

DIELECTRIC BEHAVIOUR OF 2-ACRYLAMIDO 2-METHYL PROPANE SULPHONIC ACID (AMPS) WITH AMIDE COPOLYMERS

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Abstract:-A systematic measurement of dielectric constant (ϵ) and loss ($\tan\delta$) on powder pressed pellets of AMPS with AA, MAA and MBA copolymers in composition 50/50 have been carried out in the frequency range 200Hz – 100 kHz and in the temperature range from room temperature to 180°C covering through the glass transition temperature (T_g). Relaxation peaks were observed (above T_g) from $\tan\delta$ 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.

Key words: Dielectric constant (ϵ), Dielectric loss ($\tan\delta$), AC conductivity.

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]. As no reports are available on dielectric properties of AMPS with acrylamide copolymers, an attempt is made to investigate the dielectric properties of AMPS+AA, AMPS+MAA, AMPS+MBA copolymers in 50/50 composition.

II.EXPERIMENTAL

The powder samples of AMPS with AA, MAA and MBA copolymers of 50/50 composition 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 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

The results on the measurement of dielectric constant (ϵ) and loss ($\tan\delta$) for AMPS with AA, MAA and MBA copolymers of 50/50 compositions at room temperature are given in table-1 for frequencies 200Hz and 100kHz and the variation are shown in fig.1.

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Table-1

Copolymer	ϵ at 200Hz	$\tan\delta$ at 200Hz	ϵ at 100kHz	$\tan\delta$ at 100kHz
AMPS+AA (50/50)	10.00	1.80×10^{-1}	40.00	3.00×10^{-1}
AMPS+MAA (50/50)	6.75	1.70×10^{-1}	11.50	2.60×10^{-1}
AMPS+MBA (50/50)	4.00	2.00×10^{-1}	10.00	1.20×10^{-1}

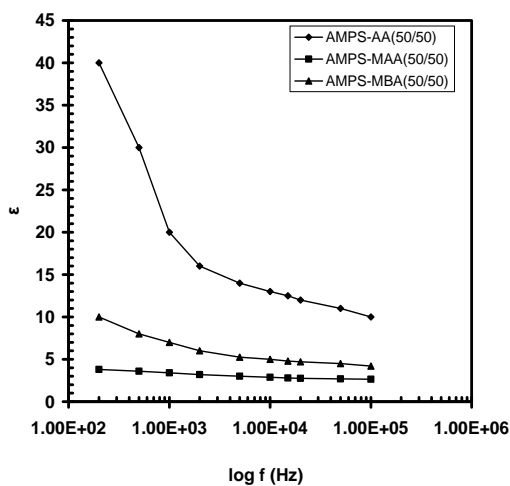


Fig1(a) Variation of ϵ with $\log f$ at room temperature

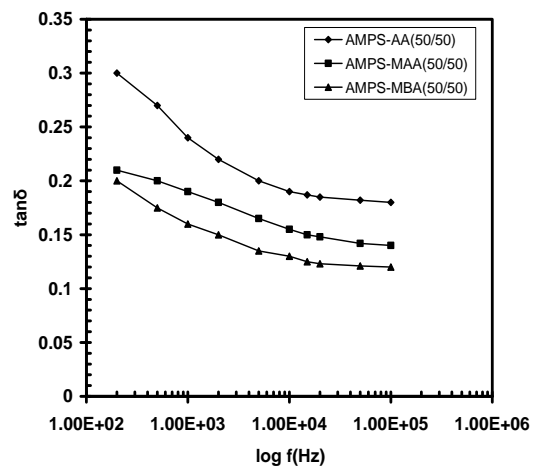


Fig1(b) Variation of $\tan\delta$ with $\log f$ at room temperature

It can be seen that both the values of ϵ and $\tan\delta$ decrease, with increase of frequency and the rate of decrease is smaller for high frequencies. Further, an enhanced variation is being observed for AMPS+AA copolymer.

It is believed that 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. On comparison among the three copolymers it is seen that an enhanced dielectric property is being established in AMPS+AA copolymer at room temperature. This may be due to more polar nature of AA than that of MAA and MBA in copolymer systems.

Figures 2(a) and 2(b) show the variation of ϵ and $\tan\delta$ respectively with temperature for AMPS+AA (50/50) and fig.2(c) for ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies. From room temperature to 40°C, ϵ is frequency and temperature dependent and increases at a slower rate. Beyond 45°C and up to 60°C ϵ decreases giving rise a peak at 45°C for all frequencies, and from 60°C to 80°C ϵ increases at a rapid rate and then decreases with increase of temperature giving rise a peak at 80°C for all frequencies. Further increase of temperature there is an increase in ϵ i.e. beyond 100°C.

The peak appeared around 45°C in ϵ for all frequencies is attributed to the slow motion of individual side chain molecular groups like NH_2 and CH_3 . The rapid increase of ϵ with temperature is attributed to

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enhanced flexibility of the polymer chain and thus the mobility of molecular chain. Beyond 80°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 phase[13].

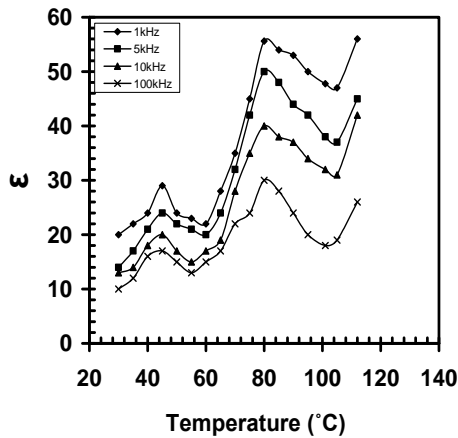


Fig.2(a). Variation of ϵ with temperature for AA-AMPS(50/50)

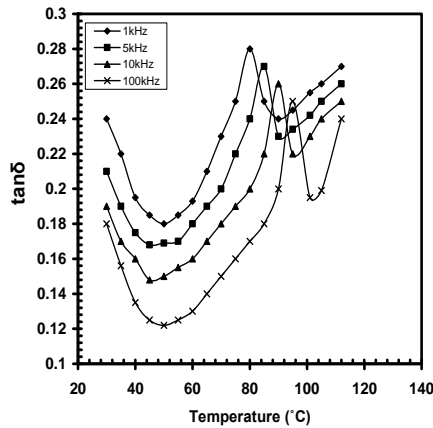


Fig. 2(b). Variation of $\tan\delta$ with temperature for AA-AMPS(50/50)

The variation of $\tan\delta$ with temperature shows a gradual decrease due to annealing effect, giving rise a dip at 50°C with increase of temperature. Beyond this temperature the increase of $\tan\delta$ is continued up to 90°C. Further increase of temperature resulted in a rapid enhancement of $\tan\delta$ giving rise relaxation peaks at 70°C, 75°C, 80°C and 90°C for 1 kHz, 5 kHz, 10 kHz and 100 kHz 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 $\tan\delta$.

The ac conductivity (σ_{ac}) has been evaluated from the data on ϵ and $\tan\delta$ as a function of temperature and plotted as $\log \sigma_{ac}$ versus reciprocal temperature (Fig 2c). A frequency and temperature dependent variation in σ_{ac} is seen up to 40°C. The trend of variation is same as that seen for ϵ and $\tan\delta$. Beyond 45°C and up to 80°C, a linear rise of conductivity is observed, because the copolymer gets softened and relatively more number of charge carriers available for conduction. Then the conductivity is found to decrease rapidly beyond 80°C entering into a disordered phase of the polymer. The overall change in conductivity is observed to be in the range between 10^{-9} to 10^{-6} (ohm-cm)⁻¹.

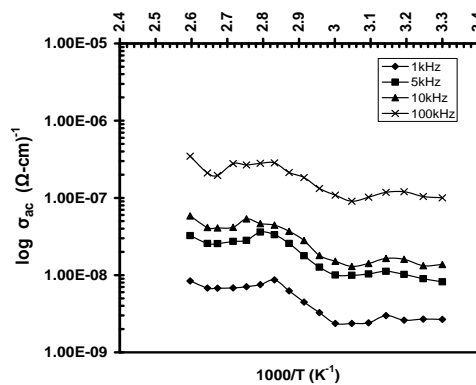


Fig. 2(c). Variation of ac conductivity with reciprocal temperature for AA-AMPS(50/50)

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Figures 3(a) and 3(b) show the typical variation of ϵ and $\tan\delta$ respectively with temperature for AMPS+MAA (50/50) and fig.3(c) for ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies. Unlike the behaviour observed in case of AMPS+AA, only one set of peaks were seen in the variation of ϵ at 80°C and without any dip in the variation of $\tan\delta$. The relaxation peaks in $\tan\delta$ have been noticed at 72°C, 75°C, 80°C and 90°C for 1 kHz, 5 kHz, 10 kHz and 100 kHz respectively beyond T_g . The ac conductivity variation is in the range of 10^{-10} to 10^{-7} (ohm-cm)⁻¹.

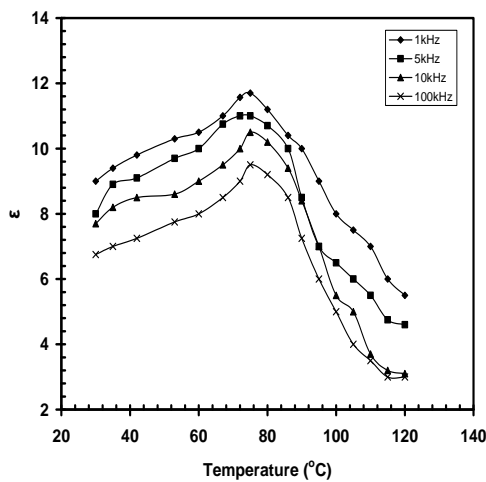


Fig. 3(a). Variation of ϵ with temperature for MAA-AMPS(50/50)

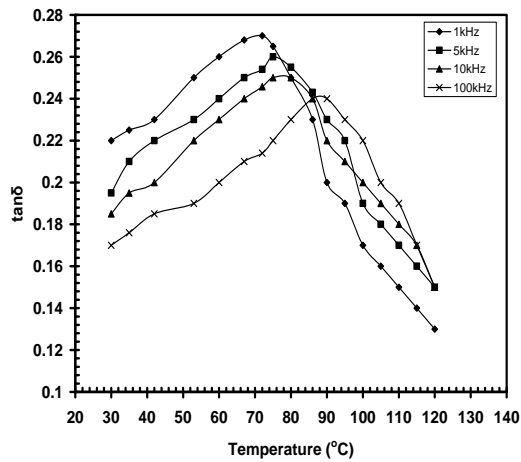


Fig. 3(b). Variation of $\tan\delta$ with temperature for MAA-AMPS(50/50)

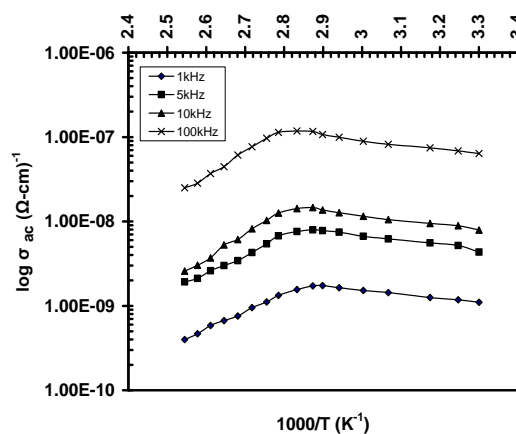


Fig. 3(c). Variation of ac conductivity with reciprocal temperature for MAA-AMPS(50/50)

Figures 4(a) and 4(b) show the typical variation of ϵ and $\tan\delta$ respectively with temperature for AMPS+MBA (50/50) and fig.4(c) for ac conductivity ($\log \sigma_{ac}$) with reciprocal temperature for four selected frequencies. A peak is observed at elevated temperatures i.e., at 70°C for all frequencies. It can be seen that $\tan\delta$ decreases from room temperature to 50°C giving rise a dip around 50°C as observed for AMPS+AA (50/50); then $\tan\delta$ started increasing giving rise α – relaxation peaks at 65°C, 70°C, 75°C and 80°C for 1 kHz, 5 kHz, 10

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kHz and 100 kHz respectively. The ac conductivity variation for AMPS-MBA is in the range of 10^{-10} to 10^{-7} (ohm-cm^{-1}), one order lower than that for AMPS+AA

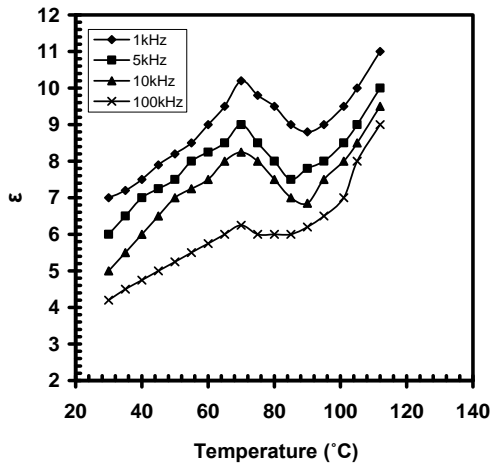


Fig. 4(a). Variation of ϵ with temperature for MBA-AMPS(50/50)

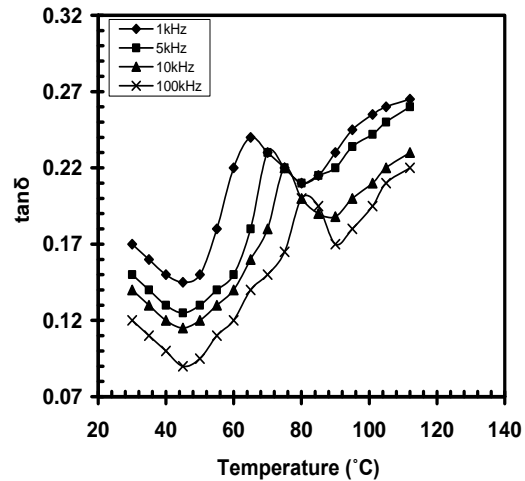


Fig. 4(b). Variation of $\tan\delta$ with temperature for MBA-AMPS(50/50)

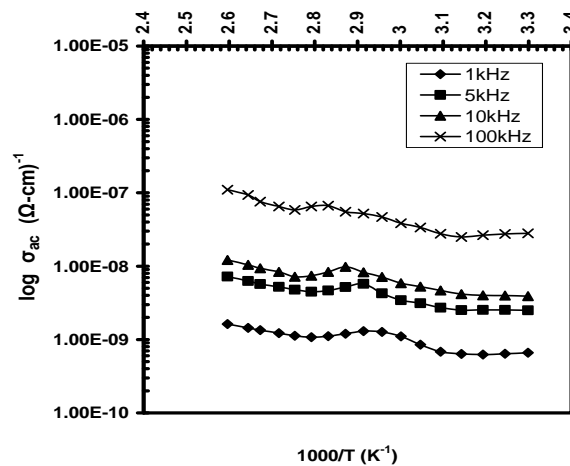


Fig. 4(c). Variation of ac conductivity with reciprocal temperature for MBA-AMPS(50/50)

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Table - 2. Comparison of the property in copolymers of AA,MAA & MBA with AMPS(50/50)

Copolymer	T _g (°C)	ε _{max} (°C)	T at tanδ _{max} for 1 kHz	T at tanδ _{max} for 5 kHz	T at tanδ _{max} for 10 kHz	T at tanδ _{max} for 100 kHz	activation energy (eV)	σ _{ac} (Ω-cm) ⁻¹
AMPS+AA (50/50)	75	80	80	85	90	95	0.86	10 ⁻⁹ to 10 ⁻⁷
AMPS+MAA (50/50)	70	75	72	75	80	90	1.00	10 ⁻¹⁰ to 10 ⁻⁸
AMPS+MBA (50/50)	60	65	65	70	75	80	1.40	10 ⁻¹⁰ to 10 ⁻⁸

IV. CONCLUSIONS

Among the copolymers AMPS+AA, AMPS+MAA and AMPS+MBA each of (50/50) composition AMPS+AA (50/50) established an enhanced dielectric property around room temperature and also around T_g, the glass transition temperature of the respective copolymer. Presence of α-methyl group in MAA of AMPS+MAA and two acrylamide groups on either side of methylene in AMPS+MBA increases the bulkiness in the side chain of the copolymer system. It is known that, the bulky groups always increase the chain mobility and act in a direction to reduce the T_g values and also α-relaxations temperatures. Accordingly it can be seen that the α- relaxation peaks observed typically for 1 kHz occurred for AMPS+AA, AMPS+MAA and AMPS+MBA at 80°C, 72°C and 65°C respectively. It can be also seen from the Table 2 that T_g values for respective systems are 75°C, 70°C and 60°C, which provides a supportive reasoning for dielectric behaviour described above.

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