Polymeric and non-polymeric nanofiber of Cinnamaldehyde from Cinnamon oil (*Cinnamomum zeylanicum*)

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**Abstract.** Encapsulation of cinnamaldehyde within polymeric and non-polymeric-based nanofiber matrix was investigated. Polyvinyl alcohol (PVA) was used as a polymeric matrix, and β-cyclodextrin (CD) was used as a non-polymeric matrix. The study is aimed to purify cinnamaldehyde from cinnamon oil and to encapsulate it within the nanofibers matrix. The purification step was carried out using spinning band distillation. On the other hand, the nanofibers were prepared through electrospinning. Three different formula were made, namely PVA/cinnamaldehyde, PVA/β-CD/cinnamaldehyde 5% and PVA/β-CD/cinnamaldehyde 10%. The yield of isolated cinnamon oil was 0.26% with 88.90% cinnamaldehyde purity in fraction III tested using GC and GC-MS. In advanced, the SEM images indicate that the average diameter of the bare nanofiber matrix was 75 nm. The diameter was decreased in the presence of cinnamon oils in all samples (range 50-65 nm). The inclusion complex formation was confirmed from FTIR data in the presence of a band at 1700 cm⁻¹ that indicate the presence of the aldehyde group in both polymeric and non-polymeric nanofibers matrix.

1. Introduction

Nanofiber has attracted an enormous amount of attention on researchers in this past decade because of their distinctive properties. Nanofiber has a few characteristics, such as having a highly porous high surface area and high encapsulation efficiency of active compound [1-6]. Because the traits itself, nanofiber can be applied in a vast field such as membrane for filtration, controlled release system, support for drug delivery, as a textile material, active food packaging [2, 4, 5, 7]. The technique used on a few research last decade was electrospinning because it’s cost-effectiveness, and it is the only process that can control the size of the fibre [8]. Electrospinning is a nanofiber preparation method by applying a high applied voltage and vaporization of the solvent principle [8, 9].

Preparation the nanofiber from polymeric and non-polymeric matrix investigated. In the principle of electrospinning, the matrix must have a high molecular weight, high concentrated, have a chain entanglement and overlapping [1, 2]. PVA with the molecular formula [CH₂-CH₂(OH)]ₙ- is a non-toxic polymeric and high biocompatible usually used as a nanofiber matrix [3, 4, 7]. β-cyclodextrin has been selected due to its sugar group, which has polymer-like properties. β-cyclodextrin is natural and non-toxic cyclic oligosaccharides that have a toroid shaped molecular which can form host-guest inclusion complexes with a variety of molecules [1-4]. The guest molecules in this study is an active compound...
from cinnamon oil called cinnamaldehyde. Commonly, cinnamaldehyde used for fragrance, flavour, and even in medical [10, 11]. In medical usage, cinnamaldehyde can obstruct the growth of glucose and against cancer cell activity because it has an aldehyde functional group [10, 11]. The purpose of current research is optimizing the isolation of cinnamaldehyde from cinnamon oils and investigating the preparation and characterization of the polymeric and non-polymeric nanofiber.

2. Materials and Method

2.1. Materials and device
Polyvinyl alcohol (PVA, 99+% hydrolyzed, Mw 89,000 – 98,000) a product from sigma-Aldrich. β-cyclodextrin (≥ 97% 1,000 – 1,300) a product from sigma-Aldrich. Cinnamon bark (Cinnamomum zeylanicum), cinnamon oil (containing 73,989% cinnamaldehyde) from Nusaroma Essential Indonesia. The materials were used without any purification.

The device is set of steam distillation, set of fractional distillation, stirrer, electrospinning (UiTM), GC-MS (QP2010 SE Shimadzu), GC (Agilent 6820 Vers. A.01.03), FTIR (Perkin Elmer, UiTM), and SEM (TM3030plus).

2.2. Isolation of Cinnamon Oil
Steam distillation was used to isolate the cinnamon oil from cinnamon bark. Firstly break 5 kg of cinnamon bark into a small piece and grind to form a powder. Take the powder into the steam distillation’s pan and distilled for approximately 15 hours. Then, separate the cinnamon oil from water using NaSO₄ salt. Count the yield and analyst the oil using GC-MS.

2.3. Isolation of Cinnamaldehyde from Cinnamon Oil
The separation of cinnamaldehyde from cinnamon oil was using pressure drop fractionation using previously published set up parameter [12]. The oil used is 250 mL and the processing time around 24 hours 32 minutes. The result of the fraction was analyzed using GC to see where the cinnamaldehyde mostly found.

2.4. Preparation Solution for Electrospinning
PVA 12% (w/v) was prepared in 5 mL distilled water, stir in a constant rate for approximately 60 min (90°C). After the PVA soluble in water, turn down the temperature into room temperature and adding 5% (w/w PVA) of cinnamaldehyde then stirred overnight. In the other hand, prepare two formula of PVA 12% (w/v) in 5 mL distilled water stir at a constant rate for approximately 60 min (90°C). After the PVA soluble in water, turn down the temperature into 60°C. Adding 39% (w/w PVA) β-cyclodextrin then stirred in a constant rate. After the solution, PVA/ β-cyclodextrin soluble, turn down the temperature into room temperature and adding 5%(w/w PVA) of cinnamaldehyde then stirred overnight. Make the solution of PVA 12% (w/v) in 5 mL distilled water for comparison.

2.5. Electrospinning
The solution was placed in 3mL syringe with metallic needle diameter 0.60 x 25 mm from Terumo. The voltage applied is 14 kV, with tip-to-collector distance is 16 cm and the federate of the solution is 0,3 mL/hour. The collector used is aluminium foil and performed in room temperature. The electrospinning takes a time about 2-3 hours.

2.6. Characterization of Nanofiber
The morphology and the fibre diameter of nanofiber were observed by SEM (TM3030plus Hitachi), the nanofiber film coated with Au using sputter coater under vacuum. The diameter of the nanofiber calculated by analysing around 100 fibres using ImageJ analyzer.

The interaction of PVA, β-cyclodextrin, and cinnamaldehyde analyzed using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer). The measurement was using ATR for the fibre, powder
and the oil. The FTIR spectra were recorded with a resolution 4 cm\(^{-1}\) with a wavenumber range 4000-650 cm\(^{-1}\) for solid phase, and 4000-450 cm\(^{-1}\) for the liquid phase.

3. Result and Discussion

3.1. Isolation of Cinnamon Oil

![GC-MS Chromatogram of Cinnamon Oil](image)

In the isolation of cinnamon oil from cinnamon bark used steam distillation method which based on its volatility. The steam will push the plant’s cells containing essential oil to let the volatile compound released. The cinnamon oil that successfully isolated is 13 mL from 4.82 kg of cinnamon bark; the yield is 0.26%. Figure 1 showed that cinnamaldehyde compound dominated the oil’s content, about 74.66% in retention time 35.273. The other compounds are 1,8 cineol (7.52%), alpha-pinene (7.44%), 2-propane-1-of-3-phenyl (4.30%), beta-pinene (3.16%), and camphene (2.91%).

3.2. Isolation of Cinnamaldehyde

In the separation of cinnamaldehyde from cinnamon oil used fractional distillation. The use of pressure reduction is intended so that cinnamaldehyde can evaporate faster than regular boiling points. The pressure used in this process is 29.8 – 30.1 mmHg and temperature 30 °C – 300 °C. This isolation produced three fractions of oil, and the first fraction appears at 160 °C – 235 °C the second fraction look at 235 °C - 245 °C and the third fraction appear at 245 °C – 280 °C. The third fraction has a cinnamonaldehde’s distinctive aroma and yellow coloured. Based form GC showed that the cinnamaldehyde compound is increasing to 88,90%, followed by decreasing the other compounds.

3.3. Fabrication of Nanofiber

Fabrication of polymeric and non-polymeric nanofiber using electrospinning successfully made by PVA and \(\beta\)-cyclodextrin. The solvent used is distilled water, explained in the previous research that water is an optimal solvent to form a nanofiber [2]. The solution that consists of PVA/\(\beta\)-cyclodextrin and distilled water are transparent and colourless, but the addition of cinnamaldehyde makes the solution turbid. This case indicates that there is an interaction between PVA, \(\beta\)-cyclodextrin, and cinnamaldehyde. The electrospinning process influenced the setting of voltage and feed rate. While making nanofiber of PVA, PVA/Cinnamaldehyde and PVA/ \(\beta\)-cyclodextrin/Cinnamaldehyde 5% used 14kV and feed rate 0.3
mL/hour resulted from an edible fibre but while it applied on PVA/β-cyclodextrin/Cinnamaldehyde 10% the stability of the electrified solution jet disturbed. This condition caused by a feed rate that is too high for this low viscosity solution. From that case, we conclude that the addition of essential oil decreasing the viscosity of the solution while the additional of β-cyclodextrin increasing the thickness. The concentration and viscosity of the solution influence the stability of the electrified solution jet during electrospinning [2, 4, 7].

3.4. Characterization of Nanofiber

![Figure 2](image)

(a) (b) (c) (d)

**Figure 2.** The representative SEM images of the nanofiber (a) PVA; (b) PVA/Cinnamaldehyde; (c) PVA/β-cyclodextrin/Cinnamaldehyde 5%; (d) PVA/β-cyclodextrin/Cinnamaldehyde 10%

**Table 1.** The Morphology of Nanofiber

| Solution                           | PVA (% w/v) | β-CD (% w/w PVA) | Cinnamaldehyde (% w/w PVA) | Average diameter (nm) | Fiber Morphology                        |
|-----------------------------------|-------------|------------------|-----------------------------|-----------------------|-----------------------------------------|
| PVA                               | 12          | 0                | 0                           | 76.57                 | Bead Free Nanofiber                    |
| PVA/Cinnamaldehyde                | 12          | 0                | 5                           | 54.56                 | Nanofiber with CD-IC crystal           |
| PVA/β-CD/Cinnamaldehyde 5%        | 12          | 39               | 5                           | 60.75                 | Nanofiber with CD-IC crystal           |
| PVA/β-CD/Cinnamaldehyde 10%       | 12          | 39               | 10                          | 58.53                 | Nanofiber with CD-IC crystal           |
Figure 2 showed the morphology and the average diameter of nanofiber that analysed by using SEM. The magnification used is 5000x, 10,000x and 20,000x, which Figure 2 showed the magnificent of 20,000x. Nanofiber from PVA was beads-free while PVA/Cinnamaldehyde, PVA/β-CD/Cinnamaldehyde 5% and PVA/β-CD/Cinnamaldehyde 10% were present beads at several random points. The present of beads can be caused by the non-optimals condition of electrospinning and lack of sufficient polymer chain entanglements and overlapping such as low viscosity [2, 8, 9, 13]. Table 1 showed the composition of the solution, the distribution diameter and the average diameter of the nanofiber. The average diameter of the nanofiber count by calculated 100 random fibre using ImageJ for windows. The diameter of the nanofiber influencing by the viscosity of the solution. The more viscous will impact to the bigger diameter size [9, 14].

Table 2. The result of IR spectrum analysis of all nanofibers with PVA

| Functional group | β-Cyclodextrin | PVA | PVA/β-CD/Cinnamaldehyde 5% | PVA/β-CD/Cinnamaldehyde 10% |
|------------------|---------------|-----|----------------------------|-----------------------------|
| O-H              | 3286          | 3237| 3294                       | 3303                        |
| C-H              | 2936          | 2911| 2936                       | 2927                        |
| C-O              | 1411          | 1444| 1402                       | 1428                        |
| C=O              | 1151          | 1052| 1085                       | 1101                        |
| α-1,4            | 921           | -   | -                          | 921                         |
| C=O              | -             | 1003| 1737                       | 1737                        |

The FTIR spectrum of PVA in Table 2 showed peaks in region 3237 cm⁻¹, 2911 cm⁻¹, 1444 cm⁻¹ that indicated as a present of O-H, C-H, and C-H stretching vibration [4, 7]. For β-cyclodextrin specific peak was on 3286 cm⁻¹ for O-H stretching vibration, 1151 cm⁻¹ and 1003 cm⁻¹ for the vibration of C-O from C-O-C called a glycosidic bond. The bands 939-916 cm⁻¹ indicated vibration of α-1,4 bond on β-cyclodextrin [4, 7]. For the presence of essential oil or cinnamaldehyde showed in the peak 1600-1700 cm⁻¹ that indicated as C=C of the aromatic ring and C=O of aldehyde [15]. As it can be seen in Figure 3
and Table 2, the characteristic absorption peak of cinnamaldehyde present in the nanofiber PVA/Cinnamaldehyde; PVA/β-CD/Cinnamaldehyde 5%; PVA/β-CD/Cinnamaldehyde 10%.

4. Conclusion
Polymeric and non-polymeric nanofiber were successfully fabricated in nanoscale were obtained under optimal condition. The polymeric substance is PVA, and the non-polymeric material is β-cyclodextrin. Furthermore, the cinnamaldehyde successfully inserted into the fibre showed by the data analyst.

Cinnamaldehyde isolated from cinnamon oil with a purity of 88.90%.

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