DEVELOPMENT OF SUPERCAPACITOR HYDROGEL FROM SELF-CROSSLINK POLYANILINE AND RICE HUSK
(RH-*grafted*-PANI)

MUHAMMAD HAZIQ BIN RUSLI

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
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MUHAMMAD HAZIQ BIN RUSLI
B. ENG. (HONS) CHEMICAL ENGINEERING
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by

Muhammad Haziq Bin Rusli

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Dissertation submitted in partial fulfilment of
the requirements for the
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Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak

CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

____
(Dr Nurul Ekmi bt Rabat)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

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

MUHAMMAD HAZIQ BIN RUSLI

ABSTRACT

Nowadays, supercapacitor has been widely used in many applications. Therefore, this research is conducted to synthesize self-crosslink polyaniline (PANI) hydrogel grafted with rice husk fiber electrode for supercapacitor. Also, this research also study the effect of rice husk fiber on water absorbency capacity and conductivity of the hydrogel. Polyaniline (PANI) hydrogel usually synthesized using cross-linkers which greatly impair the electrochemical properties of hydrogel. Eliminating the cross-linkers in synthesizing the hydrogel helps increase its electrochemical properties. Rice husk waste are abundantly dumped and causing environmental and disposal issues. Hence, it is benificial it in other useful application. Sol-gel method was chosen to synthesize the hydrogel by using ammonium persulfate (APS) as initiator, aniline hydrochloric as precursor and gelatin. Five samples of hydrogel were synthesized with 0wt%, 1.5wt%, 3wt%, 4.5wt% and 6wt% of rice husk fiber content. The resulted hydrogels were characterized by Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Water absorbency capacity test was conducted by soaking the resulted hydrogel in water for 24 hours. While conductivity test was determined using DC conductivity measurement. The highest water absorbency capacity was hydrogel with 3 wt% rice husk which obtained 96.4% absorbency. The conductivity of hydrogel decreased when rice husk content increased but within a small range from 3.120×10^{-4} to 3.306×10^{-4} $s.cm^{-1}$. Thus, the self-crosslink Polyaniline (PANI) grafted with rice husk fiber hydrogel was successfully synthesized using sol-gel method.

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LIST OF ABBREVIATIONS

APS	Ammonium persulfate
DSC	Differential Scanning Calorimetry
DI	Distilled water
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
HCl	Hydrochloric Acid
HRTEM	High Resolution Transmission Electron Microscopy
NSGH	Nitrogen-sulphur co-doped graphene hydrogel
PANI	Polyaniline
PPy	Polypyrrole
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
WAC	Water Absorbency Capacity

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Supercapacitor is a high-capacity electrochemical capacitor. Instead of long term compact energy storage such as memory backup for static random-access memory and short-term energy storage or burst-mode power delivery, supercapacitor has been used in applications that require a lot of rapid charge and discharge cycles [1]. Supercapacitors use electrostatic double-layer capacitance or electrochemical pseudocapacitance or combinations of both.

For this project, the material for the electrodes is changed to hydrogel consisting of self-crosslink polyaniline (PANI) as conductive polymer and grafted with biomass waste fiber. Hydrogel is a network of polymer chains that are hydrophilic, sometimes as a colloidal gel in which water is the dispersion. Hydrogel is highly absorbent and consists of porous structure with three-dimensional networks. Hydrogel can be embedded with conductive polymer to form a conductive hydrogel [2].

Polyaniline (PANI) hydrogel is a combination of hydrogel and conductive polymer. Due to the unique electrochemical properties of polyaniline (PANI) and porous three-dimensional (3D) structure of hydrogel, it possessed a good potential in electrochemical energy storage field. Commonly, PANI hydrogel is synthesized by two methods. The methods are implanting PANI into non-conducting polymer [3] and use various cross-linkers. However, there is a new method called self-crosslink method. Self-crosslink PANI hydrogel is synthesized without using any cross-linkers. The advantage of this hydrogel is that its electrochemical properties is not limited by the non-conductive cross-linker. It has been proven in a study that self-crosslink PANI hydrogel is a very good material for electrochemical energy storage application as electrode due to its fast electrochemical response, high specific capacitance and low electric resistance [4]. The main purpose of this project is to synthesize conductive hydrogel from self-crosslink PANI and rice husk. Rice husk is waste material from rice mill process. Rice husk is abundant in Malaysia and used as fuel to generate energy. However, rice husk may be used in other applications as biomass fiber. Thus, this project study the effect of the content of biomass fiber on water absorbency capacity and conductivity of the resulted hydrogels.

1.2 Problem Statement

Supercapacitor is commonly made up of two porous carbon electrodes held closely together which charge and discharge quickly. Supercapacitor made of these electrodes has high power and cycle ability. However, it has a low energy density which means it can store small amount of electrical energy only [5]. Thus, the material of this electrode need to be changed to improve the capacitance and energy density.

As a conducting polymer, polyaniline (PANI) is a good material as it is cheap, high conductivity and easy of synthesized [6]. PANI hydrogel, the combination of the conducting polymers and hydrogels, might provide favorable approaches for electrons, charges and ions because of both conjugated structures existed in the PANI backbones and porous framework of the hydrogel. However, the existence of the non-conducting cross-linkers would greatly impair the electrochemical performances of the resulting PANI hydrogels because the additional cross-linkers cannot contribute to the pseudocapacitance of the whole devices [4].

Rice husk is a waste resulting from the milling process of paddy rice. This waste are commonly being used as burning fuel and turned into ash. The ash contains about 85 to 90% silica which is non-degradable. In 2010, it is estimated that about 37 million rice husk ash can be obtained and in would pose a great threat to environment where it damages the land [7].

1.3 Objectives of Research

This project will be conducted to develop a supercapacitor hydrogel. There are three objectives to be achieve in this research. The first objective is to synthesize conductive self-crosslink polyaniline (PANI) hydrogel grafted with rice husk fiber.

The second objective of this research is to characterize the resulted hydrogel using Fourier Transform Infrared (FTIR), Differential Scanning Colorimetry (DSC) and Thermogravimetric Analysis (TGA).

The last objective of this research is to investigate the effect of rice husk fiber content in the hydrogel on water absorbency capacity and conductivity of the resulted hydrogel.

1.4 Scope of Research

The materials that will be used for this research include aniline hydrochloric acid as precursor, ammonium persulfate (APS) as initiator, hydrochloric acid as hydrogel purifier and rice husk as biomass fiber.

The resulted hydrogels from this project will be characterized by testing it using Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry and Thermogravimetric Analysis (TGA). The conductivity will be tested using DC conductivity measurement and water absorbency capacity will be calculated based on the equation by Ge and Wang [8].

For this project, sol-gel method will be used to produce the hydrogel. Sol-gel synthesis method is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.

CHAPTER 2

LITERATURE REVIEW

Supercapacitor is a high-capacity electrochemical capacitor. Supercapacitor is used for energy storage undergoing frequent charge and discharge cycles at high current and short duration [1]. A conventional solid dielectric of ordinary capacitor is not used in supercapacitor. Instead, supercapacitor use electrostatic double layer capacitance or electrochemical pseudocapacitance or the combination of both. Electrostatic double layer capacitance use carbon or activated carbon as electrode while electrochemical pseudocapacitance use metal oxide or conducting polymer as electrode.

Table 2.1 shows the advantage and limitation of supercapacitor. Several types of electrodes have been tried and most are based on the electrochemical double-layer capacitor concept. It is carbon-based, has an organic electrolyte that is easy to manufacture and is the most common system in use today. However, the use of conducting polymer and hydrogel as electrode has emerge as one of the promising future electrode for supercapacitor. The material of supercapacitor electrode is further discussed below.

Table 2.1 Advantages and Limitations of Supercapacitor

Advantages	Limitations
• Can be cycled millions of time • High specific power; low resistance enables high load currents • Charges in seconds. Did not require end-of-charge termination	• Low specific energy. • High self-discharge which higher than most batteries • High cost per watt

2.1 Hydrogel

Hydrogel is a network of polymer chains that are hydrophilic, sometimes as a colloidal gel in which water is the dispersion. Hydrogel is highly absorbent where it can contain over 90% of water and natural or synthetic polymeric networks. It also has porous structure and three-dimensional networks which make it a potential material in huge applications. Hydrogel can be made as a conductive hydrogel by embedding conducting polymer into aqueous gels by physically compositing or forming co-networks [2]. However, this hydrogel conductivity performance is limited due to the presence of non-conductive host matrix or leaching out of conducting polymer when the hydrogel network swells.

Figure 2.1 shows the structure of hydrogel. The polymer is cross-linked forming a porous structure. The cross-link is normally created by using cross-linkers such as non-conductive polymer. Water molecules can be absorbed and stored in between the porous structure of hydrogel. Besides water molecules can also be stored in between the porous structure such as ions and solvents.

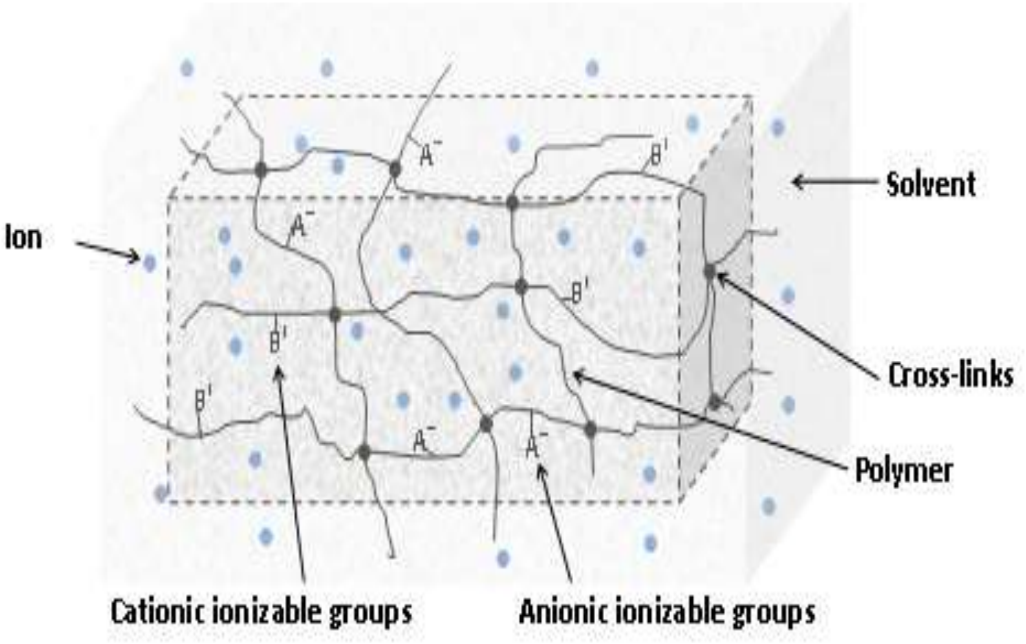


Figure 2.1 Structure of Hydrogel

2.1.1 Conductive hydrogel

In 2014, Yun Lu had synthesized elastic conductive polymer hydrogel from polypyrrole (PPy) using fast reaction and slow reaction in sequence. The elasticity of the hydrogel was very good as it can be compressed by more than 70% and recovered to its original state in 30 seconds. However, the original sponges exhibit many macro pores with the diameter of about 10 µm, which will inhibit the electrical transport. Besides, the electrical resistance of the hydrogel was affected by gel compression where it decreased gradually and the gel is compressed as what Figure 2.2 illustrates [2].

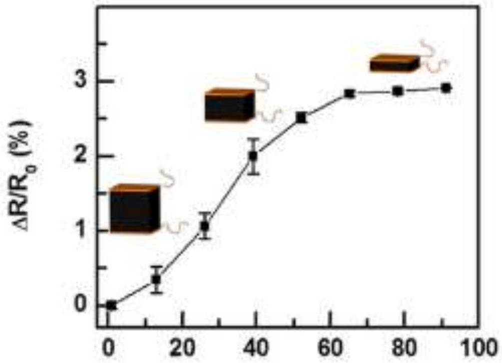


Figure 2.2 Graph of Change of electrical resistance of the PPy sponge sensor with the compression ratio

In another research, Xing and co-workers had prepared nitrogen(N), sulfur(S) co-doped graphene hydrogel by using thiocarbohydrazide as reducing and doping agents in aqueous solution. Based on field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM), it can be seen in Figure 2.3 that the hydrogels have porous structure and 3D network. This hydrogel electrode has long-term cycle stability and good electrochemical reproducibility. However, when the number of cycle increased, the capacitance of the hydrogel electrode decreased. This is due to the loss of pseudocapacitance resulted from some unstable functional group [9].

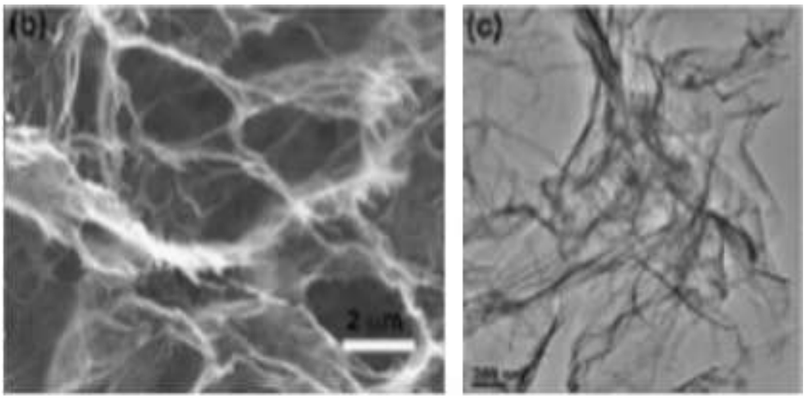


Figure 2.3 FESEM image of NSGH (left) and HRTEM image of NSGH (right)

2.2 Polyaniline (PANI)

Polyaniline (PANI) is a widely used conductive polymer. PANI provides a good service as a pseudocapacitive material. This is due to its high theoretical specific capacitance, low cost, high conductivity and ease of synthesis. It has a theoretical capacitance of 750 Farad per gram (F/g) with an assumption of 0.5 dopant per polymer unit and 0.7V potential window [6]. Besides, it exists in a variety of reversible protonation and oxidation forms, differing for electrochemical, optical or electrical properties [10].

2.2.1 Polyaniline (PANI) Supercapacitor Electrode

PANI-graphene nanofiber composite film of supercapacitor was prepared by Qiong Wu. The conductivity of the film is 5.5 x 10^2 siemens per meter (S/m), high capacitance of 210 farad per gram (F/g) at 0.3 ampere per gram (A/g) and it has good stability that high capacitance can be maintain after 800 charging/discharging [11].

A fabrication of manganese oxide nanorods–PANI composite for supercapacitor and the composite performance test was successfully done by Nirmalesh and Selladurai in 2015. Manganese oxide nanorods distributed over polyaniline (PANI) network was prepared by one step facile synthesis condition. The pH of the reactant solution was tuned using sulfuric acid. Based on Figure 2.4, for the composite material, PANI decompose at temperature between 280°C to 600°C and at temperature above 800°C the manganese dioxide composition decomposed.

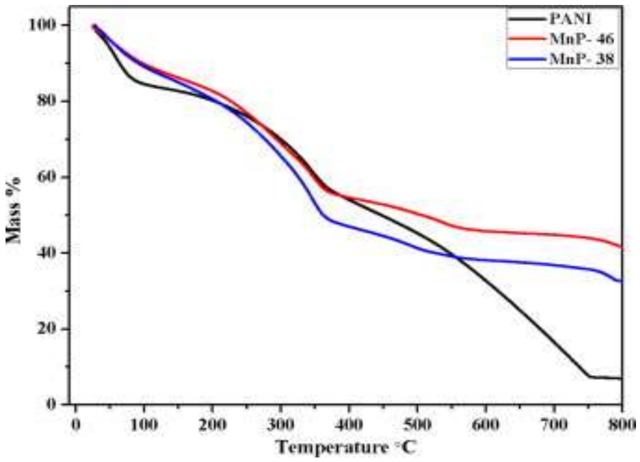


Figure 2.4 Thermogravimetric curve of Composite Material

In FTIR spectra of manganese–polyaniline composites skeletal vibrations of PANI was observed along with two sharp peaks at 533 cm−1 and 579 cm−1 characteristics of antisymmetric stretching mode of the MnO6 octahedra. Based on Field Emission Scanning Electron Microscope (FESEM) images in Figure 2.5, manganese-polyaniline composite was composed of manganese oxide cylindrical nanorods and PANI fiber like network. It was found that nanorods were oriented in random directions. However, with increase in PANI content or decrease in manganese concentration in the composite, it was found that current density of the composite decreased due to the overlapping of PANI over MnO_2 nanorods [12]. This has reduced the active sites available for charge storage.

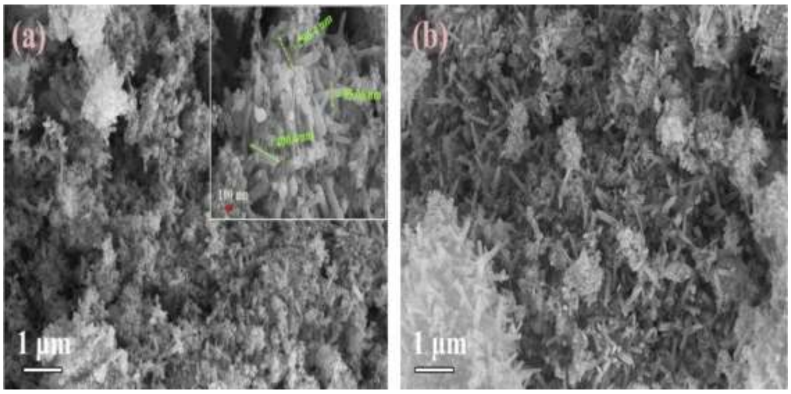


Figure 2.5 FESEM images of manganese oxide nanorod-PANI composites

In 2015, Elhalaway and co-workers conducted a research on synthesizing, characterization and electrical properties of polyaniline/gold and/or platinum core-shell nanocomposites [13]. The core-shell nanocomposites was a success based on images of scanning electron microscope (SEM) in Figure 2.6. The particles are highly branched and have taken the tree shape forming clusters groups.

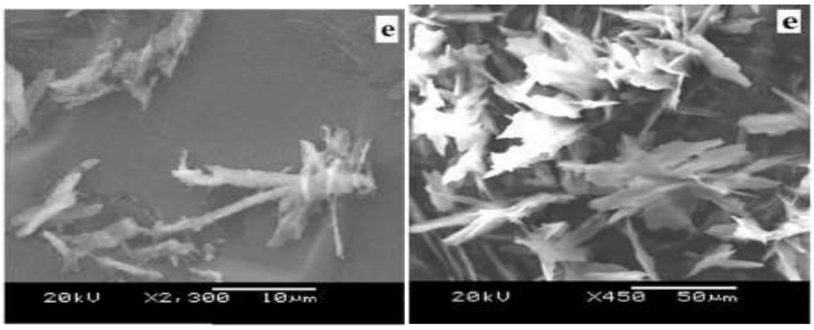


Figure 2.6 SEM images of polyaniline/gold (left) and polyaniline/platinum (right) composites

The FTIR results also showed the presence polyaniline/gold and polyaniline/platinum composites. Both have the almost the same peaks where polyaniline/platinum composite peak is slightly shifted. In the Thermogravimetric analysis (TGA), it was found that the composites were thermally stable but only until the temperature of 200°C and 210°C for polyaniline/gold and polyaniline/platinum composites respectively. Above the temperature, the composites will be completely decomposed. Figure 2.7 shows the diagram of TGA results.

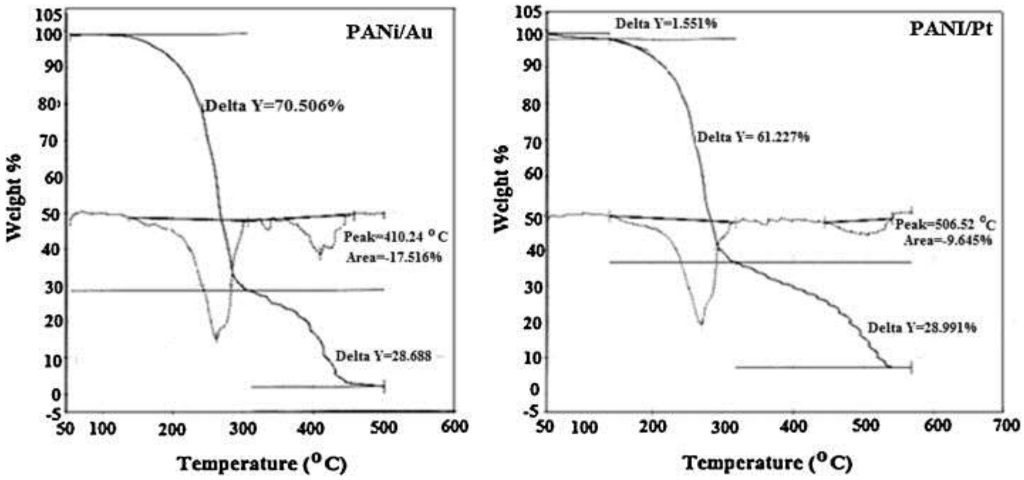


Figure 2.7 Thermogravimetric Analysis diagram of both composites

2.3 Self-crosslink polyaniline (PANI) hydrogel

A research had been made by Guo and co-workers on synthesizing self-crosslink polyaniline (PANI) hydrogel electrodes for electrochemical energy [4]. In this study, oxidative coupling reaction was used to synthesize the hydrogel by using ammonium persulfate as initiator and aniline hydrochloric salt as precursor. Figure 2.8 shows images of self-crosslink polyaniline (PANI) structure where a porous three-dimensional structure of polyaniline (PANI) is formed.

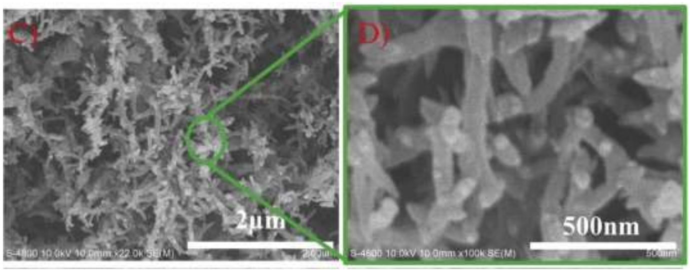


Figure 2.8 SEM images of self-crosslink polyaniline (PANI) hydrogel

Based on the Fourier Transform Infrared (FTIR) spectrum, PANI was present in the hydrogel in the form of emeraldine salt. The specific capacitances of the PANI hydrogel electrodes are greatly dependent on its doping level. The higher the doping level, the higher the specific capacitance. The density of the hydrogel also play an important role. The viscosity and mechanical strength depends on the density of gel. The higher the density, the higher the viscosity and mechanical strength. However, when the density adds up to 140 mg/ml, the PAni gel starts to become heterogeneous and reflect fragile properties because of the polymerization process is too quick to send out calorie during polymerization. Overall, the self-crosslink polyaniline (PANI) hydrogel has a fast electrochemical response, a high specific capacitance and a low electric resistance.

2.4 Rice Husk

Rice husk is the outermost layer of the paddy that is separated from rice grains during the milling process. Rice husk is available in abundance, low cost and high content of carbon. The annual production of rice husk worldwide is about 1.2×10^8 tons [14]. As a rice-producing country, Malaysia contributes tonnes of paddy rice. About 20% of the paddy rice produced is composed of rice husk [15]. Rice husk in Malaysia are mostly used as burning fuel and the resulting as is sold as fertilizer. It is also being used as animal’s feed by grounding it with broken rice. However, a lot of rice husk waste are not manage properly due to its enormous amount causing damage to land. Therefore, another applications can be used to fully utilize rice husk.

A lot of research about supercapacitor electrode from rice husk activated carbon has been made. Rice husk was converted into activated carbon by potassium hydroxide (KOH) activation. Rice husk activated carbon consists of porous structure and exhibits high surface and pore volume characteristic. Besides, it had a higher specific capacitance and longer cycling life than other biomass carbon materials [16]. However, rice husk fiber was never used in a research related to electrical energy. It was only used as a material to produce carbon.

CHAPTER 3

METHODOLOGY

3.1 Research Outline

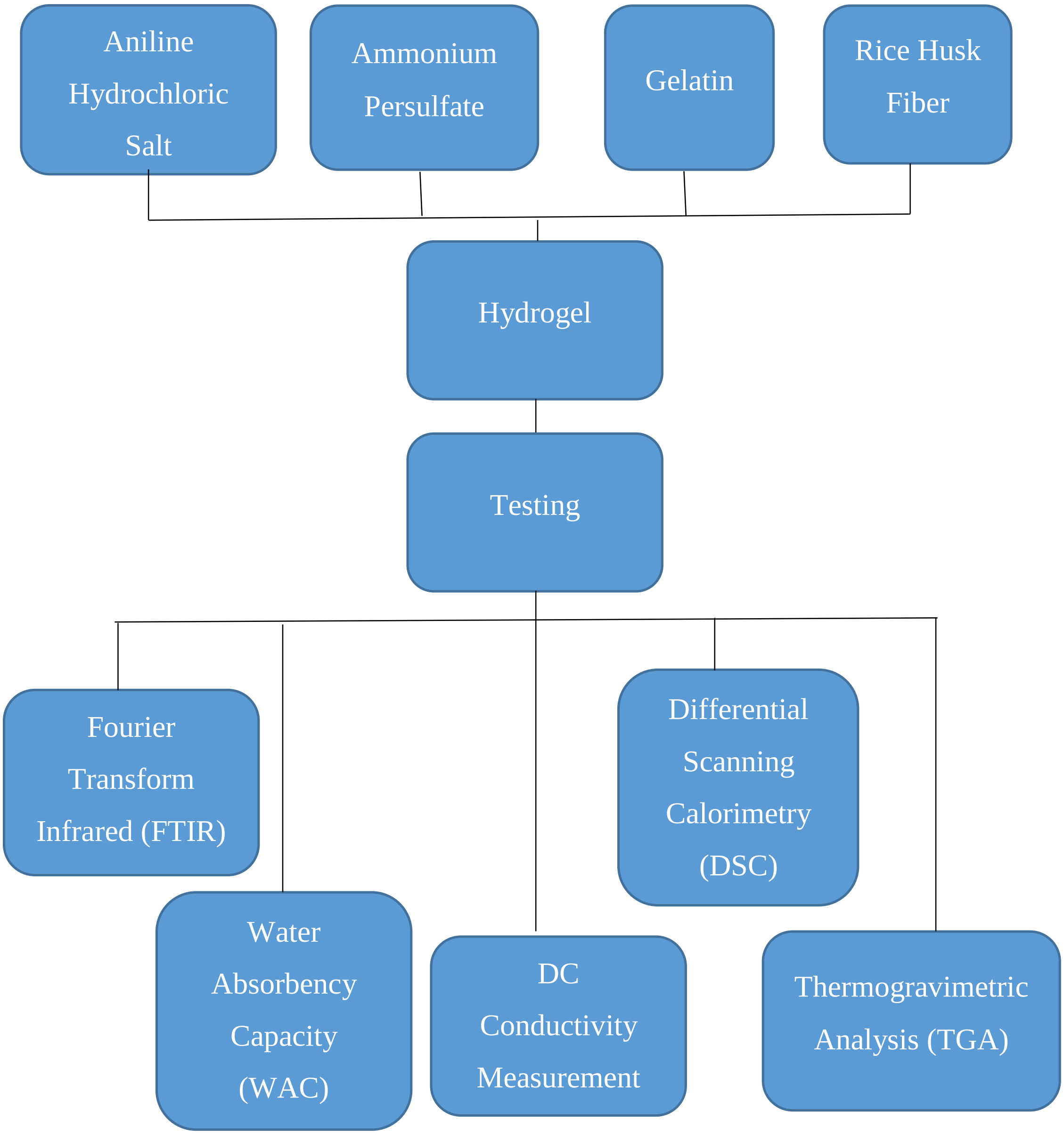
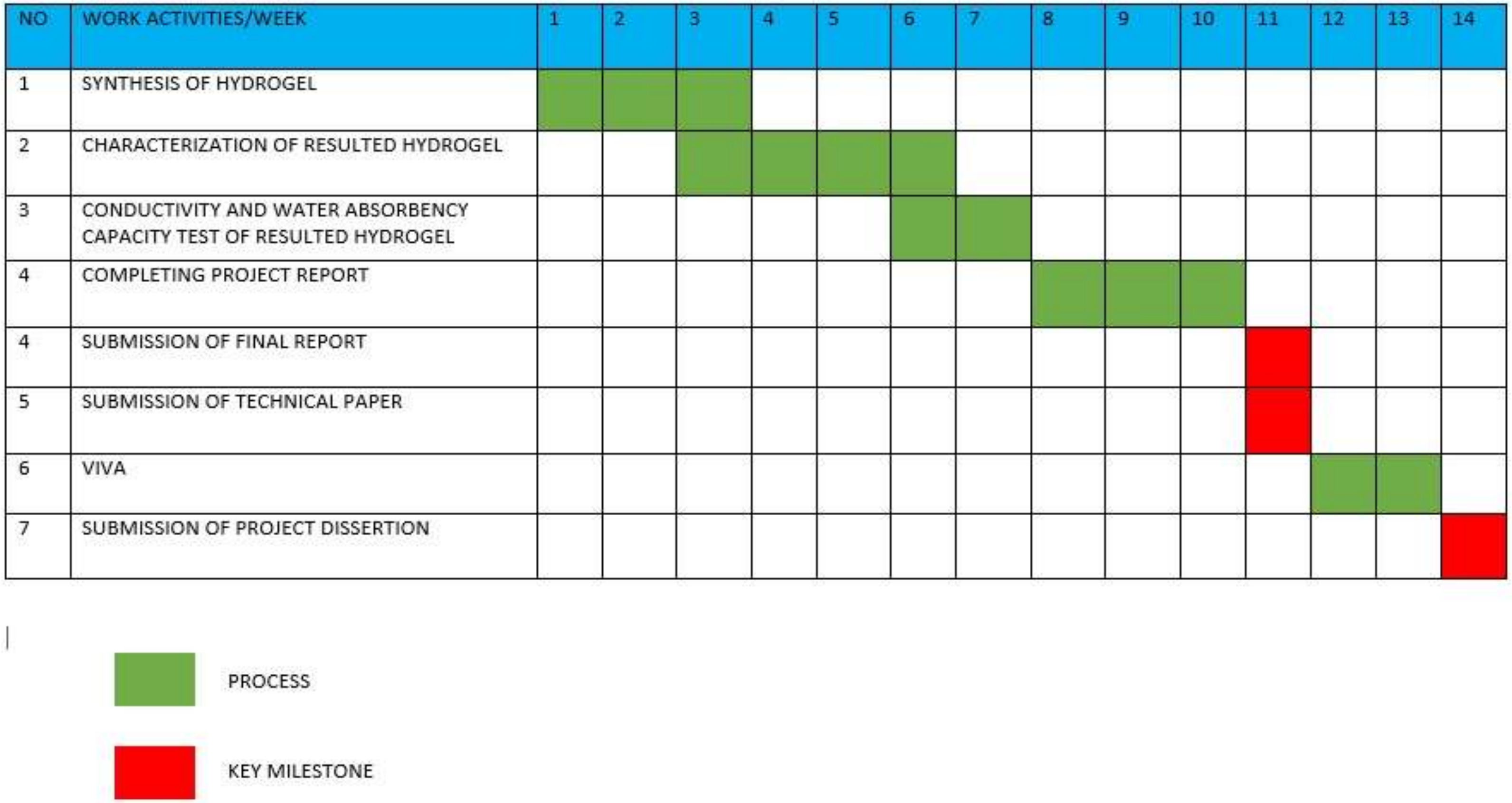


Figure 3.1 Research Outline

3.2 Gant Chart



NO	WORK ACTIVITIES/WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	SYNTHESIS OF HYDROGEL	🟩	🟩	🟩											
2	CHARACTERIZATION OF RESULTED HYDROGEL			🟩	🟩	🟩	🟩								
3	CONDUCTIVITY AND WATER ABSORBENCY CAPACITY TEST OF RESULTED HYDROGEL						🟩	🟩							
4	COMPLETING PROJECT REPORT								🟩	🟩	🟩				
4	SUBMISSION OF FINAL REPORT											🟥			
5	SUBMISSION OF TECHNICAL PAPER											🟥			
6	VIVA												🟩	🟩	
7	SUBMISSION OF PROJECT DISSERTION														🟥

🟩 PROCESS

🟥 KEY MILESTONE

Figure 3.2 Gantt Chart FYP

3.3 Materials

There are five materials that was used to synthesize the hydrogel. The main materials are aniline hydrochloric salt as precursor, ammonium persulfate as initiator and rice husk as waste fiber. Table 3.1 below shows the materials and its function.

Table 3.1 Materials and its function

Material	Function
Aniline Hydrochloric Salt	Precursor
Rice Husk	Waste Fiber
Ammonium Persulfate (APS)	Initiator
Distilled Water (DI)	Solvent
Hydrochloric Acid	Act as purifier
Gelatin	Increase gelation

3.4 Procedures

The procedure in synthesizing the hydrogel is divided into two, preparation of rice husk fiber and synthesis of hydrogel.

3.4.1 Preparation of rice husk fibre

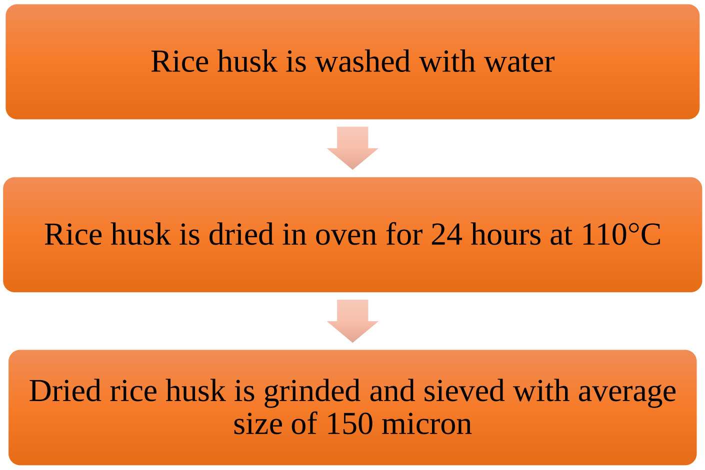


Figure 3.3 Flowchart preparation of rice husk fiber

3.4.2 Synthesis of hydrogel

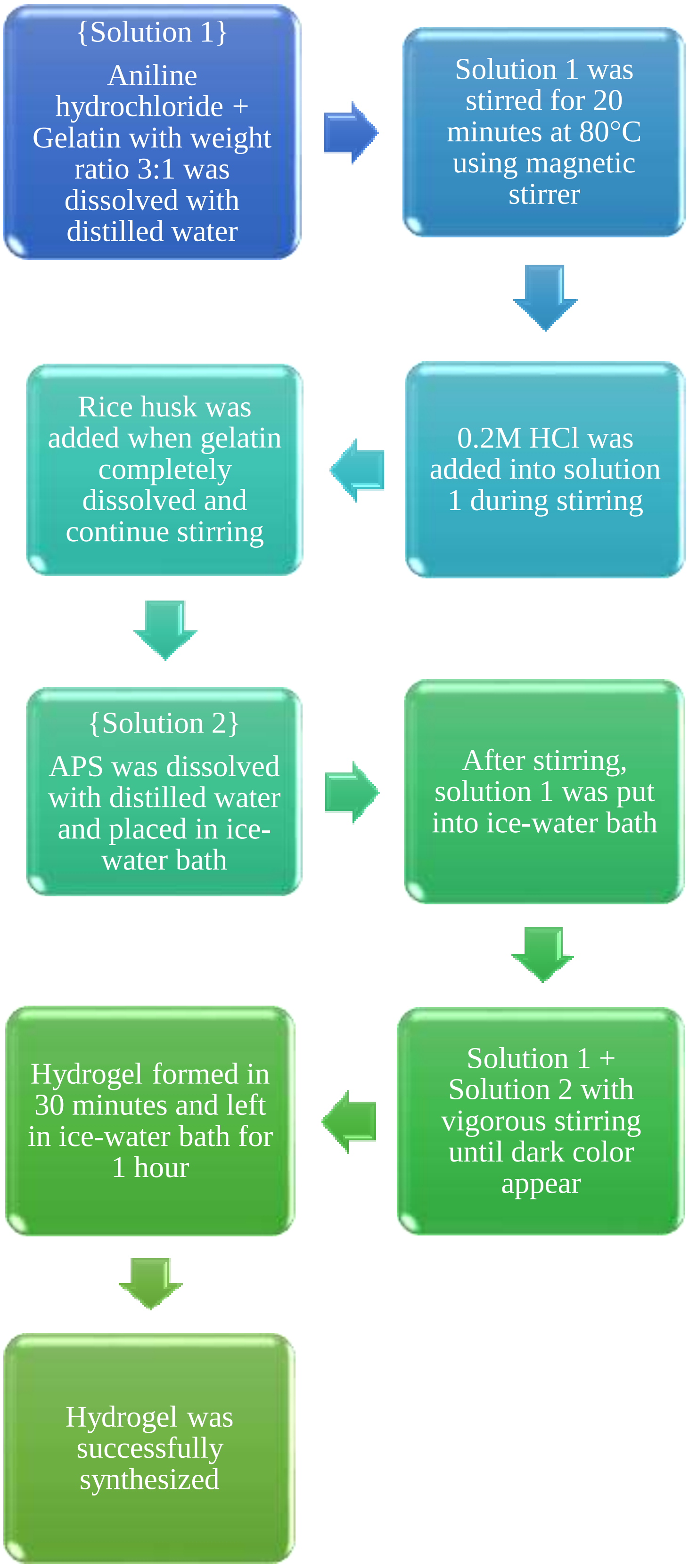


Figure 3.4 Flowchart synthesis of hydrogel

3.5 Testing

3.5.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectrum was recorded on PerkinElmer Spectrum Version 10.4.4 between 4000 and 450 cm^{-1}.

3.5.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry testing was done using equipment DSC Q2000 V24.11 Build 124. The parameter used are -50°C as starting temperature, 250°C as end temperature and 20°C per minute as heating rate.

3.5.3 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) analysis was conducted to analyze the thermal stability of the hydrogel. Weight percent loss was recorded with respect to increasing temperature.

3.5.4 DC conductivity measurement

DC conductivity measurement was conducted by mounting hydrogel with aluminium plates. The resistance of the hydrogel was recorded using multimeter. The conductivity is calculated using equation (2).

3.5.5 Water Absorbency Capacity (WAC)

Dry hydrogel was weighted and soaked into water for 24 hours. After 24 hours, the hydrogel was weighted again. Water absorbency capacity (WAC) is calculated using the formula:

$$\text{Absorbency (\%)} = \frac{W\prime - W}{W} \times 100\% \tag{1}$$

Where W'= weight of swollen resin and W= weight of dry hydrogel [8].

CHAPTER 4

RESULTS AND DISCUSSIONS

4.0 Introduction

This chapter will show the results obtained and will be discussed in detail. Two tests were conducted to examine the electrochemical properties of the hydrogel, water absorbency capacity test and conductivity test. The sample were characterized using three tests which are Direct Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy.

4.1 Water absorbency capacity

Water absorbency capacity (WAC) test was conducted by soaking the sample for 24 hours. Each sample were weighted before soaking into water and set as initial weight. After 24 hours, the sample was weighted again and set as final weight. The water absorbency capacity test were calculated using equation (1). The results are tabulated in the table below.

Table 4.1 Weight absorbency capacity (WAC) result

Rice husk weight percent (wt%)	Initial weight, W (g)	Final weight, W' (g)	WAC percentage (%)
0	2.0386	3.675	80.27
1.5	1.9834	3.708	86.9
3	2.989	5.781	96.4
4	1.9887	3.785	90.4
6	1.678	2.764	64.7

Based on Table 4.1 above, the percentage of water absorbency capacity increased from 0 wt% to 3 wt% of rice husk content. However, the percentage decreased a little at 4.5 wt% rice husk content and decreased sharply at 6 wt% of rice husk. The trending of the water absorbency capacity of the samples can be seen in figure 13 below.

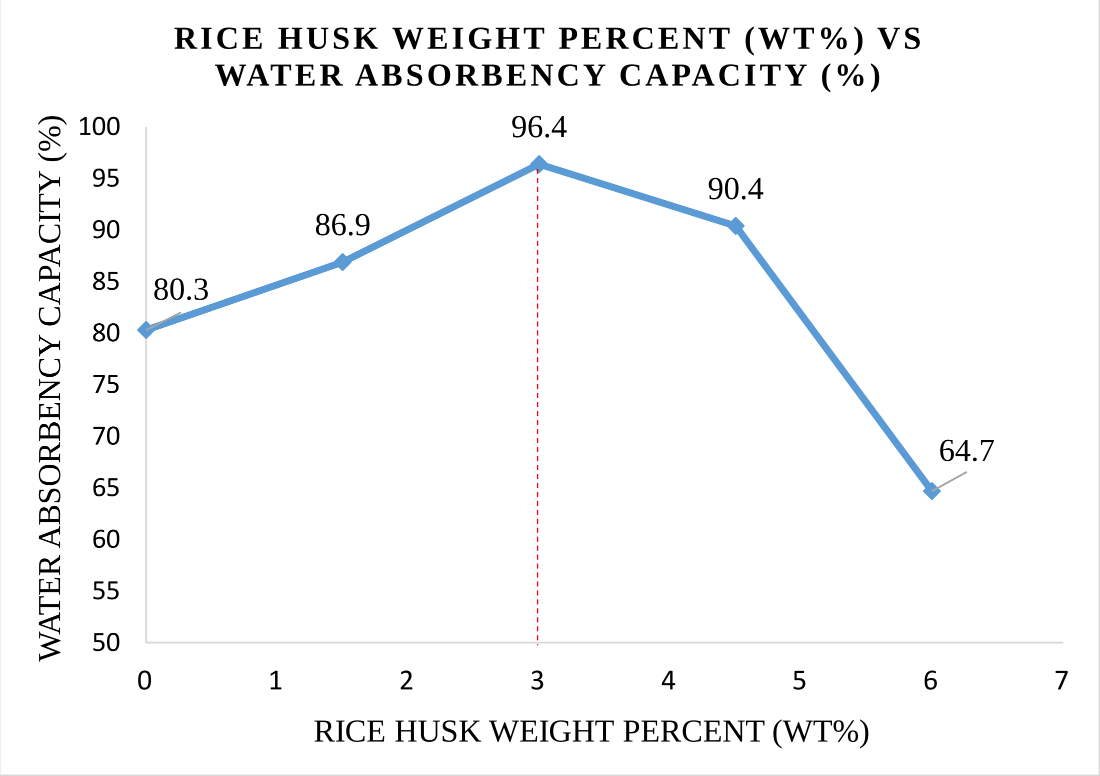


Figure 4.1 Graph of rice husk weight percent (wt%) vs water absorbency capacity (%)

Hydrogel have a porous structure thus it able to absorb and store water or ions. The presence of rice husk during the gelation of polyaniline hydrogel helped increasing the size of the pore in the hydrogel structure. Thus increasing the ability of the polyaniline hydrogel to absorb and store water or ions. That is why it can be seen from Figure 4.1 above that the water absorbency capacity of the samples are increasing as the rice husk content are increasing.

However, the water absorbency capacity started decreasing when the rice husk content is 4.5 wt%. This is due to the excessive amount of rice husk during the gelation of polyaniline hydrogel that it disrupts the porous structure of the hydrogel.

The porous structure of the polyaniline hydrogel might be blocked by the excessive amount of rice husk. Hence, the ability of the polyaniline hydrogel to absorb and store water or ions is reduced. It can be concluded that the optimum rice husk content is at 3 wt%.

4.2 Conductivity

The conductivity of the samples was calculated using the formula in equation (2) below. The sample were mounted between two aluminium plates and the resistance of the sample was measured. Using the resistance recorded, the conductivity of the hydrogel was calculated. The table 4.2 below shows the results of the conductivity test.

$$\text{Conductivity (s.cm}^{-1}) = \frac{\text{Thickness (cm)}}{\text{Area (cm}^2)\times\text{Bulk resistance }(\Omega)} \qquad (2)$$

Table 4.2 Results of conductivity test

Rice Husk Weight Percent (wt%)	Area (cm2)	Thickness (cm)	Bulk Resistance (Ω)	Conductivity (s.cm-1)
0	1	0.2	605	3.306×10^{-4}
1.5	1	0.2	621	3.221×10^{-4}
3	1	0.2	629	3.180×10^{-4}
4.5	1	0.2	634	3.155×10^{-4}
6	1	0.2	641	3.120×10^{-4}

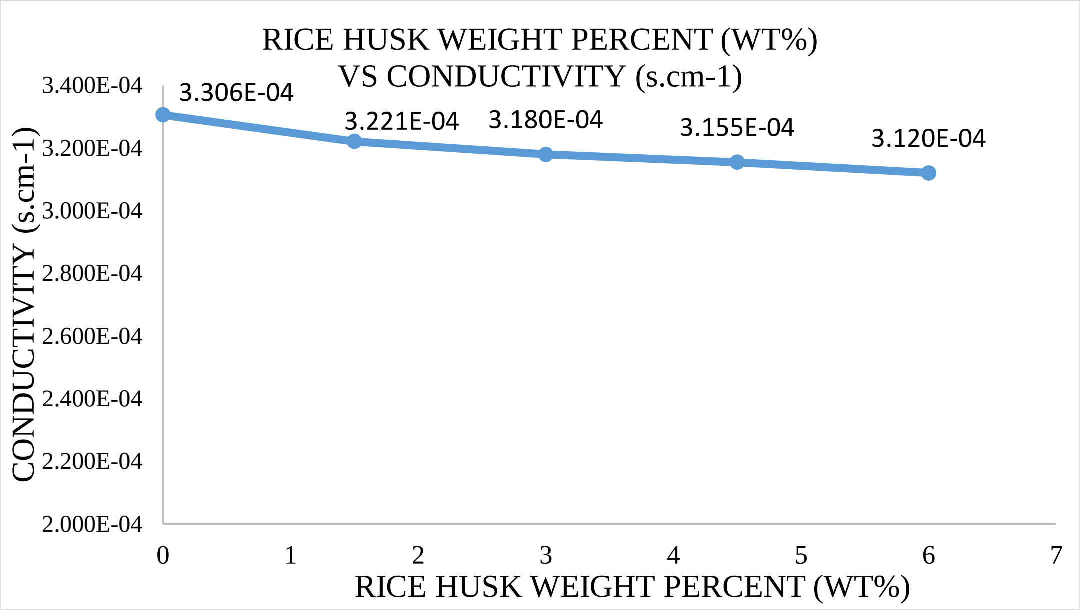


Figure 4.2 Graph of rice husk weight percent (wt%) vs conductivity (s.cm-1)

From figure 4.2 above, the samples showed result of increasing bulk resistance when the rice husk content is increasing. Resistance can be potrayed as a block that inhibits the movement of electricity. Therefore, as the resistance increase the conductivity will decrease. The presence of rice husk increased the resistance. This shows that rice husk act as a resistance in the polyaniline hydrogel. This is acceptable as rice husk does not have the property of conducting electrical energy.

However, this is not much of a concern as the difference between the conductivity of the samples were not big. The highest conductivity was 3.306E-04 s.cm-1 where rice husk content is 0 wt% and the lowest conductivity is 3.120E-04 s.cm-1 where rice husk content is 6 wt%. The trend of the conductivity of the samples can be refer at Figure 14 above. The conductivity of all samples were within the same range is due to the same amount of doping being used when synthesizing the sample. Therefore, the presence of rice husk content will not affect the conductivity in a big scale.

4.3 Differential Scanning Calorimetry (DSC)

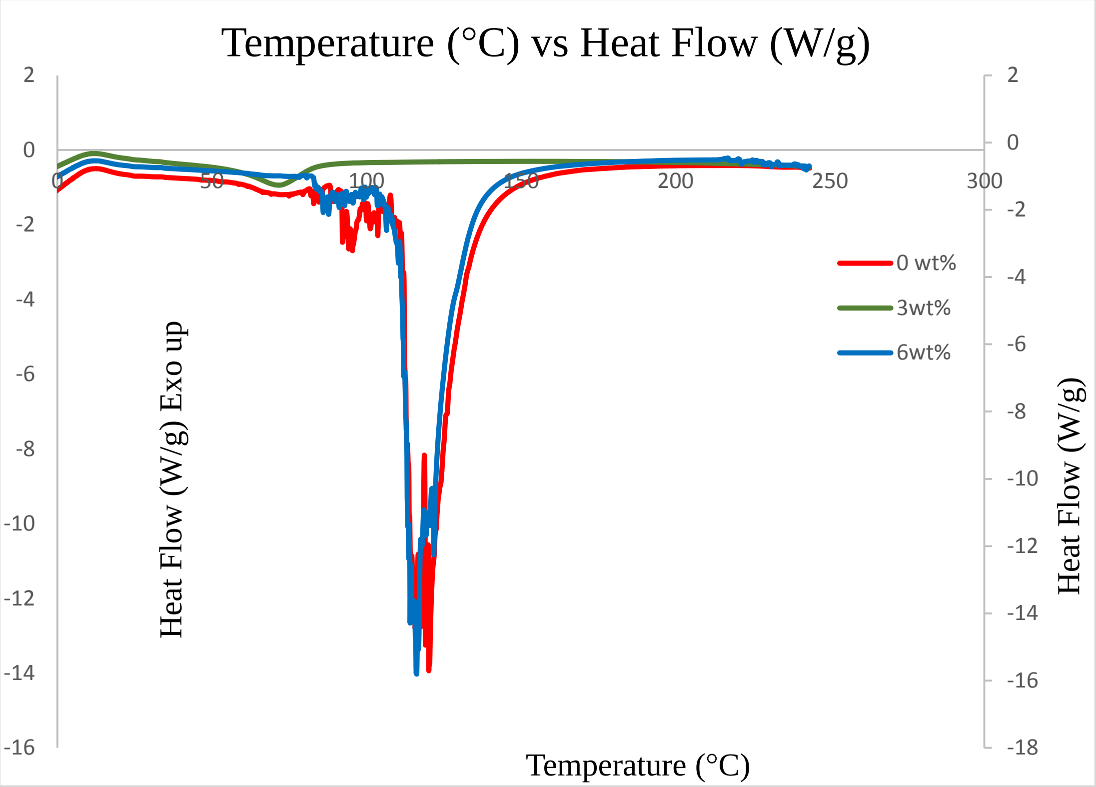


Figure 4.3 Direct Scanning Calorimetry (DSC) curve

The equipment used in this testing was DSC Q2000 V24.11 Build 124 and the method used was ramp method. DSC curve of hydrogel with 0 wt%, 3wt% and 6 wt% of rice husk content are shown in Figure 4.3 above. The Hydrogel with 0 wt% curve showed a short exothermic peak at 0°C to 25°C that indicate the degradation of PANI. A broad endothermic peak from 110°C to 165°C was also observed indicating the evaporation of water.

The curve for hydrogel with 6 wt% rice husk content showed a similar trend with 0 wt% curve but shifted about 4°C to the back. This might be because the excessive content of rice husk made the hydrogel less thermally stable. However, 3 wt% rice husk curve showed a different trend that the other two curves. It is observed that the 3 wt% rice husk hydrogel only gives a small broad endothermic peak which is different than 0 wt% and 6 wt% rice husk sample. This might be due to only a small amount of water evaporation.

If compare the results with results obtained from research by Thanpitcha and co-workers (2006) the peaks were in reverse. Endothermic peak was observed first before exothermic peak. This is due to the evaporation of water in early stages and then degradation of PANI [17]. Even though the results were in reversed, further study can be made in the future to understand more the newly self-crosslink PANI hydrogel grafted with rice husk and improve it.

4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted to determine the thermal stability of the hydrogel. Three samples which are 0 wt% rice husk, 3 wt% rice husk and 6 wt% rice husk were analyze and their thermal stability curve were compared. Figure 4.4 below shows the TGA curves.

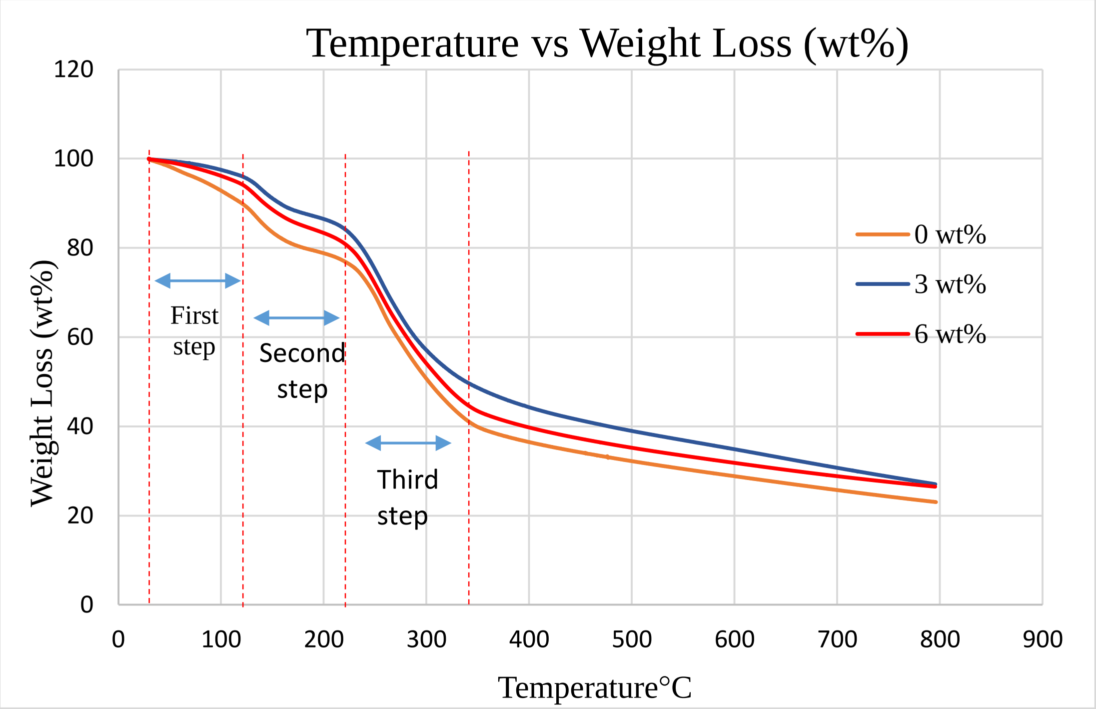


Figure 4.4 Thermogravimetric (TGA) curves

Based on the Figure 4.4 above, there are three steps of mass degradation for the hydrogel samples. The first step started from 30°C which is room temperature and ends at 127°C. This is due to the loss of water in the polymer matrix. The second step is from 128°C to 220°C where the elimination of dopant and degradation reactions. In previous study, the elimination of dopant and degradation reactions were at temperature between 220°C and 270°C [18]. The third step is a very large reduce of weight where it started from 250°C and ends at 360°C. The large reduce of weight is due to degradation polymer chain matrix and rice husk. The hydrogel samples were fully degraded from 370°C.

When comparing the samples, the curves trend are quite similar. However, the weight loss were not similar. Sample with 3 wt% of rice husk was the most thermally stable compared to 0 wt% and 6 wt% sample. However, 6 wt% sample was less thermally stable than 0 wt% sample. Therefore, the presence of rice husk in the hydrogel helps to increase the thermal stability of the hydrogel but excessive amount of it would reduce the thermal stability.

4.5 Fourier Transform Infrared (FTIR) Spectroscopy

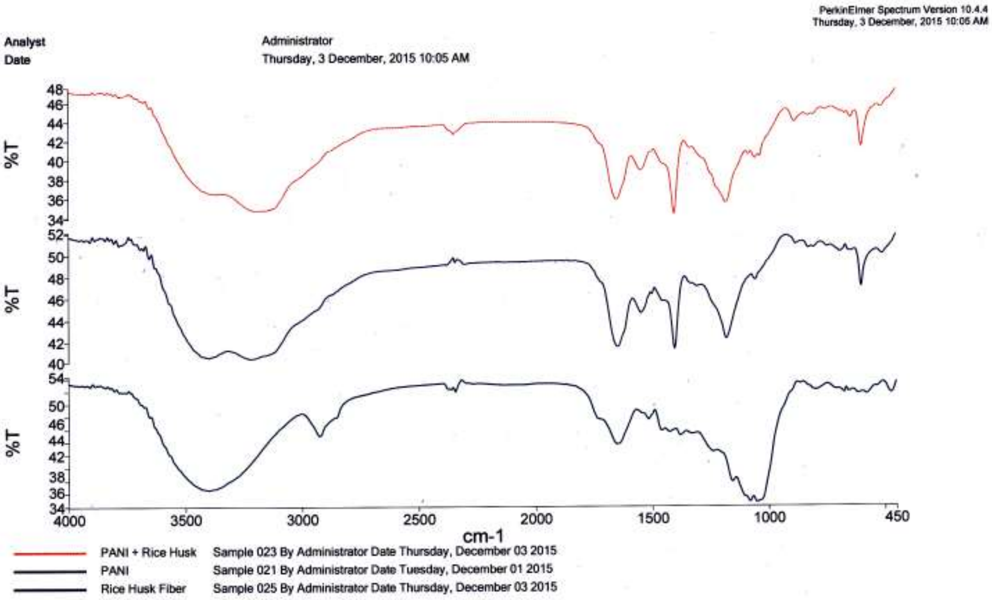


Figure 4.5 FTIR spectra of rice husk fiber, PANI, and PANI + rice husk fiber

The chemical structure of product is measured by Fourier Transform Infrared (FTIR) spectrum. The results were recorded on PerkinElmer Spectrum Version 10.4.4 between 4000 and 450 cm^{-1}. For PANI sample, two characteristic peaks located at 3408 and 3217 cm^{-1} which indicates amine stretching. A peak at 1547 and

1402 cm^{-1} corresponding to C-C stretching of benzene and quinone ring. Indications of C-N stretch aromatic amines were found at peaks 1179 and 1055 cm^{-1}. These peaks shows the characteristic peaks of PANI based on research by Guo and co-workers [4] and Wang and co-workers [19].

For rice husk fiber sample, peak at 3401 cm^{-1} indicates –OH and Si.OH functional group. Meanwhile, peaks at 2926 and 1651 cm^{-1} corresponds to C-H stretching of alkanes and C=O stretching of alkenes and aromatics respectively. Functional groups Si-O-Si and Si-H were found at peaks 1050 and 798 cm^{-1}. These tally with the peaks identified in FTIR of raw and modified rice husk [20].

From Figure 4.5 above, the peak at 3408 cm^{-1} from PANI curve is shortened at PANI + rice husk curve. This is due to presence of rice husk –OH and Si.OH functional groups. Peak at 1648 cm^{-1} from PANI curve is also shortened at PANI + rice husk curve where there is C=O stretching of alkenes and aromatic functional groups of rice husk. This shows that polyaniline (PANI) is grafted with rice husk fiber.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, self-crosslink polyaniline (PANI) grafted with rice husk fiber hydrogel was successfully synthesized using sol-gel method where no cross-linkers were used, only gelatin was used to help enhance the gelation of polyaniline. The resulted hydrogel shows a good water absorbency capacity where hydrogel with 3 wt% rice husk content recorded maximum percentage of 96.4%. From the conductivity test, it appears that the conductivity decreased when rice husk content increased. However, the difference between all 5 samples were so small that it could be neglected. The conductivity reading of the samples range from 3.120E-04 to 3.306E-04 s.cm-1.

It can be concluded that from these 2 tests that hydrogel with 3 wt% rice husk content gives the best electrochemical properties. The thermal stability of the hydrogel were not too good as it started to degrade drastically at temperature as low as 220°C. Further study and improvements can be made to increase all the properties of this hydrogel. In a nutshell, all the objectives of this research are successfully achieved.

5.2 Recommendations

In future research, it is recommended to do Scanning Electron Microscopy (SEM) characterization in order to justify the porous structure of the hydrogel. Besides, a new formula or ratio of the chemical in synthesizing the hydrogel need to be study so that a more thermally stable hydrogel could be synthesized. A proper testing for the conductivity of hydrogel also need to be conducted in future research as there are limitations to measure the conductivity in this research.

REFERENCES

[1] V. Sedlakova, J. Sikula, J. Majzner, P. Sedlak, T. Kuparowitz, B. Buergler, *et al.*, "Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion," *Journal of Power Sources,* vol. 286, pp. 58-65, 2015.

[2] Yun Lu, Weina He, and H. G. Tai Cao, Yongyi Zhang, Qingwen Li, Ziqiang Shao, Yulin Cui & Xuetong Zhang, "Elastic, Conductive, Polymeric Hydrogels and Sponges," *Scientific Reports,* vol. 4, 2014.

[3] H. Huang, X. Zeng, W. Li, H. Wang, Q. Wang, and Y. Yang, "Reinforced conducting hydrogels prepared from the in situ polymerization of aniline in an aqueous solution of sodium alginate," *Journal of Materials Chemistry A,* vol. 2, pp. 16516-16522, 2014.

[4] H. Guo, W. He, Y. Lu, and X. Zhang, "Self-crosslinked polyaniline hydrogel electrodes for electrochemical energy storage," *Carbon,* vol. 92, pp. 133-141, 2015.

[5] L. Weinstein and R. Dash, "Supercapacitor carbons," *Materials Today,* vol. 16, pp. 356-357, 2013.

[6] C. Tran, R. Singhal, D. Lawrence, and V. Kalra, "Polyaniline-coated freestanding porous carbon nanofibers as efficient hybrid electrodes for supercapacitors," *Journal of Power Sources*, vol. 293, pp. 373-379, 2015.

[7] R. Khan, A. Jabbar, I. Ahmad, W. Khan, A. N. Khan, and J. Mirza, "Reduction in environmental problems using rice-husk ash in concrete," *Construction and Building Materials,* vol. 30, pp. 360-365, 2012.

[8] H. Ge and S. Wang, "Thermal preparation of chitosan–acrylic acid superabsorbent: Optimization, characteristic and water absorbency," *Carbohydrate Polymers,* vol. 113, pp. 296-303, 2014.

[9] L.-B. Xing, S.-F. Hou, J.-L. Zhang, J. Zhou, Z. Li, W. Si, *et al.*, "A facile preparation of three dimensional N, S co-doped graphene hydrogels with thiocarbohydrazide for electrode materials in supercapacitor," *Materials Letters,* vol. 147, pp. 97-100, 2015.

[10] C. Dispenza, C. L. Presti, C. Belfiore, G. Spadaro, and S. Piazza, "Electrically conductive hydrogel composites made of polyaniline nanoparticles and poly(N-vinyl-2-pyrrolidone)," *Polymer,* vol. 47, pp. 961-971, 2006.

[11] Y. X. Qiong Wu, Zhiyi Yao, Anran Liu and Gouquan Shi, "Supercapacitors Based on Flexible Graohene/Polyaniline Nanofiber Composite Films," *2010 American Chemical Society,* vol. 4, pp. 1963-1970, 2010.

[12] A. Nirmalesh Naveen and S. Selladurai, "Fabrication and performance evaluation of symmetrical supercapacitor based on manganese oxide nanorods–PANI composite," *Materials Science in Semiconductor Processing,* vol. 40, pp. 468-478, 2015.

[13] N. Elhalawany, H. Elmelegy, and M. Nayfeh, "Synthesis, characterization and electrical properties of highly conductive polyaniline/gold and/or platinum nanocomposites," *Synthetic Metals,* vol. 205, pp. 145-152, 7// 2015.

[14] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, and M. Poliakoff, "Valorization of biomass: Deriving more value from waste," *Science,* vol. 337, pp. 695-699, 2012.

[15] A. A. M. Daifullah, B. S. Girgis, and H. M. H. Gad, "Utilization of agro-residues (rice husk) in small waste water treatment plans," *Materials Letters,* vol. 57, pp. 1723-1731, 2003.

[16] Y. Gao, L. Li, Y. Jin, Y. Wang, C. Yuan, Y. Wei, *et al.*, "Porous carbon made from rice husk as electrode material for electrochemical double layer capacitor," *Applied Energy,* vol. 153, pp. 41-47, 2015.

[17] T. Thanpitcha, A. Sirivat, A. M. Jamieson, and R. Rujiravanit, "Preparation and characterization of polyaniline/chitosan blend film," *Carbohydrate Polymers,* vol. 64, pp. 560-568, 2006.

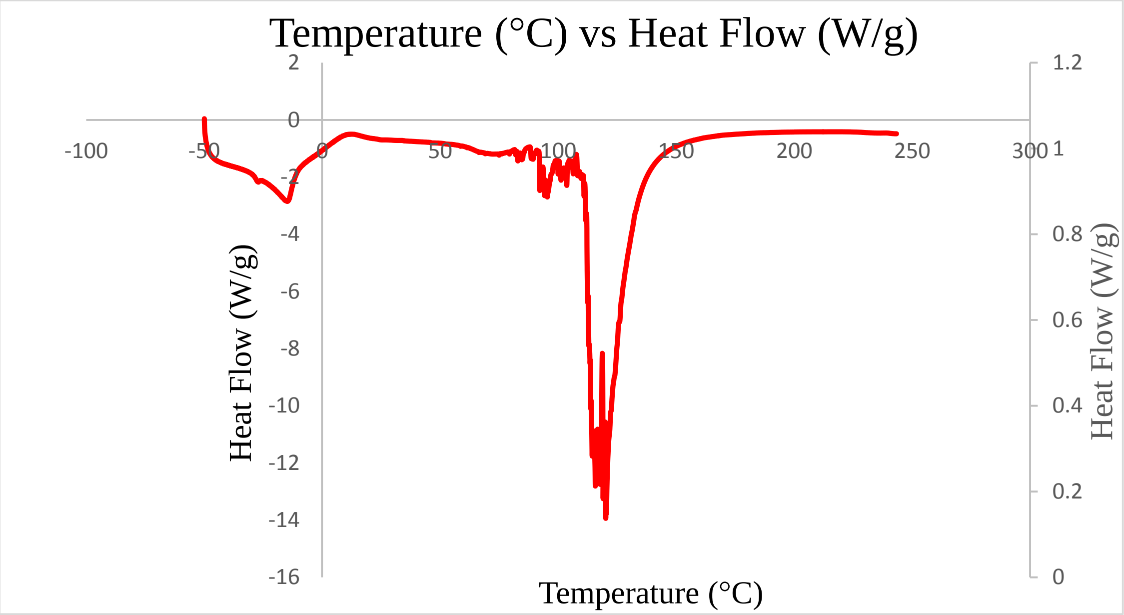
[18] J. H. O. Owino, O. A. Arotiba, P. G. L. Baker, A. Guiseppi – Elie, and E. I. Iwuoha, "Synthesis and characterization of poly (2-hydroxyethyl methacrylate)-polyaniline based hydrogel composites," *Reactive and Functional Polymers,* vol. 68, pp. 1239-1244, 2008.

[19] Q. Wang, J. Yan, Z. Fan, T. Wei, M. Zhang, and X. Jing, "Mesoporous polyaniline film on ultra-thin graphene sheets for high performance supercapacitors," *Journal of Power Sources,* vol. 247, pp. 197-203, 2014.

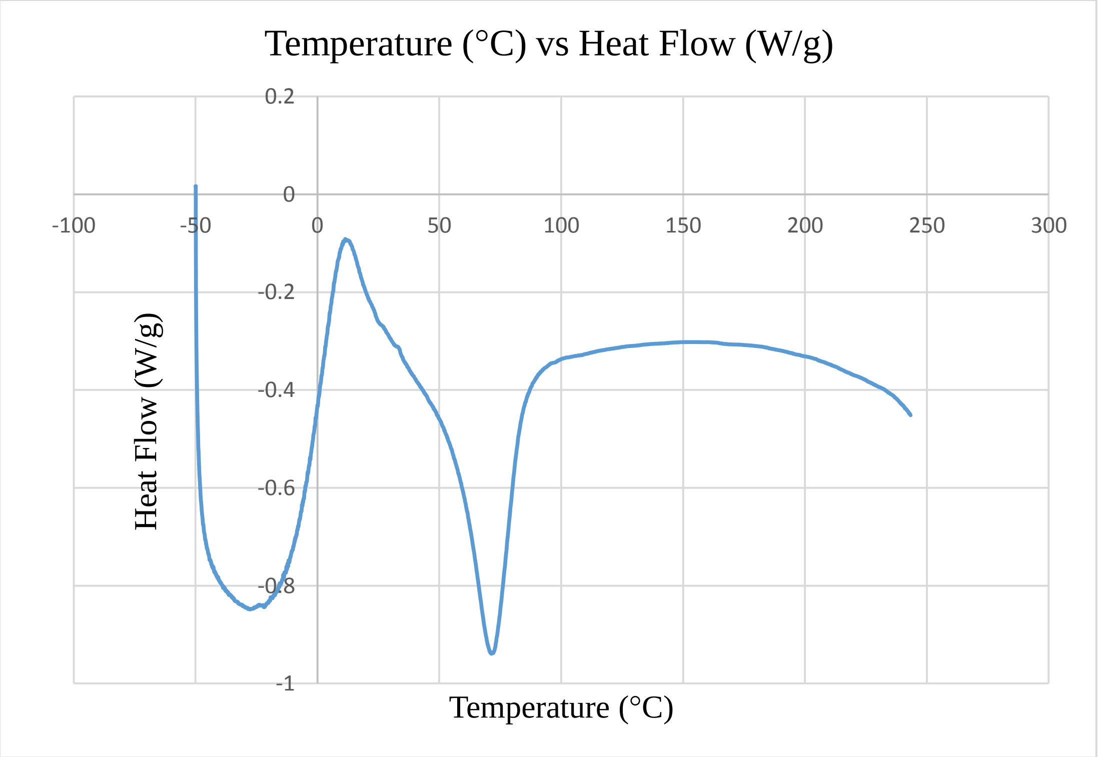
[20] S. B. Daffalla, H. Mukhtar, and M. S. Shaharun, "Characterization of Adsorbent Developed from Rice Husk: Effect of Surface Functional Group on Phenol Adsorption," *Journal of Applied Sciences,* vol. 10, pp. 1060-1067, 2010.

APPENDICES

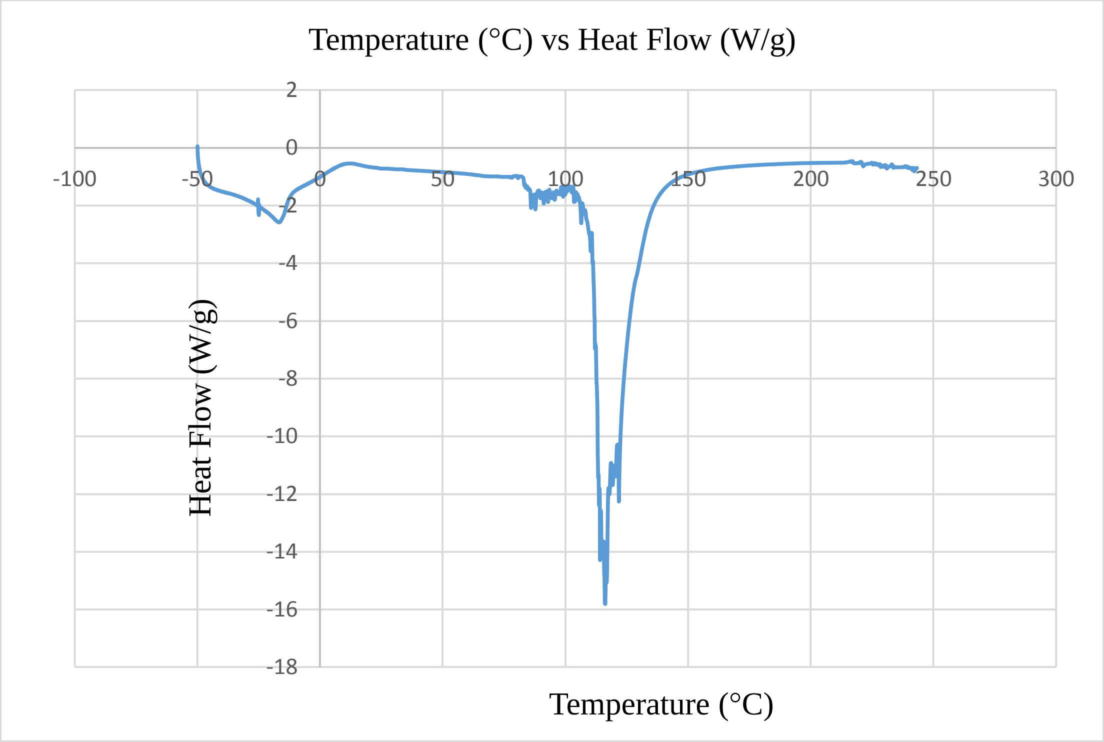
a. DSC curve of hydrogel with 0 wt% rice husk



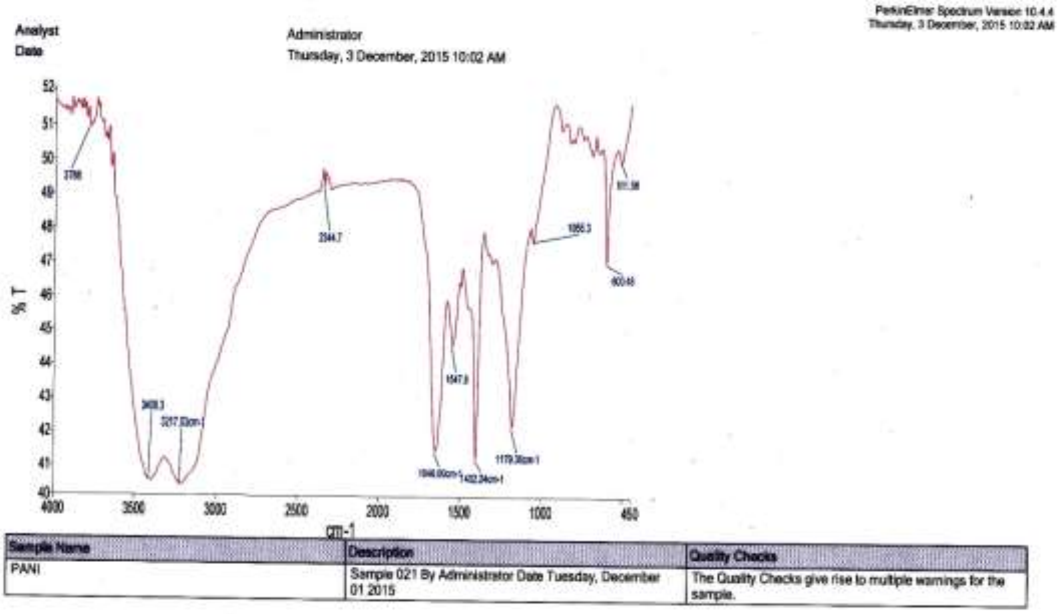
b. DSC curve of hydrogel with 3 wt% rice husk



c. DSC curve of hydrogel with 6 wt% rice husk



d. FTIR of PANI

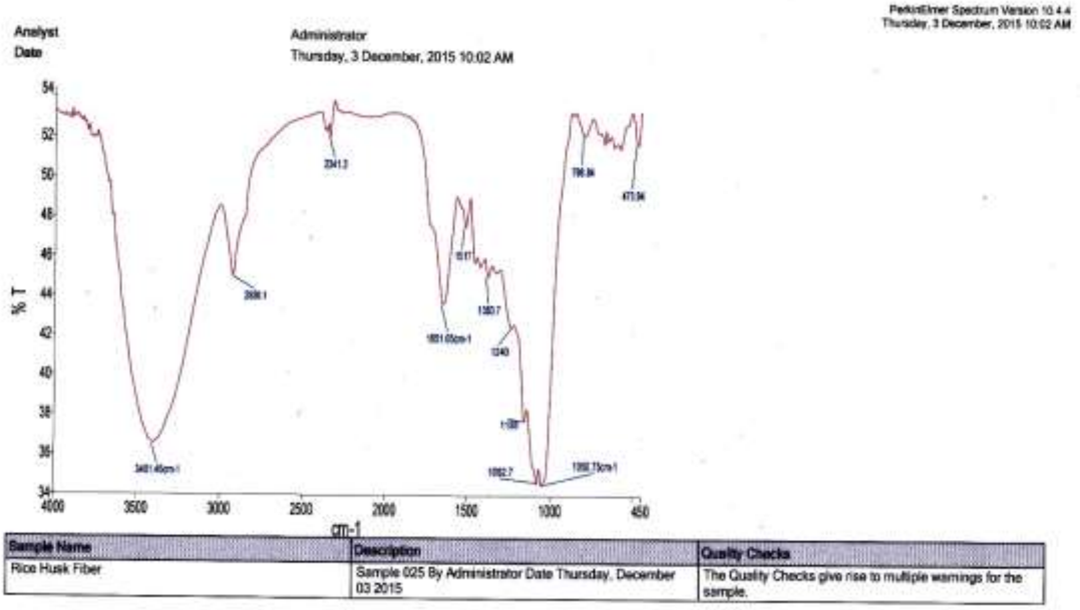


PerkinElmer Spectrum Version 10.4.4
Thursday, 3 December, 2015 10:02 AM

Analyst Administrator
Date Thursday, 3 December, 2015 10:02 AM

Sample Name	Description	Quality Checks
PANI	Sample 021 By Administrator Date Tuesday, December 01 2015	The Quality Checks give rise to multiple warnings for the sample.

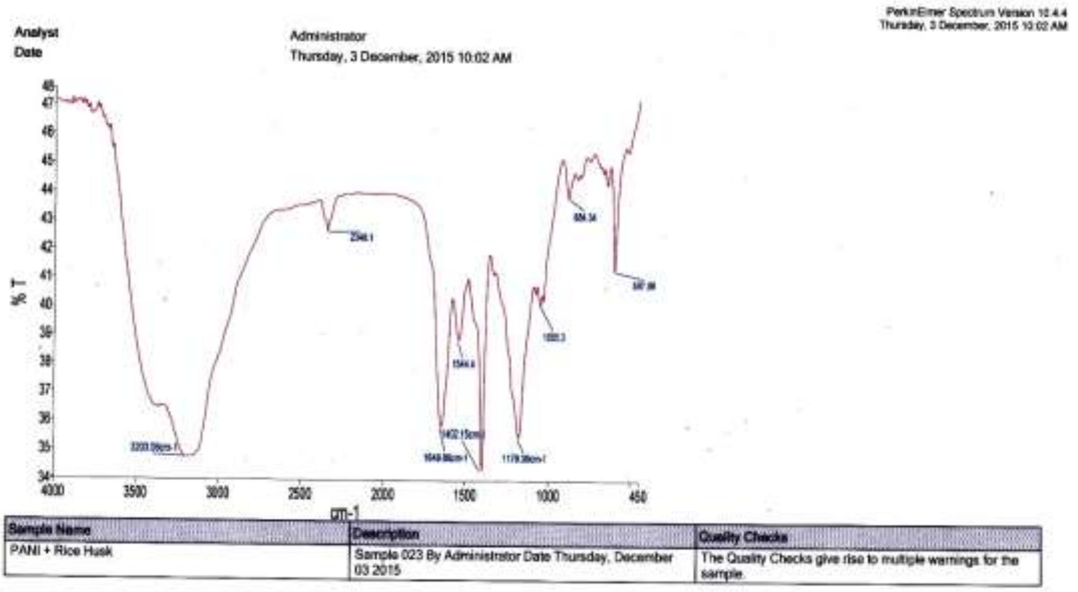
e. FTIR of rice husk



Analyst Administrator
Date Thursday, 3 December, 2015 10:02 AM

Sample Name	Description	Quality Checks
Rice Husk Fiber	Sample 025 By Administrator Date Thursday, December 03 2015	The Quality Checks give rise to multiple warnings for the sample.

f. FTIR of PANI + rice husk



Analyst Administrator
Date Thursday, 3 December, 2015 10:02 AM

Sample Name	Description	Quality Checks
PANI + Rice Husk	Sample 023 By Administrator Date Thursday, December 03 2015	The Quality Checks give rise to multiple warnings for the sample.

g. Figure of self-crosslink polyaniline grafted rice husk hydrogel