

PIEZOELECTRIC FLEXURE ELEMENT AND METHOD OF MANUFACTURE

The present invention relates to single layer polymeric piezoelectric flexure elements and to a method in increasing the flexure mode activity of such elements.

Conventional piezoelectric flexure elements typically comprise a plurality of layers of material of differing piezoelectric activity. Under the application of an external field across the thickness of such a device, small expansions and/or contractions in the planes of opposing layers are converted into relatively large deflections of the layers out of their planes. Alternatively, if an external force is applied to the device causing it to flex, a voltage is generated across the layers of the device. Piezoelectric flexure mode devices are used both as electrical-to-mechanical and mechanical-to-electrical transducers in such diverse applications as speakers, microphones, phonograph cartridges, motors, and accelerometers.

Conventionally, piezoelectric flexure mode devices are manufactured by separately uniformly poling individual sheets of piezoelectric material, then bonding the sheets together using an adhesive. This technique has long been employed for making flexure mode devices from piezoelectric ceramic materials such as lead zirconate titanate (PZT). For more information on the structural details of such devices and some of their various uses, reference may be made to the article by C.P. Germano entitled "Flexure Mode Piezoelectric Transducers", IEEE Transactions on Audio and Electro-acoustics, Vol. AU-19, No. 1, March 1971.

In recent years, considerable effort has been expended in making piezoelectric flexure elements from

various polymeric materials, such as polyvinylidene fluoride (PVF_2), which exhibit, when suitably poled, exceptionally high piezoelectric activity. As plastics, such materials are very attractive because well developed plastic manufacturing technologies may be adapted to their economical manufacture. However, as plastics, such materials are difficult to bond together, and moreover, problems in proper matching of the mechanical impedances of the adhesive and the polymeric piezoelectric material have been encountered.

One way of overcoming the above-mentioned bonding problem is disclosed in U.S. Patent No. 2,659,829 which uses the technique of non-uniformly poling a single sheet of piezoelectric material so that it behaves like a unimorph or bimorph. A slab of piezoelectric material is first poled uniformly in one direction, then the poling is relaxed in a portion of the thickness of the slab by propagating a thermal pulse to a limited depth that momentarily raises the temperature of the material above the Curie point. The resulting structure comprises a continuous slab of material having layers of different piezoelectric activity within the continuous slab. It resembles a conventional monomorph, with one layer piezoelectrically active and another layer substantially inactive. In a further embodiment, the slab is then subjected to a poling field of the opposite polarity and of such a strength so as to polarize the unpoled material but not to reverse the polarity of the already poled portion of the material. The result is a device similar to a conventional bimorph, having two layers poled in opposite directions in one continuous slab of material.

If this technique could be applied to polymeric piezoelectric materials to produce a multilayer structure in a continuous body of material, the bonding problems could likewise be resolved. Unfortunately, polymeric piezoelectric materials such as PVF₂ do not exhibit a true Curie point below the melting point of the polymer. When the thermal depolarization technique is attempted, all that results is a molten blob of plastic.

- 10 Some observers have noted that single films of PVF₂, poled under certain conditions of electric field and temperature, exhibit flexure mode behaviour attributable to a nonuniform distribution of piezoelectric activity across the thickness of the
- 15 film (see the article by H. Sussner and K. Dransfeld entitled "Importance of the Metal-Polymer Interface for the Piezoelectricity of Polyvinylidene Fluoride", Journal of Polymer Science: Polymer Physics Edition, Vol. 16, 529-543, (1978), John Wiley & Sons, Inc.).
- 20 However, the nonuniformly poled polymeric piezoelectric material produced thereby, although exhibiting some flexure mode behaviour, is not nearly as active in the flexure mode as those devices produced by bonding multiple layers of differently poled
- 25 material.

It is, therefore an object of the present invention to provide a method of nonuniformly poling polymeric material, such as PVF₂, so that its piezoelectric flexure mode activity is substantially

30 increased over that observed in the prior art.

According to the present invention there is provided a homogeneous polymeric piezoelectric material non-uniformly poled across its thickness wherein the direction of polarisation of the more strongly polarised portion of the material is inward.

The invention also provides a homogeneous piezoelectric material non-uniformly poled across its thickness wherein the polarisation directions in both halves of the material are inward.

10 The invention also provides a method of poling a sheet of polymeric material to render it non-uniformly piezoelectrically active, comprising applying an electric field across the thickness dimension of the sheet for a predetermined time and simultaneously
15 heating one surface and cooling the opposite surface to maintain a temperature gradient and to induce non-uniform poling across the thickness dimension of the sheet.

Also provided is a piezoelectric flexure element obtainable by the process of:

20 (a) applying an electric field across the thickness dimension of a sheet of polymeric material for a predetermined time, and

(b) simultaneously heating one surface and cooling the opposite surface so as to establish a
25 temperature gradient between the surfaces and to induce non-uniform poling across the thickness of the polymeric sheet.

The present invention will now be described, by way of example, with reference to the accompanying drawings, in which:-

30 Fig. 1 is a schematic diagram of apparatus for poling samples of polymeric piezoelectric material according to the methods of the present invention;

Fig. 2 is a schematic diagram showing the testing procedure employed to evaluate flexure mode activity of samples poled in the apparatus shown in Fig. 1;

Fig. 3a illustrates the poling conditions for a comparative example using no temperature gradient;

Fig. 3b is an enlarged schematic partial cross section of a sheet of a polymeric piezoelectric material poled according to the comparative example;

Figs. 4a-7a illustrate poling conditions for a series of samples of polymeric piezoelectric material poled in temperature gradients according to the methods of the present invention; and

Figs. 4b-7b are enlarged schematic partial cross sections of the samples of piezoelectric polymeric material poled according to the present invention under the conditions shown in Figs. 4a-7a respectively.

The apparatus shown in Fig. 1 includes a press, generally designated 10, having an upper platen 12 and a lower platen 14. The lower platen 14 is moved towards the upper platen 12 by a hydraulic jack 16. The temperatures of the upper and lower platens 12, 14 are independently controllable by a temperature control unit 18. The upper and lower platens 12, 14 are equipped with electrical heating elements 20 and 22 respectively and cooling tubes 24 and 26 respectively for circulating cooling fluid (e.g. chilled water). The temperature control unit 18 maintains the temperature of the respective platens 12, 14 at a desired level by supplying controlled amounts of electric current to the heaters 20, 22 and/or cooling fluid to the cooling tubes 24, 26.

A pair of poling electrodes 28 and 30, each comprising a $2 \times 2 \times \frac{1}{2}$ inch thick block of stainless steel, are disposed between the two platens 12, 14 and electrically insulated therefrom by spaced blocks of alumina 32 and 34. The alumina blocks 32, 34 provide good electrical insulation and at the same time are good thermal conductors. A sample (in sheet form) of polymeric piezoelectric material 36 is clamped between the electrodes 28 and 30. The material contacting surfaces of the electrodes 28, 30 are finished to optical flatness to ensure uniform thermal and electrical contact with the material sample. A poling field is established across the electrodes 28, 30 by a high voltage power supply 38.

Samples of polymeric piezoelectric materials poled in the apparatus described with reference to Fig. 1, are tested in the apparatus schematically illustrated in Fig. 2 to determine the extent of their flexure mode activity. A rectangular strip 40 of material approximately 3 mm x 40 mm is cut from the poled piezoelectric material 36. Aluminium electrodes 42 and 44 are deposited on the top and bottom surfaces, respectively, using standard aluminium vapour deposition techniques. One end of the resulting structure is clamped in a fixture 46 to form a cantilever piezoelectric flexure (i.e. bender) element. A voltage of alternating polarity is applied across the piezoelectric material by connecting a 300 volt AC power supply 48 across electrodes 42 and 44, thereby causing the bender 40 to deflect up and down as indicated by dotted lines in Fig. 2. The maximum deflection δ produced at the tip of the bender 40 is measured to determine the flexure mode activity of the poled sample.

The deflections produced by samples poled under various poling conditions are compared with the predicted deflection of a theoretically perfect bimorph having zero bonding layer thickness.

The theoretical deflection at the free end of such a perfect bimorph is given by:

$$\delta = 3/2 d_{31} V L^2 / t^2 \quad (1)$$

where:

δ is the deflection;

d_{31} is the piezoelectric constant that defines the strain produced in the plane of the material by an electric field perpendicular to the plane of the material;

V is the applied voltage;

L is the length of the flexure element; and

t is the overall thickness.

After a sample is tested according to the procedure described above to determine δ , equation (1) is solved for d_{31} to yield an effective d_{31}

(d_{31}^{eff}) that can be compared to the (d_{31}^{eff}) of other samples produced under various poling conditions.

In the following examples a series of samples of 90 μ m thick, uniaxially stretched PVF₂ film made from "Kynar 961" brand PVF₂ (Kynar is a trade mark of the Pennwalt Corporation) were poled in a field of 0.5 megavolt/centimeter under various temperature conditions and for various times to render them piezoelectrically active. After the samples were poled, they were tested for flexure mode activity by the method described above with reference to Fig. 2. A d_{31}^{eff} for each sample was

computed from the test results for comparison with the other samples.

Example 1

To establish a basis for comparison with samples prepared according to the method of the present invention, a first sample was poled for sixty minutes in one direction at a uniform temperature of 90°C.

Fig. 3a illustrates these poling conditions. The solid line indicates the field polarity of the top poling electrode with respect to the bottom poling electrode, and the temperatures of the top and bottom surfaces of the sample are indicated above and below the time axis, respectively. After poling, the poling field was removed and the sample returned to room temperature. The sample was then prepared and

tested for flexure mode activity, yielding a d_{31}^{eff} of 2.1×10^{-12} meters/volt (m/V), indicating some nonuniformity in the poled material. Fig. 3b

depicts a partial cross section of the material 40 poled according to Example 1. The arrows 50 and 52 are intended to indicate, in a qualitative way, the average piezoelectric activity in the top and bottom halves of the sample, respectively.

Arrows 50 and 52 are shown pointing the same direction, indicating that the polarity of piezoelectric activity is the same throughout the sample, the different length arrows indicating the existence of flexure mode activity. For piezoelectric material poled asymmetrically in one direction, any piezoelectric activity in the weaker half of the material will cancel part of the piezoelectric activity contributing to bending in the stronger half of the material.

Example 2

A second sample, prepared in accordance with the methods of the present invention, was poled for 30 minutes in one direction in a temperature gradient of 35°C. The top poling electrode was maintained at 55°C and the bottom poling electrode at 90°C. The poling conditions are illustrated in Fig. 4a. The poled sample was tested for flexure mode activity and found to have a d_{31}^{eff} of 6.2×10^{-12} m/V, an almost three-fold improvement over the comparative example (Example 1). Fig. 4b depicts the average piezoelectric activity in the top and bottom halves of a portion of the poled sample. As shown in Fig. 4b, the nonuniformity between the top and bottom halves is very pronounced, the strongest activity occurring in the portion of the material maintained at a lower temperature during poling. The activity in the portion maintained at a higher temperature is very small or nonexistent.

Example 3

A third sample, was prepared in the same manner as Example 2 with the exception that the temperature gradient across the material was in the opposite direction, with the relatively cold side being on the bottom and the relatively hot side, on top as illustrated in Fig. 5a. The poled sample, when tested for flexure mode activity, was found to have a d_{31}^{eff} of -5.9×10^{-12} m/V. The minus sign (-) in d_{31}^{eff} indicates that the sample bent in the opposite direction from the sample in Example

2. Fig. 5b depicts the average piezoelectric activity in the top and bottom halves of a portion of the sample. Again, most of the piezoelectric activity is concentrated in a portion of the material maintained at a lower temperature during poling. This configuration of nonuniformly poled polymeric piezoelectric material, i.e. with the direction of polarization of the more strongly polarised portion of the material being inward, rather than outward, is considered to be a novel structure.

Example 4

A fourth sample was similarly prepared by first poling in one direction for 30 minutes in a 35°C temperature gradient (as in Example 2), then reversing the poling field and the temperature gradient and poling for an additional 30 minutes. The temperature gradient and poling field were reversed by removing the sample from the apparatus and turning it over. These poling conditions are depicted in Fig. 6a. The poled sample was tested for flexure mode activity and found to possess a d_{31}^{eff} of 10.9×10^{-12} m/V, which is a very high flexure mode activity in a single sheet of nonuniformly poled polymeric piezoelectric material. Fig. 6b depicts the average piezoelectric activity in the top and bottom halves of a portion of the sample.

Example 5

Finally, a sample was prepared by poling in one direction for 30 minutes in a 35°C temperature gradient, then reversing the polarity of the field and the temperature gradient and poling for another 30 minutes, similar to Example 4, with the difference

that the direction of the temperature gradient and the poling field, respectively, were 180° out of phase with those employed in Example 4. The poling conditions are illustrated in Fig. 7a. The poled sample was tested and found to have a d_{31}^{eff} of -10.4×10^{-12} m/V; the minus sign (-) indicating that the sample bent in the opposite direction from the sample of Example 4. Fig. 7b depicts the average piezoelectric activity in the top and bottom halves of the sample. This configuration of poled polymeric piezoelectric material, i.e. with the polarisation directions in both halves of the material pointing inwardly, rather than outwardly, is considered to be novel.

Other experiments were performed with temperature gradients in the range of 20° to 60°C with lower temperatures in the range of 25° to 70°C . Poling fields between .80 and .25 MV/cm were employed. In all cases, the portion of the sample maintained at the lower temperature during poling was observed to be the most piezoelectrically active, independent of the direction of the poling field. Subsequent reversal of the poling direction and the temperature gradient invariably yielded an improvement of nearly a factor of two in flexure mode activity.

A plausible mechanistic explanation for the nonuniform poling produced by the temperature gradient poling method of the present invention is based on temperature dependent electrical conductivity in the piezoelectric material. Because of the temperature gradient, the electrical conductivity across the sample is highly nonuniform. When the

poling field is applied, the nonuniform conductivity causes the poling field inside the material to be highly nonuniform, concentrating the field in the colder, and hence less conductive, portion of the material. Typically, the conductivity of a polymeric piezoelectric material is temperature dependent only above its glass transition temperature (T_g). T_g for PVF_2 is approximately -40°C . According to the theory advanced above, this would imply a lower limit (T_g) on the poling temperature of a polymeric piezoelectric material. Furthermore, a polymeric piezoelectric material generally cannot be effectively poled at or near its melting temperature (T_m), thereby imposing an upper limit on poling temperature. T_m for PVF_2 is approximately 160°C . The maximum temperature gradient in which a polymeric piezoelectric material could be poled, is therefore $T_m - T_g$, with one side of the material at T_m and the other at T_g . In practice however, very large temperature gradients, of the order of 200°C , are difficult and costly to maintain and are not expected to yield significant improvements over more moderate temperature gradients.

It is presently believed that the practical upper operating limit on temperature gradient for nonuniformly poling a polymeric piezoelectric material according to the present invention is about 100°C .

On the other hand, if the temperature gradient is too small, the mechanism of temperature dependent conductivity in the polymeric piezoelectric material will not produce significant nonuniformity in the poling field within the material. It is therefore presently believed that the practical lower operating limit on temperature gradient for nonuniformly poling a polymeric piezoelectric material

according to the present invention is about 10°C. The preferred range of temperature gradients is 20°C to 60°C with the lower temperature in the range between 25°C and 70°C and no higher than 75°C.

5 The invention has been described with reference to preferred embodiments, however changes and modification may be made within the spirit and scope of the appended claims. For example, the invention has been described mainly with respect to embodiments employing poling
10 for given times in one direction then reversing the poling field and temperature gradient and poling in an opposite direction for an equal time. Unequal times in opposite directions and different temperature gradients and/or poling fields could likewise be
15 employed according to the methods of the present invention.

 The temperature gradient could be maintained during poling by means other than a press with temperature controlled poling electrodes. For example,
20 polymeric piezoelectric material could be poled according to the present invention by depositing thin electrodes on the material prior to poling and then using the deposited electrodes as poling electrodes. The temperature gradient could be maintained by
25 blowing relatively hot air onto one electrode and relatively cold air on the other.

 Furthermore, although the invention was described with reference to PVF₂, any other known polymer having piezoelectricity may be used, for
30 example, a copolymer of vinylidene fluoride and a monomer polymerizable with vinylidene fluoride, such as tetrafluoroethylene, vinylidene fluorochloride, trifluoroethylene, vinyl fluoride, chlorotrifluoroethylene, or propylene hexafluoride.



Claims

- 1 A homogeneous polymeric piezoelectric material non-uniformly poled across its thickness wherein the direction of polarisation of the more strongly polar-
5 ised portion of the material is inward.
- 2 A homogeneous polymeric piezoelectric material non-uniformly poled across its thickness wherein the polarisation directions in both halves of the material are inward.
- 10 3 A method of poling a sheet of polymeric material to render it non-uniformly piezoelectrically active, comprising applying an electric field across the thickness dimension of the sheet for a predetermined time and simultaneously heating one surface and cooling the opposite sur-
15 face to maintain a temperature gradient and to induce non-uniform poling across the thickness dimension of the sheet.
- 4 The method as claimed in claim 3 wherein the temperature gradient is within the range of 10°C to 100°C.
- 5 The method as claimed in claim 3 or 4 wherein
20 the temperature gradient is greater than 20°C and less than 60°C, and the cooler face of the sheet is maintained within the range of 25°C to 75°C.
- 6 The method as claimed in claim 3, 4 or 5 wherein the polymer material is polyvinylidene fluoride, the temper-
25 ature gradient is about 35°C, the cooler face of the sheet is maintained at about 55°C, the electric field is about 0.5 Megavolts/cm, and the predetermined time is about 30 minutes.
- 7 The method as claimed in claim 3, 4, 5 or 6
30 wherein after being subjected to the electric field and temperature gradient for a predetermined time, the polarity of the electric field and the direction of the temperature gradient are reversed for an equal period of time.
- 8 A method of poling a sheet of polymeric material
35 as claimed in claim 3 and substantially as hereinbefore described.



9 A piezoelectric flexure element obtainable by the process of:

5 (a) applying an electric field across the thickness dimension of a sheet of polymeric material for a predetermined time, and

 (b) simultaneously heating one surface and cooling the opposite surface so as to establish a temperature gradient between the surfaces and to induce non-uniform poling across the thickness of the polymeric sheet.

10 10 The element defined by claim 9 characterised in that after the electric field is applied for said predetermined time, the polarity of the field and the direction of the temperature gradient are reversed for a similar predetermined time period.

15 11 A piezo electric flexure element of polymeric material substantially as hereinbefore described with reference to, and as illustrated in Fig. 4b, 5b, 6b or 7b.
