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Dynamic Contact Angle of Modified Biopolymer Droplet on Urea Surface: Temperature Effects

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Abstract. The droplet impact behaviour provides the particle coating characterization during the coating process of controlled release fertiliser. To have a good coating uniformity around the urea granules, it is necessary to enhance the wettabitily properties between the coating material and urea surface. The biopolymer material is preferred as the coating material because this polymer may degrade and will not cause any environmental impact to the environment. Various compositions of starch/urea /borate/lignin were prepared and evaluated for the wettability properties. The wettability characteristic measured is the dynamic contact angle. The high speed Charged-Couple Device (CCD) camera was used to capture the images of this droplet impact behaviour. Temperature plays an important factor during wetting stage because the coating material must be completely dried in continuous coating process in fluidised bed. From this analysis, it indicates that a composition of starch/urea/ borate (50/15/2.5) with 10% lignin has the best wettability characteristic and thus suitable to be used as a coating material. The ideal temperature for the coating process is 60°C.

Introduction

Urea is widely used as fertiliser due to high content of nitrogen [1]. However, the solubility characteristic of urea in water has caused the nutrient excessively absorb into the soil. Therefore, the controlled release urea (CRU) is introduced to minimise the loss of nutrient into soil and optimise the nutrient by plants. The biopolymer material is preferred as the coating material because this polymer may degrade and will not cause any environmental impact to the surrounding. Starch is known as a natural polymer which is safe to the environment [2]. Recently, the research on starch-based polymer has gained lots of interest in several of applications. The biopolymer compatibility with the urea phase is an important factor in the coating process since the adhesion properties at the interface will determine the final mechanical properties of the controlled release fertiliser. Good mechanical properties such as modulus and impact strength are required to minimise attrition during the coating process and the final product must remain intact during storage and transportation. The impact behaviour of modified biopolymer droplet shows the wettability properties between the droplet and urea substrate during the coating process. Yet, less attention is given to this study in urea coating for the application in agricultural field.

The coating process of CRU is done in the fluidised bed by applying the thin film spray coating mechanism. During the coating process, the principle of film coating is applied where there are four stages involved as shown in Fig. 1. This droplet impact behaviour studied about the wetting stage at macroscopic level. The wetting phenomenon is very important because it will enhance the uniformity of coated material on urea and boost the controlled released property. One of the factors that affect the coating uniformity is the temperature inside the bed. As soon as the coating solution hit onto the particle, the droplets spread onto urea particles and wet particles collided and form liquid bridges [3]. The particles continued the dried process as they accelerated toward the expansion region in the fluidised bed. The urea particles must be completely dried before fell down in the down-bed region and repeating the same process. If too high temperature is supplied, the coating droplets will dry before it can reached the urea particle. Therefore, an optimum temperature is very crucial because it will affect the wettabilty properties between the coating material and urea particle.

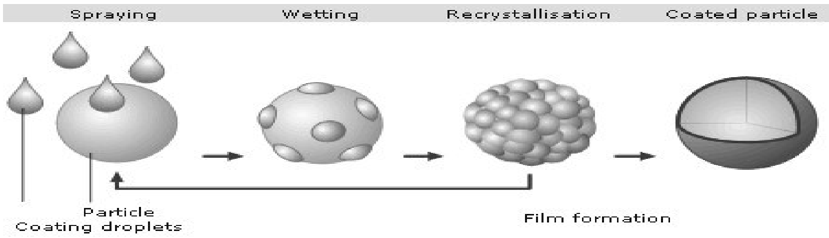


Figure 1: Principle process of film coating in fluidized bed [3].

According to Young's equation, the consideration of forces in the tangential direction which connects three interfacial tensions, γ_{sl}, γ_{sv}, and γ with the value of the equilibrium contact angle, θ. The Young's equation is given as:

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma \quad (1)$$

Eq. 1 represents the γ_{sl}, γ_{sv}, and γ as solid-liquid, solid-vapour, and liquid-vapour interfacial tensions respectively. Wetting is defined when a liquid drop spreads on a solid substrate until it reach equilibrium in shape [5]. Dynamic contact angle are associated with a moving contact line which depend on the velocity of the dynamics of spontaneous spreading. The spontaneous spreading of a liquid drop on solid surface can be determined by measuring the rate change of contact angle [6] or the diameter (contact line) of the liquid onto solid surface over time. However, the static contact angle is hard to measure as the contact line is moving against time until it dries onto urea substrate. Advancing dynamic contact angles [9,10] are measured to determine the wettabilty property of the coating material on urea surface. The objectives of this research is to determine the best formulation of coating material that has better wettability characteristic and to investigate the optimum temperature that would enhance the uniformity of CRU.

Experimental

The modified biopolymers were consists of starch, urea, borate and lignin. Starch is the main raw material, urea and borate as the cross linkers and lignin act as filler. These materials compositions were varies to enhance the wettabilty property and the controlled release mechanism. All the chemicals were analytical graded. The urea granules are provided by PETRONAS Fertilizer Kedah.

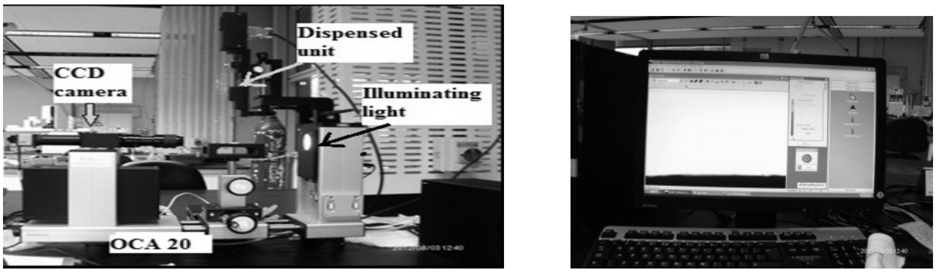
Preparation of Biopolymer Solution. The modified biopolymer solution was prepared by using mixing method. In 250ml round bottom flask, 5g of starch was dissolved in 100ml deionized water. The slurry was heated and stirred in water bath at 80°C. After 30 minutes, urea, borate and lignin were added to the mixture and continued mixing for another 3 hours. The prepared modified biopolymer solution was stored in a tight air container. Three modified biopolymer solutions were prepared by varying the composition of lignin as shown in Table 1.

Table 1: The compositions of modified biopolymer.

Solution	**Composition ratio (in 1000ml solution)**			
	Starch	Urea	Borate	Lignin
50/15/2.5	50.00	15.00	2.50	0.00
5% Lignin	50.00	15.00	2.50	3.55
10% Lignin	50.00	15.00	2.50	3.75

Preparation of Urea Surface. The urea granules were melted in petri dish at 130°C. As soon as all of the granules have been melted, the melted urea is immediately dried in the oven at 70°C for 30 minutes. The urea substrate was taken out form the dish and stored in desiccators to avoid moisture contact.

Determination of Dynamic Contact Angle. The Optical Contact Angle (OCA 20) measurement device as shown in Figure 2 was used to measure the dynamic contact angle of modified biopolymer solutions on urea substrate. 1ml syringe with 0.51mm needle tip was used to dispense the liquid with droplet size of 2mm±0.06mm. The temperature controller was adjusted with 20°C, 40°C, 60°C and 80°C. This device has a high-speed CCD camera feature to capture the high speed motion of the droplet impact. The SCA 20 software was used to conduct the experiment and analysed the digital image data obtained. The CCD camera of the OCA captured 17 – 25 frames per second. The droplet impact behaviour phenomenon was captured and recorded in a video mode. The selection data for dynamic contact angle was taken for every one second.



(a) (b)

Figure 2: The experimental setup using (a) Optical Contact Angle (OCA 20) device which is linked to (b) SCA 20 for conducting the experiment and analysis the data.

Results and Discussion

The data of dynamic contact angle of each composition solution was taken from the sequence data files of the video recorded. The sessile drop image [11] obtained is used to determine the contact angle value as seen in Fig.3 for the 10% Lignin solution which fit the Young-Laplace equation. The dynamic contact angle was measured per one second for ten seconds. The data images showed that the moving contact line of the solution on urea surface is spontaneously occurred. Thus, the coating solutions had good wettabilty properties as it continued to wet and adhere on the urea surface against time.

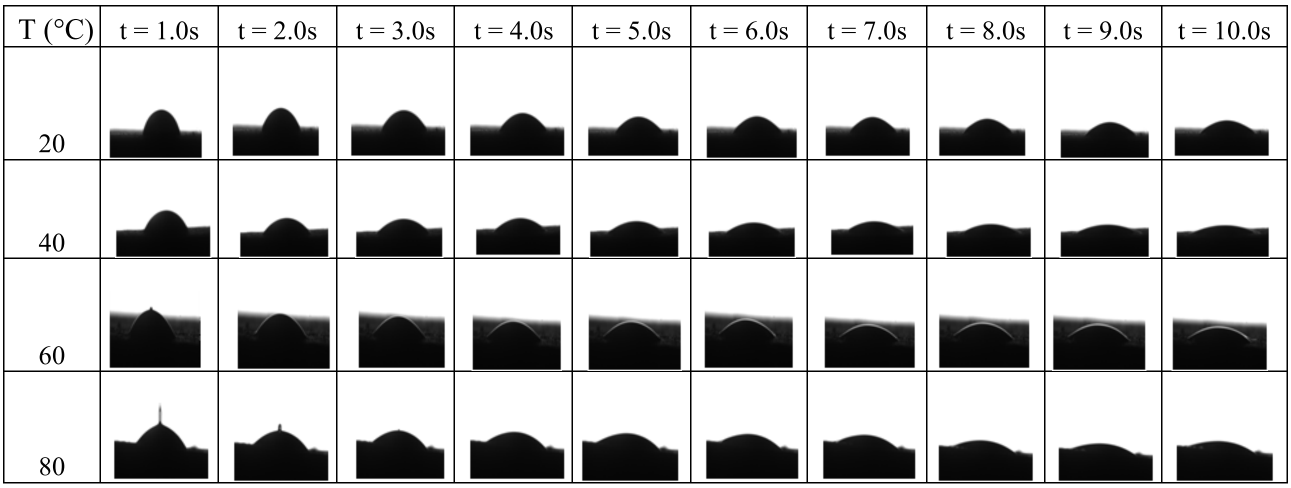


Figure 3: Sessile images of dynamic contact angle of 10% Lignin at different temperatures captured in every second.

Wettability properties of a solution would change with temperature as the viscosity, surface tension and the liquid – solid surface free energy changed. As the temperature increased, the solution becomes less viscous and the surface tension also decreased. Therefore, the biopolymer solution adhere more on urea surface and form smaller contact angle against time. Fig. 4 illustrated the graphs of dynamic contact angle against time at different temperature.

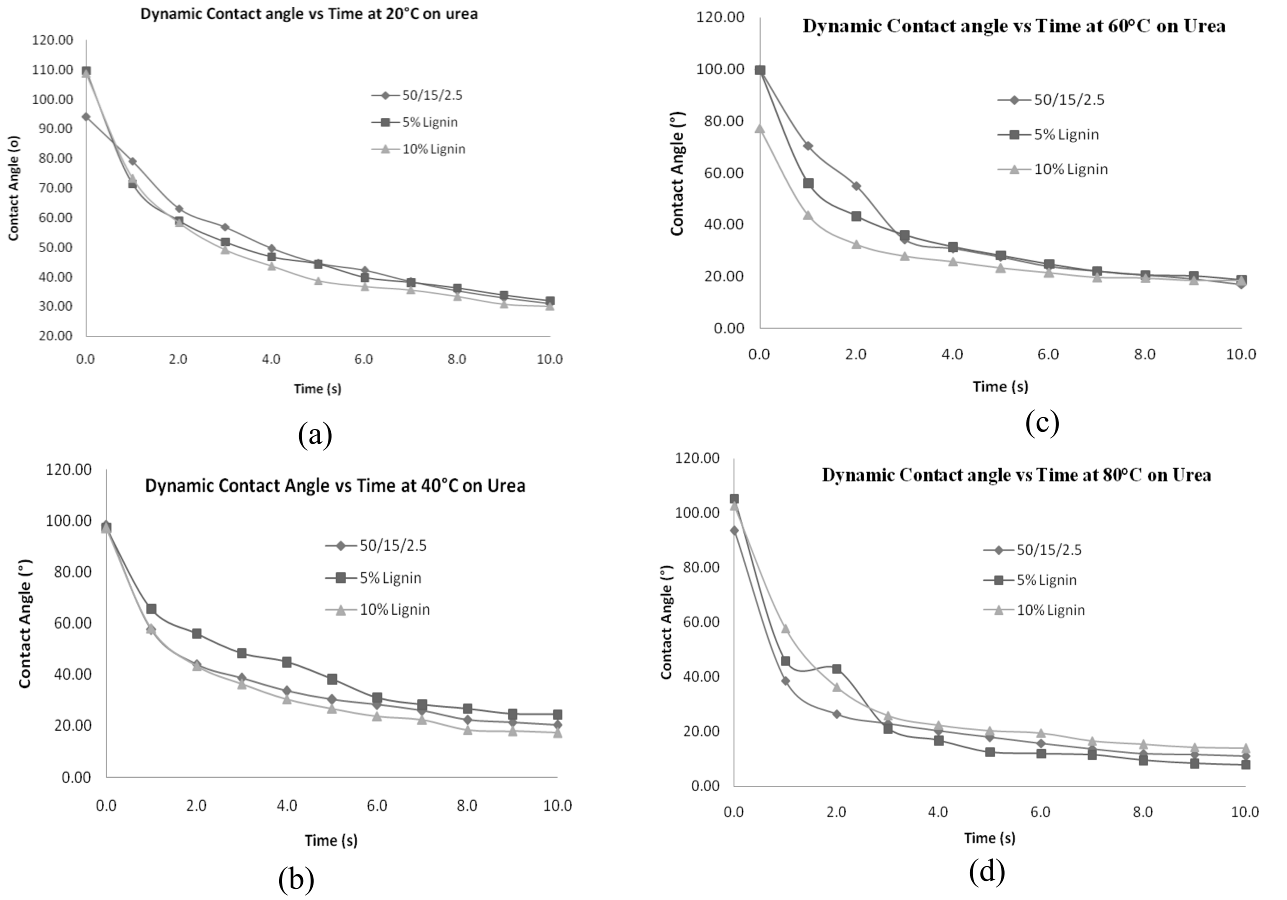


Figure 4: Dynamic contact angle of modified biopolymer solution against time at (a) 20°C, (b) 40°C, (c) 60°C and (d) 80°C

From the graphs, biopolymer solution with composition 10% Lignin has the smallest contact angle at temperature 20°C, 40°C and 60°C. It is shown that 10% Lignin solution has better wettability properties compared to 0% and 5% Lignin solutions. The surface free energy of 10% Lignin solution becomes lower as increased temperature, thus it wet and spread more on the urea surface. At 80°C, although 10% Lignin has value of contact angle, this temperature is not an ideal temperature because the biopolymer solutions tend to dry more before the droplet reached the surface. Therefore, 60°C is the most ideal temperature because the biopolymer solution has better wettabilty characteristic from 0s to 3s as this period of time is the crucial period for the solution spread on the surface during coating process in fluidised bed. After this time period, the particle would travel toward up – bed region for the coating material to spread and dry on the surface before fall down to downward region and repeat the same process again. At low temperature, the product pproduced will aggromarates as the coating material could not dry completely.

Summary

The dynamic contact angle of each coating material were measured at 20°C, 40°C , 60°C and 80°C against time from 0 second to 10 seconds. Three compositions of starch/urea/ borate (50/15/2.5) are differentiating by the lignin contain with 0%, 5% and 10%. As shown on all four graphs above, the composition of 50/15/2.5/10% lignin has better wettability properties with temperature changed. The smaller the contact angle of coating material on urea surface, the greater the wettability properties as the droplet of the coating material will spread more on the surface and enhance the uniformity of the coating layer. From this analysis, it indicates that a composition of starch/urea/ borate (50/15/2.5) with 10% lignin has the best wettability characteristic and thus suitable to be used as a coating material and 60°C is the most ideal temperature for coating process application.

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