Effects of the electric field and AlCl₃·6H₂O salt on the crystal, morphology and dielectric properties of P(VDF-HFP) fibres

P Sukwisute¹*, J Yuennan² and N Muensit²,³

1 Department of Physics, Faculty of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok, 10520, Thailand
2 Material Physics Laboratory, Department of Physics, Prince of Songkla University, Songkhla, 90112, Thailand
3 Center of Excellence in Nanotechnology for Energy (CENE), Prince of Songkla University, Songkhla, 90112, Thailand

*Corresponding author’s e-mail: pisan.su@kmitl.ac.th

Abstract. This research aims to prepare the polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)) fibres by electrospinning process with different electric fields. The aluminium chloride hexahydrate (AlCl₃·6H₂O) was filled into the fibres to act as a nucleating agent for β phase transformation. The morphology and phase transformation of the neat fibre mats with and without AlCl₃·6H₂O were investigated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The results show that the average diameter of fibres decreases with increasing electric field. The diameter of composite fibres becomes smaller compared to that of the pure P(VDF-HFP) fibre. The β phase fraction of fibre mats increases due to the applied electric field and AlCl₃·6H₂O filler. Moreover, an improvement of dielectric constant is found in the composite fibres, suggesting for mechanical sensors.

1. Introduction
Owing to the piezoelectric polymer, poly(vinylidene fluoride) (PVDF) and its copolymers like polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)) have been extensively studied in a variety of sensors and actuators because of its flexibility, light weight, thermal stability, and chemical robustness.[1] The crystal polymorphs of PVDF are often observed in a combination of four phases; α, β, γ, and δ. Among these, the electroactive β phase is the highest dipole moment and is mostly responsible for piezoelectric properties.[2] Electrospinning is an effective and simple technique to produce the α to β phases transformation in PVDF directly from solution without mechanical stretching and electrical poling processes.[3, 4] In this study, P(VDF-HFP) fibre mats were fabricated by electrospinning method. The influences of the applied electric field and aluminium chloride hexahydrate (AlCl₃·6H₂O) filler on the morphology, crystalline phase, and dielectric properties were investigated.

2. Experimental

2.1. Materials
Polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP); Solef 11010/1001; Solvay) was used as starting materials. The solvent in this work was N,N-dimethylformamide (DMF; D158550; Sigma
-Aldrich) with an impurity less than 0.1% water. Aluminium chloride hexahydrate (AlCl₃.6H₂O; 06232; Sigma-Aldrich) was adopted as a hydrated-salt additive.

2.2. Sample preparation

In this research, the P(VDF-HFP) fibre mats were fabricated by electrospinning process. To prepare the P(VDF-HFP) solution, 20 g of P(VDF-HFP) powder was first dissolved in 100 ml of DMF/acetone solvent and the mixture was continuously stirred with a magnetic bar at room temperature for 3 h. For a composite solution, 0.5 wt% AlCl₃.6H₂O filler was added to the neat P(VDF-HFP) solution because a viscosity of the solution at concentrations over 0.5 wt% was unsuitable for the electrospinning process. Afterwards, the Al/P(VDF-HFP) solution was gently stirred to make it homogeneous and transparent again.

The electrospinning apparatus was set in vertical direction consisting of a HV-power supply, 0-25 kV (Phywe Systeme GmbH & Co. KG., Germany) a syringe pump (Nz1000; New Era pump systems Inc., USA), a plastic syringe connected to a steel needle of 0.4 mm inner diameter, and an aluminium foil collector. A high electric field was applied between the needle and collector by the HV-power supply. The needle to collector distance was fixed at 15 cm. The as-prepared solution loaded in the plastic syringe was spun on the collector with a feeding rate of 1.0 ml/h controlled by a programmable syringe pump. The electrospun P(VDF-HFP) fibres were collected on the ground collector with the applied voltage of 10 and 20 kV at room temperature. The as-deposited fibres were put at room temperature for a week to evaporate the solvent before characterization. In all the conditions, the electrospun films had a thickness of 100 μm.

2.3. Characterizations

The surface morphology of electrospun fibres was examined by scanning electron microscopy (SEM; FEI Quanta 250, Thermo Scientific, USA) with an accelerating voltage of 15 kV. All the samples were coated with gold nanoparticles before the imaging. An average diameter of the fibres was measured from the SEM images using ImageJ software. In order to study the phase transformation of P(VDF-HFP) fibres, Fourier transform infrared spectroscopy (FTIR; Nicolet 8700, Thermo Scientific, USA) was scanned over the 400 to 1600 cm⁻¹ range with the attenuated total reflection (ATR) mode. For the dielectric measurement, the capacitance (C) of each sample was measured by an LCR meter (IM 3533; HIOKI, Japan) at room temperature.

3. Results and Discussion

3.1. Morphology study

Figure 1 shows the SEM images of P(VDF-HFP) electrospun fibres of filled and unfilled AlCl₃.6H₂O with the applied voltage of 10 and 20 kV. It is clearly shown the smooth and uniform and bead-free P(VDF-HFP) fibres, suggesting that the applied voltage of only 10 kV is enough to produce continuous fibres. The average fibre diameter of each sample measured by the ImageJ software is represented in figure 2. The diameter of electrospun P(VDF-HFP) fibre is remarkably reduced from 1,120 to 814 nm (unfilled Al) and 510 to 190 nm (filled Al) with the increase in applied voltage from 10 to 20 kV. The decreased diameter with increasing applied voltage can be explained in terms of the electrospinning jets during fibre production. Accordingly, the increase in applied voltage will increase the electrostatic repulsive force on the electrospinning jet leading to increased elongation of the fibres, which encourage to produce in the tiny fibres.[5]

The influence of AlCl₃.6H₂O filler was also investigated keeping constant applied voltage. The diameters of fibres of filled AlCl₃.6H₂O in P(VDF-HFP) samples are smaller than that of the unfilled samples. The adding of AlCl₃.6H₂O in the solution results in larger stretching and elongation of the jet because the charges in the composite jet can improve the electrostatic force during the electrospinning process, leading to smaller sized fibres.[6]
3.2. Polymer crystalline phase

FTIR spectra were performed in order to study the crystalline phase structure in P(VDF-HFP). In this work, the FTIR spectra of each electrospun fibre are further compared with a pristine P(VDF-HFP) film prepared by a solvent casting technique, as presented in figure 3. The absorption bands at 532, 613, 766 and 976 cm\(^{-1}\) are assigned to the \(\alpha\) phase (TGTG' conformation), while the bands at 840 and 1,275 cm\(^{-1}\) are designed to the \(\beta\) phase (TTTT conformation).\[^7, 8\] To estimate \(\beta\) phase content (\(F(\beta)\)) in P(VDF-HFP) samples, the absorbance peaks related to the \(\alpha\) phase at 766 cm\(^{-1}\) (\(A_\alpha\)) and \(\beta\) phase at 840 cm\(^{-1}\) (\(A_\beta\)) are calculated as following: \(F(\beta)=[A_\beta/(1.26A_\alpha+ A_\beta)]\times100\),\[^8\] and the results are reported in figure 4.

The pristine P(VDF-HFP) film clearly shows the bands of \(\alpha\) phase and a small peak of \(\beta\) phase at 836 cm\(^{-1}\), resulting in a mixture of both \(\alpha\) and \(\beta\) phases with the lowest \(F(\beta)\). In regard to the P(VDF-HFP) fibres, most of the peaks of \(\alpha\) phase disappear and the band of \(\beta\) phase at 1,275 becomes predominant. This suggests that the \(\alpha\) to \(\beta\) phases transformation is produced during the electrospinning process. The \(F(\beta)\) of fibres decreases with increasing applied voltage due to higher elongation forces the molecular. Moreover, the \(F(\beta)\) of fibres filled with AlCl\(_3\)-6H\(_2\)O is higher than that of the unfilled fibres. The addition of AlCl\(_3\)-6H\(_2\)O can further improve \(\beta\) phase formation because of the hydrogen bonding interaction between the water molecule in AlCl\(_3\)-6H\(_2\)O and -CF\(_2\) dipole in P(VDF-HFP) chains\[^2\]. Therefore, the electrospun P(VDF-HFP) fibre with applied voltage at 20 kV exhibits the maximum \(F(\beta)\).
3.3. Dielectric property
Table 1 presents the dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) of all samples. This value can be calculated from the relation: $\varepsilon_r = \varepsilon_0 \varepsilon_r A$, where $C$, $t$, and $A$ are the capacitance, thickness, and surface area of the sample, respectively. $\varepsilon_0$ is the permittivity of free space (8.85×10^{-12} F/m). It is obviously found that the P(VDF-HFP) fibre mats display lower dielectric constant compared to the pure film. Typically, the values of the dielectric constant of PVDF and its copolymer are mainly dependent on the $F(\beta)$ values of polymers.[9] However, the dielectric constant of electrospun fibre mats in the work does not behave in this manner because of the porosity of P(VDF-HFP) mats as seen in figure 1. The P(VDF-HFP) mats should be taken into account as multiphase materials comprising the polymer fibre networks, fillers and air gaps (voids).[10] During the dielectric measurement, the electric field was applied normal to the plane of fibre mats. The low dielectric constant of air influences on the dielectric value of these fibre mats. Therefore, an increase in the electrostatic field and an appearance of AlCl$_3$·6H$_2$O in P(VDF-HFP solution) causes the declination of dielectric constant due to the smaller diameter of fibres and larger air fraction of fibre mats. Nevertheless, the dielectric constant of AlCl$_3$·6H$_2$O/P(VDF-HFP) fibre mats still higher than that of the Fe$_3$O$_4$/PVDF fibre composite (~2.1) as previously reported.[10]

| Sample | Film | UnAl-10 kV | UnAl-20 kV | Al-10 kV | Al-20 kV |
|--------|------|------------|------------|----------|----------|
| $\varepsilon_r$ | 4.9  | 3.42       | 3.16       | 2.95     | 2.68     |
| tan $\delta$ | 0.03 | 0.12       | 0.18       | 0.22     | 0.27     |

4. Conclusion
The P(VDF-HFP) fibre mats were prepared by the electrospinning process. The influence of electric fields and AlCl$_3$·6H$_2$O salt on the morphology, phase structure, and dielectric constant was also studied. It is worthy to note that the $\beta$ phase fraction of electrospun fibres can be enhanced by increasing electric field and adding AlCl$_3$·6H$_2$O, whereas the fibre diameter tends to decrease. The dielectric constants (2.68-3.42) of the AlCl$_3$·6H$_2$O/P(VDF-HFP) mats are higher than that of Fe$_3$O$_4$/PVDF fibre (2.1), suggesting the improvement of sensing ability of the AlCl$_3$·6H$_2$O/P(VDF-HFP) mats.

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