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AC Conductivity and Dielectric Relaxation Behavior Studies of 2-Acrylamido 2-Methyl Propane Sulphonic Acid (AMPS) with Amide Copolymers: Composition Dependence

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ABSTRACT- A systematic measurement of dielectric constant (ε) and loss (tanδ) on powder pressed pellets of MAA with AMPS copolymers in composition10/90,20/80 and 50/50 have been carried out in the frequency range 200Hz – 100 kHz and in the temperature range from room temperature to180°C covering through the glass transition temperature (T_g). Relaxation peaks were observed (above T_g)from tanδ versus temperature curves. The peaks are attributed to α – relaxations. Further the peaks shift towards higher temperatures for higher frequencies. The AC conductivity has also been evaluated from the data. The results are discussed in the light of substituent effect in the copolymer.

KEYWORDS- Dielectric constant (ε), Dielectric loss (tanδ), AC conductivity, Relaxation, segmental motion

I. INTRODUCTION

The use of polymers in engineering industry as dielectric is becoming increasingly important. Polymers substituted by sulfo groups have unusual properties, allowing a wide range of applications. Introduction of the sulfo groups into fibers improves dyeability and imparts antistatic properties. Sulfo polymers are employed in biomedical systems including biomembranes[1]and blood compatible materials [2-5]. Sulfo polymers are also having potential applications in bioengineering, biomedicine, chromatography, water purification[6]and in enhanced oil recovery(EOR)[7-10] .Ranga Rao

carried out the synthesis and studied dielectric property of AMPS with Vinyl Amides[11]and Dielectric properties of AMPS with amides reported by Narender et al[12] . As no reports are available on dielectric properties of AMPS with Methacrylamide copolymers, an attempt is made to investigate the dielectric properties of AMPS-MAA, copolymers in 10/90,20/80 and 50/50 composition.

II. METHODOLOGY/EXPERIMENTAL

The powder samples of MAA with AMPS copolymers of 10/90 ,20/80 and 50/50 composition were used to prepare the pellets of suitable size for the present measurements. The dielectric constant (ε) and dielectric loss (tanδ) were measured using a GR-1620A capacitance measuring assembly in conjunction with an indigenously built three terminal high temperature cell. The measurements have been carried out in the frequency range from 200Hz to 100 kHz and in the temperature range from room temperature to 180°C, covering through the glass transition temperature (T_g).

III. RESULTS AND DISCUSSION

A. Dielectric Analysis

B. Dielectric Constant & Dielectric Loss

The Dielectric relaxation study gives the information about translational and orientation motion of mobile charge carriers in the dilectricmaterial.The dielectric constant changes with the frequency of the applied field and is also dependent on the physical properties of dielectric. The variation in the dielectric constant arise in the different frequency domains due to different dielectric polarizations, such as ionic, electronic, interfacial and orientational. The dielectric constant **ε**' expresses the charge stored in the material, while the dielectric loss **ε**" expresses the energy loss when the polarity of the electric field is rapidly reversed. The dielectric parameters a function of frequency is described by the complex dielectric permittivity which consists of real(**ε**') and imaginary(**ε**")parts.
The real and imaginary parts are correlated with each other through the following equation.

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where **ε**' and **ε**" are the real and imaginary parts which represent the components of energy storage and energy loss respectively in each cycle of the electric field and j is constant having value$(-1)^{1/2}$. The energy storage component is calculated from the following relation.

$$\varepsilon' = Cd/A\,\varepsilon_o$$

where C, d, A and ε_o (8.854×10^{-12} Fm^{-1}) are the capacitance, film thickness, surface area and permittivity of free space The capacitance C and loss factor **(tanδ orD)** can be obtained directly from the measurement . Figure 1-4 are showing the variation of energy storage component (Dielectric constant), dielectric loss and AC conductivity of MAA-AMPS copolymers synthesized for various compositions. Obviously the values of dielectric constant are decreased with increase of frequency which may due to the presence of dipoles to align themselves in the direction of the applied field[13].The high value of both **ε**' and **ε**" at lower frequencies may be attributed to the charges accumulation at the electrode-sample interface that leads to the electrode phenomena of polarization or space charge polarization/Interfacial polarization[14-15]. The energy loss (imaginary of **ε**”) is calculated by the following relation **ε**”= **ε**’(loss factor).

C. AC Conductivity

The electrical conductivity of polymers has been extensively investigated to interpret the nature of charge transfer in the materials. Polymers are good insulating materials with low conductivity, and therefore are of interest to the industry of micro-electronics. The electrical conductivity of polymers depends upon the thermally generated charge carriers. The Ac conductivity data were obtained using the following relation[17].

$\sigma_{ac} = \varepsilon_0 \varepsilon'' \omega$.

The AC conductivity is also related to the frequency as $\sigma_{ac} = A\omega^s$

Where A is a constant, w is the angular frequency, and s is the exponent which generally less than or equal to one.The value and behavior of the exponent of s versus temperature and/or frequency determines theprevailing conduction mechanism dominant in the material.

The results on the measurement of dielectric constant (ε) and loss (tanδ) for AMPS with dielectric properties of MAA-AMPS, copolymers in 10/90,20/80 and 50/50 composition at room temperature are given in table-1 for frequencies 200Hz and 100kHz and the variation are showing in figure 1 & 2.

Table 1: Values of ε and tanδ of MAA-AMPS copolymers at room temperature for frequencies 200Hz and 100 kHz

Copolymer	ε at 200Hz	tanδ at 200Hz	ε at 100kHz	tanδ at 100kHz
MAA-AMPS (10/90)	3.70	1.90×10^{-1}	2.50	1.10×10^{-1}
MAA-AMPS (20/80)	3.80	2.10×10^{-1}	2.65	1.40×10^{-1}
MAA-AMPS (50/50)	11.50	2.60×10^{-1}	6.75	1.70×10^{-1}

The variation of ε and tanδ with frequency, at room temperature for MAA-AMPS (10/90) are showing in Figure 1 & 2. It is seen from the figure that ε vary from 3.7 at 200 Hz to 2.50 at 100 kHz (Table 1). The variation in tanδ is very small i.e. from 0.19 at 200 Hz to 0.11 at 100 kHz. The small changes in ε and tanδ ensure the high purity of the polymer material and also indication of absence of space charge polarization.

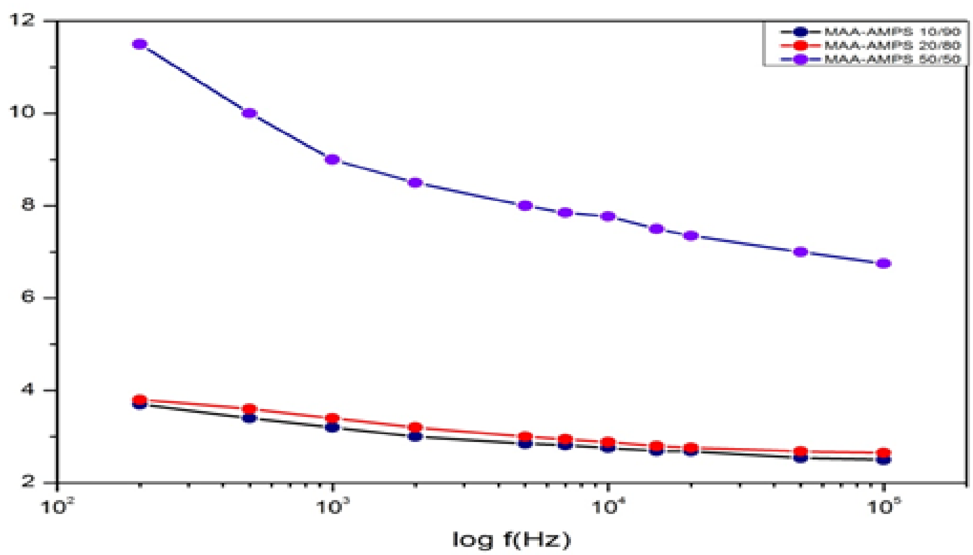

Figure 1: Variation of Ɛ with log f at room temperature

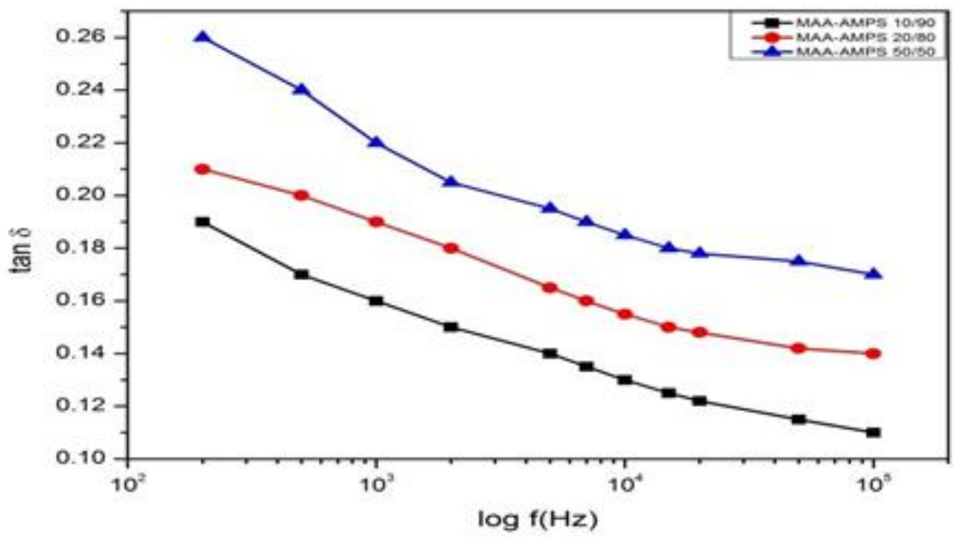

Figure 2: Variation of tanδ with log f at room temperature.

It that is believed the large value of ε at low frequencies could be due to effect of space charge polarization,[12] whereas this effect is negligible for the frequencies beyond 10kHz. It can be seen that both the values of ε and tanδ decreases, with increase of frequency and the rate of decrease is smaller for high frequencies. Comparison among the three copolymers it is seen that an enhanced dielectric property is being observed This may be due to more polar nature of MAA-AMPS (50/50) than that of MAA-AMPS (20/80) and MAA-AMPS(10/90.) in copolymer systems.

It is further seen that, strong temperature dependence starts at lower temperature for lower frequencies and at higher temperature for higher frequencies. To understand the nature of temperature dependence, the temperature coefficient of dielectric constant (TCε)is calculated for various intervals of temperatures(Table-2) for 1kHz.The temperature coefficient of dielectric constant (TCε)has been determined from room temperature Trt, up to glass transition temperature Tg, according to the relation $TC\varepsilon=1/\varepsilon_{m.p}.d\varepsilon/dt$. Where dε is the difference between dielectric constants, $\varepsilon_{m.p}$ is the dielectric constant at the mid-point of Tg and Trt.

Table 2: Variation of temperature coefficient of dielectric constant (TCε) for MAA-AMPS at 1kHz

S. No.	Temperature(ºC)	TCε $(^{o}C)^{-1}$
1	30-40	0.011
2	40-60	0.056
3	60-80	0.025
4	80-120	0.010

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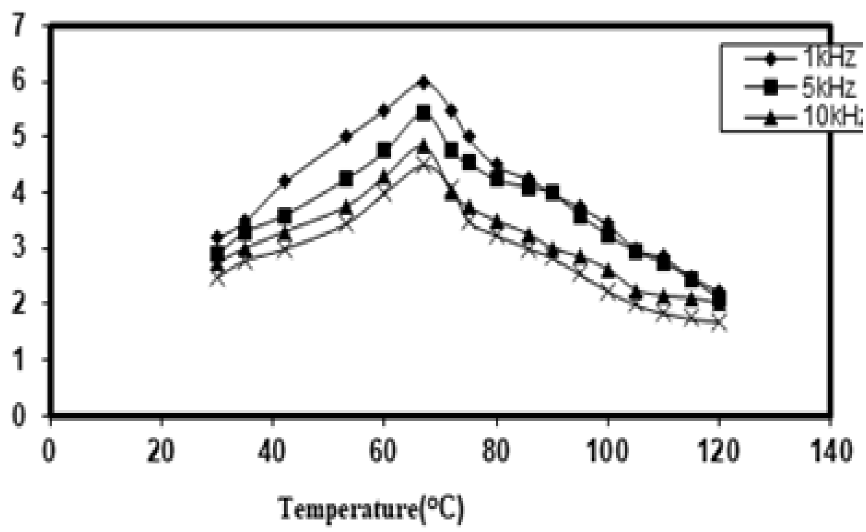

Figure 3: Variation of ε with temperature for MAA-AMPS(10/90)

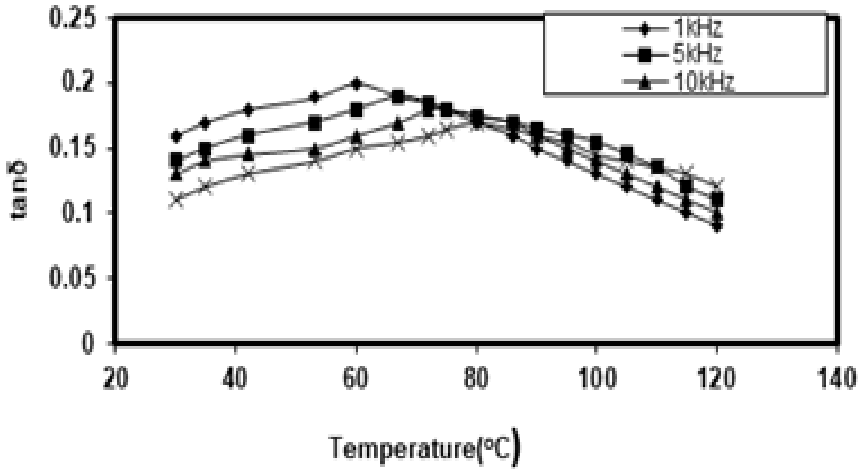

Figure 4: Variation of tanδ with temperature for MAA - AMPS (10/90)

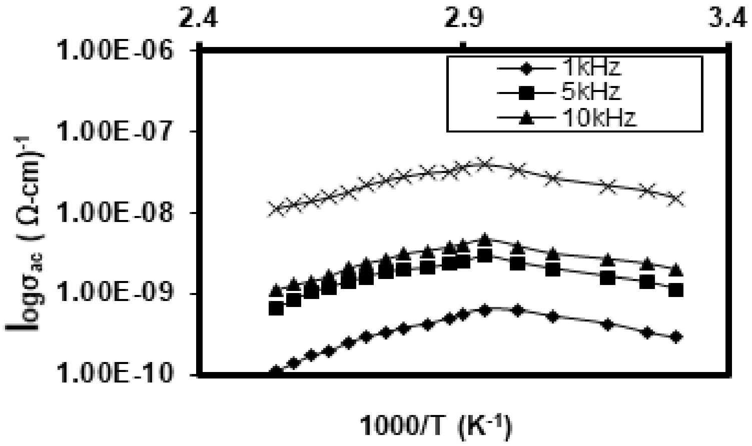

Figure 5: Variation of ac conductivity with reciprocal temperature for MAA-AMPS(10/90)

Figure 3 and 4 are showing the variation of ε and tanδ respectively with temperature for MAA-AM(PS (10/90) and figure 5 for ac conductivity (log $_{ac}$) with reciprocal temperature for four selected frequencies. From room temperature to 67ºC, ε is both frequency and temperature dependent and a linear increase of ε with temperature is observed giving rise a peak at67ºC for all frequencies. Beyond 67ºC, ε decreases in manner it increased, indicating a kind of phase change at this temperature. The increase of ε from room temperature to 67ºC is attributed to the increase of flexibility of the polymer chain. The peak observed around 67ºC indicates the transition of copolymer material from viscoelastic to rubbery

like state. Various polarizations contributing to total polarizations are also effective up to T_g resulting in a maximum value of ε a few degrees above T_g at all frequencies. Further increase of temperature caused thermal chaotic oscillations of the molecular chain and the

diminishing degree of order of orientation of dipoles, showing abrupt fall of ε and confirming the disordered phase of the polymer chain[18].

The variation of tanδ with temperature is shown in Figure 4 for different frequencies. The variation in loss is similar to that of ε and giving rise α-relaxation peaks at 60ºC, 67ºC, 75ºC and 80ºC for 1 kHz, 5 kHz, 10 kHz, and 100 kHz respectively. The peak positions shift towards higher temperatures for higher frequencies. The ac conductivity σac have been evaluated from the measured values of Ɛ and tanδ as a function of temperature. The σ ac values range from10^{-10} to 10^{-8}(Ω-cm)$^{-1}$ for the present measurement range it can be seen from the figure, that σ_{ac} is frequency and temperature dependent. The σ_{ac} values are higher for higher frequencies.

Figure 6 & 7 showing the variation of ε and tanδ respectively with temperature for MAA-AMPS (20/80) and figure 8 for ac conductivity (logσ_{ac}) with reciprocal temperature for four selected frequencies. The temperature dependence is similar to that of MAA-AMPS (10/90) with a 5-6 % enhancement in the property.

The following are the few noticeable points from the observed results.

- An enhancement in the property of ε and tanδ at room temperature is nearly 5%.

- A peak at 72ºC in ε versus temperature for all frequencies indicating the phase change in the system.
- α-relaxation peaks were noticed at 67ºC, 72ºC, 75ºC and 80ºC for 1 kHz, 5 kHz, 10 kHz and 100 kHz respectively.

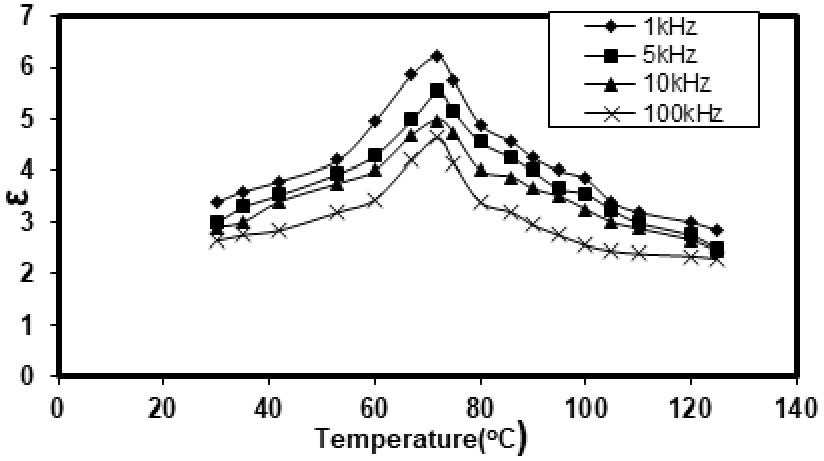

Figure 6: Variation of ε with temperature for MAA- AMPS (20/80)

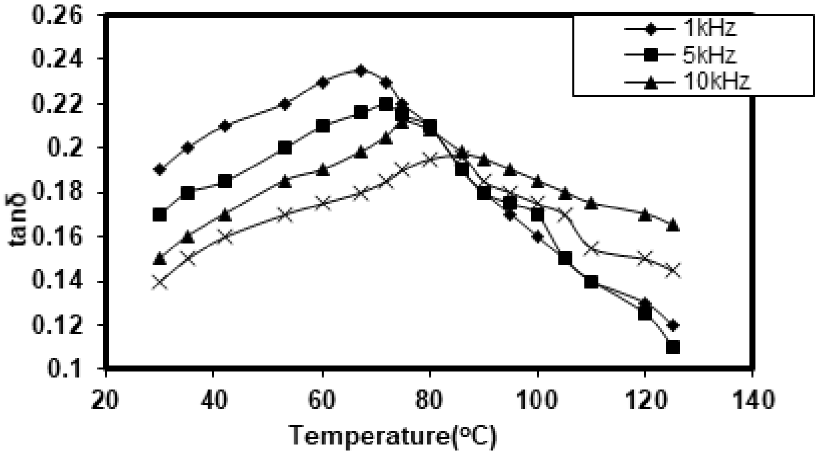

Figure 7: Variation of tanδ with temperature for MAA - AMPS (20/80)

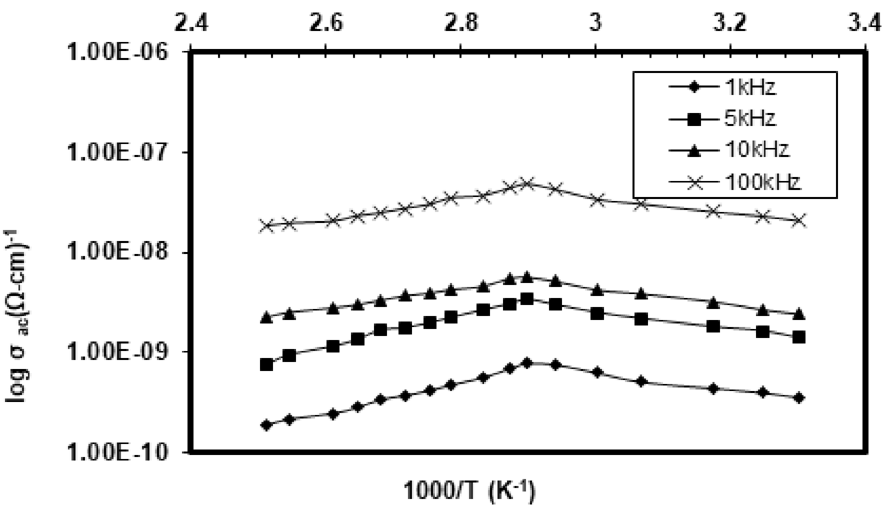

Figure 8: Variation of ac conductivity with reciprocal temperature for MAA-AMPS (20/80)

The Figure 8 shows the variation of conductivity (σ_{ac}) with reciprocal temperature. The σ_{ac} has been evaluated from the measured values of ε and tanδ as function of temperature.

The σ_{ac} Values range from 10^{-10} to10^{-8} $(\Omega\text{-cm})^{-1}$ for the present measurement range. It can be seen from the plot that the σ_{ac} is frequency and temperature dependent and further the increase of σ_{ac} is higher for higher frequencies.

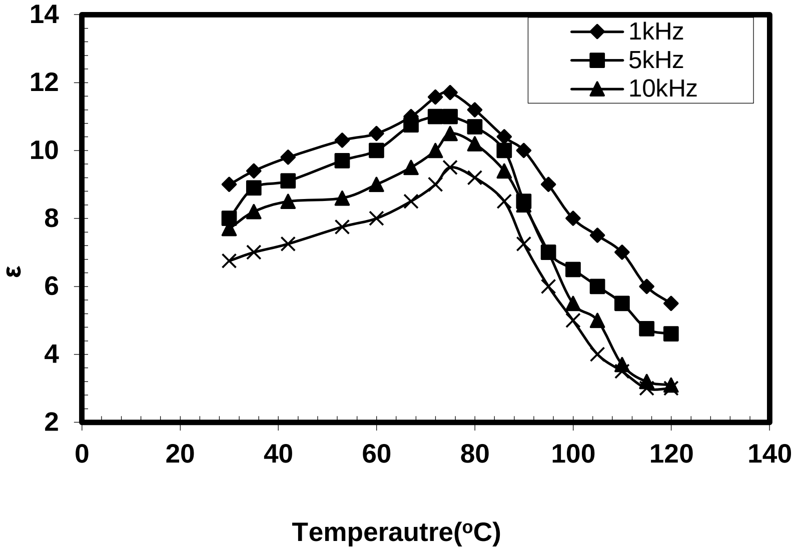

Figure 9: Variation of ε with temperature for MAA- AMPS (50/50)

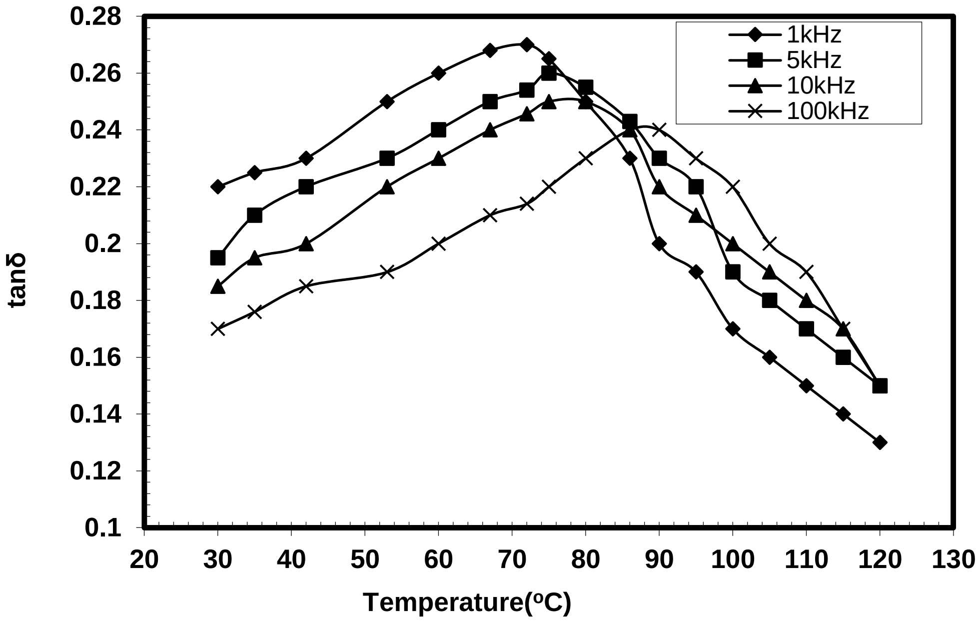

Figure 10: Variation of tanδ with temperature for MAA-AMPS (50/50)

Figures 9 and 10 are showing the variation of ε and tanδ respectively with temperature for MAA-AMPS (50/50) and figure 11 for ac conductivity (log $_{ac}$) with reciprocal temperature for four selected frequencies. From room temperature to 75°C, ε is both frequency and temperature dependent and with a slight increase of temperature ε increases at a rapid rate, giving rise a peak at 75°C for all frequencies. Beyond 75°C, ε decreases abruptly indicating a kind of phase change at this temperature (19-26).

The variation of tanδ with temperature is shown in figure 10 for different frequencies. The tanδ is both frequency and temperature dependent and increases at a slower rate giving rise α- relaxation peaks at 72°C, 75°C, 80°C and 90°C, for 1 kHz, 5 kHz, 10 kHz, and 100 kHz respectively. The peak positions shift towards higher temperatures for higher frequencies. A further increase of temperature causes decrease in tanδ, as it can be observed from the figure.

The σ_{ac} has been evaluated from the measured values of ε and tanδ as a function of temperature for various frequencies. The values range from 10^{-10} to10^{-7} $(\Omega\text{-cm})^{-1}$. It can be seen from the plot that the σ_{ac} is frequency and temperature dependent and further the increase of σ_{ac} is higher for higher frequencies.

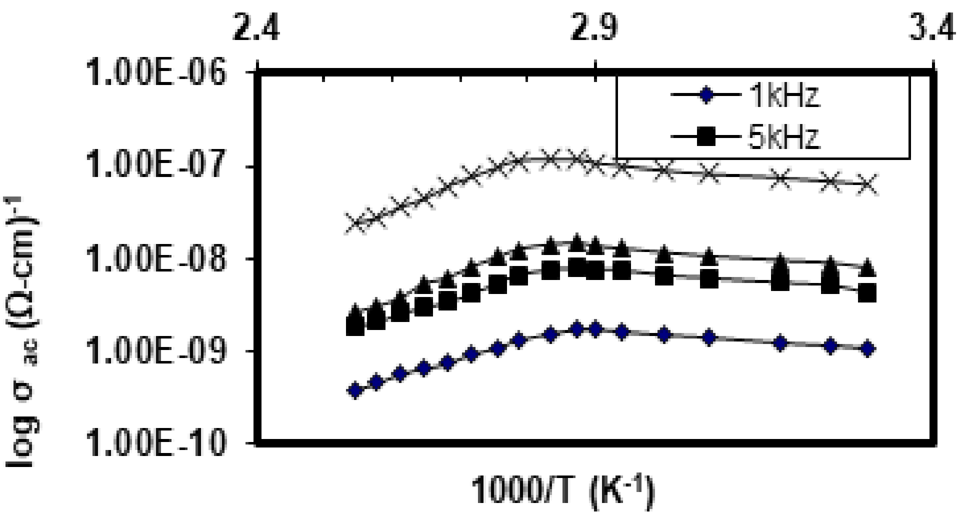

Figure 11: Variation of ac conductivity with reciprocal temperature for MAA-AMPS (50/50)

IV. CONCLUSION

A systematic measurement of dielectric constant (ε) and loss (tanδ) on powder pressed pellets of MAA with AMPS copolymers in composition10/90,20/80 and 50/50 have been carried out in the frequency range 200Hz – 100 kHz and in the temperature range from room temperature to180^{o}C covering through the glass transition temperature (T_g). Relaxation peaks were observed (above T_g) from tanδ versus temperature curves. The peaks are attributed to α – relaxations. Further the peaks shift towards higher temperatures for higher frequencies. The AC conductivity has also been evaluated from the data. The results are discussed in the light of substituent effect in the copolymer. Among the Copolymers of -MAA-AMPS (10/90), MAA-AMPS(20/80) and (50/50) compositions MAA-AMPS(50/50) established enhanced dielectric property around the room temperature and also at high temperature is due to presence alpha methyl group and increase of polar nature in MAA of MAA-AMPS(50/50) of the copolymer system.

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