STUDY ON OPTIMUM CONDITION OF EMPTY FRUIT BUNCH-GRAFT-POLY(ACRYLAMIDE) SUPERABSORBENT POLYMER COMPOSITES

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ABSTRACT

Superabsorbent polymers (SAPs) are three-dimensional networks of flexible polymer chains that carry dissociated and ionic functional group which characterized by hydrophilicity. Nowadays, many things created by industrial highlighting on environment friendly element, and using EFB which is a natural fiber to produce superabsorbent polymers are the new technique to reduce the pollution. This research is conducted to study on the optimum condition of Empty Fruit Bunch-graft-Poly(acrylamide) Superabsorbent Polymer Composite (EFB-g-PAAm SAPC). The objective of this study is to determine the optimum water absorbency of superabsorbent polymer composite (SAPC) by varied the amount of EFB, initiator, and crosslinker. EFB-g-PAAm was synthesized by graft copolymerization of monomer, acrylamide (AAm) onto EFB backbone with N, N'-methylenebisacrylamide (MBA) and ammonium persulphate (APS) acts as crosslinker and initiator. The method used to determine the water absorbency of SAPC was the tea-bag method. The results showed that optimum water absorbency of effect of filler was achieved at 196.3320 g/g with 5 wt. %. Meanwhile, the optimum water absorbency of effect of initiator and crosslinker were achieved at 218.4060 g/g and 171.2867 g/g when the amount of initiator and crosslinker were 30 wt. % and 10 wt. %, respectively. The chemical structure of the EFB-g-PAAm SAPC was characterized by FTIR spectroscopy and the surface morphological study of EFB-g-PAAm SAPC was conducted by scanning electron microscopy (SEM). Thermogravimetric Analysis (TGA) was carried out to determine the thermal properties of the synthesized superabsorbent polymer composites. In conclusion, the objective of this study has achieved where the optimum condition for the SAPC has been determined. As recommendation, in order to improve the properties of synthesis of EFB-g-poly (acrylamide), some recommendation should be considered such as parallax error needs to be avoided during the measurement of the chemicals.

KAJIAN KE ATAS KEADAAN OPTIMUM BUAH TANDAN KOSONG-CANTUM-POLI (AKRILAMIDA) POLIMER KOMPOSIT PENYERAP LAMPAU

ABSTRAK

Polimer penyerap lampau (SAP) adalah tiga dimensi rangkaian rantaian polimer fleksibel yang boleh diceraikan dan fungsi kumpulan ionik dicirikan oleh sifat hidrofilik. Kini, banyak perkara yang dicipta oleh penonjolan perindustrian pada elemen mesra alam, dengan menggunakan EFB yang merupakan serat untuk menghasilkan polimer penyerap lampau di mana ia adalah teknik yang baru untuk mengurangkan pencemaran. Kajian yang dijalankan ini adalah untuk mengkaji keadaan optimum buah tandan kosong-cantum-poli(akrilamida) polimer komposit penyerap lampau (EFB-g-PAAm SAPC). Objektif dalam kajian ini adalah untuk menentukan optimum kuantiti penyerapan air dalam bentuk polimer komposit penyerap lampau (SAPC) dengan membezakan kuantiti EFB, pemula dan pemautsilang. EFB-g-PAAm telah disintesiskan dengan menggunakan teknik 'graft copolymerization' dimana pencantuman monomer, acrylamide (AAm) ke dalam 'EFB backbone' dengan N, N'- methylenebisacrylamide (MBA) dan ammonium persulphate (APS) berfungsi sebagai pemautsilang and pemula. Kaedah yang digunakan untuk menentukan kuantiti air SAPC adalah kaedah 'tea-bag'. Keputusan yang diperolehi menunjukkan optimum kuantiti penyerapan air kesan pengisi telah dicapaikan pada 196.3320 g/g dengan 5 wt. %. Kuantiti penyerapan air yang optimum terhadap kesan pemula dan pemautsilang telah diperolehi pada 218.4060 g/g dan 171.2867 g/g apabila kuantiti pemula dan pemautsilang adalah 30 wt. % and 10 wt. %. Struktur kimia EFB-g-PAAm SAPC telah dicirikan dengan menggunakan spektroskopi jelmaan Fourier infra-merah (FTIR), manakala kajian morfologi permukaan EGB-g-PAAm SAPC telah dilakukan mengguna 'scanning electron microscopy' (SEM). Thermogravimetric Analysis (TGA) telah dijalankan untuk menentukan sifat-sifat polimer komposit penyerap lampau. Kesimpulannya, objekif kajian ini telah dicapai di mana keadaan optimum untuk SAPC telah ditentukan. Sebagai cadangan, dalam usaha untuk meningkatkan sifat-sifat buah tandan kosong-cantum-

poli(akrilamida), beberapa cadangaan perlu dipertimbangkan seperti ralat paralaks perlu dielakkan semasa pengukuran bahan kimia.

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LIST OF ABBREVIATIONS

AA	-	Acrylic acid
AAm	-	Acrylamide
APS	-	Ammonium persulfate
APT	-	Attapulgite
CMPWS	-	Chemically modified pulverized wheat straw
EFB	-	Empty fruit bunch
FFB	-	Fresh fruit bunch
FTIR	-	Fourier transform infrared spectroscopy
H^+-APT	-	Acidified attapulgite
HDTMABr	-	Hexadecyltrimethyl ammonium bromide
HDTMABr-APT	-	Organo-attapulgite
HEMA	-	Hydroxyethyl methacrylate
MBA	-	N,N’-methylenebisacrylamide
PAM	-	Polyacrylamide

PAN	-	Polyacrylonitrile
SAP	-	Superabsorbent polymer
SAPC	-	Superabsorbent polymer composites
SEM	-	Scanning electron microscopy
St	-	Starch
TGA	-	Thermogravimetric analysis
UVMT	-	Unexpanded vermiculite
WS/PAA	-	Wheat straw-g-poly(acrylic acid)

LIST OF SYMBOLS

Q_{H_2O}	-	Water absorbency of SAPC
m_1	-	Weight of dry sample
m_2	-	Weight of water-swollen sample
wt. %	-	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background of study

Superabsorbent polymers (SAPs) are three-dimensional networks of flexible polymer chains that carry dissociated and ionic functional group which characterized by hydrophilicity (Jamaludin and Hashim, 2011). These cross-linked hydrophilic polymers can swell, absorb and retain a large amount of water which is 10% up to thousands of times their dry weight in a short period in saline solution or physiological fluids (Buchholz and Graham, 1997). This absorbed water is hardly removed even under some pressure. Because of their excellent characteristics, superabsorbents are widely used in many fields, such as agriculture, horticulture, sanitary goods, and medicine (Liu et al., 2006).

Malaysia is the world's largest supplier and exporter of palm oil. The amount of production of palm oil accounted approximately 40-60% of the world total oil palm over the 25 years (Chew and Bhatia, 2008). Currently, over 3.88 million hectares of land are under oil palm cultivation and more than 368 palm mills operate in Malaysia (Idris et al., 2010). Every year, large quantities of oil palm biomass wastes which included trunks, fronds, fibers, shells and empty fruit bunches (EFBs) are generated in Malaysia (Mohammed et al., 2012). Empty fruit bunch is one of the biomass materials, which is a by-product from the palm oil industry (Rozman et al., 2004). Many studies have been carried out on the utilization of EFB, such as in compost (Dayana Amira et al., 2011), superabsorbent polymers (Jamaludin and Hashim, 2011; Nor Erma Shuhadah et al., 2011), mulching (Christopher Teh et al., 2010), composites (Rozman et al., 2004), oil products (Fan et al., 2011) and tannin extracted from EFB as rust deactivator (Mohammad Ibrahim et al., 2005).

In general, utilization of biomass in superabsorbent polymers has been attributed to several advantages. Graft copolymerization of vinyl monomers onto natural polymer is one of an efficient approach to achieve biopolymer-based superabsorbent polymer. It is due to the exceptional properties such as biocompatibility, biodegradability, renewability, and non-toxicity, with polysaccharides which is one of monomer are the main component of natural-based superabsorbent polymer (Sadeghi and Hosseinzadeh, 2008). According to the research of Ibrahim et al. (2005), grafting of vinyl monomer such as arylamide (AAm) onto EFB backbone may be used to modify and improve various properties in the original vinyl polymer such as elasticity, absorbency, ion exchange capabilities, thermal resistance and hydrophilicity.

1.2 Problem statement

In Malaysia, liquid and solid wastes that are generated by the palm oil industries such as empty fruit bunch (EFB) keeps increasing annually (Dayana Amira et al., 2011). There are about 7.3 million tons of EFB are produced every year (Chua, 1991). As reported by Singh et al. (1999), in the process of palm oil milling, one tone of fresh fruit bunches (FFB) produces about 220kg of EFB as a by-product. The high amount of wastes which were generated may cause air or land pollution and hence, increase the waste treatment cost if there is no proper way to manage these wastes (Dayana Amira et al., 2011). Therefore, it is vital to determine the ways to reuse the EFB waste. Noticed that nowadays many things created by industrial highlighting on environmental friendly element to reduce the pollution, such as by using EFB fiber to produce superabsorbent polymers. According to the research of Jamaludin et al. (2011), SAPs being prepared through the method of graft copolymerization of monomers onto the chain of natural fibers to render the SAPs to be biodegradable. Thus, environmentally friendly SAPC can be produced.

Commercialized SAP usually uses two types of monomer which are acrylic acid and acrylamide in its products. By grafted EFB onto only one of the monomers, it expected to give the same performance as the commercial one. This approve that by using EFB, the production cost of SAP could be reduce as it can be prepared by only one monomer as well as the price of EFB which considerably cheap. This research is conducted to study on the optimum condition of EFB-graft- poly(acrylamide) superabsorbent polymer composite. The amount of initiator, crosslinker and EFB are manipulated in order to determine the optimum value of water absorbency. Thus, the aim of this study is to develop the collaborative absorbent effect through the introduction of EFB in reducing the production cost and improve the water absorbency of superabsorbent composites.

1.3 Research objectives

The objective of this research is to study the optimum condition of empty fruit bunch-graft-poly(acrylamide) superabsorbent polymer composite (SAPC) by determined:

i. Effect on the amount of EFB or filler towards water absorbency.
ii. Effect on the amount of initiator, APS towards water absorbency.
iii. Effect on the amount of crosslinker, MBA towards water absorbency.

1.4 Scope of study

In order to achieve the optimum condition of empty fruit bunch-graft-poly(acrylamide) superabsorbent polymer composite (SAPC), three parameters were varied which were the amount of crosslinker, MBA, initiator, APS and filler, EFB. The polymerization technique that has been used in this research was graft copolymerization. The water absorbency of SAPC was tested by using tea bag method. The SAPC was characterized using FTIR spectroscopy and the surface morphological studies of EFB-g-

PAAm SAPC were conducted by scanning electron microscopy (SEM). The change in weight of SAPC with increasing temperature or thermal properties was measured by using Thermogravimetric Analysis (TGA).

1.5 Significance of study

EFB is acknowledged as a waste which give a bad effect to the environment if not being managed properly. In this research, EFB was used as the main material for grafting it with PAAm polymer. This research might solve the problems by investigated the optimum conditions for graft copolymerization of vinyl monomer such AAm onto the EFB backbone. Graft copolymerization of EFB will upgrade its nature characteristics of EFB fiber and can improve its commercial values.

EFB fiber is environmentally friendly compared to other synthetic fibers. Synthetic fibers which usually derived from petroleum are non biodegradable, non renewable and limited sources. The burning of these fibers may release toxic gases which bring harmful to human health. Graft copolymer of EFB render the SAPC to be biodegradable, and hence producing environmentally friendly SAPC (Jamaludin and Hashim, 2011). This study significantly reduces the cost production and improves the water absorbency of SAP. The efficiency of higher water absorbency and high retention per unit weight of SAPC are essential. Using expensive monomers or modifiers for increasing water absorbency will result in high cost, rendering the resulting SAPC will be economically unsuitable. Therefore, in order to develop cheap SAPC, an effort is made to increase the water absorbency by varying the crosslinker, initiator and amount of EFB or filler.

CHAPTER 2

LITERATURE REVIEW

2.1 Empty fruit bunch

The oil palm (Elaeis guineensis) is the dominant agriculture crop in Malaysia. It is the major source of producing edible oil which is extracted from fruits (Mohd Zuhri et al., 2010). However, palm oil mills produce a large amount of solid wastes. Research studied of Basiron (2007), reviewed that each fresh fruit bunch (FFB) processed in an oil mill produces 14% fibers, 7% shells, and 20%-25% EFB, which is the lignocellulosic fibrous medium left behind after oil extraction. It was estimated that more than two million tonnes of oil palm fiber is produced every year in Malaysia (Tan et al., 2007). According to Fan et al. (2011), EFB are the main by-products in the palm oil industry with every ton of fresh fruit bunch will produce 0.22 ton of EFB which contribute to the total amount of 2.96×10^6 ton of EFB per year. This high amount of wastes can cause land pollution. These EFB fibers can be added into the synthesizing superabsorbent polymer composite (SAPC) in order to minimize the waste. Moreover, according to

Ibrahim et al. (2005), the swelling behavior of SAPC can be increased by adding EFB fibers. Figure 2.1 and Figure 2.2 show the empty fruit bunch and empty fruit bunch fiber, respectively.

Figure 2.1 Empty fruit bunch

(Source: Anonymous, 2011)

Figure 2.2 Empty fruit bunch fiber

(Source: Anonymous, 2011)

2.1.1 Composition of oil palm empty fruit bunch

Empty Fruit Bunch is composed of 66.97% of holocellulose (cellulose and hemicelluloses) and 24.45% of lignin (Rodriguez et al., 2008). According to Raju (2005), there are very low ashes content in the EFB. This factor contributes to better performance of the fiber as a reinforcement agent in polymers. Therefore, empty fruit bunch fiber is appears to be a potential substrate for enzyme and other chemical production (Deraman, 1993). EFB is also suitable to be incorporated with SAPC as it contains hydroxyl group (OH) which can form hydrogen bond with water molecules. This is claimed by Suda (2007), that characterization of superabsorbent polymer is determined by its hydrophilicity that contain hydroxyl group.

2.2 Superabsorbent polymer composite

Superabsorbent polymer (SAP) materials which also known as hydrogels that relative to its own mass are hydrophilic networks can absorb and retain large quantity of water or aqueous solutions (Zohuriaan-Mehr and Kourosh, 2008). These ultrahigh absorbing materials can absorb deionized water as high as 1,000-100,000% (10-1000 g/g). However, according to Zohuriaan-Mehr and Kourosh, (2008) the absorption capacity of common hydrogels is not more than 100% (1 g/g). The swelling equilibrium composite can retain liquid even under some pressure (Chen and Park, 2000). The superabsorbent hydrogels have been widely used in hygiene, agriculture, horticulture, drug delivery and food storage, this is due to their superior properties comparing with traditional water absorbing materials (Chen et al., 2007; Dadhaniya et al., 2006). SAPC is synthesized by graft copolymerization of acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) monomers onto chitosan in the research of Sadeghi (2010). Liu et al. (2006) reviewed the superabsorbent nanocomposite was synthesized through the intercalation polymerization of partially neutralized acrylic acid and sodium-type montmorillonite powder.

Meanwhile, a superabsorbent hydrogel is synthesized based on starch (St) and polyacrylonitrile (PAN) in the research of Sadeghi and Hosseinzadeh (2008). Zheng et al. (2007) reviewed SAPC were synthesized by copolymerization reaction of partially neutralized acrylic acid on unexpanded vermiculite (UVMT) micropowder using MBA as crosslinker and APS as initiator. It shows that the equilibrium water absorbency increased with increasing UVMT content and the concentration of 20 wt % clay gave the best absorption. In another review of Zhang et al. (2006), a starch phosphate-graft-acrylamide/ attapulgite superabsorbent composite was prepared by graft-copolymerization among starch phosphate, acrylamide, and attapulgite in aqueous solution. This all shows that natural resource is a potential material in SAP production.

Other than that, natural fiber based superabsorbent also have been reviewed. In the research of Qureshi et al. (2011), superabsorbent hydrogel was produced from wheat straw with APS and MBA as initiator and crosslinker. Besides that, Liu et al. (2009) reviewed superabsorbent hydrogel has been synthesized with chemically modified pulverized wheat straw (CMPWS) and acrylic acid (AA) in aqueous solution. Moreover, a wheat straw-g-poly(acrylic acid) (WS/PAA) superabsorbent composite was synthesized by graft polymerization with wheat straw powder and acrylic acid in aqueous solution in the research of Liang et al. (2009).

Besides of using wheat straw fibre in synthesizing SAPC, several researches have been done by using EFB fibre as filler in synthesizing SAPC. Recent research by Nor Erma et al. (2011), reviewed that SAPC can be synthesized by graft copolymerization of the acrylic acid (AA) and acrylamide (AM) comonomer onto EFB fibre using ammonium persulfate (APS) and N, N-methylene bisacarylamide (MBA) as an initiator and crosslinker respectively. This also proved by Jamaludin and Hashim (2011) which claimed that SAPC can be synthesized by graft copolymerization of acrylamide monomer onto EFB backbone with MBA and APS acts as crosslinker and initiator respectively by using solution polymerization method. This all showed that fiber can be graft into SAP.

SAPs are generally divided into two main classes which are the synthetic (petrochemical-based) and natural (polysaccharide- and polypeptide-based). According to Sadeghi and Ghasemi (2012), even though hydrogel that synthesized from synthetic polymers, such as polyacrylate has an excellent water-absorbing, however, its toxicity and non-biodegradability might cause long period of environment problems and their use in drug delivery systems and consumer products will be limited. Recently, natural-based SAPs have attracted much attention in medical and pharmaceutical fields due to their non-toxicity, biodegradability and biocompatibility. By adding some synthetic parts onto the natural substrates like graft copolymerization of vinyl monomers on polysaccharides, the natural-based SAPs can be prepared (Zohuriaan-Mehr and Kourosh,