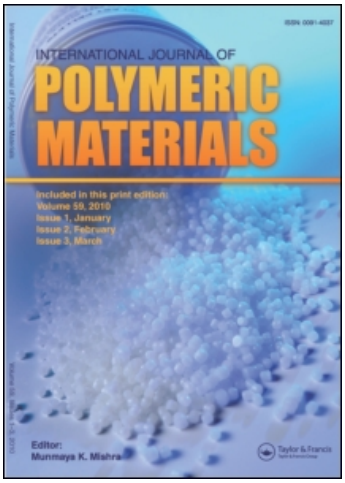

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Corona charging and pyroelectric behavior in acrylonitrile-co-methylacrylate films

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CORONA CHARGING AND PYROELECTRIC BEHAVIOR IN ACRYLONITRILE-co-METHYLACRYLATE FILMS

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Annealed and stretched films of P(AN-MA) were charged with negatively constant–voltage corona at different temperatures. Electric field induces phase transition, which is determined by the wide angle X-ray diffraction. Using the thermally stimulated depolarization technique, pyroelectric currents have been investigated in unpolarized and corona charged P(AN-MA) films over the temperature range 25 – 140°C. Stretching films produces an enhancement in pyroelectricity. The increase in crystallinity and the presence of space charge build-up during corona charging are believed to be the chief contributors to the higher pyroelectric activity in the stretched films.

Keywords: P(AN-MA), X-rays, corona, TSDC, pyroelectricity

INTRODUCTION

Corona discharge provides a good means of treating polymer surfaces, changing their physical and chemical properties. These modifications are mainly due to the action of activated neutral species generated by the corona discharge and carried to the sample surface by the corona wind. By their action, the polymer surface may change its conductivity and charge injection in the sample bulk.

Pyroelectricity is the electrical response of a material to a change in temperature. The study of the pyroelectric properties of a dielectric gives insight into the charge storage and polarization phenomena, and also throws important light on the usability of such materials in devices such as infrared radiation detection, gas analysis and thermal imaging [1 – 5]. Charge storage and polarization phenomena in polymers have been widely investigated using thermally stimulated depolarization current (TSDC) technique [6], which consists of heating the electret and measuring the so called depolarization current as a function of the temperature.

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Pyroelectric properties have been reported for many polymers [7–12] and polymer composites [13]. The pyroelectricity may arise from orientation of dipoles, change in film dimension or a reversible change in crystallinity with temperature [14]. Cyanopolymers are relatively new materials to join the family of piezoelectric polymers. The C–CN group, an essential constituent of all cyanopolymers has a large dipole moment (3.5D). It is the high value of dipole moment that has tempted many researchers to explore their piezo-, pyro- and ferroelectric properties. In the present work, we report the results from studies on pyroelectricity and thermally stimulated depolarization currents (TSDC) carried out for unpolarized and corona charged stretched acrylonitrile–methylacrylate, P(AN-MA) copolymer films. The (TSDC) and pyroelectric current I_y, were measured in both annealed and stretched samples under various charging temperatures, T_c, and charging voltage V_c. The results showed the existence of pyroelectric current during several heating and cooling processes, exclusively due to space charge effects in the material. Results obtained on variation of X-ray diffraction with annealing temperature and stretching have also been included.

MATERIAL AND EXPERIMENTAL TECHNIQUE

Acrylonitrile–methylacrylate, copolymer (94% acrylonitrile and 6% methylacrylate, $M_w = 100{,}000$ Polysci. USA) is a semi-crystalline material [15]. Films of various thickness in the range 25–35 μm as determined by digital micrometer (Miltutoyo, No. 293, 521–30, Japan), were obtained by casting technique. The material was dissolved in hot concentrated dimethylformamide. The solution was dried on a glass plate under normal atmosphere at 355 K for 24 h. A group of the cast films were annealed at 373 K for 24 hours. Another group of the films was uniaxially stretched up to three times their original length. A sandwich configuration of carbon paste-with an effective of film-carbon paste area $0.785 \times 10^{-4}\,m^2$ was used for the measurements. After the films were polarized, they were subjected to a number of heating and cooling runs at a constant heating rate of 4 K/min. in the temperature range 300 K to 440 K. The first cycle, which is irreversible, is associated with thermally stimulated depolarization current (TSDC) behavior. Subsequent cycles are reversible and give rise to pyroelectric current. TSDC and pyroelectric measurements were carried for the unstretched and stretched P(AN-MA) films. Films of P(AN-MA) were corona charged at several elevated temperatures. The negative corona electrode, which is a brush of very smooth steel fiber of diameter 0.5 mm, is connected with the negative terminal of the high voltage biasing power supply. The counter electrode is a spring sheet connected with the ground and about 2 mm spaced from the corona electrode (mostly carbon paste). The polarized films were short-circuited for 5 minutes. The discharge current being measured by keithley electrometer (610 C) and keithley Picoammeter

(Model 485). Partial heating measurements on corona charged films were carried out to determine the trap energies. Good reproducibility has been observed, except at polarizing temperature 100°C, for which a physical change in the sample's structure has been suggested. Details of experimental arrangement and measuring techniques are to be found elsewhere [16–18]. X-ray scans were obtained by X-ray diffraction Dx-30 Kyoto, with 40 kV, 30 mA, using filtered copper Cuk$_\alpha$ of wavelength 0.154 nm.

RESULTS AND DISCUSSION

X-ray Scans

Figure 1 shows four X-ray scans for unannealed; annealed; hot stretched and hot stretched followed by corona charging for P(AN-MA) films. For

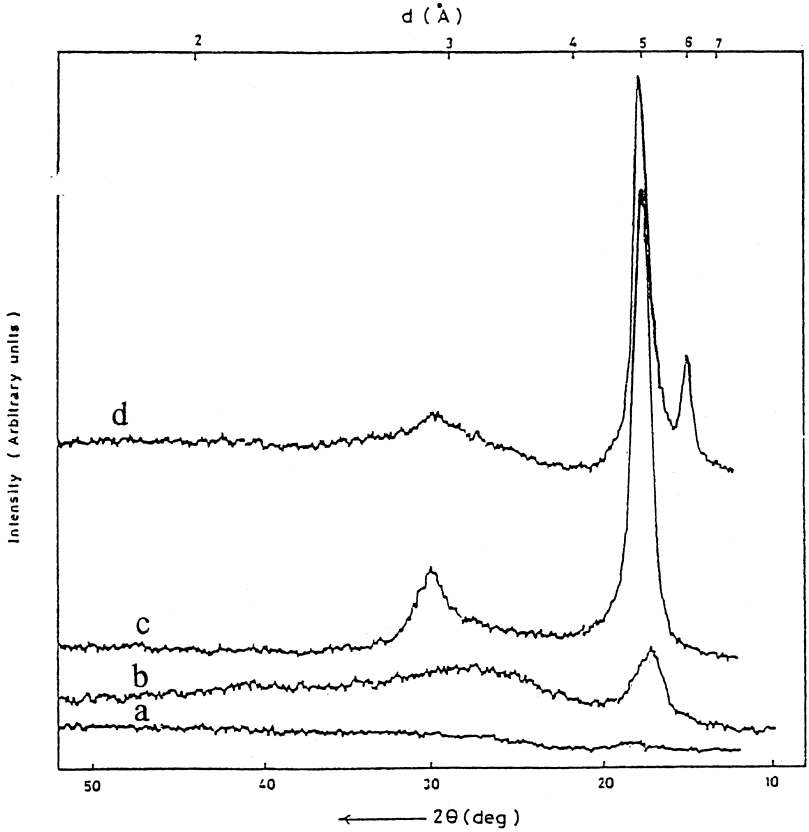

FIGURE 1 X-ray diffraction scans of P(AN-MA) (a) unannealed, (b) annealed 24 h at 373 K, (c) hot stretched at 403 K to 3 times, and (d) hot stretched and then corona charged with 4 kV voltage.

unannealed (Fig. 1a) P(AN-MA)film one observes the amorphous structure of the material. Samples annealed at 373 K for 24 h in air show crystalline peak located at $2\theta = 17.2^\circ$ (Fig. 1b). Scan *c* of the hot stretched film to 3 times its original length at 403 K shows that the peak at $2\theta = 17.2^\circ$ becomes very sharp and intense; another reflection located at $2\theta = 30.1^\circ$. During corona charging the field induces structural change and a new crystalline phase appears at $2\theta = 14.8^\circ$ as shown in Figure 1d. The crystallite size was calculated using Scherrer's relation [19]

$$t = 0.9\lambda/\beta \cos(\theta_{hkl}) \quad (1)$$

where t is the crystallite thickness that is perpendicular to the hkl plane, λ is the X-ray wavelength, β is the peak width at half height (radian) and θ_{hkl} is the Bragg angle. The average crystallite size for hot stretched and for hot stretched and then corona charged P(AN-MA) films corresponding to $2\theta = 17.2^\circ$ are 6.54 nm and 7.85 nm respectively. That is to say changes in chain conformation or crystalline structure have occurred. Hence, the appearance of a new reflection at $2\theta = 14.8^\circ$ is an experimental evidence for the effect of an electric field on the crystallization behavior of P(AN-MA). This suggests that, in fact, at least three crystalline phases may be present in hot stretched and corona charged (AN-MA) copolymer films.

THERMALLY-STIMULATED DEPOLARIZATION AND PYROELECTRIC CURRENT MEASUREMENTS

An uncharged P(AN-MA) film was heated to 413 K and was then cooled to room temperature: the procedure was repeated. A typical pattern obtained in several heating cycles is shown in Figure 2. On reheating the film (second heating cycle), the data were not reproducible and a marked change in the feature of the TSC spectrum was found. The pyroelectric current passes through maxima and then increases strongly, indicating changes in the microstructure of the film. The appearance of these peaks is related to the phase transition in the copolymer films during the cooling process from 140°C to the room temperature.

Figure 3A shows the temperature dependence of the TSDC for annealed film charged with 4 kV at the polarizing temperatures, T_p, of 309 K, and 343 K and 373 K. On the other hand Figure 3B shows the variation of the pyroelectric current (second and third heating cycle) with temperature for the specimen represented in Figure 3A. Curves 1 and 2 of Figure 3A showed a pronounced reversed peak at 145°C. The reversed peak vanishes upon the second heating of the film (curves 1 and 2 of Fig. 3B). The fact that this peak disappears during a second heating cycle of the film is explained by the relaxation of oriented dipoles. On the other hand, curve 3 in Figure 3A shows three different peaks, two normal peaks at 70 and 130 and a reversed

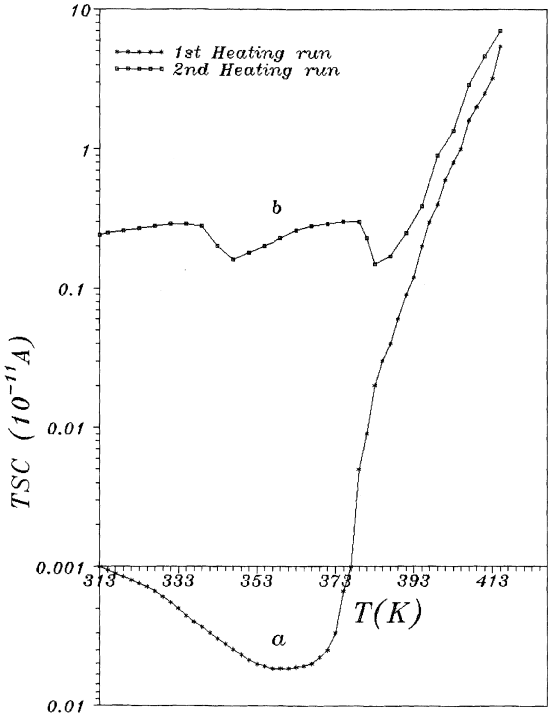

FIGURE 2 Typical short circuit curves for unpolarized P(AN-MA) films; (a) first heating run and (b) second heating run.

peak at ca. 140°C. The figure indicates that with the rise of the charging temperature, a relaxation peak appeared at higher temperature (ca. 130°C). This is because carriers in donor-like states are already activated by thermal energy during charging at elevated temperature and are then retrapped at energetically deeper level [20]. The Pyroelectric current (curves 3 and 4 of Fig. 3B) exhibited abnormal behavior. The curves showed at least two peaks. The appearance of these may be related to the structural variation during charging at elevated temperature. In fact, this is not surprising since the charging at higher temperature ($T_c > T_g$) is equivalent to annealing under field. Referring to curves 3 and 4 in Figure 3B we suggest that charging at temperature $T_c = 100°C > T_g$ ($T_g = 90°C$ as evaluated from thermal analysis measurements) results in the formation of a very broad peak. This suggests that the width of the relaxation time have been shifted to larger values due to thermally stimulated structural changes occurring in the material under high electrical stress. That is the annealing under the influence of the electric field enhance the pyroelectic activity in the film. Such an effect would clearly be expected if the major peak was dipolar in origin,

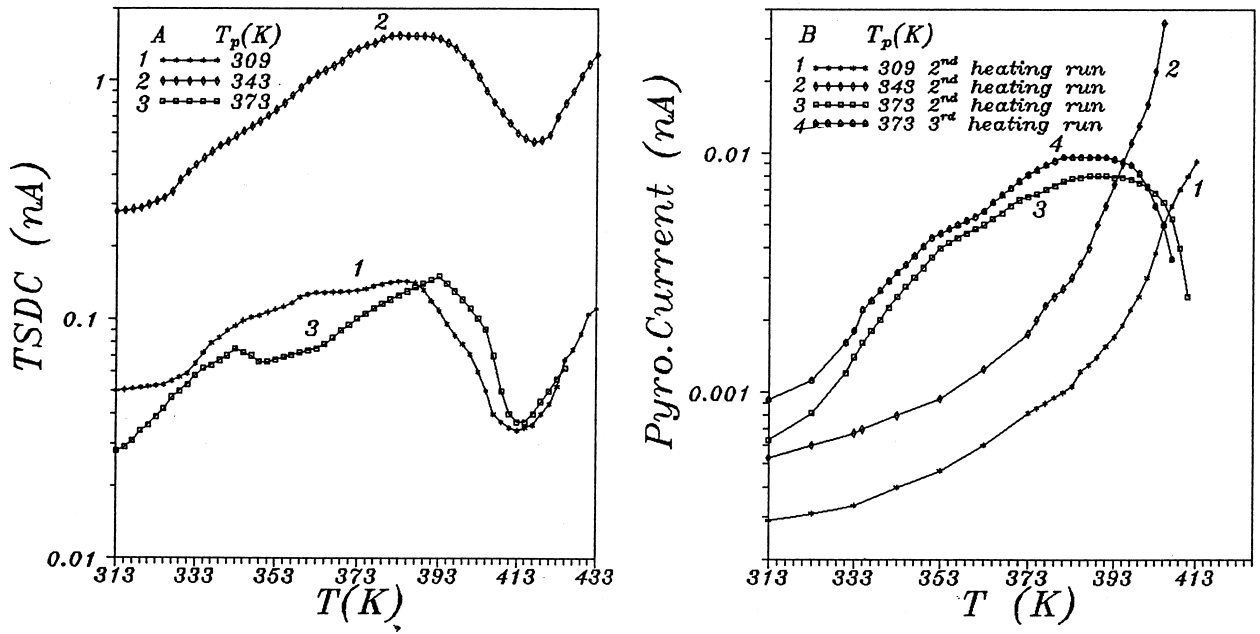

FIGURE 3 TSDC(A) and pyroelectric current (B) as a function of temperature for annealed P(AN-MA) films charged with 4 kV voltage for different charging temperatures. (Charging time is 15 min. and carbon paste as electrode).

but pyroelectricity resulting from space charge coupled with material inhomogeneities has also been discussed [21] and a model of charge injection and charge trapping at polarized crystallites is proclaimed [22].

Similar results have been obtained on changing the charging voltage (curves are not given). However, there was a certain threshold voltage of the order 3.6 kV beginning from which the film began to exhibit pyroelectric properties after the polarization procedure. The pyroelectric current increased with the charging voltage until it reached saturation. Hence, the space charge and the frozen-in dipole orientation in P(AN-MA) films could be considered to be superimposed [17].

Figures 4A and B represents the TSDC and Pyrocurrent spectra for hot stretched films. The second and third heating cycle pyroelectric currents of the stretched film polarized at 309 K are given in Figure 4B. In the second heating cycle thermogram, two maxima at 343 K and 363 K are appearing. On cooling and upon reheating (third heating cycle), the pyroelectric current manifests itself. From the point of view of surface modifications it has been proposed that the corona irradiation of polymer films have the effect of breaking bonds and creating polar groups. Therefore, the discharge currents could be attributed to a space charge build-up during the polarization. Hence the pyroelectricity left in the film after the second heating cycle may be due to a mechanism in which carriers are predominantly produced within the bulk. This indicates that these carriers could be activated from donor-like states or could originate from the ionization of impurities, which move under the influence of the field and create microscopic charge packets [23]. The fact that the pyroelectric activity, namely dipolar and volume polarization, remains nonvanishing in the temperature range 25°C – 90°C, even if many heating and cooling cycles have been done, implies that various kinds of polarization exist; a part of these originates in dipole orientation in the crystalline region.

Thermally stimulated current, TSC, was obtained by measuring the short-circuit current, $I(T)$ from the sample. In order to obtain the activation energy associated with the relaxation process, we have applied the partial heating method [24], which utilizes the initial rising part of the current during a series of heating runs. The initial rise part is exponential, proportional with the temperature. So the relation between the initial discharge current I, and the activation energy is given by

$$I = I_o \exp[-E/KT] \tag{2}$$

The variation of the apparent activation energy estimated from the slopes of the log I *vs.* $1/T$ plots as a function of the maximum temperature reached in each heating run are illustrated in Figure 5. The wide distribution of activation energies suggests that the major relaxation process originates within the amorphous phase, or at the crystal/amorphous boundaries,

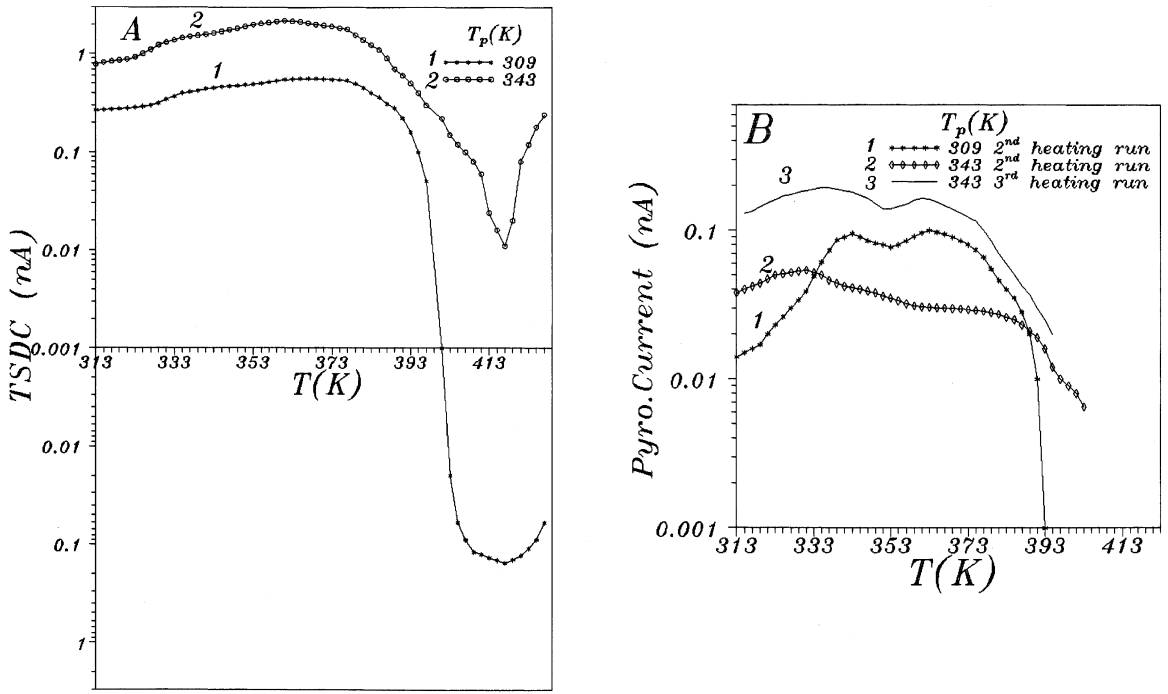

FIGURE 4 TSDC (A) and pyroelectric current (B) as a function of temperature for annealed and stretched P(AN-MA) films charged with 4 kV voltage for different charging temperatures. (Charging time is 15 min. and carbon paste as electrode).

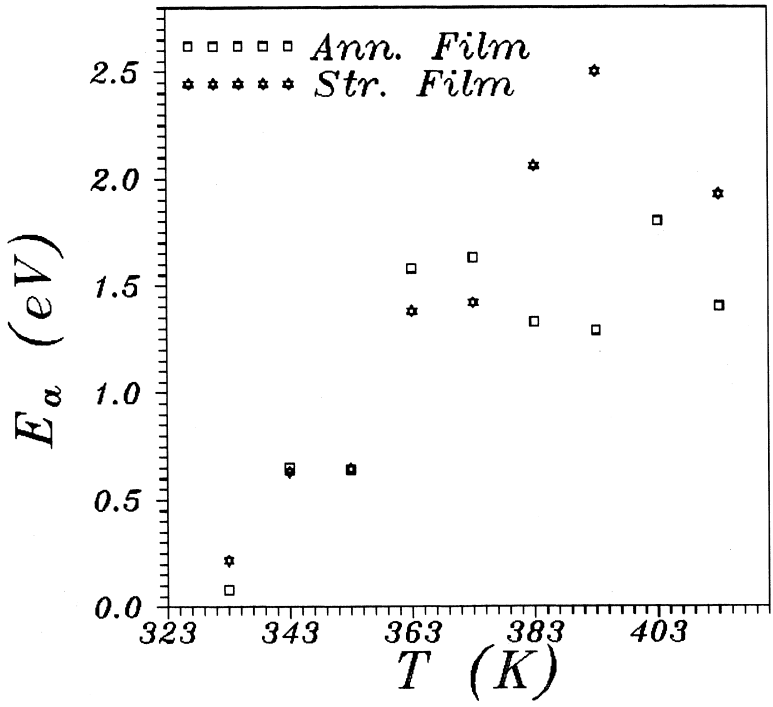

FIGURE 5 Apparent activation energies determined from the partial heating technique as a function of the maximum temperature reached in each heating run.

rather than from the structurally regular crystalline region [25]. Further, the dependence of the activation energy on the cut-off temperature indicates that the discharge currents can result in a thermally activated process from charge motion and diffusion.

CONCLUSIONS

Stretching and/or electric field induce crystal phase transformation and create a stable one in P(AN-MA) films involving a change in molecular conformation. Pyroelectric activity is greatly improved by increasing crystallinity and/or crystallite size in P(AN-MA).

Corona charge at elevated temperature is a more efficient method of poling stretched P(AN-MA) copolymer films than room temperature charging. More of the charges are injected deeper into the sample, giving rise to a higher internal field, and thus higher pyroelectric current. The space charge injected by the corona and trapped in the material implies that

various kinds of polarization exist. Hence, the discharge currents can result from charge motion and diffusion.

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