Fabrication and Characterization of Electrospun Nanofiber Films of PHA/PBAT Biopolymer Blend Containing Chilli Herbal Extracts (*Capsicum frutescens* L.)

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Abstract*—Biopolymer nanofiber film is a form of transdermal drug delivery system, which was developed from gels or creams. Films, which are flexible, can be attached to the skin body and controlled for drug release application. The synthesis of biopolymer nanofiber as a matrix for drug control release of drug and herbal extracts has been extensively attracted from many researchers until present time. In this research, we focused on the nanofiber production from the biopolymers of polyhydroxyalkanoate (PHA) and poly(butylene adipate-co-terephthalate) (PBAT) blending systems containing chilli herbal extract or capsaicum extract. This study aims to figure out the suitable proportion of the mixture of biopolymer and capsaicin and to perform the characterization. The nanofiber forming was performed by melting PHA/PBAT and capsicum extracts in dichloromethane. The weight ratio of PHA:PBAT was fixed at 60:40 and the concentration of the PHA/PBAT solutions were 5, 7.5 and 10%, respectively. The suitable concentration condition of polymer solution was at 10%, then mixing with concentration of capsicum extracts at 1, 2, 5, 10 and 20% respectively. The solutions measured by viscometer machine confirmed that the viscosity of polymer solutions blended with capsaicin affects to the nanofiber synthesis by electrospinning technique. Then, the material properties of the nanofiber films were characterized by tensile tester. It was found that the stiffness and the elongation at break of the nanofiber films are in the acceptable range of the standard. The morphology and diameter of PHA/PBAT nanofibers were characterized by scanning electron microscopy. The amount of fiber ranges about 155-680 lines and the diameter was between 240-4,820 nm, as most of the fibers fell in lower than 1 micrometer resulting in a confirm nano-scale fiber synthesis. With FTIR measurement, the nanofiber films containing capsicum extract in various numbers have a similar peak graph showing frequency ranging 1,340-1,020cm^{-1}. Therefore it can be concluded that fibers at the nanofiber and capsaicin substance molecules could be included in the nanofibers.

***Index Terms*—capsaicin, biopolymer, transdermal patch, electrospinning, nanofiber, chilli herbal extracts**

I. Introduction

Nowadays, many researches have been conducted to tackle pain relief and inflame reduction for human. Over the past several years, great advances have been made on development of herbal drug delivery systems for plant actives and extracts [1]. Polymer patch is an effective product for topical herbal drug systems to deliver active compound to skin [2]. A novel herbal formulation especially polymeric nanofibers by electrospinning has been greatly reported using bioactive and plant extracts [3]. Electrospinning has been recognized as a simple and versatile method for fabrication of polymer nanofibers [4]. Biopolymer nanofiber film is a form of transdermal drug delivery system, which was developed from gels or creams. Films, which are flexible, can be attached to the skin body and controlled for drug release application. The synthesis of biopolymer nanofiber as a matrix for drug control release of drug and herbal extracts has been extensively attracted from many researchers until present time. Capsaicin is a bioactive compound responsible for the spicy, pungent taste of hot chili peppers (*Capsicum frutescens*) [5], [6]. The bioactive compound has been employed as medicine and food additive. Currently, capsaicin, with a characteristic smell and taste, is one of the most highly consumed additives throughout the world [7], [8]. Capsaicin is associated with multiple pharmacological activities such as anti-inflammatory [9], and antioxidant [10] activities.

Polyhydroxyalkanoates (PHAs) are a family of biopolyesters that are synthesized and accumulated by many bacteria as carbon storage material [11]. The biopolyesters, after recovery and purification from the cells, can be melted and molded like conventional

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petroleum-derived thermoplastics but can be completely decomposed by microorganisms in the environment. The excellent biodegradability and biocompatibility of PHA bioplastics are desired properties for many short-life goods and applications in agriculture and health care. Blending PHAs with toughened polymers such as poly(butylene adipate-co-terephthalate) (PBAT) is a practical and economical way to improve the specific toughness up to two orders of magnitude for solid and microcellular specimens compared to neat PHA [12]. In this research, we focused on the nanofiber production from 2 types of biopolymers: polyhydroxyalkanoate (PHA) and poly(butylene adipate-co-terephthalate) (PBAT) containing chilli herbal extract or capsaicin extract. This study aims to figure out the suitable proportion of the mixture of biopolymer and capsaicin and to perform the characterization.

II. Metrials and Methods

A. Materials

Capsaicin, 99% purity, was supplied by Thai-China Flavours and Fragrances Industry Co., Ltd. (TCFF) (Nonthaburi, Thailand). Polyhydroxyalkanoate (PHA) copolymer was purchased from Sigma-Aldrich, USA, and Poly(butylene adipate-co-terephthalate) (PBAT) was purchased from Ecoflex, BASF, Germany. Dichloromethane was supplied from RCI Lab-scan, Thailand)

B. Polymer Solution Preparation

For preparation of polymer solution, the polymer mixture of PHA:PBAT was at the ratio of 60:40 dissolved in dichloromethane with concentration of 10% (w/v). Then, the capsaicin was blended at 1%, 2%, 5%, 10%, and 20% of polymer weight and mixed together with temperature at 60 ℃ for 15 min.

C. Electrospinning

A single nozzle electrospinning setup was used to prepare electrospun nanofibers. A high voltage power supply (ES60P-10W, Gamma High Voltage, Florida, USA) was attached to a metal nozzle to create a voltage difference between the metal nozzle and a grounded collector of 15-25kV. A charged metal nozzle with 0.57mm outer diameter was placed 15cm directly above the center of the 20×20cm aluminum flat grounded collector. A mechanical pump (NE-300, New York, USA) was used to deliver the solution from a plastic syringe to the metal nozzle at a rate of 1ml/hr.

D. Characterization

Scanning Electron Microscope (SEM) (JSM-6400, JEOL Ltd., Tokyo, Japan) was used to characterize electrospun fibers characteristic and size. Image J software (www.imagej.nih.gov) was used for measuring fiber diameter. The average fiber diameter and Standard Deviation (SD) were determined.

A stress-strain test of polymer films ($20\times5\times0.15mm^3$) was performed at room temperature using an Instron bench-type tensile test machine (LR5K Plus) with a strain rate of 5mm/min.

The nanofiber films were examined using the ATR-FTIR technique. They were scanned at a resolution of $4cm^{-1}$ with 64 scans over a wavenumber region of 400-$4000cm^{-1}$ using the FT-IR spectrometer (model: Nicolet 6700, DLaTGS detector, Thermo Scientific, USA). The characteristic peaks of IR spectra were recorded.

III. Results and Discussions

A. SEM Morphology, Solution Viscosity and Film Thickness of Electrospun PHA/PBAT Nanofibers Containing Capsaicin

The nanofiber forming was performed by melting PHA/PBAT and capsicum extracts in dichloromethane. The weight ratio of PHA: PBAT was fixed at 60:40 (the best property of cast film ratio) and the concentration of the PHA/PBAT solutions were 5, 7.5 and 10%, respectively shown in Table I and Fig. 1 (A-C), and applying the electrospinning for 4hr. The suitable concentration condition of polymer solution was at 10%, then mixing with concentration of capsicum extracts at 1, 2, 5, 10 and 20% respectively shown in Table II and Fig. 2 (D-H).

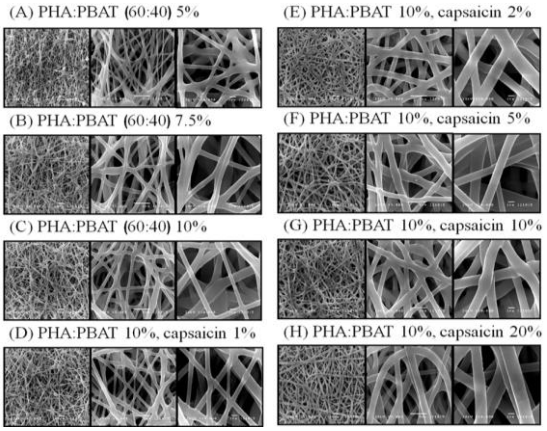


Figure 1. SEM morphology of PHA:PBAT (60:40) nanofibers at the concentration of 5% (A), 7.5% (B), and 10% (C), while the nanofiber films of 10% were loaded with capsaicin in concentration by polymer of 1% (D), 2% (E), 5% (F), 10% (G), and 20% (H), respectively. The micrograph were prepared by electrospinning technique for 4hr at SEM image of 1,000x 5,000x and 10,000x, respectively from left to right.

TABLE I. Solution Viscosity and Film Thickness of PHA:PBAT (60:40) Solutions and Nanofibers Prepared by Electrospinning Technique for 4hr at the Concentration of 5%, 7.5%, and 10%

sample	solution viscosity (cP)	thickness (mm)
PHA:PBAT 5%	32.8	0.05
PHA:PBAT 7.5%	193.6	0.09
PHA:PBAT 10%	283.3	0.13

TABLE II. Solution Viscosity and Film Thickness of PHA:PBAT (60:40) Solutions and Nanofiber Films of 10% Loaded with Capsaicin in Concentration by Polymer of 1%, 2%, 5%, 10%, and 20%, Respectively. Prepared by Electrospinning Technique for 4hr

sample	solution viscosity (cP)	thickness (mm)
capsaicin 1%	194.7	0.04
capsaicin 2%	198.1	0.12
capsaicin 5%	202.5	0.16
capsaicin 10%	206.9	0.10
capsaicin 20%	209.8	0.09

The polymer solutions measured in Table I and Table II by viscometer machine confirmed that the viscosity of polymer solutions blended with capsaicin slightly affects to the nanofiber synthesis by electrospinning technique. The amount of polymer solution has a great effect to the solution viscosity. For electrospinning process with comparable high viscosity, the 10% viscosity at 283 cP should be the most suitable concentration for the blend.

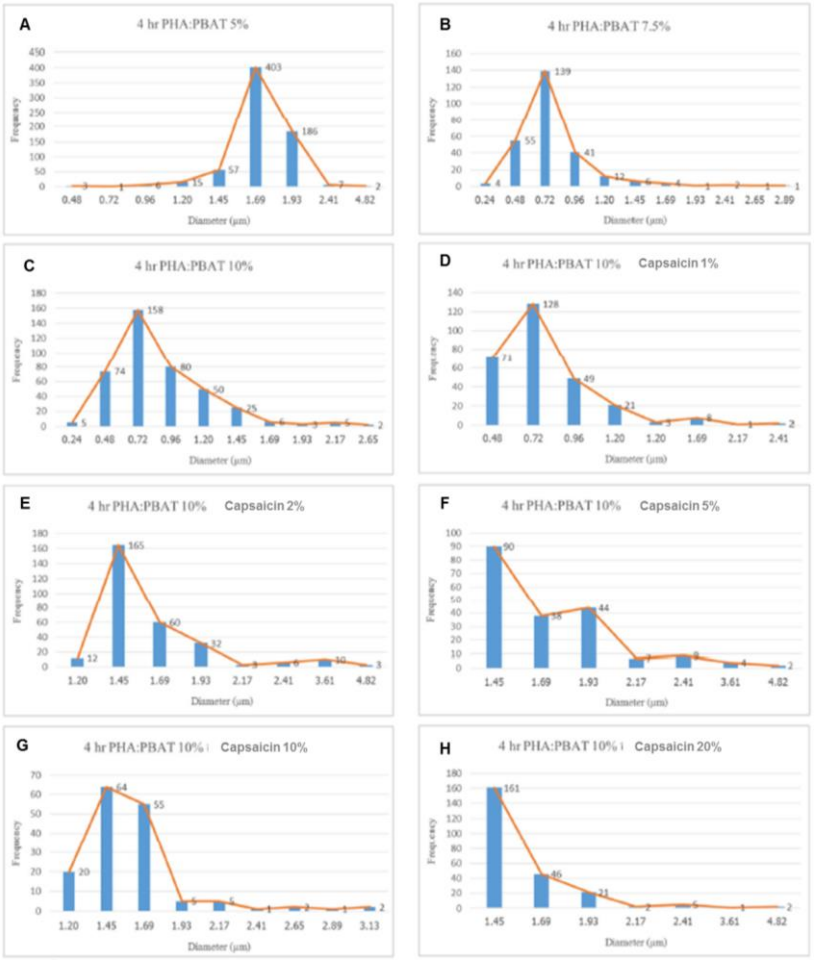


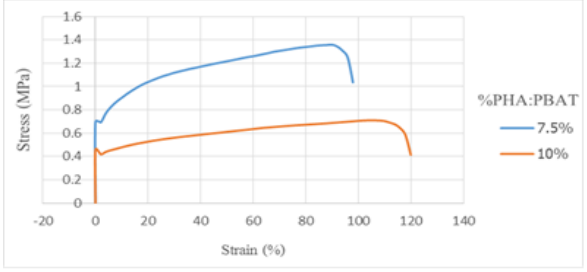
Figure 2. The relative graph between diameter and amount of nanofibers analysed from the SEM image of PHA:PBAT (60:40) nanofibers with 4hr electrospinning at the concentration of 5% (A), 7.5% (B), and 10% (C), while the nanofiber films of 10% were loaded with capsaicin in concentration by polymer of 1% (D), 2% (E), 5% (F), 10% (G), and 20% (H), respectively.

The morphology and diameter of PHA/PBAT nanofibers were characterized by Scanning Electron Microscopy (SEM). Within 1000x microscale, the amount of fiber ranges about 155-680 lines and the diameter was between 240-4,820nm, as confirmed by the counting and shown in the Fig. 2. Because most of the fibers fell in lower than 1 micrometer, it is indicated that the electrospun films fabrication resulted in a confirmed nano-scale fiber.

B. Tensile Test of Electrospun PHA/PBAT Nanofibers Containing Capsaicin

A tensile test was performed to determine the effect of capsaicin content on the mechanical properties of the PHA/PBAT nanofiber films. The films of the dimension of $20 \times 5 \times 0.15 mm^3$ was performed at room temperature using a tensile test machine with a strain rate of 5mm/min. Fig. 3 shows typical stress/strain curves with a mechanical data.

From the Fig. 3 (upper picture), electrospinning process for 4hr of PHA: PBAT (60:40) 10% is higher in elongation at break value (120%) than 7.5% (100%), but the maximum tensile strength is lower two folds (0.7MPa: 1.4MPa). As shown in Fig. 3 (lower picture), nanofiber films of 10% loaded with 20% capsaicin has the highest elongation at break value (280%) and the highest maximum tensile strength value (2.1MPa), compared with the other samples containing lower amount of capsaicin. It can be indicated that the stiffness and the elongation at break of the nanofiber films containing 20% of capsaicin or lower are in the acceptable range of the standard (1.5-6 MPa) and could be applied as a nanofiber patch for herbal medical application.



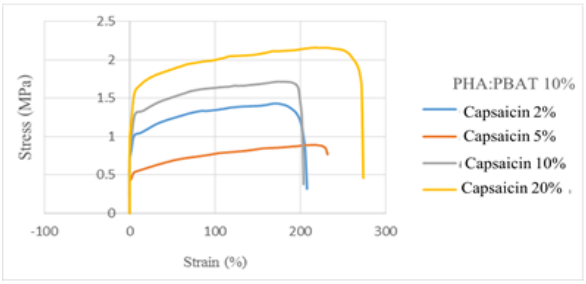


Figure 3. Typical stress-strain curves of: (above); PHA:PBAT (60:40) nanofibers at the concentration of 7.5% and 10% (below); nanofiber films of 10% loaded with capsaicin in concentration by polymer of 2%, 5%, 10%, and 20%.

C. FTIR Measurement of Electrospun PHA/PBAT Nanofibers Containing Capsaicin

An ATR-FTIR spectrum in Fig. 4 shows the completely major functional groups of pure capsaicin and PHA/PBAT nanofiber containing 20% capsaicin. With FTIR measurement, it was found that nanofiber film samples containing capsicum extract in various numbers have a similar peak showing frequency ranging 1,340-1,020cm^{-1}. The identical patterns of both FTIR spectra confirms no changeable of each ingredient in the capsaicin in the biopolymer nanofiber films. Therefore it can be concluded that fibers at the nanofiber and capsaicin substance molecules should be included in the biopolymer nanofiber.

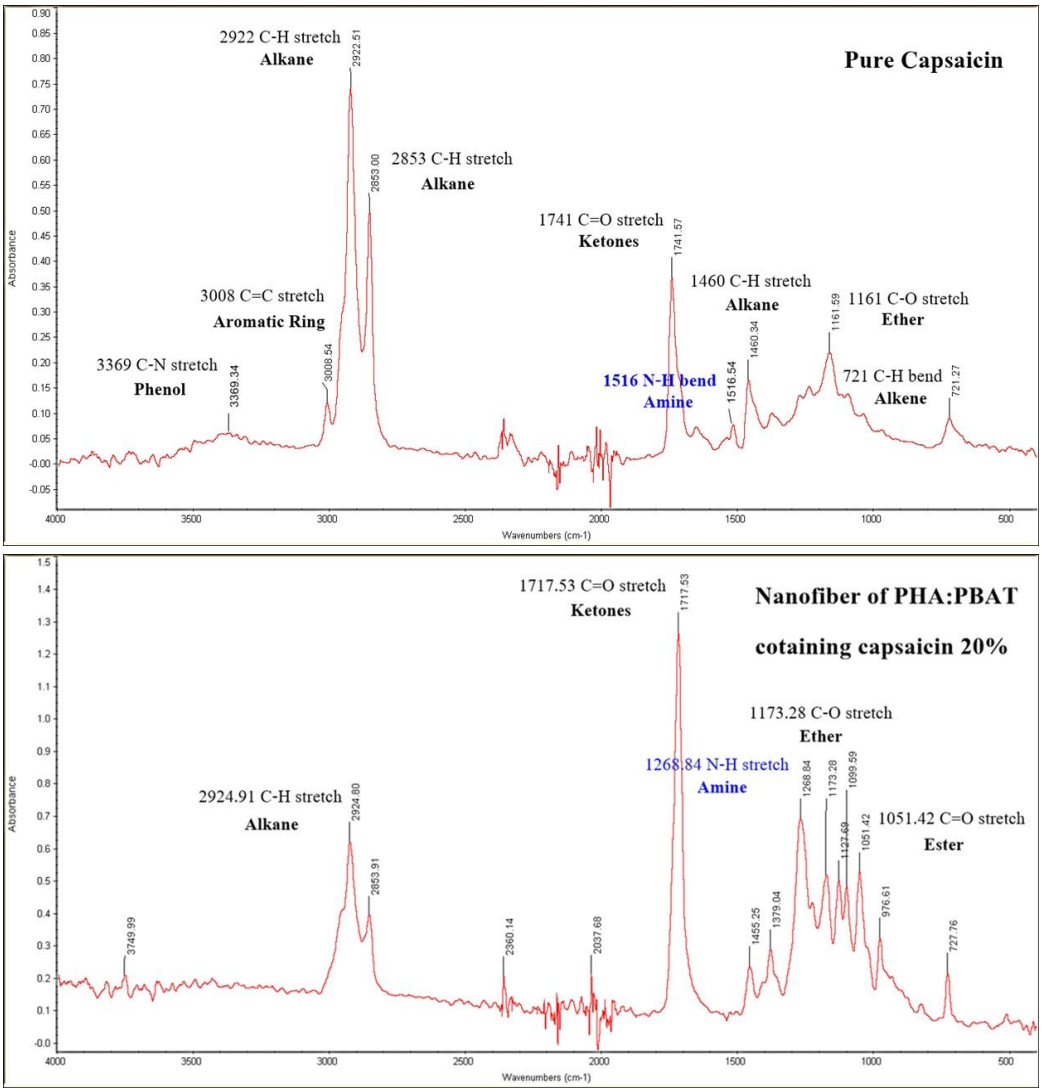


Figure 4. FTIR spectra of (above); pure capsaicin, (below); 10% PHA/PBAT nanofibers loaded with 20% capsaicin.

IV. Conclusions

We successfully prepared the PHA/PBAT nanofiber films from different capsaicin blends by electrospinning method. The nanofiber films showed a potential for alternative materials as drug release patches. The physicochemical properties such as morphology, FTIR, and tensile property indicated the compatibility of the blended ingredients. Therefore, these results have provided the feasibility of the capsaicin patches could be employed suitably for topical application.

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