

Graft Copolymerization of Methyl Methacrylate onto Oil Palm Empty Fruit Bunch Fiber Using $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ as an Initiator

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Received 20 June 2002; accepted 22 November 2002

ABSTRACT: Graft copolymerization of methyl methacrylate (MMA) onto oil palm empty fruit bunch fiber (OPEFB) was successfully carried out in aqueous medium using hydrogen peroxide as an initiator. Results from the investigation of the optimum conditions for grafting are presented. Maximum percentage of grafting was achieved when the amount of initiator, cocatalyst, and nitric acid were 5.877×10^{-3} mol, 2.63×10^{-4} mol, and 3.24×10^{-3} mol, respectively. The optimum reaction temperature was 50°C and the reaction period was 120 min. The highest percentage of

grafting and grafting efficiency were 220 and 47%, respectively, under optimum conditions. The grafted copolymer was characterized by FTIR spectroscopy and scanning electron microscopy. The presence of a band at 1730 cm^{-1} provides strong evidence of grafting. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2233–2238, 2003

Key words: graft copolymers; fibers; monomers; radical polymerization; FTIR

INTRODUCTION

In the past few decades, Malaysia produced an abundance of oil palm empty fruit bunch fiber (OPEFB), which was regarded as waste and not utilized. OPEFB was obtained after stripping off the fruits from the fruit bunch for the extraction of oil. More than 55 million tons of oil palm biomass were generated annually in Malaysia.¹ Chemical analysis of the OPEFB shows that OPEFB consists of 65% cellulose and 19% lignin.²

Chemical modification of lignocellulose material through graft copolymerization with vinyl monomer may improve the properties of the natural polymer such as water sorbency, elasticity, ion-exchange capabilities, thermal resistance, and resistance to microbiological attack.^{3,4} 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 chemical means or by irradiation.

Grafting of lignocellulose material such as jute,^{5–8} pineapple leaf,⁹ henequen,¹⁰ wheat straw,¹¹ kenaf,¹² and coir^{13,14} have been done successfully using differ-

ent types of initiator such as ceric ion, potassium permanganate, and potassium monopersulfate.

This investigation deals with synthesizing of grafted polymer onto empty fruit bunch oil palm fiber (OPEFB) with methyl methacrylate (MMA) using hydrogen peroxide as initiator.

The optimum conditions for grafting were determined by varying the reaction time, reaction temperature, and amount of monomer, initiator, cocatalyst, and acid. The presence of MMA in the products was studied by use of FTIR spectroscopy and scanning electron microscopy.

EXPERIMENTAL

Materials

Oil palm OPEFB fibers were received from Sabutek Sdn. Bhd., Malaysia. The OPEFB used in this study was ground to the mesh size of 60 ($>270 \mu\text{m}$). The OPEFB powder was soaked for 6 h and washed first with hot water and then with acetone, after which it was dried in an oven at 60°C to constant weight. This OPEFB fiber consists of 65% cellulose and 19% lignin.² Methyl methacrylate of purity more than 99% was purchased from Fluka Chemie (Buchs, Switzerland) and purified by passing through a column packed with an activated alumina to remove its inhibitor. Analytical reagent grade hydrogen peroxide was purchased from Riedel-de Haën (Seelze, Germany). Am-

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monium ferrous sulfate, an analytical-grade reagent, was obtained from BDH (Poole, UK), and used as received. Solvents and other chemicals of analytical grade were used as received from manufacturers.

Graft copolymerization

To prepare the fiber/PMMA copolymer, 1.00 g OPEFB fiber was placed in 250 mL three-neck flasks equipped with stirrer and condenser and immersed into a thermostated water bath. The OPEFB suspension was obtained by adding 100 mL of distilled water and 3.0 mL of 1.0M nitric acid with stirring. Nitrogen was purged through the OPEFB slurry to remove the presence of oxygen during the reaction. After 30 min, the required amount of ammonium ferrous sulfate and the required volume of 2.0M H₂O₂ were added. The reaction mixture was mixed for 5 min and then the required amounts of monomer (MMA) were added into the mixture. The reaction mixture was stirred under nitrogen at the chosen temperature and reaction period. Immediately after the reaction period was over the reaction flask was cooled under running tap water and the product was filtered. The crude product was washed thoroughly with distilled water and oven dried at 60°C to constant weight.

Removal of homopolymer and determination of graft level

The crude product was purified with the acetone using a Soxhlets extractor for 24 h to remove poly(methylmethacrylate) homopolymer. The pure grafted copolymers were then dried at 60°C to a constant weight. The percentage of grafting (P_g) and grafting efficiency (G_e) were determined by the following formulas, respectively:

$$P_g = \frac{W_2 - W_1}{W_1} \times 100$$

$$G_e = \frac{W_2 - W_1}{W_3 - W_1} \times 100$$

where W_1 is the weight of the original OPEFB fibers in grams, W_2 is the weight of the grafted product after copolymerization and extraction, and W_3 is the weight of the grafted product after copolymerization and before extraction (grafted product + homopolymer).

FTIR spectroscopy

Infrared (IR) spectra of the OPEFB and grafted OPEFB were recorded on a Fourier transform-IR spectrometer (Perkin-Elmer 1725, Norwalk, CT) using a KBr disk pellet.

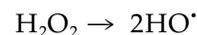
Scanning electron microscopy

The SEM photographs of the fiber surfaces of grafted PMMA onto OPEFB and ungrafted OPEFB fiber were taken using a scanning electron microscope model SEM JEOL 6400 (JEOL, Peabody, MA).

RESULTS AND DISCUSSION

Reaction mechanism

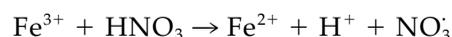
Graft polymerizations of PMMA onto OPEFB were carried out in aqueous solution using hydrogen peroxide as initiator and Fe²⁺ as cocatalyst. Grafting by chemical methods involves the formation of an active center on cellulosic fiber, which acts as the backbone. Radicals produced by decomposition of H₂O₂ may initiate the production of cellulosic fiber radical. Therefore the first step of the mechanism is the generation of radicals. Decomposition of H₂O₂ to produce radicals occurs slowly.¹⁵



Addition of Fe²⁺ into the system speeds up the decomposition of H₂O₂.⁵



The Fe³⁺ ion generated also produced radical by reacting with HNO₃.



The radical species HO· and NO₃· are expected to be reactive in the redox initiation of graft copolymerization by hydrogen abstraction from cellulosic fiber.¹⁶

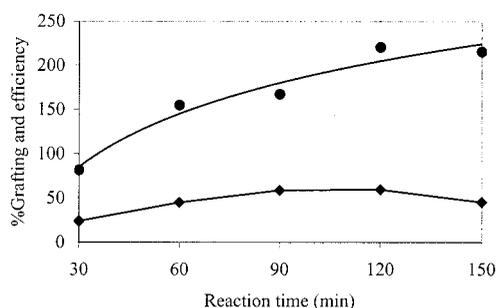
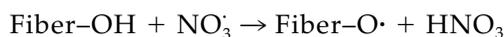
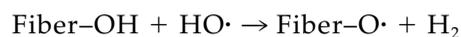


Figure 1 Effect of reaction time on the percentage of grafting and efficiency. Temperature, 50°C; MMA, 47.15 mmol; HNO₃, 3.24 mmol; H₂O₂, 3.918 mmol; Fe²⁺, 0.262 mmol; (●) grafting (%); (◆) efficiency (%).

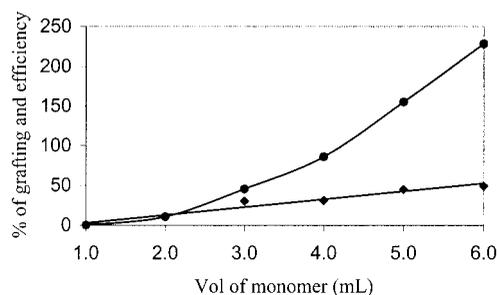
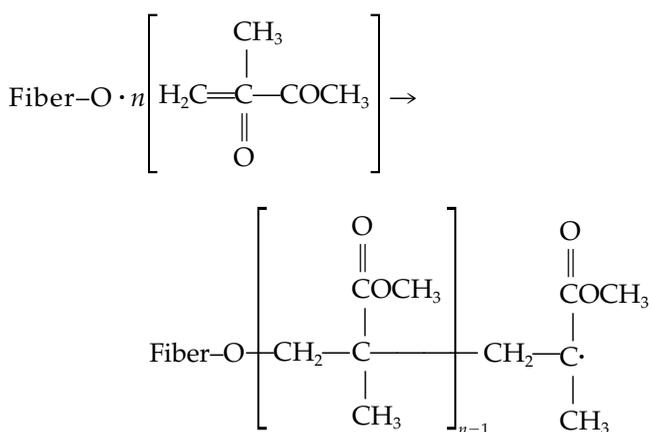


Figure 2 Effect of volume of monomer on the percentage of grafting and efficiency. Temperature, 50°C; time of reaction, 1 h; HNO₃, 3.24 mmol; H₂O₂, 3.918 mmol; Fe²⁺, 0.262 mmol; (●) grafting (%); (◆) efficiency (%).

The HO· and NO₃ radicals may also initiate the homopolymerization of MMA.

Once the cellulosic fiber radicals are produced, they react with the monomers to give the graft copolymer:



Termination of the graft copolymerization could be through a combination of the radicals or a chain transfer and polymerizations of MMA initiated by simple radicals leads to the formation of homopolymer.

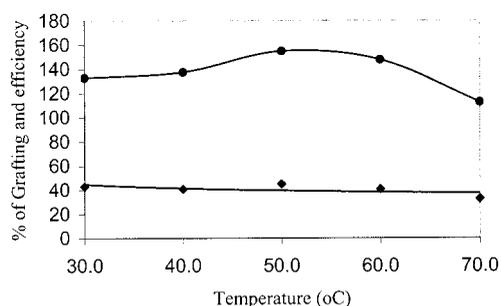


Figure 3 Effect of reaction temperature on the percentage of grafting and efficiency. Reaction time, 1 h; MMA, 47.15 mmol; HNO₃, 3.24 mmol; H₂O₂, 3.918 mmol; Fe²⁺, 0.262 mmol; (●) grafting (%); (◆) efficiency (%).

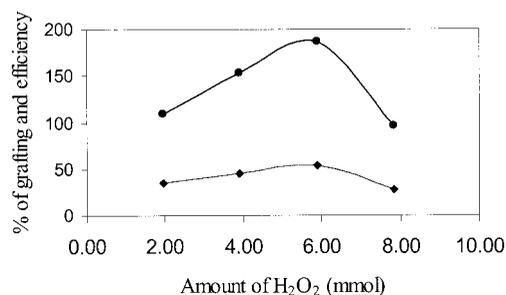


Figure 4 Effect of amount of initiator on the percentage of grafting and efficiency. Temperature, 50°C; MMA, 47.15 mmol; HNO₃, 3.24 mmol; reaction time, 1 h; Fe²⁺, 0.262 mmol; (●) grafting (%); (◆) efficiency (%).

Effect of reaction period

The effects of the reaction period on the percentage of grafting and grafting efficiency are shown in Figure 1. Percentage of grafting increases during the earlier reaction period and leveled off after 2 h. The maximum percentage of grafting was 220.6%.

This trend is in agreement with the observation reported earlier in the study of graft copolymerization of vinyl monomer onto jute fiber.^{6,8} The leveling off of grafting value is attributed to the decrease in monomer and catalyst concentration as well as to the retardation of diffusion arising from the formation of polymer at the fiber surface.¹⁷

Effect on monomer concentration

The percentage of grafting increases with the increase for the monomer from 9.43 to 56.58 mmol (1 to 6 mL), as shown in Figure 2. The percentage of grafting and grafting efficiency for 6 mL of MMA are 228.3 and 41.0%, respectively. This type of behavior is expected given that the larger the amount of monomer, the more favored will be the reaction with the backbone.¹⁸

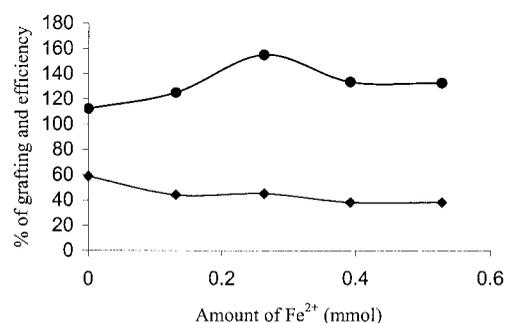


Figure 5 Effect of amount of catalyst on the percentage of grafting and efficiency. Temperature, 50°C; MMA, 47.15 mmol; HNO₃, 3.24 mmol; H₂O₂, 3.918 mmol; reaction time, 1 h; (●) grafting (%); (◆) efficiency (%).

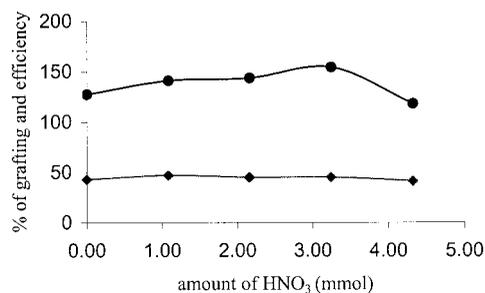


Figure 6 Effect of amount of initiator on the percentage of grafting and efficiency. Temperature, 50°C; amount of MMA, 47.15 mmol; H₂O₂, amount of 3.918 mmol; reaction time, 1 h; Fe²⁺, 0.262 mmol; (●) grafting (%); (◆) efficiency (%).

Effect of reaction temperature

The percentage of grafting increases with the increase of temperature up to 50°C and then decreases with further increase in the reaction temperature, as shown in Figure 3. The increase in grafting at higher temperature may be attributable to the swellability of OPEFB in the substrate and enhancement of rate of diffusion of the monomer with increase of the temperature. This observation is in agreement with the grafting of MMA onto jute fiber.⁶ At higher temperature probably the decomposition of peroxide increases, thus producing a lot of radicals. Some of the radicals create active centers on the lignocellulosic fiber, whereas the remaining radicals initiate the homopolymerization. This explanation is in agreement with the experimental data where the total conversion increased with temperature but the percentage of grafting decreased as the temperature increased. This result is in agreement with Lutfor et al.,¹⁹ who used ceric ammonium nitrate to graft methyl acrylate onto sago starch.

Effect of the amount of initiator

In the case of grafting initiated by a chemical initiator, the extent of grafting increases with the amount of initiator up to certain limit, then decreases.²⁰ This is attributed to the increase of free radicals with increasing initiator concentration, which enhanced the possibility of initiating reactive site on the backbone where PMMA can be grafted. The effect of the amount of H₂O₂ initiator on the percentage and efficiency of grafting of OPEFB is shown in Figure 4. The percentage of grafting increased with an increase of the amount of initiator from 1.96 to 5.88 mmol but decreased at higher amounts. The optimum percentage of grafting and efficiency are 187.3 and 40.0, respectively, at 5.88 mmol of initiator. Thereafter, the graft level decreased with further increases of the amount of initiator. At higher H₂O₂ concentrations, the decrease was expected because the decomposition of H₂O₂ increases the number of cellulosic fiber radicals, which terminated before the addition of monomer. The formation of homopolymer also contributes to a decrease in the grafting level.

Effect on the amount of cocatalyst

When grafting of OPEFB is carried out using H₂O₂ as the initiator without a cocatalyst the percentage of grafting is low. The percentage of grafting increases when ammonium ferrous sulfate, (NH₄)₂SO₄·FeSO₄·6H₂O, is added. It indicates that when H₂O₂ alone is used as initiator, its conversion into radicals is slow. Addition of Fe²⁺ into the system speeds up the decomposition of H₂O₂ and the formation of radicals.¹⁵ The percentage of grafting increases with the increase of the amount of cocatalyst up to 0.263 mmol, but decreases at higher amounts, as shown in Figure 5. This may be attribut-

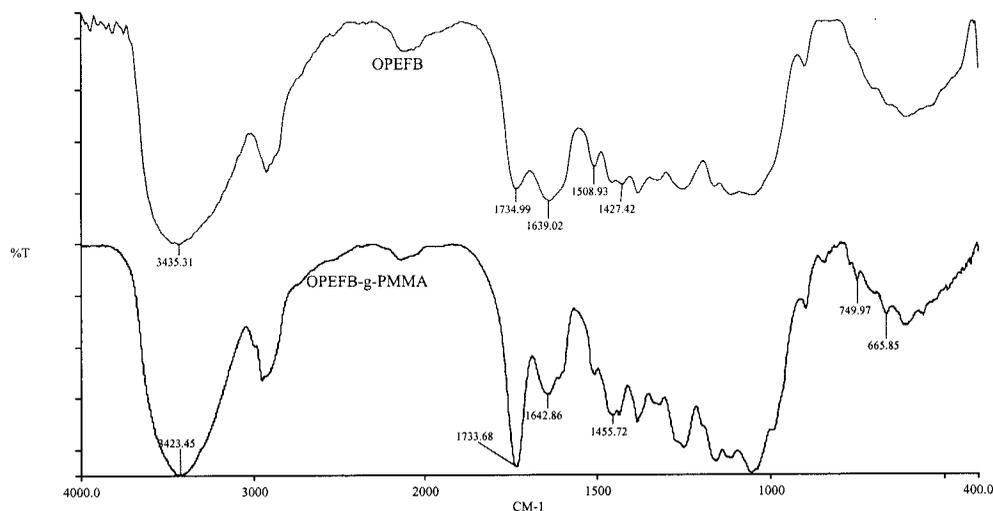


Figure 7 Infra red spectra of (a) OPEFB and (b) PMMA-g-OPEFB.

able to the presence of a large number of free radicals, which may interact with each other, causing termination and thus reducing the graft yield.²⁰

Effect on the amount of acid

The effect of the amount of acid on the percentage of grafting and grafting efficiency is shown in Figure 6. The maximum percentage of grafting (154%) is observed at 3.24 mmol of HNO₃; beyond this amount the grafting percentage decreases. The initial increase in percentage of grafting with the increase of the amount of HNO₃ may occur because acid reacts with the Fe³⁺ present in the solution to produce NO₃ radicals, which enhances the possibility of initiating a reactive site on the backbone where PMMA can be grafted. Higher amounts of acid, however, can cause degradation of the backbone as well as graft chains. The decrease in grafting may also be related to the abundance of H⁺, which may act as a free-radical terminator.¹⁹

FTIR spectroscopy

The presence of PMMA on the fiber was verified by the FTIR spectra of the OPEFB and PMMA-grafted-OPEFB, as shown in Figure 7

Both spectra show a characteristic broad absorption band of the hydroxyl group around 3500–3100 cm⁻¹. This is attributed to OH stretching vibrations of cellulose, absorbed water, hemicelluloses, and lignin constituent of OPEFB.²¹ The presence of the peak near 1730 cm⁻¹ in OPEFB spectra could be associated with C=O stretching vibration of carboxyl groups in hemicelluloses and lignin in OPEFB. The increase in intensity of the C=O peak (1730 cm⁻¹) in the spectrum of poly(MMA)-grafted-OPEFB indicates that the presence of an ester group from MMA provides strong evidence of grafting.²²

The absorption band in the 1600–1400 cm⁻¹ region in both spectra may be attributed to the presence of aromatic or benzene rings in lignin. Aliphatic and aromatic (C–H) in the plane deforma-

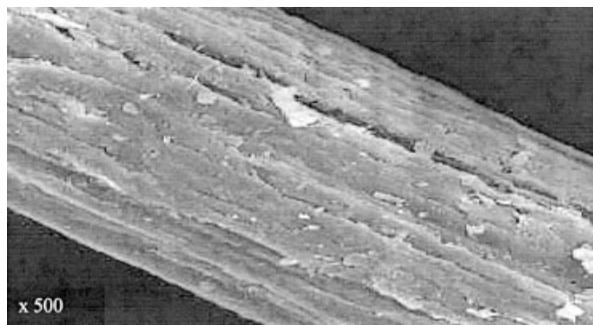


Figure 8 Scanning electron micrographs of ungrafted OPEFB fiber (×500).

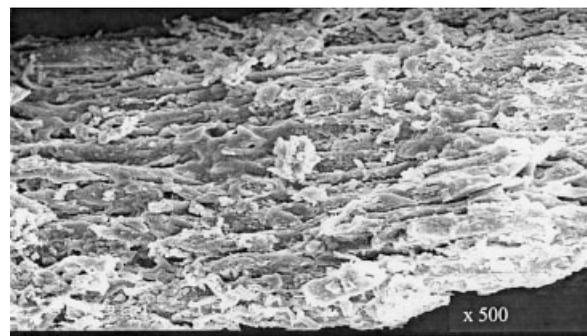


Figure 9 Scanning electron micrographs of OPEFB-g-PMMA (×500).

tion vibration of methyl, methylene, and methoxy groups in fiber can be seen near 1400–1300 cm⁻¹, whereas the band in the region of 1300–1000 cm⁻¹ indicates the C–O stretching vibration of aliphatic primary and secondary alcohols in cellulose, hemicelluloses, lignin, and primary and secondary aromatic alcohols in lignin.²³

SEM microscopy

SEM micrographs of the ungrafted OPEFB fiber and OPEFB-g-PMMA are shown in Figures 8 and 9, respectively. In Figure 8, the OPEFB surface is rough with groovelike structures observed that may be attributed to removal of intercellular binding material. After the grafting process, the surface of the fiber was homogeneously covered by PMMA. This synthetic polymer is strongly attached onto the fiber surface because it is chemically bonded.

CONCLUSIONS

The synthesis of hydrophobic monomer (MMA) grafted onto OPEFB using hydrogen peroxide as initiator was carried out. The spectroscopic data and the SEM micrograph of the purified product confirmed the presence of PMMA on the fiber.

The percentage of grafting and grafting efficiency were dependent on the amounts of the initiator (hydrogen peroxide), the monomer (MMA), the cocatalyst (Fe²⁺), and nitric acid as well as the reaction period and reaction temperature.

The optimum temperature and reaction period are 50°C and 2 h, respectively. The optimum amounts of H₂O₂, Fe²⁺, and HNO₃ are 5.88 × 10⁻³ mol, 2.63 × 10⁻⁴ mol, and 3.24 × 10⁻³ mol, respectively, with 1.00 g of OPEFB fiber. No optimum value of the monomer concentration as the graft yield was observed to increase with amount of monomer (9.43–56.58 mmol).

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