

SYNTHESIS AND SWELLING BEHAVIOUR OF BENTONITE BASED
SUPERABSORBENT POLYMER COMPOSITE

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ABSTRACT

Bentonite based superabsorbent polymer composite (SPC) was synthesized by solution polymerization of acrylic acid and acrylamide comonomer with bentonite using ammonium persulfate (APS) as an initiator and *N, N*-methylenebisacrylamide (MBA) as a crosslinker. Amount of bentonite, initiator and crosslinker were varied to get the optimum value to produce maximum water absorbency. The water absorbency determination was done by using tea-bag method. The SPC were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). The water absorbency under optimal synthesis of the SPC with Bentonite content of 10%, APS content of 0.9% and MBA content of 0.0%, it reaches more than 537 g H₂O/g in distilled water respectively.

ABSTRAK

Kajian ini adalah untuk menganalisa kelebihan sifat-sifat pada tanah liat terhadap kuantiti penyerapan air dalam bentuk 'Superabsorbent Polymer Composite' (SPC). Pembolehubah yang dikaji adalah kuantiti pemaat silangan, ammonium persulfat dan tanah liat dengan menggunakan teknik 'solution polymerization'. Bahan-bahan lain yang turut dicampur adalah *N,N*-methylenebisacrylamide (MBA) dan Ammonium Persulfat (APS). Kadar penyerapan air ditentukan melalui kaedah 'tea-bag'. Analisa struktur dilakukan menggunakan Fourier Transform Infrared Spectroscopy (FTIR) dan Thermogravimetric Analysis (TGA) untuk menganalisa kestabilan haba. Kuantiti penyerapan air terbaik adalah 537 g Air/g pada kuantiti 10% Bentonite, 0.9% kandungan APS, dan 0.0% kandungan MBA secara keseluruhannya.

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LIST OF ABBREVIATIONS

AA	Acrylic Acid
AM	Acrylamide
APS	Ammonia Persulfate
B	Bentonite
FTIR	Fourier Transformed Infrared Spectroscopy
MBA	N, N-methylenebisacrylamide
SPC	Superabsorbent Polymer Composite
TGA	Thermogravimetric Analyzer

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Superabsorbent polymer composites (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). SPC are types of loosely crosslinked hydrophilic polymer that can swell, absorb and retain a large volume of water or other fluid.

Superabsorbent polymers have been widely used in disposable diaper industry, agriculture and horticulture, sealing composites, artificial snow, drilling fluid additives, medicine for drug delivery system and others (Gohar et al., 2009). It is very highly demand from consumers because of wide application of superabsorbent polymer composites. This product can achieve 1.5 million tons per year in worldwide production.

On 1938, acrylic acid (AA) was synthesized with divinylbenzene which were thermally polymerized in aqueous medium. Then, the first generations of hydrogels were invented which were used in ophthalmology in order to developing contact lenses. That hydrogels has swelling capacity up to 40-50% which was based on hydroxyalkyl methacrylate with related monomers. On 1970s, by using starch-graft-polyacrylonitrile (SPAN), the first commercial SAP was invented at the Northern Regional Research Laboratory. The revolutions of SAP were commercialized in Japan on 1978 in order to produce feminine napkins. In Germany and France, they were employing SAP in baby

diapers in 1980. In late 1990, the production of SPC became more than one million tons due to the applications in daily life (Zohuriaan-Mehr et al., 2008).

There are three types of SAP which are synthetic SAPs, polysaccharide-based SAPs and poly (amino acid)-based SAPs. For Synthetic SAPs, these types of SAPs were derived from petrochemical origin. It is produced by using acrylic acid (AA) with its salt acrylamide (AM).

However, most of these super-absorbents are expensive synthetic polymers based on acrylic acid or acrylamide their production is dependent on the consumption of petroleum resources, and their usage may also cause a non-negligible environmental problem. Recently, some research used inorganic fillers to advance the behavior of SPC, inorganic fillers like clay can be used as substitution material (Molu et al., 2009). In this paper, we report the synthesis and swelling behavior of bentonite superabsorbent polymer composites by using solution polymerization reaction of bentonite, acrylic acid and acrylamide. Using N, N'-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator with presence of bentonite powder in aqueous solution.

Because of biodegradable and environmental friendly properties, it makes the demand of clay higher than usual. Superabsorbent polymer composites substituted with organoclay such as bentonite, it makes the price cheaper with reducing the production cost. Bentonite with the layered aluminum silicate with reactive group -OH, is the best substrate for superabsorbent material. At the end of synthesis, the result was approved that advanced SPC composite is better than pure SPC at 10% w/w of filler with water absorbency at 573.27 g/g.

1.2 PROBLEMS STATEMENTS

High production cost and non-biodegradable properties are the disadvantages of synthetic SPC. Thus, this study was proposed to solve that problem by using inorganic filler clays which is bentonite for developing the properties of superabsorbent hydrogels. By using swelling behavior, it can improve the strength and properties in

polymer matrixes just using nature materials to reduce the production cost and make it more environmental friendly.

This research was designed to determine the optimum amounts of bentonite, crosslinker and initiator in synthesizing of SPC monomer to acquire the highest value of water absorbency. Thus, the target of this research to increases the collaborative absorbent effects though the introduction of bentonite to reducing the production cost and increase the swelling capacity of superabsorbent composites.

1.3 RESEARCH OBJECTIVES

The main objective of this research is to study the optimum synthesizing condition of bentonite based SPC by determine:

- i. Effect on amount of initiator towards water absorbency.
- ii. Effect on amount of crosslinker towards water absorbency, and;
- iii. Effect on amount on inorganic clay, bentonite towards water absorbency.

1.4 SCOPE OF STUDY

(a) Material:

- i. Filler that used was bentonite.
- ii. Type of monomer of SPC is Acrylic acid (AA) and Acrylamide (AM).
- iii. Type of crosslinker for SPC is N,N'-methylenebisacrtlamide (MBA).
- iv. Type of initiator for SPC is Ammonium persulphate.
- v. In preparation of sample, three parameter was varied which are amount of initiator, amount of crosslinker and amount inorganic clay.
- vi. Polymerization technique was used in this research was solution polymerization. Moreover, it showed the comparisons between SPC and collaborative SPC with that three parameter studies.

(b) Apparatus

- i. Four-neck flask, stirrer, thermometer, sieve shaker, hot plate, nitrogen line and beakers were used for polymerization.
- ii. In water absorbency determination, tea bag and weighing scale was used.

1.5 RATIONALE AND SIGNIFICANCE

Superabsorbent polymer composite were widely used in diapers, horticulture and agriculture industries. There a lot of applications with products equipped with absorbency properties. These researches were conducted in order to improve the amount of water absorbency with substitution of bentonite collaboration. Moreover, the rationale of this paper to improve the conditions of SPC with substitution on bentonite by monitoring parameters such as initiator and crosslinker amounts. As known, synthetic superabsorbent was not a biodegradable products and environmental friendly. This bentonite based superabsorbent were resulted with reduces the cost production of SPC and increase the demand on manufacturing of collaborative SPC. It also was more biodegradable and environmental friendly suit to agriculture and horticulture field.

CHAPTER 2

LITERATURE REVIEW

2.1 SUPERABSORBENT COMPOSITES (SPC)

Superabsorbent polymers are slightly crosslinked hydrophilic polymers with a three-dimensional network structure which are capable in absorbing and retaining large amounts of aqueous fluids under some pressure. Desired features of superabsorbent consist of good swelling capacity, high swelling rate, and have good strength of swelling gel. SPC hydrogels relative to their own mass can absorb and retain extraordinary large amounts of water or aqueous solution (Zohuriaan and Kabiri, 2008).

The SAP particle shape (granule, fiber, film, etc) has to be basically preserved after water absorption and swelling, 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 SPC, will lose most of their absorbed water when they are squeezed (Zohuriaan and Kabiri, 2008).

Figure 2.1 shows that superabsorbent can retain aqueous solution up to hundreds of times their own weight even under some pressure. According to Zheng et al. (2007) has proposed that molecule structure of SPC which is loosely crosslinked hydrophilic polymer influence the water absorbency and swelling behavior of SPC. So that, superabsorbent is very useful to absorb, swell and retain some weight of aqueous solution in wide applications.

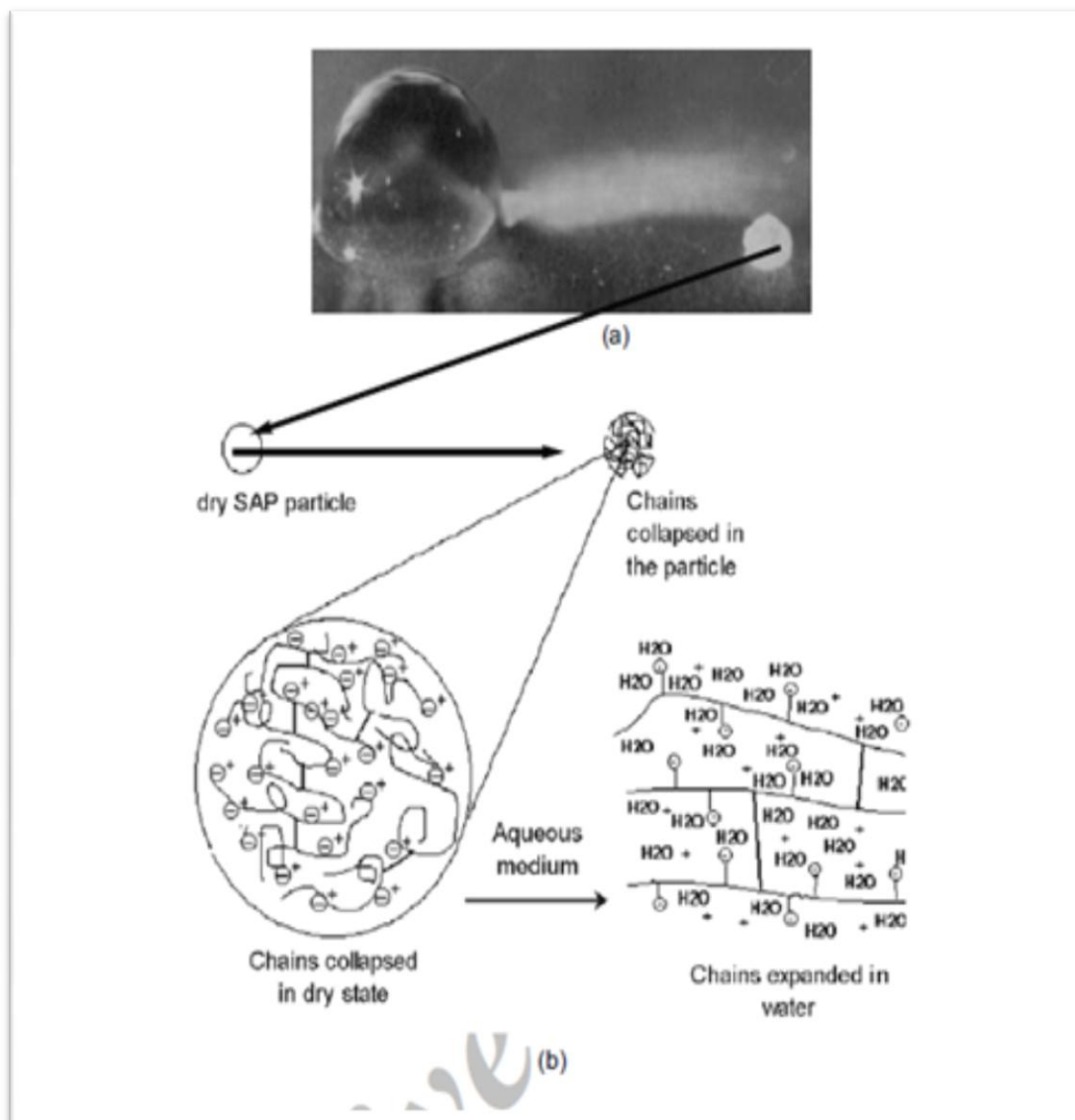


Figure 2.1: Illustration of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states

Source: Zohuriaan and Kabiri (2008)

2.2 CLAY POLYMER STRUCTURE

Clay particle sizes are in micrometer to nanometer range length scale. The small dimensions of clay particles suggest a large influence of the molecular scale behavior and interactions (particle-particle, particle-water and interlayer) on bulk mechanical properties.

According to Vimonses et al. (2009) found that a crystalline structure of clay is known as 2:1 type aluminosilicate, presenting an octahedral alumina between two tetrahedral silica layers. As a results, these parallel layer allowing water and other polar molecules to enter between layers and induce an expansion of mineral structure due to weak electrostatic forces between them. Water was polar molecules which can be interacting through dipole-dipole intermolecular force and hydrogen bonds. Thus, by this type of molecular structure will influence the water absorbency in collaborative SPC in this research. It shows that substitution of bentonite composition in SPC also contribute to the increases of water absorbency.

Inorganic fillers has been used as substitution material to improve the behaviour of SPC in past research (Molu et al., 2009 and Li and Wang, 2005). Meanwhile clays, such as kaolin, montmorillonite, attapulgite, mica, and sercite hydrotalcite have all been used for the preparation of superabsorbent composites.

The basic structural units in clays consist of the sheet formed of silica tetrahedral and octahedral unit formed of octahedrally coordinated cations (with oxygens or hydroxyls) octahedral as shown in Figure 2.2

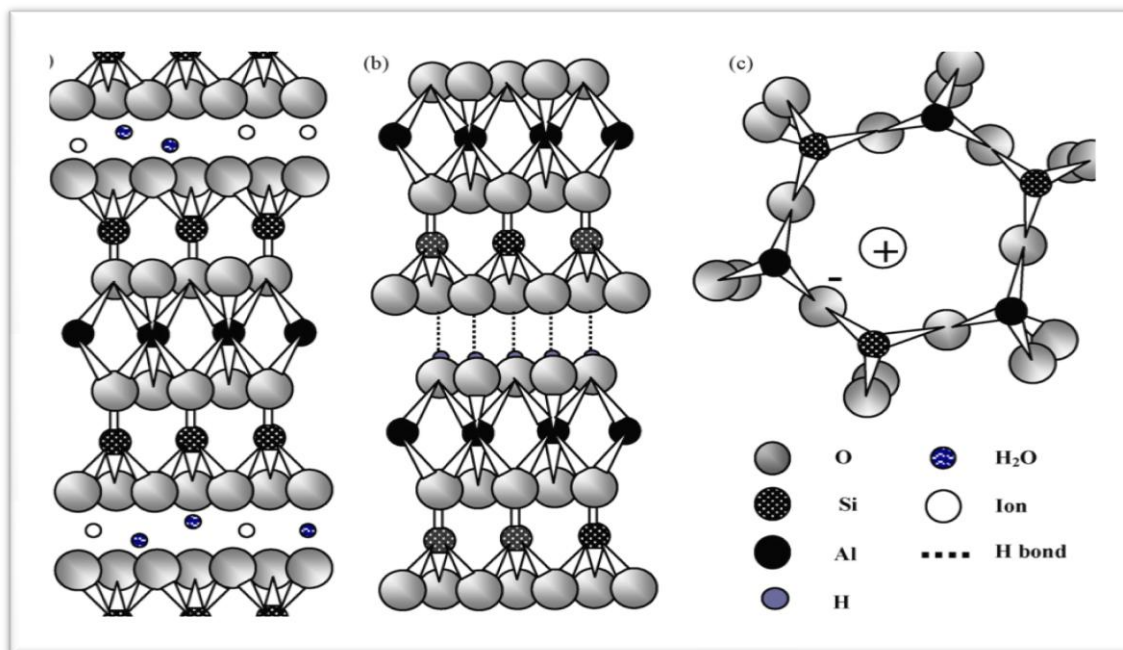


Figure 2.2: The diagram of clay minerals molecular structure (a) Bentonite (b) Koalin
(c) Zeolite

Source: Vimonses et al. (2009)

2.3 PROPERTIES OF BENTONITE

Bentonite are the cheaper, most abundant, available and organic materials. It is fine-grained clay that contains primarily montmorillonite minerals. Bentonite is come from the weathering of volcanic ash, usually in a marine environment. There comes with different colors such as light olive green, brick red, gray, cream, brown, and yellow. Bentonite usually feels greasy and slippery but its adsorbent properties make it good for used as a paste.

Moreover, Zhang and Wang (2007) reported that, clays such as kaolin, montmorillonite and mica have all been used for the preparation of superabsorbent. From this research shows that by adding clay collaborative with SPC, the water absorbency increase up to 1077 g/g. Thus, bentonite has been chosen in this research as filler to improve the water absorbency of SPC.

From the Table 2.1, bentonite have 2:1 layer type and with sheet crystal structure. It is because of Bentonite was composed of two thirds of silica elements. It also have some portions of elements such as 18.1% of Aluminium, 0.04% of Calcium, 3.5% of Iron, 1.7% of Magnesium, 7.8% of moisture, 8.3-9.1% of potential hydrogen, 0.01% Potassium, 2.3% of Sodium and 0.02% of Titanium. Moreover, Bentonite has higher value of cation exchange capacity (CEC) which is closely related with swelling capacity. Bentonites are clay rich in smectite regardless of their mode of origin which are valued for their properties such as crystal shape and size hydration and swelling, thixotropy, bonding capacity, impermeability, plasticity and tendency to react with organic compounds (Christidis, 1998).

Table 2.1: Summary of structure and properties of the most common clay minerals.

Property	Koalin	Mica	Bentonite	Attapulgitite	Chlorite
Layer type	1:1	2:1	2:1	2:1	2:1:1
Crystal Structure	Sheet	Sheet	Sheet	Sheet	Sheet
Particle shape	Hexagonal plate	Extensive plates	Flake	Needle	Plate
Particle size, microns	5-0.5	Large sheets to 0.5	2-0.1	1-0.1	1-0.1

Surface Area					
	Koalin	Mica	Bentonite	Attapulgite	Chlorite
BET-N ₂ , m ² /g	15-25	50-100	30-80	200	140
BET-H ₂ O, m ² /g	-	-	200-800	-	-
CEC, Meq/100g	3-15	10-40	80-150	12-25	10-40
Viscosity in water	Low	Low	High	High	Low
Effect of salts	Flocculates	Flocculates	Flocculates	Little or none	Flocculates

Source: Christidis (1998)

2.4 PRETREATMENT OF BENTONITE

Bentonite clays have the best adsorption properties which were used as adsorbent, decolouration agents, ion exchange, and molecular sieve catalyst (Santiago et al., 2006). The most popular ways to modified of absorptive properties of bentonite have been done by using treatment with inorganic acids and saturation of clay by using polyvalent cations method. By doing this treatment, formation of a nano-porous structure comes from acid activation of bentonite's structure was developed. Thus, stabilization was created in the clay molecular structure before it can be used in various applications.

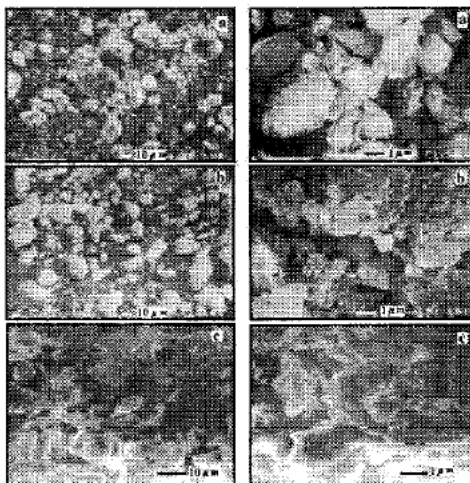


Figure 2.3: Microphotos of samples of initial bentonite clay (a), after HCl treatment of clay (b), after HCl + BaCl₂ treatment of clay and (c), with different magnifications.

Source: Vlasova et al. (2003)

According to Vlasova et al. (2003), the treatment of Bentonite clays by the diluted hydrochloric acid with $\text{pH} = 0.8$ resulted the reduction of gypsum and montmorillonite contents. Based on Figure 2.3 shows that, the mean of diffraction lines of bentonite change from 1.47 nm to 1.52nm of an intensity ratio. It's also reported HCl-treated bentonite clay make the aggregate of a clay mineral increase up to 1.9 nm, then loosening and destruction of inside aggregate porosity are visible. It also leads to formation of pores as a result of eliminating the OH-groups from interlayer space. The action of acids on bentonite is similar to the dehydration during temperature treatment of silicates layer. So, pretreatment of bentonite were important and suitable to remove the OH-groups from interlayer space and increase the water absorbency when combined with superabsorbent monomers.

2.5 INITIATOR

APS are the medium to connect among monomers which were acrylic acid (AA) and acrylamide (AM). APS will react with double bond molecular structure of AA and AM by producing free radicals sites to connect between these two monomers. Figure 2.4 shows the mechanism for grafting and production of free radicals sites by using

APS. APS is a strong oxidizing agent and a radical initiator. So, it is easy to soluble in water and endothermic reaction when dissolution of salt in water.

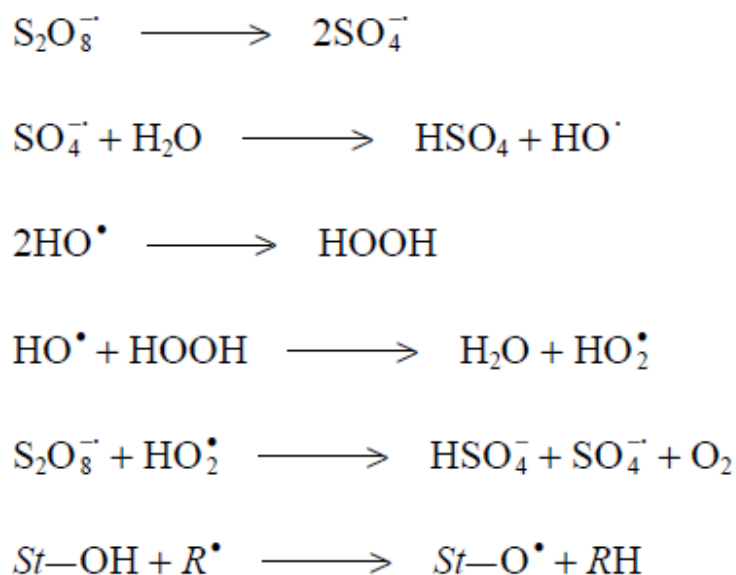


Figure 2.4: Mechanism for grafting by using APS

Source: Athawale and Rathi (2007)

Varma and Meshram (1997) reported that ammonium persulfate is an expensive and readily accessible oxidizing reagent. It is commonly used in industry for bleaching and for waste water treatment. Li and Wang (2005) also stated that by using APS at 1.0 wt%, resulted 1400 g/g of water absorbency of superabsorbent composites in distilled water.

Another research by Li et al. (2006) of 'Utilization of starch and clay for the preparation of superabsorbent composite' showed that by 0.3 wt% of APS initiator, resulted 1077 g/g of water absorbency of superabsorbent composite. All this result shows that by using and varying the amount of APS gave a good performance to the water absorbency of SPC.

2.6 CROSSLINKER

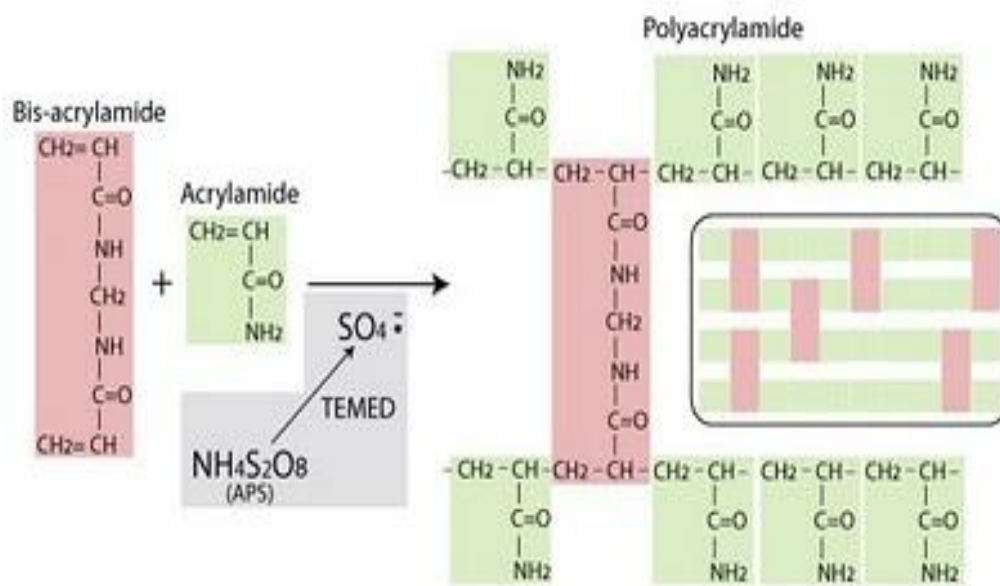


Figure 2.5: Polyacrylamide gels are formed by copolymerization of acrylamide and bis-acrylamide (“bis,” N,N'-methylene-bisacrylamide).

Source: Chrambach (1985)

N, N'-Methylenebisacrylamide, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$. (MBA) is a cross-linking agent used during the formation of polymers such as polyacrylamide. It can be in covalent bond and ionic bond. MBA was very popular medium used to connect within copolymer to form polymer. Figure 2.5 shows the copolymerization reaction of acrylamide and bis-acrylamide to form polyacrylamide. Bis-acrylamide(MBA) was functional to connect the copolymer (acrylamide) in order to form polymer. Chrambach (1985) said that, the reaction is a vinyl addition polymerization initiated by free-radical generating system. So, this reaction will allow acrylic acid, acrylamide and bentonite to grafting by using MBA when this reaction occurs. According to Li and Wang (2005), the crosslinker content will affect the space for water absorbency in SPC and the increases of crosslinker content will increased the crosslinking density of SPC. Its shows when the increases of MBA content from 0.2 to 1.0 wt% resulted decreases of water absorbency from 1400 to 200 wt%.

In other research, the water absorbency decreased with the increased of crosslinker content from 0.08 to 0.2%. Clearly, higher crosslinker content resulted in the generation of more crosslink points caused the formation of an additional network and decreased the available free volume within the superabsorbent composite (Li et al., 2006). Besides that, it is because of increase of crosslinker between copolymer will decrease the space for bentonite to substitute in SPC. So, MBA content play an important role in determining maximum water absorbency of superabsorbent polymer composites.

2.7 SOLUTION POLYMERIZATION

Solution polymerization is also known as free-radical polymerization. These processes also were general production of SPC which were acceptable for swelling properties, less expensive and faster technique (Zohuriaan-Mehr et al., 2008). Solution polymerization is a polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization reaction. The process depends on concentration of monomer, the solution does not increase in viscosity and usually use in ionic polymerization because solvent are necessary to control the polymerization. Free radical initiated polymerization of AA and its salt and AM, with crosslinker it frequently used for SAP preparation. In this research, ammonium persulphate and N,N'-methylenebisacrtlamide were initiator and crosslinker during solution polymerization process.

According to Henriquez et al. (2003) reported that chain transfer agents to control the molecular weight of polymer can be obtained by using free-radical polymerization. The monomer between acrylamide (AM) and acrylic acid (AA) will be connected with this process to produce synthetic SPC. So, ammonium persulphate (APS) was used because of strong oxidation agent.

According to Li and Wang (2005), reported that by using solution polymerization technique, the water absorbency reached maximum up to 1440 g/g of

distilled water. Besides that, the maximum swelling capacity of superabsorbent composite was reached within 60 min.

In other report by Bulut et al. (2009) said that, by using solution polymerization in process of poly AA-Bentonite superabsorbent polymer composite, achieved maximum water absorbency up to 325 g and 110 g of distilled water just in 180 and 45 min. Moreover, poly AA-Bentonite also successfully absorbed heavy metal such as Pb(II), Ni(II), Cd(II) and Cu(II). It shows that solution polymerization technique was applicable to produce superabsorbent polymer composite without disturb the absorbent properties.

By the way, in solution polymerization step, 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-Mehr et al., 2008).

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 (Zohuriaan-Mehr et al., 2008).