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Determination of the piezoelectric/pyroelectric response of polytrifluorovinyl acetate and other piezoelectric materials

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The piezoelectric and pyroelectric response characteristics for a variety of polymers and crystalline reference materials were correlated with their refractive index (n) and McGinniss equation x' values. A general predictive relationship was developed using these n and x' parameters which was then used to estimate the piezoelectric d and g constants for polytrifluorovinyl acetate. The predicted d and g values (8×10^{-12} C N^{-1} and 180×10^{-3} V m N^{-1}) were then compared with the actual experimentally determined d and g values (11×10^{-12} C N^{-1} and 100×10^{-3} V m N^{-1}) for polytrifluorovinyl acetate. Similar studies (physical and electrical property correlations with chemical structures and experimental verification of the correlations) were carried out for determining the pyroelectric coefficient of polytrifluorovinyl acetate. The McGinniss equation was shown to exhibit a higher degree of accuracy in correlating physical/electrical properties of polymers with their chemical structures as compared with other similar chemical structure/property correlation relationships reported in the literature.

(Keywords: piezoelectric activity; pyroelectric activity; polytrifluorovinyl acetate)

INTRODUCTION

The first report that piezoelectric and pyroelectric activity could be obtained from polymer films, previously subjected to direct current electric fields at elevated temperatures, was published in 1969[1]. The best known polymer film that has these properties is poly(vinyldiene fluoride) (PVDF), which has been used in detectors and loudspeaker applications[2].

The piezoelectric and pyroelectric properties of a polymer are related to the changes in electric polarization (P) with strain (S) or stress (X) and temperature (T)[3].

$$\begin{aligned} \text{polarization} = f[&(\text{permittivity})\ (\text{electric field}) \\ &+\text{piezoelectric stress constant } (g)\ (\text{strain}) \\ &+\text{piezoelectric strain constant } (d)\ (\text{stress}) \\ &+\text{pyroelectric constant } (P)\ (\text{temperature})] \end{aligned}$$

The piezoelectric response of a film material is generally described along with a reference to an axis or direction of the film:

Axis	Definition
1	Extrusion direction within the plane of the film
2	Transverse direction within the plane of the film
3	Perpendicular to the plane of the film

From a more practical situation, the g (generator) constant, or the field produced by a given stress can be defined as follows:

$$g = \frac{\text{volts/metre}}{\text{newtons/square metre}}$$

A g_{31} coefficient would describe a film that has electrodes deposited on the face or '3' surfaces with the tensile stress being applied in the '1' direction.

The d (driver) coefficient relates to the creation of an electric charge by an applied stress which also relates to the deformation of a film caused by an induced voltage.

The g and d coefficients are interrelated by the dielectric constant of the polymer:

$$g = \frac{d}{K\varepsilon^{0}}$$

where K = dielectric constant and ε^{0} = permittivity of free space.

The orientation or axis representation for the d coefficient conforms to the same definitions previously described for the g coefficients.

The purpose of this research was to develop a better understanding of how the physical and chemical structures of various polymeric and inorganic materials influence the magnitude of the d and g coefficient associated with their piezoelectric response capabilities.

EXPERIMENTAL

Synthesis of polytrifluorovinyl acetate (PTFVA)

PTFVA was prepared according to the procedures outlined in references 4 and 5. In this procedure, 50 g of trifluorovinyl acetate monomer (supplied by PCR Industries, Gainesville, FL) was distilled (b.p. 38°C) into a glass ampoule containing 0.144 g of a free radical initiator (Vazo 52 catalyst, EI DuPont de Nemours and company, Wilmington, DE). The ampoule was frozen at dry ice conditions, sealed under vacuum, and placed in a constant temperature water bath at 40°C for 24 h reaction time.

The resulting homopolymer was dissolved in dry acetone, precipitated with dry petroleum ether at 30–60°C, redried, and then stored in a vacuum desiccator for 24 h before being used in preparing films.

Film preparation

Films of PTFVA were cast by redissolving the homopolymer in dry acetone and casting the resulting solution on polyester (Mylar brand) film supports. After 10 min, the films were stripped from the Mylar support and placed in a vacuum oven to evaporate final traces of occluded solvent. Film thicknesses were in the range of 25.4–152.4 μm.

Film orientation

Cast films of PTFVA were oriented in an Instron testing apparatus according to normal procedures for uniaxial drawing, as outlined in reference 6. For the 3:1 drawing ratio the Instron speed was 1.27 cm min^{-1} at 76°C with a heat treatment of 45 min at 76°C. The 4:1 drawing ratio oriented films were oriented under the same conditions.

Electrode fixation

Aluminium metal was evaporated onto the surfaces of the film samples (oriented and unoriented) by vacuum metallizing techniques similar to those described in references 7 and 8. In these techniques, the film was held between stainless steel or plastic masks that allowed preparation of five circular (2.2 cm diameter) samples from a 7.63 cm square sheet of the film sample. The aluminium electrode film thickness was controlled to be about 100 nm, consistent with known technology for producing electrically conductive electrodes without effecting a major influence on the film modulus. This type of configuration is designed to allow measurement of the g_{33} coefficient of the film sample.

Polarizing conditions

The aluminium electrode fixed film was placed between two additional metal electrodes (aluminium) of approximately the same shape and size as the fixed aluminium electrodes but with extended arms for electrical connection. This configuration was then placed between polyimide film electrical insulation and overlaid with glass plates for further insulation and surface uniformity or flatness. The entire system was placed into a laboratory press to apply a contact pressure and a source of thermal energy.

External electrical connections were applied to the extended metal electrodes, the temperature raised to the desired value, and a d.c. voltage applied over a specified time interval. Thereafter, the samples were cooled to room temperature at the applied voltage. Additional information regarding techniques of poling and other techniques for producing piezoelectric and pyroelectric samples can be found in references 9–12.

Piezoelectric evaluation

Two accepted techniques for evaluating piezoelectric polymers are a comparator technique and a microphone calibrator technique[10]. In the comparator technique, a pulse generator initiates successive ultrasonic pulses of constant amplitude from a transducer. The ultrasonic pulses travel through an aluminium delay line and impinge on the test specimen at normal incidence. The specimen is coupled to the face of the delay line by a suitable coupling device. The incident pulses produce a voltage across the specimen if it is piezoelectric. This voltage is compared to the voltage produced when the same amplitude pulses impinge on a known standard (quartz). The specimen and the standard are thin compared with the wavelength of the impinging pulses.

Measurements are made initially on the unknown specimen. The specimen is then removed and replaced by the standard. If the signal from the standard is higher than that of the specimen, attenuation is applied until the received signal from the quartz standard equals that of the unknown. The number of decibels is read as a negative quantity. If the quartz signal is less than that of the specimen, the decibel insertion to bring the specimen to an amplitude equal to the quartz reference is read as a positive quantity. The decibel readings are designated as N_{db} in the equation:

$$\log_{10} g_{33} = N_{\mathrm{db}}/20 + \log_{10} g_{\mathrm{ref}}$$

where for the quartz reference (X – cut) $\log_{10} g_{\mathrm{ref}}$ is -1.136572.

Pyroelectric evaluation

A 3:1 oriented PTFVA film sample was polarized at 95°C for 15 min at 100 V/25.4 μm. This sample (12.6 cm^2 in area) was subjected to pyroelectric evaluation studies according to references 10, 11 and 12 with an oven set for a temperature rise of 5°C min^{-1}. The maximum current output for this sample was 2×10^{-9} A at 46°C. The pyroelectric coefficient for this sample was calculated according to $P(T) = I/(A\,\mathrm{d}T/\mathrm{d}t)$, where I = current, A = area of the sample and $\mathrm{d}T/\mathrm{d}t = 5$°C min^{-1}. The apparent pyroelectric coefficient for this sample was 1.9×10^{-9} cm^{-2} K^{-1}.

EMPIRICAL CHEMICAL STRUCTURE–PHYSICAL PROPERTY CORRELATIONS

The piezoelectric or pyroelectric response of a material depends on a number of factors such as degree of crystallization[13], dielectric constant[14], dipole alignment[15], stiffness[16], polarizability[17] and other interrelated physical/chemical property parameters[18]. Initial attempts at correlating the piezoelectric response for a variety of dissimilar materials (*Table 1*) were based on the theory that the dielectric constants and elastic stiffness of the material were the dominant parameters associated with the piezoelectric driver (d) or generator (g) constants. These attempts produced the following correlations.

$$\log d = 0.773 \log \varepsilon + 0.574 \log \text{ tensile modulus} - 0.950$$

$$\text{multiple } R = 0.89 \text{ with a standard error of estimate of } 0.61 \tag{1}$$

$$\log g = 0.554 \log \text{ tensile modulus} - 0.246 \log \varepsilon + 1.119$$

$$\text{multiple } R = 0.44 \text{ with a standard error of estimate of } 0.61 \tag{2}$$

Table 1 Properties of piezoelectric materials

Piezoelectric materials	Dielectric constant, ε (60–1000 Hz)	Refractive index, n	Density ($g\,cm^{-3}$)	Tensile modulus ($10^9\,N\,m^{-2}$)	x'	Piezoelectric driver constant, d_{31} ($10^{-12}\,C\,N^{-1}$)[a]	Piezoelectric generator constant, g_{31} ($10^{-3}\,V\,m\,N^{-1}$)[a]
Polyethylene (PE)	2.1–2.3	1.51–1.53	0.95–1	1	0	0.035	1.88
Fluorinated ethylenepropylene (FEP)	2.1–2.3	1.338	2.12–2.17	0.5	0	0.035	1.72
Polycarbonate (PC)	2.92–3.0	1.586	1.2	2.5–3.3	0.233	0.100	3.77
Polysulfone (PSUL)	3–3.3	1.633	1.24	2.5–3.6	0.277	0.350	13.2
Polyvinylchloride (PVC)	3–3.5	1.54–1.56	1.4–1.5	2.6	1.315	1.300	48.90
Nylon 11 (N11)	3–4	1.51	1.1	1.5	0.193	0.500	17.1
Polymethylmethacrylate (PMMA)	3–3.6	1.49	1.19	3.2	0.470	0.430	14.30
Polyacrylonitrile (PAN)	3.6–6.5	1.518	1.15–1.18	3.4–3.6	0.963	1.500	30.80
Polyvinylfluoride (PVF)	8–10	1.46	1.38–1.57	1	0.704	1.300	17.30
Polyvinylidene fluoride (PVF_2)	8–15	1.42	1.78–1.8	1.8–10	1.462	20–28	174
Polyvinylidene cyanamide/vinyl acetate copolymers (PVCN/PVOAC)	4.2	1.52	1.2	7.5	1.05	6	160
Barium titanate ($BaTiO_3$)	1700	2.40	5.85	110	3.87	78–180	5–12
Quartz (Q)	4.5	1.4588	2.650	77–80	1.139	2.000	50
Rochell salt (R salt)	350	1.496	1.77	17.7	3.038	150–275	90
Lead zirconate titanate (PZT)	1200	2.4–2.6	7.5	80	1.834	110	10
Ammonium dihydrogenphosphate (ADP)	15.6	1.502–1.53	1.803		2.485	24	178

[a] The piezoelectric constant values were obtained from refs 1–6

Table 2 Definition and calculation of the McGinniss equation x' parameter

Polymer	McGinniss equation parameter, x'	Remarks
PE	0	There are no dissimilar atoms in the monomer repeat unit of these polymers (no dipoles) hence x' is defined as being equal to 0
FEP	0	
PC	$\frac{\text{3 oxygen atoms}}{C_{16}H_{14}} = \frac{48}{206} = 0.233$	
PSUL	$\frac{\text{S, 4 oxygen atoms}}{C_{27}H_{22}} = \frac{96}{346} = 0.277$	
PVC	$\frac{Cl}{C_2H_3} = \frac{35.5}{27} = 1.315$	
N11	$\frac{N, O}{C_{11}H_{21}} = \frac{30}{153} = 0.196$	
PMMA	$\frac{\text{2 oxygen atoms}}{C_5H_8} = \frac{32}{68} = 0.47$	
PAN	$\frac{CN}{C_2H_3} = \frac{26}{27} = 0.963$	
PVF	$\frac{F}{C_2H_3} = \frac{19}{27} = 0.704$	
PVF_2	$\frac{2F}{C_2H_2} = \frac{38}{26} = 1.462$	
PVCN/vinyl copolymers	$\frac{2CN, 2O}{C_6H_8} = \frac{84}{80} = 1.05$	
$BaTiO_3$	$\frac{Ba, 3O}{Ti} = \frac{185}{47.90} = 3.87$	Ratio of the most electronegative atom and polarizing cation to the most electropositive element in the crystal
Q	$\frac{2O}{Si} = \frac{32}{28.1} = 1.14$	
R salt	$\frac{Na, K, 6O}{C_4H_4} = \frac{158}{52} = 3.038$	
ADP	$\frac{NH_4, 4O}{P, 2H} = \frac{82}{33} = 2.485$	
PZT	$\frac{Pb, 3O}{Zr, Ti} = \frac{255}{134} = 1.834$	

Equations (1) and (2) indicate that there is not a strong correlation between the piezoelectric response for all the materials in *Table 1* and their dielectric constant or their tensile modulus values. Attempts to correlate the piezoelectric response with dielectric constant or tensile modulus for similar materials (crystals or polymer separately and not in combination) were also not highly successful.

$$\log d\,(\text{crystals}) = 0.6754\log\varepsilon + 0.24$$

$R = 0.89$ with a standard error of estimate $= 0.44$ (3)

$$\log d\,(\text{crystals}) = -0.988\log \text{ tensile modulus} + 3.51$$

$R = -0.36$ with a standard error of estimate $= 1.13$ (4)

$$\log g\,(\text{crystals}) = -0.364\log\varepsilon + 2.34$$

$R = -0.71$ with a standard error of estimate $= 0.48$ (5)

$$\log g\,(\text{crystals}) = -1.1467\log \text{ tensile modulus} + 3.42$$

$R = -0.79$ with a standard error of estimate $= 0.39$ (6)

$$\log d\,(\text{polymers}) = 0.13\varepsilon + 0.20 \text{ tensile modulus} - 1.47$$

multiple $R = 0.90$ with a standard error of estimate $= 0.43$ (7)

$$\log g\,(\text{polymers}) = 1.181\log\varepsilon + 1.142\log \text{ tensile modulus} + 0.1$$

multiple $R = 0.88$ with a standard error of estimate $= 0.35$ (8)

It was observed that the general equation (9) (McGinniss equation) based on refractive index (n) and the ratio of the total mass of the most electronegative dissimilar atoms and polarizable cations to that of the most electropositive atoms in the crystal, molecule or monomer repeat unit of the polymer (x') (*Table 2*) correlated the piezoelectric response capabilities of the materials listed in *Table 1* with a reasonable degree of accuracy[19-21].

$$\text{Response} = C_1 n \pm C_2 x' \pm C_3 n x' \pm \text{constant} \qquad (9)$$

where n = refractive index and x' = ratio of most polarizable or most electronegative atoms to the most electropositive atoms in the structure of interest.

The first test of the predictive equation (9) was its ability to correlate well characterized physical or electrical property information such as density and dielectric constant values of all the materials listed in *Table 1*.

$$\log\varepsilon = 1.98n + 0.88x' - 0.23nx' - 2.69$$

multiple $R = 0.95$ with a standard error of estimate of 0.35 (10)

$$\text{density} = 4.89n + 0.19x' - 0.03nx' - 5.95$$

multiple $R = 0.92$ with a standard error of estimate of 0.80 (11)

The density and dielectric constants for similar materials (all crystals or all polymers) in *Table 1* could also be correlated with their refractive index and x' values as shown in the following equations:

$$\text{density (crystals)} = 4.82n - 5.12$$

$R = 0.97$ with a standard error of estimate $= 0.70$ (12)

$$\text{density (polymers)} = 25.48n^2 - 78.84n + 0.24x' + 62$$

multiple $R = 0.98$ with a standard error of estimate $= 0.08$ (13)

$$\log\varepsilon(\text{crystals}) = 0.44n^2 + 0.47$$

$R = 0.80$ with a standard error of estimate $= 0.80$ (14)

$$\varepsilon(\text{polymers}) = 4.8n + 80.59x' - 51.95nx' - 4.2$$

multiple $R = 0.94$ with a standard error of estimate $= 1.28$ (15)

Since the refractive index and x' values for all the materials listed in *Table 1* were reasonable parameters for correlating the physical or electrical properties (dielectric constant and density) of these materials (equations (10)–(15)), it was of interest to see how well these parameters correlated the piezoelectric response characteristics of these same materials.

$$\log d = 2.47n + 2.58x' - 0.96nx' - 4.67$$

multiple $R = 0.95$ with a standard error of estimate of 0.43 (16)

$$\log g = -0.94n + 1.47x' - 0.30(x')^2 + 1.90$$

multiple $R = 0.91$ with a standard error of estimate of 0.30 (17)

In one particular correlation, equation (17), the generator piezoelectric constant was more nearly approximated with the x' and $(x')^2$ parameter than with the refractive index (n) of the materials.

The piezoelectric response capabilities of individual or separate classes of materials (crystals or polymers) can also be generally well correlated with the density, refractive index and x' values of these materials[22].

RESULTS

The value of these types of predictive equations is that one should be able to select a polymer material and, by knowing its refractive index value and a calculated x' value, estimate the level of its piezoelectric response capabilities. We selected PTFVA as a test of these predictive equations. At the time of the initial structure/property correlation studies, there was no indication that anyone had reported the piezoelectric or pyroelectric properties of this polymer or any of its copolymer counterparts. The refractive index is 1.375 and its calculated x' value is 1.745. Thus, from equations (16) and (17) one would predict a piezoelectric response d_{31} value of $8\times10^{-12}\,\mathrm{C\,N^{-1}}$ and a piezoelectric g_{31} response value of $180\times10^{-3}\,\mathrm{V\,m\,N^{-1}}$ for PTFVA.

The polymer was prepared, orientated, metallized, poled and tested for its piezoelectric response capabilities (see Experimental section for details of the polymer synthesis reaction, orientation, metallization and poling conditions). The theoretical density, dielectric constant and piezoelectric response values (equations (10), (11), (13), (15), (16), (17)) and the experimentally determined values are shown in *Table 3*.

The pyroelectric constants for a series of materials, listed in *Table 4*, were correlated with their density,

Table 3 Comparison between predicted property values for PTFVA and experimentally determined values

Predicted properties	Experimentally determined values
Average density = 1.61 g cm^{-3} (equations (11) and (13))	density = 1.633 g cm^{-3}
Average dielectric constant value = 14 (equations (10) and (15))	$\varepsilon = 12$
Piezoelectric response d_{31} value = 8×10^{-12} C N^{-1} (equation (16))	$d_{33} = 2-11 \times 10^{-12}$ C N^{-1}
Piezoelectric response g_{31} value = 180×10^{-3} V m N^{-1} (equation (17))	$g_{33} = 16-100 \times 10^{-3}$ V m N^{-1}

Table 4 Pyroelectric coefficient for a series of different materials

Material	Pyroelectric coefficient ($\times 10^{-9}$ C cm^{-2} K^{-1})[a]
PVDF	4
PVF	1
PVC	0.1
PAN	0.1
$BaTiO_3$	20
PZT	50

[a] The pyroelectric coefficients were obtained from refs 1–6 and 17–19

refractive index and x' values according to equation (18):

$$\text{pyroelectric constant} = 10.16\ \text{density} - 11.77n - 4.82x' + 9.32$$

$$\text{multiple } R = 0.99, \text{ standard error of estimate} = 1.77 \qquad (18)$$

Thus, the predicted pyroelectric constant value for PTFVA from equation (18) would be 1.32×10^{-9} cm^{-2} K^{-1}. The experimentally determined value for this material was 1.9×10^{-9} cm^{-2} K^{-1}.

DISCUSSION

The piezoelectric and pyroelectric response properties of a material are influenced by a number of factors. The equations described in this study have specific parameters that appear to correlate reasonably well with the observed piezo–pyro and physical properties of different materials. The refractive index of a material gives a strong indication of how closely associated the electrons are to their respective atomic nuclei in a molecular structure. The refractive index of a molecule is also related to its dielectric constant and in polymer films is also a measure of the degree of orientation of the polymer chains (birefringence), which strongly influences piezoelectric/pyroelectric response characteristics of the film.

The McGinniss x' parameter takes into consideration that there is a dipole moment in the structure and that the dipole moment can become highly oriented in an electric field, resulting in the observed piezoelectric or pyroelectric response of the material[1]. The fact that the refractive index and the x' parameters or the interaction parameter, nx', predict other physical properties of various materials, also indicates that these particular parameters are somewhat universal in their predictive capabilities[7,8].

The empirical correlations in this study were based on the highest reported literature values (*Table 1*), and thus not all of the samples were processed under the same ideal conditions. The experimental studies with PTFVA did not always reach their predicted maximum values and the primary reason for this difference between theoretical and experimental results was the degree of orientation. As previously mentioned, the predictive equations (equations (16) and (17)) were based on the highest reported literature values for the materials shown in *Table 1*. In these studies, we were only able to orient the PTFVA film samples up to a 4:1 ratio. Higher orientation and gold electrodes rather than aluminium electrodes on the samples would have a greater probability of producing higher piezoelectric response values for PTFVA.

CONCLUSIONS

The results of this study indicate that a linear or product combination of two variables, n and x' (McGinniss equation) can be used to correlate the density, dielectric constant, piezoelectric and pyroelectric response characteristics for a wide variety of different materials. One of the advantages of these types of correlations is their ability to provide a framework by which one can begin to predict or computer model the physical properties of new materials before having to go into the laboratory and prepare exploratory samples for testing and evaluation studies.

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