

Optimized Conditions for the Grafting Reaction of Poly(methyl methacrylate) onto Oil-Palm Empty Fruit Bunch Fibers

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ABSTRACT: This article describes the graft copolymerization of poly(methyl methacrylate) (PMMA) onto oil-palm empty fruit bunches (OPEFBs) with a fiber length of less than 75 μm . The graft copolymerization was carried out under a nitrogen atmosphere by a free-radical initiation technique in an 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 Soxhlet extraction. Determining the effects of the reaction period, reaction temperature, and monomer concentration on the grafting percentage was the main objective, and they were investigated systematically. The optimum reaction period, reaction temperature, monomer concentration,

and initiator concentration were 60 min, 50°C, 47.15×10^{-3} mol, and 3.92×10^{-3} mol, respectively. The maximum percentage of grafting achieved under these optimum conditions was 173%. The presence of PMMA functional groups on OPEFB and the enormous reduction of the hydroxyl-group absorption band in PMMA-g-OPEFB spectra provided evidence of the successful grafting reaction. The improvement of the thermal stability of PMMA-g-OPEFB also showed the optimal achievement of the grafting reaction of PMMA onto OPEFB. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 847–855, 2008

Key words: FT-IR; graft copolymers; radical polymerization; renewable resources

INTRODUCTION

Currently, there are more than 3 million hectares of oil-palm plantations in Malaysia.¹ In all, about 90 million metric tons of renewable biomass (trunks, fronds, shells, palm press fibers, and empty fruit bunches) are produced each year. They are residues left after the fruit bunches are pressed at the oil mill and the oil is extracted. The solid residues, mainly oil-palm empty fruit bunches (OPEFBs), represent 9% of this total and remains unused commercially.¹ Hence, there is a growing interest in using OPEFBs as an alternative material to add value and to reduce the volume of solid waste.

OPEFB fiber is highly attractive as a reinforcement fiber for fiber-filled thermoplastic composites because of the consumer trend of using products made from eco-friendly and natural waste. Previous researchers focused on how the fiber loading, fiber size distribution, and fiber surface treatment affect the mechanical, thermal, and processability properties of the composites.^{2–6} The OPEFB fiber reported

in our previous studies was untreated with any chemical surface reagents, whereas the poly(vinyl chloride) (PVC) matrix was impact-modified with an acrylic impact modifier to improve the mechanical properties of OPEFB-filled PVC composites.^{2,5,6} Untreated OPEFB showed the ability to enhance the stiffness and reduce the fusion time of unmodified PVC composites. On the other hand, the impact and flexural strength and weathering resistance of the unmodified PVC composites decreased with the OPEFB fiber loading increasing from 0 to 40 phr. The ability of acrylic-impact-modified PVC to shear the yield before fracture improved the impact and flexural strength and greatly reduced the fusion time, even though the weathering resistance of acrylic-impact-modified PVC composites decreased.

In this study, OPEFB fiber was grafted with methyl methacrylate (MMA) for the purpose of improving the compatibility of hydrophilic OPEFB with a hydrophobic polymer matrix. Graft copolymerization is a well-established technique for the modification of the physical and chemical characteristics of polymers. Recently, the grafting copolymerization of various vinyl monomers onto natural cellulosic or lignocellulosic fibers has attracted many researchers interested in enhancing the fiber properties.^{7–9} The grafting of acrylonitrile onto pineapple

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leaf fiber improved the thermal properties of pineapple leaf fiber,⁷ whereas the grafting of acrylamide onto sisal fiber improved the water resistance of sisal fiber.⁸ The grafting of MMA onto jute fiber enhanced the mechanical properties of jute fiber.⁹ The chemical modification of a lignocellulose material through grafting copolymerization with a vinyl monomer also improved the properties of the natural fibers, such as the elasticity, ion-exchange capabilities, and resistance to microbiological attack.¹⁰

OPEFB has been grafted with various chemical reagents, including poly(butyl acrylate),¹¹ poly(methyl methacrylate) (PMMA),¹² and acrylamide.¹³ PMMA grafted onto OPEFB was studied by Ibrahim et al.,¹² and they found that the optimum reaction time of OPEFB fibers greater than 270 μm long was 2 h. In our case, the shorter copolymerization reaction time is the main interest and is more attractive in terms of cost effectiveness. Therefore, an OPEFB fiber shorter than 270 μm was used in this study. This is because an increase in the surface area of the OPEFB fiber able to react with MMA can reduce the copolymerization reaction time. Until now, no research had been done to determine the optimal conditions for the grafting copolymerization of PMMA onto OPEFB fibers less than 75 μm long. With that in mind, the main objective of this study was to determine the optimum conditions for grafting PMMA onto OPEFB with a fiber length of less than 75 μm through variations of the reaction time, reaction temperature, monomer concentration, and initiator concentration.

EXPERIMENTAL

Materials

OPEFB fibers were bought from Sabutek Sdn. Bhd. (Teluk Intan, Perak, Malaysia) and separated into different lengths with a Restsch (Haan, Deutschland) shaker. The vibration time used for separation was 10 min. The OPEFB fibers used were less than 75 μm long and were then dried in an oven at 105°C for about 24 h to a constant weight. MMA monomer, obtained from Merck Schuchardt (Hohenbrunn, Germany), was used for grafting onto OPEFB fibers. The choice of MMA was based on its hydrophobic property and its extensive use in the grafting of synthetic polymers and cellulosic fibers. Analytical-grade hydrogen peroxide (H_2O_2), produced by QR&C (Malaysia), was used as an initiator, whereas ammonium ferrous sulfate, obtained from BDH Sigma-Aldrich Chemie GmbH (Steinheim, Germany), was used as a catalyst. All solvents and other analytical-grade chemicals were used as received from the manufacturers without further purification.

Removal of the inhibitor from the monomer

MMA was purified by passage of the monomer through a column packed with activated alumina to remove its inhibitor (hydroquinone). Initially, alumina was heated in an oven at 60°C for 24 h to activate its content. A reagent bottle was first immersed in an ice bath. Then, a burette was filled with glass wool, and this was followed by activated alumina. MMA was poured into the burette through a conical funnel and was allowed to flow through the burette. The activated alumina changed in color from white to pink when the inhibitor was trapped. Purified MMA was collected in a reagent bottle, which was kept in a refrigerator below 10°C.

Preparation of PMMA-g-OPEFB

The graft copolymerization of MMA onto OPEFB fibers through a free-radical mechanism was carried out in a typical three-necked flask equipped with a magnetic stirrer. A 250-mL, three-necked flask was properly arranged and immersed in a thermostated water bath. A reflux condenser of the Graham type was attached to the three-necked flask to reduce the loss of the water medium. All the joints were properly attached, and the reaction was carried out under an atmosphere of nitrogen. A thermometer was used to ensure that the heater maintained the desired temperature. One gram of dried OPEFB together with 100 mL of distilled water was added to the three-necked flask. Water was used as the dispersion medium.¹⁴ Nitrogen was purged through the OPEFB slurry for 30 min to remove oxygen in the flask because the presence of oxygen during the reaction might terminate the free-radical mechanism. Later, the required volume of 2.0M H_2O_2 as an initiator was injected into the flask, and the mixture was left for 5 min. The required amount of the cocatalyst (ammonium ferrous sulfate) was added to the flask, and the slurry was allowed to settle for 5 min. Next, the required amount of the MMA monomer was injected into the mixture. The reaction mixture was magnetically stirred under a nitrogen atmosphere at the chosen temperature and for the chosen reaction period. When the reaction period was over, the reaction flask was immediately exposed to the ambient atmosphere, and the grafted product was filtered with a vacuum pump. The flask was washed thoroughly with distilled water to remove the grafted product stuck on the inner flask surface, and it was filtered again. Finally, the grafted product was kept in an oven at 60°C for 24 h until a constant weight was achieved. The grafted product was further treated with the Soxhlet extraction technique for the removal of the PMMA homopolymer that was formed during the reaction.

Removal of the homopolymer

PMMA homopolymer formation during the copolymerization reaction was inevitable, even though Karlsson et al.¹⁵ reported that Fe²⁺ was capable of suppressing homopolymerization. This homopolymer was an unwanted product, and it was removed from the grafted product with a Soxhlet extraction technique. Initially, the three-necked flask was filled with acetone. A few grams of boiling chips was added to the flask to avoid a burst-off of acetone during heating. A thimble used for the extraction process was preheated in an oven for 24 h before its application in the Soxhlet extractor. The preheated thimble was then kept in a desiccator to remove moisture.

Grafting percentage and grafting efficiency

For the grafting percentage and grafting efficiency calculations, the initial weight of the empty thimble was first determined. The grafted product was removed from the oven and was allowed to cool to room temperature. This grafted product was then added to the thimble, and the weight of the thimble containing the grafted product (including the PMMA homopolymer) was measured. This thimble was then inserted into a Soxhlet extractor, and the extraction process was allowed to proceed for 24 h to remove the PMMA homopolymer. Afterward, the thimble was dried in an oven at 60°C for another 24 h until a constant weight was achieved. Later, the thimble was removed from the oven and transferred immediately to the desiccator to prevent the thimble from absorbing the moisture. The thimble was allowed to cool to room temperature. Finally, the weight of the thimble and grafted product without the PMMA homopolymer was measured. The grafting percentage and grafting efficiency were determined with the following formulas:

$$\% G = [(w_3 - w_1)/(w_1)] \times 100\%$$

$$\% E = [(w_3 - w_1)/(w_2 - w_1)] \times 100\%$$

where % *G* is the grafting percentage, % *E* is the efficiency percentage, *w*₁ is the weight of the original OPEFB, *w*₂ is the weight of the grafted product after copolymerization, and *w*₃ is the weight of the grafted product after copolymerization and purification (extraction).

Fourier transform infrared (FTIR) spectroscopy

A Nicolet 5700 FTIR apparatus (Mettler–Toledo) was used to identify the related functional groups present in the OPEFB and PMMA-*g*-OPEFB fibers. The

small quantity of ungrafted OPEFB and PMMA-*g*-OPEFB fibers was used for comparison and analysis. The fiber samples were scanned from 4000 to 370 cm⁻¹ for 16 times to reduce the noise-to-signal ratio.

Thermogravimetric analysis (TGA)

The thermogravimetry (TG) experimental work was carried out with the optimized-condition sample with a PerkinElmer TGA 7 thermal analyzer. The analysis was carried out in a nitrogen atmosphere through the scanning of approximately 10 mg from 35 to 1000°C at a heating rate of 10°C/min with a nitrogen flow rate of 20 mL/min. Each sample was placed in an open alumina sample pan. Thermograms were obtained by the plotting of the residual weight percentage against the temperature.

Scanning electron microscopy (SEM)

Studies on the surface morphologies of grafted OPEFB and original OPEFB fibers were performed with a Zeiss Supra 35 VPFE scanning electron microscope. Samples were mounted on the stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. The SEM micrographs were recorded at a magnification of 1000×.

RESULTS AND DISCUSSION

Effect of the reaction time

The effect of the reaction time on the grafting parameters was studied under predetermined conditions. The study was conducted through the variation of the reaction time from 30 to 90 min with intervals of 15 min. Figure 1 shows the effect of the

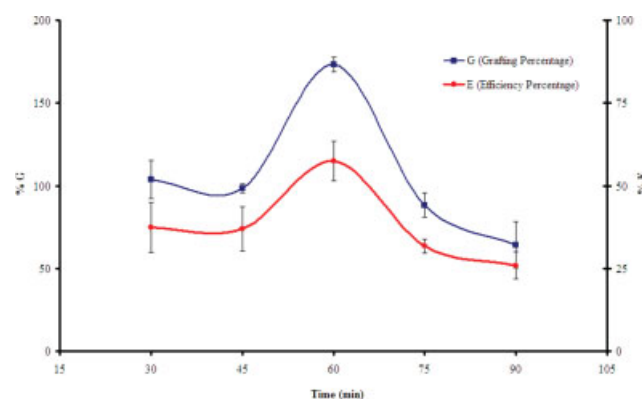


Figure 1 Effect of the reaction time on the grafting percentage (*G* %) and efficiency percentage (*E* %). The reaction conditions were as follows: reaction temperature, 50°C; MMA, 47.15 mmol; H₂O₂, 3.92 mmol; and Fe²⁺, 0.262 mmol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

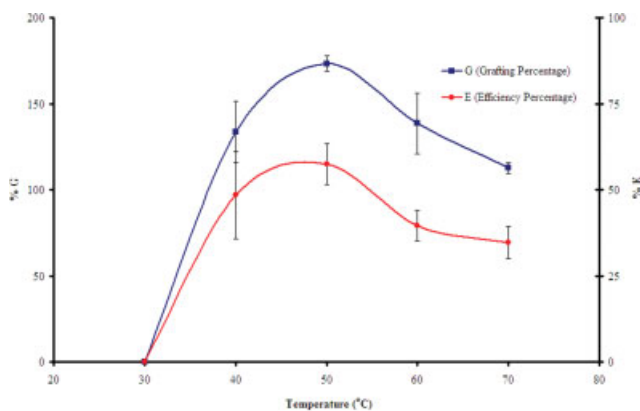


Figure 2 Effect of the reaction temperature on the grafting percentage (G %) and efficiency percentage (E %). The reaction conditions were as follows: reaction time, 60 min; MMA, 47.15 mmol; H₂O₂, 3.92 mmol; and Fe²⁺, 0.262 mmol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reaction time on the grafting and efficiency percentages. At the early stage of the copolymerization, both the grafting and efficiency percentages were relatively constant. The reaction started to take place after 45 min. Once the reaction took place, the percentage of grafting increased rapidly and decreased thereafter. The highest amount of grafting occurred with a reaction time of 60 min, with grafting and efficiency percentages of 173 and 57%, respectively. The initial increment in the grafting level with the reaction period increasing might be due to the increase in the number of active sites¹⁶ and the increase in the extension of initiation and propagation with time.¹² However, the retardation of diffusion after some polymer formed on the fiber surface and the decrease in the monomer and initiator with increasing time were the reasons for the reduction of the grafting percentage and grafting efficiency.^{17,18} The reduction also may have been due to the degradation of the grafted chain on the fiber.¹⁹ The degradation can be explained by the chain scission of the growing grafted copolymer, which probably takes place at a low temperature for a longer reaction time.

Effect of the reaction temperature

Radical copolymerization requires a thermal decomposition step for the initiator.¹⁹ This leads to the fact that the reaction temperature must be properly selected for the decomposition of the initiator to produce free radicals. The graft copolymerization was carried out from 30 to 70°C, and the results are shown in Figure 2. The graft copolymerization did not take place at reaction temperatures below 30°C. A similar observation was reported by Khan and

Ahmad.⁹ This takes into consideration the fact that peroxide initiators are known to be stable and remain inactive below 30°C. The radical copolymerization reaction started only when the initiator thermally decomposed into free radicals.¹² The decomposition rate of H₂O₂ was accelerated at a higher temperature, so more reactive sites were generated on the OPEFB and thus the initiation and propagation rates of grafting were also accelerated. Both the percentage of grafting and the efficiency increased rapidly with an increase in the reaction temperature from 40 to 50°C. When the maximum level of grafting was reached at 50°C, the grafting and efficiency percentages decreased with a further increase in the temperature. The reduction of both the grafting and efficiency percentages indicated that the increase of the homopolymer surpassed the formation of the copolymer. Because the free radicals are available in large amounts at higher temperatures, premature terminations of growing grafted chains can easily take place and restrict the formation of long chains of grafted copolymers.¹⁵ As a result of this termination, the excess free radicals actively attack the living monomers, thereby leading to an increase in homopolymer formation. This result is also in agreement with observations reported by other researchers.²⁰

Effect of the monomer concentration

The monomer concentration in the solution is one of the reaction parameters for grafting. It influences the graft copolymerization by adjoining the required number of monomer units onto the polymer chain during the reaction. To analyze the effect of the monomer concentrations, the concentrations of the initiator and metal salts were kept constant at 3.92 and 0.262 mmol, respectively. The reaction was carried out at 50°C for 60 min. The trend was plotted against the monomer concentration, as shown in Figure 3. The results show that there was no copolymerization reaction occurring at low MMA concentrations. However, the grafting percentage drastically increased with the addition of 47.15 mmol of MMA into the aqueous solution. This may be the result of an easy accumulation of the monomer in close proximity to the polymer backbone. The monomer molecules that are in the immediate vicinity of reaction sites become acceptors of cellulose radicals, resulting in chain initiation.¹⁸ Even though further additions of MMA increased the grafting percentage, the grafting efficiency remained unchanged. This may have occurred because the formation rates of the homopolymer and grafted copolymer caused by radicals were comparable. Therefore, the optimum monomer concentration was found to be 47.15 mmol of MMA.

Effect of the initiator concentration

The effect of the initiator concentration on the grafting yield was studied through the variation of the H_2O_2 concentration from 1.959 to 7.836 mmol. Figure 4 shows that the percentage of grafting and efficiency increased up to 3.92 mmol and then decreased thereafter. The increase in grafting was attributed to the increase in free radicals with an increasing initiator concentration, which could create microradicals at various sites on the backbone of OPEFB to which PMMA could be grafted. The decrease in the percentage of grafting and efficiency after 3.92 mmol may have been due to the enhanced rate of premature terminations of growing grafted chains and the formation of the homopolymer, as discussed previously in the Effect of the Reaction Temperature section.

Graft copolymerization mechanism

Graft copolymerization mechanisms of a vinyl monomer onto fibers with the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ redox initiation technique have received much attention.^{11,12,18,21} However, most authors have not thoroughly described the termination step of free-radical mechanisms. The termination mechanism scheme, therefore, is proposed in this article to give an idea of how the termination step takes place during the reaction. The grafting mechanism of OPEFB with MMA, including initiation, propagation, and termination steps, is as follows.

Initiation

In the initiation step, H_2O_2 (without the presence of Fe^{2+} salts) decomposes as follows:

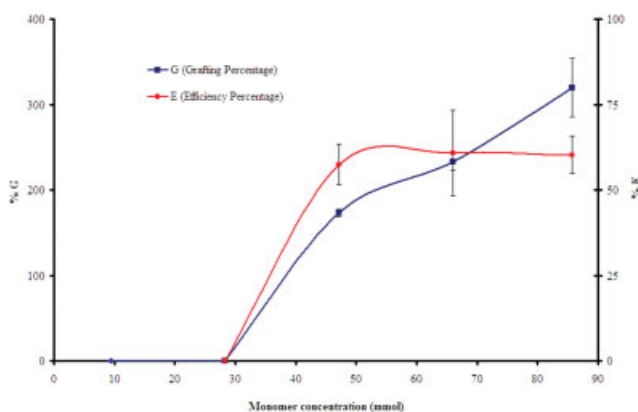


Figure 3 Effect of the monomer concentration on the grafting percentage ($G\%$) and efficiency percentage ($E\%$). The reaction conditions were as follows: reaction temperature, 50°C ; reaction time, 60 min; H_2O_2 , 3.92 mmol; and Fe^{2+} , 0.262 mmol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

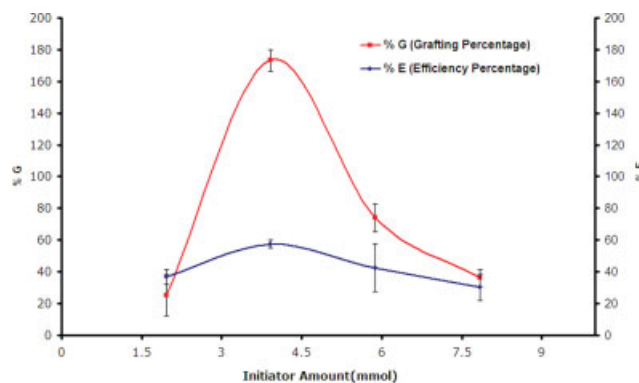
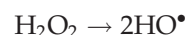


Figure 4 Effect of the initiator concentration on the grafting percentage ($G\%$) and efficiency percentage ($E\%$). The reaction conditions were as follows: reaction temperature, 50°C ; reaction time, 60 min; MMA, 47.15 mmol; and Fe^{2+} , 0.262 mmol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



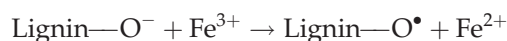
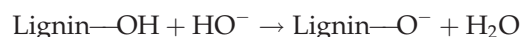
However, this decomposition of H_2O_2 occurs slowly, and ferric ion as a redox initiator pair has been suggested for enhancing the decomposition rate of H_2O_2 .²² Moreover, Fe^{2+} is able to convert hydroxyl radicals into hydroxyl ions.¹⁵ The initiation step in the presence of Fe^{2+} used in this study is as follows:



Some hydroxyl radicals generated during the initiation step (reaction 4) probably will not convert into hydroxyl ions and instead start polymerization.¹⁹ The hydroxyl radical from this step attacks cellulose to produce a macroradical of cellulose:

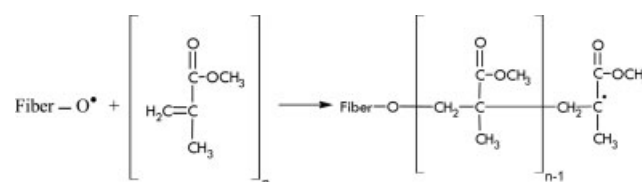


In the case of lignocellulosic material, a hydroxyl ion is wisely used with lignin to produce a macroradical of lignin:



Propagation

In the propagation step, both cellulosic backbone radicals and lignin backbone phenolic radicals produced during the initiation are in contact with the MMA monomers:



Fiber—O• denotes both cellulose and lignin radicals, and n indicates the number of repeating monomer chains.

Termination

This step is very important because it determines the length of the grafted copolymer, thus determining the level of grafting. Figure 5 shows the termination mechanism of these macroradicals.

A macroradical in a growing grafted polymer chain has three main possibilities for reaction termination: modes I, II, and III. In mode I, the growing grafted polymer chain undergoes a crosslinking reaction with an adjacent growing grafted polymer chain. This mode of termination does not affect the level of grafting. In mode II, a premature termination occurs when the macroradical growing polymer chain is grafted with a hydroxyl radical (free radical). As discussed earlier in the sections on the reaction temperature and initiator concentration, the generation of a large number of free radicals at a higher reaction temperature and initiation concentration increases the ability of premature termination to occur when the excess free radicals are prone to attack living monomers rather than the microradicals growing grafted polymer. Therefore, the grafting reaction decreases after reaching an optimum reaction temperature of 50°C, even though the temperature is increased up to 70°C. The macroradical growing grafted polymer chain is also terminated when free radicals come into contact with growing homopolymer radicals, as in mode III. A shorter grafted polymer chain length is produced from immediate termination by hydroxyl radicals (mode II), whereas a longer grafted copolymer chain length may be the result of termination with growing homopolymer radicals (mode III).

Figure 6 also shows that the growing grafted polymer chain contains a pendent double bond. Based on a model suggested by previous researchers,¹⁵ a

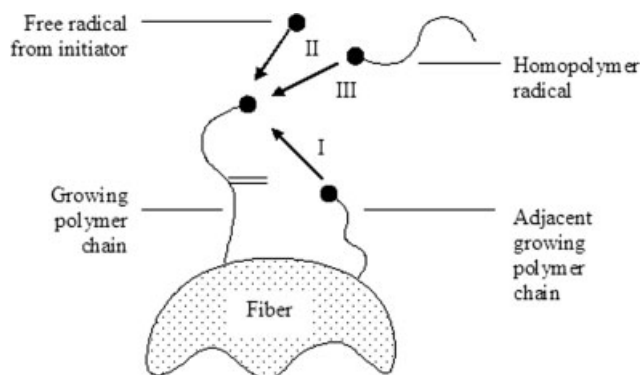


Figure 5 Model of the termination of the macroradicals.

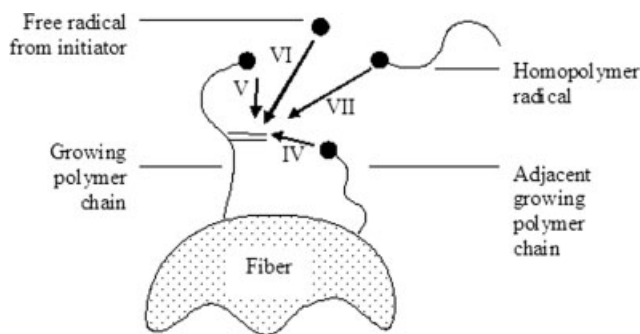


Figure 6 Model of the termination of the pendent double bond of the polymer.

proposed model of termination of pendent double bonds is shown in Figure 6.

This pendent double bond has five possibilities of reaction (modes IV, V, VI, VII, and VIII). In mode IV, the growing grafted polymer chain undergoes a crosslinking reaction with an adjacent growing grafted polymer chain. The termination of the growing grafted polymer chain may also occur by a cyclization reaction, as shown in mode V. In mode VI, this pendent double bond may react with radicals in bulk, whereas in mode VII, there is a termination reaction with growing homopolymer radicals. For mode VIII (not shown in the diagram), the pendent double bond may remain unchanged, allowing termination to take place according to mode I, II, or III. If double bonds react in accordance with modes IV, V, and VIII, the grafting yields are unchanged, whereas modes VI and VII result in an increased amount of the growing grafted polymer chain connected to the substrate and thus an increase in the grafting yield. Another interesting aspect of the termination step is probably the capacity of this growing grafted polymer chain for scission. Chain scission occurs as a result of exposing macroradicals for long periods even at lower temperatures. This leads to the reduction of the grafting percentage and grafting efficiency, as shown in Figure 1.

FTIR analysis

The presence of PMMA on the fiber was verified by FTIR spectra of OPEFB and PMMA-g-OPEFB, as shown in Figure 7. Both spectra show a characteristic absorption band of the hydroxyl group around 3500–3100 cm^{-1} . This is attributed to OH stretching vibrations of cellulose, absorbed water, hemicellulose, and lignin constituents of OPEFB. The absorption band within this range changed with the amount of grafting.¹⁰ The reduction of the hydroxyl broad absorption band in PMMA-g-OPEFB reveals that grafting successfully took place at the hydroxyl group shown in Figure 7. The presence of the peak near 1730 cm^{-1} in the OPEFB spectrum could be

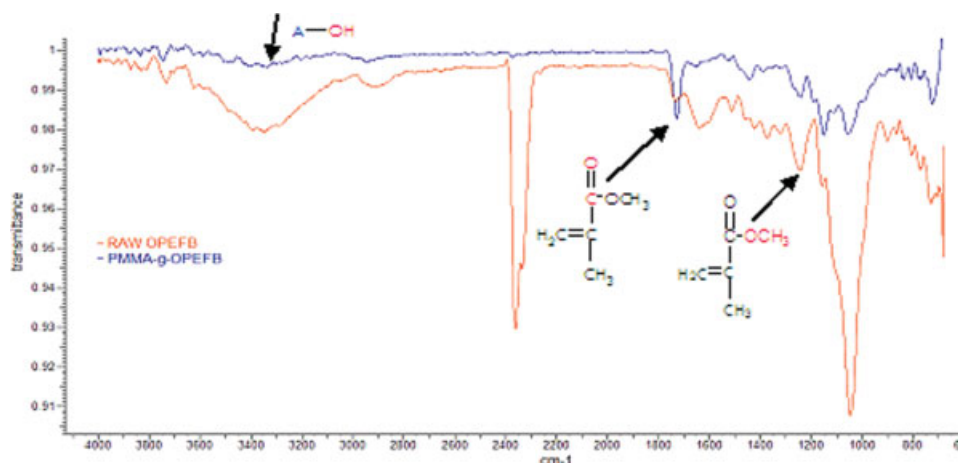


Figure 7 FTIR spectra of OPEFB and PMMA-g-OPEFB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

associated with C=O stretching of carboxyl groups in hemicellulose and lignin of OPEFB. The increase in the intensity of the C=O peak in the spectrum of PMMA-g-OPEFB indicates the presence of an ester group from MMA, providing strong evidence of PMMA grafted onto OPEFB. The increment of the intensity at a peak near 1251 cm^{-1} in the PMMA-g-OPEFB spectra may be associated with the CO—OCH₃ stretching of PMMA. This result also shows the presence of MMA functional groups in OPEFB and is in agreement with a previous report.¹²

TGA

TGA is the simplest accurate method for analyzing the thermal stability of polymers. Figures 8 and 9 show the TG and differential thermogravimetry (DTG) curves for OPEFB and PMMA-g-OPEFB, respectively.

As shown in Figure 8, the initial weight loss from 30 to 100°C was caused by the dehydration of the fiber. OPEFB and PMMA-g-OPEFB lost their weight because of the devolatilization of moisture (ca. 9.8 and 3%, respectively). The TG curve for OPEFB (in Fig. 8) shows that there were three main steps of weight loss in the range of 195–635°C. The thermal degradation of OPEFB was due to the decomposition of hemicellulose, lignin, and cellulose, which gave off volatiles. The pyrolysis of OPEFB took place initially in the hemicellulose part, which was followed by lignin and cellulose, at 207, 223, and 234°C, respectively.²³

The TG curve of PMMA-g-OPEFB (Fig. 8) reveals that only one stage of degradation occurred in the temperature range of 234–465°C with a weight loss of 85 wt %. However, from the corresponding DTG (Fig. 9), this one stage of degradation actually

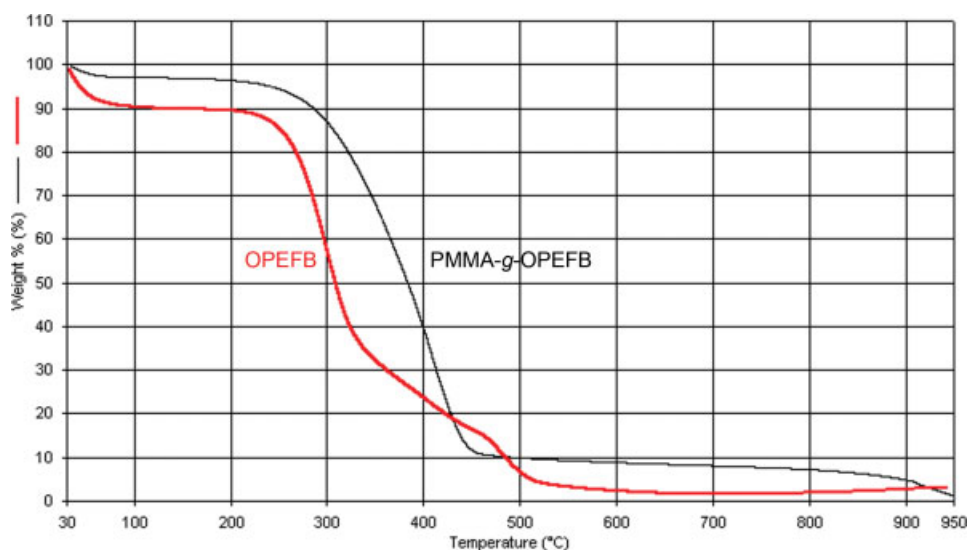


Figure 8 TG curves of OPEFB and PMMA-g-OPEFB (grafting percentage = 173%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

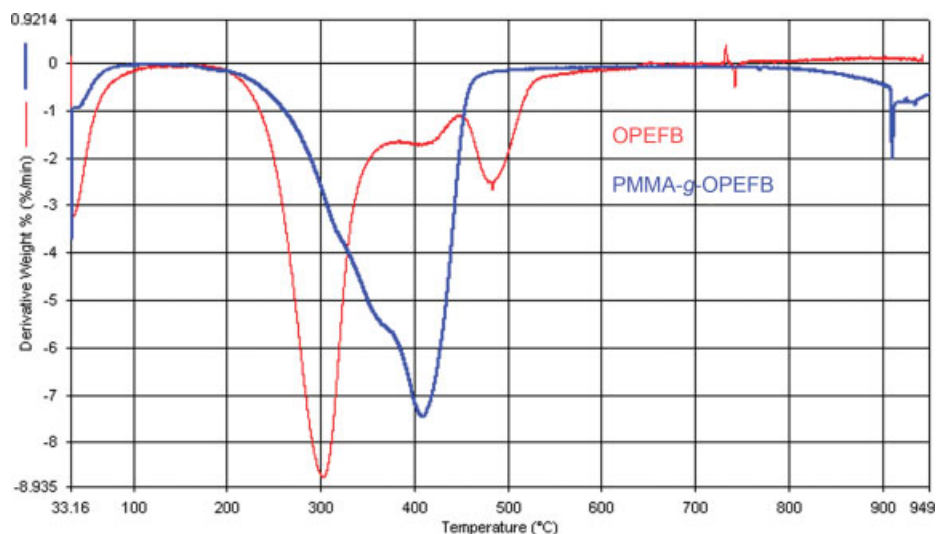


Figure 9 DTG curves of OPEFB and PMMA-g-OPEFB (grafting percentage = 173%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

consisted of two stages; the first stage (235–380°C) corresponded to PMMA.²³ As a grafted copolymer, PMMA should be initially subjected to heat during pyrolysis because it envelops the OPEFB surface (Figs. 10 and 11). The second stage can be attributed to the pyrolysis of hemicellulose, lignin, and cellulose of OPEFB, accordingly.

Table I compares the degradation temperatures at 20% weight loss for the ungrafted and grafted OPEFBs. The thermal stability of the fiber increased with grafting with PMMA. The degradation temperature of PMMA-g-OPEFB fiber was 55°C higher than that of OPEFB. A comparison of the decomposition resistance of PMMA-g-OPEFB and OPEFB is also provided in Figures 8 and 9. Both figures prove that PMMA-g-OPEFB had better thermal stability than OPEFB. This was due to the fact that PMMA enveloped the OPEFB surface with the grafting copolymerization technique. The grafted copolymer acted as an

insulative carbonaceous char barrier on the surface, thus inhibiting early degradation.⁹ Therefore, PMMA-g-OPEFB had better thermal stability than OPEFB.

SEM analysis

Figures 10 and 11 show SEM micrographs of ungrafted and grafted OPEFB fiber surfaces, respectively. Striking differences can be easily observed on the surfaces of the ungrafted and grafted OPEFB fibers. The surface of the grafted OPEFB was almost covered by PMMA after the grafting process. This shows that PMMA was attached to the fiber as it was chemically bonded.

CONCLUSIONS

The graft copolymerization of PMMA onto OPEFB was successfully carried out by free radicals with

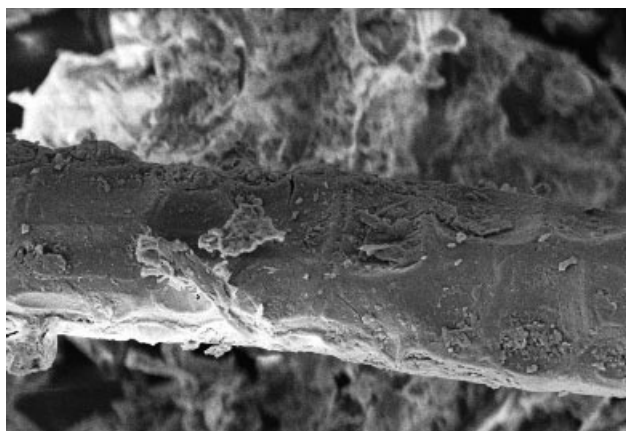


Figure 10 SEM micrograph of ungrafted OPEFB ($\times 1000$).

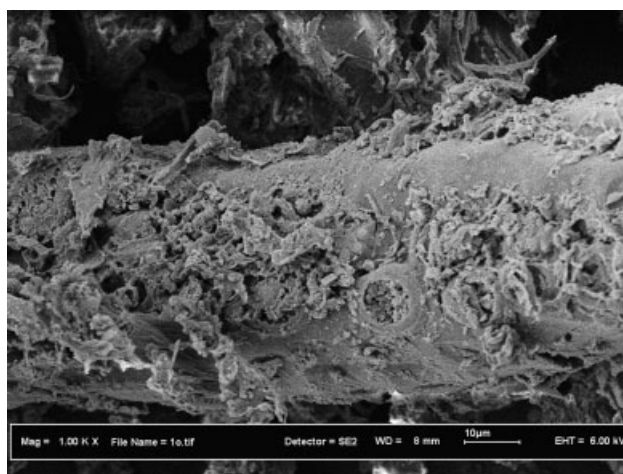


Figure 11 SEM micrograph of OPEFB-g-PMMA ($\times 1000$).

TABLE I
Thermal Degradation Temperature at 20% Weight Loss

Material	Degradation temperature (°C)
OPEFB	265
PMMA-g-OPEFB	320

H₂O₂ and ferrous ions as a redox initiator/cocatalyst system. The grafting level and efficiency were dependent on the reaction time, reaction temperature, and monomer concentration. The optimum reaction time, reaction temperature, monomer concentration, and initiator concentration were 60 min, 50°C, 47.15 × 10⁻³ mol, and 3.92 × 10⁻³ mol, respectively. The shortest optimum reaction time was achieved in comparison with previous results reported by other researchers.¹² The maximum percentage of grafting (173%) was achieved when the reaction was carried out under these optimum conditions. The presence of PMMA on the OPEFB fiber surface was confirmed by FTIR spectra, TG and DTG curves, and SEM micrographs. The PMMA-g-OPEFB fibers had better thermal resistance than OPEFB.

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