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DIELECTRIC RELAXATION BEHAVIOUR OF ACRYLONITRILE AND ETHYL METHACRYLATE (AN+EMA) 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 reveal the information about the nature of segmental motion in polymer chain. Radiation induced copolymerization of acrylonitrile with ethyl methacrylate (0.5 : 0.5 composition) was carried out in the aqueous medium at room temperature. The copolymer was characterized employing IR, ^{1}H NMR and thermal studies (DSC). A systematic measurement of dielectric constant (ε) and dielectric loss (tan δ) were made as a function of frequency in the range 100 Hz -100 KHz and as a function of temperature in the range from room temperature to 180^{o}C. Two types of relaxation peaks were observed above the glass transition temperature (T_g) and below the glass transition temperature of the copolymer. The peaks correspond to β and α relaxation respectively.

Key words: Dielectric constant, Dielectric loss, AC conductivity.

INTRODUCTION

Introduction of Ethyl methacrylate (EMA) into various copolymers appears to modify and improve the properties of a number of copolymers[1-4]. 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[5-7]. Hill and Vaughan[8], and Vargun et al.[9] reported the preparation and characterization of acrylonitrile-ethyl methacrylate copolymers. Sridevi et al.[10] reported cyclohexane corbonitrile initiated copolymerization of AN with EMA and dielectric properties at 20 KHz. Rajani et al.[11] reported reactivity ratio, thermal and dielectric properties cyclohexane corbonitrile initiated

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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 great interest to study the dielectric properties of acrylonitrile and ethyl methacrylate (EMA) copolymers' both as a function of temperature and frequency. We have discussed here the dielectric relaxation behaviour in the light of experimental results.

EXPERIMENTAL

The copolymer sample of AN-EMA in the powder form was used to prepare the pellets of the dimensions viz., 1-2 mm thickness and 1 cm diameter. The dielectric constant and loss (tan δ) 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 100 Hz 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). γ-ray induced copolymerization of acrylonitrile (AN) with ethyl methacrylate (EMA) of 50/50 composition was carried out in aqueous medium at room temperature. The overall accuracy in the measurement of dielectric constant and loss was 1% and 2% respectively.

RESULTS AND DISCUSSION

Figure 1 and 2 show the variation of dielectric constant (ε) and loss (tan δ) at room temperature as a function of frequency for AN + EMA 50/50 composition. The value of ε decreases from 3.5 at 200 Hz to 2.65 at 100 KHz. Similarly the tan δ value decreases from 0.10 at 200 Hz to 0.02 at 100 KHz.

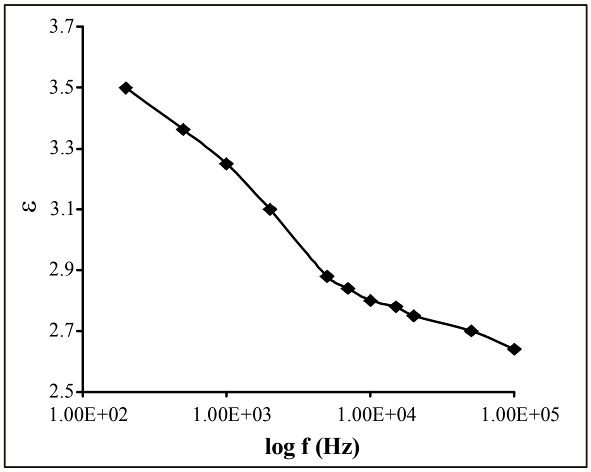

Fig. 1: Variation of ε with frequency for AN-EMA (50/50) at room temperature

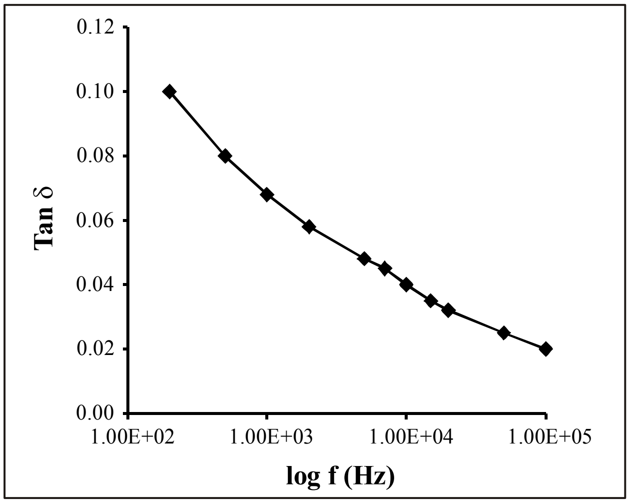

Fig. 2: Variation of tan δ with frequency for AN-EMA (50/50) at room temperature

Figure 3 shows the variation of ε with temperature for different frequencies viz; 1 KHz, 5 KHz, 10 KHz and 100 KHz. At room temperature, the value of ε is both frequency and temperature independent and decreases giving rise a peak at 40°C for all frequencies and between 50°C to 90°C the increase is at a slower rate and frequency dependent.

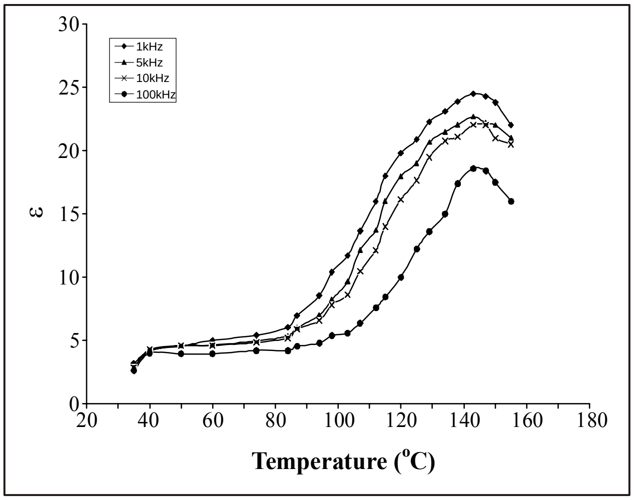

Fig. 3: Variation of ε with temperature for AN - EMA (50/50).

Beyond 90°C the value of ε increases at a rapid rate for lower frequencies and slower rate for higher frequencies reaching maximum and giving rise a peak at 140°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}[12,15].

Table 1: Variation of temperature coefficient of dielectric constant (TCε) for AN+EMA at 1 KHz

Temperature (^oC)	TCε (^oC)$^{-1}$
35-50	0.0055
50-85	0.0115
85-120	0.0343
120-143	0.00917
143-155	-0.00917

The peak appeared at lower temperature is due to individual molecular groups of the molecule. The slow increase of ε between 50^{o}C to 90^{o}C is attributed to increase in flexibility of the polymer chain and thus mobility which will in turn increases the order of orientation of dipoles with increase of temperature. This effect is more pronounced as the temperature is increased beyond 90^{o}C, as the glass transition (T_g) is approaching. The T_g determined from DSC is 113^{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[13,14].

The Figure 4 shows the variation of tan δ with temperature for different frequencies. The tan δ is both frequency and temperature dependent and decreases giving rise a peak at 50^{o}C for all frequencies. Beyond 60^{o}C and upto 85^{o}C' tan δ is temperature independent and frequency dependent. Beyond 90^{o}C the increase of tan δ is at a rapid rate upto 117^{o}C. The relaxation peaks were found at 117^{o}C, 118^{o}C, 130^{o}C and 140^{o}C for 1 KHz, 5 KHz, 10 KHz and 100 KHz respectively.

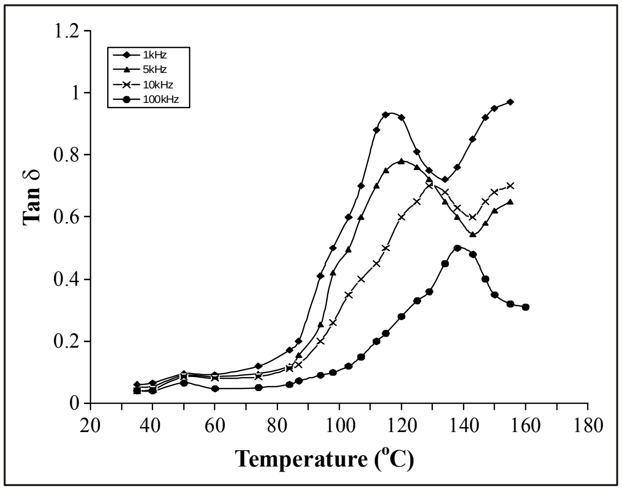

Fig. 4: Variation of tan δ with temperature for AN-EMA (50/50)

It is evident that the variation in tan δ 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 appeared around 50°C to be β- relaxation peak and attributed to the micro-Brownian motion of the ester group of the AN+EMA[14]. 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[15-17].

The plots of AC conductivity against reciprocal temperature for frequencies 1 KHz, 5 KHz, 10 KHz, and 100 KHz are shown in Fig. 5. The plots show two regions. In the first region upto a temperature of 50°C, σ_{ac} increases 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 140°C, σ_{ac} increases linearly with temperature and frequency independent. Above 140°C and upto 170°C’ the conductivity decreases at all frequencies due to similar variations in ε and tan δ. Further the conductivity values are larger for higher frequencies. The σ_{ac} values range from 10^{-10} to 10^{-6} $(\Omega\text{-cm})^{-1}$ in the present measurement.

A slow increase of AC conductivity from room temperature upto 50°C is attributed to low concentration of impurities and their mobility. A similar behavior that observed in tan δ variation reflected in conductivity between 50°C and 60°C due to the presence of pendant groups of the polymer chain. The linear increase in conductivity above 90°C and upto 140°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 is observed. Thus at higher temperatures the increase in conductivity is mainly attributed to the increase in mobility of ions in the polymeric material[18]. 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 1.50 eV.

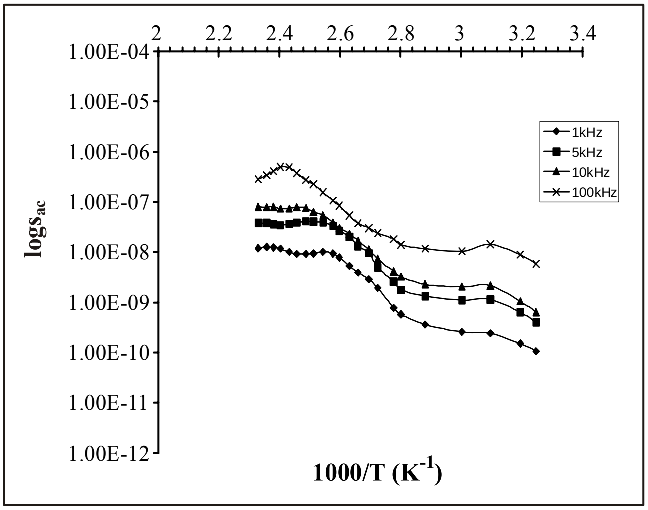

Fig. 5: Variation of AC conductivity with reciprocal temperature for AN - EMA (50/50)

CONCLUSION

The dielectric property of the AN+EMA has been studied and AC conductivity is also evaluated and studied the conduction process and molecular motions and relaxations in the polymer material.

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