

## Characterization of the Properties of Electrospun Blended Hybrid Poly (Vinyl Alcohol)\_Aloe Vera/Chitosan Nano-Emulsion Nanofibrous Membranes

Harini Sosiati<sup>1a\*</sup>, Wahyu Nur Fatihah<sup>1b</sup>, Yusmaniar<sup>2c</sup>  
and M. Budi Nur Rahman<sup>1d</sup>

<sup>1</sup>Department of Mechanical Engineering, Faculty of Engineering, Universitas Muhammadiyah Yogyakarta, Jl. Brawijaya, Kasihan, Bantul, Yogyakarta 55183, Indonesia.

<sup>2</sup>Department of Chemistry, State University of Jakarta, Jl. Rawamangun Muka, Jakarta 13220, Indonesia

<sup>a\*</sup>hsosiati@ft.ums.ac.id, <sup>b</sup>wahyunurfatihah@gmail.com, <sup>c</sup>yusmaniar@unj.ac.id,  
<sup>d</sup>budinurrahman@ums.ac.id

**Keywords:** Aloe Vera; PVA; chitosan nano-emulsion; electrospinning; nanofiber.

**Abstract.** The spinning solution of blended hybrid poly (vinyl alcohol) (PVA)\_Aloe Vera (AV) with various concentrations (0%, 3%, 10% and 15%) of chitosan nano-emulsion (CSNe) were electrospun under optimized conditions of high DC voltage 15 kV, distance of spinneret tip to collector plate 16.5 mm and spinneret diameter 0.8 mm. This work aims to manufacture the blended hybrid PVA\_AV/CSNe nanofibrous membranes and characterize the solution and fiber properties, and tensile properties of the nanofibrous membranes by varying CSNe concentrations. Scanning electron microscopy (SEM) results revealed that beads-free fiber structure featured in all electrospun membranes with relatively homogeneous fiber size distribution. An increase of CSNe concentration from 0% to 15% reduces the average fiber size from 366 nm to 180 nm and increase tensile strength from  $2.52 \pm 0.54$  MPa to  $6.18 \pm 0.15$  MPa and tensile modulus from  $7.5 \pm 1.06$  MPa to  $21.9 \pm 9.88$  MPa of the membranes, respectively. The tensile strength of the present blended hybrid PVA\_AV/CSNE nanofibrous membranes with 15% CSNe concentration and tensile modulus of that with all CSNe concentrations are included in the range of the natural skin properties: i.e. (5.00 – 30.00 MPa) and (4.6 – 20.0 MPa) for tensile strength and modulus, respectively. Such data suggest the potential use of the membranes as wound dressing material in the near future.

### Introduction

Aloe Vera (AV) is a natural plant contained Aloe gel which has the antimicrobial activity toward microbes. Chitosan (CS) is a natural biopolymer which has combination properties such as antimicrobial activity, biodegradability, and non-toxicity. However, the antimicrobial activity of AV is better than that of CS [1]. Poly (vinyl alcohol) PVA as a synthetic polymer is non-toxic, biocompatible [2] and could be smoothly blended with AV [3]. Accordingly, they are potentially used for biomedical applications such as for wound healing, wound dressing and tissue engineering.

When a large area of skin is lost, a wound has to be immediately covered to prevent a bacterial irruption and blood losses. Usually, wound dressing is specified as protective coverage positioned on an injury to enhance the healing process. It is required, therefore, a wound dressing material having the compatible properties with the natural skin. Wound dressing material should be non-toxic, have the porous structure for better air circulation around a wound, high tensile strength and low stiffness for flexibility.

Some investigations on developing the wound dressing materials have been reported [3-6]. PVA and a combination of blended PVA and AV [3], PVA and CS [4], PCL/AV\_CS [5] and PVA/AV\_HPMC [6] have been developed by the electrospinning method. However, those have mostly devoted to the influence of the solution concentration on the morphology of the produced nanofiber membranes. Solution viscosity is the function of solution concentration which is one of

some significant electrospinning parameters giving impact not only the morphology but also the mechanical property of the electrospun nanofibrous membrane [7]. Electrospinning is an effective method for fabricating the nanofiber membranes, in which the obtained membranes have unique characteristic needed for wound dressing material such as a high surface area to volume ratio and high porosity generated by self-interaction between the fibers forming the fiber networks.

Miquel *et al.* [5] have reported that mean fiber diameter of blended CS\_AV\_polyethylene oxide (PEO) (~152 nm) is smaller than that of blended CS\_PEO (~239 nm) and PCL (~385 nm). The tensile strength of PCL/CS\_AV\_PEO (~6 MPa) lower than that of PCL\_CS\_PEO (~9 MPa). Incorporation of AV in CS\_PEO produced nanofiber membranes with mechanical properties and antimicrobial activity that are compatible with the wound dressing material. Our previous study [8] on the characterization of electrospun PVA/AV nanofiber membrane resulted in beads-free fibrous structure and verified the relationship of solution concentration/viscosity and a mean fiber size and tensile properties. Enhancing the solution concentration/viscosity increased the average fiber size and decreased the tensile strength and modulus. This propensity is consistent with those reported in Ref. [7, 9]. In addition, investigation of biomaterial-based CS prepared using electrospinning method have also been extensively carried out. However, research on the incorporation of CSNe in the blended hybrid PVA\_AV was not found. CSNe with CS nanoparticles of about 50 nm was used as fillers in the PVA\_AV matrix. Uniform dispersion of CS nanoparticles in the nanofibers is expected to be able to enhance the tensile strength of the nanofiber membrane. Thus, the addition of CSNe in the blended hybrid PVA\_AV solution was presently studied to characterize the changes in properties of the electrospun blended hybrid PVA\_AV/CSNE nanofibrous membranes by varying CSNe concentrations. The produced membranes are expected to behave the properties which are compatible with a standard wound dressing material.

## Experimental Methods

**Materials and Fabrication of the Spinning Solution (PVA\_AV/CSNe).** AV and PVA used in this work were commercial extract AV powder and PVA Goshenol (PVOH/PVA, Mw: ~ 22,000 g/mol), respectively. Chitosan micro powder, sodium tripolyphosphate (STTP) and acetic acid ( $\text{CH}_3\text{COOH}$ ) were purchased from Sigma Aldrich (USA).

PVA solution (10% w/v) was prepared by dissolving 10 g PVA into 100 ml distilled water under continuous magnetic stirring at 80°C for an hour. The PVA\_AV solution was prepared by mixing 5% AV in PVA (10% w/v) and stirred at room temperature for 2 h. CSNe were prepared by dissolving CS micro powder in 1%  $\text{CH}_3\text{COOH}$  and *homogenized* by constant magnetically stirring. After that, STTP and 1%  $\text{CH}_3\text{COOH}$  were gradually added into the CS- $\text{CH}_3\text{COOH}$  solution with also constant magnetically stirring, and the solution was kept for 24 h. These chemical processes produced CS Nano-emulsion with an inhomogeneous size of the particles: i.e., CS nanoparticles (~ 50 nm) are located on the top level which was separated from CS microparticles located at the bottom. Finally, blended hybrid PVA\_AV/CSNe as a spinning solution was prepared by mixing CSNe at various concentrations (0%, 3%, 10% and 15%) in PVA\_AV solution (5% w/v) under magnetic stirring at 30-45°C for an hour. The viscosity of PVA\_AV/CSNe solution at each CSNe concentration was measured with a viscometer (Brookfield Viscometer).

**Preparation of Electrospun Blended Hybrid PVA\_AV/CSNE Nanofiber Membranes.** The spinning solution of PVA\_AV/CSNe with (0%, 3%, 10% and 15%) CSNe concentrations was fabricated to be the nanofiber membranes by electrospinning technique operating under the optimized conditions: i.e. applied DC voltage 15 kV, flow rate 0.083 ml/min, the spinneret diameter 0.6 mm and the distance from tip to the collector plate (TCD) 16.5 cm. Each membrane was fabricated for about 3 h for getting the thickness for the tensile test specimen. The thickness was measured from the cross-section of the membrane using an optical microscope (OM, Olympus BX53M).

**Characterization.** The morphology of PVA\_AV/CSNe nanofiber membranes for each CSNe concentration was characterized by scanning electron microscopy (SEM, TESCAN VEGA3 LMU). Before inserting in the specimen chamber, a surface of the membrane specimen was metallic coated with Au-Pd alloy. The ImageJ digital image analysis measured fiber diameter observed from two different regions of the membrane at each concentration variation. All PVA\_AV/CSNe nanofiber membranes were tensile tested using a testing machine (Zwick Z0.5 Germany) at a crosshead speed of 10 mm/min and a gauge length of 20 mm. Preparation of tensile test specimens was carried out according to ASTM 882.

## Results and Discussion

**The Properties of Spinning Solutions and Fibers.** It is known that in the electrospinning process the solution properties (viscosity, conductivity and surface tension) affect the morphology of fibers and also the mechanical properties of nanofiber membranes [7]. In this study, changes in fiber morphology and the tensile properties are discussed from the different viscosity of the spinning solution. The viscosity of the PVA\_AV/CSNe spinning solution at various CSNe concentrations is summarized in Table 1. As the CSNe concentration increases, the viscosity of the spinning solution PVA\_AV/CSNe decreases. Generally, the viscosity of the spinning solution is associated with the extent of polymer molecular chains entanglement within the solution [6]. The high viscosity of the solution leads too large viscoelastic and to make the jet splitting is difficult,

Tabel 1. Viscosity of AV/PVA solution at different AV concentration.

Specimen	Concentration (%)	Viscosity (cP)
PVA_AV/CSNe-0	0	849.9
PVA_AV/CSNe-3	3	729.9
PVA_AV/CSNe-10	10	379.9
PVA_AV/CSNe-15	15	359.9

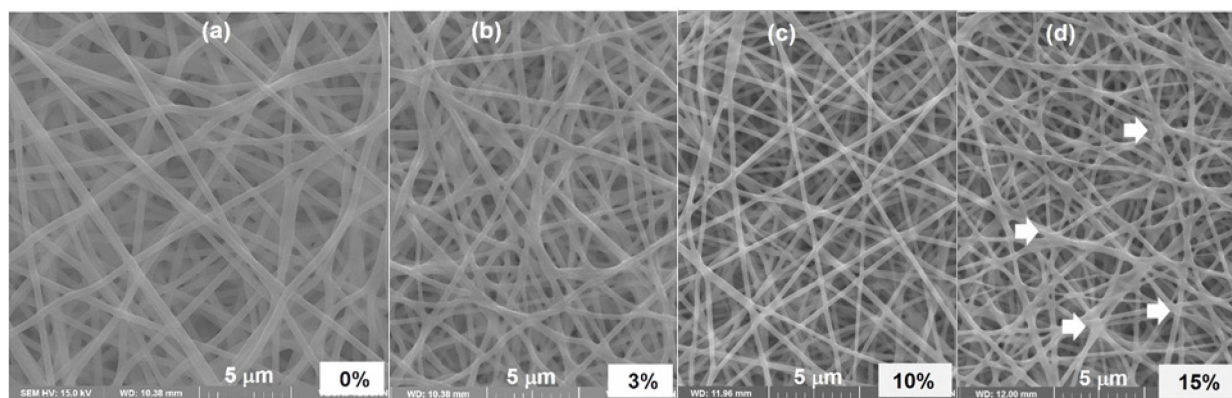


Fig. 1. SEM micrographs of blended hybrid electrospun PVA\_AV/CSNe nanofiber membranes with different CSNe concentrations. (a)0%. (b)3%. (c) 10% and (d) 15%.

resulted in wide range fiber size. Inversely, the solution with low viscosity would have a low viscoelastic and columbic repulsion forces, causing the jet break-up and may produce the beaded fiber structure [9, 10].

SEM micrographs (Fig.1) illustrate the bead-free fibrous structure for all electrospun PVA\_AV/CSNe nanofiber membranes. The addition of AV into the spinning solution plays a crucial role in affecting the produced fibers [6], leading to generate fibers without any beads. This trend is consistent with our previous and present studies: i.e. the addition of AV into the PVA solution.

Produced nanofibers (Fig.1) are related to the viscosity of the spinning solution summarized in Table 1, which are included in the range of viscosity reported by Amariei *et al.* [9]; the spinning solution with a viscosity ranging from 1 to 20 poise is considered to be a suitable condition for

electrospinning. SEM images also evidently show that fiber size distribution formed in the membrane at 0% and 10% CSNe concentrations demonstrate relatively more homogeneous compared to that at 3% and 15% CSNe concentrations.

The fiber size distribution for all produced nanofibers (Fig.2) confirmed the observation result on the SEM images (Fig.1). The addition of CSNe into the PVA\_AV solution reduced the fiber size. As the CSNe concentration increases (0%, 3%, 10% and 15%), the average of fiber size decreases (366, 286, 242 and 180 nm), respectively. In this case, the addition of CSNe concentration into the PVA\_AV solution is also ascribed to be related to the changed in the crystallinity of the spinning solution, because PVA is a semicrystalline polymer and CS is present in the crystalline phase on a crystal structure of orthorhombic [11]. The degree of crystallinity has a correlation effect on the applied voltage [12]. So at a certain applied voltage, as a viscosity of the solution is going lower, the degree of crystallinity becomes lower, resulting in smaller fiber size.

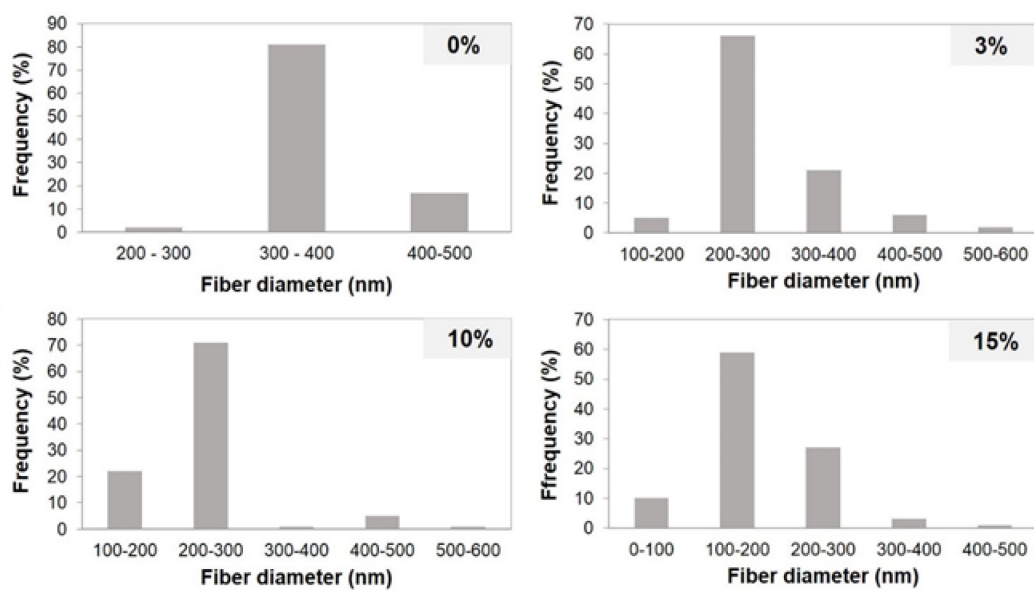


Fig. 2. Fiber size distribution for produced nanofibers of blended hybrid electrospun PVA\_AV/CSNe with different CSNe concentrations. (a) 0%. (a) 3%. (c) 10% and (d) 15%.

**Tensile Properties of Blended Hybrid PVA\_AV/CSNE Nanofiber Membranes.** The material for biomedical application should have adequate tensile properties, such as the tensile strength should be higher than 5 MPa. The relationship of tensile strength and modulus of the nanofiber membranes and CSNe concentrations (Fig. 3a) exhibit a similar trend. An increase of the CSNe concentration decreased the viscosity of the spinning solution and increased both the tensile strength and modulus which can be attributed to the change in morphology of the nanofiber membrane. The smaller is the fiber size, the tensile strength and modulus increase [12]. Principally, high mechanical properties are influenced by molecular orientation and crystallinity of the nanofiber membranes. But, an increase in mechanical properties was not considered due to increased crystallinity [13]. Therefore, the highest tensile strength of the membrane with 15% CSNe concentration obtained from this work is considered due to the lowest crystallinity, because CSNe was present in the amorphous phase as confirmed by transmission electron microscopy (TEM). Thus, the higher the CSNe concentration, the more the CS nanoparticles were distributed in the nanofibers, resulted in reducing the crystallinity of the membrane. The highest tensile strength can also be understood from the typical structure of the membrane (Fig. 4), showing the interaction between the fibers which generated high volume fraction of cross-link structures (see arrows). This typical structure seems to be beneficial in improving the tensile strength of the membranes.

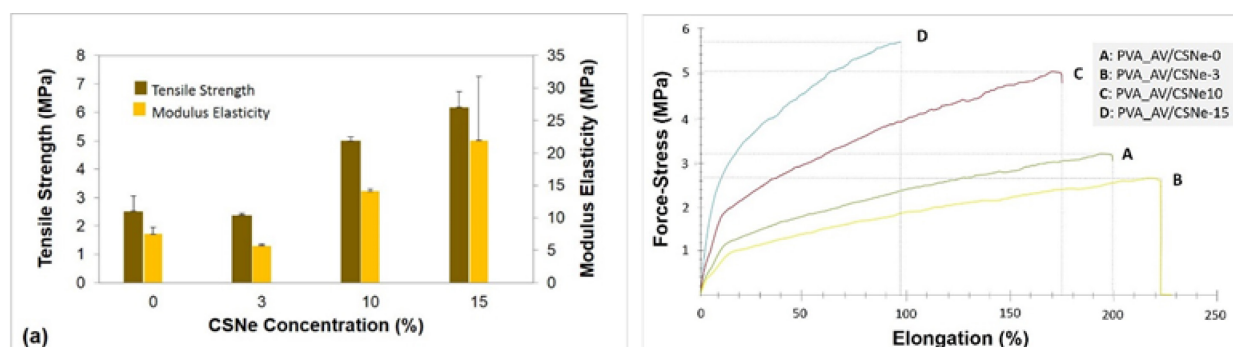


Fig. 3. (a) Tensile strength and modulus versus CSNe concentrations and (b) Force-stress versus elongation at each CSNe concentration.

Elongation at break for the membrane with 15% CSNe concentration showed the lowest (Fig. 3b), which is included in the range of the natural skin properties: i.e., 35 – 115% for elongation at break, (5.00 – 30.00 MPa) for tensile strength and (4.6 – 20.0 MPa) for Young modulus. Therefore, the best properties obtained from the present membranes were achieved by the blended hybrid PVA\_AV/CSNe nanofiber membrane with 15% CSNe concentration:  $6.18 \pm 0.15$  MPa,  $21.9 \pm 9.88$  MPa and 97% for tensile strength, Young modulus and elongation at break, respectively, although Young modulus is slightly higher than that of the native skin. However, tensile strength and a mean fiber size resulted in the membrane with 15% CSNe concentration are comparable with that reported by Miquel *et al.* [5]. Further study may be required to reach higher tensile strength and optimize a tensile modulus of the membrane.

### Acknowledgement

This study was partly supported by a research grant of “Penelitian Dasar Unggulan Perguruan Tinggi” 2018, contract no: 109/SP2H/LT/DRPM/2018 by the Directorate General of Higher Education (DIKTI), Ministry of Research, Technology and Higher Education, the Republic of Indonesia.

### Summary

1. The blended hybrid PVA\_AV/CSNe nanofiber membranes have been successfully manufactured by an electrospinning method and resulted in a beads-free fibrous structure for all concentrations (0-15%) of CSNe with relatively uniform fiber size distribution.
2. An increase of CSNe concentration added into the PVA\_AV decreased the viscosity of PVA\_AV/CSNe spinning solution. The lower the viscosity of the spinning solution, the smaller the average fiber size and the higher the tensile strength and modulus.
3. The electrospun PVA\_AV/CSNe with 15% CSNe concentration has smallest mean fiber size (180 nm) and the tensile properties: i.e.  $6.18 \pm 0.15$  MPa,  $21.9 \pm 9.88$  MPa and 97%, for tensile strength, Young modulus and elongation at break, respectively, which are comparable with the wound dressing material properties.

### References

- [1] L. Ammayappan and J. J. Moses: *Fibers and Polymers* Vol.10 (2) (2009), p. 161.
- [2] K. H. Hong: *Polym. Eng. Sci.* Vol. 47(1) (2007), p. 43.
- [3] N. A. Abdullah Shukry, K. Ahmad Sekak, M.R. Ahmad and T.J. Bustami Effendi: *Characteristic of Electrospun PVA-Aloe vera Nanofibers Produced via Electrospinning* (Proc. Int. Colloquium in Textile Engineering, Fashion, Apparel and Design, 2014).

- 
- [4] K. Paipitak, T. Pornpra, P. Mongkontalang, W. Techitdheer and W. Pecharapa: *Procedia Eng.* Vol. 8 (2011), p 101.
  - [5] S.P. Miquel, M.P. Ribeiro, P. Coutinho and I.J. Correia: *Polymers* Vol. 9 (2017), p. 183.
  - [6] I. Uslu, S. Keskin, A. Gül, T.C. Karabulut and M.L. Aksu: *Hacettepe J. Biological. Chem.*, Vol. 38 (1) (2010), p. 19.
  - [7] B. Tarus, N. Fadel, A. Al-Qufy and M. El-Messiry: *Alexandria Eng. J.* Vol. 55 (2016), p. 2975.
  - [8] H. Sosiati, A.N. Widodo and A.W. Nugroho: to be published in *J. Sains Materi Indonesia* (2018).
  - [9] N. Amariei, L.R. Manea, A.P. Berteau, A. Berteau and A. Popa: *IOP Conf. Series: Mater. Sci. Eng.* Vol. 209 (2017), p. 012092.
  - [10] S. Huan, G. Liu, G. Han, W. Cheng, Z. Fu, Q. Wu and Q. Wang: *Materials* Vol. 8, (2015), p. 2718.
  - [11] M. Ioelovic: *Res. Rev.: J. Chem.* Vol. 3 (3) (2014), p. 7.
  - [12] O. Ero-Phillips, M. Jenkins and A. Stamboulis: *Polymers* Vol. 4 (2012), p. 1331.
  - [13] A. Arinstein, M. Burman, O. Gendelman, E. Zussman: *Nat. Nanotechnol.* Vol. 2 (2007), p. 59.