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Piezoelectric Effect in Oriented Polyvinylchloride and Polyvinylflouride

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The direct piezoelectric effect has been observed in roll-elongated films of polyvinylchloride and polyvinylfluoride. The effect was produced by applying tensile stress to a clamped specimen at a fixed frequency of 20 Hz. The piezoelectric modulus g_{31} was determined to be 0.2 to 0.7 V m^{-1}/N m^{-2} in polyvinylchloride; in polyvinylfluoride $g_{31} \simeq 0.2$ V m^{-1}/N m^{-2} and $g_{32} \simeq 1$ V m^{-1}/N m^{-2}. The piezoelectric effect in these films is believed to be due to mechanical distortion of oriented dipoles, resulting from the tensile stress, and the orientation appears to differ in the two materials.

INTRODUCTION

Piezoelectricity was discovered by Pierre and Jacques Curie[1] nearly a century ago. They observed the effect in many crystals such as sodium chlorate, cane sugar, quartz, and rochelle salt, and subsequently numerous studies were made. Nevertheless, some 60 years elapsed before it was recognized that piezoelectricity could occur in other than single crystals, and the effect was demonstrated in high polymers, specifically wool keratin[2] and wood cellulose.[3]

To date, most of the work on piezoelectricity in polymers has been made on other naturally occurring biopolymers, e.g., silk fibroin[4] and bone and tendon collagen.[5] Synethetic polypeptides also have been studied.[5] These investigations have provided useful information such as the form of the piezoelectric tensor, structure, and biological processes. On the other hand, the piezoelectric moduli are generally very small and the materials not useful for engineering applications. A few measurements have been reported also on commercially available polymers.[6,7]

Recently we undertook investigations of piezoelectricity in polymers with a view towards eventual applications, e.g., as underwater transducers and physiological sensors. In bulk polyvinylchloride, electrical poling techniques were developed which resulted in activity approaching that of quartz, and its use as an underwater sound receiver was demonstrated.[8] In untreated, commercial polyvinylchloride films, the activity was found to be significant.[9] This paper reports on the attainment of substantial piezoelectricity in films of polyvinylchloride and polyvinylfluoride, previously inactive, after orientation by simple rolling; the dipole orientation appears to differ in the two materials.

EXPERIMENTAL

Samples were rectangular strips of commercially available polyvinylfluroide (Dupont's "Tedlar") and plasticized polyvinylchloride (Union Carbide). The PVF film had been cast and the PVC had been rolled during manufacture. The thicknesses of different samples of the former ranged from 0.043 to 0.13 mm, and those of the latter from 0.013 to 0.051 mm; in both cases the length (when tested between clamps) was 25 mm and the width 5 mm. Electrodes, applied to both lateral faces, were either evaporated silver or tin foil attached with dilute rubber cement, and there was no noticeable difference in their behavior. Connecting electrodes were No. 40 copper wires secured with dots of silver paste.

A rectangular coordinate system was assigned to the films. The direction of rolling is the 1 axis, which probably is also the direction in which the molecules, but not necessarily the dipoles, are oriented. The 2 axis is perpendicular to it and lies in the plane of the film; the 3 axis is perpendicular to both the 1 axis and the film plane.

The appropriate basic equation[10] of the direct piezoelectric effect is

$$E = -gT + \beta^T D.$$

An electric field E is produced by applying a stress T. The coefficient g is the piezoelectric stress modulus, β^T is the dielectric impermeability (the reciprocal of dielectric susceptibility) at constant stress, and D is the electric displacement. If E is measured under open-circuit conditions, D vanishes and the piezoelectric stress modulus can be determined from from the relation $g = -E/T$.

The direct piezoelectric effect is produced by applying an oscillatory stress to a clamped specimen along its length, and Fig. 1 is a sketch of the apparatus used. The film was clamped at both ends between spring-loaded Teflon jaws: one jaw was fas-

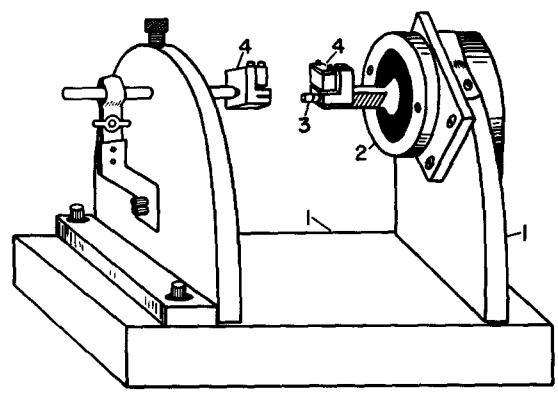

FIG. 1. Sketch of apparatus for producing direct piezoelectric effect in polymer films. (1) Brass frame; (2) shaker; (3) calibrated accelerometer; (4) spring-loaded Teflon jaws.

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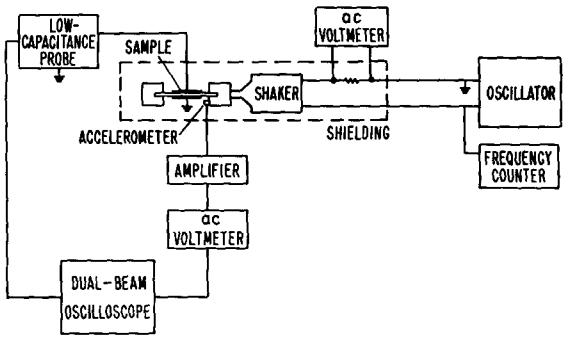

FIG. 2. Block diagram of apparatus for determination of the g modulus of polymer films.

tened to the center of the shake table of an electromagnetic shaker and the other jaw to an adjustable frame to provide suitable tension to the film.

The force exerted by a shaker on an external load is[11]

$$F = \alpha i + \beta v,$$

where αi is the total force developed by the shaker and βv is the force required to drive the internal impedance of the shaker. The internal impedance includes all impedances on the shaker side of the point where the load is attached.

The force exerted by the shaker on a mass m_1 is

$$m_1 \dot{v}_1 = \alpha i + \beta v_1,$$

where v is the velocity, i is the current in the voice coil, and α and β are constants. Similarly for a mass m_2,

$$m_2 \dot{v}_2 = \alpha i + \beta v_2,$$

where constant sinusoidal current is maintained. Solving for the constants,

$$\alpha = \dot{v}_1 \dot{v}_2 (m_1 - m_2)/(\dot{v}_2 - \dot{v}_1) i,$$

$$\beta = \omega(\dot{v}_2 m_2 - \dot{v}_1 m_1)/(\dot{v}_2 - \dot{v}_1),$$

where $\omega = 2\pi$ frequency. Thus, to calibrate the shaker, constant coil current was maintained and with different known masses in the shake table, corresponding accelerations were measured by means of a calibrated accelerometer cemented to the vibrating Teflon jaw.

Figure 2 is a block diagram of the measurement apparatus. The shaker, driven at a fixed frequency of 20 Hz, imparted a sinusoidal stress to the sample. This produced a piezoelectric voltage with the same frequency as the shaker, and the open-circuit voltage was determined with the use of the oscilloscope. The current in the voice coil was kept at the value used during the calibration of the shaker so that the force exerted could be calculated from the reading of the calibrated accelerometer.

RESULTS

Our previous work[9] on untreated polyvinylchloride films showed the g modulus to be large and suggested that dipole orientation was established by the rolling operation during manufacture. It was of interest, therefore, to investigate this premise.

Samples of polyvinylchloride were first heated at 75–80 °C for 1 h, and this was found to sufficiently remove the orientation so that piezoelectricity could not be observed. The samples were then cold rolled with a mill to a thickness of from one-third to two-thirds the original value. Some samples were not previously heated, but rolled only. After electroding, tests for piezoelectricity were made. The results are given in Table I, and our previous results[9] are included for comparison.

No piezoelectricity could be observed from untreated polyvinylfluoride tested in any orientation. A section of the same sheet was rolled (to one-fourth the original thickness) and four samples, two with the length parallel to the direction of roll and two perpendicular, were prepared. Considerable piezoelectric activity was obtained, and the results are given in Table I.

The g values obtained here are comparable to or larger than those of conventional piezoelectric materials such as ADP and Rochelle Salt.[12] Further, some are up to three times those reported by Kawai[7] for PVC and PVF after a complicated orientation procedure.

The piezoelectricity is believed due to the distortion of oriented dipoles, resulting from tensile stress. In PVC the dipoles in the molecular chains appear to become oriented in the direction of roll because little activity could be obtained in samples prepared with the length perpendicular to the direction of elongation, and maximum activity was obtained in samples in which the length and direction of elongation were parallel. In PVF, however, there appears to be considerable dipole orientation normal to the roll direction and in the plane of the film. Perhaps the apparent orientational difference between the two materials is associated with their structural differences, e.g., PVC is considered essentially amorphous and PVF highly crystalline.

TABLE I. Measured values of the piezoelectric moduli, g_{31} and g_{32} of polyvinylchloride and polyvinylfluoride films.

Sample		Film thickness (mm)	g_{31} ($V\,m^{-1}/N\,m^{-2}$)	g_{32} ($V\,m^{-1}/N\,m^{-2}$)
Polyvinyl-chloride	untreated	0.13	0.4–3	0
	heated	0.13	0	0
	heated, then rolled	0.046–0.089	0.2–0.7	slight
	rolled	0.043	0.3	slight
Polyvinyl-fluoride	untreated	0.051	0	0
	rolled	0.013	0.1–0.2	0.9–1

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