CHAPTER 1

INTRODUCTION

This chapter provide the general ideals on the subject that are going to be study including background of study, problem statement, research objectives, scope of proposed study, expected outcome and significance of proposed study.

1.0 Background of Study

Superabsorbent polymer composites(SPC) has been defined as polymeric material which exhibit the ability of swelling in water and retaining a significant fraction of water within their structure, without dissolving in water (Zohuriaan and Kabiri, 2008). The absorbed water can be released slowly when the SAP is put in dry air to maintain the moisture of the environment. Most SPC are in principle crosslinked hydrophilic polymers. Because of these unique properties, SPC have many novel potential applications and highly demand form consumer in various areas. For example, superabsorbent polymer have been widely used in disposable diaper industry, agriculture and horticulture, sealing composites, artificial snow, drilling fluid additives, medicine for drug delivery system and others (Gohar et al., 2009).

Previous study (Zohuriaan and Kabiri, 2008) reported that polysaccharides and portein are the main part of the natural based superabsorbent hydrogels that contribute to their extraordinary ability, such as biocompatibility, biodegradation, non-toxicity and renewability. However, higher production costs and low gel strength superabsorbents of this material, restrict their widespread application. Therefore, in order to reduce the production cost as well as improve the strength and stiffness properties. Inorganic compounds with low cost can be introduce as a filler in the fabrication of SAP. Recently, some research used inorganic filler to advance the behavior of SPC, inorganic fillers like EFB as can be used as subtitution material (Molu et al., 2009).

Other than that, empty fruit bunches (EFB) is becoming a popular source of fuel for renewable energy power generation (Menon. N. R. Et al 2003). The rapid depletion of fossil fuel and most developed nations are pursuing the development of biomass as an alternative method of power generation. The oil palm is the dominant agricultural crop in many countries, Malaysia alone produces approximately 47% of the world supply of palm oil and can be considered the world's largest producer and exporter of palm oil (Mohammed et al., 2011). Malaysia has a ready source of biomass in EFB conveniently collected and available for exploitation in all palm oil mills. Currently, more than 3.88 million hectares of land are under oil palm cultivation and more than 368 palm mills operate in Malaysia (Idris et al., 2010).

As OPEFB can be found easily in Malaysia, there are many researches has been conducted to utilize and determine the properties of OPEFB (Aznizam and Azman., 2009; Lim and Zaharah., 2002). For example previous study by Shafinaz and Shahrir (2011) reported the synthesized technique of oil palm empty fruit bunch-graft-polyacrylamide (OPEFB-g-AA) superabsorbent polymer composites (SPC) by using N,N'-methylenebisacrylamide (MBA*)* and Ammonium persulphate (APS) as crosslinker and initiator, respectively, via solution polymerization method. Their study also reported on the variable that affect the swelling behaviours of OPEFB-g-AA SPC such as the effect of iniatior, crooslinker and filler concentration as well as solvent quantity and the degree of neutralization on water absorbency of OPEFB-g-AA-SPC. Based on ther osbervation, they reported that advance SPC composite better than pure SPC at 10% w/w of filler with the water absorbance at 573.27 g/g (Shafinaz and Shahrir., 2011).

1.1 Problem Statement

Malaysia is the largest palm oil producer, which contributes approximately 50% of the world palm oil production. According to Chiew.Y.L (2009), there is approximately 397 palm mills are operating in Malaysia. During the milling process, a fresh fruit bunch could produces 13% of fiber, 7% of shell and 23% of EFB. By using this ratio, the total 79.7 million tonnes of fresh fruit bunch in the year of 2006 could, generates~18.33 million tonnes of EFB. Most of the EFB currently were taken back to the plantation to mulch as organic fertilizers. However, a common problem that had been faced by industry is including the problem of EFB supply chain, characteristic of EFB (high moisture content and bulky) that causing inefficient combustion and difficulty in transporting for a plant that located far away from the heat demand (Jan.H and Joseph B.P., 2010).

The disadvantage of current synthesis of SPC nowadays is high production cost and non-biodegradable properties. This problem can be solved by using the inorganic filler for creating the properties of superabsorbent polymer. Empty Fruit Bunch (EFB) can be suitable filler as it is considerably cheap and can be found abundantly in Malaysia. Besides reducing the production cost, the presence inorganic filler such as EFB in polymer matrix also could increase the strength and stiffness properties of SAP as well as make it more environmental friendly.

1.2 Objective

To study the optimum condition of empty fruit bunch-graft-polyacrylic superabsorbent polymer composites by determine:

i. Effect on amount of initiator towards water absorbency.

ii. Effect on amount of crosslinker towards water absorbency, and;

iii. Effect on amount on inorganic filler, empty fruit bunch towards water absorbency.

.3 Scope of Research

In this research, characterization Empty Fruit Bunch (EFB)-g-AA is using Fourier Transform Infrared Spectroscopy (FTIR). In this research focus on effect of parameter, amount of EFB, N,N'-Methylenebisacrylamide (MBA) and ammonium persulfate (APS) content the due to the water absorbency. In this research, all parameter are variable in six different values of concentration and amount. The materials in this research are acrylic acid is the monomer. The MBA is the cross-linker and the ammonium persulfate (APS) is the initiator. Then, empty fruit bunch (EFB) is the filler. The polymerization technique that use in this research is graft copolymerization technique. This technique is common technique use to produce SPC.

1.4 Significanse of Study

This study is focused on the characteristic and swelling behavior of synthesized OPEFB-g-AA SPC. The synthesized SAPC has benefited the system in enhancing the swelling ability while reducing the production cost and accelerate the generation of new material for special application. Other than that, positive findings from this study can also help to promote the use of oil palm fibres and it may be used to modify and improve various properties in the original vinyl polymer such as elasticity, absorbency, ion exchange capabilites, thermal resistance and hydrophilicity. Therefore we will be able to reuse the agricultural waste in the country such as oil palm fiber in turning its abundant supply from oil palm industry by products into value added products will be beneficial. The advantages of using natural fiber compared to synthetic fibers include low weight, recyclability, biodegradability and renewability. This research gives the best condition to synthesize polymer grafting so that it can be used perfectly in polymer industry.

CHAPTER 2

LITERATURE REVIEW

This chapter provide the general ideals on the subject that are going to be study including the background and introduction of reforming process, hydrogen production from methane, dry reforming of methane and the catalysts used in this study.

2.1 Superabsorbent Polymer Composites (SPC)

Superabsorbent polymers are an important class of polymers which can absorb large amount of water compared with general absorbing materials and the absorbed water is hardly removable even under pressure. Water absorbing polymers, which are classified as hydrogels that absorb aqueous solutions through hydrogen bonding with water molecules and the parameters for water absorbing polymers of the superabsorbent polymer such as crosslinker, initiator, solvent, and filler (Kabin.K., 2003).

There are many kind of methods to prepare SPC with various starting materials, such as copolymerizing hydrophilic monomer with a cross-linking agent, grafting monomer with starch, cellulose, synthetic fiber, and polysaccharide, cross-linking linear hydrophilic polymer with polyvalent metal ions or organic multifunctional group materials (Thomas et al., 2003). The product of SAP can be in the form of small particles, powder, fiber, membrane, microbeads and even liquid (Tashiro.,1989). However, synthetic polymer based SAPs like acrylamide are poor in degradability especially for applications in agriculture and horticulture, though , they alone do have large fluid absorbing capacities (Xie et al.,2008).

The SAPs can be classified with different methods likes graft copolymerization, solution polymerization and inverse suspension polymerization (Zohuriaan and Kabiri.,2008) . From a morphological point of view they can be divided into particle, powder, spherical, fiber, membrane and emulsion types. The morphology of SAP is designed to respond the different requirements of the applications. For example, the powder product can be put in the mutilayers sheet to form sanitary napkins and diapers, the particle and spherical product can be used as deodorant, fiber product can be used as antistatic electric fiber, membrane product can be used as antifost sheet and emulsion product can be used in soaking and painting.

Figure 2.2 shows that superabsorbent can absorb water up to several thousand times of its own weight even under some pressure (Zohuriaan and Kabiri.,2008). According to Shafinaz and Shahrir (2011) has proposed that molecule structure of SPC which is loosely crosslinked hydrophilic polymer possess the capability to absorb, swell and retain high capacity of fluid like water, brines and biological fluid.

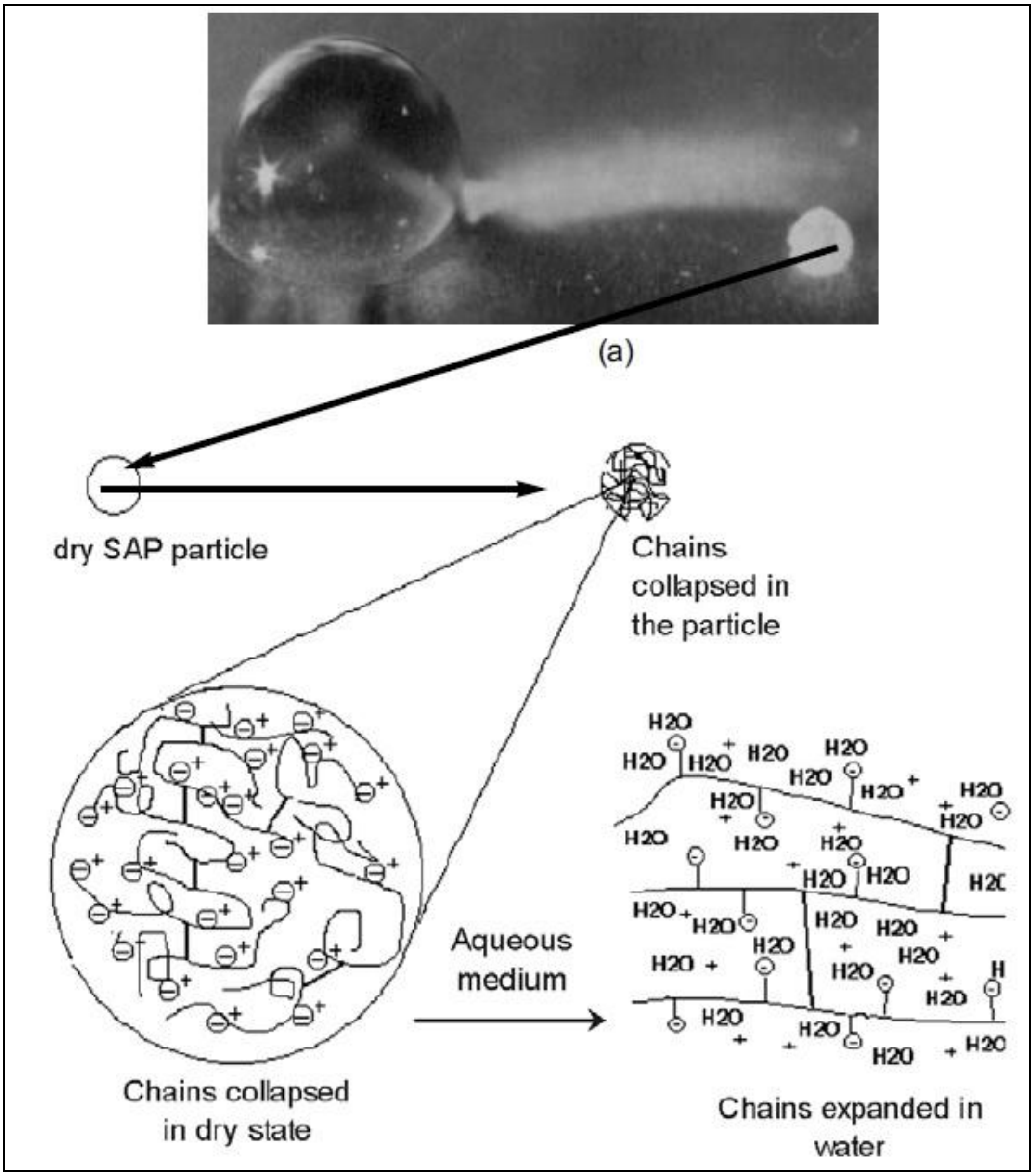

Figure 2.1: Illustration of an acrylic-based anionic superabsorbent hydrogel: (a) The SAP single particle in dry (right) and water-swollen states (left). The sample is a bead prepared from the inverse-suspension polymerization technique. (b) A schematic presentation of the SAP swelling

Source : Zohuriaan and Kabiri (2008)

2.2 Properties of Oil Palm Empty Fruit Bunch (OPEFDB)

Oil palm is widely planted commercially due to its oil-producing fruit. Its two main products are palm oil and palm kernel oil. However, in the process of obtaining these products, it will leave various agricultural waste such as oil palm fronds (OPF), trunks, mesocarp, empty fruit bunches, palm oil mill effluent, palm kernel cake and palm press. Table 2.1 show that the properties of different oil palm fibres.

Table 2.1 : Properties of different oil palm fibres

Properties	EFB	OPF	Oil Palm Trunk
Fibre length (mm)	0.67	1.03	1.37
Width of fibre (µm)	12.50	15.10	20.50
Width of lumen (µm)	7.90	8.20	17.60
Runkel ratio	0.59	0.84	0.26
Area of fibre (µm2)	75.60	126.20	86.70

Source : Rozman, Ishak and Ishiaku (2005)

A fruit bunch is where the palm fruit is embedded. An empty fruit bunch is obtained when the oil is extracted from the palm fruit leaving a bunch of fibres. According to SIRIM Berhad, Malaysia, 23% of empty fruit bunch (EFB) is obtained per tonne of fresh fruit bunch (FFB) processed in an oil palm mill. Therefore, EFB is being sold commercially to produce mattresses, car seats, insulations, composite panel products and particle boards. Figure 2.1 show that the picture of empty fruit bunch and fibrous form.

a.)

b.)

a.) An empty fruit bunch and b.) its fibrous form

Figure 2.2 : Oil palm empty fruit bunch (OPEFB)

Oil palm fibre is non-hazardous biodegradable material extracted from oil palm's empty fruit bunch (EFB). Oil palm fibre is an important lignocellulosic raw material. OPEFB fibre and oil palm mesocarp fibre are two types of fibrous materials left in the palm-oil mill.

Mesocarp fibres are left as a waste material after the oil extraction. These fibres must be cleaned from oily and dirty materials. The only current uses of this highly cellulosic material are as boiler fuel and in the preparation of potassium fertilizers.

When left on the plantation floor, these waste materials create great environmental problems. Therefore, economic utilization of these fibres will be beneficial (Sreekala et al., 1997). Table 2.2 show that the physical and mechanical properties of oil palm empty fruit bunch fibre.

Table 2.2: Physical and mechanical properties of oil palm empty fruit bunch fibre

Chemical constituents (%)	
Cellulose	65
Hemi cellulose	-
Lignin	19
Ash content	2
Physical properties of oil palm fibre	
Diameter (mm)	0.15-0.50
Density (g/mm^3)	0.7-1.55
Linear density (denier)*	2150
Tensile strength (MPa)	100-400
Young's modulus (MPa)	1000-9000
Elongation at break (%)	14
Microfibrillar angle (°)	46

* 1 denier= 1/9000 g/m

Source : Sreekala et al., 1997

2.3 Graft Copolymerization

The superabsorbent composites based on Acrylic Acid (AA) monomer will be synthesized by graft copolymerization method . The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile was synthesized using this method (Hosseinzadeh et al., 2005). One of the best methods for the synthesis of these polymers is graft copolymerization of AA as a monomers onto polysaccharides (Sugahara et al., 2001 ; Ratel et al., 1999 ; Silong et al., 2000).

Graft copolymers are the branched copolymer. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer. When chains of a polymer made of monomer B are grafted onto a polymer chain of monomer A we have a graft copolymer. However, the individual chains of a graft copolymer may be homopolymers or copolymers. The figure below show that structure of graft copolymer. Figure 2.3 show that the structure of graft copolymer.

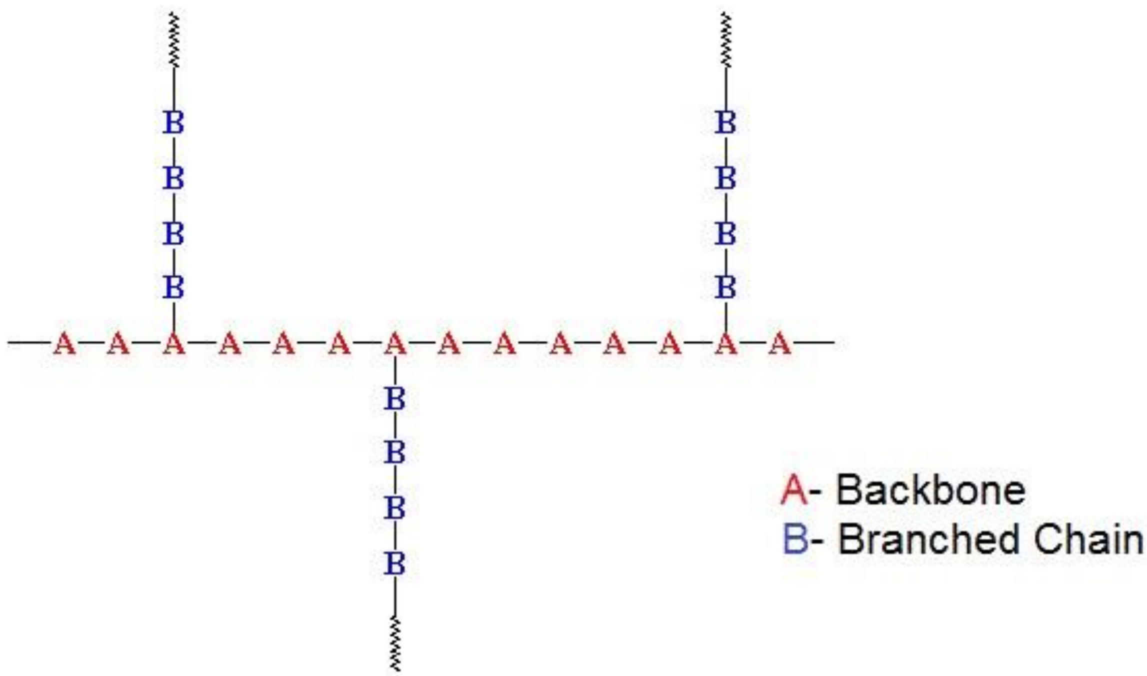

Figure 2.3: Structure of a Graft Copolymer

The typical method of graft polymerization is a free radical polymerization of various monomers onto existing polymer initiated by chemical initiators (Fanta et al., 1987). According to Zohuriaan-Mehr et al. (2008) reported that in graft copolymerization, generally a polysaccharide enters reaction with initiator by few ways.

In the way of initiation, an initiator such as persulphate may abstract hydrogen radicals from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone. This reaction is more affected by temperature compared to other method because of employing a thermal initiator.

Therefore, extensive attention has been directed towards SAPs being prepared through graft copolymerization of monomers onto the chain of such natural fibres to render the SAPs to be biodegradable, and hence producing environmentally friendly SAPC, which may offer advantages for such applications. Figure 2.4 show that the chemical structure of the reactant and general pathway to prepare an acrylic SAP network.

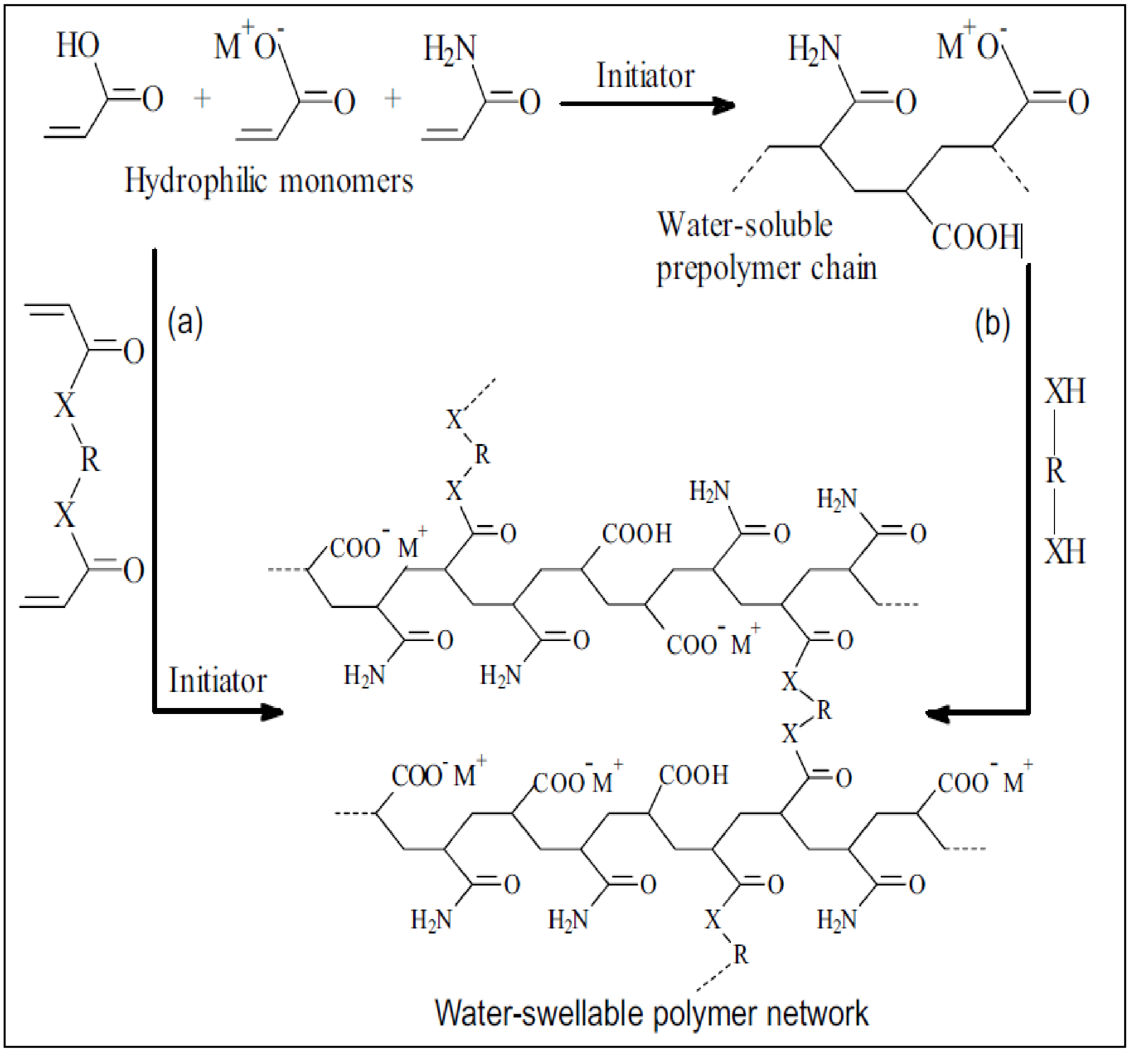

Figure 2.4 Chemical structure of the reactant and general pathways to prepare an acrylic SAP network; (a) crosslinking polymerization by a polyvinylic cross-linker, (b) cross-linking of water soluble prepolymer by a polyfunctional cross-linker.

Source : Zohuriaan and Kabiri (2008)

2.4 Water Absorbency Capacity

In this research, factors influencing water absorbency of the superabsorbent composite will be investigated, and then the optimal synthesis conditions will be obtained as follows: the effect of varying crosslinker, initiator and filler.

2.4.1 Crosslinker

The crosslinkers plays an important role in the formation of three dimensional network structures permanently to the SAPs in the polymerization process. Crosslinker density is a key control of water absorbency, and saturated absorbency of superabsorbents can be influenced greatly even with a relatively small change of the amount of crosslinker. According to (Flory.,1953), the high values of absorbency are obtained with low concentrations of crosslinkers, leading to a low crosslinking density. Increasing the crosslinking agent and subsequently, the crosslinking density results in a highly crosslinked, rigid structure that cannot be expanded to hold a large quantity of water.

As reported by Wu et al (2003), a higher concentration of crosslinker will developed a larger number of growing polymer chains by the generation of more crosslink points that caused the formation of an additional network. Thereby, water absorbency decreased with the increase in crosslinker concentration due to the available free volume within the SPC system which gets diminished and less water molecules can enters the SPC network structure. In contrast when the concentration of the crosslinker is lower than the amount of crosslinker, the water absorption capacity of the SPC was low too, as the low crosslinking SPC is unable to maintain the absorbed water and may be dissolved easily when it was immersed in water. Figure 2.5 shows that the influence of crosslinker loading on water absorbency of SPC system. From figure 2.5, since the avaibility of free volume within the SPC system gets diminished, water molecules that can enters the SPC network structure is reduced. Therefore, water absorbency decreased with the increase in crosslinker concentration. (Wu et al. 2003). In contrast, the water absorption capacity of the SPC was low too when the concentration of the crosslinker is lower than 0.15 wt% because at the low crosslinking SPC is unable to maintain the absorbed water and may be dissolved easily when it was immersed in water. The results may be due to the fact that the cross-linkage network of the SPC cannot be formed efficiently because of few crosslink points (Li et al. 2005; Wu et al. 2003; Li et al. 2007).

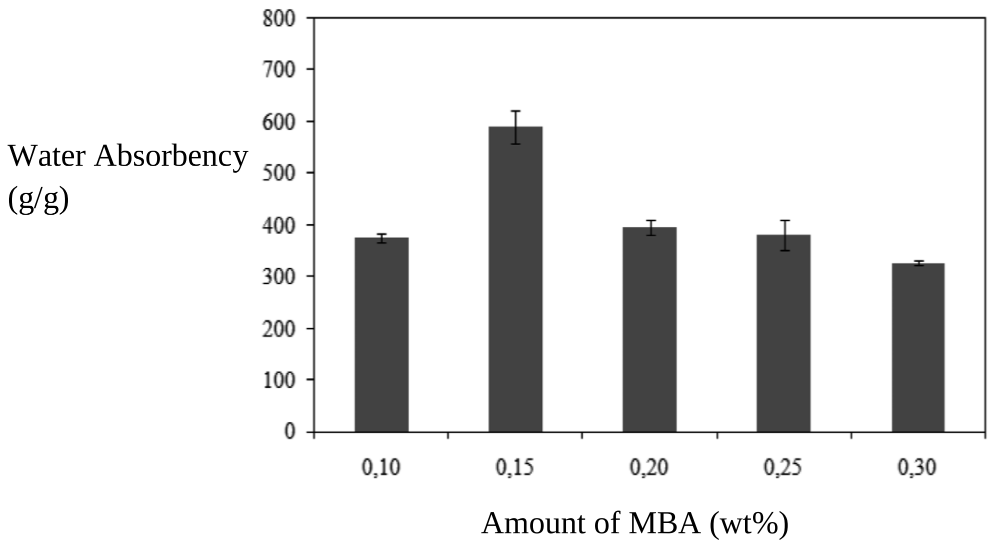

Figure 2.5 Effect of crosslinking on water absorbency

In advanced SAP, there are two main types of cross-linking, bulk and surface cross-linking. In the bulk cross-linking such a cross-linking of the polymer normally takes place during the polymerization stage of the monomer to form a network in which a cross-linking agent is actually a co-monomer with a higher functionality than the main monomer. The degree of soluble polymer is important in determining the optimum cross-linking level, since too low a cross-linking level gives high Water Absorbency Capacity (WAC) with low strength and high extractable product, while too high a cross-linking level induces low extractable product with non-tacky gel and having low WAC. To obtain an acceptable level for most SAP users, a balance is required with a small amount of extractable, high gel strength and high WAC. This type of surface crosslinking is a new process that improves the absorption against a pressure profile of the polymer gel, such as for feminine napkins. Because high swelling capacity is obtained, but poor absorption against pressure occurs due to low elastic gel strength, caused by the low core cross-linking level (Kamjornwong., 2007). In conclusion, crosslinker type and concentration has a great influence on the physical properties of SAPs.

2.4.2 Initiator

In a polymerizations, the initiator have great influence on polymerization rate as well as on the molecular weight of the resulted polymer. In the process of crosslinking polymerization reactions also, the initiator affects both the degree of crosslinking and molecular weight between two crosslinking points and contributes for the inhomogeneity in the polymer system (Murali et al., 2005). The low concentrations of initiator results in lowering of the crosslinking density as well as conversion. When the amount of initiator was higher than the optimum point, the change of the waterabsorbency became gentle and the waterabsorbency decreased slowly with the increase of the amount of initiator, likely because more graft polymerization occurred and more stable network structures were formed in the synthesized SAPC. When the concentration of the initiator was too high, there was a strong reaction with the cellulose molecular, which resulted in the decrease of the main chain length. Consequently, the waterabsorbency of the polymer dropped.

According to Li et al.(2005) and Li et al.(2008) at low concentration, the initiator were mostly utilized in producing a large number of free-radical sites on the OPEFB backbone at which the AA monomers could be grafted. Because of that, the absorbency of the graft polymer increased with the increase in initiator content because the grafting yield increases the grafted points. Otherwise, when the initiator concentration increase rates was faster, the mean kinetic chain length was decreased and the smaller polymer network space due to the generation of more radical, which lead to the decrease of water absorbency of the synthesized SAPC(Wu et al.,2003; Singhaa et al.,2008; Yu et al.,2009). Figure 2.6 show that the effect of initiator on water absorbency. From Figure 2, network structures were formed and more stable in the synthesized SPC because more graft polymerization occurred. Consequently after increase in the amount of initiator from 1.0 wt% to 1.5 wt% resulting in an increase in water absorbency. Li et al. (2005) and Li et al. (2008) stated that, a large number of free-radical sites on the OPEFB backbone at which the AAm monomers could be grafted. Therefore, the absorbency of the graft polymer increased simultaneously with the initiator content with the grafting yield and the grafted points. (Li et al. 2005; Li et al. 2008).

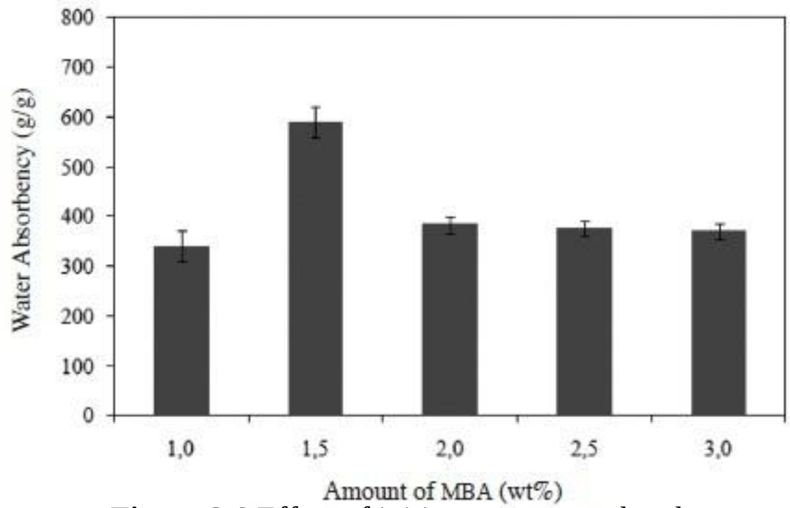

Figure 2.6 Effect of initiator on water absorbency

2.4.3 Filler

Synthesized SPC influenced of OPEFB content on the water absorbency. Water absorbency of SPC assimilate with 10 wt% OPEFB, is exactly the same with AA SPC regards the amount of water being absorb. OPEFB is the biodegradable material that exists in the synthesized SPC system which also works as another crosslinking point. Even though the water absorption capacity was lowered at 5 wt% OPEFB consequence of the amount of OPEFB does not provide enough crosslinking point within the SPC polymeric network space (Shafinaz et al.,2011). When the ability of water absorbency was enhanced as the loading increases near 10 wt%, the OH molecules on the OPEFB backbone could react with AA monomer, which advantage the system by forming a network structure. When the amount of OPEFB is suitable for the system which the 10 wt% OPEFB, the crosslink density and the network space of the SPC were almost equal to that pristine ones resulting in almost the same capacity in water absorbency.

According to Shafinaz et al. (2011), there will be reduction in the ability of water absorbency due to the increase in OPEFB amount from 10 wt% to 15 wt% which terrifically decreased the elasticity of SPC. The increasing OPEFB content package with decreasing tendency of water absorbency with may be attributed to the fact that additional OPEFB fibre in the SPC system results in the generation of more crosslink points in the polymeric network. OPEFB in the network structure has a lot of hydroxyl groups to form superfluous network point, which increases the network density of the composite where it leads to a more difficult permeation of water into the SPC system. Figure 2.7 show that the effect of filler on water absorbency.

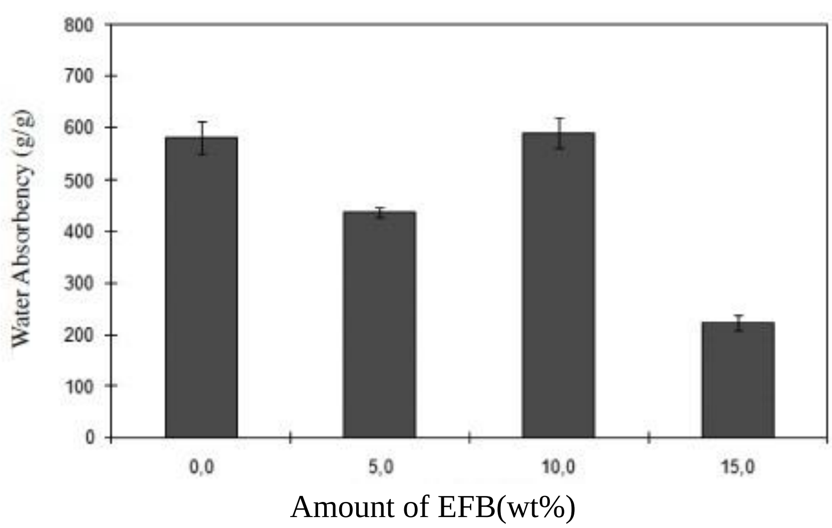

Figure 2.7 The effect of filler on water absorbency.

CHAPTER 3

METHODOLOGY

3.1 Material

In this research, the OPEFB fibre were purchased from Felda Palm Industries Sdn Bhd, Gambang, Pahang, Malaysia. Acrylic Acid was distilled under reduced pressure prior to used in order to remove inhibitor. Ammonium Persulfate (APS) and N,N-methylenebisacryamide (MBA) were used. Sodium hydroxide (NaOH) which used as neutralization agent was prepared with distilled water.

3.2 Equipment and Apparatus

3.2.1 Synthesis of SPC

For this research of synthesis of SPC, 500mL three-neck round-bottom flask with a stirrer, a condenser, a thermometer and a nitrogen line were setup. For water absorbency determination, weighing scale, tea bag and sieve shaker were used.

3.2.2 Charaterization

3.2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

The IR Spectra of the OPEFB, PAA SAPs and OPEFB-*g*-PAA SAPC samples were characterized on FTIR (Nicolet Avatar 370 DTGS) using KBr disk pellets technique. The spectra was record in the range of 4000 to 500 cm^{-1}.

3.2.2.2 Thermogravimetric Analysis (TGA)

The amount and rate of change on weight of SPC were measured by using Thermogravimetric Analysis (TGA, TAQ-500) as a function of temperature of The analysis of TGA was carried out in nitrogen atmosphere from 25-950 ^{o}C at heating rate 10 ^{o}C/min with nitrogen flow rate of 50 ml/min.

3.3 RESEACH DESIGN