

SYNTHESIS AND SWELLING BEHAVIOUR OF OIL PALM EMPTY FRUIT
BUNCH BASED SUPERABSORBENT POLYMER COMPOSITES

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ABSTRACT

Polyacrylamide-graft-oil palm Empty Fruit Bunch (PAM-g-EFB) SAP was synthesized using graft copolymerization method of acrylicamide (AM) monomer onto EFB backbone with ammonium persulphate (APS) as an initiator and N,N'-methylenebisacrylamide (MBA) as cross-linker to assist the process. Determination of water absorbency was tested using tea bag method after immersed in distilled water. The effects on amount of initiator, cross-linker and filler towards water absorbency were studied to determine the optimum condition of EFB-g-PAM SAP. The maximum water absorbency was 263g/g, 223g/g and 250g/g when the optimum condition for initiator (APS), crosslinker (MBA) and filler (EFB) were at 10wt%, respectively. The characterization of the EFB-g-PAM SAP was characterized by FTIR spectroscopy while thermal stability was indicate using TGA.

ABSTRAK

Polyakrilamida-cantum-serabut tandan kosong buah kelapa sawit (PAM-g-EFB) SAP disintesis menggunakan kaedah pengkopolimeran cantuman akrilamida (AM) monomer ke atas tulang belakang EFB dengan ammonium persulfat (APS) sebagai pemula dan N'N'-metilenabisakrilamida (MBA) sebagai pemautilang dalam membantu proses. Kebolehan daya serap air diuji menggunakan kaedah 'tea bag' selepas direndam dalam air suling. Pembolehubah seperti kuantiti pemula, pemautilang dan pengisi ke arah daya serap air dikaji untuk menentukan keadaan optimum EFB-g-PAM SAP. Daya serap air maksimum ialah 263g / g, 223g / g and 250g / g apabila keadaan optimum untuk pemula (APS), pemautilang (MBA) dan pengisi (EFB) berada pada 10wt%, masing-masing. Analisa struktur kimia EFB-g-PAM SAP telah dianalisa menggunakan spektroskopi FTIR manakala kestabilan haba dikenalpasti menggunakan TGA.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Superabsorbent polymers (SAP) are basically the materials that can absorb fluids, such as water, brines and blood, greater than their original weight, either under load or without load by forming a gel. It consists of loosely cross-linked, three-dimensional networks of flexible polymer chains that carry dissociated, ionic functional groups (Kiatkamjornwong, 2007). There are two types of SAP which are synthetic (petrochemical-based) and natural. The graft copolymerization of vinyl monomers on polysaccharides are the example of the natural based SAP where usually been prepared through addition of some synthetic parts onto the natural substrate. The greatest volume of SAP comprises full synthetic or of petrochemical origin which produced from the acrylic monomers, frequently used are acrylic acid (AA) and acrylic amide (AM) (Zohuriaan-Mehr and Kabiri, 2008). Moreover, SAP is used as an absorbent for water and aqueous solutions in the applications of hygiene products such as disposable diapers and also agriculture for example in soil conditioner.

Based on Zhang et al., (2006), among many others, AM is the most frequently used non-ionic monomer in preparing SAPs. AM is better in salt resistance performance, high capability for water absorption and biocompatibility which is non-toxicity when exposed to the body or body fluids (Marandi *et al.*, 2008). On the other hand, synthetic polymer based SAPs like AAm are poor in degradability especially for applications in agriculture and horticulture, though, they alone do have large fluid absorbing capacities (Xie and Wang, 2008).

Oil palm production in Malaysia is a major producer to the world and empty fruit bunches are one of the major solid wastes. Most commonly used for composite materials are oil palm empty fruit bunch (EFB) since it consists of fibers for a bunch and at low cost. EFB consists of 65% cellulose, 19% lignin and very low ash content through chemical analysis. Biocomposites are the materials made by combining natural fiber and non-biodegradable polymer which produce product to be more eco-friendly and known as green composites (John and Thomas, 2008). The main drawback of EFB is the degradation of properties when expose to moisture and degrading organism. However, acetylated EFB shown good performance when exposed to moisture and decay organisms (Hill *et al.*, 1998). So, EFB is a good to be used as a filler because of its highly biodegradation. Moreover, the conventional method of burning EFB for disposal purpose often creates environmental problems in that it generates severe air pollution. Hence, turning EFB abundant supply from oil palm industry by-products into value-added products will be beneficial to economic utilization (Jamaludin and Hashim, 2011).

Synthesis and manufacture of new polymeric materials which are friendlier to environment have been carried out by many researchers (Abdel-Rehim *et al.*, 2004). Besides, the SAP is prepared by utilizing the modifications of natural materials such as starch, and cellulose (Shuhadah *et al.*, 2009). Previously, there was research on preparation of SAPs using graft copolymerization of poly [acrylamide(PAAm)/ acrylic acid(PAA)] onto EFB. So, to modify and improve various properties in the original vinyl monomer polymer such as elasticity, absorbency, ion exchange capabilities, thermal resistance and hydrophilicity, grafting of vinyl monomer such as acrylic amide onto EFB may be used (Ibrahim *et al.*, 2005). Hence, the production cost and accelerates the generation of new materials for other applications can be posses by the synthesis of EFB-g-PAAm SAPs which will enhances the swelling ability.

1.2 PROBLEM STATEMENT

Many kinds of SAP with improved properties have been developed. SAP made from synthetic polymers posses excellent characteristics, but the limitations of these materials in comparison to natural based ones seems to be worth noting where it

contains toxicity and non-degradability might pose environmental problems and limit their uses. So, by using EFB in synthesizing the SAP can reduce the cost and also make the SAP based EFB more biodegradable than synthetic SAP.

1.3 OBJECTIVES

The main objectives of this research is to study the optimum conditions of oil palm empty fruit bunch (EFB) based on the superabsorbent polymer (SAP) by determine:

- a) Effect on amount of initiator towards water absorbency.
- b) Effect on amount of cross-linker towards water absorbency.
- c) Effect on amount of filler towards water absorbency.

1.4 SCOPE OF STUDY

The scopes of study of this research are:

- a) Material
 - i. EFB was used as filler.
 - ii. Ammonium per sulphate (APS) used as an initiator.
 - iii. Cross-linker used was N^oN^o-methylenebisacrylamide (MBA).
- b) Technique
 - i. The technique used in this research was solution polymerization.
- c) Characterization
 - i. The sample was characterized using FTIR (Fourier Transform Infrared) spectroscopy, TGA (Thermal Gravimetric Analysis) and SEM (Scanning Electron Microscope).
- d) Water Absorbency Testing
 - i. The tea bags method was used for the water absorbency measurement.

1.5 SIGNIFICANCE OF STUDY

Superabsorbent polymer composite (SAP) from oil palm empty fruit bunch (EFB) will become a new materials to be used in the application of agriculture, sanitary goods and horticultural. The significant of this research can reduce overall cost to produce SAP with the same quality as synthetic SAP since EFB is residue where it can be found easily at the palm oil mill around Malaysia. The addition of this research is the SAP produced has biodegradable element and reducing the environment problems and protect the earth. The swelling ability of this SAP also increases compare to the synthetic SAP proven by the recently research that had been done.

CHAPTER 2

LITERATURE REVIEW

2.1 SUPERABSORBENT POLYMER COMPOSITE (SAP)

There are two types of SAP which are synthetic (petrochemical-based) and natural. The graft copolymerization of vinyl monomers on polysaccharides are the example of the natural based SAP where usually been prepared through addition of some synthetic parts onto the natural substrate. According to Zohuriaan-Mehr and Kabiri (2008), superabsorbent polymers are slightly cross-linked hydrophilic polymers with a three-dimensional network structure which are capable of absorbing and retaining large amounts of aqueous fluids even under some pressure. Desired features of superabsorbent polymer (SAP) are high swelling capacity, high swelling rate, and good strength of the swelling gel. SAP hydrogels also known as polymeric materials which exhibit the ability of swelling in water and retaining a significant fraction of within their structure without dissolving in water or aqueous solution (Brannon-Peppas and Harland, 1990; Buchholz and Graham, 1998). Absorption capacity of common hydrogels usually not more than 100% (1g/g) but superabsorbent hydrogels can absorb deionized water as high as 1000-100000% (10-1000g/g) which can be seen on Figure 2.1. (Omidian *et al.*, 2004).

Moreover, after water absorption and swelling, SAP particle shape (granule, fibre, film, etc) has to be basically preserved, which the swollen gel strength should be high enough to prevent a loosening, mushy, or slimy state. Traditional absorbent materials such as tissue, papers and polyurethane forms unlike SAP, will lost most of their absorbed water when they are squeezed. Comparisons of water absorptiveness of

some common absorbent materials with a typical sample of a commercially available SAP nowadays are shown in the Table 2.1.

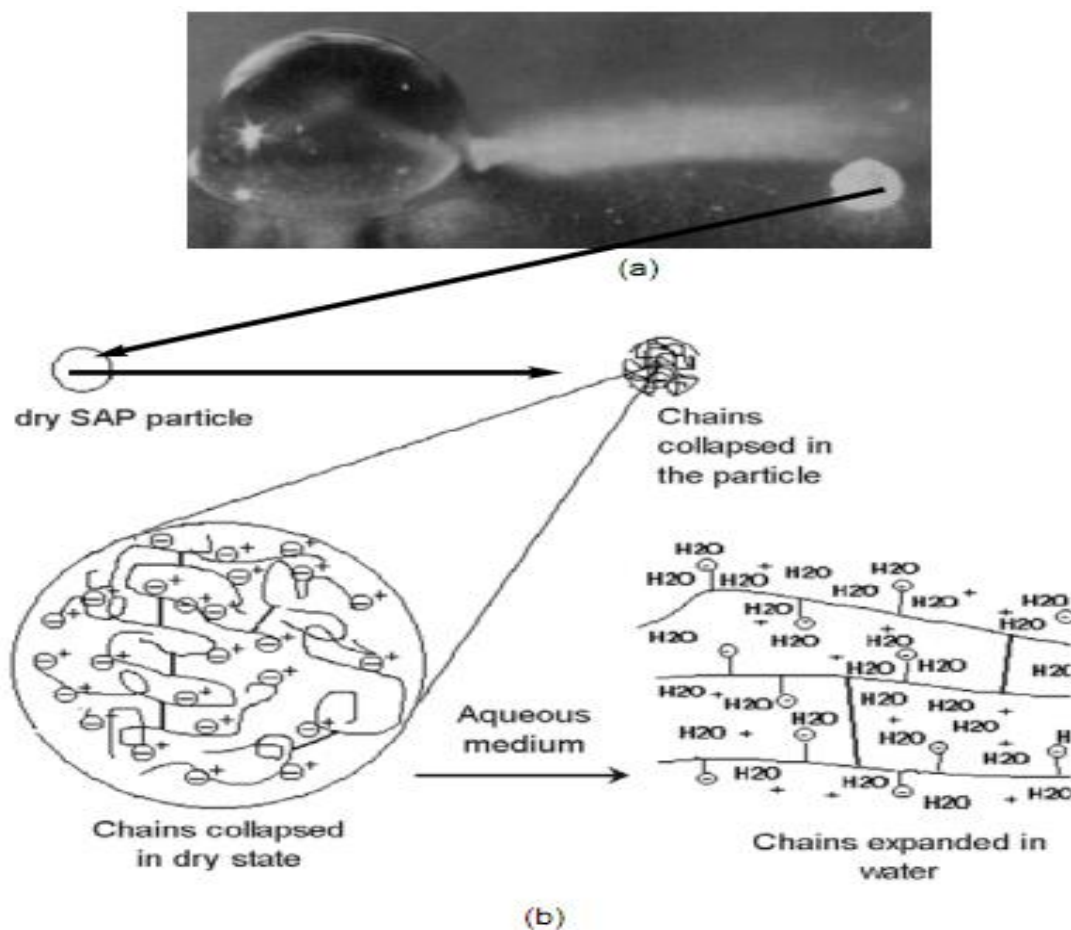


Figure 2.1: Comparison of dry SAP with swollen SAP and schematic of the SAP swelling

Absorbent Material	Water Absorbency (wt %)
Whatman No. 3 filter paper	180
Facial tissue paper	400
Soft polyurethane sponge	1050
Wood pulp fluff	1200
Cotton ball	1890
Superab A-200 ^a	20200

Table 2.1: Water absorbency of absorbent materials

2.1.1 Natural based SAP

Kiatkamjornwong et al., 2010, used cassava starch for polymer substrate, acrylamide, AM as a grafting monomer, potassium persulfate, KPS as initiator and N,N'-Methylenebisacrylamide (MBA) as crosslinker. The water absorbency of cassava starch-g-polyacrylamide which has been saponified in this experiment was 605 g/g. However, when the testing for the comparison of inorganic filler the bentonite clay SAP showed the highest water absorption of 730g/g among the China clay, 650g/g and silica, 310g/g. From the study, it shows that the pure SAP without inorganic filler still can produce high water absorbency of 605g/g but when filler was added it helps in improving the capacity of the water absorbency.

Soy and fish proteins are converted to SAP through modification by ethylenediamine tetraacetic dianhydride (EDTAD). The amino groups of the protein was crosslinked by glutaraldehyde to produce SAP. The dry gel of SAP was capable to absorb 80-300g of deionized water/g after centrifugating at 214g. The capability of SAP was depending on the extent modification, protein structure, cross link density, protein concentration and environmental conditions like pH, ionic strength and temperature (Hwang and Damodran, 1996). This research show the protein after modification could be used as polymer substrate and produce SAP with high absorption.

Starch phosphate-graft-acrylamide or attapulгите superabsorbent composite was prepared by graft-copolymerization among starch phosphate, acrylamide, and attapulгите in aqueous solution. The factors influencing water absorbency of the superabsorbent composite such as the molar ratio of NaOH to AM and the amount of starch phosphate and attapulгите were studied. Hence, the superabsorbent composite achieved the highest equilibrium water absorbency of 1268 g/g when the molar ratio of COO^- , COOH , and CONH_2 is 10:3:11, the weight ratio of AM to starch phosphate is 5:1, and 10 wt% attapulгите was incorporated. In this research, the results show that the phosphorylation of starch and the introduction of attapulгите could greatly improve equilibrium water absorbency superabsorbent composite (Raju *et al.*, 2005).

According to the research Wang and Li, 2005, water absorbency on synthesis of superabsorbent composites based on acrylic acid, acrylic amide, or inorganic clay mineral (attapulgite) was studied. When composition of 0.2% cross linker, 1.0% initiator and 10% attapulgite, the water absorbency of higher than 1400g H₂O/g, 110g H₂O/g and 0.9% NaCl. The superabsorbent contains attapulgite show higher water absorbency than polyacrylic acid-co-acrylamide. This study proved that superabsorbent composite material had improved the absorbency than the pure SAP.

The effects of vermiculite content on water absorbency were studied in a series of superabsorbent composites were synthesized by copolymerization reaction of partially neutralized acrylic acid on unexpanded vermiculite (UVMT) micropowder using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator in aqueous solution. The equilibrium water absorbency increased with increasing UVMT content and the concentration of 20 wt % clay gave the best absorption of 1232 g/g in distilled water and 89 g/g in 0.9 wt.% NaCl was obtained. In this research, the UVMT helps in improving the absorbency of water and also saline solution (Zheng *et al.*, 2007).

2.2 OIL PALM EMPTY FRUIT BUNCH (EFB) AS FILLER

According to Shinoj *et al.*, 2011, the lignocellulosic materials are from the excess of oil palm tree which can be extracted from oil palm fronds, trunks and also empty fruit bunch. EFB is the fibrous mass left after separating the fruits from fresh fruit bunches where it has 73% fibers among the various source in oil palm tree. However, these waste materials will cause tremendous environmental problems when left in field. Furthermore, the additional advantage of natural fiber than glass fiber is that it can be composted at the end of their life cycle.



Figure 2.2: Oil Palm Empty Fruit Bunch Fibrous

From the research of Jawaid et al., 2010 about the hybrid composites made from OPEFB/jute fibres, the hydrophilic properties of lignocellulosic materials and capillary action will cause the intake of water when the samples were soaked into water. It is observed that the thickness swelling for the pure EFB composite with the value of 9.12% was the highest among different types of composite. Next is the highest water absorption among the different type composite is pure EFB with the value of 21.39%. It shows that the high porosity on the surface of pure EFB composite.

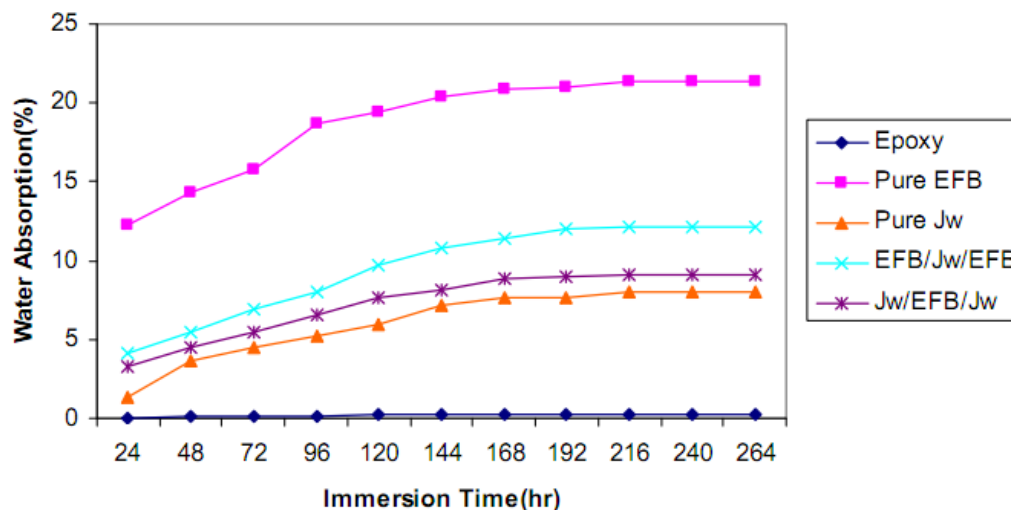


Figure 2.3: Water absorption (%) of oil palm EFB/Jute(Jw) reinforced hybrid composites

The water absorption behaviour of the polymer composite depends on the ability of the fibre to absorb water due to the presence of hydroxyl groups. Here the study shows that the pure EFB has higher potential than pure jute mate and hybrid composite (EFB/jute mate) in water absorption, this reason strengthens the usage of EFB as filler in this research.

2.2.1 Polymerization of EFB based SAP

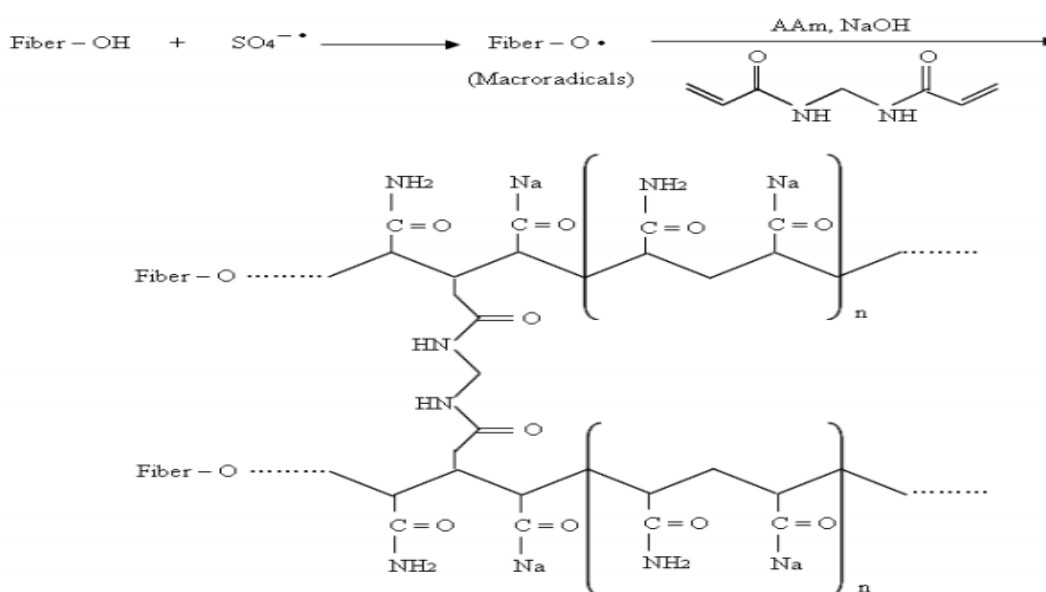


Figure 2.4: Synthesis of EFB-g-PAAm SAP

Figure 2.4 shows the mechanism for crosslinking graft polymerization of acrylamide, AM onto EFB backbones with the presence of initiator, ammonium persulphate, APS, and crosslinker, N-N' Methylbisacrylamide, MBA. Firstly, APS, the thermally dissociating was decomposed under heating of 60°C to generate sulphate radicals which also known as chain carriers. Polymeric materials containing cellulose, -OH and C-H sites are the active centers for grafting of polymeric chains onto the natural fibres backbone (Sigha *et al.*, 2008). Hence, the radical abstracts hydrogen from one of the existing hydroxyl groups in EFB backbone to form the matching macro-initiator, implying to the formation of alkoxy. C-O-C, radicals on the substrate.

After that, these macro-radicals initiate a radical polymerization of AM grafting onto the EFB backbones. Then, the active centers of EFB backbone were radically liberating the graft polymerization. In addition, the hydrolyzed amide groups in PAM were converted into carboxylate groups during neutralization which carrying negative charges. Lastly, these negatively charged groups are susceptible to the MBA where the crosslinking occurs and SAP was obtained which contain characteristic for both EFB and PAM (Jamaludin and Hashim, 2011).

2.3 POLYACRYLAMIDE AS MONOMER

According to Zhang et al., (2006), one type of water soluble polymers is polyacrylamide which it can be either dissolve to form a solution or swell in water to form a hydrogel. Presello (2006) stated said that the positioning sufficient numbers of hydrophilic functional group, amide (-CONH₂), along the backbones of side chains of polymers is the factor of its solubility. Based on research Klimchuk (1991), polyacrylamide which is the basis of the acrylamide-based polymers and derivatives can be synthesized in a few techniques. It can be synthesized via free radical polymerization technique which includes bulk, suspension, solution, emulsion, inverse emulsion and also precipitation.

Due to better salt resistance performance and its capability for water absorption and biocompatibility with non-toxicity when exposed to the body or body fluids (Marandi *et al.*, 2008) have been proven that AM is widely used in preparing SAP. So that, AM is used in the preparation of EFB based SAP in this research.

2.4 TECHNIQUE OF POLYMERIZATION

The polymerization techniques often used in preparing superabsorbent polymer (SAP) either by solution or suspension polymerization. Each of the techniques has its own advantages and disadvantage depends on the product been produced. The mechanism in preparation of SAP was shown in Figure 2.5.

According to Zohurian-Mehr and Kourosh (2008), the solution technique frequently used for SAP preparation is a free radical initiated polymerization of acrylic acid (AA) and its salts, acrylic amide (AM) with a cross-linker. Before or after the polymerization step, the carboxylic acid groups of the product are partially neutralized. There are few types of initiation often carried out by reaction of reducing agent with an oxidizing agent (redox system), or chemically with free radical azo or peroxide thermal dissociation species. The process of AA and AM with a water soluble cross-linker, e.g., N'N'-methylenebisacrylamide (MBA) in an aqueous is a straight forward process. The reactants at desired concentration about 10-70% are dissolved in water and a fast exothermic reaction yields a gel-like elastic product. Then, the product is dried and sieved to obtain the required size particles. Based on study by Kiatkamjornwong (2007), stated that the major advantage of the solution polymerization is the presence of solvent serving as a heat sink. A great variety of hydrogels has been synthesized where the SAP can be made pH-sensitive or temperature-sensitive by using solution polymerization method.

From the research of Zohurian-Mehr and Kourosh (2008), the suspension polymerization is also referred as inverse suspension because the process is water-in-oil (W/O) has been chosen. The monomers and initiator are dispersed in the hydrocarbon phase as a homogenous mixture. Each particle contains all the reactive species when the initiator dissolves in the aqueous phase and behaves like an isolated micro-batch polymerization reactor. According to Kiatkamjornwong (2007), the mixture is thermodynamically unstable and being stabilized by addition of stabilizer. Besides, the SAP with high swelling ability and fast absorption kinetics is the production of inverse suspension where it is a highly flexible and versatile technique. The products from the continuous organic phase are easily removed by filtration or centrifugation. Furthermore, it is an advantageous method because the products obtained as powder or microspheres (beads) and grinding is not required.

However, the solution method may often preferred by manufacturers for a general production of SAP with acceptable swelling properties, the less expensive and faster techniques rather than suspension techniques.

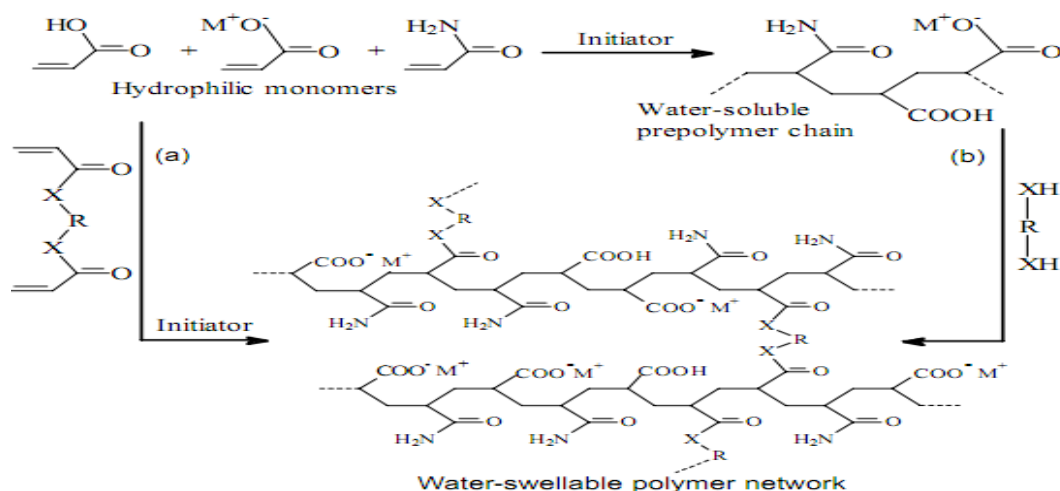


Figure 2.5: The mechanism in preparation of SAP

2.5 EFFECT OF INITIATOR

According to Ibrahim et al., 2003 and 2005, the extent of grafting increases with the amount of initiator and up to certain limit then the graft will decrease. When increasing the initiator concentration, the free radicals also increase, which enhanced the possibility of initiating reactive site of backbone where PMMA (polymethyl methacrylate) can be grafted. The effect of the amount of H₂O₂ initiator is the percentage of grafting increased with an increase of the amount of initiator but decreased at higher amount.

The optimum percentage of grafting and efficiency are 187.3 and 40.0, respectively at 5.88mmol of initiator. Hence, with further increase of amount of initiator, the graft level is decreased. The decrease was expected since the decomposition of H₂O₂ increases the number of cellulosic fiber radicals, which terminated the before the addition of monomer. So, in this research, the initiator is used to investigate the effect on the water absorbency towards the initiator.

According to Kiatkamjornwong et al., 2006, the biodegradable superabsorbent polymers were prepared by the graft copolymerization between the gelatinized starch and acrylamide/itaconic acid via foamed solution polymerization using APS and

TEMED as an oxidation-reduction initiator and co initiator, respectively, and N-MBA as a crosslinking agent. Besides, the polymer synthesized with 1.0wt % APS gave the highest water absorption of 300g/g. However, when APS concentration was higher than 1.0wt%, the gel strength is reduced because the low molecular weight branches were grafted on starch backbone lead to decreasing of water absorption. In this study, it shown that the optimum conditions of initiator was 1.0wt% of APS to produce the highest water absorption.

2.6 EFFECT OF CROSS-LINKER

According to Mohan et al., 2005, in the polymerization process, the cross-linkers play an important role in the formation of three dimensional network structures permanently to the SAP. The swelling ratio of the superabsorbent polymers will be directly affecting by this factor. This research shows the water absorbency of the AM–NMA superabsorbent copolymer as a function of cross-linker concentration. The water absorbency of the SAP increases up to a certain level as the cross-linker concentration increases and then decreases with further increase in the concentration of the cross-linker. Due to decrease in space between the copolymer chains as the cross-linker concentration increases contribute to this behaviour in both the cross-linked SAP. Thus, the cross-linker was used in the research to determine the optimum condition of the SAP.

This research shows the biodegradable superabsorbent polymers were prepared by the graft copolymerization between the gelatinized starch and acrylamide/itaconic acid via foamed solution polymerization using APS and TEMED as an oxidation-reduction initiator and co initiator, respectively, and N-MBA as a crosslinking agent. Increasing the crosslinking agent concentration in the graft copolymerization enhanced the percentages of grafting efficiency, add-on, and grafting ratio. The optimum condition of the crosslinking agent N-MBA of 2.0 wt% gave the highest water absorption of 379g/g. Thus, too many crosslinking points of the crosslinking reaction enhanced the higher gel strength but reduced the water absorption. (Kiatkamjornwong *et al.*, 2006).

CHAPTER 3

METHODOLOGY

3.1 MATERIALS AND SOLVENTS

In this research the monomer used for the production of SAP were acrylic amide (AM), N'N'-methylenebisacrylamide (MBA) as crosslinker, and ammonium persulphate (APS) as initiator, was purchased from Sigma-Aldrich. EFB was purchased from Sabutek Sdn. Bhd. at Teluk Intan, Perak. The EFB was grounded using the laboratory scale grinder machine to less than 100 μ m particle sizes. After that, the particles were washed twice with hot distilled water followed by acetone. Then the EFB that has been washed was put in the oven at 10 $^{\circ}$ C for about 24hours until the weight was constant.

3.2 APPARATUS AND EQUIPMENT

For synthesis of SAP, the apparatus that have been used were 500ml five-neck round bottom flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. The samples were characterized using FTIR (Fourier Transform Infrared) spectroscope and TGA (Thermal Gravimetric Analysis).

3.3 RESEARCH DESIGN

This research design for this study was shown in Figure 3.1.

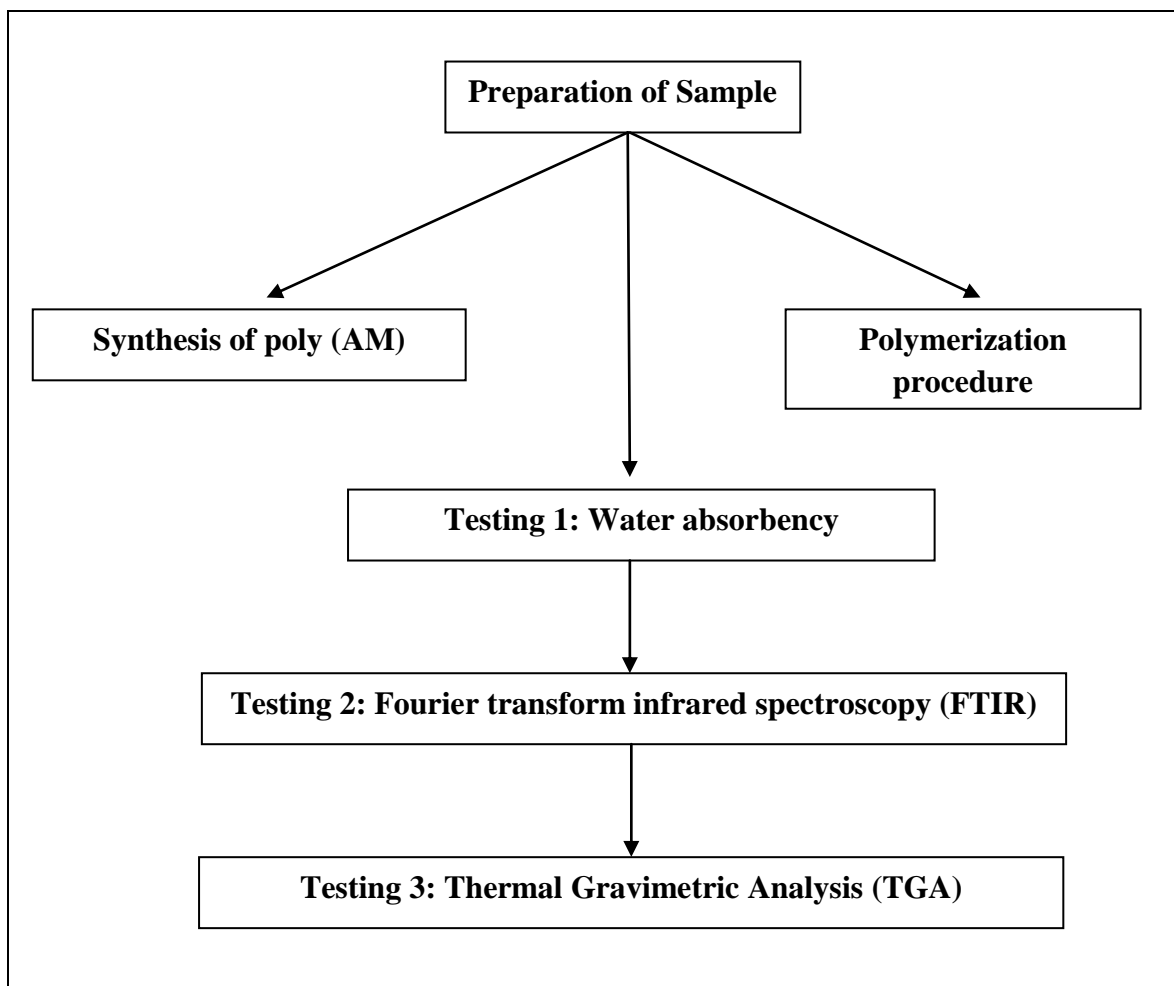


Figure 3.1: Research Design

3.4 PREPARATION OF SUPERABSORBENT POLYMER COMPOSITES

A series of samples by using fixed amount of AM and different amounts of EFB, cross linker, and initiator were prepared by the following procedure.

- i. Firstly, the synthesis apparatus, 500ml five-neck round bottom flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line, was set up in a water bath.
- ii. Then, an amount of 7.1g AM monomer (in 20ml distilled water) and 15mg MBA cross linker were introduced.
- iii. The mixture was stirred until MBA was dissolved completely and then 0.8g EFB was dispersed in the mixed solution.
- iv. After that, the solution was purged with nitrogen for 30min to remove the oxygen.
- v. Next, the mixed solution was heated to 40°C gradually and then 40mg APS, initiator was introduced to initiate the reaction. The solution was stirred vigorously and nitrogen atmosphere was maintained throughout the polymerization for 2h.
- vi. Lastly, 30ml of sodium hydroxide solution (2M) was added and the primary product was heated to almost 95°C for 1h. After saponification, the product was immersed in excess distilled water and then filtered for several times to remove unreacted reactants until pH7 was obtained.
- vii. An oven at 70°C was used to dry the product until constant weight before milled to a particle size range in 40-80mesh.
- viii. Steps 2 until 7 were repeated for different amount of initiator, cross-linker, and filler as shown in Table 2.

Sample	Initiator (APS) (wt %)	Cross-linker (MBA) (wt %)	Filler (EFB) (wt %)
1	2.5	0	0
2	5.0	0	0
3	10.0	0	0
4	15.0	0	0
5	25.0	0	0
6	0	2.5	0
7	0	5.0	0
8	0	10.0	0
9	0	15.0	0
10	0	30.0	0
11	0	0	2.5
12	0	0	5.0
13	0	0	10.0
14	0	0	15.0
15	0	0	30.0

Table 3.1: Different Amount of Parameters

3.5 PREPARATION OF PURE SUPERABSORBENT POLYMER

The procedure of preparation poly acrylic amide (PAM) superabsorbent polymer was similar to the procedure of the preparation superabsorbent polymer composite except EFB was omitted.

3.6 WATER ABSORBENCY MEASUREMENT

The measurement of water absorbency was performed by a tea bag method and the liquid absorbed was distilled water. The weight of the dry sample was marked as m_1 and weight of swollen sample as m_2 . A series of tea bags which contain weighed dry sample was immersed in the 200ml distilled water at the room temperature for 24hours.

Then, the swollen samples were filtered and hang up for 15minutes until no water drop. The ratio of the swelling was calculated using equation below:

$$\text{Water Absorbency ratio} = \frac{[m_2 - m_1]}{m_1} \quad (1)$$

3.7 CHARACTERIZATION

3.7.1 Fourier Transform Infrared Spectrometer (FTIR)

The samples were characterized using KBr disk pellets technique by FTIR, Nicolet Avatar 370 DTGS.

3.7.2 Thermal Gravimetric Analysis (TGA)

Thermal stability of samples were studied using TGA TAQ-500 with a temperature range 25-750°C at a heating rate of 10°C min⁻¹ using a dry nitrogen purge at a flow rate of 50ml min⁻¹.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 WATER ABSORBENCY CAPACITY

Table 4.1 shows the result of water absorbency

Sample	Initiator (APS) (wt %)	Cross- linker (MBA) (wt %)	Filler (Efb) (wt %)	Initial Weight, m_1 (g)	Final Weight + Filter Paper (g)	Final Weight, m_2 (g)	Water Absorbency (g/g)
0	0	0	0	0.5022	110.456	109.958	217.944
1	2.5	0	0	0.5021	80.063	79.560	157.456
2	5	0	0	0.502	109.673	109.171	216.472
3	10	0	0	0.5016	133.952	133.450	265.049
4	15	0	0	0.5031	113.045	112.541	222.696
5	25	0	0	0.5055	69.095	68.589	134.686
6	0	2.5	0	0.5023	98.065	97.562	193.231
7	0	5	0	0.5045	109.109	108.604	214.271
8	0	10	0	0.5017	113.699	113.197	224.627
9	0	15	0	0.5066	109.14	108.633	213.436
10	0	30	0	0.5045	85.385	84.880	167.246
11	0	0	2.5	0.5018	88.425	87.923	174.215
12	0	0	5	0.5015	111.585	111.083	220.502
13	0	0	10	0.5013	113.713	125.744	250.836
14	0	0	15	0.502	110.017	109.515	217.157
15	0	0	30	0.5016	70.098	69.596	137.748

Table 4.1: Water Absorbency of SAP

4.2 EFFECT OF INITIATOR

The amount of APS was varied from 2.5wt% to 25wt % was studied. The results on water absorption capacity were shown in Figure 4.1.

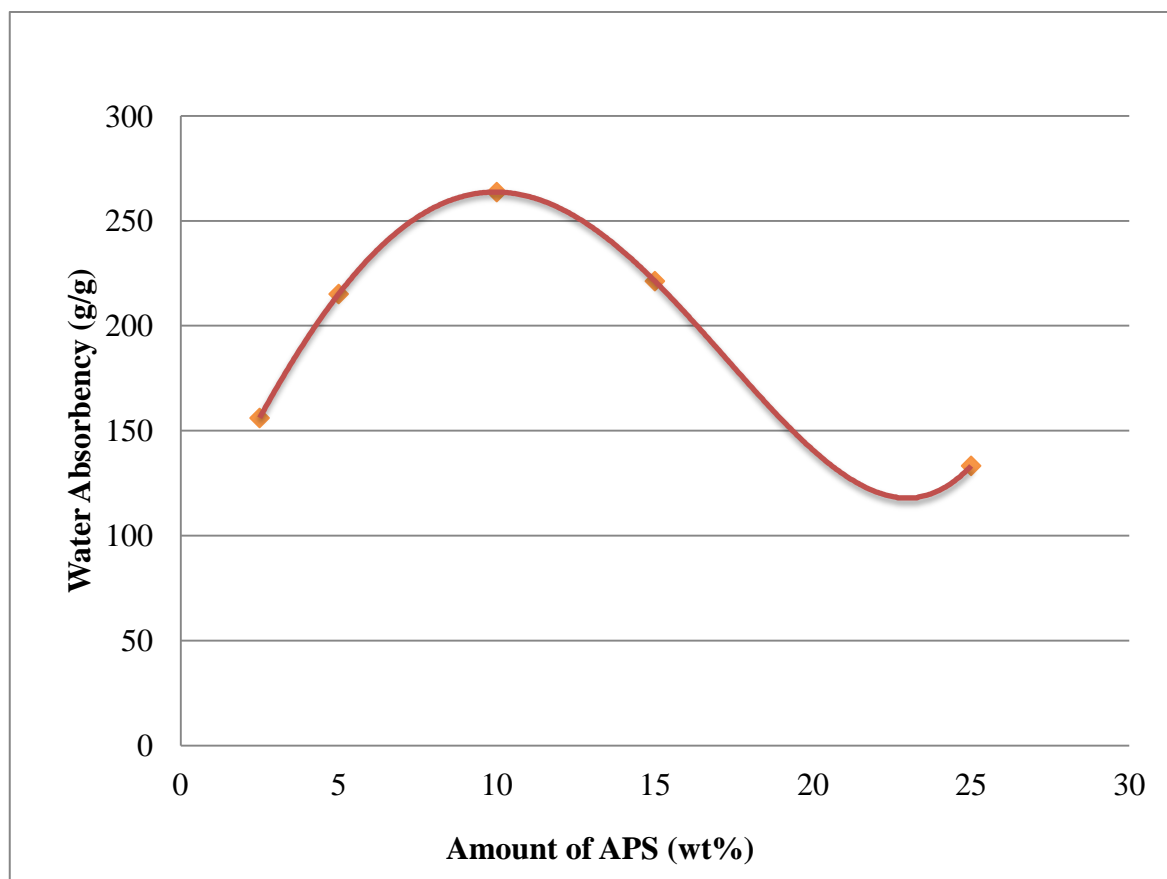


Figure 4.1: Effect of Initiator

From Figure 4.1, it can be seen that increases amount of initiator, the water absorbency was also increased, because of more graft polymerization occurred and more stable network structures were formed. The optimum content of APS was at 10wt% where it reached maximum water absorbency of 265g/g. However, further increasing of APS resulted in decreasing of water absorbency.

At low content, AM monomers could be grafted with help of the initiator in producing a large number of free-radical sites on EFB backbone. Thus, increasing the grafting yield lead to increases of the grafted points and the absorbency of polymer

increased with the initiator content increased (Li *et al.*, 2005 and 2008). When the concentration of the APS is below than 10wt%, theoretically, the graft polymerization reaction is in the slower rate where the network in the polymer is less which leads to the lower water absorbency than 10wt % (Wu *et al.*, 2003).

On the other hand, when the content of initiator is above the optimum point (10wt%), the polymerization reaction rates was faster, the mean kinetic chain length was decreased. Due to the generation of more radicals contribute to the smaller polymer network space which lead to the decrease of water absorbency of the synthesized SAP (Wu *et al.* 2003; Singha *et al.*, 2008).

4.3 EFFECT OF CROSSLINKER

The effect of the amount of MBA on water absorption capacity of the polymer was studied from 2.5wt% to 30wt% loading and the results were shown in Figure 4.2.

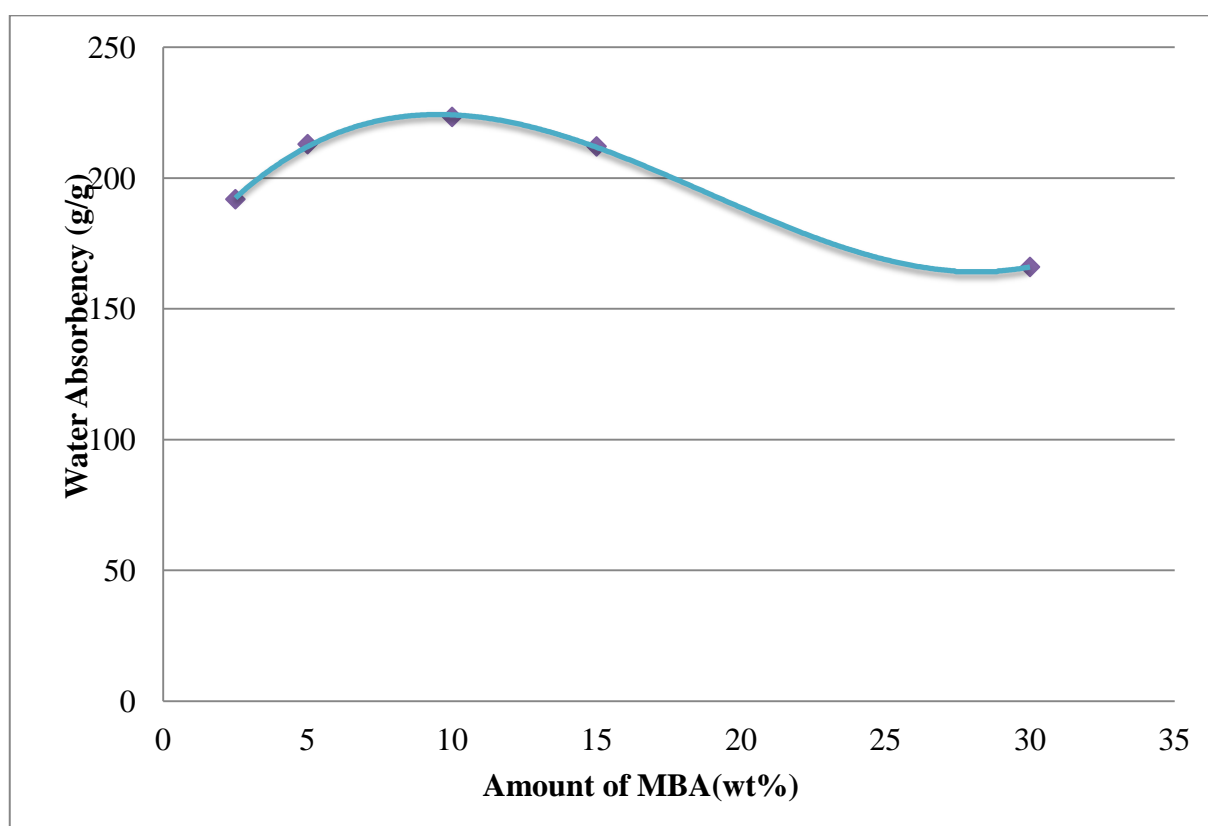


Figure 4.2: Effect of Crosslinker

From the Figure 4.2, the crosslinker content at 10 wt% showed maximum water absorbency of 224g/g. When the crosslinker exceed the 10 wt% amount, the water absorbency was decreased. From the result, a higher concentration of crosslinker produces a greater number of growing polymer chains, which involved in the formation of additional network. Therefore, increasing the crosslinker concentration decreased the water absorbency regarding to the available free volume within SAP system gets diminished and less water molecules can get through SAP network structure (Wu *et al.*, 2003). Similar phenomena have been previously reported by other researchers (Li *et al.*, 2005; Li *et al.*,2007).

On the other hand, when the crosslinker is lower than 10wt%, the low crosslinking SAP is unable to maintain the absorb water and might be dissolved easily when immersed in water. Thus, the result of the water absorption capacity of the SAP also low. This occurs may be due to few crosslink points where the fact of the cross-linkage network of SAP cannot be formed efficiently (Li *et al.*, 2005; Li *et al.*, 2007; Wu *et al.*, 2003). Hence, the concentration of the crosslinker should be higher than 10wt% because lower than that, such samples was semisoluble and almost represent as sol-gel state in water, where water cannot be tied in the network and the water absorbency can hardly be measured.

4.4 EFFECT OF FILLER

The influence amount of EFB varied from 2.5wt% to 30wt% on water absorbency of SAP system was studied and the results were shown in Figure 4.3.