Electrospun SiO$_2$/PVDF copolymer composite nanofiber: effect of SiO$_2$ content on nanostructure, morphology, and thermal property

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Abstract. A separator is an important part of lithium-ion batteries. Nanofiber separator is one promising material to improve the performance of lithium-ion batteries. SiO$_2$/cPVDF composite nanofiber was successfully synthesis by the electrosprning process. SiO$_2$ nanoparticle, cPVDF, and N-N DMac were used to synthesis composite nanofiber. SiO$_2$ content influences nanostructure, morphology, diameter and thermal property of nanofiber. Nanofiber separator prepared with the optimum condition of flow rate 0.004 mL/min, voltage 22 kV, and the distance to collector 13 cm. Structure of nanofiber separator was analyzed with ATR-FTIR. FTIR vibration band peak at 1057.8 cm$^{-1}$, 839.4 cm$^{-1}$, and 761.3 cm$^{-1}$ were related to Si-OH functional group, a distinctive $\beta$ phase crystal and $\alpha$ phase crystal, respectively. The average diameter of cPVDF nanofiber, SiO$_2$/cPVDF (0.5%) nanofiber, SiO$_2$/cPVDF (0.75%), and SiO$_2$/cPVDF (1%) were 648.3 nm, 320.6, 347.1, and 388.8 nm, respectively. Effect of addition of silica nanoparticles decreased the average diameter nanofiber. Electrospun SiO$_2$/cPVDF composite nanofiber also showed different thermal behavior under different gases conditions in TGA study, and it is observed that the nanofiber separator could stand until near 400$^\circ$C before the main chain’s degradation occur. XRD and DSC analysis showed that increasing of SiO$_2$ content decreased crystallinity of nanofiber composite. Water contact angle experimental results of SiO$_2$/cPVDF composite nanofiber revealed an improvement of hydrophobicity with the addition of SiO$_2$ on nanofiber composite.

Keyword: Lithium-ion battery, separator, composite nanofiber.

1. Introduction

In recent years, many researchers have been focus to made advanced material based on nanotechnology process, due to its excellent properties such as low basis weight, high permeability, and small pore size, which beneficial for some applications such as membrane filtration, drug delivery, catalyst carriers sensors, tissue engineering, energy storage devices, Li-Ion batteries, etc [Haddadi, 2017]. Among those nanomaterials, nanofiber has attracted great attention owing to their high surface area-to-volume ratio, which approximately thousand times higher than human hair. Several techniques are well-known to fabricate nanofiber, for example template synthesis, phase separation, and electrosprning. Due to the ease of processing and flexibility, electrosprning is more preferable than other techniques to produce nanofiber [Teo 2006, Tong 2012].

Poly(vinylidene fluoride) (PVDF) is one of interesting polymer which can be applied as the matrix for electrosprned nanocomposite, by cause of its typical characteristic such as high
chemical resistance, thermal stabilities, good dielectrical and mechanical properties [Hadaddi 2017, Obaid 2015]. To develop nanocomposite performance for specific applications, it is possible to modify them by adding inorganic nanoparticles, such as ZrO$_2$, SiO$_2$, TiO$_2$ and Al$_2$O$_3$ [Nasir 2014, Obaid 2015].

As well known today silica nanoparticle is considered to be applied in green technology application. Because modifying the silica nanoparticles is quite possible, we could control porosity, particle size, crystallinity and also the surface properties [Bharti 2011, Liberman 2014]. Moreover, silica nanoparticles has some beneficial value, which can improve material properties such as thermal stability, hydrophobicity, biocompatibility, surface properties, electrochemical properties and so on. [Bae, 2010, Dong 2015, Gomes 2016].

2. Experimental

2.1 Materials
Poly(Vinylidene Fluoride) (PVDF copolymer, Kynar S80201), N,N-Dimethylacetamide (DMAc) (Merck), SiO$_2$ (LIPI). All chemical was used without further purification.

2.2 Preparation of electrospun composite nanofibers
Various amount of SiO$_2$ nanoparticle (0.5% ; 0.75% ; 1% w/v) were added to PVDF copolymer solution in N,N DMAc as solvent and continuously stirring for one day. Before using for electrospinning, entrapped air in polymer solution was removed. 5 mL syringe with polymer solution was attached to an electrospinning machine (Zuheros nano). Some parameters of the electrospinning as follow: polymer concentration is 24% (w/v), SiO$_2$ concentration is 0.5% ; 0.75% ; 1% (w/v), nozzle-to-ground collector distance is 13 cm, applied voltage is 22 kV and flow rate is 0.004 ml/min.

2.3 Characterization
The morphology of electrospun composite nanofiber was investigated by a Scanning Electron Microscope (SEM) JEOL/JSTM-IT300, Japan. The sample was prepared with Au-coating before measurement.

The interaction between the SiO$_2$ composite and nanofiber was analyzed with Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Nicolet iS 5 ATR iD5, Thermo Scientific, USA, in the wavenumber range of 500-4000 cm$^{-1}$.

The diffraction patterns were observed by X-Ray Diffraction (XRD) Bruker D8 Advance, Germany. Samples were characterized from 2θ range between 5° to 90° with zero background and rotating anode of CuKα tube (λ=1.540 Å).

Thermal properties of composite nanofiber have explored using Differential Scanning Calorimeter (DSC) 214 Polyma, Netzsch, Germany, under inert atmosphere (pure N$_2$) with the condition of heating from -70°C until 200°C, with the heating rate of 10°C/min. The crystallinity was calculated from the DSC results by the following equation:

$$\text{Crystallinity} (%) = \frac{\Delta H_{ms}}{\Delta H_{mo}} \times 100$$

Where $\Delta H_{ms}$ is the melting enthalpy of the sample, and $\Delta H_{mo}$ is the melting enthalpy of 100% crystalline of PVDF, which specified as 105 Jg$^{-1}$.

Thermogravimetric Analysis (TGA) 209 F1 Libra, Netzsch, Germany, used to study the behavior of composites nanofiber under two different conditions. First, prepared sample was run under pure nitrogen atmosphere (inert condition) from 30°C-700°C with the heating rate of 10°C/min. Second, the prepared sample was run under an oxygen atmosphere (oxidative condition) from 30°C-700°C with the heating rate of 10°C.

The water contact angle was evaluated by drop shape method and calculated by the equation:

$$\theta = \tan^{-1}\left(\frac{h}{d}\right)$$

Where $\theta$ = contact angle, d=diameter, h=height
3. Result and Discussions

3.1 SEM

Figure 1. SEM images of (a) cPVDF, (b) cPVDF-SiO$_2$ 0.50%, (c) cPVDF-SiO$_2$ 0.75%, and (d) cPVDF-SiO$_2$ 1.00% composite nanofibers

The pristine copolymer poly (vinylidene fluoride) (cPVDF) 24% w/v nanofibers which were fabricated by electrospinning had not uniform size with bead-free fibers in the average diameter of 648.3 nm. The addition of SiO$_2$ contents in cPVDF system nanofibers affected their morphology and diameter distribution of nanofibers. Those nanoparticles decreased the average diameter of cPVDF nanofiber into 320.6, 347.1, and 388.8 nm when added SiO$_2$ 0.50%, 0.75%, and 1.00% into PVDF system nanofibers, respectively. It was also observed that a higher amount of SiO$_2$ led to heterogeneous distributed nanofibers diameter due to the repulsive force of SiO$_2$ which minimized the entanglement of polymer chains (Jung et al. 2009; Yanilmaz et al. 2013). Figure 2 showed 0.50% w/v of SiO$_2$ in the nanofiber system tended to produce a homogenous size diameter of nanofibers.
Figure 2. Diameter distribution of (a) cPVDF, (b) cPVDF-SiO₂ 0.50%, (c) cPVDF-SiO₂ 0.75%, and (d) cPVDF-SiO₂ 1.00% composite nanofibers
3.2 FTIR

Figure 3. ATR FTIR spectrum of cPVDF-SiO \textsubscript{2} composite nanofibers

IR spectrum of SiO \textsubscript{2} nanoparticles revealed a stretching vibration of silanol (Si-OH) group at 3392.7 cm\textsuperscript{-1} and stretching vibration of silicon-oxygen were observed at 1057.8 cm\textsuperscript{-1} (Jung et al. 2009), 961.8 cm\textsuperscript{-1}, and 796.5 cm\textsuperscript{-1}. Characteristic peaks of cPVDF nanofibers were showed at 1400.1 cm\textsuperscript{-1} assigned to C-F stretching vibration, 1274.2 cm\textsuperscript{-1} assigned to CF out-of-plane deformation of $\beta$-cPVDF (Bormashenko et al. 2004), CF\textsubscript{2} symmetrical stretching attributed to 1174.9 cm\textsuperscript{-1} and 1072.7 cm\textsuperscript{-1}, 877.0 cm\textsuperscript{-1} to C=CH vibration, 839.4 cm\textsuperscript{-1} assigned to CH\textsubscript{2} rocking of $\beta$ -cPVDF phase (Bormashenko et al. 2004), and 761.3 cm\textsuperscript{-1} assigned to CH\textsubscript{2} rocking of $\alpha$-cPVDF phase (Gregorio et al. 2005).
The addition of SiO₂ nanoparticles revealed small intensity peak at about 3300 cm⁻¹ as silanol group, drew α -phase formation of cPVDF with reduced β fraction, 0.83 of cPVDF nanofibers into 0.76, 0.80, and 0.69 respectively for cPVDF-SiO₂ 0.5%, cPVDF-SiO₂ 0.75%, and cPVDF-SiO₂ 1.00% beside of shifting characteristic peaks of cPVDF.

3.3 DSC Analysis

![DSC results for SiO₂-cPVDF composites nanofiber](Figure 4)

**Table 1.** Differential scanning calorimetry data for composite nanofiber cPVDF and containing SiO₂

|              | Tg (°C) | Tm (°C) | ΔHₘ (J/g) | %Xc   |
|--------------|---------|---------|-----------|-------|
| cPVDF        | -11.2   | 136.5   | 39.71     | 32.73%|
| SiO₂ 0.5%    | -9.5    | 138.5   | 35.13     | 31.66%|
| SiO₂ 0.75%   | -8.4    | 137.6   | 33.20     | 31.03%|
| SiO₂ 1%      | -5.4    | 137.9   | 33.42     | 22.21%|

From DSC measurement, the glass transition (Tg) shows a shifting into a higher temperature. Pristine cPVDF nanofiber shown the Tg point at -11.2°C and relatively increased with the addition of silica composite. The peak pattern of nanofiber also showed a change at about 55°C, which attributed to the phase transition of nanofiber. Nanofiber SiO₂/cPVDF shows a lower peak while the Tg curve of pure cPVDF nanofiber shows a higher peak. This, affected by the change of amorphous phase of the polymer as the presence of inorganic composite, which contributes to the shifting of the Tg curve.(Kim et al. 2011; Malmonge, Malmonge, and Sakamoto 2003)

In addition, the enthalpy of melting (ΔHₘ) and the crystallinity (%Xc) are decreased with the increase of SiO₂ content. This might be triggered by the existence of SiO₂ nanoparticles which retard the polymer chain rearrangement during the polymer crystal formation. The SiO₂ surface charges can also influence to the amorphous phase of the polymer, as the result of the higher nucleation rate during the solidification process (Gong et al. 2017; Kim et al. 2011).

Conversely, the presence of SiO₂ did not affect significantly to the melting temperature (Tm). The melting temperature of pure cPVDF nanofiber is 136.5° when the others present a melting peak at 138.5°C,137.6°C, 137.9°C for 0.50%, 0.75%, 1.00% of SiO₂ content respectively. The slight change of melting temperature, presumably are not related to the interaction between polymer and SiO₂ composite but by the orientation of polymer chains on the fiber, the same case is reported by (Kim et al. 2011)
3.4 TGA analysis

Figure 5. Thermograms for SiO₂-cPVDF composite nanofiber under different atmosphere

TG curve under non-interactive gases condition (pure N₂ gases), perform DTG peak at around 480°C for cPVDF nanofiber, and about 477.21°C, 484.18°C, 479.54°C for 0.50%, 0.75%, and 1.00% of SiO₂-cPVDF nanofibers respectively. Initial degradation starts at almost 450°C for nanofiber PVDF copolymer system, and relatively increase with the addition of SiO₂ composites. Furthermore, the completion appears at 500°C for those cPDVF nanofibers and SiO₂-cPVDF composite nanofibers.

Different behavior occurs in an interactive gas condition (O₂ gases). The degradation process starts at approximately 420°C for pristine cPVDF nanofiber and nearly 440°C for PVDF composite nanofibers. Meanwhile, the complete combustion performs at around 470 until 475°C for both neat nanofiber and composite nanofibers, which start and end earlier than the non-interactive gases. DTG peak present a mid-point of decomposition process at 453°C for cPVDF nanofiber, and at 459°C, 460°C, 469°C, for 0.50%, 0.75%, and 1.00% of SiO₂ content correspondingly.

Thus, the difference results between the non-interactive and interactive gases could be used as an indication in the application of nanofiber separator. Whereas, under inert ambiance (N₂ gases) the composite nanofibers separator designate the fact that it would stand until nearly 480°C before hit its degradation process. On the other side, in case the system contacts with air which contains oxygen the separator would stand until around 420°C before the degradation takes place.
3.5 XRD Analysis

Figure 6. XRD patterns for cPVDF nanofiber and SiO\textsubscript{2}-cPVDF composite nanofiber

Table 2. Percentage crystallinity of cPVDF nanofiber and SiO\textsubscript{2}-cPVDF composite nanofiber

|                  | cPVDF   | SiO\textsubscript{2} 0.50% | SiO\textsubscript{2} 0.75% | SiO\textsubscript{2} 1.00% |
|------------------|---------|---------------------------|---------------------------|---------------------------|
| Total crystallinity (%) | 54,1    | 44,9                      | 39,4                      | 35,1                      |

Figure 6 shows the X-ray diffraction of nanofibers. The diffraction patterns of silica nanoparticles show a broad peak around 22° (2θ) which attributed to amorphous structure, but it also obtains in the measurement a sharp peak at 2θ value of 29° which indicating a crystalline structure of nanosilica. The presence of crystalline peak may be assigned to re-crystallization process of silica during calcination (Deshmukh 2011).

On the other hand, pristine cPVDF nanofiber shows a shoulder peak at 2θ value of 18,1° which indicating a crystalline α phase of polymer and an intensive peak at 20,3° which contributed to crystalline β phase. It was also seen a remarkable peak at nearly 39° considering a crystalline β phase. It is as well agreed with the ATR-FTIR results which dominantly showed a distinctive β phase peak at 839.4 cm\textsuperscript{-1} and 1274.2 cm\textsuperscript{-1} but it is also confirmed that crystalline α phase presence in the polymer with showed peak at 761.3 cm\textsuperscript{-1}. (Li et al 2014, Cai et al 2017, Bormashenko et al 2004, Gregorio et al 2005)

The loading of SiO\textsubscript{2} nanoparticle in the nanofiber induced a shifting to higher intensity at the crystalline α phase peak at 2θ value of 18,1°. Identical outlines appear at small crystalline β phase
peak around 39° which going to elevate the intensity. As the SiO₂ loading risen the total crystallinity reduced. The same profile has also reported on the crystallinity value report by DSC measurement. The diminished of the percentage of crystallinity can be altered by the polymer chains re-organization and also caused the higher ionic conduction (Stephan et al 2006)

3.6 Wettability

The surface behavior of nanofiber has studied with wettability measurement. It is indicating that with the addition of SiO₂ nanoparticle the hydrophobic behavior of composite nanofibers is improved. It acquires from the measurement that cPVDF nanofiber preforms a contact angle in 116,62° and increases to 131,38°, 133,74° and 137,12° for 0.50%, 0.75%, 1.00% of SiO₂ content respectively. Increasing hydrophobicity of composite nanofibers is caused by the surface roughness of the fiber due to the presence of silica nanoparticles, which condense to the total area of solid-liquid interface (Dong et al, 2015).

4. Conclusions

Electrospun SiO₂/cPVDF copolymer composite nanofiber with average diameter of 320-380 nm was successfully prepared by electrospinning method. FTIR and XRD analysis showed that crystal structure of nanofiber composites was a mixed of a and b phase. XRD and DSC analysis revealed that increasing of SiO₂ will decrease crystallinity of nanofiber composite. The contact angle experimental revealed an improvement of hydrophobicity with the addition of SiO₂ on nanofiber composite. Electrospun SiO₂/cPVDF composite nanofiber showed different thermal stability under different gases condition, it is observed that the nanofiber separator could stand until near 400°C before the main chain degradation occur. As a result, the prepared electrospun nanofiber would be able as a promising material for Li-ion battery separator.

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