Formulation, printing and poling method for piezoelectric films based on PVDF-TrFE

Christine K. McGinn,[1, a)] Kevin A. Kam,[1] Mika-Matti Laurila,[2] Karem Lozano Montero,[2] Matti Mäntysalo,[2] Donald Lupo,[2] and Ioannis Kymissis[1]

[1)]Dept. of Electrical Engineering, 500 W 120th Street, Room 1300/MC 4712, Columbia University, New York, NY, USA 10027

[2)]Faculty of Information Technology and Communication Sciences, Tampere University, Korkeakoulunkatu 3, 33720 Tampere, Finland

Polyvinylidene flouride- trifluoroethylene (PVDF-TrFE) has been utilized widely for pressure sensing, healthcare monitoring, and energy harvesting. In order to integrate piezoelectric elements into flexible thin film electronics, researchers have studied depositing PVDF-TrFE via printing methods. Screen printing, in particular, has been utilized by several groups, but printing methodology and characterization procedures have varied significantly between works. In this work, a simple, low-cost, flexible method is described. The resulting films are characterized for their piezoelectric character and temperature tolerance. The printed films have a piezoelectric coefficient comparable to previous work (26.24 pC/N) and demonstrate no meaningful degradation in piezoelectric character up to 110C.

I. INTRODUCTION

Polyvinylidene fluoride (PVDF) and its copolymers have been critically important to flexible circuits and sensors due to its strong ferroelectric, pyroelectric, and piezoelectric character in comparison to other electroactive polymers.[1–10] What makes PVDF especially appealing for healthcare applications is that it is biocompatible, inert, and transparent.[8,11–14] As a result, it has been used in a wide variety of biomedical devices for health monitoring.[15–17]

The pure PVDF polymer has some known disadvantages. It can only be coerced into its most electroactive form, known as the β phase, under very specific conditions.[9,18] One commonly used method for crystallizing and poling the film is to simultaneously stretch and expose the film to very high voltage.[19] As a result, pure PVDF is typically purchased as freestanding sheets, which for flexible electronics means it must be the substrate or laminated. These sheets also inhibit the miniaturization of devices as they cannot be made thinner than drawn. It is known that that these freestanding sheets also deform significantly upon exposure to temperatures above a critical temperature (80 °C), which can make additive processing difficult.[5,20]

However, the PVDF copolymer polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) solves many of the processing concerns associated with the pure PVDF as it readily crystallizes into the β phase and does not require additional stretching during poling. As a consequence it lends itself to more methods of processing including spin coating and printing.[18,21,22] The facile processing does not come at cost of piezoelectric performance, as the remnant polarization and and piezoelectric d-coefficient of the copolymer are similar to that of PVDF.[9]

As many researchers look to printed devices to create flexible and stretchable sensors, devices, and displays, simple, reliable, low-cost methods for printing and characterizing PVDF-TrFE are increasingly important.[10,23–25] While the Stadlober group demonstrated some of the first and most effective printed PVDF-TrFE devices, several groups have demonstrated extensive work on screen- and inkjet-printing PVDF-TrFE.[6,7,25–32] While some use commercially available inks, these inks can be expensive and cannot easily be tailored for a specific printing system or project using dilution, evaporation, or addition or subtraction of PVDF-TrFE material. Of the groups that formulate their own ink for screen printing, the method varies significantly in concentration, solvent used, and even copolymer composition (i.e. the percentage of TrFE in the copolymer).[10,24,27,31,33] The higher the loading of PVDF-TrFE in the ink, the more ferroelectric and piezoelectric character can generally be expected, but many inks use very dilute mixtures (10 wt % or less) to facilitate the printing process.[33,34] Using dilute mixtures results in thinner films which have several adverse effects for piezoelectric capacitors, such as minimized piezoelectric and ferroelectric characteristics, lower output voltage, and a reduced density of pinholes.[23,35]

This report details a repeatable method for creating and printing PVDF-TrFE ink that is simple, low cost, and customizable for the researcher's needs. Additionally, methodology for successfully characterizing the performance of the printed films is described.

II. METHOD

A. PVDF-TrFE mixture

PVDF-TrFE powder or crystals (Piezotech, 70/30 VDF/TrFE) was weighed into mixing bottle with a sealed top and stir bar. Note that wider bottomed bottles generally work better and the stir bar should be about $\frac{2}{3}$ of the diameter of the bottom of the bottle. A typical amount used for a single batch was 1-3 g of PVDF-TrFE. Solvent was then added to create mixture with desired weight percent. For screen printing, 20

a)cm3592@columbia.edu

wt% solutions were used. A mixture of dimethylformamide (DMF) and methyl ethyl ketone (MEK) was used as the solvent for the ink. Ratios of 1:1, 3:1, 4:1, and 9:1 DMF to MEK were tested in making 20 wt% solutions for screen printing. To reduce waste and correct for errors, we weighed the DMF and MEK in separate containers from the mixing container before adding to the PVDF-TrFE container. For easier mixing, we also added the DMF before the MEK. The powder suspends well in the DMF, once the MEK is added the system gelates, and is more challenging to dilute.

After all components of the mixture are added, we placed the bottle on a hot plate and heated to 30 °C for 15 minutes, with the stir bar on a low speed continuously. After 15 minutes, we turned the heat off and left it to stir at room temperature until a clear (not cloudy) and homogeneous mixture was obtained, typically 3-12 hours.

B. Printing Procedure

The bottom electrode was printed using an inkjet printer (DMP-2801, Fujifilm Dimatix) on polyethylene napthalene (PEN) sheet using a silver nanoparticle ink (DGP 40LT-15C, Advanced Nanoproducts) with one pass for the first layer with 40 um spacing (i.e. 635 dpi pattern). A second layer was printed with the same parameters and four passes to ensure good conductivity. This film was sintered for one hour at 150 °C in a hot air oven.

While working with both the PVDF-TrFE and PEDOT:PSS ink, it was important to wear personal protective equipment, such as a respirator mask, or arrange the equipment inside an exhausted enclosure to avoid inhalation of potentially hazardous vapors. The vapors of DMF and MEK, in particular, can be carcinogenic.[36] PVDF-TrFE was screen printed using a semi-automatic screen printer (TIC SCF-300, Eickmeyer). Thermotropic liquid crystal polymers screens (V Screen Next, NBC Meshtec) with 20 μm thread and 40 μm opening width were used. Two layers were printed in order to minimize pinholes in the film. In between each layer, the film was baked at 70 °C under vacuum in a vacuum oven for five to ten minutes. After all layers were printed, final film was cured in a vacuum oven at 135 °C for one hour. The pressure in the vacuum oven was kept below 0.1 mbar. While printing, it was important to use a significant excess volume of ink and work quickly to prevent drying and sticking to the screen which can impact the print quality. Additionally, cleaning the back side of the screen immediately after print helped to increase the quality of each printed layer. To clean the screen after use, the screens were rinsed thoroughly with acetone until no traces of PVDF-TrFE/DMF/MEK mixture were left. A final rinse with IPA or water was used to remove any remaining residue from inside of the screen.

The top electrode was a single layer of screen printed PEDOT:PSS ink (Clevios S V4 STAB, Heraeus) which was cured at 90°C for 30 minutes after printing. The same printer and screen type was used as for the PVDF-TrFE layers. To help

with contacting the PEDOT:PSS film, silver paste was added to the contact pad before probing. The silver paste was cured on a hot plate at 65°C for 15 minutes.
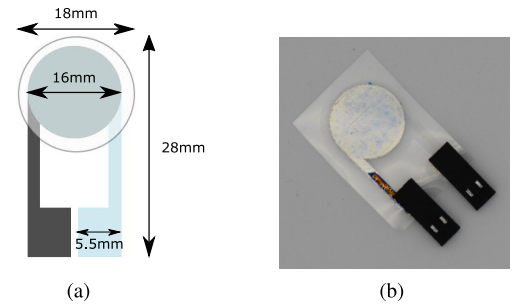

FIG. 1: (a) Detailed schematic of sample design with dimensions. (b) Image of finished device with contacts added.

C. Poling Procedure

To determine the maximum poling voltage needed, the thickness of the printed PVDF-TrFE layers was measured using a profilometer. The thickness of the piezoelectric layer was 5-15 μm depending on the mixture used with the majority of samples being $6-7$ μm.

Both AC and DC poling procedures were tested, and it was found that DC poling achieved higher piezoelectric coefficients. In both cases, the setup was the same. A function generator (33500B, Keysight) was connected to a voltage amplifier (610C, TREK) to create the high voltages needed for poling. An oscilloscope (DSOX2002A, Keysight) was connected in parallel to observe the output voltage. The output of the voltage generator was connected to probes which contacted the sample. To effectively pole the sample, a maximum electric field of 70-100 V/μm was applied. It should be noted that for DC poling, there are several commercially available supplies that could be used to execute poling.

For AC poling, the function generator was set to output an exponential sinusoid wave, which had a maximum poling field of 700 kV/cm and a frequency of 50 mHz. After the waveform finished, the source was turned off for a short time before being turned on again. In total, five waveforms were used for poling with a total duration of 300 seconds.

For DC poling, the function generator was set to output a constant voltage which was manually adjusted to set values during the poling procedure. The approach outlined by Setiadi et al was used.[37] According to their work, the optimal way to pole a PVDF-TrFE film is to alternate off and on periods, with 8 minutes on and 4 minutes off being the best ratio. In each interval the field strength is increased up to the final poling field of 100V/um. The field strength used in each interval was 20 V/μm, 40V/μm, 60V/μm, 80V/μm, and 100

V/μm. The entire process for poling a single sample then took approximately 50 minutes.

During poling, it was observed using a voltmeter that occasionally the maximum voltage could not be reached across the device, even though the device was not shorted. Additionally an open circuit would result on occasion when the voltage reached over 400V. There was often a very high input resistance to probing the devices as well, which was easily fixed with silver paste. It seemed that the PEDOT:PSS film struggled to withstand the high poling voltages, and likely needed reinforcement.

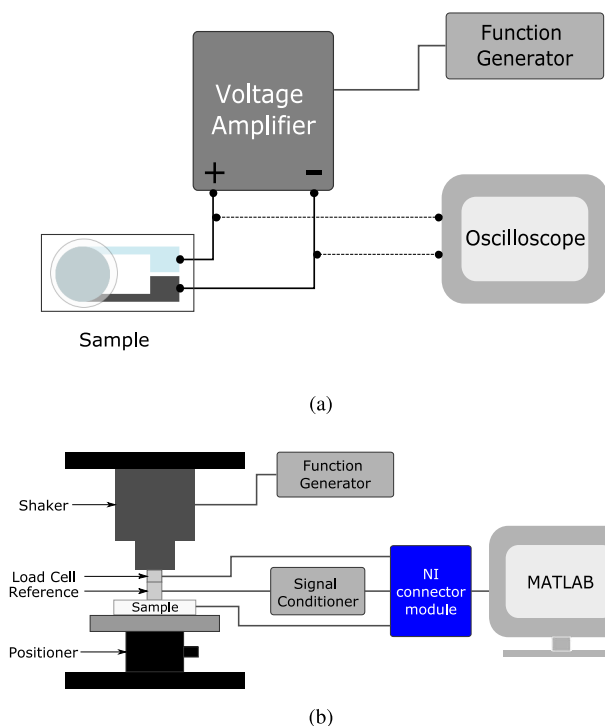### D. Piezoelectric Coefficient Measurement

(a)

(b)

FIG. 2: Schematics of (a) poling and (b) Berlincourt setups.

Samples were tested using an in-house Berlincourt setup, which is shown schematically in Fig. 2.[38–40] In a Berlincourt setup, the effective piezoelectric coefficient ($d_{33,eff}$)is measured by applying a low frequency force to a sample that is fixed to the testing surface. In order to get an accurate measurement, the frequency used was very low to avoid any material or device resonances. A reference sensor was also integrated and the final piezoelectric coefficient was determined by dividing the sample charge output with the force value measured by the reference sensor (i.e. Q/F).

To apply the low frequency force, a commercial shaker (Brüel & Kjaer Mini-Shaker Type 4810) was used. The shaker

was driven with a function generator (Tektronix AFG3101) set to apply sinusoidal force from the shaker at 1.5Vpp amplitude and 5Hz.

Before measuring, the sample was clamped down to limit any sliding or movement of the sample and prevent the piston of the shaker leaving the surface. A load cell (Measurement Specialties Inc., model number ELFS-T3E-20L) was used to observe the force between the piston of the shaker and the sample. The clamp holding the sample was adjusted until there was a static force of approximately 3N.

To observe the reference signal while the shaker was on, a commercial high sensitivity sensor (PCB Piezotronics, model number 209C02) was added and connected using a low-noise coaxial cable to a signal conditioner (PCB Piezotronics, Model 442B06).

The sample was contacted using crimp connectors (Nicomatic Crimplex). The sensor and reference were then connected to a computer using a National Instruments SCB-69 connecting block before being processed using a Matlab script to determine the charge generated per unit force.

Three separate points on the surface of each sample were tested, with three consecutive measurements done at each location. Typically, one point was the roughly in the center of the sample and the other two were to the left and right of the center. The average of all these measurements was taken as the d_{33} value for that sample.

E. Temperature Tolerance Measurements

To observe the temperature tolerance of the printed samples, two identically prepared samples were exposed to increasing temperatures for an hour at a time before testing the sample's g_{33} response.

The g_{33} response was first observed at room temperature by applying a known force to the printed sample and observing the corresponding piezoelectric response. An ADMET Universal Testing System (ADMET 5600 Testing System, ADMET ep2 controller) was used to provide regular 5N force impulses to the printed substrate. The pulse was repeated in 60 second intervals for a total of ten measurements. The exact force delivered was recorded after each impulse.

Subsequently, the samples were tested for their g_{33} response after being exposed to 40-110°C in ten degree intervals. The samples were exposed to the tested temperatures by being placed in an oven (Yamato DX 600) for one hour and immediately tested for the g_{33} response immediately after being removed from the oven.

The electrical response from the sample was recorded using a charge amplifier analog front end. The data acquisition system used in the temperature tolerance testing is shown in Fig.3 First, a custom printed circuit board (PCB) was designed and fabricated featuring a charge amplifier with an output voltage dependent on the piezoelectric charge generation using the equation shown in Equation 1.

$$V_{out} = \frac{1}{C_f} \int I dt = \frac{Q}{C_f} \tag{1}$$
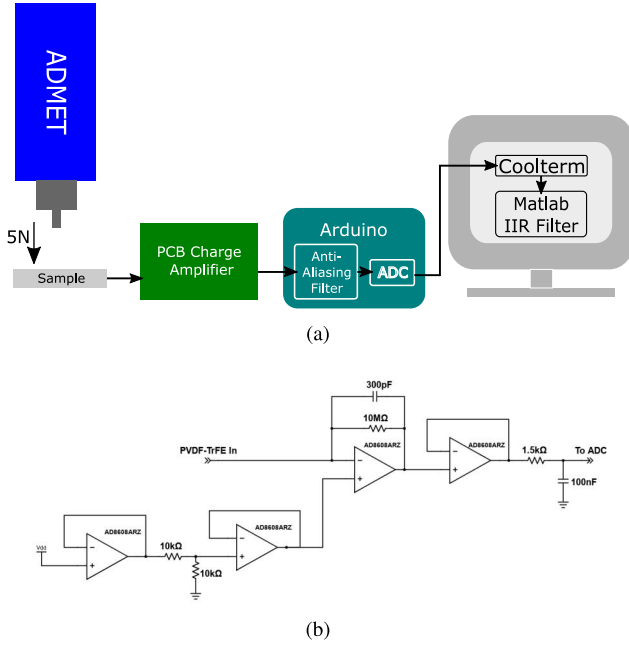
(a)

(b)

FIG. 3: a) Block diagram of heat testing system, including force generator and electronics. b) Circuit diagram of printed circuit board used in the heat testing system to amplify the charge of the PVDF-TrFE film.

TABLE I: Measured piezoelectric coefficients for different solvent ratios

Solvent Ratio (DMF:MEK)	Poling Field (V/μm)	$d_{33,eff}$ (pC/N)
1:1	90	17.89
3:1	100	26.24
4:1	60	16.84
9:1	100	22.62

III. DISCUSSION

A. Piezoelectric Coefficient

The measurement for the piezoelectric coefficient in time is shown in Fig. 4 and a summary of the measured piezoelectric coefficient for various inks is shown in Table I. The best demonstrated d_{33} values with the homemade ink were 25-27 pC/N, which is within previous literature values of 20-34 pC/N for printed PVDF-TrFE.[6] These values were demonstrated with the above processing procedure with DC poling and 4:1 and 9:1 DMF to MEK ratio homemade ink. Many other samples with homemade ink with 4:1, 1:1, and 9:1 DMF/MEK ratio were successfully poled and demonstrated d_{33} values of 10-20 pC/N. It appears then that the mixture does not have a strong influence on the piezoelectric activity of the film. However, both 4:1 and 9:1 were easy to work with on the printer so those mixtures are preferred.

The generation of charge from the piezoelectric device is directly proportional to the sheet's charge generating properties, and thus the output voltage is the charge on the feedback capacitor divided by its capacitance. Once amplified, the PVDF response voltage is fed into an anti-aliasing filter, digitized using an analog-to-digital converter (ADS1013), and finally transferred serially for post-processing. A program called CoolTerm was used to control data collection and read in the output of the Arduino/PCB. An Arduino Leonardo was used as both the I2C master to interface with the charge amplifier circuitry and the UART bridge to communicate with CoolTerm.

To smooth out the response and reduce noise harmonics of the recorded response, a 2nd order IIR band-reject filter was implemented in MATLAB to suppress all frequencies that appeared outside the band of interest. The filter was designed by taking the fast Fourier transform, observing the primary frequency of the noise, and then utilizing MATLAB's filter design tools to optimize the digital filter. To determine the g_{33} coefficient, the voltage response of the sample is divided by the input force for each impulse. The final g_{33} is taken as the average of each trial. The error is taken as the standard deviation of this average.
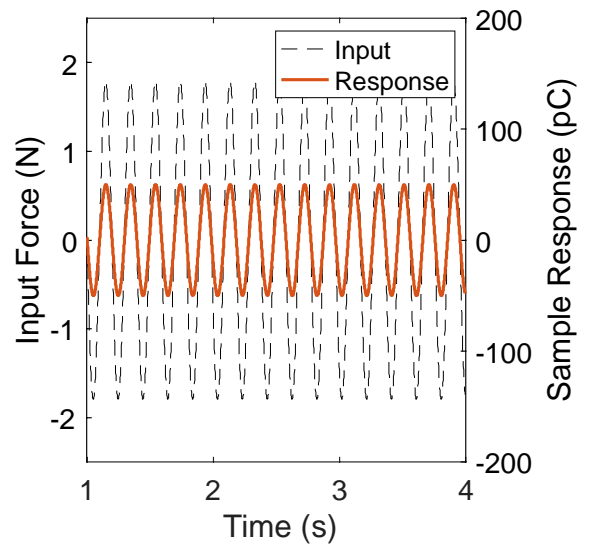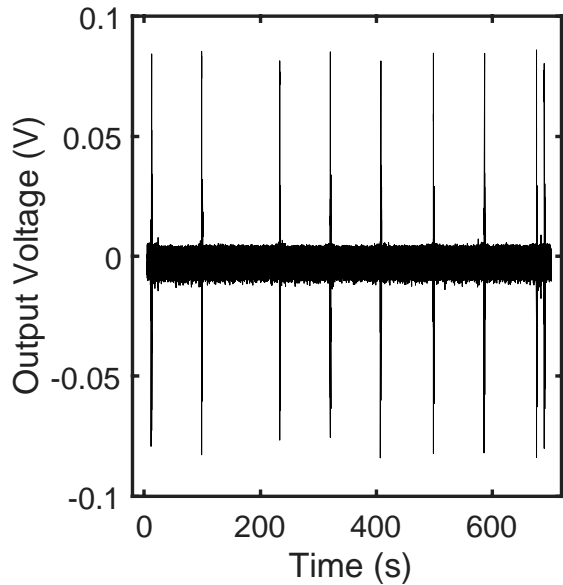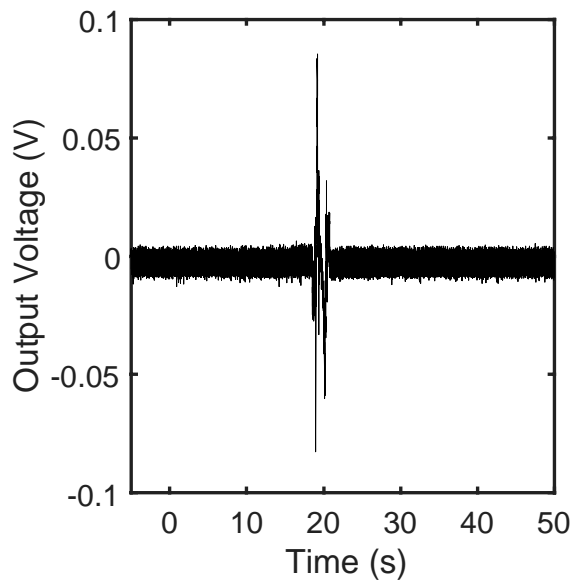

FIG. 4: Input force and sample response from piezoelectric coefficient test are shown. Sample response is shown in red on the right axis, and the input response is shown in black on the left axis.

B. Temperature Tolerance

The voltage response in time at room temperature is shown in Fig. 5a and a single response from this series is shown in Fig. 5b.


(a)

(b)

FIG. 5: (a) Sample response to repeated 5N force at room temperature. (b) Piezoelectric response of sample to single 5N force at room temperature.

The mean maximum and minimum voltage responses of the two samples at each temperature are shown in Fig. 6(a) and (b). For reference, the mean voltage during that trial is shown as well. The full response data of each sample is shown separately to demonstrate the repeatability of the measurement and
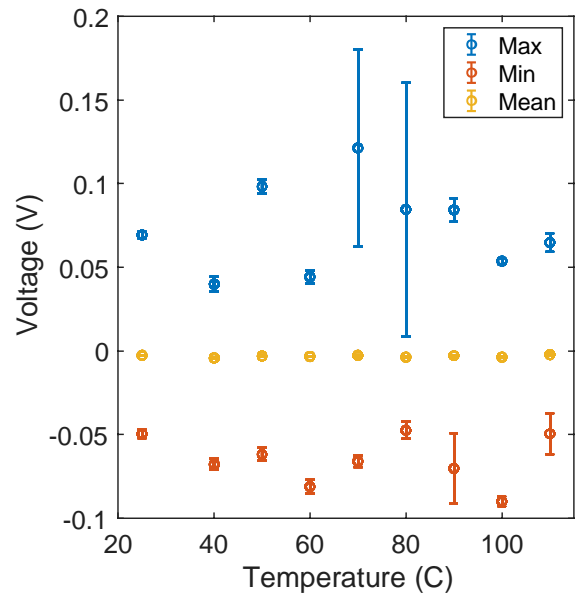
(a)
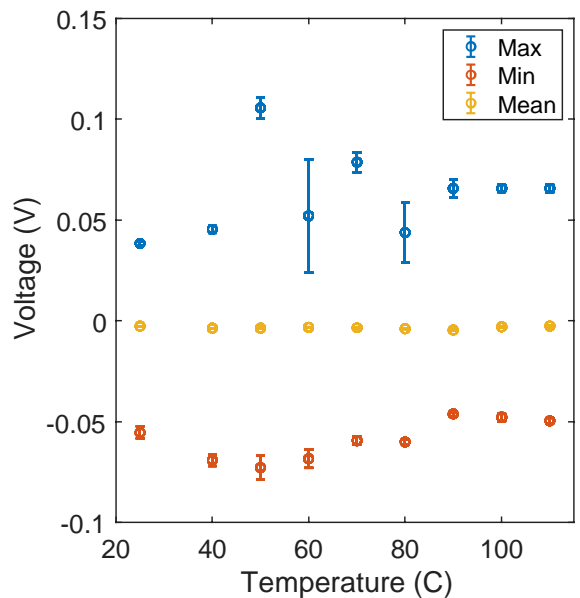
(b)

FIG. 6: Absolute voltage response to 5N force for two identically prepared samples after one hour long exposure to each increasing temperature. The data from the first sample is shown in (a) and data from the second sample is shown in (b).

avoid confusion between the data sets. The error bars shown in Fig. 6 (a) and (b) are both is the standard deviation of the repeated measurement of the voltage change at each temperature. The average g_{33} value for the two samples tested is shown in Fig. 7. The error bars here are carried forward from the voltage measurement shown in Fig. 6.

For both samples, there seems to be no significant depreciation in absolute response or g_{33} as temperature increases. Other work has established that commercially available PVDF
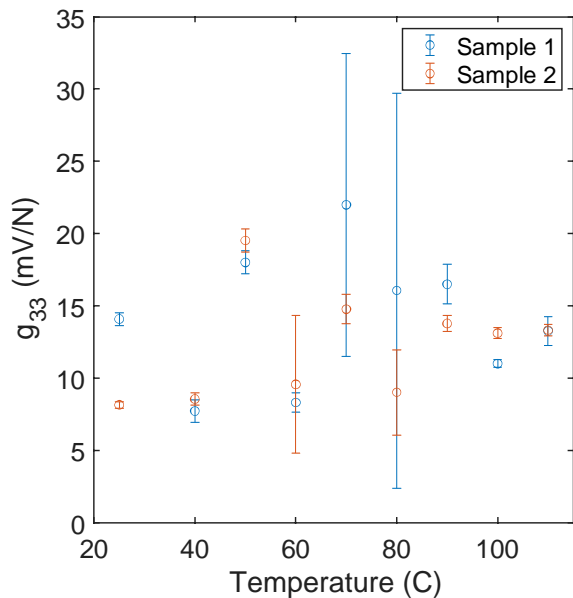
FIG. 7: g_{33} measurement of the two tested samples after
hour long exposure at increasing temperature.

sheets will physically deform after exposure to 80 °C.[5] Due
to the temperature tolerance of the PEN substrate and high
Curie point of PVDF-TrFE, the method presented here pro-
vides samples which are significantly more temperature toler-
ant than commercially available devices.

IV. AVAILABILITY

The primary advantage of the PVDF-TrFE ink mixture
described here is that it can be mixed using inexpensive and
commonly available chemicals and solvents. Commercial
ink can be significantly more expensive and offer mixed
results depending on application. In the method described,
the mixture can be tailored to work optimally for a specific
application or printing system.

The primary roadblock to most researchers of utilizing this
printing method will be access to inkjet and screen printers
and the cost of appropriate screens. Both the screens and
printers can be purchased from many sources, but the screen
printer used in this work was semi-automatic and offered
few advanced features, proving the simplicity of this method.
Screen printers are significantly less expensive than inkjet
printers, and the method for the bottom electrode could be
adapted for screen printing, which would remove the need
for the inkjet printer altogether.[41] These methods then can be
used with a variety of equipment.

The electronic systems described here for poling and
piezoelectric coefficient measurement were created by the
researchers with available laboratory equipment. Several
commercial systems are available from Radiant Technologies

or Piezotest for piezoelectric coefficient measurement, but
a similar system can be constructed using the Berlincourt
method.[42] To verify the ferroelectric character of the PVDF-
TrFE films, commercially available systems from Radiant
Technologies can be used. However, it is possible to construct
a similar system. A simplified methodology for the construc-
tion of a Sawyer-Tower circuit has been previously reported
by Qiu et al.[43,44]

V. FUTURE WORK

In future iterations of these devices, printing multiple PE-
DOT:PSS layers could help reinforce them to give them the
stability to handle the high poling voltages necessary for well
functioning devices. Alternatively, the film could be rein-
forced by printing silver ink on top of the PEDOT:PSS ink.
In order to make the device symmetric, the bottom elec-
trode could be a dual layer of silver ink on the bottom and
PEDOT:PSS on top to interface with the PVDF-TrFE layer.
Screen printing the PEDOT:PSS ink sometimes seemed to im-
pact the success of the device as it would physically deform
the PVDF-TrFE layer. Inkjet printing PEDOT:PSS might
solve this problem.

VI. CONCLUSIONS

This work describes a comprehensive method for mixing
and screen printing PVDF-TrFE inks which can be used for
a wide variety of applications and available equipment. De-
tailed methods for characterizing the resulting films have also
been discussed to verify this printing method. This stream-
lined method will enable researchers of printed electronics to
more simply and successfully integrate high quality PVDF-
TrFE polymer films into their devices for better sensors and
flexible electronics.

AUTHOR CONTRIBUTIONS

C.K.M. fabricated the PVDF-TrFE ink, printed the sam-
ples, and performed the characterization testing. M.L. assisted
C.K.M. in printing the samples and piezoelectric coefficient
characterization. K.L.M. advised and assisted in the details
and setup of the poling experiment. K.A.K. designed and im-
plemented the charge amplifier for temperature tolerance test-
ing. I.K., D.L., and M.M. advised and supervised the project.
C.K.M. wrote the manuscript with support from all authors.

ACKNOWLEDGMENTS

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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