

# Graft Copolymerization of Methyl Methacrylate onto Rubber-Wood Fiber Using H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> as an Initiator System

Faraj A. Abu-Ilaiwi,<sup>1</sup> Mansor B. Ahmad,<sup>1</sup> Nor Azowa Ibrahim,<sup>1</sup> Mohamad Zaki Ab. Rahman,<sup>1</sup> Khairul Zaman Md. Dahlan,<sup>2</sup> Wan Md. Zin Wan Yunus<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia

<sup>2</sup>Malaysian Institute for Nuclear Technology Research (MINT), Bangi, 43000 Kajang, Malaysia

Received 1 April 2002; accepted 29 August 2002

**ABSTRACT:** Methyl methacrylate (MMA) was successfully grafted onto rubber-wood fiber in a free-radical solution polymerization initiated by ferrous ion and hydrogen peroxide. The effects of the reaction parameters (reaction temperature, reaction period, influence of hydrogen peroxide, ferrous ammonium sulfate, and monomer concentrations) were investigated. The grafting percentage showed dependency on H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, and monomer concentrations, as well as reaction temperature and reaction period. The optimum reaction temperature was determined to be about

60°C and the reaction period was 60 min. The optimum concentration of H<sub>2</sub>O<sub>2</sub> was 0.03M and optimum amounts of Fe<sup>2+</sup> and MMA were 0.26 mmol and 2.36 × 10<sup>-2</sup> mol, respectively. Poly(methyl methacrylate) (PMMA) homopolymer was removed from the graft copolymer by Soxhlet extractor using acetone. The presence of PMMA on the fiber was shown by FT-IR spectroscopy and gravimetric analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2499–2503, 2003

**Key words:** graft copolymers; rubber fibers; initiators

## INTRODUCTION

Cellulose or poly(1→4,β-D-anhydroglucose) is one of the oldest and most abundant polymers on the earth. It is biodegradable, renewable by direct fixation of solar energy by plants, and can be derivatized to yield various useful products.<sup>1</sup> It is a major constituent of many natural fibers such as cotton and jute. Its main source, however, is wood where cellulose is in combination with hemicellulose and lignin in a texture, which represents a masterpiece of natural architecture. Rubber-wood (a standard name for the timber of *Hevea brasiliensis*) is a natural polymer that has gained special importance because it is cheap and plentiful. Chemical compositions of this wood showed that its main components are cellulose (67.0%) and lignin (26.0%).<sup>2</sup> The properties of cellulose may be modified and improved by both physical and chemical methods. In the last few decades, the graft copolymerization technique on natural lignocellulosic materials has gained importance in modifying the physical and chemical properties.<sup>3</sup> Modification of cellulose by graft copolymerization techniques allows one to chemically change the cellulose chain by introducing

polymeric chains that confer different structural characteristics to the initial material, which has led to new cellulosic products with improved or new properties.

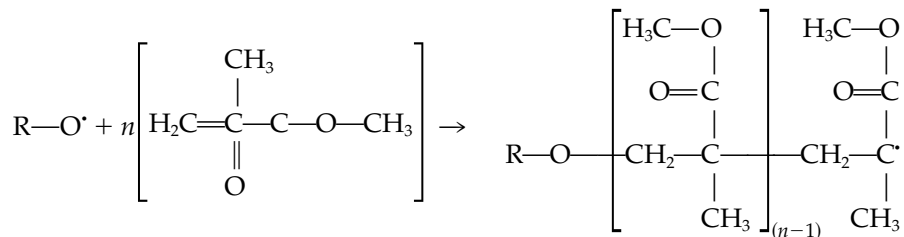
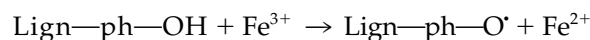
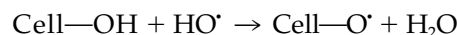
Graft copolymerization initiated by free radicals formed onto cellulose or lignocellulosic materials by chain transfer, high-energy irradiation, or redox systems were previously reviewed in the literature.<sup>4–10</sup> However, this investigation is the first work reported of grafting of poly(methyl methacrylate) (PMMA) onto rubber-wood fiber (RWF).

## EXPERIMENTAL

### Materials

RWF, obtained from Merbok MDF Sdn. Bhd. (Kedah, Malaysia) after it was ground and steamed at 170°C, was boiled with distilled water for 3 h three times to remove dust and any other water-soluble impurities. Methyl methacrylate (MMA) monomer (Fluka Chemie, Buchs, Switzerland) was purified by passing through an activated alumina column. Hydrogen peroxide was purchased from Riedel-de Haën (Seelze, Germany). Ammonium ferrous sulfate, an analytical-grade reagent, was obtained from BDH (Poole, UK) and used as received. Acetone and other chemicals used were all analytical grade.

Correspondence to: F. Abu-Ilaiwi (faraj\_ah@hotmail.com).



where R is Cell or Lign—ph

**Scheme 1** Proposed mechanism of graft copolymerization of poly(methyl methacrylate) onto rubber-wood fiber using  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  initiator (Cell—OH is cellulose and Lign—ph—OH is the phenolic hydroxyl group of lignin).

### Graft copolymerization

The graft copolymerization was carried out under nitrogen atmosphere in a 250-mL two-neck flask. About 1.0 g of RWF (size < 2.36 mm) was placed in the flask. Exactly 100 mL of dilute  $\text{H}_2\text{O}_2$  (at the chosen concentration) and specified quantity of ammonium ferrous sulfate were added. The mixture was stirred at the selected temperature in a water bath for 15 min under nitrogen atmosphere. To start the copolymerization reaction, a specified amount of monomer was added. After a chosen time interval, the homopolymer and the grafted fabric sample were filtered, washed with distilled water several times, and dried in an oven at  $60^\circ\text{C}$  to a constant weight. Finally, the sample was extracted with acetone to remove the homopolymer and dried in the oven at  $60^\circ\text{C}$  and weighed. Extraction was repeated until a constant weight was achieved.

### Characterization of RWF-g-poly(methyl methacrylate)

The presence of the MMA on the RWF was studied by FT-IR spectroscopy. The infrared spectra was recorded by Perkin-Elmer FTIR spectrophotometer (1600 series; Perkin Elmer Cetus Instruments, Norwalk, CT) using potassium bromide disk technique.

### Determination of graft level

The graft percentage (G%) was calculated as follows:

$$\text{Graft percentage (G\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where  $W_1$  and  $W_2$  denote the weights of initial RWF and purified grafted RWF, respectively.

## RESULTS AND DISCUSSION

### Graft copolymerization

Graft copolymerization of MMA onto rubber-wood fiber was carried out in a heterogeneous reaction by treating RWF with  $\text{H}_2\text{O}_2$  and ferrous ammonium sulfate solution, followed by addition of the monomer into the reaction mixture. **Scheme 1** shows the grafting mechanism of cellulose with methyl methacrylate using  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  as initiator.

### FT-IR spectroscopy

FT-IR spectra of rubber-wood fiber and RWF-g-poly(MMA) are shown in Figure 1. Broad and strong absorption bands in the  $3500\text{--}3100\text{ cm}^{-1}$  region in both spectra correspond to OH stretching vibrations of cellulose, absorbed water, hemicellulose, and lignin,<sup>11</sup> aliphatic primary and secondary alcohols found in cellulose, hemicellulose, lignin, and carboxylic acids in extract<sup>12</sup> constituents of rubber-wood fiber. The presence of the peak near  $1730\text{ cm}^{-1}$  in the RWF spectra could be associated with carbonyl (C=O) stretching vibration of carboxyl groups in hemicellulose and lignin<sup>12</sup> in rubber-wood fiber. The absorption bands in the  $1600\text{--}1400\text{ cm}^{-1}$  region in the RWF spectra may be attributed to the presence of aromatic or benzene rings in lignin.<sup>12</sup> The vibrations near  $1400\text{--}1300\text{ cm}^{-1}$  could be attributable to aliphatic and aromatic (C—H) in the plane deformation vibrations of methyl, methylene, and methoxy groups in wood.<sup>13</sup> The bands in the region  $1300\text{--}1000\text{ cm}^{-1}$  involve the (C—O) stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose, lignin, and primary and secondary aromatic alcohols in lignin.<sup>12</sup> In the grafted polymer a sharp and strong peak observed at  $1730\text{ cm}^{-1}$  refers to the carbonyl (C=O) group in MMA.

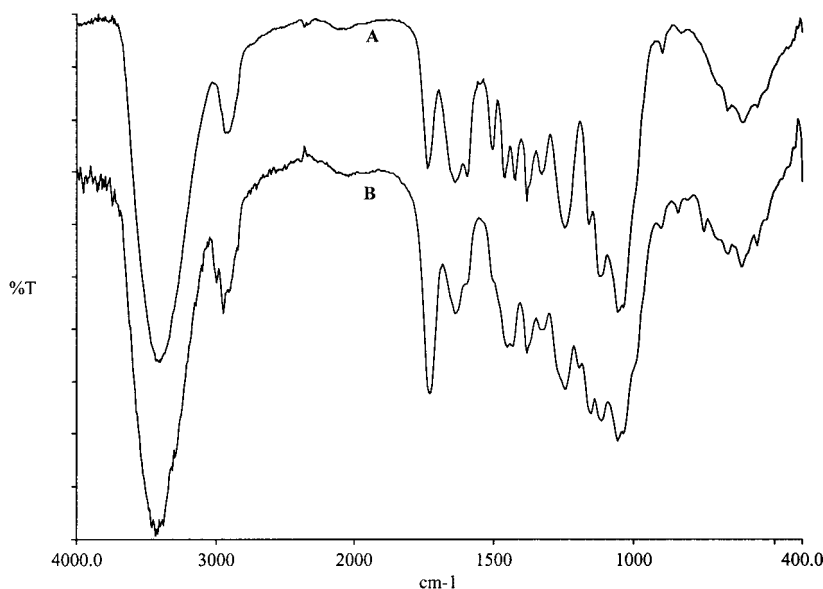


Figure 1 FT-IR spectra of rubber-wood fiber (RWF) (A) and RWF-g-PMMA (B).

Moreover, a new band at  $843\text{ cm}^{-1}$  can be seen from Figure 1(B), which indicates (C—H) stretching vibrations in MMA.<sup>14</sup>

#### Effect of reaction temperature

The graft copolymerization of MMA onto rubber-wood fiber was carried out from 30 to  $70^\circ\text{C}$  and the results are shown in Figure 2. It can be seen from the results that the  $G\%$  was increased with increasing of reaction temperature from 30 to  $60^\circ\text{C}$ . Further increasing of reaction temperature led to a decrease in grafting yield. Increase of the grafting percentage from 30 to  $60^\circ\text{C}$  could be attributable to (1) an increase in the number of the free radicals formed on the backbone, (2) an increase in the mobility of monomer molecules and their collision with backbone macroradicals, and (3) enhancement of diffusion of monomer and initiator onto the backbone structure.<sup>15</sup> Decrease of the  $G\%$

with the increase of reaction temperature after  $60^\circ\text{C}$  could result from (1) the increase of the radical termination or (2) the increase of termination of the polymeric chain.<sup>15</sup>

#### Effect of initiator concentration

Figure 3 shows the effect of the initiator ( $\text{H}_2\text{O}_2$ ) concentration on the graft percentage. It may be observed that the percentage of grafting increases with the increase of  $\text{H}_2\text{O}_2$  concentration up to  $0.03\text{M}$ , which could be the result of the increase in rate of grafting at low concentration of initiator.<sup>16</sup> Beyond this concentration, the grafting percentage decreases, which may result from the decay of the macroradicals by their reaction with the initiator and/or the increase of grafting rate at low initiator concentration. Then at higher concentration, the level of grafting achieved begins to decrease, which could be the result of (1) the decrease

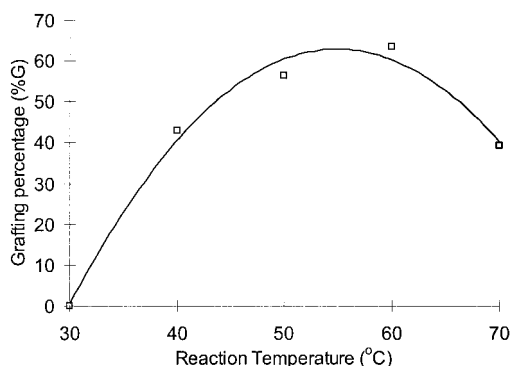


Figure 2 Effect of reaction temperature on grafting. Reaction conditions: RWF: 1.0 g;  $\text{Fe}^{2+}$ , 0.26 mmol; MMA,  $1.88 \times 10^{-2}$  mol; reaction time, 60 min.

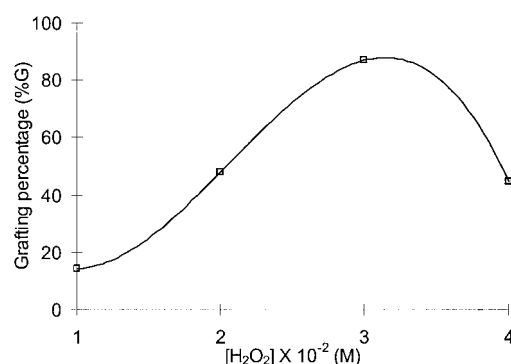
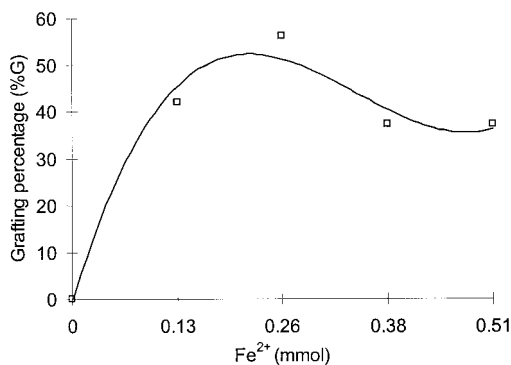


Figure 3 Effect of  $\text{H}_2\text{O}_2$  concentration on grafting. Reaction conditions: RWF, 1.0 g;  $\text{Fe}^{2+}$ , 0.26 mmol; MMA,  $1.88 \times 10^{-2}$  mol; reaction time, 60 min; reaction temperature,  $60^\circ\text{C}$ .



**Figure 4** Effect of  $\text{Fe}^{2+}$  concentration on grafting. Reaction conditions: RWF, 1.0 g;  $[\text{H}_2\text{O}_2]$ ,  $6 \times 10^{-2} \text{ M}$ ; MMA,  $1.88 \times 10^{-2} \text{ mol}$ ; reaction time, 60 min; reaction temperature,  $60^\circ\text{C}$ .

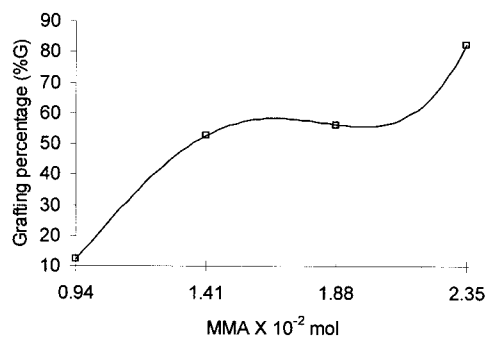
in the rate of polymerization at high initiator concentration and/or (2) the increase of homopolymer formation.<sup>14</sup> However, Nonaka et al.<sup>17</sup> used a higher concentration of  $\text{H}_2\text{O}_2$  when they grafted vinyl monomers, bearing positive charge or episulfide groups such as tributyl-4-vinylbenzylphosphonium chloride (TBVB) and methacryloyloxy-ethyl trimethyl ammonium chloride (METAC), onto Loofah fibers.

#### Effect of $\text{Fe}^{2+}$ amount

The graft percentage increases with the increase of the  $\text{Fe}^{2+}$  amount up to 0.26 mmol; beyond this amount, the graft percentage starts to decrease and then levels off. The results are shown in Figure 4. The reason for increasing of graft percentage for the amount of  $\text{Fe}^{2+}$  up to 0.26 mmol could be explained that, as the amount of  $\text{Fe}^{2+}$  is increased, more  $\text{Fe}^{2+}$  ions are available to react with  $\text{H}_2\text{O}_2$  to produce  $\text{Fe}^{3+}$  and hydroxyl radicals, which then attack lignocellulose to produce macroradicals. Produced  $\text{Fe}^{3+}$  may then react with the phenolic hydroxyl group of lignin to produce phenolic radicals and ferrous ion<sup>18</sup> (Scheme 1). The decrease in graft percentage at high concentration of  $\text{Fe}^{2+}$  is probably the result of the decrease of the initiating free radicals, attributed to the mutual combination.<sup>17</sup>

#### Effect of monomer amount

Graft copolymerization of RWF with various MMA concentrations was carried out at  $60^\circ\text{C}$  for 1 min. It was observed that the degree of grafting increased as the monomer amount was increased in the grafting reaction, reaching 82.4% at  $2.36 \times 10^{-2} \text{ mol}$  of MMA, as shown in Figure 5. The increase of grafting percentage may be a consequence of the increased grafting rate<sup>19</sup> and the gel effect.<sup>20</sup>



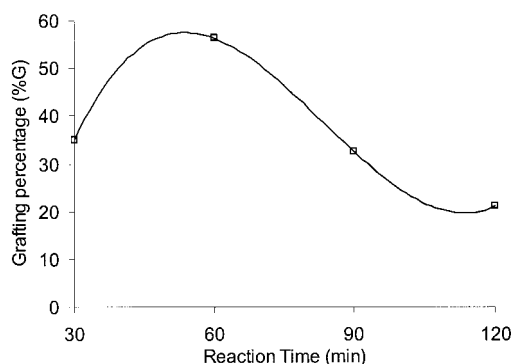
**Figure 5** Effect of monomer concentration on grafting. Reaction conditions: RWF, 1.0 g;  $[\text{H}_2\text{O}_2]$ ,  $6 \times 10^{-2} \text{ M}$ ;  $\text{Fe}^{2+}$ , 0.26 mmol; reaction time, 60 min; reaction temperature,  $60^\circ\text{C}$ .

#### Effect of reaction period

The effect of reaction period on the grafting percentage is shown in Figure 6. The highest graft percentage was 56.3% when the reaction period was 60 min. From the results, it is observed that the percentage of grafting increases with the increase of the reaction period from 30 to 60 min. This is attributed to the increase of the extent of initiation and propagation of the graft copolymerization with time.<sup>21</sup> However, beyond 60 min, the graft percentage decreases and levels off, which may be attributed to the decrease in monomer and initiator concentrations and retardation of diffusion when polymer formed on the RWF surface.<sup>22</sup> It also could be attributable to the decrease in the number of sites available for grafting.<sup>14</sup>

## CONCLUSIONS

PMMA was successfully grafted onto rubber-wood fiber by using the  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  initiator system. The optimum reaction conditions were as follows: reaction temperature,  $60^\circ\text{C}$ ; concentration of  $\text{H}_2\text{O}_2$ , 0.03M; amount of  $\text{Fe}^{2+}$ , 0.26 mmol; monomer amount,  $2.36 \times 10^{-2} \text{ mol}$ ; reaction period, 60 min. The presence of



**Figure 6** Effect of reaction time on grafting. Reaction conditions: RWF, 1.0 g;  $[\text{H}_2\text{O}_2]$ ,  $6 \times 10^{-2} \text{ M}$ ;  $\text{Fe}^{2+}$ , 0.26 mmol; MMA,  $1.88 \times 10^{-2} \text{ mol}$ ; reaction temperature,  $60^\circ\text{C}$ .

PMMA on the grafted product was indicated by FT-IR spectroscopy and gravimetric analysis.

### References

1. Premamoy, G.; Rupali, G. *Eur Polym J* 2000, 36, 625.
2. Liew, K. C. M.S. Thesis, Universiti Putra Malaysia, 1998.
3. Eromosele, I. C.; Hamogadu, T. J. *J Appl Polym Sci* 1993, 50, 645.
4. Karlsson, J. O.; Henriksson, A.; Michalek, J.; Gatenholm, P. *Polymer* 2000, 41, 1551.
5. Karlsson, J. O.; Gatenholm, P. *Macromolecules* 1999, 32, 7594.
6. Rupali, G.; Premamoy, P. *J Appl Polym Sci* 1999, 74, 1623.
7. Focher, B.; Marzetti, A.; Marsano, E.; Conio, G.; Cosani, A.; Terbojevich, M. *J Appl Polym Sci* 1998, 67, 961.
8. Hebeish, A.; El-Hilw, Z. H. *J Appl Polym Sci* 1998, 67, 739.
9. Bianchi, E.; Marsano, E.; Ricco, L.; Rasso, S. *Carbohydr Polym* 1998, 36, 313.
10. Tan, Y.; Zhang, L.; Li, Z. *J Appl Polym Sci* 1998, 69, 879.
11. Premamoy, G.; Debaprasad, D.; Asish, K. S. *J Appl Polym Sci* 1998, 68, 1139.
12. Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T. *J Appl Polym Sci* 1997, 66, 1163.
13. Khan, M. A.; Ali, K. M. I.; Basu, S. C. *J Appl Polym Sci* 1993, 49, 1547.
14. Lutfor, R.; Sidik, S.; Wan, Md. Z.; Zaki, M. ab. R.; Mansor, B. A.; Jelas, H. *J Appl Polym Sci* 2000, 76, 516.
15. Abduel Majid, K. N.; Wan, Md. Z. W. Y.; Mansor, B. A.; Mohamad, Z. ab. R. *J Appl Polym Sci* 2000, 77, 2314.
16. Stannett, V. T.; McDowall, D. J.; Gupta, B. S. *Prog Polym Sci* 1982, 10, 1.
17. Nonaka, T.; Noda, E.; Kurihara, S. *J Appl Polym Sci* 2000, 77, 1077.
18. Huang, Y.; Zhao, B.; Zheng, G.; He, S.; Gao, J. *J Appl Polym Sci* 1992, 45, 71.
19. Gao, J. P.; Tian, R. C.; Duan, M. L. *J Appl Polym Sci* 1994, 53, 1091.
20. Maji, T. K.; Banerjee, A. N. *J Appl Polym Sci* 1999, 73, 2187.
21. Shukla, S. R.; Rao, G. V.; Athalye, A. R. *J Appl Polym Sci* 1991, 42, 2163.
22. Kulkarni, A. Y.; Mehta, P. C. *J Appl Polym Sci* 1968, 12, 1321.