Roughness Study of Hydroxypropyl Cellulose Film Surface Loaded with Cinnamaldehyde/ Lauric Arginate by Atomic Force Microscopy

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Abstract. In this work, atomic force microscopy (AFM) technique was used to study the microstructure properties of hydroxypropylcellulose/ cinnamaldehyde (CDH) composite biofilm. The solution was emulsified by cationic surfactant, lauric arginate (LAE). Zetasizer analysis found that the addition of CDH-emulsified LAE increased the zeta potential of HPC-based solution from -1.31 to 10.47 (mV). Furthermore, the increasing trend was showed by the roughness of surface properties. AFM analysis revealed that the arithmetical mean deviation from the mean (Ra) and root mean square deviation from the mean (Rq) of HPC film surface enhanced by 1.7 nm and 3.63 nm respectively as addition of CDH-emulsified LAE. Any deformation in the surface properties of the biofilm might affect its barrier properties such as water resistance and light transmission.

Keyword: Biofilm, cationic surfactant, composite, surface

1 Introduction

The study on edible films have been gaining attention as one of alternative to maintain the quality of food products. Among all biomatrices, hydroxypropyl cellulose (HPC) is believed as good film-forming material that has been investigated in few numbers of studies [1]. HPC is a commonly used polymer in the food industry and has been approved by the U.S. Food and Drug Administration (FDA) as a food additive. It is used as a thickener, stabilizer, and emulsifier in a variety of food products, including baked goods, dairy products, and beverages. HPC-based edible films have been shown to be effective in encapsulating and releasing bioactive compounds, making them a promising material for

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use in functional food products. HPC possesses hydrophilic and nonionic properties where some of the OH groups are hydroxypropylated, yielding -OCH2CH(OH)CH3 groups) [2]. However, the films made of only pure HPC is not satisfied, thereby the effort to improve its performance is necessary.

The development of emulsified edible film is one of strategies. Edible films are potential vehicles for loading various beneficial active compounds including antioxidant and antimicrobial agents [3]. Cinnamaldehyde, is a very potent antimicrobial and antioxidant which may provide positive effects the pure HPC film [4, 5]. Furthermore, there has been an interest in the replacement of synthetic surfactants in the development of edible film with food grade cationic surfactant such as lauric arginate (LAE; Nα-lauroyl-L-arginine ethyl ester monohydrochloride). LAE has been listed as a generally recognized as safe (GRAS) substance and shown to be an effective antimicrobial effect [6, 7]. Incorporating lauric arginate into the edible film matrix can help to inhibit the growth of bacteria, yeasts, and molds on the surface of food products, thereby extending their shelf life and improving their safety. Additionally, lauric arginate is effective at low concentrations, which minimizes any potential negative impact on the taste, odor, or color of the food product. Therefore, the use of lauric arginate in edible film production can improve the quality and safety of food products by providing an additional barrier against microbial contamination.

Roughness study is essential in the fabrication of required edible films. This parameter is used to represent the functional of specific features such as contact angle, hydrophilicity, adhesion, water vapor barrier, etc. In this work, we prepared an emulsified film made from HPC incorporated with CDH and LAE. Their characteristics related to surface roughness were studied through AFM technique.

2 Methods

2.1 Edible Film Preparation

The HPC-film solution was made by mixing 4 % HPC powder (Nippon Soda, Japan) in distilled water with the aid of magnetic stirrer 500 rpm for 30 min. Plasticizer agent, glycerol 0.25 % v v^{-1} (FUJIFILM Wako Pure Chemical Corporation, Japan), was added and stirred for 10 min. The emulsion stock was prepared by adding 0.6 % v v^{-1} CDH (FUJIFILM Wako Pure Chemical Corporation, Japan) in the solution containing 0.04 % LAE (FUJIFILM Wako Pure Chemical Corporation, Japan) and homogenized with a high-speed homogenizer (T 25 digital ULTRA- TURRAX® - IKA, Germany) at 15 000 rpm (1 rpm = 1/60 Hz) for 2 min. Subsequently, HPC solution were homogenized with emulsion stock or distilled water (for pure HPC film), at equal ratio, at 15 000 rpm for 2 min to reach 2 % HPC containing 0.02 % LAE and 0.3 % CDH and degassed under vacuum for 15 min. The edible films were fabricated by drying each 20 ml film forming solution in silicon mold plates (8 cm × 8 cm) at oven (35 °C) for 18 h to 20 h and kept in a desiccator (50 ± 4 % RH).

2.2 Zeta potential and pH

Zeta potential was measured with a Zetasizer (Zetasizer Nano ZNP, Malvern Instruments, UK). The film forming solution was first placed into capillary zeta cell DTS1070 before measurement with five replicates.

2.3 AFM

An atomic force microscope Hitachi 5200S (Japan) was used to analyze the roughness of film surface. A sample was placed on the sample stub and sticked with double side carbon tape. The scanning was done in tapping mode equipped with cantilever type SI-DF20, frequency 0.7 Hz to 0.84 Hz, scan area 2 × 2 μm^2. Root mean square deviation from the mean (Rq) and arithmetical mean deviation from the mean (Ra) were calculated from 10 measurements of different line profiles, as Equation (1) and Equation (2).

$$Rq = \sqrt{\frac{1}{n}\sum_{i=1}^{n} Zi^2} \quad (1)$$

$$Ra = \frac{1}{n}\sum_{i=1}^{n} |Zi| \quad (2)$$

Zi = the height deviation of the i-th value, n = the total number of data points.

3 Result and discussion

3.1 Zeta potential

The zeta potential value of HPC film forming solution was negatively charged surfaces, -(1.29 ± 0.06) mV. As expected, the addition of CDH and LAE into HPC contributed to increasing of the zeta potential, (10.47 ± 0.32) mV, which was s a measure of the electrostatic repulsion between particles or surfaces in a colloidal suspension. This was directly associated with the presence of the positive charge on LAE’s protonated guanidine. It allowed that cationic LAE molecules formed complexes with the anionic cellulose molecules via electrostatic interactions. In the application, this might be a beneficial phenomenon to improve both antimicrobial activity and interaction ability with anionic food components [7]. These values indicated poor stability of the suspended colloidal dispersion. According to the theory, a zeta potential value more than ± 30 mV (negative or positive) implied physically stable dispersions because of the electrostatic repulsion [8]. This is particularly important in the case of edible films, which are often made up of a complex mixture of biopolymers that tended to separate or form clumps. In addition to improving the stability of the composite system, the increased zeta potential can also help to improve the release and diffusion properties of the film, which can be beneficial for applications such as controlled release of active compounds.

3.2 Surface roughness

AFM provides a powerful method for both qualitative and quantitative analysis of film surface roughness at nano-scale level [9]. These properties of the films are directly associated with the surface irregularities, which were usually affected by the addition of other materials. As seen in Figure 1, the surface of HPC/CDH/LAE films was relatively continuous without pores observed, contoured, and no cracks. Moreover, some droplets at nanoscale, found on the surface of emulsified film, were believed as the dispersed phase of CDH. The average value of the neat HPC (Ra = 5.26 ± 2.21, RMS = 4.65 ± 2.29) became rougher (Ra = 6.95 ± 0.66, RMS = 8.18 ± 0.78) when CDH droplets and cationic surfactant of LAE were incorporated into the main matrix. Although the opposite reports have been documented [10–12], other works found in line trends, the rougher surface for film containing essential oils [14]. Enhancement in the pattern of roughness might be corresponded to the presence of hydrophobic material aggregation and/or creaming process as the result of drying during film formation.

HPC/LAE/CDH

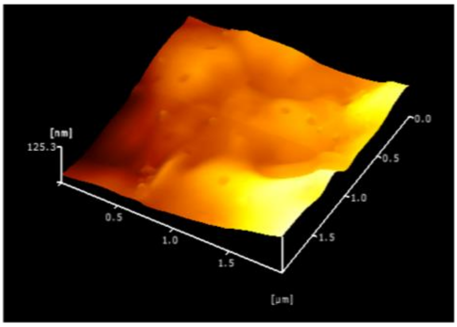

Fig 1. The 3D image of edible film surface topography

To further understand the effect of the addition of CDH/LAE, the analysis of height and line profile were done (Figure 2). The 2D topography photographs were visually seen to form uplands structures. Besides, the height profile, and vertical and horizontal line profile of HPC/CDH/LAE surface films were observed. The addition of bioactive compound emulsified with cationic surfactant were seen forming higher Z axis ranges than the film made of pure main matrix. This might represent the aggregation of hydrophobic component which was exacerbated when water content evaporated [1, 14]. Earlier investigation reported a similar phenomenon, in which the incorporation of cajuput oil into sodium alginate-based film had a higher line of Z axis profile [15].

Any changes in the surface roughness of edible film might influence the related properties. Roughness on the surface of the film can increase its mechanical strength, making it more resistant to tearing or breaking [16]. The rough surface also can improve the adhesion of the film to a substrate or to another film layer, which can be useful in layered or composite structures [17]. This enhancement in roughness increases the surface area of the film, which can improve its barrier properties against oxygen, moisture, and other gases. Depending on the application, a rough surface can provide a desirable texture or mouthfeel to the some produces. However, the roughness on the surface of the film can make it more challenging to handle and process during production and packaging such as labels or other decorations to the surface. In the case the roughness is not uniform across the film surface, it may result in an uneven distribution of active ingredients or additives. Furthermore, roughness can create more sites for microbial attachment and growth, which can increase the risk of microbial contamination [17].

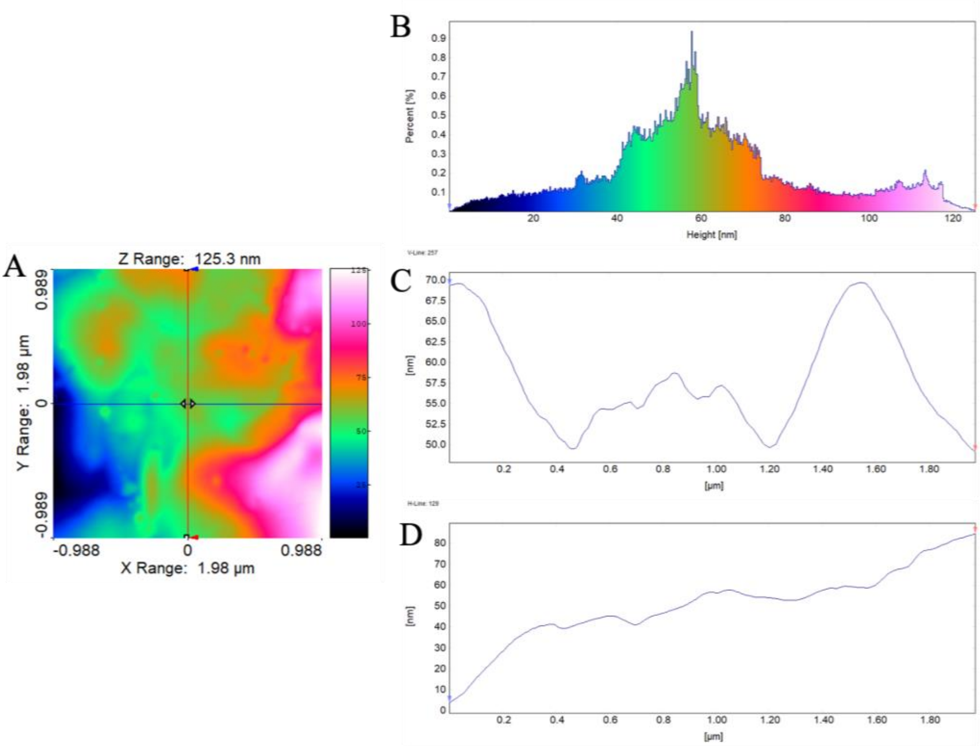

Fig 2. 2D Image (A), height profile (B), vertical (C), and horizontal (D) line profile analysis of HPC/CDH/LAE surface film

4 Conclusion

This study evaluated the influence of the addition of CDH and LAE on the HPC film surface using AFM technique. The results showed that the addition of CDH/LAE increased the zeta potential of the neat HPC film forming solution, confirmed by zetasizer analysis. AFM analysis could reveale that the roughness properties of CDH-emulsified LAE, confirmed with Ra and Rq values. Emulsification of CDH/LAE into HPC matrix might affect the properties of HPC film which have not studied yet in this work. Finally, it is important to carefully consider the advantages and disadvantages of roughness when designing an edible film for a specific application.

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