

**GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE
ONTO RICE HUSK**

KAMARUL IZHAN BIN SOH

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**Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang**

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ABSTRACT

Graft copolymerization of methyl methacrylate (MMA) onto Rice Husk (RH) was synthesized with a fiber length less than 45 μm . The graft copolymerization was carried out under a nitrogen atmosphere by a free radical initiation in aqueous medium. Hydrogen peroxide and ferrous ions were used as a redox initiator/cocatalyst system. The PMMA homopolymer that formed during the reaction was removed from the grafted copolymers by soak with acetone for 24hr. The percentage of grafting was found to be dependent on the amount of monomer; temperature and amount of hydrogen peroxide were investigated. The optimum conditions for amount of monomer, reaction temperature and amount of hydrogen peroxide were 46.94mmol, 50°C and 5.88mmol, respectively. The highest percentages of grafting and grafting efficiency were 10.8% and 77%, respectively, under optimum condition. After removal of homopolymer, the graft copolymerization (grafted fiber) was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy. The presence peak around 1666 cm^{-1} in the FTIR of the graft RH provides strong evidence of present MMA in the RH fibers. SEM reveals that the surface of the original RH fiber become rough and contained grooves and the surface of the fiber was homogenously covered by PMMA after graft copolymerization.

ABSTRAK

Pengkopolimeran cangkukkan metal metakrilat (MMA) ke Sekam Padi (RH) disintesis dengan panjang serat kurang dari 45 μM . Pengkopolimeran cangkukkan dilakukan di bawah suasana nitrogen oleh permula radikal bebas dalam medium air. Hidrogen peroksida dan ion besi digunakan sebagai permula redoks / sistem cocatalyst. Homopolimer PMMA yang terbentuk dalam tindakbalas telah dibuang dari kopolimer dicangkok dengan merendam dengan acetone untuk 24 jam. Peratus penyambungan dijumpai bergantung pada jumlah monomer; suhu dan jumlah hidrogen peroksida diselidiki. Keadaan optimum untuk jumlah monomer, suhu tindakbalas dan jumlah hidrogen peroksida adalah 46.94 mmol, 50°C, 5.88mmol, masing-masing. Peratusan tertinggi penyambungan dan tunas kecekapan adalah 10.8% dan 77%, masing-masing, di bawah keadaan optimum. Setelah penghapusan homopolimer, yang pengkopolimeran cangkukkan (dicangkokkan fiber) ditandai dengan spektroskopi inframerah transformasi Fourier (FTIR) dan imbasan mikroskop elektron. Puncak Kehadiran sekitar 1666 cm^{-1} di FTIR dari RH cangkukkan memberikan bukti kuat MMA hadir dalam serat RH. SEM mendedahkan bahawa permukaan serat RH asal menjadi alur kasar dan berisi dan permukaan serat itu homogen ditutupi oleh PMMA selepas pengkopolimeran cangkukkan.

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LIST OF ABBREVIATIONS

FTIR	-	Fourier Transform Infrared
H ₂ O	-	Water
H ₂ O ₂	-	Hydrogen Peroxide
HNO ₃	-	Nitric Acid
KBr	-	Potassium Bromide
MMA	-	Methyl Methacrylate
PMMA	-	Poly (Methyl Methacrylate)
RH	-	Rice Husk
RH-g-PMMA	-	Rice Husk grafted Poly (Methyl Methacrylate)
SEM	-	Scanning Electron Microscopy

LIST OF SYMBOLS

E%	-	Efficiency Percentage
Fe ²⁺	-	Ferrous ion
G%	-	Grafting Percentage
M	-	Molar
n	-	Number of mol
OH ⁻	-	Hydroxyl ion
OH [·]	-	Hydroxyl radical
V	-	Volume
W ₁	-	Weight of original rice husk in gram
W ₂	-	Weight of grafted product (copolymerization + extraction)
W ₃	-	Weight of grafted product (Copolymerization + before extraction)
μ	-	Micro
ρ	-	Density

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CHAPTER 1

INTRODUCTON

1.1 Background of Study

Rice cultivation yield three types of byproduct, rice husk and rice bran, rice straw, and the vegetation residue after grain harvest. Rice bran has its own commercial value as it being used as protein supplement for animals and poultry rations (Vadiveloo *et al.*, 2009). Rice husk and rice straw are continuous to remain unutilized in Malaysia.

Based on annual grain production of 2.2 million tones, the outputs of rice husk is about 0.44 million tons in Malaysia. The residue has variety of applications, whole husks as fertilizer, energy source or animal feed, husk ash (silica) in steel, cement and ceramic manufacturing and as filler in lignocellulosic fibre-thermoplastic composites. The silica (20% of ash) is present in the outer epidermal cells which are thick, highly convoluted and lignified (Park *et al.*, 2003). This constitutes a major limitation to its use as an animal feed, apart from low protein (20 g/kg, DM) and high lignocelluloses (580 g/kg, DM) contents (Beg *et al.*, 1986).

Nowdays grafting copolymer is one of the important technique that applied in field of science. Many of journal paper on grafting copolymer published nowadays which showed rapid development of graft copolymer. Graft copolymer has been done onto various types od fiber such as jute (Ferdous *et al.*, 1995), pineapple leaf (Mohanty *et al.*, 2000), wheat straw (Focher *et al.*, 1998), kenaf (Ighodola *et al.*, 1996).

Physical treatment, such as steaming under pressure or chemical treatment with acids and alkalis, breaks the covalent association between lignocellulose components, hydrolysing hemicellulose and de-polymerising lignin (Saha, 2003). By using chemical modification of lignocelluloses material through graft copolymerization with vinyl monomer may improve the properties of the natural polymerization such as water sorbency, ion-exchanger capability elasticity, thermal resistance and resistance to microbiological attack. Graft copolymerization of vinyl monomer involved the creation of free radicals on the backbone (cellulose and lignin), free radicals are formed on the lignocelluloses either by irradiation or by chemical means (Ibrahim *et al.*, 2003).

Many researches has been done on rice husk, Shih *et al.* (2009) by using PMAA and grafting into RH by graft copolymerization and Fenton's reagent act as the redox initiator. The finding stated that the rapid uptake and high adsorption capacity make the PMAA-modified rice husk a highly promising alternative adsorbent of paraquat.

Recently, graft copolymerization of different monomer onto cellulose or lignocelluloses material has been used to enhance their properties. For example acrylonitrile has been grafted onto delignified cellulose, which enhances its water absorbance (Frag *et al.*, 2002). According to Das *et al.* (2000) chemical treatment onto non-mulberry silk-Antheraea assama using potassium permanganate-oxalic acid redox system using MMA as the monomer has cause the grafted fiber were thermally more stable and more hydrophobic in nature than the ungrafted fibers.

1.2 Problem Statement

Rice husk is a by-product of rice milling process but it is a major waste product of the agricultural industry; rice husk has posed a major problem of disposal to the rice milling industry in Malaysia and elsewhere in the world.

According to the statistical data of Food and Agriculture Organization (FAO), the world annual paddy production is approximately 582 million tons. *Oryza sativa* L. husks (Rice husks) comprise 25 mass% of the rice grain and, therefore, 145 million tons of rice husks residue are produced (Stefany *et al.*, 2005), because of their commercial interest is low, rice husk somehow just being dispose, but actually rice husk can be used as a value added product by changing it into building material, fertilizer, insulation material or fuel and many more. By grafting rice husks with polymer it will increase the properties respectively.

The aim of this research is to study the optimum condition for graft copolymerization methyl methacrylate into rice husks.

1.3 Objective Of Research

The objective of this research is to study the optimum condition for grafting copolymerization of methyl methacrylate by:

- (a) Determine the effect of amount of monomer towards percentage of grafting.
- (b) Determine the effect of reaction's temperatures towards percentage of grafting.
- (c) Determine the effect of amount of initiator towards percentage of grafting.

1.4 Scopes of Study

The scopes of this research are:

(a) The main material used are :

- i) Rice husk
- ii) Methyl methacrylate

(b) Set the study parameter:

- i) Effect of amount of monomer (MMA)
- ii) Effect of reaction temperature
- iii) Effect of amount initiator (H_2O_2)

(c) The grafting process used is radical initiator.

(d) The testing of presence MMA chain in the rice husk fiber using Fourier transform-IR spectrometer (FTIR) and scanning electron microscope (SEM).

1.5 Rational and significant

The rational and significant of this research is to find the optimum condition for grafting methyl methacrylate onto rice husk. By doing chemical modification toward rice husk, it will give adding value to the fiber, chemical modification will enhance the properties of rice husk and it can be turn into some beneficial product.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Fiber

Natural fibers are hair-like threads obtained directly from plants, animals, and mineral sources. Botanically, a natural fiber is a collection of cells having long length and negligible diameter. They are obtained as continuous filaments or discrete elongated pieces similar to thread. They can be spun or twisted into yarn such as cloth and can be converted into nonwoven fabrics, such as paper or felt. An example of a commonly used natural fiber is cotton. Other examples include wool, jute, silk, hair, fur, hemp, and linen (Globalspec, 2010.).

2.1.1 Rice Husk

Rice husk (RH) is also a kind of plant natural fiber which is hard protecting coverings of grains of rice. RH is recycled to be use as a building material, fertilizer, animal food, and an alternative energy. To protect the seed during the growing seasons, the hull is made from hard materials, including opalina silica and lignin. The hull is mostly indigestible to human. During the milling process, the hull is removing from the grain to create rice. The chemical compositions of RH are shown in Table 2.1.

Table 2.1: The chemical composition of RH (Razavi *et al.*, 2006)

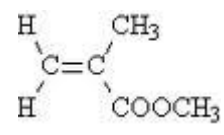
Content	% Based on weight
Cellulose	35
Hemicelluloses	25
Lignin	20
Ash	17(94% silica)
Moisture	3

2.2 Methyl Methacrylate

Methyl methacrylate is an organic compound with the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$. This colorless liquid, the methyl ester of methacrylic acid (MAA) is a monomer produced on a large scale for the production of poly (methyl methacrylate) (PMMA). The principal application, consuming approximately 80% of the MMA, is the manufacture of polymethyl methacrylate acrylic plastics (PMMA). Methyl methacrylate is also used for the production of the co-polymer methyl methacrylate-butadiene-styrene (MBS), used as a modifier for PVC (Methyl acrylate, 2010.).

Acrylate monomers are known to polymerize with great facility in the presence of a wide variety of initiator, and copolymerize with almost all types of vinyl monomer (Kaur *et al.*, 1999). Poly(methylmethacrylate) (PMMA) was selected for fibers surface modification because its compatibility with other common polymers and because its monomer have high water solubility, 1.59% vol. (Min and Ray, 1974). It is worthy to mention that even though the chemical modification of cellulose or lignocellulosics with acrylic polymers have been widely reported. The properties of methyl methacrylate are show in Table 2.2.

Table 2.2: Physical/chemical properties of Methyl methacrylate (Methyl methacrylate fact sheet, 1994)

Characteristics/properties	Data
Molecular formula	C ₅ H ₈ O ₂
Chemical structure	
Physical state	Liquid
Molecular weight	100.1
Melting point	-48°C
Boiling point	100-101°C
Water solubility	15g/L @ 25°C
Density	0.939g/cm ³
Flash point	10°C

2.3 Chemical Modification

One of major problem associated with the use of natural fiber in composites is their high moisture sensitivity leading to severe reduction of mechanical properties and delaminating. The reduction in mechanical properties may be due to poor interfacial bonding between matrices and fibers.

As an example, one difficulty that has prevented a more extended utilization of the henequen fiber is the lack of a good adhesion to most polymeric matrices. The hydrophilic nature of natural fiber adversely affects adhesion to a hydrophobic matrix and as a result, it may cause a loss of strength. To prevent this, the fiber surface has to be modified in order to promote adhesion (Herrera *et al.*, 2004).

Several methods to modify the natural fiber surface have been proposed: the graft copolymerization of monomers onto the fiber surface, the use of maleic

anhydride copolymers, alkyl succinic anhydride, stearic acid, etc. It has also been reported that the use of coupling agents such as silanes, titanates, zirconates, triazine compounds, etc. also improve fiber-matrix adhesion. Furthermore, it is also known that pre-impregnation of the fiber with the polyolefin solution will also improve adhesion (Valadez *et al.*, 1999).

Kang *et al.* (1996) has shows surface modification of polymers via graft copolymerization with specific functional monomers has been shown to be a versatile means for improving the adhesion strength in polymer laminates.

The effect of chemical treatment of rice husk with methacrylic acid (MAA) for paraquat adsorbtion has been reported by Shih *et al.* (2007). The carboxylic groups were chemically bound to the surface of the rice husk by graft copolymerization using Fenton's reagent as a redox initiator. This modification results in an increasing in adsorbent capacity of paraquat. Shengjun *et al.* (2009) has reported graft copolymerization of methyl acrylate onto pullulan using ceric ammonium nitrate as initiator has cause absorption capacity of resin decreased significantly with increasing in percentage of grafting.

2.4 Graft Copolymerization

Graft copolymer is a special type of branched copolymer which the side chains are structurally distinct from the main chain, one of graft copolymerization is between ricks husk with methyl methacrylate. An example of copolymer model is just like in figure 1, where respective monomer residues are coded A and B:

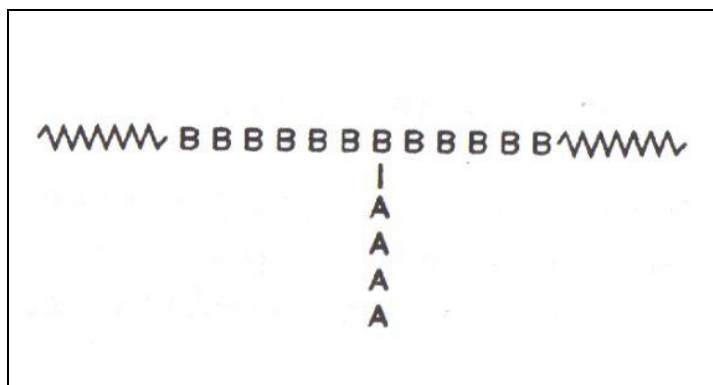


Figure 2.1: Structure of graft copolymer mode (Rudin, A., 1998)

The nature of polymer surfaces is of great importance because it is the surface that first comes into contact with the environment and therefore determines all kinds of interactions such as wettability, adhesion and biological response. Surface modification of polymers has recently turned in the direction of new areas involving the control of not only the surface chemistry but. Also the morphology in order to affect specific interactions (Ratner, 1996).

Modification of properties of natural protein fibers through graft copolymerization has become an attractive means of chemical modification of these fibers, since such treatments; in general, improve some of the disadvantages associated with these fibers. Some vital changes in properties like photoyellowing, wash and wear, wrinkle recovery, water repellency, improved dyeability, soil resistance and thermal stability can be brought about by grafting with various vinyl monomers (Samal *et al.*, 1983).

Graft copolymers are commonly used as compatibilisers in polymer blends. Their role is to stabilize the morphology of two immiscible polymers by reducing the interfacial tension and increase the adhesion between their phases (Cartier *et al.*, 2001). There are several types of interactions that can appear between compatibiliser and immiscible polymers. One of these interactions is the result of the same chemical structure of the graft copolymers and the polymers in an incompatible polymer blend (Aggarwal *et al.*, 1976). The other possibility is that graft copolymers can make chemical bonds with the polymers in the blend whose side chains contain highly reactive functional groups (such as isocyanate). For example, by toughening of styreneacrylonitrile copolymer (SAN) with ethylene propylene diene terpolymer (EPDM) it is difficult to achieve appropriate compatibility due to their chemically dissimilar structure. That will result in phase separation which is larger than the optimum interfacial bonding and poor physical properties of blends (Chaintore *et al.*, 1998).

Graft copolymerisation enables modification of polymers and has allowed formation of various materials with unique properties. Even when a low concentration one of the agents is added significant changes of the structure of the graft copolymers can be observed. Such example is addition of coagent TAC during synthesis of EPDM-g-PS graft copolymers where the TAC will prevent scission of the main chain of EPDM and then different structure of graft copolymers can be expected (Dikland *et al.*, 1993)

Grafting of vinyl monomers onto cellulose provides a potential route for significantly altering the physical and mechanical properties of polymer substrates and thus, potential end uses. Depending on the chemical structure of the grafting monomer, cellulose graft copolymers can be made hydrophilic or hydrophobic in character (Ghosh *et al.*, 1995), exhibit improved elasticity, water sorbency, ion-exchange capability, heat resistances and resistance to microbiological attack.

The grafting of vinyl monomers onto cellulose and its derivatives is generally considered to involve three steps; (1) the generation of reactive sites on substrate polymer, (2) the addition of monomer to the substrate, and (3) the propagation of that

monomer. Reactive sites on the cellulose backbone are generated by either radiation or chemical initiation methods (Ibrahim *et al.*, 2008).

Graft copolymerization reactions of cellulose are mostly carried out in aqueous and heterogeneous media. In water, the accessible, amorphous regions of cellulose swell enabling the diffusion of monomer into these regions and the subsequent grafting reactions (Hebeish and Gutrie, 1981). By either preswelling the cellulose or performing the grafting reaction in a medium in which cellulose swells, the grafting efficiency is increased as a result of the increased ratio of monomer/cellulose. Moreover, by preswelling the cellulose, the grafting efficiency can be easily controlled. Many methods, including ozonation/oxidation, alkali, amine and water pretreatments have been used to improve the accessibility of cellulose towards chemical reactions (Ibrahem and Nada, 1985).

Grafting can be performed using free radical initiators, redox system or by photochemical process. In the photochemical process, semiconductor-based photocatalyst is one of the modern methods for generation of initiating radicals in photopolymerization of vinyl monomer (Hoffman *et al.*, 1992). Mills and Hunte (1997) mention the effectiveness of these semiconductors as photocatalyst depends upon how well the radiation wavelength used corresponds to the band gap excitation energy of the semiconductor.

In case of free radical mechanism, various initiators systems like ceric ammonium nitrate (CAN), Cr(VI), ferrous-peroxy disulphate, KMnO₄–oxalic acid redox system have been used and testing by various reseacher. In comparison with other types of processes, free radical process followed by light-induced initiation has the advantage due to applicability at room temperature and its user-friendly nature (Ojah *et al.*, 2006).

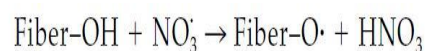
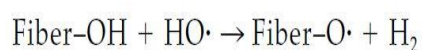
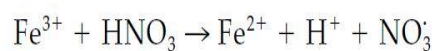
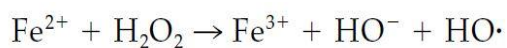
2.4.1 Free Radical Initiator Mechanism

Free radical polymerization is the typical method of graft polymerization of various monomers onto existing polymer initiated by chemical initiator or by radiation (Fanta *et al.*, 1987). During the polymerization the radical formation for initiation reactions can occur either on the backbone polymer or on the monomer to be grafted. Homopolymer will be produced if the radical formation is on monomer, therefore, initiator capable of creating radicals at various sites on the backbone are preferred (Ibrahim, N.A. *et al.*, 2005).

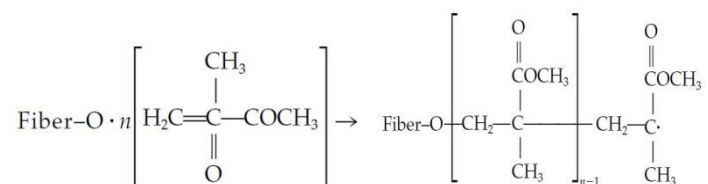
Huang *et al.* (1992) reported that lignin accelerates grafting at the initiation stage of reaction when $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was used as an initiator. As in this experiment we will be using $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ as initiators and will be carried out in aqueous solutions in the process grafting methyl methacrylate into rice husk, the flow is mechanism as shown in Figure 2.2.

Reaction Mechanism

Initiation



Propagation



Termination

It could be through a combination of the radical or a chain transfer and polymerization of MMA initiated by simple radical leads to the formation of homopolymer.

Figure 2.2: Mechanism of radical initiator of methyl methacrylate onto oil palm empty fruit bunch fiber (Ibrahim, N.A. *et al.*, 2003)

Free radical initiator, according to Ibrahim *et al.* (2003) its will consist of 3 main mechanism, that it initiation, propagation and termination. As can see in figure 2, Initiation will be starting with decomposition of H_2O_2 to produce radical occurs slowly, adding co catalyst of Fe^{2+} to the system speed up the decomposition of H_2O_2 . The decomposition of the Fe^{3+} ion generated also produce radical by reacting with HNO_3 , The radical species $HO \cdot$ and $NO_3 \cdot$ is expected to be reactive in the redox initiaotion of graft copolymerization by hydrogen abstraction from cellulisic fiber (Bhattacharyya, 1984). The production of homopolymer of MMA is may be initiated by $HO \cdot$ and $NO_3 \cdot$. Next step is the propagation, once fiber radical are produced, they react with the monomer to give the graft copolymer . Last step is termination where It could be through a combination of the radical or a chain transfer and polymerization of MMA initiated by simple radical leads to the formation of homopolymer (Ibrahim *et al.*, 2003).