

Characterization of Chemically Modified Biomass as a Coating Material for Controlled Released Urea by Contact Angle Measurement

Nur Zahirah Zulhaimi, KuZilati KuShaari, Zakaria Man

Abstract—Controlled release urea has become popular in agricultural industry as it helps to solve environmental issues and increase crop yield. Recently biomass was identified to replace the polymer used as a coating material in the conventional coated urea. In this paper spreading and contact angle of biomass droplet (lignin, cellulose and clay) on urea surface are investigated experimentally. There were two tests were conducted, sessile drop for contact angle measurement and pendant drop for contact angle measurement. A different concentration of biomass droplet was released from 30 mm above a substrate. Glass was used as a controlled substrate. Images were recorded as soon as the droplet impacted onto the urea before completely adsorb into the urea. Digitized droplets were then used to identify the droplet's surface tension and contact angle. There is large difference observed between the low surface tension and high surface tension liquids, where the wetting and spreading diameter is higher for lower surface tension. From the contact angle results, the data showed that the biomass coating films were possible as wetting liquid ($\theta < 90^\circ$). Contact angle of biomass coating material gives good indication for the wettability of a liquid on urea surface.

Keywords—Fluid,Dynamics;Droplet;Spreading;Contact Angle;Surface Tension

I. INTRODUCTION

UREA is one of the most is of the most important fertilizers of the agricultural industry. It is added to the soil to release nutrients necessary for plant growth. However, the potential hazards of fertilizers to the environment have results in stringent limitation to their use. About half of the applied fertilizers, depending on the method of application and soil condition, are lost to the environment, which results in the contamination of water [1-2]. Use of conventional fertilizers may lead to concentration levels that are too high for effective action. A high concentration may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment [3]. One method of reducing nutrient losses involves the use of controlled-release fertilizers (CRF). Controlled- or slow-release fertilizers are broadly divided into uncoated and coated products. Uncoated controlled release urea relies on inherent physical characteristics, such as low solubility, for their slow release. Coated controlled release urea mostly consists of quick-release N sources surrounded by a barrier that prevents the N from releasing rapidly into the environment. Coated products have several advantages. Some coated products offer a relatively inexpensive means to exploit slow-release characteristics. They also may offer desirable release characteristics in certain conditions. Nowadays, Polymer-coated urea (PCU) is used to coat urea for improving nitrogen (N) use efficiency (NUE). PCU is urea coated in a plastic membrane. Release of the urea is controlled by diffusion

through the membrane, and the rate is dependent on soil temperature (higher temperature faster release). Large amounts of polymers are left as residue when the nutrients are exhausted [4]. Biomass is one of the alternatives to replace PCU for coating urea. Research found that the unique characteristics of biomass combine with starch can reduce the usage of polymers as coating agent in fertilizers industries [5-7]. Not only has biodegradable characteristic, but biomass is also less expensive compared to PCU. Film coating method was found to be the most suitable method to coat urea. To ensure good coating uniformity, good wettability and droplet spreading of coating material is crucial [8-11]. Wettability is unique for every substrate and liquid. Therefore, in this paper, spreading characteristics of different biomass droplet; combining urea, starch, borate and lignin/clay/cellulose on urea surface are investigated experimentally. The study will focus on the

II. MATERIALS AND METHODS

A. Apparatus

The equipment shown in Fig.1 was used to create silhouette and an image from a side view of an impinging droplet, to video-image the silhouette, and to digitize the image. [12]. OCA 15 is a measuring device for the measurement of the static and the dynamic contact angle, the surface free energy of solids, and the surface and interfacial tension of liquids. The apparatus consisted of a light source (a halogen lighting with continuously adjustable intensity), dosing bay for installation of the optional syringe units, measuring stage (adjustable in three axis), and a high-speed video system with adapter and CCD-camera. The droplet onto the active area of the camera was magnified approximately 10 times. Falling drops were generated from a stainless steel needle (ID=0.83mm) 20mm±0.6mm above the substrates. The video image digitizer (32-bit software SCA 15) was installed in a personal computer. The system capable for control of the syringe dispenses volume, light intensity and also the tilting base assemblies. Although the syringe delivered slightly different initial droplet diameters, there was no significant effect on the results [13]

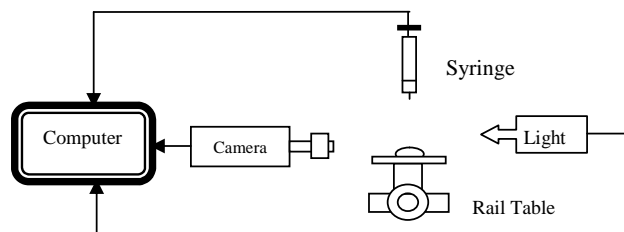


Fig. 1 Schematic diagram of OCA 15 (Video based Optical Contact Angle Measuring Instrument) [12]

Nur Zahirah Zulhaimi is with Universiti Teknologi PETRONAS, Sri Iskandar, Malaysia. (kuzilati@petronas.com.my)

B. Materials

The entire reagents used were of analytical purity. Soluble tapioca starch, borate, lignin, cellulose, clay and Urea fertilizer (PETRONAS Fertilizer Kedah) were stored with silica gel to avoid moisture.

C. Preparation of starch/Urea/Borate/lignin or Cellulose or Clay films.

Tapioca starch (5g) is dispersed in 95 ml of purified water to form starch slurry. The starch slurry is heated in a water bath of an 80 °C for 30 minutes and stirred until it gelatinize and become viscous. Borate (0.25g) and urea (2.5g) are weighed in a separate beaker and mixed to viscous starch solution. Lignin is added to the solution with different ratio of 0%, 5% and 20% under continuous heating and stirring for 3h. Same ratio applied to cellulose. For clay, the ratio is 0%, 2% and 8%. The mixture is removed from the heat, the foam is skimmed off, and the solution is stored before use for next steps.

D. Preparation of Urea substrate

100 g of Urea granules were melted in a beaker (melting temperature: 130-140 °C) about 30 min. Urea melt were then pour onto glass plate and dried inside the oven at 70°C for 1 h before stored in storage with silica gel to avoid moisture contamination.

E. Contact Angle

A flat glass plate and urea were used as the solid substrates. Immediately before measurement, the glass plate was rinse with pure water and dried in an oven. A droplet was generated at the tip of the needle, which is 20mm±0.6mm from the solid substrate. The droplet fell down and impinged upon the solid substrates. The images of the drop were then taken and processed to determine the droplet contact angles. For glass surface, the images were taken after the droplet relaxing to its static value while for urea surface, the images were taken as soon as the droplet drop onto the surface. The contact angles for different substances were then plotted into a graph against the concentration.

F. Surface Tension

1ml film substance was charged into the syringe with the 0.83 mm tip. The syringe were attached to a metal stand and suspended vertically. The syringe's tip are placed within the focus of a high speed digital camera. The backlight must be placed parallel with the tip in order to get a black body picture of the droplet spreading. The substance was dispensed automatically until a *tear drop* shape shown. The surface tensions for different substances were then plotted into a graph against the concentration.

III. RESULTS AND DISCUSSION

A. Surface Tension

Fig. 2 shows the surface tension for cellulose, clay and lignin with different concentration. As the concentration increases, the surface tension for cellulose and lignin are decreasing. On the other hand, the surface tension of clay increases with the increase in concentration. This results

shows that with increasing the concentration of lignin and cellulose, the cohesive energy present at interface reduced, molecules on the surface become more imbalance. Compared to lignin and cellulose, the cohesive energy present at interface increasing which indicate that the bonding between molecules become more stable.

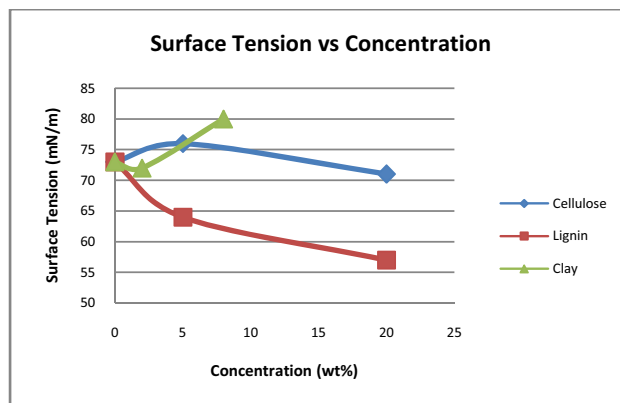


Fig. 2 Surface Tension for different concentration of biomass

B. Contact Angle

Digital frame grabber OCA 15 software was used to obtain images from side view of the CCD camera to measure the contact angle. Table 1 summarize the result of the contact angle with different biomass concentration. Fig.3-5 show the images captured for partial wetting of biomass film over glass. Fig.6-8 show the partial wetting of the films onto urea surfaces. The film (coating) thickness depends on the surface tension, withdrawal speed, substrate geometry, roughness, and liquid viscosity [14, 15].

TABLE I
DATA FOR CONTACT ANGLE AND SURFACE TENSION FOR EACH BIOMASS WITH DIFFERENT CONCENTRATION

Films	parameters	Concentration (wt%)		
		0	5	20
Cellulose	contact angle on glass (°)	64.5	80	50
	contact angle on urea (°)	37	55	47
	surface tension(mN/m)	73	76	71
Lignin	contact angle on glass (°)	64.5	65	42
	contact angle on urea (°)	37	45	24
	surface tension(mN/m)	73	64	57
Film	parameters	Concentration (wt%)		
		0	2	8
Clay	contact angle on glass (°)	64.5	48	70
	contact angle on urea (°)	37	42	55
	surface tension(mN/m)	73	72	80

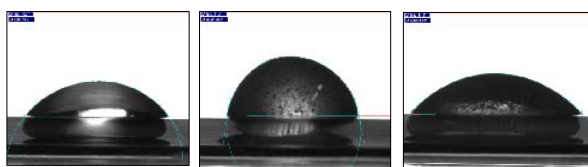


Fig. 3 Sessile drop images for (a) 0% cellulose, (b) 5% cellulose (c) 20% cellulose onto glass surface

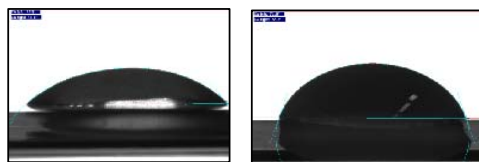


Fig. 4 Sessile drop images for (a) 2% clay, (b) 8% clay onto glass surface

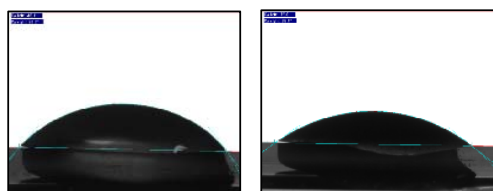


Fig. 5 Sessile drop images for (a) 5% lignin, (b) 20% lignin onto glass surface

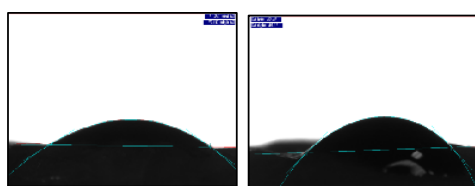


Fig. 6 Sessile drop images for (a) 0% cellulose, (b) 5% cellulose (c) 20% cellulose onto urea surface

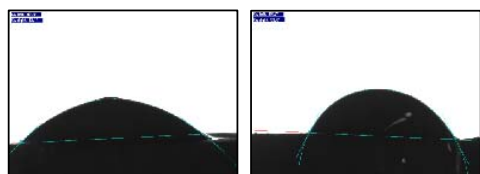


Fig. 7 Sessile drop images for (a) 2% clay, (b) 8% clay onto urea surface



Fig. 8 Sessile drop images for (a) 5% lignin, (b) 20% lignin onto urea surface

Pendant drop and sessile images of different biomass content on urea and glass surfaces were recorded. The digitized images were used to measure their contact angles and surface tensions. Fig.3, Fig.6 and Fig.9 show the images of pendant drop of cellulose, clay and lignin, respectively.



Fig. 9 Pendant drop images for (a) 0% cellulose, (b) 5% cellulose (c) 20% cellulose

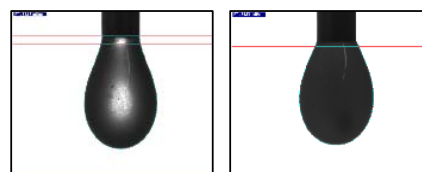


Fig. 10 Pendant drop images for (a) 2% clay, (b) 8% clay

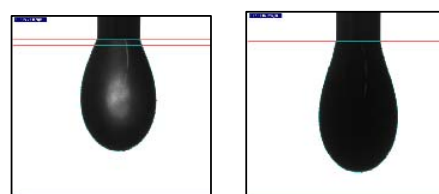


Fig. 11 Pendant drop images for (a) 5% lignin, (b) 20% lignin

Fig.12 summarizes the of the contact angle with different concentration. For the case of cellulose and lignin, as the concentration increases, the contact angle decreases. On the contrary, for the case of clay, the concentration increases with the contact angl .

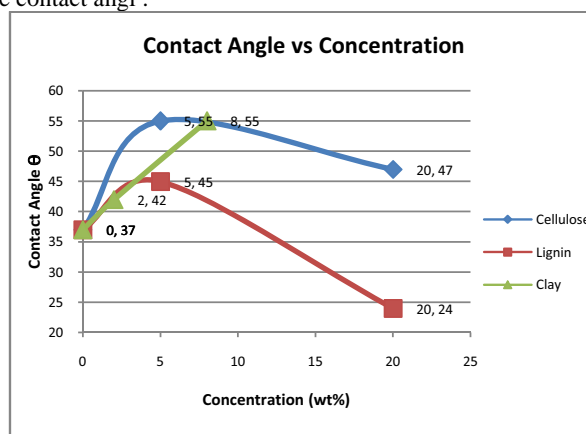


Fig. 12 Surface Tension for different concentration of biomass

From the results, increasing the concentration of cellulose and lignin will reducing the film's molecules cohesiveness, thus, reducing the contact angle. For clay, the cohesive forces between the films molecules increasing when the concentration increased. From the contact angle, physical properties of interaction between solid and liquid like wettability, affinity, adhesiveness and repellency can be studied. These results indicate that contact angles were sensitive to the surface condition and the degree of contamination. The way of change in contact angles with time depends on the surface treatments.

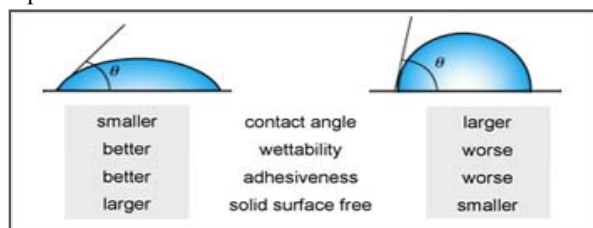


Fig. 13 Comparison between smaller and larger contact angle

TABLE II
WETTABILITY, ADHESIVENESS AND SOLID SURFACE FREE ENERGY FOR DIFFERENT BIOMASS FILM

Film	(%)	Contact Angle	Wettability	Adhesiveness	solid surface free energy
Cellulose	5	55	Worse	worse	smaller
	20	47	Better	better	larger
Lignin	5	65	Worse	worse	smaller
	20	42	Better	better	larger
Clay	2	42	Better	better	larger
	8	55	Worse	worse	smaller

C. Critical Wetting Tension

From the result we can plot Zisman's Critical Wetting tension graph as shown in Fig.14 and Table 3 to show the relationship between surface tension and contact angle. When the cosine of the contact angles is plotted against the surface tension, a more-or-less straight line is formed. This line is extrapolated to point of contact angle, θ equal to zero. When the contact angle just goes to zero, the liquid film will spread and remain continuous, this is called the critical wetting tension, or the "dyne value". From above results, 20% lignin, 20% cellulose and 2% clay mixture gives the best spreading characteristic compare to others concentration.

TABLE III
CRITICAL SURFACE TENSION FOR DIFFERENT BIOMASS

Films	Critical Surface Tension(mN/m)
Lignin	52
Cellulose	67
Clay	69

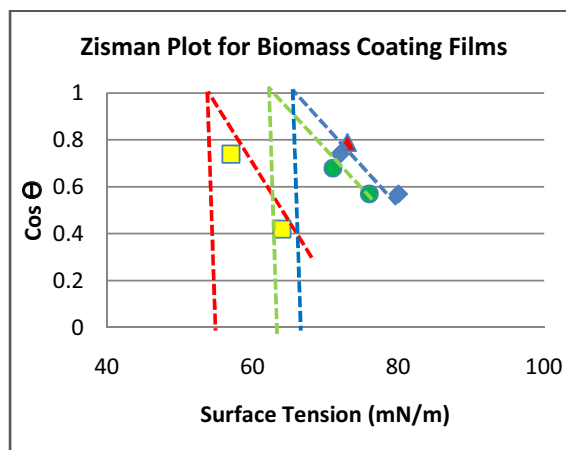


Fig. 14 Zisman's Plot (the relationship between contact angle and surface tension)

IV. CONCLUSION

The spreading of biomass coating film characteristic onto urea surface has been investigated. The differences in spreading ability when different coating materials were used could be quantified. Surface tension is an important factor that determines the ability of coating to wet and adhere to a substrate. Wetting may be defined by referring to a liquid drop resting at equilibrium on a solid surface. When the angle is greater than zero, the liquids wets the solid completely over the surface at a rate depending on a liquid viscosity and the solid roughness. Based on theory, [9] a liquid is said to wet the solid if the contact angle is less than 90° . The data showed that the biomass coating films were possible as wetting liquid ($\theta < 90^\circ$). Contact angle gives good indication for the wettability of a liquid.

REFERENCES

- [1] Iovino R., Zullo R., Rao M.A., Cassar L., Gianfreda L. Biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions (2008) *Polymer Degradation and Stability*, 93 (1), pp. 147-157.
- [2] Puechner P., Mueller W.-R., Bardtke D. Assessing the biodegradation potential of polymers in screening- and long-term test systems (1995) *Journal of Environmental Polymer Degradation*, 3 (3), pp. 133-143.
- [3] J. K. Kiran, Y. M. Khanif, H. Amminuddin, A. R. Anuar, "Effect of Controlled Release Urea on the Yield and Nitrogen Nutrition of Flooded Rice", *Comm. Soil Science and Plant Anal.*, 2010, 41, 811-819
- [4] M. Tomaszewska and A. Jarosiewicz, "Polysulfone Coating with Starch Addition in CRF Formulation," *Desalination*, 2004, 163, 247-252. [10] dr zak
- [5] Guo, M., Liu, M., Zhan, F., Wu, L. (2005). Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. *Industrial Engineering Chemistry Research*, 44, 4206-4211.
- [6] Yongsong Cao, Lu Hang, Jiuxin Chen, Ji Liang, Shengyou Long, Yitong Lu, (2005) Development of a controlled release formulation based on a starch matrix system. *International Journal of Pharmaceutics* 298 108-116
- [7] Boli Ni, Mingzhu Liu, Shaoyu Lu, (2009) Multifunctional Slow-Release Urea Fertilizer from ethylcellulose and superabsorbent coated formulation, *Chemical Engineering Journal* 155 892-898
- [8] Jonathan E Stringer, Patrick J Smith and Brian Derby. (2005) Droplet Behaviour in Inkjet Printing, School of Materials, University of Manchester.
- [9] Derrick O.N, Esio. O.Rhoda.H. (2001) Determination of contact angle from contact area of liquid droplet spreading on solid substrate.

- [10] Oukach et. al., 2010, "Deformation Behavior of a Liquid Droplet Impacting a Solid Surface," COMSOL Conference Proceedings, Paris, 2010.
- [11] Chi-Chuan HWANG, Yeau-Ren JENG, Yu-Lin HSU and Jee-Gong CHANG. (2001) Molecular Dynamics Simulation of Microscopic Droplet Spread on Rough Surfaces. Physical Society of Japan Vol. 70, No. 9, pp. 2626-2632.
- [12] F.Depypere, P. Van Oostveldt, J.G Pieters, K. Dewettinck, (2009) Quantification of microparticle coating quality by confocal laser scanning microscopy (CLSM). European journal of pharmaceutics and Biopharmaceutics 73 (2009) 179-186.
- [13] Li Chen, Zhigang Xie, Xiuli Zhuang, Xuesi Chen, Xiabin Jing, (2008) Controlled release of Urea encapsulated by starch-g-poly (L-lactide) 342-348
- [14] KuShaari, K. (2007), Coating uniformity on a pharmaceutical tablet: An experimental study and finite volume modeling of droplet impact behavior, PhD Dissertation.
- [15] Moita, A. S. H., and Moreira, A. L. N., (2003), Influence of surface properties on the dynamic behavior of impacting droplets, 9th International Conference on Liquid Atomization and Spray Systems.