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Impact Behaviour of Modified Biopolymer Droplet on Urea Surface

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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. In this study, modified biopolymer is used as the coating material for the controlled release fertilizer. Various compositions of starch:urea:borate were prepared and evaluated for the wettability properties. The wettability properties measured are the maximum spreading diameter, dynamic contact angle and surface tension. The high speed Charged Couple Device (CCD) camera was used to capture the images of this droplet impact behaviour. From this analysis, it is indicated that a composition of starch:urea:borate (50:15:2.5) has the best wettability characteristic and thus are suitable to be used as a coating material.

Key words: Wettability properties, biploymer, coating process

INTRODUCTION

The usage of controlled release urea has gained lots of interest around the world. Urea has been used as main fertilizer because it has high nitrogen content which is about 46% (Ni *et al*., 2009). However, urea is very soluble in water where all the nutrients are being absorbed into the soil excessively at early plant growth stage. Therefore, the controlled release urea is introduced to minimize the loss of nutrient into soil and optimize 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 environment. The biopolymer compatibility with the urea phase is an important factor in the coating process as 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 according to Zulhaimi *et al*. (2011). Yet, less attention is given to this study in urea coating for the application in agricultural field.

When a droplet impact on the solid substrate, the angle formed by the solid surface and the tangent line to the upper surface at the end point is called contact angle (Myers, 1990). 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) (Starov *et al*., 2007). The Young's equation is given as:

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

where, γ_{sl}, γ_{sv} and γ are solid-liquid, solid-vapour and liquid-vapour interfacial tensions, respectively. The physical properties of interaction between solid and liquid that can be obtained from contact angle measurement were the wettability, adhesiveness and solid surface free properties as shown in Fig. 1. Wetting is defined as when a liquid drop spreads on a solid substrate until it reach equilibrium in shape (Rein, 2002). Surface tension is known as the intermolecular forces to contract the surface

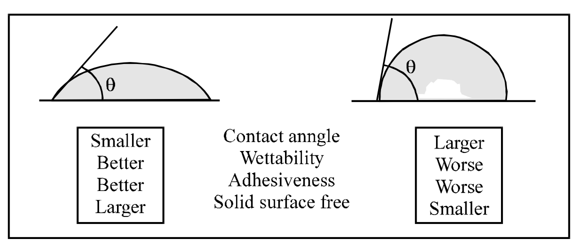

Fig. 1: Physical properties of solid-liquid interaction with contact angle (Kyowa Interface Science Co Ltd., 2007)

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where a molecule loses some cohesive interactions with its neighbours. Vadillo *et al*. (2009) mentioned that dynamic contact angle is associated with a moving contact line which depends 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 (Alteraifi *et al*., 2003) or the diameter (contact line) of the liquid onto solid surface over time. Spreading phenomena occurs if the contact angle exceeds the static contact angle during the first stage (Marengo *et al*., 2011) of the droplet impact. The spreading spontaneous behaviour (Gu and Li, 2000) and the study of the maximum spreading behaviour (Ukiwe and Kwok, 2005) are being modeled for the past years for a better understanding of the droplet impact phenomena. Other parameter, that can be determined during the second stage of the droplet impact behaviour, is the penetration rate of the liquid onto the solid porous surface.

The measurement of contact angle can be done with several methods; entropic edge detection (Atae-Allah *et al*., 2001), angle-of-contact (ASTM Standards, 2003), drop shape, sessile or pendant drop (Arashiro *et al*., 1999) and the Wilhelmy plate (Shang *et al*., 2008) methods. A new method based on the Young-Laplace equation (Stalder *et al*., 2010) is introduced for contact angle and surface tension measurement as given below:

$$\Delta P = \gamma\ (1/R_1+1/R_2) \qquad (2)$$

where, R_1 and R_2 are the principle radii of curvature at any point of the drop, γ is the surface tension and ΔP is the pressure difference across the surface.

This new method used sessile drop images to determine the contact angle and surface tension and this system can be analysed at low computational burden. Most of the measurement device recently used this method for the contact angle and surface tension measurement. This 50:15:2.5 ratio solution has the smallest contact angle where it have better wettability, adhesiveness properties and larger solid surface free energy for the liquid to spreads and adheres smoothly.

MATERIALS AND METHODS

The modified biopolymer solutions were prepared with different composition of starch, borate and urea. Urea from PETRONAS Fertilizer Kedah wass used as the urea substrate. The humidity for each material was controlled by proper storage handling. The Optical Contact Angle (OCA 20) measurement device as shown in Fig. 2a was used to measure the contact angle and surface tension of modified biopolymer solutions on urea substrate. One milliliter syringe with 0.51 mm needle tip was used to dispense the liquid with droplet size of 2±0.06 mm. This device has a high-speed and a CCD camera feature to capture the high speed motion of the droplet impact. The SCA 20 software as shown in Fig. 2b was used to conduct the experiment and analysed the digital image data obtained.

Preparation of biopolymer solution: The modified biopolymer solution was prepared by using mixing method. In 250 mL round bottom flask, 5 g of starch was dissolved in 100 mL deionized water. The slurry was heated and stirred in water bath at 80°C. After 30 min, urea and borate was added to the mixture and continued mixing

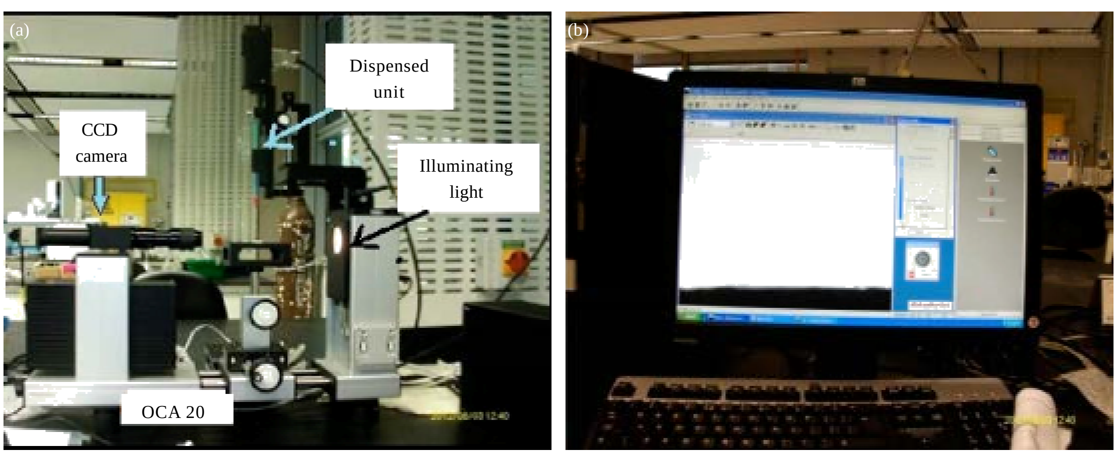

Fig. 2(a-b): Experimental setup using (a) Optical contact angle (OCA 20) device and (b) SCA 20 for conducting the experiment and analysis the data

Table 1: Contact angle and physical properties for different blending ratio

Blending ratio (starch:urea:borate)	Contact angle (°)	Wettability	Adhesiveness	Solid surfaces free energy
50:15:2.5	22.40	Better	Better	Larger
50:15:3.5	31.30	Moderate	Moderate	Large
50:15:4.5	31.40	Moderate	Moderate	Large
50:20:2.5	42.30	Worse	Worse	Smaller
50:20:3.5	33.90	Moderate	Moderate	Large
50:20:4.5	36.80	Worse	Worse	Smaller

Table 2: Dynamic contact angle across the time for different blending ratio

	Contact angle (°)					
Blending ratio (starch:urea:borate)	1.0s	2.0	3.0	4.0	5.0	6.0
	t (sec)					
50:15:2.5	49.80	34.40	27.30	30.80	28.60	26.70
50:15:3.5	58.10	55.60	44.90	43.10	39.20	37.30
50:15:4.5	71.20	62.40	47.20	48.70	46.00	39.50
50:20:2.5	85.90	67.00	64.90	61.50	59.30	55.40
50:20:3.5	69.50	60.40	59.90	47.40	46.30	45.40
50:20:4.5	62.30	57.30	41.70	38.30	34.50	32.50

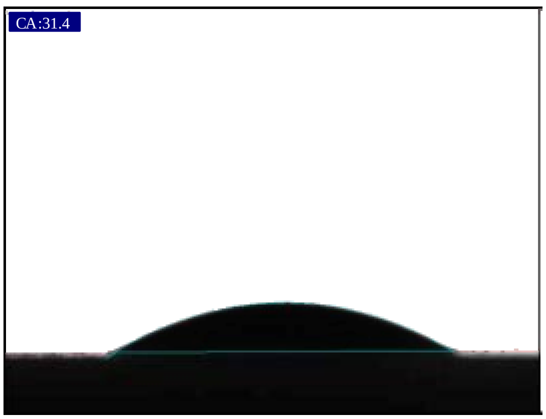

Fig. 3: Sessile drop images for the 50:15:4.5 ratio

for another 3 h and blue dye was added 30 min before finished. The ready modified biopolymer solution was stored in a tight air container.

Preparation of urea surface: The urea granules were melt in petri dish at 130°C until all melted. Immediately, the melted urea was dried inside the oven for 30 min. The urea substrate was taken out form the dish and stored in desiccators to avoid moisture.

Dynamic contact angle and maximum spreading diameter maesurement: The measurement for the dynamic contact angle was similar with the measurement steps for static contact angle. The CCD camera of the OCA captured 17 frames per second and the droplet impact behaviour studies by record it into video. The selection data for dynamic contact angle was taken for every 1 sec. This data was used to determine the maximum spreading diameter of the modified biopolymer.

RESULTS AND DISCUSSION

Contact angle: The sessile drop image was used to determine the contact angle value as shown in Fig. 3, which fit the Young-Laplace equation. Table 1 shows the data of contact angle and physical properties for different blending ratio of modified biopolymer solutions. The 50:15:2.5 blending ratio has the smallest contact angle compared to other blending ratio because it has a low surface free energy or intermolecular forces within the liquid. Therefore, it can spread more on the urea substrate. The contact increase as the composition of borate increase for the blending of 50:15 (starch: urea). But for the composition of 50:20 (starch:urea), the contact angle decrease in size with increase in composition. However, the data for the 50:20:3.5 has lower contact angle than 50:20:4.5 because there might be an error occurred during the contact angle measurement where the baseline determination of the sessile drop is inaccurate. A good wetting criteria is when the contact angle is small, the wettability is high, good adhesiveness with a larger solid surface free energy and low surface free energy. Based on all physical properties, the 50:15:2.5 ratio was chosen for having good droplet impact behaviour.

Dynamic contact angle: Table 2 shows the dynamic contact angle or the rate of contact angle change across the time. The dynamic contact angle was measured every 1 sec until 6 sec. The sessile drop images that used to measure the dynamic contact angle are shown in Fig. 4 within 6 sec for each blending ratio. Figure 5 shows the graph of dynamic contact angle versus time for different blending ratio. From the graph, it clearly show that the 50:15:2.5 has the smallest dynamic contact angle values which shows a good wettabilty properties compared to other modified biopolymer solutions. As stated before, low surface free energy caused the liquid to

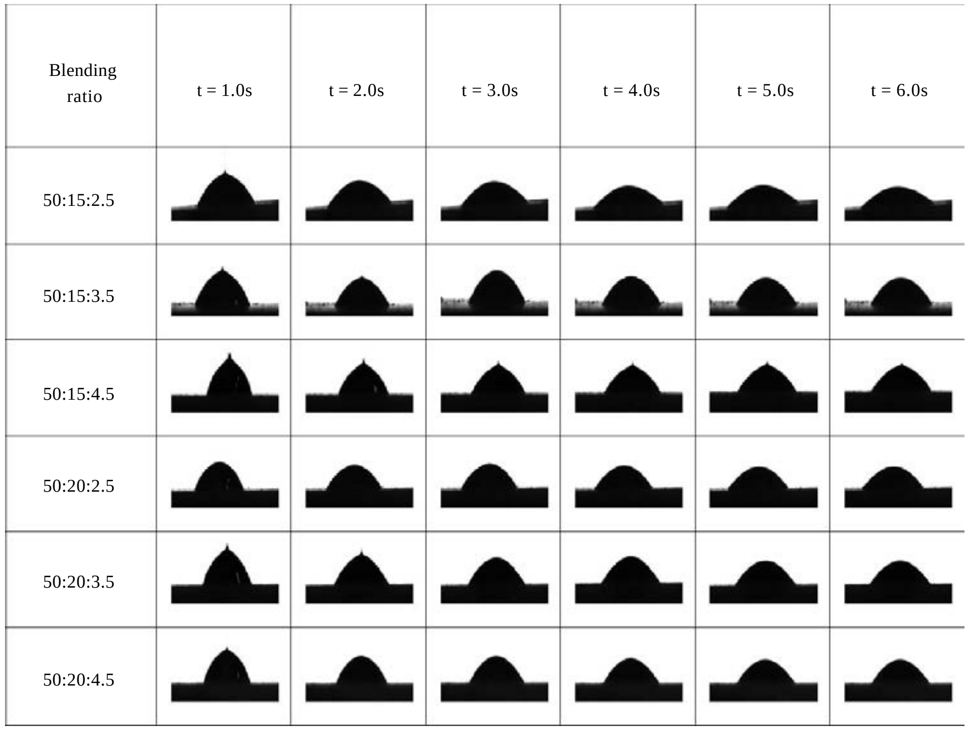

Fig. 4: Sessile drop images of biopolymer liquid within 6 sec

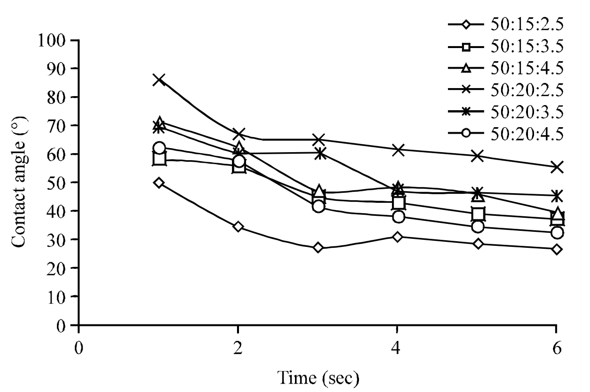

Fig. 5: Dynamic contact angle vs. time for different blending ratio

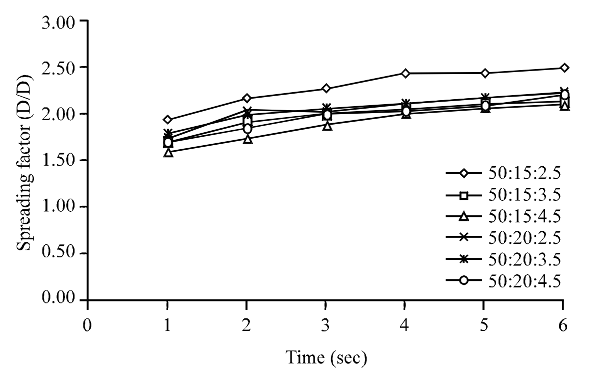

Fig. 6: Spreading factor vs. time for different blending ratio

form a small contact angle. Another factor that can affect the size of the angle is the viscosity of the liquid and the 50:15:2.5 ratio has low viscosity compared to others. Meanwhile, the 50:20:2.5 ratio has the biggest dynamic contact angle values resulting having the worse wettabilty properties because it has larger surface free energy due to high in viscosity.

Maximum spreading diameter: Several phenomena like spreading, bouncing and splashing can be observed when a droplet impact on the solid surface. Only spreading behaviour is observed when the modified biopolymer droplet collided with the urea surface. The maximum spreading behaviour explained the spreading property of the liquid on the urea surface by determined the maximum spreading diameter, Dt at certain time over the initial droplet diameter, Do prior to impact which measured as spreading factor.

From the graph in Fig. 6, most of the modified biopolymer coating solutions has similar spreading factor over the time. However, the 50:15:2.5 ratio clearly showed that it has better maximum spreading behaviour because it have the smallest static and advancing contact angle which reducing the cohesive force and increase the adhesive work of the liquid. This behaviour plays an important factor during the coating process where it will affect coating uniformity of the urea. As the droplet spread more on a surface, it provides thinner layer of coating material which in turn enhance the coating uniformity.

CONCLUSION

The impact behaviour for six different blending ratios is studied using OCA 20 device measurement. The pendant drop and sessile drop images is used to determine the surface tension and contact angle values which fit the Young-Laplace equation using the SCA 20 software. The wettability, adhesiveness, solid surface free energy, dynamic contact angle and maximum spreading behaviour were the parameters that had been investigated. As a conclusion, from all the results obtained, the most suitable composition of modified biopolymer solution to be used is the 50:15:2.5 ratio. This blending ratio solution having the smallest contact angle thus had a better wettability, adhesiveness properties and larger solid surface free energy for the liquid to spreads and adheres smoothly. The dynamic contact angle and maximum spreading behaviour also preferable the 50:15:2.5 ratio as the best coating solution because it has good droplet impact behaviour.

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