EFFECT OF NANOFILLERS ON THE SPREADING BEHAVIOUR OF BIOPOLYMER BLENDS ON UREA SURFACE

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by

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Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NURUL IZZATY FAIZZEN BINTI ZULKEFELY

ABSTRACT

Recently, the controlled release technology has been developed through coating process which helps in increasing the efficiency of fertilizer besides reducing the fertilizer's losses and minimizing environmental pollution. This paper presented new approach where a new modified biopolymer filled with nanoclay is developed and used as the coating material for the slow- or controlled-release fertilizer. The use of nanofiller is predicted to give a better spreading behavior which ensures the uniformity of coating process. Uniformity of urea coating is crucial as it will provide a steady and constant release of nutrients. Better wettability properties of a biopolymer droplet promotes formation of thin-film on urea surface and thus certifies the uniformity in coating process. Various sample consist of seven different blending ratio of modified biopolymer are prepared and evaluated for wettability properties. The wettability properties measured in this research project includes surface tension, contact angle and the maximum spreading diameter. Surface tensiometer or OCA 20 device is used to capture every single images of this droplet impact behavior. From experimental procedure, the spreading behavior of modified biopolymer on urea surface after addition of nanoclay filler is analyzed. The addition of 2% of nanoclay filler into 50/15/2.5/7.5 blending ratio had reduced the surface tension and contact angle of the droplet impact which provides the better wettability properties and spreading behaviour compared to the 50/15/2.5/7.5 blending ratio without addition of nanoclay filler. Therefore, it is proven that small amount of nanoclay filler added into the modified biopolymer solution had enhanced the spreading behavior of the droplet impact on the urea surface.

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ABBREVIATIONS AND NOMENCLATURES

CRU – Controlled-release urea

SCA 20 – Optical Contact Angle software

OCA 20 – Optical Contact Angle measurement device

CCD – Charged-coupled device

N_2O – Nitrous oxide

PNC – Polymer nanocomposites

BC – Before century

PU – Polyurethane

PCL – Polycaprolectone

MMT – Montmorillonite

SEM – Scanning electron microscopy

TEM – Transmission electron microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The relevant use of fertilizer nutrient is very crucial in achieving the high demand of production from agriculture sector. However, about more than half percent nitrogen of normal fertilizer are released to the soil and vaporized to the environment. Therefore, the applied fertilizer may not afford to supply the nutrient during the plant growth which will result in low plant yield. The frequent application of fertilizer is required in order to maintain the nutrient supply for the plant. Consequently, there will be the excess use of fertilizer which may lead to water contamination as the fertilizer is being absorbed by the soil and reach the ground or surface water. Besides, the denitrification process also occurs where the fertilizer nutrient is loss to the atmosphere as the nitrogen gas.

Nowadays, many researchers had been investigating and developing the new technology with prior to optimize the absorption of nutrient and minimize the environmental impact. Therefore, the slow- or controlled-release fertilizers are invented in order to increase the utilization of fertilizer's nutrient and increase the crop yield. The optimization of fertilizer nutrients will incredibly reduce the financial loses as well as the environmental risk sourced from agriculture sector. The controlled-release fertilizers are prepared using thin-film coatings technology. Coating ensures the release of fertilizer nutrient is controlled by diffusion.

Several aspects need to be considered in performing the coating process for example the compatibility of the coating material with the substrate, the environmental aspect and also the economics aspect of preparing the coating material. In this research, the

biopolymer blends is proposed as coating material on urea surface prior to its biodegradable property and may not cause any environmental impact.

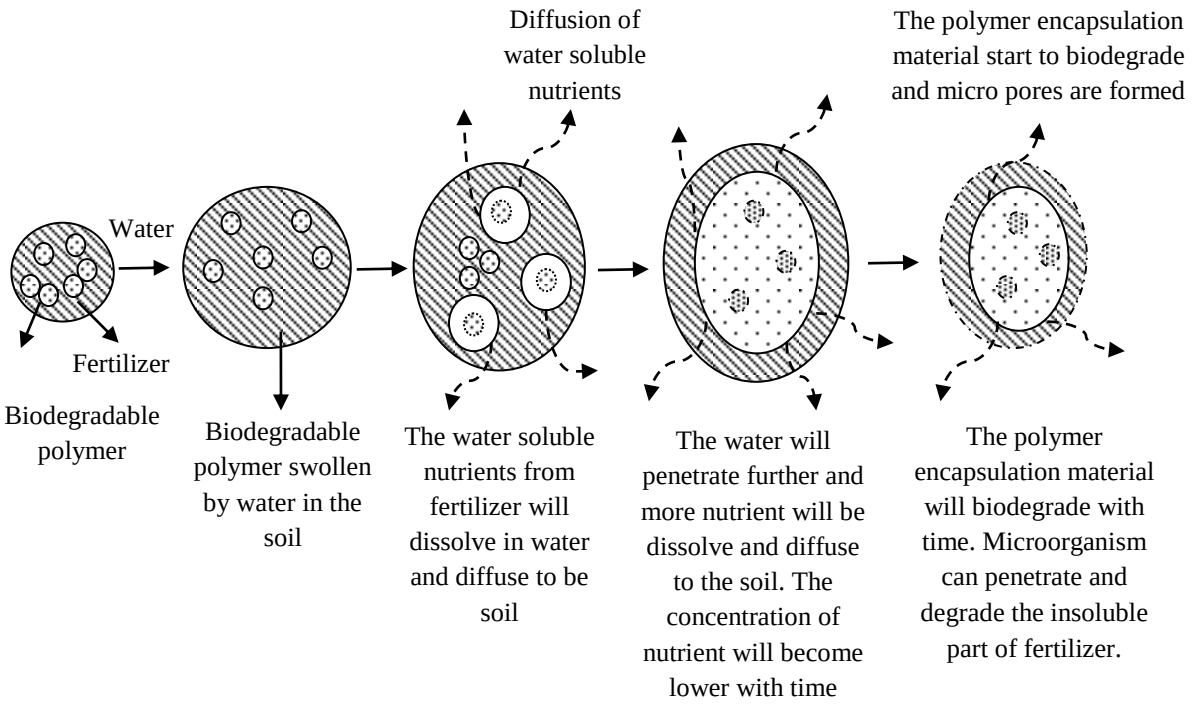


Figure 1 Mechanism of controlled release fertilizer (Munusamy et al, 2012)

Furthermore, the advanced technology nowadays promotes the development of nanocomposites in polymer in order to produce products with enhanced properties. Reinforcement by even small quantities of filler in the matrix can incredibly improved certain properties of polymer. Likewise this project research, the addition of nanoclay in the biopolymer will significantly improved the properties of biopolymer blends on the urea surface.

1.2 Problem Statement

Urea is common and widely use fertilizer as it has high nitrogen content of 46% (Ni, Liu, Lü, 2009). Furthermore, nitrogen is the most essential nutrient for the plant growth. However, urea property which is highly soluble in water results in more resource losses and less utilization by the crops. For example the demand of nutrient at the early stage of the plant growth is less compared to the plant growing season. Therefore, not all nutrients are being utilized by the crops at early stage of plant growth and most of them being released to the environment. Consequently, the deficiency of nutrient at the end of growing season occurs. Furthermore, the deficiency of nutrients during the growing season may leads to low plant yield and vast economical losses. Thus, in order to provide a steady and continuous supply of nutrients throughout the plant growth without having the excess hazardous release of nitrogen, the release of nitrogen from urea need to be controlled.

Besides, the release of nitrogen to the environment need to be controlled as the excessive nitrogen gas or nitrous oxide level in atmosphere leads to the global warming. According to 'Is Fertilizer To Blame for Global Warming' online article, climate scientist had assumed nitrogen-based fertilizer is the cause for the rising nitrous oxide level in the atmosphere as this such fertilizer promote microbes in the ground to convert nitrogen into nitrous oxide at faster rate. Therefore, in order to reduce the application of normal fertilizer while maintaining the steady supply of nutrient, the nutrient release must be controlled. According to the problem statement mentioned earlier, it shows that the development of slow- or controlled release urea (CRU) is significant prior to optimize the absorption of nutrient by the plant throughout the plant growth besides controlling the loss of nutrient into the soil or the environment.

In the process of developing the controlled-release urea, the thin-film coating technology has been used where the material form a thin layer on surface in order to modify and improved the surface properties. In order to form a thin layer coating, the coating materials need to have the desired properties of material. In this project, modified biopolymer is used as the coating material. The coating material properties are important in thin-film coating process as it will define the uniformity of spreading occur. In this

case, the uniform spreading of modified biopolymer will result in thin layer coating on the urea surface. Moreover, the spreading uniformity of modified biopolymer on urea surface consequently leads to the uniformity of diffusion or spreading of the nutrients from urea to the soil. From the study and earlier research, the coating material blended with fillers produced better physical properties. Therefore, new modified biopolymer with the addition of nanofiller is developed and the characterization is investigated in this project. The parameters used to identify the characterization of coating material include surface tension, contact angle and maximum contact angle.

1.3 Objectives

There are two objectives of this project research. The primary objective of this research is to study the effect of nanoclay filler on the spreading behavior of modified biopolymer on urea surface. As mentioned in the problem statement, the addition of nanoclay filler is aimed to modify and improve the modified biopolymer physical properties. The secondary objective is to investigate the spreading behaviour of modified biopolymer based on surface tension, contact angle and maximum spreading diameter. The combination of modified biopolymer with nanoclay filler is expected to have better physical properties which are required for coating process.

1.4 Scope of Study

In this project research, the author will focus on:

- Type and percentage of nanofiller used
- Preparation of modified biopolymer filled with nanoclay
- Preparation of urea substrate surface
- Set up and operate the surface tensiometer device and SCA20 software
- Analyzing the spreading behaviour of modified biopolymer on urea surface

1.5 Relevancy of project

This project research is executed to investigate the spreading behavior of modified biopolymer with addition of nanoclay filler on the urea surface. The main objective is to discover the effect of nanoclay on the spreading behavior of biopolymer blend. The spreading behavior is crucial in coating process as well as in the process of controlled release urea (CRU) production. Good spreading behavior will promotes to thin film formation on the urea substrate which helps to obtain the uniformity of coating during the coating process. Therefore, this project research is relevant to today's technology and knowledge.

From the previous research on nanofiller, the material's properties can be outstandingly improved with the addition of small amount of filler. The addition of nanoclay filler in the modified biopolymer is expected to produce a better spreading behavior compared to the presence modified biopolymer. As the uniformity of coating is achieved and the granular structure of urea produced is smooth, the release of nutrient from urea would be steady. Thus, the controlled release urea has more potential to be commercialized. As the controlled-release urea is commercialized, it could provides a prolong supply of nutrients. Therefore, the usage or frequency of applying the nutrients to the plant is reduced as well as the economics.

Besides, the environmental impact such as greenhouse effect and global warming that is caused by nitrous oxide could also be reduced with the less application of urea. Furthermore, it has been proven that the use of controlled release fertilizer could increase the yield of crops due to steady supply of nutrient throughout plant growing season.

In conclusion, based on the detailed justification above, this project research is relevant to be implemented for sustaining the environment as well as human betterment besides widened up the scope of knowledge on nanofiller.

1.6 Feasibility of project within scope and time frame

The feasibility study is necessary for various kinds of project. For this project research, the feasibility study highlight on scope and time frame. The project research is said to be feasible due to some reasons which are as follows:

1.6.1 Time frame

The project research can be accomplished within the time frame. The author is given 14 weeks to do the literary research, identify the problem, study and affirm the theory, detailed the methodology and collect all the information related to the project title. The final report is documented at the end of week 14. The period given is sufficient for the author to complete the project as many information could be screened out and gathered from the previous research that are related to the topic. Furthermore, another 14 weeks is provided for the author to carry out the experimental work. The matter raised is the author has to queue for surface tensiometer device which is used for the characterization of modified biopolymer. The interval between modified biopolymer preparation and characterization process need to be synchronized as it should be constant for every sample. Therefore, detailed plan should be performed so that the experimental work and the characterization process can be done without any delay. The experimental works and data analysis only takes approximately 10 weeks to be accomplished. Another four weeks are allocated for writing and compiling the report.

1.6.2 Scope

There are five scopes of study that are stated earlier. Among these scopes, the most critical part is to be familiarized with the surface tensiometer device. The author also needs to learn how to set up and operate the device before the characterization process is performed. The person in charge of the instrument will give the instruction and guidance for the better understanding. Besides, the author has to be trained how to use the Optical Contact Angle software (SCA20) in order to analyzed the surface tension and contact angle obtained from the characterization process. Analyzing the data from the device would not take much time if the author had conquered the software and instrument procedures.

CHAPTER 2

LITERATURE REVIEW

2.1 Why controlled release of urea?

More than 90% of world production of urea is used as the nitrogen-release fertilizer as urea has the highest nitrogen content (Leverich, 2010). As the property of urea is highly soluble in water, the nutrients are easily can escaped to the environment. Although urea has the highest nitrogen content, not all nutrients are being absorbed by the plant due to vaporization, surface runoff and leaching (Chen et al., 2008). KuShaari(2011) clarified that the application of commercial granular soluble fertilizer will cause the hazardous excess release of nitrogen at the beginning of plant growth and deficiency of nutrients at the end of growing season. Thus, the controlled-release urea is developed to provide a steady release of nutrients with optimal urea availability throughout the growing season. Besides, the use of controlled-release urea (CRU) not only reduces the loss of nutrients from the urea but also could increase the crops yield. It has been proven by Kiran et al., rice yields produced from the plant treated with CRU is greater and performs significantly compared to granular urea.

About 40-70% of nitrogen in normal fertilizers vaporized to the environment which not only can give high impact on economic and resource losses but also environmental pollution (Dave, Mehta, Aminabhavi, Kulkarni, & Soppimath, 1999; Guo, Liu, Zhan, & Wu, 2005; Liu Liang, Zhan, Liu, & Niu, 2007). The granular urea is easily vaporized and it is incapable to sustain the nutrient supply throughout the plant growth. Therefore, frequent application of urea is required to maintain the plant growth. In contrast, the application of urea will be reduced by using CRU as it provides prolong nutrient supply. The reduced use of urea will accordingly reduced the environmental impact as the increase of nitrous oxide levels in the atmosphere is due to nitrogen-based fertilizer *("Is*

fertilizer to blame for global warming?", 2012). The release of nitrous oxide from agriculture sector may lead to the environmental impact such as greenhouse effect and also global warming. According to the Figure 2.1, agriculture soil management are said to be the largest source of N_2O emission in the United States which covered for about 68% from the total U.S N_2O emission (*Greenhouse gas emission*, 2012).

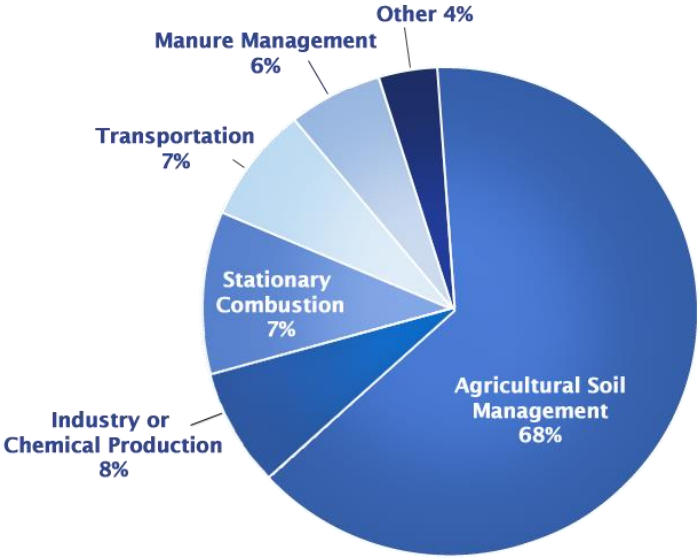


Figure 2 U.S Nitrous Oxide Emission, by source (Inventory of U.S. Greenhouse Gas Emissions and Sinks, 2012)

2.2 Thin-film coatings technology

In the process of producing the controlled release urea, a thin film coatings technology is used where the coating material formed a thin layer ranging from nanometers to several micrometers in thickness (Chen et al., 2008). There are several techniques in performing the thin-film coatings. Suherman and Angogoro (2011) argued that many researchers has been studied the coating process of urea using different techniques; fluidized bed, spouted bed, rotating drum, with various coating materials; resin, sulphur, polymers.

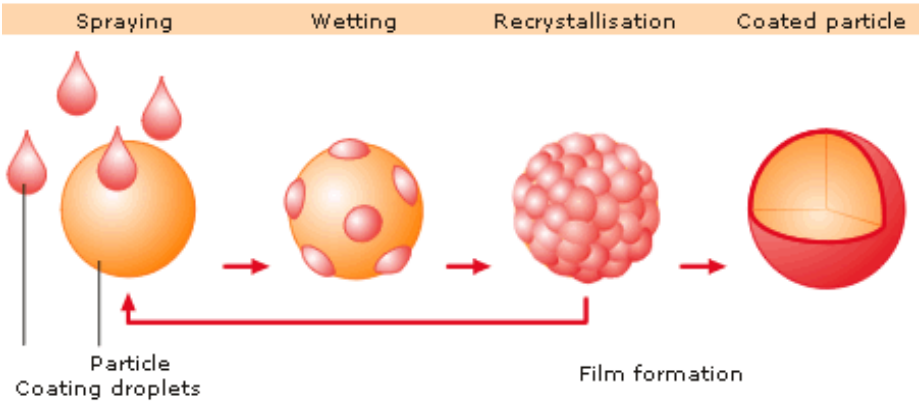


Figure 3 Fluid Bed Coating mechanism (Glatt Process Technology, 1989)

Turton, Tardos, and Ennis (1998) affirmed that during the coating process, the liquid is sprayed and mixed with the solid bed material. As the coating droplets in contact with the surface of the particles, the droplets of liquid will spread over and partially coat the solid particle. The repeated movement of particles through the spray zone will continuously coat all over the solid material which resulting in smooth and uniform coating. Therefore, the wetting of coating material on solid particle is significant to acquire uniform coating. However, if the drops do not wet the surface and blob up, it will result in unsmooth surface of solid particles and irregularities of crystal.

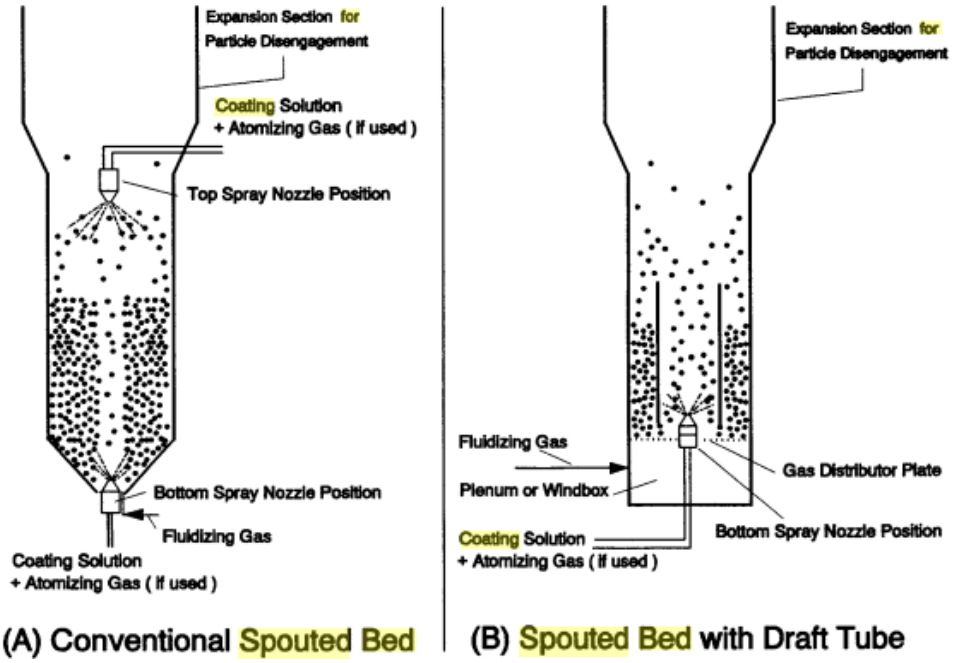


Figure 4 Spouted and fluidized bed used in coating operations (Turton et al., 1998)

As mentioned earlier, the wetting of coating material and solid particles are crucial in obtaining good spreading behavior and achieving the uniform coating. The wettability properties of material can be identified by its surface tension and contact angle. Weiss and Meisen (1983) have coated the urea with the molten sulphur to improve the wetting properties. Commonly, surfactant is used to improve the spreading and wetting of liquid on solid surface. However, in this project, nanoclay is used as the nanofiller that are believed could enhance the spreading behavior of polymer. Hence, this project research aimed to investigate the spreading behavior of modified biopolymer after the addition of nanoclay filler by examining the wettability properties of various components of modified biopolymer.

2.3 Background of Nanofillers

Recently, new technology has been developed where the modified biopolymer is used as the coating material on urea surface. Biopolymer is preferable as it is biodegradable and will not cause any environmental impact. Although the modified biopolymer is a suitable material, the compatibility between biopolymer and urea phase need to be consider as it will defined the final mechanical properties of the controlled-release urea.

Nowadays, many researchers has been terrifically focusing on the research and development in polymer nanocomposites(PNC). As an introduction, polymer nanocomposites are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small amount of nanofillers in the polymer matrix (Hedge, 2009). The properties of materials can drastically being improved or adjusted by introducing nanofillers to the composite materials.

2.4 History of nanoclay filler

The polymer-clay nanocomposites were first discovered early 1950. Recently, the interest from industry on polymer-clay nanocomposites increased due to the outstanding improvement of material properties at very low clay loading (Sapkota, 2011). The consumption of clay nanocomposites was almost achieved one-quarter in 2005 of other nanocomposites consumed as nanoclays nowadays is being used to modify the polymeric material for various applications (Uddin, 2008). Although polymer-clay

nanocomposites is newly developed, the science of clay has been existed since prehistoric. Clay, formerly known as kaoline was early found at China 3rd century BC. Uddin (2008) also stated that the special behavior of clay is its ability to swell and mold in water and remain the shape of container when dry.

To fulfill the demand of modern technology, the size of filler should be reduced to nanometer scale. The superb composite material will have incredible mechanical and physical properties for example increased in mechanical strength, enhanced in thermal stability, superior hardness and higher electric resistivity (Sreedhar, Chattopadhyay, and Swapna, 2005). Many researchers have been investigated the effect of polymer-clay nanocomposite on the physical properties of a material. Ma et al. combined an akyl ammonium modified Na-montmorillonite into the polyol and the elastomeric polyurethane-urea (PU)/clay nanocomposite discover that at 8% clay loading, tensile strength and elongation at break of PU/Clay nanocomposite increased by two and five times than the pure PU (Ma, Zhang, & Qi, 2001). Yao et al. have investigated that thermal conductivity will decrease with the increasing layered clay loading to a PU matrix. Chen et al. studied the mechanical properties when polycaprolactone (PCL)/clay nanocomposite added to PU and discovered that the crystallinity and tensile mechanical properties is strongly affected by the amount of PCL/clay.

2.5 Why choose nanoclay?

On the basis of the above background, this research proposed a new approach for developing new type of biopolymer, enhanced by nanoclay filler. Marquis et al. argued that clay-based nanocomposites provide an overall improvement in physical performances. Besides, clay-based fillers are the most widely used due to its natural abundance and easy availability. Nanoclay filled polymer matrices give great impact in mechanical and physical properties improvement even consuming in small amount of fillers (<10%). According to Ferreira et.al, the key to successful reinforcement with nanoclays is to ensure their completely dispersion and exfoliate.

Among many type of nanoclays, montmorillonite (MMT) is widely used as reinforcement because it is abundance, environmental friendly and relatively low cost.

Besides, MMT clay has potential to exfoliate in the polymer matrix and its structure exhibits the required stiffness, strength, and dimensional stability. Ferreira et.al studied that the most significant improvements in properties is reached when the filler forms a three-dimensional network, which obtained when the content of nanoclay particles reaches the threshold value at which they interact and cannot rotate freely. N.R. Savvas et al has claimed that the addition of clay slightly reduced the viscoelasticity due to distruption of chain entanglement by high aspect ratio of clay platelets and also eliminates the surface melt fracture, and postpones. X. Zhang et al studied at the same draw ratio, fiber with clay had higher crystallinity, lower orientation, improved moisture absorption and dye affinity.

2.6 Determining the spreading behavior of modified biopolymer blends

In this research orientation, the spreading behavior of biopolymer blends on urea surface is the main focus. It is aimed to identify the droplet impact behavior of biopolymer filled with nanoclay on porous surface of urea. Surface tension is one of the parameter can be used to explain the spreading behavior of liquid droplet. Surface tension of liquid droplet depend on the forces of attraction between particles of that liquid and also the gas, liquid or solid in contact with it. Besides, the surface tension can be measured as the energy required to increase the surface area of liquid by unit area. The lower surface tension, the more tendency of liquid droplet to have better spreading. The spreading of liquid droplet on solid substrate can be determined by measuring the contact angle. Contact angle is the angle formed by a liquid at the three phase boundary where a liquid, solid, and gas intersect as shown in the Figure 5.

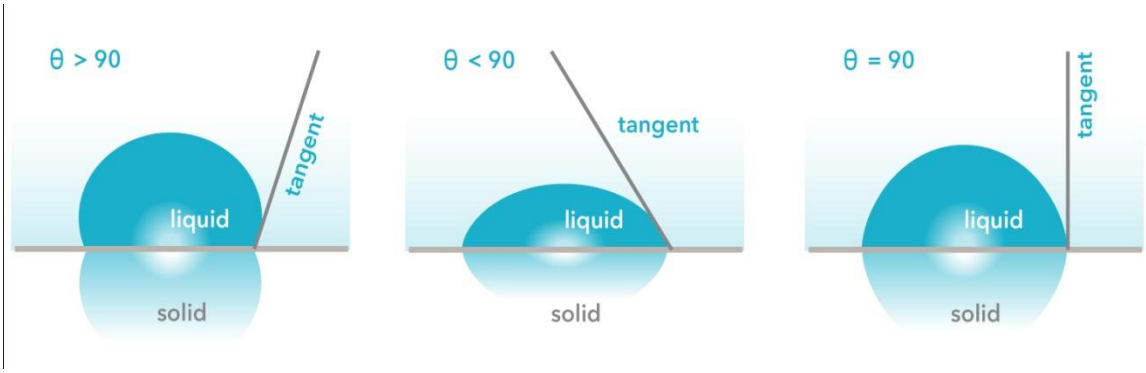


Figure 5 The angle formed by a liquid at three phase boundary where liquid, solid, gas intersect (Attension Tensiometers, 2009)

Wetting is defined when a liquid drop spreads on a solid substrate until it reach equilibrium in shape (Samsudin et al, 2012). Contact angle represents the wettability of droplet on urea substrate. Low values of contact angle indicate liquid spreads, or wets well while high contact angle indicates poor wetting. If angle less than 90 degrees wetting occurs whereas if angle is greater than 90 degrees it is said to be non-wetting. Besides, the contact angle also identifies the strength of solid/liquid and liquid/liquid interactions as shown in the Table 1.

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

Contact angle	Degree of wetting	Strength of:	
		Solid/liquid interactions	Liquid/liquid interactions
$\theta = 0$	Perfect wetting	strong	weak
$0 < \theta < 90°$	high wettability	strong	strong
		weak	weak
$90° \leq \theta < 180°$	low wettability	weak	strong
$\theta = 180°$	perfectly non-wetting	weak	strong

Zisman et al.(1999) stated that 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 under the action of three interfacial tensions (Figure 6) defines the contact angle of liquid drop on solid surface. The equilibrium contact angle can be determined from Young's equation:

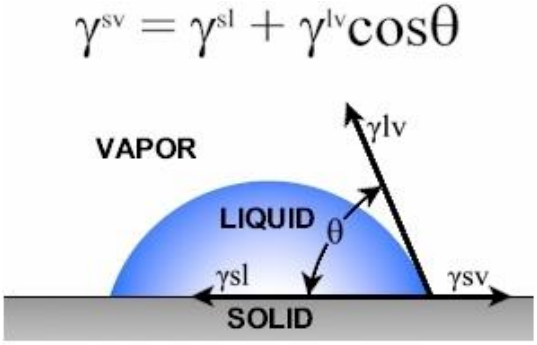


Figure 6 Illustration of contact angle and Young's equation (Rame-hart, 2012)

Figure 6 represents the γ_{sv}, γ_{sl} and γ_{lv} as solid-vapor, solid-liquid, and liquid-vapor interfacial tension respectively, θ is the contact angle. There are four direct contact angle measurement techniques which are a) sessile drop, b) captive bubble, c) sessile bubble, d) tilting plate (Myers, 1946). The most commonly used method for contact angle measurement 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 the depositing of liquid drop on solid surface occur (Njoubuenwu et al., 2007). Other properties of modified biopolymer that can be determined using the sessile drop method include wettability, absorption and surface free energy.

The measurement of single contact angle is insufficient to characterize the interaction. There could be a range of contact angles which may be discovered for any given solid/liquid interaction. When the drop expanded, the angle is said to have 'advanced' contact angle whereas the 'receded' contact angle occur is when the drop has contracted the angle. For a given system, it will be found that $\theta_A \geq \theta \geq \theta_R$ (Myers, 1946). D. Myers also stated that in the dynamic systems, the values of θ_A and θ_R depends on the velocity of wetting line movement, with increasing θ_A and θ_R decreasing. If the three phase boundary is in actual motion the angle produced are called dynamic contact angle. Alteraifi et al. (2003) argued that the rate change of contact angle is the parameter that generally used to determine the spreading kinetics of liquid drop on solid surface.

During the second stage of droplet behavior, the penetration rate of liquid onto the porous surface solid substrate can be determined (Samsudin et al., 2012). J. Schonherr and M.J. Bukovac state that the penetration of stomata by liquids depend on the surface

tension, wettability and stomata morphology. Liquids that having low surface tension resulted in zero contact angle on leaf surface and penetrate the stomata spontaneously whereas liquids with higher surface tension did not wet on leaf surface and failed to permeate the stomata.

The maximum spreading behaviour is the other aspect need to be identified in order to investigate the spreading behavior of modified biopolymer on urea surface intercalated with nanoclay filler. The maximum spreading behavior can be determined by maximum spreading diameter, where D_t at certain time over by the initial droplet diameter, D_o (Samsudin et al., 2012). Similarly, the change in contact area also indicates the maximum spreading behaviour (contact line) of liquid drop on solid surface at a given time and velocity. Samsudin et al.(2012), stated that better maximum spreading behavior is achieved when the liquid droplet impacted on the urea substrate produced the smallest static and advancing contact. The better maximum spreading behavior will ensures the uniformity of liquid spreading as well as the coating process.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology and Project Activities

In this chapter, the author will discuss the detailed research methodology for the smooth running of research project activities. This project research is mainly experimental work. Therefore, the results obtained from this research later will be compared to the literature results. The completion of literature review proceeded by experimental works. The experiment is carried out thoroughly in order to obtain accurate results. There are three main focuses in conducting the experiment which are to determine the surface tension, contact angle and maximum spreading diameter of the modified biopolymer droplet.

3.2 Experimental Procedures/Approach

3.2.1 Materials and Apparatus

The biopolymer will be prepared using a specific composition of starch, urea and borate. Samsudin et al., 2012 has been proved that the best coating solution is the biopolymer with the blending ratios of 50/15/2.5 which refer to the ratio of starch, urea and borate respectively. This blending ratio solution is proven to have good droplet impact behavior as it results in smallest contact angle which indicates better wettability and adhesive properties. Better wettability of modified biololymer on the urea surface will ensures the uniformity of spreading behavior and consequently resulted in uniformity of coating process (Turton, Tardos, & Ennis, 1998). Besides, the range of 1 to 6% of nanoclay and also 10% lignin are proposed to be used in this project research. The nanoclay and lignin will be blends together with the biopolymer to produce the modified biopolymer. All these materials are stored in tight air container as the proper storage handling is required in order to maintain the humidity of each material.

3.2.2 Preparation of urea substrate

The main apparatus used to prepare urea substrate are petri dish and hotplate. The hotplate used to provide heat to melts the urea granules in the petri dish and the petri dish have to withstand up to temperature of 150^{o}C. The urea granules are melted in petri dish at 130^{o}C until all urea granules melted. Immediately, the melted urea is dried inside the oven at the temperature range of 65 - 70^{o}C for 30 minutes. The dried urea substrate is then taken out from the dish and stored in the desiccators to avoid moisture (Samsudin et al., 2012).

Figure 7 The flow diagram of urea substrate preparation

3.2.3 Preparation of Modified Biopolymer Solution

The biopolymer solution is prepared with blending ratio of 50/15/2.5 of starch, urea and borate respectively. Firstly, 5g of starch is dissolved with 100mL of deionized water in 250mL round-bottom flask. The slurry is heated and stirred in the water bath at 80^{o}C. Urea, borate, 10% lignin and nanoclay are added to the mixture after 30 minutes of heating and continued mixing for another 3 hours. Add blue dye 30 minutes before finished if required. The purpose of blue dye is to give colors in order to differentiate the uncoated urea with coated urea after the coating process. The readily modified biopolymer solution is stored in tight air container. The duration between solution preparation and characterization process is made constant between 2 – 3 days as different time duration may affect the result obtained. Figure 8 shows the process flow diagram of modified biopolymer solution preparation whereas Table 2 shows the exact amount of materials used to prepare the desired coating formulations.

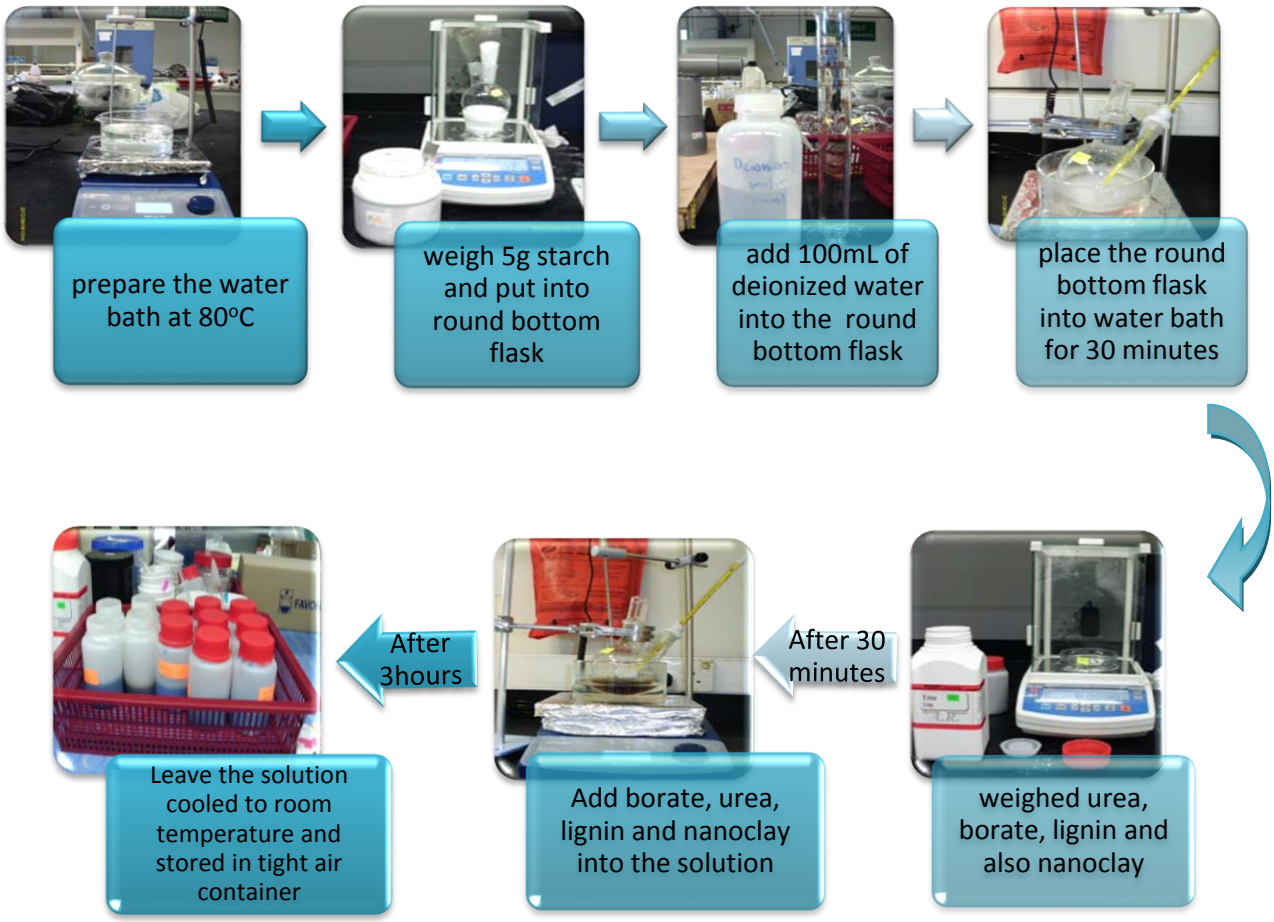


Figure 8 The flow diagram of modified biopolymer solution preparation

Table 2 Weight of material for 1000 mL of deionized water

Blending ratio starch/urea/borate/lignin (g) + nanoclay	Amount of nanoclay (g)	Addition of bromothylmol blue
50/15/2.5/7.5	-	No
50/15/2.5/7.5	-	Yes
50/15/2.5/7.5 + 1% nanoclay	0.758	No
50/15/2.5/7.5 + 2% nanoclay	1.531	No
50/15/2.5/7.5 + 3% nanoclay	2.320	No
50/15/2.5/7.5 + 4% nanoclay	3.125	No
50/15/2.5/7.5 + 5% nanoclay	3.947	No
50/15/2.5/7.5 + 6% nanoclay	4.787	No

3.2.4 Characterization of modified biopolymer solution

The characterization of new modified biopolymer solutions spreading behavior on urea substrate will be measured using OCA 20 (Optical Contact Angle) measurement device as shown in Figure 7. OCA 20 also known as surface tensiometer provide various kind of measure method for example, pendant drop, sessile drop, spinning drop, weigh based method, and etc. OCA 20 is mainly designed to measure the surface tension, static or dynamic contact angle, and surface free energy by tensiometry or geometric analysis of the shape of a meniscus (Myers, 1946). This measurement device comprise of 1mL syringe with 0.51mm needle tip that will be used to dispense the liquid with droplet size of 2mm±0.06mm (Samsudin et al., 2012). This device comes with high-speed, a CCD (Charged-Coupled Device) camera to capture the speed motion of the droplet impact. Besides, this CCD camera is capable to capture up to 17 frames per second and it use SCA software to perform the experiment and analyzed the digital image data obtained.

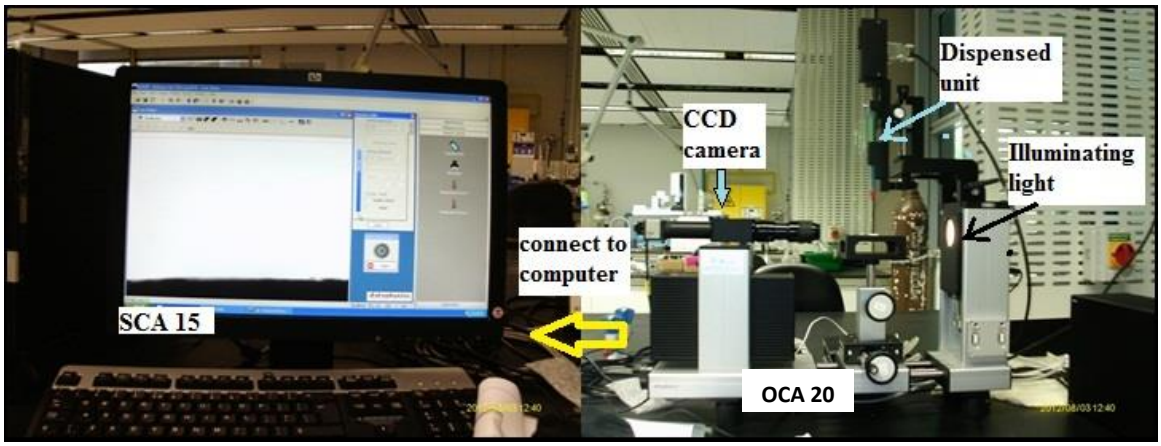


Figure 9 The Optical Contact Angle (OCA) device (Samsudin et al., 2012)

Surface tension measurement

The picture button is then clicked and the modified biopolymer is dispensed until the white spot appeared in the pendant drop image. The surface tension is measured directly by the measurement tool using the pendant drop method.

Contact angle measurement

The position of urea substrate is adjusted to obtain a clear image. The picture button is then clicked and the modified biopolymer is dispensed at dosing rate of 2.00 µl so that the gravitational effect is negligible. The modified biopolymer droplet impact is recorded. The contact angle measurement is carried out using the sessile drop method and is measured when it reached the equilibrium or static contact angle which fit the Laplace-Young method (Samsudin et al., 2012).

Maximum spreading diameter measurement

The droplet impact behavior of modified biopolymer on urea surface can be observed and identified as the CCD camera of OCA 20 can captured up to 17 frames per second. The initial droplet and the diameter of liquid drop after a certain time are recorded. The maximum spreading diameter can be determined by D_t / D_o where D_t at certain time over by the initial droplet diameter, D_o (Samsudin et al., 2012).

3.3 Key Milestones

Planned Completed On-going

PROJECT FLOW/TASK	Jan-13		Feb-13				March-13				April-13				May-13				June-13				July-13				Aug-13			
	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
SELECTION OF PROJECT TOPIC																														
- Meeting with supervisor																														
PRELIMINARY RESEARCH WORK																														
Gather all the information related to the topic																														
Define the material and apparatus																														
EXTENDED PROPOSAL																														
Define the problem statement and objectives																														
Literature review and Detailed the methodology																														
Submission of Extended Proposal																														
Prepare the slide for presentation																														
PROPOSAL DEFENCE																														
PROJECT WORK CONTINUES																														
Understand the problem statement																														
Preparation of urea substrate																														
Preparation of modified biopolymer																														

Characterization process																														
INTERIM REPORT																														
Detailed literature and methodology																														
Submission of Interim Draft report																														
Final report modification																														
Submission of Interim Report																														
EXPERIMENTAL WORK CONTINUES																														
Preparation of modified biopolymer (sample 1,2 & 3)																														
Characterization of sample 1, 2 & 3																														
PROGRESS REPORT																														
Submission of progress report																														
EXPERIMENTAL WORK CONTINUES																														
Preparation of urea substrate																														
Preparation of modified biopolymer (Sample 3, 4, 5)																														
Characterization and analysis of sample 3, 4 & 5																														
PRE-SEDEX																														
Preparation of poster presentation																														
DISSERTATION REPORT																														
Submission of draft report																														
Submission of dissertation																														
Submission of technical paper																														
ORAL PRESENTATION																														
PROJECT DISSERTATION SUBMISSION																														

3.4 Gantt Chart

Timelines for FYPI

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	■	■													
2	Preliminary Research Work and Literature Review		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Preparation for Oral Proposal Defence							■								
5	Oral Proposal Defence Presentation									■						
6	Detailed Literature Review									■	■	■	■	■		
7	Preparation of Interim Report			■	■	■	■	■		■	■	■	■	■		
8	Submission of Interim Draft Report														●	
9	Submission of Interim Final Report															●

● Suggested milestone

■ Process

Table 3 Gantt Chart for FYP I

Timelines for FYPII

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continues	■	■	■	■	■	■	■								
2	Submission of Progress Report							●								
3	Project Work Continues									■	■	■	■	■		
4	Pre-SEDEX											●				
5	Submission of Draft Report												●			
6	Submission of Dissertation (soft bound)													●		
7	Submission of Technical Paper													●		
8	Oral Presentation														●	
9	Submission of Project Dissertation (Hard Bound)															●

● Suggested milestone

■ Process

Table 4 Gantt chart for FYP II

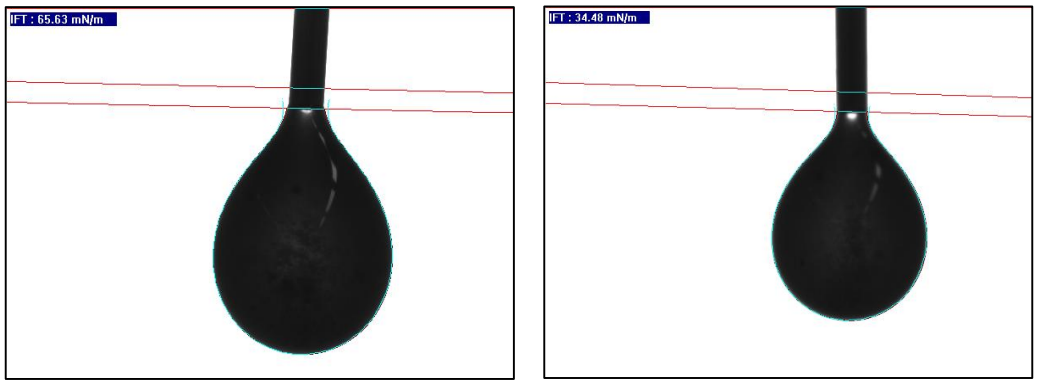
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Modified biopolymer blends with the addition of nanoclay filler

4.1.1 Surface tension and contact angle measurement

The pendant drop image is used to determine the surface tension of certain liquid whereas the contact angle can be obtained by using sessile drop image. The droplet impact behavior of seven different blending ratios of modified biopolymer solutions are tested on the urea substrate and also glass surface. Since the characteristic of urea are porous and dissolutive, the solutions tend to immediately penetrate into the urea substrate and slightly disturbed the spreading process. Therefore, the droplet impact is firstly tested on glass surface to study the spreading characteristic. Figure 10 below shows the comparison of surface tension between blending ratio of 50/15/2.5/7.5 and 50/15/2.5/7.5 with 2% nanoclay filler using pendant drop test.



Blending ratio without nanoclay | Blending ratio with 2% nanoclay filler

Figure 10 Surface tension of 50/15/2.5/7.5 blending ratio and 50/15/2.5/7.5 ratio with 2% nanoclay filler using pendant drop test

Table 5 Surface tension and contact angle of seven different blending ratios

Blending ratio (starch/urea/borate/lignin)	**Surface tension (mN/m)**	**Contact angle (°)**	
		Glass surface	**Urea substrate**
50/15/2.5/7.5	64.18	55.90	13.47
50/15/2.5/7.5 + 1% nanoclay	63.21	52.93	12.97
50/15/2.5/7.5 + 2% nanoclay	62.59	48.4	12.53
50/15/2.5/7.5 + 3% nanoclay	63.05	49.2	14.2
50/15/2.5/7.5 + 4% nanoclay	63.33	50.3	14.6
50/15/2.5/7.5 + 5% nanoclay	63.44	48.0	16.0
50/15/2.5/7.5 + 6% nanoclay	63.48	60.3	16.4

Table 5 shows result of surface tension and contact angle measurement that indicate the physical properties of seven different blending ratio of modified biopolymer solutions. From the result obtained, the 50/15/2.5/7.5 blending ratio with addition of 2% nanoclay has the smallest surface tension and contact angle compared to the other six blending ratios. The addition of 2% nanoclay filler slightly reduced the surface tension and contact angle to 62.59 mN/m and 12.53^{o} respectively. As mention earlier, surface tension depends on the forces of attraction between particles of that liquid and also the gas, liquid or solid in contact with it. The lower surface tension will result in better spreading as the tendency of liquid surface to resist the external forces is less. The modified biopolymer droplet with low surface tension spreads more on urea substrate. The contact angle is interrelated with the wettability properties of modified biopolymer. Low contact angle value represent better wettability properties as the droplet is allowed to spread more. Therefore, it is proven that although small amount of nanoclay filler is added, it can improve the physical properties of the modified biopolymer solutions.

Figure 11 shows the result of surface tension analysis whereas Figure 12 and Figure 13 shows the result of contact angles analysis.

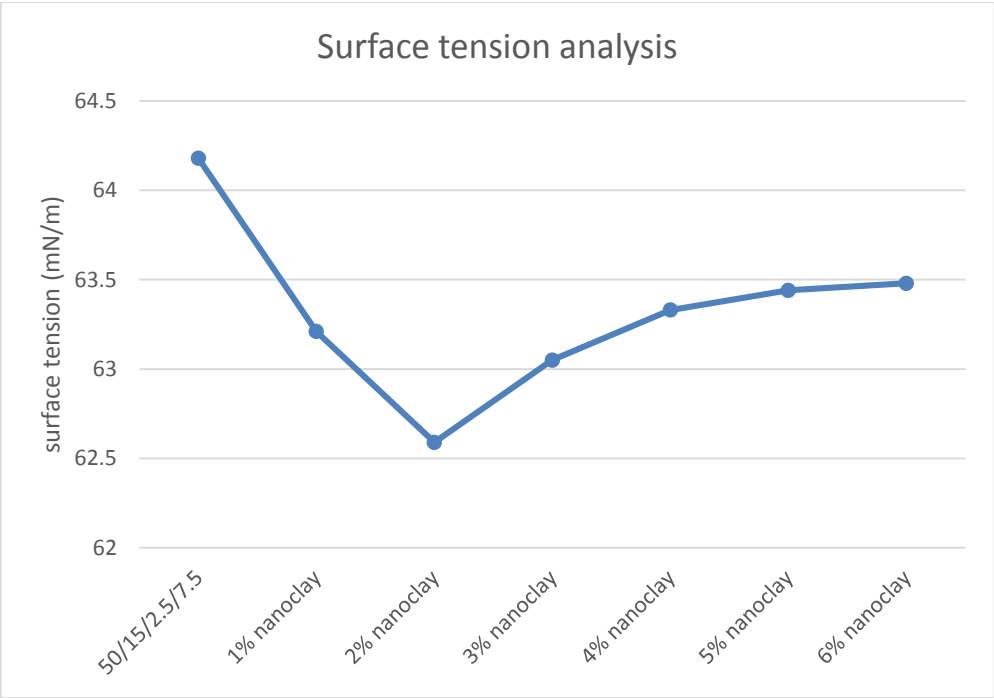


Figure 11 The graph of surface tension analysis for seven blending ratios of modified biopolymer solutions

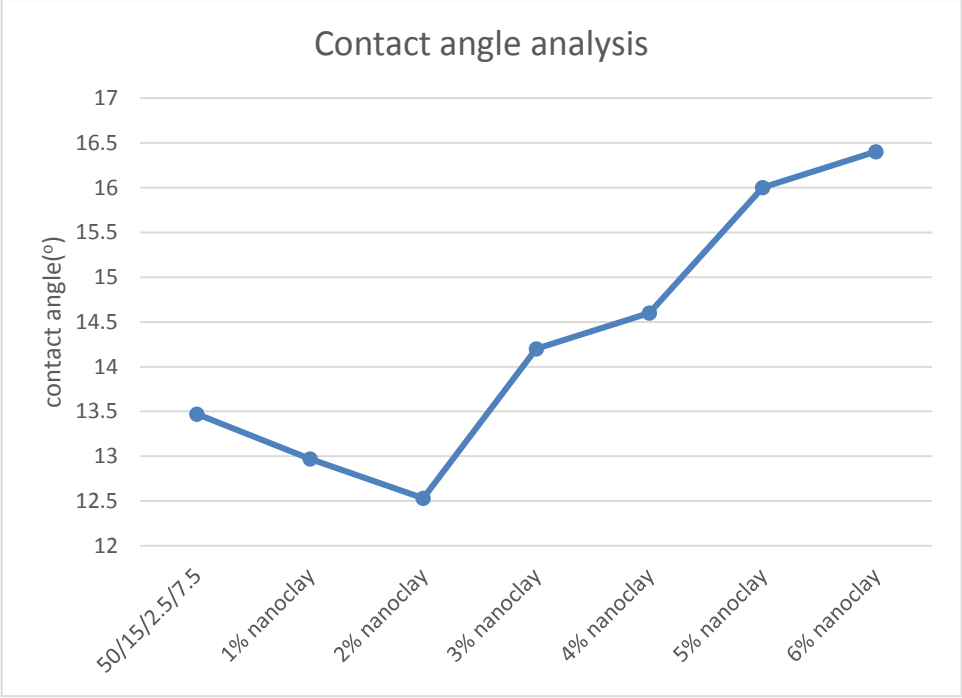


Figure 12 The graph of contact angle analysis for seven blending ratios of modified biopolymer solutions on urea surface

From the graph in both figures above, the surface tension and contact angle proportionally decrease with the addition of 1% and 2% nanoclay. The surface tension started to increase with the addition of 3% nanoclay filler and the surface tension become approximately constant after the addition of 4%, 5% and 6% nanoclay filler. Meanwhile, the contact angle started to increase after the addition of 3% nanoclay and become even worse compared to the solutions without addition of nanoclay filler.

This occurrence might be related to the crosslinking between starch and lignin in the modified biopolymer itself. The starch component is hydrophilic and thus permeable to urea substrate as urea is water-based component. In contrast, the lignin is more hydrophobic. The crosslinking of starch by lignin will help to reduce the penetration of modified biopolymer into urea substrate which consequently reduce the disturbance on spreading process. Hydrophobes contain low water-soluble molecules and usually it is non-polar molecules that did not interact with water molecules (UC Davis ChemWiki, n.d.). Kauzmann, W. discovered that non-polar molecules tend to cluster up together instead of allocating itself in water medium. Therefore, nanoclay filler is added as the compatibilizer for immiscible biopolymer blends. The mechanism of compatibilization by nanoclay works differently according to the immiscible biopolymer blends. The addition of 2% nanoclay filler able to reduce the contact angle and surface tension of modified biopolymer as the dispersion of nanoclay in the biopolymer matrix occurs very well and it act as efficient compatibilizer. Above 3% nanoclay loading resulted in higher contact angle as compared to modified biopolymer without nanoclay filler might be due to high content of nanoclay molecules disturbed the crosslinking that occur in the biopolymer matrix. This discussion can be proved by further study on nanoclay dispersion and morphology of nanocomposites through scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Since the urea properties itself are porous and dissolutive, the modified biopolymer may easily penetrate into the urea substrate and disturbed the spreading of a biopolymer droplet. Therefore, the spreading behavior of modified biopolymer on glass(solid) surface is studied. The result is tabulated in Table 5 and illustrated in Figure 13.

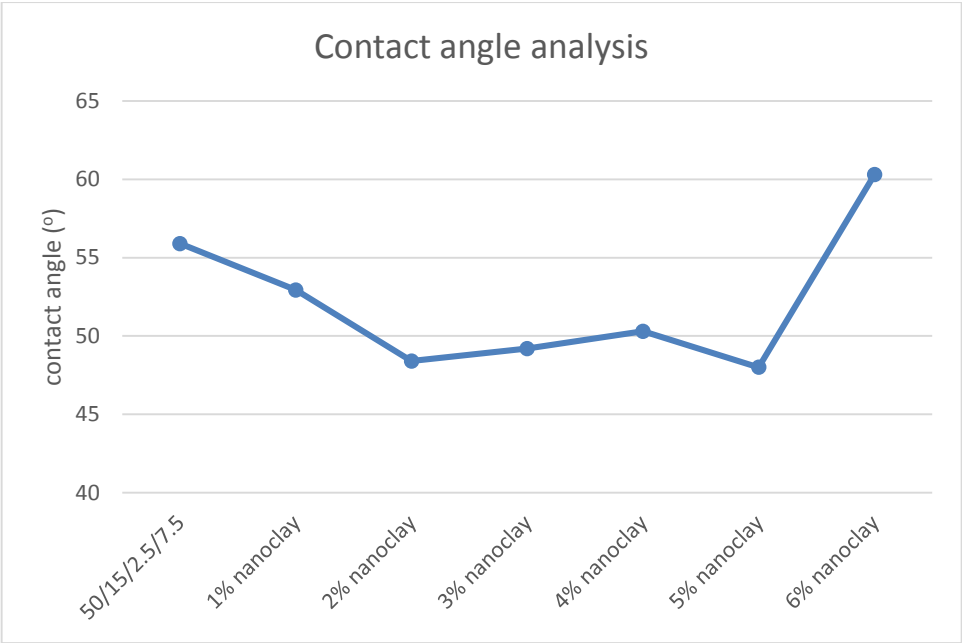


Figure 13 The graph of contact angle analysis for seven blending ratios of modified biopolymer solutions on glass surface

Based on the graph in Figure 13, the contact angle of modified biopolymer on glass surface decreased with the addition of 1% and 2% of nanoclay filler and the contact angle start to increase with the increasing percentage of nanoclay filler added. Therefore, the study of droplet impact on glass surface has support the data obtained for the modified biopolymer droplet impact on urea substrate. However, the contact angle of modified biopolymer with addition of 5% nanoclay filler is slightly lower than addition of 4% nanoclay filler due to systematic error. The error might be due to inaccuracy of baseline determination of sessile drop during the contact angle measurement or unsmooth surface of urea substrate. Future research can be done by increasing the percentage of nanoclay filler added in order to get better result data and to have a strong data support on the spreading behavior occur on glass surface.

The desired physical properties for coating material are the modified biopolymer droplet with better wettability characteristic. Based on result obtained, the 50/15/2.5/7.5 blending ratio of modified biopolymer with addition of 2% nanoclay filler has the best physical properties to achieve good droplet impact behavior as well as spreading characteristic.

4.1.2 Maximum spreading diameter

There are several phenomena of the droplet impact behavior on solid surface such as splashing, spreading, receding, and bouncing (Yarin, 2006). In the case of modified biopolymer droplet impact on urea surface, only spreading behavior can be observed. Therefore, the maximum spreading diameter is considered as another parameter that can also be used to explain the spreading properties of modified biopolymer solutions. The diameter was measured from one second until seven second. The sessile drop image is captured for every one second and the diameter of droplet each second is measured. The spreading factor is calculated by taking the ratio between spreading diameter at certain time, D_t and spreading diameter of the initial droplet, D_o. The spreading factor obtained is tabulated in the Table 6.

Table 6 The data of spreading factor across time for seven different blending ratio of modified biopolymer

Blending ratio (starch/urea/borate/lignin)	**Spreading factor (D_t/D_o)**						
	***t* = 1s**	**t = 2s**	***t* = 3s**	***t* = 4s**	***t* = 5s**	***t* = 6s**	***t* = 7s**
50/15/2.5/7.5	2.143	2.313	2.452	2.538	2.584	2.603	2.629
50/15/2.5/7.5 + 1% nanoclay	2.108	2.331	2.462	2.537	2.638	2.671	2.693
50/15/2.5/7.5 + 2% nanoclay	2.201	2.370	2.504	2.606	2.673	2.694	2.714
50/15/2.5/7.5 + 3% nanoclay	2.104	2.271	2.362	2.484	2.573	2.623	2.63
50/15/2.5/7.5 + 4% nanoclay	2.063	2.341	2.434	2.510	2.578	2.610	2.637
50/15/2.5/7.5 + 5% nanoclay	2.128	2.295	2.386	2.497	2.541	2.569	2.587
50/15/2.5/7.5 + 6% nanoclay	2.062	2.255	2.368	2.430	2.460	2.485	2.507

Figure 14 shows the spreading factor of seven blending ratios of modified biopolymer solutions. Based on the graph, it clearly illustrate that the addition of 2% gives the highest spreading factor followed by 1% addition of nanoclay which represent a good spreading properties compared to the other modified biopolymer blends. A good

spreading behavior of modified biopolymer solution is crucial for coating process as it helps to form a thin layer of coating material which accordingly gives a better coating uniformity of urea. Besides, the spreading factor become lower as the percentage of nanoclay increase. From the graph, it can be concluded that the spreading behaviour of modified biopolymer solution with addition of 3% nanoclay and above are even worst compared to the modified biopolymer solution without nanoclay filler. This phenomenon occur due the high percentage of nanoclay filler has disturbed the crosslinking of starch by lignin which consequently not allow the modified biopolymer to spread more. The modified biopolymer filled with nanoclay only takes up to ten seconds to achieve its equilibrium whereas droplet impact behavior of modified biopolymer without nanoclay filler takes a long time to reach equilibrium in shape.

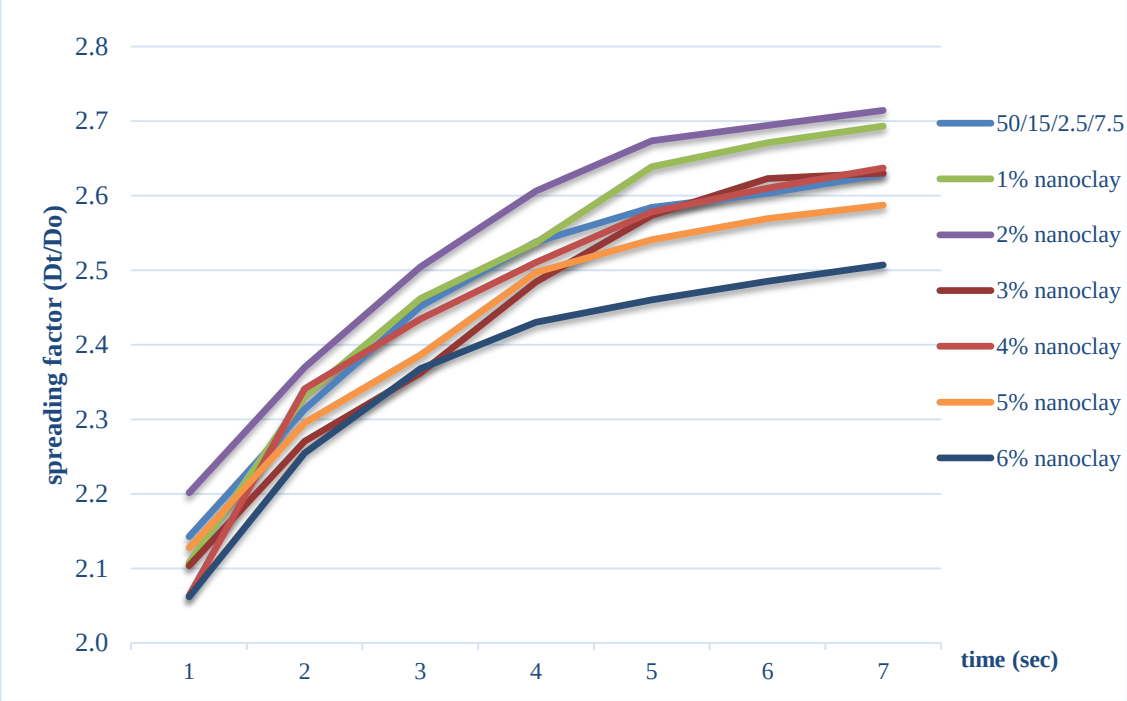


Figure 14 The graph of spreading factor versus time

From the result obtained, the 50/15/2.5/7.5 blending ratio with addition of 6% nanoclay shows the smallest maximum spreading diameter and gives the worse droplet impact spreading behavior. Figure 15 below obviously shown the spreading behavior of modified biopolymer with addition of 2% nanoclay filler formed almost thin layer of modified biopolymer on the urea surface. This characteristic of droplet is required in order to obtain thin layer coating process.

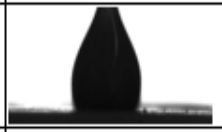
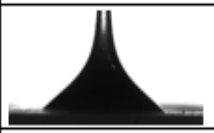
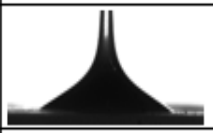
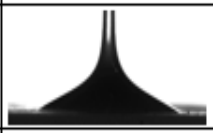
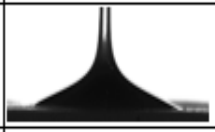
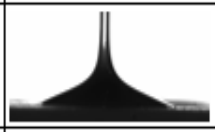
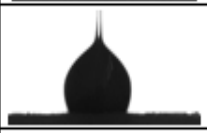
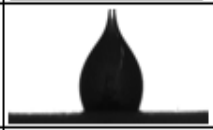
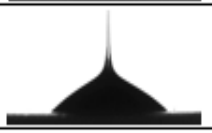
Blending ratio	t =1s	t = 2s	t = 3s	t = 4s	t = 5s	t = 6s	t = 7s
50/15/2.5/7.5							
50/15/2.5/7.5 + 1% nanoclay							
50/15/2.5/7.5 + 2% nanoclay							
50/15/2.5/7.5 + 3% nanoclay							
50/15/2.5/7.5 + 4% nanoclay							
50/15/2.5/7.5 + 5% nanoclay							
50/15/2.5/7.5 + 6% nanoclay							

Figure 15 The spreading behavior of seven modified biopolymer blends on urea surface

4.2 Modified biopolymer blends with the addition of 6% bromothymolblue

4.1.1 Surface tension and contact angle measurement

Another finding is discovered where the addition of 6% bromothymolblue could slightly modify the physical properties of the modified biopolymer solution. Table 7 shows the comparison of surface tension and contact angle between the 50/15/2.5/7.5 blending ratio and 50/15/2.5/7.5 blending ratio with the addition of bromothymolblue. The addition of bromothymolblue has decrease the surface tension of 50/15/2.5/7.5 blending ratio to 48.71 mN/m.

As per discussed earlier, low surface tension represent the weak intermolecular forces within the liquid that will enable the liquid to spread faster and easily dispersed. It can be proved when the droplet impact is tested on the glass surface. From the result obtained, the blending ratio added with the 6% bromothylmolblue which has lower surface tension spread more on glass surface compared to 50/15/2.5/7.5 blending ratio. Although low surface tension is believed might enhanced the spreading behavior of biopolymer droplet, high contact angle is formed when 6% bromothymolblue added into the modified biopolymer solution is dispensed on urea surface. The presence of bromothymolblue in the biopolymer blends cause the droplet unable to penetrate into the urea surface. This might be due to the incompatibility between composition modified biopolymer droplet and porous surface of urea or due to inappropriate percentage of bromothylmol blue added.

Table 7 Surface tension and contact angle of two different blending ratios of modified biopolymer

Blending ratio (starch/urea/borate/lignin)	**Surface tension (mN/m)**	**Contact angle (°)**	
		Glass surface	**Urea substrate**
50/15/2.5/7.5	64.18	55.90	13.47
50/15/2.5/7.5 + 6% bromothymolblue	48.71	47.77	22.40

4.1.2 Maximum spreading diameter

The maximum spreading diameter across time for two different modified biopolymer blends is tabulated in the Table 8 below. From the observation, the blending ratio with addition of bromothymolblue is much less viscous and it spreads faster compared to the 50/15/2.5/7.5 blending ratio. The viscosity of liquid droplet also affects the spreading behavior of liquid droplet. More viscous the liquid droplet results in smaller maximum spreading diameter as it inhibit the spreading of liquid. In contrast, the spreading factor of blending ratio with addition of bromothymolblue is smaller than 50/15/2.5/7.5 blending ratio although it has low viscosity compared to 50/15/2.5/7.5 blending ratio. This phenomenon occur might be due to the properties of bromothylmolblue that incapable to penetrate into the urea substrate. The spreading behavior of 50/15/2.5/7.5 blending ratio is affected by the porousity and dissolutive properties of urea that slightly help in reducing the contact angle between the liquid and solid surface.

Table 8 The spreading factor versus time for two different blending ratios of modified biopolymer

Blending ratio (starch/urea/borate/lignin)	**Spreading factor (D_t/D_0)**						
	***t* = 1s**	***t* = 2s**	***t* = 3s**	***t* = 4s**	***t* = 5s**	***t* = 6s**	***t* = 7s**
50/15/2.5/7.5	2.143	2.313	2.452	2.538	2.577	2.589	2.716
50/15/2.5/7.5 + 6% bromothymol blue	1.704	1.847	1.898	1.969	2.010	2.010	2.010

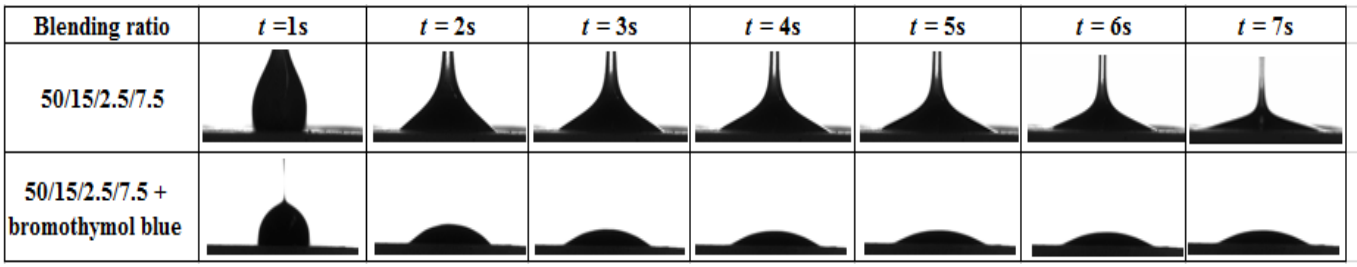


Figure 16 The spreading behavior of modified biopolymer blends and biopolymer blends with the addition of 6% bromothymolblue

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In conclusion, seven different blending ratios of modified biopolymer are prepared with the range of 0 to 6% nanoclay filler are added. As mentioned earlier, the uniformity of coating depends on the spreading behavior of coating materials. The spreading behavior of each blending ratio of modified biopolymer is observed and analyzed from the characterization process using SCA20. The analysis and data obtained had identified the physical properties of each different coating formulations. From the result obtained, it can be concluded that 50/15/2.5/7.5 blending ratio of modified biopolymer with addition of 2% nanoclay filler gives the best wettability properties and better spreading behavior of a liquid droplet impact. Besides, 2% addition of nanoclay filler resulted in greatest maximum spreading diameter compared to the other blending ratios. The results and discussion in the previous chapter had proved that the addition of small amount of nanoclay filler into the modified biopolymer improved the spreading behavior of liquid droplet on urea surface. Thus, the expected result and the objectives of this research are achieved.

There are several recommendations prior to improve this project research in the future. The first suggestion is the characterization of modified biopolymer solutions has to be done several times. During surface tension and contact angle measurement, there are several parameters that need to be kept constant such as surrounding temperature, density, dosing rate, size of needle and minimize the disturbance. Furthermore, the accurate determination of baseline will give better result in determining the contact angle of the droplet impact. Further study on the morphological and rheological characterization of the modified biopolymer with the presence of nanoclay filler can be done via transmission electron microscopy (TEM) and scanning electron microscopy (SEM) in order to have strong support of result data.

This project research can be expand and continue in the future where the best spreading behavior of modified biopolymer can be used in application of urea coatings by using the fluidized bed. Future research can be done by investigating the element present in the nanoclay filler that could enhanced the properties of biopolymer solutions. Besides, another research can be done to discover the alternative or substance that could act as the same element present in the nanoclay filler which are more economically feasible.

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