

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Photograft Copolymerization of Methyl Methacrylate (MMA) on Bleached Jute Fiber Using Ferric Sulfate, $\text{Fe}_2(\text{SO}_4)_3$, as Initiator in Limited Aqueous System

Premamoy Ghosh^a; Sankar Kumar Paul^a

^a Department of Plastics and Rubber Technology, Calcutta University, Calcutta, India

To cite this Article Ghosh, Premamoy and Paul, Sankar Kumar(1983) 'Photograft Copolymerization of Methyl Methacrylate (MMA) on Bleached Jute Fiber Using Ferric Sulfate, $\text{Fe}_2(\text{SO}_4)_3$, as Initiator in Limited Aqueous System', *Journal of Macromolecular Science, Part A*, 20: 2, 169 – 178

To link to this Article: DOI: 10.1080/00222338308069957

URL: <http://dx.doi.org/10.1080/00222338308069957>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photograft Copolymerization of Methyl Methacrylate (MMA) on Bleached Jute Fiber Using Ferric Sulfate, $\text{Fe}_2(\text{SO}_4)_3$, as Initiator in Limited Aqueous System

PREMAMOY GHOSH and SANKAR KUMAR PAUL

Department of Plastics and Rubber Technology
Calcutta University
Calcutta 700009, India

ABSTRACT

The polymerization of methyl methacrylate in the presence of bleached jute with $\text{Fe}_2(\text{SO}_4)_3$ as initiator under visible light was studied. In order to establish the optimum reaction conditions for graft copolymerization of MMA on bleached jute, the variables studied were copper number of bleached jute to give a measure of the degree of oxidation effected by bleaching (hypochlorite treatment), initiator concentration, monomer concentration, amount of bleached jute, and time of polymerization. The reaction mechanisms for graft copolymer and homopolymer formation are discussed. Percent total conversion, % grafting, and grafting efficiency (%) under different conditions are evaluated and compared. High grafting efficiency (~80%) along with high conversion (~80% in 2-3 h) and high % grafting were readily obtained.

INTRODUCTION

Jute fiber, an agricultural product, is facing tough competition from synthetic fibers as the latter often offer certain advantages in terms of many physical properties, durability, and production economics. Graft copolymerization of vinyl monomers on jute fiber has therefore been receiving considerable attention in recent years to incorporate desired properties. A few reports are available so far on modification of jute fiber by graft copolymerization of vinyl monomers. Roy [1] graft-copolymerized methyl methacrylate (MMA) and acrylonitrile (AN) on hollocellulose (delignified jute) using ceric-ion initiation and reported % grafting of 30% for MMA and 20% for AN. Jabbar [2] recently reported % grafting of 18.86% for defatted jute and 133.2% for bleached jute in graft copolymerization of MMA on defatted and bleached jute using ceric-ion initiation and showed that lower % grafting on defatted jute was due to a higher lignin content in defatted jute than in bleached jute. Efforts have also been made to modify jute fiber by graft copolymerization of vinyl monomers using ionizing radiation [3, 4]. Agarwal [5, 6] studied graft copolymerization of four vinyl monomers on jute fiber using gamma rays and reported % grafting of 86% for MMA, 83% for AN, 33% for vinyl acetate, and 53% for styrene. In most of the above reports, a low intake of vinyl monomers on jute was observed and very few studies have been made on graft copolymerization of vinyl monomers on jute fiber under visible light in the presence of an initiator. There remains wide scope for further investigations in this area. With a view to obtain high % grafting and grafting efficiency (%), we studied the graft copolymerization of MMA on bleached jute using $\text{Fe}_2(\text{SO}_4)_3$ as initiator under visible light in a limited aqueous system.

EXPERIMENTAL

Materials

Fresh jute fiber, supplied by Jute Technological Research Institute, Regent Park, Calcutta, was used. Monomer methyl methacrylate (MMA) was purified following a standard procedure [7]. $\text{Fe}_2(\text{SO}_4)_3$ (Riedel) was used. Sodium hypochlorite (NaOCl) was prepared in the laboratory following the procedure of Palmer [8]. All other ingredients used were of analytical grade.

Preparation of Bleached Jute

Fresh jute was extracted with an alcohol-benzene (1:1) mixture for 48 h at room temperature. The extracted jute is called "defatted jute."

Bleached jute was prepared from defatted jute according to the procedure of Roy [9] using NaOCl instead of sodium chlorite. Bleaching of jute was allowed to continue for different time periods (1, 2, 2.5, and 3 h) to obtain four bleached jute samples. The copper numbers of the bleached jute samples were determined using Braidy's method [10].

Graft Copolymerization

A weighed amount of bleached jute (~ 0.2 g) was taken in a Corning borosilicate glass test tube to which freshly prepared aqueous acidic (H_2SO_4) ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, a solution of known concentration was added, and the jute sample was allowed to soak for 20 min. The test tube and the contents were then flushed with purified nitrogen gas followed by addition of a known volume of MMA. The test tube was then stoppered tightly and placed between a pair of tube lamps (40 W, Philips India Ltd.), and polymerization was allowed to continue for specific time periods. The contents of the test tube were then filtered on a previously weighed sintered bed crucible under suction, washed profusely with water, and then dried at 50°C under vacuum to constant weight. The dried polymer is called "gross polymer."

The gross polymer was then extracted with benzene under reflux conditions to remove free polymethyl methacrylate (PMMA). The apparent graft copolymer in the residue containing true graft copolymer (jute/PMMA) and unreacted jute was then subjected to acid (72% H_2SO_4) hydrolysis in the cold to separate the grafted PMMA according to the procedure described earlier [11]. Percent grafting, % total conversion, and grafting efficiency (%) were then calculated [11].

RESULTS AND DISCUSSION

The results are shown in Table 1 and Figs. 1-5. The effect of varying the copper number of the bleached jute fiber, initiator concentration, monomer concentration, bleached jute fiber content, and time of polymerization on the grafting parameters were studied.

Effect of Variation of Copper Number of Bleached Jute Fiber

Treatment of jute with NaOCl yielded bleached jute through a process of oxidation whereby coloring matter and lignin were removed. At the same time, treatment with the oxidizing agent NaOCl is likely to bring about uncontrolled oxidation of the jute cellulose, producing mainly aldehyde groups ($-\text{CHO}$) on the C_2 - C_3 positions of the glucopyranose ring, giving rise to an enhanced copper number for the bleached jute fiber (Table 1).

TABLE 1. Oxidation (bleaching) of Jute with NaOCl Solution

Expt No.	Bleaching time (h)	Copper number by Braidy's method
1	0.0 (defatted jute without bleaching)	2.6
2	1.0	8.4
3	2.0	13.5
4	2.5	20.5
5	3.0	31.6

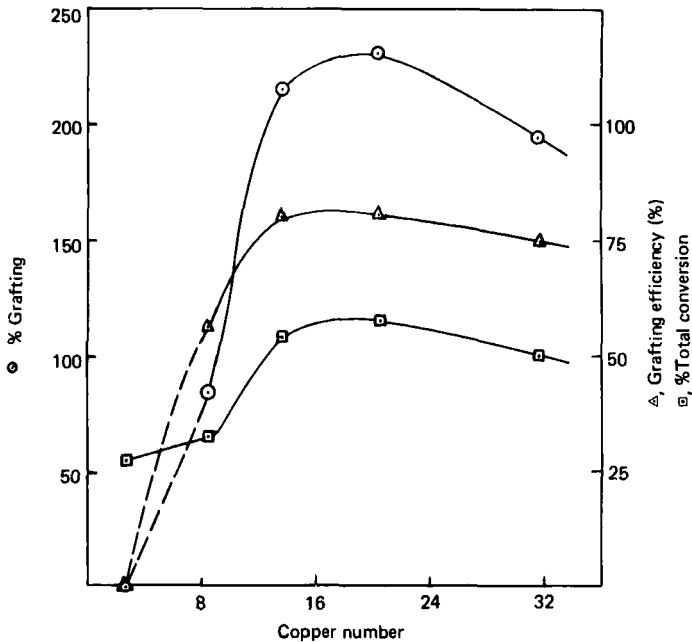


FIG. 1. Photograft copolymerization of MMA on bleached jute fiber at 32°C using $\text{Fe}_2(\text{SO}_4)_3$ as initiator. Effect of variation of copper number of bleached jute fiber on grafting parameters. Bleached jute fiber, 0.2 g; water, 5.5 mL; $[\text{Fe}_2(\text{SO}_4)_3]$, 1.56×10^{-3} mol/L; MMA, 1 mL; time, 120 min; total volume (liquid), 6.5 mL.

Results showing the effects of the variation of the copper number of the bleached fiber on the grafting parameters are presented in Fig. 1. Percent grafting increases with an increase in copper number up to a certain level (copper number = 20.5), the copper number of defatted unbleached jute being 2.6, and beyond this point it decreases. Percent total conversion and grafting efficiency also show a similar trend. The above observation on % grafting is in close agreement with Ghosh [11] and Todda [12]. A decreasing trend in % grafting for a given time in the higher range of copper number, i.e., at high -CHO contents in bleached jute cellulose, is probably due to a pronounced retarding effect of -CHO groups in highly oxidized samples.

Effect of Variation of Initiator, $\text{Fe}_2(\text{SO}_4)_3$, Concentration

Results showing the effect of variation of initiator concentration on the grafting parameters are presented in Fig. 2. Percent grafting and

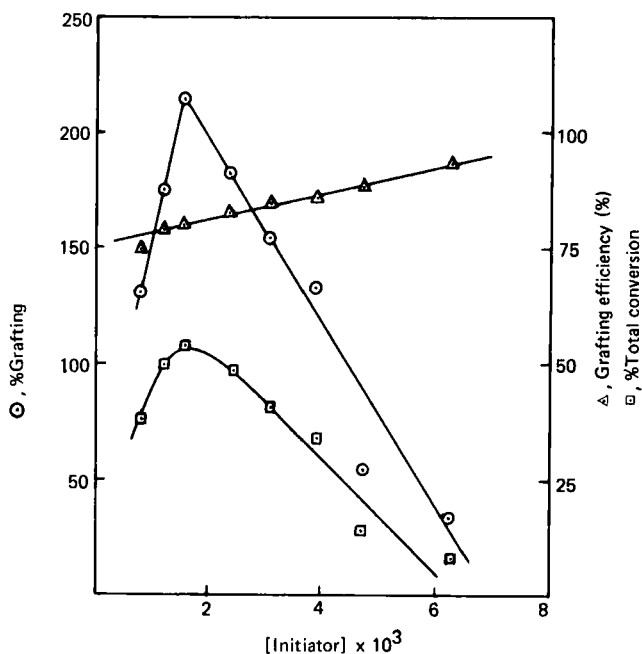


FIG. 2. Photograft copolymerization of MMA on bleached jute fiber at 32°C using $\text{Fe}_2(\text{SO}_4)_3$ as initiator. Effect of variation of $[\text{Fe}_2(\text{SO}_4)_3]$ on grafting parameters. Bleached jute fiber, 0.2 g; copper number, 20.5; water, 5.5 mL; MMA, 1 mL; time, 120 min; total volume (liquid), 6.5 mL.

% total conversion increase with an increase in $\text{Fe}_2(\text{SO}_4)_3$ concentration up to a certain point, $[\text{Fe}_2(\text{SO}_4)_3] \leq 1.5 \times 10^{-3}$ mol/L, and beyond this point both these parameters fall sharply. However, it is interesting to note that grafting efficiency follows an increasing trend with increasing $\text{Fe}_2(\text{SO}_4)_3$ concentration over the whole range of the initiator concentration studied. The above observation (both the % grafting and % total conversion curves passing through a maximum) can be reasonably understood on the basis of pronounced initiator (ferric) termination, particularly at high $[\text{Fe}^{3+}]$ [13].

Effect of Variation of Monomer (MMA) Concentration

Related results are shown in Fig. 3. Percent grafting increases linearly and grafting efficiency remains more or less steady with an increase in monomer concentration. Percent total conversion also expectedly follows an increasing trend with an increase in the amount of monomer.

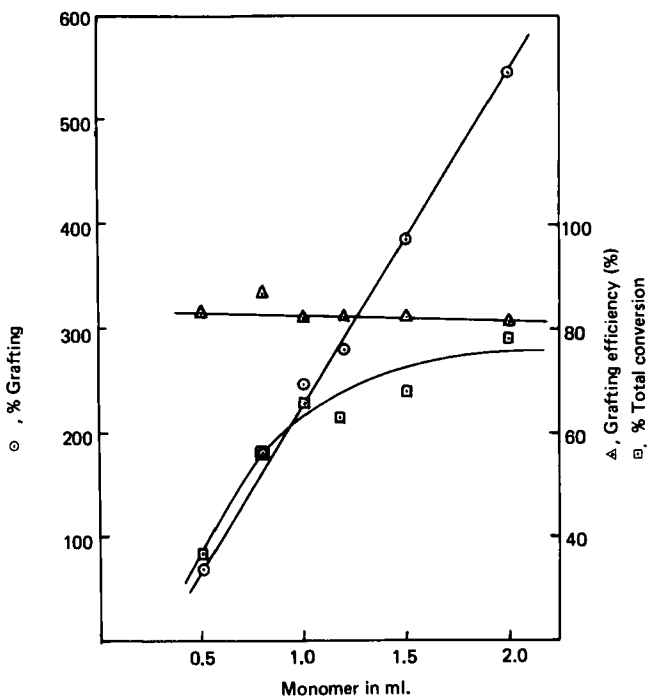


FIG. 3. Photograft copolymerization of MMA on bleached jute fiber at 32°C using $\text{Fe}_2(\text{SO}_4)_3$ as initiator. Effect of variation of MMA on grafting parameters. Bleached jute fiber, 0.2 g; copper number, 20.5; water, 5.5 mL; $[\text{Fe}_2(\text{SO}_4)_3]$, 1.56×10^{-3} mol/L; time, 120 min; total volume (liquid), 6.5 mL.

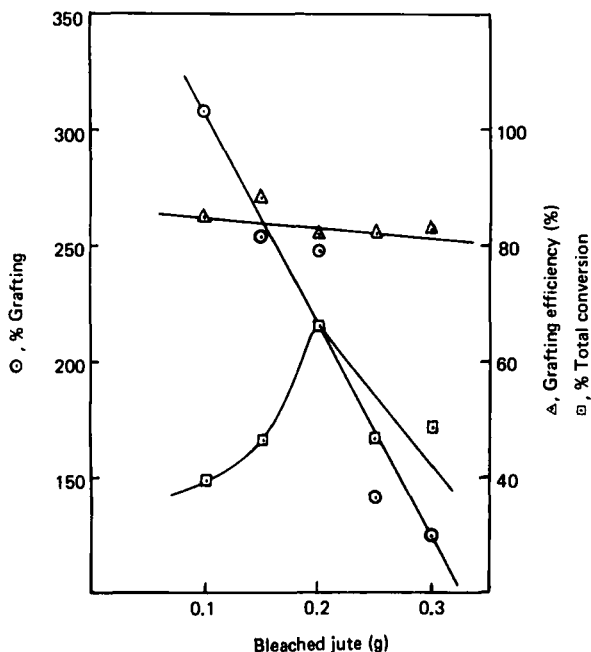


FIG. 4. Photograft copolymerization of MMA on bleached jute fiber at 32°C using $\text{Fe}_2(\text{SO}_4)_3$ as initiator. Effect of variation of bleached jute fiber content on grafting parameters. Copper number, 20.5; water, 5.5 mL; $[\text{Fe}_2(\text{SO}_4)_3]$, 1.56×10^{-3} mol/L; MMA, 1 mL; time, 120 min; total volume (liquid), 6.5 mL.

Effect of Variation of Bleached Jute Content

Results are shown in Fig. 4. Percent grafting decreases quite expectedly with an increase in the amount of bleached jute, the effect being just the reverse of what was observed for an increase in monomer concentration (Fig. 3). The grafting efficiency, however, shows a marginal decreasing trend over the full range of jute variation. The % total conversion, on the other hand, increases up to bleached jute = 0.2007 g and thereafter tends to drop off. For a high content of bleached jute (0.2 g), the concentration of $-\text{CHO}$ groups becomes high enough in the polymerization system to exhibit a pronounced retardation effect, leading to a drop in the % total conversion.

Effect of Variation of Polymerization Time

The graft copolymerization of MMA on bleached jute fiber as a function of grafting time is presented in Fig. 5. Percent grafting increases

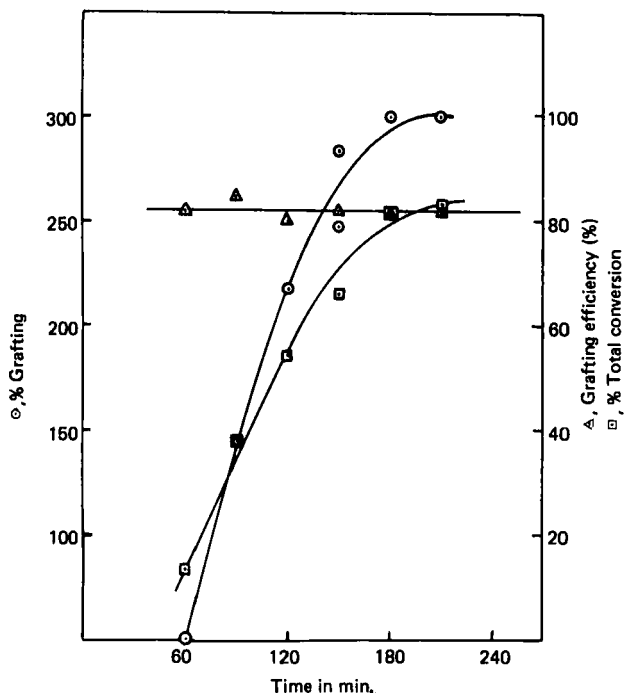


FIG. 5. Photograft copolymerization of MMA on bleached jute fiber at 32°C using $\text{Fe}_2(\text{SO}_4)_3$ as initiator. Effect of variation time on grafting parameters. Bleached jute fiber, 0.2 g; copper number, 20.5; water, 5.5 mL; $[\text{Fe}_2(\text{SO}_4)_3]$, 1.56×10^{-3} mol/L; MMA, 1 mL; total volume (liquid), 6.5 mL.

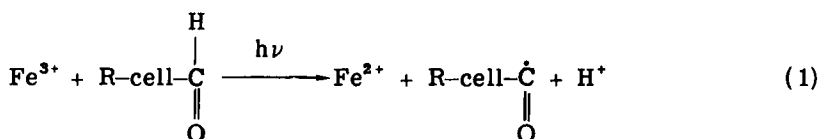
with an increase in time up to 180 min. Beyond this time it tends to level off but the grafting efficiency, which is quite high (80–81%), remains steady over the time period studied. However, % total conversion expectedly increases with an increase in time of polymerization with the usual leveling off trend at a later stage, due probably to initiator and monomer depletion.

Mechanism

By the use of bleaching, lignin present in the defatted jute was practically removed (as shown by a negative response to the test for lignin with acidified ammonium vanadate solution), particularly for bleached jute samples having a copper number ≥ 10 . The degree of oxidation of the bleached jute samples is reflected in their copper number; the higher the copper number, the higher is the degree of oxidation. Be-

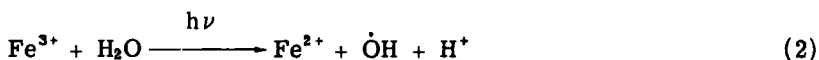
sides generation of aldehydic groups on the C₂-C₃ position of the glucopyranose rings, variable proportions of ketonic and carboxylic groups are also likely to be generated on the bleached jute samples due to uncontrolled oxidation by NaOCl. Thus the jute fiber becomes more prone to initiator (Fe³⁺) attack.

Fe₂(SO₄)₃ is incapable of inducing graft copolymerization of MMA on bleached jute in the dark at 40°C but can do so in the presence of visible or near ultraviolet light at 40°C or lower temperatures. Generation of radical sites on the bleached jute may be considered to take place in the following way:



Reaction (1) does not measurably take place in the dark. The electron transfer reaction, however, takes place on photoactivation, Fe³⁺ being highly photosensitive [14], and high rates of polymerization (% total conversion) and grafting transformations were therefore observed in the photoactivated system.

Formation of homopolymer (PMMA) may arise due to generation of OH radicals in the photosystem according to



However, Reaction (2) is likely to occur with limited ease in an acidic medium. Ferric ion adsorbed on jute cellulose passes with difficulty in aqueous solution because of the ionic bond [15] established between cellulose and ferric ion, and thus the bulk of the photoactivation reactions of ferric ion are likely to take place on the jute cellulose, giving a low probability of homopolymer formation. The high grafting efficiencies observed in the present system are very much in agreement with the above viewpoints.

REFERENCES

- [1] P. K. Roy, *J. Appl. Polym. Sci.*, **12**, 1787 (1968).
- [2] M. A. Jabbar and M. M. Haque, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1447 (1980).
- [3] S. K. Majumder and W. H. Rapson, *Text. Res. J.*, **34**, 1007, 1015 (1964).
- [4] M. H. Awan and M. A. Hussain, cited in *Impregnated Fibrous Materials Reports of a Study Group*, International Atomic Energy Agency (Vienna), 1968, p. 267.

- [5] S. R. Agarwal and A. Sreenivasan, Indian J. Technol., 12, 456 (1974).
- [6] S. R. Agarwal and A. Sreenivasan, Ibid., 12, 460 (1974).
- [7] P. Ghosh and A. N. Banerjee, J. Polym. Sci., Polym. Chem. Ed., 12, 375 (1974).
- [8] W. G. Palmer, Experimental Inorganic Chemistry, Cambridge University Press, 1965, p. 463.
- [9] P. K. Roy, J. Appl. Polym. Sci., 12, 2593 (1969).
- [10] R. L. Wistler, Carbohydrate Chemistry, Vol. III, Academic, New York, 1963.
- [11] P. Ghosh and T. K. Ghosh, J. Macromol. Sci.-Chem., A17, 847 (1982).
- [12] T. Todda, J. Polym. Sci., 58, 411 (1962).
- [13] A. R. Mukherjee, R. Pal, A. M. Biswas, and S. Maity, Ibid., Part A-1, 5, 135 (1967).
- [14] Y. Ogiwara and H. Kabota, Ibid., 9, 2549 (1971).
- [15] Y. Ogiwara and H. Kabota, Ibid., A-1, 7, 2087 (1969).

Accepted by editor December 12, 1982

Received for publication January 12, 1983