

The Effect Of Fillers On Physical Properties Of Biopolymer Nanocomposite Material
For Urea Coating

by

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

(AP Dr. Ku Zilati Ku Shaari)

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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.

(MUHAMMAD NURHANAFI BIN AZLAN)

ABSTRACT

The concept of slow release fertilizers (SRF) is the latest technology available in fertilizer industries since 1963. The objective of this technology is to gradually release the nitrogen and other nutrients from the urea granules through a coating material so that the volume of nitrogen as well as other nutrients to be absorbed by crops can be maximized and the nutrients loss into the soil through leaching will be minimized. There are many types of coating materials that had been used such as wax, sulfur and polymer but they are not environmentally friendly.

A biopolymer nanocomposite material has been developed from starch, citric acid and polyvinyl alcohol (PVA) to be the coating material for the urea granules since it is more environmental friendly compared to the other coating materials. However, the problem arises when urea granules that had been coated by the biopolymer nanocomposite materials have rough surface. This is not a good characteristic for a coating material because as the surface is rough, the rate of nutrients release through the coating material will not be equally the same from one point to another.

In order to overcome this problem, fillers which are bentonite, kaolin, halloysite and nanoclay were mixed together with the biopolymer nanocomposite materials. The weight percentage of fillers added are varies from 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% while the ratio of PVA/starch/citric acid used is 1:3:2 respectively. The effect of fillers on biopolymer coating material in term of its water solubility, degree of swelling and surface roughness had been studied. The experimental results showed that the addition of 2 wt.% of halloysite reinforced into biopolymer material had the lowest percentage of degree of swelling and water solubility. The smoothest surface of biopolymer film was achieved when the biopolymer material mixed with 2 wt.% of halloysite.

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CHAPTER 1: INTRODUCTION

1.1 Background of Study

The costs of raw materials for urea fertilizer especially nitrogen have increased substantially over the past five years which then make the production cost also increase. Many fertilizer industries also are facing difficulties in producing better urea fertilizers that come with high efficiency of releasing the nutrients from granules to the crops as well as to minimize the negative impacts of the urea fertilizers to the environment. Urea is the most famous fertilizers that favorably used in the worldwide compare to other nitrogen fertilizers because urea has the highest nitrogen content which is approximately 46% and the production cost of urea fertilizer also is the lowest compare to other fertilizers [1].

However, after the fertilizers are mixed and dissolved with water in soil, the nutrients that are seeping out from the urea granules are not completely absorbed by the plants because some of the nutrients are vaporized into the atmosphere and some are loss through leaching which resulted that the amount of urea that is being absorbed by plants is approximately below 50% [2]. Once urea is in contact with water, it will immediately soluble and dissolve with the water and it turns out that the amount of nutrients that are being absorbed into the soil are too much to be absorbed for the plants at one time especially when it is at early plant growth stage.

Thus, this is where the slow release fertilizer is being invented whereby this concept is the latest and technically have the best fertilizer technology because by having the coating material on the urea granules, it will gradually release the nutrients into the soil and excessive amount of nutrients that are being absorbed into the soil can be prevented so that the amount of nutrients that are available in the soil is at optimum level and meets the plant need. Besides, SRF technology also successfully minimizes leaching and subsequently enhances the efficiency of the fertilizer usage by the plants [3].

There are numerous varieties of polymers that can be used as the coating material and this project will be using starch, citric acid and polyvinyl alcohol (PVA) since this biopolymer material will be degradable and not cause any negative impact to the environment. Starch is effectively cross-linked with citric acid which improves its

strength about 150% higher than non-cross-linked films and its strength is better compare to the other most cross-linked starch and synthetic polymer blended films previously developed [4]. The topography surface of the film is observed under scanning electron microscope (SEM) and the result showed that the film is homogenous without any pores or cracks but the tensile strength of the film will eventually decrease when the amount of citric acid used is exceeding its optimum amount. Besides, biopolymer films that are made up of rice starch and PVA with a ratio of 2:8 showed the highest tensile strength [5].

Previous study showed that by adding citric acid into starch/PVA biopolymer solution, it will further enhances the properties of the film compared to by adding glycerol or sorbitol [6]. However, over the past years, fillers had been added to the polymeric material due to its ability to reinforce the mechanical and physical properties. Thus, this project will be developed and discovered the best biopolymer film to be used as coating material for urea granules by adding four different types of fillers which are bentonite, kaolin, halloysite and nanoclay with weight percentage that varies from 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.%. The blending ratios of starch/PVA/citric acid used are kept constant at 3:1:2.

1.2 Problem Statement

Biopolymer solutions that consist of starch, citric acid and polyvinyl alcohol (PVA) have a great cross linking characteristic among all of them. Studies showed that biopolymer material that developed from these materials have the best combination since it has the highest tensile strength, elongation and have the lowest water solubility. However, this biopolymer film has a rough surface when it was coated on the urea granules which are not a good quality as a coating material. Thus, there are four types of fillers that will be mixed together with the biopolymer materials in order to enhance the surface roughness of the biopolymer coating material.

1.3 Objectives

The objective of this project is to study the effect of four different types of fillers on biopolymer coating material in term of its water solubility, degree of swelling and

surface roughness. There are four fillers that will be added into the biopolymer materials which are bentonite, kaolin, halloysite and nanoclay. Each of these fillers will be mixed together with the starch, PVA and citric acid with different blending ratio.

1.4 Scope of Study

The three main materials in this project are starch, citric acid, PVA and four types of fillers which are bentonite, kaolin, halloysite and nanoclay will be added into those materials. The blending ratio would be 3:2:1 for starch, citric acid and PVA respectively and addition of 1 wt.%, 2 wt.% , 3 wt.% and 4% for each filler. The scope of study is as below:

- Effect of fillers on the biopolymer coating material in term of water solubility and degree of swelling will be identified and characterized by using swelling test and water solubility test.
- Characterization of biopolymer film surface topography which is the surface roughness can be identified by using Scanning Electron Microscopes (SEM).

1.5 Project Feasibility

This project will study the effects of four types of fillers which are bentonite, kaolin, halloysite and nanoclay to biopolymer coating material in term of degree of swelling, water solubility and surface roughness. The biopolymer coating materials consist of starch, citric acid and PVA. Each of the filler will be added to the biopolymer material with different blending ratio of its mass compositions that will vary from 1%, 2%, 3% and 4%. The effects of the filler on its surface roughness will be identified by using SEM. SRF technology needs good characteristics of a coating material so that the nutrients release from the urea granules will fulfill the nutrients need of the plants at right time. The characteristics like surface roughness, degree of swelling and water solubility will put into consideration so that a better coating material for the urea could be developed. Thus, this project seems to be in the same track and goal with nowadays' research for the enhancement of the SRF technology in agriculture industries especially the coating materials

CHAPTER 2: LITERATURE REVIEW

2.1 Filler

Technically fillers can be considered as additives to be mixed with polymer materials in order to enhance the properties of the polymer [7]. Filler which is usually micron-sized is incorporated into composite materials to improve their properties. There are a few primary functions of fillers that can be identified which are to modify mechanical properties of polymer, fire retardants, modify electric and magnetic property, surface property modifiers and solvent permeability. Over the few years, there are group of nano-engineered polymeric materials that have become as alternatives to the conventionally filled polymers and polymer blends [8]. The best quality of this new type of fillers in polymeric nanocomposites is their ability to improve their overall properties but only need low amount of total filler loading [9].

2.2 Bentonite

Bentonite is a rock formed of plastic clays which composed mainly of montmorillonite clay minerals [10]. There are a lot of uses for bentonite like as a bonding material in the preparation of molding sand for the production of iron, steel and non-ferrous casting and cat litter. Bentonite also can be produced as paste formation due to its absorption/adsorption criteria such as industrial protective creams, calamine lotion, wet compresses, and ant irritants for eczema.

Natural bentonite was used as filler in styrene-butadiene rubber (SBR) composites since it contain Sodium (Na) and Calcium (Ca) and both of the cations can be exchanged with other ions which are Strontium (Sr), Copper (Cu), Barium (Ba) and double cations copper-barium (Cu-Ba) [11]. Different type of ion exchange bentonites (IEB) were mixed in SBR matrix to study the effect of the bentonite as reinforcing filler. Clay is a common substance that has been used as functional filler in rubber application because it is inexpensive filler which able to reduce polymer consumption as well as the composite cost [12]. Clay also able to stiffen the uncured rubber and reinforces cured rubber by

increasing the stiffness, improve the resistance to abrasion and tear as well as tensile strength of the vulcanizate [13].

In order a filler to be a good reinforcing agent, there are three main factors which are particle size, structure and surface characteristics [13]. The morphology of natural bentonite and IEBs are shown in the Figure 1.

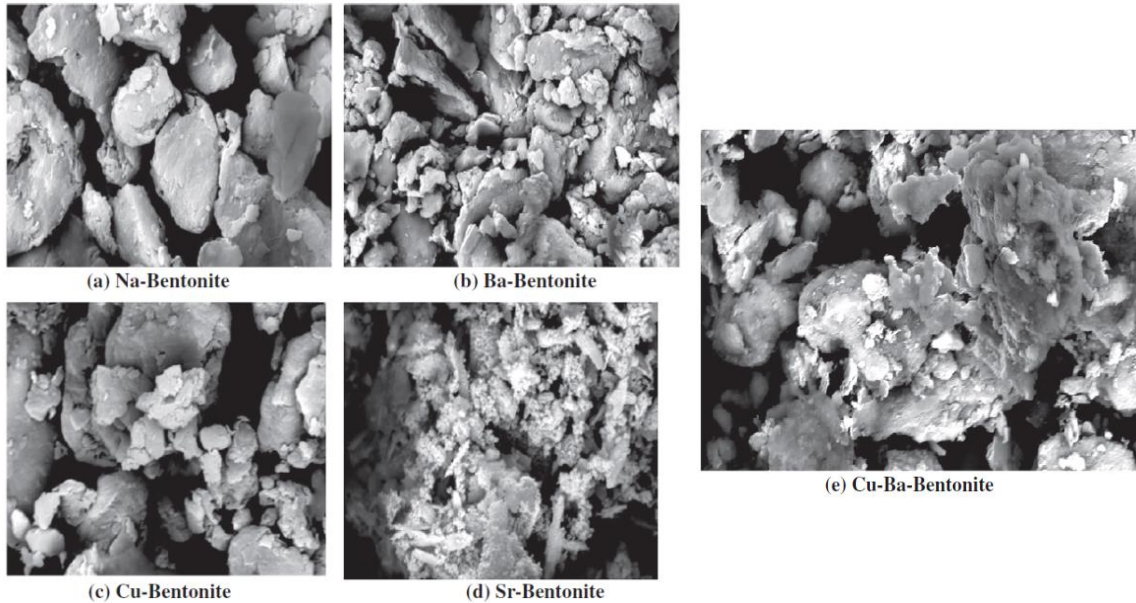


Figure 1: SEM micrographs of ion-exchange bentonites at magnification 2×10^3 [11].

One of the famous natural clay is bentonite which had been studied extensively as ideal mineral for preparation of organomodified fillers and it was found that bentonite also possesses a unique quality of having the ability of cation exchanging capacity (CEC) [11]. The advantages of using ion exchange clays or pigment are it is most naturally abundant, easily synthesized, cheap and environmentally friendly [14]. Styrene-butadiene rubber (SBR) was inferior in terms of physic mechanical characteristics with reinforcing filler even though it has good process ability, heat aging and abrasion resistance [11].

Table 1: Rubber formulation containing different concentrations of the prepared (IEB) [11].

Formulation no.	S0	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17
Control	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Natural bentonite	-	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba-bentonite	-	-	5	10	15	20	-	-	-	-	-	-	-	-	-	-	-	-
Sr-bentonite	-	-	-	-	-	-	5	10	15	20	-	-	-	-	-	-	-	-
Cu-bentonite	-	-	-	-	-	-	-	-	-	-	5	10	15	20	-	-	-	-
Cu-Ba-bentonite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	10	15	20

Base recipe in phr (parts per hundred parts of rubber): SBR 100; stearic acid 2; zinc oxide 5; CBS 1.5; and sulfur 2.

The formulation of the NBR with the natural bentonite as well as the other IEBs are shown in the Table 1. The effect of adding IEBs which have different cations to SBR matrix on the rheometric characteristics were identified as shown in the Table 2.

Table 2: Rheometric characteristics of SBR compound [11].

Rheometric characteristics	S0	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17
M_L (dN m)	5.5	10	12	12	14	14	12	13.5	14	13.5	11	10	8	7	11	9	8	8
M_H (dN m)	30	36	42	46	50	48	40.5	44	49	47	38	36	33	32	39	36	35	33
T_{90} (min)	12	18	16	18	19	18	17	19	19	19	16	16	15	15	16	16	16	16
TS_2 (min)	2	7	9	11.5	13	12	9.5	12	12.5	12.5	8.5	8.5	5	5	8.5	7	6	6
CRI (min^{-1})	10	11.11	14.29	15.38	16.67	16.67	13.33	14.29	15.38	15.38	13.33	13.33	10	10	13.33	11.11	10	10
α_f	-	0.306	2.86	3.88	4.22	3.16	2.86	3.67	3.81	2.55	2.04	1.02	0.136	0.1	2.86	1.02	0.68	0.102

(M_L) is Minimum torque, (M_H) is maximum torque, (T_{90}) is optimum cure time, (TS_2) is scorch time, and (CRI) is cure rate index.

Table 2 shows the rheometric characteristics of SBR compound by using natural bentonite and IEBs as filler in SBR and it can be conclude that the rubber compounds containing the ion exchanged Ba and Sr bentonites (IEBs) are exhibiting a better mechanical properties among the groups with an optimum loading of 15 phr [11].

Other than that, bentonite clay and polyacrylonitrile (PAN) had been used as nanoceramic active filler to be mixed with composite polymer electrolytes (CPE) and the properties of the CPEs was investigated [15]. Since the last 25 years, researches were being done in order to develop highly efficient polymer electrolytes to be used for high power source systems [16]. In order to increase the ionic conductivity of the electrolyte, low molecular weight organic liquid as plasticizers were used but the mechanical properties were low. One of the ways to increase the properties of polymer electrolyte is the CPE which is mixed with the ceramic fillers as additive [17].

Table 3: Composition of the films (wt%) [15].

Sample	Bentonite-Li ⁺ -PAN	Bentonite-Li ⁺	PAN	PPC
1	3	-	15	82
2	5	-	15	80
3	7	-	15	78
4	-	3	15	82
5	-	5	15	80
6	-	7	15	78

Table 3 shows there are six samples of films and its thickness was about 0.03-0.1 cm. All the samples which have six different blending ratio of PAN, polypropylene carbonate (PPC) and Bentonite-Li⁺ were experimented in order to determine ionic conductivity of the CPE.

Table 4: conductivity composite (at 25°C) [15].

Sample	σ (S/cm)	E_a (KJ/mol)	E_a (e.v)
Bentonite(LiPAN)3%	4.80×10^{-7}	57.2	0.59
Bentonite(LiPAN)5%	4.20×10^{-6}	17.3	0.18
Bentonite(LiPAN)7%	1.23×10^{-6}	48.0	0.49
BentoniteLi 3%	9.12×10^{-8}	32.9	0.34
BentoniteLi 5%	2.33×10^{-7}	48.7	0.51
BentoniteLi 7%	1.97×10^{-7}	31.2	0.32

Based on the conductivity result from Table 4, the maximum value of the conductivity of prepared CPEs is at 4.2×10^{-6} S/cm when the concentration of Bentonite-Li⁺-PAN is 5%. Thus, the ionic conductivity of the CPEs using Bentonite-Li⁺-PAN as filler is about one order of magnitude higher than using Bentonite-Li⁺ at the same condition. Bentonite-Li⁺-PAN is a better filler compared with the Bentonite-Li⁺ is due to the weaker interaction of the carrier with aluminosilicate matrix produced by the presence of the polymer in the coordination of the carrier [15].

2.3 Kaolin

Just like bentonite, kaolin is one of the clay materials that have been widely used in many industrial applications. Kaolin is also as filler for the production of rubber, plastics and pigments, in the refractory materials, cosmetics, pharmaceutical, food industries and also for the production of synthetic zeolites [18]. Kaolin has relatively low viscosity at high solid concentrations which particularly important in paint application and paper coating [19].

In recent studies, the inventions of biodegradable polymers have got many attentions of researches around the globe. However, starches that can be derived from agriculture crops such as cassava, rice, potato and corn are classical renewable materials and can be produced to foam polymers through common thermoplastics processing such as extrusion [20]. However, there are still a few disadvantages of starch foam that being discovered which is has poor mechanical properties, poor thermal stability and high water adsorption [21]. Thus, numerous numbers of experiments had been conducted by mixing different kind of additives in order to increase the properties of starch foam [22]. In order to improve the properties of the starch foam, there were many researched have been done by using different type of fibers such as aspen [23], corn [21], cellulose [24], kraft [25], jute and flax fibers [26]. These fibers are able to enhance the mechanical properties and water absorption of starch foam because of their strong interaction between the fibers and the starch matrix [22].

Kaolin is a natural clay and it has complex structures consisting of octahedral sheets of $\text{AlO}_2(\text{OH})_4$ and tetrahedral sheets of SiO_4 [27]. Kaolin which acts as a filler had been added into the starch foam and subsequently it lowers the water absorption ability of the starch/kaolin foam compared to the pure starch foam and results from SEM also confirmed that larger cell size and good dispersion of kaolin in the starch/kaolin foam [22].

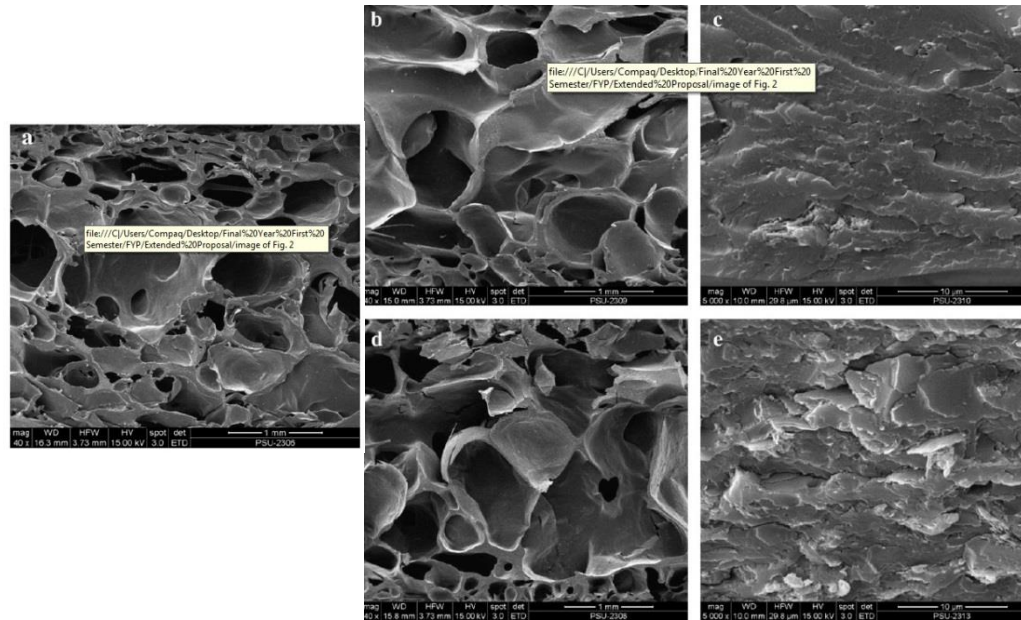


Figure 2: SEM micrographs of cross-sections of (a) starch foam, 40× and (b) kaolin/starch foam with; 3 m% kaolin, 40× and (c) 5000× and (d) 15 m% kaolin, 40× and (e) 5000× [22].

Figure 2 shows the SEM micrograph of cross-section of starch and kaolin/starch foams which contain different blending ration of kaolin. Figure 2a shows that the starch foam has a smaller and denser cell structure. However, for Figures 2b-c and 2d-e which contain 3m% and 15m% of kaolin respectively show that they have different cell size and structure from the starch foam itself. The cell size of the starch foam was only $0.37 \pm 0.23\text{mm}$ while the cell size of kaolin/starch foams with 3m% and 15m% of kaolin content were increase to $0.57 \pm 0.16\text{mm}$ and $0.81 \pm 0.7\text{mm}$ respectively. After the kaolin being mixed together with the starch, the cell size of the foams was increased because kaolin delayed the thermal collapse of the steam bubble and encourages the formation of larger foam cells [22].

Other than that, Figure 3 shows the effect of the time of aging and the kaolin content on the water absorption of starch foam as well as kaolin/starch foams.

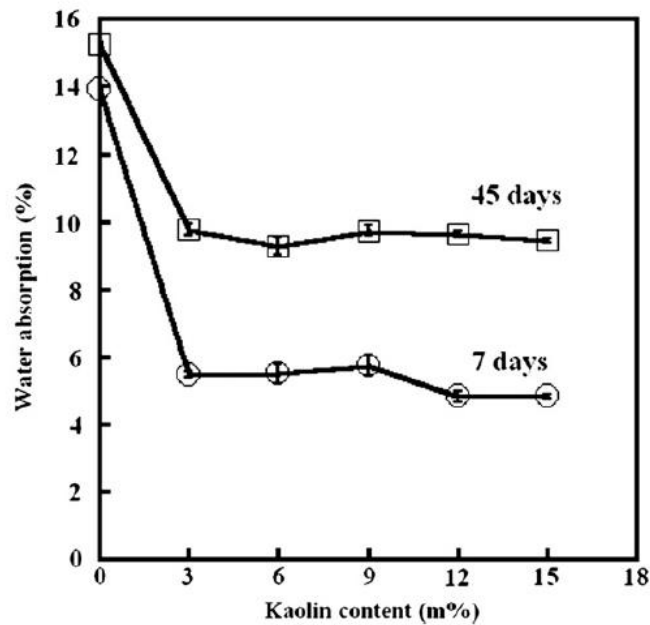


Figure 3: The ability of starch and kaolin foam to absorb water [22].

Based on the graph, the water absorption of starch foam without any kaolin were 13.91% and 15.25% after aging for 7 and 45 days respectively. Since the starch foam was stored for a long period of time, a lot of water will be absorbed due to the acts as plasticizers and affect the properties of the starch foam [28]. However, it is different for starch/kaolin foam because it has lower water absorption compared to the starch foam. At 3m% of kaolin content in starch/kaolin foam, the water absorption was 5.46 % and 9.79 % after aging for 7 and 45 days respectively. The water absorption is slightly decreased when the kaolin content was increased since the kaolin act as an obstrucater in the matrix [29]. Thus, it was concluded that the kaolin did inhibit water absorption [22].

Other than that, Kaolin also had been mixed together with phosphoric acid and starch to prepare a flat ceramic membrane [30]. Ceramic membrane is used for ultrafiltration and microfiltration to remove particles, microorganism and colloidal materials suspensions [31]. There are many advantages of porous ceramic membranes which are a good thermal, chemical and mechanical resistance controllable microstructure and being slightly hazardous for the environment. Kaolin, phosphoric acid (PA) and starch were

mixed together to form the flat ceramic membrane support [30]. The raw materials used to form the ceramic membrane support have its specific functions attributed. Kaolin exhibits low plasticity and high refractory properties to the membrane [32]. Regulation of porous texture in the ceramic is realized by starch that would release the CO₂ gas under sintering condition [33]. The porosity of the membrane was contributed by the path of the released CO₂. Other than that, PA will acts as a binder that increase membrane mechanical strength [30]. In order to study the porosity, permeability and mechanical properties of the ceramic membrane, the effect of phosphoric acid (PA) content into the ceramic membrane has taken into account. The amount of added phosphoric acid was gradually increased from 0 to 15wt%.

Table 5: The effect of amount of phosphoric acid (PA) added into the ceramic membrane [30].

Mass% PA	Permeability (L h ⁻¹ m ⁻² bar ⁻¹)	Rupture strength (MPa)	Porosity (%)
0	8.62	6.66	37.88
2.5	14.24	9.42	33.99
5	17.95	15.00	29.70
10	15.65	12.84	30.87
15	12.16	10.23	34.78

From table 5, the result showed that the minimum porosity and the maximum rupture strength were found in the composition containing 5-10 % of phosphoric acid. However, the permeability is increase as the amount of the PA increases. The porosity of the ceramic membrane decreases as its permeability increases and this obeyed the Poiseuille and Darcy's laws [33]. Thus, the increasing amount of PA content up to 5 mass % resulted to an enhancing the rupture strength and the permeability but to a decrease of the porosity of the kaolin/starch/PA ceramic membrane [30].

2.4 Nanoclay

In recent years, there is increasing interest at polymer-clay nanocomposites due to the significant improvements of material properties at very low clay loading [34]. Moisture absorption of polymer materials can be minimized by mixing nanoclay together with the polymer materials due to its excellent gas/moisture barrier properties [35]. Besides, there was a first report stated that the water absorption rate of a nanoclay/polymer composite

could be minimized by approximately 40% as compared to a neat polymer [36]. Moreover, the water absorption for polymer/nanoclay composite was decreased to 80% [37].

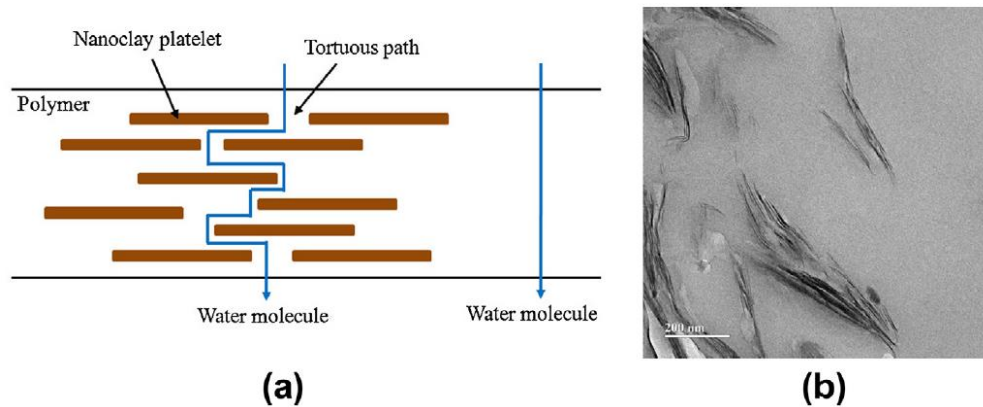


Figure 4: Moisture barrier characteristic of nanoclay platelets in the epoxy structure: (a) interrupted path of water molecule into the polymer structure; (b) TEM image of the nanoclay platelets [35].

Figure 4 shows that the nanoclay platelet in the epoxy will act as a barrier for the penetration of water molecules into the structure as it has a very high aspect ratio [35]. The epoxy/nanoclay composite were mix with the different blending ratio of the nanoclay that varies its weight fractions which are 0 %, 1 % 3 % and 5 %. Figure 5 shows the graph of water absorption of the nanoclay/epoxy composites for different wt.% of nanoclay.

Thus, the amount moisture absorption into the nanoclay/epoxy composite decreased when the wt.% of the nanoclay increased since the nanoclay platelets block the penetration of water molecules into the epoxy structure. Furthermore, nanosized clay platelets also help to restrict the molecular dynamics of polymer chains, thus slowing down the relaxation of the polymer chains and this would explained why a small amount of nanoclay reinforcement able to retard the penetration of water molecules through polymer chains [38, 39].

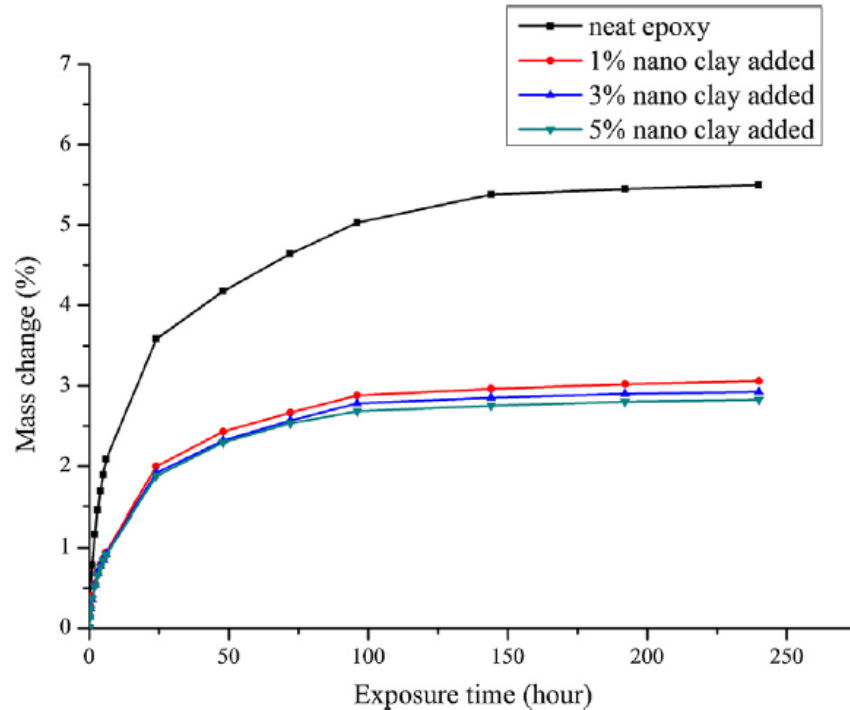


Figure 5: weight gain of nanoclay/epoxy adhesive verse moisture exposure time [35].

Figure 6 shows the SEM images of the nanoclay/epoxy composites fracture surfaces. As the nanoclay wt% increased, rougher fracture surfaces and more evident crack bifurcation nearby the nanoclay could be found. Thus, it can be concluded that the improvement of the fracture toughness and strength of the nanoclay/epoxy composite come from the retardation of crack propagation due to bifurcation around the nanoclay in tensile loading [40]. From the images, it were clearly seen that the 5 wt.% of nanoclay did not well dispersed as the nanoclay of 1 wt.% and 3 wt.% since the nanoclay platelets were almost not exfoliated. The optimum amount of nanoclay would about 3 % because it has the best dispersion and the nanoclay platelets filled nearly entire epoxy polymer area compared to 1 % and 5 % of nanoclay [35].

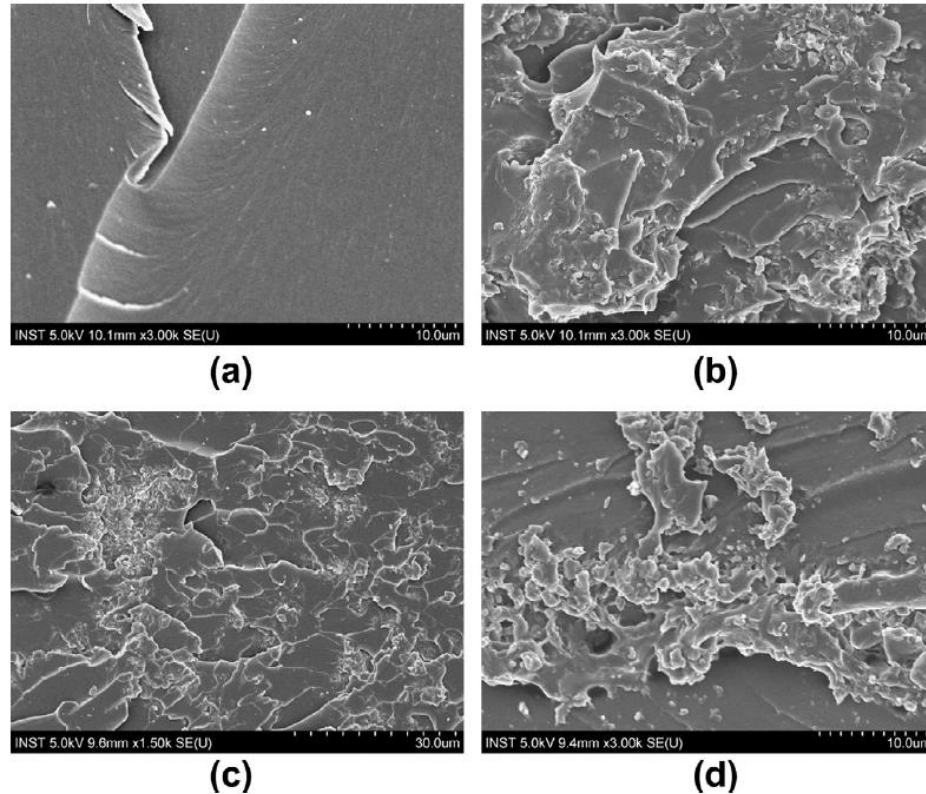


Figure 6: Fracture surface of nanoclay/epoxy composite with respect to the nanoclay wt.%: (a) 0%; (b) 1%; (c) 3%; (d) 5% [35].

Besides, nanoclay which act as filler has been added into chitin based polyurethane bio-nanocomposite (PUBNC) through intercalation in order to synthesize high-performance chitin based PUBNC [41]. Polyurethane has many type of potential for commercial applications as it can be molded, injected, extruded and recycled [42]. By using the optical microscope (OM), the effect of the nanoclay contents on the morphological patterns and intercalation structure of the chitin based PUBNC has been investigated. Figure 7 shows the series of OM images for PUNBC with different compositions of added nanoclay. From the pictures, it is obviously showed that the nanoclays are fully dispersed and clearly visible on the surface of PUBNCs samples.

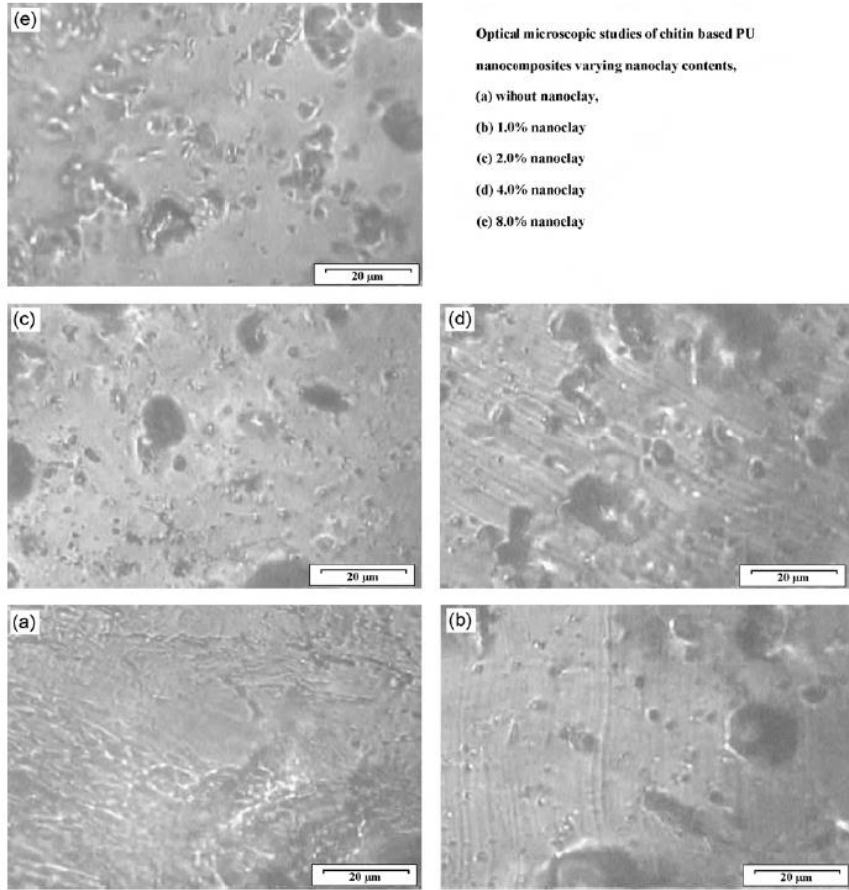


Figure 7: Optical microscopic studies of chitin based PU bio-nanocomposites varying nanoclay contents: (a) PUBNC1; without nanoclay, (b) PUBNC2; 1.0% nanoclay, (c) PUBNC3; 2.0% nanoclay, (d) PUBNC4; 4.0% nanoclay, and (e) PUBNC5; 8.0% nanoclay [41].

CHAPTER 3: METHODOLOGY

3.1 Experiment Methodology

3.1.1 Substances and Chemicals used

Substances and chemicals that are being used in this experiment are:

1. Tapioca starch
2. Polyvinyl Alcohol (PVA)
3. Citric acid
4. Bentonite
5. Kaolin
6. Nanoclay
7. Halloysite
8. Deionized water
9. Water bath

3.1.2 Tools and Equipment

In order to mix the biopolymer materials together with the fillers, the tools and equipment involved would be:

1. 250 ml of two neck round bottom flask
2. 100 ml of measuring cylinder
3. Magnetic hot plate stirrer
4. Thermometer
5. 100 ml beaker
6. Teflon mould (100 mm X 100 mm X 30 mm)
7. Petri dish

The mixed solution will be poured on a Teflon mould for 20 gram. The Teflon mould is then put into an oven at 120 °C for two hours. The dried film is taken out and let it cool to room temperature before it is being tested for characterization as well as put under the SEM.

3.2. Properties of Biopolymer Films

3.2.1 Surface Roughness

In order to identify the surface topography and roughness of the biopolymer film, the films would be examined under the Scanning Electron Microscope (SEM). The SEM would display the micrographs of cross section for all biopolymer that has been mixed with different mass composition of added fillers.



Figure 8: Scanning Electron Microscope (SEM)

3.2.2 Degree of Swelling

The values of degree of swelling can be determined for polymers that have certain limitation values of its swelling properties because polymers that have zero value on its swelling properties will begin to dissolve once immersed in the solvent. In order to calculate degree of swelling of the dried blend film with different percentage of added filler, the film will be first cut into 30mm \times 30mm before it will then be immersed in 50 ml of deionized water in a petri dish at room temperature of 25 °C. After the film reached equilibrium which is approximately after 24 hours, the film will be taken out from the petri dish and moisture on the surface of the film will be removed, and the weight of the films is measured.

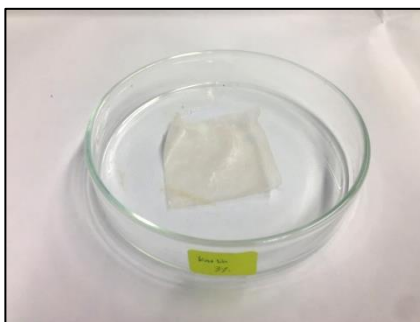


Figure 9: Biopolymer film with 30mm \times 30mm dimension

The percentage of degree of swelling (DS) of the film was calculated as:

$$DS = \frac{W_f - W_i}{W_i} \times 100\% \quad (1)$$

Where W_f is the weight of the blend film at the absorbing equilibrium, and W_i is the first dry weight of the film. This test is a simple and low-cost technique for characterizing the polymer networks, degree of cross-linking as well as degree of hydration. Figure 9 shows the image of biopolymer film before immersed into 50 ml of deionized water.

3.2.3. Water Solubility

In order to calculate the percentage of water solubility of the biopolymer films, the swelled films were dried again for 24 hours at 60 °C after the moisture at the surface of the films had been removed. The water solubility (S) of the film was calculated by the following equation:

$$S = \frac{W_i - W_d}{W_i} \times 100\% \quad (2)$$

Where, W_i is the weight of the swelled film while W_d is the weight of the dried biopolymer film after taken out from the oven. Figure 10 below shows the image of biopolymer film after it is dried at 60 °C for 24 hours.

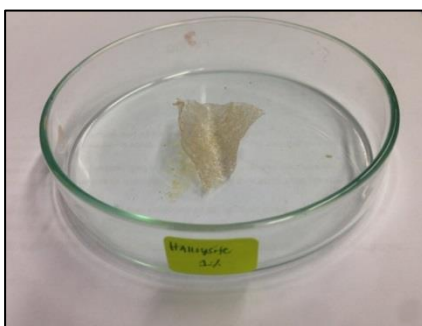


Figure 10: Dried biopolymer film with 30mm × 30mm dimension

3.2.4 Design Matrix

Table 6: Design matrix of the experiment

No	Starch (g)	Citric Acid (g)	PVA (g)	Kaolin (wt.%)	Bentonite (wt.%)	Nanoclay (wt.%)	Halloysite (wt.%)
1	3	2	1	0	0	0	0
2	3	2	1	1	0	0	0
3	3	2	1	2	0	0	0
4	3	2	1	3	0	0	0
5	3	2	1	4	0	0	0
6	3	2	1	0	1	0	0
7	3	2	1	0	2	0	0
8	3	2	1	0	3	0	0
9	3	2	1	0	4	0	0
10	3	2	1	0	0	0	1
11	3	2	1	0	0	0	2
12	3	2	1	0	0	0	3
13	3	2	1	0	0	0	4
14	3	2	1	0	0	1	0
15	3	2	1	0	0	2	0
16	3	2	1	0	0	3	0
17	3	2	1	0	0	4	0

Table 6 shows the design matrix for experiment which indicates the percentage amount of filler that will be mixed together with the other materials which are starch, citric acid and PVA. The amounts of those materials are kept constant while the weight percent of the fillers that will be added are varies from 1%, 2%, 3% and 4%.

3.2.5 Proposed Experiment Procedure

The experiment is planned to be conducted for about six hours. Taken the previous researched work as guidance [6], proposed procedures of preparing the biopolymer coating material are as follows:

- 1) Heat water bath at 90 °C.
- 2) Put 40ml deionised water in the 250 ml of two necks round bottom flask and place it on the magnetic hot plate stirrer.
- 3) Put 1g PVA into the flask after the temperature of the water bath reach 90 °C.
- 4) Stir for 15 minutes at 300 rpm.
- 5) Dissolve the selected filler according to its corresponding percentage in 30ml deionised water.
- 6) Add 3g tapioca starch into the solution and stir them until well mixed.
- 7) Pour this filler/tapioca starch solution into the flask. Stir for 1hour at 90 °C.
- 8) Cool down the temperature of the solution to 30 °C
- 9) Dissolve 2 gram of citric acid in 10 ml of deionised water.
- 10) Add citric acid solution into the flask.
- 11) Continue stir at room temperature for 1 hour.
- 12) Pour the biopolymer mixture into the teflon mould for 20 gram.
- 13) Put the biopolymer mixture into the oven at 120 °C for two hours.

CHAPTER 4: RESULT AND DISCUSSION

4.1 Percentage of Degree of Swelling

Figure 11 shows the graph of degree of swelling (DS) of the biopolymer film that consist of starch, citric acid and PVA with ratio of 3:2:1 respectively and filler which had been added from 1 wt.% to 4 wt.%. Generally, from the graph we can see that the percentages of DS value for the biopolymer films are decreasing as the percentage of fillers increase. After the films are immersed into the 50 ml deionized water, rather than completely dissolve, it absorbed a small amount of the deionized water and subsequently swell since the water molecules penetrated into the cross-linked polymer networks.

There are two forces involved in the extension of the degree of swelling in polymers. Once the polymer films immersed into the water, the free energy of mixing will cause the water molecules to penetrate and try to dilute the biopolymer films. Then, the polymer chains in the cross-linked polymers start to elongate and at the same time it generate an elastic retractive force in order to oppose the deformation by the swelling action. The volumetric swelling will be finally achieved a steady state once both of the forces do balance each other.

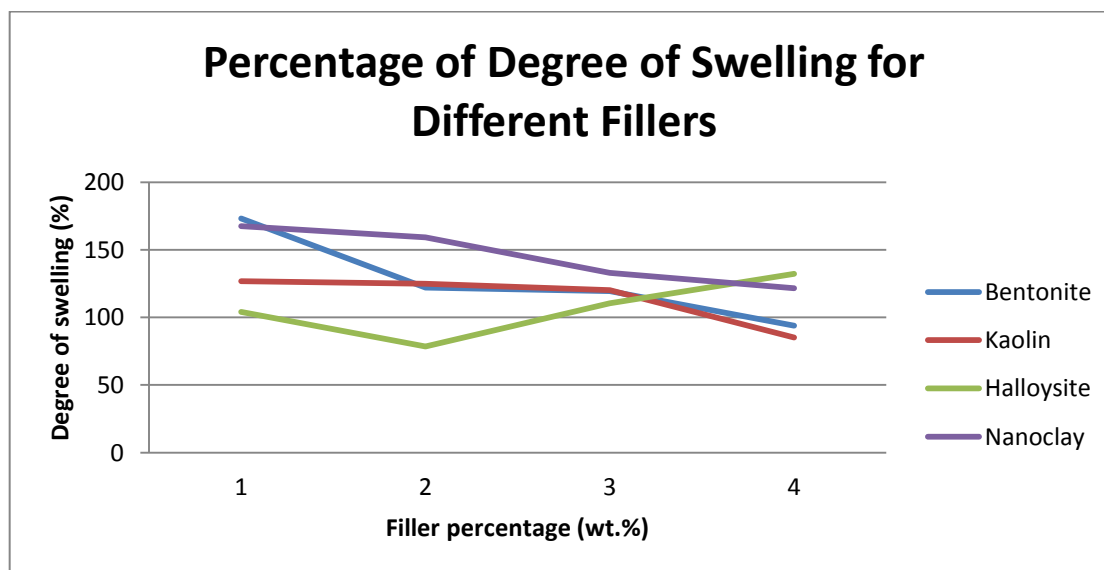


Figure 11: Percentage of degree of swelling for different fillers

From figure 11, the graph shows that the percentage of DS value for biopolymer films that are being added with kaolin, bentonite and nanoclay is decreasing as the weight percentage of those fillers are increasing. However, the lowest percentage of DS value goes to biopolymer film that is being added with 2 wt.% of halloysite which is 78.6164 % followed by 4 wt.% of kaolin, 4 wt.% of bentonite and 4 wt.% of nanoclay which are 85.185 %, 99.939 % and 121.62 % respectively. Compare with other fillers, the trend of halloysite graph is different since the percentage of DS values for halloysite are only decreasing from 1 wt.% to 2 wt.% but suddenly increase towards 3 wt.% and 4 wt.%. Thus, optimum wt.% values for halloysite to be added with the biopolymer film is at 2 wt.% while others are at 4 wt.%.

From previous studies, it was explained that the degree of swelling of a polymer is affected by the flexibility and mobility of polymer chains, molecular size of the solvent, temperature and cross-linking agent type [43]. The room temperature where the DS test carried out is fixed at 25 °C and deionized water is fixed as the solvent. However, the molecular weight of the biopolymer films are varies since different types of fillers are added to the biopolymer film.

A cross-link is a bond that links one polymer chain to another. As the amount of cross-linking increases, the polymer becomes less flexible and its hardness increases. In order to promote the cross-linking properties between polymers chain, an agent will be added into the polymer solution. So, acetic acid is added since both PVA and starch are the biopolymers and it would act as the monomer which cross-linked by hydrogen bonding between both PVA and starch [6]. The flexibility of the biopolymer film is further decrease while its hardness is further increase by adding the filler.

As we can see from the graph, the best percentage of DS value for kaolin, bentonite and nanoclay is at the 4 wt.% because when the amount of fillers added into the biopolymer film is increasing, more hydrogen molecules will be able to form the hydrogen bonding between cross-linker polymer network of the biopolymer film. However, the best percentage DS value for halloysite is at 2 wt.% but since halloysite has the highest number of hydrogen molecules compare to the other fillers, it is bonded and exhibited

more structured cross-linked between the biopolymer network which the make the biopolymer film has the lowest swelling properties.

The optimum percentage of DS value for halloysite is at 2 wt.% while towards 3 wt.% and 4 wt.%, the percentage of DS values are suddenly increase. This is because halloysite exhibit a similar composition as kaolin except that it contains additional water molecules between the alumino-silicate layers with a hollow tubular and cylindrical structure that is formed by tetrahedral sheet of silica and octahedral sheet of alumina which turn it to cylindrical shape [44]. At 2 wt.%, the amount halloysite at this much is the most optimum because halloysite nanotubes will form a covalent bond with the citric acid through hydrogen bond which then cross-linked the polymers chain. However, as the amount of halloysite added into the biopolymer solution increases to 3 wt.%, there will be more halloysite nanotubes available which attracts more citric acid molecules to form a covalent bond and subsequently less cross-linkers are available to bond with the polymers chain.

4.2 Percentage of Water Solubility

The dissolution of polymers in a solvent may take up several days or weeks and not all polymers can be dissolved. It was discovered that the water solubility of polymers in solvent depends not only on their physical properties, but also on their chemical structure, such as polarity, molecular weight, branching, crosslinking degree, and crystallinity. Figure 11 below shows the water solubility percentage of the biopolymer films added with 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% of 4 different fillers.

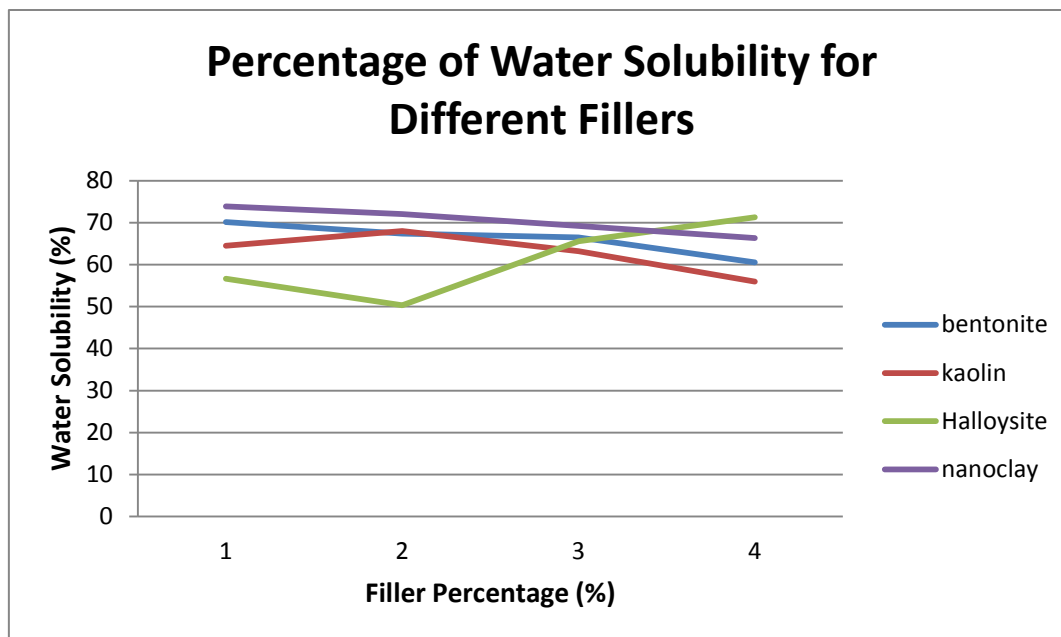


Figure 12: Percentage of water solubility for different fillers.

From the graph, it shows that as we increase the amount of fillers added into the biopolymer films, the percentage of water solubility is decreasing. The trend of the graph is the same as the percentage for DS values which shows the biopolymer film has the best percentage of water solubility when 2 wt.% of halloysite is added while other fillers are 4 wt.%.

Water solubility can be defined as the maximum amount of the chemical substance which in this case is the biopolymer film that will dissolve in pure water at specified temperature. The molecular weight of polymers plays an important role in their water solubility. It was discovered that in a given solvent at a particular temperature, as molecular weight increases, the solubility of a polymer decreases [45]. This same behavior is also noticed as crosslinking degree increases, since strongly cross-linked polymers will inhibit the interaction between polymer chains and solvent molecules, preventing those polymer chains from being transported into solution.

Table 7: Chemical formula and molecular weight of each material

Materials	Chemical formula	Molecular weight (g/mol)
Water	H ₂ O	18.02
Kaolin	Al ₂ Si ₂ O ₅ (OH) ₄	258.168
Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄ .2H ₂ O	294.2
Bentonite	Al ₂ O ₃ .2(SiO ₂).H ₂ O	240.152
Nanoclay	Al ₂ O ₆ SiH ₂	180.1

Table 7 shows the molecular weight of the fillers and we can see that halloysite has the highest of value of molecular weight which is 294.2 g/mol followed by kaolin, bentonite and nanoclay which are 258.169 g/mol, 240.152 g/mol and 180.1 g/mol respectively. Thus, it clearly shows that as the molecular weight of the biopolymer film is increase, its water solubility properties also decreases. This is because as the molecular weight of the biopolymer film is increased, the crystalline regions in the biopolymer structure will become compacted as the filler acts as a resistor in the matrix to prevent the water molecules from penetrating into the biopolymer network.

4.3 Surface Morphology under SEM

Figures 13, 14, 15 and 16 below show the surface morphology of bentonite, halloysite, kaolin and nanoclay respectively at 4 wt.% under SEM.

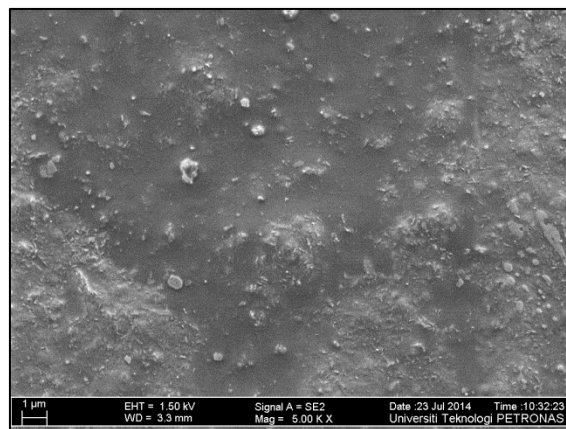


Figure 13: 4 wt. % Bentonite with 5.0 k magnification

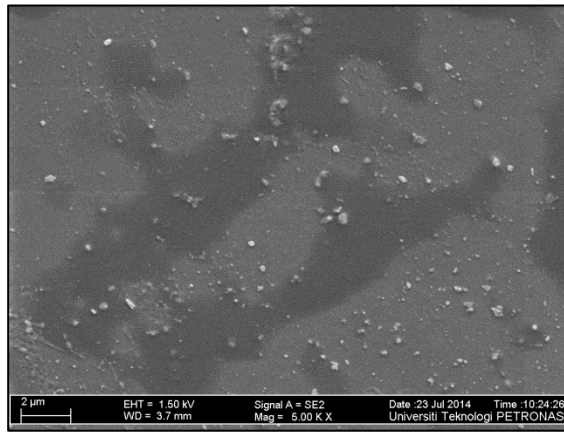


Figure 14: 4 wt. % Halloysite with 5.0 k magnification



Figure 15: 4 wt. % Kaolin with 5.0 k magnification

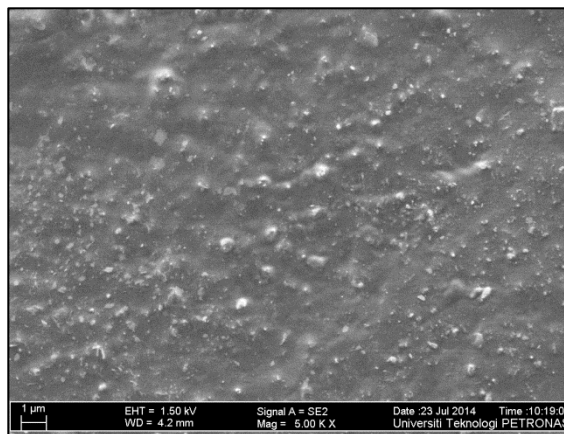


Figure 16: 4 wt. % Nanoclay with 5.0 k magnification

From the result of both degree of swelling and water solubility, it shows that at 4 wt.% of fillers added into the biopolymer film, kaolin exhibited the best result followed by bentonite, nanoclay and halloysite. These films are then put under the SEM in order to observe the surface composition and topography.

As shown from figures above, the distribution of biopolymer film structure for 4 wt.% of kaolin has the most uniform and well-dispersed compared to the other fillers. At this amount, the kaolin almost perfectly filled the entire biopolymer area and it formed the hydrogen bonds between the citric acid and hold the polymer chains [35]. Both 4 wt.% nanoclay and 4 wt.% bentonite have irregular and rougher surface compared to 4 wt.% kaolin and 4 wt.% halloysite.

However, 4 wt.% halloysite has a very smooth surface topography just like the 4 wt.% kaolin but from Figure 14, it clearly shows that the presence of immiscible system whereby two different chemical structures are not chemically mixed together [35]. This result indicates that excess amount of halloysite was added into the biopolymer solution. The halloysite molecules are failed to cross-link with the polymers chain and did hydrogen bond with the citric acid molecules.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The slow release fertilizer (SRF) technology had been further improvised in order to reduce the negative impact to the environment as well as minimizing the cost production of urea fertilizers. This project seems really important as it deals with one of the way to improve the technology of fertilizers industries as well as minimizing the negative impact from fertilizers to the environment. In order to produce a best slow release fertilizer, it would be depends on the type of its coating material. This study is aiming to produce a green technology for the fertilizers industries which is a biopolymer coating material that is an environmental friendly coating material.

Both starch and PVA are biopolymers that have been widely used nowadays. In order to exhibit a cross-link between those two polymers chain, citric acid must be added so that the polymers chain would be cross-linked by the hydrogen bond. However, the degree of swelling, water solubility and surface roughness are the most important criteria that a coating material should have. Therefore, this project research is carried out to achieve desired properties of biopolymer coating material for urea fertilizers.

This project is relevant to its objective, which is to identify the best filler to be mixed with the biopolymer solution in order to formulate a coating material that has the best properties in term of degree of swelling, water solubility and surface roughness. The favorable characteristic of biopolymer film as a coating material for urea fertilizer must has the abilities to resist the swell and has low water solubility. As the film is immersed into the water, the water molecules will be in contact with the film surface and then slowly penetrating into the polymeric network. The film will start expanding or swelling and subsequently allowing more water molecules to penetrate within the biopolymer network. However, the coating material would not simply dissolve after swelled as the crystalline regions in the biopolymer structure are compacted and the filler acts as a resistor in the matrix. A good coating material would have a weak swelling property as well low degree of water solubility. Furthermore, the material also must have a smoother surface topography so that the releases of fertilizers through the coating material have the same rate.

The result shows that 2 wt.% halloysite has the lowest percentage of degree of swelling and water solubility compare to the other fillers. However, for the result of surface topography under SEM also shows that kaolin has smoother surface compared to the other fillers at 4 wt.%. The results and discussion in the previous chapter proved that the addition amount of bentonite, halloysite, kaolin and nanoclay added into the biopolymer solution did improved the percentage of water solubility, degree of swelling of the film. Therefore, it can be concluded that the expected result and the objectives of this project is successfully achieved.

As for recommendations, this project can be further improvised by increasing the number of test in when analyzing the percentage of degree of swelling and percentage of water solubility. The test should be done at least 3 times so that any inappropriate data can be identified and the test can be repeated. Method of preparing the biopolymer solution also must be alter by allowing more heating time of the PVA in the deionized water so that the PVA will be fully dissolved in the deionized water before proceed to the next step. Before that, the step of putting the PVA into the heating flask must be very carefully handled in order to prevent the PVA from melt due to the hot water vapor and immediately stick to head of the flask. Moreover, the filler must be stir vigorously in the deionized water so that it will dissolve completely before pour into the PVA solution.

This project also can be continued in the future by adjusting the ratio of PVA/citric acid/starch. Besides, the amount of fillers added into the biopolymer solution can be increased to more than 4 wt.% so that a better biopolymer film as coating material might be produced. There are many other types of filler and additives that are available which have better molecular structure and more economically feasible that can be used to be mixed with this biopolymer solution to produce the coating materials for urea fertilizers.

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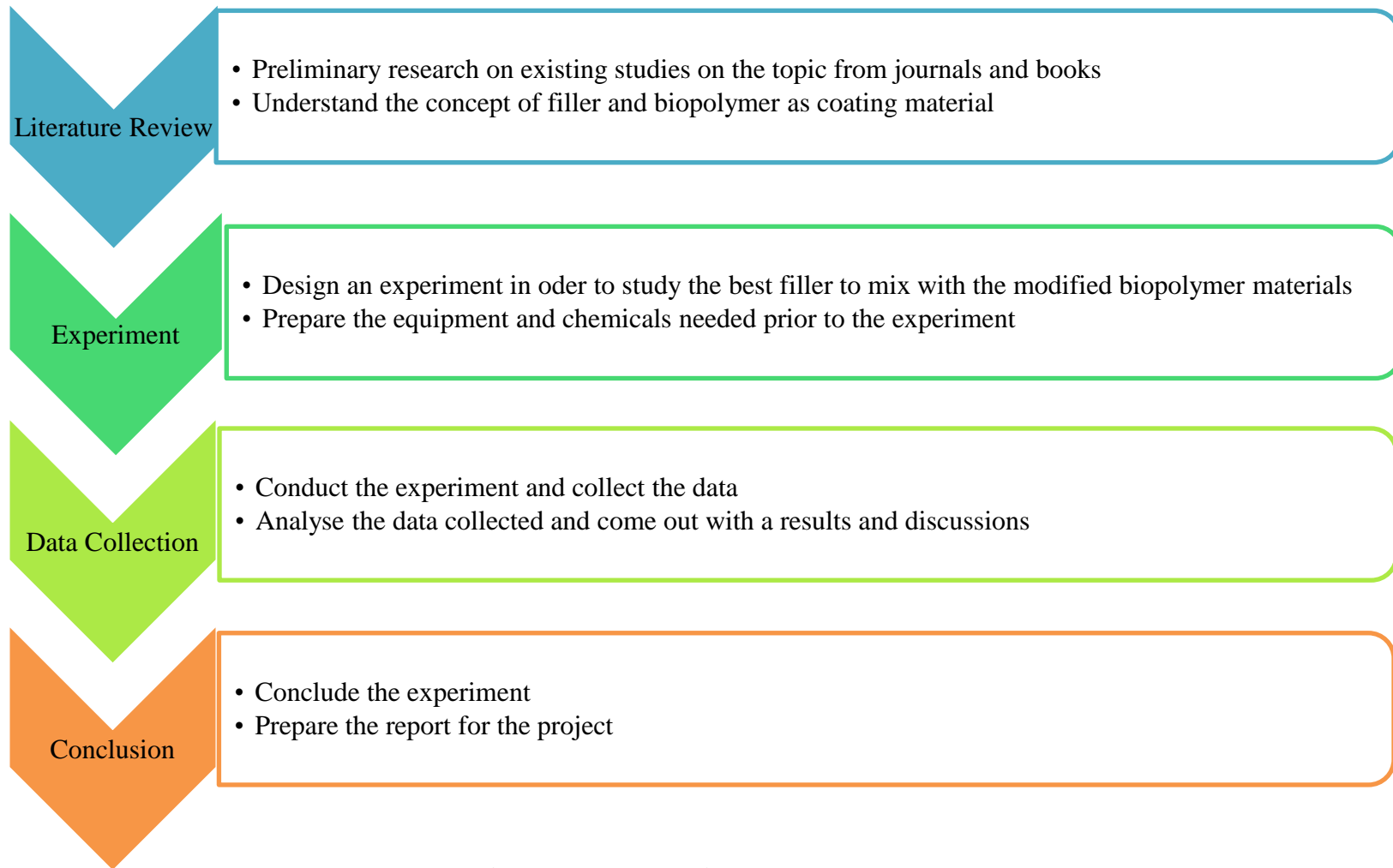
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CHAPTER 7: APPENDICES

APPENDIX I: Project Flowchart

APPENDIX II: Gantt Chart and Key Milestone for FYP I

APPENDIX III: Gantt Chart and Key Milestone for FYP II



APPENDIX I: Project Flowchart

No	Detail work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■												
2	Preliminary Research Work			■	■	■	■	■							
3	Submission of Extended Proposal								●						
4	Proposal Defence									●					
5	Project Work Continues								■	■	■	■	■		
6	Submission of Interim Draft Report													●	
7	Submission of Interim Report														●



Process



Suggested Milestone

APPENDIX II: Gantt Chart and Key Milestone for FYP I

No	Detail work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■								
2	Submission Progress Report								●							
3	Project Work Continues								■	■	■	■	■			
4	Pre - EDX											●				
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)															●

 Process
  Suggested Milestone

APPENDIX III: Gantt Chart and Key Milestone for FYP II