Temperature and Substrate Dependence of Piezoelectric Sensitivity for PVDF Films

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1 Abstract

The piezoelectric sensitivity, via both the direct and converse effects, for commercial polyvinylidene fluoride (PVDF) films is measured as a function of temperature and frequency, for two substrates, nylon and aluminum. The average effective sensitivity for the PVDF on nylon was 29 pm/V for both direct and converse effect, independent of frequency over 0.5 to 200 Hz. Direct effect sensitivity on aluminum substrate was about a factor of five greater. Analysis of effects of substrate's thermal and elastic constraint disclosed insufficient effect to account for the observed increase of sensitivity. Flexoelectric effects were considered as the cause. The direct and converse sensitivity increased at approximately 2% per degree Celsius over the frequency range 0.5 to 200 Hz. **Adapted from Faust, D. and Lakes, R. S., "Temperature and Substrate Dependence of Piezoelectric Sensitivity for PVDF films", Ferroelectrics, 481(1), 1-9, Sept. (2015).**

2 Introduction

Piezoelectric materials produce an electric field proportional to an applied mechanical stress. Conversely, these materials deform mechanically at the same rate when an electric field is applied [1]. In particular, the strain ϵ_{ij} depends upon stress σ_{kl} via the elastic compliance J_{ijkl}, and upon electric field $\mathcal{E}_k$ in piezoelectric materials with modulus tensor d_{kij}. Strain also depends on temperature change ΔT via the thermal expansion α_{ij}. The electric displacement vector $\mathcal{D}_i$ depends on electric field via K_{ij}, the dielectric tensor at constant stress and temperature. In some materials such as PVDF it depends on temperature change ΔT via the pyroelectric effect; p_i is the pyroelectric coefficient at constant stress. Piezoelectric materials are anisotropic; they always have a chiral asymmetry.

$$\epsilon_{ij} = J_{ijkl}\sigma_{kl} + d_{kij}\mathcal{E}_k + \alpha_{ij}\Delta T \tag{1}$$

$$\mathcal{D}_i = d_{ijk}\sigma_{jk} + K_{ij}\mathcal{E}_j + p_i\Delta T \tag{2}$$

Piezoelectricity in stretched and poled polyvinylidene fluoride (PVDF) was first demonstrated in 1969. This discovery sparked further research into the pyro, piezo and ferroelectricity of PVDF and other polymers [2]. PVDF is a piezoelectric polymer that is used for sonic and ultrasonic transducers, sensors and actuators. PVDF has a piezoelectric sensitivity, d_{33}, of -20 pC/N. The units of pC/N and pm/V are interchangeable. The d_{33} coefficient corresponds to the charge measured perpendicular to the poling direction when the force is also applied perpendicular to the poling direction [3].

The piezoelectric sensitivity of PVDF is dependent on temperature. Between the glass transition temperature (-40 °C) and the breakdown of the piezoelectric film (80 °C), the magnitude of the sensitivity increases with temperature [4]. This is independent of PVDF's pyroelectricity, in which the material generates charge in response to a fluctuating temperature [6].

3 Methods

3.1 Equipment

The PVDF films, purchased from Goodfellow, were 28 μm thick and 12.5 mm wide. The d_{33} piezoelectric coefficient was reported as approximately 20 pC/N [7]. Charges for the direct effect were measured using a Kistler 5010 Charge Amplifier and a TDS 3014B digital oscilloscope. An SRS SR560 high-low pass filter was used to minimize noise in the experiments. For the converse effect, an SRS DS345 function generator, a SR850 DSP lock-in amplifier and a fiber optic displacement sensor (MTI 2000 Fotonic Sensor) were used. The temperature of the PVDF film was controlled using a Cambion (Cambridge, MA) thermoelectric module and measured using an Omega 871A Digital Thermometer with Type K thermocouples.

3.2 Procedure

For the first series of tests, the PVDF film was mounted onto a 44.45 mm diameter polymer cylinder. The film was secured in place using a UHU acid free glue-stick (manufactured in Allemagne). The piezoelectric sensitivity was measured using both the direct and converse effect at room temperature (23 °C). A 4 Ohm speaker was mounted above the PVDF film with a 12.7 mm diameter polycarbonate rod transmitting force from the speaker to the piezoelectric element. The frequency at which the speaker moved was controlled using an SRS DS345 function generator. The entire system was enclosed in a small plexiglass chamber to isolate the PVDF film from any air currents in the room. This chamber was filled with mineral wool insulation to minimize temperature gradients. Measurements with two thermocouples confirmed the temperature difference above and below the specimen was less than 1 °C. A small preload of 0.5 N was applied to the polycarbonate rod to keep it in place over the PVDF film. The piezoelectric sample was securely fastened to a Newport 270 vertical stage to allow for fine adjustments underneath the speaker [8]. The speaker was calibrated by applying a known current and measuring the force via an analytical balance. A nominal input voltage of 20 V p-p from a 50 ohm source impedance was used. The charge amplifier was set to a medium time constant (10 seconds) and the same time constant was used for the lock-in amplifier. The charge amplifier's sensitivity was set to 1 V for every 100 pC. For this setup, the signal-to-noise ratio was approximately 50.

Piezoelectric sensitivity was first measured using the direct effect, then, via the converse effect. The function generator was used to supply a 20 V p-p sine wave directly to the PVDF film. A small mirror was glued with cyanoacrylate to the surface, allowing a fiber optic displacement sensor to be used to measure the displacement of the piezoelectric in response to the input voltage [5]. Once again, a plexiglass enclosure filled with insulation was used to shield the PVDF film and maintain uniform temperature. The signal-to-noise ratio for this method was much lower, at $5 * 10^{-3}$. Therefore a lock-in amplifier with a long time constant of 100 seconds was used to cut through the noise to measure the amplitude of the displacement.

Once the piezoelectric sensitivity had been successfully measured over a range of frequencies for both methods, the PVDF film was mounted on an aluminum substrate. Two surface textures were used: smooth aluminum and a layer of tin beads 3 mm in diameter; this allowed evaluation of whether gradient effects (flexoelectric sensitivity) might contribute to the output. Initial measurements using the aluminum substrate revealed a much higher sensitivity than using the polymer substrate. Therefore further studies were done to ascertain whether ground loops or image charges would obtrude in the results. Reversal of the lead wires had no effect. Changing the ground wire for the charge amplifier had no effect. A fast Fourier transform of the signal showed no additional sources of noise or error as compared to the previous results with the nylon substrate. It was concluded that electrical errors were not responsible for the observed sensitivity.

The aluminum sheet was then mounted on a thermoelectric module to allow for heating and cooling. The top surface of the PVDF was covered with a layer of Omegatherm 201 thermal paste and, as indicated above, a layer of 3 mm Sn beads. On top of the tin beads another Al sheet was fixed in place. A foam copper block 6 mm thick was attached to the top aluminum sheet. This configuration was done to enable a concurrent series of experiments, to be reported elsewhere. Type K thermocouples were placed on both surfaces of the PVDF film to measure any temperature differences across the film. With the additional layers on top of the PVDF, the amount of noise present increased by a factor of ten. The signal-to-noise ratio for the direct effect sensitivity was 5. The ratio for the converse effect remained unchanged. As above, a lock in amplifier was used to extract the signal.

After testing was completed with the thermoelectric module, a second form of heating was used. Insulation was added to the walls of the enclosure and forced hot air was used to create a uniform temperature inside the enclosure and the converse piezoelectric coefficient was measured.

4 Results

The average sensitivity for PVDF piezoelectric mounted on the polymer cylinder was $d_{33}^{\mathrm{eff}} = 29.2 \pm 1$ pC/N (Figure 1). All sensitivity values reported are magnitudes. This was for the direct effect measured over 0.5 to 25 Hz. The average sensitivity measured using the converse effect was $d_{33}^{\mathrm{eff}} = 28.6 \pm 1.5$ pm/V. This was over the frequency range 1 to 25 Hz. Sensitivity values via the direct and converse effects are equal within the resolution of the measurements.

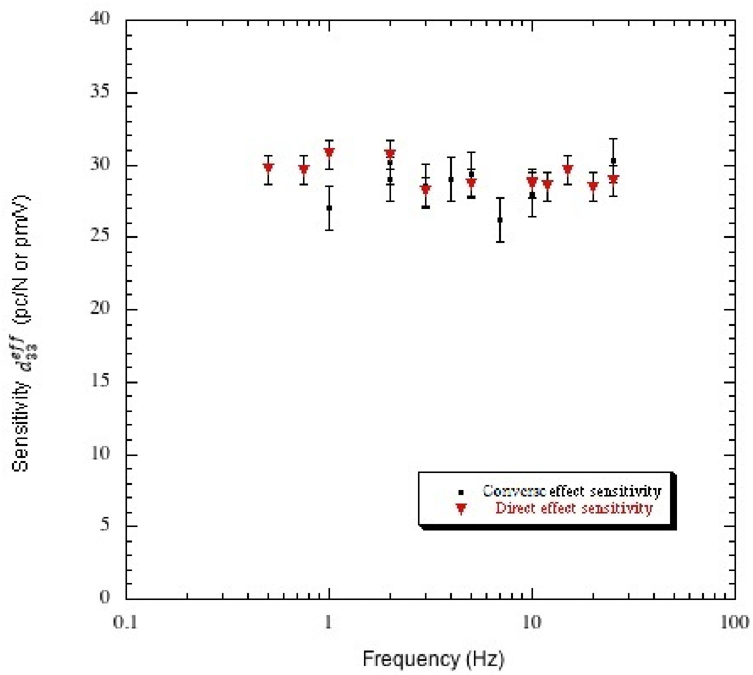

Figure 1: Sensitivity d_{33}^{eff} of PVDF as a function of frequency, measured at room temperature (23 °C); polymer substrate.

Mounting the PVDF on aluminum caused the sensitivity as measured by the direct effect to increase significantly. Over 0.667 to 10 Hz, the average sensitivity was 167 ± 2 pC/N. The procedure used to measure the sensitivity was the same as the procedure for the PVDF mounted on the polymer. The only difference was changing the substrate material. The sensitivity measured using the converse effect was $d_{33}^{\mathrm{eff}} = 31.7 \pm 0.75$ at 200 Hz. The frequency at which the measurements were made had to be increased from the previous substrate. Increased noise from the additional layers reduced the accuracy of the measurements at lower frequencies.

The effect of temperature on the sensitivity is shown in Figure 2. Over the temperature and frequency range chosen, the sensitivity increases at a rate of 5 pC/N per degree Celsius. This corresponds to an increase of approximately 3% per degree. As shown, the sensitivity only depends on the temperature and not on the frequency, within the resolution of the measurements.

Despite the much larger overall sensitivity for the PVDF mounted on aluminum, the increase in sensitivity with temperature is similar whether the direct or converse effect is used. Figure 3 shows the same trend when measuring the sensitivity with the converse effect. Results show that over this temperature range, sensitivity increases at approximately 2%/ °C as compared to the 3%/ °C cited above. That is four times larger than the 0.5%/ °C reported for other PVDF sensors [9].

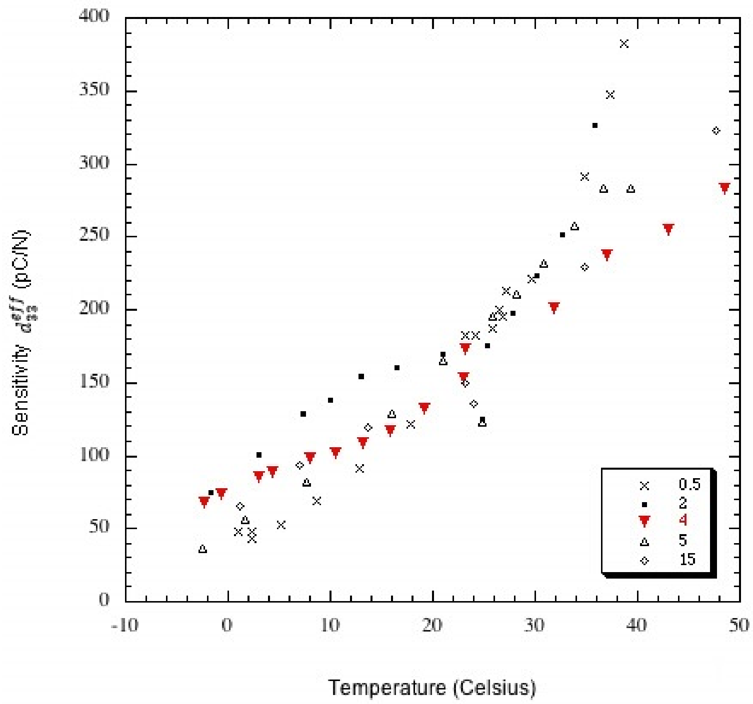

Figure 2: Sensitivity d_{33}^{eff} of PVDF as a function of temperature at 0.5, 2, 4, 5, 15 Hz using the direct effect on aluminum substrate.

Figure 3 shows a comparison of the two different heating methods. The same relationship between temperature and sensitivity is present. The temperature range obtained via the thermoelectric device was approximately 0 °C to 45 °C. The upper limit was set by the melting temperature of the glue, not by the thermoelectric module. The hot air flow approach was more limited in temperature range as the PVDF could not be cooled below room temperature.

Figure 4 shows a comparison of the piezoelectric sensitivities measured at ambient temperatures via the direct effect for PVDF mounted on aluminum. For both the rough and smooth tests, the experimental conditions were the same, except for the contact surface smoothness. The time constant used for the charge amplifier was changed to 0.1 seconds from 10 seconds for the testing with the tin beads. This change in surface roughness had about a 12% effect on effective sensitivity.

5 Analysis

Analysis of boundary conditions was conducted to evaluate possible reasons for the enhanced sensitivity of PVDF on aluminum substrate. Different boundary conditions can change the measured piezoelectric sensitivity. As shown in Equation 3, the relationship between adiabatic (d_{ijk}^S) and isothermal (d_{ijk}^T) piezoelectric coefficients depends upon the pyroelectric coefficient (p), the heat capacity (T/C) and the thermal expansion (α)[1]. The calculated thermal time constant for the PVDF film is 300 μs [11]. This time constant corresponds to a cut-off frequency of 600 Hz for the PVDF in a heat bath of infinite conductivity. Frequencies used during experimentation were kept well below 600 Hz. In practice, the thermal conductivity is much faster in aluminum than nylon but both substrates have finite heat transfer rates. The values used in Equation 4 were $p = 27 * 10^{-6} \frac{C}{m^2 K}$, $\alpha = 100 * 10^{-6} K^{-1}$, $T = 300K$, $C = 2.3 * 10^6 \frac{J}{m^3 K}$, and $d = -20 * 10^{-12} \frac{C}{N}$.

$$d_{ijk}^S - d_{ijk}^T = -p_i^\sigma (T/C^{\sigma,E}) \alpha_{jk}^E \tag{3}$$

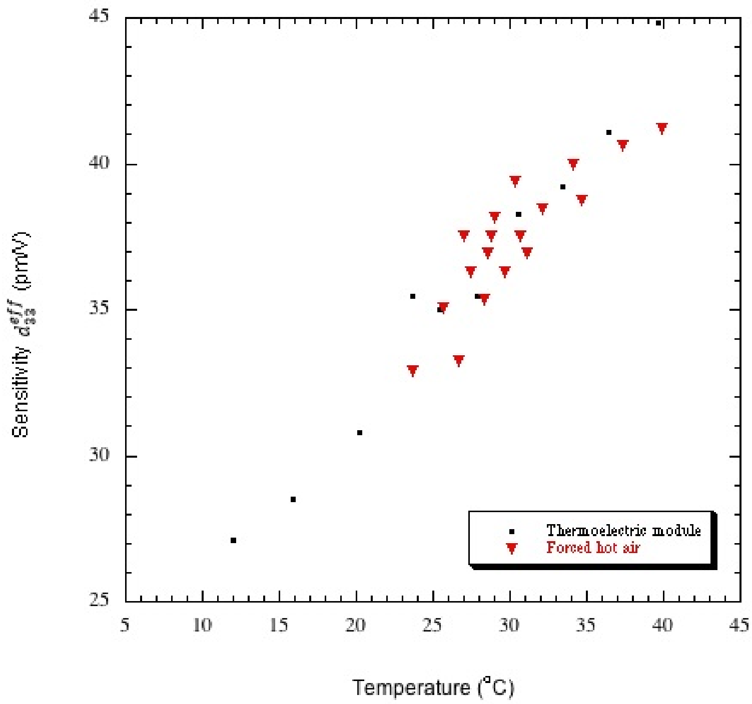

Figure 3: Sensitivity d_{33}^{eff} as a function of temperature on aluminum substrate. Both heating methods follow a similar trend.

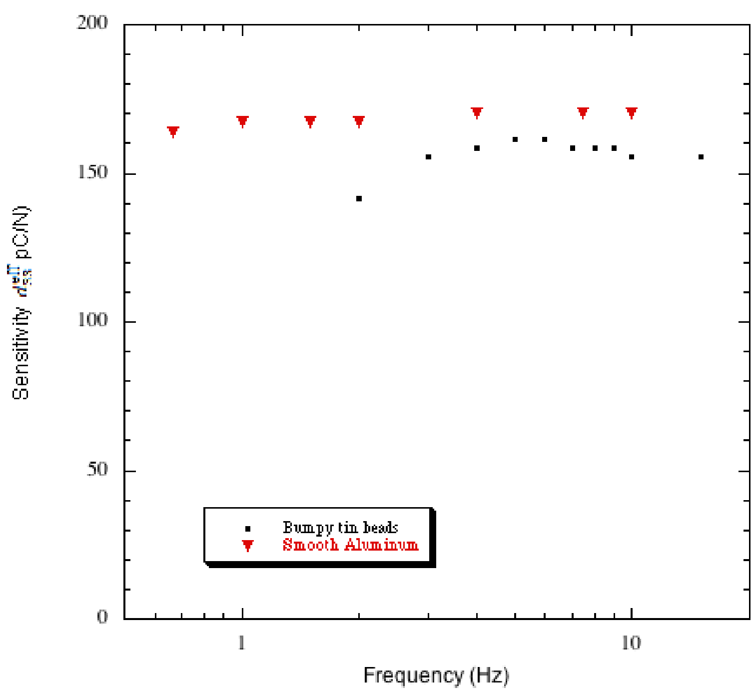

Figure 4: Sensitivity d_{33}^{eff} of PVDF as a function of frequency on aluminum substrate for contact with a smooth surface and with a surface of tin beads.

$$\Gamma_h = \frac{p\alpha}{(C/T)d} \tag{4}$$

This results in a relative difference of $1.8 * 10^{-2}$ between the adiabatic and isothermal piezoelectric sensitivities. This small difference cannot account for the large measured difference in the direct effect sensitivity. Moreover, all the results were obtained at frequencies well below the thermal transition frequency of 600 Hz. In any case, other changes appeared to have a much larger effect on the piezoelectric sensitivity. When switching from nylon to aluminum, the mechanical boundary conditions changed as well. The PVDF strip is partially constrained to the substrate by the glue.

Larger effects are known in other variables. For example, Equation 5 gives the relationship between constant stress and constant strain pyroelectric coefficients which depends upon the thermal expansion (α), the piezoelectric coefficient (d), and the elastic compliance (S)[1]. The value used for S in Equation 6 was $(2 * 10^9 \text{ Pa})^{-1}$.

$$p_i^{\epsilon} - p_i^{\sigma} = -\alpha_{jk}^{E} c_{jklm}^{E,T} d_{ilm}^{T} \tag{5}$$

$$\Gamma_h = \frac{d\alpha}{Sp} \tag{6}$$

The relative difference calculated in Equation 6 is 0.15. Although pyroelectric measurements were not made, this illustrates that in some cases effects of constraint can be large. This difference was further minimized by allowing the PVDF to reach a constant temperature before measuring the sensitivity.

Another important consideration in the measurement of the piezoelectric sensitivity is that the film is fixed to a substrate of different stiffness. The PVDF film can only expand and contract perpendicular to the surface if the substrate is stiff. Therefore, the measured piezoelectric sensitivity is only an effective coefficient[12]. The resulting equations could not be directly applied to a PVDF film. More terms were necessary due to PVDF's anisotropy[13]. Equations 7 and 8 show the relationship for the effective piezoelectric coefficient due to constraints for the converse effect and direct effect respectively:

$$\epsilon_3/E_3 = d_{33}^{eff}|_{converse} = d_{33} + \frac{d_{32}(s_{12}s_{13} - s_{11}s_{23}) + d_{31}(s_{12}s_{23} - s_{22}s_{13})}{s_{11}s_{22} - s_{12}^2} \tag{7}$$

$$D_3/T_3 = d_{33}^{eff}|_{direct} = d_{33} - (d_{31} + d_{32})\frac{(s_{13} + \nu/Y)}{(s_{11} + s_{12})} \tag{8}$$

where s_{11}, s_{12}, s_{13}, s_{22} and s_{23} are the mechanical compliances. ϵ is the strain and E is the electric field. D is the polarization linked to displacement and T is the applied stress. Y is the Young's modulus of the substrate and ν its Poisson's ratio. For PVDF $s_{11} = 3.65 * 10^{-10}$ Pa^{-1}, $s_{12} = -1.1 * 10^{-10}$ Pa^{-1}, $s_{13} = -2.09 * 10^{-10}$ Pa^{-1}, $s_{22} = 4.24 * 10^{-10}$ Pa^{-1} and $s_{23} = -1.92 * 10^{-10}$ Pa^{-1} [14]. $d_{33} = -30$ pC/N and $d_{31} = 20$ pC/N [7]. These values can vary by up to ± 5 pC/N. For PVDF d_{32} is much smaller at 2 pC/N. The assumed values are $Y = 69$ GPa and $\nu = 0.35$ for aluminum and $Y = 3$ GPa and $\nu = 0.4$ for Nylon.

Using reported values for PVDF's mechanical compliances, the expected values are $d_{33}^{eff}|_{converse} = -13.3$ pC/N and $d_{33}^{eff}|_{direct} = -14.7$ pC/N for the PVDF mounted on aluminum. The expected value is $d_{33}^{eff}|_{direct} = -22.9$ pC/N for the PVDF mounted on nylon. These results, however, are sensitive to any variance in the mechanical compliance of the PVDF. Such variance is expected in comparisons of materials from different sources. Also, commercial material will vary from one batch to another. Increasing s_{11} by 25% to $4.56 * 10^{-10}$ Pa^{-1} changes $d_{33}^{eff}|_{converse}$ from -13.3 to -16.7 pC/N and changes $d_{33}^{eff}|_{direct}$ from -14.7 to -17 pC/N for an aluminum substrate. Decreasing s_{12} by 25% to $8.25 * 10^{-11}$ Pa^{-1} changes $d_{33}^{eff}|_{converse}$ from -13.3 to -14.7 pC/N and changes $d_{33}^{eff}|_{direct}$ from -14.7 to -16 pC/N for an aluminum substrate. Decreasing s_{13} by 25% to $-1.57 * 10^{-11}$ Pa^{-1} changes $d_{33}^{eff}|_{converse}$ from -13.3 to -16.5 pC/N and changes $d_{33}^{eff}|_{direct}$ from -14.7 to -16.9 pC/N for an aluminum substrate. Variations in the piezoelectric coefficients can also change the expected effective sensitivity. Changing d_{31} by 5 pC/N to 15 pC/N changes $d_{33}^{eff}|_{converse}$ from -13.3 to –17.2 pC/N and changes $d_{33}^{eff}|_{direct}$ from -14.7 to -18.1 pC/N for PVDF on aluminum. Overall, these possible variations in mechanical properties of commercial PVDF result in $d_{33}^{eff}|_{converse}$ changing from -13.3 pC/N to -22.3 pC/N and $d_{33}^{eff}|_{direct}$ changing from -14.7 pC/N to -21.9 pC/N.

From this analysis it can be concluded that the mechanical properties of the aluminum substrate cannot account for the increased $d_{33}^{eff}|_{direct}$ piezoelectric coefficient.

6 Discussion

Piezoelectric sensitivity measured on polymer substrate showed direct and converse effects to be in close agreement. Measurements of the PVDF sensitivity mounted on a polymer using a direct and converse methods and the measured sensitivity for the PVDF mounted on aluminum using the converse effect had magnitudes of 29.2, 28.6, and 31.7 pC/N respectively. Based on thermodynamic arguments, the direct and converse effects should cause the same response in the material [1]. This was evident when the PVDF was mounted on the polymer substrate. Changing the substrate to aluminum changed this apparent behavior. The PVDF's effective sensitivity is approximately five times stronger in response to a mechanical force instead of an electric field. In the analysis section, considerations of the changing boundary conditions in switching from a polymer substrate to an aluminum one could not account for this large increase in sensitivity. Specifically, variations on the mechanical compliances did not have a large enough effect on expected piezoelectric sensitivity to account for the observed difference. Other effects may contribute. For example, ferroelectric materials [15] including PVDF [16] are sensitive to gradients of strain. Such behavior is currently called flexoelectric. Local indentations can contribute to such effects. Indeed, experiments were done using two contact surfaces of different roughness. In view of the thinness of the polymer film (28 μm), details of surface roughness may be pertinent in this context. Indeed, shaped constituents or contacts have been considered in the context of designed composites [17]. Regardless of origin, substrate dependence of d_{33}^{eff} could be used in applications for which enhanced sensitivity is desirable.

For all conditions, piezoelectric sensitivity increased with temperature. Two heating methods were used: a thermoelectric module and forced hot air. In both cases, temperature gradients were minimized. As shown in figure 3, the different heating methods did not cause any discernable differences in the sensitivity when measured using the converse effect. The sensitivity also increased with temperature at all frequencies tested using the direct effect.

While PVDF piezoelectrics have lower sensitivities than ceramic piezoelectrics, they are cost effective in many applications. They also can be advantageous in matching acoustic impedance. By adjusting conditions such as the operating temperature, and choosing appropriate substrate materials the sensitivity of PVDF can be increased to levels comparable to ceramic piezoelectrics.

7 Conclusion

The effective sensitivity for the PVDF on nylon was 29 pm/V for both direct and converse effect. This was independent of frequency over 0.5 to 200 Hz. Direct effect sensitivity on aluminum substrate was about a factor of five greater. Analysis of the effects of mechanical and thermal constraint of the substrate cannot account for all of this increase. Flexoelectric effects are a possible cause. Surface roughness had about a 12% effect on effective sensitivity. Substrate dependent enhancement of properties may be useful in applications.

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