

Piezoelectricity in acrylonitrile/methylacrylate copolymer

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SUMMARY

The piezoelectric strain coefficient d_{31} of stretched and unstretched acrylonitrile/methylacrylate copolymer films has been investigated as a function of poling conditions. The maximum d_{31} values obtained for stretched and unstretched films were around 3 and 0.85 pC/N, respectively. The time stability of piezoelectricity is relatively low.

INTRODUCTION

Piezoelectric properties have been investigated for a variety of polymers (1). The polymer with the strongest piezoelectric activity in the stretched and poled form is poly(vinylidene fluoride) (PVDF). The mechanism of piezoelectricity in PVDF is not yet fully understood, but the most investigators explained the effects by dipole orientation. Whereas the $-CF_2-$ group of the PVDF monomer unit has a dipole moment of 2.1 D, the nitril side group of poly(acrylonitrile) (PAN) has a dipole moment of about 3.5 D. If these dipoles can be oriented by an applied electric field, a piezoelectric activity of PAN can be expected. Indeed it could be observed (2,3).

The aim of the present paper was, to investigate the piezoelectric behaviour in more detail, especially its dependence on the poling conditions. Owing to the better processability instead of acrylonitrile homopolymer a copolymer of acrylonitrile (~93 %) and methylacrylate (6-7 %) (P(AN-MA)) was used.

EXPERIMENTAL

The polymer with a molecular weight of $M_w = 5 \times 10^4$ was synthesized by solution polymerisation. Films were cast from a 4 wt% dimethylformamide solution under normal atmosphere at 42 °C. Some of the films were then uniaxially stretched by hot-zone drawing where drawing temperature and draw ratio were 90 °C and $\lambda \approx 4$, respectively. All films were dried in an evacuated oven at 95 °C for 24 h to remove residual solvent. The sample thickness varied from 10 to 15 μ m. Aluminium electrodes were vacuum deposited onto both sides. The samples were poled by applying d.c. electric fields. After poling at higher temperatures, the films were cooled slowly down to room temperature under applied field. The measurement of d_{31} was carried out by a quasistatic charge integration technique at room temperature two days after poling.

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RESULTS

Fig. 1 shows the measured poling field strength E_p dependence of the d_{31} coefficient for stretched and unstretched

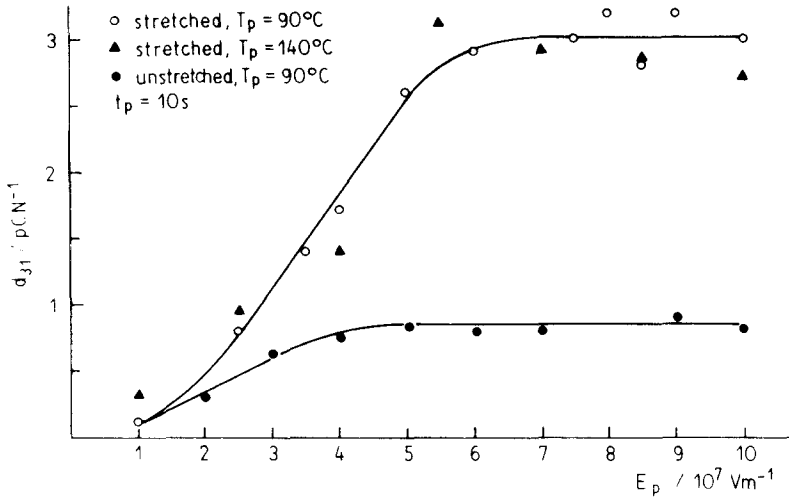


FIGURE 1 Poling field strength dependence of d_{31} coefficient.

films. The poling time t_p was chosen as 10 s. In the case of stretched films two different poling temperatures of $T_p = 90^\circ\text{C}$ and 140°C , respectively were used. It can be seen that the piezoelectric activity is not influenced by increasing the poling temperature. Before a saturation value is reached around $E_p = 6 \times 10^7 \text{ V/m}$, the d_{31} coefficient exhibits a nearly linear dependence on E_p .

In a second experiment the poling time was varied between 10 s and 25 min. For stretched samples poled at 90°C under $E_p = 8 \times 10^7 \text{ V/m}$ a value of $d_{31} \approx 3 \text{ pC/N}$ was found independent of t_p . From this it was decided to use 10 s as the standard poling time for the next set of experiments.

The piezoelectric activity strongly depends on the poling temperature as shown in Fig. 2. Very little activity is found unless T_p is greater than a critical value of about 50°C . At $E_p = 8 \times 10^7 \text{ V/m}$ d_{31} increases sharply when the poling temperature exceeds $\approx 65^\circ\text{C}$ and reaches its saturation value around 80°C . This threshold behaviour also explains the T_p -independence of the $d_{31}(E_p)$ -dependencies in Fig. 1.

To obtain information on the stability of the piezoelectric properties the storage time dependence of d_{31} at room temperature and normal atmosphere was investigated. The results are given in Fig. 3. The piezoelectric decay follows logarithmic kinetics as was found also for PVDF (4). d_{31} decays to about 87 % of its initial value after a storage time of 42d and to 68 % after 200 d. The isothermal investigations were

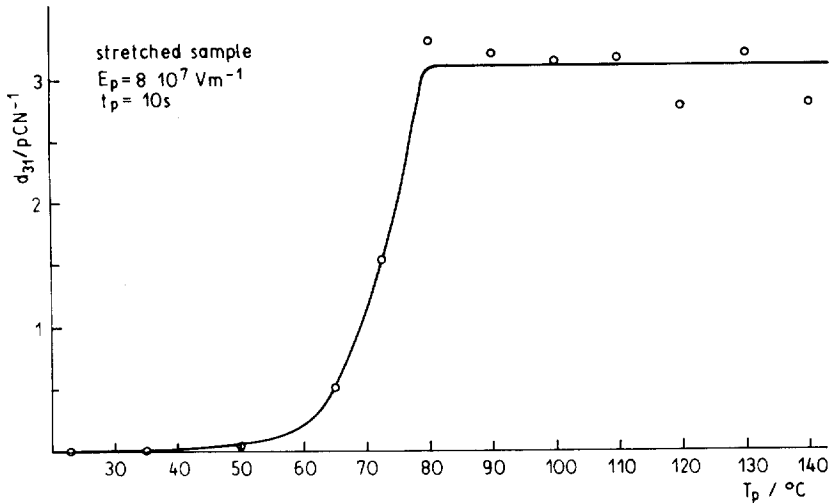


FIGURE 2 Poling temperature dependence of d_{31} coefficient.

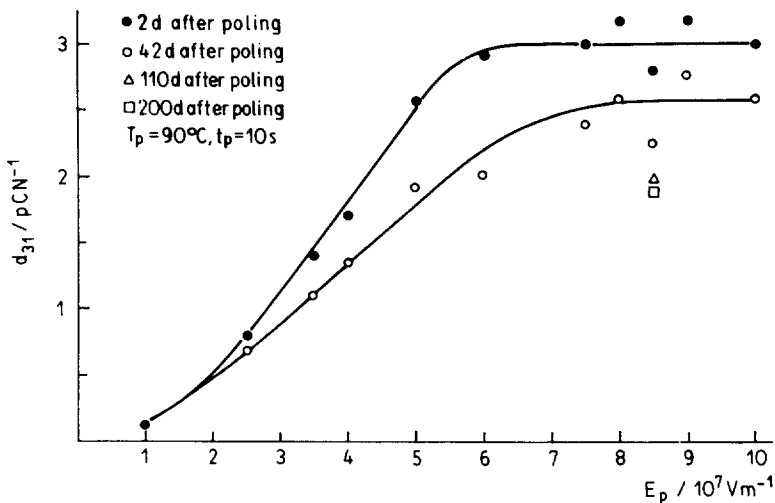


FIGURE 3 Storage time dependence of d_{31} coefficient for differently poled samples.

supplemented by additional thermally stimulated measurements. For this end an initially poled sample was annealed stepwise at rising temperatures T_a for 30 min and cooled down to room temperature. After each annealing step the residual d_{31} coefficient was estimated. This procedure was carried out on

three samples which were previously stored different times (2d, 7d, 200d) at room temperature. Fig. 4 shows the plots

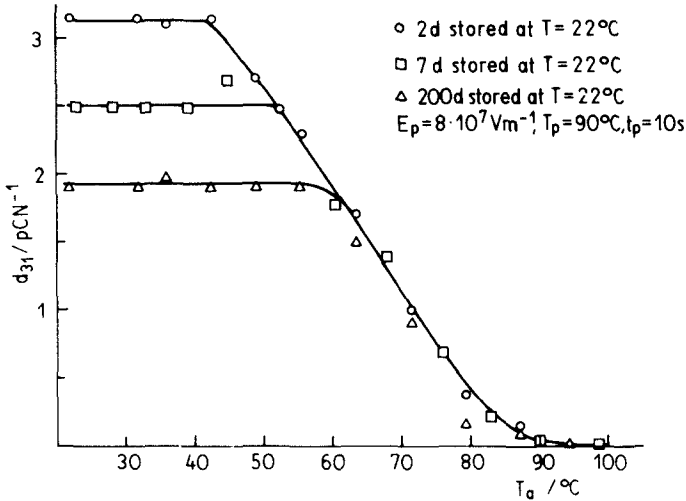


FIGURE 4 Annealing temperature dependence of d_{31} coefficient for differently stored samples.

of d_{31} versus T_a . We note a nearly linear decay of d_{31} after an initial constant plateau. For aged samples the loss of piezoelectricity sets in at higher temperatures compared with the fresh sample. However the initial value of d_{31} is smaller originating in the foregoing isothermal aging (Fig. 1). The most conspicuous fact is the sample history independent linear loss of piezoelectricity at higher temperatures. The behaviour refers to some kind of temperature-time-equivalency. If the piezoelectricity yet relaxes irreversibly at room temperature as was demonstrated, then it should be possible to obtain a piezoelectric activity after large poling times at room temperature. Indeed we found $d_{31}=0.25$ pC/N on a sample poled for 25 min.

CONCLUSIONS

The maximum observed values for d_{31} of about 3 pC/N are comparable with the values previously reported for AN homopolymer (2), but still one order of magnitude less than the values obtained for oriented PVDF films. In contrast to Hall et al. (5) which suggest that PAN should not show any piezoelectricity as the result of the cancellation of dipoles due to the helical conformation (6), our samples show an appreciable piezoelectric activity. It appears likely that this is a result of copolymerization of AN, because the introduction of the comonomer enhances the internal mobility of polymer segments, reducing the sequences of AN molecules capable of interacting with neighbouring sequences (6). Stretching of specimens, which causes chain alignment clearly en-

hanced the piezoelectricity. The observed saturation of d_{31} for poling fields exceeding $E_p \approx 6 \times 10^7$ V/m is obviously related to limited inner fields in the films during poling caused by partial breakdown processes. So far the nature of the piezoelectricity is not clear. Polarization in PAN is commonly taken as arising from a combination of a preferential orientation of dipoles and from space charge effects (2). Further investigations to gain insight into the mechanisms are in progress.

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REFERENCES

1. T. Furukawa, Proc. 5th Intern. Symp. Electrets, Heidelberg 1985, p. 883 (IEEE, New York, 1985).
2. H. Ueda and S.H. Carr, Polym. J. 16, 661(1984).
3. H. v. Berlepsch, W. Künstler and R. Danz, submitted to Ferroelectrics.
4. A.G. Kolbeck, J. Polym. Sci., Poly. Phys. Ed. 20, 1987 (1982).
5. H.K. Hall jr., R.J.H. Chan, J. Oku, O.R. Hughes, J. Scheinbeim and B. Newman, Polymer Bull. 17, 135(1987).
6. G. Henrici-Olivé and S. Olivé, Adv. Polym. Sci. 32, 124 (1979).