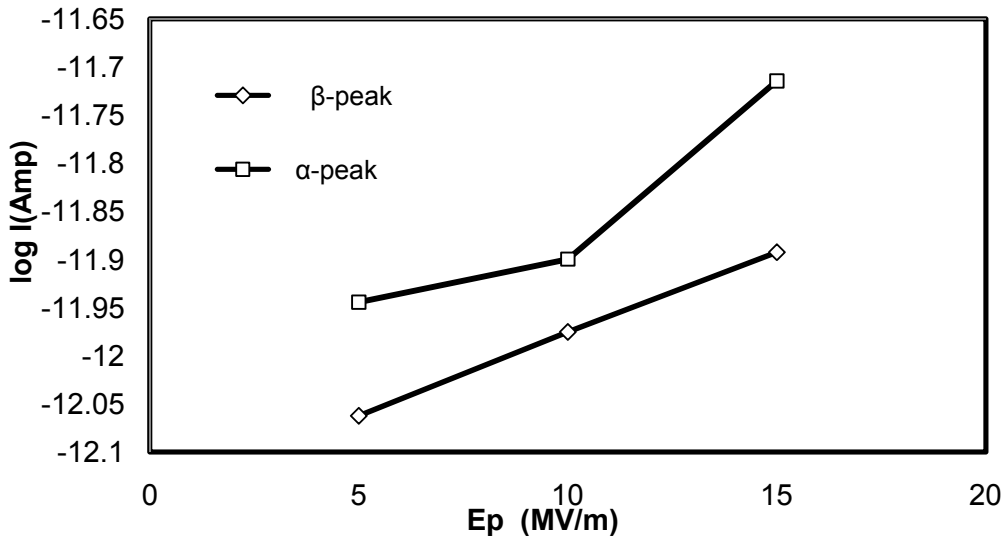

Fig .No.4 log I versus Ep at constant polarising temp. Tp=60°C

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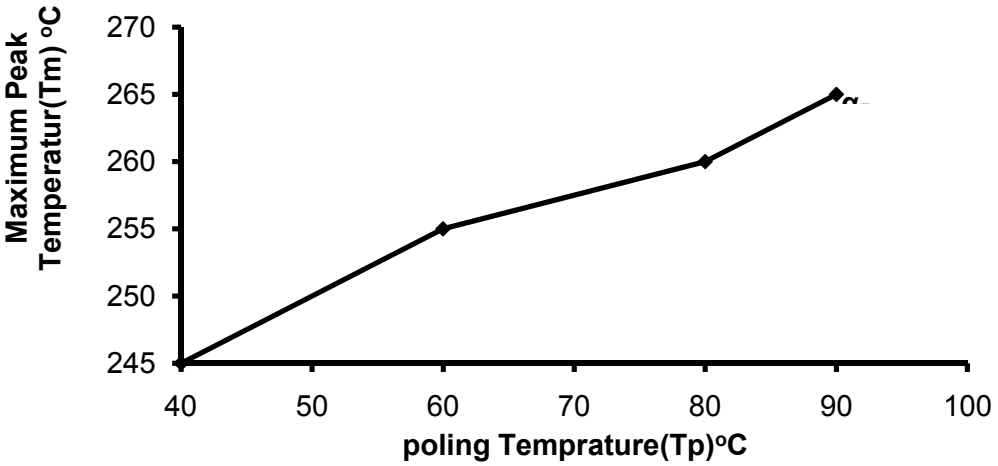

Fig No. 5: Poling temperature(Tp) versus maximum peak temperature(Tm) for doped MAA doped EC

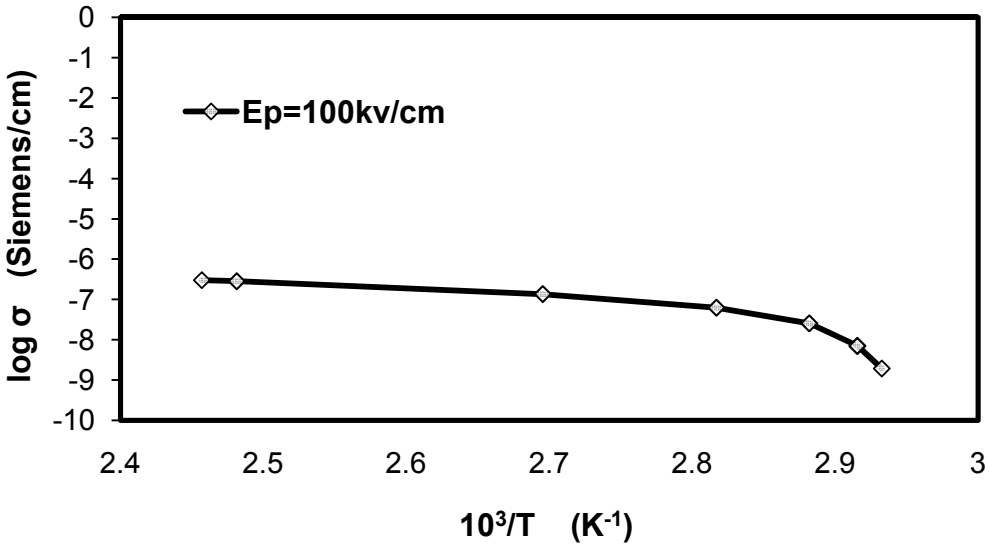

Fig no.6: Arrhenius plot(Temprature dependance of conductivity for doped MAA Ethyl Cellulose

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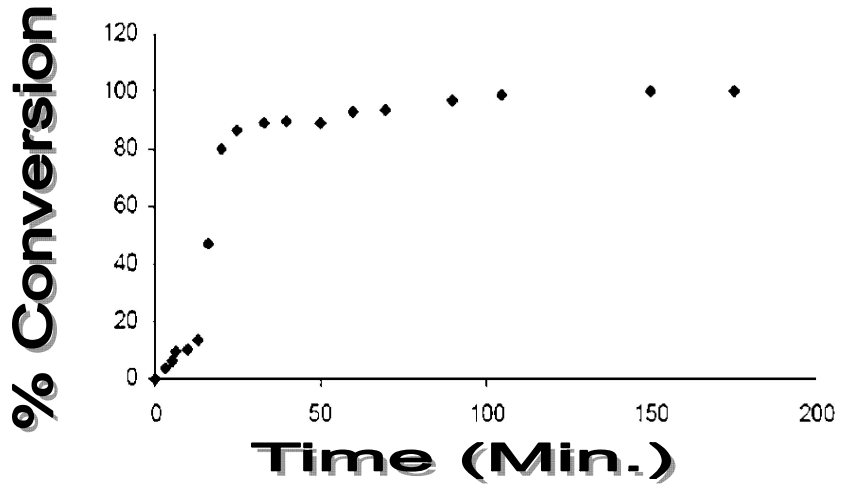

Fig. No 7.: Monitoring of polymerization process of Methyl Acrylic Acid (MMA) doped Ethyl Cellulose (EC)

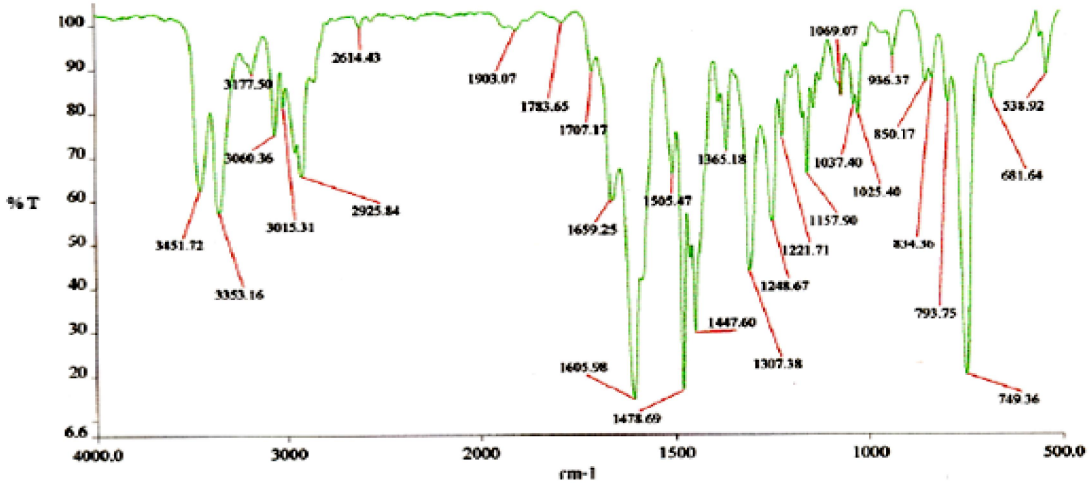

Fig. No. 8: Infrared Spectroscopy of MMA doped EC

Table 1: Depolarization kinetic data for doped MAA ethyle cellulose (EC) samples at 40°C with various polarizing fields. Sample thickness 25µm for Al-Al System

Polarizing Field	β-peak				α-peak					
(Ep) MV/m	Peak Current (Amp.)	Peak Temp. (°C)	Activation Energy (eV)	Relaxation Time(τ) (sec)	Charge Released Coul.(Q)	Peak Current (Amp.)	Peak Temp (°C)	Activation Energy (eV)	Relaxation Time(τ) (sec)	Charge Released Coul.(Q)
05	8.66×10^{-13}	50	0.234	2.8×10^{5}	4.6×10^{-9}	1.13×10^{-12}	100	0.554	5.6×10^{5}	1.2×10^{-8}

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10	$1.09x10^{-12}$	50	0.233	$1.6x10^{6}$	$6.6x10^{-9}$	$1.25x10^{-12}$	120	0.528	$4.8x10^{6}$	$3.4x10^{-8}$
15	$1.28x10^{-12}$	50	0.232	$6.2x10^{6}$	$6.8x10^{-9}$	$1.9x10^{-12}$	120	0.511	$3.2x10^{6}$	$4.2x10^{-8}$

Table 2: Depolarization kinetic data for doped MAA ethyle cellulose (EC) samples at a polarizing field 10MV/m with various polarizing temperatures i.e. 40, 60, 80 & 90°C respectively.

Polarizing field Ep(MV/m)	Polarizing temperature Tp(°C)	Peaks	Peak temperature Tm(°C)	Activation energy E(eV)	Charge released Q(C)	Relaxation time τ(s)	Peak current Im (A)
10	40	β α	145 280	0.34 0.65	6.7 17.8	0.35 0.68	0.27 42.0
10	60	β α	175 240	0.33 0.62	2.89 24.9	0.69 0.41	2.01 46.3
10	80	β α	--- 280	---- 0.64	------ 10.8	----- 0.32	------- 54.6
10	90	β α	130 275	0.31 0.64	0.77 14.3	0.30 0.18	1.10 41.0

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