Formation of Carbon Fibres From Polymer Poly(vinyl alcohol)/Acetylene Black using Electrospinning Method

R A Yuniar¹, W Widiyastuti¹*, H Setyawan¹, H Purwaningsih¹, S Machmudah¹ and D Anggoro²

¹Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia
²Department of Physics, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

*E-mail: widi@chem-eng.its.ac.id

Abstract. Carbon fibres are important materials due to their excellent properties. Carbon fibres were formed by blending Poly(vinyl alcohol) (PVA) and a high conductivity material of Acetylene black (AB). Electrospinning technique was used to fabricate PVA and AB solutions in demineralized water. Electrospinning is an efficient technique for the formation of polymer nanofibers. The effects of solution concentration and AB contents on morphological appearance and diameter of those as-spun fibres were investigated by scanning electron microscopy (SEM). Iodine treatment on the fabricated PVA/AB composite was successfully achieved in order to build up the carbonization process and retained their original fibrous structure. The mass of iodinated nanofibers at 80 °C for 24 h increased about 130 %. The mechanism of iodine uptake by electrospun PVA/AB fibres have been obtained by thermal behaviour and its morphological characteristics. It was found that iodine treatment played an important role in changing the morphological structure during the carbonization process. With the iodine treatment of PVA/AB precursor fibres successfully converted into thin carbon fibres and SEM analysis confirmed that the diameter of fibres was about 290 nm. The resulted pure fibres and iodine treatments show guarantee for production carbon fibres.

1. Introduction
Nano-scale technology is called nanotechnology has changed the paradigm and the way of view of technology because the material is designed and arranged in the order of atomic per atom or molecules, so that it is found a material that has special superior properties to the existing material. Rapid developments in the application of nanotechnology in the industrial world indicate that the world is currently leading to the revolution of nanotechnology, one of which is nanofiber. Nanofiber has a large surface area to the ratio of the volume of the solution and has a large absorption with small pore size [1]. Nanofibers have the advantage of physical characteristics that can be utilized in various aspects such as healthcare, biotechnology, energy storage application and textile [2]. There are several techniques to produce nanofibers, such as drawing [3], template synthesis [4], phase separation [5] and electrospinning technique was the most frequently used [6].
Among several techniques, electrospinning is a simple and efficient technology for the formation of electrostatic polymer nanowires utilizing electric power to produce fibres of nano-sized diameters. This
technique has received much attention due to the flexibility of the materials used and its ability to produce fibers in the submicron range. Electrospinning is the only technique available for the production of fibers with very small diameters [7]; hence electrospinning can be a main alternative technique. Carbon is a material widely used as an electrochemical support because it has high conductivity, thermal and chemical stability and surface characteristics that can be changed [8]. Carbon nanofibers produced from electrospinning technique have attracted due to their superior characterization such as high-modulus, high-resistance [9], flexibility and their special morphology nanomaterials [10]. Today the development of carbon materials is directed towards nano meter-sized carbon by modifying the pore structure and surface [11]. Carbon fibers from polymer/organic or polymer/inorganic composite have been developed by electrospinning cause of their potential properties such as mechanical and electrical conductivity. The composites of PVA/lignin [12] and PVA/Carbon black [13] have been investigated as electrode material. Their investigations claimed having good electro-properties. Poly(vinyl alcohol) (PVA) has a fairly high carbon content and has a hydroxyl group in the polymer chain so that PVA is great for precursor in carbon material. PVA is a resin made from the incorporation of vinyl acetate molecules (polymerization), by partial hydrolysis of the catalyzing ester. The physical properties of the polymerization product depend on the degree of polymerization and degree of hydrolysis. PVA fibers have good tensile and bending strength [14]. Carbon fibers from electrospun PVA nanofibers when heated at a higher temperature than their melting point will result in low carbon. Therefore, PVA percussion requires high thermal stability between 100-290 °C [15]. On the other hand, iodine can be used for PVA stabilizer in order that at high temperature carbonization, PVA kept on it structure and hard to melt. This is due to that the addition of iodine treatment can modify the bonds in PVA hydrocarbons into double bonds such as polyene [16]. Some studies have compared halogen compounds such as bromine to iodine. Iodine treatment has resulted more superior than bromine due to bromine treatments is only non-selective while using iodine treatment selectively to aromatics. Thus, iodine is good stabilizer suited to treat a material for carbonization. According to previous studies, iodine treatments have no yet been examined toward PVA/Acetylene black composite. Thus, in this paper, electrospinning of PVA blended with acetylene black (AB) dissolved in distilled water to produce precursor fibers was investigated. The effects of iodine treatment on PVA/AB composite electrospun fibers are then investigated in order to produce carbon nanofibers.

2. Materials and Methods

2.1. Spin Dope Solution
PVA powder was used technical grade, acetylene black powder and iodine crystal was purchased from SAP chemicals. Spin dope PVA solution were prepared by the addition PVA powder (concentration ranging between 5 and 15 % w/v with 5 % w/v increment) which dissolved in distilled water at 85 °C under constant stirring for an hour. In order to blend solution of PVA and AB were prepared by adding a weighed amount of AB in PVA aqueous solutions followed by sonication at 50 °C for 2 hours. After sonication, the mixture was mechanically stirred at 85 °C for 30 minutes then cooling down to room temperature. AB was varied amount 0, 5, 10 and 15 wt. % based on the weight of PVA powder to obtain the effect of AB content in PVA solution.

2.2. Electrospinning of nanofibers
The polymer solution was carried out in an OneMed plastic 50 ml syringe with needle an inner diameter 0.6 mm. The steady flow rate was maintained by the ColeParmer Instrument Co. syringe pump at 1 ml per hour. As shown in Figure 1, a high voltage power supply was connected the needle and the collector. The applied voltage at 10 kV was applied to the polymer solution using 10 kV was applied onto a collection device. Collection device was wrapped by a square 15 cm x 30 cm of aluminium foil around rotating cylinder. The distance from needle to collector was 10 cm.
2.3. Iodine treatment
An electrospun nanofibers PVA/AB were peeled off from aluminium foil on cylinder collector placed into a sealed glass jar. The glass jar was contained iodine crystal placed in an oven at 80 °C for 24 hours to vaporize the iodine. After iodine treatment, sealed glass jar from the oven was removed and then was cooled at room temperature. For a few moments the remaining iodine vapour in the jar recrystallized after which electrospun nanofibers can be removed from the jar. The samples of PVA/AB iodine treatment and non-treated was carbonized in a Lindberg tubular furnace with heating operation: (i) 30 – 200 °C; (ii) 200 – 400 °C; (iii) 400 – 600 °C, each step holding for 15 minutes. (iv) 600 – 800 °C, the temperature was held for an hour. A constant N₂ flow was maintained during carbonization. For their morphology, the samples were observed using FEI-Inspect S50 Scanning Electron Microscope (SEM). ImageJ software was used for analysing images and calculating fibre diameters from at least 40 randomly selected.

3. Results and Discussion

3.1. Nanofibers of PVA
Many factors or parameters affected the morphology of the nanofiber, for example electrospinning process, the distance between the needle to collector, viscosity, flowrate, applied voltage [6]. Ambient parameters such as temperature [17] and relative humidity play role to the morphology nanofibers [18]. Figure 2 shows the SEM images that described the morphological as spun nanofibers from various concentrations. Electrospinning of the 5 and 10 % w/v PVA resulted in the formation of beaded fibres, because the solution has low viscosity.

![Figure 1. Schematic of the electrospinning process](image)

![Figure 2. SEM images of electrospun PVA fibres with concentrations: (a) 5, (b) 10, and (c) 15 % w/v](image)
Figure 2 shows the results of SEM analysis of PVA concentration variables, where Figure 2a shows the formation of relatively non-homogeneous fibres both in shape and size at a concentration of 5 % w/v. It was observed that there were large and oval beaded in the middle of the fibres and at the vertex between fibres. The concentration of PVA 10 % w/v produces relatively homogeneous fibres in shape and size as shown in Figure 2b. However, it can still be observed that there are beaded at several points along the fibre and fibre point vertices. If the concentration is added up to 15 % w/v, it produces fibres that are finer morphologically and more homogeneous. There is no observation of beaded along the fibres and knot points. The concentration and the viscosity of the solution is too low hence the charged liquid could not form fibres instead of droplets [13]. At the concentration of 10 % w/v PVA, the number of beaded fibres decreased as the viscosity increased. The lower viscosity of solution, the lower viscoelastic force because the coulomb repulsion force worked. Increasing the concentration of solution led to the uniform fibres without beads. This is due to the solution has low viscosity that increased the viscoelastic force and it may cause the coulomb repulsion force broke the charged jet much uniform. Increasing PVA concentration up to 15 % w/v resulted smooth nanofibers and uniform in size about 220 nm, as shown in Figure 2c. The fibre of 15 % w/v PVA had oriented-nanofibers. In this composition, solution had optimum viscosity correlated with applied voltage and distance of needle to collector.

3.2. Nanofibers of PVA/AB composite
The purpose of Acetylene Black added to the PVA solution is to increase carbon sources because PVA has low carbon yield when exposed to high temperatures and is expected to increase the conductivity of carbon fibres. Figure 3 shows the results of SEM observations on 15 % w/v PVA samples added with concentration variables AB. The addition of 5 wt. % has been able to change the morphology of PVA fibres to be larger and not smooth on the surface. The shape of the fibre also changes from straight to slightly curly-fibre. Increasing of AB 10 wt. % produces fibre that is relatively heterogeneous in size because there are large and many small sized fibres. While the fibre surface is no longer smooth. While the addition of AB to 15 wt. % produces a fibre that is not homogeneous in size and morphology. An increase in AB addition of up to 15 wt. % causes changes in the morphology and size of PVA/AB composite fibres.

Figure 3. SEM images of electrospun PVA/AB fibres with various AB contents: (a) 0 wt. %, (b) 5 wt. %, (c) 10 wt. %; (d) 15 wt. %
The homogenous of particles in solution is the important factor in electrospinning polymer/inorganic composite. Sonication is an effective way for mixing polymer/inorganic composite [13]. The electrospinning of PVA/AB composite resulted grey coloured fibre mats. On the other hand, only PVA fibre mats had white colour. The grey colour of 15 wt. % AB was darker than others sample.

Figure 3 shows the SEM images of PVA/AB nanofibers with various AB amount of 0, 5, 10, and 15 wt. % to PVA powder weight with 15 % w/v. The average diameter of PVA/AB composite is almost similar for all samples at around 280 nm. Sample with 5 wt. % AB had smoother fibre than that of higher wt. % AB. Non uniform surface morphologies were found for 10 and 15 wt. % AB. The same phenomenon was also observed for polyacrylonitrile (PAN)/silica composite in which increasing the silica content exhibited more non uniform surface fibres [19].

3.3. Effect of iodine treatment on PVA/AB nanofibers

Figure 4a shows that the nanofiber structure was broken when the origin PVA/AB nanofiber was heated at temperature 200 °C under N₂ atmosphere. Increasing the carbonization temperature at 300 °C led to the further broken fibre structure becoming nanosized spherical particles as shown in Figure 4b. Furthermore, as depicted in Figure 4c, increasing the carbonization temperature at 450 °C made the particle size was smaller. PVA is one of the higher carbon content among vinyl alcohol polymers but on the other hand PVA has low carbon yield due to it melts before carbonization temperature [16]. The PVA thermally decomposed into the volatile low molecular weight molecules. The chains of PVA were pyrolyzed during carbonization. Therefore, PVA needs pre-treatment or additive to produce sustainable form of fibre and high carbon yield [20].

Iodine treatment can be considered to take over losing of carbon yield followed by carbonization. The iodine absorption of the PVA/AB mats were investigated through carbonization the samples with treated and untreated iodine. The weight of PVA/AB mats before and after iodine treatment were 0.541 and 1.242 gram, respectively. The 1:4 ratio of iodine crystals to PVA/AB mats was added into sealed glass jar. After 24 h of treating with vapour of iodine crystals, the colour of PVA/AB mats was changed from a grey to dark brown and the weight of PVA/AB mats increased about 50 wt. %.

As shown in Figures 5a and 5b, SEM images of PVA/AB mats prepared with iodine treatment at 80 °C for 24 hours for before and after carbonization, respectively, have almost the same structure fibre with non-homogeneous fibre diameters. Iodine treatment has a significant effect to sustain nanofiber structures after carbonization. A similar effect was investigated for pure of PVA nanofibers [20]. They found that during carbonization with iodine treatment for 24 hours, nanofibers can maintain the original nanofibers without melting. It can be explained that during the carbonization, PVA turned into a stable cyclic aromatic structure with intermolecular cross-linked resulted polyyene structure by dehydration.
PVA. Conversely, if the iodine process was carried out only 3-10 hours, the neat PVA entirely melted to form a solid layer and cracking in the structure of morphology.

![Figure 5. SEM images PVA/AB mats after iodine treatment: (a) before and (b) after carbonization](image)

### 4. Conclusion

Effective methods have been found to fabricate carbon fibres from PVA/AB composite nanofibers using electrospinning techniques. The average diameter of the as-spun pure PVA was around 220 nm. The effect of AB content on PVA/AB composite influenced the diameter and their morphological structure. The average diameter of the PVA/AB nanofibers was around 280 nm. In the process of carbonization at 800 °C with iodine treatment for 24 hours played a very important role to maintain the nanofiber structure without melting. The ratio of nanofibers of PVA/AB mats to iodine crystals used in iodine treatment was 1:4 which resulted in diameter after carbonization at around 300 nm.

### Acknowledgments

Research Grant sponsored by Directorate of Research and Community Services, Directorate General of Strengthening Research and Development, Ministry of Research Technology and Higher Education, Republic Indonesia (No. 128/SP2H/PTNBH/DRPM/2018) is gratefully acknowledged.

### References

[1] Liu W and Adanur S 2009 *Text. Res. J.* **80** 124–34

[2] Ramakrishna S, Fujihara K, Teo W, Yong T and Ramaseshan R 2006 *Mater. Today* **9** 40–50

[3] Ondarçuhu T and Joachim C 1998 *Europhys. Lett.* **42** 215–20

[4] Feng J J 2002 *Phys. Fluids* **14** 3912–3926

[5] Ma P X and Zhang R 1999 *J. Biomed. Mater. Res.* **46** 60–72

[6] Bhardwaj N and Kundu S C 2010 *Biotecnolog. Adv.* **28** 325–47

[7] Dersch R, Steinhart M, Boudriot U, Greiner A and Wendorff J H 2005 *Polym. Adv. Technol.* **16** 276–82

[8] Huggins T M, Pietron J J, Wang H, Jason Z and Biffinger J C 2015 *Bioresour. Technol.* **195** 147–53

[9] Setton R, Bernier P and Lefrant S 2002 *Carbon Molecules and Materials* (London and New York: Taylor and Francis Inc) p 489

[10] Tanabe Y and Yasuda E 2000 *Carbon N. Y.* **38** 329–34

[11] Ma X, Elbohy H, Sigdel S, Lai C, Qiao Q and Fong H 2016 *RSC Adv.* **6** 11481–7

[12] Lai C, Zhou Z, Zhang L, Wang X, Zhou Q, Zhao Y, Wang Y, Wu X F, Zhu Z and Fong H 2014 *J. Power Sources* **247** 134–41

[13] Chuangchote S, Sirivat A and Supaphol P 2007 *Nanotechnol.* **18** 145705

[14] Du E, Dong S and Sun J 2018 *Chem. Eng. Trans.* **66** 1057–62

[15] Bin Y, Chen Q, Nakamura Y, Tsuda K and Matsuo M 2007 *Carbon N. Y.* **45** 1330–9

[16] Donnet J, Wang T K, Rebouliat S and Peng J 1998 *Carbon fibers* (New York: Marcell Dekker Inc.)
[17] Pelipenko J, Kristl J, Janković B, Baumgartner S and Kocebek P 2013 *Int. J. Pharm.* **456** 125–34
[18] Fuenmayor C A, Mascheroni E, Cosio M S, Piergiovanni L, Benedetti S, Ortenzi M, Schiraldi A and Mannino S 2013 *Chem. Eng. Trans.* **32** 1771–6
[19] Ji L, Saquing C, Khan S A and Zhang X 2008 *Nanotechnol.* **19** 085605
[20] Fatema U K, Uddin A J, Uemura K and Gotoh Y 2011 *Text. Res. J.* **81** 659–72