The Effect of Beeswax and Chitosan Concentrations as Superhydrophobic Coating on Wound Dressing

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Abstract: One of the factors that caused the wound dressing to be wet is water permeability through wound dressing pores. A wet wound dressing must be replaced frequently in order to prevent infection. On the other side, the recurring replacement of wound dressing increases the amount of infectious waste. As a consequence, one of wound dressing called Hypafix is coated with the beeswax-chitosan mixture to obtain a waterproof ability by a facile method. The purpose of this study is to determine the effect of concentrations of beeswax and chitosan solutions as a superhydrophobic coating material on Hypafix and analyze the waterproof characteristics. There are two models of research, beeswax concentration (0, 0.25, 0.5, 2, 2.5%wt/v) with constant concentration of chitosan 0.5%wt/v, and chitosan concentration (0, 0.25, 0.5, 2, 2.5%wt/v) with fixed concentration of beeswax 0.5%wt/v. The contact angle (θ), hysteresis, morphology of film, and functional group analysis were characterized. The results showed that the contact angle was significantly increased with increasing beeswax and chitosan concentrations but decreased at a concentration of 3%wt/v. The lowest hysteresis of the sample was successfully obtained at 1.3° with θ~151.2° using beeswax/chitosan concentration of (2.5 : 0.5) %wt/v. Scanning Electron Microscope (SEM) showed that the film covered the gauze fibers. Hence the surface was rougher and also increased contact angle as explained in Cassie-Baxter Theory. Furthermore, FTIR indicated that the layers formed on the fibre by both beeswax and chitosan compounds, while they contributed to the Hypafix surface superhydrophobicity in beeswax and chitosan optimum concentrations.

1 INTRODUCTION

Several strategies are needed for wound care. The ability of the dressing to maintain the moisture of the wound, absorb exudate, and remove dead tissue must be considered (Setiyawan, 2016). The wound that loses its moisture will cause damage to the tissue, while for a wound that contains a lot of exudates, an absorbent must be applied to keep the moisture. The more exudates produced, then the frequency for changing the bandages will be higher. In addition, the moisture of dressing is affected by the amount of water that hits the dressing. Water seeping into the dressing will increase the moisture inside and resulting in an increase in the frequency of dressing replacements, even though the exudate absorbed was still very low. Thus, a waterproof patch is needed to reduce the intensity of the dressing replacement.

In recent years, researchers have been established modern wound dressing not only to cover the wound but aid the function of the wound. This dressing is focused both on keeping the wound moisture and promote healing. One of modern wound dressing can be classified as interactive wound dressings. They are semi-occlusive or occlusive that focused more on preventing the skin from losing moisture by forming a protective film over the epidermis (Degreef, 1998). Occlusive dressings are widely used to support the wound healing process. Occlusion develops the microenvironment of a wound and increases the rate of repithelialization (Fernandez-Castro et al., 2017).

Hypafix[a] One of the most common modern dressing is a white, thin, elastic, adhesive coated

[a] Hypafix (Registered Trade Mark): supplied by BSN Medical, Inc., Charlotte, NC, United States.

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non-woven polyester film permeable to both air and moisture in order to minimize the risk of maceration. This dressing still has hydrophilic properties, which can cause water to be absorbed from the outside. Water that contacts with a hydrophilic surface will wet the surface when dripped on it. Wet wound dressing can induce wound infection so that it should be replaced often. However, the wound dressing is one of infectious waste; hence its amount has to be reduced as medical waste. In contrast, when a surface has hydrophobic property, water will not wet the surface (Wenten et al., 2015). Therefore, a wettability property modification on a wound dressing surface is conducted to reduce the amount of infectious waste. A method is proposed to make a waterproof dressing by modified its outer side to become hydrophobic. One of the parameters that can be measured to determine the hydrophobicity of a material is the contact angle. Material, which has a contact angle above 90^o, can be categorized as hydrophobic materials (Butruk et al., 2011). If the contact angle exceeds 150^o, the material can be categorized into superhydrophobic material. By forming a superhydrophobic layer, it will be difficult for water to seep through the pore pads.

Commercially, there are some waterproof wound dressings that are widely used in the world. Mostly, those kinds of dressings have hydrophobic abilities due to Durable Water Repellent (DWR) coating on their fabric. However, in general, a key substance resulting in a waterproof surface is contained fluor. Based on previous studies, the fluor-based substances are hazardous for human health, so their application on wound dressing is not suggested. On the other hand, Chemical Vapor Deposition (CVD) method provides a very thin water repellant film with no use of hazardous regeants. Nonetheless, this method is categorized as a sophisticated method and needs a vacuum condition. Based on the background, a facile method using no harmful material is induced to modify the surface of the wound dressing. A mixture of beeswax and chitosan can be used as one of the candidates to form a hydrophobic coating material. El-Bisi reported that the addition of beeswax into chitosan on cotton fabric could increase the contact angle of up to 152^o (El-Bisi et al., 2016). Beeswax and chitosan have anti-microbial properties that are widely used for medical purposes.

Beeswax is a pure wax formed from a beehive derived from *Apis mellifera* bees, which contain ester almost 70%. Esters have a non-polar group that has the ability to bind water relatively small. A study has been reported that beeswax has a contact angle between 100^o-110^o (Naderizadeh et al., 2019).

Chitosan has hydroxyl and amine groups along the chain. This causes chitosan to be very effective for adsorbing cations from organic substances, especially proteins and fats (Lee et al., 2001). Moreover, chitosan polymer contains a positively charged amino group that can bind to negatively charged via ionic or hydrogen bond. These bonds cause chitosan to be difficult to bind to water (Setiani et al., 2013). It has been reported that chitosan has a contact angle between 70^o-91^o (Farris et al., 2011).

In the present work, we describe the effect of chitosan and beeswax mixture concentration to develop a superhydrophobic coating on Hypafix. The morphology, hysteresis, and contact angle were studied in detail.

2 EXPERIMENTAL METHODS

2.1 Synthesis of Superhydrophobic Layer

Beeswax (*Apis mellifera*) solution was prepared by dissolving beeswax in 2-propanol (Merck, 98% purity). Prior to use, 2-propanol was preheated for 30 minutes at 75°C. Moreover, chitosan (degree of deacetylation = 79%) solution was prepared to dissolve in 1% (v/v) acetic acid solution (Merck, 98% purity) at room temperature with a stirring speed of 1000 rpm for 1 hour and further heated for 30 minutes at 75°C. Then, beeswax solution and chitosan solution are mixed at 75°C with a stirring speed of 1200 rpm for 2 hours. After that, the whole mixture was homogenized for 30 minutes by Ultrasonic. Last, *Carboxymethyl Cellulose* (CMC) with high molecular weight (262.19 g mol^{-1}) added in the mixture, and homogenization is continued for 60 min. The mixture was obtained from two experiment models. First, different concentration of beeswax solution (0.25%, 0.5%, 2%, 2,5%) in wt/v were mixed with fixed concentration of chitosan solution (0.5% wt/v). Second, different concentration of chitosan solution (0.25%, 0.5%, 2%, 2,5%) in wt/v were mixed with fixed concentration of beeswax solution (0.5% wt/v).

2.2 Coatings Preparation

The mixture coatings were prepared by the casting method in the outer layer of gauze (*Hypafix*). After the deposition process, the samples were dried at room temperature for 20 hours. Thus, the patch with coatings was obtained.

2.3 Coatings Characterization

2.3.1 Contact Angle Measurements

To evaluate the surface hydrophobicity of patch with coatings, contact angles were determined by dropping ten microliters of water on the surface of the patch that has been coated with superhydrophobic material. Then, the picture of the surface of the patch was taken using a camera (Nikon D5500), and the results of the images were analyzed using ImageJ software to determine the right and left contact angle values. The reported contact angle results were the average values from the right and left contact angle values. Measurement was performed three times.

2.3.2 Contact Angle Hysteresis Measurements

The contact angle hysteresis measurements have the same procedure as the one previously described for contact angle measurements. However, the hysteresis measurements were not carried out on a flat surface, but rather a surface with an angle of 10° from the flat surface. Thus, the values of the front angle and rear angle are obtained. The reported contact angle results in the difference between the two angles.

2.3.3 Morphology

In order to know the surface of the patch which is coated with a mixture of beeswax-chitosan, the patch with coatings were visualized using a scanning electron microscope (SEM Tescan Vega3 LMU) at PT Gestrindo Sakti Utama, Jakarta

2.3.4 Functional Group

Functional group analysis was performed to determine the functional group on the beeswax-chitosan mixture. The analysis was carried out using Fourier Transform Infrared Spectroscopy (FTIR PerkinElmer type Spectrum Two) at PT DKSH Indonesia, Jakarta.

3 RESULTS AND DISCUSSION

3.1 Characteristic of the Coating Solution

Naturally, beeswax consists of no polar groups in its structure. This characteristic makes beeswax is difficult to bind water molecules. On the other hand, chitosan reduces the water affinity that results in no permeation of drops on the substrate (Mohamed et al., 2011). When beeswax and chitosan are mixed, the hydrophobic behavior is improved to be superhydrophobic. Superhydrophobic ability is produced by bonding between NH_3^+ groups from chitosan and fatty acids from beeswax that has anions. This bond is categorized as an ionic bond. In order to form NH_3^+ polycationic, chitosan has been dissolved in acetic acid 1% v/v. Carboxymethyl cellulose (CMC), as an emulsifier, is needed to homogenize the beeswax-chitosan mixture. After sonication, beeswax droplets in the solution become smaller, and they are adsorbed by CMC. This mechanism prevents the coalescence of small droplets from being the bigger ones (Dickinson, 2009).

3.2 Wetting Properties

The ordinary Hypafix is permeable to water, as shown in Fig. 1. Drops come through pores, and it corresponds to the increase of moisture content in wound dressing. Besides, a wet wound dressing should be replaced with the new one. Frequent replacement of wound dressing can lead to infectious waste pollution

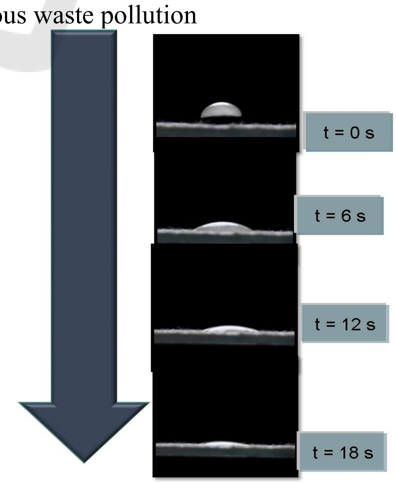
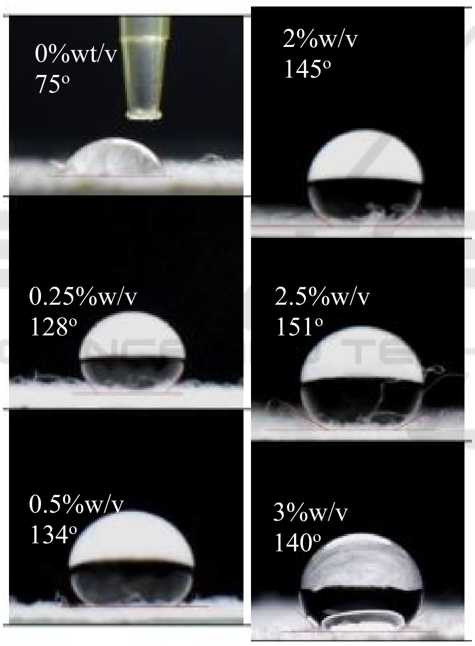


Figure 1. The water drop behavior on the ordinary Hypafix

In contrast, when Hypafix is coated by beeswax-chitosan mixture, drops permeation does not exist, and the drops have a static contact angle on a flat plane. The variations of beeswax and chitosan concentrations evidently affect the coating wettability properties. They are summarized in Fig.2 and Fig.3. In Fig. 2, beeswax concentration varies from 0 to 3% wt/v. The increase of beeswax concentration leads to a higher contact angle due to many fatty acids compounds provided by the beeswax bond with NH_3^+ groups. The highest contact angle,151o, is resulted from 2,5% wt/v of beeswax. However, the contact angle decreases to 140^o when beeswax is added up to 3% wt/v. This reduction relates to NH_3^+ groups' lack of availability to bond with fatty acids, so the superhydrophobicity is majorly contributed from the nonpolar beeswax structure (Supeni and Irawan, 2012).

(a)



(b)

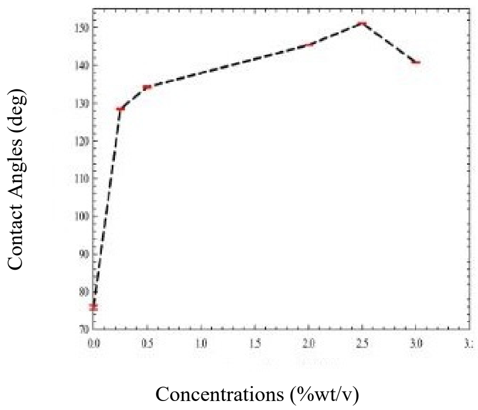
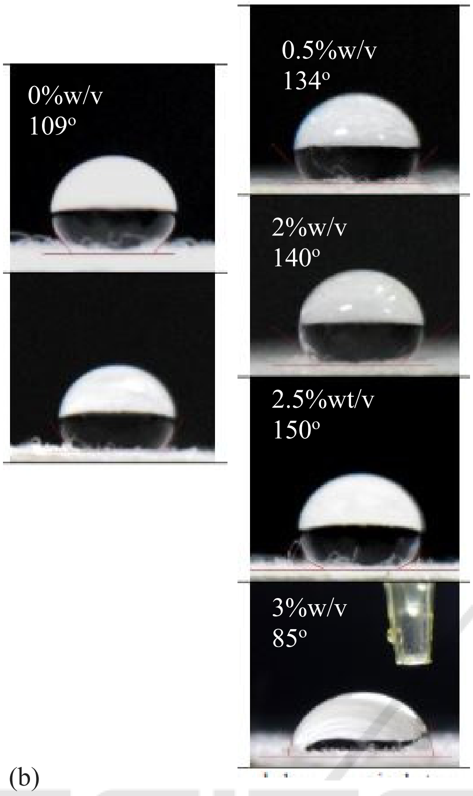


Figure.2. (a) The variations of beeswax concentrations and the fixed chitosan concentration (0.5%w/v) affect the contact angles. (b) Graphic of contact angles and beeswax concentrations.

The other result is conducted from variations of chitosan concentration and fixed beeswax concentration (0,5% wt/v), as shown in Fig 3. The high concentration of chitosan refers to many NH_3^+ groups. These groups bond with anions of fatty acids to modify the wettability from hydrophobic to superhydrophibic. The contact angle of 150^o is reached when chitosan is 2,5% wt/v. Nonetheless, the high concentration of chitosan (3% wt/v) changes the wettability from superhydrophobic to hydrophilic (85^o). This contact angle is in a range of the chitosan one, which is 70-90^o (Farris et al., 2011). This phenomenon corresponds to the domination of NH_3^+ groups with small nonpolar structures from beeswax. In addition, there is a lack of bonding between NH_3^+ groups and fatty acid, which can conduct the hydrophobicity.

(a)



(b)

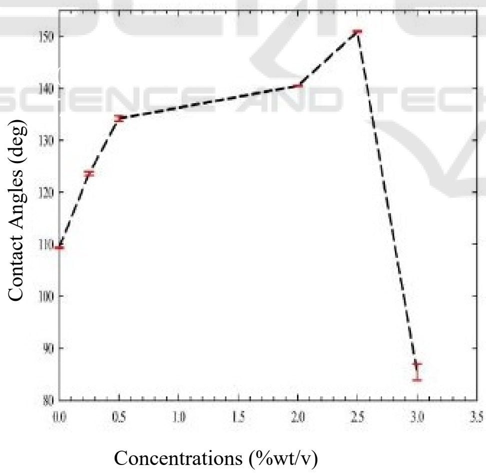


Figure.3. (a) The variations of chitosan concentrations and the fixed beeswax concentration (0.5%w/v) affect the contact angles. (b) Graphic of contact angles and chitosan concentrations.

In further, contact angle hysteresis is also evaluated on the coated substrate. It is conducted by the tilted-plane method. This test represents an initial confirmation of whether the drops are pinning or not. From Fig.4, it is shown that the hysteresis is small, around one to four degrees. The results potray that drops can easily slide on the Hypafix. The small gap between the front and rear angles indicates that the hysteresis is small. Small hysteresis corresponds to almost no defects that exist on the surface. The existence of defects is one of the sources for capillary force, which will sustain the drop on the surface. In simple words, small hysteresis relates to weak capillary force.

In other perspectives, higher contact angle induces drops to have an almost perfectly round shape, so there is no big difference between the front and rear angles. The shape also affects the movement of the drop. When it has hydrophobic or superhydrophobic wettability, the drop movement is dominated by a rolling mechanism than a sliding one (Wenten et al., 2015).

Figure.4 Contact angle hysteresis of variations beeswax concentration and fixed chitosan concentration (0.5%w/v)

3.3 Physicochemical Properties of Superhydrophobic Coating

Functional group analysis by FTIR shows that the coating consists of beeswax and chitosan, as represented in Figure. 5 and Figure 6

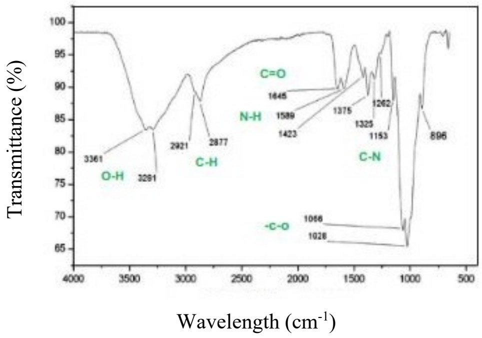


Figure.5. FTIR Spectrum of chitosan (2.5%w/v) and beeswax (0.5%w/v).

Based on Fig.5, in wavelength of 3361-3291 cm^{-1}, there is vibration from hydrogen bonding between O-H in chitosan. The alkanes in chitosan that composed of C-H and N-H are shown in 2921-2877 cm^{-1} and 1589 cm^{-1}, respectively. The primary amine and primary amide (C=O in (-$NHCOCH_3$) bond) are also detected in 1153 cm^{-1} and 1645 cm^{-1} absorbances, respectively. The data of wavelength is cited from Sigma-Aldrich. The later indicates that there is a bond between NH3+ groups and beeswax anions (Wittriansyah et al., 2018).

The functional group in beeswax is shown in Fig.6. The primary functional groups of beeswax are indicated as asymmetric C-H (CH_2), C=O carbonil, and C-O esther in 2800-2900 cm^{-1}, 1750 cm^{-1}, and 1100 cm^{-1} respectively (Lambert et al., 1998; El-Bisi et al., 2016; Hromis et al., 2011). The key that shows if there is a bond between chitosan and beeswax is primary amide or C=O. This functional group is found in 1460 cm^{-1} absorbance. In those samples, it can be known that beeswax-chitosan are mixed uniformly.

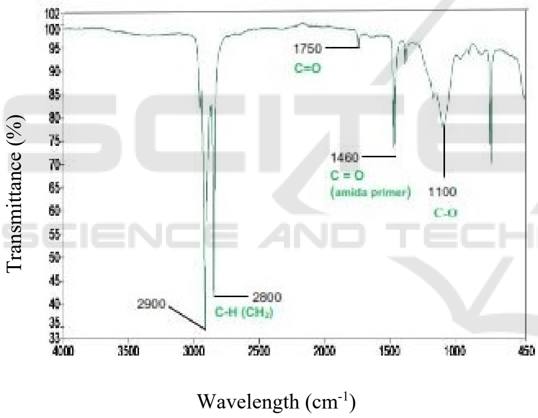


Figure.6. FTIR Spectrum of beeswax (2.5%w/v) and chitosan (0.5%w/v).

To analyze the morphology of coating on the substrate, the Scanning Electron Microscope is used as the instrument, and the result is shown in Fig.7 (a). The superhydrophobic coating does not clog the pores. Hence the wound dressing still has a breathable characteristic, which keeps air circulation around the wound. It can be distinguished that the coated substrate has a film that covers its fibers. The film contributes to the roughness of the surface. This roughness contributes to the superhydrophobicity, as described in Cassie-Baxter Theory that illustrated in Fig.7 (b). The roughness creates pockets filled by air. When drop placed on the rough surface, the interaction between air-substrate is stronger than drop-substrate interaction. It relates to the higher surface tension between the drop and substrate. Hence it makes the drop tends to have a round shape and has a high contact angle.

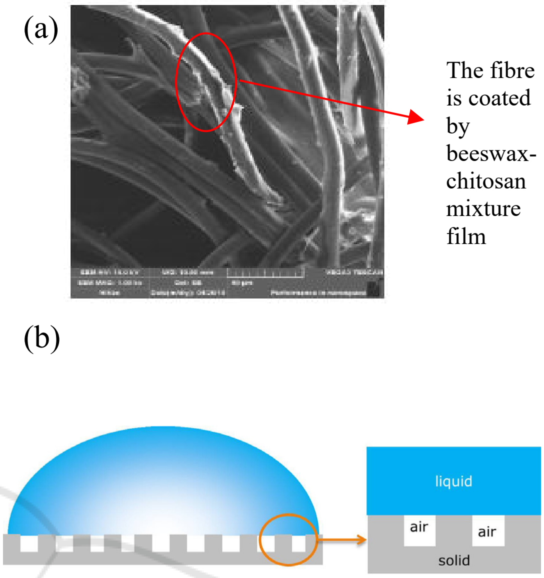


Figure.7. (a) Surface morphology of beeswax-chitosan (0.5%wt/v-2.5%wt/v) in 1000x zoom. (b) Illustration of the Cassie-Baxter Model

4 CONCLUSION

The superhydrophobic coating on a Hypafix is produced by a mixture of beeswax and chitosan. The variations of beeswax and chitosan concentrations in the mixture affect the wettability properties of the coating. It can be concluded that beeswax is the hydrophobic agent that has 151° of contact angle in 2.5% wt/v. It is also convinced when beeswax is 3% wt/v, the superhydrophobicity is maintained in 140.8° despite the contact angle decreases from the early value. Although chitosan also has a close contact angle in the same concentration (2.5% wt/v), chitosan is not the primary compound to obtain superhydrophobicity due to the change of wettability into hydrophilic (Contact angle=85°) when the NH_3^+ groups are dominated (3% wt/v).

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