EFFECT OF HEXANE TREATMENT AND UNIAXIAL STRETCHING ON BENDING ELECTRICITY OF POLYVINYLIDENE FLUORIDE (PVDF)

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Abstract
The effect of hexane treatment and uniaxial stretching in polyvinylidene fluoride (PVDF) film was studied. The quantity, β_{31}, defined as the bending piezoelectric stress constant, was calculated. After hexane treatment and uniaxial stretching of the PVDF film, the value of β_{31} was 5.75 mV/m and 8.00 mV/m for draw ratio of 1.5 and 2.5 was recorded. Fourier transform Infra-red (FTIR) spectrophotometry was used for structural investigations.

Key words: Polyvinylidene fluoride (PVDF), bending piezoelectric stress constant β_{31}, Fourier Transform infra-red (FTIR) spectrophotometry, iodine doping, hexane treatment, uniaxial stretching.

1.0   Introduction

Piezoelectric and pyroelectric polymer electrets (Sessler,1987; Lang,1995) are found more and more in industrial applications . Interest in the electric properties of PVDF began in 1969 when Kawai (Kawai, 1969) showed that thin films that had been poled exhibited a very large piezoelectric coefficient (Kepler and Anderson,1978 ; Luongo,1972) pCN-1, a value which is about ten times larger than had been observed in any other polymer.

PVDF has the advantage of long term stability of its piezoelectricity at room temperature and its mechanical flexibility. Bending (or flexure) piezoelectricity in poled polymer films has been investigated by several authors (Furukawa et al.,1968;Kawai and Heiji,1970;Ibe,1974;Furukawa, 1976; Fukada et al., 1987). These studies were arrived at by determining the piezoelectric activity induced by bending deformation of polymer. While tensile piezoelectricity has been investigated in detail, the origin of bending piezoelectricity is not yet fully understood. When a poled polymer film is subjected to bending deformation, the electrical displacement consists of two components, one proportional to stress (as in the case of elevation) and the other proportional to the stress gradient (Litt et al., 1977; Zoon and Zoon and Liu, 1978; Lang,1974).

The latter effect is characterized by a bending piezoelectric strain constant b31 which depends on the structure of the polymer (Kawai and Heiji, 1970). Commercial polymer films contain various impurities such as antioxidants, residual catalysts, phenanthrene, benzoic acid, aromatic ketone such as benzophenone and some impurities introduced during manufacturer (Umemura et al., 1982; Ronarch and Haridoss, 1981). Hexane has been shown to have greatest permeation rate through polyethylene (Ronarch and Hridoss, 1981). Also it is established that the steady state electrical conductivity in polyethylene is significantly reduced on hexane treatment possibly because of a reduction in the density of impurity hopping sites for the charge carriers (Foss and Dannhauser,1963).

Here we have carried out investigations on untreated and hexane treated PVDF films with the aim of determining the effect of β31 on bending piezoelectricity.

Changes in voltage against film bending have been used to establish the effect of the β31on the induced current.

1.1   Experimental

Commercial PVDF film of 40mm thickness were obtained from Kureha Industrial Chemical Company; Japan.

Hexane treatment was performed by keeping the PVDF sample in hexane for 24 hours at room temperature. Aluminium electrodes of thickness about 500 Å were vacuum deposited on one surface of the virgin and hexane treated samples.

Fourier transform infra-red (FTIR) spectra of the virgin and hexane treated PVDF films were recorded using a Shimadzu FTIR–8400 Fourier transform infra-red spectrophotometer.

Uniaxial stressing of the samples was performed with the aid of a film stretching frame shown in Fig. 1. Sample specimens of sizes 44 mm x 7 mm were locked at the grips of the stretching frame before being extended. 2 mm portions of the sample under grips were covered by emery cloth to improve the gripping and to prevent heat damage from the hot metal grips. The frame was then placed in an air circulated oven set at 45oC, 55oC and 65oC. The same were left to heat for 5 minutes after which the oven door was partially open and sample stretched at ratios 1.5, 2.0 and 2.5 for the temperature settings of 45oC, 55oC and 65oC respectively by rotating the lever arm of the frame. The samples were then left to cool while under tension.
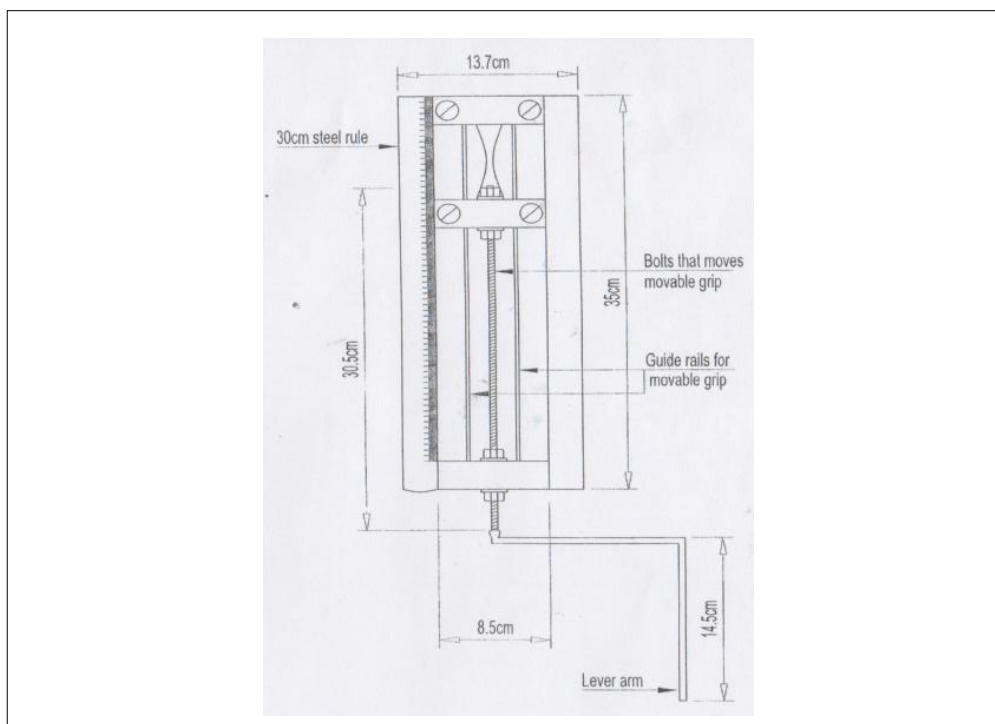

Figure 1: The film-stretching frame

The experiments for the determination of β31 values were carried out under room temperature using horizontal deflection of the lower end of the film by eccentrically rotating the micrometer screw gauge. Piezoelectric bending measurements were carried out using a cantilever beam of length 1, width w and thickness t. Deflection D2 is imposed at the end of the beam as shown in Fig. 2.
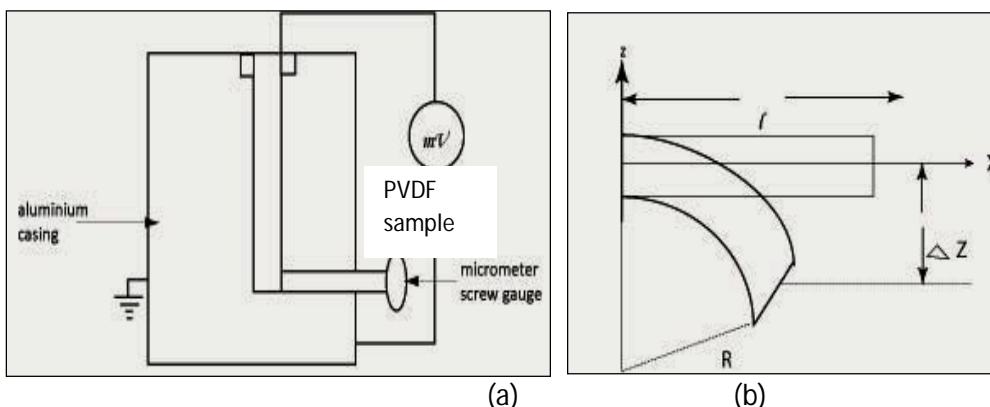
(a)   (b)

Fig 2. (a) Schematic diagram of the measuring device and (b) geometry of the
experiment cantilever beam of length l and thickness t deflected by ΔZ

The induced electric displacement D3 in the direction of the Z axis is given by

$$D_3 = \epsilon_3 E_3 + \beta_{31} (1/R) \dotfill (1)$$

$$\frac{d D_3}{dz} = \overline{\varepsilon_3 E_3} + \beta_{31} \left(\frac{1}{R}\right) \dotfill (2)$$

Where E3 and ε3 are the z-direction components of electric field intensity and the permittivity of the PVDF film, respectively, and R is the radius of curvature of the displacement D. Since 1/R is equal to the thickness gradient of the strain in x–direction, dDs/dz. the quantity b31 is defined as the bending piezoelectric stress constant. In a non-uniform polarized dielectric Gauss's law dD3/dz=0 yields D3 = constant while E3ε3 must be replaced by the average E3 ε3. For constant ε3 and under short-circuit conditions E3 ε3 = 0 and one obtains the electrode charge induced by bending as . Since for small deflections,   one obtains

$$\beta_{31} = \frac{l}{2w} \left(Q/\Delta Z\right) \dotfill (3)$$

But the induced charge Q is proportional to the voltage V, i.e, so that

$$\beta_{31} = \frac{l}{2w} . k. \frac{V}{\Delta Z}, \dotfill (4)$$

where k is a constant

Hence $\beta_{31} = constant \times V/\Delta Z$ $\dotfill (5)$

The deflection DZ of the sample was measured and the corresponding value of

voltage v was noted. This was repeated for several values of deflection DZ.

2.0   Results and Discussion

Figure 3(a) and Figure 3(b) show the FTIR scans for virgin and hexane treated PVDF films, respectively. Weak peaks in the virgin sample (Figure 3(a)) are eliminated with hexane treatment (Figure 3(b)).
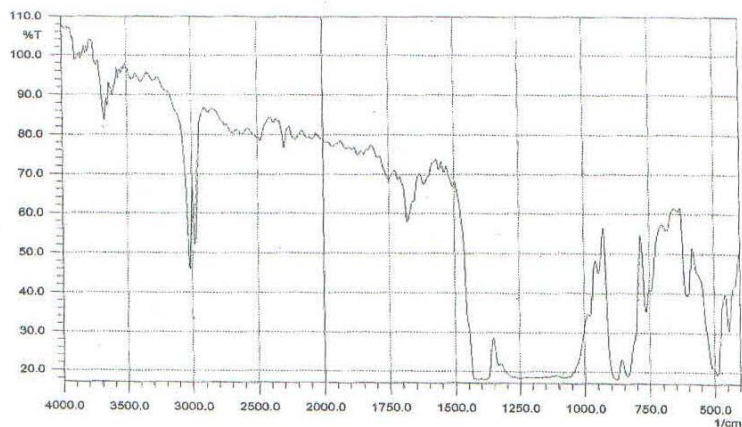

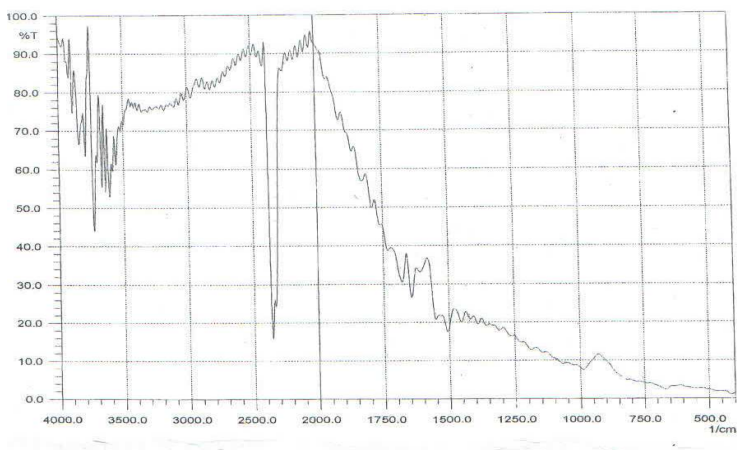*Figure 3(a): FTIR spectrum of virgin PVDF sample*

Figure 3(b): FTIR spectrum of hexane treated PVDF sample

Therefore these peaks probably belong to the impurities present in the sample. The impurities could be low molecular weight hydrocarbons, antioxidants and other impurities introduced during the manufacturing process. The exact nature of impurities reached out is uncertain (Umemura *et al.,* 1982; Ronarch and Haridoss, 1981). A shift of 3019.4 cm^{-1} peak towards lower wave number is observed after hexane treatment.
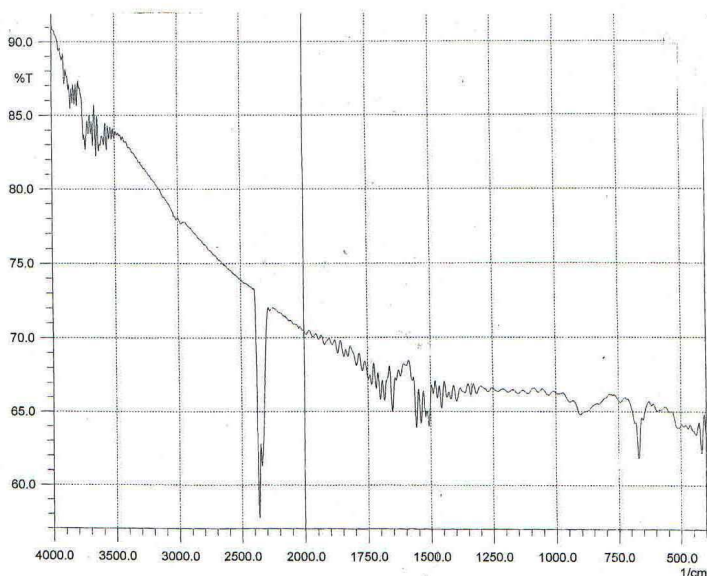
Figure 4:   FTIR spectrum of hexane treated and stretched virgin PVDF sample at 45°C and a stretching ratio of 2.5

Figure 4 show FTIR spectrum of hexane treated and stretched PVDF sample at a temperature of 45oC and a stretching ratio of 2.5. Absorption peaks at 3650 and 1653cm-1 were observed while weak peaks were eliminated. The disappearance of these peaks can be attributed to both hexane treatment and stretching.
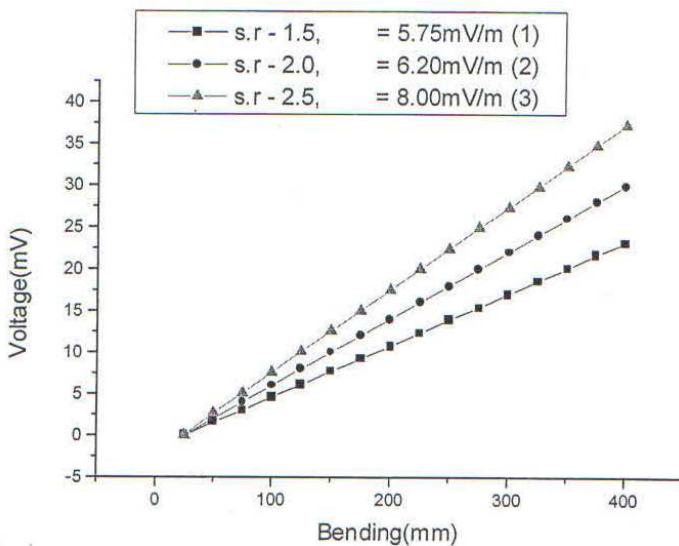

Figure 5:   Graph of change in voltage against bending for unpoled stretched PVDF sample at 45°C and stretching ratios 1.5, 2.0 and 2.5

Figure 5 shows a comparison of a change in voltage against bending for a stretched PVDF sample at 45oC with varying stretching ratios of 1.5, 2.0 and 2.5 (plots 1, 2 and 3 respectively). An increase of 2.25 in b31 was observed in plots 1 and 3 respectively.
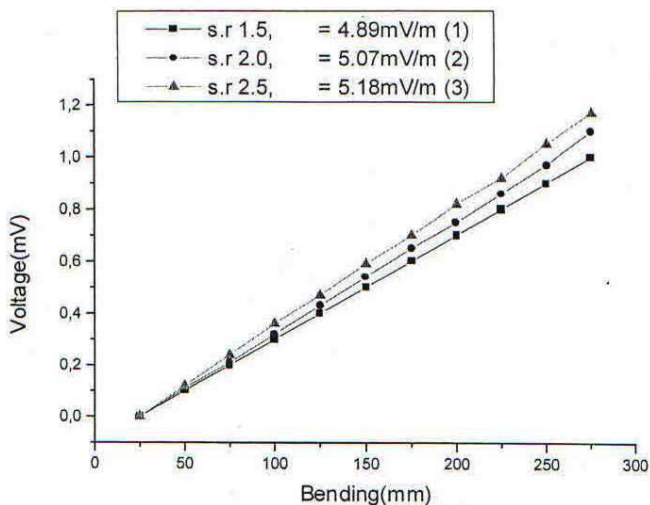

Figure 6: Graph of change in voltage against bending for unpoled stretched PVDF sample at 55ºC and stretching ratios 1.5, 2.0 and 2.5

Figure 6 shows a change in voltage against bending for a stretched PVDF sample at a temperature of 55oC and at stretched ratios of 1.5, 2.0 and 2.5 (plots 1, 2 and 3 respectively). The b31 varied from4.89 mV/m (Plot 1) to 5.18 mV/m (Plot 3).
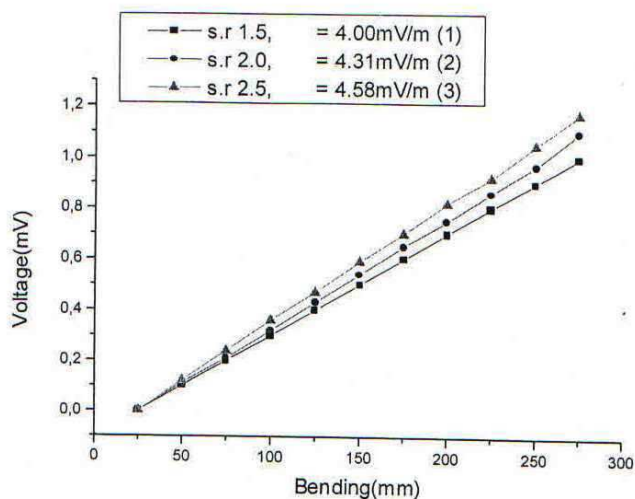

Figure 7: Graph of change in voltage against bending for unpoled stretched PVDF sample at 65ºC and stretching ratios 1.5, 2.0 and 2.5

Figure 7 shows a comparison of a change in voltage against bending for a stretched PVDF sample at 65oC with varying stretching ratios of 1.5, 2.0 and 2.5, plots 1, 2 and 3 respectively. The b31 varied from4.00 mV/m (plot 1) to 4.58 mV/m (plot 3).

3.0   Conclusion
Hexane treatment and uniaxial stretching greatly increases the b31 in polyvinylidene fluoride. The elimination of weak peaks and the shift of 3019.4 cm-1 peak towards lower wave number can be attributed to hexane treatment. b31 is optimum at temperature of 45 oC and increases with increase in draw ratios for different temperatures.

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