SYNTHESIS AND SWELLING BEHAVIOUR OF BENTONITE BASED SUPERABSORBENT POLYMER COMPOSITE

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ABSTRACT

This study is about synthesis and swelling behavior of bentonite based superabsorbent polymer (SAP) camposite. The main objective of this research is to study the optimum condition of producing bentonite based SAP by determine the effect of amount of initiator, cross-linker, and filler content towards water absorbency of the SAP. Superabsorbent polymer composite was synthesis by solution polymerization reaction of bentonite micropowder into monomer Acrylic acid (AA) using ammonium persulfate (APS) as initiator and *N,N'*-metylene bisacrylamide (MBA) as cross-linker in aqueous solution. The superabsorbent polymer was characterized by using Fourier Transform Infra Red (FTIR) and Thermogravimetric Analysis (TGA). The water absorbency test for the SAP also performed. The result showed, optimum content to produce SAP were at 30 % initiator, 10 % cross-linker and 20 % filler with water absorbency of 573.3 g/g, 457.3 g/g and 485.4 g/g in distilled water respectively.

ABSTRAK

Kajian ini adalah tentang sintesis dan tingkah laku penyerapan komposit polimer super serapan (SAP) berasaskan bentonite. Objektif utama kajian ini adalah untuk mengkaji keadaan optimum bagi menghasilkan SAP berasaskan bentonite dengan menentukan kesan jumlah pemula, pemaut silang, dan kandungan pengisi terhadap resapan air SAP. Komposit polimer super serapan disintesis melalui tindak balas pempolimeran larutan serbuk bentonit ke dalam monomer Akrilik asid (AA) menggunakan ammonium persulfat (APS) sebagai pemula dan *N*, *N'*-metylene bisacrylamide (MBA) sebagai pemaut silang dalam larutan akueus. Komposit polimer super serapan telah dicirikan dengan menggunakan 'Fourier Transform Infrared' (FTIR) dan 'Thermogravimmetry Anaysis' (TGA). Ujian penyerapan air untuk SAP juga dilakukan. Keputusan menunjukkan, keadaan optimum untuk menghasilkan SAP ialah dengan kandungan 30% pemula, 10% pemaut silang dan 20% pengisi dengan penyerapan air 573.3 g/g, 457.3 g/g dan 485.4 g/g masing-masing di dalam air suling.

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LIST OF SYMBOLS

^{o}C	Degree Celsius
$^{o}C/min$	Degree celcius per minute
%	Percent
f	Effectiveness of initiator
v	Kinetic chain length
k_p	Polymerization constant
k_d	Decomposition constant
k_t	Termination constant
$[C]$	Initial concentration of cross-linker
$[I]$	Initial concentration of intiator
$[M]$	Initial concentration of monomer

LIST OF ABBREVATION

AA	Acrylic acid
AM	Acrylamide
APS	Ammonium persulfate
BT	Bentonite
MBA	*N,N'*-methylene bisacrylamide
μm	micro meter
mm	mili meter
mL	mili litre
Md	Mass of dry sample, *g*
Ms	Mass of swollen sample, *g*
Q	Water absorbency, *g/g*
g	Gram
g/g	gram per gram

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Superabsorbent polymers (SAP) are loosely cross linked hydrophilic polymers that can absorb, swell and retain aqueous solution up to hundreds of times their own weight (Santiago *et al.*, 2007). SAPs are derived from monomers to form longer chain molecule called polymer initiated by initiator in the presence of cross linking agent. Due to their superior properties, they are widely use in hygienic, agricultural, medical, and pharmaceutical fields. As the water absorbency in these applications is crucial, the technology of enhancing the performance of SAP is rapidly developed.

There are generally two types of SAP which are natural and synthetic SAP. Natural absorbents are including cotton, wood pulp, and also plant fibres. According to Gale Encyclopaedia of Science, until 1980's, the natural absorbent products are only having maximum 20 times their weight water retention capacity. The introduction of synthetic SAP later has improved the development of industries in many ways. Relatively, synthetic SAP can absorb much more water compare to natural SAP. Many of the existing SAP are produced by cross-linking of unsaturated carboxylic acid monomers including acrylic acid, or methacrylic acid, with acrylamide which is derived from petroleum oil, the non-renewable raw material as mentioned by S. Weerawarna (2009).

However, the hazardous material content in the product has also increased the concern of many parties. As reported by US Environmental Protection Agency (EPA, 1994) in chemical summary for acrylamide, the acrylamide used in production of human sanitary products and diapers are very carcinogenic when exposed to human. Other effects of acrylamide are indicated neurotoxicity causing drowsiness, parathesias in the fingers, numbness, and also ataxia.

As mentioned before, this material is also one of petroleum based chemical derivatives which has very high cost as the petroleum is limited and expensive. Despite of their wide use, development of lower cost, biodegradable and high water absorbency characteristic SAP has attracted great attention.

1.2 PROBLEM STATEMENT

Massive production of synthetic polymers nowadays leads to many environmental issues. The present of synthetic component in the polymer material made them non biodegradable. On top of that, the hazardous material content in SAP product such as sanitary product will threaten consumers. Moreover, the petroleum based monomers are also required high cost of purchasing.

Recently, there are many researches regarding to these problems. This is including introduction of natural material as filler and also the reduction of hazardous monomer in production of SAP product. Recent inventions lead to replace acrylamide with fibers or other inorganic materials such as clay as an alternative in order to improve the polymer produced. Furthermore, many studies have come out to reduce the consumption of hazardous monomers and also the addition of filler as alternatives. The clay that has been used in this research is bentonite which has become natural abundance and low cost (Bulut, 2009). This study is to produce SAP using only one monomer only and bentonite as filler to produce at least the same quality as pure SAP.

1.3 RESEARCH OBJECTIVES

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

i) The effect of initiator content towards water absorbency.

ii) The effect of cross-linker content towards water absorbency.

iii) The effect of filler content towards water absorbency.

1.4 SCOPE STUDIED

The scopes of this research were:

a) Materials

   i. The monomer used is acrylic acid (AA)
   ii. The cross linking agent used is *N,N'*-methylene bisacrylamide (MBA)
   iii. The initiator used is ammonium persulfate (APS)
   iv. The filler used is bentonite

b) Parameters that has been varied

   i. The amount of initiator content in the SAP
   ii. The amount of cross-linker content in the SAP
   iii. The amount of filler content in the SAP

c) Sample preparation technique

   The SAP has been prepared using solution polymerization technique with reaction temperature of 70 ^{o}C.

d) Water absorbency testing techniques

   The swelling behaviour of SAP produced has been tested using tea bag method

e) Characterization

   Sample SAP has been characterized using:

   i. Fourier Transform Infra Red (FTIR)
   ii. Thermogravimetric Analyzer (TGA)

1.5 SIGNIFICANT OF STUDY

The main aim of this study is to use only one monomer in producing SAP and also bentonite as the filler. By reducing one monomer, it is expected that the product produced is more degradable as compared to copolymerization of two monomers based SAP. This also can reduce the significant effect of hazardous materials to human health and environment. Other than that, reducing one material also means reducing the cost of raw material in the production of SAP product.

Furthermore, the use of bentonite as filler is because of their abundance, thigh water absorbency characteristic. It is expected to increase the water absorbency of the product with no economic burden.

CHAPTER 2

LITERATURE REVIEW

2.1 SUPERABSORBENT POLYMER (SAP)

Superabsorbent polymers (SAP) are three dimensionally cross-linked hydrophilic polymers that can swell and retain extremely huge amount of water. SAP hydrogel has been defined as polymeric structure that can absorb 100 – 100,000 % of water relative to its weight and retain water within its structure without been dissolve (Zohourian and Kabiri, 2008). Figure 2.1 shows the illustration of SAP in dry and water swollen state

Figure 2.1: Dry SAP (right) and Water swollen state SAP (left)

Source: Omidian (1997)

2.2 SWELLING MECHANISM OF SAP

When the water is swelling into the SAP molecules, the SAP structure expended as shown in Figure 2.2. There are several mechanisms that contribute on water swelling in SAP structure. According to report written by Elliot (2011) for BASF Company on superabsorbent polymer, the main factors of swelling phenomena in SAP structure are hydration and hydrogen bonding.

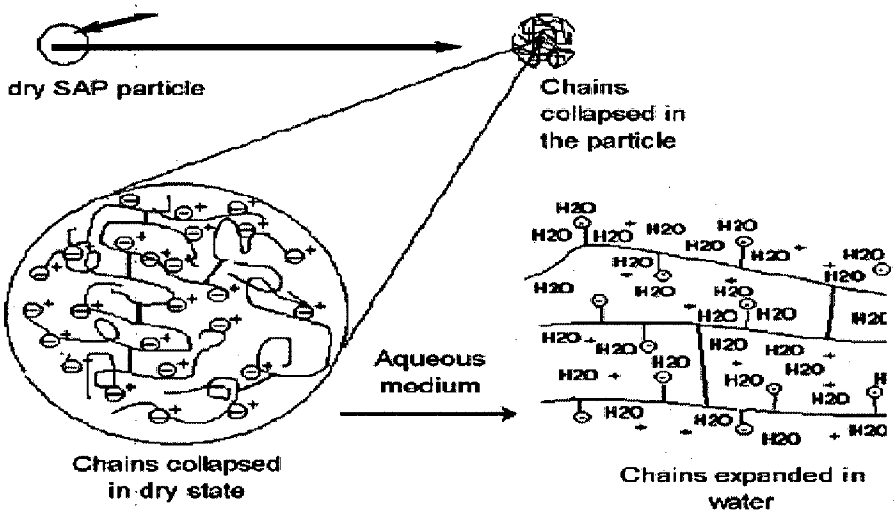

Figure 2.2: Schematic presentation of SAP swelling

Source: Zohourian and Kabiri (2008)

2.2.1 Hydration Mechanism of Water Swelling

The hydrophilic groups in the SAP backbone has contribute to the formation of hydration in the molecules when water is added to the SAP. This is due to the interaction between polymer and water. The examples of hydrophilic groups in the SAP are COO^- and Na^+ ions. The interaction of these ions towards polar molecules in water is shown in Figure 2.3.

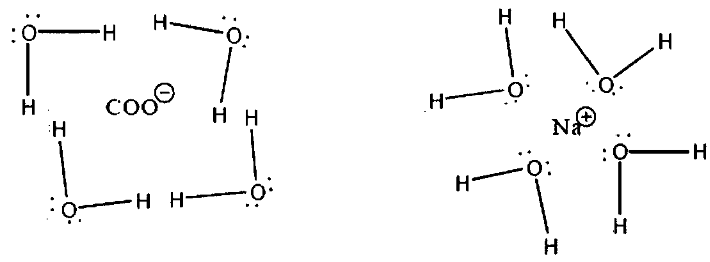

Figure 2.3: Hydration in SAP molecule

(a): Attraction of COO^- ion with hydrogen in water

(b) Attraction of Na^+ ion with oxygen in water

Source: Elliot

The attractions of these hydrophilic ions towards water molecules make the water swell into the polymer chain.

2.3 POLYMERIZATION TECHNIQUES

Generally there are two ways of producing SAP either using chemical or non chemical initiator. For chemically initiated polymerization, common technique used is solution polymerization. According to Kiatkamjornwong (2007) in his article stated that in this technique, monomer is dissolve in polymeric solution where chemical initiator is added later to give free radical to the monomer. The polymerization of SAP will continue to form longer change molecule. As the cross linking agent present in the mixture, the polymer molecule will then connected each other. This article also mention about irradiation polymerization. This technique of polymerization use high energy of radiation as an initiator instead of using chemical initiator.

According to Gao (2003) in the study of Superabsorbent Polymer Composite (SAPC) Materials and their Industrial and High-Tech Application have used the irradiation polymerization method. In this study they have used AA and AM as monomer, MBA as cross-linking agent and also bentonite as the filler. Then the solution is initiated by electron beam to generate free radicals from the monomer to start the polymerization reaction. Based on this research, the optimum condition of producing SAP using this technique of polymerization has been obtained.

Another research by Li and Wang., (2005) on utilization of starch and clay for the preparation of superabsorbent composite has used the solution polymerization technique. In this study, they also use AA as monomer. The chemical initiator used is APS, cross-linking agent used is MBA and attapulgite is used as filler. In the study, the monomer is partially neutralized before the polymerization as in Figure 2.4. Then, with the presence of water soluble cross-linker N-N' methylene bisacrylamide (MBA), the initiator has been added. In this research, the optimum condition of producing SAP also achieved.

By comparing both techniques, it shows that solution polymerization can be considered as the most appropriate technique to apply in this research. This is due to the irradiation polymerization technique will give higher cost and also more complicated to apply.

2.4 POLYMERIZATION MECHANISM OF POLY(ACRYLIC ACID–BENTONITE) (PAA-BT) SAP

In synthesis of PAA based SAP, the monomer (AA) has been partially neutralized before polymerized. This is to produce sodium acrylate for polymerization. The presence of sodium in the monomer molecule will increase the osmotic pressure in the SAP (Elliot). The process is shown in Figure 2.4.

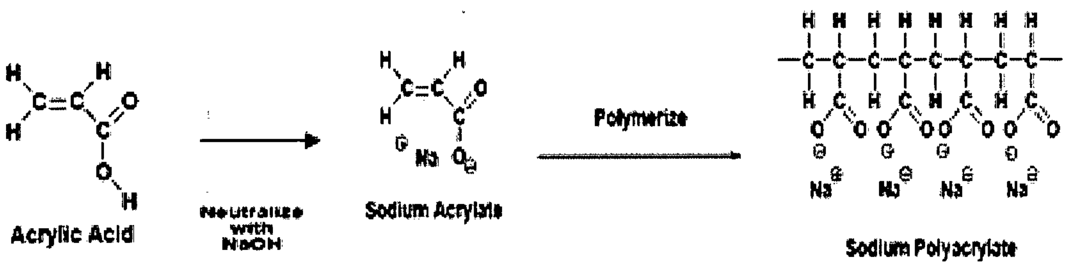

Figure 2.4: Polymerization of Acrylic acid (AA)

Source: Cash (2007)

The addition of water soluble cross-linker in production of SAP is to provide network points in the SAP structure to form three dimensional cross-linked molecules Li et al. (2007). Then, the addition of initiator into the monomer solution is to start the polymerization. The initiator will be decomposed by heat to produce free radicals. Then the reaction propagate to form longer chain polymer molecules of PAA-BT.

2.5 EFFECT OF INITIATOR, CROSS-LINKER, AND FILLER TOWARDS WATER ABSORBENCY

In polymerization process, initiator will induced to form radicals to start the reaction of the monomers to form longer chain molecules. The cross-linker is added to transform the SAP molecule into three dimension molecule to enhance the water absorbency. The filler presence will help the water absorbency and increase the thermal stability of the SAP. In order to get the optimum condition of polymerization of SAP the exact amount of initiator, cross-linker and filler have been determined.

A research by Bulut et.al (2009), on synthesis of clay based superabsorbent composite and its sorption capability using AA as monomer, MBA as cross linker, APS as initiator and bentonite as filler. The optimum condition obtained from the study is 352 *g/g* water absorbency in distilled water. The result also shown that the water absorbency is very much depending on the amount of initiator as been followed in this study.

Another research by Santiago et.al (2007) on preparation of composites and nanocomposites based on bentonite and poly(sodium acrylate) has use amount of filler as variable parameter. This study is conducted to determine the effect of amount of bentonite on the swelling behaviour with optimum condition of 995 *g/g* water absorbency. In this study, the result obtained shows that the addition of small quantity of bentonite increased the water absorbency of SAP However, at higher concentration of Bentonite, the water absorbency increased as the clay amount increased. This shown that variation of clay amount will affect the water absorbency of SAP.

Furthermore, Li et al. (2007) in their study of utilization of starch and clay for the preparation of superabsorbent composite have proved that the amount of initiator, cross-linker and filler will affect the water absorbency of SAP produced. Based on the result obtained, the optimum water absorbency achieved is 1077 g/g in distilled water. The result indicated that increasing initial concentration of initiator increased the water absorbency until effective amount achieved. Then, further increasing of initiator gave decreasing in water absorbency. The result also proved that the addition of cross-linker and filler decreased the water absorbency of SAP. However the presence of filler in SAP enhanced water absorbency as compared to SAP without clay filler. It is proved that the amount of initiator, cross-linker and filler gave direct effect to water absorbency of SAP.

By reviewing those study that has been conducted above, the water absorbency of SAP is depend on the amount of initiator, cross-linker, and also filler used. So, in order to obtain the optimum condition of SAP towards water absorbency, this study has been conducted by varying those parameters in synthesis of SAP.

2.6 BENTONITE CLAY

Bentonite is a family of clay minerals that has layer structure of tetrahedral and octahedral coordination (Natural Sodium Bentonite, 2011). The minerals are found in flat particles of fine grain aggregate forms and also characterised by expansibility, absorption of water and organic molecules, and considerable cation exchange properties (Anthony *et al.*, 2011).

Montmorillonite is the active ingredients in bentonite. It is a hydrosilicate of aluminium and magnesium, morphologically composed of octahedral alumina trapped between two layers of tetrahedral silicate (Samsuri and Abdullah, 2002). The structure montmorillonite is shows in Figure 2.5 and Figure 2.6.

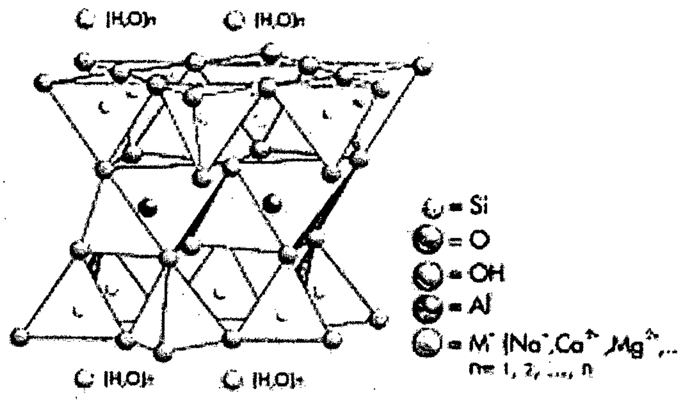

Figure 2.5: Three dimensional structure of bentonite

Source: Natural Sodium Bentonite

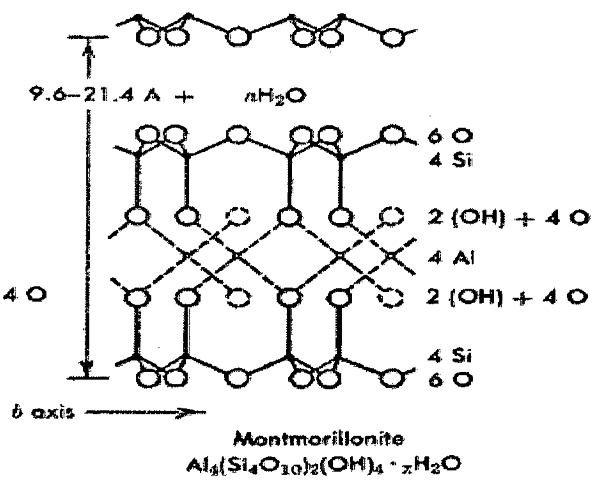

Figure 2.6: Layers between bentonite structure

Source: Floor, (2000)

Montmorillonite is expansible clay mineral with permanent layer negative charge. Due to the open and hydrated interlayer, cations may present within the interlayer to balance the negative charges (Anthony *et al.*, 2011). When the structure is in contact with water, ions are exchanged and water penetrates between the layers. This can lead to interlayer swelling. This is proved that the clay structure can enhance the water absorbency in SAP.Selection of bentonite clay as filler in this study is due to this characteristic of bentonite.

CHAPTER 3

METHODOLOGY

3.1 MATERIAL

Acrylic acid (AA) was used as monomer to synthesis SAP. The acid is chemically pure and purchased from Merck. This acid is also partially neutralized with a sodium hydroxide (NaOH). Ammonium persulfate (APS) is used as an initiator, is an analytical grade purchased from Sigma-Aldrich. The cross-linker used is N,N'-methylene bisacrylamide (MBA) also obtained from Aldrich. The MBA is chemically pure and is used as purchased.

The clay used as filler in this study is bentonite micropowder purchased from Merck which has been milled through 320 mesh screen. Then, the meshed clay powder is treated with 37% hydrochloric acid (HCl) before further use.

3.2 EQUIPMENTS

In preparation of SAP, the equipments used were 250 mL three-neck-flask equipped with stirrer, condenser, thermometer, and nitrogen line, water bath, mesh and oven. The equipments use for characterization of SAP were including Fourier Transform Infra Red (FTIR) and Thermo Gravimetry Analyzer (TGA).

3.3 RESEARCH DESIGN

Research design for this study is shown in Figure 3.1.

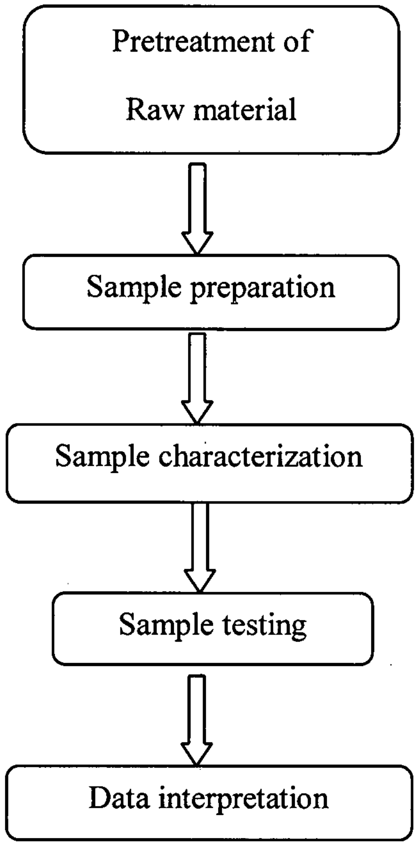

Figure 3.1: Research design

3.4 PRETREATMENT OF RAW MATERIAL

Before being used in the sample preparation, the bentonite was firstly milled through 320 mesh screen. Then, the meshed clay powder was treated with 37% hydrochloric acid (HCl) for 48 hours. It is then washed with distilled water until pH 7 to remove the residual HCl. Then, the clay powder was filtrated and dried at 105 °C for 8 hours before prior use.

3.5 PREPARATION OF BENTONITE BASED SUPERABSORBENT

SAP was prepared through solution polymerization of betonite onto PAA in the presence of MBA as cross-linker and APS as initiator. Acrylic acid (4mL) was dissolved in 20 mL distilled water and then neutralized with 4.6 mL of 5M NaOH solution in a three-neck-flask equipped with a stirrer, condenser, thermometer, and nitrogen line. Bentonite powder (0.72g) was then dispersed in the above monomer solution. Then, under nitrogen atmosphere, the cross-linker MBA (14.3 mg) was added to the AA-bentonite mixture solution. The solution is then stirred at room temperature until the MBA is completely dissolved. The water bath was heated to 70 °C. After that, the initiator APS (79.2g) was added to the solution while the solution is vigorously stirred. The polymerization reaction is allowed to proceed for 2 hours at 70 °C to ensure full consumption of the monomer. After 2 hours of the reaction, the resulting rubbery gel was removed from the flask and was cut into pieces about 2-5 mm. Then, the pieces have been washed with distilled water several times. After precipitated, the sample was then dried in oven at 40 °C to a constant weight before any test. The resulting SAP is then stored away from moisture, heat and light.

3.6 PREPARATION OF CROSS-LINKED POLYACRYLIC ACID (PURE SAP)

Preparation of pure SAP is similar to that of preparation of bentonite based superabsorbent except bentonite is omitted.

3.7 FTIR CHARACTERIZATION

The IR spectra of the SAP were recorded on a FTIR (thermo, Nicolet, NEXUS, TM) by using KBr pallet. Result has been plotted as in Figure 4.4.