

# Stabilization of PVA/Chitosan/TiO<sub>2</sub> Nanofiber Membrane with Heat Treatment and Glutaraldehyde Crosslink

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**Abstract.** PVA/chitosan/TiO<sub>2</sub> nanofiber membrane have been prepared by electrospinning method. PVA/Chitosan/TiO<sub>2</sub> nanofibers are poor stability in water. In this paper, the stabilization of PVA/chitosan/TiO<sub>2</sub> nanofiber membrane was improved by heat treatment and GA crosslink. The structure and morphology of PVA/chitosan/TiO<sub>2</sub> nanofibers were characterized by FTIR, SEM, and EDAX. The result showed that the stabilization methods affected the morphology of nanofiber membranes and their stability in water. Heat treatment reduces fiber diameter and membrane pore size, in contrast, GA crosslink increase fiber diameter and membrane pore size. Stability in water of nanofiber membranes was examined by immersing in the water for 24 h. The SEM result shows that after immersing in water for 24 h, PVA/Chitosan/TiO<sub>2</sub> nanofibers without stabilization rapidly shrink and dissolve after dipped in water and finally form transparent gel shape material with a grain of TiO<sub>2</sub> nanoparticle. PVA/Chitosan/TiO<sub>2</sub> nanofibers with heat treatment don't dissolve after immersing but present a certain degree of aggregation and swelling, which indicates that heat treatment can improve the stability of the fiber but still low. Meanwhile, PVA/Chitosan/TiO<sub>2</sub> nanofibers with GA crosslink do not dissolve and change morphology and fiber diameter after immersing 24 h. It indicates that PVA/Chitosan/TiO<sub>2</sub> nanofibers with GA crosslink have excellent stability in water.

**Keywords.** Chitosan, GA crosslink, heat treatment, nanofibers, PVA, Stabilization, and TiO<sub>2</sub>.

## 1. Introduction

Polyvinyl alcohol (PVA) as a hydrophilic polymer with partial crystallization has a lot of advantages such as chemical resistance, excellent biocompatibility, high melting point, non-toxic, simple processing, and high water permeability [1]. On the other hand, chitosan (CS) is an organic polymer which has the properties of non-toxic, biocompatible, biodegradable, biofunctional, and hydrophilic [2]. Moreover, CS has been used as an antimicrobial and antiviral material in the fields of biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science, and textiles because of its advantageous in biological properties [3]. It has been reported that the combination between PVA and CS can be produced nanofibers by electrospinning [4].



Electrospinning is a technique using electrostatic force to produce fine fibers from a polymer solution, fibers produced from this electrospinning have a small diameter (micrometer or nanometers) and a surface area higher than that obtained from conventional spinning process [5, 6]. Electrospun nanofiber has excellent characteristics such as the vast surface area to volume ratio and high porosity with small pore sizes [7]. Other reports, TiO<sub>2</sub> fibers showed high surface-to-volume ratios and a high number of active surface sites for effective photocatalytic [8, 9]. Chitosan nanofibers could become a new material for virus removal in drinking water applications. Some other applications of chitosan-based chitosan nanofibers including; PVA/chitosan nanofibers were used as a membrane to remove metal ions in a fixed-bed reactor, in particular for the adsorption of metals nickel and cobalt [10]. Chitosan nanofibers combined with TiO<sub>2</sub> is used for adsorption of heavy metal ions Pb (II) and Cu (II) [11].

Titanium dioxide (TiO<sub>2</sub>) has been successfully studied for photovoltaic application [12]. Moreover, TiO<sub>2</sub> has also been used as photocatalytic due to its chemical stability and availability in commercial [13]. The size of TiO<sub>2</sub> could be reduced to increase the reactive surface area for some applications [14]. In particular, wastewater treatment for environmental preservation based on TiO<sub>2</sub> powder has been applied in photocatalytic for reducing many organic pollutants effectively. However, this still leaves some problems when applied in environments such as rivers, lakes, and sea [15]. The main problem was due to the difficulty of recovery after the photocatalytic treatment process. In this case, the TiO<sub>2</sub> particles were not easy to separate from the waste [16]. To overcome this problem, we developed photocatalytic based nanofibers synthesized using electrospinning methods [17].

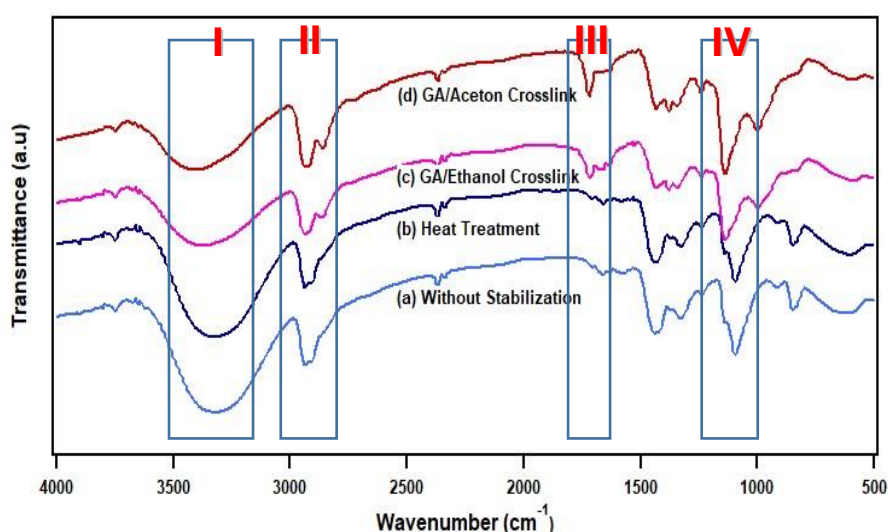
Many applications of PVA/TiO<sub>2</sub>/chitosan nanofibers, such as a membrane for filtration, membrane adsorption, for and membrane for photocatalytic application. For this application nanofiber membrane must provide high stability especially in water. The stabilization method can use chemical cross-linking agents or physical treatment methods to improve the water stability of nanofibers membrane [18 – 20]. In this paper, we studied the various stabilization method to increase the stability of the nanofiber membrane in water. This paper also discusses the effect of stabilization method and on the morphology of the nanofibers membrane especially diameter and porosity of nanofibers membrane.

## 2. Materials and methods

All material was used without further purification: PVA (Mw: 89.000 g·mol<sup>-1</sup> to 98.000 g·mol<sup>-1</sup>, 99 % hydrolyzed), Chitosan (medium molecule weight), Titanium (IV) oxide, anatase, nanopowder < 25 nm particle size, 99.7 % trace metal basis, Glutaraldehyde solution 50 wt% in H<sub>2</sub>O, and tetramethylammonium hydroxide (TMAH). All of them purchased from Sigma-Aldrich. PVA/TiO<sub>2</sub> electrospun solution was prepared by dissolving TiO<sub>2</sub> nanoparticle in deionized water at 90 °C for 1 h in magnetic stirrer and adding TMAH solution with ratio TiO<sub>2</sub> to TMAH of 10:1. TiO<sub>2</sub> dispersion adding with PVA powder and then blending the PVA and TiO<sub>2</sub> at a ratio of 4:1. And then stirring them for 1 h at 90 °C. Chitosan (1 wt%) was dissolved in 2 % acetic acid solution at 45 °C for 1 h in magnetic stirrer. PVA/TiO<sub>2</sub>/Chitosan solution was obtained by blending the PVA/TiO<sub>2</sub> and Chitosan solution at a ratio of 85:15 and then stirring them for 1 h at 45 °C and then sonicated them for 3 h. The prepared PVA/TiO<sub>2</sub>/Chitosan solution was then loaded into a 12-mL plastic syringe equipped with a 0.4-mm needle diameter. A high voltage of 15 kV, with a tip-collector distance of 14 cm, was applied to the solution and fiber collected on the plane collector [21]. Electrospun nanofibers were stabilized with various stabilization method, i.e., Heat treatment and GA crosslinked. Heat treatment was done by heating the fiber membrane in a furnace at 135 °C for 4 h. GA crosslinked were done by immersing in a solution of 2.5 wt% Glutaraldehyde solution (volume ratios of Glu (aq): acetone/ethanol: HCl (aq) = 1:2:0.01) at 40 °C for 4 h. Characterizations of PVA/TiO<sub>2</sub> nanofibers using FTIR and SEM-EDAX. FTIR (Shimadzu, Type: IR Prestige21) were used to determine the functional group of PVA/Chitosan/TiO<sub>2</sub> nanofiber. The nanofibers surface morphology was studied using SEM (FEI, Type: Inspect-S50). Image processing software was used for measuring the diameter of the nanofibers captured in the SEM micrograph. The EDAX used to investigate the content elements of electrospun fibers, especially presence of TiO<sub>2</sub> nanoparticle on the fibers.

### 3. Results and discussion

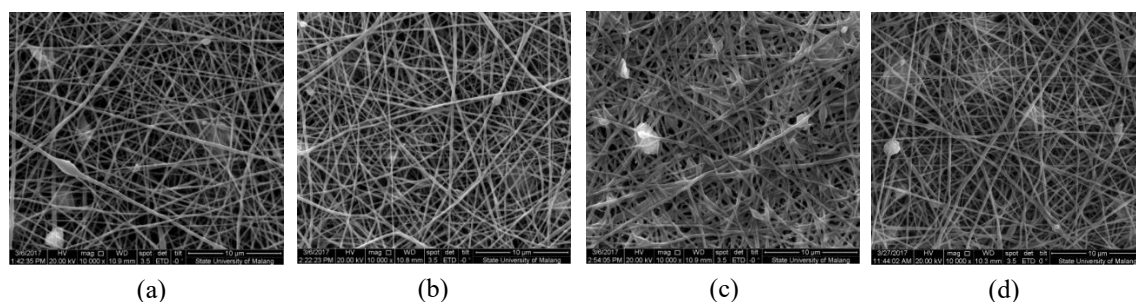
The FTIR spectra of PVA/TiO<sub>2</sub>/Chitosan nanofiber with various stabilization method are shown in Figure 1. The FTIR spectra for all sample is same. The Broadband at 3200-3550 cm<sup>-1</sup> indicates the O-H stretching. The peaks at 2931.8 cm<sup>-1</sup> indicate C-H- stretching. The peaks at 1342.46 cm<sup>-1</sup> indicate the CH banding. The broad absorption bands at 1095.57 cm<sup>-1</sup> indicate the C-O stretching [10]. The peaks at 856.39 cm<sup>-1</sup> were assigned C-C vibrations of PVA [22]. The chitosan vibration occurs in the broadband at 3425.58 cm<sup>-1</sup> which is due to the OH stretching. The band at 1573.91 cm<sup>-1</sup> is assigned for the NH bending (amide II) (NH<sub>2</sub>) while the small peak at 1658.78 cm<sup>-1</sup> indicates the C=O stretching (amide I) O=C-NHR. The bands at 2924.09 cm<sup>-1</sup> were assigned C-H stretching [23]. The band at 1381.03 cm<sup>-1</sup> is due to CH<sub>3</sub> wagging. The vibrational band observed at 2924.09 cm<sup>-1</sup> is associated with the C-H stretching from alkyl groups. The absorption corresponding to the C-O stretching occurs at 1080.14 cm<sup>-1</sup>, and broadband around (550 to 800) cm<sup>-1</sup> is attributed to the Ti-O-Ti band [24].



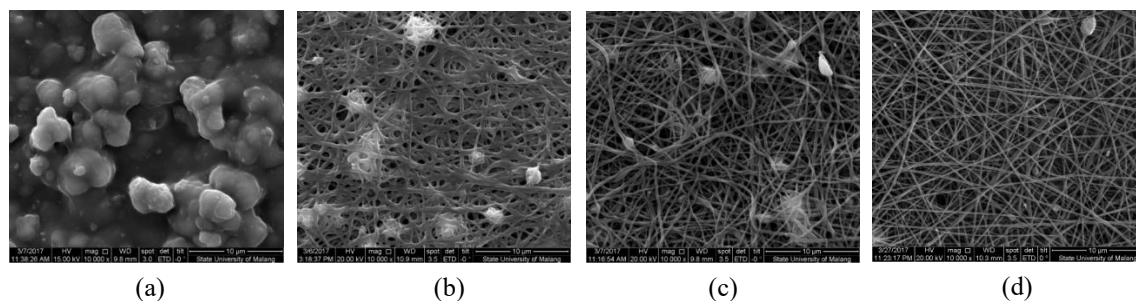
**Figure 1.** FTIR spectra of PVA/TiO<sub>2</sub>/Chi nanofibers (a) without stabilization (b) heat treatment, (c) GA crosslink with ethanol, (d) GA crosslink with acetone.,

Effect of stabilization method regarding FTIR results seen at wavelengths around 1720 cm<sup>-1</sup> and 1095 cm<sup>-1</sup> (area III and IV). The PVA/TiO<sub>2</sub>/Chi nanofibers with the GA crosslink show a new peak at the wavelength of 1720 cm<sup>-1</sup>, this peak indicates the presence of C = O stretching of GA and 2870 cm<sup>-1</sup> (area II) C-H stretching of GA. While The PVA/TiO<sub>2</sub>/Chi nanofibers without stabilization and heat treatment the fibers do not show up. In The PVA/TiO<sub>2</sub>/Chi nanofibers with crosslink GA, there was a shift from 1095 cm<sup>-1</sup> to 1141 cm<sup>-1</sup>. It indicates the interaction between C-O from PVA and C-O from GA [25].

PVA is readily soluble in water, so the PVA/TiO<sub>2</sub>/Chitosan nanofiber is also readily soluble in water and will be damaged if it is used for applications in water. Therefore, this research is preserved/stabilized so that the resulting nanofiber will be stable/insoluble when applied to the liquid, especially for photocatalytic application. In this study there are several stabilization methods used are heat treatment and GA crosslink. The SEM image of PVA/TiO<sub>2</sub>/Chitosan nanofibers with various stabilization method is shown in Figure 2. Figure 2 shows that the PVA/TiO<sub>2</sub>/Chitosan nanofiber with heat treatment is compacted and has a smaller diameter, while the crosslink GA nanofiber results in wrapping so that the resulting fiber has a larger diameter. Nanofiber results of crosslink GA by using acetone solvent have a cleaner surface than those using ethanol solvent.

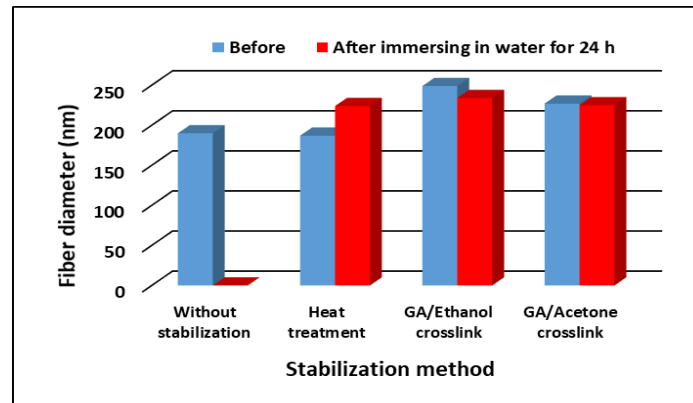


**Figure 2.** SEM image of PVA/TiO<sub>2</sub>/Chi nanofibers before immersing in water (a) without stabilization (b) heat treatment, (c) GA crosslink with ethanol, (d) GA crosslink with acetone.



**Figure 3.** SEM image of PVA/TiO<sub>2</sub>/Chi nanofibers after immersing in water for 20 days (a) without stabilization (b) heat treatment, (c) GA crosslink with ethanol, (d) GA crosslink with acetone.

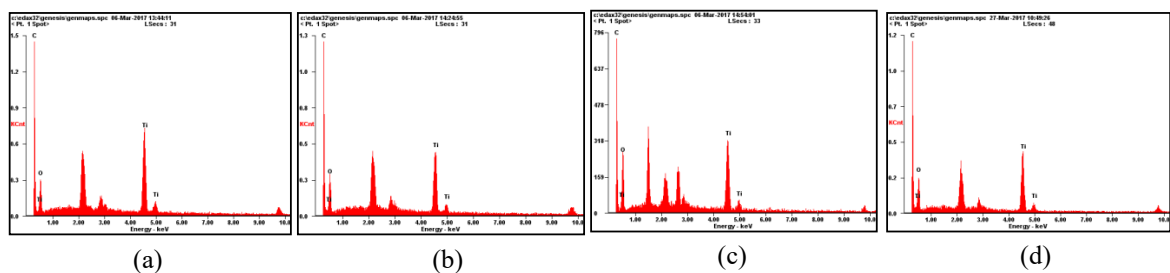
The stabilized nanofiber was tested for water resistance by immersing in water for 24 h. Figure 3a showed that the nanofiber without stabilization dissolves in the water so that none of the fibers are visible and only particles of TiO<sub>2</sub> in the gel solution are visible. Nanofiber with heat treatment has low stability, as shown in Figure 3b the fibers still exist but it starts to deteriorate and swell due to water uptake. Nanofibers with heat treatment do not dissolve after soaking but present a certain degree of aggregation and swelling, which indicates that heat treatment can improve the water stability of fibers as well as the degree of physical stabilization and crystallization [1]. Nanofiber with crosslink GA has high stability as shown in Figure 3c and Figure 3d. The fiber is still intact with the same morphological form as before soaked in water, no damage at all in fiber. Stabilization with crosslink GA has high stability. Chemical crosslinking of PVA nanofibers treated in GA/methanol shown in this work is apparently more useful in stabilizing them against disintegration in water [26]. It is considered to be applied in the fiber because fiber will be used for photocatalyst application which directly contacts to water.



**Figure 4.** Fibers diameter of PVA/TiO<sub>2</sub>/Chi nanofibers before and After immersing in water for 20 days with various stabilization method.

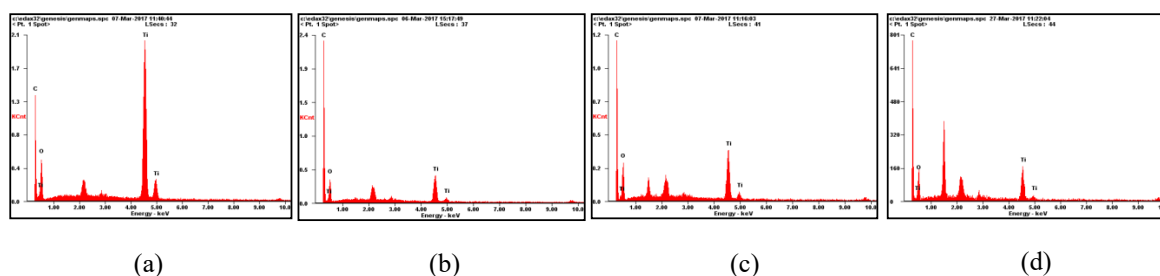
The result of the diameter analysis is shown in Figure 4. The nanofiber without stabilization has a diameter of 190 nm, and after being soaked for 20 days, one of fiber diameter is detectable. Nanofiber with heat treatment has a diameter of 187 nm, and after soaked for 20 days, the diameter of the fiber enlarged about of 224 nm because of fiber have swelling due to immersion in the water. Nanofiber with a crosslinked acid with ethanol as a solvent having a diameter of 249 nm, and after being soaked for 20 days, the fiber diameter decreased to 234 nm, this is because most of the GA did not react in the crosslinking process dissolved in the water during immersion. Nanofiber with a crosslinked acid with ethanol as a solvent having a diameter of 227 nm, and after soaking for 20 days, the fiber diameter has not changed in size. It shows the high stability of this nanofiber.

The EDAX was used to investigate the content elements of electrospun fibers. EDAX result of the PVA/TiO<sub>2</sub>/Chi composite nanofibers before water-immersion tested is shown in Figure 5 and after water-immersion tested is shown in Figure 6. The summary results are listed in Table 1.



**Figure 5.** SEM-EDAX of PVA/TiO<sub>2</sub>/Chi nanofibers before immersing in water (a) without stabilization (b) heat treatment, (c) GA crosslink with ethanol, and (d) GA crosslink with acetone.





**Figure 6.** SEM-EDAX of PVA/TiO<sub>2</sub>/Chi nanofibers after immersing in water (a) without stabilization (b) heat treatment, (c) GA crosslink with ethanol, and (d) GA crosslink with acetone

**Table 1.** Summary of EDAX of PVA/TiO<sub>2</sub>/Chi nanofibers before and after immersing in water.

SEM-EDAX	without stabilization	heat treatment	GA crosslink with ethanol	GA crosslink with acetone
<b>Before immersing in H<sub>2</sub>O</b>				
<b>C</b>	49.23 %	50.47 %	44.51 %	58.95 %
<b>O</b>	26.86 %	29.87 %	36.30 %	28.28 %
<b>Ti</b>	23.90 %	19.66 %	19.19 %	12.77 %
<b>After immersing in H<sub>2</sub>O</b>				
<b>C</b>	30.90 %	62.83 %	53.65 %	58.55 %
<b>O</b>	29.94 %	25.06 %	30.49 %	28.68 %
<b>Ti</b>	39.16 %	12.12 %	15.86 %	12.77 %

The elemental analysis reveals the presence of TiO<sub>2</sub> nanoparticle on the fibers, the element ratio of C, O, and Ti for PVA/TiO<sub>2</sub>/Chi nanofibers before stabilization are 49.23 %, 26.86 %, and 23.90 % respectively in the entire area of PVA/TiO<sub>2</sub>/Chi nanofibers. It proves that the nanofiber is containing TiO<sub>2</sub>. Results of EDAX nanofiber PVA/TiO<sub>2</sub>/Chi without stabilization showed that the Ti composition increased from 23 % to 39 % while the composition C decreased after immersion. It suggests that after immersion some of the polymer (PVA) dissolves in water and the fibers become damaged so that the remaining ones are TiO<sub>2</sub> which is enveloped in a gel solution of PVA. The results of EDAX nanofiber PVA/TiO<sub>2</sub>/Chi with heat treatment stabilization method showed that the Ti composition decreased from 19 % to 12 % while the composition C increase from 50 % to 62 % after immersion. This suggests that after partial immersion of the polymer (PVA) absorbs water so that it is swelling and the diameter of the fiber enlarges and the fiber swells. Results of EDAX nanofiber PVA/TiO<sub>2</sub>/Chi with GA crosslink stabilization method show that the composition of Ti and C and O is relatively fixed. It shows that before and after immersion of fiber condition still no change of composition nor change of surface morphology of fiber. It shows that nanofiber PVA/TiO<sub>2</sub>/Chi with GA crosslink stabilization method has high stability when applied in water.

#### 4. Conclusions

The PVA/Chitosan/TiO<sub>2</sub> nanofibers were successfully stabilized in water with various stabilization method. The SEM results show that the nanofiber formed with a smooth surface with a diameter of 190 nm and has grains of TiO<sub>2</sub> particles in it. These results are supported by EDAX results which show a high TiO<sub>2</sub> content in fiber reaching 23 %. The SEM result shows that after immersing in water for 24 h, PVA/Chitosan/TiO<sub>2</sub> nanofibers without stabilization rapidly shrink and dissolve after dipped in water and finally form transparent gel shape material with a grain of TiO<sub>2</sub> nanoparticle. PVA/Chitosan/TiO<sub>2</sub> nanofibers with heat treatment don't dissolve after immersing but present a

certain degree of aggregation and swelling, which indicates that heat treatment can improve the stability of the fiber but still low. While PVA/Chitosan/TiO<sub>2</sub> nanofibers with GA crosslink don't dissolve and no change form of the fiber after immersing 24 h and same as before immersing. It indicates that PVA/Chitosan/TiO<sub>2</sub> nanofibers with GA crosslink have excellent stability in water. Nanofiber with GA crosslinks has better morphology when using acetone as a solvent than ethanol. The nanofiber stabilization results indicate that the stabilization method with GA crosslink is proven to have high resilience or stability in the water, which will be very useful for maintaining fiber durability when used for photocatalytic applications.

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