GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO OIL PALM EMPTY FRUIT BUNCH

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ABSTRACT

Graft copolymerization of Methyl Methacrylate (MMA) onto Oil Palm Empty fruit Bunch (OPEFB) fiber has been successfully carried out using hydrogen peroxide (H_2O_2) as an initiators and ferrous ammonium sulfate as catalyst in an aqueous medium. The effects of reaction temperature, reaction period and amount of initiators on the percentage of grafting were investigated. The results show that the percentage of grafting depends on reaction period and temperature as well as amount of initiator. The maximum percentage of grafting was obtained when the reaction was carried out using 5.00×10^{-3} mol of H_20_2 .The optimum reaction period was 120 minutes and the reaction temperature was 65ºC**.** The highest percentage of grafting and grafting efficiency was 30.51% and 85.30% respectively under optimum conditions. The presence of the functional group in the grafted polymers was characterized by FTIR spectroscopy and scanning electron microscope. The increasing in intensity at band 1730 cm^{-1} indicates that the MMA was grafted successfully on OPEFB.

ABSTRAK

Pempolimeran cangkuk Metil Metakrilat (MMA) ke atas gentian tandan kosong kelapa sawit (OPEFB) telah dijalankan dengan jayanya, dengan menggunakan hydrogen peroksida sebagai pemula dan ferrus ammonium sulfat sebagai pemangkin dalam larutan akueus. Daripada kajian ini, di dapati bahawa peratus pencangkukan metal metakrilat ke atas gentian OPEFB bergantung kepada suhu tindak balas, jangka masa tindak balas dan kepekatan hydrogen peroksida. Kajian ini mendapati peratusan pempolimeran pada tahap maksimum apabila menggunakan 5.00×10^{-3} mol H_2O_2. Keadaan optimum terhasil pada tempoh tindak balas selama 120 minit pada suhu 65ºC. peratusan pempolimeran tertinggi ialah 30.51% dan peratusan efisyen sebanyak 85.30% pada keadaan optimum. Kehadiran kumpulan berfungsi pada polimer yang telah bercangkuk dikesan oleh FTIR Spektroskopi dan mikroskop pengimbasan electron. Peningkatan keamatan pada puncak 1730 cm^{-1} menunjukkan bahawa MMA telah dicangkukan pada OPEFB dengan jayanya.

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LIST OF ABBREVIATIONS

°C	Degree celcius
EFB	Empty Fruit Bunch
Fe^{2+}	Ammonium Ferrous Sulphate
FFB	Fresh Fruit Bunch
FTIR	Fourier Transform Infra Red
H_2O_2	Hydrogen Peroxide
MMA	Methyl Methacrylate
MPOC	Malaysian Palm Oil Promotion Council
OPEFB	Oil Palm Empty Fruit Bunch
POME	Palm Oil Mill Effluent
SEM	Scanning Electron Microscopy
SIRIM	Standards and Industrial Research Institute of Malaysia
HNO_3	Nitric Acid
N_2	Nitrogen

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CHAPTER 1

INTRODUCTION

1.1 Background Of Study

In recent years there has been increasing demand for a new material with friendly environmental impact. This demand has lead to a great interest in the plant derived materials such as natural fibers as the raw material for the production of conventional and advanced polymer materials. In Malaysia oil palm empty fruit bunch (OPEFB) fiber waste was produced in millions of tonnes every year and can lead to unhealthy environmental impact. Oil palm empty fruit bunch (OPEFB) fiber is an important type of fibrous material left in the palm oil mill. It is obtained after the removal of oil seeds from fruit bunch for oil extraction and extracted by the retting process of the empty fruit bunch. OPEFB is an important lignocelluloses raw material which can be used for the preparation of cost effective and environmental friendly composite material.

Naturally, polymers are derived from organic materials include silk, wood, rubber, cotton, and oil palm empty fruit bunch. The properties of these fibers are limited by their natural state, so polymerization may improve the properties of the natural polymer such as water absorbency, elasticity, ion-exchange capabilities, thermal resistance, and mechanical strength. Oil palm empty fruit bunch consist of 65% cellulose and 19% lignin (Sreekala *et al*., 2000). It was also found to have very low ash content. These factors contribute to better performance of the fiber as a reinforcement agent in polymers.

Surface modification of natural fiber by graft copolymerization is one of the most widely used techniques. Graft copolymerization of vinyl monomer onto empty fruit bunch oil palm fiber involves the creation of free radicals on the lignocelluloses backbone. The advantage of free radical polymerization is, it take place in water media with good yield of the final product. Graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch will carry out in aqueous medium, using hydrogen peroxide as an initiator.

Some of parameters will be manipulated to investigate their effect to the grafting process. By manipulated each parameter that may effect to the grafting process, the optimum condition for that process was obtained. As a result, a good OPEFB grafting product can be produce in very effective ways with low cost, low energy, less time and good yield.

1.2 Problem Statement

Oil palm production is a major agricultural industry in Malaysia. In 2006, Malaysia becomes the world’s largest palm oil exporter after Indonesia with 41% of world palm oil production, and 43% of world export. Also 11% and 25% of the world's total production and exports of oils and fats (MPOC, 2009). From these huge amounts of production, 23% of Empty Fruit Bunch (EFB) produces per tonne of Fresh Fruit Bunch (FFB) processed in oil palm mill (SIRIM, 2009). This number is increase year by year. The abundance of palm oil waste contributes too many other problems.

A large field area was filled with palm oil waste and it is very high in volume and mounting in palm oil mill. At the same time it will give bad effect to the environment. A small amount of EFB was used in the plantation as mulch and organic fertilizer to the palm oil trees. However, this method is not feasible due to exorbitant collection and transportation cost as well as difficulty in spreading uniformly over the land (Alam *et al.*, 2009). The disposal of EFB as solid waste by open dumping in lowland area poses great environmental problems such as sol pollution as well as ground water pollution. Meanwhile disposal by proper sanitary landfill will be costly. The other of disposal of EFB is burning illegally. The conventional method of burning these residues often create environmental problems in that it generates severe air pollution and is prohibited by the Environment Protection Act (SIRIM, 2009).

The special characteristics of OPEFB are clean, biodegradable and compatible compare to many other fibers from other wood species. The advantages of using natural fiber compared to synthetic fibers include low weight, recyclability, biodegradability and renewability. But, some of the properties of natural fiber may not as good as synthetic fiber in terms of mechanical properties. High moisture content in OPEFB may limit its ability as thermal resistance and its resistance to microbiological attack. Polymerization of OPEFB with a hydrophobic monomer may improve its properties rather than before. If the improvement of OPEFB’s natural character could be done, Malaysia therefore has a great potential in turning its abundant supply of oil palm industry by-products into value-added product.

1.3 Objectives

The main objective of this research is to study the optimum conditions for graft copolymerization of methyl methacrylate onto OPEFB by;

i) Determine the effect of reaction period to the graft copolymerization of OPEFB.

ii) Determine the effect of temperature to the graft copolymerization of OPEFB

iii) Determine the effect of the amount of initiator to the graft copolymerization of OPEFB.

1.4 Scope Of Study

The scopes of this research are:

a) Materials :

   i) Type of fiber is oil palm empty fruit bunch (OPEFB)

   ii) Type of monomer is Methyl Methacrylate

   iii) Type of initiator is Hydrogen Peroxide

b) Equipments used for characterization is Fourier Transform Infra Red Spectrometer (FTIR) and Scanning Electron Microscope (SEM).

c) The parameters involved are reaction period, temperature and amount of initiator.

d) Type of grafting is Free Radical Polymerization.

1.5 Significance of Study

In this research, OPEFB was used as the main material for grafting with MMA polymer. OPEFB was acknowledged as a waste which will give bad effect to the environment. This research might resolve the problems by investigate the optimum conditions for graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch. Graft copolymerization of OPEFB will upgrade its natural characteristics of OPEFB fiber and can improve its commercial values.

By turning OPEFB waste to commercial product, it will reduce its amounts which always increase year by year. By reducing the OPEFB waste, environmental problems which can cause many health problems should be solve in an effective ways. At the same time, it also will contribute to the economics growth in Malaysia by producing new material that can full fill global needs for more environmentally product in life today.

OPEFB fiber is environmentally friendly compared to other synthetic fibers. Synthetic fibers usually derived from petroleum as their main sources are non biodegradable, non renewable and limited sources the burning of synthetic fibers may release toxic gases which harmful for health environment due to green house effect. The development of biopolymer likes OPEFB is an important step to overcome all that issues. The advantages of using natural fiber compared to synthetic fibers include low weight, recyclability, biodegradability, and renewability. This research gives the best condition to synthesize polymer grafting so that it can be used perfectly in polymer industry

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Fibers

2.1.1 Classification of Natural Fibers

Fiber is a class of hair-like materials that are continuous filaments or are in discrete elongated pieces, similar to pieces of thread. There are three types of fibers; natural fibers, cellulose fibers and synthetic fibers. Each fiber has a unique composition and its own set of physical properties which can be differentiate between one fibers to another fiber. Synthetic fibers are mass produced from petrochemicals to uniform strengths, lengths and colors, easily customized for specific applications only. The disadvantages of synthetic fiber are it is non biodegradable, non reusable and harmful to the environment due to the toxic gas release when burning. Natural fiber is biodegradable, reusable and environment friendly make natural fiber took place in the market demand today. Research and development on natural fiber to improve its quality had been done from recent year until now.

2.1.2 Properties of Natural Fiber

Mohanty *et al.* (2005) was reported that, all natural fiber whether woods or non woods types are cellulosic in nature. Cellulose is a hydrophilic glucan polymer, consisting of a linear chain of 1, 4- ß anhydroglucose units which contain alcoholic hydroxyl group. Therefore, all natural fibers are hydrophilic in nature.

Cellulose fibers exhibit a highly polar surface due to the presence of hydroxyl group. These hydroxyl groups enable the formation of hydrogen bonds in the interface of reinforced composite materials. On the other hand, the high polarity in cellulose fiber surface is the reason for their hydrophilic behavior (Bellmann *et al.*, 2004).

The structure and chemical make-up of natural fibers varies greatly and depend on the source and many processing variables (Craig *et al.*, 2005). Table 2.1 showed the chemical composition (%) for selected natural fibers.

Table 2.1: Chemical Composition (%) of Selected Natural Fibers (Craig *et al.*, 2004)

Species	Cellulose (Wt %)	Lignin (Wt %)	Pectin (Wt %)
Flax	65 – 85	1 - 4	5 - 12
Kenaf	45 – 57	8 - 13	3 - 5
Sisal	50 – 64	-	-
Jute	45 – 63	12 - 25	4 - 10
Hardwood	40 – 50	20 - 30	0 - 1
Softwood	40 – 45	36 - 34	0 - 2
OPEFB	65	19	-
Cotton	85 – 90	-	0 – 1
Abaca	56 – 63	12 - 13	1

2.2 Oil Palm Empty Fruit Bunch (OPEFB)

2.2.1 Introduction

Empty Fruit Bunch (EFB) is solid waste generated in palm oil mill. Behind the production of crude palm oil and palm kernel oil, the oil palm industry also generates a large amount of waste and by-product in form of EFB and palm oil mill effluent (POME). At the palm oil mills, about 20% crude palm oil and 1.6% palm kernel oil are recovered from fresh fruit while the rest 78.4% is leaving as biomass including EFB fiber (Basiron, 2005).

Due to abundant of EFB produce each production, EFB become a major problem in palm oil mills. Over the last decade, EFB wastes have attracted attention from the academic world to investigate and find the alternative to EFB. Ridzuan *et al.* (2002) reported that EFB is possibly suitable for medium density fiberboard (MDF). Other researchers also investigate the uses of EFB and the number of possible uses include;

i. Possibly suitable for medium density fiberboard (MDF).
ii. As substrates for the cultivation of Pleurotus *Ostreatus* (Mohd Tabi' *et al.*, 2008).
iii. Potential source of xylose which can be raw material for production of xylitol (Rahman *et al.*, 2007).
iv. Production of citric acid from OPEFB by solid state bioconversion using *Aspergillus Niger* (Alam *et al.*, 2009).

2.2.2 Properties of OPEFB

The OPEFB biomass contains cellulose, hemicelluloses and lignin. Sreekala *et al.* (2003) also do the investigation on OPEFB, and the result is shown in the Table 2.2 below:

Table 2.2: Chemical and Physical Composition of OPEFB Fiber (Sreekala *et al.*, 2003).

Composition	**Quantity**
Lignin content (%)	19
Cellulose content (%)	65
Density (g/cc)	0.7 – 1.55
Diameter (µm)	$0.015 \times 10^4 – 0.05 \times 10^4$
Ash content (%)	2

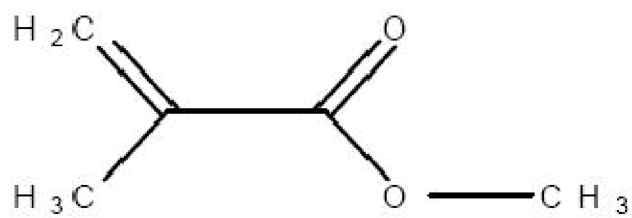
Yusoff *et al.* (2009) had concluded that, it is good to use natural fiber such as OPEFB due to low cost, low density, biodegradable and non abrasive properties. In order to upgrade the quality of natural polymer, chemical modification of lignocelluloses material through polymerization process with hydrophilic, vinyl monomer may improve the properties of the natural polymer such as water absorbency, elasticity, ion-exchange capabilities, thermal resistance and resistance to microbiological attack. So, the polymerization of OPEFB may upgrade its properties and at the same time may improve its quality.

2.3 Methyl Methacrylate

Methyl Methacrylate (MMA) is a volatile synthetic chemical that widely used in the production of cast acrylic sheet, acrylic emulsions, and molding and extrusion resins. Polymers and copolymers of methyl methacrylate are also used in waterborne, solvent, and undisclosed surface coatings, adhesives, sealants, leather and paper coatings, inks, floor polishes, textile finishes, dental prostheses, surgical bone cements, and leaded acrylic radiation shields and in the preparation of synthetic fingernails and orthotic shoe inserts.

MMA is colorless, volatile liquid, with a characteristic odor that has been describe as fragrant, fruity, acrid, pungent or onion-like. The empirical formula of MMA is $C_5H_8O_2$ with relatively high vapor pressure (4 kPa at 20 ^{0}C). The purity of commercial methyl methacrylate is typically 99.9%. Inhibitors added for storage and transportation are usually 2–100 ppm methyl ether of hydroquinone and 25–100 ppm hydroquinone, although other phenolic inhibitors, such as dimethyl *tert*-butylphenol, may also be used. Additional physical/ chemical properties of MMA are presented in Table 2.3 below.

Table 2.3: Physical and chemical properties of MMA

IUPAC name	methyl 2-methylprop-2-enoate
Structural formula	
Molecular formula	$C_5H_8O_2$
Molecular weight	100.12 g/mol
Density	0.94 g/cm^3
Melting point	-48 ^{0}C (225 K)
Boiling point	101^{0}C (374 K)
Flash point	2^{0}C (auto ignition 435^{0}C)
Solubility in water	1.5 g/ 100 ml water
Main hazard	Flammable

➢ Source : - International Chemical Assessment Document, United Nation Environment Programme, WHO, Geneva 1998
- NICNAS Existing Chemicals Information Sheet, Department of Health and Ageing, Australian Government.

2.4 Graft Copolymerization Technique

There are many types of polymerization techniques such as free radical polymerization, redox polymerization, ionic polymerization, atomic transfer radical polymerization and coordination polymerization. Free radical polymerization is widely use rather than other techniques. The simplest way to catalyze the polymerization reaction that leads to an addition polymer is to add a source of a free radical to the monomer. The advantage of free radical polymerization is, it take place in water media with good yield of the final product.

The term free radical is used to describe a family of very reactive, short-lived components of a reaction that contain one or more unpaired electrons. In the presence of a free radical, addition polymers form by a chain-reaction mechanism that contains chain-initiation, chain-propagation, and chain- termination steps (Ibrahim *et al*., 2003a). Figure 2.1 show the reaction mechanism of free radical graft copolymerization:

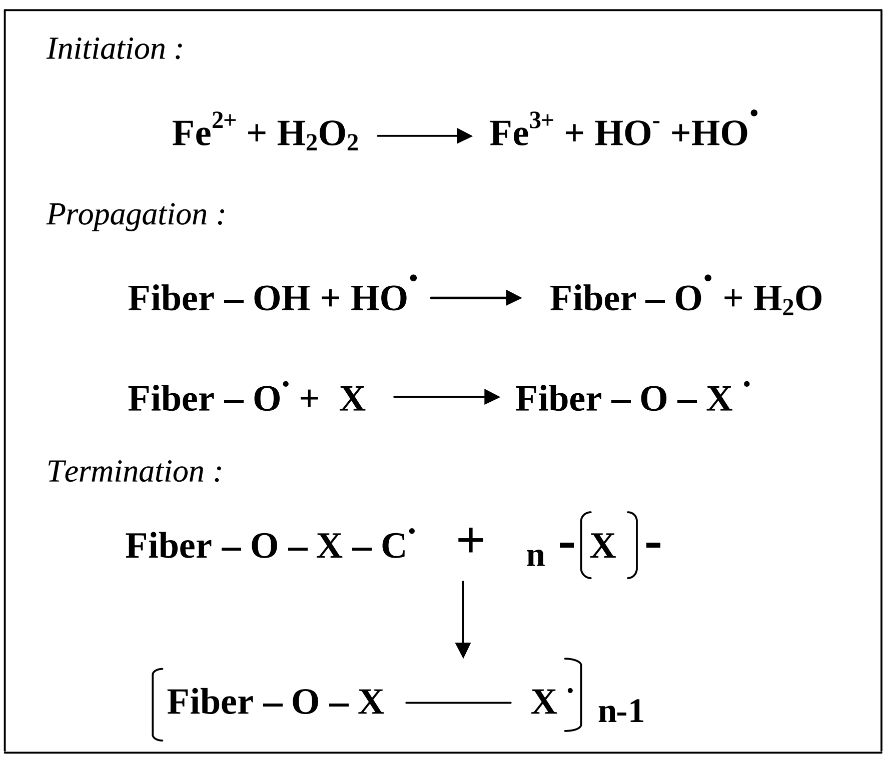


Figure 2.1: Reaction mechanism of free radical graft copolymerization

Bai *et al.* (2009) had studied graft copolymerization of Styrene onto Poly (vinyl alcohol) initiated by Potassium Diperiodatocuprate (III). Some of the graft reactions are implemented in aqueous medium by redox reaction using ceric ammonium nitrate, ammonium persulphate and potassium persulphate as initiator. The redox system can directly initiate graft copolymerization of vinyl monomer onto macromolecule with high grafting efficiency. The efficiency of ceric ammonium nitrate as initiator is superior, but because of its high cost, its application is very limited.

Peng *et al.* (2005) investigated the surface- initiated atom transfer radical polymerization (SI-ATRP) of styrene on chitosan particles reported that, the percentage of grafting for ATRP reaction is higher than other reaction. ATRP also not create relatively large amount of free radical in solution, which encourage the formation of homopolymer. Homopolymer is the unwanted product in polymerization. But the weakness of ATRP is that reactions are more complicated to be run and high in cost. Usually, ATRP run under organic solution rather that free radical reaction which can be run in aqueous solution easily.

2.5 Grafting Acrylic Monomer Onto Natural Fiber

There are many research have been done on OPEFB to upgrade its natural properties, and previous researches had prove that the chemical modifications on OPEFB and other fiber by polymerization process will improve its properties to achieve certain quality required. By grafting with hydrophobic monomer, the water absorbency of natural fiber can be reduced to the certain level.

Wu *et al.* (2008) had proved that polymerization of natural fiber, pullulan can improve their properties by grafting it with MMA. Pullulan is a fiber which is similar as EFB species. By using ceric ammonium nitrate as initiator, the research found that water absorbency capacity of the fiber decrease significantly with the increasing in percentage of grafting. This is due to increasing of the hydrophobic monomer on pullulan fiber.

In order to improve the mechanical properties the biocomposites of OPEFB, Hamid *et al.* (2010) was modified it by grafting with methyl methacrylate (MMA). In this study, in order to improve the adhesion between OPEFB and other polymer, the OPEFB fiber was made hydrophobic by grafting with hydrophobic monomer, methyl methacrylate. The modification of fiber was carried out at 70ºC under nitrogen atmosphere by using hydrogen peroxide as an initiator and Fe^{2+} as catalyst.

2.6 Characterization of Grafting

2.6.1 Percentage of Grafting and Efficiency

In order to determine whether OPEFB is successfully grafted the percentage of grafting (P_g) and grafting efficiency (G_e) is determined by the following formula:

$$Pg = \frac{W2-W1}{W1} \times 100 \qquad \text{Equation (1)}$$

$$Ge = \frac{W2-W1}{W3-W1} \times 100 \qquad \text{Equation (2)}$$

Where W_1 is the weight of the original fibers in grams, W_2 is the weight of fibers after grafting and extraction, W_3 is the weight of fibers after grafting and before extraction (Ibrahim *et al*., 2003b). To reduce large error in percentage of grafting and efficiency, fiber need to be handled carefully to avoid many weight losses that will effect to the result.