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. Digitalized 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 (θ < 90º). 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]. Not only has biodegradable characteristic, but biomass is considered as 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 impending 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 droplets were generated from a stainless steel needle (1D=0.8mm) 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]](image-url)
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 ºC) 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 statics 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 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.

![Surface Tension vs Concentration](image)

<table>
<thead>
<tr>
<th>Films</th>
<th>parameters</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Cellulose</td>
<td>contact angle on glass (°)</td>
<td>64.5</td>
</tr>
<tr>
<td></td>
<td>contact angle on urea (°)</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>surface tension (mN/m)</td>
<td>73</td>
</tr>
<tr>
<td>Lignin</td>
<td>contact angle on glass (°)</td>
<td>64.5</td>
</tr>
<tr>
<td></td>
<td>contact angle on urea (°)</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>surface tension (mN/m)</td>
<td>73</td>
</tr>
<tr>
<td>Clay</td>
<td>contact angle on glass (°)</td>
<td>64.5</td>
</tr>
<tr>
<td></td>
<td>contact angle on urea (°)</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>surface tension (mN/m)</td>
<td>73</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>TABLE I DATA FOR CONTACT ANGLE AND SURFACE TENSION FOR EACH BIOMASS WITH DIFFERENT CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Films</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td></td>
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<tr>
<td>Cellulose</td>
</tr>
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<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>Lignin</td>
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<td></td>
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<tr>
<td>Clay</td>
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</tbody>
</table>
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. 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

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 angle.

![Contact Angle vs Concentration](image)

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](image)

**TABLE II**

<table>
<thead>
<tr>
<th>Film</th>
<th>Contact Angle (%)</th>
<th>Wettability</th>
<th>Adhesiveness</th>
<th>Solid Surface Free Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose 5</td>
<td>55</td>
<td>Worse</td>
<td>worse</td>
<td>smaller</td>
</tr>
<tr>
<td>20</td>
<td>47</td>
<td>Better</td>
<td>better</td>
<td>larger</td>
</tr>
<tr>
<td>Lignin 5</td>
<td>65</td>
<td>Worse</td>
<td>worse</td>
<td>smaller</td>
</tr>
<tr>
<td>20</td>
<td>42</td>
<td>Better</td>
<td>better</td>
<td>larger</td>
</tr>
<tr>
<td>Clay 2</td>
<td>42</td>
<td>Better</td>
<td>better</td>
<td>larger</td>
</tr>
<tr>
<td>8</td>
<td>55</td>
<td>Worse</td>
<td>worse</td>
<td>smaller</td>
</tr>
</tbody>
</table>

**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.

![Fig. 14 Zisman’s Plot (the relationship between contact angle and surface tension)](image)

<table>
<thead>
<tr>
<th>Films</th>
<th>Critical Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>52</td>
</tr>
<tr>
<td>Cellulose</td>
<td>67</td>
</tr>
<tr>
<td>Clay</td>
<td>69</td>
</tr>
</tbody>
</table>

**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 then 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 90º. The data showed that the biomass coating films were possible as wetting liquid (θ < 90º). Contact angle gives good indication for the wettability of a liquid.

**REFERENCES**


