EFFECT OF PH SOLUTION ON THE WATER ABSORBENCY OF SUPERABSORBENT POLYMER COMPOSITE

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project report and in my opinion this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedicated to

My beloved parents

for their endless love and support.

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Thank you.

ABSTRACT

Nowadays, superabsorbent polymer composite (SAPC) has been world widely known because of its capacity in contributing beneficial applications in daily life. In this study, Poly Oil Palm Empty Fruit Bunch-co-Acrylamide superabsorbent polymer composite (OPEFB-AM-SAPC) was synthesized by solution polymerization of the Acrylamide (AM) monomer onto OPEFB fibre using Ammonium Persulphate (APS) and N, N-methylene bisacrylamide (MBA) which act as an initiator and crosslinker, respectively. The effects of different pH solution and filler amount towards water absorbency have been identified by studying the optimum condition of each parameter towards water absorbency capacity of polymer. For a parameter of pH solution, the maximum water absorbency was observed at pH 4 for fixed filler amounts. Meanwhile, for the effect of different filler loading, the optimum water absorbency of OPEFB-AM-SAPC was achieved at 2.5 wt% of filler loadings which reveals the well-organized loosely polymeric structure with multiple porous structures that suitable for penetration of water into the polymeric network. These multiple porous structures lead for high water uptake within the network. On the other hand, the characterizations of OPEFB-SAPCs have been carried out by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Field Emission Scanning Electron Microscopy (FESEM). The thermogravimetry analysis result of OPEFB-SAPC at 2.5% filler loading indicate that the SAPC shows a three stage degradation, which unlike the dense unorganized rigid structure been exhibited by the 12.5 wt% filler loading. Meanwhile, FTIR analysis shows OPEFB-SAPC (2.5 wt %) has sharp peak of bonding curves compared to OPEFB-SAPC (12.5 wt%).

ABSTRAK

Pada masa sekarang, penyerap polimer gel (SAPC) telah diketahui secara umum dan meluas kerana kebolehannya yang menyumbangkan banyak kelebihan dalam kehidupan seharian. Di dalam penyelidikan ini, penyerap polimer gel (SAPC) bedasarkan tandan kosong buah kelapa sawit (EFB) disentesiskan menggunakan kaedah pempolimeran cantuman akrilamida (AM) monomer ke atas tulang belakang OPEFB dengan ammonium persulfat (APS) sebagai pemangkin dan N'N'-metilenabisakrilamida (MBA) sebagai pemautsilang dalam membantu proses. Kesan kuantiti pengisi (filler) dan kesan larutan pH yang berbeza terhadap kebolehan daya serap air dipelajari untuk menentukan keadaan kuantiti maksimum kebolehan daya serap air OPEFB-SAPC. Kebolehan daya serap air paling tinggi untuk larutan pH adalah 4 untuk kuantiti pengisi (filler) yang tetap. Selepas itu, daya serap air OPEFB-SAPC paling maksimum adalah 2.5 wt%. Manakala, analisa struktur kimia OPEFB-SAPC dianalisis menggunakan spektroskopi FTIR, TGA dan FESEM.

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LIST OF ABBREVIATIONS

AM	Acrylamide
APS	Ammonium Persulphate
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HCl	Hydrochloric Acid
MBA	N,N’-methylenebisacrylamide
NaOH	Sodium Hydroxide
N_2	Nitrogen
OPEFB	Oil Palm Empty Fruit Bunch
SAP	Superabsorbent Polymer
SAPC	Superabsorbent Polymer Composite
SPAN	Starch-graft-polyacrylonitrile
TGA	Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Superabsorbent are three-dimensional a cross-linked network of hydrophilic polymers that can absorb large quantities of water, saline or physiological solutions while the absorbed solutions are not removable even under pressure (Hossein et al., 2011). Based on study by Gadallah et al., (2012), to function as an absorbent for aqueous fluids, a polymer must have certain properties which is must be hydrophilic and the polymer must swell in aqueous fluids but must not dissolve. According to Zohuriaan and Kabiri, (2008), the synthesis of the first water-absorbent polymer goes back to 1938 when acrylic acid (AA) and divinylbenzene were thermally polymerized in an aqueous medium. In the late 1950s, the first generation of hydrogels was appeared. These hydrogels were mainly based on hydroxyalkyl methacrylate and related monomers with swelling capacity up to 40-50%. They were used in developing contact lenses which have made a revolution in ophthalmology. The first commercial SAP was produced through alkaline hydrolysis of starch-graft-polyacrylonitrile (SPAN). The hydrolyzed product (HSPAN) was developed in the 1970s at the Northern Regional Research Laboratory of the US Department of Agriculture. Expenses and inherent structural disadvantage (lack of sufficient gel strength) of this product are taken as the major factors of its early market defeat. Commercial production of SAP began in Japan in 1978 for use in feminine napkins.

Because of the superior properties of SAPs, they have found extensive applications such as disposable diapers, feminine napkins, drug delivery systems, and soil for agriculture and horticulture. For the majority of applications, the superabsorbent polymers have to possess high absorption capacity and elevated swelling rate and show a strong swollen gel. Hydrogels with high mechanical strength are required in some applications such as artificial cartilage, controlled drug delivery, hygiene and agricultural uses (Hossein et al., 2011). Recently, based on research from Xie and Wang (2009), the usage of superabsorbent as water managing materials for the renewal of arid and desert environment has attracted great attention as they can reduce water consumption for irrigation, improve fertilizer retention in soil, lower the mortality rate of plants, and increase plant growth rate.

Furthermore, SAPs are used also as scaffolds in tissue engineering where they may have human cells in order to repair tissue. Superabsorbent polymers have the ability to sense environmental changes, like changes of pH and temperature. Hydrophilic networks that are responsive to some molecules, such as glucose or antigens can be used as biosensors as well as in drug systems, disposable sanitary products (for example, diapers, incontinence articles, feminine hygiene products, airlaids and absorbent dressings), and in controlled release drugs. Superabsorbent polymers were also employed in various applications, such as household articles, sealing materials, humectants for agricultural products for soil conditioning, oil-drilling, anti-condensation coatings, water-storing materials in agriculture, absorbent paper products, bandages and surgical pads, pet litter, wound dressings, and as chemical absorbents. Furthermore, they are used in food packaging applications (Jaber, 2012).

In general, there are two types of SAP that available in the market which are synthetic (petrochemical-based) and natural. The graft copolymerization of vinyl monomers on polysaccharides is the example of the natural based SAP where usually been prepared through addition of some synthetic parts onto the natural substrates. 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). This superabsorbent polymer can be prepared by various techniques such as bulk polymerization, suspension-inverse suspension polymerization and polymerization by irradiation. However, the frequently common method used for SAP preparation is solution polymerization technique which 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 a reducing agent with an oxidizing agent (redox system) or chemically with free-radical azo or peroxide thermal dissociative species or. Additionally, radiation is sometimes used for initiating the polymerization. The solution polymerization of AA and AM with a water-soluble cross-linker, e.g., MBA in an aqueous solution is a straight forward process. The reactants are dissolved in water at desired concentrations, mostly about 10-70% and a fast exothermic reaction yields a gel-like elastic product. Then, the product is dried and sieved in order to obtain the required particle size (Zohuriaan-Mehr and Kabiri, 2008). Based on study by Kiatkamjornwong (2007), the major advantage of 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 this method as well.

Currently, material’s biodegradability has been widely focused on due to the renewed attention towards environmental protection issues. Approximately, 90% of superabsorbent materials are used in disposable articles which most of them are synthetic polymers that are poor in degradability. Poor degradability will eventually leads to the environmental problem. However, according to previous work (Zhang et al., 2007); the degree of degradability of this superabsorbent polymer could be improved by incorporation of biodegradable and renewable natural sources such as starch, cellulose, and chitosan. It was believed that incorporation of biodegradable element is a convenient way to improve biodegradability of corresponding superabsorbent materials. Natural- based SAP polymers have attracted much attention in medical and pharmaceutical fields because of their non-toxicity, biocompatibility and biodegradability (Sadeghi, 2012). Moreover, the introduction of low cost inorganic fillers such as natural filler into a polymer matrix could increase their strength and stiffness properties as well as reduced the production cost (Hossein et al., 2011).

Therefore, this study has been carried out by utilization of natural filler in order to improve the absorbency capacity and their strength. For examples, in Malaysia, agricultural waste materials such as oil palm wastes, paddy straw and rice husk are increasing each year leading to disposal problem and need to manage in a proper way. The conventional method of burning OPEFB for disposal purpose often creates environmental problems in that it generates severe air pollution. Thus, economic utilization of OPEFB in turning its abundant supply from oil palm industry by-products into value-added products will be beneficial. Therefore, grafting of vinyl monomer such as AA or AM onto OPEFB backbone may be used to modify and improve various properties in the original vinyl polymer such as elasticity, absorbency, ion exchange capabilities, thermal resistance and hydrophilicity. The synthesized SAPC has benefited the system by enhancing the swelling ability while reducing the production cost, more environmental friendly and accelerate the generation of new materials for special applications (Hashim and Jamaludin, 2011).

1.2 PROBLEM STATEMENT

Nowadays, development of SAP has been improved from time to time. SAPC made from synthetic polymers possess good characteristics but it is not environmental friendly since it contains toxicity and non-degradability. SAP based on acrylic acid and acrylamide are poor in degradability in application of agriculture and horticulture. As an alternative way, OPEFB used as the filler in SAPC and lower the cost production. Additionally, SAPC that will be produced is biogradable and easy to dispose so it does not pollute the surrounding environment. This SAPC is also able to absorb water higher than synthetic SAPC with proved from recently research that had been going through. Thus, OPEFB based on SAPC may become a new invention to be used in widely agriculture, sanitary goods as well as in horticulture field.

1.3 OBJECTIVE

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

a) Effect on different of pH solutions towards water absorbency.

b) Effect on amount of filler towards water absorbency.

1.4 SCOPE OF STUDY

The effects of filler amount and effect of different pH solution towards water absorbency have been studied to determine the optimum condition for water absorbency capacity of OPEFB-SAPC. A few parameters required to be controlled in this research which is by fixing pH solutions at pH 2 up to pH 10 while varying amount of filler at range of 5 wt% to 12.5 wt%. In this research, SAPC were synthesized by using solution polymerization with acrylamide (AM) was used as the monomer, ammonium persulphate (APS) was used as the initiator as well as N’N’-methylenebisacrylamide (MBA) as a crooslinker. In sample preparation, three flasks equipped with a stirrer, condenser, thermometer, and nitrogen line were used. The samples were characterized by using FTIR (Fourier Transform Infrared) spectroscopy to indicate functional groups, TGA (Thermal Gravimetric Analysis) to indicate thermal stability of samples and FESEM (Field Emission Scanning Electron Microscope) to examine morphology of superabsorbent polymer composite (SAPC). Finally, the tea-bag method was used to measure the amount of water absorbency.

1.5 SIGNIFICANCE OF STUDY

Superabsorbent polymer composite (SAPC) from oil palm empty fruit bunch (OPEFB) become 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 SAPC with the same quality as superabsorbent polymer synthetic since OPEFB is residue where it can be found easily at the palm oil mill around Malaysia. The addition of this research is the SAPC 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 which has been proved by the recently research that had been done.

CHAPTER 2

LITERATURE REVIEW

2.1 SUPERABSORBENT POLYMER COMPOSITE (SAP)

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 water within their structure without dissolving in water or aqueous solution (Brannon-Peppas and Harland, 1990; Buchholz and Graham, 1998). 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. 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).

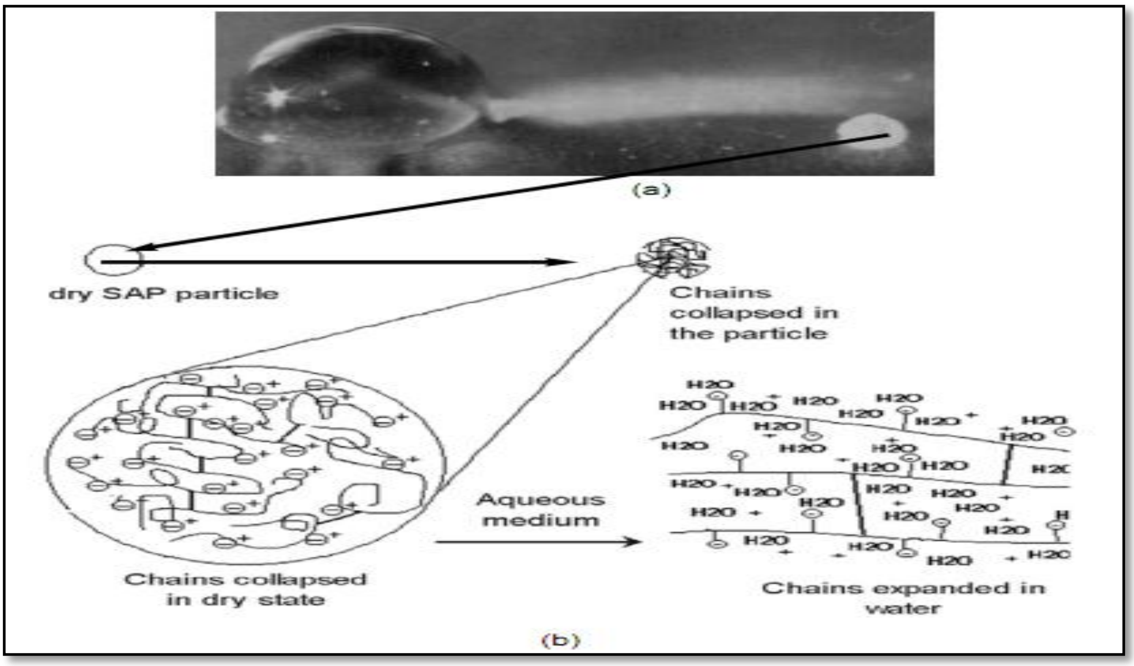


Figure 2.1: Comparison of dry SAP with swollen SAP and schematic of the SAP swelling

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.

Table 2.1: Water absorbency of absorbent materials

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

2.2 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 730 g/g among the China clay, 650 g/g and silica, 310 g/g. From the study, it shows that the pure SAP without inorganic filler still can produce high water absorbency of 605 g/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 tetraaceticdianhydride (EDTAD). The amino groups of the protein was crosslinked by glutaraldehyde to produce SAP. The dry gel of SAP was capable to absorb 80-300 g of deionized water/g after centrifugating at 214 g. The water absorbency capabality 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 that the protein after modification could be used as polymer substrate and produce SAP with high water absorption.

Starch phosphate-graft-acrylamide or attapulgite superabsorbent composite was prepared by graft-copolymerization among starch phosphate, acrylamide, and attapulgite in aqueous solution (Raju et al., 2005). 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 attapulgite 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% attapulgite was incorporated. In this research, the results show that the phosphorylation of starch and the introduction of attapulgite could greatly improve equilibrium water absorbency superabsorbent composite.

The effects of vermiculite content on water absorbency were studied by Zheng et al. (2007), in a series of superabsorbent composites that were synthesized by copolymerization reaction. This copolymerization reaction was occurred between a 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. They found that 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. From the result obtained in this research, it is found that the UVMT helps in improving the absorbency of water and also saline solution.

2.3 OIL PALM EMPTY FRUIT BUNCH (OPEFB)

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. OPEFB 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, they found that the hydrophilic properties of lignocellulosic materials and capillary action will cause the intake of water when the samples were soaked into water. It is also observed that the thickness swelling for the pure OPEFB composite with the value of 9.12 % was the highest water absorption among different types of composite. The next highest water absorption among the different type composite is pure OPEFB with the value of 21.39 % which resulted from the high porosity on the surface of pure OPEFB composite.

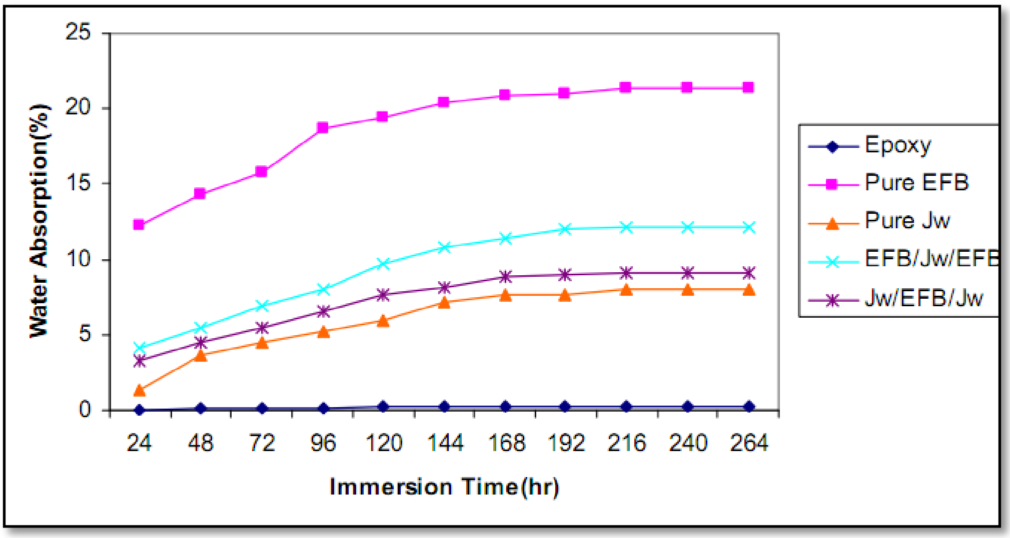


Figure 2.3: Water absorption (%) of OPEFB reinforced hybrid composites

Moreover, according to Jawaid et al. (2010), 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. From their study, it shows that the pure OPEFB has higher potential than pure jute mate and hybrid composite (OPEFB/jute mate) in water absorption, which by this reason strengthens the usage of OPEFB as filler in this research.

2.4 TECHNIQUE OF POLYMERIZATIO N

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.

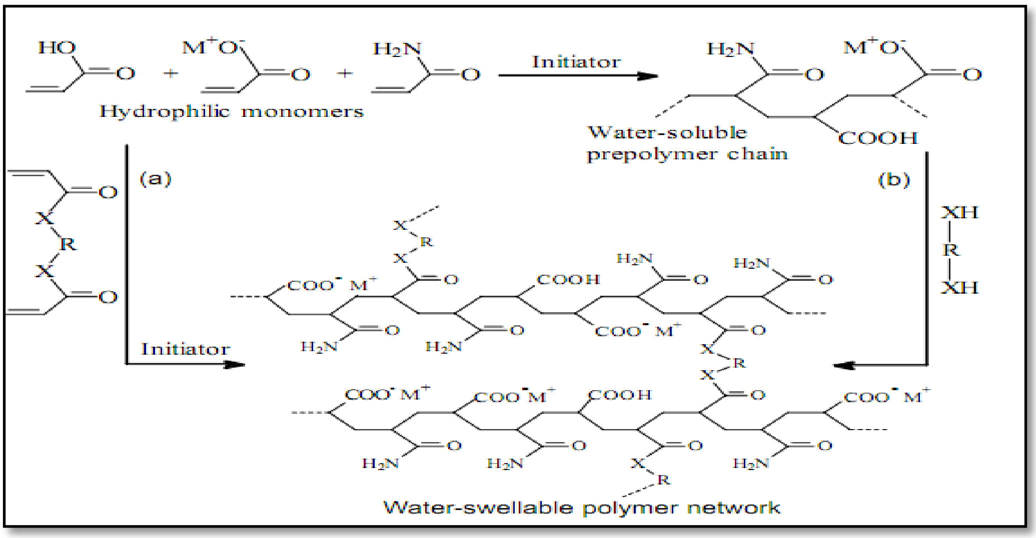


Figure 2.5: The mechanism in preparation of SAP

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 thermodically 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.

2.5 GENERAL REACTION AND MECHANISM OF SAPC

The superabsorbent composite, was prepared by graft copolymerization of acrylic acid onto carrageenan in the presence of a crosslinking crosslinking agent and powdery kaolin. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate radicals that abstract hydrogen from one of the functional groups in side chains of carrageenan backbones. So, this persulfate-saccharide redox system results in active centres capable to radically initiate polymerization of acrylic acid led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure (Sadeghi et al., 2012).

In addition, other cross-linking agent were also used including 1, 4-butanediol diglycidyl ether (1, 4-BDGE), and ethylene glycol diacrylate (EGDA). Ethylene glycol diacrylate was chosen because it is a well-known cross-linking agent that is reported in the literature as a cross-linking agent for superabsorbent polymers. 1, 4-Butanediol diglycidyl ether was used for the first time as cross-linking agent for superabsorbent polymer.

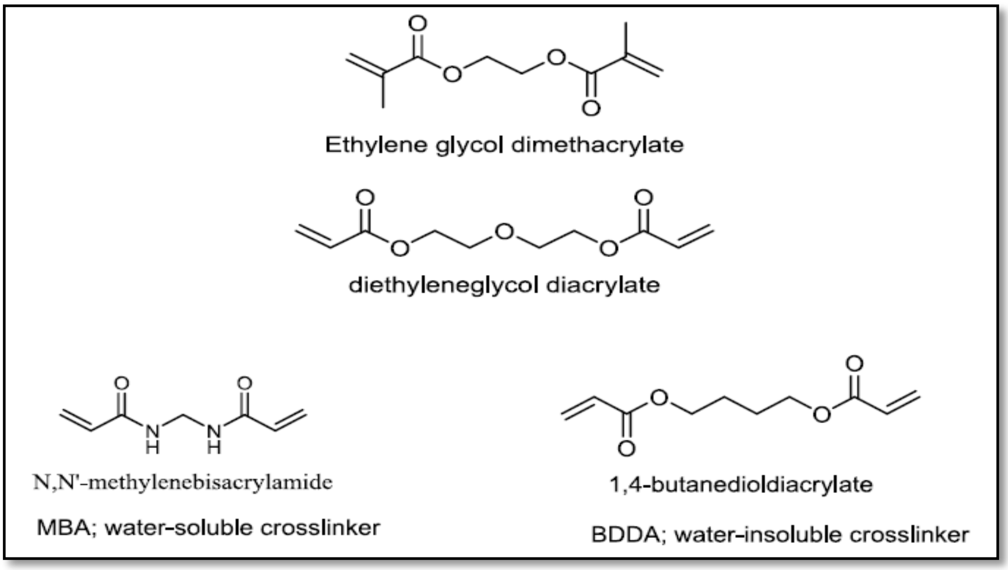


Figure 2.6: Structures of some of the cross-linking agents

There are three principal bonding types that are used to bind the polymer chains together: covalent, ionic, and hydrogen bonds. Two basic methods are used to introduce covalent crosslinks. First, covalent crosslinks are formed when the major monomers (e.g., acrylic acid) is copolymerized with a di-,tri-, or tetra – vinyl monomer for instance N,N-methylenebis(acrylamide), 1,1,1-trimethylolpropanetriacrylate, or as well as tetraallyloxyethane, in a free radical initiated addition polymerization.

Covalent cross-links are also introduced by reacting the polymer chains with a di- or tri - functional reagents that reacts with the carboxylic acid groups by means of a condensation or addition reaction. Second, ionic cross-links are formed by reacting a polyvalent ion of opposite charge with the charged polymer chains. The crosslink forms as a result of charge association of the unlike charges. Because the bond is formed by ion association (charge neutralization) the chemical structure of the cross-linker is less important in determining the placement of the cross-links compared with covalent cross-links. If ionic components are present in the liquid to be absorbed, ion exchange may occur with the ionic cross-links, which may alter the nature of the crosslinks and the behaviour of the polymer in ways that may be unforeseen. Also because the interionic reaction is very fast. The incorporation of the crosslink and the resulting structure of the crosslinked polymer can be difficult to control.

The third type of crosslink is the physical crosslink, which is usually formed by means of hydrogen bonding of segments of one chain with the segments of another chain is shown (Jaber, 2012).

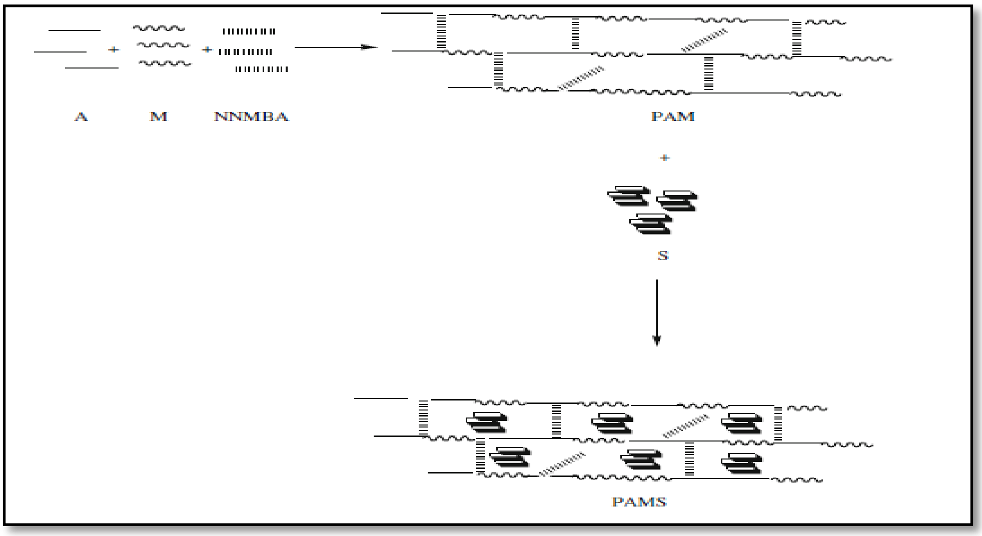


Figure 2.7: Preparation of poly(acrylamide/maleic acid) hydrogel (PAM), and Poly (acrylamide/maleic acid)-sepiolite composite hydrogel (PAMS). (A Acrylamide, M maleic acid, NNMBA N,N0- methylenebisacryl amide, S sepiolite)

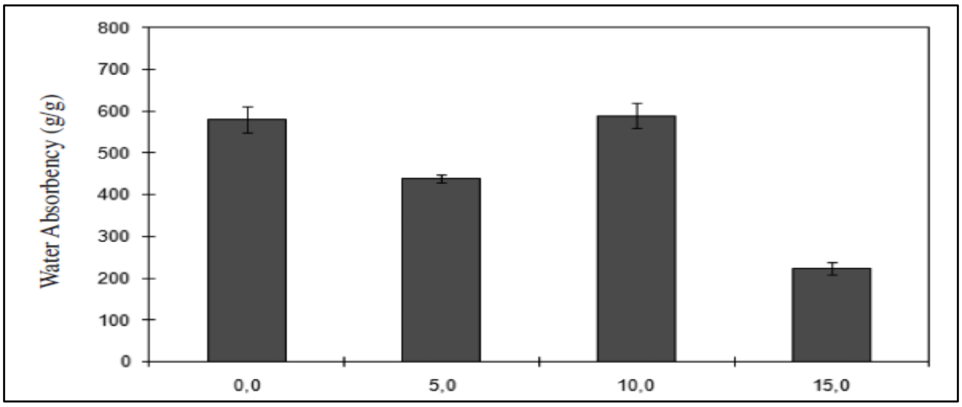
Source: (Oztop et al., 2009)

Poly(acrylamide/maleic acid)–sepiolite composite hydrogels were prepared by free radical crosslinking and copolymerization of acrylamide, sepiolite and maleic acid with a small amount crosslinker (NNMBA) in aqueous solution. APS and TEMED were used as the initiator and the accelerator, respectively. At polymerization, the possible step is a reaction amongst AAm and anionic comonomer, M and crosslinker molecules by the process of the unpaired electron transfer to the monomeric units, so that they in turn become reactive. Another monomer or comonomers can be attached and activated in the same way resulting in a three dimensional network. Sepiolite molecules can be incorporated into chains simultaneously (Oztop et al., 2009).

2.6 EFFECT OF FILLER (OPEFB) AMOUNT

The influences of oil palm empty fruit bunch towards water absorbency give a strong effect in synthesizing the superabsorbent polymer composites. According to Shafinaz and Shahrir (2011), small amount of filler (5 wt% of OPEFB) does not provide enough crosslinking point within the SAPC polymeric network space, thus decreased the water absorption capacity. However, the increasing of OPEFB filler contents (10 wt% of OPEFB) enhance the ability of water absorbency due to the OH molecules on the OPEFB backbone could react with AAm monomer, which benefit the system by forming a network structure.

Moreover, as further increase in OPEFB amount from 10 wt% to 15 wt% reduce the ability of water absorbency due to the decreasing in elasticity of SAPC. This may be attributed to the fact that additional OPEFB fibre in the SAPC system results in the generation of more crosslink points in the polymeric network. This is because it contains a lot of hydroxyl groups to form superfluous network point, hence increases the network density of the composite which it leads to a more difficult permeation of water into the SAPC system.



Amount of OPEFB (wt %)

Figure 2.8: The effect of filler amount towards water absorbency

2.7 EFFECT OF pH SOLUTION

The interactions among the counter ions within OPEFB superabsorbent polymers composites have substantial influences on the shrinking and expansion of the network of the polymer. The concentration of both the counter anions and counter cations are essentially controlled by the dissociation of charged groups along the polymer backbone and are expected to be significantly affected by the pH value in the solution. (Yu et al., 2010).

Based on study reported by Hossein et al., (2011) at pH less than 4, mostly the carboxylate anions are protonated, so that the main anion repulsive forces are eliminated and thus swelling values are decreased. However, some of attractive interactions (H-O hydrogen bonding) decreased in water absorbencies. Meanwhile, at higher pH range of 5 to 8, some of carboxylate groups are ionized and the electrostatic repulsion between COO– groups causes an increasing of the swelling behaviour. Then, the reason of the swelling-loss at highly basic solutions higher than pH 8 is “charge screening effect” of excess Na+ in the swelling media, which shields the carboxylate anions as well as to prevent effective anion repulsion.

CHAPTER 3

METHODOLOGY

3.1 MATERIALS AND SOLVENTS

In this research, Acrylamide (AM) was used as the monomer, while N'N'-Methylene Bisacrylamide (MBA) and Ammonium Persulphate (APS) were used as the initiator and crosslinker, respectively to synthesize Superabsorbent Polymer Composite (SAPC). All the chemicals were purchased from Sigma-Aldrich while the Nitrogen (N_2) was purchased from Air Product Malaysia.

In this study, the OPEFB was used as filler in preparing the SAPC and it was purchased from the LKPP. The OPEFB has been treated first and OPEFB in powder form was used with the size less than 315µm. Meanwhile, the sodium hydroxide (NaOH) and acid hydrochloric (HCl) were used to prepare the buffer solution in determining the water absorbency test.

3.2 APPARATUS AND EQUIPMENT

For synthesis of SAPC, the apparatus and equipment used were 500ml three-neck round bottom flasks which equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Meanwhile, series of tea bag and pH meter was used in measuring the water absorbency.

The samples were characterized by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Field Emission Scanning Electron Microscopy (FESEM).

3.3 RESEARCH DESIGN

Process flow chart is shown as follows:

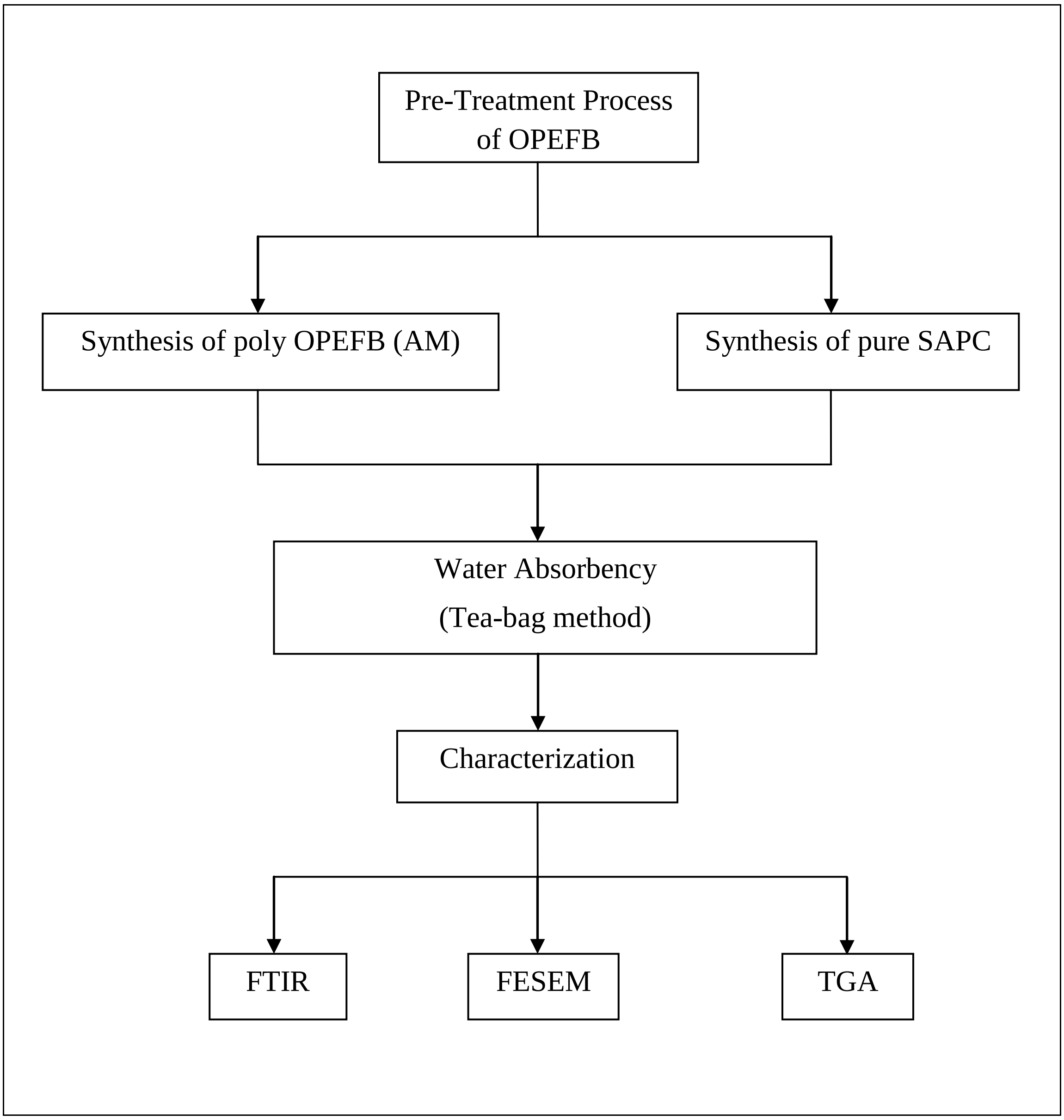


Figure 3.1: Process flow chart for synthesis of SAPC

3.4 SAMPLE PREPARATION

3.4.1 Pre-Treatment of Oil Palm Empty Fruit Bunch (OPEFB)

Oil palm empty fruit bunch was treated in order to produce clean filler without impurities in preparation of SAPC. Firstly, 120 g of OPEFB was weighed. Then, the weighed OPEFB was soaked with 3.74% (w/v) solution of NaOH at a ratio of 1:15 (w/v) of OPEFB: NaOH solution and was put in the ultrasonic bath for a period of 2 hours at $80^{\circ}C$ and ultrasonic power of 9. The OPEFB was then washed in continuous flow water flow until pH 7 was attained. Next, the pH was neutralized using few drops of dilute acetic acid until pH 7 was reached i.e the water no longer show any alkalinity. OPEFB was then dried in air for 10 hours after it was oven dried at $60^{\circ}C$. The crushing of OPEFB was carried out using a blender to have a uniform size. Finally, a mechanical sieve shaker was used to separate the particles in order to obtain a uniform size of less than 315 µm.

3.4.2 Preparation of Oil Palm Empty Fruit Bunch Based Superabsorbent Polymer Composites (OPEFB-SAPC)

A series of samples with different amounts of OPEFB were prepared by the following procedures:

i. Firstly, the synthesis apparatus, 500ml three-neck round bottom flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line, were set up in a water bath.

ii. OPEFB (0.98 g) was dissolved in 20 ml of distilled water and it was poured into the three-neck round bottom flask. The temperature and the speed of magnetic stirrer were set up at 80ºC and 300 rpm respectively.

iii. Acrylamide AM (2.13 g) was dissolved in 16 ml of distilled water and was added into the previous partial solution in the flask. Then, the crosslinking agent, MBA (0.05 g) was added to the AM mixture solution and it was stirred at the temperature of 80ºC about 30 minutes.

iv. Next, the water bath was heated slowly in order to maintain the temperature with effective stirring after initiator APS (0.02 g) was introduced into the mixture.

v. The product was washed several times with distilled water after 2 hours of the reaction and dried in the oven at the temperature of 60ºC for 24 hours.

vi. Finally, the product was milled and screened. All samples that were produced have a particle size in the range of $315\mu m$.

vii. Step (i) until (vi) were repeated with different values of filler loadings (OPEFB).

3.4.3 Preparation of Pure Superabsorbent Polymer Composites (SAPC)

The procedure of preparation poly acrylamide (PAM) superabsorbent polymer was similar to the preparation of superabsorbent polymer composite except OPEFB was omitted.

3.4.4 Preparation of Buffer Solution

This experiment has been conducted at different pH values range between pH 2 until pH 12. The buffer solution had been prepared by mixing NaOH with distilled water for alkaline condition as well as mixing of HCl with distilled water for acidic condition to the desired base and acidic pH values. The value of pH solutions were measured by using the pH meter.

3.5 WATER ABSORBENCY MEASUREMENT

The measurement of water absorbency had been carry out by using the tea bag method by immersing pH solution which was fixed at pH 2 until pH 12 respectively while varying the amount of OPEFB in order to achieve the optimum condition for water absorbency capacity of OPEFB-SAPC.

Initially, a series of tea bags containing weighed dry sample (0.4 g) were immersed in 600ml of pH solutions at the room temperature for a period of 24 hours. Then, the tea bags were hung up for 1 hour in order to remove excess solution until no liquid was dropped off. The water absorbency, Q of samples was calculated according to this equation Eq. (1):

$$\text{Water Absorbency, Q (g/g)} = \frac{(m_2 - m_1)}{m_1} \qquad (1)$$

where m_1 and m_2 were represented of the dry and the swollen sample, respectively.

3.6 CHARACTERIZATION

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a measurement technique in determining the functional groups contains in SAPC. The samples were recorded on the FTIR (Thermo Nicolet NEXUS TM) by using KBr disk pellets technique. The IR spectra were recorded in the range of 4000 to 500 cm^{-1}.

3.6.2 Thermal Gravimetric Analysis (TGA)

TGA function is to determine the weight loss or gain because of the thermal degradation of OPEFB backbone which is due to dehydrogenation, decomposition and oxidation. Thermal stability of samples were carried out by using TGA (TAQ-500) with a temperature range of 50 to $750^{o}C$ at a heating rate of $10^{o}C\ min^{-1}$ as well as with dry nitrogen purged at a flow rate of 50ml/min.

3.6.3 Field Emission Scanning Electron Microscopy (FESEM)

The FESEM (JEOL) surface morphology of the OPEFB-SAPC was taken at several magnifications of X500, X1000, X1500 and X2000.

CHAPTER 4

RESULTS

4.1 Water Absorbency testing in pH Solution

Based on the result shown in Figure 4.1, it can be seen that the water absorbency increased rapidly from pH 2 to pH 4 and then decreased gradually from pH 6 to pH 10 for each OPEFB filler loading. From the graph, pH 4 was observed to produce the optimum condition for water absorbency in pH solutions. This is because most hydrogel swells at acidic pH 2 to pH 4, above which the swelling decreases as the pH approaches the basic side. At acidic pH, it can be presumed that the pendent groups became protonated and therefore, the charge density on the gel increased. Thus, cause an increase in the number of mobile counter ions within the gel which invariably increased the internal osmotic pressure relative to the external solution leading to high swelling (Nisha et al., 2011).

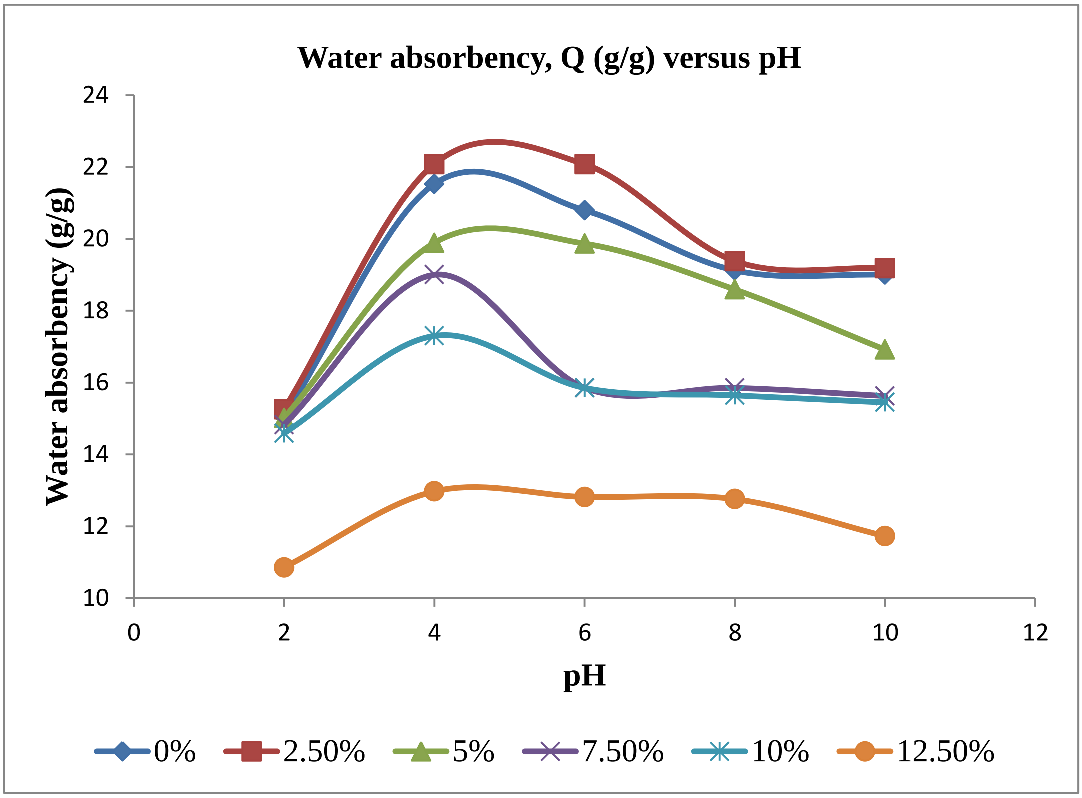


Figure 4.1: Graph of water absorbency versus pH solution.

In a similar research, it was reported the swelling behaviour of Bentonite SAPC was maximum at the pH range between 3.5 and 4.5. The carboxyl (COOH) groups of the adsorbent ionized in the pH range 3.5 to 4.5 and changed to carboxylate (COO-) groups and possessed a negative charge. Thus, the maximum adsorption of Bentonite SAPC in the pH range 3.5-4.5 was due to strong electrostatic interaction between negative charges in the adsorbent surface and positively charged Bentonite SAPC molecules. In addition, a decrease in the adsorption of Bentonite SAPC is experienced in the pH range >4.5, due to the fact that the surface charge of the adsorbent becomes more negative at higher pH values and caused greater electrostatic repulsion toward the more negatively charged of Bentonite SAPC (Anirudhan et al. (2011).

Moreover, Tan and Chen (2006) through the study of Carboxymethylchitosan-g-poly (acrylic acid) copolymer reported that under acidic conditions, the swelling behaviour was controlled mainly by the –NH2 and –NH–R groups at C-2 of carboxymethylchitosan. As the basic amine groups were readily protonated, the charge density on the polymer chains was increased and the osmotic pressure inside the network was enhanced by electrostatic repulsion between the inside and outside of the network was balanced by the swelling of the polymer, and the swelling ratio was higher around pH 4. However, under conditions of high acidity (pH <4), the charge of the ammonium cations was shielded by the screening effect of the Cl^-, counter ions, and efficient repulsion were prevented. Thus a remarkable decrease in equilibrium swelling is observed which similar observed via this research.

As studied in like manner. It has been observed that as pH is lowered to the strongly acidic region; -COO- is transformed to -COOH, thus decreasing the charge density on the network. The concomitant decreased in mobile counter ion content of the network sharply decreased the internal osmotic pressure, thereby reducing water absorbency as reported in Superabsorbent composite containing sodium humate researched by Zheng et al., (2008). Furthermore, Zheng et al., (2008) also explained that as pH is increased to the strongly basic region, most of the -COOH changed into the -COO-, and then the screening effect of the counter ion on the poly anionic chain is more evident, leading also to a decrease in water absorbency. Generally, the pH value of agricultural soils was within 5 to 8, at which the water absorbencies of OPEFB SAPC remained constant. Thus, this characteristic makes the superabsorbent composite a suitable candidate for agriculture as well as horticulture.

Generally, it has been noticed that the effect of pH solution on water absorbency, is a consequence of both the attractive or repulsive electrostatic interactions and hydrogen bonding which occurs within the network structure of the super absorbent polymers.

4.2 Effect of Filler on Water Absorbency

Based on the result obtained in Figure 4.2, it shows that the water absorbency of OPEFB filler loading for each pH fixed increased from 0 wt% to 2.5 wt% and then decreasing rapidly from 2.5 wt% to 12.5 wt%. From observation, 2.5 wt% is the optimum condition for water absorbency of filler loadings. The water absorption capacity decreased from 0 wt% to 2.5 wt% because the amount of filler does not provide sufficient crosslinking point within the polymeric network space. However, as the loading increased up to 2.5 wt%, the water absorbency enhanced, due to the existence of AAm monomer that able to react with OH molecules on the OPEFB by forming a network structure. Further increase in OPEFB amount from 2.5 wt% to 12.5 wt% decreased the elasticity of SAPC, and hence reduced the ability in water absorbency. The decreasing tendency of water absorbency with increasing OPEFB content occurred with additional OPEFB fibre in the SAPC system results in the generation of more crosslink points in the polymeric network. This is because OPEFB in the network structure has a lot of hydroxyl groups to form excessive network point, which increases the network density of the composite where it leads to a more difficult permeation of water into the SAPC system (Shafinaz and Shahrir, 2011).

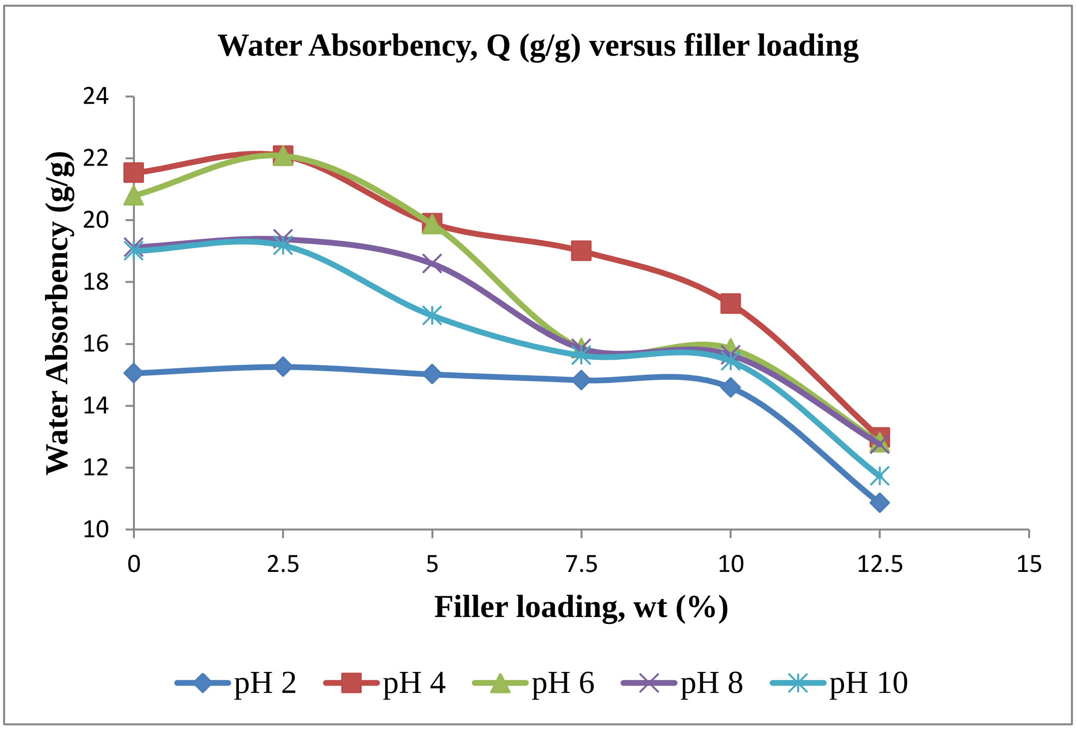


Figure 4.2: Graph of water absorbency versus filler loading.

Apart from that, these results have been proved with Field Emission Spectroscopy Electron Microscopy (FESEM) at several different magnifications which consist of x500µm, x1000µm and x2000µm. The differences of surface morphology were observed between the lowest and highest filler contents. Those samples were 2.5 wt% (0.98 g) and 12.5 wt% (5.46 g) have been observed and shown in Figure (a), Figure (b) and Figure (c) respectively.

The surface morphology at 12.5 wt% of filler contents indicated a smooth and dense surface which leads to less water absorbency compare to 2.5 wt% of filler contents indicated coarse and undulant surface that leads to higher water absorbency. This surface Figure (a) is suitable for penetration of water into the polymeric network, which leads to high water uptake within the network (Bhattacharya et al., 2011).

Based on Figure (a) the sample possessed well organized and revealed multiple porous structure as well as loosely polymeric structure. As reported by Sadeghi, (2011) in ‘Synthesis, and investigation of swelling behaviour natural based superabsorbent composites with high thermal resistance’ these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. Then, Figure (c) possessed unorganized and rigid polymeric structure without showing porous structure. This happened due to the higher extent of the crosslinking within the polymeric matrix structure (Bhattacharya et al., 2011).

From Figure (c) and Figure (a), the OPEFB-SAPC samples consist of rigid polymeric structure and a loosely polymeric structure on the surface. This can be proved the polymerization had occurred among the monomer, crosslinker as well as filler resulted in the water absorbency uptake in the polymeric network. The increasing of filler loading in the product encourages the network structure from rigid structure towards loosely structure and hence contributed to the highest water absorbency within polymeric network.

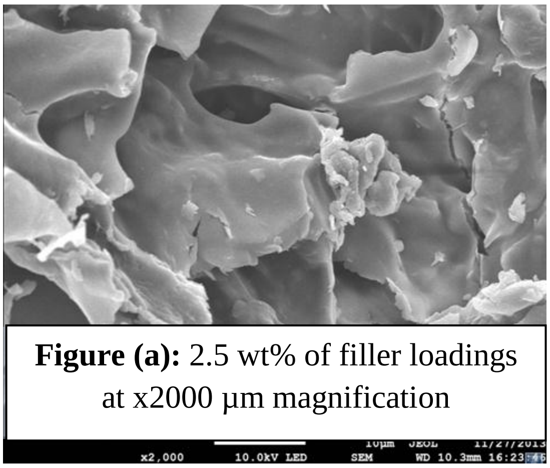


Figure (a): 2.5 wt% of filler loadings at x2000 µm magnification

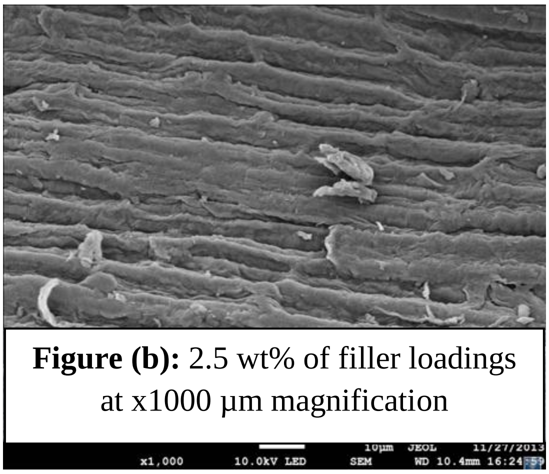


Figure (b): 2.5 wt% of filler loadings at x1000 µm magnification

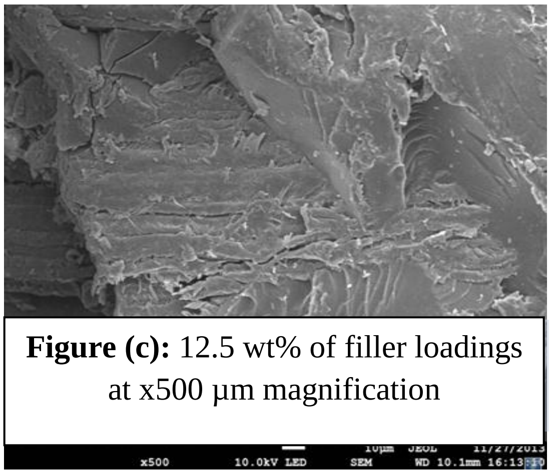


Figure (c): 12.5 wt% of filler loadings at x500 µm magnification

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

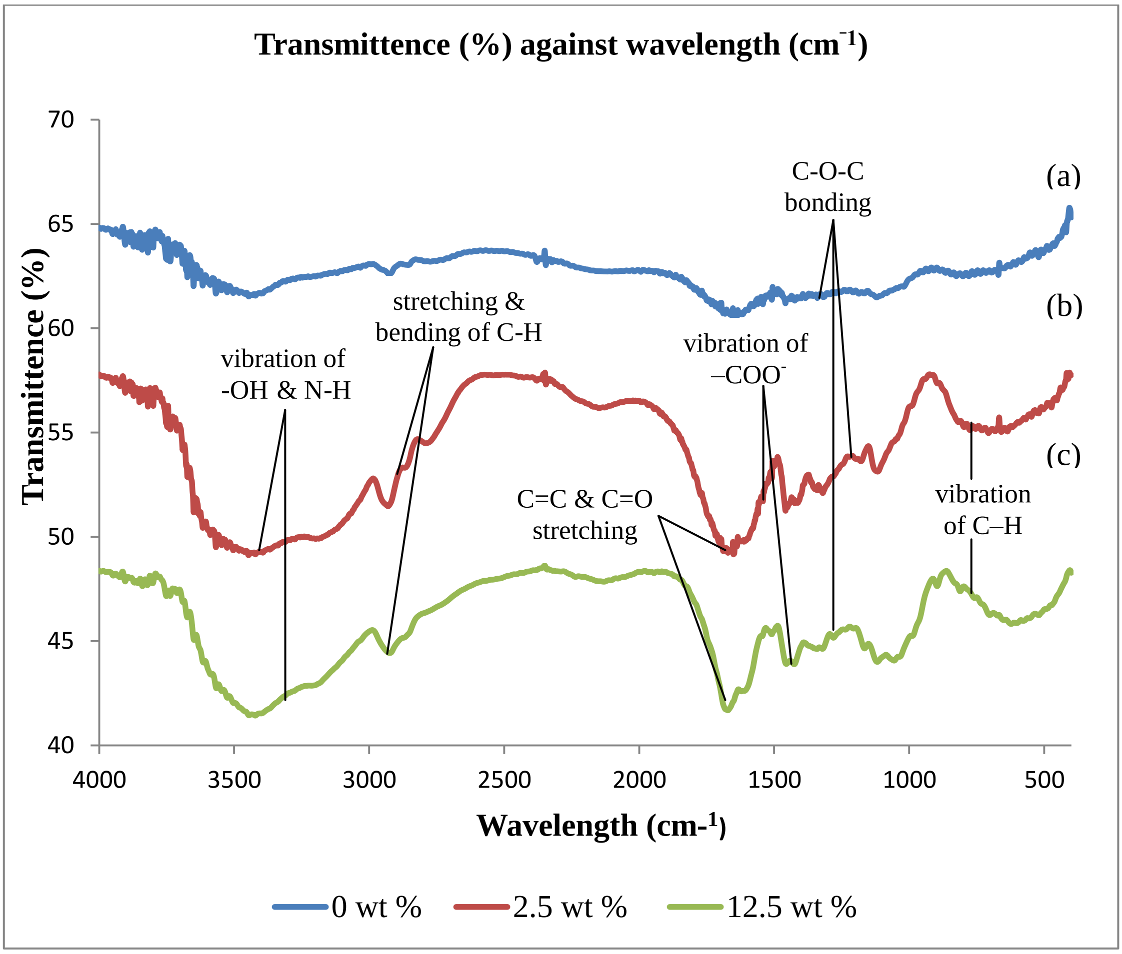


Figure 4.6: FTIR spectra of (a) pure SAPC, (b) OPEFB-SAPC (2.5 wt %) and (c) OPEFB-SAPC (12.5 wt %)

The FTIR analysis was carried out to confirm the chemical structure of the prepared graft copolymer. Infrared spectra of (a) OPEFB-SAPC (2.5 wt%) and (b) OPEFB-SAPC (12.5 wt%) are shown in Figure 4.6 respectively. The spectrum of OPEFB-SAPC (2.5 wt%) and OPEFB-SAPC (12.5 wt%) show a broad absorption band at 3447.12 cm^{-1} and a sharp absorption band at 3422.14 cm^{-1} respectively which assigned to the stretching vibration of -OH and N-H groups. This could be attributed to O-H stretching vibrations of cellulose, absorbed water, and hemicellulose as well as lignin constituent of OPEFB (Ibrahim et al. 2003a). Besides, the OH stretching vibrations are overlapped by N-H stretching vibrations due to the presence of methylene–bisacrylamide (Bajpai et al., 2011).

The presence of peak at 2930.41 cm-1 for OPEFB-SAPC (2.5 wt%) and 2924.03 cm^{-1} for OPEFB-SAPC (12.5 wt%) are ascribed to stretching of C-H groups and bending of C-H groups absorption bands that may be present in methyl and methylene groups in cellulose (Bajpai et al., 2011). From there, the intensity of the absorption peak around those are from the stretching vibration of C–H of carboxymethyl which is increased significantly after introducing the long carboxymethyl in OPEFB chain (Yu et al., 2010).

The peaks were observed at 1671.28cm-1 and 1671.94 cm-1 for both polymers, and the long peak shows that OPEFB-SAPC (2.5 wt%) of filler contents incorporated with optimum OPEFB compare to the higher OPEFB-SAPC (12.5 wt%) of filler contents which is due to the cellulose and silica content in OPEFB. These absorption peaks were attributed to the asymmetric extension vibration of $–COO^-$ coincided with the extension vibration of C=O of amide I band at 1 (Yu et al., 2009).

Moreover, the C=C and C=O stretching of carbonyl groups which presence in the aromatic rings in hemicellulose and lignin in OPEFB, as well as C=O asymmetric stretching of carboxylate anions which exist in amide functional groups in the SAPC network seems to be appeared at the same broad absorption band of around 1700-1600 cm^{-1} regions for both spectra. (Ibrahim et al. 2003 and Ibrahim et al. 2005). The aliphatic and aromatic groups in the plane deformation vibration of methyl, methylene and methoxy groups in OPEFB can be seen around 1425-1110 cm^{-1}. The synthesized OPEFB-SAPC comprises OPEFB backbone grafted with poly-acrylamide that carry both amide and carboxylate as functional groups, and was shown in the peak around 1300-1100 cm^{-1} which is due to the C-O-C bonding between OPEFB and the side chains (Ibrahim et al. 2003).

Both curves have been observed show peaks around 1458 $cm^{-1}$and 1426 cm^{-1} and it shows sharp peak observed at 2.5 wt% of filler contents compare to 12.5 wt% of filler contents. This may be occurred because the increasing of extension vibration of –

COO^-. In a similar research it was reported that the strength of the peak at 1450 cm^{-1} contributed to the symmetrical extension vibration of $–COO^-$ and the peak at 1308 cm^{-1} assigned to the extension vibration of C-O is greatly increased and the absorption peak at 1323 cm^{-1} was contribute to the stretching and bending vibrations of the C–N bond of the amide III band and the intensity was notably increased after the reaction (Chen and Tan, 2006).

Furthermore, absorption peak at 706.34 cm^{-1}, 658.91 cm^{-1} and 622.66 cm^{-1} shows shifted curve in both polymers. The OPEFB-SAPC (2.5 wt %) is more shifted to the left compared to the OPEFB-SAPC (12.5 wt %) because of filler contents and it may be attributed to the planar rocking vibration of C–H of the long carbon chain appeared (Chen and Tan, 2006). On the other hand, another evidence of grafting could be seen from the peaks that appeared after 1000 cm^{-1} which was due to the stretching of the CH_2-CH_2 groups (Ibrahim et al. 2003).

This Table 4.1 shows the value of intensity at wavenumber for both curves which exhibit the significance of adding sufficient filler contents in SAPC. From Table 4, it can be seen that OPEFB-SAPC (2.5 wt %) possess higher value of intensity than OPEFB-SAPC (12.5 wt %). This is because of the sufficient cellulose and silica content within OPEFB-SAPC which results in the highest water absorbency.

Table 4.1: Intensity value at same wavenumber

Wavenumber (cm^{-1})	Intensity (%T)	
	OPEFB-SAPC (2.5 wt%)	OPEFB-SAPC (12.5 wt%)
4000	57.80	48.40
3600	50.40	43.80
1650	49.20	42.10

4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a simple and accurate method to study the decomposition pattern and thermal stability of polymers over a wide range of temperature. TGA curves of (a) pure SAPC, (b) OPEFB-SAPC containing 2.5 wt% (c) and OPEFB-SAPC containing 12.5 wt% (c) were presented in Figure 4.7, respectively. Both introduction of filler contents show a similar loss between 50 ºC, to 250 ºC, correspond a loss of water existed in these samples. The introduction of filler loadings on thermal stability of OPEFB-SAPC were observed as from the graph, it shows OPEFB-SAPC (2.5 wt %) of filler contents starts to dope at 500 ºC while for OPEFB-SAPC (12.5 wt %) the doped begins at 340 ºC earlier. From the graph, it can be seen that the doped of OPEFB-SAPC (2.5 wt %) occurred twice compare others due to higher amount of crosslinker was added during polymerization. Besides, the result indicated that as temperature increased, the weight loss also decreased due to the loss of moisture as well as breaking bond occurred in OPEFB-SAPC.

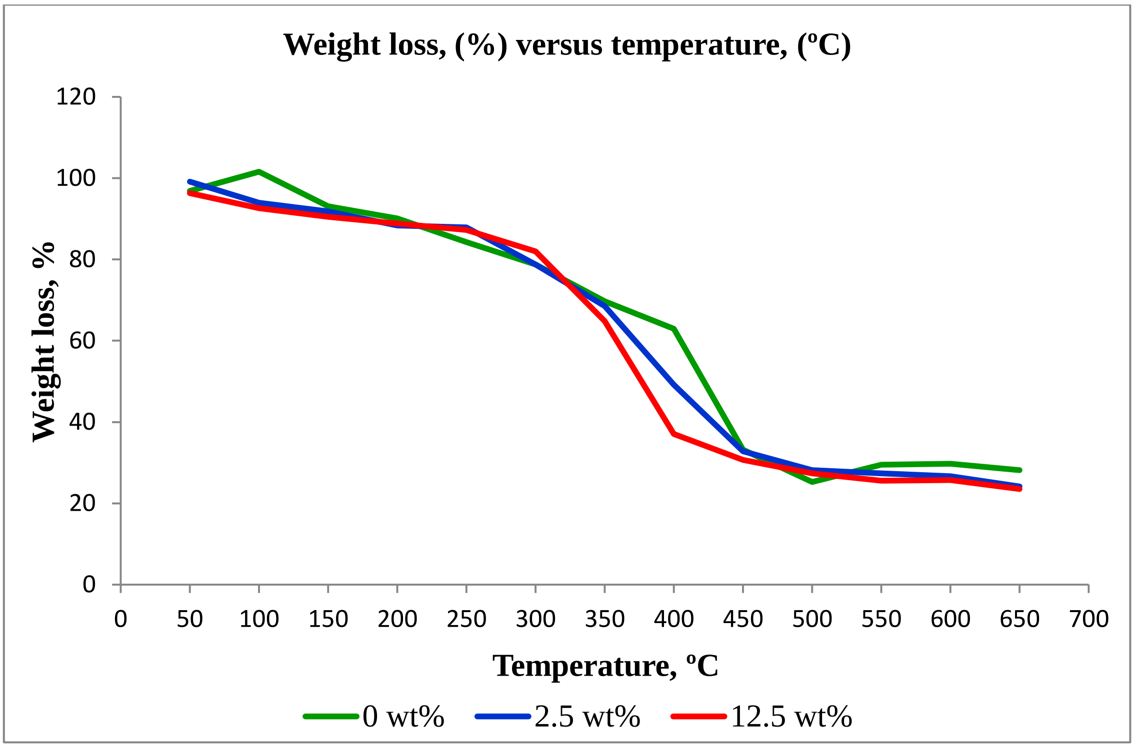


Figure 4.7: TGA curves of pure SAPC, OPEFB-SAPC (2.5 wt %) and OPEFB-SAPC (12.5 wt %) of filler loadings

Based on the Figure 4.7, it has been observed that the initial decomposition temperature of OPEFB-SAPC (2.5 wt%) of filler loadings was 340 ºC (70% weight loss) then, the final decomposition temperature was 500 ºC (28% weight loss) and the maximum rate temperature of weight loss was at 500 ºC (21% weight loss). Meanwhile, the initial decomposition temperature of OPEFB-SAPC (12.5 wt %) of filler loadings was 340 ºC (69% weight loss) then, the final decomposition temperature of OPEFB-SAPC (12.5 wt %) of filler loadings was 500 ºC (28% weight loss) and the maximum rate temperature of weight loss was at 500 ºC (42% weight loss).

Moreover, as can be seen from Figure 4.7, OPEFB-SAPC (12.5 wt %) shows a four-stage thermal decomposition process as well as the pure SAPC. As the temperature increased to 250ºC, the weight of samples decreased gradually implying a loss of moisture, dehydration of saccharide rings and breaking of C–O–C glycosidic bonds in the main chain of OPEFB-SAPC as similar study reported by (Zhang et al., 2007). There is a sharp weight loss with increasing temperature from 250º C to 400º C and 50% of sample was lost within this temperature range.

Besides, there was no obvious difference between OPEFB-SAPC (2.5 wt %) and OPEFB-SAPC (12.5 wt %) as the temperature was below 250 ºC. With further increasing temperature from 340 ºC to 500 ºC, OPEFB-SAPC (12.5 wt%) exhibits a second step decomposition implying the decomposition of carboxyl groups of OPEFB-SAPC chains which similar research from Chitosan-g-poly (acrylic acid)/ attapulgite superabsorbent composite study by Zhang et al., (2007). Lastly, the third stage occurred within the temperature range from 500 ºC to 700ºC with the decreasing of weight loss about 10.25%.

However, from this graph too, OPEFB-SAPC (2.5 wt%) shows a lower weight loss and smaller total weight loss between the temperature 50ºC and 750ºC compare to OPEFB-SAPC (12.5 wt%). From there, it can be seen OPEFB-SAPC (2.5 wt%) exhibits three-stages thermal decomposition where the first one was from 340ºC to 500ºC with the weight loss about 21% which also implying a loss of moisture, dehydration of saccharide rings and breaking of C–O–C glycosidic bonds (Zhang et al., 2007). Secondly, the decomposition occurred within the temperature of 500ºC to 700ºC with the weight loss about 10.25 % which was lower compared to OPEFB-SAPC (12.5 wt %).

In a similar research it was reported there were three types of decomposition regions of the composite. Firstly for the first region was in the range of 20 to 200 ºC due to water loss, which is adsorbed both on the surface and in the pores of the composite. Then followed by the second region; the weight loss within the temperature of 200 to 400 ºC that can be attributed to the thermal decomposition of amide side groups of acrylamide and crosslinker on the network. Lastly, for the third region at 400 ºC represented a substantial mass loss and was generally attributed to main chain of composite breakdown (Oztop et al., 2009).

The incorporation of OPEFB filler contents gave advantage in enhancing the thermal stability of OPEFB-SAPC. This phenomenon occurred may be attributed that the OPEFB particles improve the barrier by physically impeding the passage of gases through the matrix, called as a tortuous path. The enhanced barrier characteristics which benefits from the hindered diffusion pathways through the Unexpended Vermiculite, will lead to improve thermal stability impedance with UVMT particles act as the heat barrier as reported by Zheng et al., (2007).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Oil palm empty fruit bunch Superabsorbent Polymer Composite (OPEFB) was synthesized by using solution polymerization technique of acrylamide onto OPEFB micro powder by mixing N, N-methylene-bisacrylamide (MBA) as the crosslinking agent and ammonium persulphate (APS) as the initiator in aqueous solution. The research project has been successfully achieved in studying the optimum condition of OPEFB based on the superabsorbent polymer composite by determining the effect of pH solution as well as the effect of filler loadings towards the water absorbency. As a result, pH 4 is the highest optimum condition of water absorbency. Meanwhile, OPEFB-SAPC (2.5 wt% of filler loading) reveals the well-organized loosely polymeric structure with multiple porous structures suitable for penetration of water into the polymeric network, which leads to high water uptake within the network was the optimum filler contents compared with OPEFB-SAPC (12.5 wt%) of filler contents. The samples were characterized by using Field Emission Electron Microscopy (FESEM), Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR). The thermogravimetry analysis result indicate that the OPEFB-SAPC the well-organized loosely polymeric structure with multiple porous structures of the 2.5 wt% of filler loading shows a three stage degradation, unlike the dense unorganized rigid structure been exhibited by the 12.5 wt% filler loading. Then, FTIR analysis shows OPEFB-SAPC (2.5 wt %) has sharp peak of bonding curves compared to OPEFB-SAPC (12.5 wt %). Therefore, this research has proved that the OPEFB-SAPC was able to enhance the water absorbency uptake for better contributions in various applications widely which useful to the environmental friendly.

5.2 RECOMMENDATIONS

There are several improvements are required to be considered as follows:

i. Ensure treated OPEFB filler is grind in size around 100 µm in better mixing during polymerization process.

ii. The neck bottom flask has to be closed tightly with the stoppers in order to reduce the exposure of polymerization samples to the oxygen.

iii. Constant water supply must be flow continuously to the condenser during polymerization process in order to maintain the temperature inside the neck bottom flask so that the liquid from the solution mixture will not be evaporated and disturb the occurrence of the polymer.

iv. The period time of tea bag step need to be hanged up longer than one hour to ensure there is no liquid drop off so that it will not effect in measuring water absorbency of swollen sample.

v. The synthesized of OPEFB-SAPC should be repeated in triplicate samples in order to obtain more accurate result.

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APPENDIX A

Table A1: Summary data of water absorbency testing

Filler loading, wt(%)	WEIGHT BEFORE (g)									
	Empty Tea Bag					Empty Tea Bag + Dried Sample				
pH	2	4	6	8	10	2	4	6	8	10
0.0	1.133	1.144	1.133	1.140	1.156	1.533	1.544	1.533	1.540	1.556
2.5	1.126	1.161	1.146	1.154	1.136	1.526	1.561	1.546	1.554	1.536
5.0	1.139	1.133	1.122	1.152	1.126	1.539	1.533	1.522	1.552	1.526
7.5	1.142	1.142	1.134	1.133	1.135	1.542	1.542	1.534	1.533	1.535
10.0	1.156	1.138	1.142	1.158	1.523	1.556	1.538	1.542	1.558	1.923
12.5	1.132	1.146	1.178	1.124	1.136	1.532	1.546	1.578	1.524	1.536

Filler loading, wt(%)	WEIGHT AFTER (g)									
	Tea Bag + Swollen Sample					Swollen Sample				
pH	2	4	6	8	10	2	4	6	8	10
0.0	7.953	10.554	10.25	9.588	9.556	6.420	9.010	8.717	8.048	8.000
2.5	8.028	10.793	10.776	9.706	9.608	6.502	9.232	9.230	8.152	8.072
5.0	7.945	9.888	9.868	9.388	8.692	6.406	8.355	8.346	7.836	7.166
7.5	7.872	9.542	9.392	8.273	8.185	6.330	8.000	7.858	6.740	6.650
10.0	7.791	8.851	8.283	8.215	8.101	6.235	7.313	6.741	6.657	6.178
12.5	6.274	7.314	7.104	9.98	6.625	4.742	5.768	5.526	8.456	5.089

Filler loading, wt(%)	WEIGHT ABSORBENCY (g/g)				
pH	2	4	6	8	10
0.0	15.050	21.525	20.793	10.120	19.000
2.5	15.255	22.080	22.075	10.380	19.180
5.0	15.015	19.888	19.865	9.590	16.915
7.5	14.825	19.000	18.645	6.850	15.625
10.0	14.588	17.283	15.853	6.643	14.445
12.5	10.855	13.420	12.815	11.140	11.723

Table A.2: Statistical analysis

t-Test: Two-Sample Assuming Equal Variances

	Variable 1	*Variable 2*
Mean	19.594	12.2236
Variance	7.84492	0.82823
Observations	5	5
Pooled Variance	4.33657	
Hypothesized Mean Difference	0	
df	8	
t Stat	5.59613	
P(T<=t) one-tail	0.00026	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.00051	
t Critical two-tail	2.306	

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Filler loading 0 wt%	5	95.49	19.098	6.2899
Filler loading 2.5 wt%	5	97.97	19.594	7.8449
Filler loading 5.0 wt%	5	90.27	18.055	4.3659
Filler loading 7.5 wt%	5	81.15	16.231	2.5749
Filler loading 10.0 wt%	5	78.82	15.765	0.9650
Filler loading 12.5 wt%	5	61.12	12.224	0.8282
pH 2	6	85.59	14.265	2.8410
pH 4	6	112.8	18.794	11.130
pH 6	6	107.3	17.875	12.782
pH 8	6	101.3	16.89	6.7596
pH 10	6	97.89	16.315	7.6194

ANOVA

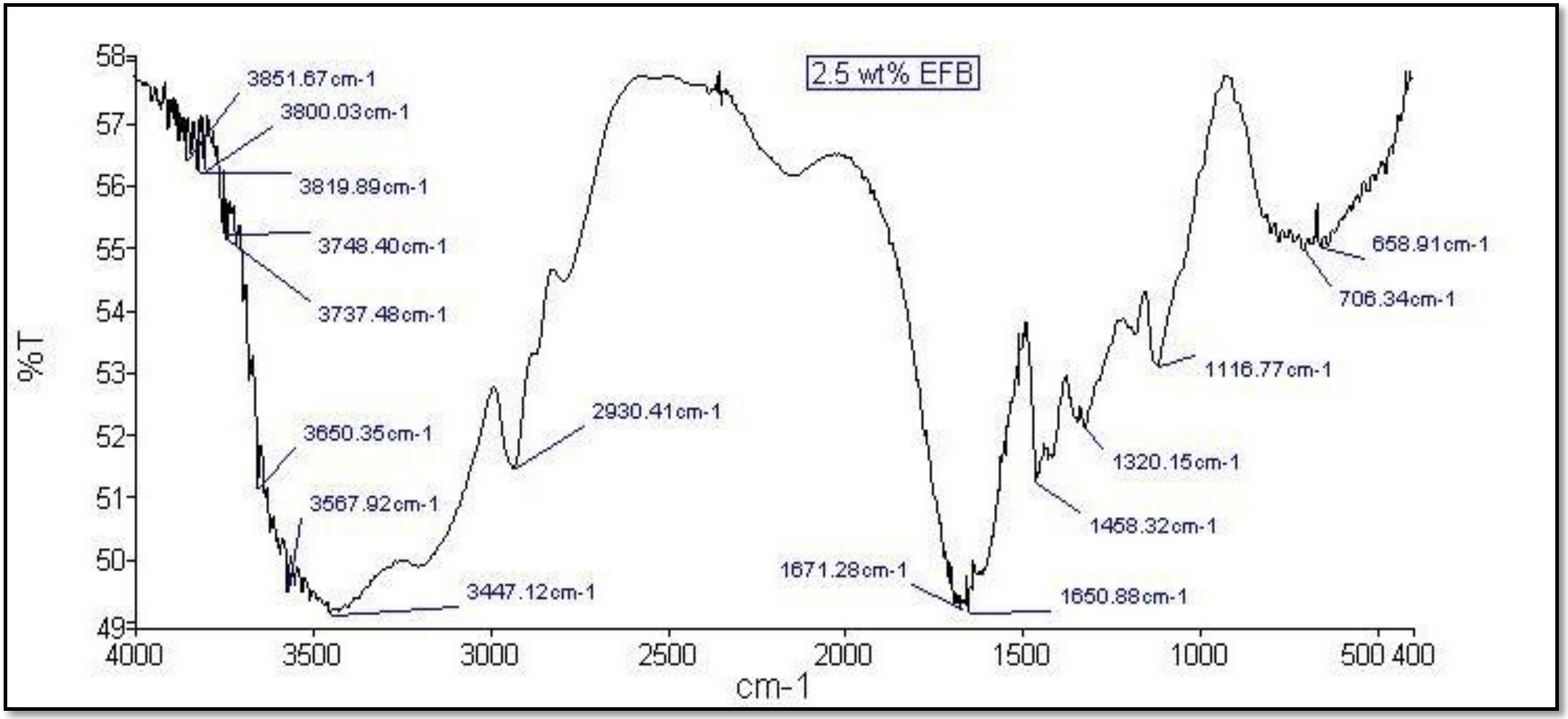
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	185	5	36.994	35.763	2.607E-09	2.711
Columns	71	4	17.697	17.107	3.06E-06	2.866
Error	20.7	20	1.0344			
Total	276	29				

Filler loading (wt %) / pH	**Water Absorbency (g/g) for 0 wt %**					**Water Absorbency (g/g) for 2.5 wt%**				
	2	**4**	**6**	**8**	**10**	**2**	**4**	**6**	**8**	**10**
Trials	15.170	20.895	21.360	19.756	18.920	16.220	23.377	21.380	19.917	18.207
	14.980	21.416	20.507	18.223	19.310	14.321	21.070	22.188	18.904	19.173
	15.000	22.260	20.512	19.381	18.770	15.224	21.790	22.657	19.319	20.160
N	3	3	3	3	3	3	3	3	3	3
Average	15.050	21.525	20.793	19.120	19.000	15.255	22.080	22.075	19.380	19.180
STDEV	0.104	0.691	0.491	0.799	0.279	0.950	1.180	0.646	0.509	0.977
SE	0.060	0.399	0.284	0.461	0.161	0.548	0.681	0.373	0.294	0.564

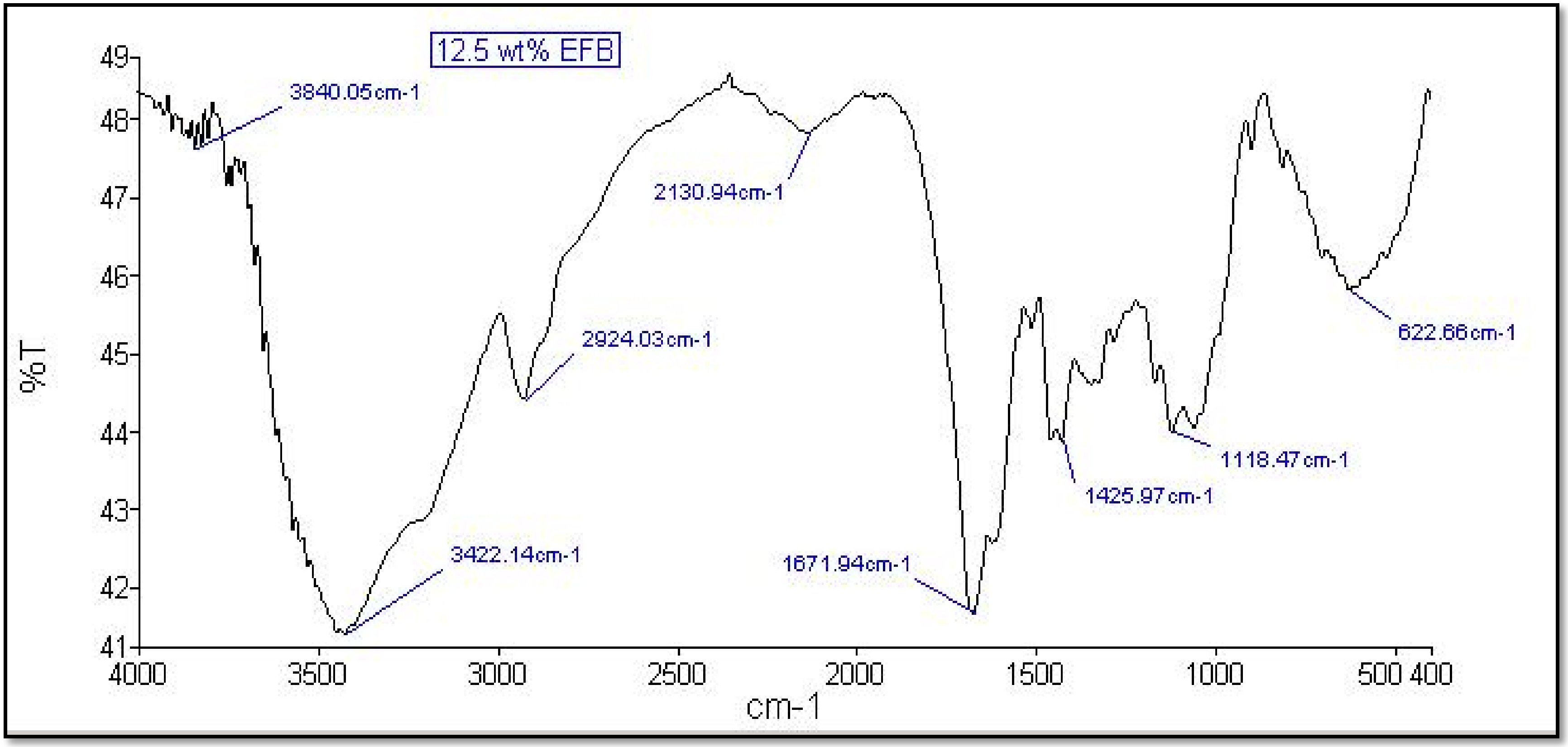
Filler loading (wt %) / pH	**Water Absorbency (g/g) for 5.0 wt %**					**Water Absorbency (g/g) for 7.5 wt %**				
	2	**4**	**6**	**8**	**10**	**2**	**4**	**6**	**8**	**10**
Trials	15.297	18.945	19.526	18.320	17.114	14.443	18.695	16.299	16.542	16.048
	14.944	20.013	19.519	18.708	16.816	15.926	19.714	15.248	15.630	15.517
	14.804	20.710	20.550	18.742	16.815	14.106	18.590	16.012	15.378	15.310
N	3	3	3	3	3	3	3	3	3	3
Average	15.015	19.888	19.865	18.590	16.915	14.825	19.000	15.853	15.850	15.625
STDEV	0.254	0.887	0.593	0.234	0.172	0.968	0.621	0.543	0.612	0.381
SE	0.147	0.512	0.343	0.135	0.100	0.559	0.358	0.314	0.354	0.220

Filler loading (wt %) / pH	**Water Absorbency (g/g) for 10.0 wt %**					**Water Absorbency (g/g) for 12.5 wt %**				
	2	**4**	**6**	**8**	**10**	**2**	**4**	**6**	**8**	**10**
10.0	14.294	17.047	15.292	16.326	15.876	11.838	12.409	13.437	12.194	12.720
	13.658	17.318	16.640	15.728	15.286	10.491	13.484	12.823	12.720	11.103
	15.812	17.53	15.618	14.875	15.173	10.236	13.02	12.185	13.351	11.346
N	3	3	3	3	3	3	3	3	3	3
Average	14.588	17.298	15.850	15.643	15.445	10.855	12.970	12.815	12.755	11.723
STDEV	1.107	0.242	0.703	0.729	0.378	0.861	0.539	0.626	0.579	0.872
SE	0.639	0.140	0.406	0.421	0.218	0.497	0.311	0.361	0.334	0.503

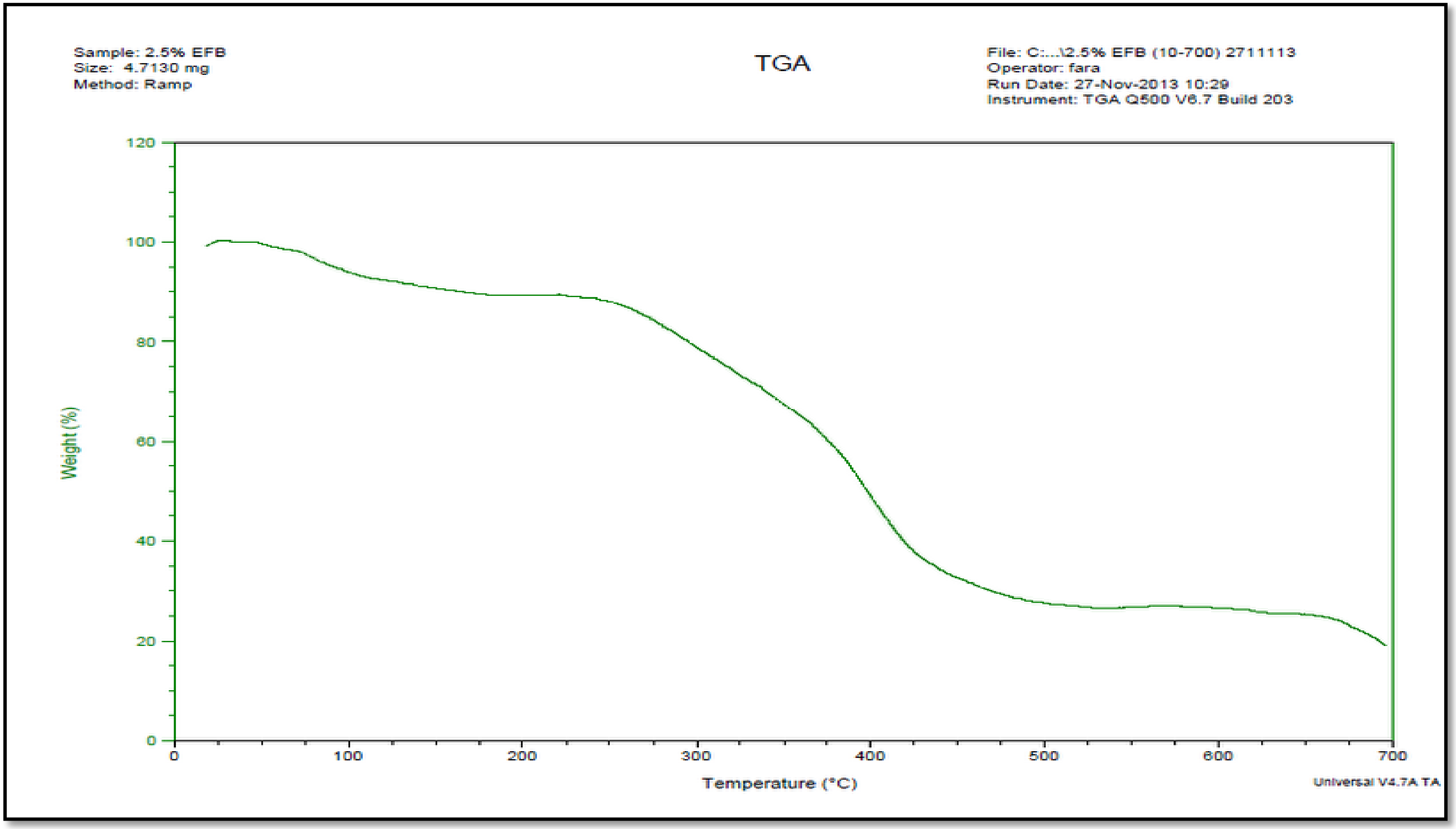
APPENDIX B



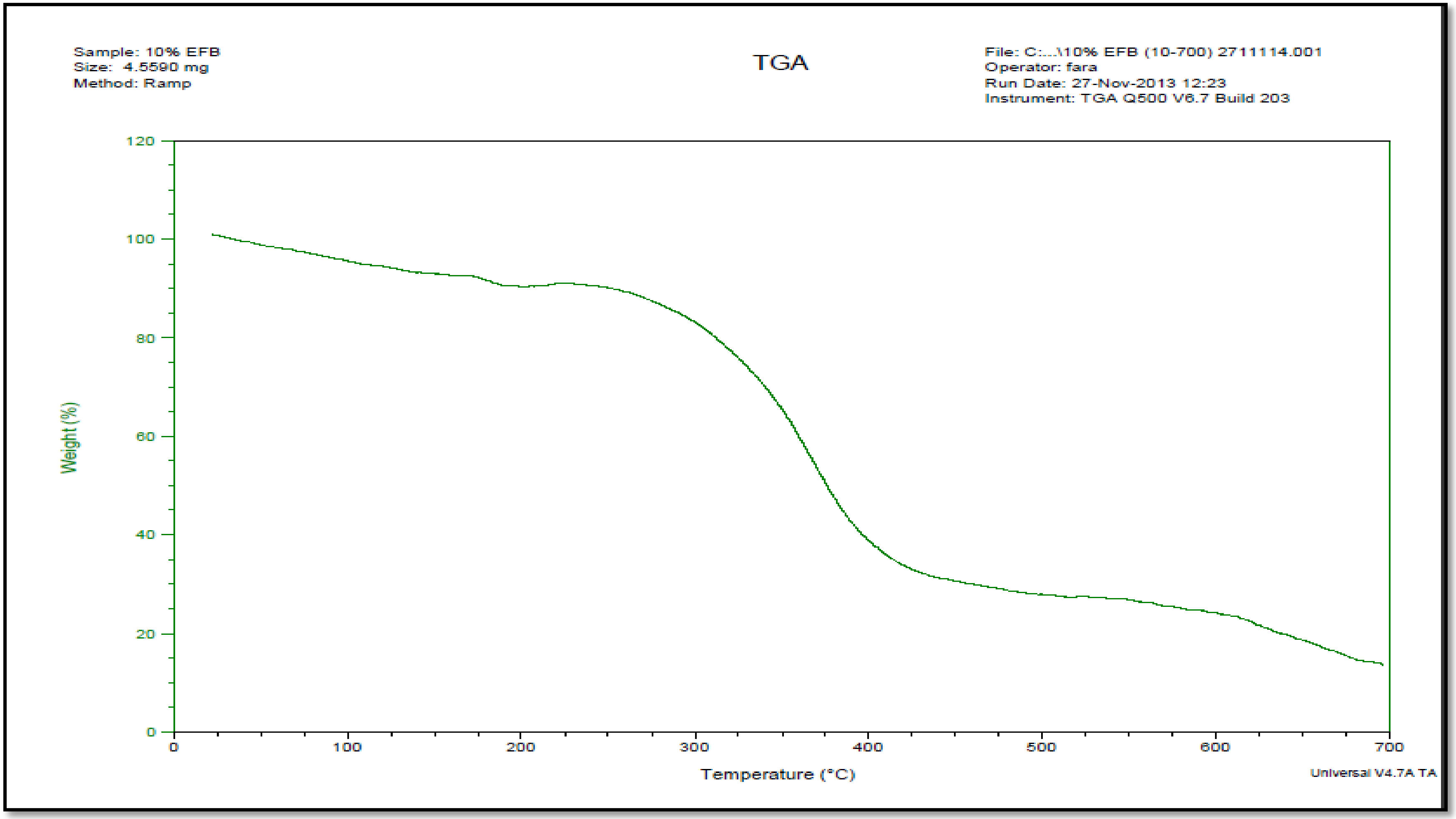
Appendix B1: Fourier Transform Infrared Spectroscopy (FTIR) for OPEFB-SAPC (2.5 wt %)



Appendix B2: Fourier Transform Infrared Spectroscopy (FTIR) for OPEFB-SAPC (12.5 wt %)



Appendix B3: Thermal Gravimetric Analysis for OPEFB-SAPC (2.5 wt %)



Appendix B4: Thermal Gravimetric Analysis for OPEFB-SAPC (12.5 wt %)

APPENDIX C

MATERIALS, APPARATUS AND EQUIPMENTS

Appendix C1: Chemicals and OPEFB filler

Appendix C1: Polymerization process apparatus

Appendix C3: Sieve shaker

Appendix C4: pH meter

Appendix C5: Analytical balance

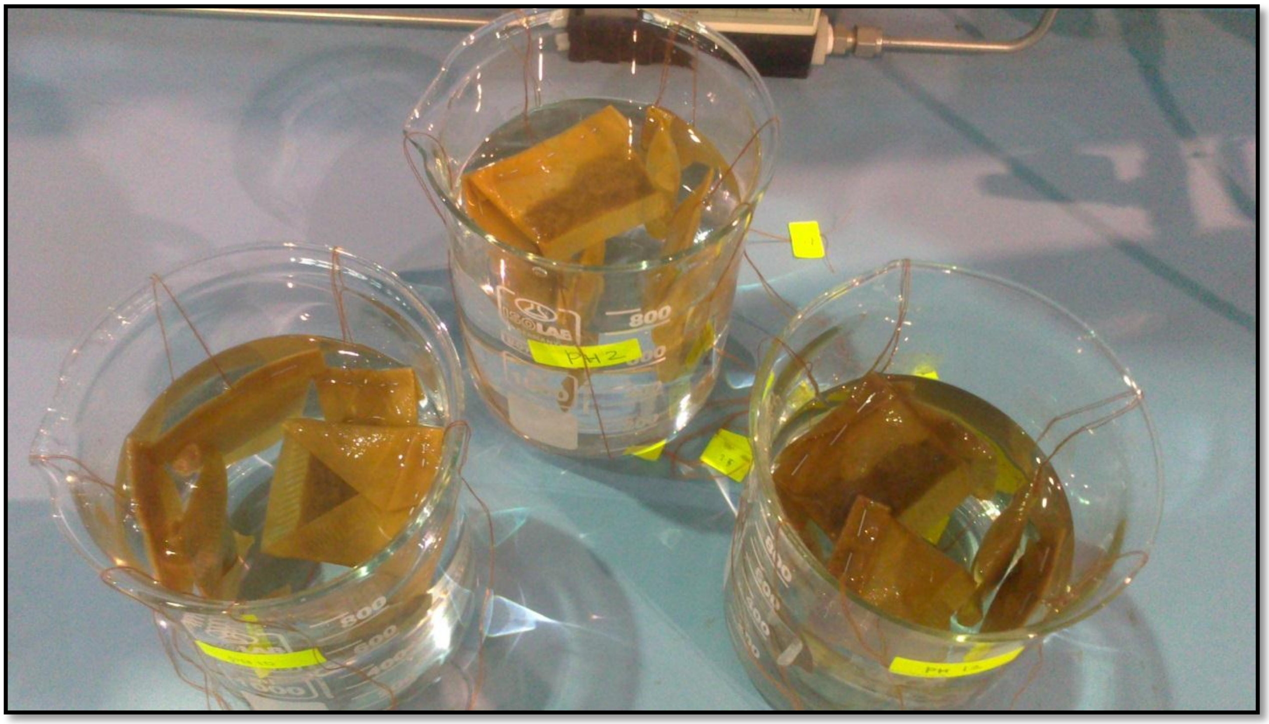
APPENDIX D

OPEFB SUPERABSORBENT POLYMER COMPOSITE

Appendix D1: Fresh OPEFB-SAPC

APPENDIX E

WATER ABSORBENCY TEST



Appendix E1: Tea-bag Method

APPENDIX F

CHARACTERIZATION

Appendix F1: FTIR

Appendix F2: TGA

Appendix F3: FESEM