

EFFECT OF PRE-ANNEALED MgO ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF PVDF/MgO BULK FILM

A. N. ARSHAD^a, N. M. A. ZULAIKHA^a, M. N. SARIP^c, E. Z. E. ZAHARAH^a, M. RUSOP^b, M. D. ROZANA^{a,*}

^aFaculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^bNANO-SciTech Centre (NST), Institute of Science (IOS), Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^cFaculty of Applied Sciences, Universiti Teknologi MARA Cawangan Perlis, 02600 Arau, Perlis, Malaysia

MgO nanofillers were pre-annealed at temperatures of 200°C (AN200), 300°C (AN300) and 400°C (AN400) prior to utilization. Resistivity values, ρ showed significant increment to 8% for AN200 ($13.3 \times 10^7 \Omega \cdot \text{cm}$). With increasing annealing temperatures of MgO, ρ gradually decreased to $10.3 \times 10^7 \Omega \cdot \text{cm}$ and $8.5 \times 10^7 \Omega \cdot \text{cm}$ for AN300 and AN400 respectively. FTIR spectra for AN200 showed sharp peak at 1180 cm^{-1} representing β -crystal in PVDF. AN300 and AN400 showed shift from β - to γ -crystal at peak 1198 cm^{-1} for PVDF. XRD pattern for AN200 showed an improved in intensity for β -crystal PVDF at $2\theta=20.04^\circ$. Further increment to 300°C and 400°C, presence of γ -PVDF at $2\theta=20.26^\circ$ was evident. This suggests that 200°C is the optimized annealing temperature for MgO nanofillers.

(Received August 23, 2018; Accepted November 9, 2018)

Keywords: PVDF, MgO, Nanocomposites, Resistivity value, Structural properties

1. Introduction

PVDF is a semicrystalline polymer with complex polymorphism comprising at least four crystalline phases of α -, β -, δ -, and γ -phases. Amongst these phases, β -crystal of PVDF is the most desirable crystal structure due to its considerable polarization of $22 \mu\text{C}/\text{cm}^2$ and its large dipole moment ($7 \times 1030 \text{ C}\cdot\text{m}$), making PVDF a suitable material for storing charges. Previous study reported that preparation of PVDF films via solution casting method will result in combination of polar (β - and γ -) and non-polar (α - and δ -) phases of PVDF crystal. However, the β -PVDF can further be improved via annealing treatment, addition / incorporation of micro- and nano-fillers, and by dissolving in polar solvents. In addition, polymer composites composed of a polymeric materials embeded with nano- or micro-fillers are widely used in applications of capacitors, biosensors, thermal sensors and tunable actuators. The study on the incorporation of nano-fillers into polymeric materials are still being investigated as these nanocomposites material has improved chemical and physical properties. They also have excellent resistance towards solvents as well as improved in thermal resistance, with enhance electrical properties. Due to its nano-sizes, these nano-fillers have relatively large surface area per unit weight.

Semiconductor oxide fillers such as titanium dioxide, zirconium oxide and zinc oxide incorporated in PVDF are typical nano-fillers used in enhancing the electrical properties of PVDF. The oxide material, currently being investigated for its effect in PVDF is Magnesium Oxide (MgO). MgO is an insulating filler with cubic structure, and chemical inert, electrical insulative, and high temperature stability; as well as high thermal conductivity. MgO have high dielectric constant of 9.6 at 1kHz, with wide band gap (7.8eV) and high breakdown field of 12MV/cm; making MgO a promising material to be used as a dielectric layer.

*Corresponding author: rozanadahan@gmail.com

Annealing is a common heat treatment process for fillers for modifying its crystal structure and surface property. Post annealing process for composites materials is typically used for matrix and fillers that can withstand high annealing temperatures (300-500C) . For polymer matrix such as PVDF incorporated with oxide filler, high annealing temperature can cause degradation of the polymer composite. Therefore, in most study, the oxide fillers are preannealed before inclusion in the polymer matrix . Hence, pre-annealed MgO nanofillers was utilized in this study prior to inclusion in PVDF. The pre annealing temperatures was set in the range of 200°C to 400°C. The PVDF/MgO was investigated for their structural and electrical properties.

2. Experimental

PVDF powder and MgO nanofillers with particle size <50nm were used as purchased. The MgO fillers were dispersed in PVDF solution, dissolved in N, N-dimethylformamide (DMF, System).

The unfilled PVDF films, 1 μ m thick were prepared by solution casting. The PVDF (0.6g) was first dissolved in 20mL of DMF solvent and stirred constantly for 48h at ambient temperature. Upon complete dissolution, the unfilled PVDF solution was poured into a glass petri dish. The crystallization process was initiated with further annealing at 100°C for 1 h. In previous study, it is established that PVDF with 7 wt.% enhanced electrical properties with improved polar crystals . Hence, MgO nanofillers of 7 wt.% loading was used and pre-annealed to 200°C (AN200), 300°C (AN300) and 400°C (AN400) prior to incorporation in PVDF. The film sample is denoted in Table 1.

Table 1. Films denotations for PVDF, UN, AN200, AN300 and AN400

Films	Denotations	Descriptions
Unfilled PVDF	PVDF	Neat PVDF
Un-annealed PVDF/MgO	UN	MgO nanofillers pre-annealed at 400°C for 1 hour
Annealed PVDF/MgO at 200°C	AN200	MgO nanofillers pre-annealed at 200°C for 1 hour
Annealed PVDF/MgO at 300°C	AN300	MgO nanofillers pre-annealed at 300°C for 1 hour
Annealed PVDF/MgO at 400°C	AN400	MgO nanofillers pre-annealed at 400°C for 1 hour

Fourier transform infrared spectrometer (Perkin Almer) in ATR mode and X-ray diffractometer (Malvern Panalytical's) were used to determine the functional groups and crystallization behavior of the polymer composites film. The electrical properties of PVDF and PVDF/MgO films were measured using dielectric spectroscopy (Hioki) and the resistivity values were re-plotted using OriginLab software.

3. Results and discussion

The crystalline phase of PVDF and PVDF/MgO films were characterized by FTIR (Fig. 1) and XRD (Fig. 2). From Fig. 1, PVDF shows crystalline phases of α -, β -, and γ -crystals that coexist in PVDF with presence of absorption peaks; 1403 cm^{-1} , 1070 cm^{-1} and 840 cm^{-1} . A formation of sharp adsorption peak at 1180 cm^{-1} can be observed for AN200 film, indicating stretching of -CH₂ bond of β -phase PVDF, which aid in improving the polar properties of PVDF.

However, the emergence of α -phase at absorption band of 765 cm^{-1} and 976 cm^{-1} can be observed for respective AN300 and AN400 films. AN300 also shows a shifting at absorption peak of 1180 cm^{-1} from β -phase to γ -phase (1198 cm^{-1}).

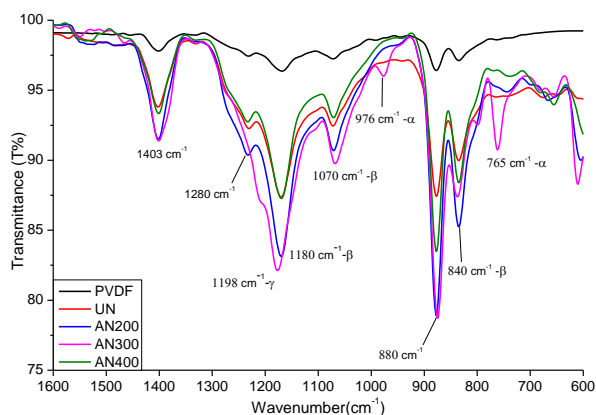


Fig. 1. ATR-FTIR spectra for (i) PVDF, (ii) UN, (iii) AN200, (iv) AN300 and (v) AN400 of PVDF/MgO films

The findings were further analyzed using the XRD pattern shown in Fig. 2. It can be observed that XRD pattern for PVDF and UN films have low and broad intensity peaks as compared to MgO crystal. From 2θ range of 10° to 30° , unfilled PVDF and PVDF/MgO films showed polymorphism, indicating the presence of both polar and non-polar crystal phase of PVDF. Diffraction peak at $2\theta = 18.6^\circ$, assigned to (100) crystal planes of α -phase, a non-polar phase of PVDF. Meanwhile, the β - and γ -phase (polar) are observed at the superposition point of the peaks located at 20.4° and 22.5° , associated to (110) and (200) crystal planes.

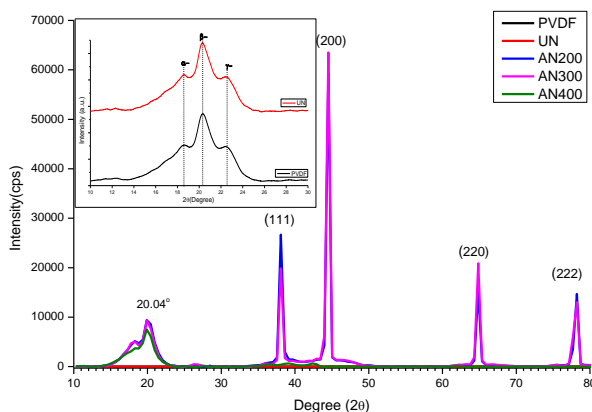


Fig. 2. XRD pattern for PVDF and pre-annealed PVDF/MgO films for UN, AN200, AN300 and AN400, and inset shows XRD pattern for PVDF and UN films with 2θ from 10° to 30° .

Sharp diffraction peak at (111), (200), (222) and (220) plane for MgO were observed at $2\theta = 38^\circ$, 45° , and 65° . From these peaks, (200) plane showed the highest intensity value for AN200 and AN300 films. Reduction in intensities at these planes can be observed for AN400 films, indicating either a change in MgO crystal phase which may be finer in crystals structure caused by high annealing temperature (400°C). From the JCPDS data (JCPDS file: 45-0946), MgO nanofillers annealed at 200°C (AN200) may produce cubic structure while AN300 and AN400 produced hexagonal structure. However, for low energy loss, cubic structure crystals are preferable for their electrical properties [16].

Fig. 3 shows the resistivity value, (ρ) of Unfilled PVDF, UN, AN200, AN300 and AN400 films. The ρ were observed to increase from $0.9 \times 10^7 \Omega \cdot \text{cm}$ to $13.3 \times 10^7 \Omega \cdot \text{cm}$ for UN and AN200. Nevertheless, upon increasing the annealing temperatures of MgO nanofillers, the ρ for AN300 and AN400 films decreased to $10.3 \times 10^7 \Omega \cdot \text{cm}$ and $8.5 \times 10^7 \Omega \cdot \text{cm}$, respectively. This reduction of ρ was expected due to occurrence of non-polar phases as evident in FTIR spectra and XRD pattern. Thus, 200°C suggests the optimum annealing temperature for MgO nanofillers.

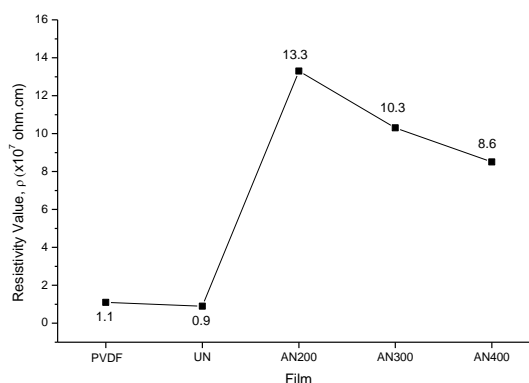


Fig. 3. Resistivity value (ρ) for PVDF, UN, AN200, AN300 and AN400 films.

4. Conclusions

PVDF and PVDF/MgO composite film using pre-annealed MgO nanofillers (200°C , 300°C , and 400°C) were investigated. The annealing temperature at 200°C was proposed to be the optimum annealing temperature for MgO nanofillers. The results showed enhancement of resistivity value from $1.1 \times 10^7 \Omega \cdot \text{cm}$ (UN) to $13.3 \times 10^7 \Omega \cdot \text{cm}$ for AN200 film. These findings were supported by FTIR spectra, which showed sharp absorption bands of β -phase crystal in AN200 films at wavenumber of 840 cm^{-1} , 1070 cm^{-1} and 1180 cm^{-1} . The XRD pattern also indicates high β -crystal of PVDF for AN200 film at 20.4° . Enhanced in resistivity value and polar crystals of AN200 film suggests that PVDF/MgO annealed at 200°C is a suitable film used for electronic based devices.

Acknowledgements

This research was fully supported by BESTARI Grant from Research Management Center (RMC), Faculty of Applied Sciences, Nano-SciTech (NST), Institute of Science, and Nano-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA, Malaysia. Our highest appreciation goes to Microwave Research Institute (RMI), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM) for their assistance in sample preparation. Our special thanks also goes to MyBrain15 (MyP.hD), Ministry of Higher Education for funding this research.

References

- [1] J. H. Nan, S. Qian, X. Jing, S. Guangmei, Rui, *Polymer Testing* **57**, 302 (2017).
- [2] J. Lee, S. Lim, *Journal of Industrial and Engineering Chemistry In Press*, (2018).
- [3] A. N. Arshad, M. D. Rozana, M. H. M. Wahid, M. K. A. Mahmood, M. N. Sarip, Z. Habibah, M. Rusop, *AIP Conference Proceedings* **1963**(1), 020010 (2018).
- [4] W. C. Gan, W. H. A. Majid, T. Furukawa, *Polymer* **82**, 156 (2016).
- [5] N. Meng, Mao Rui, Tu Wei, Zhu Xiaojing, M. Rory Wilson, Emiliano Bilotti, Michael Reece,

- J. Polymer **100**, 69 (2016).
- [6] D. M. Dhevi, A. A. Prabu, K. J. Kim, *Vibrational Spectroscopy* **94**, 74-82.
- [7] A. Z. Ashar, K. S. Narayan, *Organic Electronics* **42**, 8 (2017).
- [8] M. Kutz, "Handbook of Materials Selection" John Wiley USA, 1497 (2002).
- [9] K. S. Tan, W. C. Gan, T. S. Velayutham, W. H. Abd Majid, *Smart Material Structure* **23**, 11 (2014).
- [10] F. Wang, Z. An, J. Tang, F. Cao, Y. Li, C. Li, *Chalcogenide Letters* **13**(10), 459 (2016).
- [11] S. Rudzhiah, N. S. Mohamed, *Key Engineering Materials* **594-595**, 604 (2014).
- [12] T. Yu, K. Y. Wang, Y. T. Chen, M. L. Sheu, H. Chen, *Chalcogenide Letters* **14**(4), 119 (2017).
- [13] H. Kausar, Y. Muhamad Kamil, T. Mohamad Fariz Mohamad, S. Bouchta, A. Zainal Arifin, M. Ahmad Azmin, *Materials Research Express* **4**(8), 085908 (2017).
- [14] S. J. Oh, N. Kim, Y. T. Lee, *Journal of Membrane Science* **345**(1-2), 13 (2009).
- [15] H. Rekik, Z. Ghallabi, I. Royaud, M. Arous, G. Seytre, G. Boiteux, A. Kallel, *Composites Part B: Engineering* **45**(1), 1199 (2013).
- [16] J. Y. Chen, W. H. Hsu, C. L. Huang, *Journal of Alloys and Compounds* **504**(1), 284 (2010).
- [17] N. A. Rejab, A. Z. A. Azhar, K. S. Kian, M. M. Ratnam, Z. A. Ahmad, *Materials Science and Engineering: A* **595**(0), 18 (2014).
- [18] S. Choubey, A. Kaushik, K. Tiwary, *Chalcogenide Letters* **15**(3), 125 (2018).
- [19] D. T. Mustafa, N. Kamarulzaman, N. F. Chayed, N. H. Badar, M. F. M. Taib, Ibrahim, A. B. M. A., *Journal of Computational and Theoretical Nanoscience* **14**(6), 2591 (2017).
- [20] N. Kamarulzaman, N. F. Chayed, N. H. Badar, *AIP Conference Proceedings* **1711**(1), 040004 (2016).
- [21] Z. Habibah, A. N. Arshad, M. H. Wahid, L. N. Ismail, R. A. Bakar, M. H. Mamat, M. Rusop, 10th IEEE International Conference on Semiconductor Electronics (ICSE), 73 (2012).
- [22] A. H. S. Rana, S. B. Chang, H. U. Chae, H. S. Kim, *Journal of Alloys and Compounds* **729**, 571 (2017).
- [23] P. Rodnyi, K. Chernenko, O. Klimova, V. Galkin, A. Makeenko, E. Gorokhova, D. Buettner, W. Keur, H. Wiczorek, *Radiation Measurements* **90**, 136 (2016).
- [24] Y. R. Sui, Y. P. Song, Y. J. Wu, J. H. Lang, X. W. Meng, S. Q. Lv, B. Yao, J. H. Yang, *Ceramics International* **42**(14), 15166 (2016).
- [25] M. D. Rozana, A. N. Arshad, M. H. Wahid, Z. Habibah, L. N. Ismail, M. N. Sarip, M. Rusop, Business, IEEE Symposium on Engineering and Industrial Applications (ISBEIA), (2012).