SYNTHESIS AND SWELLING BEHAVIOR OF BENTONITE BASED SUPERABSORBENT POLYMER COMPOSITES

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ABSTRACT

A novel superabsorbent polymer composite (SPC) was synthesized by solution polymerization reaction of partially neutralized acrylic acid (AA) and acrylamide (AM) on bentonite micropowder using N,N-methylenediacrylamide (MDA) as croslinker and ammonium peroxodisulfate (APS) as an initiator in aqueous solution. Poly (acrylamide-co-acrylic acid) [poly (AM-co-AA)]-based bentonite SPC were prepared by varying the cross-linking agent composition amount in the range of 0.00% to 1.80%. The effect of Bentonite as filler in weight percentages range of 0.00% to 1.40% on the water absorbency of the hydrogels was also studied by keeping two monomers content constant. The synthesized hydrogels were characterized by FTIR dan SEM. The effect of amount of Bentonite and crosslinker on the water absorbency of AM-AAc-Bentonite was investigated to different physiological fluids which are; deionized water, NaOH solution pH 13.75 and HNO_3 solution pH 2.10. An optimum condition which is highest percentages of swelling behavior were obtained with bentonite composition at about 1.00% wt, crosslinker composition in range 1.20-1.40% wt and the best fluid immersed in distilled water. The water absorbency of poly(AA-co-AM)/bentonite was found to be 3821.57, 822.15 and 675.72g H_2O g in distilled water, alkali solution and acid solution.

ABSTRAK

Sebuah novel komposit polimer superabsorbent (SPC) disintesis dengan menetralisiki pempolimeran larutan asid akrilat (AA) dan akrilamida (AM) terhadap serbuk micro Bentonite dengan menggunakan N,N-methylenediacrylamide (MDA) sebagai agen penyambung, dan peroxdisulfate ammonium (APS) sebagai pemangkin dalam larutan cecair. Poli(asid akrilat-co-akrilamida)[poli(AA-co-AM)] SPC berasakan Bentonite dikaji dengan menvariasikan jumlah berat komposisi agen penyilang dalam julat diantara 0.00% hingga 1.80%. Pengaruh komposisi Bentonite sebagai agen pemanbah dalam julat diantara 0.00% hingga 1.40% terhadap kadar serapan air di dalam larutan cecair dengan memalarkan kandungan monomer-monomer yang digunakan. Sifat sistesis hidrogel dibuktikan dengan menggunakan FTIR dan SEM. Pengaruh jumlah Bentonite dan agen penyilang terhadap kadar penyerapan AM-AAc-Bentonite dikaji di dalam cecair fisiologi yang berbeza iaitu air deionisasi, larutan NaOH dan larutan HNO_3 dengan nilai pH 13.75 dan 2.10. Keadaan optimum dikenalpasti melalui nilai peratusan tertinggi terhadap kadar sifat pengembangan yang diperolehi adalah pada tahap komposisi Bentonite sekitar 1.00%, komposisi agen penyilang sekitar 1.20-1.40% dan cecair rendaman terbaik adalah dalam air deionisasi. Daya serap air poli(AA-co-AM)/Bentonite dikenalpasti menjadi 3821.57 dan 675.72 g H_2Og dalam air deionisasi, larutan alkali dan larutan asid.

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FTIR	-	Fourier Transforms Infrared Spectroscopy
SEM	-	Scanning Electron Microscopy

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Superabsorbent polymer composite (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, 2008a). SPC are types of loosely crosslinked hydrophilic polymer that can swell, absorb and retain a large volume of water or other fluid. Desired features of superabsorbents are high swelling capacity, high swelling rate, and good strength of the swelling gel. SPC hydrogels relative to their own mass can absorbs and retain extraordinary large amounts of water or aqueous solution (Zohuriaan and Kabiri, 2008b).

Reviewed by Zohurian and Kabiri (2008c) stated that traditional absorbent materials (such as tissue papers and polyurethane foams) unlike SPC, will lost most of their absorbed water when they are squeezed. Table 1.1 compares water absorptiveness of some common absorbent materials with a typical sample of a commercially available SPC.

Table 1.1: Water absorbency of some common absorbent materials in comparison with a typical commercial SPC sample (Zohuriaan and Kabiri, 2008d)

Absorbent Material	**Water Absorbency (wt%)**
Whatman No. 3 filter paper	180
Facial tissue paper	400
Soft polyurethane sponge	1050
Wood pulp fluff	1200
Cotton ball	1890
Superb A-200[a]	20200

Because of it properties, they widely used in the fields of personal care products, biomaterials, biosorbents, agriculture and so on (Gohar *et al.*, 2009). For examples these materials, firstly applied in the United States as water retention agents in agriculture, were developed in Japan in the mid 1970s in the personal care and hygienic products disposable diapers, sanitary, napkins, surgical pads, etc. It is well known that there are many water absorbing materials such as pulp, paper, cotton and etc which were conventionally used as sanitary towel and diaper. In addition to the healthcare products, they are used in soil conditioning and as artificial soils for hydroponics, as controlled release agents for skiing area, and other numerous applications (Zohuriaan and Kabiri, 2008; Kabiri *et al.*, 2003).

Recently, the applications of hydrogels are grown extensively. Hydrogels that are responsive to specific molecules, such as glucose or antigens can be used as biosensors as well as in drug delivery systems (DDS). These kinds of hydrogels are also used as controlled release delivery devices for boi-active agents and agrochemicals. Contact lenses are also based on hydrogels (Zohuriaan and Kabiri, 2008e)

SPC are originally divided into two main classes which are synthesis (petrochemical-based) and natural. Usually, most of the superabsorbent are frequently produced from acrylic acid (AA) its salts and acrylamide (AM) via solution or inverse-suspension polymerization techniques (Zohuriaan and Kabiri, 2008f). Recently, some researched used inorganic fillers to advance the behaviour of SPC, inorganic fillers like clay can be used as substitution material (Molu.*et al.*, 2009a; Li and Wang, 2005). Clays such as kaolin, montmorillonite (MMT), attapulgite, mica, bentonite, and sercite hydrotalcite have all been used in the preparation of SPC. In this study MMT will be used as filler. At the end of synthesis, the result will be approved whether advance SPC composite better than pure SPC.

Several papers have been published to review SPC hydrogel materials, each with own individual outlook. As a general framework, synthetic methods and properties of hydrogel networks were reviewed. Synthetic, semi-synthetic and biopolymeric hydrogels were also briefly reviewed by Zohurian and Kabiri (2008g). Theoretically, there is a wide range of inorganic materials with expandable layers available for utilization for the preparation of SPC. In recent years, the study of organic-inorganic nanocomposites has become a very important field. Currently, reinforcing polymers with small amounts of smectite clays has attracted increasing interest, because the derived heterostructural materials exhibit impressive mechanical, thermal, optical, and other properties that increase their technological values (Suda, 2007a).

Other than using organic clay as the filler on the synthesis of SPC there are other types of filler or additive use in other research such as used starch, rice husk, organic fiber and others. For example, SPC obtained from shellfish waste have also been reviewed by Dutkiewicz (2002). Teli and Nilesh (2010) have reviewed the SPC materials based on the Amaranthus starch. A review profile of water absorbing resins based on graft copolymers of acrylic acid and gelatinized starch was presented by Atawale *et al.* (2001). Peng *et al.* (2007) has elaborated the uses of SPC based on graft copolymerization blending based on acrylamide (AM), diallydimethylammonium chloride (DMDAAC) and sodium starch sulfate (SSS) (Peng *et al.*, 2008).

In another review by Zhang *et al.* (2006), the chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composite was prepared by graft polymerization with chitosan, acrylic acid and attapulgite in aqueous solution, using N,N-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. The factors influencing water absorbency of the superabsorbent composite were investigated, such as average molecular weight of chitosan, weight ratio of acrylic acid to chitosan, dewatering method, the amount of crosslinker and attapulgite have been discussed in detail (Zhang *et al.*, 2005).

1.2 Problem Statements

Recently Superabsorbent polymers composite (SPC) have been used and applied but it still have a negative feature in some application fields because of the high production cost. Thus, study is conducted to overcome this negative point by using, inorganic filler clay which is Bentonite for developing the properties of superabsorbent hydrogels. The abundance of bentonite and its low cost are likely to make it a strong candidate as filler and additive. The resulting product is poly(acrylic acid-co-acrylamide)/bentonite SPC were synthesized by solution polymerization reaction of Acrylic acid (AA) and Acrylamide (AM) on bentonite using MDA and APS as initiator in aqueous solution. It was be used as low cost material and improve the strength properties in the polymer matrixes, which can be measured by the swelling behavior.

This study will be conducted to determine the optimum value for amount of Bentonite, crosslinker and initiator in synthesizing of SPC monomer to obtain the high value of water absorbency. Thus, the aims of this study to develop the collaborative absorbent effect through the introduction of Bentonite in reducing the production cost and improved the swelling capacity of superabsorbent composites.

Review the swelling behavior of SPC in different type of physiological fluid. How the different conditions of physiological fluid can give effect on the swelling behavior of the SPC whether it enhance or declining the swelling rate.

1.3 Objectives

This research focused on studied the optimum synthesizing condition of clay based SPC by determined:

i. Effect on amount of inorganic clay, Bentonite towards water absorbency.
ii. Effect on amount of crosslinker towards water absorbency.
iii. Effect on water absorbency to different types of physiological fluids.

Use of expensive monomers/modifiers for increasing water absorbency will result in increased cost, rendering the resulting SPC economically unsuitable. In order to develop cheap SPC based on AA and AM in the present study an effort was made to increase the water absorbency by optimizing the cross-linking parameters, such as initiator and cross-linker (Singhal *et al.*, 2009a).

1.4 Scope of Study

The scopes of this research are:

a) Materials

i. Filler that used is Bentonite
ii. Type of monomer for SPC were Acrylic acid (AA) and Acrylamide (AM)
iii. Type of crosslinker agent for SPC was N,N'-methylenediacrylamide (MDA)
iv. Type of initiator for SPC was Ammonium peroxodisulfate (APS)
v. Different types of physiological fluid; distilled water, Sodium hydroxide (NaOH) solution pH 13.75, and Nitric acid (HNO_3) solution pH 2.10.

b) Parameters

For sample preparation, three parameters was varied which are amount of crosslinker, amount of inorganic clay and types of physiological fluids. Analysis will be analyzed by using Bentonite contents in range 0.0 wt% to 1.4 wt%, for amount of MDA contents evaluate in range of 0.0 wt% to 1.8 wt% and for types of physiological fluids was investigated to deionized water, NaOH solution pH 13.75 and HNO_3 solution pH 2.10.

c) Apparatus

For making sample three-neck flask was used equipped with a stirrer, condenser, thermometer, and nitrogen line.

d) Preparation technique

Polymerization technique was used in this research was solution polymerization.

e) Characterization

The IR spectra of the sample products were characterized by FTIR and the water absorbency was investigated to different physiological fluids which are deionized water, NaOH solution pH 13.75 and HNO_3 solution pH 2.10.

1.5 Rationale and Significance

The rationales of doing this study were to improve the properties of SPC with substitution of Bentonite by monitoring parameters, so that collaborative SPC can be used effectively. According to Li and Wang (2005a) on Synthesis and properties of clay based superabsorbent composites stated that the water absorbency of the poly (acrylic acid)/attapulgite superabsorbent composite in distilled water was greatly improved as compared with crosslinked poly (acrylic acid) superabsorbent polymer, it proved that collaborative absorbent effect through the information of filler.

To open up opportunities to increase the demand on manufacturing the collaborative SPC as proven by previous researchers that SPC is useful a lot. In order to reduce the cost production and improve the efficiency which is high water absorbency and retention per unit weight of SPC are essential. Because of use expensive monomers or modifiers for increasing water absorbency will result in increase cost, rendering the resulting SPC economically unsuitable. In order to develop cheap SPC based on AA and AM an effort was made to increase the water absorbency by optimizing the cross-linking parameters, which is addition of filler and cross-linker (Singhal *et al.,* 2009b).

CHAPTER 2

LITERATURE REVIEW

2.1 Inorganic Clay powder

2.1.1 Bentonite Clay Powder

Bentonite is a smectite type clay mineral and swells in water. Because of the swelling property, only small amount of bentonite can be suspended in water. This may limit certain applications of bentonite.

Clay particle sizes are in the micrometer to nanometer range length scale. The small dimensions of clay particles suggest a large influence of the molecular scale behaviour and interactions (particle-particle, particle-water and interlayer) on bulk mechanical properties. The basic structural units in clays consist of the sheet formed of silica tetrahedral and the octahedral units formed of octahedrally coordinated cations (with oxygens or hydroxyls) octahedral as show in Figure 2.1.

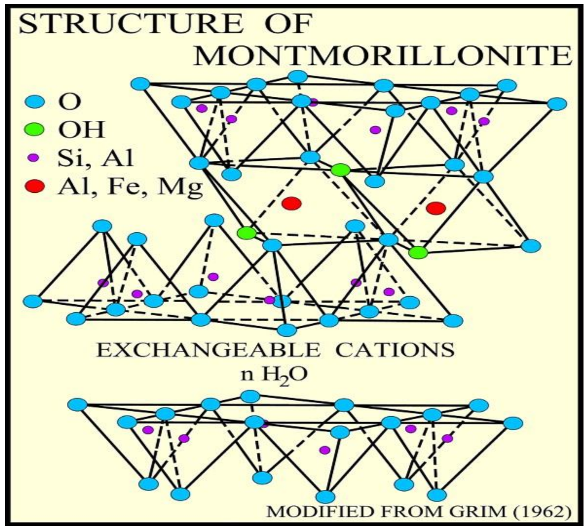

Figure 2.1: Schematic of montmorillonite structure (Katti, 2000)

To advance the behavior of SPC, inorganic fillers can be used to be substitute material as research before (Molu *et al.*, 2009b; Li and Wang, 2005b). Clays, such as kaolin, montmorillonite, attapulgite, mica, bentonite and sercite hydrotalcite have all been used for the preparation of superabsorbent composites.

Bentonite is a naturally occurring material consisting predominantly of the clay mineral montmorillonite. Montmorillonite is a materials species in the family of sheet silicates called smectites. Smectites are three layer clays minerals. They consist of two tetradral layers of interconnected SiO_4 tetrahedrons which enclose a central $M(O,OH)_6$ –octahedron layer (M=Al, Fe, Mg and others). The silicate layers have a slightly negative charge that is compensated by exchangeable ions in the intermediate layers. The charge is so weak that the cations (in natural form, predominantly Ca^{2+-}, Mg^{2+-} or Na^{+-} ions) can be adsorbed with an associated hydrate shell (innercrystalline swelling). (European Bentonite Producers Association, 2005)

An essential characteristic of all smectite minerals is their ability to absorb tremendous amounts of water and other liquids into their sheet structures. This gives bentonite extraordinary swelling and adhesive properties that are exploited commercially by many industries. The ability of smectite to absorb water is due in part to by the inherently small grain size of individual smectite crystals (typically much less that 2μ) and to the fact that individual sheets possess a negative surface charge which tends to attract polar molecules as show in Figure 2.1. This negative charge is also responsible for another essential attribute of smectite, its ability to absorb positively charged ions from solutions, an attribute which, like adhesion, is also exploited commercially. (Anonymous, 2005)

2.2 Application of Superabsorbent Polymer Composites

SPC are moderately crosslinked hydrophilic polymer material, which can imbibe and retain a large amount of aqueous solution. Owning to their excellent characteristic, SPC have been used in many fields such as healthcare products, agriculture and horticulture, waste water treatment, medical, and other numerous applications. Figure 2.3 shows the summary application SPC application in various fields. (Molu *et al*., 2009c; Liu and Wang, 2008; Kabiri *et al.*, 2009)

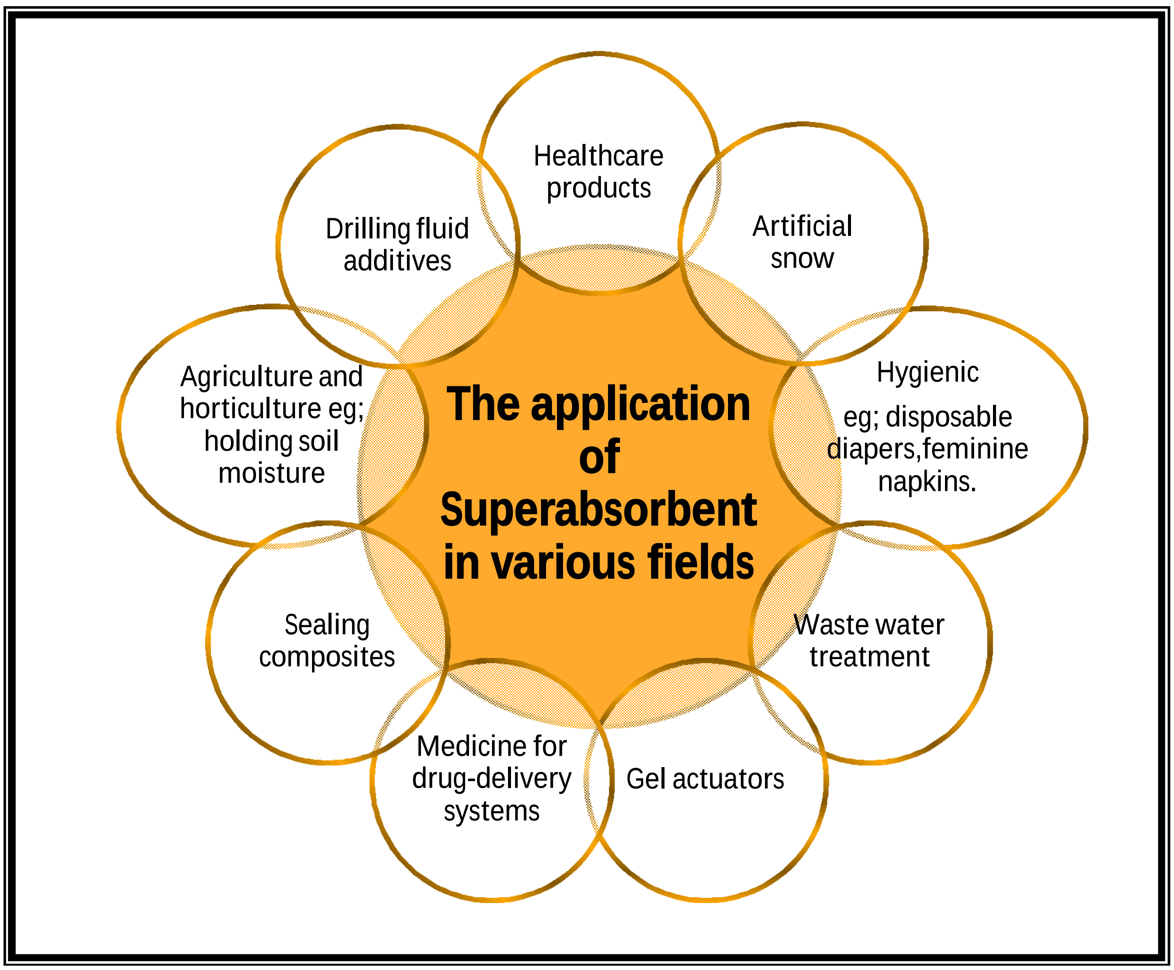

Figure 2.3: The application of SPC in various fields (Molu *et al.*, 2009d; Liu and Wang, 2008a; Kabiri *et al.,* 2009a)

Chemistry and physics of agricultural hydrogels were reviewed by Kazanskii and Dubrovskii (1992). Singal *et al.* (2009c) discuss widely about SPC on background, types, chemical and physical properties, testing method uses and applied research work.

2.3 Superabsorbent Polymer Composites

SPC hydrogels relative to their own mass can absorbs and retain extraordinary large amounts of water or aqueous solution. 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% (1g/g) (Zohuriaan and Kabiri, 2008h). Structure for SPC hydrogels are given in Figure 2.4. SPC originally divided into two main classes which is synthetic (e.g., petrochemical based) and natural (e.g., polysaccharide- and polypeptide-based) (Zohuriaan and Kabiri, 2008i)

They are polymers which are characterized by hydrophilicity containing carboxylic acid, carboxamide, hydroxyl, amine, imide groups and so on, insoluble in water, and are cross-linked polyelectrolytes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogen bonds, increasing the entropy of the network to make the Superabsorbent polymer (SAP) swell tremendously. The factors that supply absorbing power to polymers are osmotic pressure, based on movable counter-ions, and affinity between the polymer electrolyte and water (Suda, 2007b)

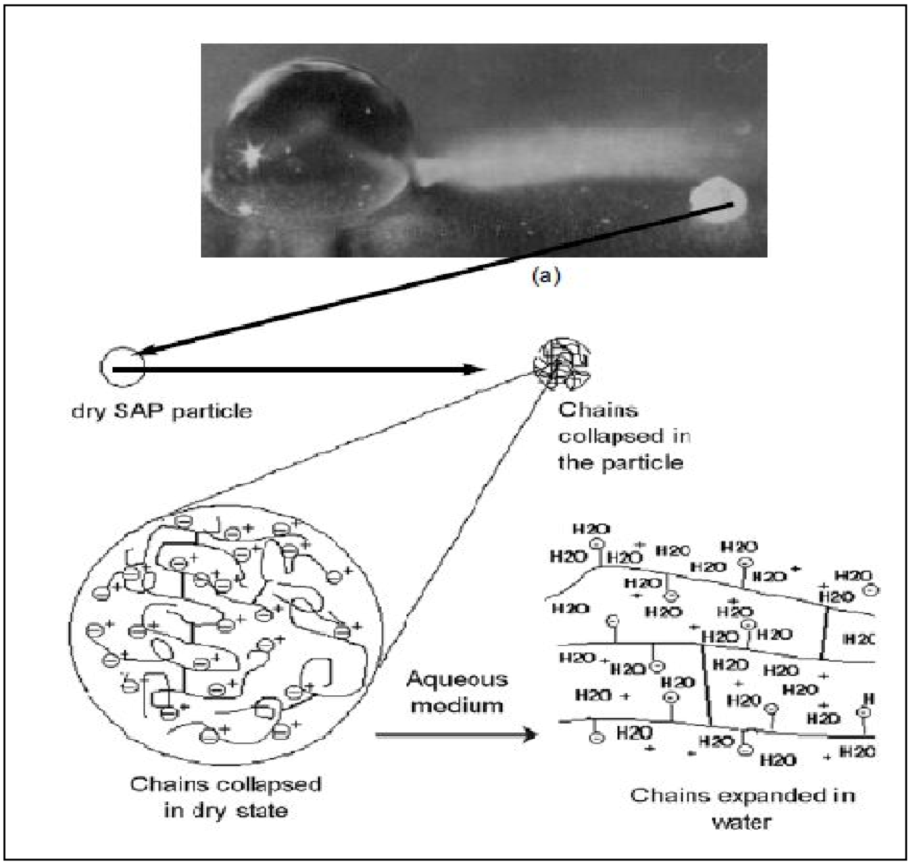

Figure 2.4: A visual comparison of the SPC single particle in dry (right) and swollen state (left) (Zohuriaan and Kabiri, 2008j).

There are many kind of methods to prepare SPC with various starting materials, such as copolymerizing hydrophilic monomer with a cross-linking agent, grafting monomer with starch, cellulose, synthetic fiber, and polysaccharide, cross-linking linear hydrophilic polymer with polyvalent metal ions or organic multifunctional group materials and others (Thomas *et al.*, 2003a).