

# Surface effects in corona-charged polyvinylidene fluoride

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Biaxially oriented films of polyvinylidene fluoride  $[-(\text{CH}_2-\text{CF}_2)_n-\dots; \text{PVDF}]$  of thickness  $25\ \mu\text{m}$ , originally containing both the  $\alpha$  and  $\beta$  crystal forms, have been corona charged at room temperature to surface potentials of up to 10 kV using positive and negative corona. The behaviour of the optical density of the  $\alpha$ -form infra-red band at  $796\ \text{cm}^{-1}$ , measured in the transmission mode, was found to be inverse to that of the piezoelectric coefficient,  $g_{31}$ , with increasing charging voltage. Attenuated total reflection (ATR) measurements on the same samples indicated that the extent of poling close to the surface which received the corona charge was less than that close to the earthed surface and less than that of the bulk. The results support a mechanism of dipole orientation for the origin of piezoelectricity in PVDF.

## 1. Introduction

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer which may exist simultaneously in at least two crystalline forms [1] – the  $\alpha$ -form (or Form II) and the  $\beta$ -form (also known as Form I). In the  $\beta$ -form the PVDF chains take up a nearly planar zig-zag conformation and they line up parallel to one another in their unit cell. PVDF is inherently polar owing to the large dipole moment of the C–F bond. In the  $\beta$ -form a major component of this moment is normal to the long molecular axis and because the unit cell is polar (dipole alignment) [1] a single crystal of the  $\beta$ -form may be expected to exhibit spontaneous polarization even in the absence of an applied field [2]. The  $\alpha$ -form molecules have a TGTG' conformation and have a smaller net dipole moment perpendicular to the chain axis than the  $\beta$ -form, but they pack into an anti-parallel array [1] so that the unit cell is non-polar and should not be expected to give rise to spontaneous polarization [2].

Thin films of PVDF can be made to exhibit piezoelectric properties after suitable poling procedures usually involving the application of

a high d.c. field at an elevated temperature for an extended period of time. Early workers [3] suggested that in poled films containing a mixture of  $\alpha$  and  $\beta$  crystallites the piezoelectricity may increase with increasing  $\beta$  content. Such an observation is consistent with a dipolar orientation model for the origin of piezoelectricity in this polymer. However, there are several examples in the literature of experiments using so-called "blocking" electrodes [3, 4] or sandwich arrangements [5, 6] which suggest that charge injection at the positive electrode may be an important requirement for poling. The importance of the metal–polymer interface [7] and the choice of electrode materials [8, 9] have been emphasized.

Significant piezoelectric response has been reported from predominantly  $\alpha$ -form samples and a mechanism of conversion from  $\alpha$  to  $\beta$  during the poling process has been proposed [10]. Southgate [11] used a corona charging technique (at room temperature) to pole samples containing both  $\alpha$ - and  $\beta$ -forms. Changes in the infra-red spectrum were observed consistent with a decrease in the  $\alpha$  content and, after annealing, an increase in the  $\beta$  content. It has since been shown by X-ray

diffraction techniques that a conversion of the  $\alpha$ -form to the  $\beta$ -form during poling may take place via an intermediate polar  $\alpha'$ -form [12, 13] in which the unit cell dimensions are unaltered but the symmetry is changed by the rotation of alternate chains into a parallel, polar arrangement. It was also found that the observed increase in piezoelectric behaviour was consistent with the proposed structural change [12, 13].

However, to produce the structural changes mentioned above it was necessary to use very high corona or plasma fields which are likely to produce charge injection which may, in turn, give rise to local field perturbations, especially close to the film surfaces. In the present study an attempt has been made to correlate changes in the infra-red spectrum with the degree of poling. Also, by probing the structure close to the surfaces of the PVDF film using the ATR technique it has been possible to examine non-uniformity of poling and to establish the relevance of the interfaces to the poling process.

## 2. Experimental

The PVDF film used in this study was 25  $\mu\text{m}$  thick biaxially oriented capacitor-grade film supplied by the Kureha Chemical Company of Japan and was similar to that employed in previous work [12]. I.r. spectra and X-ray diffraction data indicated the presence of both  $\alpha$ - and  $\beta$ -forms. Test sheets of the polymer film were each furnished with five circular aluminium electrodes of 5 cm diameter by vacuum evaporation onto one side only. Corona charging was performed on the non-metallized film face at 20°C using apparatus described previously [12]. The samples were each charged for 5 min. Each sheet was subjected to either a series of positive or negative corona charging processes. One sample on each sheet was not charged and was a reference standard for subsequent infra-red spectroscopic examination. The other four samples were charged to 2.5, 5.0, 7.5 and 10 kV respectively. After charging, the samples were shorted for 24 h between aluminium plates.

The aluminium was dissolved from the films using concentrated sodium hydroxide solution at room temperature, and a 4 mm  $\times$  9 mm specimen was cut from the centre of each of the 5 previously metallized regions for attenuated total reflection (ATR) spectroscopic examination. The long axis of the specimen was along the roll

direction of the film. Care was taken to designate the "metallized" face of each sample. Infra-red ATR spectra were recorded from both faces of each specimen using an RIIC Micro-ATR Unit Type TR5 equipped with a KRS-5 (TlBr-TlI) prism. All infra-red spectra were taken with a Perkin-Elmer Model 137 spectrophotometer (range 4000 to 667  $\text{cm}^{-1}$ ); this instrument incorporates a sodium chloride prism monochromator and hence corrections for polarization were not required. Transmission infra-red spectra were obtained on areas close to the ATR specimens and with the roll direction of the film vertical in the sample holder.

The five samples were then remetallized on both faces with aluminium by vacuum evaporation. Strips  $\sim$  5 cm long by 1 cm wide were cut from each sample so as to include the regions used for the transmission infra-red spectra. The piezoelectric coefficients,  $g_{31}$ , were measured by vibrating the strips at 20 Hz under ambient conditions using a Brüel and Kjaer mini-shaker Type 4810 and monitoring both the voltage across the film faces and the force applied to the film. The force was measured by a Kistler 9203 quartz force transducer mounted in-line with the film and feeding a Kistler 5001 charge amplifier. The film voltage was measured using an Ancom 15A31 high impedance op-amp coupled with either a Tektronix 502A oscilloscope or a Bryans Southern Instrument Transcribe 10 double transient signal recorder.

## 3. Results and discussion

To illustrate the main i.r. bands of present interest in PVDF, Fig. 1 shows a transmission i.r. spectrum between 1500 and 700  $\text{cm}^{-1}$  for a 9  $\mu\text{m}$  biaxially oriented PVDF film. Spectral changes were found to occur on corona charging at both positive and

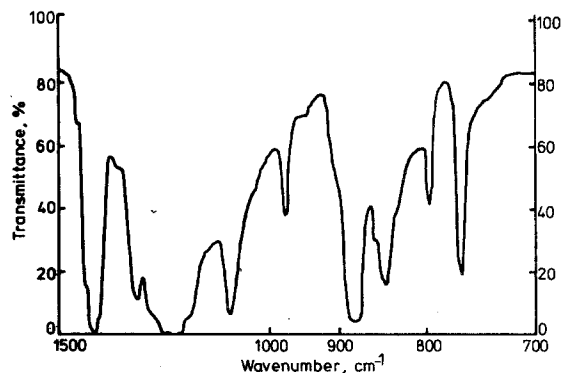


Figure 1 Transmission infra-red spectrum of 9  $\mu\text{m}$  biaxially oriented PVDF film.

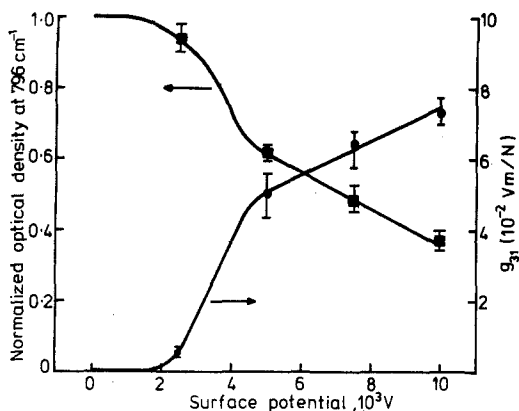


Figure 2 Normalized transmission optical density at  $796\text{ cm}^{-1}$ , and piezoelectric coefficient  $g_{31}$ , plotted against surface potential for  $25\text{ }\mu\text{m}$  biaxially oriented PVDF film.

negative potentials. The most significant changes were reductions in the bands at  $976$ ,  $796$  and  $765\text{ cm}^{-1}$ , in agreement with other workers [11, 13]. These three bands are due to the  $\alpha$ -form, corresponding to  $\text{CH}_2$  twisting,  $\text{CH}_2$  rocking, and a combination of  $\text{CF}_2$  bending and skeletal bending respectively [14]; their observed decrease after charging would suggest a decrease in the  $\alpha$ -form content.

The band at  $796\text{ cm}^{-1}$  was chosen for quantitative study. The optical density (OD) of this band was measured in the transmission mode for two series of positive and one of negative corona charging runs, and the results normalized by dividing by the OD of the PVDF reference standard. Fig. 2 shows the normalized optical densities as a function of charging potential. Also shown, for comparison, are the measured values of the  $g_{31}$  coefficient for the same samples. The bars indicate the spread of results obtained from the three runs. No difference was observed between corona charging with positive or negative potentials. It may be observed that the piezoelectric coefficient increases with charging potential in a manner similar to the decrease of the OD. The larger change occurs between potentials of  $2.5$  and  $5\text{ kV}$ , showing an interesting correlation with recent proposals for the formation of an intermediate polar  $\alpha$ -form [12, 13, 15].

Fig. 3 shows the ATR spectrum obtained from the face of a sample that had received corona charging to a potential of  $+10\text{ kV}$ . In Fig. 4 is shown the ATR spectrum of the same sample as in Fig. 3, but obtained on the face that was previously metallized and at earth potential.

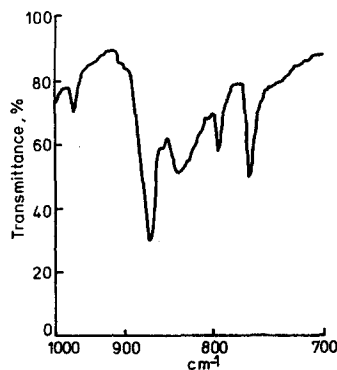


Figure 3 ATR spectrum of unmetallized surface after corona charging to a potential of  $10\text{ kV}$ .

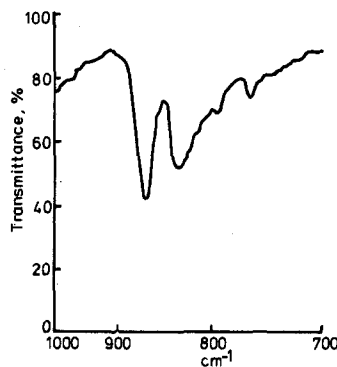


Figure 4 ATR spectrum of earthed surface of Fig. 3 specimen, after removal of Al metallization.

Differences in the bands assigned to the  $\alpha$ -form may readily be seen. To quantify the effect, the band at  $796\text{ cm}^{-1}$  was again chosen for study. The OD of this band was again normalized by division by the OD obtained from the ATR of the reference standard; in this way any marked extraneous effects due to initial differences in the  $\alpha$ -form content of the two faces of the starting material and the effects of aluminium metallization and subsequent dissolution were removed.

In the ATR technique the spectrum is obtained from a surface region of the sample. The depth of penetration ( $d_p$ ), defined as the distance required for the electric field amplitude of the internally reflected ray to fall to  $e^{-1}$  of its value at the surface, can be calculated [16] and is given by

$$d_p = \frac{\lambda_1}{2\pi (\sin^2\theta - n_{21}^2)^{1/2}} \quad (1)$$

where  $\lambda_1 = \lambda/n_1$  is the wavelength in the KRS-5 prism,  $n_{21} = n_2/n_1$  is the ratio of the refractive indices of PVDF and KRS-5, and  $\theta$  is the angle of incidence of the ray to the prism. In all the

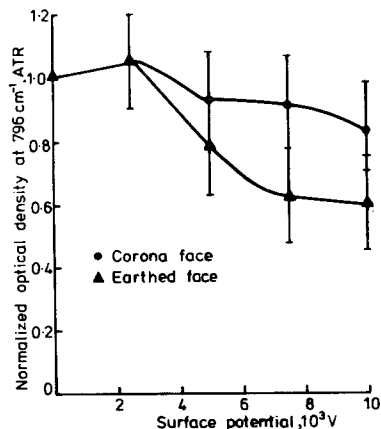


Figure 5 Normalized ATR OD at  $796\text{ cm}^{-1}$  for corona and earthed surfaces plotted against surface potential for positive corona.

ATR measurements  $\theta$  was chosen to be  $45^\circ$ . Using the values  $n_1 = 2.40$  and  $n_2 = 1.42$ , the depth of penetration at the wavelength  $\lambda = 12.6\ \mu\text{m}$  (corresponding to the band at  $796\text{ cm}^{-1}$ ) is found from Equation 1 to be  $2.2\ \mu\text{m}$ . Therefore the spectra in Figs. 3 and 4 are from surface regions representing about 10% of the sample thickness.

Fig. 5 shows the normalization OD of the  $796\text{ cm}^{-1}$  absorption band for both surfaces of the film as a function of charging potential for positive corona charges. By comparison with the transmission i.r. data given in Fig. 2 it may be observed that the changes in structure of the two surfaces are not so pronounced as those occurring in the bulk of the sample. In particular, the surface that received the corona charges undergoes little change compared to the original sample even at the highest potential, indicating a reduced field in the corona facing surface compared to the highest overall applied field of  $4 \times 10^8\ \text{V m}^{-1}$ .

The situation is not dissimilar for the case of negative corona as shown in Fig. 6, although the trends with increasing potential are not so clear and the behaviour of the corona face at lower fields appears to be anomalous. This latter effect may possibly be due to a different charge injection mechanism operating at the lower fields. However, the differences between the corona side, the earthed (metallized) side and the bulk for the highest potential are as significant as for the positive corona case, again showing a much greater change in the  $\alpha$ -form content near the earthed side than the corona side and indicating a non-uniform field distribution across the film during polishing.

There are a few earlier reports [6, 17, 19] on

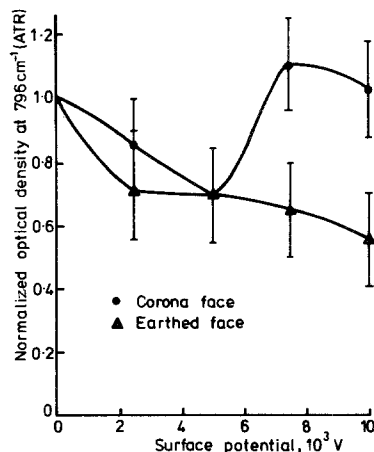


Figure 6 As Fig. 5, but for negative corona.

non-uniformity of charge distribution on poling thin films of PVDF, all referring to the use of conventional thermal poling techniques. Davis *et al.* [17], using a thermal pulse technique [18], reported non-uniformity in a copolymer of vinylidene fluoride and tetrafluoroethylene; however, they found evidence for a uniform distribution of charge in PVDF homopolymer. Day *et al.* [19] studied the responsivity and uniformity of polarization of PVDF pyroelectric detectors; they observed a high degree of non-uniformity of poling through the thickness of the sample at low poling fields ( $< 1.25 \times 10^8\ \text{V m}^{-1}$ ), but uniform poling of a  $6\ \mu\text{m}$  biaxially oriented Kureha PVDF film was obtained at fields greater than  $1.7 \times 10^8\ \text{V m}^{-1}$ .

It is possible that homocharge arising from ionized gases in the air (or their reaction products with atmospheric water) may be driven into the sample at high fields, so creating a non-uniform field distribution near the corona face. The predominant ions involved would be  $\text{CO}_3^-$  in the case of negative corona [20] and  $\text{H}^+(\text{H}_2\text{O})_n$  for positive corona [21] under ambient laboratory conditions.

#### 4. Conclusions

(1) It has been found that corona poling of biaxial PVDF film results in a decrease in  $\alpha$ -form crystallite content. This is probably accompanied by other structural changes [11] not investigated here.

(2) The change in  $\alpha$ -form content is markedly greater near the metallized (earthed) face than near the unmetallized (corona charged) face, indicating a non-uniform field in the specimen on poling.

(3) The piezoelectric coefficient  $g_{31}$  increases progressively with poling potential, concomitant with decline of the  $\alpha$ -content. This is consistent with a structural origin (orientation of dipoles) for the piezoelectric effect.

(4) The above results apply equally to positive and negative corona. This again suggests that the piezoelectric effect in PVDF is not primarily caused by the presence of residual injected charge, but is due rather to the field-induced orientation of molecular dipoles.

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