

Effect of Mechanical Treatment Temperature on Electrical Properties and Crystallite Size of PVDF Film

Ambran Hartono^{1*}, Suparno Satira², Mitra Djamal², Ramli Ramli³, Herman Bahar², Edi Sanjaya¹

¹Department of Physics, Faculty of Science and Technology, Islamic State University Syarif Hidayatullah, Jakarta, Indonesia

²Theoretical High Energy Physics and Instrumentation Research Group, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Bandung, Indonesia

³Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Padang, Indonesia

Email: *ambranhartono@yahoo.com

Received January 11, 2013; revised February 16, 2013; accepted February 25, 2013

ABSTRACT

Fabrication of PVDF films has been making using Hot Roll Press. Preparation of samples carried out for nine different temperatures. This condition is carried out to see the effect of temperature fabrication on electrical properties and crystallite size of PVDF films. The electrical properties like as surface resistivity are discussion focus in this paper. Surface resistivity properties of PVDF can be improved by mechanical treatment on the varying film thickness and the temperature. To obtain the diffraction pattern of sample characterization is performed using X-Ray Diffraction. Crystallite size of PVDF films calculate from broadening pattern of X-Ray Diffraction. Furthermore, from the diffraction pattern calculated β fraction and crystallite size, for calculation to determine the crystallite size of the sample by using the Scherrer equation. Has been obtained an increase piezoelectric properties of PVDF films that characterized by increasing β fraction. Have been obtained β fraction increased from 25.4% up to 44% for temperatures of 130°C up to 170°C, respectively. Resistivity value has been obtained at temperature 130°C up to 170°C, decreased from $1.23 \times 10^4 \Omega\text{m}$ up to $0.21 \times 10^4 \Omega\text{m}$ respectively. From the experimental results and the calculation of crystallite sizes obtained for the samples with temperature 130°C up to 170°C respectively are increased from 7.2 nm up to 20.54 nm. These results indicate that mechanical treatment caused increase β fraction and decrease surface resistivity. Increasing temperatures will also increase the size of the crystallite of the sample. This happens because with the increasing temperature causes the higher the degree of crystallization of PVDF film sample is formed, so that the crystallite size also increases.

Keywords: Crystallite Size; PVDF; Roll Hot Press; Scherrer Equation; Surface Resistivity; Temperature Different; XRD

1. Introduction

Recently, the development of manufacturing technology and utilization of polymer films are increasing rapidly, especially polyvinylidene fluoride (PVDF) polymer. PVDF is a material typically used for applications requiring high purity when compared to other fluoropolymer. PVDF easier to melt due to have a low melting point [1]. PVDF can be synthesized from the gaseous VDF monomers via free radical polymerization process are shown in **Figure 1**.

PVDF polymer has three solid molecule structures that are β -phase, α -phase and γ -phase [2]. Chain agglomerations of α -phase in PVDF are shown in **Figure 2**.

α -phase of PVDF polymer have TGTG type conformation structure [2]. PVDF polymer with β -phase mole-

cule structure is shown in **Figure 3**.

Recently, PVDF with β -phase structure are widely developed due to molecules with this structure provides the greatest piezoelectric effect compared with other phase.

β -phase have planar zig-zag formation which all trans (TTTT) [3] with deflection small because of fluor atoms bonded by nearest monomer.

The electrical properties like as piezoelectric are related to the β fraction PVDF polymer and surface resis-

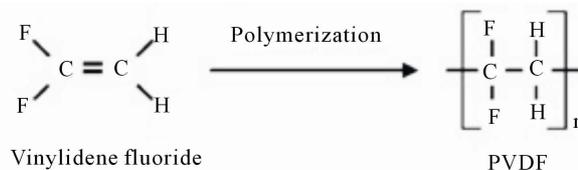


Figure 1. Polymerization process.

*Corresponding author.

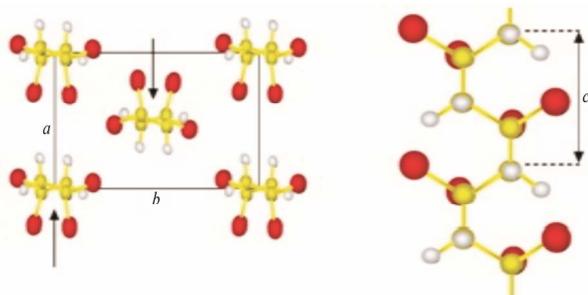


Figure 2. Chain structure of α -phase in PVDF.

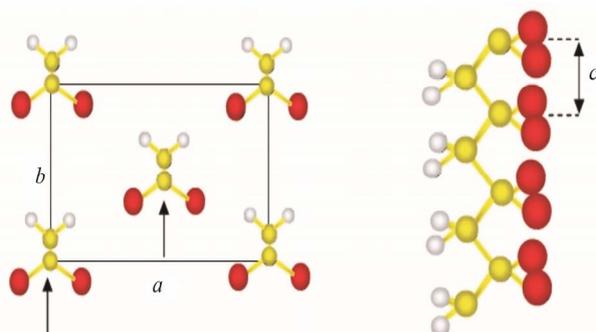


Figure 3. Chain structure of β -phase in PVDF.

tivity. Recently, PVDF with β -phase structure are widely developed due to molecules with this structure provides the greatest piezoelectric effect compared with other phase [4]. The α phase obtained by the crystallization of melt can be transformed to the β phase by mechanical deformation [2]. Drawing at lower temperatures to the natural draw ratio of ~ 4 and at higher temperatures to higher draw ratios (>4) favors the transformation from α to β phase [5-8]. From WAXD and FTIR studies, it is clear that there is α phase transformation during stretching and stretching at lower temperature to draw ratio of 4 or to higher draw ratios at higher temperature results in higher β phase contents [9,10].

The most common polymorph produced during crystallization from the melt is the α -form; it is essentially the sole crystalline obtained at all temperatures up to $\sim 150^\circ\text{C}$. Its crystallization kinetics have been studied by Gianotti *et al.* [11] in the range $147^\circ\text{C} - 165^\circ\text{C}$, by Nakamura *et al.* [12], between $148^\circ\text{C} - 155^\circ\text{C}$ and by Mancarella and Martuscelli [13] between 134°C and 149°C . The dependence of crystalline and amorphous specific volume on temperature has been systematically studied by Nakagawa and Ishida [14].

Until now research on PVDF piezoelectric properties is still being developed, both in terms of increasing the piezoelectric material and the analysis of physical parameters related to the amount of beta fraction of the sample as well as in its application to sensors. In our research conducted by making a thin layer of material

PVDF polymer with Roll Hot Press for several different temperatures. Having obtained samples were then carried out characterization using XRD to analyze the influence of different temperatures on the manufacture of crystallite size of PVDF films [15].

Surface Resistivity value of PVDF film calculated by measurement using I-V meter. Electro active polymers, especially polyvinylidene fluoride, its polyvinylidene fluoride trifluoroethylene copolymer and cellular polymer ferroelectrics'—have interesting and useful piezoelectric and pyroelectric properties [16].

2. Experiment

In the experiments performed and characterization of PVDF film using such equipment; Roll Hot Press machine, micrometer screw, IV meter and X-Ray Diffraction. Initially, the PVDF samples in powder form were placed on the engine cylinder is then heated until it melts and then hot press roll device is operated to obtain a thin film. Fabrication of PVDF films made for variations in temperature from 130°C to 170°C . PVDF film thickness was measured with a micrometer screw, the surface resistivity of film obtained by four point probes that was realized using I-V meter, β fraction and the crystalline phase is determined by using the X-Ray Diffraction. Roll hot press machine are shown in **Figure 4**.

The scheme of four point probes is shown in **Figure 5**.



Figure 4. Roll hot press machine.

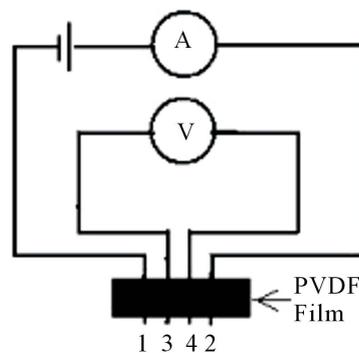


Figure 5. The point four probe scheme.

3. Results and Discussion

PVDF films have been obtained with thicknesses of 13 μm as shown in **Figure 6**. Characterization results performed on samples by using XRD.

X-Ray Diffraction characterization results of sample for temperature variation from 130°C to 170°C as shown in **Figure 7**.

XRD characterization results of sample with temperature at 130°C as shown in **Figure 8**.

While the results for the characterization of the sample for temperature at 135°C as shown in **Figure 9**.

Calculation to determine the amount of beta fraction of each sample using the Equation (1):

$$F(\beta) = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}} \times 100\% \quad (1)$$

From this characterization obtained β fraction of sample for temperature variation 130°C to 170°C are shown in **Table 1**. Graph of increasing β fraction with increas-



Figure 6. PVDF film produced.

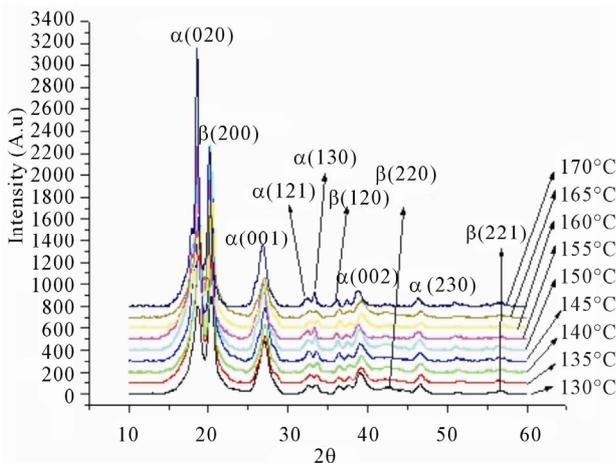


Figure 7. XRD results for sample at 130°C to 170°C.

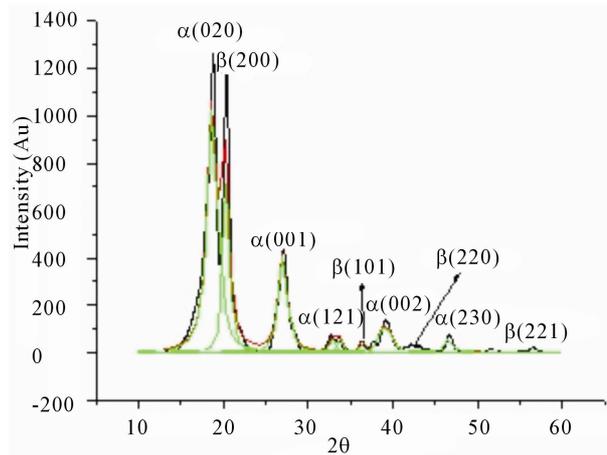


Figure 8. XRD results for sample at 130°C.

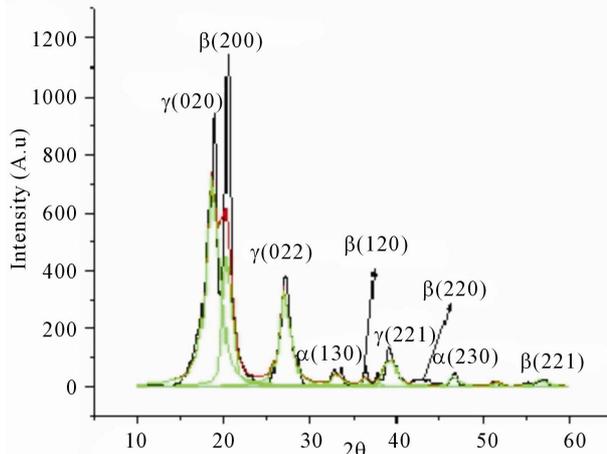


Figure 9. XRD results for sample at 135°C.

ing temperature is shown in **Figure 10**.

The increase in temperature causes an increase in polarity due to the dipole orientation resulting in the transformation of the structure occurs. It is characterized by the addition of β fraction [17].

The results of current-voltage measurements for the same thickness of 13 nm with a temperature variation of 130°C to 170°C are shown in **Figure 11**.

The results of resistivity measurements show that the applied voltage is proportional to the increase in current, in accordance with Ohm's law.

$$R = \frac{V}{I} \quad (2)$$

where R is resistance (Ω), V is applied voltage (V) and I is current (A).

The value of R can obtained from I-V curve gradient. Resistivity of sample calculated by Equation (3):

$$\rho = 2\pi RS \quad (3)$$

Table 1. β fraction of sample for temperature variation from 130°C up to 170°C.

No	Temperature (°C)	β Fraction (%)
1	130	25.4
2	135	26.34
3	140	27.51
4	145	29.23
5	150	29.56
6	155	35.5
7	160	39.13
8	165	41.07
9	170	44

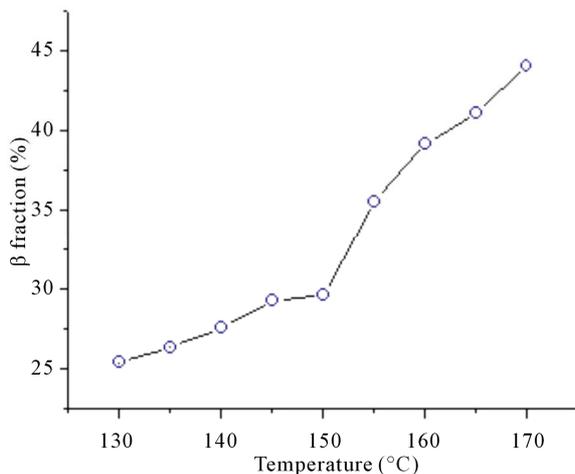


Figure 10. Graph of β fraction increase to the temperature from 130°C to 170°C.

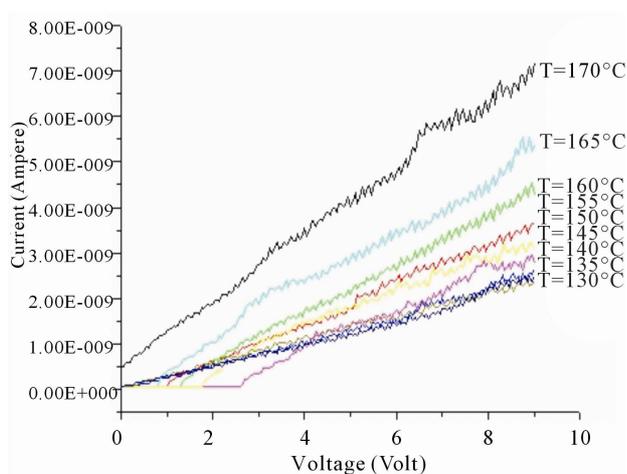


Figure 11. I-V curve of sample for variation temperature from 130°C to 170°C.

where ρ is resistivity (Ωm) and S is distance between the electrodes (5 mm). Surface Resistivity values of PVDF film for temperature 130°C to 170°C are decreased from $1.23 \times 10^4 \Omega\text{m}$ to $0.21 \times 10^4 \Omega\text{m}$ respectively. Graph of surface resistivity versus temperature are shown in **Figure 12**.

While the temperature increase causes a decrease in the resistivity value, which indicates that there has been an increase in piezoelectric properties.

Crystallite size of PVDF film is determined by using Scherrer equation. Scherrer has derived an expression for broadening of x-ray diffraction peaks due only to small crystallite sizes [18]:

$$B_{\text{cris}} = \frac{k\lambda}{L \cos \theta} \quad (4)$$

where λ is the wavelength of the x-ray used, θ is the Bragg angle, L is the “average” crystallite size measured in a direction perpendicular to the surface of the specimen, and k is a constant. Equation (4) is commonly known as the Scherrer equation and was derived based on uniform size. However, this equation is now frequently used to estimate the crystallite sizes of both cubic and noncubic materials. The constant k has been determined to vary between 0.89 and 1.39, but is usually taken as close to unity, the assumption that $k = 1.0$ is generally justifiable.

In experiment for fabrication temperature is 130°C, this pattern was indexed, and we found that these three reflections have indices (020), (200) and (001) at the 2θ value of 18.67, 20.405, and 27.09, respectively. From this characterization and calculation has produces crystallite size is 7.2 nm.

From second experiment for fabrication temperature is 135°C, we found that these three reflections have indi-

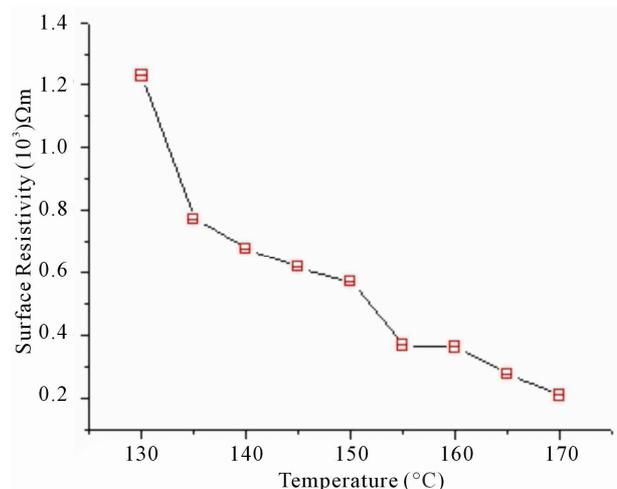


Figure 12. Graph resistivity as a function of temperature from 130°C to 170°C.

ces (020), (200) and (002) at the 2θ value of 18.72, 20.51, and 27.19, respectively. From this characterization and calculation has produces crystallite size is 7.9 nm. From the diffraction pattern for temperature 140°C, we found that these three reflections have indices (020), (200) and (022) at the 2θ value of 18.63, 20.40, and 27.08 respectively. From this characterization and calculation has produces crystallite size is 19 nm [15].

Completely experimental results from this experiment are shown in **Table 2**.

These results show that increasing temperatures will

Table 2. Crystallite size for each sample.

Temperature	2θ	hkl	B_c (rad) $\cos\theta$ ($\times 10^{-2}$)	Crystallite size (nm)
130°C	18.67	020	2.27	7.2
	20.405	200	1.76	
	27.09	001	2.42	
135°C	18.72	020	2.25	7.9
	20.51	200	2.09	
	27.19	002	1.5	
140°C	18.63	020	2.41	8.7
	20.40	200	1.61	
	27.08	022	1.57	
145°C	18.72	020	2.032	10.93
	20.51	200	1.093	
	27.18	022	1.102	
150°C	18.49	020	0.84	14
	20.225	200	1.241	
	26.92	022	1.181	
155°C	18.57	020	1.436	14.67
	20.37	200	0.809	
	27.00	022	0.901	
160°C	18.50	020	0.510	19
	20.31	200	0.335	
	26.99	022	1.677	
165°C	18.80	020	0.414	19.7
	20.44	200	0.99	
	27.08	022	1.065	
170°C	17.75	110	0.276	20.54
	18.56	020	1.253	
	20.12	200	0.731	

also increase the size of the crystallite of the sample. This happens because with the increasing temperature causes the higher the degree of crystallization of PVDF film sample is formed, so that the crystallite size also increases.

4. Conclusion

Has been successfully produced PVDF films with using roll hot press. XRD characterization showed increase in the β fraction when the temperature is raised. PVDF films showed a decrease in resistivity for every increase of temperature. This indicates that mechanical treatment to produce film thickness and temperature has a strong influence on the β fraction of PVDF films. Increasing of temperatures will also increase the size of the crystallite of the sample. This happens because with the increasing temperature causes the higher the degree of crystallization of PVDF film sample is formed, so that the crystallite size also increases.

5. Acknowledgements

The authors thank to Mr. Priambodo as laborant at Integrated Centre Laboratory of State Islamic University (UIN JAKARTA) for support in X-Ray Diffraction Characterization.

REFERENCES

- [1] C. L. Radiman, "Kimia Polimer," Penerbit ITB, Bandung, 2004, pp. 5-20.
- [2] A. J. Lovinger, "Poly(Vinylidene fluoride)," In: D. C. Bassett, Ed., *Development in Crystalline Polymers*, Applied Science Publisher, London, 1982, pp. 195-261.
- [3] A. J. Lovinger, "Poyivinylidene Fluoride," Applied Science Publisher, London, 1981, p. 202.
- [4] A. Hartono, S. Satira, M. Djamil, Ramli and E. Sanjaya, "Effect of Mechanical Treatment Temperature and Layer Thickness on Piezoelectric Properties PVDF Film," *Proceedings of APS*, 2012.
- [5] K. Matsushige, K. Nagata, S. Imada and T. Takemura, "The II-I Crystal Transformation of Poly(vinylidene fluoride) under Tensile and Compressional Stresses," *Polymer*, Vol. 21, No. 12, 1980, pp. 1391-1397. [doi:10.1016/0032-3861\(80\)90138-X](https://doi.org/10.1016/0032-3861(80)90138-X)
- [6] J. C. Mcgrath, "High Effective Draw as a Route to Increased Stiffness and Electrical Response in Poly(vinylidene fluoride)," *Polymer*, Vol. 21, No. 8, 1980, pp. 855-857. [doi:10.1016/0032-3861\(80\)90237-2](https://doi.org/10.1016/0032-3861(80)90237-2)
- [7] J. Humphreys, et al., "A Study of the Drawing Behavior of Polyvinylidene Fluoride," *Journal of Applied Polymer Science*, Vol. 30, No. 10, 1985, pp. 4069-4079. [doi:10.1002/app.1985.070301010](https://doi.org/10.1002/app.1985.070301010)
- [8] T. Hsu and P. J. Geil, "Deformation and Transformation Mechanisms of Poly(vinylidene fluoride) (PVF₂)," *Journal of Materials Science*, Vol. 24, No. 4, 1989, pp. 1219-

1232. [doi:10.1007/BF02397050](https://doi.org/10.1007/BF02397050)
- [9] V. Sencadas, V. M. Moreira, S. Lanceros-Mendez, A. S. Pouzada and R. Gregorio Jr., " α - to- β Transformation on PVDF Films Obtained by Uniaxial Stretch," *Materials Science Forum*, Vol. 514-516, 2006, pp. 872-876. [doi:10.4028/www.scientific.net/MSF.514-516.872](https://doi.org/10.4028/www.scientific.net/MSF.514-516.872)
- [10] R. P. Vijayakumar, D. V. Khakhar and A. Misra, "Studies on A to B Phase Transformations in Mechanically Deformed PVDF Films," *Journal of Applied Polymer Science*, Vol. 117, 2010, pp. 3491-3497.
- [11] G. Gianotti, A. Capizzi and V. Zamboni, *Chim. e Industr.*, Vol. 55, 1973, 1973, p. 501.
- [12] S. Nakamura, T. Sasaki, J. Funamoto and K. Matsuzaki, "Dynamic Cooling and Isothermal Crystallizations of Poly(vinylidene fluoride) from the Melt," *Die Makromolekulare Chemie*, Vol. 176, No. 11, 1975, pp. 3471-3481. [doi:10.1002/macp.1975.021761128](https://doi.org/10.1002/macp.1975.021761128)
- [13] C. Mancarella and E. Martuscelli, "Crystallization Kinetics of Poly(vinylidene fluoride)," *Polymer*, Vol. 18, No. 12, 1977, pp. 1240-1242.
- [doi:10.1016/0032-3861\(77\)90286-5](https://doi.org/10.1016/0032-3861(77)90286-5)
- [14] K. Nakagawa and Y. Ishida, "Estimation of Amorphous Specific Volume of Poly(vinylidene fluoride) as a Function of Temperature," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, Vol. 251, No. 2, 1973, pp. 103-107. [doi:10.1007/BF01498933](https://doi.org/10.1007/BF01498933)
- [15] A. Hartono, S. Satira, M. Djamal, R. Ramli, H. Bahar and E. Sanjaya, "Effect of Fabrication Temperature on Crystallite Size of PVDF Film," *Proceedings of ICMNS*, 2012.
- [16] S. B. Lang and S. Muensit, "Review of Some Lesser-Known Applications of Piezoelectric and Pyroelectric Polymers," *Applied Physics A*, Vol. 85, No. 2, 2006, pp. 125-134. [doi:10.1007/s00339-006-3688-8](https://doi.org/10.1007/s00339-006-3688-8)
- [17] A. Hartono, R. Ramli and M. D. dan S. Satira, "Pengaruh Temperatur Perlakuan Mekanik Terhadap Jumlah Fraksi β dan Resistivitas Permukaan Lapisan PVDF," *BKS PTN-BMIPA-2012*, Universitas Negeri Medan, Medan, 2012, pp. 17-22.
- [18] C. Suryanarayana and M. G. Norton, "X-Ray Diffraction a Practical Approach," Plenum Press, New York, 1998.