JOURNAL OF MATERIALS SCIENCE **34** (1999) 5397–5401

Piezoelectricity and polarization studies in unstretched san copolymer films

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The piezoelectricity and charge storage in unstretched corona poled poly (styrene-co-acrylonitrile) films have been investigated under different poling conditions. The piezoelectric coefficient d_{31} has been measured as a function of poling field (E_p) and poling temperature (T_p) and the maximum value of $d_{31} \cong 1.0$ pC/N has been obtained at $E_p \cong 46$ MV/m and $T_p = 85\,^\circ$C. The Frolich equation for dipolar polarization has been applied for quantitative analysis of the thermally stimulated current (TSC). The g-factor $= 1.7$ has been obtained, suggesting cooperative dipolar relaxation. The Young's modulus has been measured to be $\cong 0.45$ GPa. The dipolar polarization from the TSC and the elastic modulus of the films have been correlated to the piezoelectricity through the modified equation for d_{31} for amorphous SAN films. It has been concluded that the mechanisms of the dimensional and the local field effects are involved in the piezoelectric phenomenon.

1. Introduction

Cyanopolymers are relatively new materials to join the family of piezoelectric polymers, the domain which was till recently dominated by PVDF and its copolymers [1, 2], PVC [3, 4], PMMA [5], and odd-Nylons [6]. The C—CN group, an essential constituent of all cyanopolymers has a large dipole moment (3.5 D). It is the high value of dipole moment that has tempted many researchers to explore their piezo-, pyro-, and ferroelectric properties.

The two very important cyano homopolymers polyacrylonitrile and poly (vinylidene cyanide) exhibit very low piezo activity. The low piezoelectric coefficient $d_{31} = 0.57$ pC/N in PAN is due to small orientation of the —CN dipoles in the presence of poling field because of unfavourable structure and hindering effect of dipole-dipole interchain and intrachain interactions [7–12]. In addition to this, their strong affinity for water molecules, which acts as plasticizer in these polymer films. It is also known to lower the glass transition temperature, and increases the electrical conduction in polymer films which in turn lowers the remnant polarization in these films [13].

Copolymerization of acrylonitrile with other monomers like methylacrylate, vinylidene cyanide, allyl cyanide is known to improve its piezo-, pyro- and ferroelectric activity [14–16]. The other cyano copolymers which have been studied include poly (vinylidene cyanide-co-vinyl acetate), poly (vinylidene cyanide - co-vinyl benzoate) and poly (vinylidene cyanide-co-vinyl pivarate) [17]. These polymers have a very good potential for use in fabrication of pressure sensors, IR detectors, night vision devices, and switching type materials [18].

The copolymer of acrylonitrile and styrene (SAN) has better chemical resistance, higher softening point, better tensile and dielectric strength than polystyrene. This copolymer also has better barrier properties for water absorption than PAN [19–20].

In this paper, the results of the piezoelectric and thermally stimulated current studies (TSC) in unstretched corona poled SAN films have been presented. The poling conditions have been optimized with respect to d_{31}. The results of the piezoelectric studies, the TSC and the mechanical properties have been correlated to obtain better understanding of the mechanism of piezoelectricity in these films.

2. Experimental

Poly (styrene-co-acrylonitrile) of Monsanto, Korea was obtained through Messrs PSA polymers, New Delhi. The films of 50–60 μm thickness were obtained by dissolving 500–600 mg of SAN granules in acetone and pouring the solution on to clean glass plates kept at 45 °C for 12 h. The films were further annealed at 90 °C to remove the residual solvent. Annealing process also reduces the internal stresses and increases the isotropy of the film.

The X-ray scans of the unstretched SAN films were undertaken using Philips X-ray diffractometer PW 1710 using Ni filtered CuK_α radiations of wavelength 1.54 Å. The X-ray scan of the unstretched SAN (figure not shown) exhibits two broad peaks around at $2\theta = 12$

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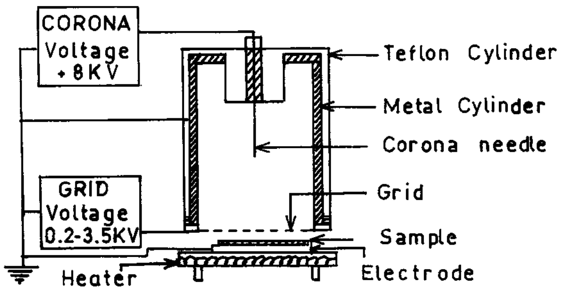

Figure 1 Schematic diagram of corona charging set up.

and 20°. The crystallinity ≅25% of the polymer film was estimated from the X-ray scan using Hinrichsen's method [21]. This implies that the SAN is predominantly amorphous.

The DSC studies on the unstretched SAN were carried out on Stanton Red Croft DSC 1500. The linear heating rate kept was 10 °C/min and the weight of the sample used was 10 mg. The glass transition T_g was determined to be 108 °C.

The Young's modulus for the unstretched SAN film was measured using Monsanto tensometer type W. The average value of the elastic modulus for the unstretched SAN film was 0.45 GPa.

For inducing piezoelectric activity, the SAN films were positively corona charged under different poling conditions. The schematic diagram of the corona charging set up is shown in Fig. 1. The grid is kept at about 4 mm distance from the surface of the film to be corona charged. A voltage of 8 kV was used at the corona needle and grid voltage is varied to obtain the desired poling field.

The rectangular aluminium electrodes of area 1.5 cm^2 were vacuum coated on both the sides of the corona charged film for piezoelectric measurements. The piezoelectric coefficient d_{31} was measured using quasi-static method [22].

The circular aluminium electrodes of area 0.78 cm^2 were vacuum deposited on each side of the poled films for the short circuit thermally stimulated current (TSC) studies. The TSC measurements were carried out in the ambient laboratory conditions in the temperature range 30–120 °C. The TSC was measured using a Keithley 610C electrometer and a chart recorder. The linear heating rate of 2 °C/min was used in the TSC experiments.

3. Results and discussion

The dependence of the piezoelectric coefficient d_{31} on the poling field is illustrated in Fig. 2, where the poling temperature $T_p = 85$ °C was kept constant. It is observed that d_{31} increases with the increase in the poling field. The maximum value of $d_{31} = 1.0$ pC/N in the poled unstretched SAN films at $E_p = 46$ MV/m has been obtained. The increase in d_{31} with E_p can be understood to be due to greater dipolar orientation in the sample with increasing poling field. At higher poling fields, the value of d_{31} falls down beyond 46 MV/m.

Fig. 3 shows the variation of d_{31} with poling temperature (T_p), whereas the poling field $E_p \cong 46$ MV/m was kept constant. The d_{31} has been observed to increase with poling temperature. The maximum value (1.0 pC/N) has been obtained at $T_p = 85$ °C.

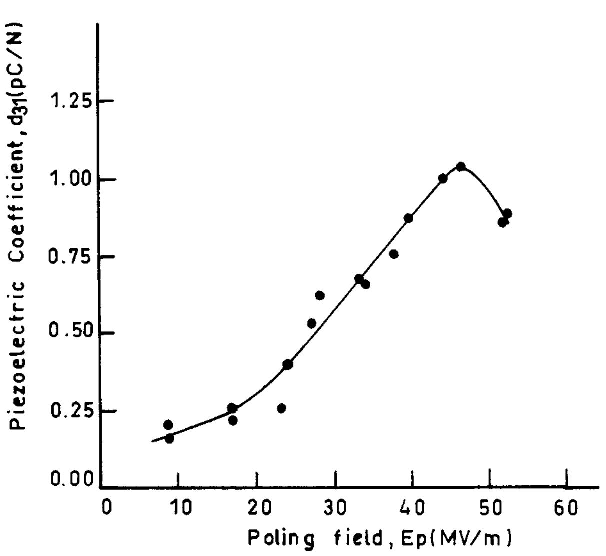

Figure 2 Dependence of d_{31} on poling field, E_p for the unstretched corona poled SAN film. $T_p = 85$ °C is kept constant.

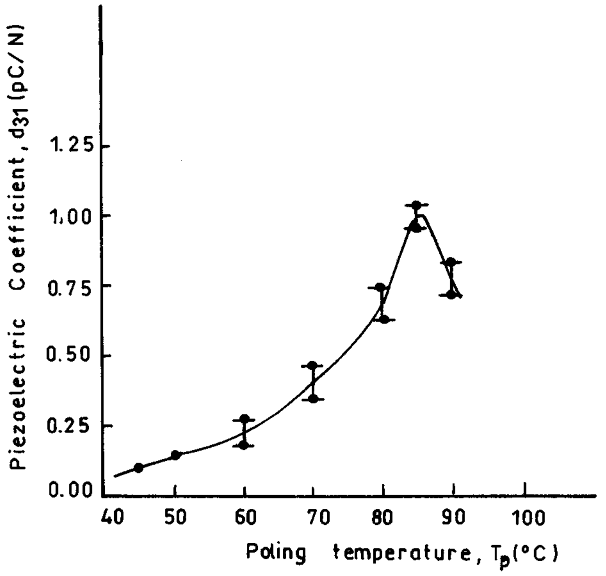

Figure 3 Variation of d_{31} with poling temperature, T_p. $E_p = 46$ MV/m was kept constant.

Thermally stimulated current experiments were performed to obtain information about the kind of polarization involved and its contribution to the piezoelectricity in SAN films. Fig. 4 shows typical TSC curves of the unstretched SAN films corona poled at different poling fields; and poling temperature 85 °C was kept constant. All the TSC curves show two peaks, the stronger peak is centered at temperature ≅97 ± 1.5 °C and the weak shoulder peak occurs around 103 °C.

The thermally stimulated currents can arise from dipolar disorientation of the dipoles in the poled films. Their contribution to the TSC can be estimated from the total charge Q released, given by,

$$Q = \int_0^\infty I(t)\,dt \tag{1}$$

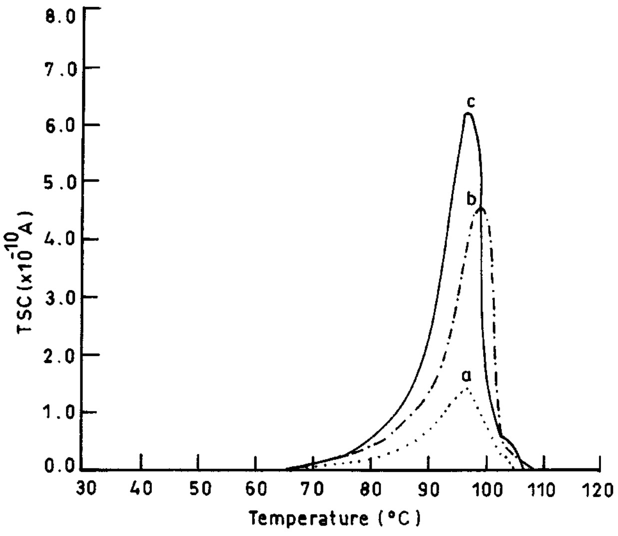

Figure 4 Typical short circuit TSC of the unstretched SAN films corona poled at different poling fields. (a) 22.5 MV/m, (b) 35 MV/m and (c) 46.2 MV/m.

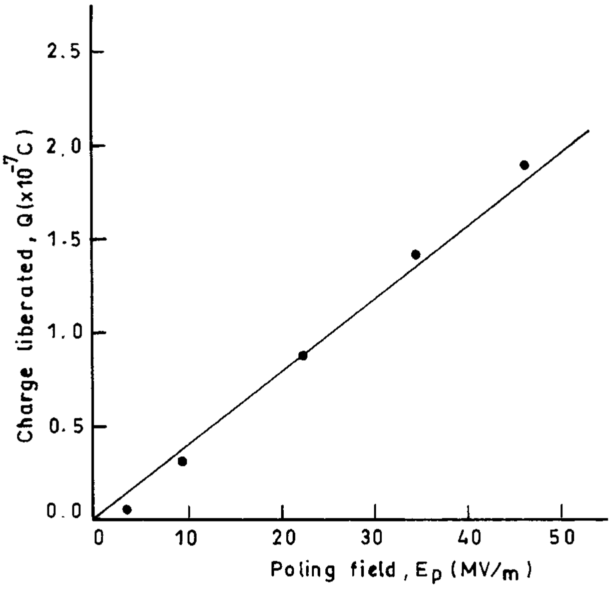

Figure 5 Plot of total integrated charge released (Q) during TSC versus poling field E_p. $T_p = 85\,^\circ$C was held constant.

where $I(t)$ is the current and t is the time. Thus the stored charge during poling process is proportional to the area under the TSC curve. The plot of Q versus E_p shows a linear dependence as shown in Fig. 5. This indicates that the dipolar polarization is stored in the poled SAN films. The increase in the polarization (Q/A), where A is the electrode area of the film, is responsible for the increase in d_{31} with the poling field (Fig. 2).

To further test the origin of the TSC peak, the TSC experiment was performed on two SAN samples of different thicknesses poled at $T_p = 85\,^\circ$C and $E_p = 25$ MV/m. The corresponding TSC curves are shown in Fig. 6. It is observed that the TSC peak position is independent of the film thickness, characteristic of the dipole peak [23].

Fig. 7 shows the TSC thermograms for the SAN films corona poled at different poling temperatures; the poling field $E_p \cong 46$ MV/m was held constant. Two significant observations can be made from these curves. Firstly, the area under the peak i.e., polarization in the SAN film increases with poling temperature which could be due to the greater alignment of dipoles in the field direction at higher poling temperatures. The area under the peak is maximum for the films poled at 85 °C

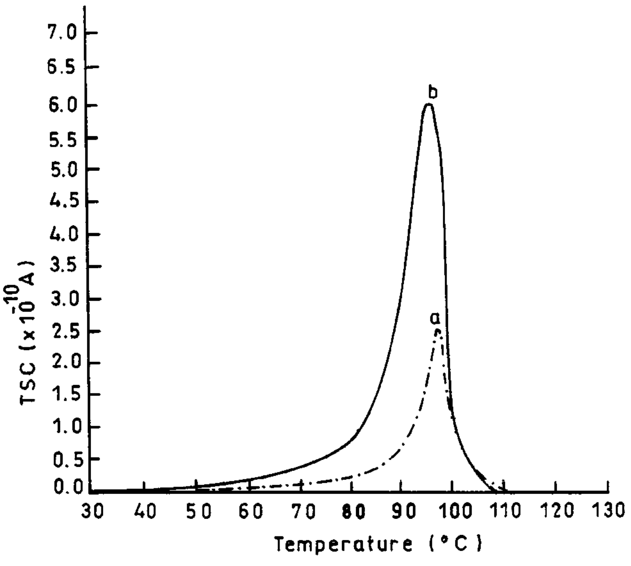

Figure 6 Short circuit TSC curves of unstretched corona poled SAN films of different thickness. (a) 30 μm and (b) 80 μm. Poling parameters. $E_p = 25$ MV/m and $T_p = 85\,^\circ$C are kept constant.

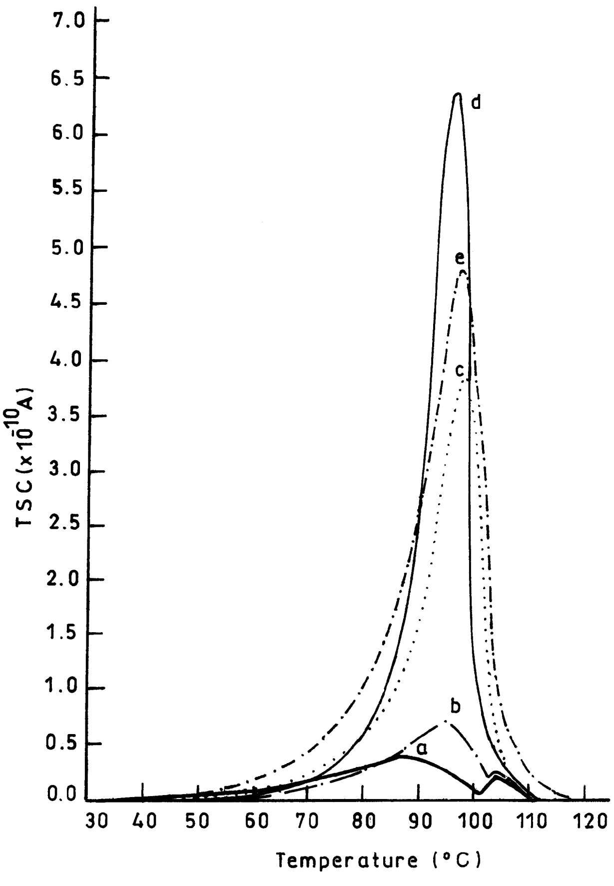

Figure 7 Typical short circuit TSC curves of unstretched SAN films corona poled at different poling temperatures. (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 85 °C and (e) 90 °C. $E_p = 45$ MV/m has been kept constant.

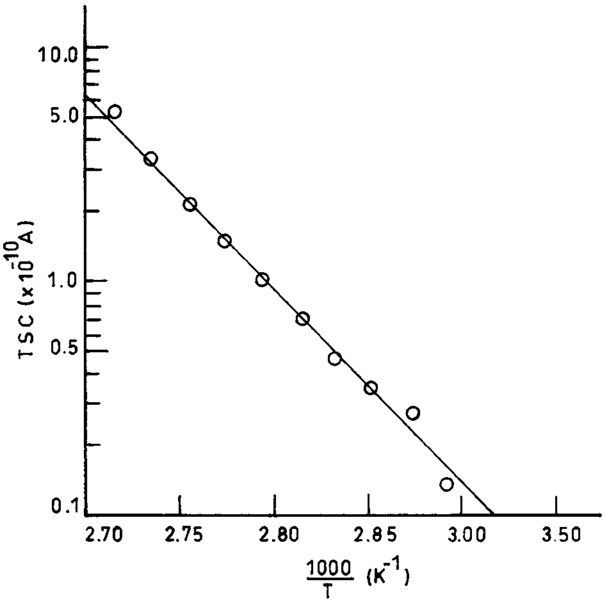

Figure 8 Arrhenious plot of TSC versus T^{-1}.

and it decreases for the films poled at higher temperatures. A similar trend was observed in the plot of d_{31} versus T_p (Fig. 3) showing a maximum at $T_p = 85\,^\circ C$. Second major observation is that the peak shifts to higher temperature as the poling temperature is increased. As poling temperature approaches the T_g, the shift in the low temperature peak position is arrested. However, the shift in the position of high-temperature peak with the increase in the poling temperature is almost negligible. The origin of the low-temperature peak could be the disorientation of dipoles due to the mobility of smaller segments of the polymer chain. This peak could be designated as β peak. The second peak near T_g could arise due to dipole disorientation due to the motion of the large segment of the main chain. This peak is thus designated as α peak.

The second peak also lies close to the glass transition temperature which can be associated with cooperative motion of chain segments. A peak shifting with poling temperature has also been observed in other polymers like polyethersulfone [24].

The activation energy was estimated using initial rise method [25] from the TSC curve of SAN film poled at optimum conditions i.e., $E_p = 46$ MV/m and $T_p = 85\,^\circ C$. The Arrehenius plot of the current versus T^{-1} is shown in Fig. 8 which gives activation energy $\cong$1.64 eV. The high value of activation energy indicates that cooperative motion of large chain segment is involved during the depolarization process.

The density of SAN, $d = 1.08 \pm .01$ g/cc was measured using the flotation method. Our previous IR studies show that these SAN samples contain 28% acrylonitrile content [26]. Thus the dipole density N, due to the nitrile group is $1.2 \times 10^{27}/m^3$ in the SAN samples.

The poling process involves the application of high electric field at elevated temperature. During this process, the dipole alignment under the influence of the field will result in conformational changes in the polymer, which could alter the local dipole environment. This effect is accounted for in the Frölich polarization equation given below in terms of g factor [27],

$$P_r = \frac{N\mu^2 E_p}{kT_p} \frac{\varepsilon_s(n^2+2)^2}{9(2\varepsilon_s + n^2)} \cdot g \qquad (2)$$

where N is the dipole density, μ is the dipole moment, E_p is the poling field, ε_s is the dielectric constant at low frequency, n is the refractive index of SAN copolymer, k is the Boltzmann's constant, P_r is the remnant polarization. Using, $P_r = 2.4 \times 10^{-3}$ cm^{-2}, $N = 1.2 \times 10^{27}/m^3$, $\mu = 1.165 \times 10^{-29}$ cm (3.5 D), $\varepsilon_s = 10.8$, $n = 1.57$ [19], $E_p = 46$ MV/m, $k = 1.38 \times 10^{-23}$ J/K and $T_P = 358$ K in Equation 2 provides $g = 1.7$. The value of g in excess of unity implies that some cooperative dipole motion is involved. The high value of TSC activation energy also suggests the cooperative dipole relaxation.

The model to account piezoelectricity in the poled amorphous polymers have been developed by Mopsik and Broadhurst [28]. Their expression for the hydrostatic pressure piezoelectric coefficient d_P can be approximated as [29],

$$d_p = \frac{P_r \beta \varepsilon_\infty}{3} \qquad (3)$$

where P_r is the remnant polarization, β is the isothermal compressibility and ε_∞ is the high frequency dielectric constant. In the present context, Equation 3 has to be modified as the stress applied here was along the X-axis (giving experimental piezoelectric coefficient d_{31}). The following equation for β can be used [30] for unstretched amorphous polymer,

$$\beta = \frac{3(1-2\nu)}{E} \qquad (4)$$

where E is the elastic modulus and ν is the Poisson's ratio and replacing d_p by d_{31} in Equation 3, this gives,

$$d_{31} = \frac{P_r \varepsilon_\infty (1-2\nu)}{E} \qquad (5)$$

Using present experimental data i.e., $P_r = 2.4$ mC/m^2, $E = 0.45$ GPa, $\varepsilon_\infty = 3$ [19], $d_{31} = 1.0$ pC/N in Equation 5, gives $\nu \cong 0.47$. The Poisson's ratio depends upon amorphous state of the polymer, is usually found in the range 0.3–0.5 [31] for temperatures below T_g. This value suggests that the basic mechanism of piezoelectricity in SAN also involves the dimensional effect in addition to the local field effect.

4. Conclusions

The maximum value of piezoelectric coefficient $d_{31} = 1.0$ pC/N has been obtained at poling parameters, $E_p = 46$ MV/m, and $T_p = 85°C$ in SAN films. The dipolar orientation is the main contributor to the TSC peaks and the piezoelectricity in SAN. Application of Frölich theory to the TSC gives $g = 1.7$, suggesting the cooperative dipole relaxation. The piezoelectricity in

SAN films has been attributed to the dimensional and the local field effects.

Acknowledgement

One of the authors, J. S. Hundal wish to thank the All India Council for Technical Education, New Delhi for providing fellowship under Quality Improvement Programme.

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Received 30 May 1997
and accepted 23 March 1999