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Dielectric Relaxation Studies of EMA,MMA&BMA with 2-Acrylamido 2- Methyl Propane Sulphonic Acid(AMPS)Copolymers

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ABSTRACT-Dielectric properties of EMA,MMA&BMA with AMPS in composition (50/50) have been studied over frequency range from 100Hz to 100kHz and temperature range from room temperature to 180^{o}C.The Copolymers characterized by DSC. The frequency dependence of the dielectric constant and dielectric loss has been investigated. Dielectric constant decreases with increasing frequency and increases with temperature. AC Conductivity calculated and data were analyzed. The AC Conductivity increases with increasing temperature and frequency. The present report deals with a systematic study of dielectric property of EMA,MMA&BMA with AMPS as a function of both frequency and temperature.

Two sets of relaxation peaks are noticed one slightly above room temperature and other at elevated temperature. The peaks are β- and α-relaxations, attributed to microBrownian motion of segments of the main chain of the copolymer. The results are discussed in the light of segmental motion of main chain of the copolymer. The AC conductivity has also been evaluated from the data. The results are discussed in the light of substituent effect in the copolymer.

KEYWORDS-
Dielectricconstant(ε),Dielectricloss(tanδ),ACconductivity , Relaxation, segmental motion

1. INTRODUCTION

In engineering industry polymers are very useful 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].

Acrylic copolymers with epoxy functional groups as pendant units have become increasingly relevant in a variety of applications, including coatings and biomaterials, as well as starting materials for photo-cross-linkage polymers. After crocross-linking the epoxy pendant groups, glycidyl methacrylate copolymers can be utilized to control fouling on ship hulls and other surfaces in contact with the marine environment. They may also have enhanced electrical and mechanical properties [8]. Dielectric studies were performed on certain homopolymers containing various alkyl methacrylate and their copolymers, either in solid form or in dilute solution, to investigate the dielectric behaviour and relaxation process involved during heating as the applied frequency was increased [9]. As no reports are available on the dielectric properties of AMPS with acrylate copolymers, an attempt is made to investigate the dielectric propertiesof Ethylemethacrylate(EMA) , Methylmethacrylate(MMA)&Butyle methacrylate(BMA) with AMPS, copolymers in 50/50 composition.

2. METHODOLOGY/EXPERIMENTAL

The powder samples of EMA,MMA&BMA with AMPS in compositions 50/50 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^{o}C, covering through the glass transition temperature (Tg).

3. RESULTS AND DISCUSSION

3.1 Dielectric Analysis

The dielectric relaxation study gives the valuable and sufficient information about orientational and translational motion of mobile charge carriers in the dielectric. The dielectric constant (ε’) changes with the frequency dispersion of the applied field and is also dependent on the physical properties of the dielectrics. dielectric constant (ε’) Variation of the dielectric constant(ε’) arose in 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 [10].

The complex dielectric permittivity ε*can be calculated by ε*= ε’-j ε”. Where ε’ is the real (relative permittivity or dielectric constant) and ε” is the imaginary (dielectric loss) parts of the complex dielectric permittivity. The dielectric permittivity analysis provides information on the transport properties of ions in the polymer. The real part of the permittivity measures the alignment of dipoles and the imaginary part represents required to align the dipoles and to move ions [11]. The low frequency dispersion region is due to the accumulation of charges at the electrode-polymer interface. In the low frequency region, conductance losses predominated due to unavoidable electrode polarization. In the high frequency region, both spectra show decreasing magnitude that is saturated at very high frequency in the frequency range studied. This is due to the rapid, periodic reversal of field applied at the electrode-polymer interface which reduces the contribution of carriers to the dielectric permittivity.

The results on the measurements of dielectric constant (ε) for MMA,EMA&BMA with AMPS in compositions (50/50) at room temperature are tabulated in Table 1. for frequencies 200Hz and 100kHz and the variation are shown in fig.1&2. For all the cases the ε decreases with frequency in usual manner (Fig.1). The variation of tanδ at room temperature as a function of frequency (Fig. 2).

Table 1: Dielectric constant (ε) and loss (tanδ) for MMA,EMA& BMA withAMPS (50/50) at room temperature

Copolymer	εat200Hz	tanδat200Hz	ε at100kHz	tanδat100kHz
MMA-AMPS(50/50)	3.60	8.50 x10^{-2}	3.00	4.20x10^{-2}
EMA-AMPS(50/50)	2.60	6.00 x10^{-2}	2.10	1.95 x10^{-1}
BMA-AMPS(50/50)	2.47	5.00x10^{-2}	1.98	1.69 x10^{-1}

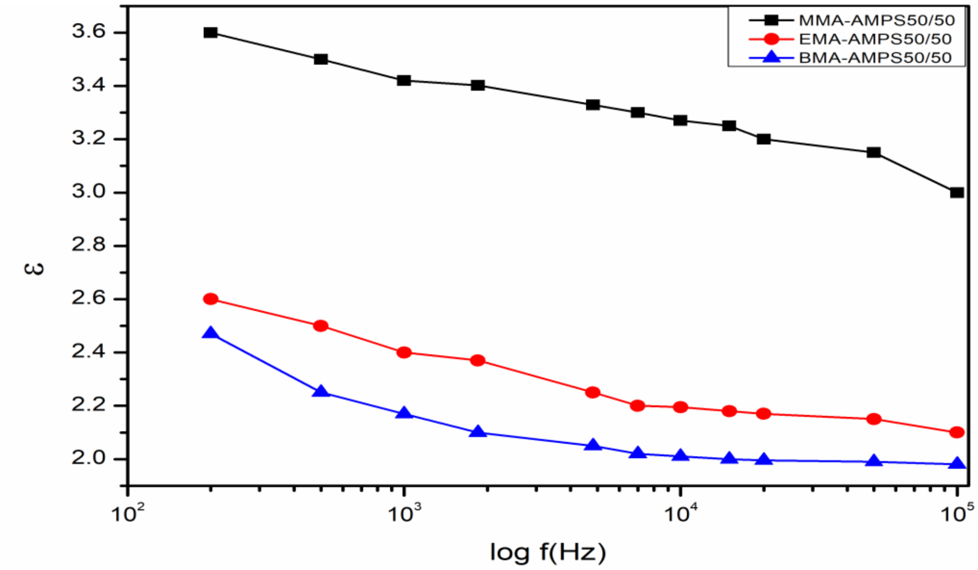

Figure 1: Variation of Ɛ with frequency at room temperature

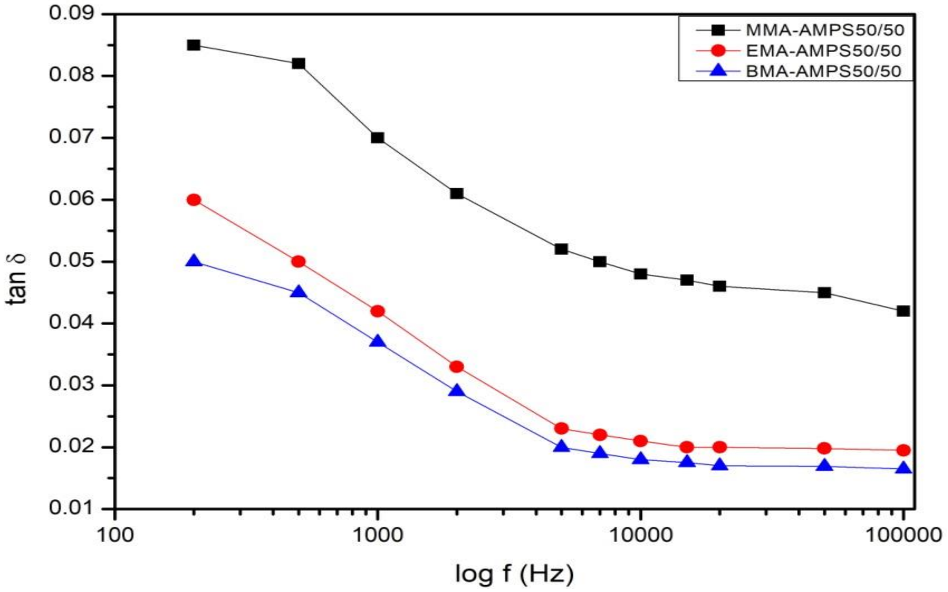

Figure 2: Variation of tanδ with frequency at room temperature

The higher magnitudes of ε for frequencies less than 10 KHz is attributed to the space charge polarization and spurious effects. Above 10 KHz the ε is attributed to the combined effect of other types of polarizations [12]. The appearance of peaks in tanδ at 1 KHz is attributed to interfacial relaxation (Maxwell-Wagner effect) [13]. The variation of ε and tanδ at room temperature as a function of frequency show a constant decreasing trend with increase of non-polar content from MMA-AMPS to BMA-AMPS.

The variation of ε and tanδ with frequency at room temperature for MMA-AMPS (50/50), EMA-AMPS (50/50) and BMA-AMPS (50/50) are shown in Figures 1 & 2. A usual frequency dependent behaviour with a small change in ε and tanδ is observed in all the three cases.

Figures 3& 4 show the typical variation of ε and tanδ respectively with temperature for MMA-AMPS at four different frequencies. From the figures, it can be seen that the variation of ε and tanδ with temperature shows two peaks one slightly above room temperature and another above glass transition temperature. The peaks appeared at the same temperature in the ε versus temperature curves. In the case tanδ versus temperature, a shift in relaxation frequencies is observed only at elevated temperatures. Whereas the shift may be unnoticeable around room temperature. A Similar behaviour is noticed in the case of copolymers of EMA-AMPS (50/50)& BMA-AMPS(50/50).

The low and high-temperature peaks are attributed to β- and α-relaxations respectively. β- Relaxation peaks without shift in peak positions with frequency are due to the micro-Brownian motion of the pendant epoxy and carbonyl groups of the acrylate polymer back bone accompanied by the local distortion of the main chain. α- relaxation peak,i.e., dipolar relaxation, above Tg with shift in peak position are known to occur due to segmental motion of molecular chains[14-16].Further the peaks shift towards higher temperatures for higher frequencies. At each temperature tanδ was found to increase with increasing frequency and attained a maximum value (tanδmax), then decrease with further increase of frequency. At low frequencies, the dipoles are ablein phase change of electric field and hence the power losses are low. As the frequency is increased the dipole reorientation cannot be completed in the time available and the dipole becomes out of phase with the electric field, hence, the power loss is maximum. The internal friction leads to the generation of heat. Further, the increase of frequency results in no time for substantial dipole moment, so the power losses are reduced. It is also observed that the maximum of tanδ decreased with increase of temperature. This is attributed to increase in mobility of the chains at higher temperature, resulting in low power loss.

It is can be seen from the figures that, with increasing temperature, the value of dielectric constant increases. The charge distribution as well as the statistical thermal motion of the polar groups plays a clear role in determining the dielectric behavior of the polymers. The dielectric constant in case of polar polymers starts to decrease at a specific critical frequency and at lower temperatures the dipole molecules cannot orient themselves. The increase of dielectric constant with temperature may be related to the known phenomenon of increasing the polarization with increasing temperature as is observed in many materials [17-21]. Increasing the temperature will improve the polymer segmental mobility, hence, facilitates the orientation of the dipoles and increase the dielectric constant as a result.

It is further seen that, strong temperature dependence starts at a lower temperature for lower frequencies and at a higher temperature for higher frequencies. To understand the nature of temperature dependence, the temperature coefficient of the 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 TCε=1/εm.p..dε/dt. Where dε is the difference between dielectric constants, εm.p is the dielectric constant at the midpoint of Tg and Trt.

Table 2: Variation of temperature coefficient of dielectric constant (TCε) for MMA-AMPS,EMA-AMPS&BMA-AMPS at 1kHz

Sno	Temperature(^{o}C)	MMA-AMPS TCε (^{o}C)$^{-1}$	EMA-AMPS TCε (^{o}C)$^{-1}$	BMA-AMPS TCε (^{o}C)$^{-1}$
1	30-50	0.012	0.011	0.10
2	50-80	0.10	0.090	0.09
3	80-100	0.33	0.022	0.95
4	100-120	0.35	0.055	0.75
5	120-140	0.55	0.058	0.59

The variation of ε as a function of temperature at different frequencies for MMA-AMPS (50/50), EMA-AMPS (50/50) and BMA-AMPS (50/50) is shown in Figures 3,6&9 respectively. It is seen that the variation in ε is both frequency and temperature dependent giving rise two sets of peaks, the first set around 45^{o}C and the second set of peaks at temperatures 120^{o}C, 115^{o}C and 98^{o}C for MMA-AMPS, EMA-AMPS and BMA-AMPS respectively, with a slight decrease in property moving from MMA-AMPS to BMA-AMPS .

The variation of tanδ as a function of temperature at different frequencies for these samples is given in Figures 4,7&10. It is seen that the usual behaviour is observed in the variation of tanδ with temperature at different frequencies giving rise α-relaxations as shown in Table 3. Further the peak temperatures shift towards lower temperatures exhibiting a diminishing dielectric behaviour from MMA-AMPS to BMA-AMPS via EMA-AMPS. As the size of the alkyl group in the side chain is increasing, the relaxation peaks are shifting towards lower temperatures from MMA-AMPS to BMA-AMPS in the series. This behaviour is similar to that of variation of the T_g values listed in Table 3.

The conductivity plots as a function of reciprocal temperature are shown in Figures 5,8&11 respectively. The conductivity variation is observed to be temperature and frequency dependent in all the three cases. While the conductivity variation is 10^{-10} to 10^{-8} (Ω-cm)$^{-1}$ for MMA-AMPS, 10^{-11} to 10^{-9} (Ω-cm)$^{-1}$ for EMA-AMPS, whereas the variation is 10^{-11} to 10^{-9} (Ω-cm)$^{-1}$ for BMA-AMPS[16-21].

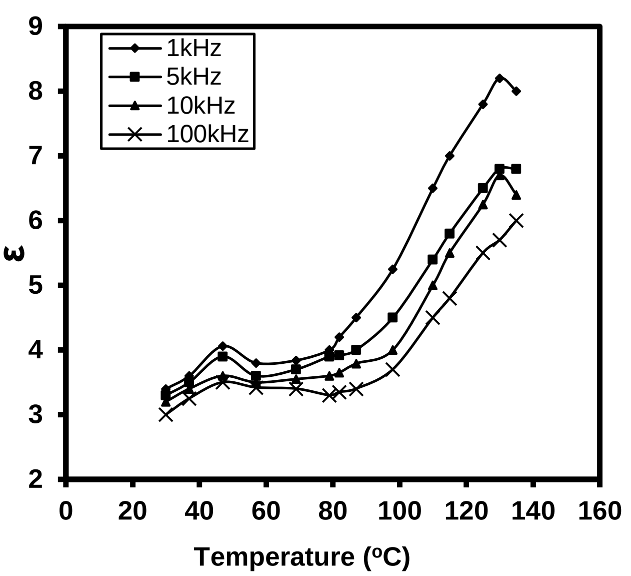

Figure 3: Variation of ε with temperature for MMA-AMPS (50/50)

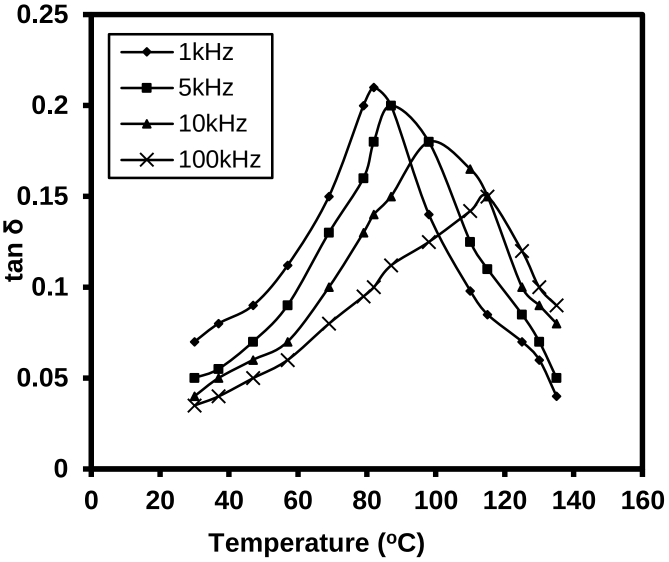

Figure 4: Variation of tan δ with temperature for MMA-AMPS (50/50)

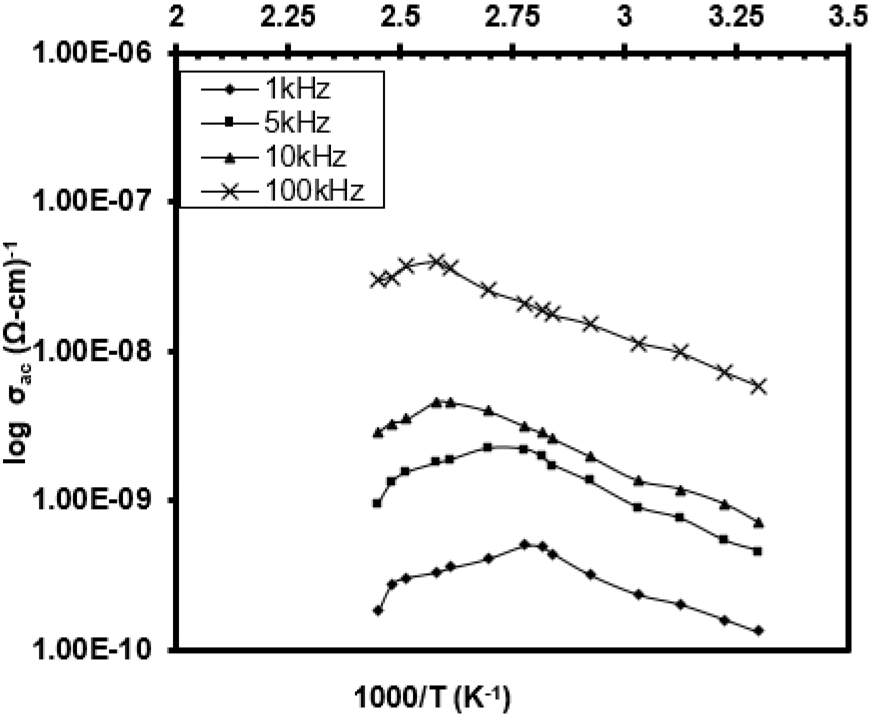

Figure 5: Variation of ac conductivity with reciprocal tempeaturte for MMA-AMPS (50/50)

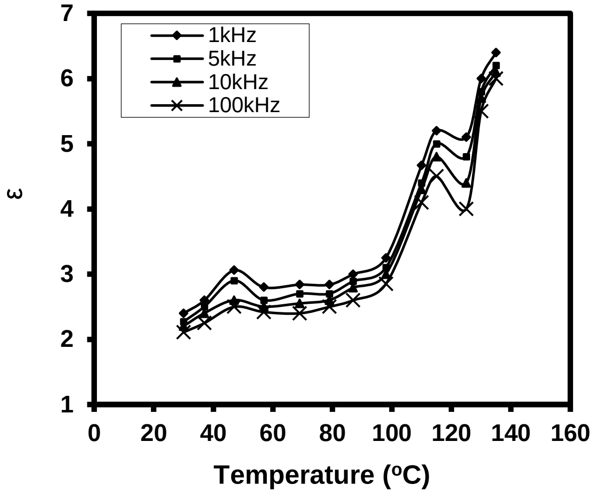

Figure 6: Variation of ε with temperaturefor EMA-AMPS (50/50)

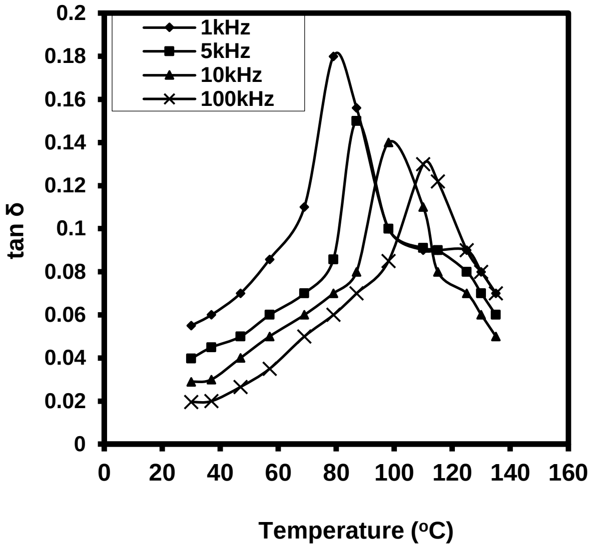

Figure 7: Variation of tan δ with temperature for EMA-AMPS (50/50)

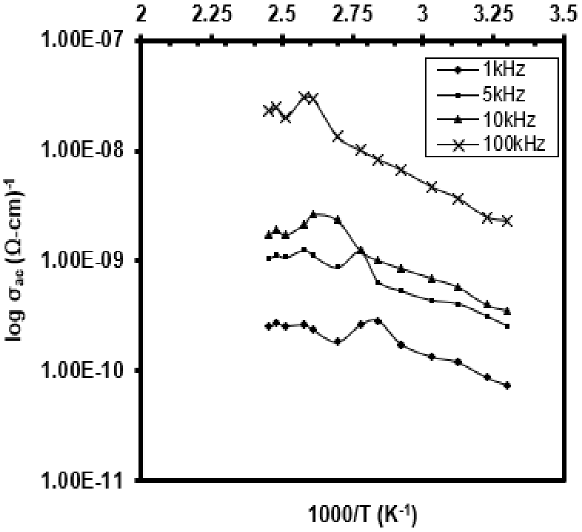

Figure 8: Variation of ac conductivity with reciprocal temperature for EMA-AMPS (50/50)

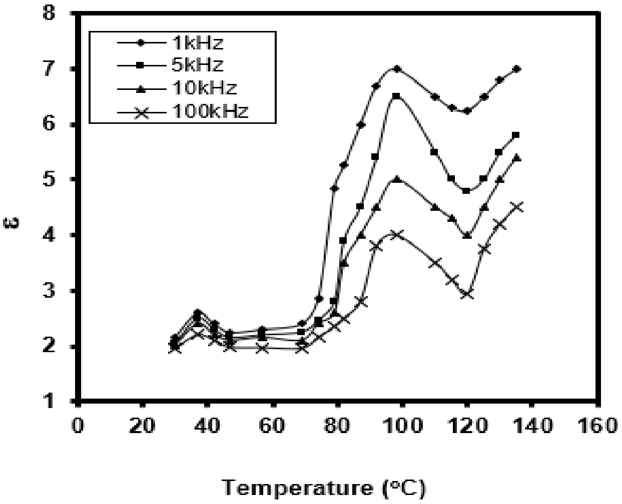

Figure 9: Variation of e with temperaturefor BMA – AMPS(50/50)

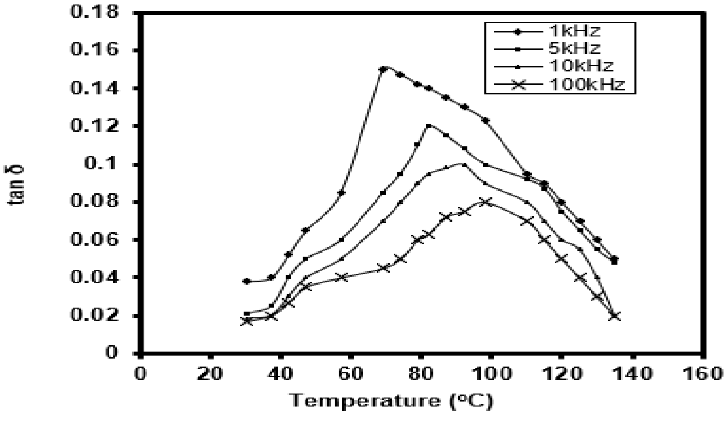

Figure 10: Variation of tan δ with temperature for BMA-AMPS (50/50)

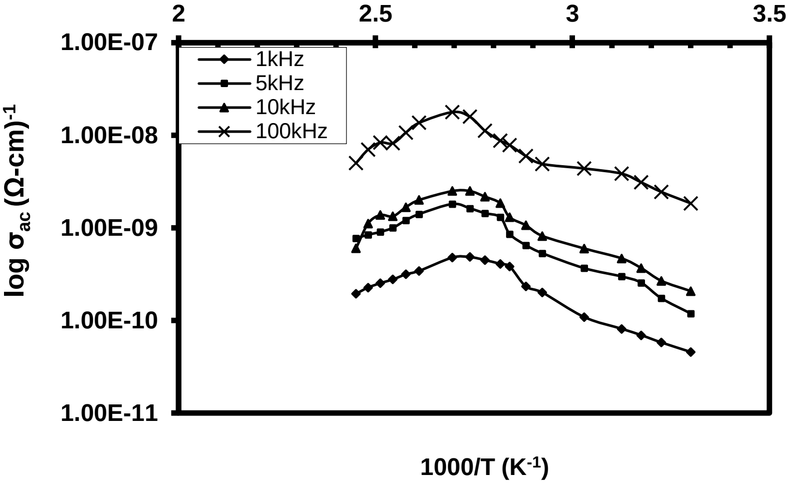

Figure 11: Variation of ac conductivity with reciprocal temperature for BMA-AMPS (50/50)

Table 3: Comparison for different properties of MMA, EMA, and BMA with AMPS (50/50)

Copolymer	T_g (^oC)	ε_{max} (^oC)	T at $\tan\delta_{max}$ for 1kHz	T at $\tan\delta_{max}$ for 5kHz	T at $\tan\delta_{max}$ for 10 kHz	T at $\tan\delta_{max}$ for 100 kHz	ctivation energy (eV)	$\sigma_{ac(\Omega\text{-cm})}^{-1}$
MMA-AMPS(50/50)	80	120	82	87	98	115	0.86	10^{-10} to10^{-8}
EMA-AMPS (50/50)	75	115	79	85	96	100	1.00	10^{-11} to10^{-8}
BMA-AMPS (50/50)	65	98	69	82	92	98	1.40	10^{-11} to10^{-8}

4. CONCLUSION

Dielectric properties of EMA,MMA&BMA with AMPS in composition (50/50) have been studied over frequency range from 100Hz to 100kHz and temperature range from room temperature to 180oC. The frequency dependence of the dielectric constant and dielectric loss has been investigated. Dielectric constant decreases with increasing frequency and increases with temperature. AC Conductivity calculated and data were analyzed. The AC Conductivity increases with increasing temperature and frequency.

Two sets of relaxation peaks are noticed one slightly above room temperature and other at elevated temperature. The peaks are β - and α –relaxations, attributed to micro Brownian motion of segments of the main chain of the copolymer. The results are discussed in the light of segmental motion of main chain of the copolymer. The AC conductivity has also been evaluated from the data. The results are discussed in the light of substituent effect in the copolymer.

It can be seen that in the copolymers of MMA-AMPS (50/50), EMA-AMPS (50/50) and BMA-AMPS (50/50) a diminishing nature in over all dielectric property is noticed. Though steric hindrance increases the Tg value in all the three copolymers under study, the increase in size of the alkyl group causes the decrease in Tg values. As the size of alkyl group in the side chain increases, they force the main chain apart increasing the free volume and reducing Tg. The dielectric relaxation peak temperatures also followed the same trend in the present study which is in consonance with the Tg values of the copolymers. In addition to the usual behaviour the appearance of first set of peaks around 45ºC in ε for all frequencies is attributed to the slow motion of individual side chain molecular groups of the respective copolymer system. i.e. the low and high-temperature peaks are attributed to β- and α- relaxations respectively. β-Relaxation peaks without a shift in peak positions with frequency are due to micro-Brownian motion of the pendant epoxy and carbonyl groups of the acrylate polymer backbone accompanied by the local distortion of the main chain. α-relaxation peak,i.e., dipolar relaxation, above Tg with a shift in peak position are known to occur due to segmental motion of molecular chains.

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