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Procedia Engineering 170 (2017) 14 – 18

Procedia Engineering

www.elsevier.com/locate/procedia

Engineering Physics International Conference, EPIC 2016

Rotary Forcespun Polyvinylpyrrolidone (PVP) Fibers as a Mangosteen Pericarp Extracts Carrier

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Abstract

The pericarp of Mangosteen (*Garcinia mangostana L.*) contains xanthone compounds such as α-mangostin, β-mangostin, γ-mangostin, which act as high-level antioxidants [1]. In this study, the mangosteen extract was integrated to PVP fibers to form a composite by means of rotary forcespinning method aiming to increase the bioavailability and solubility of the extract. The goal of this study was to produce composite fibers with mangosteen extracts as the active ingredient. The mangosteen extract was mixed into PVP solution with the various ratio (1:0.08, 1:0.10 and 1:0.12) to achieve the best result in term of morphology and antioxidant activity. The morphology and diameter of the fibers were analyzed using scanning electron microscope (SEM). The SEM image analysis confirmed the formation of bead-free, crystal-free, and aggregate-free fibers hence proving the perfect loading of the mangosteen extract into the PVP fibers. Beside SEM analysis, the fibers also underwent Fourier transform infrared (FTIR) analysis and antioxidant test using DPPH assay. From the FTIR analysis, it has been found that there was an interaction between the PVP and the extract in the fiber while the DPPH assay test has proven that the extract still retained its antioxidant ability although already being integrated into the fiber.

Peer-review under responsibility of the organizing committee of the Engineering Physics International Conference 2016
Keywords: Mangosteen extract; polyvinylpyrrolidone; rotary forcespinning; fiber; antioxidant.

1. Introduction

The pericarp of mangosteen (Garcinia L Mangostana) contains xanthone compounds such as α-mangostin, β- mangostin, γ-mangostin. Other compounds in mangosteen pericarp are anthocyanin, pectin, tannin, and resin. Xanthone are phenolic compounds which have so many medical benefits and have been reported as strong antioxidant compounds [1]. However, mangosteen extract has poor bioavailability and low solubility in water which limits their therapeutic application [2].

In recent years, many researchers have thoroughly examined polymeric fibers with diameter in micro to nano scale and the have been the center of interest in many studies. Nanofibers and microfibers are great inventions in material engineering since they can be applied for medical applications, such as for drug delivery, tissue engineering, scaffolding material, biocatalyst and wound dressing [3]. The polymeric fibers have many special characteristics, for example, they have extremely large surface per unit volume, low density and high porosity [4]. The fibers themselves consist of aligned chains of polymers. One example of polymers that can be synthesized into fibers is polyvinylpyrrolidone (PVP), which is soluble in water and other polar solvents [5]. It was reported that PVP can be successfully synthesized the nanofibers [6].

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Peer-review under responsibility of the organizing committee of the Engineering Physics International Conference 2016
doi:10.1016/j.proeng.2017.03.003

One of the methods that used to obtain the fibers is rotary forcespinning. Which use centrifugal force eject the fibers from the reservoir [7]. By combining the centrifugal force and other parameters like the internal diameter of the needle, the distance between the needle of the reservoir into collector, concentration of solutions, and flow rate, the rotary forcespinning technique is a versatile method to produce fiber. The high rotational speed of rotary forcespinning also ensures that the solutions will be dried up in faster rate to obtain fibers. Hence, the use of rotary forcespinning may improve production rate, this method is promising to produce the fibers in mass scale.

To prove that the fibers, which contained extract of mangosteen could be applied in drug delivery, the fibers underwent several tests. For the morphology and diameter, the fibers were analyzed using scanning electron microscopy (SEM). To investigate the existing functional groups, FTIR (Fourier Transform Infra Red) test was conducted. Lastly, to determine whether the composite fibers have functional groups of a phenolic compound as one of the antioxidant agent, the test on antioxidant activity was conducted using 1,1-diphenyl-2-picrylhydrazyl (DPPH) assay.

The goal of this study was to produce fibers loaded by mangosteen extracts through rotary forcespinning method and to confirm that the antioxidant activity was still retained by the composite fibers.

2. Methods

2.1. Materials

PVP with molecular weight 1,300,000 gram/mol was purchased from Sigma Aldrich. The mangosteen pericarps were purchased from local market in Bandung, Indonesia. The ethanol with 96% purity was purchased from Sakura Pharmacy store.

2.2. Fabrication of the Fibers

The precursor solution was made by mixing PVP solution and extract solution. PVP solution was made by stirring PVP in ethanol for at least an hour at temperature 40°C. The concentration of both PVP solution and mangosteen extract in ethanol were fixed at 10 % (w/w). The mangosteen extract were added into PVP solution with various ratio 1 : 0.08; 1 : 0.10 and 1 : 0.12. The mixed solution was stirred for 1.5 hours.

The precursor solutions were inserted into a single nozzle syringe with an internal diameter of 0.45 mm. The hole diameter of the reservoir was 0.6 mm, the distance between hole and collector was 10 cm, the speed of rotation was 28,000 rpm and the humidity inside the chamber was maintained at 40% so the solvent completely dried up and the fibers did not contract. The rotary forcespun process was conducted with flow rate at 30 ml/h and at temperature 35°C.

2.3. Characterization of the Fibers

The morphology of the fibers was observed by Scanning Electron Microscope/SEM (Jeol JCM-6000 NeoScope Benchtop made in Japan) with excitation voltage 15 kV. The images were achieved at 2,000 times magnification. The existing functional groups of fibers were identified using Fourier Transform Infra Red/FTIR analysis (ALPHA FT-IR Platinum ATR A220/D-01), the measurement was done in the range of wavenumber from 500 to 4000 cm^{-1}. The level of antioxidant activity was tested using DPPH assay. The fibers were tested against DPPH by mixing 50 ppm of fibers in ethanol with 50 ppm of DPPH in ethanol at volumetric ratio 1 : 1. The mixture was incubated for 30 minutes at room temperature. The antioxidant activity of the composite fibers was determined using AGILENT 8453 UV-Visible Spectroscopy. The absorbance region of the DPPH under UV-Vis spectroscopy is between 400 to 800 nm. In this research, a fixed wavelength at 515 nm was monitored closely which is the peak UV-Vis characteristic of DPPH. The antioxidant activity was expressed as the percentage of the decrease of DPPH in comparison to the control condition, according to the following equation :

$$\%AA = \frac{A_{control} - A_{sample}}{A_{control}} \times 100\% \quad (1)$$

Where $A_{control}$ is the absorbance values of DPPH solution, meanwhile A_{sample} is the absorbance values of testing fibers and mangosteen extract solution.

3. Results and Discussion

The morphologies of the rotary forcespun fibers given by different concentration of solution are shown in Fig 1 while the average diameters are provided in Table 1. The composite fibers made from the mixing of PVP and mangosteen extract solution had a smaller diameter compared to fibers made from PVP solution only. As the concentration of mangosteen extract increased, the diameter of the fibers decreased since the weight concentration of the polymer in the total solution decreased. The concentration of polymer decreased due to the additional solvent coming from the extract solution. The concentration of polymer is associated with viscosity of the solution and chain entanglement of polymer. When the concentration of polymer increased, the viscosity and chain entanglement increased as well. When the viscosity was high, the bending instability was set in for longer distance as the jet of solution emerged from the hole of the reservoir. As the result, the jet path was reduced and the bending instability was spread over the smaller area. Reduced jet path means that there was less stretching of the mixture solution resulting in larger fiber [8]. However, the size distribution of fibers was relatively larger as the fibers diameter was bigger as well.

Table 1. Average diameter of the obtained fibers

Fiber Formulation	$\overline{dF}$ (μm) ± σ*
Pure PVP solution (10%)	2.23 ± 1.42
Mangosteen extracts loaded PVP with ratio 1:0.08	2.18 ± 1.29
Mangosteen extracts loaded PVP with ratio 1:0.10	1.66 ± 1.37
Mangosteen extracts loaded PVP with ratio 1:0.12	1.43 ± 1.52

$\overline{dF}$ = geometry mean; σ* = geometry standard deviation

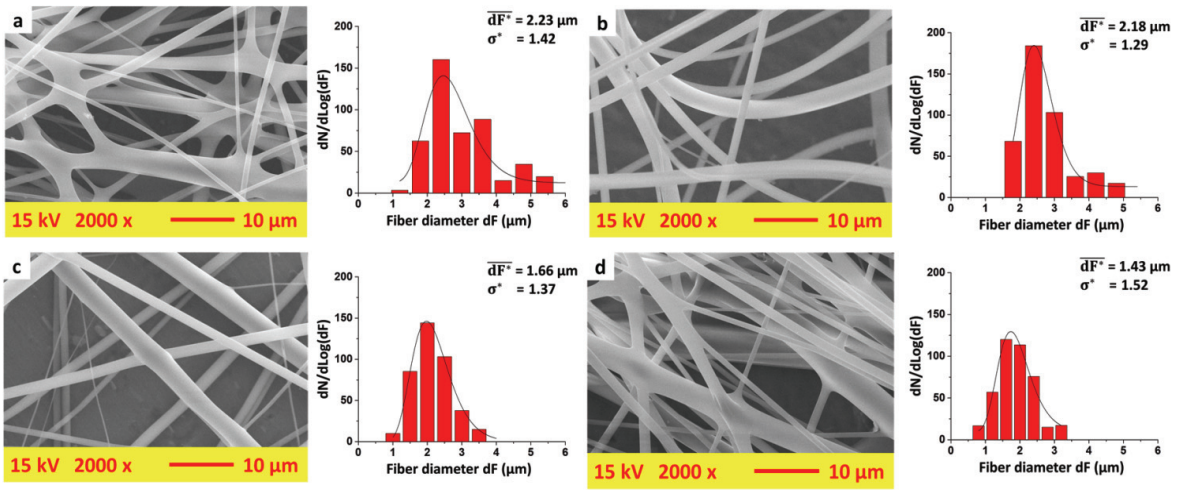

Fig. 1. SEM image and distribution curve of (a) Pure PVP, mangosteen extract loaded PVP with ratio (b) 1 : 0.08, (c) 1 : 0.10, (d) 1 : 0.12

All produced fibers were bead-free and did not have crystallized extract, or aggregates of extract at the appearance. Hence the mangosteen extract was loaded successfully into the fibers [9].

To prove that the fibers did really contain mangosteen extract, the fibers were analyzed using FT-IR and the spectrum was shown in Figure 2. The FT-IR spectrum of mangosteen extract in liquid form shows that there was strong and broad peak appear in the spectrum at 3327 cm^{-1}, the band refers to corresponding O-H stretch and H- bonded of phenolic hydroxyl and alcoholic compounds.

The peak 2944 and 2833 cm^{-1}, indicated that there were C-H asymmetric stretch and C-H symmetric stretch respectively. The presence of C=O stretch from carboxyl acid compounds can be identified from the peak at 1644 cm^{-1}. There was N-O asymmetric stretch at 1463 cm^{-1} and C-Cl from alkyl halides compounds at 765 cm^{-1}.

For pure PVP fibers, there was an O-H stretch at 3416 cm^{-1}. Supposedly, there was no O-H stretch since PVP did not have an O-H function from its formula. This was caused by imperfect evaporation of the solvent or there was a contact between fiber mats surface and the environment (air and water vapor). Since PVP is a hydrophilic polymer, so it can easily catch the water molecule from the environment. The C-H asymmetric stretch occurred at 2951 cm^{-1}. There was C=O stretch at 1646 cm^{-1}, since the contact between fiber mats PVP and environment occurred. At 1422 cm^{-1} C-H bend deformation was identified and there was proven C-H wagging and C-N stretch shown by the peak at 1288 cm^{-1}.

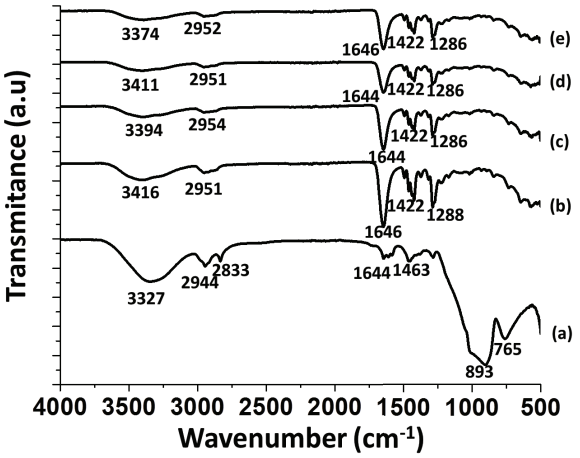

Fig. 2. FT-IR Spectrum (a) GM extracts liquid form, (b) Pure PVP, mangosteen extract loaded PVP with ratio (c) 1 : 0.08, (d) 1 : 0.10, (e) 1 : 0.12

For all spectrum of PVP fibers containing mangosteen extract, there was O-H stretch and H-bonded at 3394 cm^{-1} (ratio 1 : 0.08), 3411 cm^{-1} (ratio 1 : 0.10) and 3374 cm^{-1} (ratio 1 : 0.12). O-H stretch and H-bonded was occurred because there were phenolic compounds from mangosteen extract. Hence, it indicated the presence of interaction between PVP molecules and mangosteen extract molecules and this caused shift of wavenumber for pure PVP fibers and fibers containing mangosteen extract due to the interaction. From the FT-IR analysis, fibers containing mangosteen extract have a phenolic compound that is one of an antioxidant compound [10].

To investigate the antioxidant activity of the composite fibers, the fibers underwent antioxidant activity test using DPPH assay. The results are shown in Table 2.

Table 2. Antioxidant activity of the fiber mats containing mangosteen extract

Fiber Formulation	Absorbance of Antioxidant (%)
Pure GM extracts (10%)	60.96 ± 14.56
Mangosteen extracts loaded PVP with ratio 1:0.08	26.27 ± 1.44
Mangosteen extracts loaded PVP with ratio 1:0.10	27.16 ± 15.23
Mangosteen extracts loaded PVP with ratio 1:0.12	28.29 ± 2.11

For the liquid solution of mangosteen extract, the absorbance value was high indicating that the liquid has many antioxidant compounds. But for the PVP fibers loaded by mangosteen extract, the absorbance value decreased which mean the antioxidant activity decreased as well. This was caused by the decrease of concentration of mangosteen extract when being loaded into PVP fibers. The antioxidant activity would increase as the ratio of mangosteen extract which was added into PVP solution increased.

4. Conclusion

The fibers were successfully produced by rotary forcespinning method. The average diameter of fibers was in micrometer scale range. All fibers were bead-free and did not have crystallized extract, or aggregates of extract at the appearance. Hence the mangosteen extract was successfully loaded into the fibers. As proven by the FT-IR analysis, there were insignificant peak shift of wavenumber between pure PVP and mangosteen extract loaded PVP fibers which initially thought may be large due to the

interaction between PVP and mangosteen extract molecules. The fibers containing mangosteen extract had phenolic compounds which was known as antioxidant compounds and was approved by the result of antioxidant activity test.

Acknowledgements

This research was financially supported by Directorate of Research and Community Engagement of Ministry of Research, Technology and Higher Education, Indonesia under the University's Excellent Research (PUPT). Grant in the fiscal years of 2015-2016.

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