

Chemical Modification of Pineapple Leaf Fiber: Graft Copolymerization of Acrylonitrile onto Defatted Pineapple Leaf Fibers

A. K. MOHANTY,^{1,*} P. C. TRIPATHY,² M. MISRA,² S. PARIJA,² S. SAHOO²

¹ Technical University of Berlin, Institute of Nonmetallic Materials, Polymer Physics, Englische Str. 20, D-10587 Berlin, Germany

² Laboratory of Polymer Science, Department of Chemistry, Ravenshaw College, Cuttack - 753 003, Orissa, India

Received 12 March 1999; accepted 18 April 1999

ABSTRACT: Graft copolymerization of acrylonitrile (AN) onto defatted pineapple leaf fiber (PALF) was studied using a CuSO_4 and KIO_4 combination as an initiator in an aqueous medium in the temperature range 30–50°C. The effects of the concentration of potassium periodate, CuSO_4 , and monomer on the graft yield were investigated. The effects of time, temperature, amount of some inorganic salts, and organic solvents on the graft yield are also reported. A combination of $\text{Cu}^{+2}-\text{IO}_4^-$ in an aqueous medium with an IO_4^- concentration of 0.005 mol L⁻¹ and Cu^{+2} concentration of 0.002 mol L⁻¹ produced optimum grafting for use of 0.1 g defatted PALF with a fiber-to-liquor ratio of 1:50 at 50°C for 2 h. However, KIO_4 and CuSO_4 failed to induce polymerization of AN in the presence of PALF when used separately. FTIR and thermogravimetric analysis of the defatted and AN-grafted PALF were carried out. Grafting improved the thermal stability of PALF. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3035–3043, 2000

Key words: graft copolymerization; acrylonitrile; pineapple leaf fiber; copper–periodate system; defatted PALF

INTRODUCTION

Graft copolymerization onto lignocellulosic fibers is of considerable importance for the physico-chemical modification and improvement in the textile performance of fibers.¹ The synthetic graft copolymer of natural macromolecules like silk, wool, cotton, jute, etc., exhibit excellent properties in addition to showing their original properties.²

Pineapple leaf fiber (PALF) is obtained from the leaves of the plant *Anannus cosmosum* be-

longing to the family *Bromelliaceae*. PALF is largely cultivated in tropical countries. India has over 87,200 hectares (estimated) of land under pineapple cultivation.³ PALF is multicellular and lignocellulosic like jute fiber,⁴ containing α -cellulose, hemicellulose, and lignin associated with each other in a manner not clearly known.⁵ It also contains other minor constituents such as fat, wax, pectin, uronic anhydride, pentosan, and inorganic substances.⁶ PALF is finer than is jute but is 10 times coarser than is cotton fiber. PALF has a ribbonlike structure and is cemented together by lignin, pentosanlike materials, which contribute to the strength of the fiber.

PALF seems to be an important fiber for building up agro-based industry, but this potential source of fiber has not been properly utilized be-

Correspondence to: A. K. Mohanty, Michigan State University, Composite Materials and Structures Center, 2100 Engineering Building, East Lansing, MI 48824. e-mail: mohantya@egr.msu.edu

Contract grant sponsor: DST, Government of India.

Journal of Applied Polymer Science, Vol. 77, 3035–3043 (2000)
© 2000 John Wiley & Sons, Inc.

cause of the lack of adequate information about its physicochemical properties. Since this fiber contains about 70% cellulose,⁷ the arrangement of molecules in the fibers is similar to that of cotton cellulosic fibers. PALF could be successfully spun in a cotton spinning system with slight modifications to produce 100% PALF yarns⁸ which are used to make fabrics, mops, carpets, etc. Ghosh and Sinha⁹ measured some physical characteristics of PALF and its tensile behavior was studied by Chakravarty et al.¹⁰ Datta et al.¹¹ found the range of crystallinity to be from 0.63 to 0.68 and showed that its dielectric behavior was comparable to that of jute.¹² Some of the physical properties of PALF influencing the textile performance of PALF were studied by Saha et al.¹³ IO_4^- was reported to induce vinyl grafting on cellulose¹⁴ and wool.¹⁵ It was reported earlier that a combination of Cu^{+2} and IO_4^- can induce graft copolymerization on lignocellulosic fibers like jute¹⁶ and coir.¹⁷ There is scope for using this initiator system for vinyl grafting on PALF, another important lignocellulosic fiber. The present article deals with the study of a Cu^{+2} and potassium periodate combination as an initiator for the graft copolymerization of acrylonitrile (AN) onto defatted PALF in an aqueous medium.

EXPERIMENTAL

Materials

PALF was collected from SITRA, Coimbatore, India. The defatted PALF was obtained after successive extraction procedures as mentioned below. The fibers were first subjected to Soxhlet extraction with acetone for 24 h, followed by washing with distilled water and air-drying. The fibers were then extracted in a 1:2 mixture of alcohol and benzene for 16 h to dewax the sample, followed by washing with distilled water and air-drying to obtain the defatted PALF for grafting.

The AN monomer was washed with 5% NaOH and 3% orthophosphoric acid followed by repeated washing with conductivity water, dried over anhydrous calcium chloride, and finally stored in a refrigerator for use. The conductivity water was used for the preparation of all solutions. All chemicals like potassium periodate, CuSO_4 , etc., were of AnalaR grade and were used as such without further purification. A solution of KIO_4 and CuSO_4 were prepared by dissolving the required

quantities of KIO_4 and CuSO_4 in the conductivity water.

Graft Copolymerization

The graft copolymerization reactions were carried out at the desired temperatures (in a constant temperature bath) in a Pyrex vessel having B24/29 standard joints equipped with gas inlet and outlet tubes for passage of N_2 . At first, the defatted PALF was soaked with an appropriate quantity of the monomer (AN) for about 10 min. The CuSO_4 solution and conductivity water of appropriate quantities were added successively into the vessel. The vessel containing the above reaction mixture and another vessel containing the IO_4^- solution were separately deaerated by passing N_2 for 20 min. Then, the required amount of the IO_4^- solution was finally added into the vessel containing the reactant mixture. A fiber: liquor ratio of 1:50 was maintained for each experiment. Homopolymerization and copolymerization were started after addition of the IO_4^- solution. After a specified period, the reactions were arrested by quenching the vessels in ice-cold water.

The grafted samples were washed well by extraction with several portions of water, given a light soaping to remove the loosely adhering PAN homopolymers, then washed and air-dried. It was observed that, on further extraction with dimethylformamide (DMF) for about 24 h at 30°C, this grafted sample showed a negligible weight loss, which was also reported earlier.¹⁸⁻²⁰ Hence, all the results are based on an increase in the weight of the fiber after grafting. The percentage of grafting was calculated on a dry weight basis and determined by storing the materials in weighing bottles over P_2O_5 at room temperature in a vacuum desiccator until a constant weight was obtained:

% of graft yield =

$$\frac{\text{dry weight of grafted fiber} - \text{dry weight of defatted fiber}}{\text{dry weight of defatted fiber}} \times 100$$

FTIR Spectra

FTIR spectra in the form of KBr pellets of fiber samples were recorded on a JASCO-5300 FTIR spectrometer.

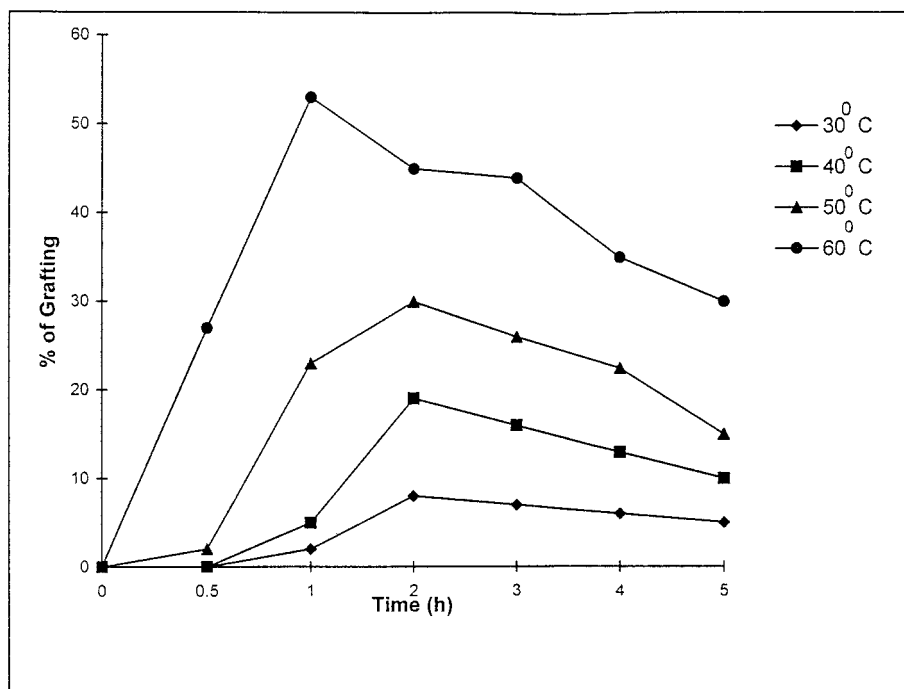


Figure 1 Effect of variation of time on graft yield: PALF = 0.1 g; $[\text{IO}_4^-]$ = 0.005 mol L^{-1} ; $[\text{AN}]$ = 0.759 mol L^{-1} ; $[\text{Cu}^{+2}]$ = 0.002 mol L^{-1} .

Thermogravimetric Analysis (TGA)

TGA curves of fiber samples were recorded on a Shimadzu DT thermal analyzer with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The results of the graft copolymerization of AN onto defatted PALF at three different temperatures are shown in the figures. It is observed that IO_4^- and Cu^{+2} failed to induce grafting of AN onto PALF when used separately. Similar findings were reported for jute¹⁶ and coir.¹⁷ The combination of both Cu^{+2} and IO_4^- in an aqueous medium is effective in inducing the graft copolymerization of AN onto PALF.

Effect of Variation of Time

Figure 1 shows the effect of time on the graft yield at four different temperatures (30, 40, 50, and 60°C). In each case, the graft yield increased steadily with time up to 2 h, then leveled off and thereafter decreased to some extent. However, a large decrease in the graft yield was observed from

50 to 30% at 60°C over 4 h. The appreciable decrease in the graft yield at higher temperature, that is, 60°C, may be due to the delinking of the graft PAN chain from the cellulose backbone. Beyond an optimum time period, the polymer graft at the cellulose backbone acts as a barrier in preventing further diffusion of the monomer onto the fiber and, hence, the graft yield is leveled off. The optimum graft yield was found within 2 h of the experiment. Similar observations were reported for the graft copolymerization of AN onto jute fibers using different redox systems as the initiator.^{18,19}

Effects of IO_4^- Ion Concentration

Relevant data are presented graphically (Fig. 2), showing the effect of the IO_4^- concentration on the graft yield at three different temperatures. It was observed that the graft yield increased by increasing the concentration of the IO_4^- ion up to 0.005 mol L^{-1} . This trend of increasing graft yield may be due to the creation of a greater number of grafting sites with an increase in the oxidant. However, the most balanced and desired graft yield is obtained at 0.005 mol L^{-1} of IO_4^- concentration. When the IO_4^- ion concentration further

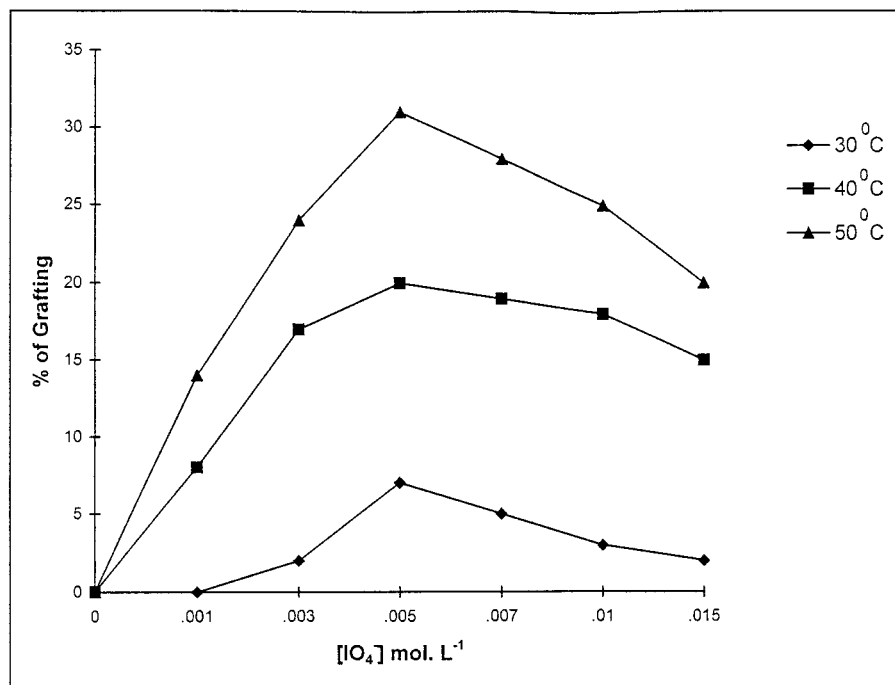


Figure 2 Effect of variation of oxidant on graft yield: PALF = 0.1 g; [AN] = 0.759 mol L⁻¹; [Cu⁺²] = 0.002 mol L⁻¹; time = 2 h.

increased, the graft yield decreased due to the formation of an increased amount of homopolymers.

Effect of Cu⁺² Ion Concentration

It is observed that neither KIO₄ nor Cu⁺² induced graft copolymerization of AN in the presence of PALF when used separately. However, Cu⁺² coupled with IO₄⁻ is an effective redox system as an initiator. The effect of Cu⁺² was studied by varying the concentration of Cu⁺² from 0.0005 to 0.005 mol L⁻¹. The graft yield increased with the Cu⁺² concentration up to 0.002 mol L⁻¹, then decreased (Fig. 3). The decreased trend in the graft yield may be due to formation of an increased amount of homopolymers and a rapid rate of termination.

Effect of Monomer Concentration

The effect of the variation of the AN (monomer) concentration on the grafting percentage at three different temperatures is represented in Figure 4. It is observed that the graft yield increases with increase in the monomer concentration. Similar observations were also reported in V⁵⁺-cyclohex-

anone-initiated grafting of AN onto acetylated jute,¹⁸ Ce(IV)-NAG-initiated grafting of AN onto chemically modified PALF,²¹ and Cu⁺²-IO₄⁻-initiated grafting of AN onto jute fiber.

Effect of Fiber Amount

The effect of the variation of the PALF amount on the graft yield for three different temperatures is shown in Figure 5. The graft yield is found to increase steadily with increase in the fiber amount and attained a maximum yield at 0.1 g. The increase in the graft yield may be due to the greater surface area for better diffusion of the monomer with an increase in the fiber amount. With further increase in the fiber amount, the grafting percentage decreases. The decrease in the graft yield beyond the optimum amount may be due to the insufficient quantity of monomer for the greater amount of fiber, thereby giving minimal diffusion of the monomer.

Effect of Reaction Medium

The graft copolymerization of the vinyl monomer is greatly influenced by the reaction medium. The

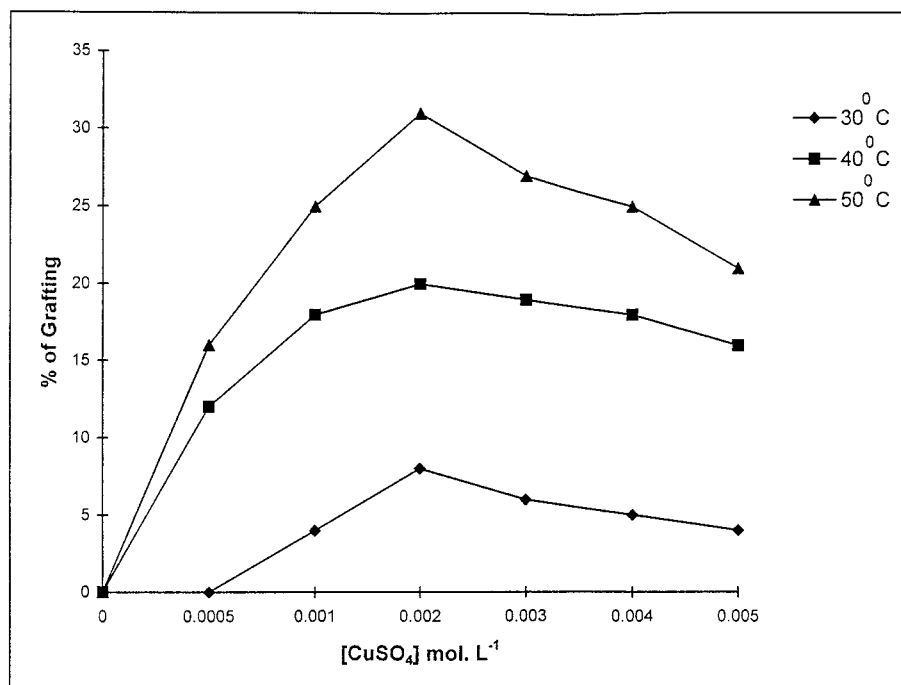


Figure 3 Effect of variation of CuSO_4 on graft yield: PALF = 0.1 g $[\text{IO}_4^-] = 0.005 \text{ mol L}^{-1}$; $[\text{AN}] = 0.759 \text{ mol L}^{-1}$; time = 2 h.

effect of different inorganic salts and organic solvents is reported in Table I. The graft yield is in the following order when an equivalent molar

concentration of some salts are added into the reaction mixture: $\text{Ba}(\text{NO}_3)_2 = \text{KNO}_3 > \text{Al}_2(\text{SO}_4)_3 > \text{control} > \text{Pb}(\text{NO}_3)_2 > \text{Na}_2\text{SO}_4$. Similarly, the

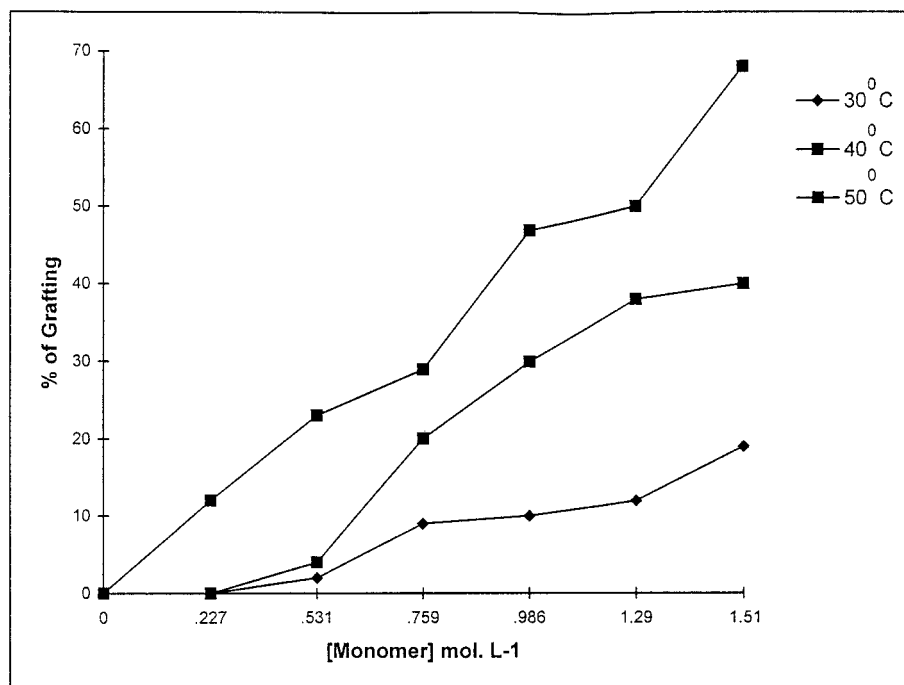


Figure 4 Effect of variation of monomer on graft yield: PALF = 0.1 g $[\text{IO}_4^-] = 0.005 \text{ mol L}^{-1}$; $[\text{Cu}^{+2}] = 0.002 \text{ mol L}^{-1}$; time = 2 h.

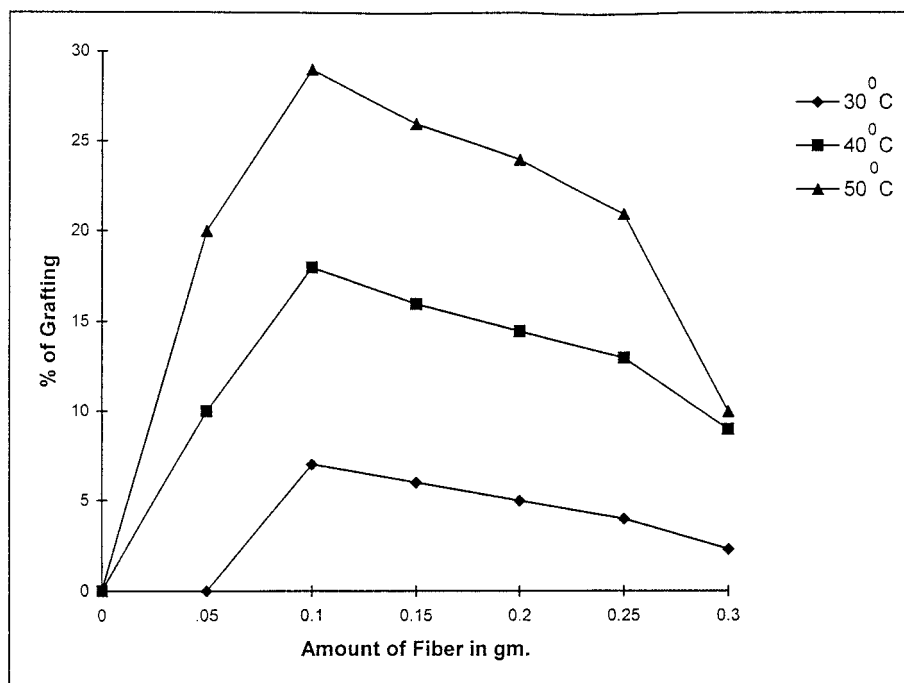


Figure 5 Effect of variation of fiber on graft yield: $[\text{IO}_4^-] = 0.005 \text{ mol L}^{-1}$; $[\text{AN}] = 0.759 \text{ mol L}^{-1}$; $[\text{Cu}^{+2}] = 0.002 \text{ mol L}^{-1}$; time = 2 h.

effect of various organic solvents when added in equal proportions (5% v/v) is in the following order: control > DMF = diethyl ether > benzene > methanol > Glacial (Gl) acetic acid.

The presence of a nonaqueous solvent brings about a decrease in graft yield compared to the control carried out in the aqueous medium. Since AN has greater solubility in the nonaqueous solvent than in the aqueous medium, it is partitioned between the added solvent and the aqueous phase. The depletion in the monomer concentration in the aqueous phase results in a decrease in the rate of grafting and, hence, a decrease in

the graft yield. It is to be noted that the grafting reaction takes place in the aqueous phase in the presence of the $\text{Cu}^{+2}-\text{IO}_4^-$ system. The lower percentage of graft yield than that of the control is attributed to the ionic dissociation of the added electrolyte, which interferes with the usual polymerization reaction, resulting in the premature termination of the growing chains.

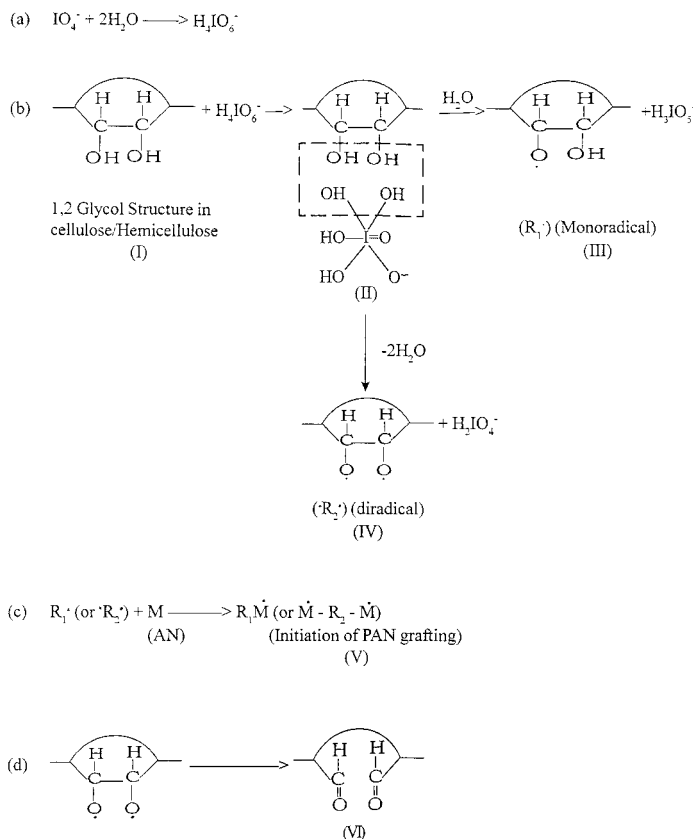
Reaction Mechanism

The periodate ion alone fails to induce graft copolymerization onto PALF, while in combination with

Table I Effect on Reaction Medium

No. Experimental Set	Effect of Salt (1 g)	% of Grafting	Effect of Solvent (1 mL)	% of Grafting
1	Control	31	Control	31
2	Na_2SO_4	0	MeOH	10
3	$\text{Al}_2(\text{SO}_4)_3$	50	DMF	20
4	KNO_3	55	Gl acetic acid	1
5	$\text{Ba}(\text{NO}_3)_2$	55	Benzene	13
6	$\text{Pb}(\text{NO}_3)_2$	2	Diethyl ether	20

$[\text{AN}] = 0.759 \text{ mol L}^{-1}$; $[\text{IO}_4^-] = 0.005 \text{ mol L}^{-1}$; $[\text{Cu}^{+2}] = 0.002 \text{ mol L}^{-1}$; PALF = 0.1; time = 2 h; temperature = 40°C.


Scheme 1

the Cu^{+2} ion, it induces graft copolymerization. This might be due to the following reasons: First, the phenolic structure of lignin acts as a strong inhibitor to kill the free radicals formed from the periodate. The periodate ion, being a strong oxidant, reacts with lignin and converts it to its quinonoid form. The reaction between the phenolic structure of the lignin and periodate ion has already been established.²² However, in the presence of the Cu^{+2} ion, the lignin is bound with the metal ion¹⁶ and, thus, the inhibiting action of lignin is prevented. As a result, IO_4^- becomes free to produce free radicals and to induce grafting of AN onto PALF. The mechanism of grafting is proposed in Scheme 1. The reaction between IO_4^- and the cellulosic constituent on PALF is by a free-radical mechanism, causing initiation of vinyl grafting (V) on them in the presence of the monomer while culminating in their oxidation to the dialdehyde state (VI) in the absence of the monomer.²³

Characterization

FTIR Spectra

FITR spectra of defatted PALF and that of AN-grafted PALF are shown in Figure 6. The defatted

PALF [Fig. 6(a)] and AN-grafted PALF [Fig. 6(b)] show the characteristic broad absorption band of $-\text{OH}$ groups around 3600 cm^{-1} . From Figure 6(b), it is observed that AN-grafted PALF shows an additional band at 2238.8 cm^{-1} for the nitrile group, confirming the occurrence of grafting. Similar observations were obtained for AN-grafted PALF for other initiator systems.²⁰

Thermal Property

The thermal behavior of defatted as well as of AN-grafted PALF was examined by thermogravimetric analysis (TGA). The TGA curves of the original defatted PALF and AN-grafted (higher percentage) PALF are shown Figure 7(a,b), respectively. It is clearly observed that the grafting has improved the thermal stability of PALF. In both curves, the various steps of decompositions are marked as 1, 2, 3, etc. To compare the thermal stability, we chose step 2 in both curves. In Figure 7(a) under step 2, the decomposition ranges from 265 to 370°C , amounting 86.6% weight loss. However, in Figure 7(b) under step 2, the decomposition ranges from 232.5 to 377°C , amounting to only a 74.4% weight loss. The thermal analysis of

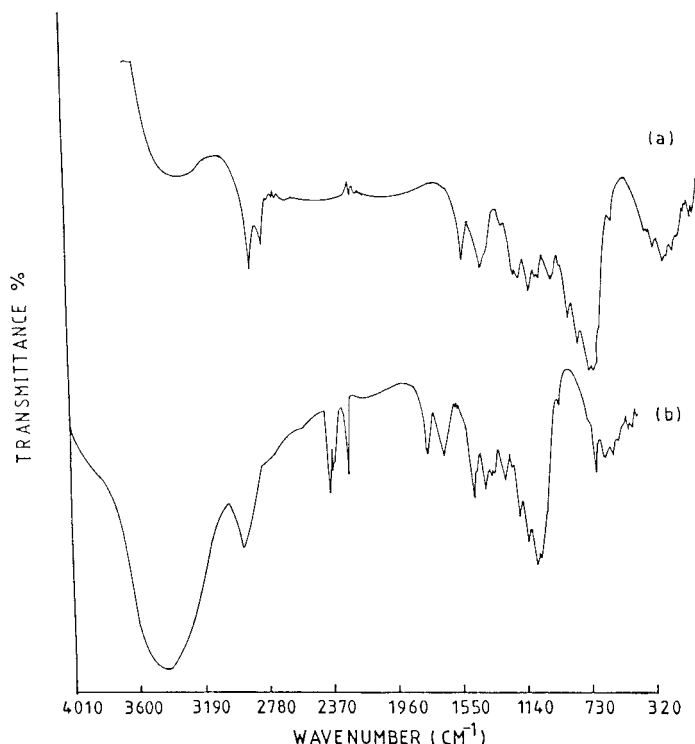


Figure 6 (a) IR spectra of defatted PALF; (b) IR spectra of AN-grafted PALF.

different chemically treated PALF was also reported by Rajendran and Chellamani.²⁴

CONCLUSIONS

From these studies, it is concluded that a combination of $\text{Cu}^{+2} - \text{IO}_4^-$ in an aqueous medium with

$[\text{IO}_4^-] = 0.005 \text{ mol L}^{-1}$ and $\text{Cu}^{+2} = 0.002 \text{ mol L}^{-1}$ produced optimum grafting with 0.1 g defatted PALF with a fiber-to-liquor ratio of 1:50 at 50°C for 2 h. It is also concluded that neither KIO_4 nor CuSO_4 alone can induce the polymerization of AN to the PALF surface. Comparison of the FTIR spectra of defatted as well as grafted PALF proves the occurrence of grafting onto PALF. From the thermal analysis, it is concluded that grafting improves the thermal stability of PALF.

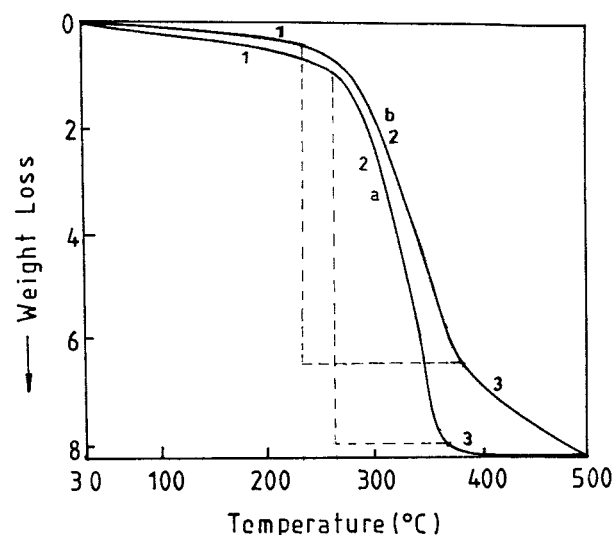


Figure 7 (a) TGA curve of defatted PALF; (b) TGA curve of AN-grafted PALF.

The authors are thankful to Ms. Indira Doraiswami of SITRA, Coimbatore, for providing the PALF sample. Help rendered by RSIC, Nagpur, and RSIC, Chandigarh, are gratefully acknowledged. Two of the authors (A. K. M.; M. M.) are thankful to the DST, Government of India, for the financial grant to carry out this piece of research.

REFERENCES

1. Watt, I. C. *J Macromol Sci Rev Macromol Chem* 1970, 5175.
2. Tripathy, S. S.; Jena, S.; Mishra, S. B.; Padhi, N. P.; Singh, B. C. *J Appl Polym Sci* 1985, 30, 1399–1406.
3. Doraiswamy, I.; Chellamani, P.; Gunasekaran, R. *South India Text Res Assoc Coimbatore* 1993, 38(2), 1.

4. Bhaduri, S. K.; Sen, S. K.; Dasgupta, P. C. *Indian Pulp Pap* 1979, 34, 15.
5. Saha, S. C.; Das, B. K.; Ray, P. K.; Pandey, C. M.; Goswami, K. *J Appl Polym Sci* 1991, 43, 1885.
6. Ghosh, S. K.; Sinha, M. K.; Dey, S. K.; Bhaduri, S. K. *Text Trends* 1982, 24(10), 49.
7. Mukherjee, P. S.; Satyanaryan, K. G. *J Mater Sci* 1986, 21, 51.
8. Terminal report of the UNDP (United Nations Development Programme) Assisted Project, 1991.
9. Ghosh, S. K.; Sinha, M. K. *Indian Text J* 1977, Nov, 111.
10. Chakravarty, A. C.; Sinha, M. K.; Ghosh, S. K.; Das, B. K. *Indian Text J* 1978, Jan, 95.
11. Datta, A. K.; Samantaray, B. K.; Bhattacharjee, S. *J Mater Sci Lett* 1978, 3, 67.
12. Datta, A. K.; Mukherjee, P. S.; Mitra, G. B. *J Mater Sci* 1990, 15, 1856.
13. Saha, S. C.; Das, B. K.; Ray, P. K.; Pandey, S. N.; Goswami, K. *J Appl Polym Sci* 1993, 50, 555.
14. Toda, T. *J Polym Sci* 1962, 58, 411.
15. Kantouch, A.; Hebeish, A.; Bendak, A. *Text Res J* 1972, 42, 7.
16. Ghosh, P.; Ganguly, P. K.; Bhaduri, S. K. *Eur Polym J* 1994, 30, 749.
17. Rout, J.; Misra, M.; Mohanty, A. K. *J Adv Technol* 1999, 10, 1-9.
18. Mohanty, A. K.; Patnaik, S.; Singh, B. C.; Misra, M. *J Appl Polym Sci* 1989, 37, 1171.
19. Mohanty, A. K.; Misra, M. *Angew Macromol Chem* 1996, 225, 1.
20. Patra, C. M.; Singh, B. C. *J Appl Polym Sci* 1994, 52, 1557.
21. Mohanty, A. K.; Parija, S.; Misra, M. *J Appl Polym Sci* 1996, 60, 931.
22. Adler, E.; Falkehay, I.; Smith, B. *Acta Chem Scand* 1962, 16, 529.
23. Waters, W. A. *Trans Faraday Soc* 1946, 42, 184.
24. Rajendran, S.; Chellamani, P. *Indian Text J* 1992, Oct, 82.