Atomic force microscopy study of surface microstructure properties of hydroxypropylcellulose/cinnamaldehyde composite biofilm

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Abstract. This study used atomic force microscopy (AFM) to examine the microstructure properties of a composite biofilm made of hydroxypropylcellulose (HPC) and cinnamaldehyde (CDH). The zeta potential of the HPC-based solution was found to decrease from -1.31 to -3.24 (mV) with the addition of CDH-emulsified CDH, according to Zetasizer analysis. Additionally, the roughness of the surface properties showed an increasing trend. AFM analysis indicated that the surface roughness of the HPC film increased by 1.31 and 4.01 nm in terms of arithmetical mean deviation from the mean (Ra) and root mean square deviation from the mean (Rq), respectively, with the addition of CDH-emulsified CDH. Changes in the surface properties of the biofilm could affect its barrier properties, such as water resistance and light transmission.

1 Introduction

Edible films have become a popular focus of research as a potential solution for maintaining food quality. Hydroxypropyl cellulose (HPC), a biomaterial, has been identified as a promising film-forming material and has been the subject of a limited number of studies [1]. HPC has both hydrophilic and nonionic properties due to the hydroxypropylation of some of its OH groups, resulting in -OCH2CH(OH)CH3 groups. However, using pure HPC for filmmaking does not produce satisfactory results; hence further efforts to enhance its performance are necessary.

The utilization of emulsified edible film is considered as a strategy, whereby edible films can serve as potential carriers for various active compounds that are beneficial,

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including antioxidant and antimicrobial agents, as indicated by Abdollahi et al. (2012) [2]. Cinnamaldehyde, an exceptional bioactive compound that has been investigated, is the major component in cinnamon essential oil, a plant extract [3,4]. It possesses strong antimicrobial and antioxidant properties, which may have positive impacts on the pure HPC film [3,5].

Studying roughness is crucial when producing edible films, as it indicates the functionality of certain features like contact angle, hydrophilicity, adhesion, and water vapor barrier. This study produced an emulsified film composed of HPC and CDH, and the surface roughness characteristics were analyzed using the AFM technique.

2 Methods

To produce the HPC-film solution, a mixture was prepared by combining 4% HPC powder from Nippon Soda, Japan, with distilled water and stirring the mixture with a magnetic stirrer at 500 rpm for 30 minutes. A plasticizer agent, glycerol 0.25% v/v from FUJIFILM Wako Pure Chemical Corporation in Japan, was then added and stirred for 10 minutes. An emulsion stock was prepared by adding 0.6% v/v CDH from FUJIFILM Wako Pure Chemical Corporation in Japan to a solution containing 0.4% Tween 80 from the same company and homogenizing the mixture with a high-speed homogenizer from T 25 digital ULTRA-TURRAX® - IKA in Germany at 15,000 rpm for 2 minutes. Afterwards, the HPC solution was homogenized with either the emulsion stock or distilled water (for pure HPC film) in equal ratios at 15,000 rpm for 2 minutes to achieve 2% HPC and 0.3% CDH, and the mixture was degassed under vacuum for 15 minutes. The resulting film-forming solution was poured into silicon mold plates measuring 8x8 cm and each containing 20 ml of solution, and the plates were dried in an oven at 35°C for 18-20 hours. The dried films were then stored in a desiccator with a relative humidity of 50 ± 4%.

The Zetasizer Nano ZNP, made by Malvern Instruments in the UK, was used to measure the Zeta potential of the film-forming solution. The solution was placed in capillary zeta cell DTS1070 before being measured five times.

To analyze the roughness of the film surface, an atomic force microscope Hitachi 5200S from Japan was used. A sample was attached to a sample stub using double-sided carbon tape and scanned in tapping mode using a cantilever type SI-DF20 with a frequency of 0.7-0.84 Hz and a scan area of 2x2 μm2. The Rq and Ra were calculated from 10 measurements of different line profiles.

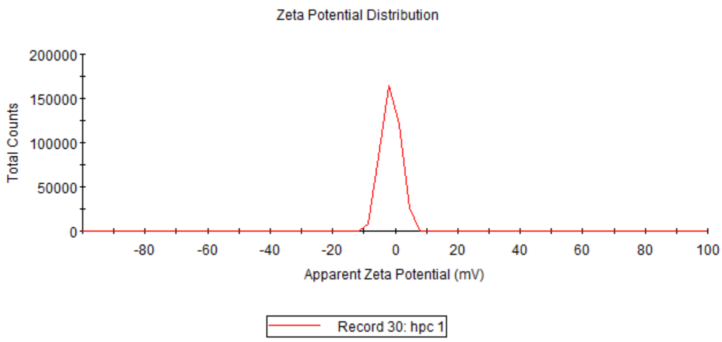
$$Rq = \sqrt{\frac{1}{n}\sum_{i=1}^{n} Zi^2} \tag{1}$$

$$Ra = \frac{1}{n}\sum_{i=1}^{n} |Zi| \tag{2}$$

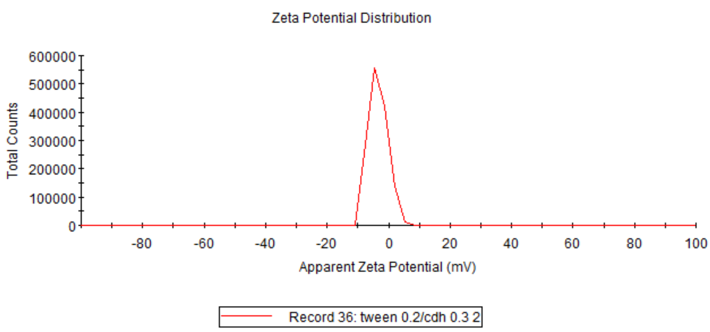
Zi = the height deviation of the i-th value, n = the total number of data points.

3 Result and Discussion

The film-forming solution of HPC had a zeta potential value of -1.31 ± 0.06 mV, indicating a negatively charged surface. The introduction of CDH into the solution resulted in a reduction of the zeta potential to -3.24 ± 0.08 mV (Fig 1). These values suggest that the colloidal dispersion was not stable. As per the theory, when the zeta potential value is more than ±30 mV (negative or positive), it indicates stable dispersions due to electrostatic repulsion [6].



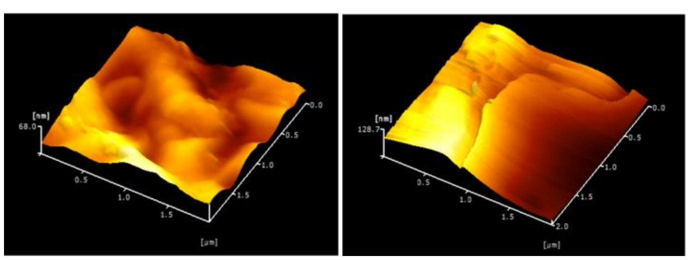
(a)



(b)

Fig 1. The zeta potential of HPC (a) and HPC/CDH (b) films

Previous report stated that AFM was a highly effective technique for evaluating film surface roughness at the nano-scale level, both qualitatively and quantitatively [7]. These surface properties were directly influenced by irregularities, which were often caused by the incorporation of other materials.



(a) (b)

Fig 2. The 3D image of the surface microstructure of HPC (a) and HPC/CDH (b) films

Fig 2 shows that both the HPC and HPC/CDH films have relatively smooth surfaces with no visible pores or cracks. The HPC/CDH film exhibited an increasingly rough surface, with some uplands believed to be the dispersed phase of CDH in the emulsified film. The addition of CDH to the main matrix resulted in a rougher surface, as evidenced by the increase in Ra and Ra values. The average value of the neat HPC (Ra = 5.25 ± 2.21nm, Rq = 4.55 ± 2.29 nm) became rougher (Ra = 6.57 ± 1.06 nm, Rq = 8.56 ± 1.13 nm) when CDH was incorporated into the main matrix. While some studies have reported contradictory results, such as the rougher surface of films containing essential oils [8,9,10], other works have found similar trends [11]. The increase in roughness may be attributed to the presence of hydrophobic material aggregation and/or creaming during film formation and drying.

In order to gain a better understanding of the impact of adding essential oil, researchers analyzed the height and line profile of the film's surface (as shown in Fig 3). The researchers observed that the 2D topography photographs displayed raised structures, and the height profile and vertical and horizontal line profile of the film with added bioactive compound (CDH) were higher compared to the pure HPC film. The addition of the bioactive compound emulsified regular surfactant (Tween 80) resulted in a higher range of the Z axis, indicating the aggregation of hydrophobic components, which became more apparent as the water content evaporated [1,12,13,14]. This phenomenon has been previously reported in studies involving the incorporation of cajuput oil into sodium alginate-based film [15]. Any changes in the surface roughness of the edible film could potentially affect properties such as water and light barrier, as well as mechanical and physical characteristics.

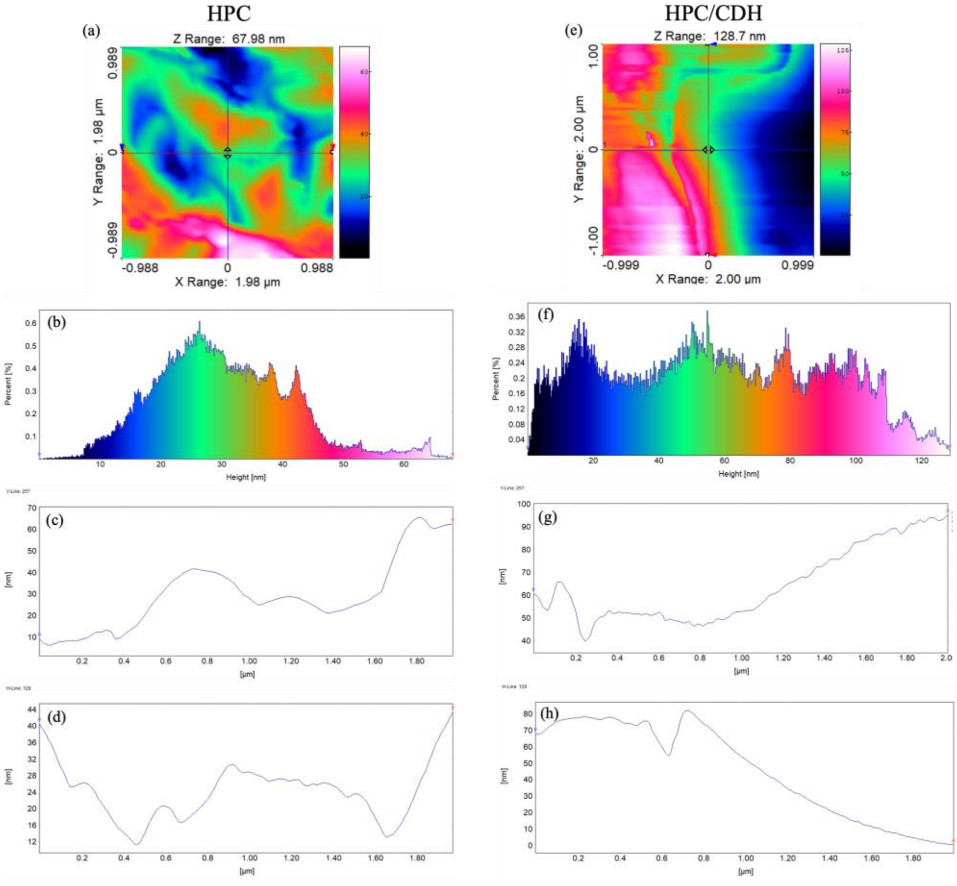


Fig 3. 2D Image (a, e), height profile (b, f), vertical (c, g), and horizontal (d, h) line profile analysis of surface films

4 Conclusion

In our research, we examined how the surface of HPC film was affected by the introduction of CDH using the AFM technique. The findings indicated that the zeta potential of the HPC film-forming solution decreased when CDH was added, which was verified through Zetasizer analysis. Additionally, the roughness characteristics of HPC increased as CDH was introduced, as indicated by Ra and Rq values observed in AFM analysis. However, we did not explore how the barrier properties of the HPC film, such as its water resistance and light transmission, may be affected by the incorporation of CDH.

5 Acknowledgment

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