

# MICROSTRUCTURE AND PHASE OF POLY(VINYLIDEN FLUORIDE) FILMS BY ELECTROPHORETIC DEPOSITION: EFFECT OF POLYMER DISPERSION STIRRING CONDITIONS

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**ABSTRACT:** Electrophoretic deposition (EPD) technique was applied to conformably deposit piezoelectric PVDF film on uneven surface target. Nevertheless, optimization of polymer dispersion preparation process is crucial to achieve an even and uniform PVDF film. Sedimentation test showed PVDF polymer dispersions were more stable and well-dispersed in DMF than in MEK. Higher stirring temperature and shorter stirring time in MEK further decreased the PVDF dispersion stability and produced higher degree of agglomerated PVDF chain. As a result, MEK-based dispersion produced thick and fully coverage films whereas, the DMF-based dispersions produced thin but partial coverage films. Thus, the degree of dispersibility of the PVDF dispersions had a profound influence on the deposited films' microstructure. FTIR spectra indicated the presence of electroactive  $\beta$  phase in DMF-derived deposit, and a mixture of  $\alpha$  and  $\beta$  phases in the MEK-derived films.

**KEYWORDS:** *PVDF Coating, Piezoelectric Materials, Solution Casting, Zeta Potential, and Phase Transformation.*

## 1.0 INTRODUCTION

Polymeric poly(vinylidene fluoride) (PVDF) [1] is a piezoelectric polymer which potentially replaces lead zirconate titanate (PZT) [2] as a vibration or heat sensor and energy harvesting devices in the health care related application. This is because the PVDF has a superior mechanical flexibility, lower fabrication cost and nontoxicity as compared to PZT. Micron-range thickness PVDF films have been prepared using several conventional techniques which include spin-coating [3-5], solution casting [3,6], and roll press [7] techniques. Nevertheless, electrophoretic deposition (EPD) technique is proposed as an alternative if not a better technique for polymer films fabrication due to its advantages of applying uniform film thickness on uneven and complex substrate surface.

Polymer dispersion preparation process for EPD involves a simple set-up. However, process optimization is crucial for achieving dense PVDF film. Stirring conditions are main processing parameters to disperse polymer chains in the organic medium. Thus, the current paper reported on the effect of stirring temperature and time of the PVDF polymer dispersion on the surface microstructure and phase of PVDF films deposited by EPD.

## 2.0 METHODOLOGY

PVDF powder (99.99 wt% purity, particle size = 2  $\mu\text{m}$ , Sigma-Aldrich) was dispersed by ultrasound and dissolved in Dimethyl Formamide (DMF, 99.8 vol%, Sigma-Aldrich) or Methyl Ethyl Ketone (MEK, 99.5 vol%, Merck) by magnetic stirring. Different elevated stirring temperatures and time were used to prepare the PVDF dispersions with fixed concentration of 0.57 wt%. Details of the PVDF dispersions parameters are shown in Table 1.

Table 1: List of PVDF dispersions and their parameters (i.e. solvents, stirring temperatures and times)

Dispersion	Solvent	Stirring Temperature ( $^{\circ}\text{C}$ )	Stirring Time (hr)
1	DMF	80	8
2	DMF	120	2
3	DMF	120	8
4	MEK	53	8
5	MEK	64	2
6	MEK	64	8

Sedimentation test was performed to characterize the prepared dispersions. 10 mL of each as-prepared dispersion was enclosed in different 15 mL glass vials (height = 150 mm, diameter = 16 mm) and were placed on a bench at vertical orientation. Then, PVDF sediment height formed at the bottom of the glass vials was measured each day (i.e. 24 hr), until the seventh day.

Cathodic EPD was performed on ITO-coated glass substrate (working electrode, dimensions: 2.0cm  $\times$  1.0cm  $\times$  1.0mm) using DC power supply (OWL EC1000XL2, Thermo Fisher Scientific). Stainless steel plate was placed as a counter electrode (grade: AISI314, dimensions: 2.0cm  $\times$  1.0 cm  $\times$  0.4mm), at fixed electrode separation of 1 cm from the substrate. Both electrodes were then immersed into the PVDF dispersion. Then, a constant voltage of 80 V was applied on the EPD set-up for 20 min to obtain PVDF films.

Their surface microstructures were captured using scanning electron microscopy (scanning electron mode, accelerating voltage = 15 kV, Evo 50, Carl Zeis). The distribution of PVDF films was determined using Energy-Dispersive Microanalysis (EDS, Oxford Instrument) integrated to Field-emission Scanning Electron Microscope (FESEM, 3 kV accelerating voltage, secondary electron emission mode, Merlin compact-60-25, Carl Zeis). Phase identification was determined using Fourier Transform Infrared (FTIR) spectrometer (FT/IR-6100, Jasco).

### **3.0 RESULTS AND DISCUSSION**

Figure 1 shows the sedimentation test results of PVDF dispersion in MEK and DMF media prepared using different stirring temperatures and times. All the PVDF dispersions in the MEK medium exhibited a progressive increase in their sediment height with a longer suspension period. However, all the DMF-based PVDF dispersions did not sink after 7 days period, resulting in zero sediment height. The PVDF sediment height was built by the PVDF particles sedimentation. A high sediment height implied a high degree of particles agglomeration. This is because the agglomerates were arranged poorly during sedimentation, creating a high sediment porosity (equivalence to high sedimentation height) [8]. A more stable PVDF dispersion tended to sediment at later time (i.e. lower sedimentation rate, thus dispersed at a longer suspension period), indicating a higher PVDF dispersion stability [8,9]. The dispersion stability was maintained by the electrostatic repulsions between the charged PVDF polymers [8]. Therefore, the DMF-based PVDF dispersions were considered more stable and well-dispersed than the MEK-based PVDF dispersions. It had been reported that the PVDF particles were dissolved completely in the DMF medium [10] because of the penetration of the DMF molecules through the PVDF particles, resulting in a stable polymer chains dispersion (i.e. zero sediment height). However, the PVDF particles were partially dissolved in the MEK right up to the elevated temperature at 60°C [10]. The undissolved PVDFs became the nuclei for the precipitation of PVDF agglomerates in the MEK medium during the cooling stage.

The sediment height increase rate of MEK-based suspensions at the studied suspension period represented the degree of the PVDF dispersion instability in the MEK medium. The PVDF dispersions prepared at a high stirring temperature (i.e. 64°C) and/or time (i.e. 8 hr) exhibited higher sedimentation rates than the dispersions prepared at 53°C, thus, high stirring temperature and long stirring

time created poor stability dispersions with highly agglomerated PVDF particles. Nevertheless, a shorter stirring time at 64°C created a higher degree of particles agglomeration. The dispersion prepared at 2 hr demonstrated a higher sediment height than the 8 hr at the 7th suspension day. The former also exhibited a lower height increase rate, probably due to the steric stabilization effect of the agglomerated particles bonding network in the dispersion media [11].

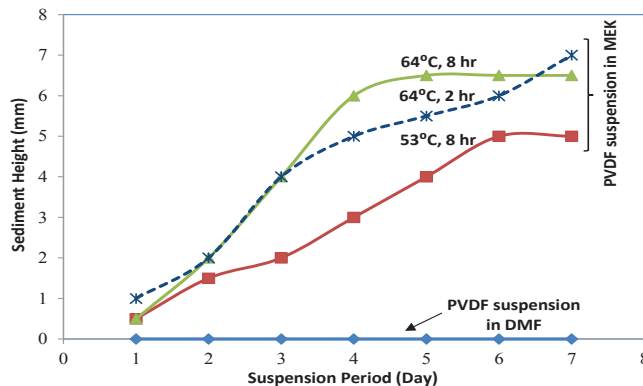


Figure 1: Sedimentation test results of PVDF dispersion in MEK and DMF media prepared using different stirring temperature and times

The microstructural observations (see Figures 2 and 3) shows EPD using MEK based dispersion formed thick fully coverage films with high surface roughness. Indirect characterization of surface roughness of the deposited PVDF films using UV-vis spectroscopy had been reported in details in our previous paper [9]. However, thin and partial surface coverage films were deposited using DMF-derived dispersion. The microstructures showed high deposition thickness of agglomerated PVDF polymers using MEK medium and low deposition thickness using DMF medium. The MEK-derived films' thicknesses were  $6.41 \pm 3.13 \mu\text{m}$  for 53°C-8 hr,  $3.90 \pm 0.91 \mu\text{m}$  for 64°C-2 hr, and  $6.41 \pm 3.13 \mu\text{m}$  for 53°C-8 hr samples. The PVDF films derived from the DMF medium were not measured due to low thickness. The microstructural difference of those films could be explained in terms of their polymer dispersion stabilities before EPD.

The low dispersion stability of MEK-based PVDF dispersion indicated that PVDF particles were not completely dissolved into the smallest and stable form of polymer chains. Thus, the dispersion easily formed agglomeration with time which in turns accelerated

PVDF film deposition. It appears that the degree of PVDF chain agglomeration in the dispersion influenced the microstructure of deposited film. Dispersion with higher degree of agglomeration and lower stability produced porous microstructural film.

The low PVDF deposition of DMF-based PVDF dispersion (see Figure 2) was due to high stability of PVDF chains in DMF medium, which was consistent with the sedimentation test result. Another reason is the PVDF chains might have very low (or negligible) net surface charges, thus, had a weak electrophoretic mobility to initiate PVDF deposition. However, it is believed that small amount of PVDF chains collided with electrode in the vicinity, producing layered deposition through polymer agglomeration and accumulation mechanism [9].

In the meantime, Figure 3 shows the topological view of PVDF films deposited using MEK and DMF solvents and different stirring conditions (i.e. temperature and time). The deposition of PVDF particulates which had size larger than as-received PVDF particles (i.e. average size of 200 nm). As-received PVDF particles were expected to be fully dissolved in DMF at the current stirring temperatures (i.e. above critical dissolution temperature of 40°C) [12]. Nevertheless, dispersion with higher stirring temperatures and time produced larger particulates, implying that PVDF dissolution in DMF media may vary with different stirring conditions. It was expected that dispersion prepared using higher stirring temperature and longer stirring time produced a higher degree of dissolved PVDF chains, enabling the polymer chains to align well to selected nucleation sites on the ITO surface. This, in turn, might accelerate the growth of PVDF agglomerates on the substrate.

PVDF phases of deposited PVDF films were identified through FTIR spectra (see Figure 4). Electroactive  $\beta$  peaks were detected at 420, 506, 535, 578, 875, 1189 and 1400  $\text{cm}^{-1}$  [13-15]. Whereas,  $\alpha$  peaks were observed at 496, 606, 757 and 975  $\text{cm}^{-1}$  [13,14]. The spectra showed MEK-derived films consisted of  $\alpha$  and  $\beta$  phases. A comparison of FTIR peaks of the films showed the  $\beta$  concentrations increased with the increase of stirring temperature and time. On the contrary, only  $\beta$  phase was detected in DMF-derived films. The  $\beta$  phase concentration of the DMF-derived films did not vary significantly with the stirring temperatures and time.

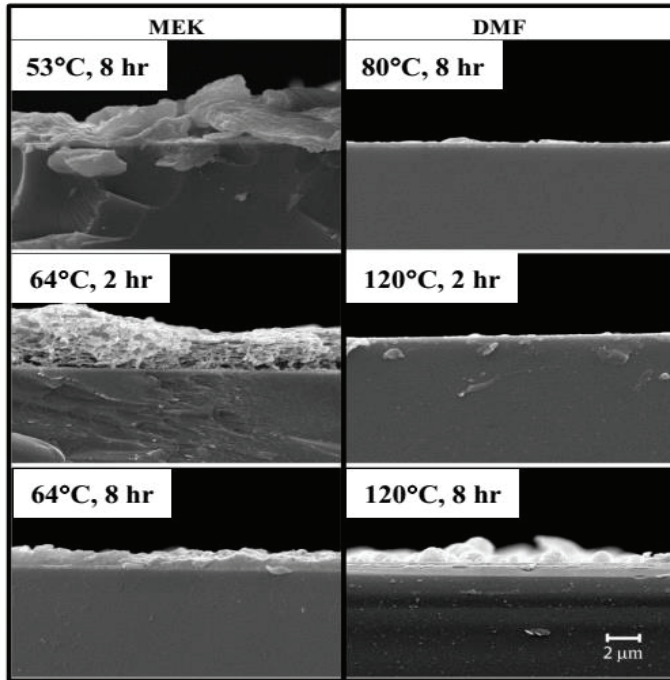


Figure 2: Cross-sectional views of PVDF films deposited using MEK and DMF solvents and different stirring conditions (i.e. temperature and time)

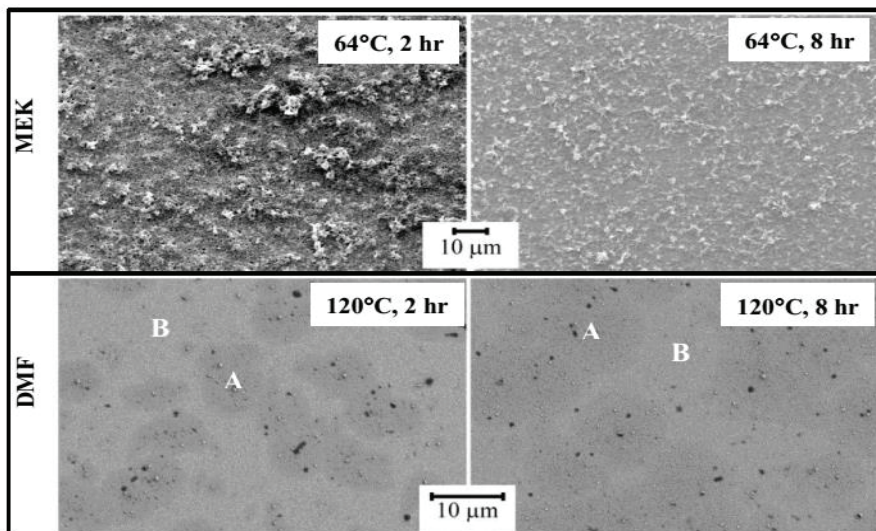


Figure 3: Topological view of PVDF films deposited using MEK and DMF solvents and different stirring conditions (i.e. temperature and time). Partial surface coverage films were deposited using DMF-based dispersion. Areas with film coverage regions are in darker colour (labeled as A) and bare substrate regions are in brighter regions (labeled as B).

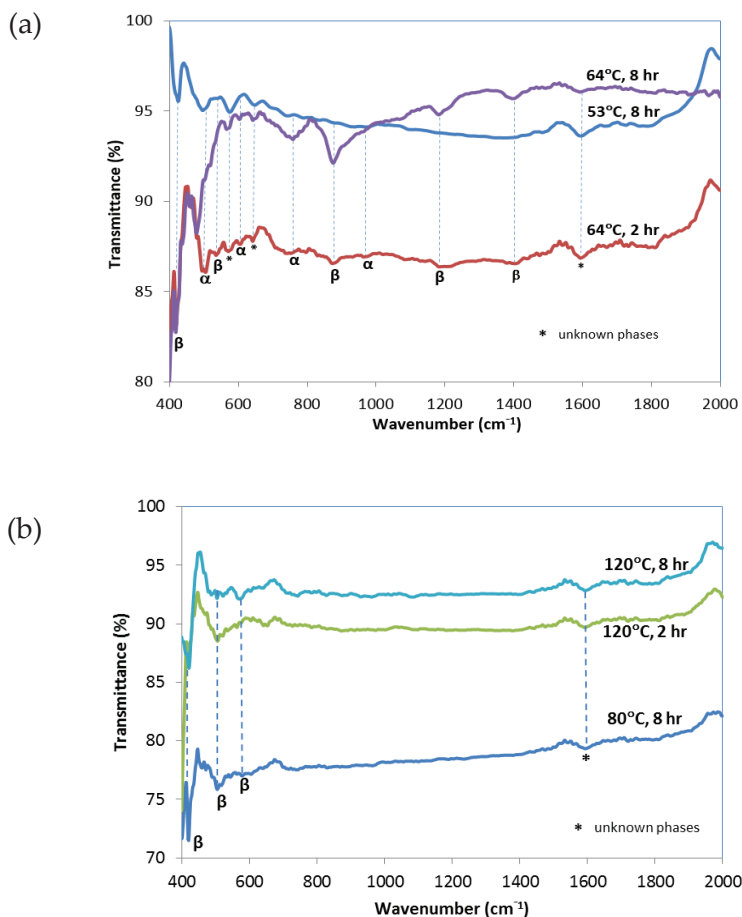


Figure 4: FTIR transmittance spectra of PVDF films deposited using: (a) MEK, and (b) DMF-based PVDF dispersion

#### 4.0 CONCLUSION

Microstructure and phase of PVDF films deposited by EPD are controlled by the selection of organic solvents, as well as stirring temperature and time of PVDF polymer dispersion. PVDF dispersions prepared using DMF solvent are more stable and more dispersed than PVDF dispersion prepared using MEK solvent. Thus, EPD using the former dispersion produces low PVDF deposit with incomplete surface coverage as compared to larger PVDF deposits produced by the latter dispersion. Stirring temperature and time of PVDF dispersion affect the degree of PVDF polymer agglomeration in the MEK solvent. MEK-based dispersion with higher stirring temperature produces less stable and more agglomerated PVDF dispersion, which

in turn, produces films with higher surface roughness and porosity feature. The dispersion with a longer stirring time has less agglomerated dispersion, giving a smoother film surface. It appears that only electroactive  $\beta$  phase is detected in film prepared using DMF-based dispersion but  $\alpha$  and  $\beta$  mixed phases are formed in the MEK-based film.

## ACKNOWLEDGMENTS

The authors would like to thank Universiti Teknikal Malaysia Melaka and Ministry of Higher Education Malaysia for the financial supports (Grant No. 06-01-14-SF00087 L00018. The authors also acknowledge Morphology Laboratory, Centre for Research and Innovation Management, Universiti Kebangsaan Malaysia for the FESEM characterization service. The authors also appreciate the supports given by Carbon Research Technology (CRT) research group.

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