# SYNTHESIS AND SWELLING BEHAVIOR OF RICE HUSK BASED SUPERABSORBENT POLYMER COMPOSITE

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## ABSTRACT

Superabsorbent polymer composites (SPC) based on acrylic acid and rice husk (RH) was synthesized through a solution polymerization to improve water absorbency and reduce production cost. The SPC was characterized using Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). The objectives of this research to synthesis RH based SPC by determine the effect of amount RH, and cross-linker agent N,N'-methylenebisacrylamide (MBA), towards swelling behavior of SPC in water and saline solution. Experiments have been done by used RH contents in range of 576 to 864 mg and for amount of NMBA content evaluate in range of 11.44 to 22.88 mg. The swelling behaviors have been investigated by measured the water absorption of rice husk-g-poly (acrylic acid). The water absorbency determined by using tea-bag method. The result showed as the amount of RH was increased, the water absorbency also increase. The maximum absorbency 4.8745 g/g in distilled water was obtained. The effect of MBA content result show the water absorption increases with increase of the cross-linker amount in the range of from 11.44 to 14.3 mg. Then, water absorption decreases with further increased of cross-linker amount. The maximum absorbency of 4.221 g/g in distilled water was obtained. The swelling behavior in saline solution also has been investigated. The result shows that water absorbency give insignificant value in saline solution compare to absorbency value in distilled water.

## ABSTRAK

Komposit polimer superpenyerapan (KPS) berasaskan asid akrilat dan sekam padi (SP) disintesis melalui pempolimeran larutan untuk meningkatkan daya serap air dan mengurangkan kos pengeluaran. The KPS disifatkan dengan menggunakan spektroskopi Fourier transform infrared spectroscopy (FTIR) dan Scanning electron microscopy (SEM). Tujuan penyelidikan ini adalah untuk mengsintesis SP berdasarkan KPS dengan menentukan pengaruh jumlah SP, dan N, N'-methylenebisacrylamide (MBA), terhadap perilaku pengembangan KPS dalam air dan larutan garam. Eksperimen ini telah dilakukan dengan jumlah SP yang digunakan adalah dalam julat 576-864 mg dan untuk jumlah MBA pula ialah dalam julat 11,44-22,88 mg. Perilaku pengembangan telah diselidik dengan mengira jumlah penyerapan air. Daya serap air ditentukan dengan menggunakan kaedah teh-beg. Keputusan menunjukkan apabila jumlah SP bertambah, daya serap air akan meningkat. Daya serap maksimum yang telah dicapai adalah sebanyak 4,8745 g / g didalam air suling manakala pengaruh hasil kandungan MBA pula menunjukkan penyerapan air meningkat dengan peningkatan jumlah MBA dalam julat 11,44-14,3 mg. Kemudian, penyerapan air menurun dengan peningkatkan jumlah MBA. Daya serap maksimum sebanyak 4,221 g / g dalam air suling telah diperolehi. Perilaku penyerapan air di larutan garam juga telah dikaji. Keputusan kajian menunjukkan bahawa air yang diserap oleh larutan garam lebih sedikit berbanding dengan nilai serapan dalam air suling.

# TABLE OF CONTENTS

TABLE OF CONTENTS

## LIST OF TABLE

## LIST OF FIGURE

# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| AA | - | Acrylic Acid |
| AM | - | Acrylamide |
| APS | - | Ammonium Persulfate |
| $CaCl_2$ | - | Calcium Chloride |
| CTS | - | Chitosan |
| CTS-g-PAA/APT | - | Chitosan-g-poly(acrylic acid)/attapulgite |
| FTIR | - | Fourier Transform Infrared Spectroscopy |
| NaCl | - | Sodium Chloride |
| MBA | - | N,N'-Methylenebisacrylamide |
| $MgCl_2$ | - | Magnesium Chloride |
| RH | - | Rice Husk |
| RHF | - | Rice Husk Filler |
| RH-g-PAA | - | Rice Husk-g-poly(acrylic acid) |
| SPC | - | Superabsorbent Polymer Composite |
| St-poly (NaAA-co-AAm) | - | Starch-poly(sodium acrylate-co-acrylamide) |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| $Ca_{2+}$ | - | Calcium ion |
| *m* | - | Mass |
| M | - | Molar (mole/$cm^3$) |
| $Mg^{2+}$ | - | Magnesium ion |
| Q | - | Absorbency |
| *Q* | - | Degree of Swelling |
| wt. % | - | Weight percentage |

## LIST OF APPENDIX

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Superabsorbent polymers are lightly cross linked hydrophilic polymers that have ability to absorb, swell and retain large quantities of water. With the superior properties, superabsorbent polymers are applying in many sectors compared to the traditional absorbent such as sponge, cotton and pulp (Zhang *et al.*, 2006). SPC are originally divided into two main classes which are synthetic (petrochemical-based) and natural. Most of the superabsorbent polymers composite are frequently produced from acrylic acid (AA) and acrylamide (AM) as the salt via solution polymerization techniques (Zohuriaan-Mehr and Kabiri, 2008).

The conventional superabsorbent polymers based on expensive fully petroleum-based polymers (Wang *et al.*, 2009). This shows that the conventional superabsorbent polymers have high cost in production. And also give bad effects to the environments and living organisms. Therefore, many research on new filler have used to fill in the superabsorbent polymers composite (SPC) like starch and clay.

In recent years, the preparation of superabsorbent polymers composites (SPC) has great attention because of their relatively low production cost and high water absorbency (Bulut *et al.*, 2009). In this context, rice husk (RH) will be filled in the SPC. RH is an agricultural waste material abundantly available in Malaysia which is one of rice-producing countries. RH is suitable being use as filler in the SPC because RH is a hydrophilic material that can absorb amount of water. The hydrophilic characteristics of RH have been reviewed. Besides that, RH is biodegradable waste therefore the SPC with RH filler will be easy to dispose.

## 1.2 Problem Statement

Recently, superabsorbent polymers composite (SPC) had high interested because of it low cost production but SPC still not environmental friendly. Xei and Wang (2009) stated that synthetic superabsorbent based on acrylic acid and acrylamide were poor in degradability for application in agriculture and horticulture. As an alternative, RH will be used as filler in SPC. The rice husk has hydrophilic characteristic that suitable as filler to the SPC. Besides that, RH is biodegradable material and as we all know that Malaysia is rice producing country. Lee *et al.* (2005) estimated the rice husk been abundant is about 3.6 million tons per annually.

The aim of this research is to determine the rice husk based superabsorbent polymers composite are the great and low cost producing superabsorbent polymers composite.

## 1.3 Objectives

The objective of this research:

a) Synthesis and characterize RH-g-PAA.
b) Study swelling behavior RH-g-PAA in water and saline solution.

## 1.4 Scope of Study

In this research, characterization RH-g-PAA is using Fourier Transform Infrared Spectroscopy (FTIR).

In this research focus on effect of parameter, amount of rice husk and N,N'-Methylenebisacrylamide (MBA) content the due to the water and saline solution absorbency. In this research, all parameter are variable in five different values of concentration and amount.

The materials in this research are acrylic acid and acrylamide are the monomer. The MBA is the cross-linker and the ammonium persulfate (APS) is the initiator. Then, rice husk (RH) is the filler.

The polymerization technique that use in this research is solution polymerization technique. This technique is common technique use to produce SPC.

## 1.5 Significance of Study

This research has gain high interest to find an alternative way to overcome the problem of SPC encountered which is not environmental friendly. Nowadays a lot of SPC that have been produced cause damage to environment and living organism. RH is known as biodegradable material that can be easy to be dispose. Besides that, by using RH as filler it will reduce production cost of SPC.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Superabsorbent polymers are lightly cross linked hydrophilic polymers that have ability to absorb, swell and retain large quantities of water. With the superior properties, superabsorbent polymers are applying in many sectors compared to the traditional absorbent such as sponge, cotton and pulp (Zhang *et al.,* 2006).

Zohuriaan-Mehr and Kabiri (2008), report that the water absorbency of superabsorbent polymers are categorized into two main classes based on the major mechanism of chemical and physical absorptions. The chemical absorbers catch water via chemical reaction converting their entire nature.

The physical absorbers imbibe water via four main mechanisms,

(i) Reversible changes of their crystal structure
(ii) Physical entrapment of water via capillary forces in their macro-porous structure
(iii) A combination of the mechanism (ii) and hydration of functional groups.
(iv) The mechanism which may be anticipated by combination of mechanisms of (ii) and (iii) and essentially dissolution and thermodynamically favoured expansion of the macro- molecular chains limited by crosslinkages.

Visual and schematic illustrations of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states are given in Figure 2.1.

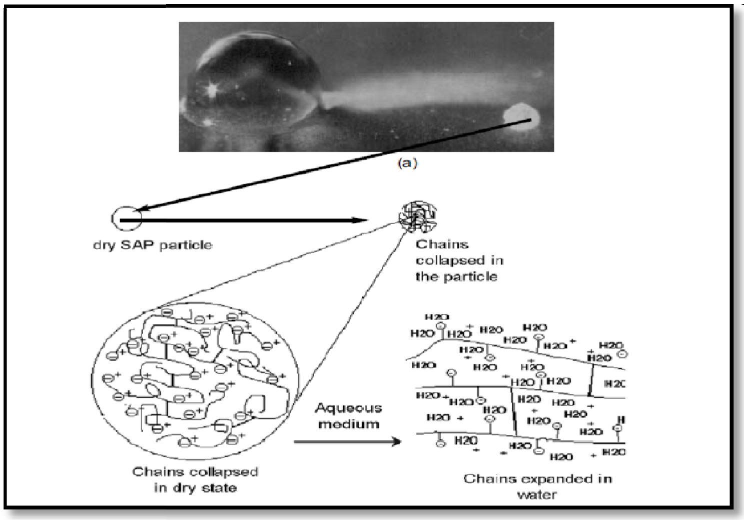


**FIGURE 2.1:** Illustration of a typical acrylic-based anionic SPC material: (a) A visual comparison of the SPC single particle in dry (right) and swollen state (left). The sample is a bead prepared from the inverse-suspension polymerization technique. (b) A schematic presentation of the SPC swelling. (Zohuriaan-Mehr and Kabiri, 2008).

## 2.2 Rice Husk

Warren and Farrell (1990), did researched to determine the component in the rice husk. The result of the research as shwon in Table 2.1. In FTIR analysis, Prachayawarakom and Yaembunying (2005) reported the peak positions obtained from rice husk (RH) component as shows in Figure 2.2 (b) are at 3250-3500 cm-1, 1700-1750 cm-1 and 1400 1600 cm-1, assigned to O-H stretching, C=O stretching of hemicelluloses and lignin and C=C stretching of aromatic carbon.

Prachayawarakorn and Yaembunying (2005) reported cellulose and hemicelluloses components are the main source for absorbing water in the RH. That means, celluloses and hemicelluloses component in RH was functioned as a hydrophilic agent shows in Figure 2.3. In the figure shows the peak pattern from 2992 to 1734 differently by comparing before recycling (a) to the second recycled time (b) and the forth recycled time. Based on that figure shows the hemicelluloses decrease as increase recycled time of product. When the hemicelluloses content decrease in RH, the water absorbency also decrease. The result shows in the Figure 2.4 where the lowest water absorbency is Rice husk-filled polypropylenes recycled fourth times.

**Table 2.1:** Percentage weight of rice husk component (Warren and Farrell, 1990)

| | Celluloses (%wt) | Hemicelluloses (%wt) | Lignin (%wt) | Ash (%wt) |
|---|---|---|---|---|
| Rice Husk | 35 | 35 | 20 | 10 |

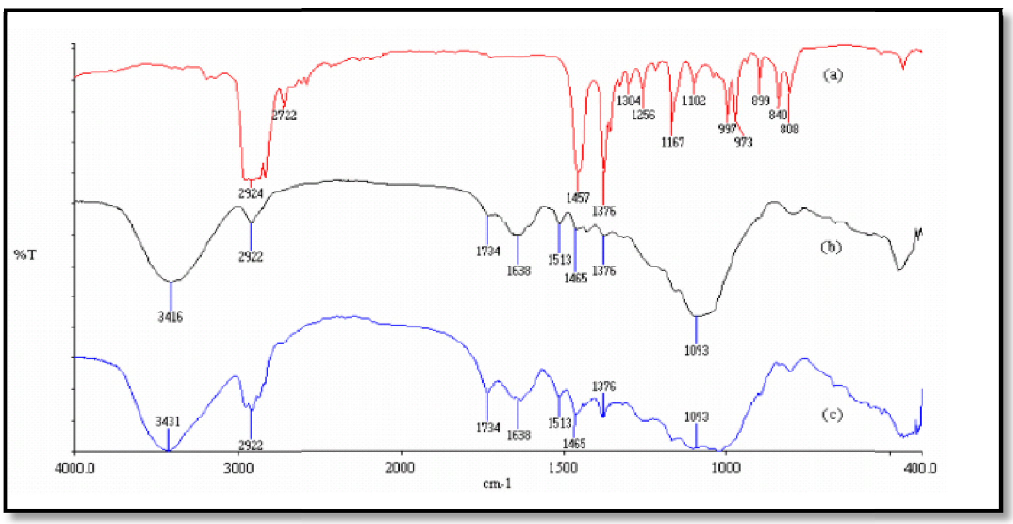


**Figure 2.2:** FTIR spectra for (a) polypropylene (b) rice husk and (c) rice husk-filled polypropylene (Prachayawarakorn and Yaembunying, 2005)

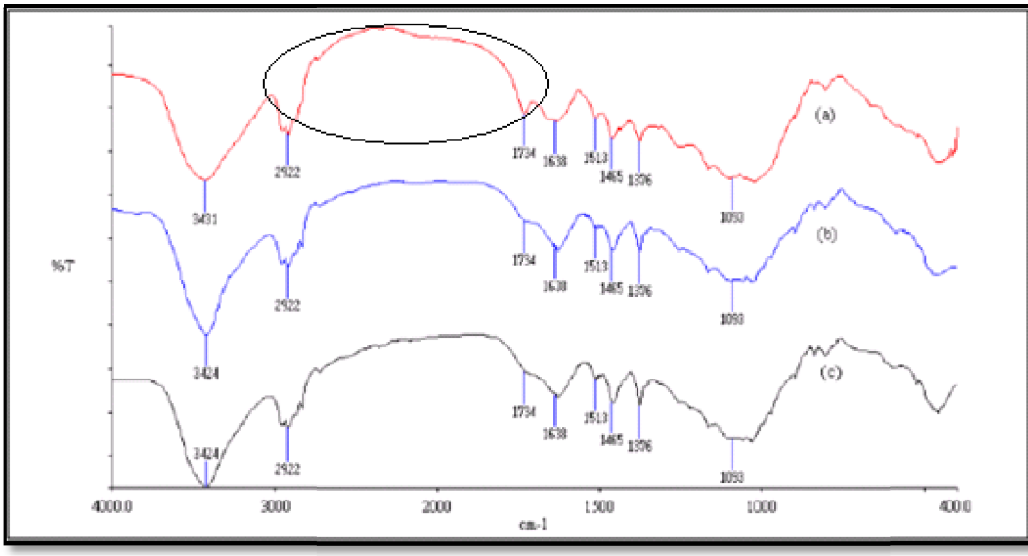


**Figure 2.3:** FTIR spectra for rice husk-filled polypropylene upon recycling (a) before recycling (b) the 2nd recycled time and (c) the 4th recycled time. (Prachayawarakorn and Yaembunying, 2005)

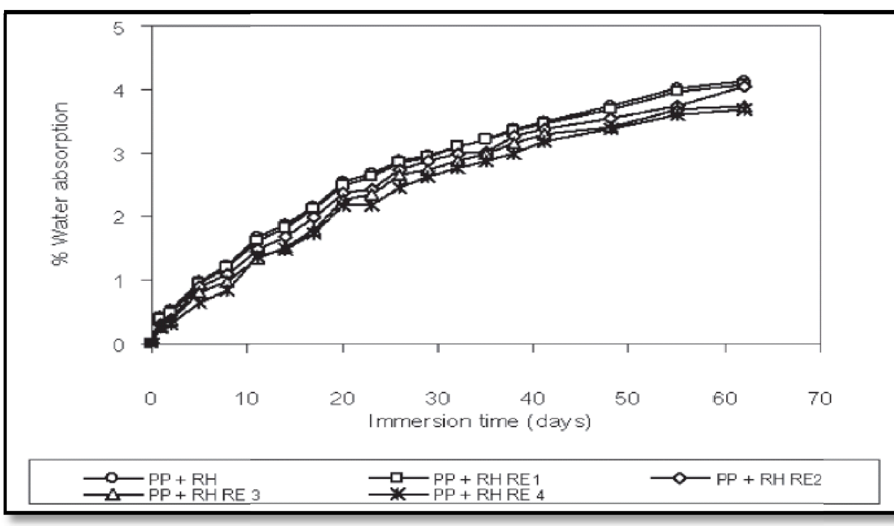


**Figure 2.4:** Percentage of water absorption rice husk-filled polypropylene with water immersion time upon recycling. **(**Prachayawarakorn and Yaembunying, 2005)

## 2.3 Effect of Parameter Contents

### 2.3.1 Rice husk content effect in swelling behavior

Rosa *et al.* (2009) report that, increasing RH concentration and increasing water contact time greatly increased water absorption, as illustrated in Figure 2.5. In this figure shows the increases of RH content from 1% to 4% and then the water absorbency increase due to time.

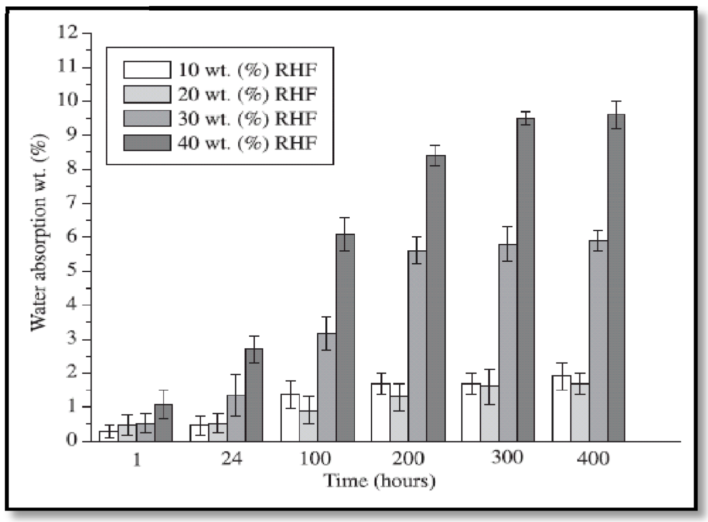


**Figure 2.5:** Water absorption at different RHF loadings. (Rosa *et al.,* 2009)

### 2.3.2 N-N'-methylenebisacrylamide contents in swelling behavior

In the polymerization process, cross-linking process is a final process of polymerization. N-N'-methylenebisacrylamide (MBA) will be used as a cross-linking agent. In this polymerization process MBA act as cross-linker to link two copolymer chains that produce from the initiation process as shown in Figure 2.6 (Zohuriaan-Mehr and Kabiri, 2008).

Flory's network theory stated that cross-linking density is a key factor influencing water absorbency of superabsorbent polymers composite. Wu *et al.* (2007)

study on factors influencing water absorbency of the chitosan-*g*-poly(acrylic acid)/attapulgite superabsorbent composites such as average molecular weight of chitosan, weight ratio of acrylic acid to chitosan, dewatering method, the amount of crosslinker and attapulgite. From the result, the water absorbency decrease from 450 to 120 g/g as increase the MBA content from 1.0 to 3.0 % that shows in Figure 2.7. This because too much cross-linker content, this would result in a decrease in the space between the copolymer chains, the resulted highly cross-linked rigid structure cannot be expanded and hold a large quantity of water. Therefore, the water absorbency will decrease. Liu *et al.* (2009) also discuss about the cross-linker content effect to absorbencies. From the result, the water absorbencies increase with tiny increasing of cross-linker content in the range of 0.02–0.15 wt%. Then, water absorbencies decreased with further increase of cross-linker content from 0.15 to 0.27 wt% shown in Figure 2.8.

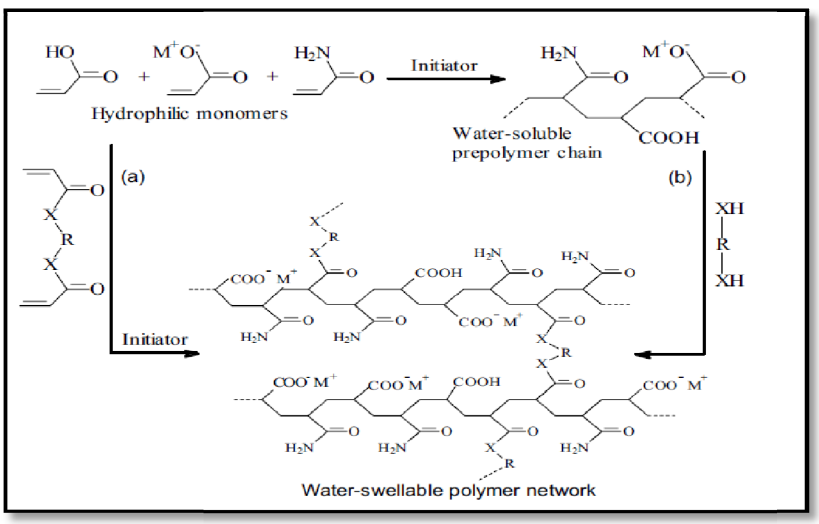


**Figure 2.6:** Cross-linking process. (Zohuriaan-Mehr and Kabiri, 2008)

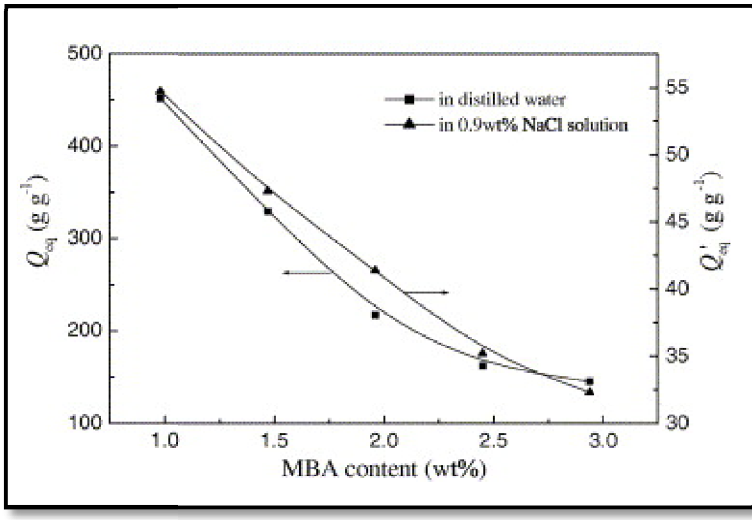


**Figure 2.7:** Variation of water absorbency for the CTS-*g*-PAA/APT superabsorbent composite with MBA content. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9 × $10^4$; APT content is 10 wt%; dewatered with methanol. (Zhang *et al.,* 2006)

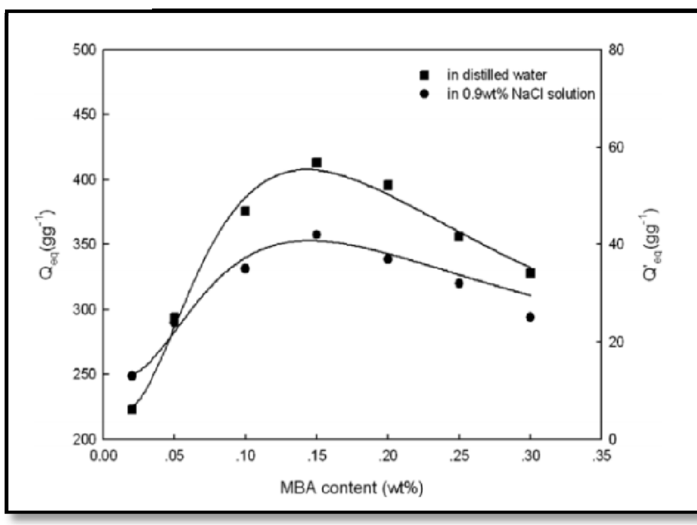


**Figure 2.8:** Effect of amount MBA on the absorbencies. (Liu *et al.,* 2009)

## 2.4 Swelling Behavior in Saline Solution

Lanthong *et al.* (2006) reported that the water absorption capacity decreases with increasing the ionic strength of the saline solutions. The presence of ions in the solution surrounding the network counteracts the mutual repulsion of the fixed ion on the network itself, and the decrease of the osmotic pressure difference between SPC and external solution. The effect of the ionic strength on the water absorbency can be expressed by Flory's equation;

$$Q^{5/3} = [(i/2v_u S^{*1/2})^2 + (\tfrac{1}{2} - \chi_1)/v_1]/(v_e/V_0),$$

Equation 4.1

Where $Q$ is the degree of swelling, $i/v$u is the charge density of polymer, S* is the ionic strength of solution, $(1/2\text{-}X_1)/v_1$, is the polymer-solvent affinity, $v$e/$V_0$ is the crosslinking density.

According this equation 4.1, when the ionic strength of saline solution increases, the water absorbency decreases. The ionic strength of the solution depends on both the mobile ions and their valence or oxidation state. Small quantities of divalent or trivalent ions can drastically decrease the swelling values. The decreases are more significant by $Mg^{2+}$ or $Ca^{2+}$ ions, which can be additionally caused by the complex formation ability of carboxamide or carboxylate groups including intramolecular and intermolecular complex formations. Additionally, cations were able to neutralize several charges inside the SPC. As the result crosslink density increase, then the swelling behavior decrease. The result of water absorption in saline solution shown in Table 2.2 depends on ionic strength.

Sadeghi and Hosseinzadeh (2008) also reported the present additional cations in the solution environment which cause a non-perfect anion-anion electrostatic repulsion. As the result the osmotic pressure decrease, then the swelling behavior decrease. The result of water absorption in saline solution shown in Figure 2.9. From the figure show that the water absorption decreases as increase the saline solution concentration.

**Table 2.2:** Effect of salt solution on water absorption. (Lanthong *et al.,* (2006)

| Solution | Ionic strength (mol-ion $dm^{-3}$) | Water absorption ($g\ g^{-1}$) |
|---|---|---|
| Distilled water | – | 379 ± 10 |
| 0.9% w $v^{-1}$ NaCl solution | 0.154 | 36 ± 1 |
| 0.9% w $v^{-1}$ $MgCl_2$ solution | 0.2836 | 11 ± 1 |
| 0.9% w $v^{-1}$ $CaCl_2$ solution | 0.2433 | 4 ± 2 |

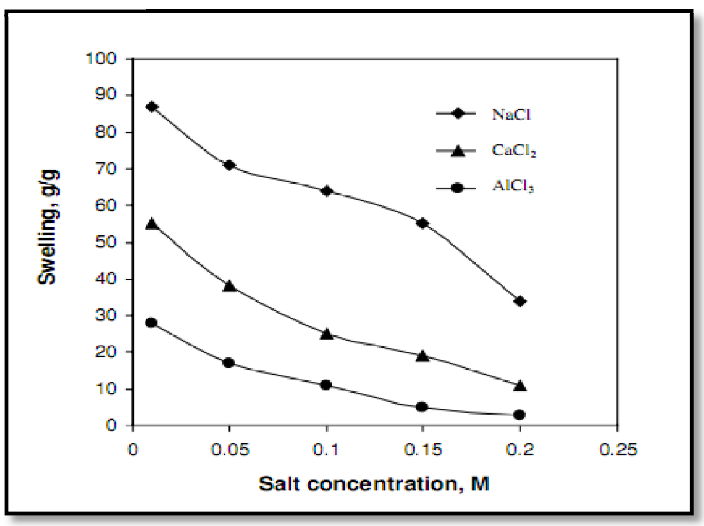


**Figure 2.9:** Swelling capacity variation of the St-poly (NaAA-co-AAm) superabsorbent in saline solutions of varying concentration. (Sadeghi and Hosseinzadeh, 2008)

# CHAPTER 3

# METHODOLOGY

## 3.1 Raw Material

Acrylic acid (R&M Chemical) and Ammonium persulfate (APS, R&M Chemical). *N,N*-methylenebisacrylamide (MBA, R&M Chemical) will be used as purchased. The rice husk was supplied from Rice Mill Sdn Bhd, Malaysia. The rice husk had been screened and milled 45-100 micrometer using sieve shaker.

## 3.2 Preparation of Samples

First steps, 4 ml acrylic acid was dissolved in 15 ml distilled water and then neutralized with 6 ml of sodium hydroxide solution (5 M) in a four-neck flask equipped with a stirrer, condenser, thermometer, and nitrogen line.0.576 g of rice husk powder was added in the solution. Under a nitrogen atmosphere, 14.3 mg the crosslinker (MBA) was added to the mixture solution and the mixed solution was stirred at room temperature for 30 min. The water bath was heated slowly to 70 °C with effective stirring after radical 71.3 mg of initiator APS was introduced to the mixed solution. After 3 h of the reaction, the resulting product was washed several times with distilled water, dried in oven at 70 °C to a constant weight. The contents of parameters used in hydrogel synthesis show in Table 3.4.

**Table 3.1:** Contents of RH and MBA in synthesis SPC

| **Sample code** | **Rice Husk (g)** | **MBA (mg)** | **APS (mg)** |
|---|---|---|---|
| AI | 0.576 | | |
| A2 | 0.648 | | |
| A3 | 0.72 | 14.3 | 71.3 |
| A4 | 0.792 | | |
| A5 | 0.864 | | |
| B1 | | 11.44 | |
| B2 | | 14.3 | |
| B3 | 0.72 | 17.16 | 71.3 |
| B4 | | 20.02 | |
| B5 | | 22.88 | |

## 3.3 Samples Characterization

### 3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to investigate the presence of RH in RH-g-PAA. The infrared spectrum of polymer was recorded with Fourier Transform Infrared Spectrometer (Thermo Nicolet 3700 FTIR). Scanning was carried out from 4000-400 $cm^{-1}$.

## 3.4 Swelling Behavior

In swelling behavior RH-g-PAA was determined by water and saline solution absorbency. Molu *et al*. (2009) stated that water and saline solution absorbency measurement was performed by weighing the initial mass of composite ($m_o$) and was been determined at the time *t* ($m_t$) of gel will be immersed in the water and saline solution at the room temperature. Q represent as the absorbency.

$$Q = \left[ \frac{m_t - m_o}{m_o} \right] \qquad \text{Equation 3.1}$$

### 3.4.1 Tea-bag Method

This method is the most conventional, fast, and suitable for limited amounts of samples (*m*= 0.01 g +/- 0.005). The RH-g-PAA sample was placed into a tea-bag and the bag was dipped in an excess amount of water or saline solution. The swelling capacity is calculated by equation (3.1). The method's precision had been determined to be around ±3.5% (Zohuriaan-Mehr and Kabiri, 2008).

### 3.4.1 Swelling in water solution

The samples were dipped in 250 ml water for one hour to reach equilibrium swelling. Then excess solution was removed by hanging the bag until no liquid was dropped off.

### 3.4.2 Swelling in saline solution

The saline solution (0.5M) was prepared 73.05 g of NaCl was dissolved in 250 ml distilled water. Then, the samples were dipped in NaCl solution for one hour to reach equilibrium swelling. Then excess solution was removed by hanging the bag until no liquid was dropped off.