Electrical and Structural Properties of PVDF/Mgo (7%) Nanocomposites Thin Films at Various Annealing Temperatures

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***Abstract*—Poly (vinylideneflouride)/nano-magnesium oxide (PVDF/MgO) film with 7% MgO loading percentage was annealed at various annealing temperatures ranging from 70°C to 150°C. The PVDF/MgO thin film was fabricated using spin coating technique with a metal-insulator-metal (MIM) configuration. The dielectric and electric properties of PVDF/MgO with respect to annealing temperatures was studied. The PVDF/MgO nanocomposites thin films annealed at temperature of 70°C (AN70-PVDF/MgO) showed an improvement in the properties; dielectric constant value of 26 at 1 kHz frequency compared to un-annealed sample (UN-PVDF/MgO), which is 21 at the same frequency. As the annealing temperatures were increased from 90°C (AN90) to 150°C (AN150-PVDF/MgO), the dielectric constant values were found to gradually decreased from 25 to 12 respectively, which was lower than the UN-PVDF/MgO thin films. AN70-PVDF/MgO also produced relatively low tangent loss (tan δ). The resistivity value of AN70-PVDF/MgO was also found to increase from $3.08x10^4$ Ω.cm (UN- PVDF/MgO) to $4.55x10^4$ Ω.cm. The increased in the dielectric constant, with low tangent loss and high resistivity value suggests that 70°C was the favorable annealing temperature for PVDF/MgO film suitable for the application in electronic devices such as low frequency capacitor.**

***Index Terms*: PVDF, Nanocomposites, Dielectric, Resistivity, ATR-FTIR**

I. INTRODUCTION

Poly (vinylideneflouride) (PVDF) is one of the important semi-crystalline polymers, and has attracted much attention during past several decades due to its good mechanical and high piezoelectricity; making PVDF a favorable material to be used as a dielectric layer for electronic devices. PVDF was known for its polymorphism structures, consisting of four crystal phases known as α-, β-, γ-, and δ-phase. Amongst this polymorphism, β-phase of PVDF is the most desired crystal structure due to its large dipole moment. The dielectric constant for PVDF is 9 at frequency of 10^3 Hz, which was higher compared to other semi-crystalline polymer. However, β-phase crystal cannot be simply obtained. In order to obtain the high β-phase crystals, PVDF film requires treatment under certain conditions, such as mechanical drawing at low temperature, melt crystallization at high pressure, electro spinning from pure or composite PVDF fibers or modification with nano-particles [1]. The addition of nano-particle created hybrid materials, also known as nanocomposites. This hybridization has generated great interest amongst researchers due to its simplicity and positive results [2-4].

Nano-composites are currently used in many fields of research, such as in thin-film capacitors, biosensors, thermal sensors and tunable actuators [5, 6]. The hybrid materials from organic polymers and metal oxide offer different chemical and physical properties such as excellent solvent resistance properties, thermal resistance, and improved electrical properties. Due to their nano sizes, these particles have relatively huge surface area per unit weight. Metal oxides nano-particles such as titanium dioxide, zirconium oxide and zinc oxide incorporated in PVDF are typical nano-particles used in improving the electrical properties of PVDF [7-9].

The oxide material, currently being investigated for its effect in PVDF is that of Magnesium Oxide (MgO) [10-12]. MgO is an inorganic filler with cubic structure, has excellent properties such as chemical inertness, electrical insulation, and high temperature stability; as well as high thermal conductivity [13]. It is a favorable insulative material of high dielectric constant (9.6), wide band gap (7.8eV) and high breakdown field of 12MV/cm; making MgO a promising material to be used as a dielectric layer [14, 15]. In our previous study, the optimized MgO filler loading in PVDF was established as 7 (wt.%) [12].

Thus for this research, nano-MgO with 7 wt.% were dispersed in PVDF, and annealed at various annealing temperature ranging from 70°C to 150°C, and the nanocomposites film were investigated for its electrical and structural properties.

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II. EXPERIMENTAL SETUP

Poly(vinylideneflouride) (PVDF) powder (Mw~534,000) and Magnesium Oxide (MgO) nanofillers with diameter of <50nm, both supplied by Sigma-Aldrich, were used to prepare the PVDF/MgO with 7% (wt.%) nanocomposites thin films. Prior to utilization, nano-MgO was pre-treated at temperature of 300°C for 1 hour. N,N-dimethylformamide (DMF) solvent was purchased from Systerm, and was used to dissolve PVDF. The PVDF powders were dissolved in DMF at concentration of 30 g/L, and 7 wt.% of nano-MgO were dispersed in PVDF solutions. Subsequently, the PVDF/MgO solution was stirred for 48 hours at temperature of 70ºC.

Aluminum-glass (Al-glass) substrates were prepared by evaporating 30nm Aluminum (Al) on clean glass slides and were used throughout this study as Al-glass substrates for spin coating of PVDF/MgO. The spin coated PVDF/MgO films of average thickness 375nm were then annealed at various temperatures. These temperatures were based on the DSC spectrum shown in Figure 1.

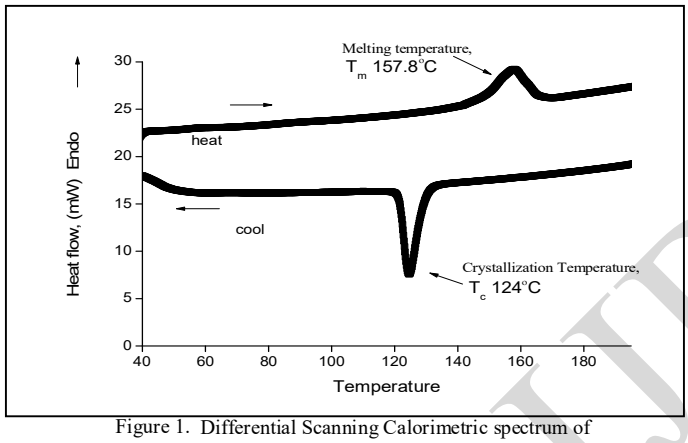


Figure 1. Differential Scanning Calorimetric spectrum of Poly(vinylideneflouride) (PVDF)

From Figure 1, the melting temperature (T_m) of PVDF is 157.8ºC and crystallinity temperature (T_c) is 124ºC. The temperature obtained was utilized as the temperature range for the annealing process of PVDF/MgO nanocomposite thin films. The thin films were annealed in an oven for an hour at temperature of of 70°C, 90°C, 110°C, 130°C, and 150°C and were rapidly removed from the oven upon completion of annealing process.

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR, Perkin Elmer) spectra were used to investigate the polymorphism of annealed PVDF/MgO thin films. Aluminum electrodes of 30nm thick were evaporated on the annealed PVDF/MgO thin films by thermal evaporation method (Edward Auto-A306 Turbo), also known as the top electrode. This created a metal-insulator-metal (MIM) configuration. The MIM configuration for annealed PVDF/MgO thin films used for electrical measurements is shown in Figure 2.

The dielectric properties of annealed PVDF/MgO thin films were measured using Impedance Analyzer Spectroscopy (Solartron Analytical 1260A) at frequency of 10^1 to 10^6 Hz, with ZView® software for data acquisition. Resistivity values were determined using two point probe of the I-V measurement (Bukoh Keiki) at an applied voltage from -2 to 2V. The voltage step was set to 0.01 V with a fixed plate temperature of 25ºC.

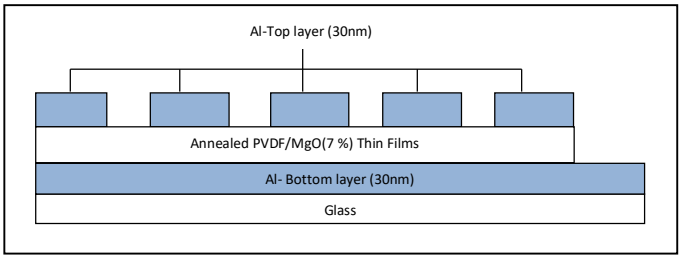


Figure 2. MIM configurations of annealed PVDF/MgO thin films for electrical measurements

III. RESULT AND DISCUSSION

A. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

The ATR-FTIR spectra of un-annealed PVDF/MgO (UN-PVDF/MgO) film, as well as annealed PVDF/MgO film of annealing temperature ranged from 70°C to 150°C is shown in Figure 3. The UN-PVDF/MgO film shows an absorption band at 1403cm^{-1}, which indicates an in-plane bending of -CH_2. Upon annealing, broader absorption peak at 1403cm^{-1} was observed. Shift in the absorption bands from 1220cm^{-1} to 1180cm^{-1} can be observed for AN70-PVDF/MgO nanocomposites thin film. The band indicates a change from wagging to rocking of -CH_2 bond, which also referred to the β-phase of PVDF.

AN70-PVDF/MgO nanocomposites thin films also showed a sharp peak at absorption band at 840cm^{-1}, indicating a significant presence of β-phase of PVDF. This finding was supported by Gregorio et., al. [16, 17]. The absorption band at 1280cm^{-1} represents the bonding of –CN group, belonging to the DMF which was used as a solvent for dissolving PVDF and dispersing MgO nano-filler.

However, as the annealing temperatures were increased from 90°C to 150°C, the absorption band shifted from 1180cm^{-1} to 1220cm^{-1} indicating transformation from polar β-phase crystals to polar γ-phase crystals. The reduction in transmittance for adsorption band at 880 cm^{-1} and 840cm^{-1} as well as the presence of α-phase PVDF at absorption band 796cm^{-1} were also observed. Table 1 shows the characteristic bands with respect to specific vibrational modes and crystalline phases for annealed PVDF/MgO nanocomposites thin films.

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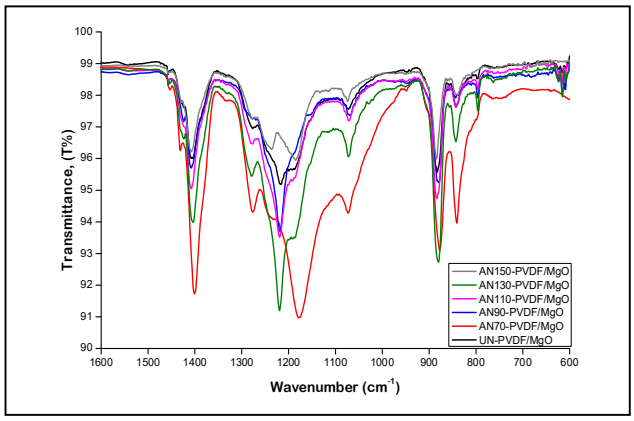


Figure 3. FTIR spectra of un-annealed and annealed PVDF/MgO thin films

Table 1. Characteristic bands with respect to specific vibrational modes and crystalline phases for annealed PVDF/MgO nanocomposites thin films.

Wavenumber (Cm^{-1})	Group	Vibration	Comments	References
1403	$-CH_2$	In-plane bending		[18, 19]
1220	$-CH_2$	Rocking	β- or γ-phase	[20]
1180	CF2	Stretching		[11]
1170			α-phase	[21]
1072	C-C-C	Bending		[22]
880	$-CF_2$	$-CF_2$ stretching		[21, 23]
840	CH_2 and CF_2	CH_2 rocking and CF_2 stretching	β-phase	[16]

B. Dielectric Constant and Tangent Loss

Figure 4 shows the dielectric constant values of un-annealed and annealed PVDF/MgO thin films against frequency. The frequency used can be divided to three phases which are low frequency (10^1 - 10^3 Hz), mid frequency (10^3 – 10^5 Hz) and high frequency (10^5 - 10^6 Hz). At low frequency region (10^1 Hz to 1 kHz), the dielectric constant of UN-PVDF and UN-PVDF/MgO nanocomposites were observed to decrease with increasing in frequency as shown in Figure 4. The dielectric constant was observed to saturate at mid frequency (10^3 – 10^5 Hz), before decreasing gradually at high frequency of 10^5 - 10^6 Hz. At low frequency (10^1 Hz), the dielectric constant observed were high due to the orientation polarization experienced by the PVDF chain structure that possessed permanent dipole moment.

The dielectric constant of UN-PVDF/MgO was 21 at 1 kHz, and upon annealing of PVDF/MgO thin films at 70°C, the dielectric constant of AN70-PVDF/MgO was enhanced to 26 at the same frequency. The enhancement in dielectric constant of AN70-PVDF/MgO was contributed by the presence of β-phase crystals and the diminishing of α-phase crystals, as evident in ATR-FTIR (Figure 2).

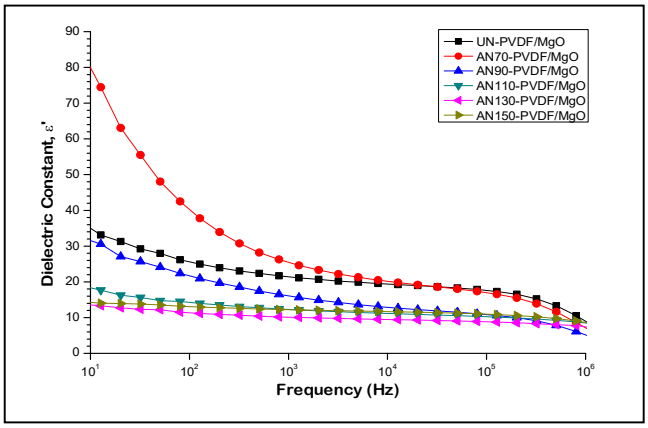


Figure 4. Dielectric constant against frequency plots for un-annealed and annealed PVDF/MgO thin films.

In addition, as observed from the FTIR spectra, annealing of AN70-PVDF/MgO at 70ºC, resulted in an improved of the molecules alignment, which caused highly ordered molecular chain packing. This resulted in an increased in the dipole density as well as polarization, leading to increase in the dielectric constant value.

Nonetheless, upon increasing the annealing temperature to 90°C, the dielectric constant of AN90-PVDF/MgO was observed to reduce to 20, which was slightly lower than UN-PVDF/MgO. Further increment in the annealing temperature for the AN110-PVDF/MgO, AN130-PVDF/MgO and AN150-PVDF/MgO, caused further reduction in the dielectric constant values to 13, 11 and 12 respectively, and measured at 1 kHz frequency. The reduction in the dielectric constant value upon annealing at temperatures of ≥ 90°C, may be affected by the shifting at adsorption band from 1180cm^{-1} to 1220 cm^{-1} as observed in Figure 3, indicating a shifting from β- to γ-phases.

It is known that PVDF can be polarized when subjected to an electric field. The quantity of the accumulated charges is very much dependent on the polarity of PVDF. When MgO nano-fillers were included in PVDF, the polarizations of nanocomposites were found to increase in comparison to unfilled PVDF. This may be due to the dipolar contribution of MgO nano-fillers. In low frequency region, apart from the polarization due to annealing of the PVDF and MgO nano-filler, the space charge polarization also plays a major role in increasing the dielectric constant of the nanocomposites. Space charge polarization is a dielectric polarization which occurs in heterogeneous materials. In this study, the space charge polarization at low frequency between PVDF and MgO nanofillers was observed to decrease significantly upon annealing at high temperatures (≥ 90°C), as observed in Figure 4.

Meanwhile, the dielectric constant curve at high frequencies (10^5 Hz to 10^6 Hz) for UN- PVDF/MgO, AN70-PVDF/MgO, and

AN90-PVDF/MgO were found to decrease, which indicates that nanocomposites were experiencing dipole polarization. Hence, this suggests at high frequency, dipoles oscillated at a faster speed, thus reducing the time required for polar switching. Table 1 shows the dielectric constant value for the annealed PVDF/MgO at these annealing temperatures, measured at 1 kHz frequency.

Table 2. Dielectric constant value of annealed PVDF/MgO nanocomposites thin films measured at 1 kHz.

PVDF/MGO (7%) ANNEALED AT VARIOUS TEMPERATURES	DIELECTRIC CONSTANT VALUE AT 1 KHZ
UN	21
AN70- PVDF/MgO	26
AN90- PVDF/MgO	20
AN110- PVDF/MgO	13
AN130- PVDF/MgO	11
AN150- PVDF/MgO	12

Figure 5 shows the curve of tangent loss versus frequency for UN-PVDF/MgO, AN70-PVDF/MgO, AN90-PVDF/MgO, AN110-PVDF/MgO, AN130-PVDF/Mg and AN150-PVDF/MgO. The AN70-PVDF/MgO film showed an increase in the tangent loss value from 0.1 (UN-PVDF/MgO) to 0.3 at 1 kHz frequency. Further increment in the annealing temperature (>70°C) showed a decrease in the tangent loss value. Low value of tan δ is preferred as this indicates low energy is dissipated from the dielectric material. The slight increment in the tangent loss in AN70-PVDF/MgO film is negligible and can be considered as low in magnitude for a dielectric layer. This theory was supported by Dang et al.[24].

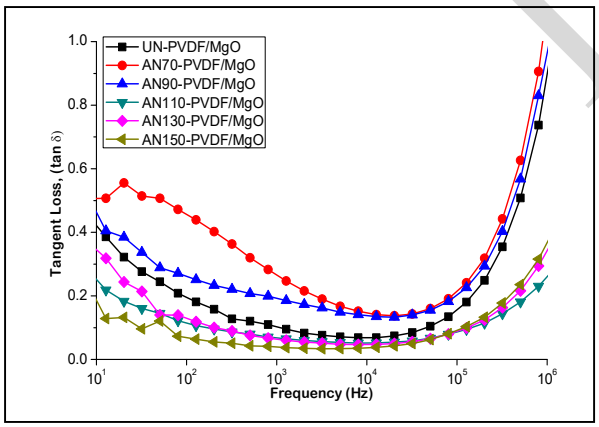


Figure 5. Tangent loss (tan δ) against frequency for un-annealed and annealed PVDF-MgO

C. Resistivity Value

Resistivity values for UN-PVDF/MgO and annealed PVDF/MgO at various annealing temperatures are shown in Figure 6. It can be observed that for AN70-PVDF/MgO, the resistivity value was improved to 4.55×10^4 Ω.cm, in comparison to UN-PVDF/MgO, which was 3.08×10^4 Ω.cm. Further increment of the annealing temperature to 90°C, caused a reduction in resistivity value for the annealed PVDF/MgO thin films.

The resistivity value was observed to decrease gradually to 4.10×10^4 Ω.cm for AN90-PVDF/MgO, and 3.63×10^4 Ω.cm for AN110-PVDF/MgO. Upon increasing the annealing temperatures to 130°C and 150°C, the resistivity values were observed to progressively decrease to 1.3×10^4 Ω.cm (AN130-PVDF/MgO) and 7.68×10^4 Ω.cm (AN150-PVDF/MgO), which were lower than the resistivity value of UN-PVDF/MgO. Thus, annealing at temperatures above 90°C did not assist in enhancing the resistivity value of the annealed PVDF/MgO film.

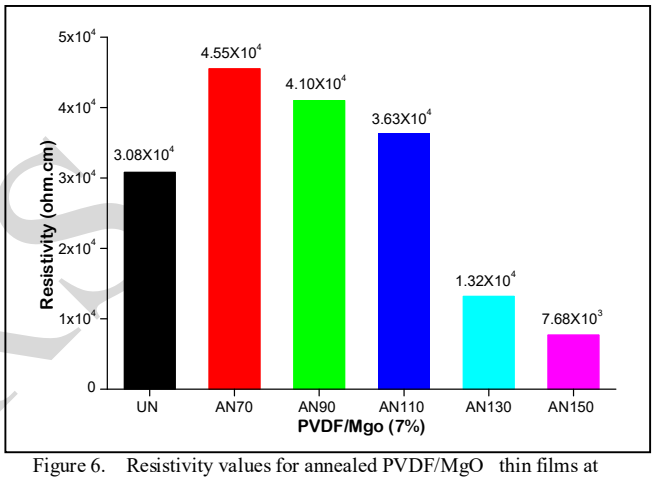


Figure 6. Resistivity values for annealed PVDF/MgO thin films at temperatures of 70, 90, 110, 130, and 150°C

IV. CONCLUSION

The dielectric properties of annealed PVDF/MgO thin films showed a gradual increment of the dielectric constant values from 21 (AN70) to 26 (AN70-PVDF/MgO) at 1 kHz frequency, with enhanced in the resistivity value from 3.08×10^4 Ω.cm to 4.55×10^4 Ω.cm, contributed to the presence of β-phase crystals. Nonetheless, further increase of the annealing temperatures to above 90°C showed fluctuations in the dielectric permittivity and resistivity values of PVDF/MgO (7%). The AN70-PVDF/MgO film is established as the optimized annealed film with enhanced β-phase PVDF crystals.

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