

Fabrication and Characterization of PVC-Based Nanofiber Membranes for Water Filtration Application

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Abstract

Polyvinyl chloride (PVC) dissolved in N-dimethylacetamide (DMAC) and filled with polyvinyl pyrrolidone (PVP) has been studied for water treatment applications due to the material being hydrophobic, rigid, and biodegradable. However, it does not have antibacterial properties. The chitosan nanoparticles (CSNPs) as a natural antibacterial polymer are added into PEO/PVC blend to fabricate nanofiber membranes for well water filtration. We investigate the effects of adding PEO and CSNPs to PVC on the morphology, tensile properties, water contact angle, and water filtration efficiency of the nanofiber membranes. The PEO-PVC polymer solutions are dissolved in DMAC by varying concentrations of 0, 1, 2, 3, and 4% PEO (w/w), then fabricated to be the nanofiber membranes by the electrospinning technique. The PEO/PVC membrane's contact angle decreases with the PEO concentration and by adding 1% CSNPs. This trend aligns with the average nanofiber diameter but is opposite to the tensile strength. The 1% CSNPs/4% PEO/PVC membrane has shown 78% and 92% efficiency in filtering Coliform and Colitinja bacteria in the well water, respectively.

INTRODUCTION

Water is one of the vital human demands in daily life, especially water for cooking and drinking must be bacteria or pollutant free. In recent years, water contamination has become a severe problem that we must be aware of because numerous people can die from unsafe water. The water problem is increasing globally annually due to population and industrialization (Homaeigohar & Elbahri, 2014; Tlili & Alkanhal, 2019), which leads many people to have insufficient access to clean water, particularly in developing countries in rural areas.

Related to the filtration system, the electrospun nanofibrous membrane can be an excellent chance to be the water filtration material. Some studies used nanofiber membranes as air (Sosiati et al., 2022^a) and water (Ma & Hsiao, 2018; Tang et al., 2022) filter applications. In this case, the outstanding properties of nanofiber membranes are a high surface area-to-volume ratio and high porosity with an average nanofiber diameter ranging from 100 nm to 500 nm. However, the nanofiber membrane must not be fully hydrophobic or super-hydrophobic for water filter applications.

It is well known that polyvinyl chloride (PVC) is used for various applications, including the filtration system (Pham et al., 2021). The natural properties of the chloride functional group make PVC super-hydrophobic (Chen et al., 2009), leading to pure PVC cannot be used for water filtration. In this case, PVC is dissolved in some solvent types, such as dimethylacetamide (DMA), dimethylformamide (DMF), and tetrahydrofuran (THF) (Grause et al., 2017). The electrospun nanofiber membrane of PVC dissolved in DMAC results in a high-water contact angle of 135° (Alarifi et al., 2018). To use PVC as water filter materials, adding hydrophilic materials are required.

Research has been carried out on the electrospun nanofiber membrane of polyvinylpyrrolidone (PVP)/PVC for water filtration (Alarifi et al., 2018; Asmatulu et al., 2013; Bhran et al., 2018). Adding PVP to PVC was varied

by 0, 2, and 5 wt.%. PVP is a water-soluble material. Therefore, adding PVP reduced the water contact angle of the PVP/PEO nanofibrous membranes from 135.23° to 129.81° and then 123.25°, leading to its use for water filtration Alarifi et al. study (2018). Another study of PVP/PVC nanofiber membranes by adding PVP of 2, 3, 4, and 5 wt.% (Asmatulu et al., 2013) had a similar trend in reducing the water contact angle to the (Alarifi et al., 2018) study. However, the membrane with 5 wt.% PVP in PVC resulted in a water contact angle of around 16°, much lower than that from the Alarifi et al. study (2018). Those studies utilized DMAC as a PVC solvent, and their PVP/PVC membranes were used to filter dam water, wastewater (Alarifi et al., 2018), and lake water (Asmatulu et al., 2013). They explored turbidity, total suspended solids (TSS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD₅). They indicated that the nanofiber membrane has potentially been used as a water filter medium and to good challenge to replace RO partially (Alarifi et al., 2018). The nanofiber membrane, with a 16° water contact angle, makes it potentially perfect for water filtration and preventing contaminants in many wastewaters (Asmatulu et al., 2013). Additionally, the PVP/PVC nanofiber membranes in which PVC was dissolved in THF resulted in water contact angles of approximately 38° for the membrane with 4 wt.% PVP in PVC and 70° for the membrane without PVP (Bhran et al., 2018). This study showed that the membrane with 4 wt.% PVP has better tensile properties than those without PVP, but both membranes have almost similarly high total dissolved solids (TDS) efficiency of around 98%. However, higher hydrophilicity and porosity belonging to the membrane with PVP make it better than the other one.

According to those previous reports, no study has added antibacterial and hydrophilic materials to PVC. PVC tends to be stiff and brittle. Therefore, the present work has added polyethylene oxide (PEO) to PVC because PEO is a hydrophilic polymer (Rošic et al., 2011) and has high tensile strain (Sosiati et al., 2022^a). Besides, chitosan nanoparticles (CSNPs) were also added to PEO-PVC, which is well-known that chitosan has excellent antibacterial properties (Felt et al., 1998). We have explored the nanofibrous membranes made of PVC, PEO/PVC, and CSNPs/PEO/PVC to filter well water. This study evaluated the water contact angle, tensile properties, and efficiency in inhibiting Coliform and Colitinja bacteria and compared them to the previous results.

EXPERIMENTAL METHOD

PVC (high molecular weight) and PEO (Mw: 100 g/mole) were purchased from Sigma Aldrich (USA). While N, N-Dimethylacetamide (DMAC), and chitosan nanoparticles (CSNPs) (~ 50 nm) were supplied from EMSURE, Germany, and ANHUI MINMETALS DEVELOPMENT I/E Co., Ltd, China, respectively. The particle size was confirmed by transmission electron microscopy (TEM) (Sosiati et al., 2022^b) and the CSNPs are present as a semicrystalline phase.

PVC was dissolved in DMAC at a ratio of 15: 85% (w/w) and continued by mixing them on a hot plate stirrer at 400 rpm and 60°C for an hour, then cooled to room temperature. This solution is ready to run in an electrospinning machine used as an initial state. After that, PEO was dissolved in water at a 4% concentration. The PEO and PVC solutions were blended with PEO concentrations of 1, 2, 3, and 4 (wt.%), conducting at the same condition as the PVC solution. Besides, adding CSNPs to the PEO/PVC solution was performed after evaluating the PEO/PVC nanofiber membrane's water contact angle. In this case, 1 wt.% CSNPs were added to PEO/PVC having the smallest contact angle. All the polymer solutions were prepared to be the nanofiber membranes by an electrospinning technique, operating at a CD voltage of 15 kV, needle tip and collector distance (TCD) of 14 cm, and a needle diameter of 0.8 mm.

The nanofiber membrane's water contact angles were measured and evaluated. The evaluation result was then used as base data for making the CSNPs in the PEO-PVC solution. As a result, there are three nanofiber membrane specimens: i.e. PVC, PEO/PVC, and CSNPs/PEO/PVC. Their tensile test was conducted following

the ASTM D882 using a universal testing machine (UTM, Zwick 0.5), and seven membrane specimens were made for each case. At the same time, scanning electron microscopy (SEM, JSM 6510) was used to examine nanofiber morphology. The nanofiber diameter measurement was on a 100-nanofiber for each membrane specimen by ImageJ software.

The water filtration was conducted only on the CSNPs/PEO/PVC membrane using a simple apparatus for low-pressure filtration (Fig.1) to filter Coliform and Colitinja bacteria contained in well water to measure the efficiency of inhibiting the bacteria. Water was obtained from a well in Yogyakarta, Indonesia (Fig.2). 100 ml of the well water was filtered for around 7 hours because the nanofiber structure of the membrane seemed dense. In this case, SEM was used to characterize the CSNPs/PEO/PVC membranes before and after water filtration. At the same time, 100 ml of the filtered water was subjected to the water test to determine the water filtration efficiency, calculated by the following equation.

$$\eta = (N_{\text{after}}/N_{\text{before}}) \times 100\% \quad (1)$$

where η is the water filtration efficiency, and N_{after} and N_{before} are the number of bacteria after and before filtration (MPN), respectively. MPN is a unit of the most probable number.



Figure 1. Water filtration apparatus



Figure 2. Well, as a water source of water filtration test

RESULTS AND DISCUSSION

Figure 3 shows the difference in water contact angle of PVC, PEO/PVC, and CSNPs/PEO/PVC, and Table 1 summarizes their measurement results. The contact angle value of the PVC membrane is the highest (134.46°), almost similar to that resulting in a previous study (135.23°) (Alarifi et al., 2018), leading to a superhydrophobic one. Adding PEO to PVC by 1, 2, 3, and 4% gradually decreased the water contact angle and reached the smallest contact angle of 96.11° by adding 4% PEO, meaning the membrane becomes partially hydrophilic. However, this achievement was higher than the earlier study (Asmatulu et al., 2013), which added 4% PVP to PVC: i.e., 58.51°, and reached a very small contact angle of 16.12° by adding 5% PVP to PVC. Another study (Alarifi et al., 2018) showed a higher value of 123° for a similar condition. Adding 5% PEO to PVC could not be conducted in the current study because the viscosity of the polymer solution was too high, leading to impossible running by electrospinning. According to the results (Table 1), the PVC, PEO-4%/PVC, and

CSNPs-1%/PEO-4%/PVC membranes were chosen to compare their nanofiber morphologies, mechanical properties, and filtration efficiency based on the hydrophilicity of the membrane.

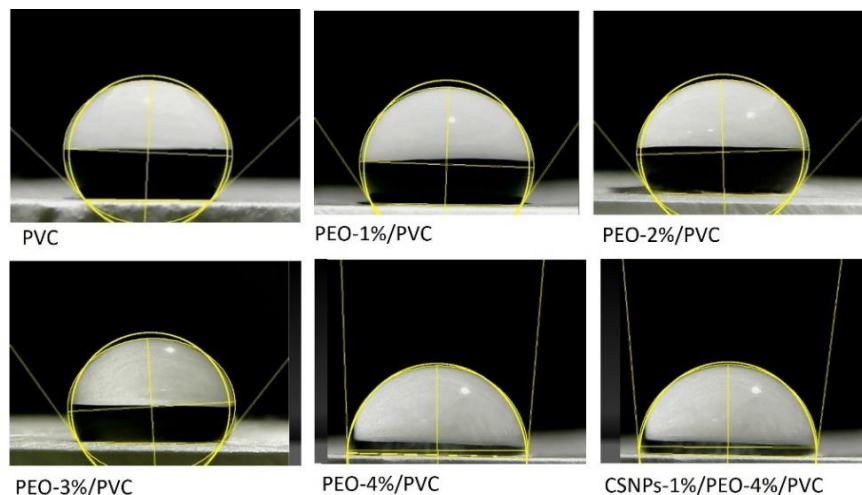


Figure 3. Water contact angles of the PVC-based nanofiber membranes

Table 1. The contact angle values for all membrane specimens

No	Membrane specimens	Average contact angle (°)
1	Neat PVC	134.46
2	PEO-1%/PVC	129.53
3	PEO-2%/PVC	124.50
4	PEO-3%/PVC	117.26
5	PEO-4%/PVC	96.11
6	CSNPs-1%/PEO-4%/PVC	94.18

Figure 4 depicts SEM images of their nanofiber morphologies. The fibers show a uniform distribution and are continuously straight, especially after adding PEO and CSNPs + PEO to PVC. But a few beads formed in the PEO/PVC membrane, which differs from the fiber morphology formed in the PVP/PEO membrane studied by (Asmatulu et al., 2013), which was not continuously straight. Fiber morphology has a correlating effect on the mechanical property of the membrane. The average fiber diameter (Fig. 5) shows that the fiber size of the PVC membrane is considerably larger (~500 nm) than those of polyvinyl alcohol (PVA) (Sosiati et al., 2022^c and PEO (Sosiati et al., 2022^b) because PVC solution tends to be more viscous than PVA and PEO. Introducing PEO to PVC reduces the fiber diameter and further decreases by adding CSNPs (Fig.5). In this case, CSNPs could significantly diminish the fiber diameter of CSNPs/PEO nanofiber membranes, as reported in our previous study (Sosiati et al., 2022^b).

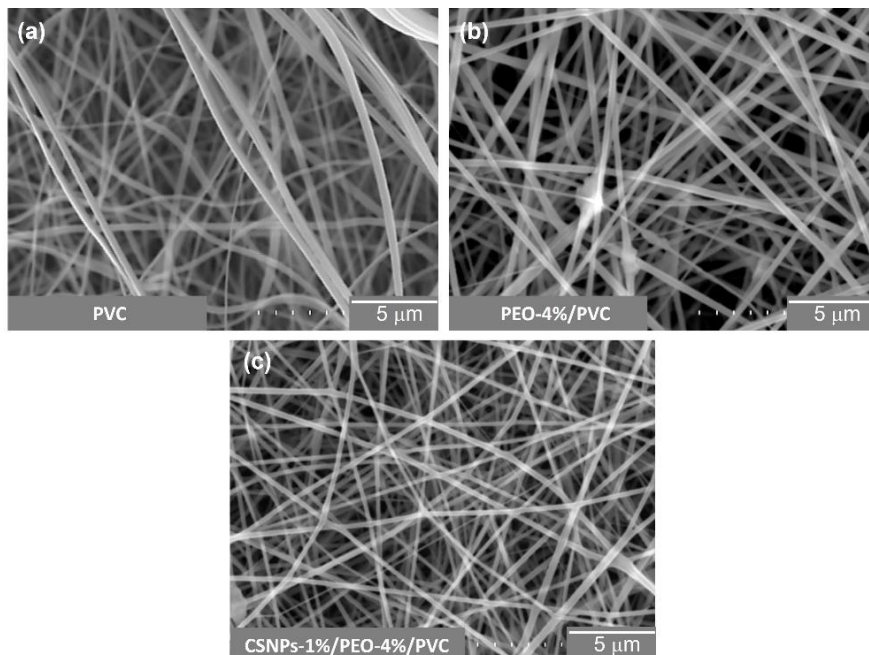


Figure 4. SEM micrographs of fiber morphologies formed in PVC (a), PEO-4%/PVC (b), and CSNPs-1%/PEO-4%/PVC (c) nanofiber membranes

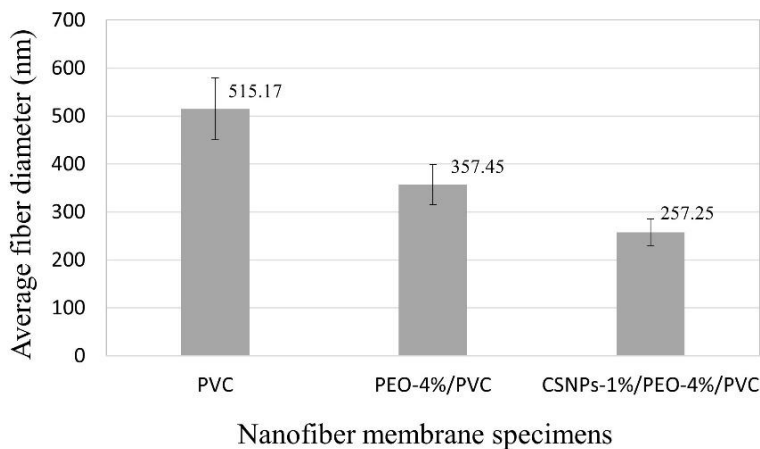


Figure 5. The average fiber diameter of the nanofiber membrane specimens

The membrane’s tensile properties (Fig. 6) show that the tensile strength increases by adding PEO to PVC and further increases by adding CSNPs to PEO-PVC. These changes are attributed to the fiber morphology and diameter in Fig. 4 and Fig. 5, respectively. The smaller the average fiber diameter, making the chance to form a higher density of cross-linked fiber and the higher the tensile strength of the membrane. The higher tensile strain of the PEO-4%/PEO membrane than the PVC membrane was due to the high PEO tensile strain (Sosiati et al., 2022^a), and the rigidity of CSNPs led to reducing the tensile strain and enhancing the CSNPs-1%/PEO-4%/PVC membrane’s stiffness.

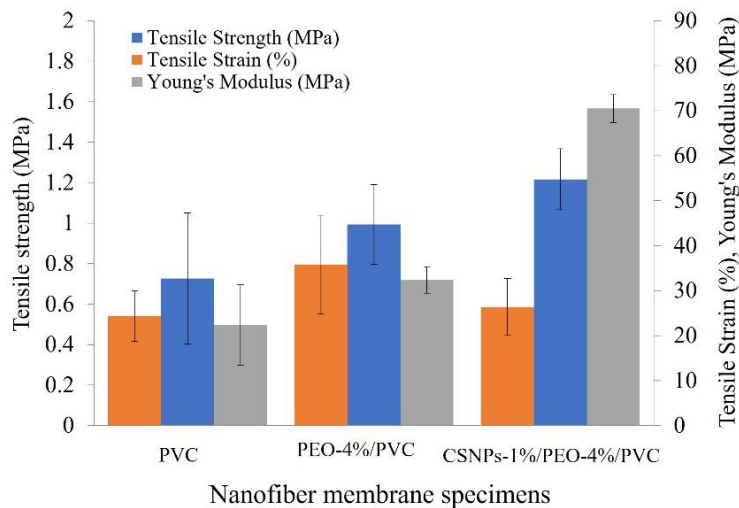


Figure 6. Tensile properties of the nanofiber membrane specimens

Based on those results, the PEO-4%/PVC and CSNPs-1%/PEO-4%/PVC membranes are hydrophilic and can filter water under low pressure. However, by considering the membrane's ability to inhibit the bacteria's activity, the CSNPs-1%/PEO-4%/PVC membrane was applied to filter the well water, and the result is shown in Table 2. Evaluating the filtration efficiency in inhibiting the Coliform and Colitinja bacteria resulted in ~ 78% and ~ 92%, respectively.

Table 2. The results of the water purification test of CSNPs-1%/PEO-4%/PVC membrane

Water specimen	Before the water filtration test		After the water filtration test	
	Coliform bacteria (MPN/100 ml)	Colitinja bacteria (MPN/100 ml)	Coliform bacteria (MPN/100 ml)	Colitinja bacteria (MPN/100 ml)
The well water	≥ 1600	≥ 1600	350	150

After water purification, the surface morphology of the CSNPs-1%/PEO-4%/PVC membrane shows the presence of microorganism-like bacteria (Fig. 7). The bacteria size is around 2–3 μm , relatively small. Therefore, other bacteria may be inside the membrane because the electrospun membrane was formed in layers. Although the number of filtered bacteria was considerably high, filtered water quality still needs to be included in the standard of hygiene sanitary water. The quality standard requires 50 MPN/100 ml Coliform and 0 MPN/100 ml Colitinja bacteria in the water. The filtration efficiency resulting in this study indicates the potential use of the membrane as the water filter material. However, the membrane's wettability should be improved to reduce the filtration test time and to achieve the filtered water quality included in the hygiene standard by repeating the filtration process.

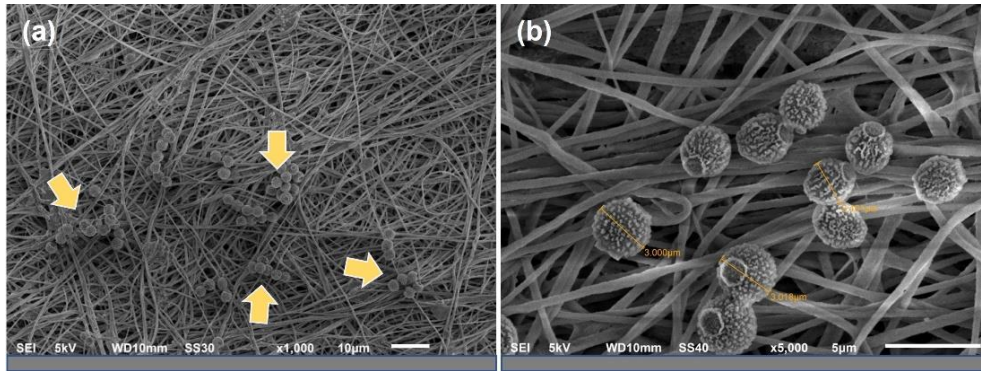


Figure 7. SEM micrographs of the microorganism-like bacteria's morphology on the CSNPs-1%/PEO-4%/PVC membrane in a low magnification (a) and higher magnification showing evident surface morphology (b)

CONCLUSION

Adding 1% CSNPs and 4% PEO to PVC reduced the fiber's diameter, increasing the nanofiber membrane's hydrophilicity and tensile properties. At the same time, the tensile strain decreased due to the brittle nature of chitosan. The smaller the average fiber's diameter led to improving the membrane's tensile strength and modulus.

The considerably high-water filtration efficiency achieved by the CSNPs-1%/PEO-4%/PVC membrane to filter Coliform and Colitinja bacteria suggests its potential use as the water filter material. However, improving the membrane's wettability is required to diminish the filtration test time and to achieve the filtered water quality included in the hygiene standard.

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