Wettability Properties of Biopolymer Coated Urea with Addition of Fillers

by

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Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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ABSTRACT

Introduction of control release urea (CRU) in agriculture gives good significant impact toward environmental and economic. The main objective of control release urea is to minimize the nutrient loss into soil through leaching and to increase efficiency of nutrient usage. There are many type of coating material has been introduced and applied for control release urea. For this research the biopolymer composite material has been developed as coating material because the biopolymer composite is more environmental friendly compared other coating material. However, the combination of biopolymer coating materials which are starch, polyvinyl alcohol (PVA) and citric acid do not give a good steady released of urea.

Coating uniformity of coated urea is crucial to allow urea to be released at steady rate. The good coating uniformity from thin-film technique needs to have good wettability properties of biopolymer coating material. In order to improve the wettability properties, fillers from Bentonite, Kaolin, Nanoclay Bentonite and Halloysite Nanoclay is mixed at certain percent with other biopolymer coating materials. Thus, the purpose of this research is to study the wettability properties of biopolymer coated urea with addition of fillers. Therefore, wettability properties, contact angle and spreading behaviour is investigated. The experimental matrix is designed by varying the type and percentage of fillers added into biopolymer composite. The wettability properties are characterized by using Optical Contact Angle (OCA) and SCA20 software.

ACKNOWLEDGEMENT

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Table of Contents

Lists of Figure and Table

CHAPTER 1

INTRODUCTION

1.1 Background Study

Nowadays, agriculture is a major economic contribution to the some countries. The development of agriculture is rapidly progress because of the technology is developed respectively. According to the Food and Agriculture Organization (FAO), fertilizer globally contributes 40% to 60% to yield increases. Many researches on the fertilizer have been done to produce the product for with the huge quantity and best quality. Subsequently, the values of the fertilizer have increased by year. The overuse and inefficient use of fertilizer has generated negative environmental consequences, such as water eutrophication and pollution (Ferng, 2009).

The fertilizer like urea has been commonly used in domestic uses as it has high amount of nitrogen. The properties of urea is very soluble in water, thus the nutrients are being absorbed into soil excessively during early plant growth stage. These problems are overcome by introducing the control release fertilizer technique where the release of nutrient from urea is controlled with several techniques. Control release urea is granules coated with a mixture of several materials which will reduce the releasing time of nutrients and control the amount of nutrients released to plant accordingly. The coating will ensure the release of fertilizer nutrient is controlled by diffusion. There are many coating material that can be used to control the release of urea. However, the biopolymer coated urea is highly preferable due to its biodegradable property and may not cause any environmental impact to nature.

Therefore, there are several types of polymers that can be used as coating material for this control release technique. In this research, the combination of starch, polyvinyl alcohol (PVA) and citric acid were tested and could give a better function as cross-linking agents (Menzel et al., 2013) and (Shi et al., 2008). However, the ability of coating material to give a steady release is depended on the uniformity of coating layer. Therefore, it is crucial to study the wettability properties in order to have the good

coating uniformity for coated urea. Thus, this experiment will be investigated by the presence of different fillers in biopolymer coating material which are Bentonites, Kaolin, Nanoclay Bentonite and Halloysite Nanoclay.

1.2 Problem statement

Coating uniformity is crucial to have urea to be released at the required time. Therefore, in order to have good coating uniformity by a thin layer film technique it is important to have good wettability properties. The addition of fillers found help to improve the wettability properties. The study of wettability for single droplet of biopolymer with addition of fillers will help to find out the best fillers composition.

1.3 Objective

The aim of the project is to study the wettability of biopolymer coated urea with variant use of fillers. The filler that we study are Bentonites, Kaolin, Nanoclay Bentonite and Halloysite Nanoclay. Besides that, different percentage of fillers (1%, 2%, 3% and 4%) is also being investigated. The wettability properties for each of biopolymer addition fillers are investigated.

- Surface tension and Contact angle
- Spreading behavior

1.4 Scope of Study

The experiment will use starch, polyvinyl alcohol (PVA) and citric acid with different fillers; Bentonites, Kaolin, Nanoclay Bentonite and Halloysite Nanoclay to check the wettability properties of the biopolymer coating solution. The wettability characterization is measured and analyzed with the optical contact angle (OCA 20) device to measure the dynamic contact angle. Aside from it, the spreading diameter is measured with the high-speed CCD camera feature to capture the high speed motion of the droplet impact. The SCA 20 software is used to conduct experiment and analyst the final digital image data. The experiment is repeated for different percentage of filler.

1.5 Feasibility of Project

This project is completed to investigate the wettability property of modified biopolymer with varies fillers as a coating material for coated urea. The main objective is to discover the effect of varies fillers on the wettability property of biopolymer blend. Good wettability property will ensure the good spreading behavior which is crucial in coating process as well as in the process of controlled release urea (CRU) production. Besides, a good spreading behavior will promotes to perfect thin film formation on the urea substrate which helps to obtain the uniformity of coating during coating process. Thus, the project research is relevant to today's development and knowledge especially in controlled-release urea (CRU) technology.

CHAPTER 2

LITERATURE REVIEW

2.1 Significant of Control Release Urea

About half of world crop yields attributed to natural or synthetic fertilizers (Stewart, Dibb, Johnston, & Smyth, 2005). In the past, controlled release fertilizers is considered too expensive to use in small area of production, but the recent development of lower-cost polymer coated urea products has led to consideration of their use in a wide range especially in agriculture sectors (Nelson, Scharf, Bundy, & Tracy, 2008). Nowadays, over 90 percent of the world's production of urea is used for fertilizer-related products ("Urea Supplier - The Chemical Company," 2014). The benefit development of urea will give significant impact on the world crop production in the future. The implication of urea usage started when the high content of nitrogen in urea is very soluble in water, thus the nutrient in urea easily wash up to the environment. As a result of that, not all nutrient from urea are being absorbed by the plant due to vaporization, surface runoff and leaching (Chen, Xie, Zhuang, Chen, & Jing, 2008).It is found that, the usage of commercial granular soluble fertilizer will cause the hazardous excess release of nitrogen at the beginning of plant growth and deficiency of nutrient at the end of the growing season Therefore, the control release urea technology is introduced to give a steady release of nutrients for the optimum urea availability during growing season (Zulhaimi, KuShaari, & Man, 2011). Besides, the use of controlled-release urea able to maximize the efficiency of urea use, optimize crop production and minimize the negative impact excess urea on the environment (Grant et al., 2012).

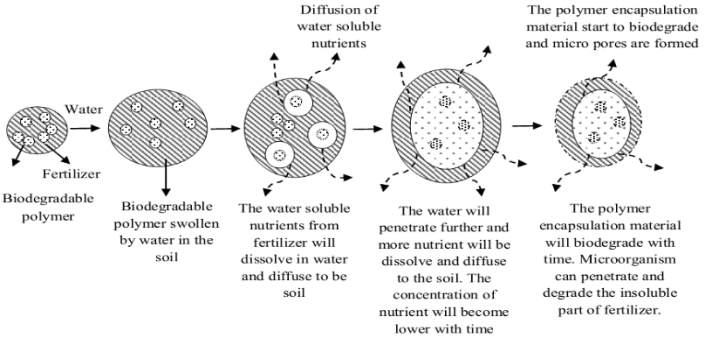


Figure 1: Mechanism of controlled release fertilizer (Munusamy et al, 2012)

2.2 Fillers

Filler is defining as something added to augment weight or size or fill space. At the earlier, usages of fillers is important as a raw material in papermaking industry (Büchner, 1989) . Usually, composite material will consist of two components, the matrix and the filler. The matrix and filler are holds together to form the bulk of the material where the filler is impregnated in the matrix. The fillers can dispersed in the polymer matrix quite homogenously (Pradhan et al., 2013). The well dispersed of filler in composite matrix help to avoid zones of weaker cohesion where defects will happen upon stressing (Othman, Ismail, & Mariatti, 2006). Basically, fillers can be categorized into two types based on performance which are extender and functional fillers. The extender fillers is likely to occupy in between space and mainly used for low formulation cost. On the other hand, functional fillers have a definite and required function in the formulation. Combination of two materials can give advantage of the good characteristics of each of the materials. There are several type of filler where the named of composite match with the filler type; particulate, short fiber, long fiber and laminate. Recently, it has been found that the addition of Cr content in Ni-Cr filler can improve the wettability on SiC ceramic (Y. Mao, Mombello, & Baroni, 2011). The interfacial reaction occur between SiC and Ni-Cr filler during the wetting process decrease the interfacial free energy of the system thus the wettability will improved significantly. The application of fillers in industry is widely applied and recognized.

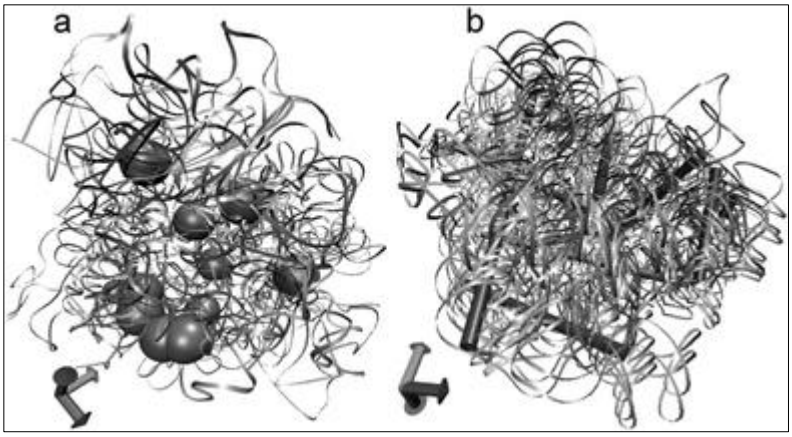


Figure 2: 3D schematic demonstration of nanocomposite system with spherical filler and tubular filler (Xu et al., 2010)

2.2.1 Bentonite as fillers.

Bentonite clay is fine-grained rock that primarily composed of montmorillonite minerals. The formation of bentonite is produced by the alteration of rhyolites volcanic ash. Besides that, bentonite has a strong colloidal properties and its volume increases a few time when coming into contact with water. Furthermore, the other properties of bentonite are good for hydration, swelling, water absorption, viscosity and thixotropic that make it valuable material for a wide range of uses and application including pharmaceuticals (Collins, 2014). Much of bentonite's usefulness in the drilling and geotechnical engineering industry comes from its unique rheological properties (Hosterman, 1985). The application of bentonite as filler is widely used by many industries. For example, sodium bentonite which enables the clay to bring filler effect on cemented material, thus refining its pore spaces and reinforcing its structures. Furthermore, the application of sodium bentonite as to maximize the filler and pozzolanic effect of stabilized peat help to improve peat in geological condition of swampy area especially for highway construction (Wong, Hashim, & Ali, 2013)..Therefore, the wide application of bentonite as filler can possibly be good filler for urea coating composite material.

2.2.2 Kaolin

Kaolin or China clay, alumina silicate is widely used in making of paint, plastics, paper and many other products. Because of its natural state whiteness, soft powder, fine particle size and plate like structure, kaolin is suitable as a coating, functional fillers, extender, ceramic raw material, and catalyst. The properties of kaolin which remains chemically inert over a wide pH range thus it will offer excellent coverage when it is used as pigment in coated film. Besides, the kaolin's particle size distribution helps to control packing density so it will give a good spreading in paint. Therefore, it will enhance to increase the spreading diameter for solution coating process. Kaolin is hydrophilic and can be dispersed in water but it also can be chemically modified so that it will become hydrophobic. The modified kaolin are being used in paints, plastic and ink production as they disperse and wet out rapidly therefore it have better suspension properties and give superior water resistance and reduced viscosities (Murray, 1991). The good property of it can be tested as potential filler for urea coating composite material.

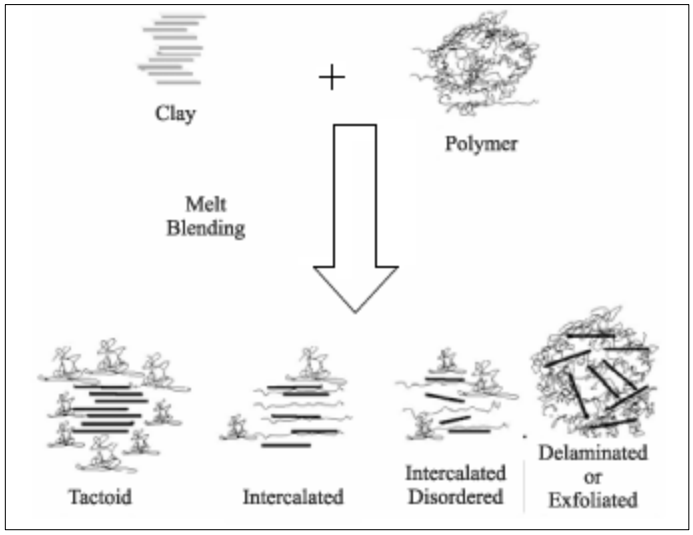


Figure 3: Schematic illustration of terminology used to describe clay and polymer formed (Fornes & Paul, 2003)

2.2.3 Nanoclay Composite Fillers

The usage of nano-scale (particle size < 2µm) composite started in the early 1950. Since that the nanocomposite technology gives a lot enhancement to the product in industry. The polymer nanocomposite are polymer (thermoplastics, thermosets or elastomers) that have been reinforced with small amount of nanofiller in the polymer matrix (Bhat, Hegde, Kamath, & Deshpande, 2008). The use of nanoclay filled polymer matrix give significant improvement to mechanical and physical properties even by introducing small amounts of filler (<10wt.%) (Ferreira, Reis, Costa, Richardson, & Richardson, 2011) .The addition of nanoclay is found can help to increase the wettability in contact angle (Hegde, 2009). Recently, there are a study that shown that the usage of nanoparticle as additives can modify the wettability of polymer surface. The nanoparticle like nanoclay can be used to modify the chemical composition of the surface and later will affecting the intermolecular interactions between solid and water like wetting behavior (Manoudis & Karapanagiotis, 2014). Figure 4 shown the basic structural unit of clay minerals which is a layer comprising a silica tetrahedral sheet and alumina octahedral sheet. According to Floody et al. (2009) natural nanoclay have a great potential for industrial and environmental application.

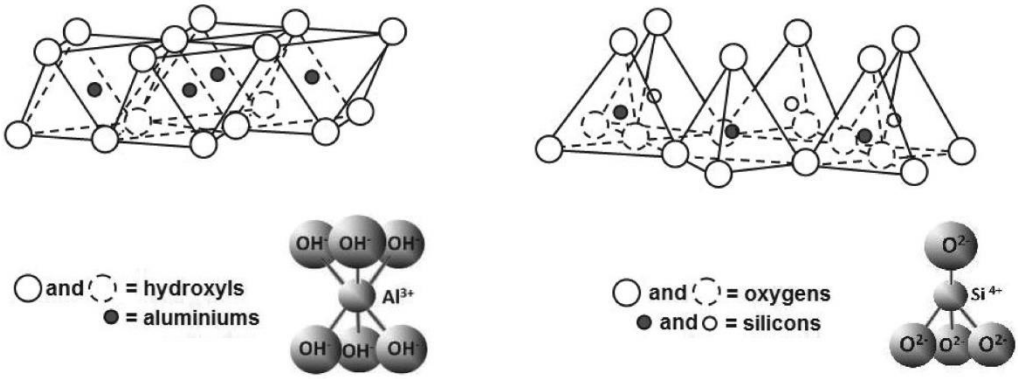


Figure 4: Some Structures of nanoclay (Floody, Theng, Reyes, & Mora, 2009)

2.3 Wettability characterization of composite

The wettability or interphase behavior is defines as a study of characterization on how a liquid deposited on a solid (or liquid) substrate spread out. The sample preservation, preparation, storage and test conditions are important since wettability is sensitive to oxidation (Glover, 2014). The wettability can be estimated by determine the spreading diameter of liquid on substrate and contact angle with young's modulus equation. Therefore, low values of contact angle indicate liquid spreads, or wets well while high contact angle indicate poor wetting. If the contact angle is greater than 90 degrees it is said to be non-wetting. Besides, the contact angle also can check on the strength of solid/liquid interactions as summarize by table below.

Table 1: The relation between contact angle, wetting and strength of solid/liquid and liquid/liquid interaction (Schonherr & Bukavac, 1972)

Contact angle	Degree of Wetting	Strength of	
		Solid/Liquid Interactions	Liquid/Liquid interactions
$\theta = 0°$	Perfect wetting	Strong	Weak
$\theta < 0\ 90°$	High wettability	Strong	Strong
		Weak	Weak
$90° < \theta < 180°$	Low wettability	Weak	Strong
$\theta < 180°$	Perfectly non-wetting	Weak	Strong

According to Zisman et al.(1991), the theoretical description of contact angle is the angle (tangent) of a liquid drop with the solid surface at the base. The mechanical equilibrium of the liquid drop is under the action of three interfacial tensions where it is defines the contact angle of liquid drop on solid surface.

The equilibrium contact angle is determined by Young's equation. The interfacial tensions are solid-vapor γsv, solid-liquid γsl, and liquid vapor γlv and θ is the contact angle. According to Myers (1946) there are four direct contact angle measurement techniques which are sissile drop,

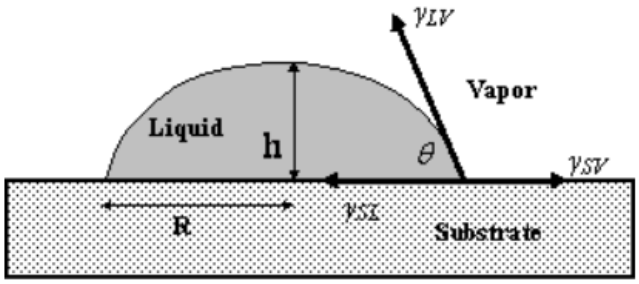


Figure 5: Schematic diagram of three interfacial tensions

captive bubble, sissile bubble and tilting plate. The common used method for measurement of contact angle is the sessile drop method which is by measuring the angle between the solid surface and the tangent to the drop profile at the drop edge during depositing of liquid drop on solid surface occur (Njobuenwu, Oboho, & Gumus, 2007). Other than that, the maximum spreading behavior is other character that needs to be identified in wettability characterization. The maximum spreading behavior can be measured by identified the maximum spreading diameter, where D_t at certain time over by the initial droplet diameter, D_o (Samsudin, Ku Shaari, Man, & Sufian, 2012). According to Samsudin et al. (2012) when the liquid droplet impacted on the urea substrate produced the smallest static it shows that the maximum spreading behavior is achieved. The better wettability will ensures the uniformity of liquid spreading as well as the coating quality. The wettability relationship is when low contact angle will give high spreading diameter factor and low surface tension which indicate of good wettability properties

CHAPTER 3

METHODOLOGY

3.3 Experiment Procedure/Approach

3.3.1 Preparation of Modified Biopolymer coating material

The modified coated biopolymer material is prepared with the blending ratio 1/2/3 of polyvinyl alcohol (PVA), citric acid and starch and several weight percent of differences type of fillers like Kaolin, Bentonite, Halloysite nanoclay and Nanoclay Bentonite with total weight of 1%, 2%, 3% and 4%. The further detail about the blending ratio is explained in experimental matrix attached below. The preparation of modified biopolymer coating solution started with the 40ml of deionized (DI) water is added into 2 neck flask and heated in water bath at 90°C. Then, 1g of polyvinyl alcohol (PVA) is added into the flask and the mixture is stirred for 15 minutes with magnetic stirrer bar rotating at 300rpm. Later, 3g of tapioca starch is added with 30ml of DI water and at the same time fillers is added. The mixture is continuously stirred for 1.0 hours at the same temperature of 90°C. The 90°C temperature is the best temperature for polyvinyl alcohol to dissolve completely. Next, the mixture is cooled down to the room temperature of 30°C. Then, another 2g of citric acid and 10ml of water is added into mixture. Finally the mixture stirred at room temperature for 1 hour. After the process is done then the readily modified solution is stored in a tight air container. Therefore the duration between solution preparation and characterization process is made constant between 2 – 3 days as the result may affected by the time different.

3.3.2 Preparation of Urea Substrate

The sample of urea surface for urea granules is made to prepare for characterization of wettability of modified biopolymer solution later. The apparatus used to prepare urea substrate are aluminum dish and hotplate. The hotplate is used to heat and melts the urea granules in aluminum dish. The urea granules are melted at 130°C until the urea granules melts to become a solution in aluminum dish. After that, the melted urea is dried inside the oven at the temperature of 60°C – 70°C for 30 minutes. Later, the dried urea substrate is taken out form the dish and stored in package to avoid from moisture. (Samsudin et al., 2012).

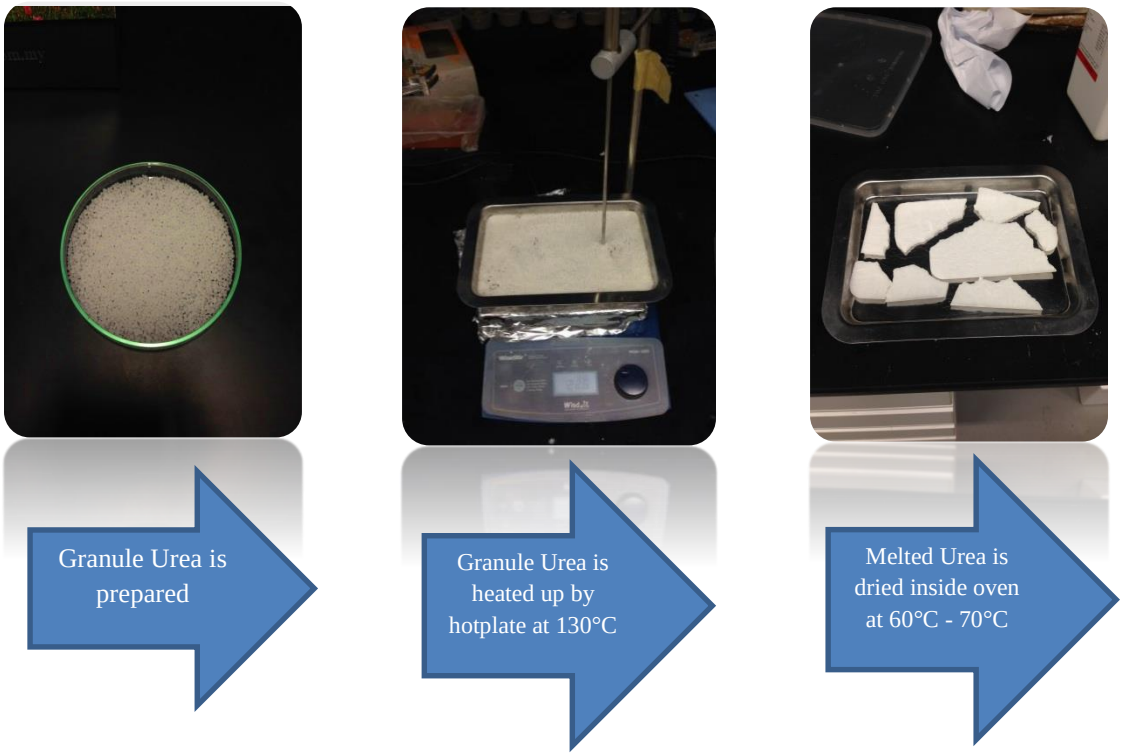


Figure 6: Preparing Urea Substrate

3.3.3 Characterization of modified biopolymer solution

The characterization of new modified biopolymer solution wetting behavior is measured by using OCA 20 (Optical Contact angle) measurement device. The OCA 20 generally can provide various kind of surface or interfacial measurement. Besides that, it is also can provide a representation of wetting envelopes and work of adhesion or contact angle diagram. The device is assembled with 1mL syringe with 0.51mm needle tip that will be used to dispense the liquid with droplet size range of 2mm to 0,06mm (Samsudin et al., 2012). Other than that, the device also equipped with high-speed, a Charged-Coupled Device (CCD) camera to capture the high speed motion of the droplet impact. The CCD camera is capable to capture up to 30 frames per second and build-in software, SCA software is used to analyze the high speed digital image data obtained. Commonly, the sessile drop method is the standard method used to measure contact angles with OCA20 device.

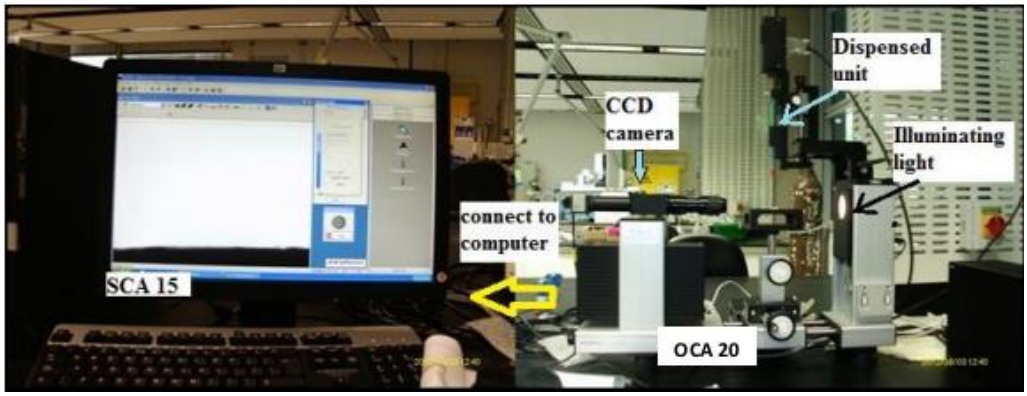


Figure 7: Optical Contact Angle (OCA20) device

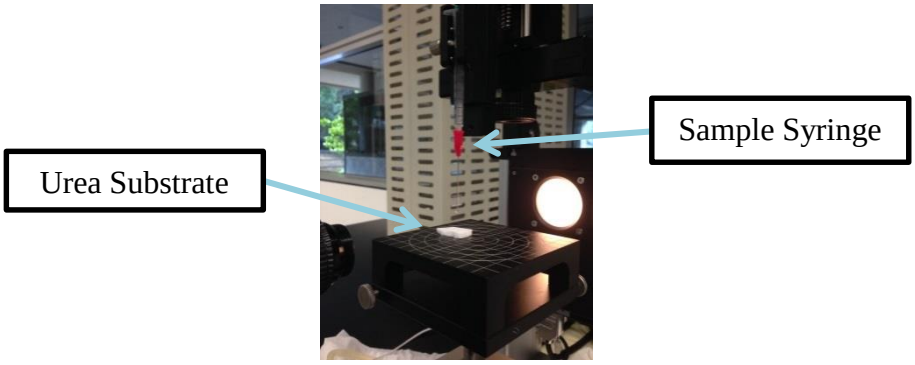


Figure 8: Dispensed Unit

3.3.4 Surface tension and contact angle measurement

From the software of SCA, the image is capture by the build-in camera video in OCA20 device. Later the image will snapped and the surface tension is measured by the measurement tool using the pendant drop method. Next, for the contact angle measurement, the position of urea substrate is calibrated to obtain the clear and sharp focus of images. Next, the syringe contains of modified biopolymer is positioned into OCA20 device. The modified biopolymer is dispensed at dosing rate of 2.00 µl therefore the gravitational effect can be negligible. The contact angle is measure using the sessile drop method. The sessile drop is illuminated from one side using a diffuse light source and viewed from the other side of the contour of the drop is observed. The baseline is first detected to indicate where the droplet boundary line then the droplet shape is determined and the contact angles can be calculated. The calculation of surface tension is calculated based the Young-Laplace equation using these contact angle measurement (Samsudin et al., 2012).

3.3.5 Maximum spreading

The spreading behavior is observed by calculating the maximum spreading diameter factor by using same OCA20 device. The spreading diameter measurement is determined after the initial droplet and the diameter of liquid drop after a certain time are recorded. The calculation of maximum spreading diameter can be measured by Dt / Do where Dt at certain time over by the initial droplet diameter, Do (Samsudin et al., 2012).

CHAPTER 4

RESULT & DISCUSSION

In order to study the wettability of the modified coated urea solution the surface tension, contact angle and spreading diameter is observed. As the number of sample for each of fillers is huge the summary of the result is tabulated and analyzed in graph and table

4.1 Surface tension and contact angle measurement

By using the OCA20 device the images result of surface tension and contact angle measurement can be identified. The pendant drop image is used to determine the surface tension (Stauffer, 1965) and according to Samsudin et al. (2012) the measurement of surface tension is calculated based the Young-Laplace equation using these contact angle measurement. Besides that, the contact angle of modified biopolymer solution is evaluated by using sessile drop image. The angle of from the shape of each droplet is highlighted so that the contact angle can be observed and evaluated. The sessile drop image is captured at 6 second with rate of 30 frames per second after the droplet drop into urea substrate surface. In order to simulate the result with the real coating surface condition, the droplet is tested on the industry urea substrate surface. The comparison of industry's urea substrate surface images is observed and pictures shown that they are slighly have similar surface condition in between granule and flat surfaces.

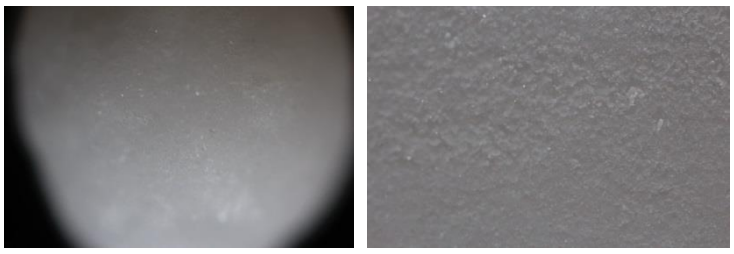
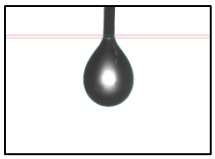
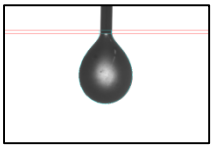
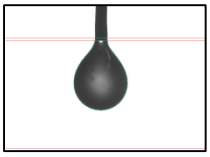
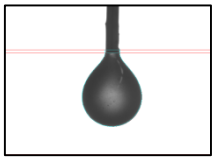
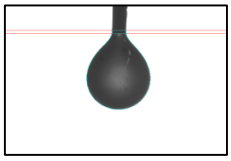
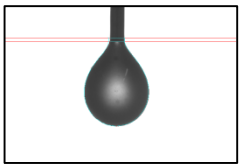
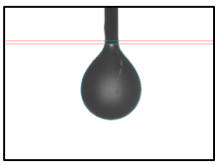
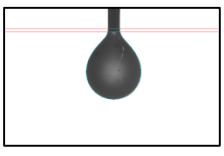
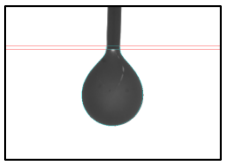
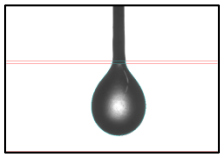
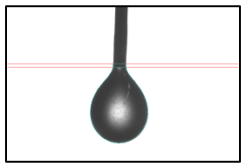
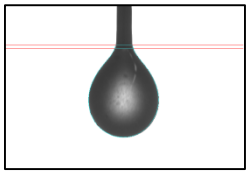
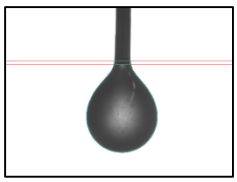
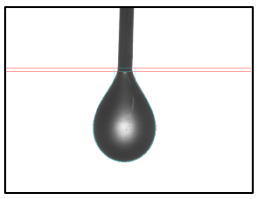
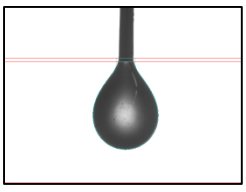
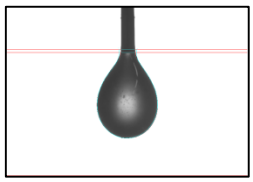


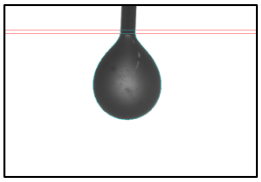
Figure 9 Granule and flat Urea Substrate Surface images

The SCA software provides both of surface tension and contact angle values for each modified biopolymer solution sample images. The total images of pendant drop and sessile drop image obtained is shown in the next tables.

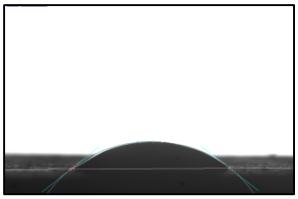
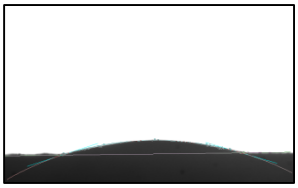
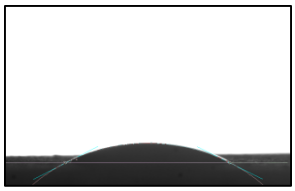
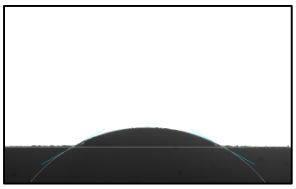
Pendant Drop Images

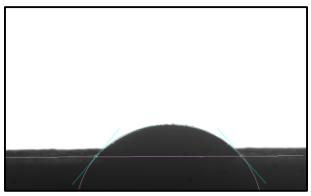
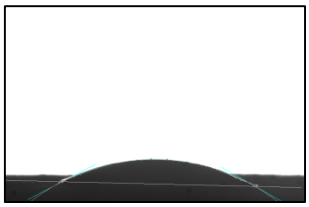
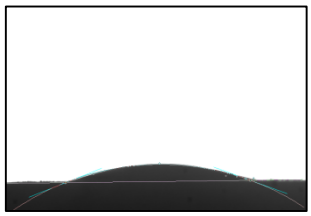
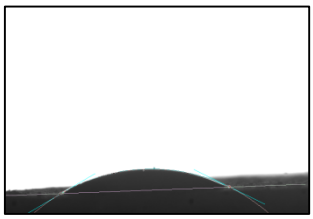
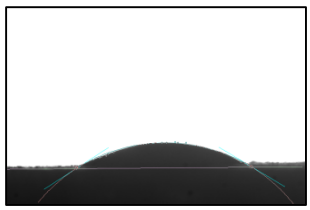
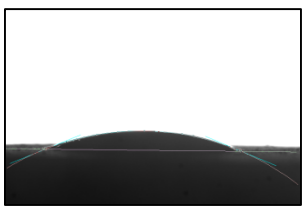
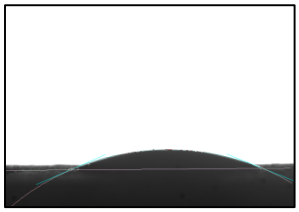
Filler	Surface tension (mN/m)	Images
No Filler	48.42	
1% Bentonite	55.89	
2% Bentonite	50.19	
3% Bentonite	55.74	
4% Bentonite	54.89	
1% Kaolin	52.30	
2% Kaolin	50.75	
3% Kaolin	55.21	

4% Kaolin	53.24	
1% Halloysite Nanoclay	53.10	
2% Halloysite Nanoclay	52.89	
3% Halloysite Nanoclay	52.94	
4% Halloysite Nanoclay	54.78	
1% Nanoclay Bentonite	39.92	
2% Nanoclay Bentonite	48.50	
3% Nanoclay Bentonite	46.25	

4% Nanoclay Bentonite	56.05	

Sessile Drop Images

Fillers	**Contact Angle (°)**		**Images**
	Left	**Right**	
No Filler	**40.1**	**40.1**	
1% Bentonite	**18.9**	**18.9**	
2% Bentonite	**29.3**	**29.3**	
3% Bentonite	**31.1**	**31.1**	
4% Bentonite	**23.1**	**23.1**	

1% Kaolin	**52.1**	**52.1**	
2% Kaolin	**29.6**	**29.6**	
3% Kaolin	**20.8**	**20.8**	
4% Kaolin	**28.2**	**28.2**	
1% Halloysite Nanoclay	**33.0**	**33.0**	
2% Halloysite Nanoclay	**23.1**	**23.1**	
3% Halloysite Nanoclay	**22.8**	**22.8**	

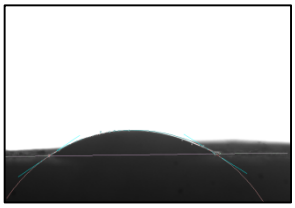
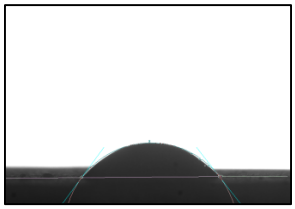
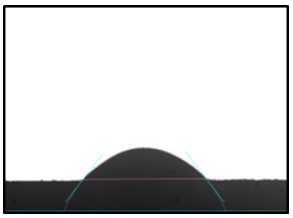
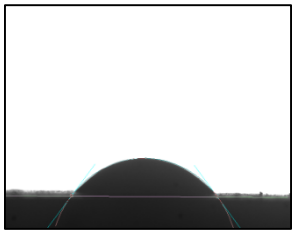
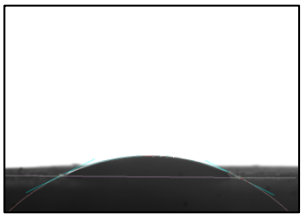
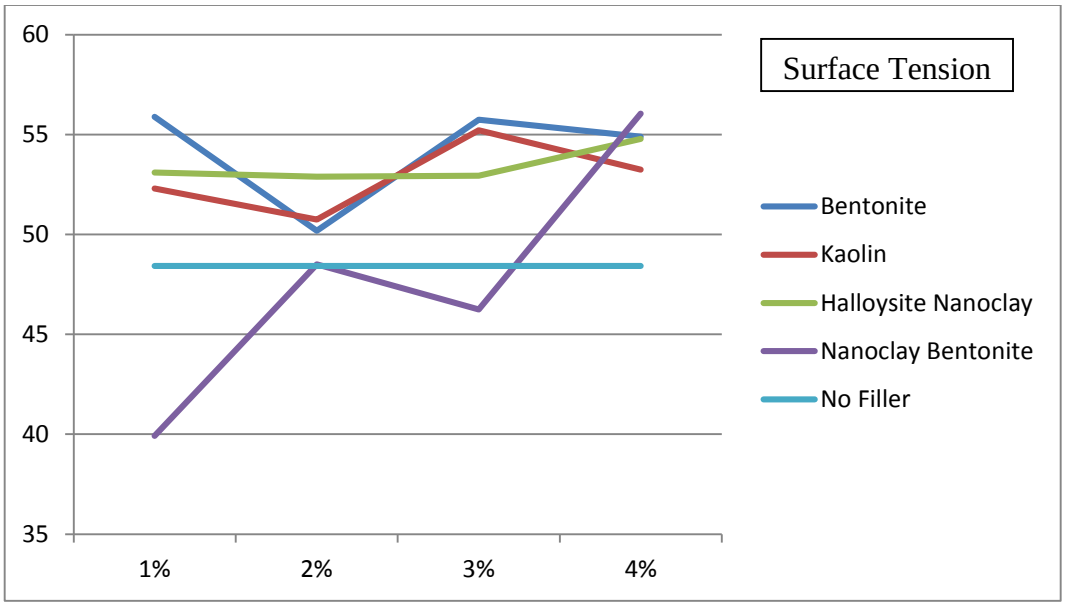
4% Halloysite Nanoclay	**33.0**	**33.0**	
1% Nanoclay Bentonite	**52.0**	**52.0**	
2% Nanoclay Bentonite	**51.0**	**51.0**	
3% Nanoclay Bentonite	**50.1**	**50.1**	
4% Nanoclay Bentonite	**25.6**	**25.6**	

Table 2 Contact angle measurement



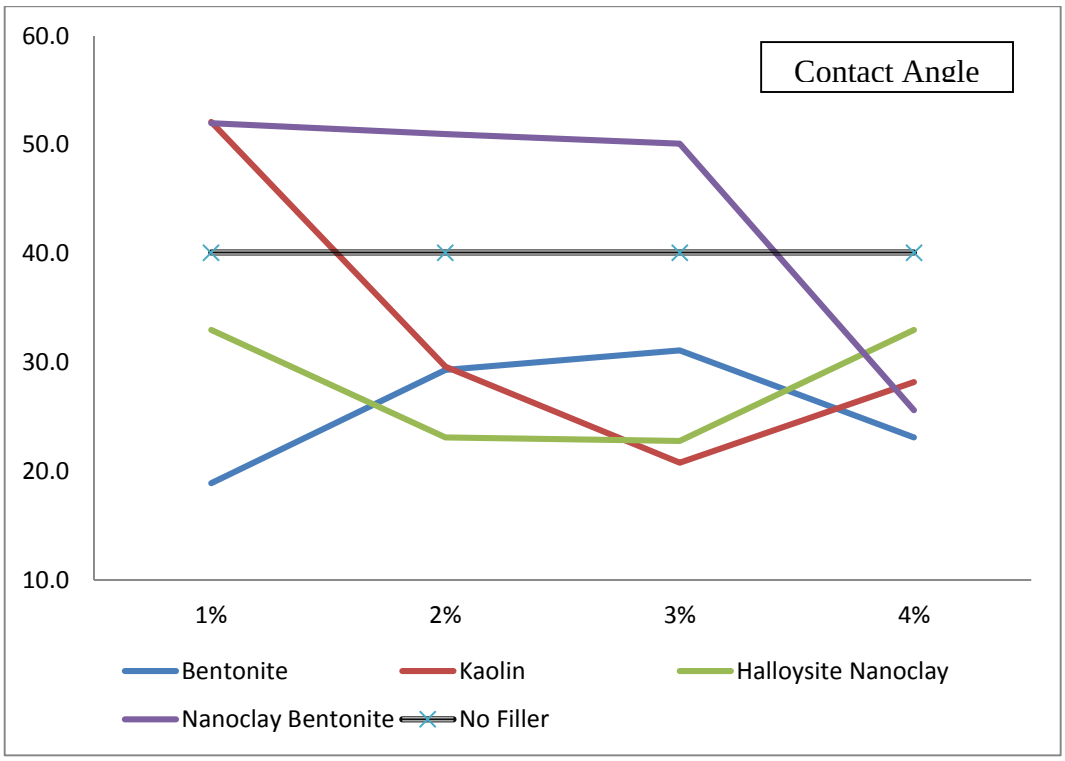


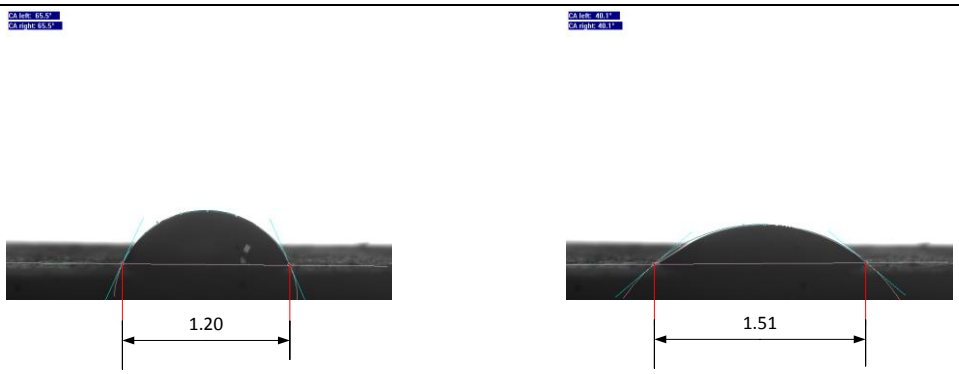
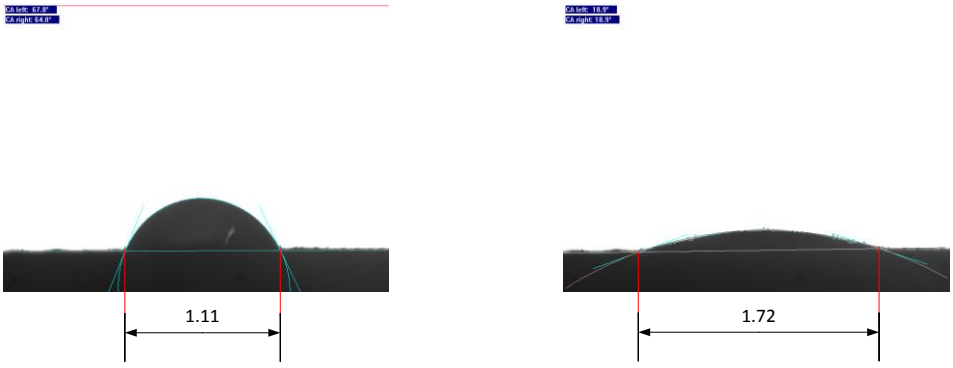
Figure 10: Surface Tension and Contact Angle analysis

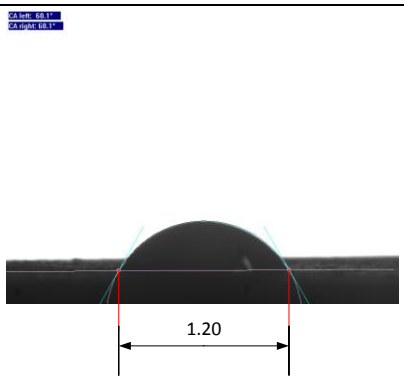
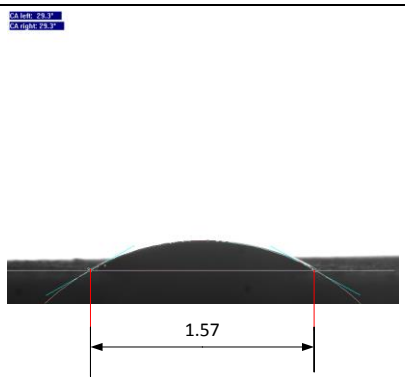
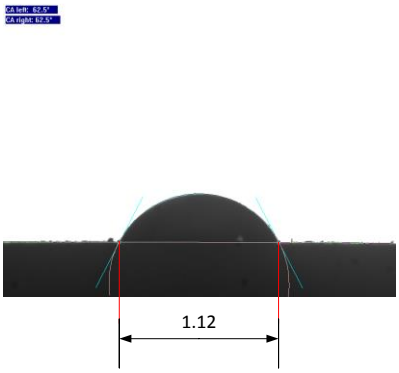
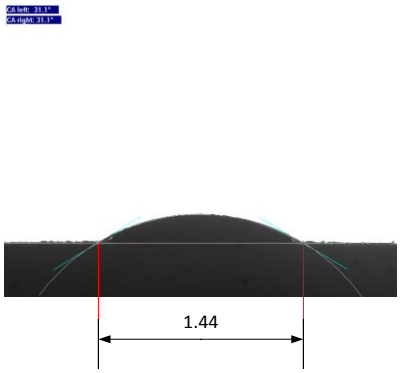
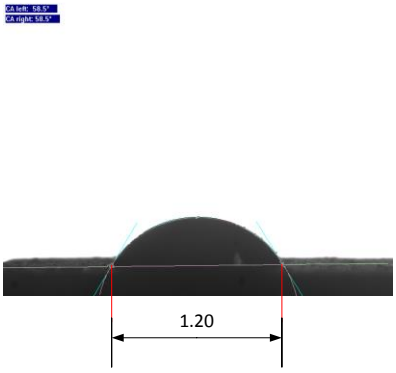
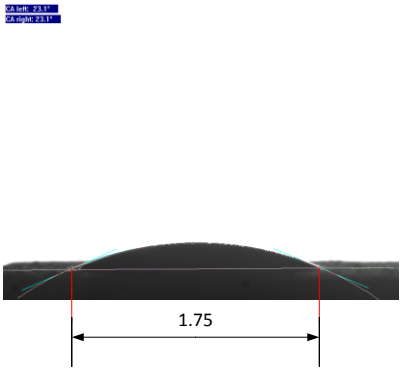
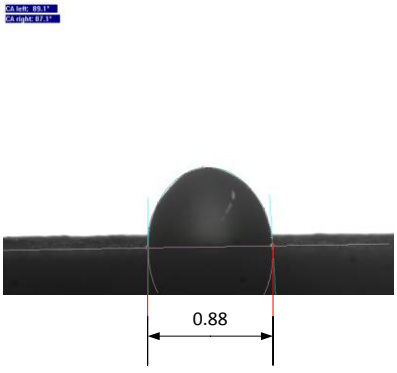
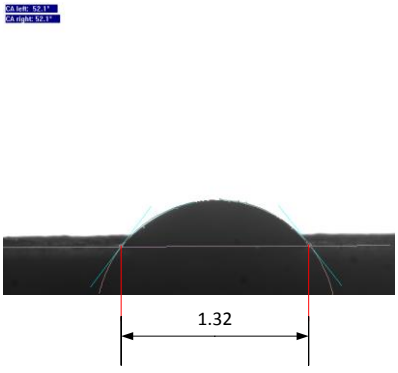
From the Figure 10, we have summarized and conclude the Surface Tension and Contact Angle measurements at each of percentages and type of fillers including without fillers. The low surface tension and less than 90° will indicate for good wettability property. From the surface tension result analysis obtained, the addition of 1% Nanoclay Bentonite filler in coating solution gives the smallest surface tension compared to the other filler. Besides that, only 1% and 3 % of Nanoclay Bentonite give the surface tension below to non-filler coating solution with 39.92 mN/m and 46.25 mN/m respectively. Meanwhile, 1% of bentonite gives the smallest value for contact angle analysis.

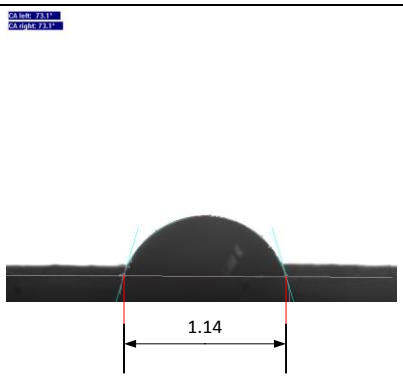
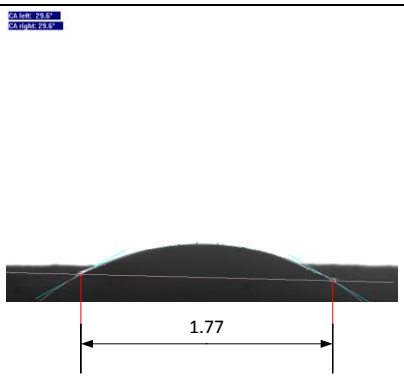
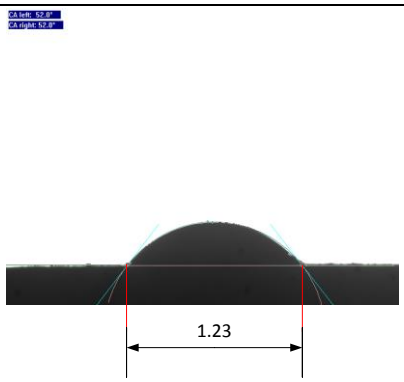
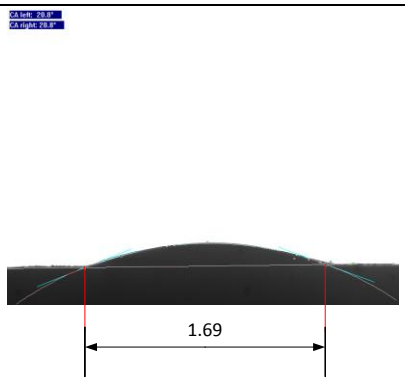
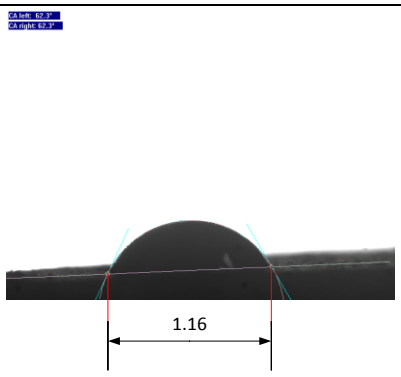
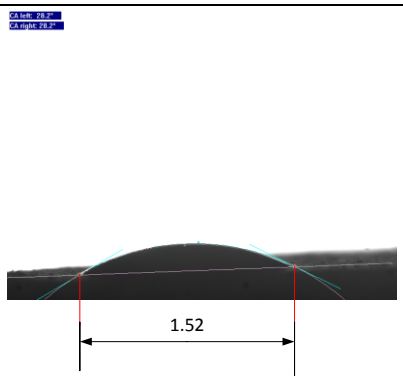
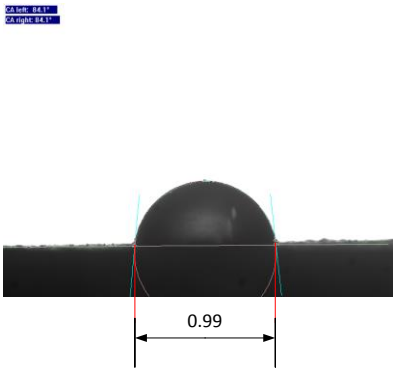
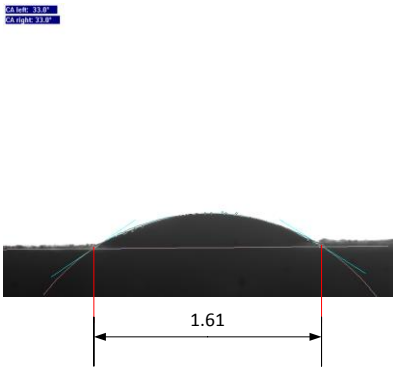
The smallest values of surface tension and contact angle indicated that the intermolecular force in between of biopolymer molecules is being reduced by addition of fillers. The fillers molecules simply polymerize with biopolymer molecule and later increase the distance between biopolymer molecules. As the intermolecular force between the molecules been reduced, then the modified coated solution will be dispersed more and it will have smaller contact angle. Therefore, it has a good wettability property. From the result we also found that the relationship between surface tension and contact angle is not right. Both should have same low value of surface tension and contact angle in order to consider it have a good wettability properties. . As the Young-Dupré stated that, the contact angle can be related to the work of adhesion and interfacial or surface tension. As the value of contact angle become smaller then the surface tension also low. The surface tension given by the software might not correct because of the baseline indication may not precise but the contact angle's result should have accurate values since the contact angle value can be clarify using manually calculated. Therefore, we can consider that 1%, 2%, 3% of Nanoclay Bentonite and 1% of Kaolin is not having good wetting property based on the contact angle analysis. Again, based on contact angle analysis 2%, 3% and 4% of kaolin and other fillers except Nanoclay Bentonite give good indication of contact angle which provide less than non-filler contact angle.

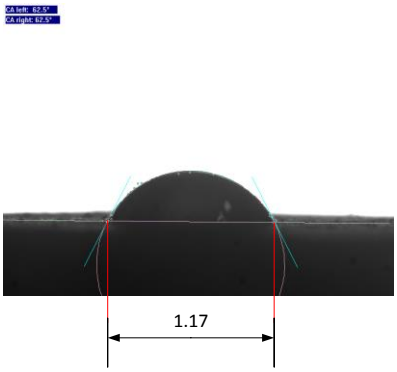
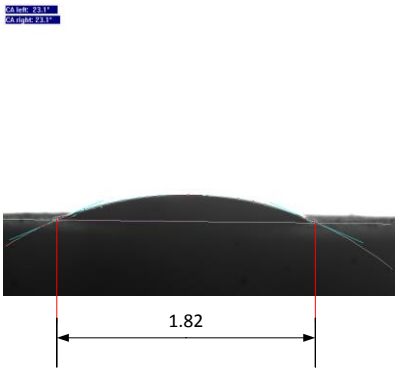
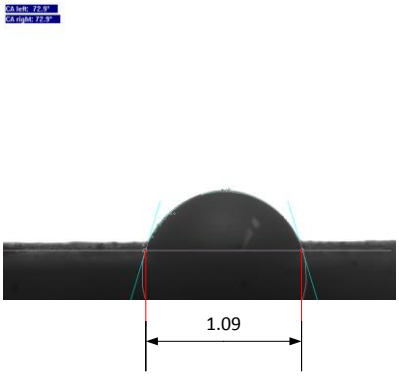
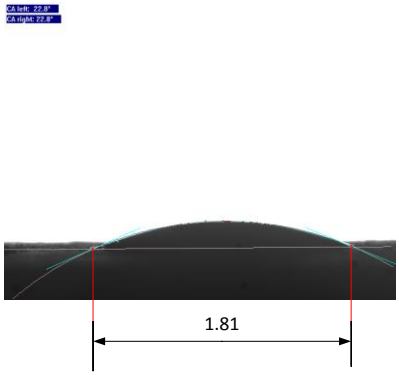
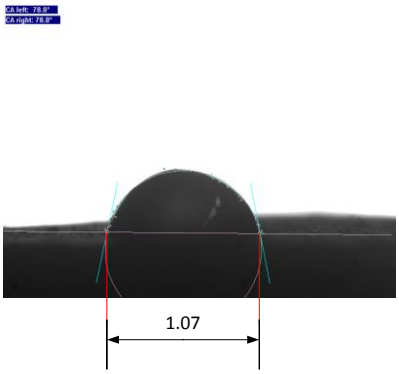
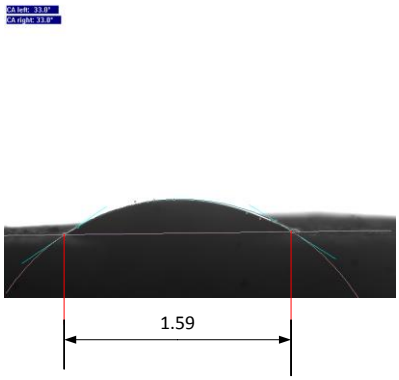
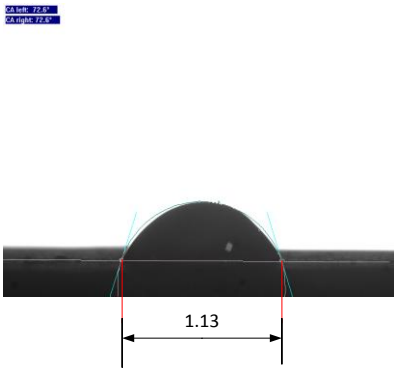
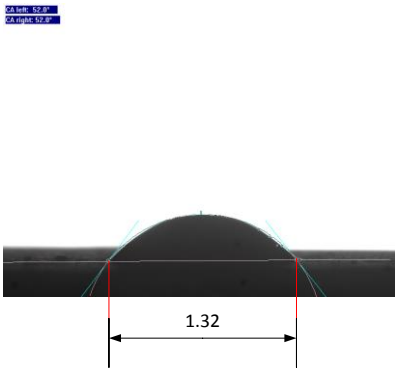
4.2 Spreading Diameter measurement

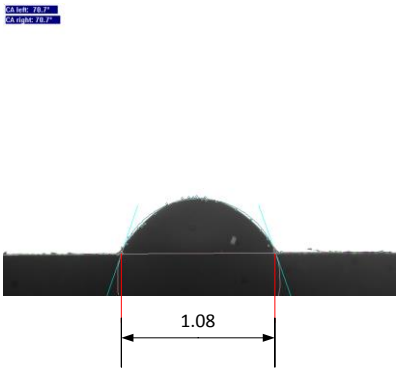
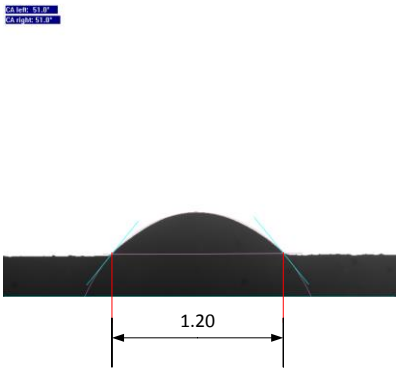
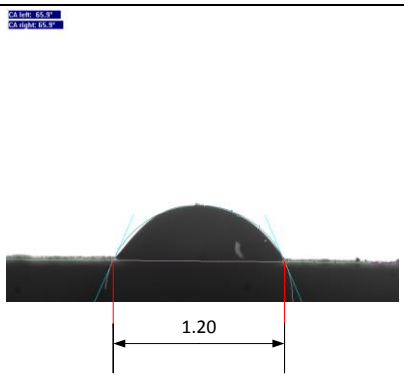
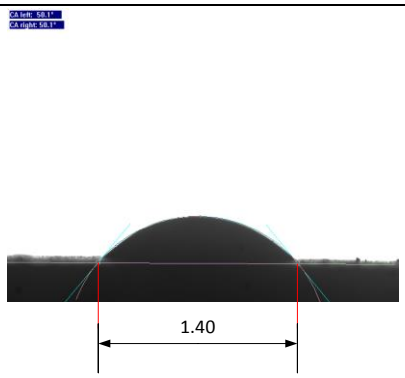
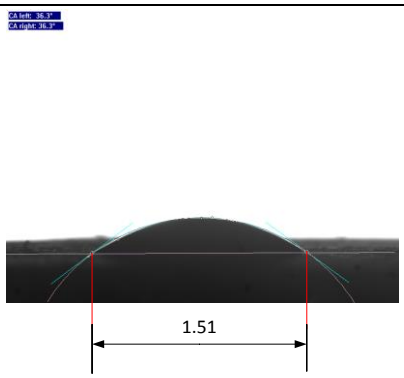
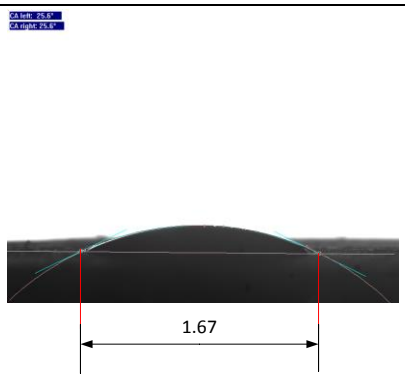
The droplet impact behavior on the solid surface is important in wettability study where the spreading diameter of droplet impact is observed. The sessile drop image at each second is captured and spreading diameter of the image is calculated. The maximum spreading diameter factor is obtained by taking the ration between spreading diameter at certain time, Dt and spreading diameter of the initial droplet, Do (Samsudin et al., 2012). All spreading diameter factor is compared with other different type and percentages of fillers.

Fillers	Image (Do & Dt)	Dmax
0% Filler		1.51/1.20 = 1.26
1% Bentonite		1.72/1.11 = 1.55

2% Bentonite			1.57/1.20 = 1.31
3% Bentonite			1.44/1.12 = 1.29
4% Bentonite			1.75/1.20 = 1.46
1% Kaolin			1.32/0.88 = 1.50

2% Kaolin			1.77/1.14 = 1.55
3% Kaolin			1.69/1.23 = 1.37
4% Kaolin			1.52/1.16 = 1.31
1% Halloysite Nanoclay			1.61/0.99 = 1.63

2% Halloysite Nanoclay			1.82/1.17 = 1.56
3% Halloysite Nanoclay			1.81/1.09 = 1.66
4% Halloysite Nanoclay			1.59/1.07 = 1.49
1% Nanoclay Bentonite			1.32/1.13 = 1.17

2% Nanoclay Bentonite			1.20/1.08 = 1.11
3% Nanoclay Bentonite			1.40/1.20 = 1.17
4% Nanoclay Bentonite			1.67/1.51 = 1.11

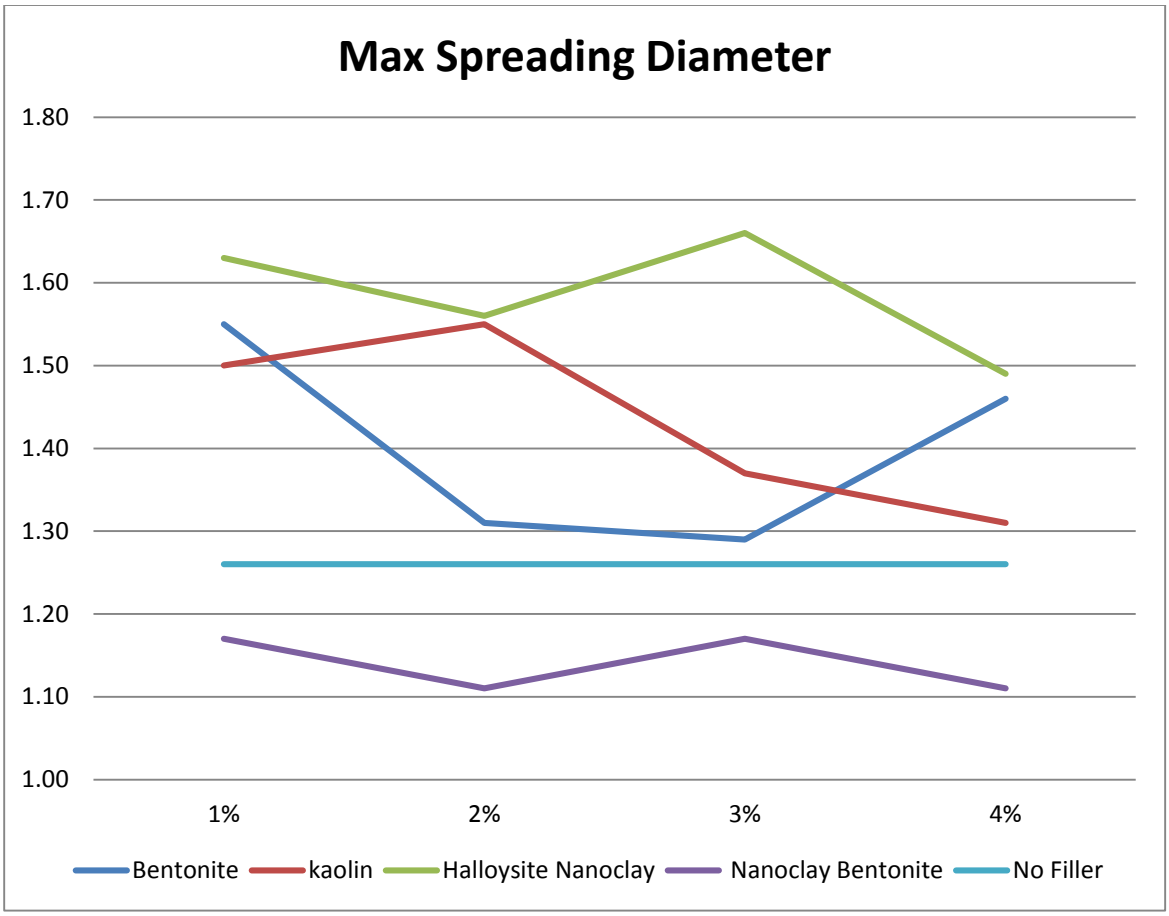


Table 3 The Spreading diameter factor of modified biopolymer solutions

Table 4 shows the comparison of spreading factor between other type of fillers and percentages. Based on the graph, most of percentage of Halloysite Nanoclay fillers gives the highest maximum spreading diameter compared to the other fillers. Addition of Nanoclay Bentonite filler does not give any significant improvement on maximum spreading diameter factor because it was plotted under the non-fillers coating solution. The addition of kaolin as fillers is optimum at 2% and other percentages gives worse spreading diameter factor. A good spreading behavior of modified biopolymer is important in coating process where it will form a thin layer of coating material which later will gives a better coating uniformity of granule urea. Based on the Table 4, 3% of Halloysite Nanoclay gives the optimum spreading diameter factor. The optimum spreading diameter factor can be explained as it shows that 3% of Halloysite Nanoclay is much less viscous and it spreads faster compared other fillers. According T. Mao, Kuhn, and Tran (1997) the maximum spread of droplet upon impact depended strongly

on the liquid viscosity and the liquid contact angle. The more viscous the liquid droplet gives smaller maximum spreading diameter. As mention earlier, the addition of 3% Halloysite Nanoclay able to lower the intermolecular force in between biopolymer molecules. Thus, it makes the biopolymer solution become less viscous and gives droplet of biopolymer solution to disperse more. Lastly, the contact angle analysis show a significant improves on the wettability properties of modified biopolymer after adding fillers except Nanoclay Bentonite. The addition of fillers, Kaolin, Bentonite and Halloysite Nanoclay able to enhance wettability give a good uniformity as coating layer.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Objective relevancy

The application of control release urea (CRU) in agriculture is important as it is able increase efficiency of fertilizer usage besides reducing the environmental side effect. A good control release urea will provide the necessary nutrient to the plant growth accordingly. For example, early stages of plant growth need only a few amount of nutrients from fertilizer and otherwise. If the excessive nutrient is not absorbed by the plant it will later wash out into soil thus it will waste the nutrients. Therefore, it is crucial to control the release and give a steady supply of nutrient to the plant. In controlled release urea, the urea must be coated to ensure the coated layer can provide slow release of nutrient from nutrient. Therefore, the coating layer thickness and uniformity must be good and smooth in order to allow the nutrient equally distributed.

This study is relevant to its objective, which is to formulate a new coating material composition with addition of fillers and study the wettability effect of on that modified coated biopolymer addition of fillers. This wettability study also included spreading behavior of modified coated biopolymer addition of fillers on the urea surface. The characterization of modified biopolymer addition with filler is done using Optical Contact Angle (OCA) machine. The image data is observed and analyzed by using SCA20. The analysis and data obtained had identified the wettability property of surface tension, contact angle and also spreading diameter factor at each type of filler addition. From the result, it is clearly proved that the addition of fillers into the modified biopolymer able to improve wettability properties except for Nanoclay Bentonite filler. From the contact angle measurement it shown that Bentonite, Kaolin and Halloysite Nanoclay give a good low contact angle, but the most optimum are 1% bentonite and 3% kaolin. Spreading diameter graph it shown that 3% of Halloysite Nanoclay give a highest spreading diameter compared to others. The surface tension measurement need more clarification in future. From both characterizations Halloysite Nanoclay give the best spreading diameter, 1.66 and good low contact, 22.8 °.

Therefore, Halloysite Nanoclay is potential to give the better coating uniformity that later will able give a good steady release for controlled release urea method. Therefore, it can be concluded that the expected result and the objective of this researches is achieved.

5.2 Suggested future work for expansion and continuation

For the future work, some recommendation needs to be considered as it will improve the result. Firstly, the results of the characterization have to repeat several times for more consistent values. The image data from the Optical Contact Angle (OCA) need to take more as the values of calibration do not consistent especially contact angle and surface tension calculation. The proper determination of baseline for surface tension and contact angle will improvise the vales of result. In analyzing data from SCA20, several parameter need to be define correctly and kept constant such as surrounding temperature, density, dosing rate, size of needle and position of calibration.

Next, for preparing the modified biopolymer the weighing of material such as starch, citric acid, polyvinyl alcohol and other fillers need precise by using more accurate weigh machine especially when the weigh involves smaller scales. The suitable size for magnetic mixer and rate for mixing need be constant to ensure the mixing is evenly distributed and mixed well. Instead of using bottom round neck flask as medium for mixing the beaker also provide better for mixing as it will directly contact with hot plate device. Besides that, heating will distribute more evenly when beaker is put directly on hot plate. Other than that, the range of fillers percentages should be increased more to study the effect of high percentage of filler on the wettability properties.

This project research can be expand and continue in the future in order to find the best fillers which gives better wettability properties of modified biopolymer solution. The best wettability properties of biopolymer addition of fillers can be used in application of urea coating for controlled release urea. Besides, future research should discover more alternative or material like fillers which could give same function and more economically feasible.

CHAPTER 6

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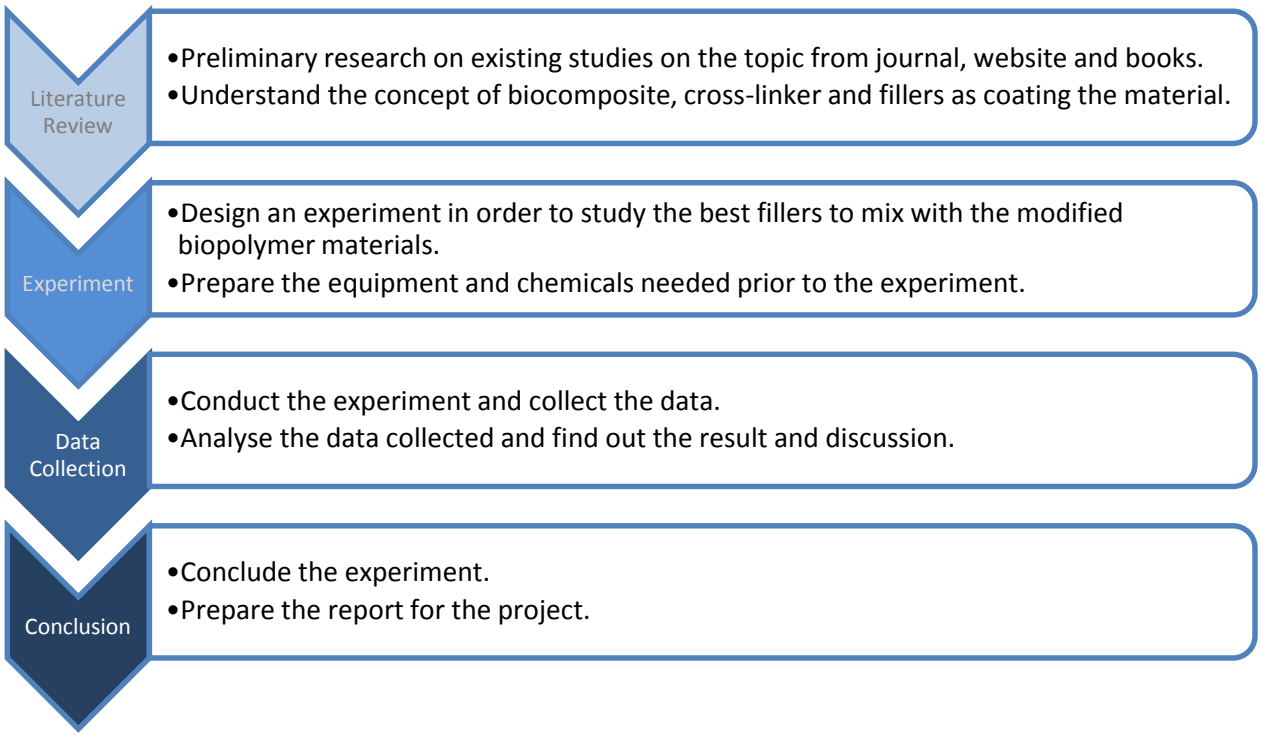
CHAPTER 7

APPENDIXES

7.1 Project Flow Chart



7.2 Gantt Chart and Key Milestone

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■								
2	Submission of Progress Report							■								
3	Project Work Continues							■	■	■	■	■	■			
4	Pre-SEDEX										■					
5	Submission of Draft Final Report											■				
6	Submission of Dissertation (Soft bound)												■			
7	Submission of Technical Paper												■	■		
	Viva														●	
	Submission of Project Dissertation (Hard bound)															●

■	Progress
●	Suggested Milestone

7.3 Experimental Table Matrix

No.	Starch	Citric Acid	PVA	Kaolin (%)	Bentonite (%)	Halloysite nanoclay (%)	Nanoclay Bentonite (%)
1	3	2	1	1	0	0	0
2	3	2	1	2	0	0	0
3	3	2	1	3	0	0	0
4	3	2	1	4	0	0	0
5	3	2	1	0	1	0	0
6	3	2	1	0	2	0	0
7	3	2	1	0	3	0	0
8	3	2	1	0	4	0	0
9	3	2	1	0	0	1	0
10	3	2	1	0	0	2	0
11	3	2	1	0	0	3	0
12	3	2	1	0	0	4	0
13	3	2	1	0	0	0	1
14	3	2	1	0	0	0	2
15	3	2	1	0	0	0	3
16	3	2	1	0	0	0	4