

DNA increases the β -phase content of PVDF films

Valerie Rennoll¹, Sea On Lee², Ugur Erturun¹, Stephen D. Fried², and James West¹

¹Dept. of Electrical and Computer Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

²Dept. of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

Abstract—Deoxyribonucleic acid (DNA) has been shown to interact with poly(vinylidene fluoride) (PVDF), resulting in increased electroactive β -phase content and piezoelectric response under certain casting conditions. While the use of DNA as a self-poling agent has the potential to eliminate the need for additional stretching and poling steps in piezoelectric PVDF films, the mechanism through which DNA poles PVDF is not yet well understood, hindering the optimization of the process. Here, we performed a study to screen the effects of drying temperature, amount of nucleic acid additive, weight percentage of PVDF, spin-casting speed, and molecular weight of PVDF on spin-cast PVDF-DNA hybrid films. The phase composition and piezoelectric response of the resulting films were quantified using Fourier-transform infrared spectroscopy (FTIR) and a piezoelectric meter, respectively. We found that DNA has a significant influence on the PVDF films' β -phase content; however, this effect is masked at low drying temperatures. While DNA facilitates the formation of the electroactive β -phase of PVDF, we could not find evidence that DNA enhances PVDF's piezoelectric response. These results conflict with previous literature, which reported that DNA aligns the dipoles of PVDF such that the films exhibited a significant piezoelectric response. Overall, this study identifies that nucleic acid additives – under certain casting conditions – have an important effect on PVDF film phase composition.

I. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has one of the highest responses among piezoelectric polymers and is highly valued for sensor, energy harvesting, and filter applications. The arrangement of hydrogen and fluorine atoms along the carbon backbone determine PVDF's phase composition. While the non-polar α -phase is more commonly found, the β -phase is preferred due to its substantial permanent dipole moment and subsequent piezoelectric response.

In order to increase the β -phase content and piezoelectric response, PVDF is commonly processed through combined mechanical stretching and electrical poling [1]. This process converts the thermodynamically stable α -phase to the β -phase while also aligning the dipoles of the polymer. To minimize the processing required to obtain piezoelectric PVDF films, there have been a number of efforts dedicated to increasing the β -phase with a variety of additives, including platinum nanoparticles [2] and ZnO nanorods [3].

One particularly notable nontoxic and biocompatible additive that has been introduced into PVDF films is deoxyribonucleic acid (DNA) [4]. Tamang and co-workers demonstrated that DNA interacts with PVDF, resulting in increased electroactive β -phase content and piezoelectric response. However, the aforementioned report left unclear what potential

interactions exist between the addition of DNA and the casting conditions, and if the combination thereof impacts the phase composition of the films. For spin or drop-casted PVDF films specifically, the phase composition is typically dependent on a number of ambient and casting parameters, including humidity [5], drying temperature [6], solvent [7], PVDF concentration [6], and PVDF molecular weight [8].

A more systematic study on the interactions between casting conditions and addition of DNA in PVDF films is necessary to fully understand and optimize the use of DNA as a poling agent. In the following, we present a 'design of experiments' study to understand the impact of PVDF molecular weight and concentration, drying temperature, added DNA mass, and spin speed on the phase composition and piezoelectric response of spin-cast PVDF films.

II. MATERIALS AND METHODS

Spin-cast PVDF films were fabricated following a fractional factorial design and characterized. A statistical model was fitted to the phase composition data to determine the factors that enhance the electroactive β -phase content of the films.

A. Design of experiments

Factorial designs vary the levels of all factors simultaneously to allow interactions between factors to be interpolated [9]. A full factorial design requires examination of all combinations of design factors. In contrast, fractional factorial designs require a smaller subset of experiments, but can still screen the factors that have the greatest impact on the response. The fractional design cannot analyze all high-order interactions between multiple factors; however, it is generally assumed that these high-order interactions either do not exist or are negligible in comparison to the individual factor effects [9].

In order to assess the dominant factors on the β -phase content of PVDF films, a resolution V, two-level, half-fraction factorial design was used. The factors, listed in Table I with their levels, included (i) PVDF molecular weight; (ii) PVDF solution concentration; (iii) drying temperature; (iv) DNA mass; and (v) spin speed. The design was created with 1 center point and 1 block, requiring the fabrication of 17 samples. The conditions for each sample were determined using Minitab [10] and are shown in Table II.

B. Materials

To limit the effects of residual water on the phase composition to the fullest extent possible prior to film casting,

Factor	Levels		
	Low (-)	Center (0)	High (+)
PVDF molecular weight	180,000 Da	275,000 Da	530,000 Da
Drying temperature	22°C	60°C	100°C
Spin speed	100 rpm	500 rpm	1000 rpm
PVDF solution concentration	15 wt%	20 wt%	25 wt%
DNA mass	0 µg	10 µg	50 µg

TABLE I: Levels of each factor used in the half-fraction factorial design.

efforts were made to reduce the exposure of the materials to moisture. Lyophilized calf thymus DNA was purchased from Sigma-Aldrich and resuspended in deionized water. 50 µg of DNA was aliquoted into a centrifuge tube, reduced to dryness in a centrifugal concentrator (Eppendorf Vacufuge Plus) for 3 hours, and stored in a desiccator overnight to remove residual solvent. PVDF pellets purchased from Sigma-Aldrich were also stored in a desiccator for one week prior to solution preparation. Anhydrous dimethylformamide (DMF) purchased from Sigma-Aldrich was removed using a Schlenk line and stored under nitrogen gas.

C. Film fabrication

Solutions of 15, 20, and 25 wt% (w/v) PVDF-DMF were mixed on a hot plate at 100°C for 90 minutes. For samples with DNA added, 3 mL of solution was transferred to the DNA centrifuge tube and vortexed. 3 mL of each solution was spin-cast (Best Tools Smart Coater 200) on a silicon wafer at speeds of 100, 500, or 1000 rpm for 20 seconds at an acceleration of 200 rpm/s. The samples were immediately transferred to a hot plate and dried at 22, 60, or 100°C. Room temperature samples were given 18 hours to dry, while 60 and 100°C samples were given 4 hours to dry. The samples were prepared in a clean room with the relative humidity between 30 and 40%.

D. Characterization

The fabricated PVDF films were characterized by three different metrics: film thickness was measured, phase composition was assessed, and piezoelectric response was recorded. The thickness was measured using a stylus profiler (KLA-Tencor D-300) and averaged from two positions on the film. The vibrational spectrum of the films was measured using Fourier transform infrared spectroscopy (ThermoNicolet Nexus 670 FTIR Spectrometer) in the attenuated total reflection mode. For free standing films, the spectrum was measured a total of four times, two times each on the top and bottom surface at randomly chosen positions. For films that were too thin to be removed from the silicon wafer, the spectrum was measured in triplicate on the top surface of the film. For each measurement, 32 scans were performed in the 4000 - 400 cm^{-1} range with 2 cm^{-1} resolution. The collected spectra were all processed using an advanced baseline correction in Spectragryph [11].

The piezoelectric charge constants (d_{33}) of the PVDF films (10mm² surface area) were measured with a piezoelectric meter (PolyK PKD3-2000). The preload applied to the sample was monitored with the meter's force sensor to 2 ± 0.05

N. The reported d_{33} values were obtained by averaging the measured coefficient from the top and bottom of the film.

E. Phase analysis and modeling

The percentages of α , β , and γ phases were quantified following the procedure in [12], which uses the peak-to-valley height ratio between the peaks at 1275 and 1234 cm^{-1} . The peak positions were identified using the 'idpeaks' function from [13] in Matlab. Using the phase composition calculations, a model for the β -phase content with all factors was fitted to the data using Minitab. The model was reduced until factors with a p-value (calculated from F-distribution in Minitab) greater than the significance value (0.05) were removed.

III. RESULTS

Films dried at room temperature were opaque or cloudy white, while films dried at elevated temperatures were transparent. This change in opacity with drying temperature has been noted previously and is caused by moisture in the surrounding environment [14]. At low drying temperatures, humidified air diffuses into the film and phase separation occurs between water in the air and PVDF. The films had an average thickness of 50 µm. While the majority of films were free standing, samples 7 through 11 were too thin to be removed from the silicon wafer.

A. Phase composition

The calculated average percentages of α , β , and γ phases for the PVDF samples are shown in Table II. The β -phase percentage of the samples ranged from 0 to 36.8%. For comparison, a commercial piezoelectric PVDF film (PolyK PVDF-P040) was measured and analyzed using the same method and found to have an average β -phase percentage of 85.6%. Figure 1 shows examples of the FTIR spectra for PVDF-DNA sample 2 and a commercial PVDF sample. In general, the phase composition was non-uniform throughout the sample and varied based on position and surface the measurement was taken from. This has been previously noted and is related to differences in solvent evaporation rates across the film [15].

The fitted model for β -phase content included coefficients for the terms shown in Figure 2, which indicates that drying temperature, drying temperature/PVDF concentration, and DNA mass had the greatest effect on the β -phase content. The main factor effects are illustrated in Figure 3: β -phase content increased with increasing drying temperature, spin speed, DNA mass, and PVDF concentration, but decreased with increasing PVDF molecular weight. Figure 4 shows the significant interactions between drying temperature and DNA mass, spin speed, and PVDF concentration. The interaction between drying temperature and DNA mass shows that the β -phase content is significantly increased when both factors are at high levels, indicating that DNA is only effective at increasing the β -phase content when the drying temperature is high.

The model had an R^2 value of 60% and the residual plots are shown in Figure 5. The low model fit is attributed to the

Sample	Molecular weight (Da)	Drying temp. (°C)	DNA mass (μg)	Spin speed (rpm)	PVDF conc. (wt%)	β%	γ%	α%	d_{33} (pC/N)
1	(+)	(+)	(+)	(+)	(+)	36.8	12.5	50.7	0.5
2	(+)	(+)	(-)	(-)	(+)	7.6	71.7	20.8	0.9
3	(+)	(+)	(+)	(-)	(-)	16.3	54.5	29.1	2.9
4	(+)	(-)	(+)	(-)	(+)	0.0	90.2	9.8	0.6
5	(-)	(+)	(+)	(-)	(+)	23.3	37.0	39.6	0.5
6	(-)	(+)	(-)	(+)	(+)	33.4	0.0	66.6	0.8
7	(-)	(-)	(-)	(-)	(+)	0.0	87.9	12.1	-
8	(-)	(-)	(-)	(+)	(-)	22.2	60.0	17.8	-
9	(-)	(-)	(+)	(-)	(-)	17.6	74.1	8.2	-
10	(-)	(-)	(+)	(+)	(+)	1.4	87.9	10.7	-
11	(+)	(-)	(+)	(+)	(-)	2.2	87.9	9.9	-
12	(+)	(-)	(-)	(+)	(+)	0.0	90.3	9.7	0.8
13	(-)	(+)	(-)	(-)	(-)	0.0	76.3	23.7	1.6
14	(+)	(+)	(-)	(+)	(-)	0.7	70.4	28.8	1.0
15	(+)	(-)	(-)	(-)	(-)	0.0	90.1	9.9	1.1
16	(0)	(0)	(0)	(0)	(0)	0.0	86.4	13.6	1.1
17	(-)	(+)	(+)	(+)	(-)	33.8	0.0	66.2	0.8

TABLE II: The fabrication conditions for each sample in the half-fraction factorial design with the calculated phase composition and measured piezoelectric response. The low, center, and high levels are represented by (-), (0), and (+), respectively.

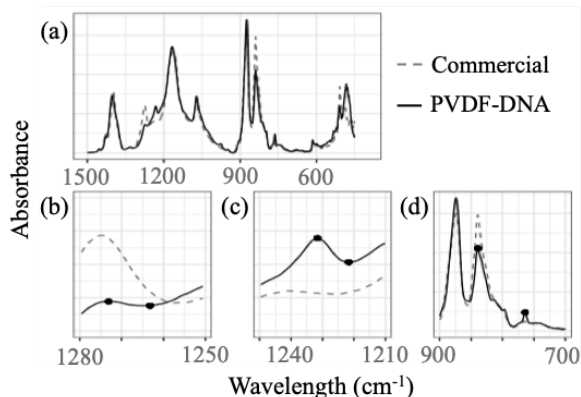


Fig. 1: FTIR spectrum of commercial sample and PVDF-DNA sample 2 acquired by attenuated total reflection with peak markers used for phase calculation. (a) Full range of 400-1500 cm^{-1} . (b) Detail of 1280-1250 cm^{-1} region, indicative of the β -phase. (c) Detail of the 1250-1210 cm^{-1} region, indicative of the γ -phase. (d) Detail of the 900-700 cm^{-1} region, indicative of the α , β , and γ -phases.

non-uniformity of the phase composition at different positions of the sample.

B. Piezoelectric response

Prior to measuring the piezoelectric response of the fabricated PVDF films, the piezoelectric meter was calibrated and validated with a commercial piezoelectric PVDF film. The measured d_{33} of the film was 27.4 pC/N, which agrees with the manufacturer's given response of greater than 25 pC/N.

The d_{33} was measured for free standing films (samples 7 through 11 excluded) and the results are included in Table II. The maximum and average d_{33} of all measured films was 2.9 and 1.0 pC/N, respectively. Despite the the promotion of β -phase formation, the addition of DNA did not enhance the piezoelectric response across the thickness of the films. While more studies are necessary to understand the low piezoelectric

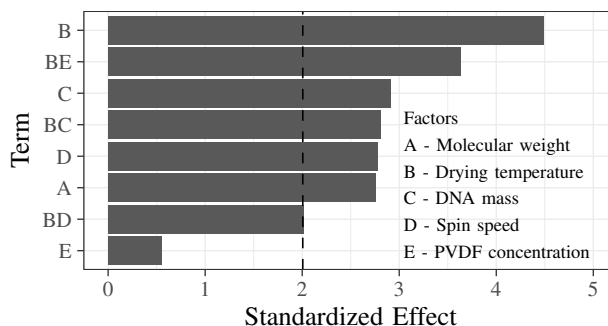


Fig. 2: The standardized effects (t-statistic to test the null hypothesis that the factor effect is 0) of the factors included in the model for the β -phase content. Factors with standardized effects that cross the reference line are statistically significant. Larger standardized effects indicate greater impacts on the response.

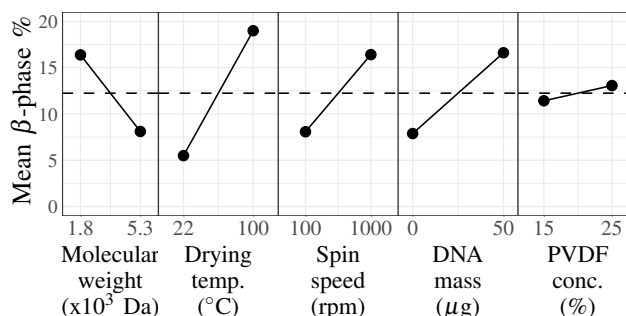


Fig. 3: The main effects of the factors included in the β -phase content model. The plot indicates the response mean for each value of a variable. Steeper slopes indicate a greater impact on the response. The reference line indicates the overall mean of the response.

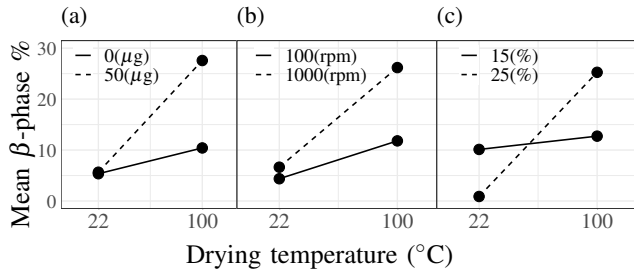


Fig. 4: Plot indicating the significant interactions between drying temperature and a second factor on the mean response. (a) DNA mass - the addition of DNA only impacts the response at high drying temperatures. (b) Spin speed - higher spin speed only impacts the response at high drying temperatures. (c) PVDF solution concentration - a higher concentration increases the mean response at high drying temperatures.

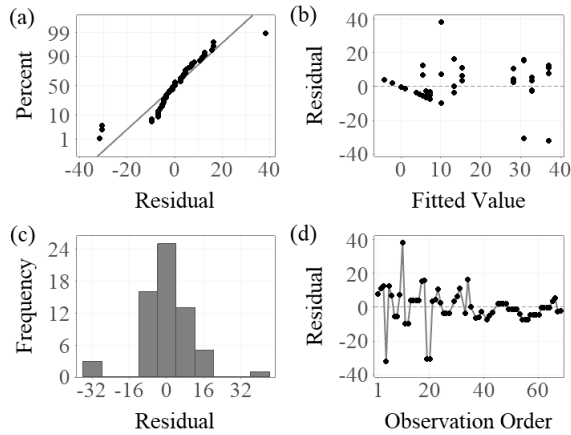


Fig. 5: Residual plots: (a) normal probability plot to assess normal distribution, (b) versus fit to assess constant variance, (c) histogram to detect outliers, and (d) versus order to address correlation. Overall, the residuals are normally distributed with constant variance, but there are several outliers that may decrease the model fit.

response, it is possible that (1) the films had low crystallinity and/or (2) the dipoles were randomly distributed throughout the film.

IV. DISCUSSION

By finding new methods to enhance the piezoelectricity of PVDF without substantial processing, it would be possible to decrease processing costs and make the polymer more widely and cheaply available. Here, a follow-up study is performed to more thoroughly investigate how the casting conditions impact the phase composition and piezoelectric response of films with DNA added. We find that in order for spin-cast PVDF films with DNA to be comparable to commercially available piezoelectric PVDF films, further optimization is required. Although DNA had a significant impact on the phase composition, it was not shown to increase the piezoelectric response of PVDF films. While the possibility of poling

PVDF with DNA rather than an electric field is intriguing, the complex interactions that occur between PVDF and DNA under varied casting conditions must be understood in greater detail. While this preliminary study used a limited parameter space without technical replicates, it nevertheless demonstrates that several factors, including DNA, can enhance the β -phase content of PVDF films.

ACKNOWLEDGMENT

We would like to acknowledge the IEEE DEIS graduate fellowship and Johns Hopkins University Discovery Award for their support. We would also like to thank Dr. Sherri Rennoll for her thoughtful discussions on the project.

REFERENCES

- [1] T. Kaura, R. Nath, and M. M. Perlman, "Simultaneous stretching and corona poling of PVDF films," vol. 24, no. 10, pp. 1848–1852, 1991.
- [2] S. K. Ghosh, M. M. Alam, and D. Mandal, "The in situ formation of platinum nanoparticles and their catalytic role in electroactive phase formation in poly(vinylidene fluoride): a simple preparation of multifunctional poly(vinylidene fluoride) films doped with platinum nanoparticles," *RSC Advances*, vol. 4, no. 79, pp. 41 886–41 894, 2014.
- [3] H. H. Singh, S. Singh, and N. Khare, "Enhanced β -phase in PVDF polymer nanocomposite and its application for nanogenerator," *Polymers for Advanced Technologies*, vol. 29, no. 1, pp. 143–150, 2018.
- [4] A. Tamang, S. K. Ghosh, S. Garain, M. M. Alam, J. Haeberle, K. Henkel, D. Schmeisser, and D. Mandal, "DNA-assisted β -phase nucleation and alignment of molecular dipoles in PVDF film: A realization of self-poled bioinspired flexible polymer nanogenerator for portable electronic devices," *ACS Applied Materials & Interfaces*, vol. 7, no. 30, pp. 16 143–16 147, 2015.
- [5] M. Benz and W. B. Euler, "Determination of the crystalline phases of poly(vinylidene fluoride) under different preparation conditions using differential scanning calorimetry and infrared spectroscopy," *Journal of Applied Polymer Science*, vol. 89, no. 4, pp. 1093–1100, 2003.
- [6] J. C. C. Ferreira, T. S. Monteiro, A. C. Lopes, C. M. Costa, M. M. Silva, A. V. Machado, and S. Lanceros-Mendez, "Variation of the physicochemical and morphological characteristics of solvent casted poly(vinylidene fluoride) along its binary phase diagram with dimethylformamide," *Journal of Non-Crystalline Solids*, vol. 412, pp. 16–23, 2015.
- [7] X. Li, Y. Wang, T. He, Q. Hu, and Y. Yang, "Preparation of PVDF flexible piezoelectric film with high β -phase content by matching solvent dipole moment and crystallization temperature," *Journal of Materials Science: Materials in Electronics*, vol. 30, no. 22, pp. 20 174–20 180, 2019.
- [8] Y. Zhao, W. Yang, Y. Zhou, Y. Chen, Y. Yang, J. Xu, and Y. Jiang, "Influence of molecular weight on the dielectric and energy storage properties of poly(vinylidene fluoride)," *Electronic Materials Letters*, vol. 12, no. 6, pp. 779–783, 2016.
- [9] R. F. Gunst and R. L. Mason, "Fractional factorial design," *WIREs Computational Statistics*, vol. 1, no. 2, pp. 234–244, 2009.
- [10] Minitab, "Minitab 19 statistical software," Computer software, 2020.
- [11] F. Menges, "Spectragryph - optical spectroscopy software," Version 1.2, 2019.
- [12] X. Cai, T. Lei, D. Sun, and L. Lin, "A critical analysis of the α , β , and γ phases in poly(vinylidene fluoride) using FTIR," *RSC Advances*, vol. 7, no. 25, pp. 15 382–15 389, 2017.
- [13] T. O'Haver, *Pragmatic Introduction to Signal Processing*, 2020.
- [14] M. Li, I. Katsouras, C. Piliugu, G. Glasser, I. Lieberwirth, P. W. M. Blom, and D. M. de Leeuw, "Controlling the microstructure of poly(vinylidene-fluoride) (PVDF) thin films for microelectronics," *J. Mater. Chem. C*, vol. 1, pp. 7695–7702, 2013.
- [15] D. L. Chinaglia, R. Gregorio Jr., J. C. Stefanello, R. A. Pisani Altafim, W. Wirges, F. Wang, and R. Gerhard, "Influence of the solvent evaporation rate on the crystalline phases of solution-cast poly(vinylidene fluoride) films," *Journal of Applied Polymer Science*, vol. 116, no. 2, pp. 785–791, 2010.