Synthesis and Characterization of Copolymer Poly(vinylidene fluoride)/Graphene Nanofiber

Muhammad Nasir*, Triannisa Rahmawati, Indriyati, Fitri Dara, Desak Gede Sri Andayani
Research Unit for Clean Technology, Indonesia Institute of Sciences (LIPI), Cisitu-Sangkuriang, Bandung 40135, Indonesia

*Corresponding author: mnasir71@yahoo.com

Abstract. The copolymer poly(vinylidene fluoride)/graphene (cPVDF/graphene) nanofibers were fabricated using the electrospinning method. The concentration of cPVDF was fixed at 24% (wt.%), graphene 0.01-0.1% (wt.%) in N,N-dimethylacetamide (N,N-DMAC). Characterization was conducted to analyse the effect of graphene concentration and electrospinning parameter of cPVDF/graphene using SEM-EDS, ATR-FTIR, TG-DSC, and XRD. Electrosprinning parameters (applied voltage, the distance between nozzle and collector, flow rate) affected nanofiber diameter, beads formation, β-crystal phase formation in the flow rate variation, the nanofiber produced is at the size of the nanometer and at optimum conditions, almost no beads are found, as well as homogeneous. SEM images showed that the presence of graphene and applied electrosprinning parameter affected morphology and an average diameter of nanofibers. FTIR and XRD pattern indicated that β-crystal phase of cPVDF was dominant than α-phase, which was followed by increasing the crystallinity when graphene added. Graphene also influenced the thermal behaviour of composite nanofibers which was supported by TG-DTG and DSC thermograms. Hydrophobicity of cPVDF nanofibers increased with more graphene content. These composite nanofibers have potential application to solve environmental problems.

1. Introduction
Approximately most of 97.5% hydrosphere in oceans is the combined mass of water on, above, and under the surface, in which only 2.5% of the hydrosphere is freshwater. This freshwater can be found in glaciers, permanent snow, mountainous regions, lakes, rivers, and ground water[1]. Along with the development of the world, the need for freshwater increases. Moreover, the increase of population, industry, and water pollution are the concern for the world to demands water treatment technology. There are several ways to overcome this problem, likes constructing the reservoir, use water effectively, and diversion of water needs. On the other hand, escalation water treatment technologies are the target for the environmental engineer, and membrane separation technology has been a concern to solve water crisis[2].

Membrane separation process is a filtration process to separate molecules with different sizes by using pressure as driving force. Polluted water can be treated by using membrane. The polluted water forced by pressure through the semipermeable membrane to separate material based on membrane pore size. This process has several advantages in the applications, such as high efficiency, low cost, can
separate in a wide range, can be used for a wide range of application[2,3], and applied in industrial scale such as reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), and nanofiltration (NF)[3].

A semi-crystalline and piezolectric poly(vinylidene fluoride) or PVDF is a polymer with –(CH₂CF₂)ₙ–repeating unit that widely used in the separation and purification. This hydrophobic polymer generally has five difference polymorphs: α, β, γ, δ, and ε[4,5], but α, β, γ are the most common obtained phase of PVDF[5,6], in which every polymer crystal phase give significant effect to intrinsic properties of PVDF with the degree of crystallinity between 35 to 70%[7]. This crystallinity depends on molecular weight, thermal history, molecular weight distribution, polymerization method, and cooling rates[8]. PVDF has exceptional properties, such as high thermal stability, mechanical strength, high chemical, and excellent aging resistance[9,10] that make this polymer widely used as raw material and suitable for membrane filtration and purification. Although PVDF nature properties have been hydrophobic, in purpose to increase hydrophobicity, another hydrophobic material needed.

Graphene is material with C-C structure that makes this material highly hydrophobic. This material has one atom thick, two-dimensional sheets of carbon atoms[11], hexagonal lattice with sp² hybridization[12].The techniques developed to synthesize graphene can be divided into five major methods, like mechanical cleavage, chemical method, epitaxial growth, total organic synthesis, and chemical vapor deposition (CVD)[13]. This material can be used as graphene bulbs, graphene battery, drug carriers, hydrogen storage materials, graphene superconductors, and graphene chips[14]. Because of its outstanding property of graphene, i.e.: high thermal stability, high mechanical properties, flexible, transparent, and hydrophobic, this material used to mix with PVDF to produce more hydrophobic membrane.

There are several methods to produce membrane, which is the conventional method through casting solution and electrospinning. Electrospinning has attracted interest of academia and industry, because of its ability to produce ultrafine fiber[15] with diameter range from few micrometer to tens of nanometers and high versatility and potential for application in many fields[16] than the conventional method. Nevertheless, to reach optimum nanofiber, the electrospinning parameter must be optimized for every polymer solution. This electrospinning parameter encompasses voltage, flow rate, and the distance between collector and nozzle.

In this study, we analyzed the effect of graphene concentration and electrospinning parameter to get optimum nanofiber morphology. Applied voltage, flow rate, the distance between collector and nozzle was varied to get optimum nanofiber using electrospinning method. This research also analyzed the diameter average, diameter distribution, crystallinity, thermal characteristic, and hydrophobicity nanofiber at optimum condition. SEM-EDS, ATR-FTIR, TG-DSC, XRD, and water contact angle were conducted to analyzed nanofiber characteristics.

2. Experimental method

2.1. Materials
Copolymer poly(vinylidene fluoride) (cPVDF) as nanofiber polymer material was purchased from Kynar flex® 2801-00 ARKEMA Inc. USA. N, N-dimethylacetamide (N, N-DMAC) as solvent was obtained from Merck. Graphene was supplied by Graphene Supermarket in form of nano powder multilayer flakes. All materials were used without further purification.

2.2. Solution preparation and electrospinning of cPVDF/graphene
The electrospinning solutions with different graphene concentrations were prepared using N,N-DMAC as solvent. cPVDF powder was fixed at 24 wt%, while graphene varied at 0.01; 0.05; and 0.1 wt%. Both of materials were mixed with N,N-DMAC using magnetic stirrer at room temperature until homogenous. During electrospinning, every sample was optimized by varying flow rate (0.5; 1.0; 1.5; and 2.0 μL/min), voltage (16, 19, 22, and 25 kV), and distance between nozzle and collector (12.5; 14.5 cm). The nanofiber product was characterized using SEM-EDS, to select the nanofiber-based on beads, branch, homogeneity, and diameter for each graphene concentration. Furthermore, an optimized nanofiber was
characterized using ATR-FTIR, XRD, TG-DTG, DSC, and contact angle. All electrospinning process was done at controlled room temperature and humidity.

2.3. Characterization
The surface morphology of nanofiber was studied with scanning electron microscopy-energy dispersive spectroscopy (SEM JEOL JSM IT-300) at 20.0 kV accelerating voltage for scanning the surface, whereas the electron dispersive spectroscopy (EDS) used to monitor the % composition of sample qualitatively. Fiber diameter, fiber diameter distribution, and the average diameter of fiber were calculated using Image J software. 125 points were taken to calculate nanofiber diameters. Thermal characteristics of cPVDF/graphene nanofiber were determined by thermogravimetric-differential thermal gravimetric using TGA 209 Lybra (Netzsch), in which sample was heated from room temperature to 900 °C for 10 °C/min of heating rate under N₂ gas. Fourier transform infrared (FT-IR) in attenuated total reflectance (ATR) mode from Thermo Scientific Nicolet iS5 and x-ray diffraction (XRD) Bruker D8 ADVANCE were used to observe the functional group in the sample, the diffraction peak of nanofiber, and crystallinity. XRD analysis was performed from the 20 range between 10° to 70° with the rotating anode CuKα tube (λ = 1.5418 Å). Differential scanning calorimetry using DSC 214 Polyma NETZSCH Germany. This instrument performed at room temperature until 275 °C for 10 °C/min of heating rate under N₂ gas. The contact angle measured to quantify sample hydrophobicity and Image J conducted to calculate the contact angle value.

3. Results and discussion
3.1. Nanofiber morphology
SEM-EDS were carried out to investigate the effect of graphene concentration and electrospinning parameter to the nanofiber morphology. The morphology of nanofiber was analyzed to get optimum nanofiber for every specific graphene concentration.

![Figure 1](image-link)  
**Figure 1.** Morphology and diameter distribution of nanofiber using SEM. Image (left) and diameter distribution (right) of the effect of graphene concentration on nanofiber morphology. (a) pure cPVDF, (b) graphene 0.01%, (c) graphene 0.05%, and (d) graphene 0.1%. The number in white colour is diameter average.

3.1.1. The effect of graphene concentration on nanofiber morphology. Figure 1 shows typical SEM images of pure cPVDF and cPVDF/graphene at different graphene concentration with same
electrospinning parameter condition on the left, and diameter distribution on the right. The electrospinning parameter was 19 kV (voltage), 1 µL/min (flow rate), and 14.5 cm (distance between collector drum and nozzle). At different graphene concentration, electrospun nanofibers can show different nanofiber morphologies, such as branch, bead, nanofiber diameter, porous, and homogeneity. On this cases, all nanofiber in these results had randomly fibrous morphology, except for graphene 0.01% a little bit aligned. As predicted, although electrospinning parameter design in the same condition, graphene concentration significantly affect nanofiber morphology as image resulted. The most significant morphology is evident from Figure 1(c). At this nanofiber condition (graphene 0.05%), highly beaded, branch, and inhomogeneous nanofibers were produced. This surface scanning was different compared to pure cPVDF and another nanofiber. However, the calculation of the diameter as shown in Figure 1 on the right side provided that all fibers have a diameter in the nanometer scale. Furthermore, the addition of reduced nanofiber diameter than pure nanofiber. This condition in consequence of the increase of charge density that generates a higher elongation force to the ejected jets[5].

3.1.2. The effect of flow rate to nanofiber morphology. Applied voltage, flow rate, and the distance between collector and nozzle were varied to get optimum nanofiber using electrospinning method. Figure 2 shows typical SEM images of pure cPVDF and cPVDF/graphene 0.05% at different electrospinning flow rate condition (left), and diameter distribution (right). The difference of electrospinning flow rate has changed the morphology of nanofibers, shown in Figure 2(a), 2(b) and 2(c). This nanofibers contains excessively beads, branches, and heterogeneous in size. However, the calculation of the diameter, as shown in the right side of Figure 1, provided that all fibers have a diameter in the nanometer scale. The other variation such as voltage and distance from the nozzle to the collector were also observed. These variations also produce different nanofibers morphologies, with different levels of beads and branches.

![Figure 2. Scanning Electron Microscopy (SEM) images of nanofibers. Image (left) and diameter distribution (right) of electrospinning flow rate variation to nanofiber morphology. (a) pure cPVDF 0.5 µL/min, (b) 1.0 µL/min, (c) 1.5 µL/min, and (d) 2.0 µL/min, when graphene concentration 0.05%. The number in white colour is diameter average.](image)

From observations on the influence of variations in graphene concentration and optimization of the parameters of the electrospinning tool, it was obtained that each polymer solution has optimum conditions for producing nanofibers shown in SEM results on Figure 3. Furthermore, high and low applied voltage made the polymer solution did not be electrospun, whereas high and low flow rate caused beads and abroad range of nanofiber diameter.
3.2. Crystallinity

ATR-FTIR, XRD was conducted to measure the crystallinity of nanofibers at the optimum state. Figure 4 shows the results of measurements using ATR-FTIR. The analysis showed that both of pure cPVDF and nanofiber with added graphene, there were three crystalline phases, such as α, β, and γ. In the spectra, α-crystal phase appeared around 612 cm⁻¹ and 762 cm⁻¹ with low intensity, β-crystal phase around 837 cm⁻¹ with high intensity, 1276 cm⁻¹ with low intensity, and the crystallization phase of γ-crystal phase around 1429 cm⁻¹ with low intensity, and other crystal phase peaks with very low intensity. Thus, it was in line with the literature of FTIR measurements for these three phases[17,18,19]. The band at around 612 cm⁻¹ was assigned to a mixed mode of CF² bending vibration. The band at around 762 cm⁻¹ was related to in-plane bending or rocking vibration. The band at around 837 cm⁻¹ was related to a mixed of CH⁡2 rocking and CF² asymmetric stretching. The band at around 1276 cm⁻¹ was assigned to C-F stretching vibration[20]. From the result of FTIR spectra, it was known that nanofibers are dominated by β-crystal phase. Crystallinity data from FTIR measurements were confirmed by XRD data. The total crystallinity of nanofibers 37.1%; 37.5%; 45.0%; 55.2% for pure cPVDF; graphene 0.01%; 0.05%; and 0.1% respectively. This measurement indicated that the addition of graphene increase nanofiber crystallinity, in which as much as graphene added to the polymer, the resulted nanofibers more crystalline. The XRD diffractogram as shown in Figure 5. The XRD diffractogram reflected that a value of 2θ around 20.4° was assigned to orthorhombicβ-crystal phase[18], while 18.4°, 36.5° and 41.2° were assigned to monoclinicα-crystal phase, but the α-crystal phase intensity was not as strong as β-crystal phase. Thus, the results of the xrd data show that β-crystal phase was the dominant crystal phase in nanofibers and the corresponding FTIR spectra is in good agreement with XRD diffractogram to analyzed the crystalline phase. The α-crystal phase is phase kinetically favorable, this phase frequently observed in membranes, while β crystal phase thermodynamically more stable and seldom observed in membranes[21,22].
The 2nd International Conference on Chemistry and Material Science (IC2MS)  
IOP Conf. Series: Materials Science and Engineering 833 (2020) 012079  
doi:10.1088/1757-899X/833/1/012079

3.3. Thermal characteristic

The thermal characteristics of the nanofibers were characterized using TG-DTG and DSC. TGA spectra exhibited that decomposition occurred at for all nanofibers, it was started with the loss of moisture or solvent material between the room temperature until below 200°C, followed by decomposition of the polymer. Every composite produced the same trend of decomposition. As Figure 6 showed, pure cPVDF nanofiber consists of volatilization and loss of moisture or solvent bellows 200°C, followed by the decomposition of nanofiber cPVDF between 200-699.7 °C with a mass loss more than 92%. In which at small addition of graphene, the thermal stability decrease, while at more graphene added, the thermal stability increase. These phenomena under study. The DTG spectra was attached to confirm TGA spectra (Figure 7). The spectra described that nanofiber has the same tendency on decomposition rate. Furthermore, analysis results using DSC show that the addition of small graphene increases the melting point, whereas the addition of more graphene decreases the melting point. DSC measurement results as in Figure 8. From the results of this analysis, it was known that the average melting point of nanofiber was at a temperature of 144 °C with an endothermic process.
3.4. Hydrophobicity

Nanofiber water contact angle analysis was carried out to determine the hydrophobicity of nanofiber before and after graphene was added at certain concentrations. Contact angle calculation is done using Image J software. From the calculation results, it is known that the addition of graphene increases the water contact angle[10]. The higher amount of graphene mixed into the solution, the higher hydrophobicity of the nanofibers produced. The water contact angle values is 134.2; 134.7; 138.1; and 139.0 for pure cPVDF, graphene 0.01%, graphene 0.05%, and graphene 0.1% respectively.

4. Conclusions

In this study, nanofiber has been fabricated using electrospinning method. The effect of variations in graphene concentration with fixed electrospinning parameters has investigated. The variations in the electrospinning parameters including variations in voltage, flow rates, and the distance between the drum collector and the nozzle had been investigated. It was known that variations in graphene concentration and the electrospinning parameters affect the morphology of the nanofiber. In the optimum conditions, the nanofibers are homogenous, unbranched, and free of beads. The addition of graphene decreasing the average diameter of the nanofiber, and as the amount of graphene increases, the higher hydrophobicity of the nanofiber produced. Based on the results of the ATR-FTIR and XRD analysis, all variations in graphene concentration are dominated by the β-crystal phase. Thermal analysis found that the reaction was endothermic with 144 °C average of melting point.

Acknowledgements

This research acknowledges Ministry of Research, Technology, and Higher Education of the Republic of Indonesia and Indonesian Institute of Sciences.

References

[1] Della Sala DA 2018 Elsevier Inc.
[2] Shi L 2014 University of Delaware
[3] Cui ZF, Jiang Y, and Field RW 2010 Elsevier Ltd
[4] Lovinger AJ 1982 Macromolecules 15 1 40-44
[5] Abolhasani MM, Shirvanimoghaddam K, and Naebe M. 2017 Compos. Sci. Technol. 138 49-56
[6] Tan X, Rodrigue D. 2019 Polymers (Basel) 11 7 1160
[7] Liu F, Hashim NA, Liu Y, Abed MRM, and Li K 2011 J. Memb. Sci. 375 1-2 1-27
[8] Roussel S, McElroy KL, and Judovits LH 1992 Polym. Eng. Sci. 32 17 1300-1308
[9] Kang GD and Cao YM 2014 J Memb Sci. 463 145-165
[10] Yuan X, Li W, Liu H, Han N, and Zhang X 2016 Compos. Commun. 2 5-8
[11] Soldano C, Mahmood A, and Dujardin E 2010 Carbon N Y. 48 8 2127-2150
[12] Zhen Z, and Zhu H 2018 Elsevier Inc
[13] Kim J-KZQ 2013 Graphene for Transparent Conductors. 53
[14] Ren S, Rong P, and Yu Q 2018 Ceram Int. 44 11 11940-11955
[15] Wang L, and Ryan AJ 2011 Electrospinning Tissue Regen. 3 33
[16] Bhardwaj N, and Kundu SC2010 Biotechnol. Adv. 28 3 325-347
[17] Shao H, Fang J, Wang H, and Lin T 2015 RSC Adv. 5 19 14345-14350
[18] Cai X, Lei T, Sun D, and Lin L 2017 RSC Adv. 7 25 15382-15389
[19] Issa A, Al-Maadeed M, Luyt A, Ponnamma D, and Hassan M 2017 Carbon. 3430
[20] Lanceros-Méndez S, Mano JF, Costa AM, and Schmidt VH 2001 J. Macromol. Sci - Phys. 40 B 3-4 517-527
[21] Cui Z, Hassankiadeh NT, Zhuang Y, Drioli E, and Lee YM 2015 Prog. Polym. Sci. 5194-126
[22] Correia HMG and Ramos MMD 2005 Comput. Mater. Sci. 33 1-3 224-229