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# The Influence of Photoinitiator on the Characteristics of Electrospun Poly (vinyl alcohol)/Chitosan Based Nanofibers

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Abstract. Poly (vinyl alcohol)/chitosan (PVA/CS) based nanofibers have non-toxic, compatible and antimicrobial properties that can be used in various applications. This research focused on the impact of benzophenone (BP) as a photoinitiator on the characteristics of electrospun PVA/CS based nanofibers. The electrospun PVA/CS nanofibers were crosslinked by the combination of immersion in glutaraldehyde (GA) solution and UV light irradiation with/without the addition of BP. The influence of BP was studied by scanning electron microscopy (SEM), fourier transform infrared (FTIR) spectroscopy, and pure water permeability analysis. The results showed that the average diameter and swelling degree of photocrosslinked nanofibers were decreased, while the pure water flux increased due to BP addition. FT-IR data confirmed that the BP was successfully blended with the presence of ketones group peak on 1655 cm<sup>-1</sup>. The change in morphology was observed by SEM investigations.

Keywords. Benzophenone, chitosan, electrospinning, nanofibers, and poly(vinyl alcohol).

#### 1. Introduction

Electrospinning has been rapidly developed in recent years because it can generate consistently polymer fibers ranging from tens to microns in diameter, depending on the polymer and processing conditions. The nanofibers prepared by electrospinning method have many advantages such as very large surface area-to-volume ratio, high porosity with very small pore size and malleability to produce different morphologies [1,2]. Due to these advantages, electrospun nanofibers have widely been investigated in the last ten years for biomedical, sensors, filter media, electrochemical energy storage and other industrial applications [2–6].

An electrospinning system consists of three major components, (i) a high voltage power supply, (ii) a spinneret, and (iii) a grounded collecting plate [2]. In an electrospinning process, a high voltage is applied to the tip of the polymer solution or melted polymer. As the intensity of the electric potential is increased, the droplet formed at the tip deforms into a conical shape. Once polymer surface tension at the top of the cone is reduced to a critical level, an electrically charged jet of fine fluid is ejected. The solvent within the ejected solution begins to evaporate, or the polymer melt begins to solidify. As a result, nanofibers are produced and eventually deposited on a grounded collector [7].

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Chitosan (CS), a (1-4)-linked 2-amino-2-deoxy-ù-D-glucopyranose, is one of the most abundant natural polysaccharides. It has excellent biocompatibility, biodegradable property, nontoxicity and ease of solubility in organic acids [1]. However, electrospinning of pure chitosan has some constraints, such as difficult to form continuous fiber jets during electrospinning. This is due to the repulsive forces between the ionic groups and high surface tension of the polymer solution as a result from the high viscosity of chitosan even in moderate concentration [7]. To overcome this constraint, chitosan is commonly blended with another synthetic polymer prior to electrospinning, e.g., poly(vinyl alcohol) (PVA). PVA is a non-toxic, water-soluble, biocompatible, and biodegradable synthetic polymer, which is widely used in the biomedical field. PVA has a high fiber forming and hydrophilic properties [1,8].

In this study, PVA/CS blend nanofiber membranes were prepared by electrospinning method. In order to improve stability, PVA/CS nanofibers were further treated by the post-treatments. The electrospun PVA/CS nanofibers were crosslinked by the combination of immersion in glutaraldehyde (GA) solution and UV light irradiation with/without the addition of BP.

#### 2. Materials and methods

#### 2.1. Materials

Polyvinyl alcohol (Mw =130.000 g/mol, 99 % hydrolyzed) and glutaraldehyde solution (1% in water) were purchased from Sigma Aldrich. Chitosan (Mw = (1,680,000 to 1,750,000) g/mol, 80.4% deacetylated) was purchased from local Indonesian company. Benzophenone was purchased from Fluka Analitycal, while acetic acid was purchased from Merck Chemical.

#### 2.2. Electrospinning and Post-treatment

PVA solution with 6 wt%, 7 wt%, and 8 wt% concentrations were prepared using distilled water at 80 °C and stirred for 2 h. A 2 wt% chitosan solution using 2 % acetic acid aqueous solution was also prepared. These two solutions were subsequently mixed with PVA/chitosan ratio was 3:1.

Electrospinning of the polymer solutions was carried out using Nachriebe 600 Electrospinning by a set-up consisting of a syringe (3 mL) and needle (3-cm long and flat tip), a ground electrode and a high voltage supply (18 kV). Polymer solutions were electrospun at a feeding rate of 0.7 mL/h and a tip-to-collector distance of 12 cm. A grounded stationary rectangular metal collector covered by a piece of aluminum foil was used for the nanofibre deposition. In the post-treatment experiments, electrospun PVA/CS nanofibres were immersed in 3 % glutaraldehyde solution for 2 h at room temperature. Then the treated samples were dried at room temperature for 24 h. The dried samples were exposed to UV light at 256 nm wavelength with or without addition of benzophenone.

#### 2.3. Characterization

The viscosity of the polymer solutions was measured using Brookfield DV-E viscometer with spindletype 5 at 50 rpm. The morphology of the electrospun PVA nanofibers was characterized using scanning electron microscopy (SEM, JEOL-JSM 6510LA). Fiber diameters were determined using Image J (IJ 1.46r) software. They were measured by drawing lines perpendicular to the fiber axis on the SEM images. The pixel values of the lies were converted to diameter values. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using IRPrestige-21 Shimadzu spectrometer. The permeability of nanofiber membrane was measured using amicon cell with dead-end filtration mode at a pressure of 0.3 kg/cm<sup>2</sup>.

### 3. Results and discussion

### 3.1. Effect of PVA/CS Concentration on Viscosity of Electrospinning Solution

Blending of chitosan and PVA electrospinning solution directly affected the resultant properties of the solutions. Figure 1 shows the dependence of the viscosity on its concentration. It was found that its

viscosity increased linearly with increasing concentration. This result is in accordance with what has been conducted by Paipitak *et al.* [8]. This result is essential for the optimization of nanofiber formation of this composite material.



Figure 1. The viscosity of PVA/CS electrospinning solution as a function of PVA concentration.

3.2. Effect of PVA/CS Concentration and Photoinitiator on Morphology of Electrospun Nanofibers SEM micrographs and fiber diameter distribution histograms of the nanofibres result are presented in Figure 2. We found that increasing the viscosity increased the average diameter of the fiber. Similar results were reported by several authors [9,10]. The higher onentration used, the thiker average diameter was resulted, i.e., 222 nm, 315 nm and 461nm for PVA 6 %, 7 %, and 8 %, respectively.

Electrospun nanofiber with PVA concentration of 7 % had a narrower size distribution compared to 6 % and 8 % concentrations. It means PVA 7 % nanofiber had more homogenous fiber diameters. However, the addition of concentration led to increasing bead sizes in electrospun nanofiber.



**Figure 2.** SEM images of the samples after electrospinning and fiber diameter distribution histograms (left to right: 6 %, 7 %, and 8 % concentration)

Post-treatment of the PVA/chitosan nanofibers with glutaraldehyde and UV irradiation showed morphological changes in the microstructure of the membrane (Figure 3). Combination of physical and chemical crosslink could affect the diameter of the fibers. This impact was shown by both post-treatments where mean fiber diameter decrease to 150 nm to 200 nm. In the other hand, addition of benzophenone as photoinitiator decreased the average diameter of the fibers. This phenomenon may be caused by benzophenone which initiates surface polymerization by giving a radical surface [11]. Major photocrosslink processes occurred on membrane surface causing shrinkage of fibers. The

radical surface from benzophenone allowed the photocrosslink process take places and reduced the average diameter of the fibers [12].



**Figure 3.** SEM images of the samples after post-treatment and fiber diameter distribution histograms (left to right, nonposttreatment; without photoinitiator; with photoinitiator)

#### 3.3. Effect of Photoinitiator on Permeability of Electrospun Nanofibers

It is seen from Figure 4 that the post-treatment caused membrane became insoluble in water. Hence permeability analysis could be investigated. The edge of nonpost-treatment membrane dissolved in the water, so the permeability analysis could not be examined. The results showed that the photoinitiator addition increased the permeability of the nanofibers. UV irradiation caused the polymer chain broke and formed free radical which led to cross-link reaction. The photoinitiator formed more free radical and the crosslinking process which led to the improvement of pore size of nanofibers and flux increase, respectively [13]. SEM results also confirmed that the electrospun nanofibers with the addition of photoinitiator have a larger pore size which leads to increase the water flux.



Figure 4. Permeability of water in nanofibers

3.4. Effect of Photoinitiator to Chemical Characteristic of Electrospun Nanofibers

The FTIR spectra exhibit overlapping broad bands of OH group and NH group at (3200 to 3600) cm<sup>-1</sup>, CH at ~2923 cm<sup>-1</sup>, CH<sub>3</sub> at ~1375 cm<sup>-1</sup>, CH<sub>2</sub> bend at ~1465, cm<sup>-1</sup>, and CN group at (1025 to 1200) cm<sup>-1</sup> which is characteristic of CS and PVA blend nanofiber (Figure 5). The peak of glutaraldehyde as post-treatment solution appears in 1643 cm<sup>-1</sup>. This band probably imine group that usually appears in ~1661 cm<sup>-1</sup>. This imine resulted from the reaction between the amine group in chitosan and the aldehyde group on the glutaraldehyde [14]. The IR spectra also show the increase in corresponding groups at

 $\sim$ 1993 cm<sup>-1</sup> that indicate ether/acetal (-COC) group. The appearance of the ether/acetal peak indicates that the acetylation reaction occurred between aldehyde and hydroxyl in the PVA [4]. The acetal groups peak as the sign of crosslinking process between PVA, chitosan, and glutaraldehyde appeared in 1140 cm<sup>-1</sup>. The addition of benzophenone as photoinitiator caused the appearance of 1655 cm<sup>-1</sup> peak which related to the presence of ketones group of benzophenone [10].



Figure 5. FTIR Spectra results of Electrospun nanofibers

#### 4. Conclusions

The electrospun PVA/CS nanofibers have been prepared. The increase in polymer viscosity increased the diameter of the fiber and formed larger beads. The addition of benzophenone as photoinitiator decreased the average diameter of the fibers. The photoinitiator addition increased the permeability of the nanofibers. FTIR analysis exhibited the existence of relevant functional groups of PVA, chitosan, glutaraldehyde, and benzophenone in the composites. The crosslinked structure was observed for the electrospun PVA/Chitosan nanofibers treated with benzophenone as a photoinitiator.

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