
Synthesis and Property Characterization of Pineapple Leaf Fiber Based Natural Fiber Copolymers *via* Grafting

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SUMMARY

Natural fiber copolymers were prepared by grafting hydrophobic monomer, methyl methacrylate (MMA), onto chemically modified pineapple leaf fiber (PALF) using a complex initiating system: Cu (II) SO₄ / histidine / ammonium persulfate (APS) in an aqueous medium. The overall activation energy (E_a) of grafting was computed to be 21.8 kJ mol⁻¹. The PALF-g-PMMA copolymers so obtained were characterized by FT-IR, their thermal behaviour by TGA and their morphology by scanning electron microscopy (SEM). Their tensile strength, elongation and tenacity were measured. The extent of water absorption by the grafted PALF showed that grafting of MMA imparts hydrophobicity onto PALFs. The biodegradation of the copolymers was evaluated in sludge water and soil and by using cultured microorganisms.

INTRODUCTION

Natural fiber composites are very cost-effective materials especially for the building and construction industry, packaging, automobile and railway coach interiors and storage devices. Composites, with light weight, high strength to weight ratio and stiffness property are replacing conventional materials like metals, wood, etc. Materials scientists all over the world have focused their attention on natural composites reinforced with jute, sisal, coir, pineapple, etc. primarily for their light weight, recycling potential, attractiveness to green customers and to cut down the cost of raw materials as well. Pineapple leaf fiber (PALF), a multicellular lignocellulosic fiber^{1,2} obtained from the leaf of the plant, *Annanus comosus*, contains α-cellulose (68.5%), hemicellulose (18.8%), lignin (6.04%), pectin (1.1%), fat and wax (3.2%), ash (0.9%) and other substances like proteins, organic acids, etc (1.46%)³.

In order to develop composites and copolymers with better mechanical properties and environmental performance, it is necessary to impart hydrophobicity

to the natural fibers by chemical reaction with suitable agents. Graft copolymerization, a promising technique for the modification of the physical and chemical characteristics of fibers, is adopted by many researchers for the attachment of various monomers onto jute, wool, cotton, and many lignocellulosic materials⁴⁻⁸. However, to the best of our knowledge, there has been little work on the grafting of synthetic polymers onto PALF, or using a complex initiating system, except our own report⁴ on the grafting of AM onto jute pulp using Cu (II) / glycine / KHSO₅ complex initiating system.

In the present work, the authors have modified PALF with 8% NaOH and 0.5% sodium chlorite (NaClO₂) in order to remove the lignin, which is a retarder of chemical grafting⁹. Previous work had shown that the resulting modified fibers showed better thermal stability¹⁰. These modified PALFs were then grafted with a hydrophobic monomer, methyl methacrylate, using a different complex initiating system Cu (II) / histidine / ammonium persulfate (APS) which had already been used as an effective system in the emulsion homopolymerization of MMA¹¹. The commercially important properties of the grafted samples were characterized, focusing special attention on their water absorption, surface morphology, biodegradability, dyeability, etc. for future application as an agro waste and to reduce the environmental pollution caused by plastics waste¹²⁻¹³.

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EXPERIMENTAL

Materials

Pineapple leaf fiber (PALF) was obtained from the National Institute of Research on Jute and Allied Fiber Technology, ICAR, Kolkata, India. One portion of PALF samples was treated with 8% NaOH and one with 0.5% NaClO₂ separately in two containers overnight. These fibers were then washed properly with deionised water and were neutralized with 0.1% HCl. The fibers were finally dried in a vacuum oven at 60°C for 24 h. The purpose of the alkali treatment was to remove lignin from the raw samples and thus enhance the possibility of grafting of various monomers onto the fiber backbone.

The monomer MMA was obtained from BDH, UK and was purified as reported earlier¹⁴. Histidine was obtained from SRL, India and was used as received. All other reagents used were of BDH (AR) grade and were used after purification by standard techniques.

Graft Copolymerization

PALF (~ 0.1 g) was presoaked in MMA for 30 min at various concentrations in a polymerization tube with a joint for passing nitrogen gas. The requisite amount of Cu(II)SO₄ and histidine were added. The reaction vessels were deaerated by passing nitrogen gas for

15 min and then sealed with a rubber septum. The vessels were kept in a constant temperature bath until the mixture attained thermal equilibrium. Then the required amount of initiator, APS, was injected carefully into the reaction system. (Table 1) Turbidity appeared within 10 min of the reaction time. After the desired time, the polymerization reaction was stopped by using an ice bath followed by the addition of a small amount of hydroquinone. The graft polymer thus obtained was washed thoroughly with deionised water to remove unreacted APS, Cu (II), histidine and hydroquinone.

The gross polymer thus obtained was refluxed with benzene for 24 h at 40°C to remove homopolymer. The resulting PALF-g-PMMA was dried in a vacuum oven overnight at 40° - 50°C till it attained a constant weight. The percentage graft yield (G%) and rate of grafting (R_g) were calculated from the initial weight of PALF (W_i) and the weight of PALF-g-PMMA (W_g) as:

$$G\% = [(W_g - W_i)/W_i] \times 100$$

$$R_g = (w \times 1000) / (V \times t \times M)$$

where W_g = weight of the grafted sample, W_i = weight of the fiber charged, w = weight of the monomer, V = total volume of the system, t = time of the reaction in seconds, M = molar mass of the monomer.

Table 1 Effect of concentrations of ammonium persulfate (APS), methyl methacrylate (MMA), histidine and CuSO₄ on the % grafting and the rate of grafting (R_g) at 50°C for 3 h with fiber weight, 0.1 g; NaOH, 8% (w/v); NaClO₂, 0.5% (w/v)

[MMA] mol dm ⁻³	[APS]x10 ³ mol dm ⁻³	[CuSO ₄] x 10 ³ mol dm ⁻³	[Histidine] x 10 ³ mol dm ⁻³	% grafting		R _g x 10 ⁵ mol dm ⁻³ s ⁻¹	
				NaOH	NaClO ₂	NaOH	NaClO ₂
0.47	10.0	10.0	10.0	43.68	64.7	0.2	0.29
0.94	10.0	10.0	10.0	69.70	88.5	0.32	0.40
1.41	10.0	10.0	10.0	88.80	110.2	0.41	0.51
1.88	10.0	10.0	10.0	114.0	131.6	0.52	0.60
2.35	10.0	10.0	10.0	118.0	153.2	0.54	0.70
0.94	5.0	10.0	10.0	-	40.8	-	0.19
0.94	15.0	10.0	10.0	-	78.1	-	0.36
0.94	20.0	10.0	10.0	-	93.8	-	0.43
0.94	25.0	10.0	10.0	-	106.2	-	0.49
0.94	10.0	5.0	10.0	-	35.5	-	0.16
0.94	10.0	15.0	10.0	-	82.7	-	0.38
0.94	10.0	20.0	10.0	-	63.9	-	0.29
0.94	10.0	25.0	10.0	-	44.5	-	0.20
0.94	10.0	10.0	5.0	-	39.6	-	0.18
0.94	10.0	10.0	15.0	-	74.2	-	0.34
0.94	10.0	10.0	20.0	-	60.1	-	0.27
0.94	10.0	10.0	25.0	-	48.7	-	0.22

Characterization and Properties

(i) Infrared spectra (IR)

The FT-IR spectra of the alkali treated PALF, PMMA homopolymer and PALF-g-PMMA copolymer were taken using KBr pellets and a Perkin Elmer Paragon 500 FT-IR spectrophotometer.

(ii) Thermogravimetric analysis (TGA)

TGA of the samples was carried out using a Shimadzu DTG-50 thermal analyzer. The samples were heated to a temperature of 500°C at the rate of 10°C per min starting from room temperature (30°C).

(iii) Tensile behaviour

The tensile behaviour of the raw PALF, alkali treated PALF and the grafted PALF copolymer were determined by measuring the tensile strength following the method of Haque and Habibuddowla¹⁵. The tensile strength was determined from the tenacity and elongation at break by using the following relationship:

Tensile strength = (tenacity at break / elongation at break) × 100

The tenacity was expressed as g/den. After conditioning the samples, they were combed. Fiber aggregates of uniform length were taken and their weight and length were determined. Their tensile strength was determined by means of a Dutrons tensile tester, Brand-20 Kgf capacity.

(iv) Scanning electron microscopy (SEM)

The SEM micrographs of PALF and grafted PALF copolymers were recorded by a Jeol, Ltd, Japan, Model 5200 scanning electron microscope at magnifications of 1,500 and 5,000.

(v) Water absorption

The water absorption (W_{abs}) of the raw PALF and the grafted PALF copolymer was determined by immersing the dry samples ($W_0 = 0.1$ g each) in deionised water at 30°C for 7, 15, 21 and 28 days. After the required time the samples were strained for 30 min to eliminate of nonabsorbed water and then the weight of the swollen samples (W_s) was recorded. The absorption was calculated as

$$\% W_{\text{abs}} (\text{g/g}) = [(W_s - W_0) / W_0] \times 100$$

(vi) Biodegradation

The biodegradation of raw PALF and the grafted PALF copolymer were studied in sludge water, soil burial and a bacteria culture medium in order to compare the extent of biodegradation under these conditions.

Sludge water degradation

0.1 g of the fiber samples were immersed in the supernatant liquid from standard activated sludge and incubated at 40°C. The activated sludge was collected from a waste dump area. It was centrifuged and the supernatant liquid was taken for detailed study.

Soil burial degradation

Soil burial is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. For the soil burial test, the samples were buried in the soil for up to one year and at predetermined intervals, they were recovered from the soil, cleaned with a buffer / ethanol solution and dried in a vacuum oven. The dried samples were weighed to determine the weight loss.

Cultured medium degradation

A culture medium was prepared by taking Agar nutrient medium. In the medium *Bacillus cereus* gram positive bacteria was cultured. The broth so prepared was kept in an incubator at about 40°C for 2 h. Then 0.1 g each of PALF and the grafted PALF copolymer at different grafting percentage were added.

All the above systems were monitored for periods of 7, 14, 21 and 28 days. After the required time period the samples were washed repeatedly with lukewarm deionised water and dried in a vacuum oven at 35-40°C for 24 h before being weighed to determine the weight loss.

(vii) Dyeing properties

The dyeability of the raw PALF and the grafted PALF copolymer was studied using 1% (w/v) ethanolic solution of a dye i.e., Erichrome black T. Then 5% (w/v) NaOH solution was added to the dye as described in earlier reports¹². Copper complexes are suitable for mordanting cellulosic fibers such as cotton, linen, ramie, pineapple fiber, etc.¹³. To mordant the fiber it is first treated with a boiling solution of CuSO_4 in the presence of a reducing agent such as oxalic acid. The

mordant fiber is then dipped in the solution of the dye as prepared above so as to precipitate the insoluble coloured lake on the fiber. After dyeing, the fibers were rinsed sequentially with cold–hot–cold water, stored at 40°C for 12 h and then dipped in 10% (w/v) NaCl solution.

RESULTS AND DISCUSSION

(i) Effect of NaOH and NaClO₂ on graft yield

The grafting of MMA onto PALF, washed by both NaOH and NaClO₂, was studied using various systems at 50°C for 3–4 h with and without the complex catalysts and initiators. From this it was clear that the PALF treated with NaClO₂ gave a better grafting yield than washing with NaOH. (Table 1) This may be because NaClO₂ has a bleaching action and so the PALF treated with NaClO₂ is more lignin free than it is when washed with NaOH. Thus, the lower the lignin content, the higher the grafting rate.

(ii) Effect of complex catalyst

It has been found that the percentage grafting yield of various initiating systems is in the following order:

{(Cu (II) / histidine), nil} < {(APS / histidine), 20.2%} < {(APS), 20.4%} < {(APS / Cu (II)), 21.8%} < {(Cu (II) / histidine / APS), 69.7%}

Thus the system Cu (II) / histidine / APS were chosen for detailed morphological and kinetic studies on the grafting of MMA onto chemically modified PALF. The novel catalytic action of the Cu (II) / histidine complex on the facile decomposition of APS has already been reported by us¹¹ in the context of the emulsion homopolymerization of MMA.

(iii) Effect of grafting time and temperature on grafting yield

Figure 1 shows the effect of time on the grafting percentage at 50°C, keeping the concentrations of MMA, APS, Cu (II) SO₄ and histidine constant. It was found that up to the 4 h stage, the percentage grafting showed a regular increase and after 4 h it showed a dead end polymerization tendency. This could be due to the high activity of the initiator at the initial period of the reaction or to the partial dissolution of the grafted fibers during the prolonged incubation period, and is in accordance with observations reported earlier during the graft copolymerization of MMA onto chemically modified coir fibers¹⁶.

On increasing the temperature, from 35°C to 70°C, the rate of grafting showed a regular increase. The overall activation energy (E_a) of grafting was calculated to be 21.8 kJ mol⁻¹ from the Arrhenius plot (Figure 2).

(iv) Effect of monomer, initiator, Cu (II) and histidine concentrations

The effect of monomer concentration on the grafting percentage and the rate of grafting, R_g, was investigated by changing [MMA] from 0.47 - 2.36 mol dm⁻³, as shown in Table 1. From the double logarithmic graph, the rate of grafting was found to be 0.6 order-dependent on the monomer concentration.

Figure 1 Variation of % grafting with reaction time for Cu(II) - histidine complex catalyzed grafting of PMMA with fiber = 0.1g, [CuSO₄] = 10 × 10⁻³ mol dm⁻³, [Histidine] = 10 × 10⁻³ mol dm⁻³, [MMA] = 0.94 mol dm⁻³, [APS] = 10 × 10⁻³ mol dm⁻³ at 50°C

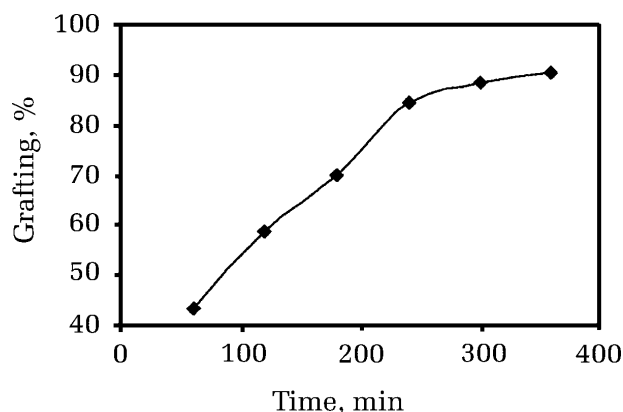
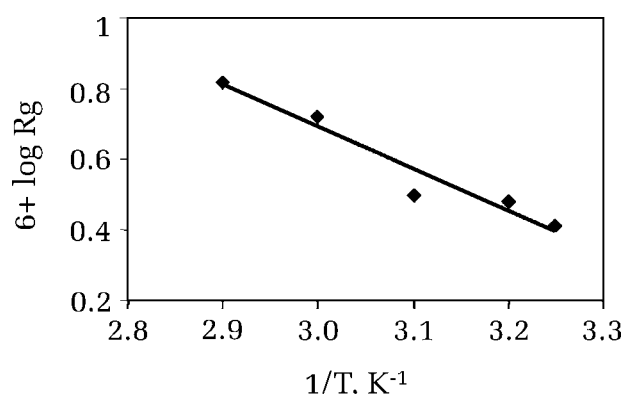


Figure 2 Arrhenius plot of log R_g vs. 1/T at fiber = 0.1 g, [CuSO₄] = 10 × 10⁻³ mol dm⁻³, [Histidine] = 10 × 10⁻³ mol dm⁻³, [MMA] = 0.94 mol dm⁻³, [APS] = 10 × 10⁻³ mol dm⁻³



The effect of APS concentration on the rate of grafting has been studied by varying the concentration of APS in the range of 5.0×10^{-3} – 10.0×10^{-3} mol dm⁻³. The results are tabulated in Table 1. In the above range the percentage grafting and the rate of grafting were found to increase with the increase in concentration of active free radicals. The double logarithmic graph of R_g against [APS] determined the overall rate to be 0.6 power-dependent on [APS].

The rate of grafting was studied as a function of Cu (II) SO₄ concentration and histidine concentration, both in the range 5.0×10^{-3} to 25.0×10^{-3} mol dm⁻³. The double logarithmic graphs reveal that the grafting reaction is 0.95 (\approx first) order-dependent on Cu (II) and 0.85 order-dependent on histidine concentrations.

(v) Characterization and properties of the grafted copolymers

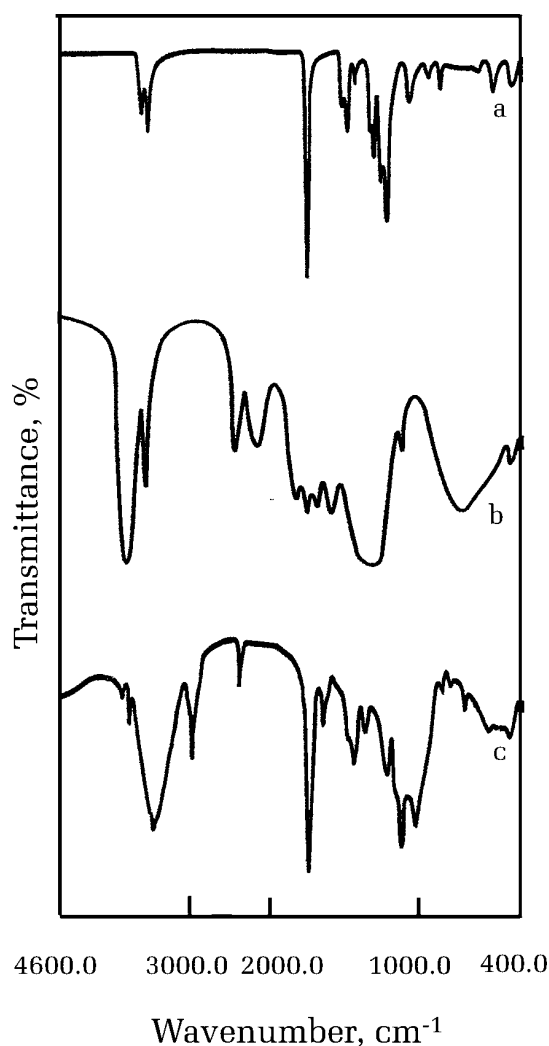
FT-IR spectra

From the FT-IR spectra of the grafted composites (Figure 3) a strong broad peak at 3447 cm^{-1} shows the characteristic H-bond (OH)_{str} vibration as observed in the spectra of PALF reported earlier². The presence of sharp bands near 1734 cm^{-1} and 1647 cm^{-1} indicate the presence of a carbonyl group ($>\text{C}=\text{O}$)_{str} acquired from the monomer. Also, there is a combination band attributed to the α,β -unsaturated ester at around 1196 cm^{-1} and 1151 cm^{-1} . There are other bands near 2953 cm^{-1} corresponding to the normal (C-H)_{str}, 1456 cm^{-1} for (C-C)_{str}, 1386 cm^{-1} for (C-H)_{def} and 1063 cm^{-1} for (C-O)_{str}.

Thermal properties

The thermal behaviour of the ungrafted fiber and the grafted fibers were studied by comparing their primary thermograms (TGA curves). The primary thermograms of the raw PALF, alkali treated PALF and PALF – g – PMMA copolymer are shown in Figure 4. From the curves the temperature of decomposition (T_D) were found out to be 345°C for raw fiber, 352°C for alkali treated fiber and 390°C for the grafted copolymer. Again between $30 - 250^\circ\text{C}$ there is a 7.5% weight loss for raw fiber, 6% for alkali treated fiber and a mere 2.5% for the grafted fiber. This may be due to the loss of water. This indicates that the grafting of the fiber decreases the moisture regaining capacity, thus imparting hydrophobicity to the fiber. After that there is a sharp degradation till the residual mass is 6% for raw fiber, 10% in alkali treated fiber and 17.5% for

Figure 3 FT-IR curves of (a) PMMA homopolymer, (b) alkali treated PALF and (c) PALF - g - PMMA copolymer



grafted fiber at temperature of 345°C , 352°C and 390°C respectively. Thus the T_D values and the residual mass indicate that on grafting, the fiber copolymer becomes somewhat resistant to heat.

Tensile behaviour

The strength of the raw, chemically modified and grafted copolymer was calculated and is presented in Table 2. The decrease in tensile strength due to alkali treatment was not only compensated but enhanced by the grafting of PMMA onto the fiber backbone, which imparted 10 – 50% improvement in tensile strength. Similar effects were observed for the elongation and tenacity of the grafted copolymers and the raw fibers.

Samples	% grafting	Elongation at break (BL%)	Tenacity g/den	Tensile strength N/m ²	Tensile strength after 12 months soil burial N/m ²	% strength retained
Raw PALF	0	0.26	0.092	3.54	0.42	11.87
Alkali (NaClO ₂) treated PALF ^r	0	0.32	0.103	3.32	0.34	10.23
Modified PALF	67.7	0.48	0.212	4.42	0.47	10.64
– g – PMMA	110.2	0.55	0.260	4.73	0.63	13.33
composites	153.2	0.63	0.324	5.14	0.78	15.16

Figure 4 TGA curves of raw PALF (a), alkali treated PALF (b), and PALF-g-PMMA copolymer (c)

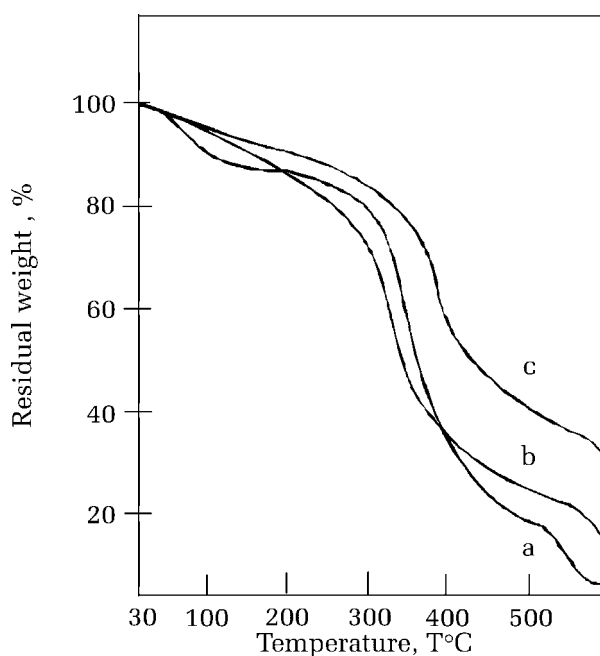
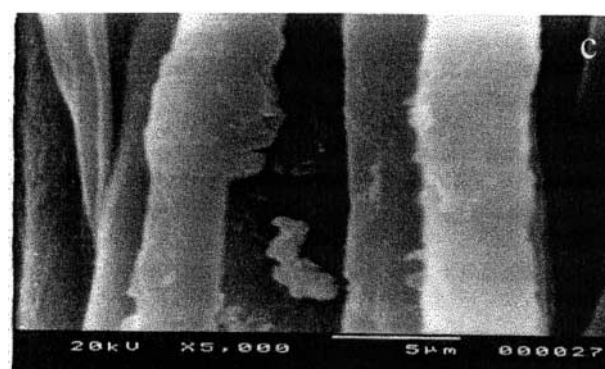
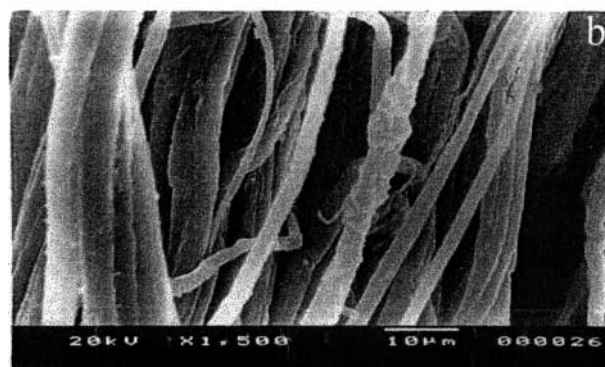
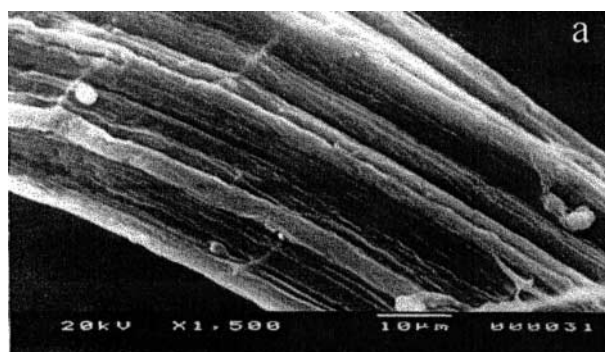


Figure 5 SEM micrographs of alkali treated PALF (a), PALF – g – PMMA copolymer at two magnifications, x1500 (b) and x5000 (c)



Surface morphology by SEM

The SEM micrographs of alkali treated PALF and grafted PALF copolymers are shown in Figure 5(a-c). Figure 5a shows the strands of the alkali-treated PALF. The surface of the fiber was smooth and uniform. On grafting with PMMA the surface morphology changed (Figure 5b). On further magnification (Figure 5c) it is seen that the PMMA has penetrated into the lumens, as shown by the white interior of the fiber strand, as seen in the grafting of polyacrylamide onto jute pulp¹⁷.

Water absorption

The amounts of water regained in the grafted samples were less than for the raw PALF. The water absorption decreased with increased grafting of PMMA onto PALF. It was observed that within a time period of 15 days there was a tremendous uptake of water and after that the uptake decreased until the saturation point, as shown in Figure 6. But in the case of raw PALF the water uptake was more uniform. This demonstrates that the grafting of hydrophobic monomer imparts hydrophobicity to PALF.

Biodegradation

The weight losses due to microbial degradation of raw PALF and grafted PALF copolymer are shown in Table 3. In the bacterial medium the weight loss was very high and the bacteria were responsible for the degradation of the fiber as well as the grafted

fibers. Again with the increase in Rg the weight loss due to degradation decreases, indicating that the microbial degradation becomes slower on grafting of a hydrophobic monomer onto a natural fiber.

The results are in good agreement with the decrease in tensile strength after one year's soil burial, as recorded in Table 2. Furthermore, the weight loss and tensile strength lowering reveals that an increase in grafting of a hydrophobic monomer onto the fiber matrix decreases the rate of biodegradation, making them more resistant to bacterial or fungal attack. Hence, from all three tests (Table 3), the hydrophobicity of the PMMA plastics plays an important role in the biodegradability of the copolymers. As the effect of hydrophobicity on biodegradability of the copolymers followed the same trend as it did on water absorption (Figure 6), the biodegradability was directly proportional to the water absorbency of the copolymers.

Dyeing

After keeping the dyed fibers (both raw and grafted) in NaCl for 12 h and then washing them properly with water and soap and giving further exposure to sunlight, it was found that the colour of the dyed fiber remained intact, even after prolonged exposure to sunlight. Moreover the grafted fibers were found to be more strongly dyed than the raw fibers.

MECHANISM

The mode of initiator decomposition¹¹, the chain initiation and termination mechanisms of graft copolymerization involving the novel catalytic system Cu (II) / histidine / APS can be interpreted as follows:

Figure 6 Water absorption of various grafted copolymers and raw fiber for a time period of 7, 15, 21 and 28 days (◆) Fiber, (■) 67.7%, (□) 110.2%, (▲) 153.2% grafted PALF

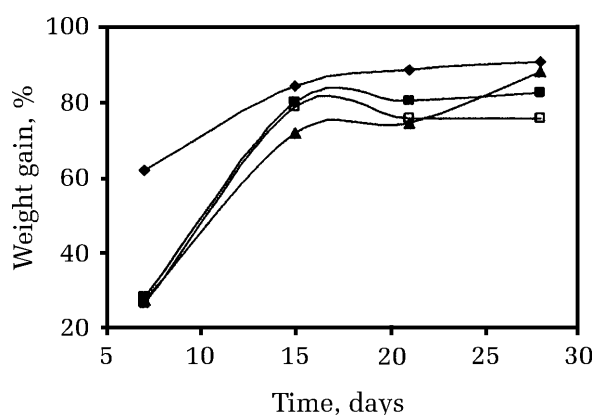
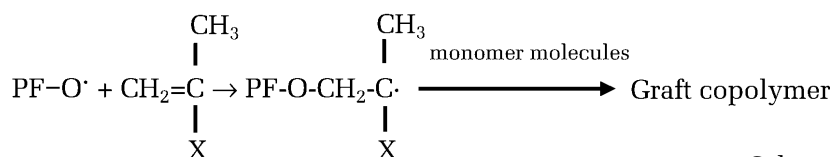
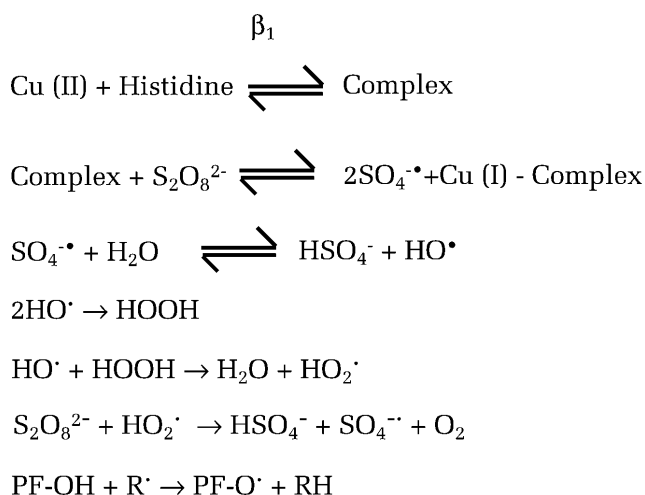


Table 3 Biodegradation studies of raw fiber and grafted fiber copolymer in sludge water, soil and a bacterial medium

Time period	% Weight loss (initial weight of samples = 0.1 g)											
	Raw Fiber			Copolymer 1 (67.7% grafting)			Copolymer 2 (110.2% grafting)			Copolymer 3 (153.2% grafting)		
	Sludge water	Soil burial	<i>Bacillus cereus</i>	Sludge water	Soil burial	<i>Bacillus cereus</i>	Sludge water	Soil burial	<i>Bacillus cereus</i>	Sludge water	Soil burial	<i>Bacillus cereus</i>
7 days	14	1.8	28	23	1.5	36	22	1.2	34	21	1.0	31
15 days	24	2.6	43	25	2.0	40	22	1.8	38	20	1.5	32
21 days	27	3.0	39	29	2.8	42	25	2.2	38	22	2.0	23
28 days	36	4.0	48	31	3.3	44	27	3.0	45	23	2.8	25
6 months	-	28.0	-	-	21.0	-	-	18.0	-	-	13.0	-
12 months	-	48.0	-	-	32.0	-	-	29.0	-	-	22.0	-



where PF - OH = PALF with terminal -OH groups

R[•] = Free radical species, e.g. HO[•] and HO₂[•]

X = -COOCH₃

Applying steady state principles and assuming mutual termination, the rate expression is as follows: $R_g \propto [\text{Cu(II)}]^{0.95}[\text{Histidine}]^{0.85}[\text{APS}]^{0.6}[\text{MMA}]^{0.6}$.

CONCLUSIONS

Natural fiber is a candidate for making copolymers and composites, especially for partial replacement of high cost glass fibers for low load bearing appliances. As such, the commercial exploitation of PALF-copolymer and composites for non-structural applications has excellent potential. Also with increasing emphasis on fuel efficiency, natural fiber such as PALF based copolymers and composites will enjoy wider applications in automobiles and railway coaches. PALF - g - PMMA copolymers show outstanding thermal, tensile, water absorbency, dyeability and eco-friendly biodegradation properties when placed in sludge water, soil or cultured microorganisms. The fiber grafted with hydrophobic PMMA shows improved resistance to water absorption and biodegradation, which opens the door to industrial applications.

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REFERENCES

1. Mishra S.P., A Textbook of Fiber Science and Technology, New Age International Publishers, New Delhi, 1st edition, (2000).
2. Saha S. C., Das B. K., Ray P. K., Pandey S. N. and Goswami K., J. Appl. Polym. Sci., 43 (1991) 1885.
3. Bhaduri S. K., Sen S. K. and Dasgupta P. C., Indian Pulp Paper, 34 (1979) 15.
4. Sahoo P. K., Swain S. K. and Debsarkar N. L., J. Appl. Polym. Sci., 83 (2002) 1963.
5. Sakurada I., Res. Rep. Jpn. Cotton Tech. Inst., 56 (1962) 1.
6. Sakurada I., Okada T. and Ikada Y., Cell Chem. Technol., 6 (1972) 35.
7. Sahoo P. K., Giri G. and Samal R. K., J. Appl. Polym. Sci., 40(3-4) (1990) 471.
8. Mohanty A. K., J. Macromol. Sci., Rev. Macromol. Chem. Phys., 27(3) (1987) 593.
9. Kubota H. and Ogiwara Y., J. Appl. Polym. Sci., 13 (1969) 1569.
10. Samal R. K. and Ray Mukul C., J. Polym. Mater., 15 (1998) 27.
11. Sahoo P. K., Sahu G. C. and Swain S. K., Polymer J. (Japan), 35(4) (2003) 364.
12. Oktem T., Seventekin N., Ayhan H. and Piskin E., Indian J. Fiber and Textile Research, 27 (2002) 161.
13. Sharma B. K., Industrial Chemistry, Goel Publishing House, Meerut, 9th edition, (1997).
14. Sahoo P. K., Bhattacharya S. P. and Samal R. K., Eur. Polym. J., 21 (1985) 499.
15. Haque M. M. and Habibuddowla Md., J. Sci. Indian Res. (Bangladesh), 15 (1980) 64.
16. Rout J., Mishra M. and Mohanty A. K., Polym Adv. Technol., 10 (1999) 336.
17. Sahoo P. K., Mohapatra R., Debsarkar N. L., Sahoo A. and Swain S. K., Intl. J. Polym. Anal. Charact., 000 (2003) 000 (in press).