Electrical Conductivity Improvement of Polyvinyl Alcohol Nanofiber by Solvent Vapour Treatment

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Abstract— The electrical conductivity of polyvinyl alcohol (PVA) electrospun nanofibers is naturally low. For an electrical device application, it requires high enough conductivity. The objective of this study is to improve the electrical conductivity of electrospun PVA nanofibers with and without poly (3,4-ethylenedioxytriophene): polystyrene sulfonate (PEDOT:PSS) by exposure polar solvent of dimethyl sulfoxide (DMSO). For this purpose, the nanofibers were deposited on a substrate with patterned electrodes. The distance between two electrodes is 2 mm. The sheet resistance of the PVA nanofibers was measured by using two-point probe connected to a source measurement unit of Keithley SMU-2400. As a result, the conductivity of PVA electrospun nanofibers increases from 0.03 μS/cm to 1.20 μS/cm by increasing the PVA concentration from 8 to 10 wt%. More significant improvement is also achieved by mixing PVA and PEDOT:PSS to be 110 μS/cm after being exposure DMSO. This improvement has been confirmed using the scanning electron microscopy (SEM) images, where a solvent-induced fusion occurs at the nanofiber junction points after DMSO treatment. The stability of electrical conductivity, however, of electrospun PVA nanofibers is better than that of electrospun PVA/PEDOT:PSS nanofibers after exposure DMSO.

Keywords— nanofiber; polyvinyl alcohol; electrical conductivity; DMSO; solvent vapour treatment

I. INTRODUCTION

Electrospinning is a simple, reproducible, and continuous technique for the preparation of nanofibers from solutions of polymers with controllable morphology [1]–[3]. Nanofiber has been widely used in many fields, such as affinity membranes [1], drug release [4], tissue scaffolds [5], wound dressing [5], protective clothing agent [6], energy [7], electronic device [7] and composite reinforcement [8]. The electrical properties of nanofiber become an interesting object to investigate due to the important properties for electrical device application such photovoltaic device (PVs) [3],[9], organic LEDs (OLEDs) [10], and sensors [11]–[13]. The electrical conductivity of polymers typically is poor ($\sim 10^{-3} \; \mu Scm^{-1}$) [14].

A lot of methods have been applied for improving the electrical conductivity of polymers, such as blend with another conductive polymer [15], [16], dipping on low concentrated solvent [17], co-solvent addition [18], change of solvent [19], [20], and solvent vapour treatment [21], [22].

The polar solvents like dimethylsulfoxide (DMSO) [23], dimethyl formamide (DMF) [23] or ethylene glycol (EG) [24] have also been used for improving the electrical conductivity of the polymer. Polar-solvent vapour treatment was reported as a better method than the conventional solvent additive methods for improving the electrical conductivity of thin-film polymer [22].

Poly (vinyl alcohol) or PVA has been known as one of the common polymers used as a solution for electrospinning technique [25]–[28]. The advantages of PVA includes non-toxic, water-soluble, strong film forming, very high dielectric strength, and dopant dependent electrical and optical properties [29]. Based on these properties, the electrical conductivity of PVA either as a thin film or as nanofiber mat is naturally low.

Solvent vapour treatment was commonly used for improving the electrical conductivity of PEDOT:PSS thin film. Ouyang et al. (2004) improved the electrical conductivity of PEDOT:PSS film significantly from 0.4 to 143 S/cm after exposure DMSO vapour. It is expected due to the

conformational change of the PEDOT chains and the driving force of the interaction between the dipoles of the organic compound and the PEDOT chains [19]. In another work Yeo et. al (2012) reported that the improvement in the conductivity of PEDOT:PSS film was due to significant phase separation between excess PSS and PEDOT chain resulted in a spontaneous dimensional connection between the conducting PEDOT chain and higher work function [22].

In this study, we report our attempts to improve the electrical conductivity of electrospun PVA nanofibers by adding PEDOT:PSS and subsequently by exposure DMSO vapour. The electrical conductivity of the nanofibers was measured using two-point probe method connected to the source measurement unit of Keithley SMU-2400.

II. MATERIALS AND METHOD

A. Materials

The main materials used in this study included PVA with a molecular weight (M_w = 85.000 – 124.000), 99%+ degree of hydrolysis, 99%+ degree of polymerization was purchased from Sigma-Aldrich, while poly (3,4-ethylenedioxytriophene) doped with poly (styrene sulfonate) PH1000 was purchased from Heraeus C Stark. The PH1000 means that the concentration of PEDOT:PSS in solution is 1.3 wt%, while the PEDOT:PSS ratio is 2:5. Dimethyl sulfoxide (DMSO) solvent was purchased from Merck Germany. Meanwhile, ethylene glycol (EG) solvent was purchased from PT Brataco Indonesia All the above materials were used without any further purification and treatment.

B. Electrospinning Nanofiber

Two preparation steps of PVA solution for electrospinning were carried out. First, PVA powder was dissolved in distilled water at a temperature of 95 °C for 2 h and stirred at a moderate speed to obtain a homogenous solution. Second, the 10-12 wt% PVA solution was then mixed with PEDOT:PSS aqueous dispersion with a ratio of 40:60 (v/v) and followed by stirring at ambient temperature for 45 min. The detail of these compositions is listed in Table 1.
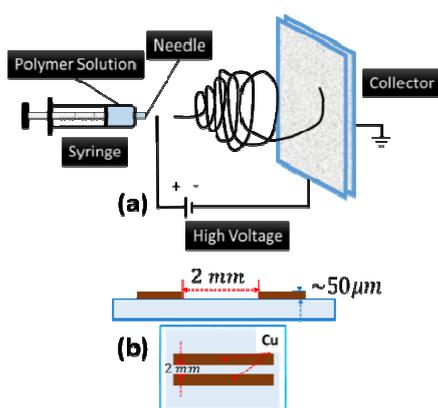

Fig. 1. Schematic diagram of (a) electrospinning system and (b) substrate with a patterned electrode

Each solution was then transferred into 10 mL syringe for electrospinning process. A schematic electrospinning machine to fabricate nanofibers and substrate with patterned electrodes

place at the collector is shown in Fig. 1. The electrospinning process took place at ambient temperature. We used copper (Cu) metals as electrodes with the distance between the electrodes, and the length of the electrode was 2 mm and 2 cm, respectively.

During the electrospinning process, a DC voltage of 15 kV was applied. The distance between the needle and the collector was set as 10 cm. The electrospinning process was carried out for 30 minutes to get a suitable thickness of nanofiber mat. Finally, all electrospun nanofibers were annealed at 60 °C for 15 min to remove the residual solvent.

C. Solvent Vapour Treatment

The schematic diagram for illustration of solvent vapour treatment is shown in Fig. 2. The nanofiber mat then cut into smaller coupon (about 3 cm x 3 cm) and place at the top of beaker glass (50 mL) with 10 mL DMSO. The DMSO then evaporate with hot plate stirrer at temperature solution set to 30 - 45 °C. The process was carried out for 2 h while the current-voltage is measured.
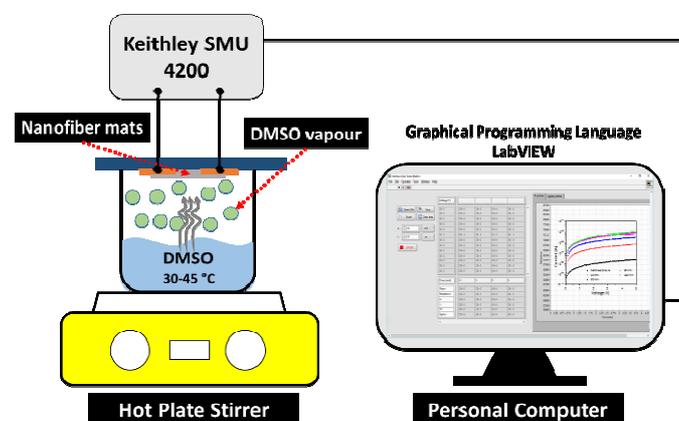

Fig. 2. Schematic diagram of solvent vapour treatment and electrical conductivity measurement.

D. Measurement and Characterization

The current-voltage characteristics during vapour treatment were recorded directly using two probes connected to the source measurement unit of Keithley SMU-2400 with graphical programming language LabVIEW. The resistance of the nanofibers was calculated by the slope of current-voltage measured. The electrical conductivity of nanofibers was calculated by American System for Testing Material Standard ASTM 1844 [30]

$$\sigma = \frac{1}{d} \frac{l}{R.w} \qquad (1)$$

where, σ is the electrical conductivity (S/m), R is resistance (Ω), l is the distance between electrodes (m), w is the length of contact electrodes (m), and d is the thickness of the nanofiber (m). The thickness and morphology of nanofibers was measured with scanning electron microscope (SEM) of JEOL JSM-6510 operate at 15 kV. Prior to SEM, sample were sputter coated for 70 s with platinum using a JEOL fine coater. Based on the SEM photos, fiber diameters distribution and

thickness of the nanofibers were analysed using an image visualization software ImageJ.

III. RESULTS AND DISCUSSION

A. Electrical Properties and Morphology

From the cross-section characterized using SEM, the thickness of the nanofiber mat is estimated to be 6 μm (Fig. 3(a)). Equation 1 is used to calculate the electrical conductivity of the nanofibers since the direct measurement parameter is current-voltage or sheet resistance.

TABLE I
SAMPLE COMPOSITION USED IN ELECTROSPINNING PROCESS

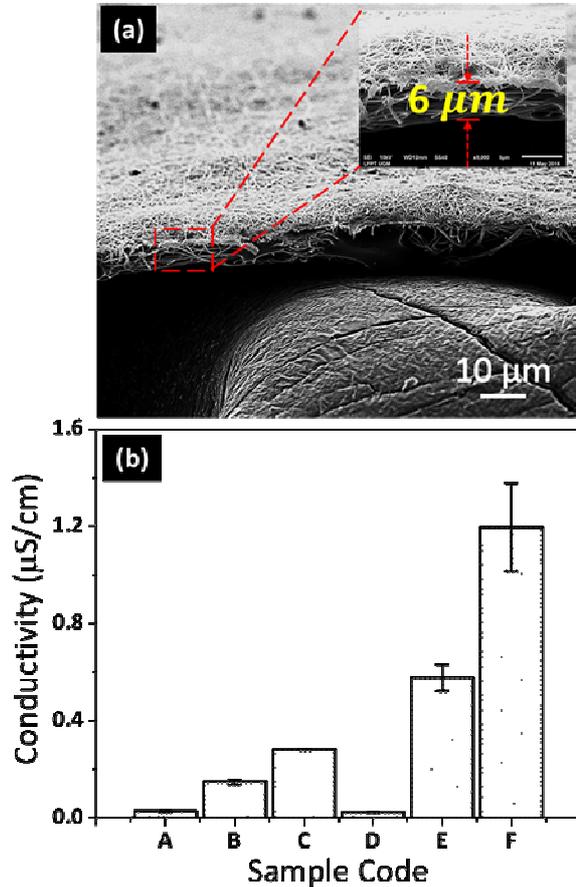| Sample Code	PVA concentration (%)	Mixing ratio (v/v)	
		PVA	PEDOT:PSS
A	8	100	0
B	9	100	0
C	10	100	0
D	10	60	40
E	11	60	40
F	12	60	40

Fig. 3. (a) SEM image of cross-section of sample C; (b) conductivity of samples

As shown in Fig. 3(b), the electrical conductivity increases by increasing PVA concentration (sample A, B, and C). More increase of the electrical conductivity is achieved by adding PEDOT:PSS (sample E and F). The electrical conductivity of sample D, however, is lower than that of sample C. It may be due to decreasing in the solution viscosity as an effect of adding PEDOT:PSS in the PVA solution. In this case, PEDOT:PSS is known to have a low viscosity so that adding more PEDOT:PSS to PVA solution results in decreasing the viscosity of polymer solution. A polymer with low viscosity tends to form beaded nanofibers. The presence of beads leads a decrease in the electrical conductivity of nanofibers.

The increase in the concentration of the PVA solution yields the larger diameter of the nanofiber. Nanofiber with a larger diameter will have a higher electrical conductivity. This result is in agreement with the previous report [31].

From Fig. 3(b), it is found that the electrical conductivities of PVA nanofiber mats (sample A, B, and C) are 0.03 μS/cm, 0.15 μS/cm, and 0.28 μS/cm, respectively. For comparison, the electrical conductivity of nanofiber mats made from PVA blended with PEDOT:PSS (sample E and F) increases significantly up to 0.57 μS/cm and 1.20 μS/cm, respectively.
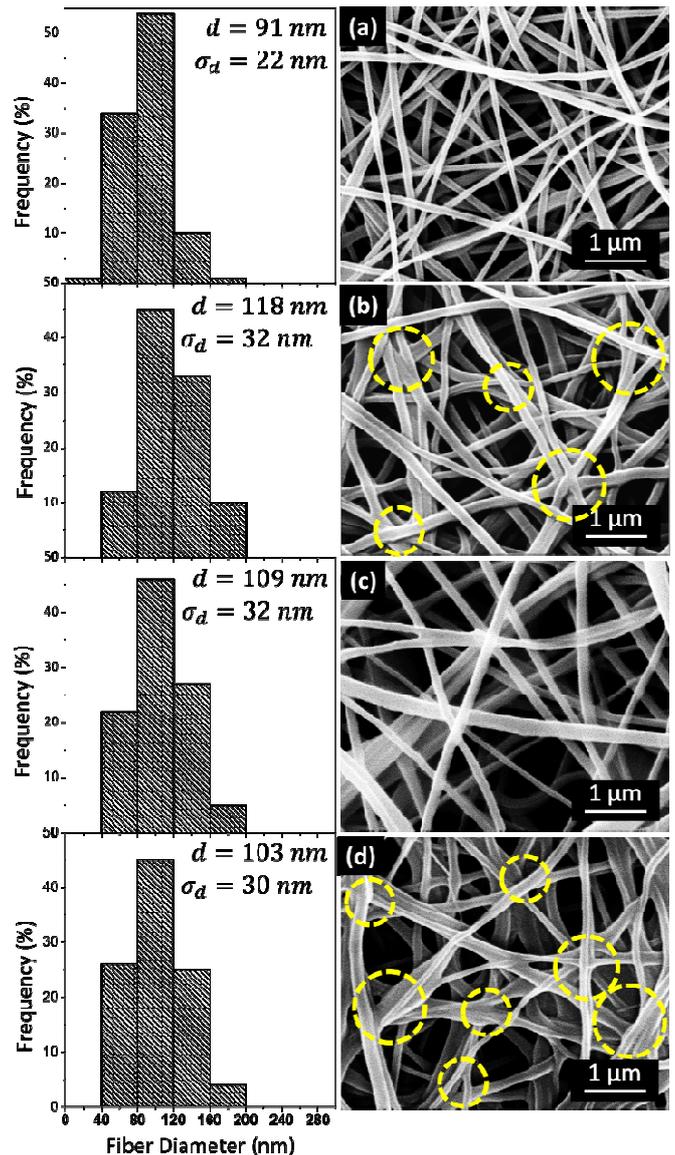

Fig. 4. SEM image and nanofiber diameter distribution, (a) sample C before, (b) after exposure DMSO at 40 °C for 2h; (c) sample F before, (d) after exposure DMSO at 40 °C for 2h

Figures 4 (a and b) show the SEM images of PVA nanofiber mat (sample C) before and after exposure DMSO, respectively. On the other hand, Fig. 4 (c and d) show the SEM images of PEDOT:PSS/PVA nanofiber mats (sample F)

before and after exposure DMSO. By exposure DMSO, the diameter of PVA nanofiber (sample C) increase from (91 ± 22) nm to (118 ± 32) nm. Meanwhile the PEDOT:PSS/PVA nanofiber relatively same (~100 nm). The SEM images show that the nanofiber mats appeared to swell after exposure DMSO. It is in accordance with other reports [32].

The electrical conductivity of nanofibers can be correlated to the morphology as shown in Fig. 4. In this case, the increase in the electrical conductivity of PVA nanofibers can be attributed to solvent-induced fusion at the nanofiber junction points [32]. In other words, the condensation of DMSO vapour during the treatment could keep the electrospun nanofiber mat relatively ''wet'', resulting in a fusion between the contacts of inter-nanofiber. Another effect of DMSO vapour is to swell affecting larger the surface density of electrospun nanofiber. These two effects yield the charge transfer becomes easier to flow from one nanofiber to others and satisfy the hopping mechanism [33], [34]. Figure 4(b) and 4(d) also show that fusion occurred among some of the nanofiber junctions, as indicated by the yellow circle. This fusion occurs because the solvent can condense at these junctions and slightly dissolve the polymer to facilitate fusion.
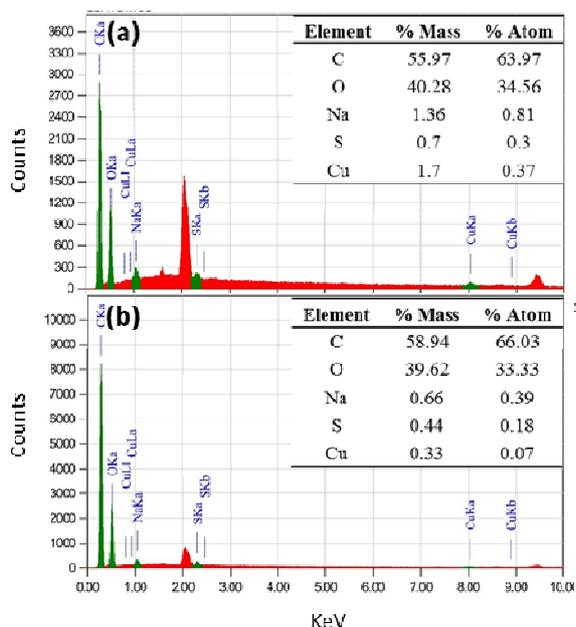

Fig. 5. EDS result of sample C (a) before, (b) after exposure DMSO for 2 h at temperature 40 °C

The change in nanofiber morphology after exposure DMSO might have a role in improving the conductivity of nanofibers. The SEM-EDS results show in Fig. 5 indicated the composition element on the surface of nanofiber did not change. This result indicated that there is no interacting bond between DMSO vapour and the surface of nanofibers.

B. Effect Solvent Vapour on Conductivity nanofiber

The effect of solvent vapour on the electrical conductivity of nanofiber was measured dynamically for 2 h evaporation and 2 h after evaporation, consecutively as shown in Fig. 6. The observation after evaporation become crucial since the effect of vapour solvent just momentarily. For the next discussion, we use sample C and sample F for comparison because of optimum electrical conductivity.
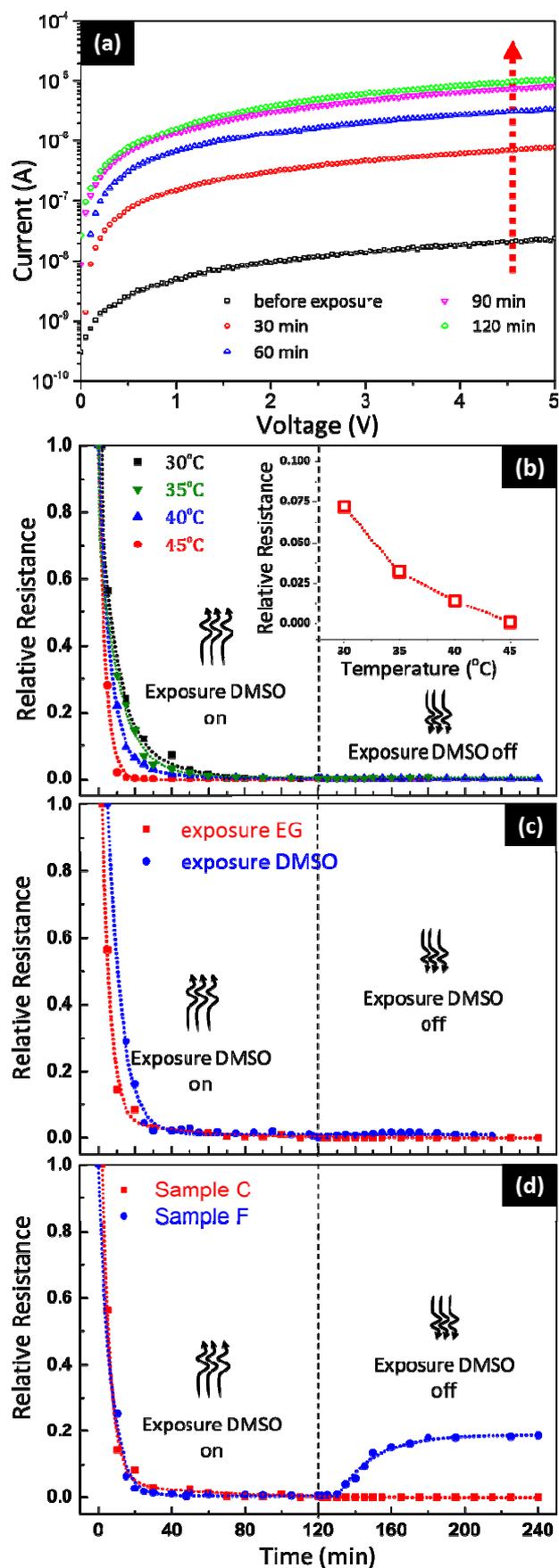

Fig. 6. (a) I-V Characteristics of sample C exposure DMSO at 40 °C, (b) relative resistance of sample C exposure DMSO various temperature (insert relative resistance vs temperature at min 40), (c) sample C with various exposure solvent at 40 °C, (d) sample C and F exposure DMSO at 40 °C.

Figure 6(a) shows the current-voltage characteristic of sample C exposure with DMSO at 40 °C for a different exposure time. Because of the huge difference in the magnitude of the current among the treatment samples, the I–V curves are shown logarithmically. The resistance decreases by increasing of exposure time as shown in Fig 6.

From Fig. 6(b) we also see that the difference of DMSO temperature makes the difference rate of reducing the resistance of nanofiber mats. The higher exposure temperature leads to higher evaporation rate, which affects decreasing the resistance of nanofiber mat (inset Fig 6(b)).

Effect of various solvent (EG or DMSO) for a vapour was also investigated. As shown in shown in Fig. 6(c), the relative resistance of sample C under exposure EG decreases faster than that of under exposure DMSO. It is due to the higher electronegativity of EG as compared to DMSO. The effect of exposure DMSO on nanofiber PEDOT:PSS/PVA (sample F) is shown in Fig. 6(d). Here, the sample F appears to be unstable after exposure DMSO.

During the vapour exposure, DMSO vapour condenses at the nanofiber junction points. It results in slightly dissolving the polymer to facilitate fusion and to change the morphological and conformational of nanofibers mats. This change then causes the improvement of electrical conductivity of nanofiber. In this case, DMSO vapour facilitates electron mobility to improve the electrical conductivity of nanofiber. From Fig. 7(a), it is clear that the conductivity is significantly improved after exposure DMSO for all samples. The highest electrical conductivity improvement is achieved by the sample with an evaporating temperature of 40 °C, which is increase from $0.07\ \mu S cm^{-1}$ to $36\ \mu S cm^{-1}$ after two-hour exposure with DMSO.
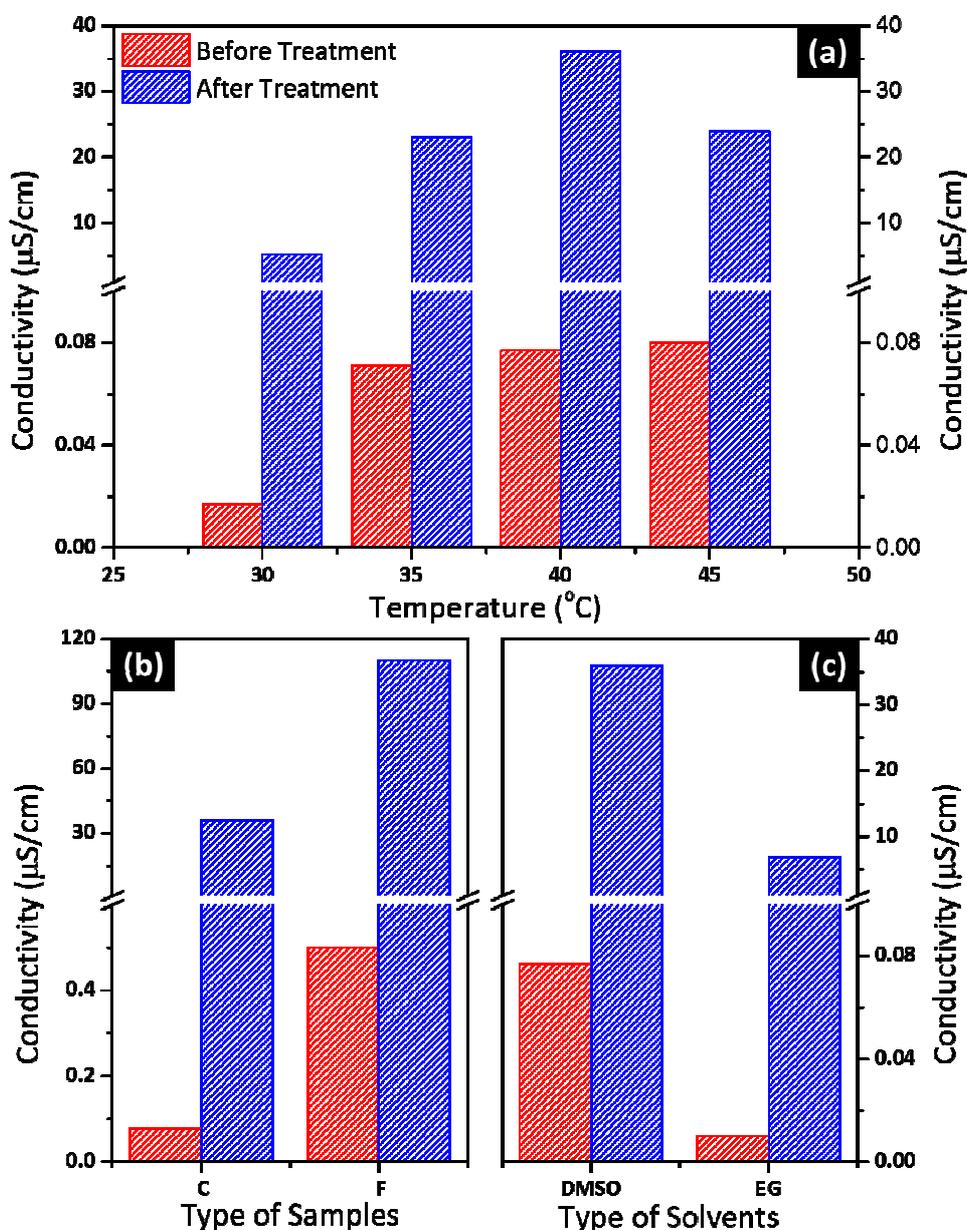

Fig. 7. Summary of conductivity improvement of (a) sample C with various DMSO temperatures, (b) Type of sample exposure DMSO at 40 °C, and (c) sample C with a different type of solvent used.

The effects of different samples and solvent during vapour treatment on the electrical conductivity are shown in Fig. 7(b and c). The PEDOT:PSS/PVA nanofibers (sample F) shows high conductivity after exposure DMSO (sample F is more conductive than sample C). The electrical conductivity of sample F increases significantly from 0.5 μScm^{-1} to 110 μScm^{-1} after exposure DMSO at a temperature of 40 °C for 2h. Figure. 7(c) indicates that DMSO is better than EG for vapour treatment.

IV. CONCLUSIONS

The electrical conductivity of PVA nanofiber has been significantly improved by adding PEDOT:PSS and solvent vapour treatment of DMSO or EG. We found that DMSO is better than EG for vapour treatment. In this case, DMSO vapour can induce a morphological and conformational change in nanofibers, which results in electrical conductivity improvement. Solvent-induced fusion at the nanofiber junction points and change on nanofiber conformation are clearly observed in the SEM image of nanofiber mat. The used of a polar solvent such DMSO in solvent vapour treatment can be an effective method process for improving the conductivity of nanofibers.

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