The morphology and scaling law model of polyvinylidene fluoride/carbon fiber using electrospinning technique

The morphology and scaling law model of polyvinylidene fluoride/carbon fiber using electrospinning technique

J Jauhari[1], M R Almafie[2], M Annisa[2], A Mataram[3], L Marlina[2], M K N A Idjan[4], and I Sriyanti[1,2*]

[1]Laboratory of Instrumentation and Nanotechnology Applications, Faculty of Computer Science, Sriwijaya University, Palembang, Indonesia
[2]Department of Physics Education, Sriwijaya University, Palembang, Indonesia
[3]Department of Mechanical Engineering, Sriwijaya University, Palembang, Indonesia
[4] Senior High School of 1 Palembang, Indonesia

*Corresponding author: ida_sriyanti@unsri.ac.id

Abstract. Electrospinning is a simple process used for polymer fibers that have diameters ranging from micro to nanometers. The purpose of this study was to investigate the morphology and scaling law model of Polyvinylidene Fluoride/Carbon (PVDF/Carbon) fiber math. Fiber is made by variations in concentration 15% w/w (FPC1) , 18% w/w (FPC2), 21% w/w (FPC3) and 24% w/w (FPC4) by adding of 2% (w / w) carbon in each solution. The electrospinning process parameters used are 10 kV voltage, needle tip distance and collector 12 cm, and flowrate 0.1 ml / hour. The results showed that the morphology of FPC1-FPC2 fibers was in the form of bead and the morphology of FPC3-FPC4 are structure free bead. The avarege diameters of FPC1, FPC2, FPC3 and FPC4 are 910 nm, 1123 nm, 1349 nm and 1506 nm, respectively. The scaling law models result R Square (R^2) of the experiment was 0.9992, indicating a very linear model relationship between theory and experiment. Polyvinylidene Fluoride/Carbon (PVDF/Carbon) fiber composite will be used as water filtration.
Keywords: Fiber, Morphology, Scaling Law.

1. Introdution

Electrospinning is a simple process used for polymer fibers that have diameters ranging from micro to nanometers [1–3]. The process of making fibers is carried out by spraying a polymer solution using a high voltage electrostatic field and is supported by a solution flow pump mechanism. Fabrication via electrospinning can produce continuous fibers for large-scale, practical-efficient use and easy-to-control dimensions [1–3]. The nanofibers are controlled by using electrospinning to produce a fine dense fiber with a very small diameter, large surface area, and very small pore size. These properties cause nanofibers to be used for various applications, such as filtration [4,5], water filtration [6], wound dressing[6,9], drug delivery [2,6,9] dan tissue enggenering [1,6].

Many of the polymers used to produce fibers have been successfully used by various studies using electrospinning methods for example, Poly (acrylonitrile) [9], Poly (ether sulfone) [10], Poly (vinyl alcohol) [1,6] and Poly (vinylidene Flouride) [10,11]. Polyvinylidene Fluoride (PVDF) has hydrophobic properties, and this polymer has a larger molecule than other conventional polymer membranes for example, PVP, PVA or PPL [11–13], so that this polymer is difficult to electrospinning. Therefore, to

stabilize the properties of PVDF by mixing carbon materials. The new nature of mixing the two materials can be utilized and used as an engineering material for air and water filters because they have hydrophilic functional groups such as carboxyl, epoxy, and hydroxyl [15]. Thus, the synthesis of the two materials is suitable combined.

Previous research results have reported pure PVDF electrospun with carbon [15–17], obtained the marphology of the fiber in the form of beadless fibers with a diameter of 80-160 [16-17], and pure PVPDF research has also produced beadless fibers in diameter 150-400 [17]. However, morphological studies and prediction of fiber diameter size models using mathematical models are still few. According to Jauhari (2020), a prediction is important in order to overcome the risk of failure of the formation of the fiber polymer mat so that a stable diameter is produced [13–15]. The complex system is understood through modeling the law of scale (SL) by combining process parameters (flow rate, concentration, conductivity, electricity, inertia, surface tension, and viscosity) [14,15,21]. In this study, we will discuss the morphology of PVDF / carbon fibers and the prediction of fiber size using a scaling law model.

2. Experimental Method

2.1 Materials

Polyvinylidene fluoride (PVDF, MW 58,000) was purchased from Sigma Aldrich, Singapore. NN-Dimethylformamide (DMF, assay 99.0% min) was purchased from Sigma Aldrich, Singapore. Carbon is obtained from Brataco Chemicals, Indonesia.

2.2 Preparation Reduction Graphene (rGO).

Three grams of carbon and 18 grams of KmnO4 to which H2SO4: H3PO4 solution was added (360: 40 mL v / v) was stirred at 50 ^{o}C for 12 hours. Then the solution is added to 30 mL H_2O_2 30% then deposited for 1 day. Furthermore, the solution is centrifuged at a rotation speed of 3,000 - 4,000 rpm for 15-20 minutes and decanted to separate the filtrate and the residue. The residue was washed in 200 mL of distilled water, then washed 2 times with 200 mL HCl 30%, 200 mL aceton, and 200 mL ethanol. The residue was dried, so that solid Graphene Oxide (GO) was obtained. GO was dissolved in 100 mL of distilled water at 1% (w / v) and heated to boiling. Next, stirrer the solution by adding 5% (w / v) ascorbic acid at 60 ^{o}C for 2 hours. After that, it is centrifuged at a rotation speed of 3,000-4,000 rpm for 15-20 minutes and the residue is dried at 100 ^{o}C until the final result is Graphene.

2.3 Synthesis of Fiber

Polyvinylidene Fluoride/carbon (PVDF/carbon) fibers were prepared by dissolving PVDF with various concentrations, namely 15% (w/w), 18% (w/w), 21% (w/w) and 24% (w/w) and the addition of carbon by 2% (w/w). Then dissolved using DMF solvent on hotplate-magnetic stirring (Therumo Sci., Japan) with a temperature of 80^{o}C, for 24 hours and a constant speed of 300 rpm and labeled FPC 1, FPC 2, FPC 3, and FPC 4 in each solution. The solution was transferred into a 10 ml syringe equipped (Terumo, Japan) and spun using electrospinning (Nanolab ES / DS 106, Malaysia). The process parameters used were a flow rate of 3.33 µl per minute, a high voltage of 13 kV, the distance between the needle tip of the collector drum of 10 cm, and the fiber rotating of 250 rpm. Also, the humidity is kept constant in the room at 45% and the temperature is 25^{o}C. At the time of collection of fibers can use the camera to monitor Taylor Cone that formed on the tip of the syringe.

The morphology of FPC 1, FPC 2, and FPC 3 fibers was observed using a fluorescence microscope (MiF) (Optika B-380 Material Science MET, Italy). The diameter size analysis used ImageJ 1.52a software (National Institutes of Health, USA), and the analysis results were made of normal distribution using OriginPro 2018 software (OriginLab Corporation, USA).

2.4 Scaling Law Model

Scaling Law (SL) is a law that expresses physical phenomena that occur when the size of a device or material is reduced. SL has been widely applied in solid matter physics to describe the size of polymers

and particles that make up solid materials. The polymer diameter that has been synthesized using electrospinning, according to SL, will be in the form of charge voltage, solution density, molecular weight, flow rate function, electrical conductivity, polymer volume fraction, and dielectric constant. The Scaling law (SL) model can be explained in the theoretical prediction of the diameter of particles and fibers using the following equation [15,16] :

$$D_{drop} = G(\kappa)\left(\kappa\varepsilon_0\frac{Q}{K}\right)^{\frac{1}{3}} \quad (1)$$

$$G(\kappa) = -10{,}9\kappa^{-\frac{6}{5}} + 4{,}08\kappa^{-\frac{1}{3}} \quad (2)$$

Description of the equation:

D_{drop}	=	droplet diameter	K	=	electrical conductivity (S/m)
ε_0	=	permeability (8.85 x 10^{-12} C^2 / Nm^2)	Q	=	flow speed (µL / min)
κ	=	dielectric constant	$G(\kappa)$	=	dimensional function

Equation (1) the prediction of droplet size, equation (2) the prediction of polymer particle size [16–19]. The dielectric constant values were determined but predicted for the viscosity values, polymer particle size, and droplet size. Where the evaluation results are used to explain that with polymer control and the appropriate process parameters will produce polymer particles with stable sizes and controlled properties that can be produced.

3. Results and Discussion

3.1 Morphology and Distribution of PVDF/rGO Fiber

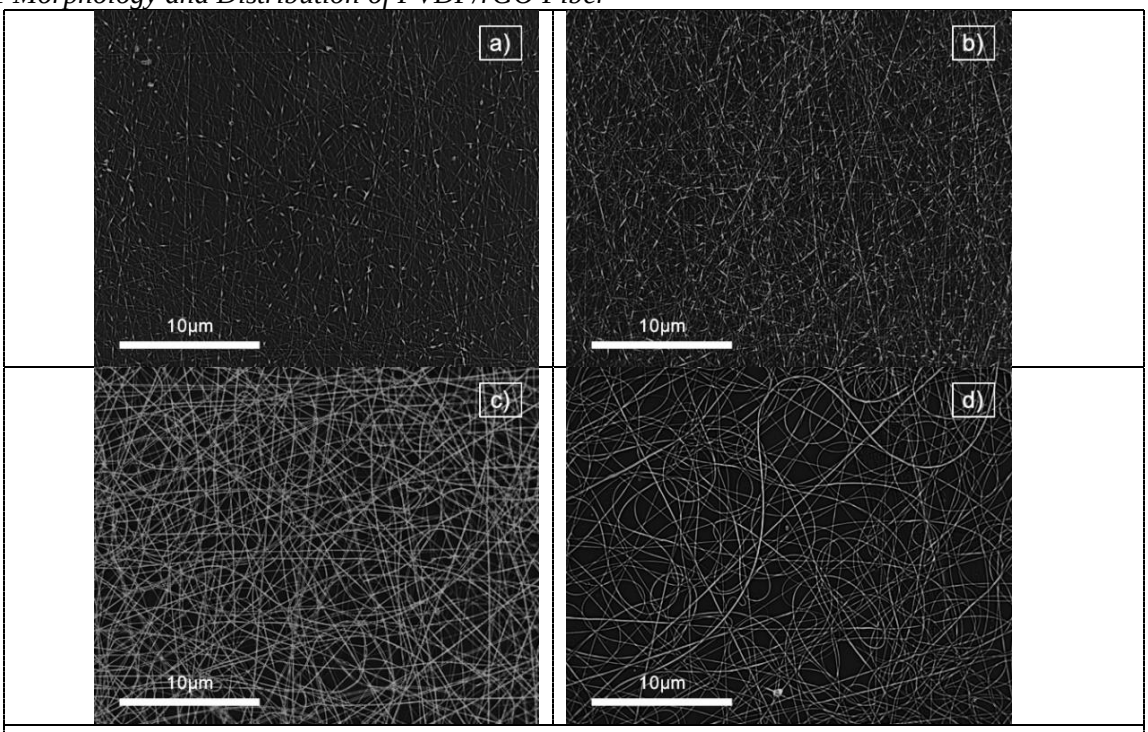

Figure 1. Morphology of PVDF/carbon (a) FPC 1, (b) FPC 2, (c) FPC 3 dan (d) FPC4 fiber.

The MiF images of FPC1, FPC2, FPC3, and FPC 4 fiber math are shown in figure 1. The variations of PVDF/carbon 15% (w/w), 18% (w/w), 21% (w/w) and 24 % (w/w) and the addition of carbon by 2%

(w/w). The process parameters used were the flow rate of 3.33 µl per minute, high voltage 13 kV, The distance between the needle tip of the collector drum of 10 cm, and fiber rotating of 250 rpm. The observed morphology is shaped like a continuous, regular strand. The results of MiF were successful in confirming that the lowest concentrations in this study, namely 15% and 18%, showed bead structures in FPC 1 and FPC 2 fibers. Meanwhile, at high concentrations, namely 21% and 24% showed a bead-free structure in FPC 3 and FPC 4 fibers. The formation of beads was related to viscosity and surface area. Solutions with low polymer concentration have low viscosity and few polymer chain bonds so that the elongation process when electric spinning was not perfect, this causes the formation of fiber beads [3,20]. Besides, increasing the surface tension has the effect of reducing the surface area of the mass unit of the solution [9,21]. When the free solvent molecules were in a high polymer concentration, there was a tendency for the solvent molecules to gather and form fibers with beads [3,9]. The size distribution of the diameter with the distribution of fiber diameter sizes ranging from 550 to 1800 is shown in Figure 2.

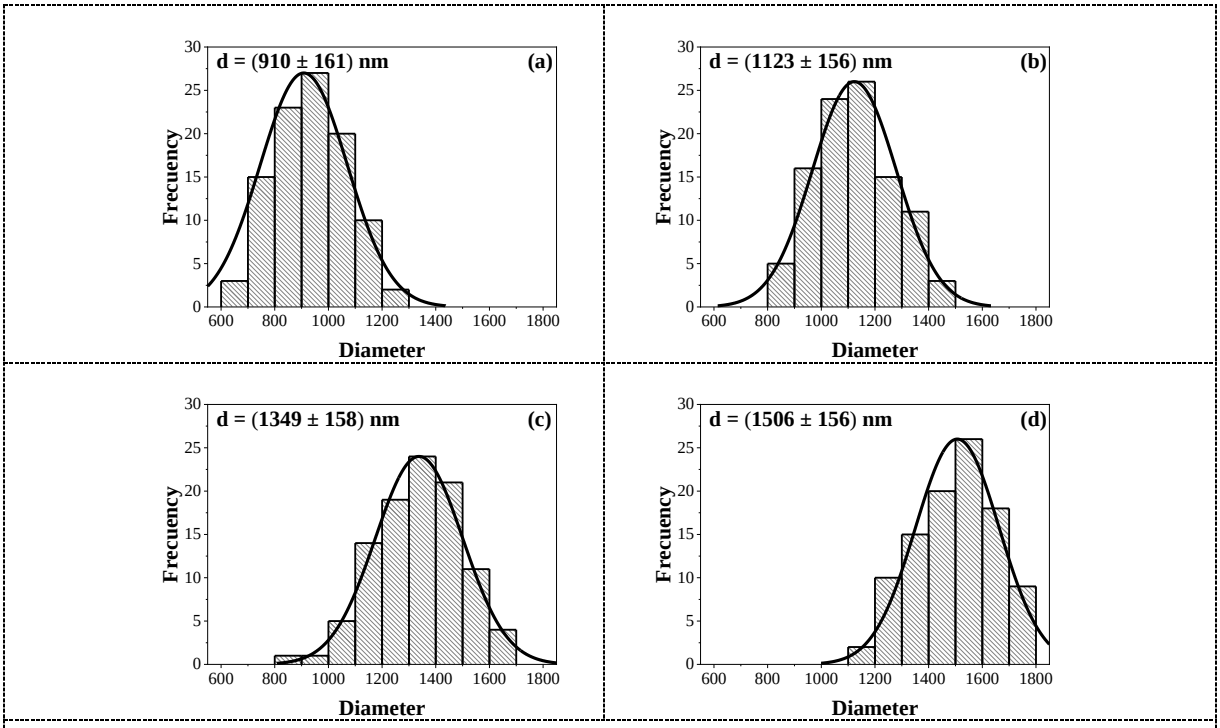

Figure 2. Distribution diameter of PVDF/rGO (a) FPC1, (b) FPC2, (c) FPC3 dan (d) FPC4 fiber.

The observed distribution of the diameter of FPC1, FPC2, FPC3 and FPC4 fibers had a coefficient of variance (cv) with prices of 0.16, 0.17, 0.12, and 0.09. Homogeneity occured when the ratio between the standard deviation and the mean diameter of the fibers was less than 0.3 [22,23]. The results of cv confirm that all fiber distributions were homogeneous. The mean diameters (d) of FPC1, FPC2, FPC3 and FPC 4 fiber math were found to be 910 nm, 1123 nm, 1349 nm and 1506 nm. Meanwhile, the standard deviation was 161 nm, 156 nm, 158 nm and 156 nm. It has been observed that increasing the concentration of the polymer solution results in a larger mean diameter. This is related to the increasing of polymer chains in solution when the concentration was higher [20,24]. The addition of 2% (w/w) carbon also significantly affected the total solution concentration while increasing the average fiber diameter. This was confirmed through previous studies, that pure PVDF had an average diameter ranging from 200-400 nm. In addition, the stretching of the fibers by the Coulomb force took less time because the high concentration solution dries faster.

3.2. Scaling Law Model of PVDF/carbon Fiber

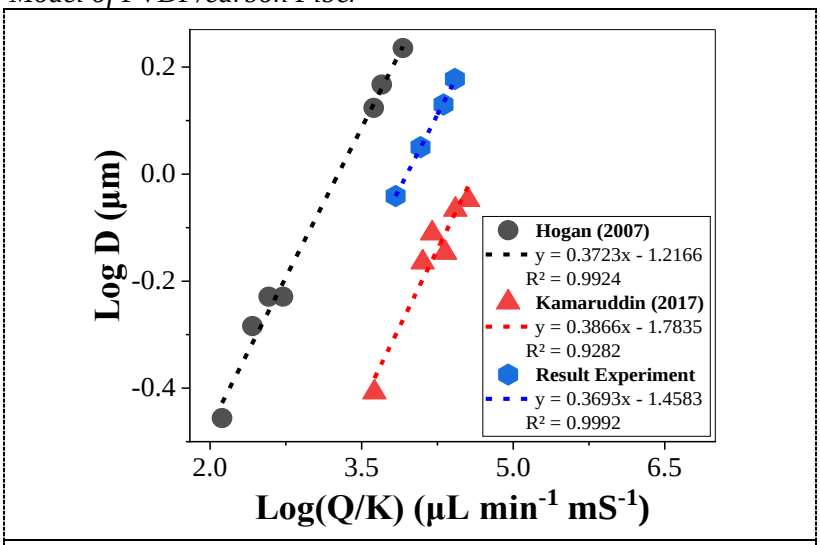

Figure 3. The logarithm of the fiber diameter measures for both empirical data and theoretical calculations as a function of the flow rate of electrical conductivity

The logarithms of fiber diameter measurements for both empirical data and theoretical calculations as a function of flow rate against electrical conductivity are shown in Figure 3. The Circle, the triangle and the hexagon are data obtained from previous studies of pure polymer [20], PVP/ETH composites [19] and experimental results. The experimental linear fitting data for the Q/K logarithm lies in the range 104 to 105. Prediction of the diameter size of the PVDF/carbon fibers from FPC1, FPC2, FPC3 and FPC 4 determines the electrical conductivity value of 0.00048 S/m, 0.00027 S/m, 0.00016 S/m and 0.00012 S/m. The logarithmic value of the flow rate per electrical conductivity (Q/K) results in 3.8971, 4.0829, 4.3109, and 4.4229 also the logarithmic values of the fiber diameter are -0.041, 0.0504, 0.1300 and 0.1778. The dotted line is shown as the approximate size of the fiber diameter as predicted from equation 1 and equation 2 [20,21]. The result of R Square (R^2) experiment approach is 0.9992, it is understood that the fiber diameter is in very good condition and more or less in accordance with the theoretical model. Thus, controlling the fiber diameter can be done by adjusting the parameters of the electrospinning process, namely electrical conductivity and flow rate.

4. Conclusion

The Morphology and Scaling Law Model of Polyvinylidene Fluoride/carbon (PVDF/carbon) fiber have been successfully produced and predicted using electrospinning techniques. Nanofiber was produced optimally with variations in the concentration of PVDF of 15% (w/w), 18% (w/w), 21% (w/w) and 24% (w/w) with the addition of carbon with a concentration of 2% (w/w). The process parameters of electrospinning, namely the distance between the tip of the collector drum needle were 10 cm, the flow rate was 3.33 µl per minute, the high voltage was 13 kV. MiF results have been shown a concentration of 15% and 18% were bead fiber structure and 21% and 24% were free to structure beads. The mean diameters of the FPC1, FPC2, FPC3 and FPC 4 fiber math were found to be 910 nm, 1123 nm, 1349 nm and 1506 nm, respectively. Besides, the results have been shown that the average fiber diameter was in very good condition and appropriate with the theoretical model developed in previous studies.

Reference

[1] Almafie M R, Nawawi Z, Jauhari J and Sriyanti I 2020 Electrospun of Poly (vinyl alcohol)/Potassium hydroxide (PVA/KOH) nanofiber composites using the electrospinning method *IOP Conference Series: Materials Science and Engineering* **8** 50

[2] Sriyanti I, Edikresnha D, Rahma A, Munir M M, Rachmawati H and Khairurrijal K 2018 Mangosteen pericarp extract embedded in electrospun PVP nanofiber mats: Physicochemical properties and release mechanism of α-mangostin *Int. J. Nanomedicine* **13** 4927–41
[3] Ramakrishna S, Fujihara K, Teo W-E, Lim T-C and Ma Z 2005 *An Introduction to Electrospinning and Nanofibers* (World Scientific Publishing)
[4] Xue J, Xie J, Liu W and Xia Y 2017 Electrospun Nanofibers: New Concepts, Materials, and Applications *Acc. Chem. Res.* **50** 1976–87
[5] Jauhari J, Suharli A J, Saputra R, Nawawi Z and Sriyanti I 2020 Polyvinylpyrollidone/Cellulose Acetate (PVA/CA) Fiber Size Prediction Using Scaling Law Model *J. Phys. Conf. Ser.* **1467**
[6] Naragund V 2018 Electrospinning of Polyacrylonitrile Nanofiber Membrane for Bacteria Removal *J. Mater. Sci. Appl.* **4** 68–74
[7] Jauhari J, Wiranata S, Rahma A, Nawawi Z and Sriyanti I 2019 Polyvinylpyrrolidone/cellulose acetate nanofibers synthesized using electrospinning method and their characteristics *Mater. Res. Express* **6** 64002
[8] Aruan N M, Sriyanti I, Edikresnha D, Suciati T, Munir M M and Khairurrijal 2017 Polyvinyl Alcohol/Soursop Leaves Extract Composite Nanofibers Synthesized Using Electrospinning Technique and their Potential as Antibacterial Wound Dressing *Procedia Eng.* **170** 31–5
[9] Wang W, Zheng Y, Jin X, Sun Y, Lu B, Wang H, Fang J, Shao H and Lin T 2019 Unexpectedly high piezoelectricity of electrospun polyacrylonitrile nanofiber membranes *Nano Energy* **56** 588–94
[10] Wang H, Wang X, Fan T, Zhou R, Li J, Long Y, Zhuang X and Cheng B 2020 Fabrication of electrospun sulfonated poly(ether sulfone) nanofibers with amino modified SiO2 nanosphere for optimization of nanochannels in proton exchange membrane *Solid State Ionics* **349** 115300
[11] Samsure N A, Hashim N A, Nik Sulaiman N M and Chee C Y 2016 Alkaline etching treatment of PVDF membrane for water filtration *RSC Adv.* **6** 22153–60
[12] Nasreen S A A N, Sundarrajan S, Syed Nizar S A, Balamurugan R and Ramakrishna S 2014 In situ polymerization of PVDF-HEMA polymers: Electrospun membranes with improved flux and antifouling properties for water filtration *Polym. J.* **46** 167–74
[13] Thongphud A and Paosawatyanyong B 2008 Improvement of Hydrophobic Properties of the Electrospun PVA fabrics by SF 6 Plasma Treatment **57** 625–8
[14] Prince J A, Rana D, Singh G, Matsuura T, Kai T J and Shanmugasundaram T S 2013 Effect of Hydrophobic Surface Modifying Macromolecules on Differently Produced PVDF Membranes for Direct Contact Membrane Distillation Environmental & Water Technology Centre of Innovation , Ngee Ann Polytechnic , 535 Industrial Membrane Research Institut *Chem. Eng. J.*
[15] Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y and Wu Y 2007 Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide **45** 1558–65
[16] Zhao Y, Xu Z, Shan M, Min C, Zhou B, Li Y, Li B, Liu L and Qian X 2013 Effect of graphite oxide and multi-walled carbon nanotubes on the microstructure and performance of PVDF membranes *Sep. Purif. Technol.* **103** 78–83
[17] Li Y, Cheng C, Bai S, Jing L, Zhao Z and Liu L 2019 *The performance of Pd-rGO electro-deposited PVDF/carbon fiber cloth composite membrane in MBR/MFC coupled system* vol 365 (Elsevier B.V.)
[18] Zhou Z and Wu X F 2015 Electrospinning superhydrophobic-superoleophilic fibrous PVDF membranes for high-efficiency water-oil separation *Mater. Lett.* **160** 423–7
[19] Kamaruddin, Sriyanti I, Edikresnha D, Munir M M and Khairurrijal K 2018 Electrosprayed Polyvinylpyrrolidone (PVP) Submicron Particles Loaded by Green Tea Extracts *IOP Conf. Ser. Mater. Sci. Eng.* **367** 12036
[20] Hogan C J, Yun K M, Chen D-R, Lenggoro I W, Biswas P and Okuyama K 2007 Controlled size polymer particle production via electrohydrodynamic atomization *Colloids Surfaces A Physicochem. Eng. Asp.* **311** 67–76

[21] Sriyanti I, Marlina L and Jauhari J 2020 Optimization of The Electrospinning Process for Preparation of Nanofibers From Poly (Vinyl Alcohol) (PVA) and Chromolaena odorata L . Extrac (COE) **16** 47–56
[22] Widiyandari H, Hogan Jr. C J, Yun K M, Iskandar F, Biswas P and Okuyama K 2007 Production of Narrow-Size-Distribution Polymer-Pigment-Nanoparticle Composites via Electrohydrodynamic Atomization *Macromol. Mater. Eng.* **292** 495–502
[23] Sriyanti I, Agustini M, Jauhari J, Sukemi S and Nawawi Z 2020 Electrospun Nylon-6 Nanofibers and Their Characteristics *J. Ilm. Pendidik. Fis. Al-Biruni* **9** 9–19
[24] Sriyanti I and Jauhari J 2019 Electrospun of poly(vinyl alcohol) nanofiber as carrier of Garcinia mangostana L. pericarp extract *J. Phys. Conf. Ser.* **1170**
[25] Matulevicius J, Kliucininkas L, Prasauskas T, Buivydiene D and Martuzevicius D 2016 The comparative study of aerosol filtration by electrospun polyamide, polyvinyl acetate, polyacrylonitrile and cellulose acetate nanofiber media *J. Aerosol Sci.* **92** 27–37
[26] Sriyanti I, Edikresnha D, Rahma A, Munir M M, Rachmawati H and Khairurrijal K 2017 Correlation between Structures and Antioxidant Activities of Polyvinylpyrrolidone/ Garcinia mangostana L. Extract Composite Nanofiber Mats Prepared Using Electrospinnin *J. Nanomater.* **2017**
[27] Liu Y-J, Tan J, Yu S-Y, Yousefzadeh M, Lyu T, Jiao Z-W, Li H and Ramakrishna S 2020 High-efficiency preparation of polypropylene nanofiber by melt differential centrifugal electrospinning *J. Appl. Polym. Sci.* **137** 48299

Acknowledgments
This research was supported by Sriwijaya University, The republic of Indonesia under the University's Excellence Research (PUPT) Grant in the fiscal year 2020. This research was supported by BPDPKS, the Republic of Indonesia under the Research and Development of Palm Oil in the fiscal year 2020.