

Ce(IV)-*N*-Acetylglycine Initiated Graft Copolymerization of Acrylonitrile onto Chemically Modified Pineapple Leaf Fibers

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SYNOPSIS

Graft copolymerization of acrylonitrile (AN) onto chemically modified pineapple leaf fiber (PALF) was studied using Ce(IV) and *N*-acetylglycine (NAG) combination as initiator in the temperature range 40–60°C. The effects of concentration of monomer, Ce(IV), and NAG on graft yield have been studied. Besides the effects of time, temperature, acid, amount of PALF, some inorganic salts and organic solvents on graft yield have been investigated. FTIR and scanning electron microscopy of PALF and grafted PALF have been studied. Grafting has improved the thermal stability of PALF. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pineapple leaf fiber (PALF) is multicellular and lignocellulosic like jute fiber.¹ It is obtained from the leaves of the plant *Anannus cosmosum* belonging to the Bromeliaceae family. PALF is largely cultivated in tropical countries, mainly for its fruits. According to estimates available, India has over 87,200 hectares of land under pineapple cultivation.² PALF is finer than jute but is 10 times coarser than cotton fiber. PALF seems to be an important fiber for building up the agro-based industry, but this potential source of fiber from agrowaste has not been properly utilized because of the lack of adequate knowledge of its physical and chemical properties. Chemically, PALF is lignocellulosic in nature,^{1,3} containing α -cellulose, hemicellulose, and lignin being associated with each other in a manner not clearly known.⁴ It also contains other minor constituents such as fat, wax, pectin, uronic anhydride, pentosan, coloring matter, and inorganic substances.⁵ PALF has a ribbon-like structure and is cemented together by materials like lignin and pentosan, which contribute to the strength of the fiber.

Since this fiber contains about 70% cellulose,⁶ the arrangement of molecules in the fibers is similar to cotton cellulosic fibers. One of the South India Textile Research Association's (SITRA) findings⁸ revealed that PALF could be successfully spun in a cotton spinning system with slight modifications to produce 100% PALF yarn and blends with other natural and synthetic fibers, especially with cotton. The yarns thus produced were used to make fabrics, carpets, mops, curtains, etc. Some physical characteristics of the fiber were measured by Ghosh and Sinha,⁹ and Chakravarty et al.¹⁰ studied its tensile behavior. Datta et al.¹¹ found the range of its crystallinity to be from 0.63 to 0.68 and showed that its dielectric behavior was comparable to jute.¹² Saha et al.¹³ studied some physical properties of PALF influencing its textile behavior.

Graft copolymerization of vinyl monomers onto lignocellulosic fibers^{14,15} using ceric ion as initiator has gained considerable importance. Many research publications^{16–20} on graft copolymerization of vinyl monomers onto jute are available in the literature. Recently we²¹ have reported graft copolymerization of methyl methacrylate (MMA) onto PALF, another important lignocellulosic fiber. The present paper deals with the study of Ce(IV) and NAG combinations as initiator for graft copolymerization of AN onto chemically modified PALF in an aqueous medium.

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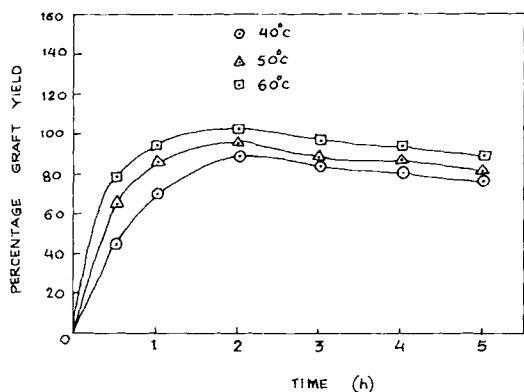


Figure 1 Effect of time on graft yield. PALF = 0.1 g, [AN] = 0.751 mol L⁻¹, [Ce(IV)] = 0.025 mol L⁻¹, [NAG] = 0.005 mol L⁻¹, [H₂SO₄] = 0.25 mol L⁻¹.

EXPERIMENTAL

Materials

Pineapple leaf fibers were received from SITRA, Coimbatore, India. The chemically modified pineapple leaf fibers were obtained after all the successive chemical treatments as mentioned below. The fibers were first subjected to soxhlet extraction with acetone for about 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. The defatted fibers thus obtained were then treated with 5% NaOH for 45 min, thoroughly washed with distilled water, and then air dried. Then the fibers were soaked with ethylene diamine for 30 min, washed, and air dried. Finally the fibers were treated with 60% ZnCl₂ so-

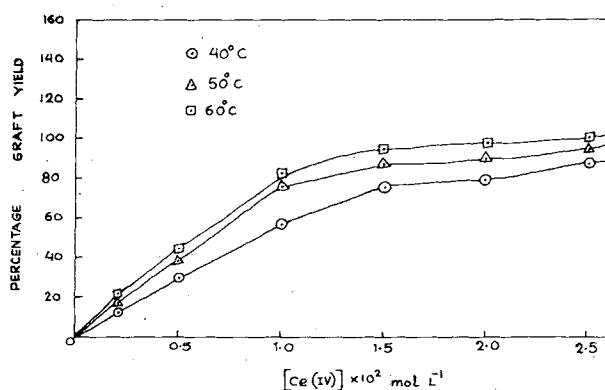


Figure 2 Effect of metal ion concentration. PALF = 0.1 g, [AN] = 0.751 mol L⁻¹, [NAG] = 0.005 mol L⁻¹, [H₂SO₄] = 0.25 mol L⁻¹, time = 2 h.

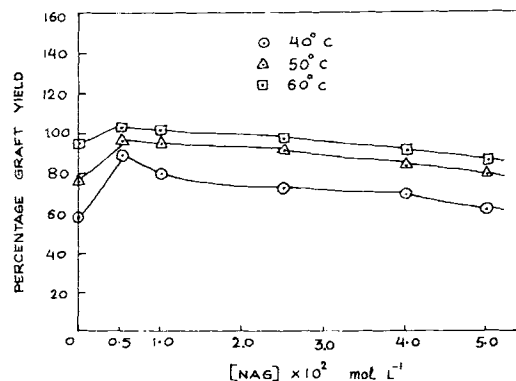


Figure 3 Effect of NAG concentration. PALF = 0.1 g, [AN] = 0.751 mol L⁻¹, [Ce(IV)] = 0.025 mol L⁻¹, [H₂SO₄] = 0.25 mol L⁻¹, time = 2 h.

lution at 20–25°C for 4 h, washed thoroughly with distilled water, and air dried. These chemically modified pineapple leaf fibers thus obtained were used for grafting.

AN monomer (M) 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 refrigerator for use. The conductivity water used to prepare all solutions was prepared by redistilling distilled water over alkaline KMnO₄ in an all glass pyrex unit. All other chemicals used, i.e., ceric ammonium sulfate (CAS), NAG, H₂SO₄ etc., were of A.R. grade and were used as such without further purification. A 0.1 mol L⁻¹ of "Ce(IV)" was prepared by dissolving required quantity of CAS in 1 mol L⁻¹ sulfuric acid. Similarly a 0.1 mol L⁻¹ solution of NAG was prepared in conductivity water.

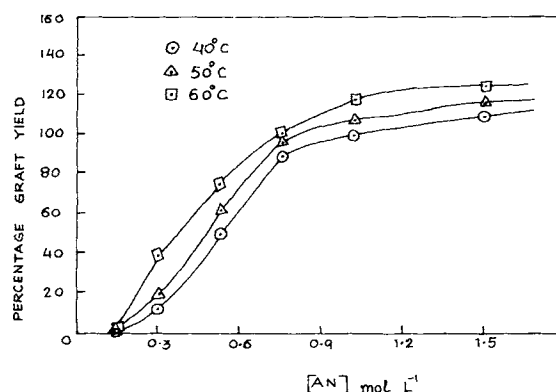


Figure 4 Effect of monomer concentration. PALF = 0.1 g, [Ce(IV)] = 0.025 mol L⁻¹, [NAG] = 0.005 mol L⁻¹, [H₂SO₄] = 0.25, time = 2 h.

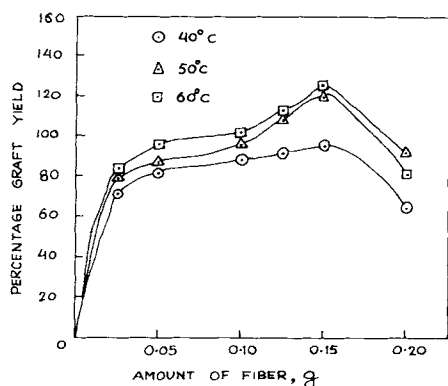


Figure 5 Effect of PALF amount. $[AN] = 0.751 \text{ mol L}^{-1}$, $[Ce(IV)] = 0.025 \text{ mol L}^{-1}$, $[NAG] = 0.005 \text{ mol L}^{-1}$, $[H_2SO_4] = 0.25 \text{ mol L}^{-1}$, time = 2 h.

Graft Copolymerization

The graft copolymerization reactions were carried out at the desired temperature (in a constant temperature bath) in pyrex vessels having B_{24/29} standard joints equipped with gas inlet and outlet tubes for passage of nitrogen. At first the required amount of chemically modified PALF was taken in the reaction vessel into which an appropriate quantity of monomer was added and the fibers were allowed to soak with the monomer for about 10 min. Then other reagents, i.e., NAG, followed by sulfuric acid (when required), and finally conductivity water in appropriate quantities were added into the vessels.

The vessel containing the above mentioned reactants mixture and another vessel containing Ce(IV) solution were separately deaerated by passing nitrogen for 20 min. Then the required amount of Ce(IV) solution was added into the vessel containing the reactants mixture. Homopolymerization and graft copolymerization were started after adding

Ce(IV) solution. In all the experiments the total liquor volume was adjusted to 20 mL by adding conductivity water and the absolute concentrations of all the reactants were calculated for 20 mL of reactant solutions. The reactions were carried out at 40, 50, and 60°C for the desired time, after which reactions were arrested by quenching the vessels in ice-cold water.

Then the grafted samples were washed well by extraction with several portions of water, given a light soaping to remove the loosely adhering polyacrylonitrile homopolymer, then washed, and dried. It was also observed that on further extraction with dimethyl formamide (DMF) for about 24 h at 30°C, the grafted samples showed a negligible weight loss. This observation has also been reported earlier.¹⁸⁻²⁰ Hence, all the results are based on the increase in weight of the fiber after grafting, followed by thorough soaping and washing. The percentage of grafting was calculated on a dry weight basis, and determined by storing the materials in weighing bottles over P₂O₅ at room temperature in a vacuum desiccator until a constant weight was obtained.

$$\% \text{ Graft yield} = \frac{\text{dry wt of grafted PALF} - \text{dry wt of original PALF}}{\text{dry wt of original PALF}} \times 100$$

FTIR Spectra

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

Scanning Electron Microscopy (SEM)

SEM of fiber samples were recorded using a JEOL-JSM 35 CF scanning electron microscopy.

Table I^a Effect of Reaction Medium on Grafting

| Effect of Sulfuric Acid (Temperature = 50°C) | | Effect of Solvent and Salt (Temperature = 50°C) | | | |
|---|------------|---|------------|---|------------|
| [H ₂ SO ₄] | % Grafting | Solvent 5% (v/v) | % Grafting | [Salt] 0.1 mol L ⁻¹ | % Grafting |
| 0.25 | 88.0 | Control | 88.0 | ZnSO ₄ | 114.3 |
| 0.30 | 84.2 | DMF | 84.8 | CuSO ₄ | 100.1 |
| 0.40 | 80.1 | Ether | 73.1 | Ba(NO ₃) ₂ | 99.9 |
| 0.50 | 72.8 | Acetic acid | 65.8 | Al ₂ (SO ₄) ₃ | 89.2 |
| 0.60 | 62.9 | Methanol | 42.1 | Control | 88.0 |
| 0.75 | 59.8 | Benzene | 25.6 | Na ₂ SO ₃ | 81.5 |
| | | Acetone | 7.2 | | |

^a PALF = 0.1 g, $[AN] = 0.7510 \text{ mol L}^{-1}$, $[Ce(IV)] = 0.025 \text{ mol L}^{-1}$, $[NAG] = 0.005 \text{ mol L}^{-1}$, $[H_2SO_4] = 0.25 \text{ mol L}^{-1}$, time = 2 h.

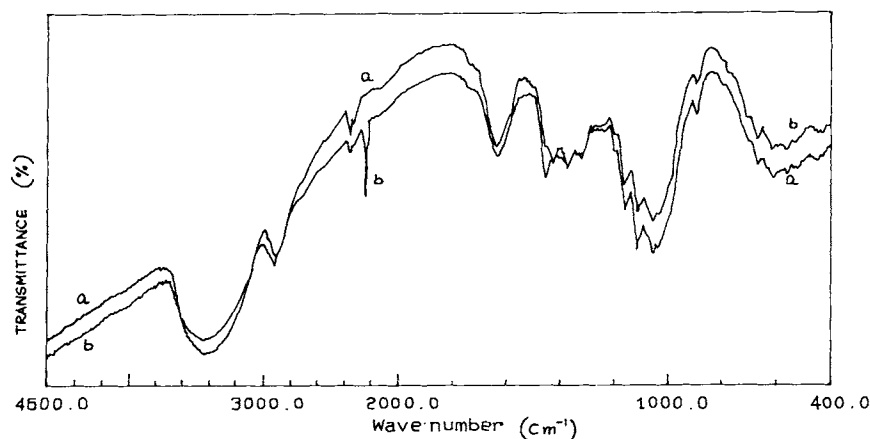


Figure 6 FTIR spectra of (a) original chemically modified PALF and (b) AN-grafted PALF.

Thermogravimetry Analysis (TGA)

TGA curves of fiber samples were recorded on a Shimadzu DT 40 thermal analyzer.

RESULTS AND DISCUSSION

Effect of Variation of Time

Figure 1 shows the effect of time on graft yield at three different temperatures (40, 50, and 60°C). In each case, the graft yield increased steadily with time up to 2 h, leveled off, and thereafter decreased to some extent. This may be attributed to the partial dissolution of the grafted fiber on prolonged exposure to the temperature of 40–60°C. Thus an optimum graft yield is obtained within 2–3 h. Similar observations have also been reported earlier^{18,19} while studying graft copolymerization of acrylonitrile onto jute fibers using different redox initiating systems.

Effect of Metal Ion Concentration

The effect of variation of metal ion (Ce^{4+}) concentration on graft yield, at three different temperatures, while keeping the concentrations of all other reagents fixed is shown in Figure 2. It is observed that percentage graft yield increases by increasing the concentration of $\text{Ce}(\text{IV})$ from 0.002 to 0.025 mol L^{-1} . This trend of increased graft yield is attributed to the creation of a greater number of grafting sites with increase of oxidant, i.e., $\text{Ce}(\text{IV})$ concentration. A similar observation has also been reported in peroxydisulfate-thiourea initiated grafting of AN onto

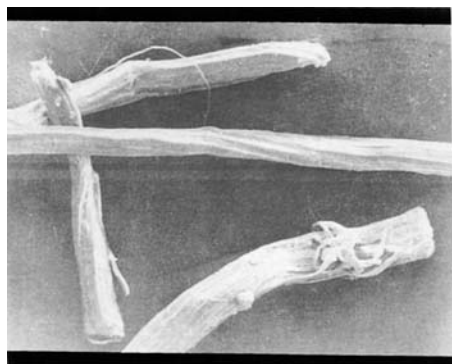
jute.¹⁹ However, the present observation is quite different from our previous communication, i.e., increase of oxidant (V^{5+}) concentration consistently decreased the graft yield.

Effect of NAG Concentration

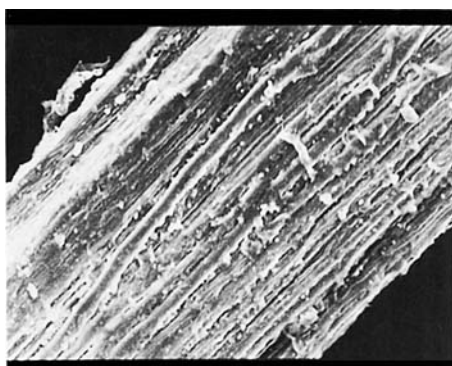
It is experimentally observed that $\text{Ce}(\text{IV})$ itself also initiates grafting of AN onto PALF. Since $\text{Ce}(\text{IV})$ coupled with *N*-acetyl glycine (NAG) is an effective redox system,²⁰ in the present investigation we have chosen this initiating system. The effect of the organic substrate has been studied by varying the concentration of NAG over a range of 0 to 0.05 mol L^{-1} . The percentage graft yield increases with NAG concentration up to 0.005 mol L^{-1} and then decreases (Fig. 3). The decreasing trend in graft yield may be attributed to the formation of an increased amount of homopolymer and rapid rate of termination and/or formation of radical scavenger at higher NAG concentration.²⁰

Effect of Monomer Concentration

The effect of variation of monomer (AN) concentration on the percentage of graft yield is shown in Figure 4. It is observed that the percent grafting increases with increase of monomer concentration from 0.1502 to 1.502 mol L^{-1} . Similar observations have also been reported in V^{5+} -cyclohexanone initiated grafting of AN onto acetylated jute¹⁸ and $\text{S}_2\text{O}_8^{2-}$ -ferrous ammonium sulfate initiated grafting of AN onto chemically modified bleached jute.¹⁹ However, in the case of grafting of AN onto jute using $\text{Ce}(\text{IV})$ -hippuric acid redox system,¹⁵ the



(a)



(b)



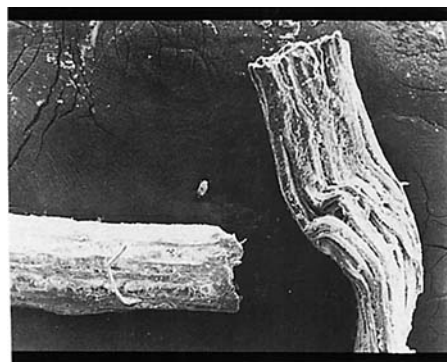
(c)

Figure 7 Scanning electron microscopy of original chemically modified PALF: (a) magnification $\times 200$, (b) magnification $\times 1000$, (c) magnification $\times 2000$.

graft yield was found to increase with increase of monomer concentration up to an optimum value beyond which it decreased.

Effect of PALF Amount

The effect of variation in the amount of pineapple leaf fiber (PALF) on percentage of graft yield is



(a)



(b)



(c)

Figure 8 Scanning electron microscopy of AN-grafted PALF: (a) magnification $\times 200$, (b) magnification $\times 1000$, (c) magnification $\times 2000$.

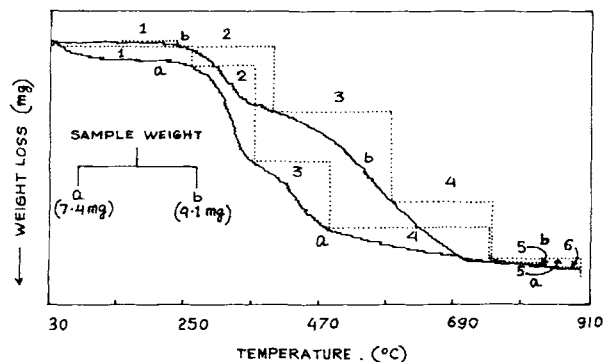


Figure 9 TGA curves of (a) original chemically modified PALF and (b) AN-grafted PALF (100.5% graft yield).

shown in Figure 5. The graft yield is found to increase with increase in amount of fibers up to an optimum value beyond which the graft yield shows a decreasing trend. The highest yield is obtained when the fiber amount is 0.150 g. This type of observation is quite contrary to previous communications on grafting onto jute fibers using different redox systems, where it is reported that graft yield either increases^{19,23} by increasing the fiber amount or decreases^{15,20} by increasing the fiber amount. Probably the rate of termination becomes faster than that of initiation with an increase in PALF amount beyond an optimum value due to abstraction of hydrogen²⁴ under the present experimental conditions.

Effect of Reaction Medium

The reaction medium plays an important role in the graft copolymerization reaction. In the present study, the graft yield decreases with an increase in sulfuric acid concentration (Table I). The increase in concentration of acid is not only unfavorable to grafting, but also it destroys some of the useful properties of the fibers.

The graft yield follows the following order when various solvents are added in equal proportions (5% v/v): control > DMF > diethyl ether > acetic acid > methanol > benzene > acetone.

Similarly, the effect of some salts when added in equivalent molar concentrations follows the order $\text{ZnSO}_4 > \text{CuSO}_4 \approx \text{Ba}(\text{NO}_3)_2 > \text{Al}_2(\text{SO}_4)_3 > \text{control} > \text{Na}_2\text{SO}_3$.

Table I reveals the above results. Similar types of studies have been reported in earlier publications.^{19,20}

REACTION MECHANISM

In the present system, it is proposed that Ce(IV) ions in sulfuric acid medium interact with NAG ($\text{CH}_3-\text{CO}-\text{NH}-\text{CH}_2-\text{COOH}$) to form a complex. The complex then dissociates in a slower step, thereby generating a free radical. This free radical abstracts hydrogen from a PALF macromolecule (FH), yielding a macroradical (F^*) that can add monomer to form grafted PALF.

CHARACTERIZATION

FTIR Spectra

FTIR spectra of chemically modified PALF and that of AN-grafted PALF are shown in Figure 6. The infrared spectra of raw and different chemically modified pineapple leaf fibers have been reported.⁴

In the present investigation it is observed that the original ungrafted PALF [Fig. 6(a)] and AN-grafted PALF [Fig. 6(b)] show the characteristic broad absorption band of hydroxyl groups around $3200-3600 \text{ cm}^{-1}$. From Figure 6(b) it is observed that AN-grafted PALF shows an additional band for the nitrile group at 2243.4 cm^{-1} , thereby confirming the occurrence of grafting. One might have expected the intensity of $-\text{OH}$ peaks to be reduced as a result of grafting, since it is a probable site for grafting. This, however, is not observed. Possibly, due to the large concentration of $-\text{OH}$ groups of PALF, small differences in concentration as a result of grafting are not detected. Similar observations have also been reported in IR spectra of AN-grafted¹⁵ and MMA-grafted²³ jute.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) of the original chemically modified PALF and AN-grafted PALF at different magnifications ($\times 200$, $\times 1000$, and $\times 2000$) are shown in Figures 7 and 8, respectively. Comparison of micrographs of the original PALF and AN-grafted PALF shows that a considerable amount of polyacrylonitrile is deposited onto the PALF surface.

Thermal Property

The TGA curves of original chemically modified PALF and AN-grafted PALF (100.5% GY) are shown in Figure 9. It is clearly observed that grafting

has improved the thermal stability of PALF. In both curves [Fig. 9(a), (b)] the various steps of decompositions have been marked as 1, 2, 3, etc. To compare thermal stability we have chosen step 2 in both curves. In Figure 9(a) under step 2 the decomposition ranges from 258.9 to 360°C amounting to 55.74% weight loss. However, in Figure 9(b) under step 2 it is computed that the decomposition ranges from 236.8 to 395.2°C amounting to only 30.90% weight loss. However, the details of the effect of increase in graft yield on thermal stability will be reported in our future communication. The thermal analysis of different chemically treated PALF has also been reported by Rajendran and Chellamani.²⁵

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