CHAPTER 1
INTRODUCTION

1.1 Background

The impact and spreading of liquid drops on impermeable solid surfaces is an everyday experience, whether in daily life e.g., raindrops on a window panel, painting industrial, agricultural as well as printing. The topic has been the subject of many experimental and theoretical studies, and much progress has been made recently in explaining the phenomena [8, 15, 16]. In this paper, spreading characteristics of different biomass droplet; combining urea, starch, borate and lignin/clay/cellulose on urea surface are investigated experimentally.

Urea coating, fertilizers are one of the most important products of the agricultural industry. They are 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 (*O.A.Salman, 1989*). 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 *(K. El Rafaie et. al., 1996).* 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 products rely on inherent physical characteristics, such as low solubility, for their slow release.

Coated products mostly consist of quick-release N sources surrounded by a barrier that prevents the N from releasing rapidly into the environment. Both coated and uncoated products are different in mechanisms, but similar (though not identical) end results. 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).

Biomass is one of the alternatives to replace PCU for coating urea. Research believes that the unique characteristics of biomass combine with starch can reduce the usage of polymers as coating agent in fertilizers industries. However, it is impossible to coat urea with biomass without using suitable method. Pellet coating processes are usually driven by fairly well optimized procedures, while coating suspension sprayed on pallets and adverse effects, such as agglomeration, can not been seen during coating process and are only detected at the very end of the process, when it is too late for any adjustments of the coating process (*Miha et. al., 2010*) .The aim of this study is to determine the biomass droplet spreading characteristic in order to understand the biomass coating behaviour that can improve the coating uniformity.

1.2 Problem Statement

Improper Coating can cause problems such as cracking, caking, segregation and poor fertilizers performance. Coating suspension sprayed on pallets and adverse effects, such as agglomeration, can not been seen during coating process and are only detected at the very end of the process, when it is too late for any adjustments of the process.(*MihaMozina, Dejan Tomazevic, stanko;2010*)

1.3 Objectives

To identified the biomass droplet's optimum spreading characteristic based of:

- Surface tension
- Contact angle
- Penetration rate and wet ability

1.4 Scope of Study

This study is conducted to develop a new approach for preparing a new type of slow release fertilizer coating using natural and biodegradable polymer. The scope of work for this project is confined to the study of starch/lignin, starch/cellulose and starch/clay blends for urea fertilizer release only. The timeframe for this study is 1 year and will be done in two phase:

1. In the first phase, the project will be more on studying and reviewing information on the journals and experiments report available in the net and library.

2. As for the second phase, by using all information and data gained from the first phase, a proper experiment will be done to achieve the objectives stated earlier. The project will be in the form of laboratory experiments. It composes of two stages which are experiment and data analyzing stage.

CHAPTER 2
LITERATURE REVIEW

2.1 Controlled Released Fertilizer

In agrochemicals industry, a controlled-release fertilizer (CRF) is a new trend in international fertilizer research and recently a growing trend to regulating fertilizer consumption. The CRF can be physically prepared from the granules of the soluble fertilizers by coating them with materials, which reduce their dissolution rate.

Droplet impact and spreading is an important phenomenon that contributes to the quality of the coatings. *(Stephen et. al., 2009).* The higher the spreading ability, the efficient the coating characteristic for the substances, where we can reduce material cost as well as resident time inside the reactor.

The differences in coating quality when different coating materials were used could be quantified. (*P. Van Oostveldt b, J.G. Pieters c, K. Dewettinck, 2009*).Surface tension is an important factor that determines the ability of coating to wet and adhere to a substrate. Wetting may be defined by reference to a liquid drop resting in equilibrium on a solid surface. The smaller the contact angle, the better the wetting. 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 surface roughness.

The equilibrium contact angle for a liquid drop sitting an ideally smooth, homogeneous, flat, and non-deformable surface is related to various interfacial tensions by Young`s *equation 2.2:*

$$0 = \gamma_{SV} - \gamma_{SL} - \gamma \cos\theta_C$$

It can be concluded that for a spontaneous wetting to occur, the surface tension of the liquid must be greater than the surface tension of the solid. It is also possible for the liquid to spread and wet a solid surface when angle is greater than zero, but this requires the application of a force to the liquid.

2.2 Techniques for measuring Contact Angle

There are several techniques exist to determine the contact angle, principal among them being the Wilhelmy Plate Method and Goniometry.

2.2.1 Wilhelmy Plate Method

This technique can be used to measure the contact angle if the surface tension of the liquid is known. Similarly, if the contact angle for a solid-liquid pair is known, the surface tension of the liquid can be obtained using this method. Wilhelmy plate method essentially used to measure the surface tension using a standardized plate with a ring/plate tensiometer. The plate is moved towards the surface until the meniscus connects with it (figure) The change in the weight of the plate (ΔW) occurs because of the liquid adhering to the plate. This change in weight is measured and with the knowledge of the wetted perimeter (p), the contact angle (θ) is measured from *equation 2.1:*

$$\sigma \cos(\theta) = \Delta W / p$$

This method is not suitable for rough and porous substrate such as urea surface. The fibrous surface of urea coupled with pores makes it difficult to measure the perimeter and may also result in wicking of the fluid into the Urea which result in incorrect weight measurements producing incorrect contact angle results. However, there is a modification of this method, which called the Single Fiber Wilhelmy method in which the plate is replaced by a single fiber of the substrate. The single fiber however is not an accurate representation of the actual urea surface.

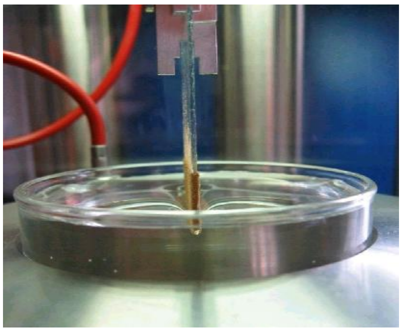


Figure 1: Measurement of the solid-liquid contact angle with the Wilhelmy Plate Method

(Jörg Bachmann,Juan Carlos Ramirez Flores ,2006-2009)

2.2.2 Goniometry

For this method, an image of the drop is obtained and contact angle is measured from the drop image. An elementary method is to draw a tangent and the solid-liquid interface along the drop profile and measure the contact angle. Captive-drop goniometry (CDG) was implemented using a home-built goniometer, as described elsewhere.*(Bain, C. D.; Troughton,,1989)* Briefly, CDG involved capturing the droplet on the test surface with a fine needle connected to a 50µL syringe. θa or θr was read by adding or withdrawing water from the drop, respectively. Contact angles were measured from images captured by a CCD camera when observable motion had ceased. This method is very crude and the obtained angle is dependent on the judgement of the user and hence this method is not suitable for scientific application.

2.3 Droplet Spreading Behaviour

The ability to produce controlled uniform droplets provides an opportunity to study the spreading and solidification behavior of individual droplets. The spreading behavior of individual droplets may be influenced by numerous parameters. These parameters include the droplet material, temperature, impact velocity, as well as the substrate temperature, material and surface condition.

Understanding how these parameters affect the spreading and solidification behavior of individual droplets can lead to greater insight in the creation of high quality deposited parts. *(Tasos Karahalios,1999)* Immediately after droplet impact, the drop may spread to a considerably greater extent than predicted by equilibrium because of the kinetic energy of the droplet in flight. Simulations of droplet impact showed that the maximum droplet spread decreased linearly with equilibrium contact angle. At equilibrium a droplet in contact with a substrate will form a spherical cap of contact angle, and base diameter, d_{eqm}.

The equilibrium contact angle is determined by the balance of the surface energies of the free droplet surface, the free substrate surface and the droplet/substrate interface, as expressed by the Young-Dupr equation (*M.E Schrader,1995)*

Assuming conservation of mass, the ratio, eqm, of the spherical droplet diameter, d, and the cap diameter, d_{eqm}, can be calculated using *equation 2.3:*

$$\frac{d_{eqm}}{d} = \beta_{eqm} = \sqrt[3]{\frac{8}{tan\left(\frac{\theta}{2}\right)\left(3 + tan^2\left(\frac{\theta}{2}\right)\right)}}$$

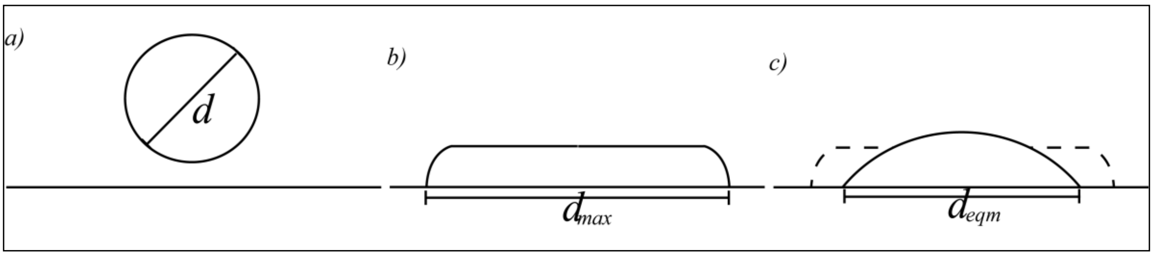


Figure 2: Schematic diagram showing a) undeformed droplet, b) droplet at maximum spread diameter and c) droplet at equilibrium on a substrate (Jonathan E Stringer,2005)

The spreading dynamics of a liquid on a solid surface are determined by different physical and chemical disciplines. Surface wetting occurs in many practical processes, e.g. surface coating, casting, laser cutting, floating screening, rubbing, adhering, lubrication, interface active agent and capillary action.

Due to extensive applications, the spreading of a liquid on a solid surface has been, and continues to be, the subject of considerable research e5orts, both theoretically and experimentally. In conventional macroscopic theory, the three-phase equilibrium contact angles, which exist between the liquid droplets, the solid surface and the air, can be determined by Youngs equation.

In this way the motion trend of a droplet spread may be observed qualitatively. However, if droplets spread on a solid surface which has a non-slip boundary condition, a contradiction occurs since this boundary prevents movement of the contact line between the solid and the liquid. *(Dussan et al.13, 1974).*

The increasing viscosity lowered the maximum spreading ratio, due to increased dissipation of energy during the impact of the droplet. The variable viscosity did not have a systematic influence on the reduction of max with equilibrium contact angle.

The amount of influence that equilibrium contact angle has on max is large when compared to previous studies *(M. Pasandideh-Fard, Y.M. Qiao, S. Chandra and J. Mostaghami, 1996)* This is because of the small droplet size and relatively low impact velocity, resulting in surface energy having a much more significant role in determining how the droplet spreads.

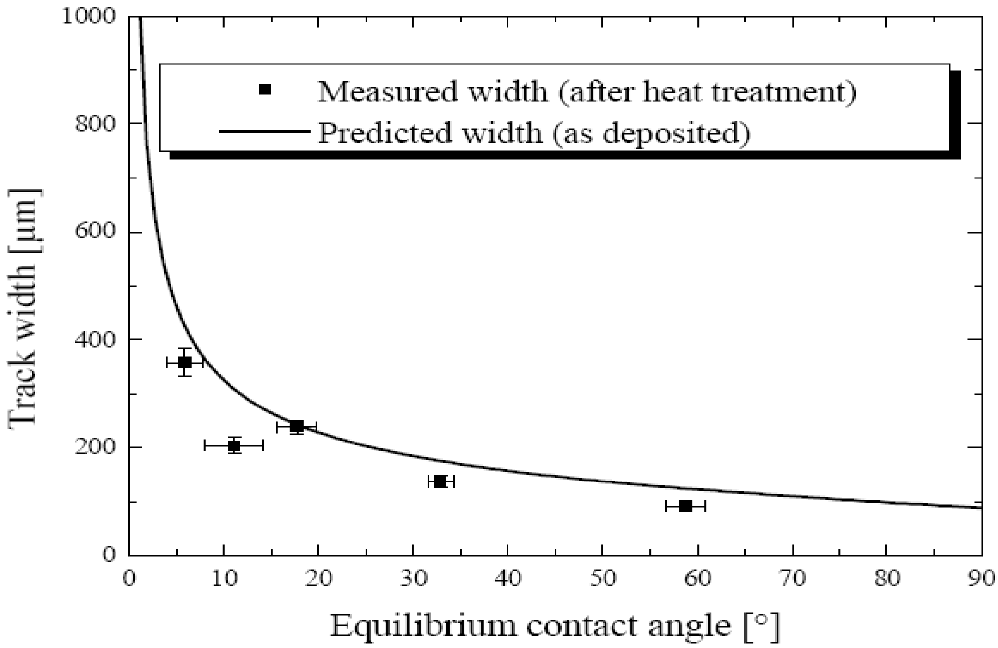


Figure 3: A graph showing the relationship between contact angle and final track width. Each data point represents a different substrate.

(Chi-Chuan HWANG,(2001)

Spreading is described by the dimensionless term of spread factor, n(t) = d(t)/d0, which is the spread diameter relative to the droplet diameter prior to impact.

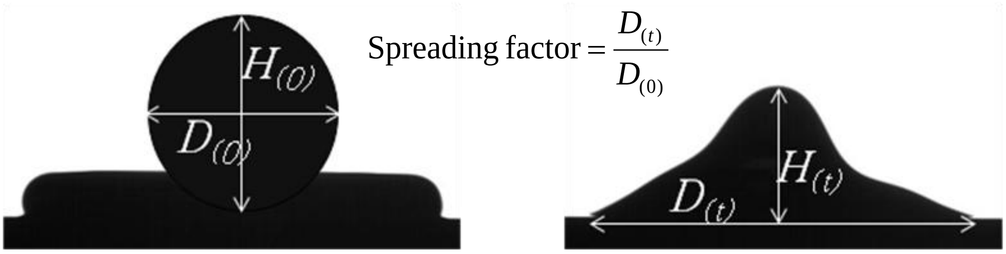


Figure 4 : Droplet and Spreading Height and Diameter (Dr Ku Zilati Ku Shaari 2007)

Of most interest to researchers are the maximum and final spread factors, n_{max} and n_{end}, where n_{max} is largely influenced by the balance between the inertia of the collision and the viscous dissipation, and n_{end} is mostly influenced by the interfacial equilibrium.

This has the processing advantage where only the coating formulation need be manipulated to obtain the best spreading characteristics and avoid the extra processing step to modify the chemical characteristics of the substrate surface.

CHAPTER 3
METHODOLOGY/PROJECT WORK

3.1 Research Methodology

3.1.1. OCA 15 (Video based Optical Contact Angle Measuring Instrument)

Contact angle measuring device for the measurement of the static and the dynamic contact angle, the surface free energy of solids, and the surface and the interfacial tension of liquids. The apparatus consisted of a droplet production system and an image acquisition system (Figure 5).

Figure5: OCA 15 in block 4

A single droplet was allowed to form at the tip of 1ml syringe and to fall over a predetermined vertical height on to the test surface. Although the syringe delivered slightly different initial droplet diameters, there was no significant effect on the results *(Werner, 2005)*

- The Coating Material used was Urea/Borate/Starch combine with different type of biomass with different composition :
  - Cellulose (5% - 20%)
  - Clay (2% - 8%)
  - Lignin (5% - 20%)

3.1.2 Substrate Preparation

Urea fertilizer, obtained from PETRONAS Fertilizer Kedah was selected as the test surface because it mimics urea fertilizer which widely used as coated fertilizer in industry. The physical surfaces of urea granules may be smooth or may contain pores, wrinkles and cracks.

A number of researchers have studied the effects of surface roughness *(Scheller and Bousfield, 1995, Shakeri and Chandra 2002)* and surface porosity/infiltration *(Hilman et al.2002, Reis et al., 2004)* on droplet impact and spreading and coating quality. In this work, it is necessary to imitate urea granules surface to remove the effects of surface irregularities.

3.1.3 Preparation of Urea Surface

The substrate was Urea fertilizers, obtained from PETRONAS Fertilizer Kedah.

Procedure:

1. Melt urea granules using beaker and hot plate (temperature: 130 -140 degC)

Figure 6: Melting Urea Granules

2. Pour into a plate and dried in a vacuum oven at 70-C for 30-min
3. Stored inside a container contain silica gel to absorb moist from the surrounding air.

Figure 7: Urea flakes

3.1.4 Sessile and Pendant Drop test

- ***Equipment :*** Optical Contact-measuring device (OCA 15)
- ***Temperature:*** 22-14 degC
- ***Methodology of Sessile Drop***

1. Charge biomass mixture solution into a 1ml syringe Attach the syringe to a metal stand and suspended vertically by micromanipulator on top of the urea layer. The micromanipulator is used to adjust the position of the needle tip of the syringe carefully above the urea layer.
2. Position the tip of the syringe few millimeters from the surface of the urea layer to eliminate impact effect when the droplet was released.
3. Place the urea layer on an optical stand within the focus of a high speed digital camera. Place backlight parallel with the urea layer in order to get a black body picture of the droplet spreading. Calculate the contact angle and plot graph for each substance.

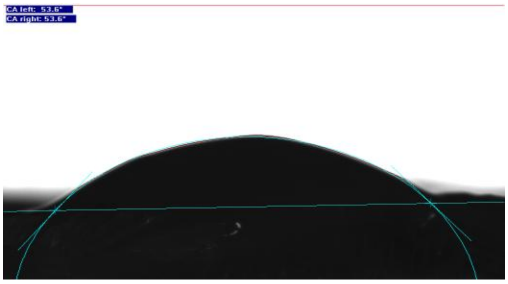


Figure 8: sessile drop image

Figure 9: Pendant drop image

- ***Methodology of Pendant Drop***

1. Charge biomass mixture solution into a 1ml syringe with the 0.83 mm tip .
2. Attach the syringe to a metal stand and suspended vertically.
3. Place the syringe`s tip within the focus of a high speed digital camera. Place backlight parallel with the tip in order to get a black body picture of the droplet spreading.
4. Dispense automatically the biomass droplet until a *tear drop* shape shown.
5. Calculate the surface tension and plot graph for each substance.

The important dates for Final Year Project 2 are as follow:

Table 1: Key Milestone

	Date
Project Work	Week 1-Week 12
Submission of progress report	13th July 2011
Pre EDX	Week 11
Submission of Draft Report	Week 12
Submission of softbound and Technical Paper	Week 13
Oral presentation	Week 14
Submission of hardbound	Week15

3.4 Gantt Chart

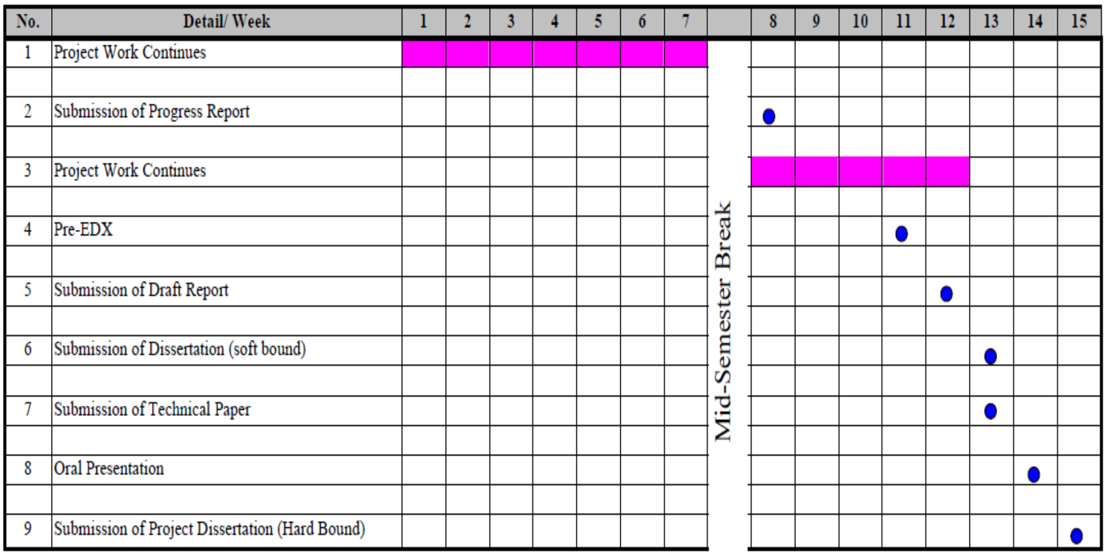


Figure 10: Gantt chart

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Surface tension and contact angle analysis.

4.1.1 *Urea/Starch/Borate/Cellulose* Surface Tension analysis.

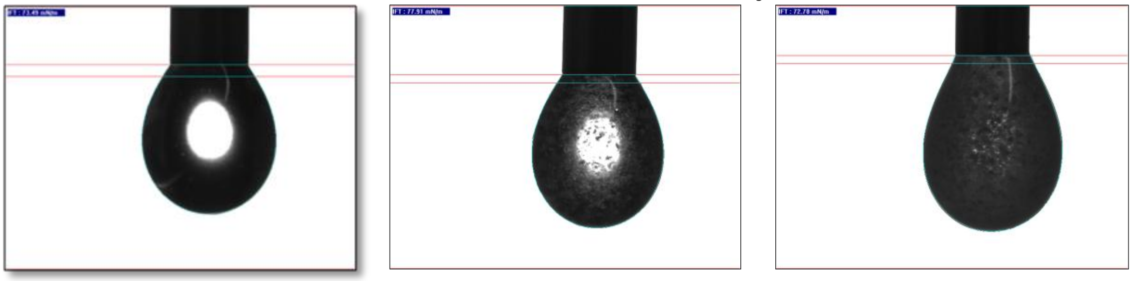


Figure 11: (a) 0% cellulose (b) 5% cellulose (c) 20% cellulose

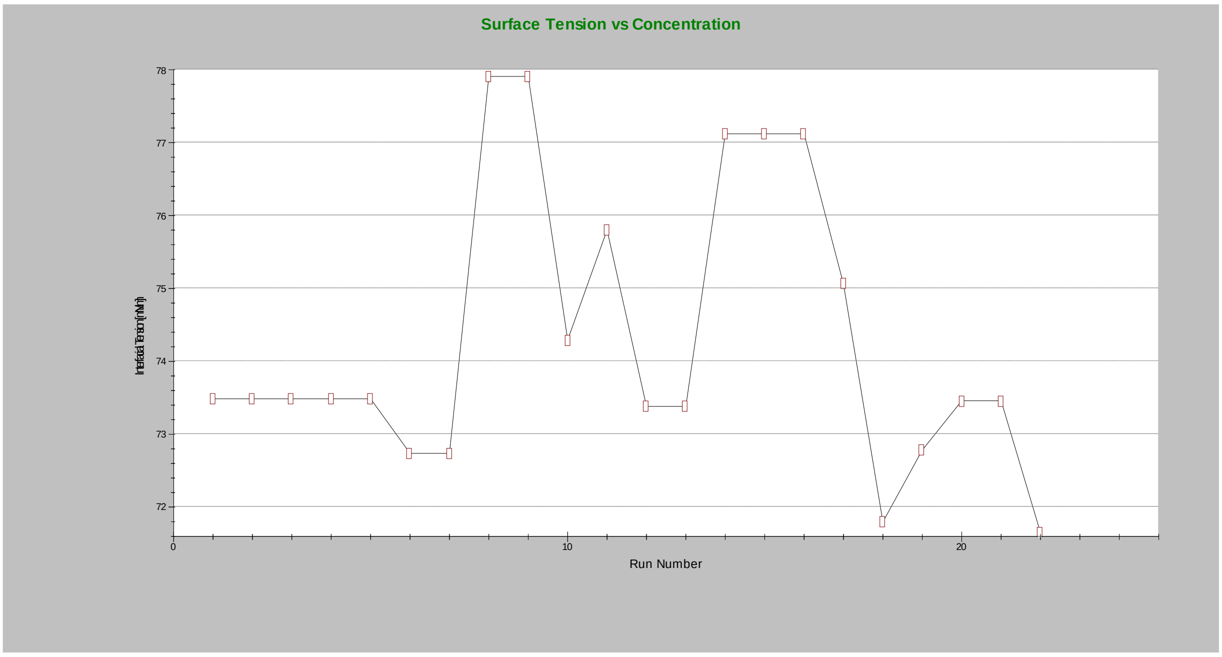


Figure 12: Surface tension versus cellulose concentration graph.

From above results, surface tension for 5% cellulose gives the highest value compared to 0% and 20% cellulose. Increasing the concentration of cellulose will result in reducing the surface tension for the mixture, thus, increasing the droplet spreading efficiency onto urea surface.

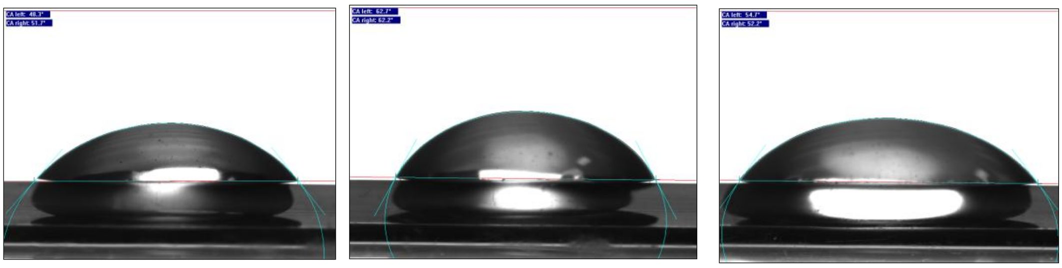
Surface tension statistics:

- 0% cellulose : 72-73 mN/m
- 5% cellulose : 75-77 mN/m
- 20%cellulose : 71-72 mN/m

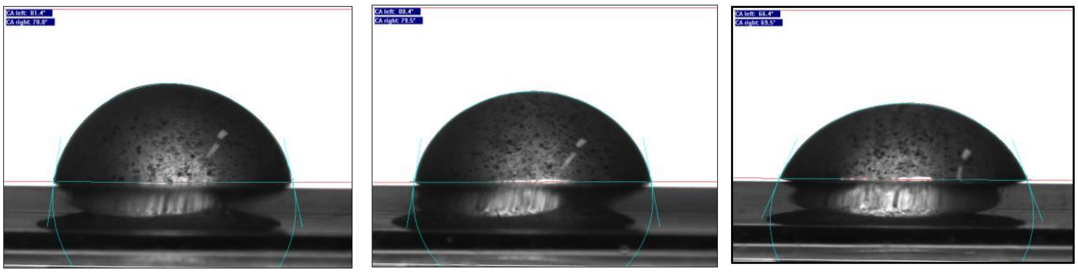
4.1.2 *Urea/Starch/Borate/Cellulose* contact angle`s analysis.

4.1.2.1 On Glass surface:

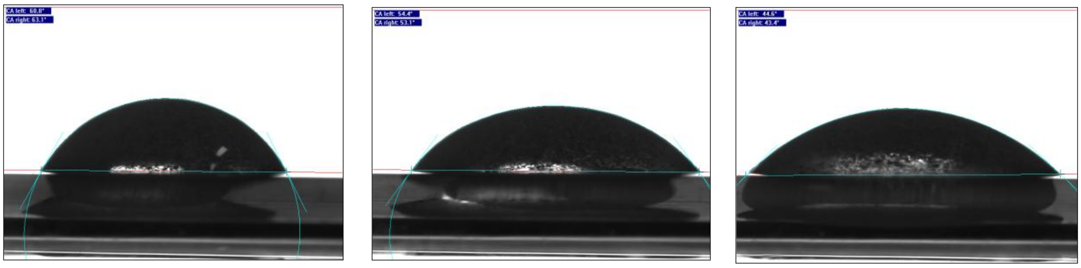
(a) 0% cellulose



(b) 5% cellulose



(c) 20% cellulose



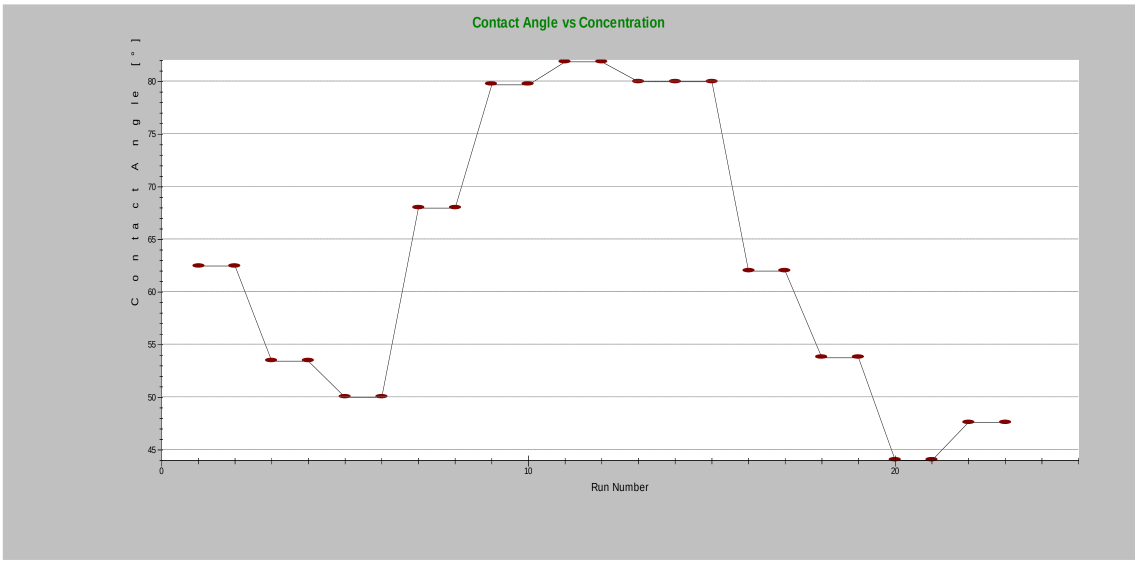


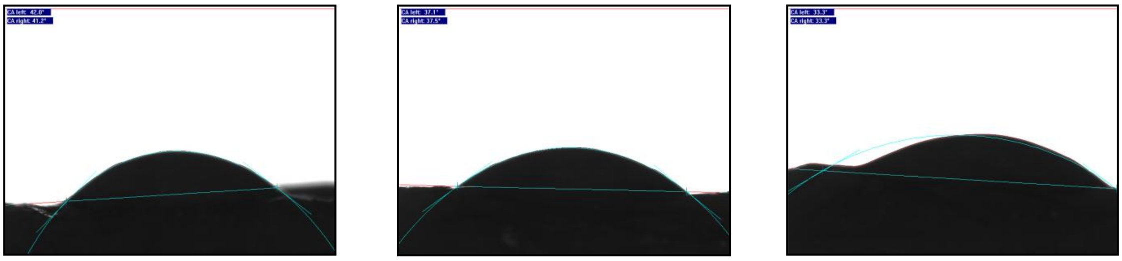
Figure 13: contact angle (on glass surface) versus cellulose concentration graph.

For contact angle, the result above shown that 5% cellulose gives the higher contact angle compared to 20%.
Contact angle statistics:

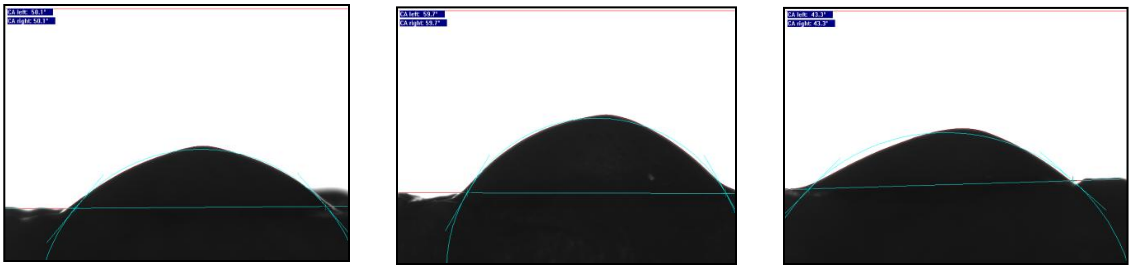
- 0% cellulose : 62-67 °
- 5% cellulose : 79-81 °
- 20%cellulose : 47-53 °

4.1.2.2 On Urea surface:

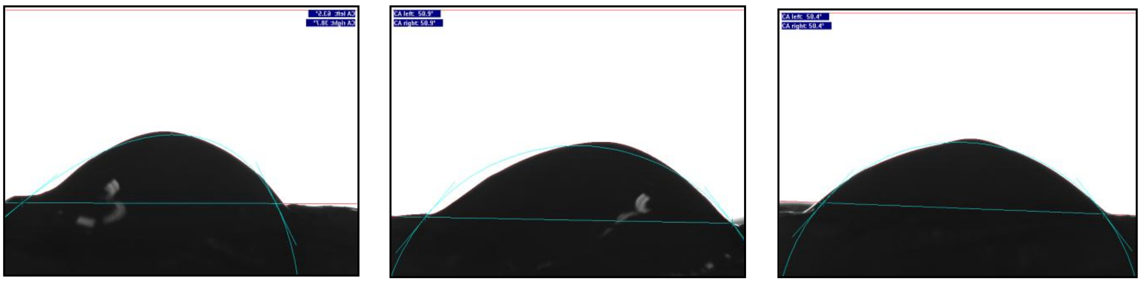
(a) 0% cellulose



(b) 5% cellulose



(c) 20% cellulose



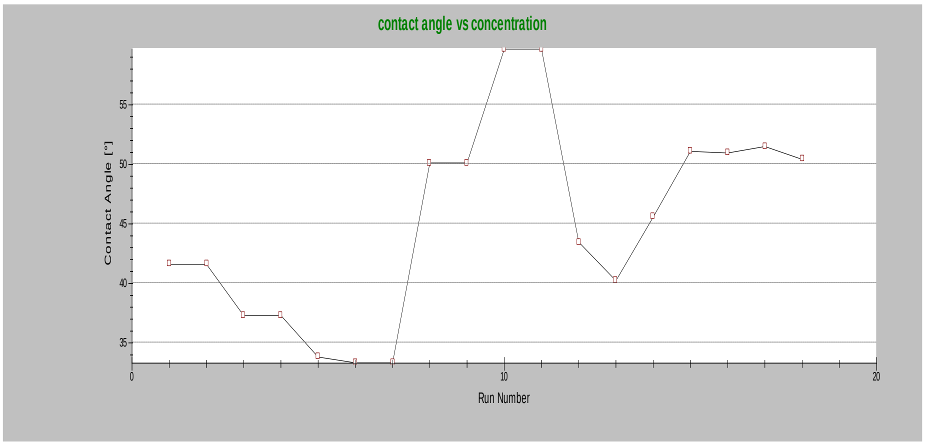


Figure 14: contact angle (on glass surface) versus cellulose concentration graph.

For contact angle, the result above shown that 5% cellulose gives the higher contact angle compared to 20%.
Contact angle statistics:

- 0% cellulose : 33-41 °
- 5% cellulose : 50-59 °
- 20%cellulose : 47-53 °

4.1.3 Urea*/Starch/Borate/Clay* Surface Tension analysis.

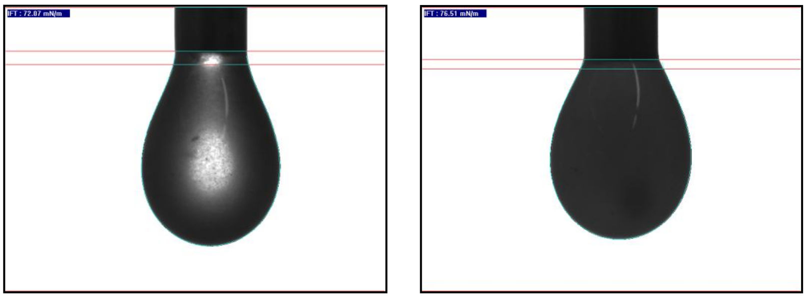


Figure 15: (a) 2% clay (c) 8% clay

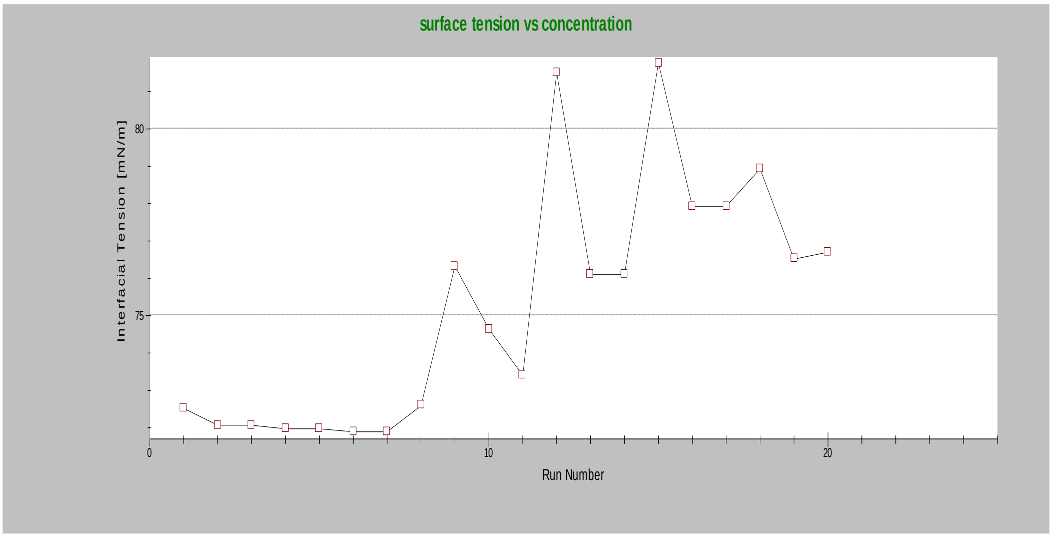


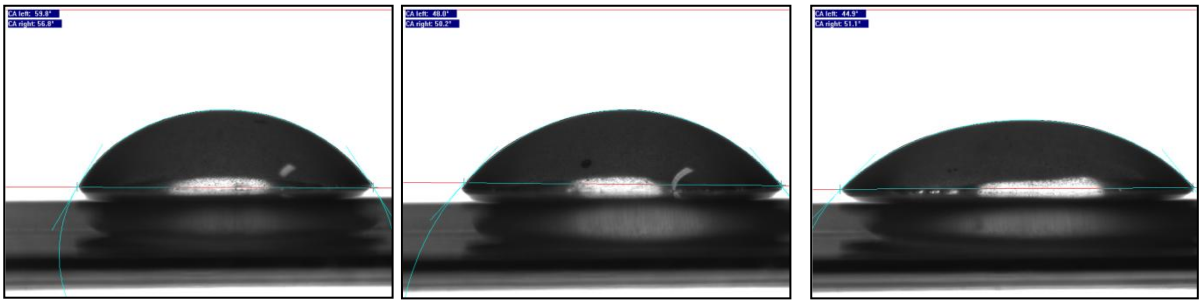
Figure 16: Surface tension versus cellulose concentration graph

Surface tension for 8% clay gives the highest value compared to 2% clay. Increasing the concentration of clay will result in increasing the surface tension for the mixture, thus, reducing the droplet spreading efficiency onto urea surface.
Surface tension statistics:

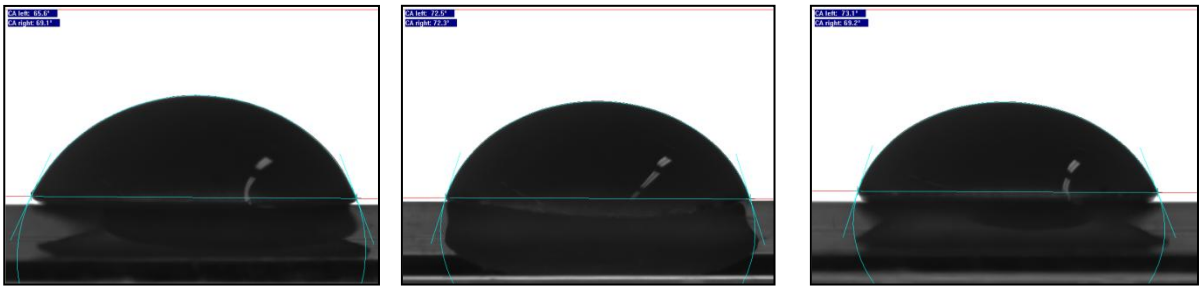
- 2% clay : 71-73 mN/m
- 8% clay : 76-81 mN/m

4.1.2.1 On Glass surface:

(a) 2% clay



(a) 8% clay



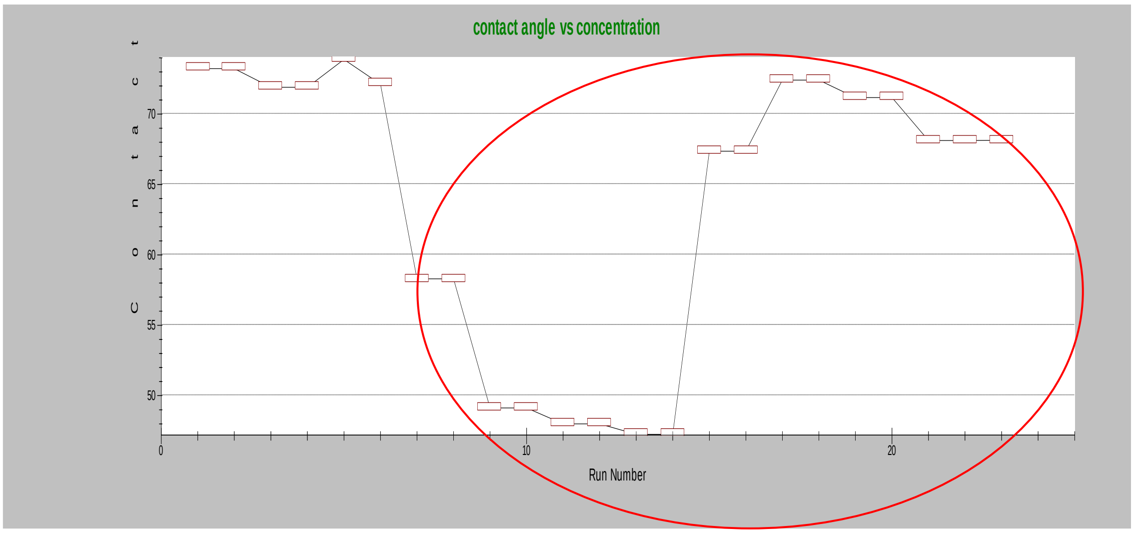


Figure 16: contact angle (on glass surface) versus clay concentration graph.

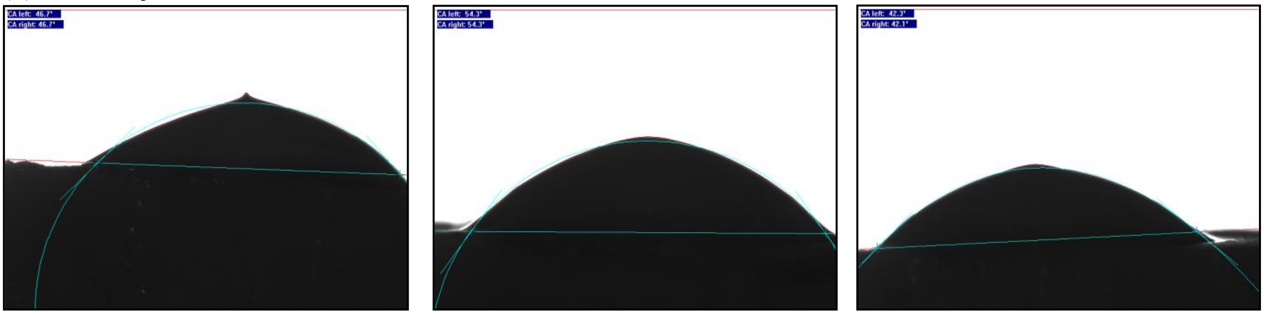
For contact angle, the result above shown that 8% clay gives the higher contact angle compared to 2%.

Contact angle statistics:

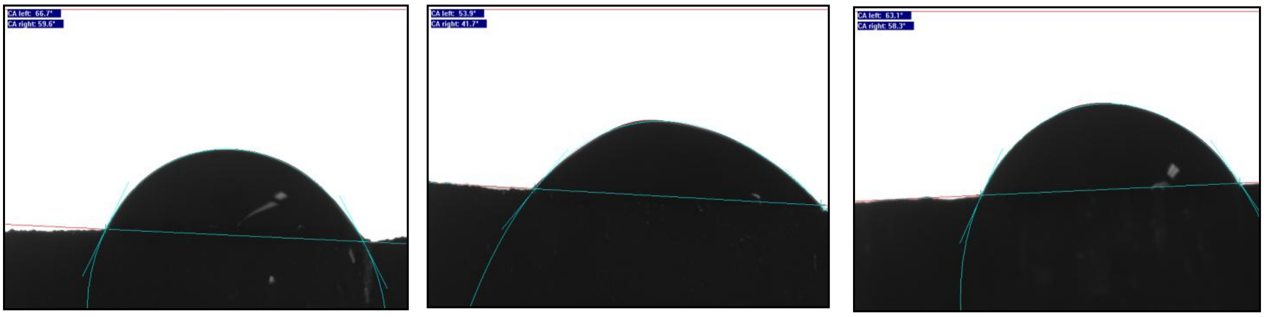
- 2% clay : 47-49 °
- 8% clay : 67-72 °

4.1.2.1 On Urea surface:

(a) 2% clay



(b) 8% clay



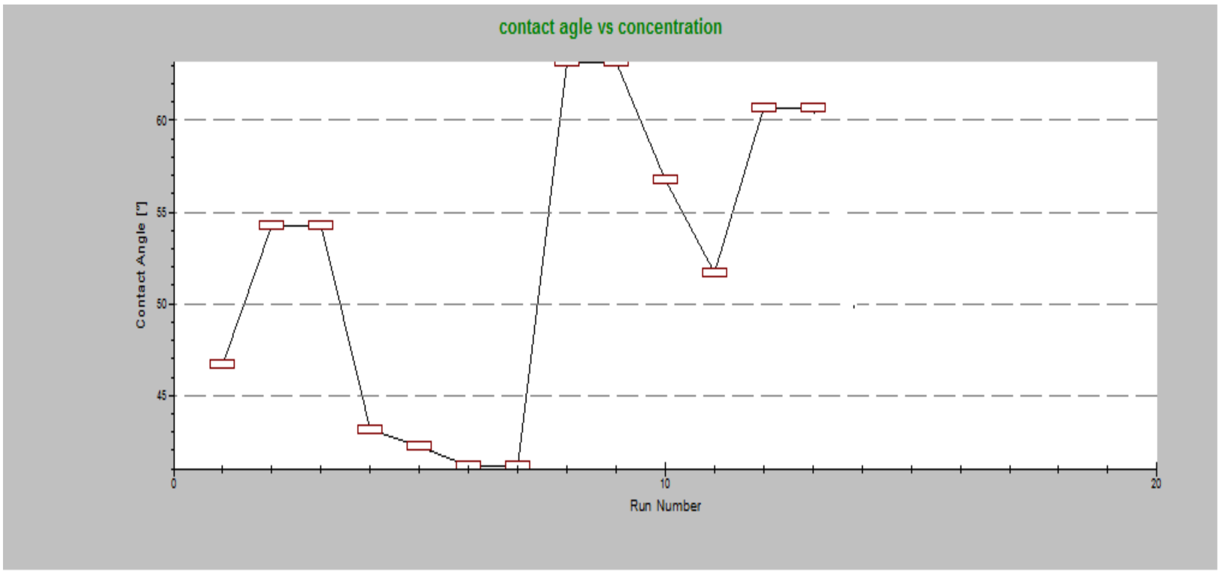


Figure 17: contact angle (on urea surface) versus clay concentration graph

For contact angle, the result above shown that 8% clay gives the higher contact angle compared to 2%.

Contact angle statistics:

- 2% clay : 41-43 °
- 8% clay : 47-63 °

4.1.1 *Urea/Starch/Borate/lignin* Surface Tension analysis.

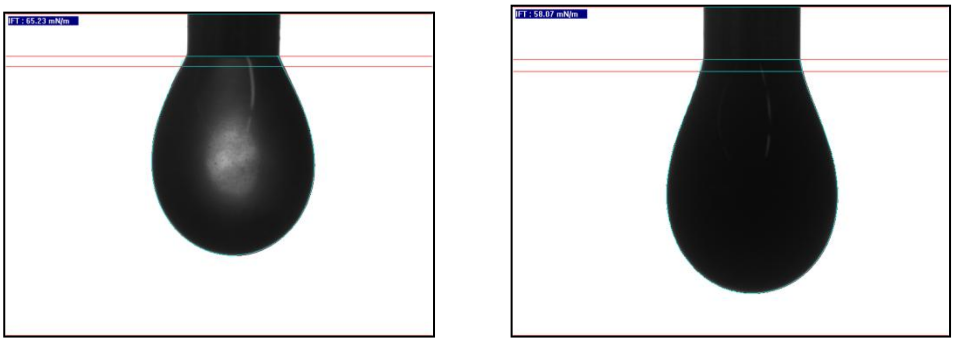


Figure18: (a) 5% lignin (c) 20% lignin

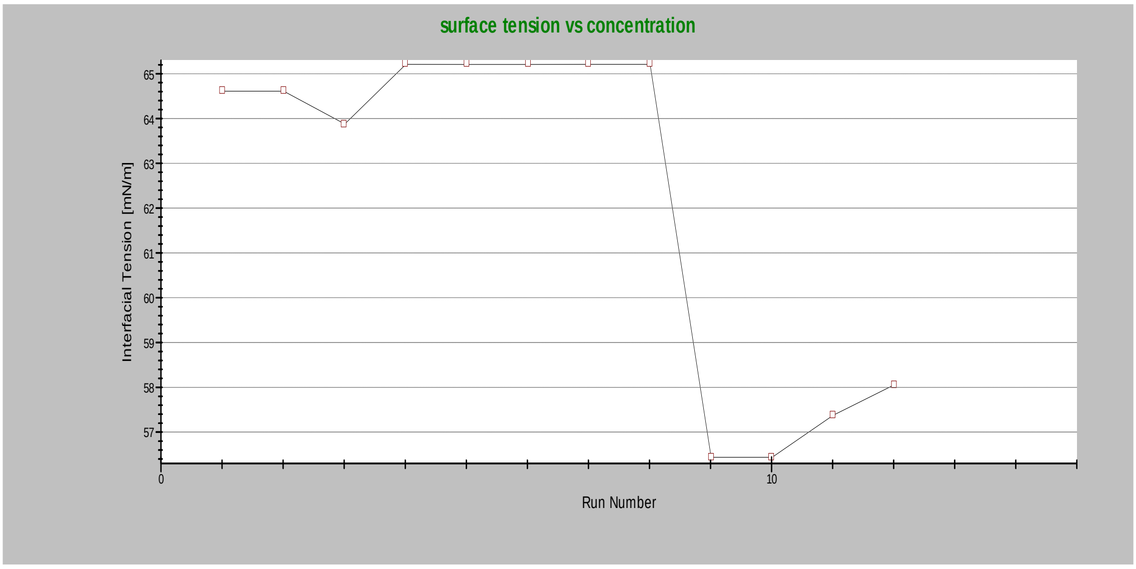


Figure 19: surface tension (on glass surface) versus lignin concentration graph

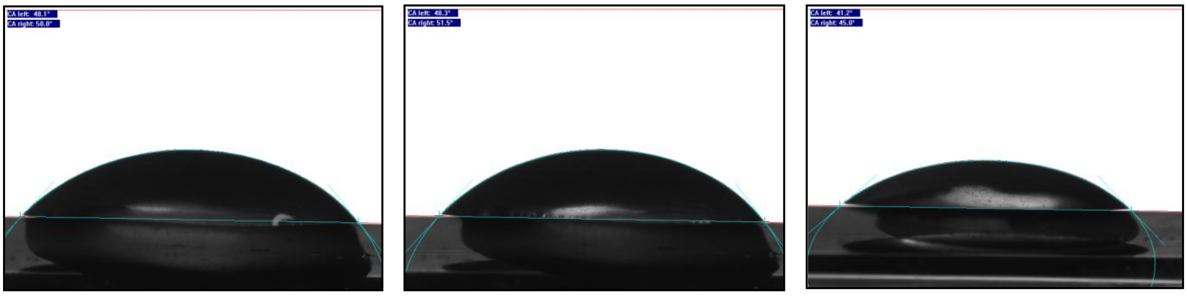
Surface tension for 5% lignin gives the highest value compared to 20% lignin. Increasing the concentration of lignin will result in decreasing the surface tension for the mixture, thus, increasing the droplet spreading efficiency onto urea surface.

Surface tension statistics:

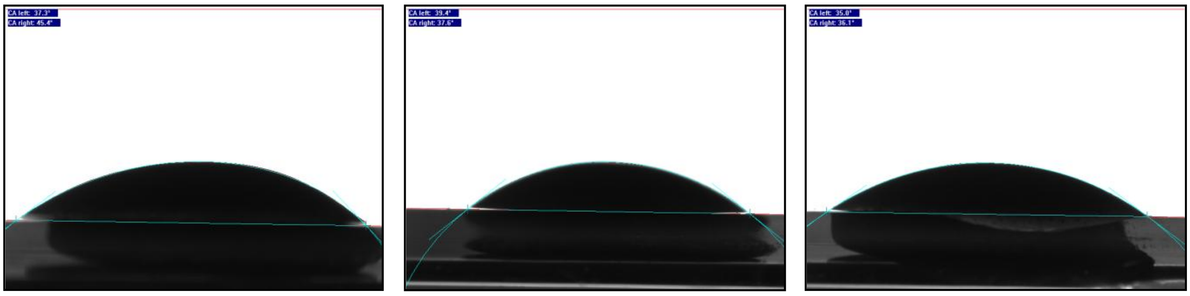
- 5% lignin : 63-65 mN/m
- 20% lignin: 56-58 mN/m

4.1.2.1 On Glass surface:

(a) 5% lignin



(a) 20% lignin



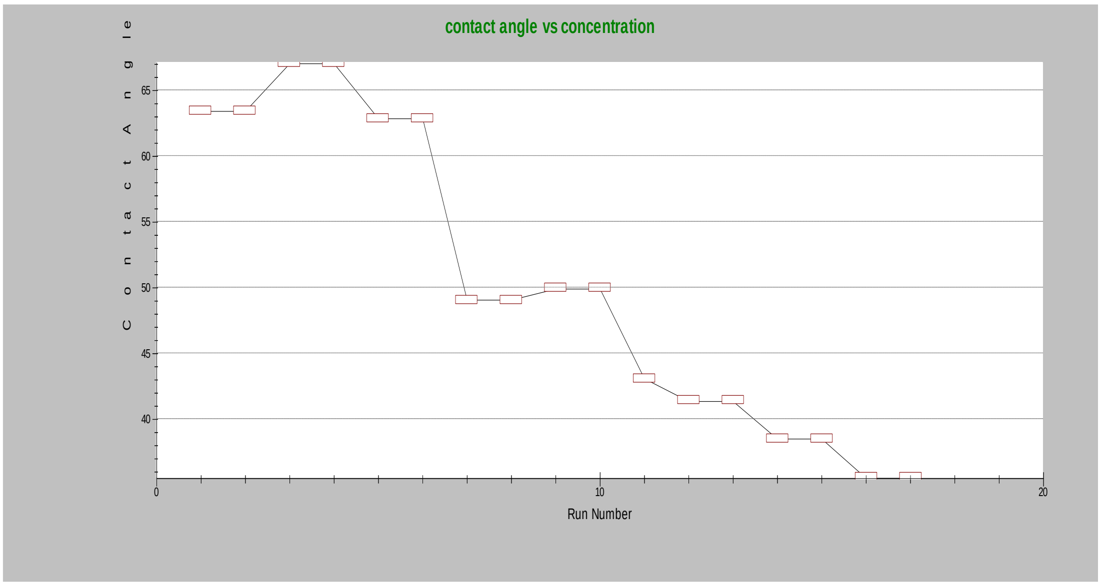


Figure 21: contact angle (on glass surface) versus lignin concentration graph

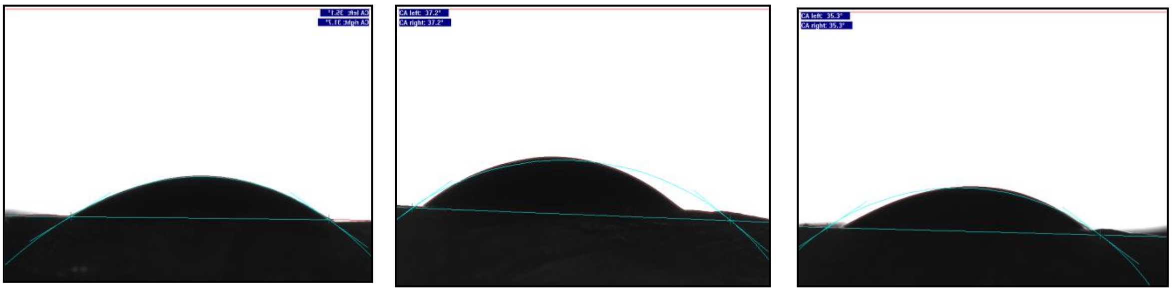
Contact Angle for 5 % lignin gives the highest value compared to 20% lignin. Increasing the concentration of lignin will result in decreasing the surface tension for the mixture, thus, increasing the droplet spreading efficiency onto urea surface.

Contact angle statistics:

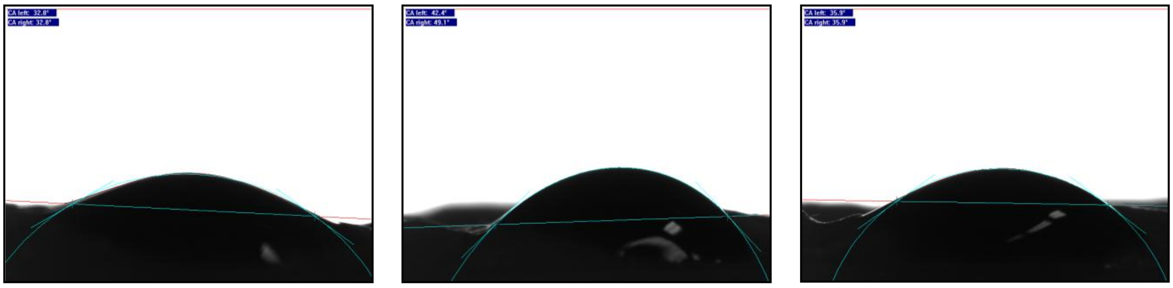
- 5% lignin : 63-67 °
- 20% lignin : 35-49 °

4.1.2.1 On Urea surface:

(a) 5% lignin



(a) 20% lignin



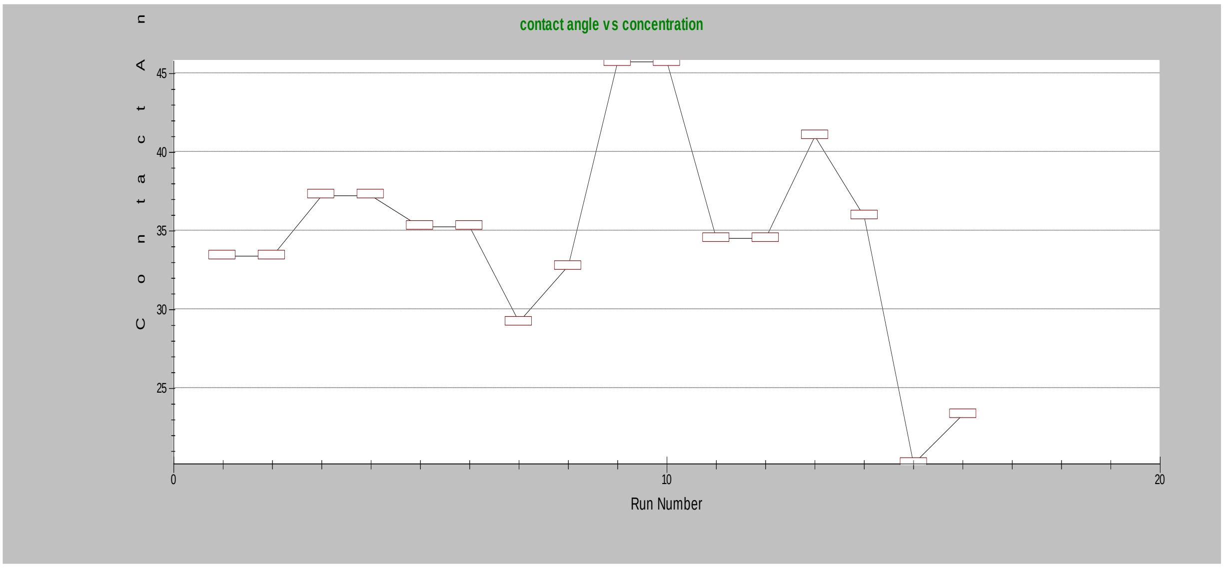


Figure 22: contact angle (on urea surface) versus lignin concentration graph

Contact angle for 5% lignin gives the highest value compared to 20% lignin. Increasing the concentration of lignin will result in decreasing the surface tension for the mixture, thus, increasing the droplet spreading efficiency onto urea surface. Contact angle statistics:

- 5% lignin : 33-37 °
- 20% lignin : 20-35 °

4.2 DISCUSSION

A. Surface Tension

Fig. 3, Fig 9 and **Fig 15** 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 while for clay, the surface tension increasing. 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.

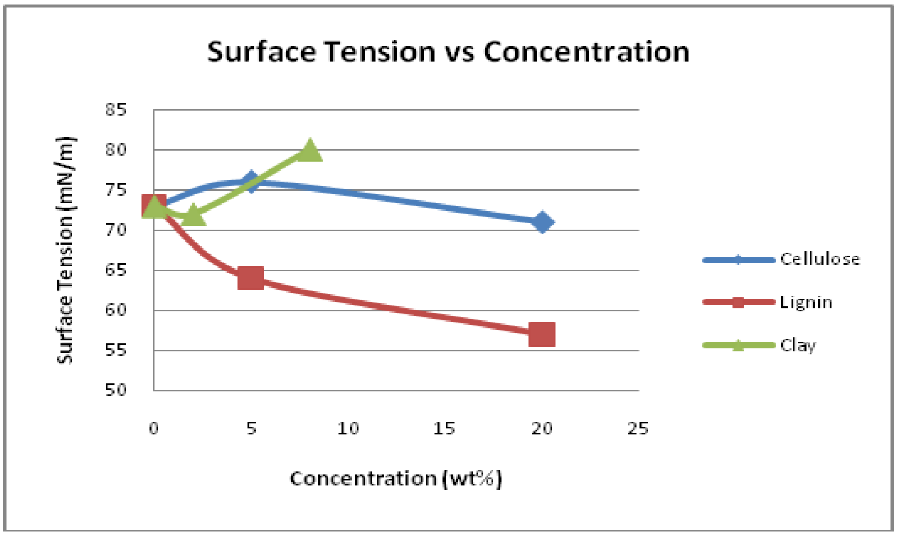


Figure.23: Surface Tension for different concentration of biomass.

B. Contact Angle

OCA 15 software; a digital frame grabber was used to obtain images from side view of the CCD camera for measuring the contact angle. **Fig.4, Fig.10** and **Fig16** shows the images captured for partial wetting of biomass film over glass. **Fig.6, Fig.12 and Fig.18** shows the partial wetting of the films onto urea surfaces. The film (coating) thickness depends upon the surface tension, withdrawal speed, substrate geometry, roughness, and melts viscosity [25, 26].

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

Table 2: contact angle and surface tension for different type and concentration for biomass droplet.

For cellulose and lignin, as the concentration increases, the contact angle is decreasing, contact area increasing. Different observation for clay, as the concentration increases, the contact angle is increasing, contact area decreasing.

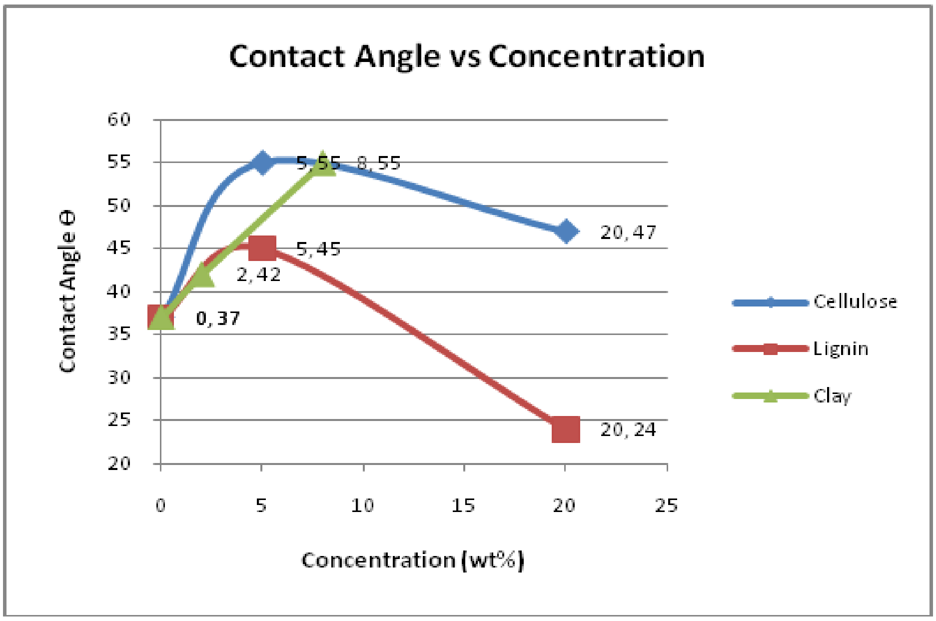


Figure 24: Surface Tension for different concentration of biomass.

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.

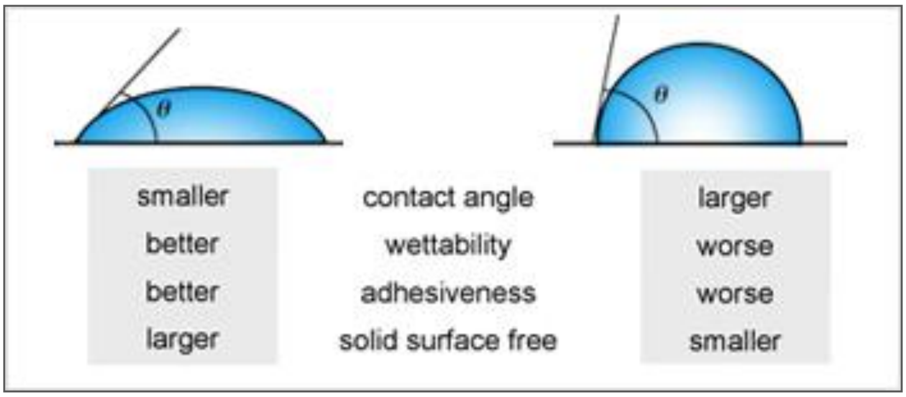


Figure 25: comparison between smaller and larger contact angle (KYOWA Interface Science 2007)

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

Table 3 : wettability, adhesiveness and solid surface free energy for different biomass film.

C. Critical Wetting Tension

From the result we can plot Zisman`s Critical Wetting tension graph in order 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.

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

Table 4 Critical Surface tension for different biomass

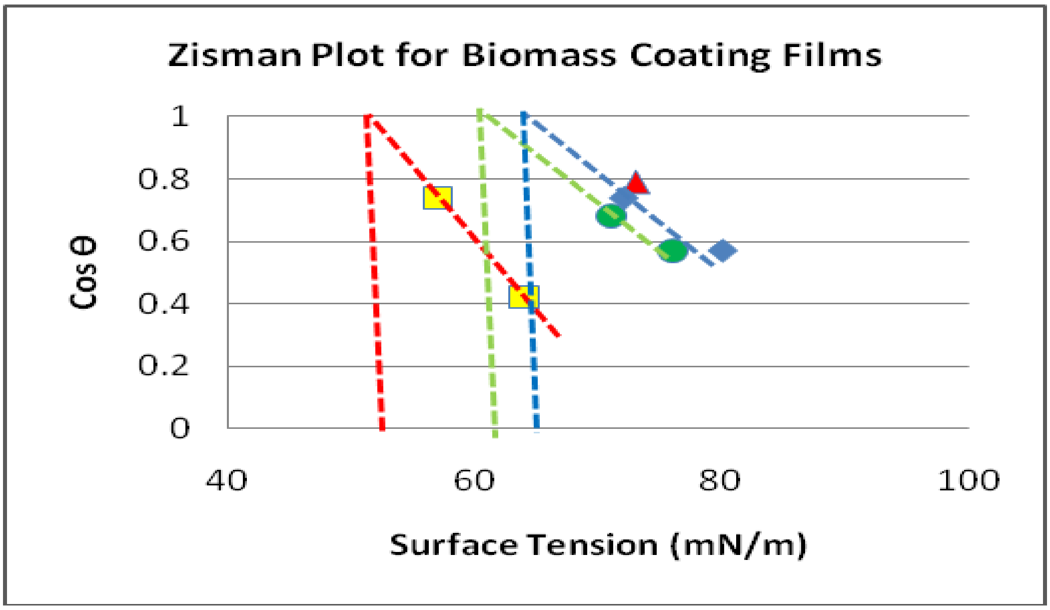


Figure 26: Zisman`s Plot (the relationship between contact angle and surface tension)

CHAPTER 5
CONCLUSION AND RECOMMENDATION

The Video based Optical Contact Angle Measuring Instrument (OCA 15) was found to be very useful tool for investigating the characteristics of biomass droplet; surface tension and contact angle. Surface tension is an important factor that determines the ability of coating to wet and adhere to a substrate. Wetting may be defined by reference to a liquid drop resting in equilibrium on a solid surface. There is a large difference observed between the low surface tension and high surface tension liquids. The lower the surface tension has higher spreading efficiency. This can be rationalized as a result of the lower contact angle formed the lower surface tension liquid.

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 e defined by reference to a liquid drop resting in 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, [6] 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 ($\theta < 90^{\circ}$). Contact angle gives good indication for the wettablity of a liquid.

RECOMMENDATION

The study for *Biomass Droplet characteristic* should be done further research on:

1. Penetration of the droplet behavior and droplet evaporation.
2. Study the effect of biomass droplet properties at different temperature i.e., 110°C as well as 120°C

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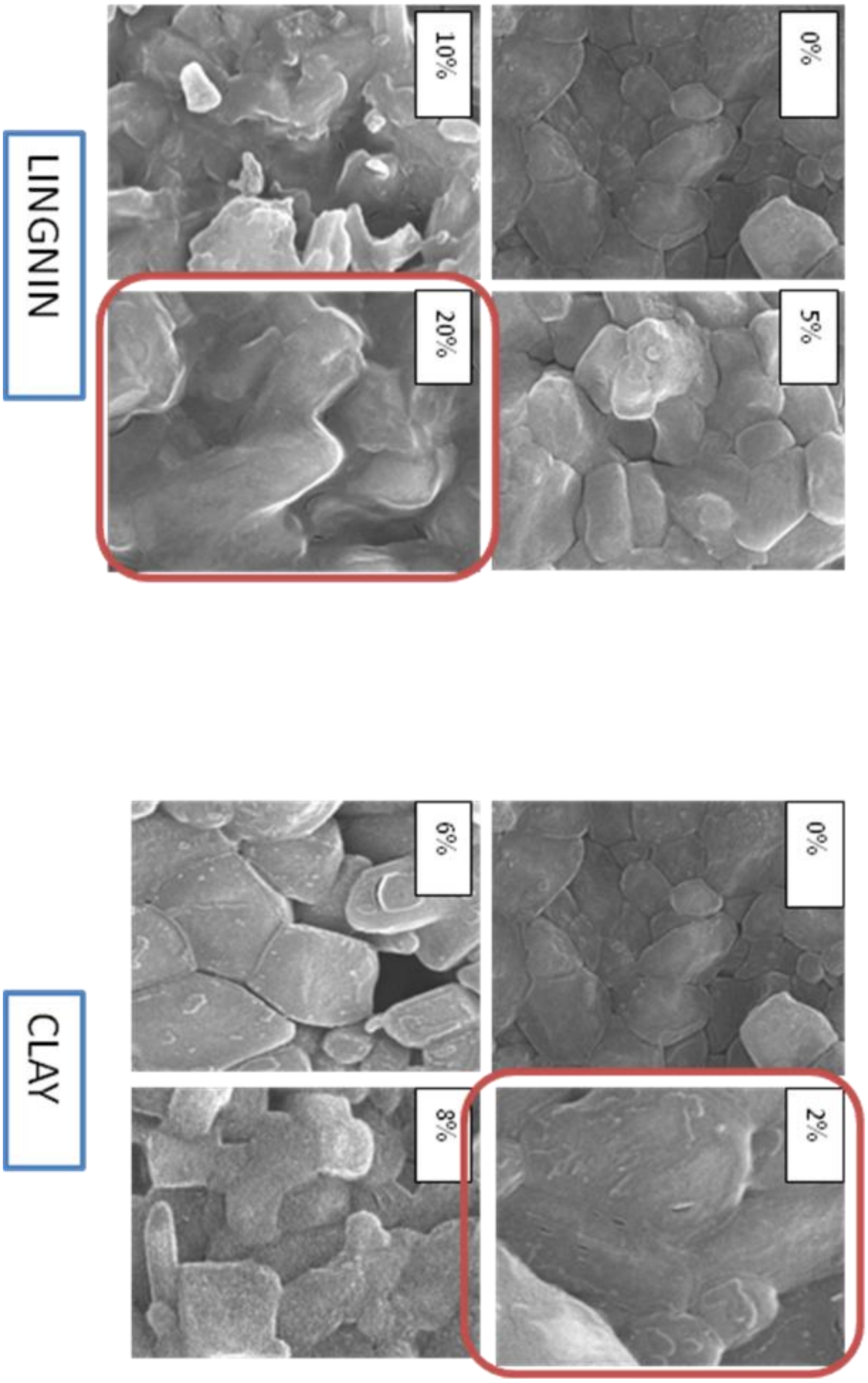
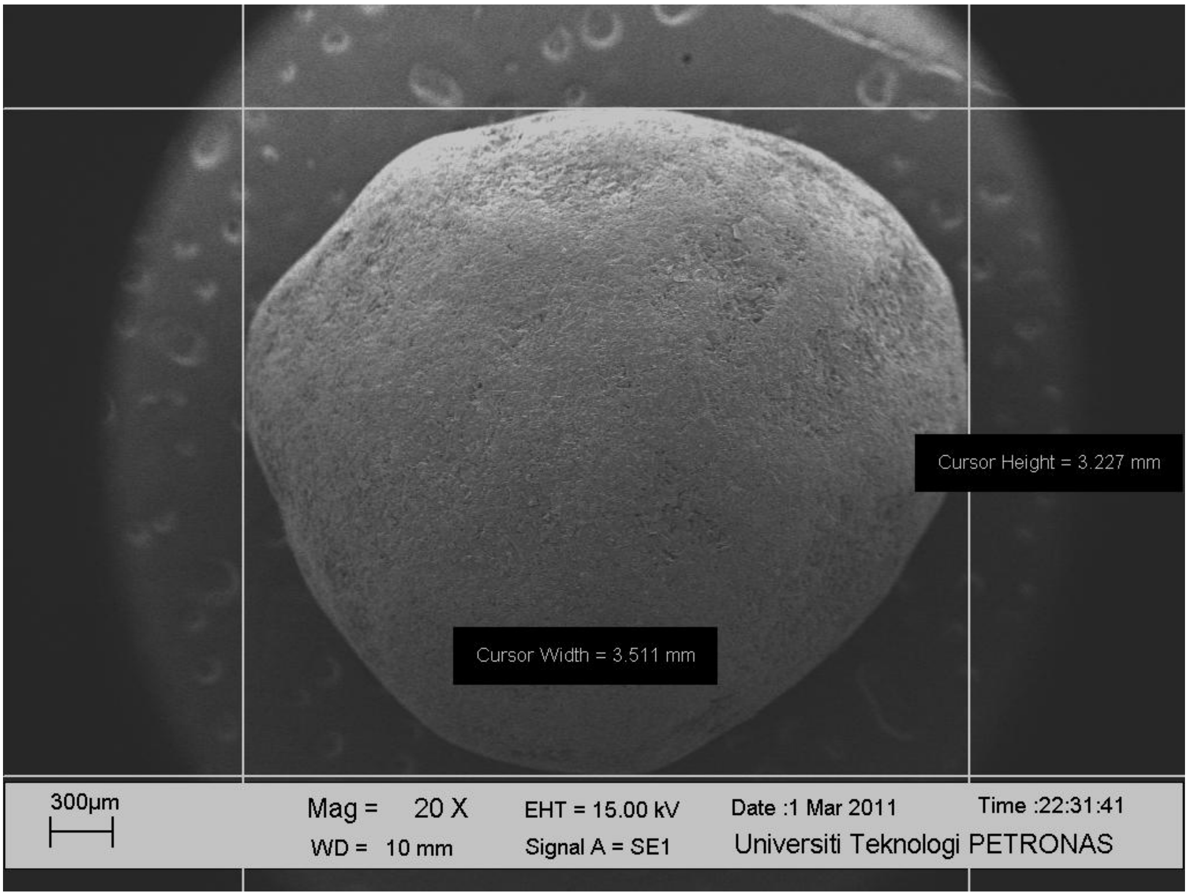
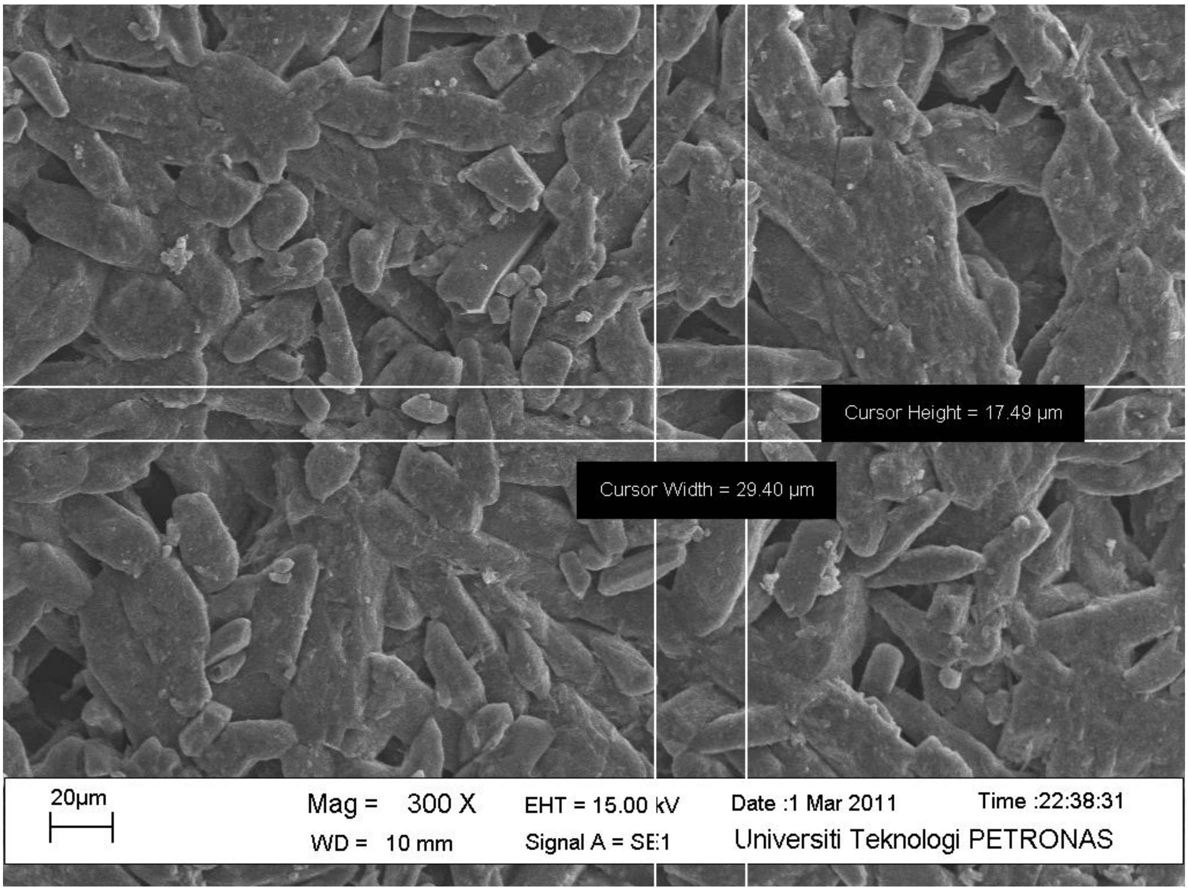
APPENDICES



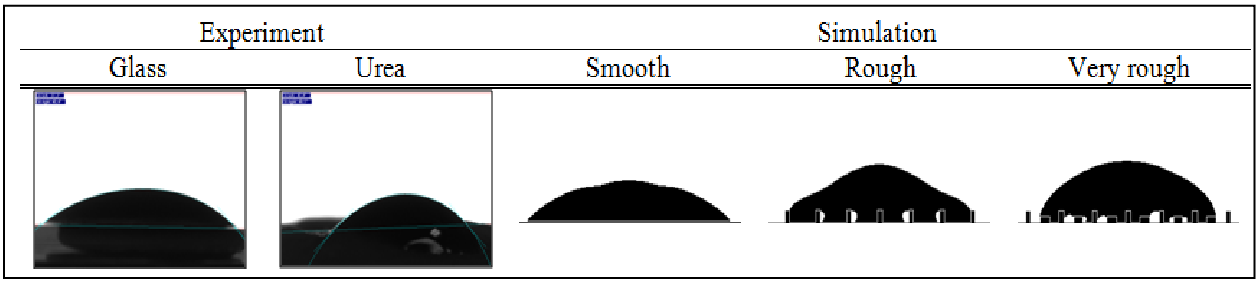
Appendix 1: SEM images for Lignin and Clay



Appendix 2: *Urea granules at 20x*



Appendix 3: *SEM images for Urea Surface at 300x*



Appendix 4: *Comparison between experiment and simulation of droplet onto smooth (glass) and rough (urea) surface.*