

Studies on Dielectric relaxation and AC Conductivity of 3-Methoxy-4-(2-Hydroxy-3-Methacryloxy-Propoxy) Benzaldehyde (MH) and Methacrylamide (MAA) Copolymers: Composition Dependence

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ABSTRACT- Systematic measurement of dielectric constant (ϵ) and loss ($\tan\delta$) on powder pressed pellets of MH and MAA copolymers in composition 10/90, 20/80, 50/50 have been carried out in the frequency range 200Hz-100kHz and in the temperature range from room temperature to 180°C covering through the glass transition temperature, T_g . Two sets of relaxation peaks one slightly above room temperature and the other slightly above T_g are noticed from $\tan\delta$ versus temperature curves for different frequencies. The peaks are attributed to β - and α -relaxations. Further the peaks shift towards higher temperatures with increase of MH content in the copolymer. The enhanced dielectric behavior is observed in the case of MH-MAA (50/50). The results are discussed in the light of increase in MH content in the copolymer.

Keywords- Dielectric constant (ϵ), Dielectric loss ($\tan\delta$), AC conductivity. Relaxation, segmental motion.

I INTRODUCTION

The use of polymers in engineering industry is becoming increasingly important, the copolymer of acryl amide and acrylic acid salts, substituted acrylamide are associative in nature and are finding applications in oil recovery, drilling fluids coatings and cosmetic applications[1-6] Many researchers are working on copolymerization of acrylamide with ionic[7], zwitterionic, neutral and acrylamide monomers by different synthetic routes. Synthesis and characterization of acrylic copolymers with N-phenyl methacrylamide and methylmethacrylate was studied by Reddy et al [8,9] and Narender et al[10] studied the dielectric studies on AMPS with amide copolymers, no reports are available on dielectric properties study on these materials. In this paper a systematic measurement of dielectric constant (ϵ) and dielectric loss ($\tan\delta$) on powder pressed pellets of MH-MAA copolymers in compositions 10/90, 20/80 and 50/50 and the results obtained there on are reported. The ac conductivity has also been evaluated from the dielectric data. The observed dielectric behaviour is

explained in terms of the polar nature of the constituents of the copolymer system.

II MATERIALS & METHODS/EXPERIMENTAL

The powder samples of MH - MAA copolymer of different compositions were used to prepare the pellets of suitable size for the present measurements. The dielectric constant (ϵ) and dielectric loss ($\tan\delta$) were measured using a GR-1620A capacitance measuring assembly in conjunction with an indigenously built three terminal cell. The temperature is controlled using a CERAMO (REX-90) temperature controller. The measurements have been carried out in the frequency range from 200Hz to 100kHz and in the temperature range from room temperature to 180°C covering through the glass transition temperature (T_g). The T_g values for MH-MAA(10/90), MH-MAA(20/80) and MH-MAA (50/50) are 107°C, 112°C, and 128°C respectively.

III RESULTS & DISCUSSION

A. Dielectric Analysis

The Dielectric relaxation study gives the information about translational and orientation motion of mobile charge carriers in the dielectric material. 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.

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

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.

$$\epsilon' = Cd/A \epsilon_0$$

where C , d , A and ϵ_0 ($8.854 \times 10^{-12} \text{Fm}^{-1}$) are the capacitance, film thickness, surface area and permittivity of free space. The capacitance C and loss factor ($\tan\delta$ or D) can be obtained directly from the measurement. Figure 1-4 shows the variation of energy storage component (Dielectric constant), dielectric loss and AC conductivity of MH-MAA copolymers synthesized for various compositions. Obviously the values of dielectric constant are decreased with increase of frequency which may be due to the presence of dipoles to align themselves in the direction of the applied field [11]. 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 [12-15]. The energy loss (imaginary of ϵ'') is calculated by the following relation $\epsilon'' = \epsilon'(\text{loss factor})$

B. 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 [16].

$$\sigma_{ac} = \epsilon_0 \epsilon'' \omega$$

The AC conductivity is also related to the frequency as

$$\sigma_{ac} = A \omega^s$$

Where A is a constant, ω 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 the prevailing conduction mechanism dominant in the material.

The results on the measurement of dielectric constant (ϵ) and loss ($\tan\delta$) for MH-MAA copolymer of different compositions at room temperature are tabulated in Table-1.

Table-1: Values of ϵ and $\tan\delta$ of MH-MAA copolymers at room temperature for frequencies 200Hz and 100 kHz

Copolymer	ϵ at 200Hz	$\tan\delta$ at 200Hz	ϵ at 100kHz	$\tan\delta$ at 100kHz
MH-MAA(10/90)	3.46	3×10^{-2}	3.20	1×10^{-3}
MH-MAA(20/80)	3.56	4×10^{-2}	3.27	1×10^{-3}
MH-MAA(50/50)	10.11	2×10^{-1}	4.72	2×10^{-2}

Figures 1(a) and 1(b) show the variation of ϵ and $\tan\delta$ at room temperature as a function of frequency for MH-MAA copolymer of the compositions 10/90, 20/80 and 50/50. It can be seen that a small change in ϵ and $\tan\delta$ for the compositions of the copolymer 10/90 and 20/80, while significant increase in ϵ and $\tan\delta$ is observed in case of composition 50/50 with increase in frequency from 200Hz to 100kHz. It is believed that the large value of ϵ at low frequencies for 50/50 could be due to combined effect of space charge polarization and increase in MH content of relatively more polar nature. Influence of space charge polarization (interfacial polarization) is more at lower frequencies resulting in higher values of ϵ , whereas this effect is negligible for the frequencies beyond 10kHz. In the low frequency region below 10kHz the spurious effects will also result in increase of polarization. Even at room temperature there exist charge carriers that can migrate for some distance through the dielectric. When they are embedded in their motion either because they are trapped in the material or on interface, they give rise to space charges. These charges result in macroscopic field distortion, which is called space charge polarization. The presence of space charge polarization is manifested as an increase in dielectric constant (ϵ) of the sample [12-15].

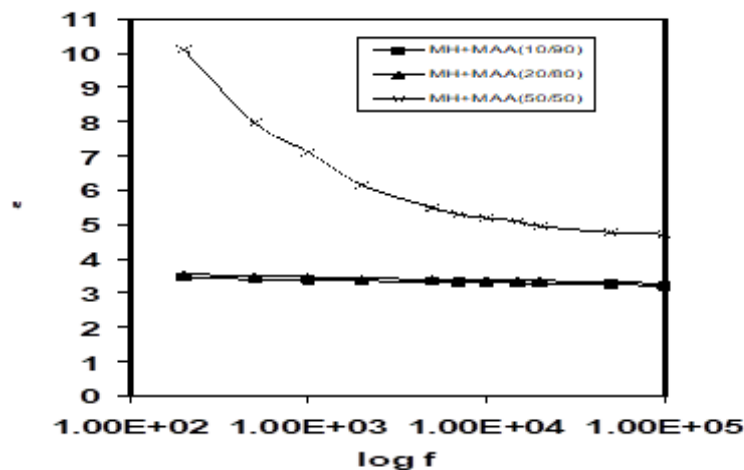


Fig. 1(a) Variation of ϵ with $\log f$ at room temperature

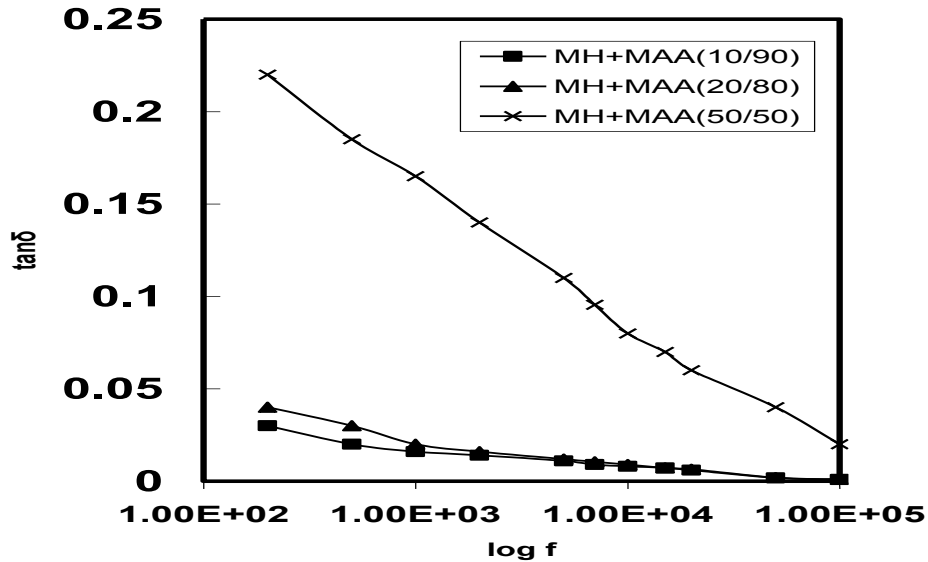


Fig. 1(b) Variation of tanδ with log f at room temperature

Figures 2(a) and 2(b) show the variation of ϵ and $\tan\delta$ respectively with temperature for MH-MAA (10/90) and Fig.2(c) for the variation of ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies. From room temperature to 100°C, ϵ is found to be frequency independent and with a small increase of ϵ with temperature at a slower rate. Beyond 100°C a frequency dependent increase in ϵ is seen up to 160°C and a rapid rise in ϵ is seen above 160°C giving rise a peak at 169°C for all frequencies. For lower frequencies i.e., 1 kHz and less than 1 kHz the increase of ϵ is at a faster rate, starting from 140°C and giving rise a peak at the same temperature. This increase of ϵ with temperature is attributed to enhanced flexibility of the polymer chain and thus giving rise enhanced polarization effects. Beyond 169°C, ϵ decreases abruptly indicating a kind of phase change at this temperature i.e. viscoelastic to rubbery like state. This decrease is due to thermal chaotic oscillations of the polymer chain beyond T_g confirming the disordered [17-19]. 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 ($TC\epsilon$) is calculated for various intervals of temperatures (Table-2) for 1kHz. The temperature coefficient of dielectric constant ($TC\epsilon$) has been determined from room temperature Trt , up to glass transition temperature Tg , according to the relation $TC\epsilon = 1/\epsilon_{m.p.} d\epsilon/dt$. Where $d\epsilon$ is the difference between dielectric constants, $\epsilon_{m.p}$ is the dielectric constant at the mid point of Tg and Trt .

Table 2. Variation of temperature coefficient of dielectric constant ($TC\epsilon$) for MH-MAA at 1kHz

Sno	Temperature(°C)	$TC\epsilon$ (°C ⁻¹)
1	30-50	0.012
2	50-77	0.026
3	77-100	0.037
4	100-140	0.052
5	140-164	0.058
6	164-179	0.031

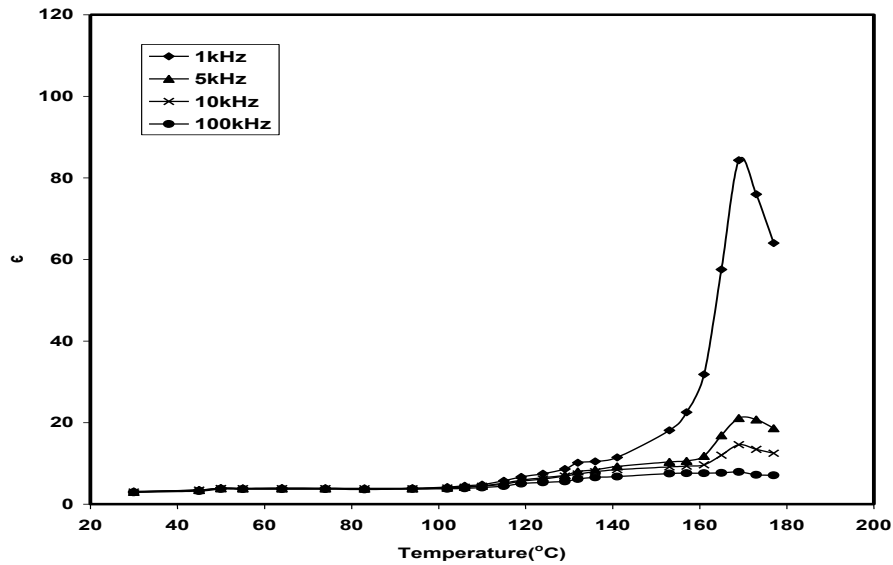


Fig.2(a) - Variation of ϵ with temperature for MH+MAA (10/90)

The variation of $\tan\delta$ with temperature show up a gradual increase giving rise a low intensity peak at 45°C for all frequencies and it is frequency dependent and the nature of behavior is believed to be β - relaxation which occur due to localized motion of the polymer chain. Beyond this temperature also the same behaviour of increase in $\tan\delta$ is continued up to 110°C. Further increase of temperature resulted in a rapid enhancement of $\tan\delta$ giving rise relaxation peaks at 129°C, 132°C, 136°C and 142°C for 1

kHz, 5kHz, 10kHz and 100kHz respectively. The relaxations are known to be α -relaxations, which occur due to segmental motion of polymer main chain above T_g . The peak positions shift towards higher temperatures for higher frequencies. Further increase of temperature caused a decrease in $\tan\delta$. [20-25]

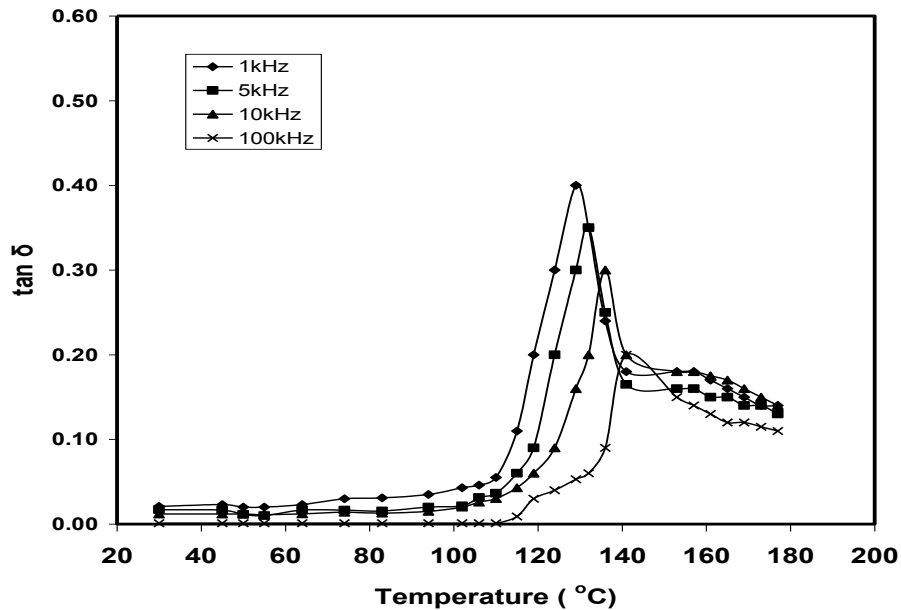


Fig.2(b) -Variation of $\tan \delta$ with temperature for MH+MAA (10/90)

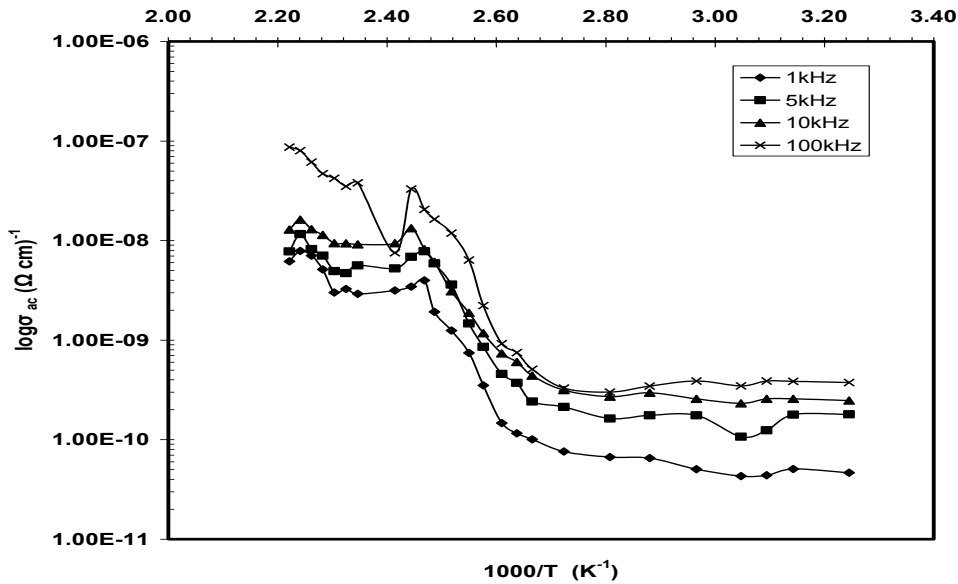


Fig. 2(c) -Variation of ac conductivity with reciprocal temperature for MH+MAA (10/90)

The ac conductivity (σ_{ac}) has been evaluated from the data on ϵ and $\tan\delta$ as a function of temperature and plotted as $\log \sigma_{ac}$ vs reciprocal temperature (Fig 2c). A frequency dependent and temperature independent variation in σ_{ac} is seen below 110°C. The trend of variation is same as that seen for $\tan\delta$ but beyond 110°C, a linear rise of conductivity is observed with an increase of two orders, because the copolymer gets softened beyond this temperature and relatively more number of charge carriers available for

conduction due to increase in mobility of molecular chain. The conductivity is found to decrease rapidly beyond the temperature 140°C (approx.) entering into a disordered phase of the polymer. The overall change in conductivity is observed to be the range 10^{-11} to 10^{-8} (ohm-cm) $^{-1}$. [20-25]. Figures 3(a) and 3(b) show the typical variation of ϵ and $\tan\delta$ respectively with temperature for MH-MAA (20/80) and 3(c) for the variation of ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies.

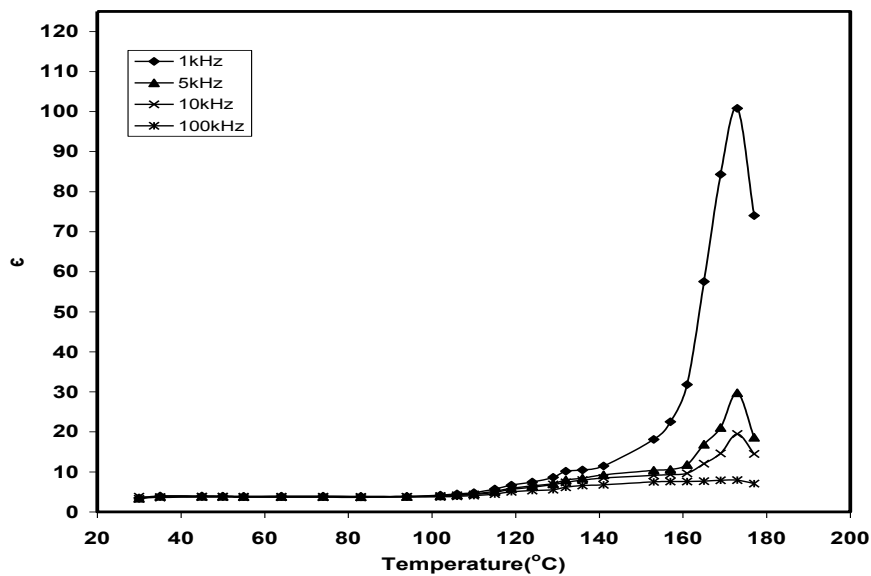


Fig. 3(a) - Variation of ϵ with temperature for MH+MAA (20/80)

A similar behaviour has been noticed with a slight enhancement in the variation of ϵ , $\tan\delta$ and ac conductivity with temperature as that of MH-MAA (10/90). A peak is

observed at 173°C for all frequencies, in the variation of ϵ with temperature and the α -relaxation peaks in $\tan\delta$ vs temperature curves have been noticed at 132°C,

136°C, 141°C and 153°C for 1 kHz, 5 kHz, 10 kHz and 100 kHz respectively beyond T_g . In addition a low intensity β -peak appeared in $\tan\delta$ vs temperature curves at 40°C for all

frequencies. In ac conductivity vs temperature curves these peaks were not seen for MH-MAA(10/90) & MH-MAA(20/80).

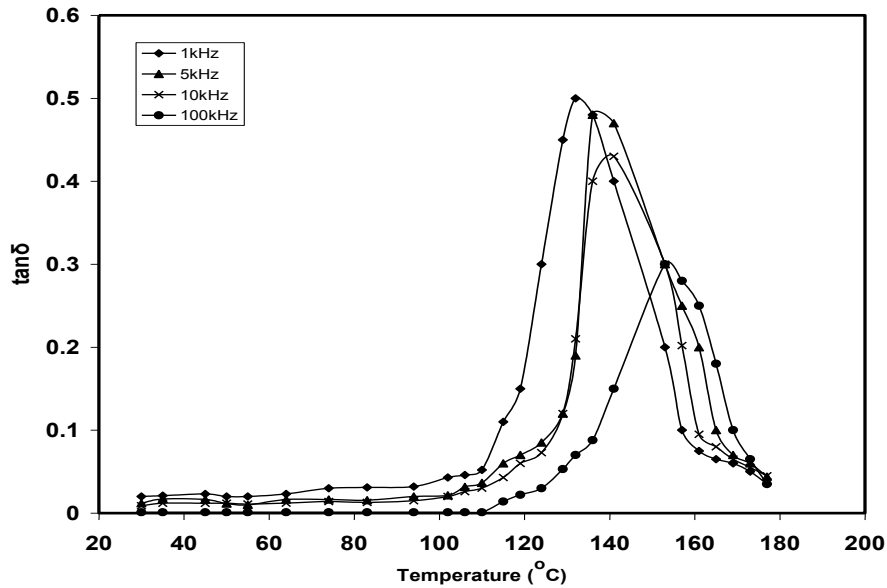


Fig. 3(b) - Variation of $\tan\delta$ with temperature for MH+MAA (20/80)

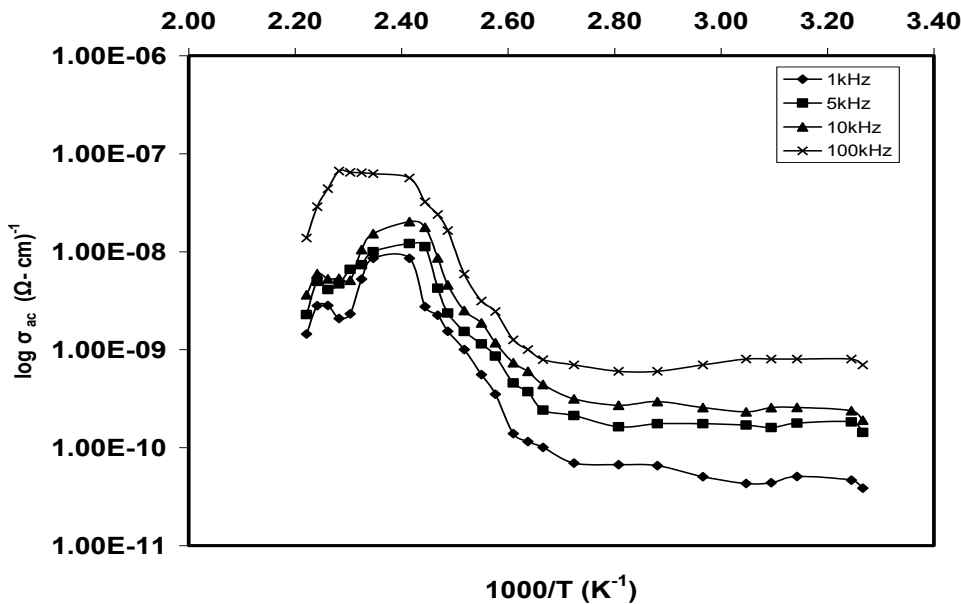


Fig. 3(c) - Variation of ac conductivity with reciprocal temperature for MH+MAA (20/80)

Figures 4(a) and 4(b) show the typical variation of ϵ and $\tan\delta$ respectively with temperature for MH-MAA (50/50) and 4(c) for the variation of ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies. An enhanced behaviour in dielectric property has been noticed for the copolymer of MH-MAA (50/50). A clear and

frequency dependent β -relaxation peaks appeared around 40°C in both ϵ and $\tan\delta$ versus temperature curves which were not seen for MH-MAA(10/90) & MH-MAA(20/80). temperature curves which were not seen for MH-MAA(10/90) & MH-MAA(20/80).

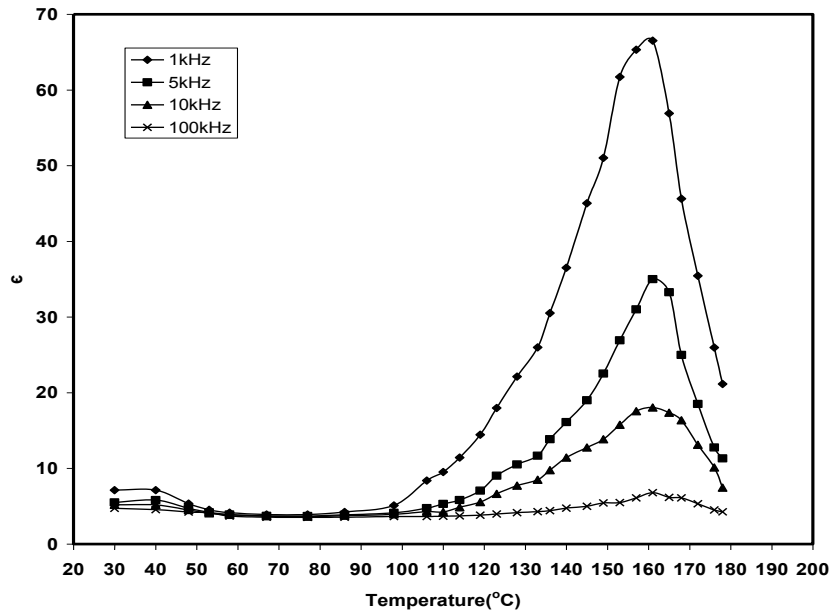


Fig. 4(a) - Variation of ϵ with temperature for MH+MAA (50/50)

The variation in ϵ is found to be both frequency and temperature independent in the temperature range between 60°C and 90°C. Beyond 90°C ϵ increases at a rapid rate and it is frequency dependent, giving rise a peak at 160°C for all frequencies, which is an indication of a phase change from viscoelastic to rubbery state. The α -relaxation peaks

appeared in $\tan\delta$ at 149°C, 153°C, 157°C and 165°C for 1 kHz, 5 kHz, 10 kHz and 100 kHz respectively beyond T_g . The ac conductivity variation is both temperature and frequency dependent in the entire range of measurement. The range of ac conductivity for this copolymer MH-MAA(50/50) is 10^{-10} to 10^{-7} (ohm-cm)⁻¹.

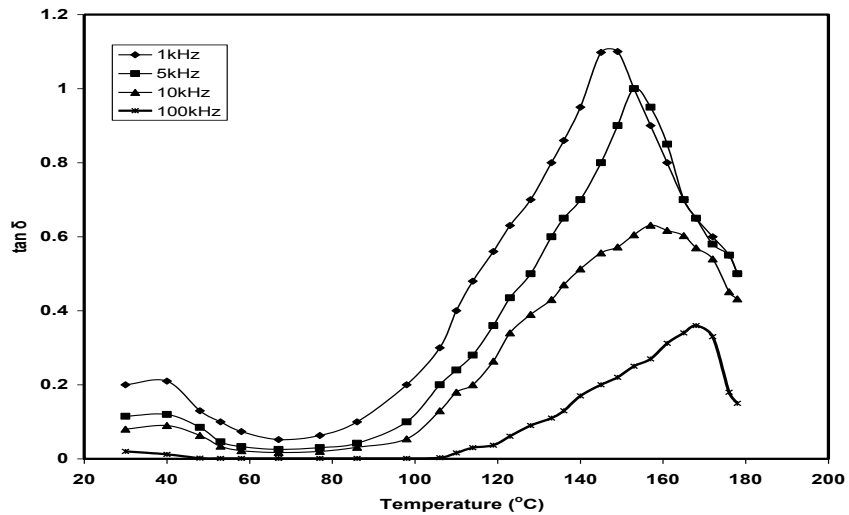


Fig. 4(b) - Variation of $\tan \delta$ with temperature for MH+MAA (50/50)

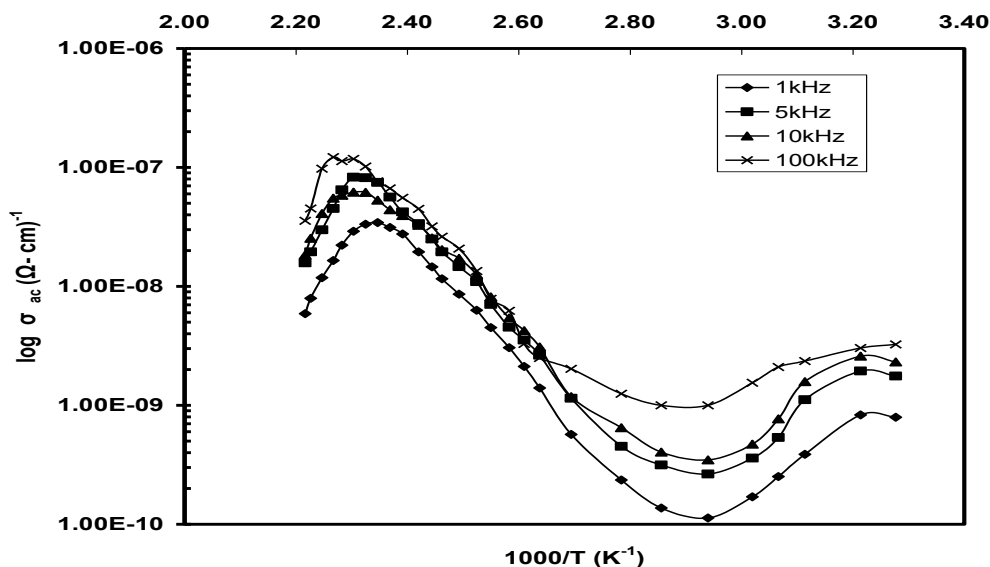


Fig. 4(c) - Variation of ac conductivity with reciprocal temperature for MH+MAA (50/50)

IV CONCLUSION

On careful comparison of the copolymer system for three compositions the following conclusions are drawn in the light of increase in polar nature of the MH content of the copolymer system.

1. A similar dielectric behaviour is noticed for MH-MAA (10/90) and MH-MAA (20/80) while the enhanced one in MH-MAA (50/50). The enhanced variation in ϵ is attributed due to increase of polar nature with increase of MH content in the copolymer MH-MAA (50/50).

2. From the curves of $\tan\delta$ versus temperature the low temperature peak appeared around 40°C in the copolymer system is attributed to micro-Brownian motion of the polymer back bone and referred as β -relaxation. Further a more intense peak has been noticed for MH-MAA (50/50) composition, than that noticed for other two compositions due to relatively more polar nature of MH content. The high temperature relaxation peaks which shift towards higher temperatures for higher frequencies are assigned to be α -relaxation peaks, which usually occur above T_g . With increase of MH content in the copolymer the α -relaxation shifts towards higher temperatures at a given frequency. For instance at 1 kHz it can be seen that the peak positions noticed for MH-MAA 10/90, 20/80 and 50/50 are 129°C, 132°C, 149°C respectively.

3. The ac conductivity follows nearly the similar variations as that of $\tan\delta$ with temperature for different compositions. As seen from the curves of $\log \sigma_{ac}$ versus reciprocal temperature the behaviour of σ_{ac} at low temperature is temperature independent and frequency dependent for MH-MAA (10/90) and (20/80), whereas for 50/50 the behaviour is both temperature and frequency dependent.

Approximately an increase of one order in conductivity is being noticed in case of MH-MAA (50/50) due to its enhanced property in ϵ and $\tan\delta$, with increase of MH content in MH-MAA(50/50)

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