Synthesis and Characterization of Rotary Forcespun Polyvinylpyrrolidone Fibers Loaded by Garlic (*Allium sativum*) Extract

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**Abstract.** Garlic (*Allium sativum*) is one of the plants traditionally used for food supplement, natural medicine, and a food flavoring. Garlic has been proven to exhibit many important pharmacological activities that bring benefits for human health such as antioxidant, antimicrobial, antithrombotic, antihypertensive, cancer prevention, and lipid-lowering effects. However, the organosulfur compounds that contribute the previously mentioned activities have a high rate of degradability. In this paper, composite fibers of garlic extract encapsulated in polyvinylpyrrolidone (PVP) fibers are reported. The fibers were synthesized using the rotary forcespinning technique to protect organosulfur compounds from degradations and to maintain their antioxidant properties. The precursor solution was prepared by mixing 15% PVP in 50% ethanol (w/w) with garlic extract (GAE) in the ratio of 10:1, 10:3, and 10:5 (w/w). Microscopy images showed that the average diameter of fibers increases with increasing viscosity, which was the result of the higher polymer-to-extract ratio. All the fibers had smooth surfaces with no beads. The coefficient of variance (CV) of each fibers distribution was lower than 0.3, which marks the uniformity of the fibers formed. Analyses of the Fourier Transform Infrared (FT-IR) spectra proved some peak differences between the PVP fibers and the PVP fibers loaded with GAE, one of them is the peak at wavenumber 1034 cm⁻¹ indicating the presence of sulfoxide functional groups.

**Keywords:** polyvinylpyrrolidone, rotary forcespinning, garlic, composite fiber

1. **Introduction**

Garlic (*Allium sativum*) has been widely cultivated and used for culinary and medicinal purposes in many regions of the world for centuries. Garlic is rich of organosulfur derivatives such as allicin, diallyl disulfide, diallyl sulfide, and allixin, which are a group of volatile compounds that can be found in the Allium family (garlic, onion, leek, and chive) [1]. These organosulfur compounds are responsible for garlic’s typical flavor, aroma, and potential health benefits. These compounds contribute to garlic’s health beneficial properties: antimicrobial, antithrombotic [2], antihypertensive, cancer preventive, and lipid-lowering effects [3,4]. Apart from its high volatility and degradability, the problem of these
compounds in their use as functional food is their distinctive pungent aroma when consumed. This can potentially be eliminated or reduced by encapsulation using polymers [5].

Polyvinylpyrrolidone (PVP) is one of the synthetic excipients that is hydrophilic (nonionic) and is often used in pharmaceutical formulations. The advantage of using this material as a binding polymer is its small particle size, which ranges between 1-100 nm. Therefore it can pass through the filtration process in the kidney so that it does not accumulate in the body. PVP is also a biocompatible polymer that can produce stable compound associations with various active ingredients [6]. Another advantage of using PVP is that this polymer is easily soluble in a variety of solvents that can be consumed orally, such as water and ethanol [7].

As the carrier of medicinal materials, micro to nano-sized fibers have unique properties, mainly because of the high surface-to-mass ratio compared to ordinary fibers. These special properties make them suitable for a variety of medical applications, such as drug delivery systems, body tissue scaffolding, membrane filters, wound dressings, and consumer products [8]. Many techniques have been used to produce micro- to nano-sized fibers, one of them is the electrospinning technique. Electrospinning is probably the most studied nanofiber production method recently. Although this method is quite popular for the production of nanofibers, electrospinning is not the ideal method because it has a low production rate. Therefore, it is not suitable for the massive production of nanofibers. Moreover, because this method uses high voltage, the production process is sensitive to the conductivity of the precursor solution [9]. Therefore, it is not suitable for several natural extract solutions, which have a high conductivity.

Rotary forcespinning is another rapid method of producing fibers with high productivity, more stable jet, eco-friendly, and free from high voltage. Moreover, this method has the potential to be scaled up, can be used repeatedly, and can also control the diameter of the fibers it produces [10]. For producing micro or nano-sized fibers using the rotary forcespinning, a precursor solution is needed with a certain concentration of polymer. The working principle of rotary forcespinning uses a centrifugal force combined with hydrostatic pressure to force the precursor solution out of the reservoir nozzle to counter against the capillary force [11]. The high rotational speed of rotary forcespinning dries the precursor solution, producing the fibers in high production rate.

Several studies have used rotary forcespinning for producing styrofoam fibers [12, 13] and PVP-based fibers [11, 14], but micro- and nano-sized PVP:GAE fibers made by using the rotary forcespinning have never been reported. In this preliminary study, we obtained PVP fibers loaded with garlic extract (GAE) and characterized the fibers morphology, functional groups, and viscosity. The morphologies of PVP and PVP:GAE fibers were characterized by using a microscope. Fourier Transform Infra-Red (FT-IR) spectrometer was used to detect the presence of functional groups of PVP and PVP:GAE composite fibers. Viscosity measurement was also done to determine the effect of the solution viscosity on the diameter of the fibers formed.

2. Methods

2.1. Materials
Polyvinylpyrrolidone (PVP) with a molecular weight of 1,300,000 g mol⁻¹ was purchased from Sigma Aldrich, and ethanol analysis grade was purchased from Merck. Deionized water was obtained from the Department of Chemistry, Bandung Institute of Technology. Fresh single clove garlic (*Allium sativum*) was purchased from the local market in Bandung, Indonesia, and was stored at 4 °C.

2.2. Extraction of Garlic
Garlic extract (GAE) was prepared by using ethanol maceration technique. First, the garlic skin was peeled and separated from the cloves. Peeled garlic was washed with distilled water to remove the remaining dirt. Then, following the garlic extraction method demonstrated by Fujisawa et al. (2008), as much as 30 grams of garlic were crushed using a blender for 10 minutes. The crushed garlic was macerated for one to three nights at room temperature with 30 grams of ethanol 20% (w/w) [15]. The ethanolic garlic extract was centrifuged at 4,600 rpm for 30 minutes. The supernatant was then filtered.
using filter paper to get a clearer extract solution. The filtrate was collected and stored in the refrigerator for experimental use and FT-IR analysis.

2.3. Fabrication of Fibers
To obtain PVP:GAE composite fibers, PVP solution was made by dissolving PVP with a concentration of 15% (w/w) in ethanol 50% (w/w) as the solvent. The PVP and ethanol were stirred using a magnetic stirrer at 40°C until a homogeneous solution was acquired. The precursor solution was then made by mixing PVP solution with four variations of extract solution: a) PVP 15% as the control solution, PVP 15% loaded with garlic extract with a ratio of b) 10:1, c) 10:3, and d) 10:5 (w/w). The precursor solution was loaded into a 10 ml syringe. The solution was then loaded into a rotary forcespinning reservoir equipped with a 0.4 mm nozzle using a pump with a solution flow rate of 10 ml h⁻¹. The distance between the nozzle and the fiber collector was 4 cm. The fibers were synthesized in ambient temperature and humidity. The rotary forcespinning process lasted for approximately 30 - 60 minutes to obtain samples. The viscosity measurements of the precursor solutions were carried out by using Ostwald Viscometer (Fisher).

2.4. Characterization of Fibers
Morphology and diameter of the obtained PVP:GAE fibers were observed using an optical microscope (Trinocular, XSZ-107E) equipped with a camera (Hayear). Images of the fibers were obtained with a 400× magnification and captured for measuring the diameter of the fibers. Meanwhile, to identify the existing functional groups, the fibers and the garlic extract solution were subjected to Fourier Transform Infra-Red (FT-IR) spectrometer (Bruker, Alpha), recorded in the wavenumber ranging from 500 to 4000 cm⁻¹, and analyzed using Opus software.

3. Results and Discussion

3.1 Rotary Forcespin Fibers
Fiber syntheses from the PVP and PVP:GAE solutions have been successfully carried out using the rotary forcespinning technique. In the production process, there were two main parameters affecting the fibers’ morphology, such as solution parameters and process parameters. The solution parameters consisted of the concentration of the polymer and the extraction method. The process parameters were the rotational speed, flow rate, the diameter of the needle, the diameter of the nozzle, and the distance from the nozzle to the collector. All parameters were made constant, and only the concentration of the solution was varied, which affected the viscosity of the solution.

Figure 1 shows the microscopic image of the fibers synthesized using the rotary forcespinning technique with several polymers to extract ratios. It can be seen that, for all concentrations, the fibers formed had a smooth surface with no beads formed, and no aggregates formed. Table 1 shows the relationship between precursor solution, viscosity, and average diameter. Based on the fiber diameter measurement, it is known that PVP fiber has the highest average diameter, followed by PVP fibers which are loaded with garlic extract of 10:1, 10:3, then 10:5 (w/w), with consecutive average diameters of 1.58, 1.40, 1.38, and 1.22 μm. Each fiber has shown CV (Coefficient of Variance) lower than 0.3. Therefore, all the fibers were uniform.

Figure 2 shows the relationship between solution viscosity and average fiber diameter. It was found that a lower solution viscosity results in a smaller average fiber diameter. The fiber with the highest average diameter (PVP fiber) was obtained from the highest precursor solution viscosity, while the fiber with the lowest average diameter (PVP:GAE 10:5) was from the lowest precursor solution viscosity. The solution viscosity decreased with the increase of PVP to garlic extract ratio, this was due to the addition of solvent obtained from addition of the extract solution, therefore lowering the PVP concentration in the precursor solution. It has been known in other studies that viscosity has a reasonably consistent influence on fiber diameter. The viscosity of the solution itself has a role as a force to counter against the centrifuge force and capillary force that occurs in the rotary force-spinning technique to cause thinning and stretching of the solution [16].
Figure 1. Microscope images of the fibers at 400x magnification and fibers distribution curve of (a) PVP 15 wt%, PVP 15 wt% loaded with garlic extract with ratio of (b) 10 : 1, (c) 10 : 3, and (d) 10 : 5 (w/w).

Table 1. Characteristics of rotary forcespun fibers

| Precursor solution | Viscosity (cP) | $\bar{d}$ [μm] | CV     | Fibers’ homogeneity |
|--------------------|---------------|----------------|--------|---------------------|
| PVP                | 811.7         | 1.58 ± 0.30    | 0.19   | Uniform             |
| PVP:GAE 10:1       | 724.3         | 1.40 ± 0.25    | 0.18   | Uniform             |
| PVP:GAE 10:3       | 538.5         | 1.38 ± 0.27    | 0.20   | Uniform             |
| PVP:GAE 10:5       | 357.4         | 1.22 ± 0.24    | 0.20   | Uniform             |

Figure 2. The relationship between viscosity and fiber diameter.

Figure 3. FT-IR spectra (a) garlic extract (GAE) and PVP loaded by GAE (PVP:GAE) with ratios of (b) 10:5, (c) 10:3, (d) 10:1 (w/w), and (e) PVP.
3.2 FT-IR Characteristics of Fibers

FT-IR analysis was conducted to observe the functional groups available in PVP and PVP:GAE composite fibers and to prove that PVP:GAE fiber produced actually contains components of garlic extract. Figure 3(a) shows the FT-IR spectrum of garlic extract that has a broad peak at 3281-3391 cm⁻¹ representing an O-H stretching vibration of the solvent ethanol, water, and phenol [17]. The PVP fibers and PVP:GAE fibers also showed the same peaks at the same wavenumber but with smaller intensity, due to imperfect solvent evaporation when fabricating the fiber with the rotary forcespinning. The garlic extract loaded in PVP was dissolved in water and ethanol. Therefore the spectrum at these wavenumbers showed a very broad peak. There was also a peak detected in PVP and PVP:GAE samples at around 2919 cm⁻¹, which marks an O-H stretching vibration overlapping with C-H, indicating the presence of carboxylic acid and its derivatives. At the GAE sample, this peak did not appear, but was slightly visible and sticks to the broad peak next to it.

All samples had a quite sharp peak at wavenumbers of 1637-1650 cm⁻¹, which mark the presence of C=O stretching vibration, and indicate the presence of amide I band because of the peptide bond modulated by the secondary structure (α-helix, β-sheet, etc.) [18]. The peak for PVP and PVP:GAE with a ratio of 10:5 lies at 1650 cm⁻¹, meanwhile the peak for PVP:GAE with a ratio of 10:3 and 10:1 lies at 1648 cm⁻¹. This shift of peak could be caused by the presence of GAE component, in which the peak of the GAE lies at 1637 cm⁻¹.

In the PVP and PVP:GAE samples, there were several small peaks, but the most intense peaks were found at 1422 cm⁻¹ and 1287 cm⁻¹, and these peaks were only slightly detected in the GAE spectrum, where the highest intensity was at 1407 cm⁻¹. Overall, from the reference, the peak ranging from 1395-1440 cm⁻¹ indicated the presence of C-O-H deformation bending vibration of carboxylic acid, while the peaks at the range of 1350-1470 cm⁻¹ represented CH₂ deformation bending vibration which marks the appearance of alkanes in the PVP chemical structure. Then, in the range of 1330-1430 cm⁻¹ there was an O-H bending vibration that indicated the presence of alcohol and phenol functional groups. Lastly, the range of 1000-1300 cm⁻¹ marked the presence of O-C stretching vibration, indicating the presence of a carboxylic acid functional group [19].

In the FTIR spectrum of GAE, there was a sharp peak detected at 1016 cm⁻¹, which marked the C-O stretching vibrations of alcohols and phenols, followed by a small sloping peak at 1057 cm⁻¹. This peak was also shown by the PVP:GAE fibers with the ratios of 10:5, 10:3, and 10:1, which was at 1034 cm⁻¹, but in the PVP fibers the peak did not appear. From the reference, at 1050-1200 cm⁻¹ there was a C=S stretching vibration that explains the presence of thiocarbonyl functional groups that only detected in the GAE sample. Then the peaks at 1030-1060 cm⁻¹ indicated the S=O stretching vibration, which marks the signature of garlic component for all the samples, except the PVP fibers [20]. The peaks in the range of 1030-1200 cm⁻¹ increased with increasing the concentration of GAE in the PVP fibers.

4. Conclusion

All fibers have been successfully produced from the mixture of PVP and garlic extract (GAE) precursor solution using the rotary forcespinning method. The average diameter of the fibers was in the micrometer scale range. All fibers were smooth, with no beads or aggregates formed. The GAE has been successfully loaded into the fiber; as evidenced by the FT-IR spectra, there were differences in the peaks between PVP and the PVP:GAE fibers. The viscosity of the precursor solution was proven to affect the fiber diameter.

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