Dielectric relaxation behaviour and ac conductivity of acrylonitrile and Vinyl propionate (an-vp) copolymers

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Abstract- Acrylonitrile based copolymers have a variety of industrial applications and attracted the attention of material researchers with increasing interest in recent years to study their electrical properties with respect to their homopolymers. The dielectric relaxation studies as a function of temperature and frequency of the applied field reveals the information about the nature of segmental motion in polymer chain.

A systematic measurement of dielectric constant (ε) and dielectric loss (tanδ) on powder pressed pellets of AN-VP copolymer in composition 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 on slight above room temperature and the other slightly above T_g are noticed from tanδ versus temperature curves for different frequencies. The peaks are attributed to β- and α- relaxations. Temperature coefficient of dielectric constant (TCε) is evaluated to understand the nature of the temperature dependence, AC conductivity is evaluated to understand the conduction process. Activation energy is calculated from loss (tanδ) versus temperature curves and $\log\omega_p$ versus reciprocal temperature curves. Activation energy is also calculated from Arrehenius plots.

Index Terms- dielectric constant, dielectric loss, ac conductivity, activation energy.

I. INTRODUCTION

Acrylonitrile based copolymers have become the materials of considerable interest in recent years owing to their technological importance. The study of the dielectric properties of these polymers helps in understanding the intra and intermolecular interaction in macromolecules[1-3]. Hill, N.E[4].and Elif Vargun, et al.[5], reported the preparation and characterization of Acrylonitrile- Ethyl Methacrylate copolymers, Sridevi, et al [6]. reported cyclohexane corbonitrile initiated copolymerization of AN with EMA and dielectric properties at 20kHz and Rajani kumar,et al.[7], reported reactivity ratio, thermal and dielectric properties cyclohexane corbonitrile initiated AN with Vinyl Propionate. No detailed dielectric properties have been reported on these materials. With this in view, the authors felt that it would be of the greater interest to study the dielectric properties of acrylonitrile and Vinyl propionate copolymers' both as a function of temperature and frequency. We discuss the dielectric relaxation behaviour in the light of experimental results.

II. EXPERIMENTAL

The copolymer sample of AN-VP in the powder form was used to prepare the pellets of the dimensions viz., 1-2 mm thickness and 1cm diameter. The dielectric constant and loss (tanδ) were measured on these pellets using GR-1620A Capacitance measuring assembly in conjunction with a laboratory build three terminal cell. The measurements were carried out in the frequency range 100Hz to 100 kHz and temperature range from room temperature to 180°C. The glass transition temperature T_g was determined by Differential Scanning Calorimetry (DSC) technique. (Mettler Toledo SR System). The overall accuracy in the measurement of dielectric constant and loss was 1% and 2% respectively.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the variation of dielectric constant (ε) and loss (tanδ) at room temperature as a function of frequency for AN-VP 50/50 composition. The dielectric constant varies from 4.5 at 200Hz to 3.6 at 100 kHz and ε decreases at a rapid rate up to 10 kHz and decreases at a slower rate beyond 10 kHz. The influence of space charge polarization is more at lower frequencies resulting in higher value of ε, where as this effect is negligible for the frequencies beyond 10 kHz[8]. Similarly the tanδ value decreases from 0.12 at 200Hz to 0.04 at 100 kHz.

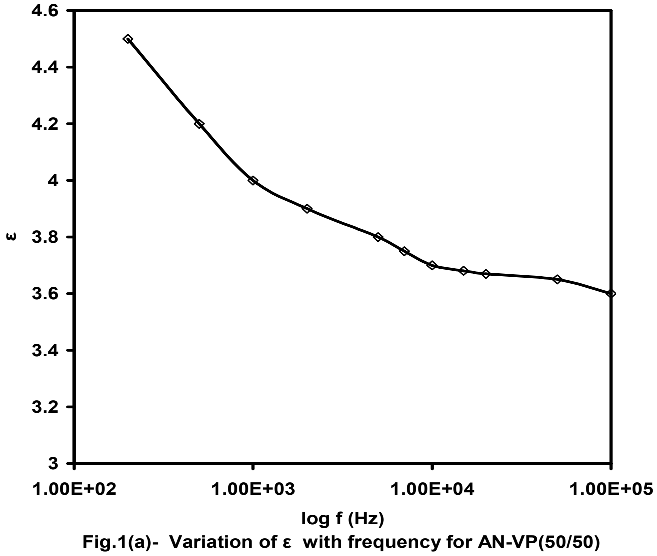

Fig.1(a)- Variation of ε with frequency for AN-VP(50/50) at room tempereture

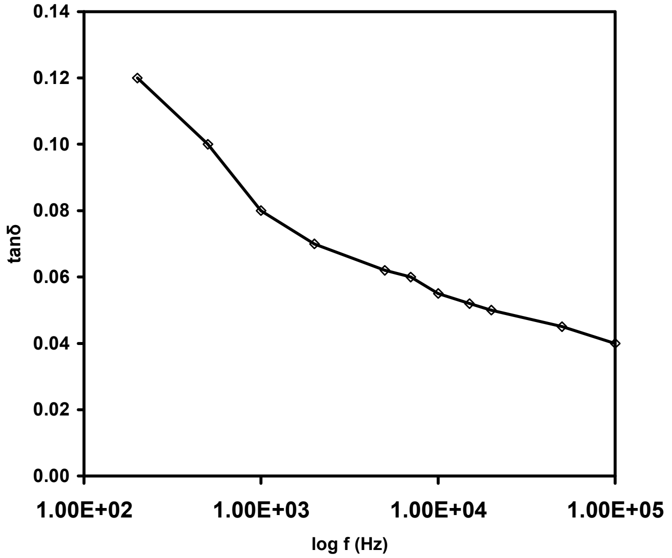

Fig.1b.Variation of tanδ with frequency for AN - VP (50/50) at room temperature

Figure 2 shows the variation of ε with temperature for different frequencies. At room temperature the value of ε is both frequency dependent and temperature independent up to 90^{o}C, beyond 90^{o}C the increase of ε is at a rapid rate for lower frequencies and slower rate for higher frequencies, reaching maximum and giving rise a peak at 145^o C for all frequencies.

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 temperature (Table 1) for 1 kHz. The temperature coefficient of dielectric constant (TCε) has been determined from room temperature T_{rt}, up to glass transition temperature T_g ,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 T_g and T_{rt}[9,10].

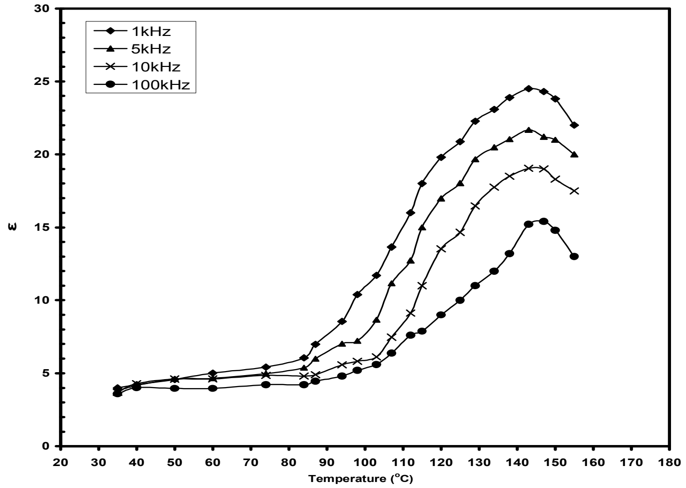

Fig. 2- Variation of ε with temperature for AN - VP(50/50)

Table 1: Variation of temperature coefficient of Dielectric constant (TCε) for AN-VP at 1 kHz

temperature (^{o}C)	TCε (^{o}C)$^{-1}$
35-84	0.0092
84-112	0.0417
112-143	0.0123
143-155	-0.00875

The dielectric constant (ε) is unaffected by temperature from room temperature to 90^{o}C, At lower temperature molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interaction.[11,] Beyond 90^{o}C the increase of ε is at a rapid rate is attributed to, more and more dipole groups are released and the mobility polymer segments increases, as the order of the orientation of dipoles increases with increase in temperature. The T_g determined from DSC is 115^{o}C. Various polarizations contribution to total polarization is also effective up to few degrees above T_g resulting in a maximum value of ε for all frequencies. Further increase of temperature causes chaotic thermal oscillations of the molecule and the diminishing degree of order of orientation of dipoles, confirming the disordered phase of the polymer chain above T_g i.e. in the rubber like state[10, 12].

The Figure 3 shows the variation of tanδ with temperature for different frequencies. The tanδ is both frequency and temperature dependent and decreases giving rise a peak at 50^{o}C for all frequencies. Beyond 60^{o}C and up to 85^{o}C tanδ is temperature independent and frequency dependent.

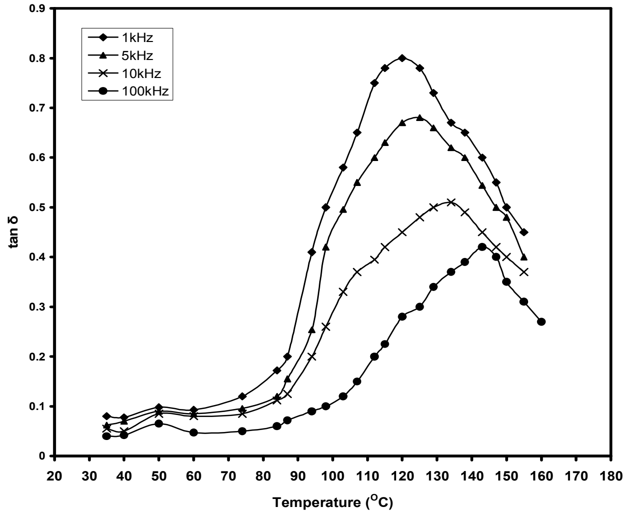

Fig. 3-Variation of tanδ with temperature for AN-VP(50/50)

Beyond 90^{o}C the increase of tanδ is at a rapid rate up to 117^{o}C. The relaxation peaks were found at 120^{o}C, 125^{o}C, 134^{o}C and 143^{o}C for 1 kHz, 5 kHz, 10 kHz and 100 kHz respectively.

It is evident that the variation in tanδ was found to be higher for low frequencies and smaller for higher frequencies. Further the peaks shifted towards higher temperatures for higher frequencies, giving rise relaxation behaviour in the material. The peaks that appeared around 50°C to be β- relaxation peak and attributed to the micro-Brownian motion of the individual molecular groups[13]. It is to be noted that there is no shift in peak position with frequency. The peaks that appeared at high temperatures are believed to be α- relaxation peaks, are due to flexible motion of main chain segment[13, 14, 15].

The activation energies for relaxation are calculated and given in Table 4.2. It is seen from the table that the activation energies for the relaxation process in the low frequency region i.e., up to 10 kHz shows a decrease and then in the high frequency region i.e., beyond 20 kHz there is an increase. The activation energy was obtained from (Method I) the slope of log ω_p versus 1/T plot (Fig 4) is 1.55 eV. Further the relaxation time (τ) for the process is found to be larger for low frequencies and smaller for high frequencies. The average of activation energy evaluated from $\tan\delta_{max}$versus temperature (Method II) is 1.54 eV, which is found to be in good agreement with the value obtained from first method.

The plots of AC conductivity against reciprocal temperature for frequencies 1 kHz, 5 kHz, 10 kHz, and 100 kHz are shown in Figure 5. The plots show two regions. In the first region up to a temperature of 50°C, σ_{ac} increase at slower rate and in the second region i.e. 50°C-60°C, a decrease in conductivity with increase of temperature is observed for all frequencies. In the temperature range between 90°C and 145°C, σ_{ac} increases linearly with temperature and frequency independent. Above 145°C and up to 170°C the conductivity decreases at all frequencies due to similar variations in ε and tanδ. Further the conductivity values are larger for higher frequencies. The σ_{ac} values range from 10^{-10} to 10^{-7} (Ω-cm)$^{-1}$.

Table 4.2: Values of activation energy and relaxation time for AN-VP (50/50) for 1 kHz

S.No	frequency (kHz)	Peak temperature(K)	$\tan\delta_{max}$	activation energy (eV)	relaxation time (τ) sec.
1	f_1 =1	393	0.8	1.88	1.272 X 10^{-4}
	f_2=5	398	0.68		….
2	f_2=5	398	0.68	0.50	2.163 X10^{-5}
	f_3=10	407	0.51		….
3	f_3=10	407	0.51	1.51	8.113 X10^{-6}
	f_4=100	416	0.42		6.681 X10^{-7}

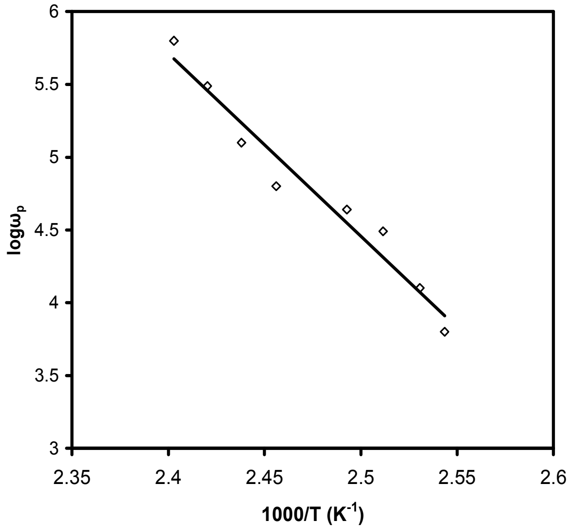

Fig.4- plot of log ωp verses reciprocal temperature for AN-VP(50/50)

A slow increase of ac conductivity from room temperature up to 50°C is attributed to low concentration of impurities and their mobility. A similar behavior that observed in tanδ variation reflected in conductivity between 50°C and 60°C due to the

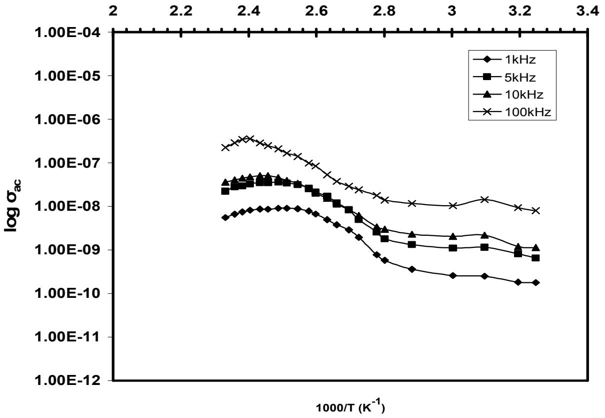

Fig. 5- Variation of ac conductivity with reciprocal temperature for AN-VP(50/50)

presence of pendant groups of the polymer chain. The linear increase in conductivity above 90°C and upto145°C is due to high concentration of thermally generated charge carriers in the polymer chain. These carriers can move more easily into the volume of the sample resulting in large currents and hence an increase in conductivity. Thus at higher temperatures the increase in conductivity is mainly attributed to the increase in mobility of ions in the polymeric material[16]. Beyond 140°C the decrease in conductivity is attributed to disordered motion of the charge carriers. The activation energy for the conduction process for the linear portion of the graph in the temperature range 90°C – 140°C is estimated from the slope. The activation energy thus obtained is 1.61 eV.

IV. CONCLUSION

The dielectric property of the AN-VP has been studied and ac conductivity is also evaluated and studied the conduction process and molecular motions and relaxations in the polymer material. Nature of temperature dependence of ε has been studied. Relaxation time is found to be larger for low frequencies and smaller for high frequencies.

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