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INFLUENCE OF TEMPERATURE ON CRYSTALLINE STRUCTURE OF POLYVINYLIDENE FLUORIDE

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***Abstract*— This study report the effect of temperature on the crystalline phases of PVDF from N,N- dimethylaformamide (DMF) solution. PVDF thin films were prepared via a spin coating of a PVDF/DMF solution. The films were annealed at 60°C, 90°C, 110°C and 140°C for 5 hours addition to the room temperature 30°C. The morphology of the PVDF thin films which investigated by using SEM spectroscopy. It appeared that the surface rough and micro-pore and spherulitic structure. The size of micro-pore reduced with increasing the annealing temperature. The crystalline structures of PVDF thin films were investigated by using the XRD and FTIR techniques which seemed the change in the crystalline phase with a variation annealing temperatures**

***Index Terms*— Annealing, β-Phase, Crystalline Structure, PVDF, Thin film.**

I. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) was widely used in different application because of its high piezoelectric, payroelectric and ferroelectric properties. PVDF has at least five different crystalline phases, namely α, β, γ, δ and ε, according to the conformation of the chains and their molecular packing at different temperatures[1],[2]. The existence of the different phases in PVDF depends on fabricating conditions such as solvent, technique of casting, stretching of thin films and annealing conditions. PVDF in β-phase was widely used as smart materials in various applications, especially as sensors and actuator devices[3]. The molecules and structure of β-phase provides the greatest piezoelectric effect compared with the other phase structure[4]. The high percent (91%) of β-phase obtained by using highly polar solvent hexamethylphosphoramide (HMPA) by drying films cast at temperature between 60 and 140°C[5],[6]. Ramasundaram et al & Kang et al used spin coating to obtain thin films of β-Phase[7],[8]. Sencadas et al used mechanical stretching with a stretch ratio of 5, the high percent of β-phase obtained at 80°C[9]. Satapathy obtained the maximum percentage of β-Phase by using polar solvent dimethylsulfoxide (DMSO) at annealing at 90°C for 5h, and obtained different phases of PVDF when change the solution temperature[10]. Annealed at 90°C for 5h by using Acetone as solvent, Bhatti et al obtained a maximum β-phase in the rapidly dried PVDF films[11]. During stretching at 90°C, maximum content of β-phase was obtained[12].

The objective of this work to verify the influence of annealing temperature on the crystalline phase of PVDF thin film using DMF as a solvent prepared by a spin coating technique. The morphology of PVDF thin films was investigated using scanning electron microscopy SEM. The phase of the PVDF thin films were measured with X-ray diffraction (XRD) and Fourier transforms infrared (FTIR) spectroscopy.

I. METHOD

PVDF in powder as received from (SIGMA-ALDRICH) was dissolved in N,N-dimethylformamide (DMF 99.5%) to make (10wt %) solution, by using a magnetic stirrer with angular velocity 400 rpm, heating 60°C and time 30 min. The PVDF film was deposited on a glass substrate by spin-coating. Before spin-coating, the substrate must be cleaned. The cleaning of substrate achieved by using an ultrasonic bath involves immersing the substrate in an acetone, ethanol and de-ionized water for 10 min for each one after that dried it. Then, the PVDF solution was deposited by spin-coated on the substrate with angular velocity1000 rpm for 30s. The samples were dried in a dry box at 26°C for one day.

The dried samples were annealed at 60, 90, 110 and 140°C for 5 hours. By using scanning electron microscopy (SEM) model EVO MA10, the morphology and thicknesses of the films were determined. XRD and FTIR were used to determine the phases of the samples. The model of the XRD was Bruker D8 Advance diffractometer operating at 40kV and 40mA producing CuK$_{\alpha 1}$ wavelength of 0.15406nm and model FTIR Perkin Elmer spectrum 400, with resolution 4 cm^{-1} respectively.

II. RESULTS AND DISCISION

A. Morphology

The SEM photograph with different magnification of PVDF thin films at room temperature 30°C and at annealing temperature 60, 90, 110 and 140°C was shown in Fig. 1. It shows from this figure that all samples were rough and contained micro-pore and spherulitic structure. The speriulities present on the surface of the thin film referred to β–phase. It appeared that, with increasing the annealing temperature, the density of speriulities increase and the porous decrease. The nature pores was evidence for interaction between the solvent and polymer and illustrates the effect of temperature on the crystalline structure. This occur due to the evaporation rate of solvent, where, at lower annealing temperature, the evaporation rate of DMF is slower and produce the pores. With increasing annealing temperature, the evaporation rate increase and causing the reducing of the pores. The sizes of micro-pores differ with varying the temperatures. At room temperature 30^{o}C, the size of the pores was 1µm in diameter and increased with increasing the annealing temperature to become 2.4µm in 110^{o}C. The speriulities diameter increase with increasing the temperature[13],[14]. The size of speriulities reflect the kinetics of the polymer, where determined by the rate of the nucleation and growth. The increasing in the size of speriulities attributed to decrease in the nucleation rate and an increase in the growth rate of these speriulities. At 140^{o}C, the pores were eliminates and the thin film appeared transparent. This refer the predominance of the α–phase. Hence, the increase of the annealing temperature leading to increasing the solvent evaporation rate and in turn to faster crystallization of the film, which leads to preferential formation of the α-phase[15].

Figure 2 shows the micrograph of the SEM cross section of thin films without annealing at 30^{o}C and with annealed at different temperature. It's conformed the porous nature of the PVDF thin films and the top and lower surface of the films are not uniform. The thicknesses of thin films range between10-14µm.

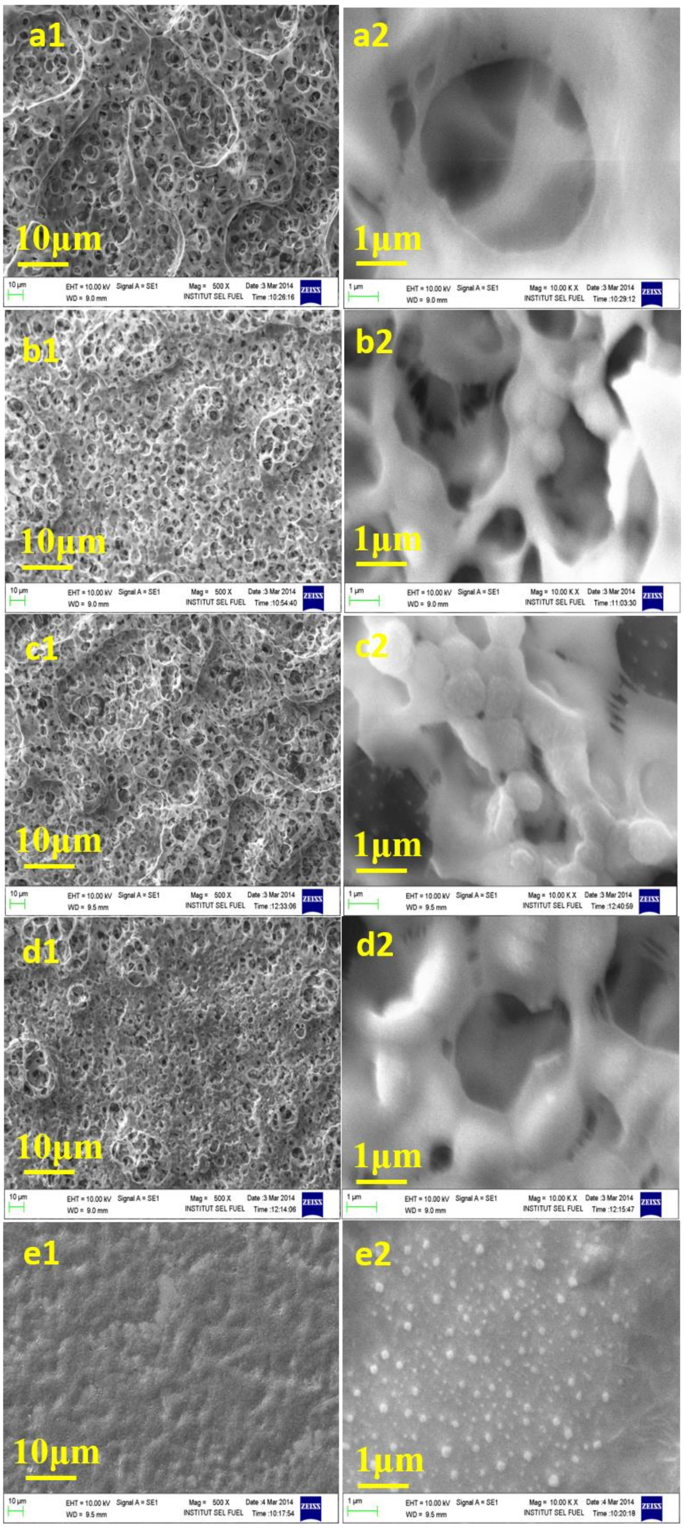

Fig. 1 SEM micrograph of the PVDF thin film (a) 30^{o}C; (b) 60^{o}C; (c) 90^{o}C; (d) 110^{o}C; (e) 140^{o}C

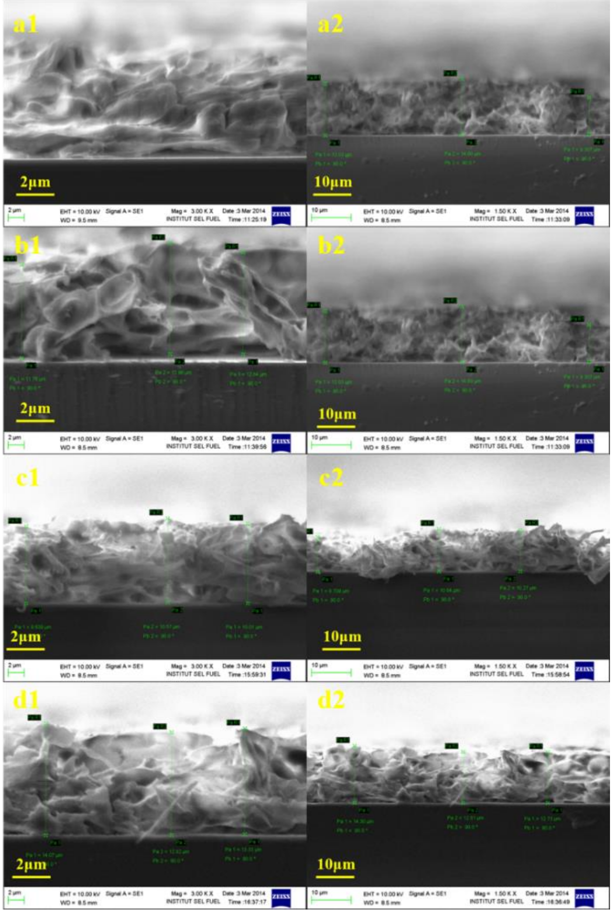

Fig. 2 SEM micrograph of the cross section of PVDF thin films, (a) 30°C; (b) 60°C; (c) 90°C; (d) 110°C

B. Crystalline Structure

Figure 3 shows the X-ray diffraction spectrum of PVDF thin films without annealing at 30°C and with annealing at 60, 90, 110 and 140°C for 5 hours. At 30°C, the high intensity appeared at $2\theta=20.1^{o}$ and 20.6^{o}, where $2\theta=20.1^{o}$ corresponding the reflection to diffraction from the plane (110) which represent α-phase and reflect the plans (200/110) which refer to the β-phase. The peak at $2\theta=20.6^{o}$ (200/110) this value represent the β-phase[16]. At 60°C, $2\theta=20.3^{o}$ conforming the reflection to diffraction from the plans (200/110) and characterize the β-phase[17]. At annealing temperature 90°C and 110°C, $2\theta=20.5^{o}$ (110)(200) and $2\theta= 20.5^{o}$& 20.9^{o} respectively corresponding the β-phase. The crystalline phase at annealing temperature 140°C represents the α-Phase, where $2\theta=19.9^{o}$ (110) which evident to obtained this phase at a point near the melting temperature. The crystalline phase in PVDF is determined by the crystalline temperature, however, the chain mobility is effected by change the temperature. At 30°C, the temperature is not enough to destroy the crystalline order of PVDF thin film and the thermal energy is not sufficient to rotate CF_2 dipoles. So, the chain conformation is trancs (T) and gaucg (G)[12]. The chain conformation aligned either in TTTGTTTG, TGTG or TTT which represent the γ, α and β-phase respectively. At 30°C, the phase was mixed of α and β. When the PVDF thin film annealed, namely at 60, 90 and 110°C, the CF_2 dipoles rotate due to the thermal energy which cause chain mobility to take the conformation TTT. At high annealing temperature 140°C, the chain motion become more active and reorientation the chain in the crystalline region through the trans-gauche conformational interchange[13]. So more stable α-phase reappears in the PVDF thin films due to distortion in crystalline region and reorientation of chains.

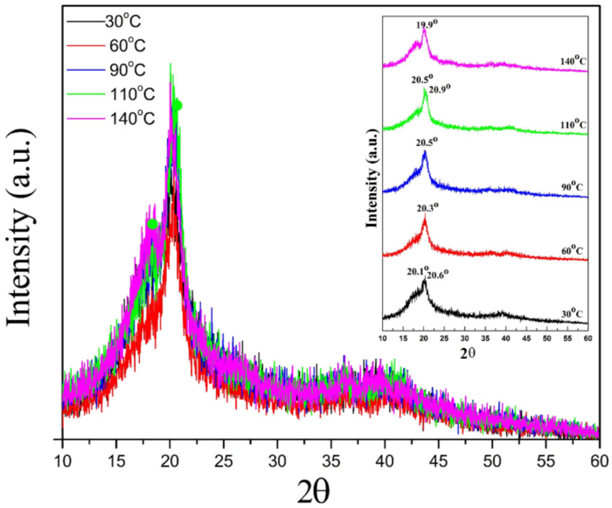

Fig. 3 X- ray diffractograms of PVDF thin films

The valuable information about the crystalline structure of PVDF also obtained via FTIR. According to the previous work, the peaks of α-Phase identify 490, 530, 615, 766, 795, 974, 1149, 1210, 1383, 1402, 1432 and 1455 cm^{-1}. The peaks at 511, 840 and 1275– 1279 cm^{-1} are characteristics of β-phase[18],[19]. It is very complicated to separate the γ and β-phase using FTIR spectroscopy, because molecular vibration peaks of γ-phase are very close to β-phase. So, only two peaks 1279 and 1234 cm^{-1} can be clearly used to characterized forms β and γ respectively[18]. Figure 4 shows the FTIR spectra of PVDF thin films at 30°C and at annealing temperature 60, 90, 110 and 140°C for 5 hours. The spectra appears at the peaks 840, 875, 1071, 1171, 1232, 1276, 1401 and 1429cm^{-1} and addition 761cm^{-1} at 30 and 140°C but the high intensity is differ between to cases. The existence the peak at 761cm^{-1} and 840cm^{-1} in 30°C confirm that the phase in this case was mixed of α and β-phase. At annealing temperature 60, 90 and 110°C, the crystalline phase was the β-phase, because most peaks belong to the β-phase and the shape of carve is very sharp with high intensity and addition eliminate the peak at 761cm^{-1}. At 110°C, the phase is α-phase due to existence the peak at 761cm^{-1} and all the peaks have low intensity compared to other annealing temperature.

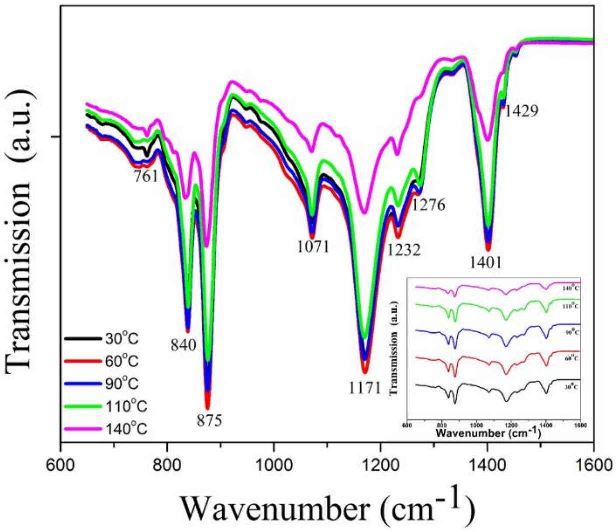

Fig. 4 FTIR spectra of PVDF thin films

III. CONCLUSION

In this work it has been observed that the phase of PVDF thin film can be change by annealed the samples. The β–phase which is important for piezoelectric application can be obtained by this process at specific annealing temperature. The SEM morphology of the PVDF thin films appears rough and contained micro-porous and spherulitic structure. The present of the speriulities on the surface of the thin film indicate that the phase of PVDF is the β–phase. By increasing the annealing temperatures the sizes of micro-pores become smaller and spherulitic diameter increased. According to the XRD and FTIR analysis, the crystalline phase of PVDF thin films at 30ºC is mixed of the α and β-phase. At annealing temperature 60, 90 and 110ºC, the phase transform to the β-phase. At annealed at 140ºC, the phase convert from β to the α-phase.

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REFERENCES

[1] R. Gregorio, "Determination of the ??, ??, and ?? crystalline phases of poly(vinylidene fluoride) films prepared at different conditions," J. Appl. Polym. Sci., vol. 100, pp. 3272–3279, 2006.

[2] X. S. and Z. R. X. Cao, J. Ma, "Effect of TiO2 nanoparticle size on the performance of PVDF membrane," Appl. Surf. Sci., vol. 253, no. 4, pp. 2003–2010, 2006.

[3] Q. Z. Y. Bar-Cohen, "Electroactive polymer actuators and sensors," MRS Bull., vol. 33, pp. 173–181, 2008.

[4] R. and E. S. A. Hartono, S. Satira, M. Djamal, "Effect of Mechanical Treatment Temperature and Layer Thickness on Piezoelctic Properties PVDF Film," Proc. APS, 2012.

[5] R. Gregorio and D. S. Borges, "Effect of crystallization rate on the formation of the polymorphs of solution cast poly(vinylidene fluoride)," Polymer (Guildf)., vol. 49, pp. 4009–4016, 2008.

[6] Y. K. a Low, N. Meenubharathi, N. D. Niphadkar, F. Y. C. Boey, and K. W. Ng, "A- and B-Poly(Vinylidene Fluoride) Evoke Different Cellular Behaviours.," J. Biomater. Sci. Polym. Ed., vol. 22, no. 12, pp. 1651–1667, 2011.

[7] J. S. Ramasundaram, S.; Yoon, S.; Kim, K.J.; Lee, "Direct preparation of nanoscale thin films of poly(vinylidene fluoride) containing β-crystalline phase by heat-controlled spin coating.," Macromol. Chem. Phys 2008, 209, 2516–2526. - Open Access Library, 2008. [Online]. Available: http://www.oalib.com/references/9273762. [Accessed: 22-Apr-2015].

[8] S. J. Kang, Y. J. Park, J. Sung, P. S. Jo, C. Park, K. J. Kim, and B. O. Cho, "Spin cast ferroelectric beta poly(vinylidene fluoride) thin films via rapid thermal annealing," Appl. Phys. Lett., vol. 92, no. 1, p. 012921, Jan. 2008.

[9] V. Sencadas, R. Gregorio, and S. Lanceros-Mendez, "to β Phase Transformation and Microestructural Changes of PVDF Films Induced by Uniaxial Stretch," J. Macromol. Sci. Part B, vol. 48, no. 3, pp. 514–525, 2009.

[10] S. Satapathy, S. Pawar, P. K. Gupta, and K. B. RVarma, "Effect of annealing on phase transition in poly(vinylidene fluoride) films prepared using polar solvent," Bull. Mater. Sci., vol. 34, no. 4, pp. 727–733, 2011.

[11] Imtiaz Noor Bhatti, M. Banerjee, and Ilyas Noor Bhatti, "Effect of Annealing and Time of Crystallization on Structural and \nOptical Properties of PVDF Thin Film Using Acetone as Solvent," IOSR J. Appl. Phys. , vol. 4, no. 4, pp. 42–47, 2013.

[12] a. Salimi and a. a. Yousefi, "FTIR studies of ??-phase crystal formation in stretched PVDF films," Polym. Test., vol. 22, pp. 699–704, 2003.

[13] R. Gregorio, Jr. and M. Cestari, "Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride)," J. Polym. Sci. Part B Polym. Phys., vol. 32, no. 5, pp. 859–870, Apr. 1994.

[14] R. Gregorio and E. M. Ueno, "Effect of crystalline phase, orientation and temperature on the dielectric properties of poly (vinylidene fluoride) (PVDF)," J. Mater. Sci., vol. 34, pp. 4489–4500, 1999.

[15] S. Satapathy, P. K. Gupta, S. Pawar, and K. B. R. Varma, "Crystallization of Beta-phase Poly (vinylidene fluoride) films using dimethyl sulfoxide (DMSO) solvent and at suitable annealing condition," p. 18, 2008.

[16] W. A. Yee, M. Kotaki, Y. Liu, and X. Lu, "Morphology, polymorphism behavior and molecular orientation of electrospun poly(vinylidene fluoride) fibers," Polymer (Guildf)., vol. 48, no. 2, pp. 512–521, Jan. 2007.

[17] V. Ostaševičius, I. Milašauskaite, R. Daukševičius, V. Baltrušaitis, V. Grigaliunas, and I. Prosyčevas, “Experimental characterization of material structure of piezoelectric PVDF polymer,” Mechanika, vol. 86, no. 6, pp. 78–82, 2010.

[18] T. Boccaccio, a. Bottino, G. Capannelli, and P. Piaggio, “Characterization of PVDF membranes by vibrational spectroscopy,” J. Memb. Sci., vol. 210, no. 2, pp. 315–329, 2002.

[19] Y. Bormashenko, R. Pogreb, O. Stanevsky, and E. Bormashenko, “Vibrational spectrum of PVDF and its interpretation,” Polym. Test., vol. 23, no. 7, pp. 791–796, 2004.