SYNTHESIS AND SWELLING BEHAVIOUR OF RICE HUSK BASED SUPERABSORBENT POLYMER COMPOSITE

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Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirements for the degree of Bachelor of Engineering

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JANUARY 2012

ABSTRACT

This research is about *Synthesis and Swelling Behaviour of Rice Husk Based Superabsorbent Polymer Composite (SPC).* In this research, the results for swelling behavior of SPC were reported. The objectives of the research are to study the optimum synthesizing condition of rice husk based SPC by determining the effect on amount of initiator, crosslinker and rice husk towards water absorbency. SPC sample is prepared by solution polymerization technique where acrylic acid-acrylamide-rice husk (AA-AM-RH) mixture is reacted with N,N-methylenebisacrylamide (MBA) and Ammonium persulfate (APS) under nitrogen atmosphere with effective stirring for 3 hours of reaction. Data for analytical evaluation were thoroughly analyzed. The water absorbency of the SPC samples was determined by tea-bag method. The SPC were characterized by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Thermogravimetric Analysis (TGA). The result of the 3 parameters involved yield a bell shape graph where there is an optimum value of these 3 parameters towards maximum water absorbency of SPC. The optimum content to produce highest yield of water absorbency are 1wt% of APS content, 1wt% of MBA content and 20wt% of rice husk content which achieved 22.219g/g, 12.823g/g, and 11.109g/g of water absorbency respectively. This study showed a new method in utilizing crops residues such as rice husk in the production of superabsorbent material.

ABSTRAK

Kajian ini adalah mengenai sinstesis dan sifat penyerapan hampas padi berasaskan super penyerap polimer komposit (SPC). Objektif kajian ini adalah untuk mengkaji keadaan sintesis optimum untuk hampas padi berasaskan SPC dengan menentukan kesan pada amaun initiator, crosslinker dan hampas padi terhadap daya penyerapan air. Sampel SPC disediakan dengan teknik 'Solution Polymerization' di mana campuran asid akrilik-acrylamide-hampas padi (AA-AM-RH) bertindak balas dengan N,N-methylenebisacrylamide (MBA) dan Ammonium Persulfate (APS) dalam keadaan nitrogen dengan pengacauan berkesan selama 3 jam. Daya penyerapan kuantiti air oleh sampel SPC ditentukan dengan teknik 'Tea-Beg'. Pencirian sampel SPC akan ditentukan menggunakan 'Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) dan Thermogravimetric Analysis (TGA)'. Keputusan untuk 3 parameter mempamerkan graf berbentuk loceng di mana terdapat satu nilai optimum untuk 3 parameter tersebut yang menunjukan nilai penyerapan kuantiti air secara maksimum. Nilai optimum tersebut ialah 1wt% APS (22.219g/g), 1wt% MBA(12.823g/g) dan 20wt% hampas padi (11.109g/g). Kajian ini menunjukkan idea baru iaitu meggunakan sisa-sisa tanaman seperti hampas padi dalam penghasilan SPC.

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LIST OF ABBREVIATIONS

AA.	Acrylic Acid
AM	Acrylamide
APS	Ammonia Persulfate
FTIR	Fourier Transformed Infrared Spectrocopy
MBA	N,N-methylenebisacrylamide
RH	Rice Husk
SEM	Scanning Electron Microscopy
SPC	Superabsorbent Polymer Composite
TGA	Thermogravimetric Analyzer

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Superabsorbent polymer composites (SPC) are polymers that can absorb and retain extremely large amounts of liquid relative to their own mass. In other words, SPC has been defined 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 (Zohuriaan and Kabiri, 2008).

Because of its properties, they are widely used in fields of personal care products, biomaterials, biosorbents, and agriculture and so on (Gohar *et al.*, 2009). For example, SPC can be used as personal disposable hygiene products, such as baby diapers, adult protective underwear and sanitary napkins. SPC is also used for blocking water penetration in underground power or communications cable, horticultural water retention agents, control of spill and waste aqueous fluid. Besides that, in motion picture and stage production, SPC is also used as artificial snow.

The synthesis of the first water-absorbent polymer was in 1938 where acrylic acid (AA) and divinylbenzene were thermally polymerized in an aqueous medium. The first generation of hydrogels was invented in late 1950 where they are mainly based on hydroxyalkyl methacrylate and related monomers with swelling capacity up to 40-50 %. Later on, the first commercial SPC was produced through alkaline hydrolysis of starch-graft-polyacrylonitrile. Major commercial production of SPC began in Japan in 1978 for use in feminine napkins (Zohuriaan and Kabiri, 2008).

SPC is usually produced from acrylic acid (AA) and acrylamide (AM) via solution or inverse-suspension polymerization techniques (Zohuriaan and Kabiri, 2008).

Recently, some research used inorganic fillers to advance the behavior of SPC (Molu *et al*., 2009). Rice husk which is inorganic filler was used in the synthesizing of SPC. At the end of synthesis, the result approved whether collaborative SPC was able to be biodegradable and strengthen the superabsorbent behaviour.

1.2 PROBLEM STATEMENT

Nowadays, the worlds are going to the greenery. In order to achieve that, green product is being produced where it can be decomposed. However, in industry, most of the superabsorbents being produced are non-biodegradable and need high production cost. Thus, research had been conducted to overcome this negative point by using rice husk for developing the properties of superabsorbent. With this, it can be used as low cost material and improve the strength properties of the SPC. Rice husk is chosen because of it properties of being able to be biodegradable and cheap.

This study was conducted to determine the optimum value for amount of rice husk, crosslinker and initiator in synthesizing SPC to obtain the high value of water absorbency and produce biodegradable SPC by developing a collaborative absorbent effect through introduction of rice husk as filler.

1.3 RESEARCH OBJECTIVES

The main objectives of this research were to study the optimum synthesizing condition of rice husk based SPC by determining the:

a) Effect on amount of initiator towards water absorbency,
b) Effect on amount of crosslinker towards water absorbency,
c) Effect on amount of rice husk towards water absorbency.

1.4 SCOPE OF STUDY

This research aim is to study of characterization of rice husk based onto superabsorbent polymer composite. Three elements have been identified to limit the scope of study:

1.4.1 Materials

a) Filler used was common rice husk.
b) Type of monomers for SPC were acrylic acid (AA) and acrylamide (AM)
c) Type of crosslinker agent for SPC was N,N'-methylenebisacrtlamide (MBA)
d) Type of initiator for SPC was ammonium persulphate (APS)

1.4.2 Method/Technique

The technique used in the study was solution polymerization where it was used to produce SPC sample. Besides that, teabag method was used to determine the water absorbency of SPC sample.

1.4.3 Characterization

Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Thermal Gravimetric Analysis (TGA) were used in the study of the SPC sample characterization.

1.5 RATIONALE AND SIGNIFICANCE OF STUDY

The significances of conducting the study were to improve the properties of SPC with introduction of rice husk by monitoring the parameters, so that collaborative SPC can be used effectively. Besides that, it was to reduce the cost of material as rice husk is easy to obtain and lastly it was to produce a biodegradable SPC. The novelty of this research is introduction of rice husk as filler into SPC.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

A review of literature was performed to identify studies relevant to the topic. The main source for the literature search was the Science Direct website. The review was organized chronologically to offer insight to how past research efforts have laid the groundwork for subsequent studies, including the present research effort. The review was detailed so that the present research effort can be properly tailored to add to the present body of literature as well as to justly the scope and direction of the present research effort.

2.2 SUPERABSORBENT POLYMER COMPOSITES (SPC)

Superabsorbent polymer composites (SPC) are hydrophilic and three dimensional networks exhibit the ability to highly swell in water, saline or biological fluids and retain significant fraction of them within their structure but they do not dissolve in water (Nor Erma Shuhadah, *et al.*, 2009). These ultrahigh absorbing materials can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g) (Zohuriaan and Kabiri, 2008).

Traditional absorbent materials such as tissue, papers and polyurethane forms unlike SPC, will lost most of their absorbed water when they are squeezed (Zohuriaan and Kabiri, 2008). An illustration of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states is shown in Figure 2.1.

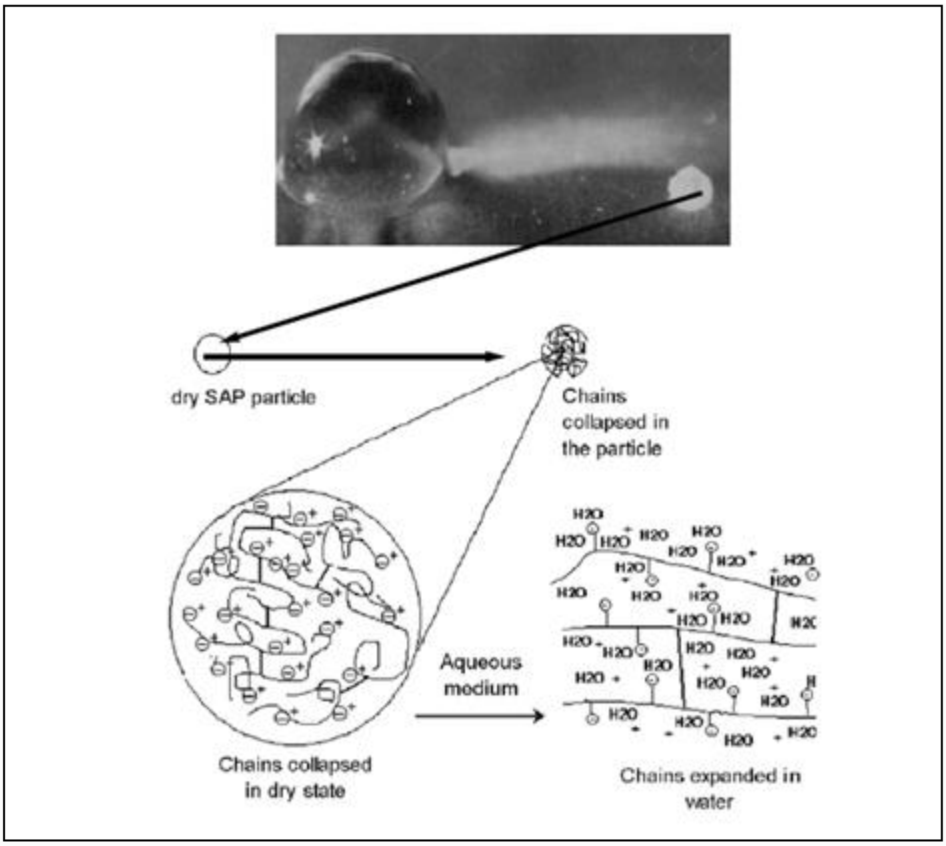

Figure 2.1: Illustration of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states.

Source: Zohuriaan and Kabiri (2008)

The Figure 2.1 above shows the visual transformation of a dry SPC particle (top right) to a swollen state (top left). The swelling occurred because of the water molecules are trapped in the network chain of SPC.

Nowadays, production of polymer superabsorbent composites has received popular demand because of their relative low production cost and high water absorbency. Recently many organic materials have been incorporated with superabsorbent polymer such as clay, cellulose and starch. The results show that the water absorbency of the poly (acrylic acid)/attapulgite superabsorbent composite in distilled water was increased tremendously as compared with crosslinked poly (acrylic acid) superabsorbent polymer. However, there is only a slightly increase in the water absorbing ability of superabsorbent composite in saline solutions (Li and Wang, 2005).

The water absorbing ability of a superabsorbent in saline solution is very important for many applications. For example, it is being used to produce diaper. Thus, the synthesis of new superabsorbent composite which has high water absorbency in both distilled water and saline solution is still being research.

Many kinds of material have been used for preparing superabsorbents. And most of the traditional water absorbing materials are acrylic acid and acrylamide-based products. They have poor degradability (Ma *et al*., 2011). About 90% of super-absorbents are used in disposal products and most of them are disposed by landfills or by inceneration (Kiatkamjornwong *et al*., 2002). This gave rise to environmental problem with super-absorbent polymers. In order to solve those problems, considerable attention has been paid to the naturally available resources such as polysaccharides and inorganic clay mineral (Li *et al*., 2007). It has good commercial and environmental value with the advantages of low cost, renewable and biodegradable polysaccharides for deriving super-absorbents (Pourjavadi and Mahdavinia, 2006; Yoshimura *et al*., 2005).

Acrylamide is a kind of nonionic monomer and has great advantage on its good salt-resistant performance as a raw material for superabsorbent. Attapulgite, as a good substrate for superabsorbent composite materials, is a layered aluminium silicate with reactive groups –OH on the surface. To reduce costs and improve the comprehensive water absorbing properties of the superabsorbent materials, acrylic acid and acrylamide copolymer are added onto attapulgite (Li and Wang, 2005). Absorbent material unlike SPC such as tissue and polyurethane will lose most of their absorbed water when they are squeezed (Zohuriaan and Kabiri, 2008).

SPC can be classified into four groups based on the basis of presence or absence of electrical charge located in the cross-linked chain. They are (1) non-ionic, (2) ionic, including anionic and catons, (3) amphoteric electrolyte, ampholytic containing both acidic and basic group and (4) zwitterions, polybetaines containing both anionic and cationic groups in each structural repeating unit. In commercial, most of SPC are from anionic type.

On the other hands, SPC can also be categorized based on the type of monomeric unit used in their chemical structure. They are categorized into (1) cross-linked polyacrylates and polyacrylamides, (b) hydrolyzed cellulose-polyacrylonitrile

(PAN) or starch-PAN graph copolymers and (c) cross-linked copolymers of maleic anhydride.

Besides that, SPC can be divided into two classes, which is (1) synthetic (petrochemical based) and (2) natural. For natural, it can be divided into two main groups that is (a) hydrogels based on polysaccharides and (b) hydrogels based on polypeptides (proteins).

In conclusion, when the term "superabsorbent" is mentioned without specifying its type, it implies that it is the anionic acrylic that comprises a copolymeric network based on the partially neutralized acrylic acid (AA) or acrylamide (AM) (Zohuriaan and Kabiri, 2008).

2.3 RICE HUSK

Using expensive monomer/modifiers for increasing water absorbency will result in increased cost, causing the economy of SPC not promising. In order to develop cheap SPC based on AA and AM, study is being conducted to increase the water absorbency by optimizing the crosslinking parameters, such as initiator and crosslinker (Singhal *et al*., 2009). Rice husk (RH) is one of the natural fillers that offer a number of advantages over inorganic fillers since they are biodegradable, low cost, recyclable and renewable.

Rice husk is an agricultural waste which can be easily obtained from the rice mills after the separation of rice from paddy. Rice husk is available in plenty and almost free of cost. The reason rice husk is chose to be added into SPC is because rice husk has good adsorptive properties (Lakshmi *et al*., 2009).

The use of modified rice husks as adsorbent also is a good choice because of its negligible raw material costs and its ability of biodegradable. Rice husk is more natural and poison free when compared to those commonly used in on-linesystems, in which the pre-concentration is usually carried out by employing potentially hazardous chemicals such as organic solvents and/or chelating agents (Tarley *et al*., 2004).

Table 2.1 shows the Chemical composition and physical properties of hydrochloric acid treated rice husk (ADR) and untreated rice husk ash (RHA) (Feng *et al*., 2003). From the table 2.1, fused silica, SiO_2 constitutes the highest percentage in chemical composition of rice husk. SiO_2 is highly cross linked three dimensional structures. One of the properties of SiO_2 is of it chemical inertness. This contribute to it function as a filler in SPC.

Table 2.1: Chemical composition and physical properties of hydrochloric acid treated rice husk (ADR) and untreated rice husk ash (RHA).

	ADR	RHA
Loss on ignition (%)	2.65	2.31
SiO_2 (%)	96	92.40
Al_2O_3 (%)	0.1	0.30
Fe_2O_3 (%)	0.2	0.40
CaO (%)	0.2	0.70
MgO (%)	<0.1	0.30
Na_2O (%)	0.03	0.07
K_2O (%)	0.16	2.54
SO_3 (%)		
P_2O_5 (%)	0.18	0.51
MnO (%)	0.02	0.11
Cl (%)	0.01	0.11
Specific gravity (g/cm^3)	2.12	2.10
Specific surface, Blaine (m^2/kg)		
Nitrogen adsorption (m^2/g)	311	110
Median grain size (μm)	7.2	7.40
Change in electrical conductivity (mS/cm)	8.43	4.75

[a] Conducted by X-ray fluorescence analysis.

Source: Feng *et al*. (2003)

2.4 INITIATOR

The first step in producing polymers by free radical polymerization is initiation. This step begins when an initiator decomposes into free radicals in the presence of monomers. The instability of carbon-carbon double bonds in the monomer makes them susceptible to reaction with the unpaired electrons in the radical. In this reaction, the active center of the radical "grabs" one of the electrons from the double bond of the monomer, leaving an unpaired electron to appear as a new active center at the end of the chain. Usually ammonia persulphate (APS) is used as the initiator in the polymerization process.

The amount of initiator content will affect toward water absorbency of SPC. From journal "Synthesis and properties of clay-based superabsorbent composite" (Li and Wang, 2005), it states that the water absorbency increases as APC content rises from 0.2 wt % to 1.0 wt % and decreases with further increase in the content of APS. The maximum absorbency is at 1.0 wt %. This shows parameter of initiator give significant effect towards water absorbency of SPC.

From journal "Synthesis and characterization of a novel cellulose-g-poly (acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste" (Wu *et al.*, 2011), it states that, the water absorbency initially increased and reached the maximum point of 872 g/g distilled water, 481 g/g natural rainwater, and 89 g/g 0.9 wt% NaCl solution at an APS to cellulose ratio of 0.1 g/g. With the further increase of initiator amount, the water absorbency decreased. It shows that mass ratio of the initiator; APS to cellulose will give effect on water absorbency.

On the other hands, the effect of the initiator, ammonium persulphate (APS), on the water absorbencies of super-absorbent composite was also shown in journal "Synthesis and characterization of a novel super-absorbent based on chemically modified pulverized wheat straw and acrylic acid" (Liu *et al.*, 2009). The maximum absorbency is at 1.1 wt% of APS (407 g/g in distilled water and 39 g/g in 0.9 wt% NaCl solution). The absorbencies increased with the increase of APS amount from 0.54 wt% to 1.1 wt%. Above optimum point (1.1 wt %), increased of APS will result in the decreased of swelling capacity of super-absorbent composite. It can be seen that the parameter of initiator has great influence on the polymer absorbencies.

2.5 CROSSLINKER

Cross-links are bonds that link one polymer chain to another. They can be covalent bonds or ionic bonds. "Polymer chains" can refer to synthetic polymers or natural polymers such as proteins. When the term "cross-linking" is used in the synthetic polymer science field, it usually refers to the use of cross-links to promote a difference in the polymers' physical properties. Commonly, ammonia persulphate (APS) is used as crosslinker in the polymerization reaction.

From previous study (Zhang *et al*., 2006), it mentioned that the water absorbency decreases with increasing crosslinker amount from 0.10 to 0.20 wt% of APS. However, water absorbency decreases sharply with further decreasing the crosslinker content below 0.10 wt% of APS. This clearly implies that amount of crosslinker is also a factor that can affect the water absorbency.

According to Li and Wang (2005), when the crosslinker, MBA content in SPC is increased above the optimum value, the water absorbency of SPC will decrease. The reason being is that the crosslinking density of the SPC increases as crosslinker content increases. This would result in a decrease in the space between copolymer chains and lead a decrease in water absorbency. Below the optimum value, the absorbency of SPC is diminished because of an increase of soluble material. This means, crosslinker is one of the parameter that gives significant effect towards water absorbency of SPC.

2.6 POLYMERIZATION TECHNIQUES

The most common type of addition polymerization is free radical polymerization. A free radical is simply a molecule with an unpaired electron. The tendency for this free radical to gain an additional electron in order to form a pair makes it highly reactive so that it breaks the bond on another molecule by stealing an electron. Free radicals are often created by the division of an initiator into two fragments along a single bond.

One of the techniques is solution polymerization. Solution polymerization is a polymerization process in which the monomers and the polymerization initiators are dissolved in a non monomeric liquid solvent at the beginning of the polymerization reaction. The process depends on concentration of monomer. Free radical initiated polymerization of AA and its salt and AM, with crosslinker is frequently used for SPC preparation. The carboxylic acid groups of the product are partially neutralized before or after the polymerization step. Initiation is most often carried out chemically with free-radical azo or peroxide thermal dissociative species or by reaction of a reducing agent with an oxidizing agent (redox system). (Zohuriaan and Kabiri, 2008). SPC are produced by reaction of acylic acid (AA) and acrylamide (AM) on attapulgite micropowder using N,N-methylene-bisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in an aqueous solution (Li and Wang, 2005).

Solution polymerization is a straight process which is the reactants is dissolved in water at desired concentrations, usually about 10-70%. Its yield a gel-like elastic product with fast exothermic reaction which is dried and the macro-porous mass is pulverized and sieved to obtain the required particle size. This method usually suffers from the necessity to handle a rubbery/solid reaction product, lack of a sufficient reaction control, non-exact particle distribution and increasing the sol content mainly due to undesired effects of hydrolytic and thermal cleavage. Solution polymerization is always preferred to be used in manufacturing of SPC because of it cost effective and fast production process (Zohuriaan and Kabiri, 2008). Figure 2.2 shows two general pathways to prepare acrylic SPC network which simultaneous polymerization and crosslinking by polyvinylic cross-linker, and crosslinking of water-soluble prepolymer by a polyfunctional cross-linker (Zohuriaan and Kabiri, 2008).

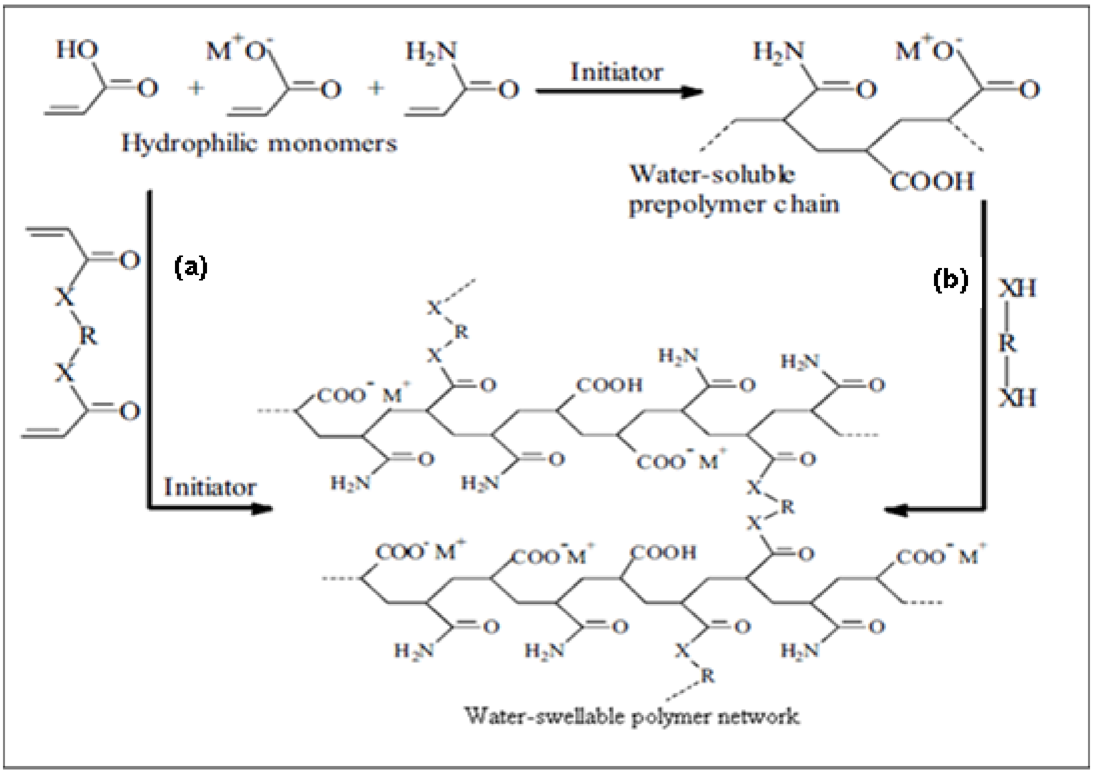

Figure 2.2: Chemical structure of the reactants and general pathways to prepare an acrylic SPC network; (a) crosslinking polymerization by a polyvinylic cross-linker, (b) cross-linking of water soluble prepolymer by a polyfunctional cross-linker.

Source: Zohuriaan and Kabiri (2008)

Apart from that, graft copolymerization is another type of polymerization other than solution polymerization. Generally, polysaccharide-based SPC can be divided into two groups which is (a) direct cross-linking of polysaccharide, and (b) graft copolymerization of suitable vinyl monomer on polysaccharide in presence of a cross-linker.

In graft copolymerization, usually a polysaccharide enters reaction with initiator by either of two different methods. The first method is that the neighboring OHs on the saccharide units and the initiator interact to form redox pair-based complexes. These complexes are then dissociated to produce carbon radical on the polysaccharide substrate through homogenous cleavage of the saccharide C-C bonds. These free radicals initiate the graft polymerization of the vinyl monomers nd cross-linker on the substrate.

For second method, the initiator such as persulphate can abstract hydrogen radical from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone. From those both methods, the second method is more sensitive by temperature changes compared to first method.

Figure 2.3 and 2.4 show the diagram of two groups of graft copolymerization which is (a) direct cross-linking of polysaccharide, and (b) graft copolymerization of suitable vinyl monomer on polysaccharide in presence of a cross-linker.

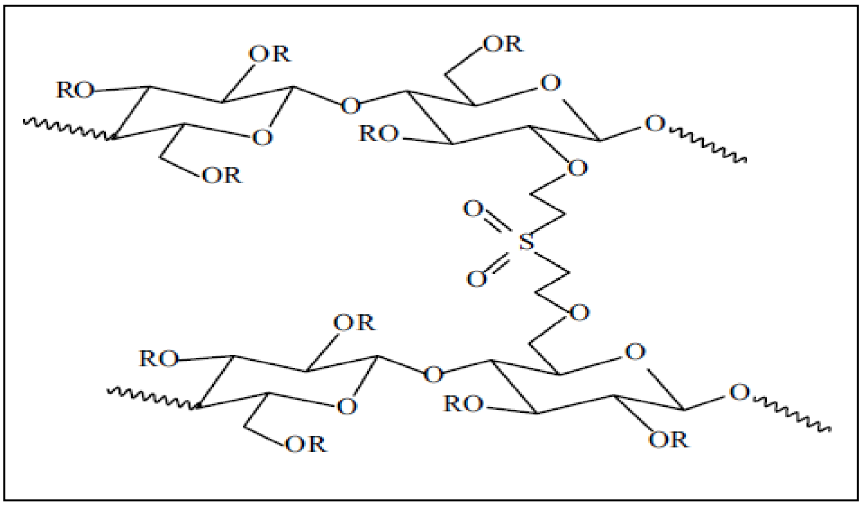

Figure 2.3: Typical cellulose based SPC prepared via direct cross-linking of sodium carboxymethyl cellulose (CMC; R=H, $COO^{-}Na^{+}$) or hydroxyethyl cellulose (HEC; R=H, CH_2CH_2OH)

Source: Zohuriaan and Kabiri (2008)

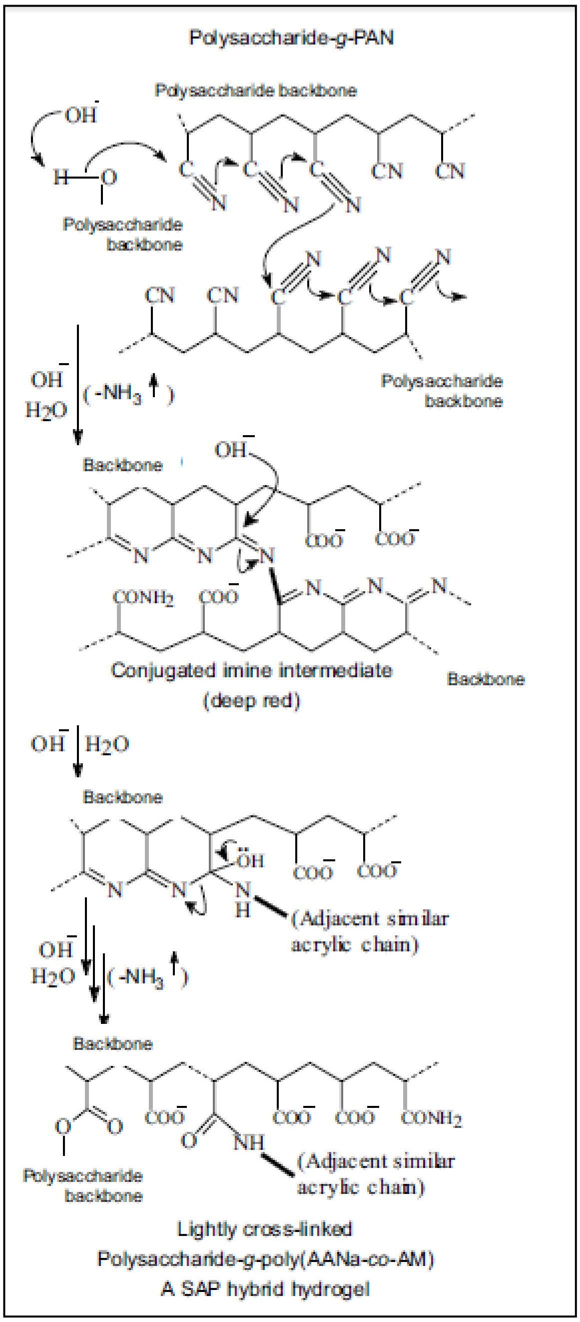

Figure 2.4: Mechanism of in-situ cross-linking during the alkaline hydrolysis of polysaccharide-g-PAN copolymer to yield superabsorbing hybrid material

Source: Zohuriaan and Kabiri (2008)