

Chemically Induced Graft Copolymerization of Acrylonitrile Onto Lignocellulosic Fibers

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ABSTRACT: The grafting of vinyl monomers is an important method for replacing hydrophilic hydroxyl groups present on the surface of natural fibers by hydrophobic polymer chains. It improves the compatibility of natural fibers with polymer matrixes during the fabrication of natural-fiber-reinforced polymer composites. This article deals with the graft copolymerization of acrylonitrile onto *Agave americana* fibers in air in the presence of ceric ammonium nitrate as a redox initiator. A maximum percentage grafting of 24% was obtained after the optimization of various reaction parameters, including the reaction time, temperature, and concentrations of nitric acid, initiator, and monomer. The graft

copolymers obtained under the optimum conditions were then subjected to the evaluation of different physicochemical properties, including swelling behavior in different solvents, moisture absorption behavior under different humidity levels, and chemical resistance. The graft copolymers were further characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermal analysis (thermogravimetric analysis/differential thermal analysis), and X-ray diffraction techniques. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1891–1898, 2012

Key words: fibers; graft copolymers; infrared spectroscopy

INTRODUCTION

The need for natural biomass-based materials has been felt by the research community as these materials are a good alternative for the continuously depleting conventional petroleum resources. However, the complete replacement of petroleum-based products by natural biomass-based products is not possible; therefore, a wise solution would be a combination of petroleum-based synthetic products and biomass-based natural products to develop materials that could be used in wide applications economically.

Traditional composite materials use synthetic fibers, such as glass, aramid, and carbon fibers, as reinforcements. Although synthetic-fiber-reinforced composite materials exhibit fairly good mechanical properties, they are not ecofriendly. The burning of substances derived from the fossil products releases a large amount of carbon dioxide into the atmosphere, which is believed to be the root cause of the greenhouse effect.¹ In light of the interest in reducing the environmental impact of materials and the pressure to decrease mankind's dependence on fossil-based products, there is increasing interest in maximizing the use

of materials that are renewable and can be recycled.² The use of agricultural materials as raw materials in industry not only provides an ecofriendly renewable resource but also generates a nonfood source of economic development for rural areas.

The use of natural fibers as reinforcements in composite materials has also been supported by a number of advantages, including their renewable nature, low density, high specific strength, good thermal properties, nonabrasive nature, biodegradability, impact resistance, flexibility, abundance in nature, and less skin and respiratory irritation, over synthetic fibers.^{3–10} Despite the large number of advantages of natural fibers, they also possess disadvantages, including high moisture absorbance, lesser resistance to chemicals, and low compatibility with polymer matrixes; these limit their use in polymer-matrix-based composites.¹¹ The property of high moisture absorption of hydrophilic natural fibers limits their applications because of formation of weak fiber–matrix interactions.¹²

There are a number of methods, such as mercerization, silane treatment, acetylation, benzylation, isocyanate treatment, and graft copolymerization,^{13–17} which have been used by various researchers all over the world to modify the surface of the natural fibers. Among these methods, graft copolymerization is most extensively used for natural-fiber surface modification. Many workers have carried out the graft copolymerizations of different monomers on various natural fibers with different initiator systems.^{18–24} Mishra et al.²⁵ studied the graft copolymerization of acrylonitrile onto sisal fibers in the

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presence of NaIO_4 and CuSO_4 as initiator systems in aqueous media. The reaction medium, treatment time, initiator concentration, monomer concentration, and even fiber loading influenced the graft yield. Chauhan et al.²⁶ graft-copolymerized methyl methacrylate onto jute fiber in the presence of ceric ions as initiators.

Grafting is an attractive method for incorporating many desired properties into the backbone of polymers while retaining the original properties. Properties, such as the swelling behavior in different solvents, moisture absorption behavior, solubility behavior, thermal resistance, and resistance to chemicals, can be improved by the grafting of different vinyl monomers onto natural lignocellulosic fibers. There are a number of techniques, including chemical, radiation, photoinitiated, plasma induced, and enzymatic grafting, which have been exercised by researchers in the past.^{27–29}

The initiator plays a very important role in chemically induced graft copolymerization as it generates the reactive species necessary to initiate the grafting reaction. Grafting by chemical methods may proceed either by a free-radical mechanism or by an ionic method. Free radicals are generated by the initiators and transferred to the backbone to react with monomers to result in the formation of graft copolymers. The free radicals may be either generated in the reaction medium through a redox reaction and then transferred to the backbone or generated by the direct oxidation of the backbone by certain transition-metal ions, such as Ce^{4+} , Cr^{6+} , and V^{5+} . In the later case, the redox potential of the metal ions is an important parameter in determining the grafting efficiency. In general, metal ions with lower oxidation potentials result in better graft efficiency. The metal ions are supposed to form an ion-polymer chelate complex, which dissociates via one electron transfer to produce free radicals.³⁰

The graft copolymerization of methyl methacrylate on to *Agave americana* fibers under pressure in the presence of ceric ions as initiators was reported earlier.³¹ A percentage grafting (P_g) of 13.6% was obtained, and it was observed that the grafting of methyl methacrylate on to agave fiber resulted in improved physicochemical and thermal properties. In this study, the graft copolymerization of acrylonitrile was carried out in air in the presence of ceric ions as initiators. In this work, we aimed to study the effect of changes in the monomer and the reaction conditions on the percentage graft yield and physicochemical properties of *A. americana* fibers. These lignocellulosic fibers occur abundantly in this region and are used for domestic purposes, such as making ropes, woven carpets, and bags, by the native people. These fibers can be used economically and commercially as a replacement for synthetic fibers during the fabrication of composites. Therefore, this research work will help to ensure the proper utilization of this natural wealth, which would otherwise be wasted.

EXPERIMENTAL

Materials used

A. americana fibers were extracted from the leaves of *A. americana* plants growing in the vicinity of the National Institute of Technology Hamirpur (Himachal Pradesh) by a water retting method. The leaves had dimensions of $250 \times 20 \times 5 \text{ cm}^3$. The average chemical constituents of the agave fibers were cellulose = 65.2%, hemicellulose = 32.1%, and lignin = 2.7%.³²

The fibers thus obtained were thoroughly washed with detergent and then with water several times to remove impurities. The fibers were then Soxhlet-extracted with acetone for 72 h after combing was done to remove the waxes and other soluble impurities from the surface of the fibers. All of the chemicals used were analytical grade and were used as received. A Libror AEG-220 electronic balance (Shimadzu, Naka-gyo-Ku, Kyoto, Japan) was used for weighing.

Methods

Graft copolymerization of the acrylonitrile onto agave fibers

A. americana fibers (0.5 g) were immersed in 100 mL of distilled water for 24 h before the grafting reaction. A known amount of initiator ceric ammonium nitrate (CAN) dissolved in an optimized concentration ($2.77 \times 10^{-1} \text{ mol/L}$) of nitric acid was then added to the reaction mixture. This was followed by the addition of monomer, and the contents of the reaction mixture were stirred constantly at a definite temperature for an optimized time interval. The homopolymer was removed with the help of dimethyl formamide, and the grafted fibers thus obtained were thoroughly washed with distilled water and dried at 60°C until a constant weight was reached. P_g and the percentage efficiency (P_e) were calculated as reported.³³

$$P_g = \frac{W_g - W}{W} \times 100$$

$$P_e = \frac{W_g - W}{W_m} \times 100$$

where W , W_g , and W_m are the weights of the ungrafted fiber, grafted fiber, and monomer, respectively.

Physicochemical studies

Swelling behavior

Known initial weights (W_i 's) of the grafted and raw fibers were immersed in different solvents for 24 h for swelling. The swollen fibers were then taken out of the solvents, and the excess solvent was removed by wiping with the help of filter paper. The final weights (W_f 's) of the samples were noted, and the

percentage swelling was calculated according to the following formula:

$$\text{Swelling}(\%) = \frac{W_f - W_i}{W_i} \times 100$$

Moisture absorption studies

The grafted and raw fibers were dried in a hot-air oven at 60°C to a constant weight before the moisture absorption studies were carried out. Known amounts of the samples (W_1) of both the grafted and raw fibers were kept at a particular humidity level in a humidity chamber (Swastika) for 2 h. The samples were then again weighed to determine the final weight (W_2). The humidity studies were performed at relative humidities ranging between 20 and 100%. The percentage moisture absorption (M_{abs}) was calculated according to the following formula:

$$M_{\text{abs}}(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

Chemical resistance studies

The chemical resistances of the grafted and raw fibers were studied as a function of the weight loss of the fibers. Known weights of the raw and grafted fibers (W_1 's) were immersed in known amounts of acids and bases of known strengths for 24 h. The samples were washed thoroughly with distilled water and dried in a hot-air oven at 60°C to a constant weight. The final weights of the samples subjected to the attack of chemicals (W_2 's) were determined:

$$\text{Weight loss}(\%) = \frac{W_1 - W_2}{W_1} \times 100$$

RESULTS AND DISCUSSION

Because of the presence of a vast network of hydrogen bonding in lignocellulosic fibers such as *A. americana*, monomer molecules cannot penetrate the surface of the fibers easily. Therefore, the fibers were immersed in water for 24 h before the graft copolymerization reaction; this led to the swelling of the fibers and an increase in the surface area.

Ceric ions formed the complex with the carbon chains of the polymeric backbone and generated free radicals. Therefore, ceric ions played an important role in initiating the graft copolymerization of acrylonitrile onto the *A. americana* fibers. The hydroxyl groups present on C-2, C-3, C-6, and C-H were the active sites for grafting. Ceric ions formed chelate complexes with the cellulose molecules through hydroxyl groups at the C-2 and C-3 of glucose units. Ce(IV) ions were reduced to Ce(III) by the breakage of bonds and the transfer of electrons from the cellulose molecule, as a result of which free-radical sites were

generated on the backbone. The free radicals were also generated in the monomer chains; they were then transferred to the free-radical reactive sites present on the backbone and formed the graft copolymer.³⁴ Nitric acid also played a vital role in the grafting process, as it prevented the formation of bulkier $[\text{Ce}-\text{O}-\text{Ce}]^{+6}$ ions, which are not able to form chelate complexes with cellulose molecules of the fibers.³⁵

Optimization of the different reaction parameters during the grafting of acrylonitrile onto *A. americana* fibers

The extent of grafting onto the cellulosic fiber was influenced by a number of parameters, including the reaction time, temperature, and concentrations of the monomer, the initiator, and nitric acid (Table I).

It was observed that the percentage graft yield increased with increasing reaction time and temperature up to a limiting value. The optimum values obtained for the reaction time and temperature were 60 min and 45°C, respectively, at which a maximum percentage graft yield of 24% was obtained. When the time and reaction temperature were increased beyond these critical values, a decrease in the graft yield was observed. It was probably due to the occurrence of various side-chain reactions, along with the graft copolymerization reaction. Further, at elevated temperatures, the strength of the fiber decreased; this also affected the percentage graft yield.

Grafting was also found to increase with an initial rise in the concentration of acrylonitrile, reaching maximum at an optimum value. With a further increase in the concentration of acrylonitrile, the graft yield showed a decline; this may have been due to the increased viscosity of the reaction medium.

During the optimization of the initiator and nitric acid concentration, similar behavior was observed. From the experimental studies, it was revealed that a linear increase was observed with initial increases in the concentrations of initiator and nitric acid. After reaching the optimum value at 0.500 g and 2.77×10^{-1} mol/L, the graft yield decreased with further increases in concentration.

With the initial increase in the initiator concentration, more Ce(IV) ions were available to generate free-radical sites on the backbone; this resulted in the increase in the graft yield. However, when the concentration exceeded the critical value, the excess Ce(IV) ions terminated the chain reaction by accepting the electrons from monomer radicals thus responsible for the reduced graft yield.

In aqueous media, there existed an equilibrium between Ce^{4+} ions and bulkier $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ ions, which were not able to form a chelate complex with the carbon chains on the backbone. Nitric acid broke the bulkier complex ion and shifted the equilibrium toward

TABLE I
Optimization of the Reaction Parameters for the Grafting of Acrylonitrile onto *A. americana* Fibers

Sample	Time (min)	Temperature (°C)	Monomer (mol/L)	CAN (mmol/L)	Nitric acid (mol/L)	P_g	P_e
1	30	45	2.92	8.77	2.77	16.7	5.18
2	60	45	2.92	8.77	2.77	23.9	7.42
3	90	45	2.92	8.77	2.77	22.4	6.96
4	120	45	2.92	8.77	2.77	18.3	5.68
5	150	45	2.92	8.77	2.77	16.6	5.14
6	60	25	2.92	8.77	2.77	17.9	5.55
7	60	35	2.92	8.77	2.77	18.9	5.86
8	60	55	2.92	8.77	2.77	21.4	6.63
9	60	65	2.92	8.77	2.77	18.3	5.68
10	60	45	2.92	4.38	2.77	13.5	4.19
11	60	45	2.92	6.58	2.77	21.7	6.73
12	60	45	2.92	10.96	2.77	22	6.86
13	60	45	2.92	13.15	2.77	16.3	5.06
14	60	45	2.92	8.77	1.38	17.7	5.49
15	60	45	2.92	8.77	2.07	18.7	5.81
16	60	45	2.92	8.77	3.46	12.7	3.95
17	60	45	2.92	8.77	4.15	7.6	2.34
18	60	45	0.73	8.77	2.77	1.9	0.61
19	60	45	1.46	8.77	2.77	2.3	0.72
20	60	45	2.19	8.77	2.77	5.6	1.73
21	60	45	3.65	8.77	2.77	24	4.86

the formation of Ce^{4+} ions; this may have been the reason for the increase in the graft yield with the initial increase in the concentration of nitric acid. However, at high concentrations ($>2.77 \times 10^{-1}$ mol/L), nitric acid oxidized the cellulosic fiber and caused the degeneration of free radicals.

Studies of some physicochemical properties

The physicochemical properties, such as swelling behavior in different solvents, moisture absorption behavior under different humidity levels, and resistance to chemicals, of the grafted and ungrafted fibers were studied.

The swelling behavior of the raw and grafted fibers was studied in different solvents, such as water, ethanol, dimethylformamide (DMF), and carbon tetrachloride. It was observed that the raw and grafted fibers showed different trends in swelling. The raw fibers showed maximum swelling in water, and the percentage swelling decreased with increasing percentage graft. This may have been due to the greater affinity of the polar $-OH$ groups present in the raw fiber toward water. Further, as the percentage graft increased, $-OH$ groups were gradually replaced by polyacrylonitrile [poly(AN)] chains; this resulted in the decrease in percentage swelling. Similarly, the grafted fibers showed maximum swelling in carbon tetrachloride, which increased with percentage graft. This may have been due to the greater affinity of poly(AN) chains toward a nonpolar solvent, such as carbon tetrachloride. Trends in the swelling behavior of the raw and grafted fibers are shown in Table II.

The samples of both raw and grafted fibers with different values of percentage graft were subjected to

the influence of different humidity levels for definite time intervals. From the humidity studies of the raw and agave-g-poly(AN) fibers, we observed that the raw fibers absorbed moisture to the maximum extent at a given humidity level. This may have been due to the greater affinity of water molecules toward hydroxyl groups in the lignocellulosic fibers, which resulted in greater moisture absorption. Further moisture absorption behavior was found to decrease as the percentage graft increases. This may have been due to the incorporation of hydrophobic poly(AN) chains in the fiber, which have lesser affinity toward moisture. The moisture absorption behavior of raw and grafted *A. americana* fibers is shown in Table III.

Both the raw and grafted fibers were evaluated for the attack of acids and bases of different strengths. It was observed from the results of the chemical resistance studies that grafted fibers were more resistant to the attack of chemicals. This may have been due to the fact that due to grafting, the reactive sites, which were prone to attack by chemicals, were blocked by the poly(AN) chains. Further, with increasing P_g , the fibers showed a lower percentage weight loss at a

TABLE II
Swelling Behavior of the Raw and Grafted Fibers

Sample	P_g	Swelling (%)			
		Water	Ethanol	DMF	CCl_4
1	0	98.4	61.2	29.8	13.4
2	5.6	68.2	53.7	34.7	48.3
3	12.7	47.2	38.7	56.3	56.8
4	18.7	42.6	32.6	58.4	73.2
5	21.4	33.8	29.5	62.3	82.6
6	24	31.4	27.9	68.9	87.0

TABLE III
Moisture Absorption Behavior of the Raw and Grafted Fibers

Sample	P_g	M_{abs} at different humidity levels (%)			
		20	40	60	80
1	0	0.42	5.84	8.53	12.85
2	5.6	0.37	3.87	6.25	10.65
3	12.7	0.31	3.21	4.92	8.73
4	18.7	0.27	2.67	3.88	6.87
5	21.4	0.21	2.10	3.15	6.21
6	24	0.17	1.82	2.93	5.78

given strength of acid or base. The acid and base resistance behavior of the raw and grafted fibers is shown in Tables IV and V, respectively.

Characterization of the graft copolymers

Characterization by Fourier transform infrared spectroscopy

The graft copolymerization of acrylonitrile onto agave fibers was confirmed with the help of Fourier transform infrared spectroscopic studies. The IR spectra of the raw and grafted fibers (24 P_g) were recorded with the help of a PerkinElmer spectrophotometer (Massachusetts, USA) with KBr pellets over a range of 4000–500 cm^{-1} with a resolution of 2 cm^{-1} (Fig. 1).

The IR spectrum of the raw fiber showed a broad peak at 3397.1 cm^{-1} due to bonded $-\text{OH}$ groups of cellulosic fiber and peaks at 2918.1, 1432.01, and at 1054.9 cm^{-1} due to $-\text{CH}_2$, $\text{C}-\text{C}$, and $\text{C}-\text{O}$ stretching movements. However, an additional peak at 2245.1 cm^{-1} was observed in the grafted fiber, which was due to the presence of $-\text{C}\equiv\text{N}$ groups of acrylonitrile.

Characterization by scanning electron microscopy (SEM)

Figures 2 and 3 show the scanning electron micrographs of the raw and grafted fibers (24 P_g), respectively. Scanning electron micrographs of the raw and grafted fibers were recorded on a Leo electron microscopy machine (Cambridge, UK) (VP-425-35). From these figures, it is clear that the surface morphology of the fiber changed upon grafting. The surface of the

TABLE IV
Acid Resistance Behavior of the Raw and Grafted Fibers

Sample	P_g	Weight loss (%)			
		0.25N HCl	0.5N HCl	0.75N HCl	1.0N HCl
1	0	7.15	11.3	14.30	20.22
2	7.6	6.87	10.35	12.20	16.60
3	12.7	5.23	9.05	11.30	14.00
4	18.7	4.13	8.74	10.24	13.07
5	21.4	3.27	7.16	9.66	12.28
6	24	2.92	6.87	8.51	10.80

TABLE V
Base Resistance Behavior of the Raw and Grafted Fibers

Sample	P_g	Weight loss (%)			
		0.5N NaOH	1.0N NaOH	1.5N NaOH	2.0N NaOH
1	0	14.26	16.87	22.54	27.82
2	7.6	13.78	14.27	18.52	23.19
3	12.7	11.78	12.56	16.96	19.87
4	18.7	10.39	12.07	14.85	16.35
5	21.4	9.54	11.63	13.36	15.05
6	24	8.23	9.87	11.42	13.61

grafted fiber became uneven; this was probably due to the incorporation of poly(AN) chains on the surface of the natural fibers as a result of graft copolymerization.³⁶ Moreover, the surface morphology of the grafted fibers changed because of the penetration of new functionalities into the micropores present on the surface of raw fibers.

Characterization by thermal analysis

Thermal studies were performed in air at a heating rate of 10°C/min with a PerkinElmer (Pyris Diamond) thermal analyzer. The thermal decomposition behavior of raw and grafted fibers ($P_g = 24$) is shown in Figures 4 and 5, respectively.

In the thermogram of raw fiber, the first mass loss (6%) between 26 to 99°C was due to the removal of water. In this case, a two-stage decomposition was observed, the first decomposition with a maximum weight loss between 240 and 346°C (50.6%), which may have been due to the depolymerization of cellulose and the rupture of glycosidic linkages. The second decomposition stage between 346 and 432°C (32.3%) corresponded to the degradation of lignin and the oxidation of char. The second decomposition stage also coincided with the exothermic peak in the differential thermal analysis (DTA) curve at 439°C (237.2 μV). The initial and final decomposition temperatures of raw fiber were 240 and 432°C, respectively.

Similarly, the grafted fiber also showed two-stage decomposition. During the first stage of decomposition, almost the same behavior was observed in the cases of both raw and grafted fibers; this showed that the backbone structure was not affected during graft copolymerization. The second decomposition stage corresponded to 349–550°C with 43% weight loss; this could have been due to the degradation of poly(AN) on the surface of the grafted fiber. Both the first and second decomposition stages were supported by exothermic peaks in DTA curves at 395°C (86.6 μV) and 474°C (68.6 μV), respectively.

X-ray diffraction (XRD) studies

XRD studies were performed on an X-ray diffractometer (Bruker D8 Advance). XRD studies were

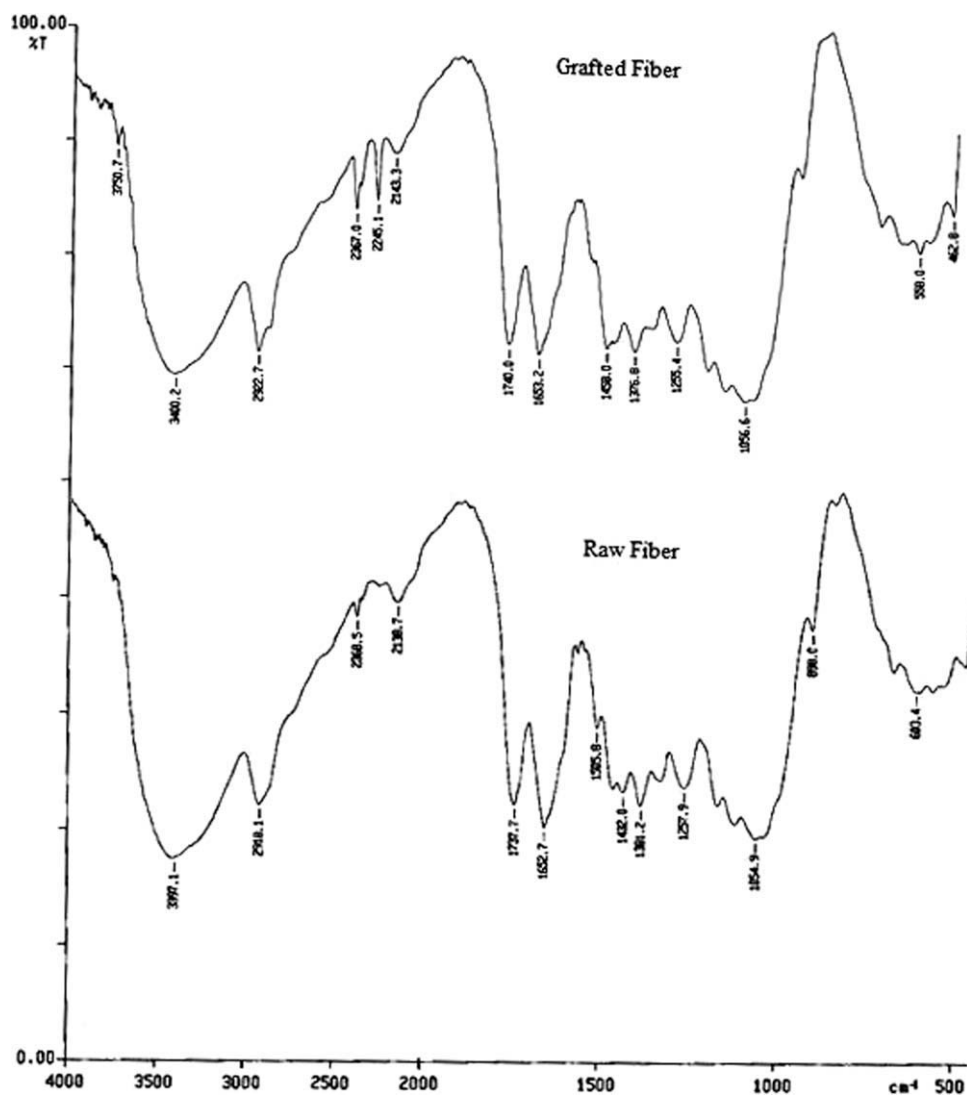


Figure 1 IR spectra of the raw and grafted fibers.

carried out with $\text{Cu K}\alpha$ (1.5418 \AA) radiation, a Ni filter, and a scintillation counter as a detector at 40 kV and 40 mA on rotation from 5 to 50° at the 2θ scale.

The crystallinity index (CI) was determined with wide-angle XRD counts at 2θ angles close to 22° and 18° . The counter reading of the peak intensity close

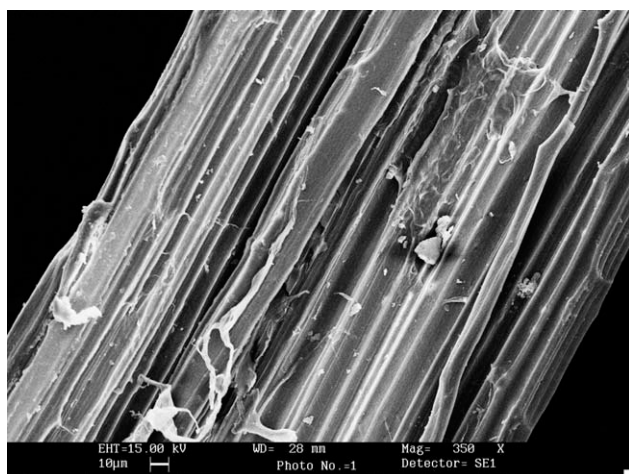


Figure 2 SEM of the raw fiber.

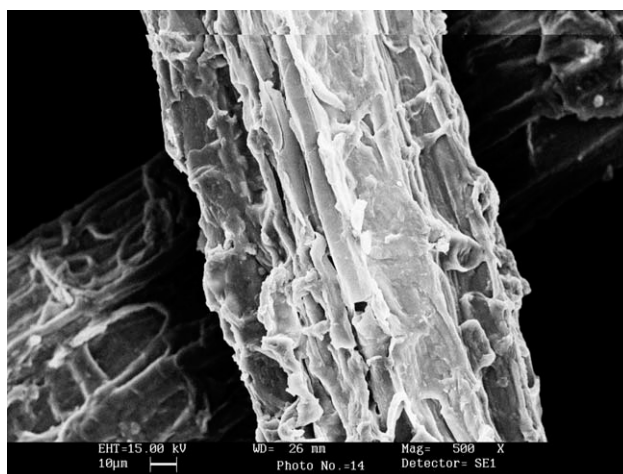


Figure 3 SEM of the grafted fiber.

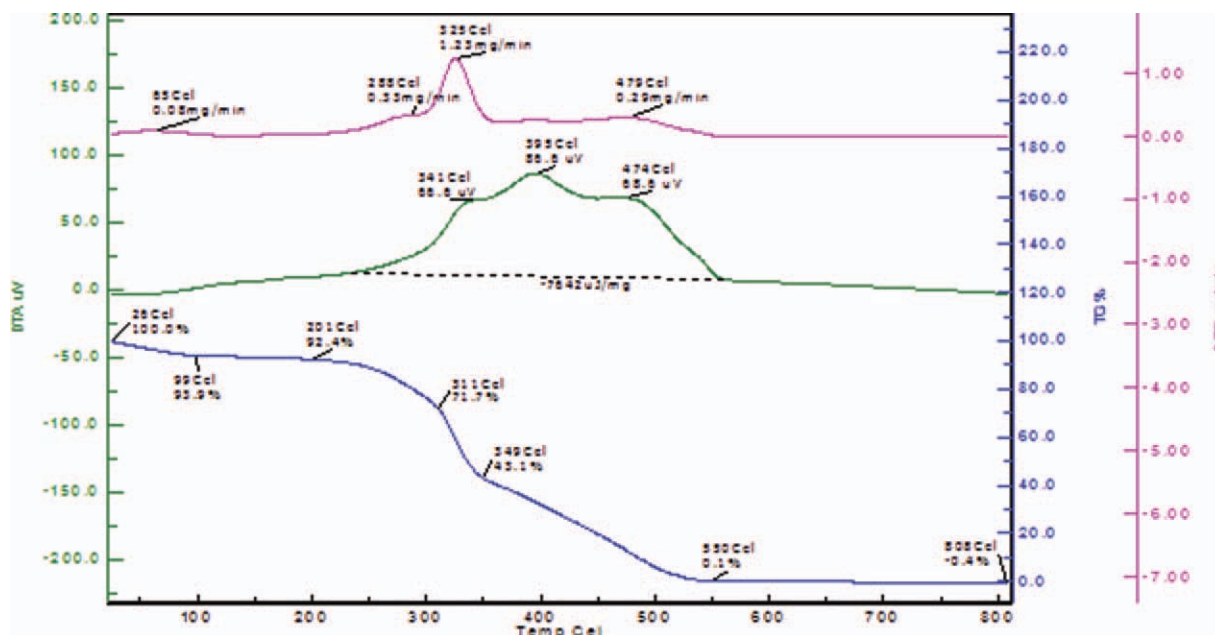


Figure 4 Thermogram of the raw fiber (DTG = differential thermogravimetry; TG = thermogravimetry). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to 22 and 18° is said to represent the crystalline material and amorphous material in cellulose, respectively.³⁷ The percentage crystallinity [C_r (%)] and CI were calculated with the following formulas:

$$C_r(\%) = \frac{I_C}{I_C + I_A} \times 100$$

$$CI = \frac{I_C - I_A}{I_C}$$

where I_C and I_A are the crystalline and amorphous intensities, respectively, at the 2θ scales close to 22 and 18°.

The C_r values of the raw and grafted fibers ($P_g = 24\%$) were 67.92 and 64.16%, respectively (Table VI). C_r of the agave fiber decreased upon grafting; this may have been due to a disturbance in the crystal lattice of the raw fiber due to incorporation of poly(AN) chains into the reactive sites.

CONCLUSIONS

The studies carried out in this research work revealed that a higher graft yield ($P_g = 24$) was

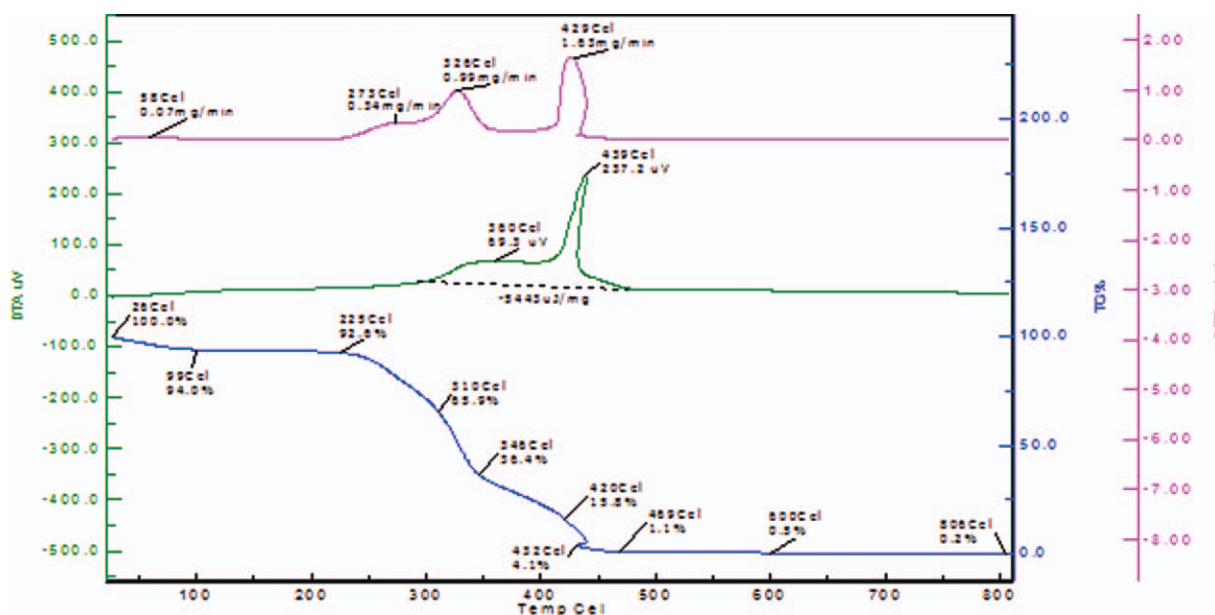


Figure 5 Thermogram of the grafted fiber. (DTG = differential thermogravimetry; TG = thermogravimetry). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
 C_r and CI Values of the Raw Fiber and
Agave-g-Poly(AN)

Sample	$I_{C22.03^\circ}$	$I_{A14.22^\circ}$	C_r (%)	CI
Raw fiber	97.6	46.1	67.92	0.53
Sample	$I_{C22.18^\circ}$	$I_{A14.22^\circ}$	C_r (%)	CI
Agave-g-poly(AN)	100	53.9	64.97	0.46

obtained when compared with the grafting carried out under pressure conditions ($P_g = 17.5$), as reported in a previous work. From the study of the physicochemical properties, it was clear that these properties were improved upon graft copolymerization of fibers with acrylonitrile. The swelling behavior in polar solvents such as water and ethanol and the moisture absorption behavior of the fibers decreased with increases in P_g . However, the swelling behavior in DMF and CCl_4 and the chemical resistance increased with P_g .

Graft copolymerization also resulted in the increase in the thermal stability of the fibers. C_r and CI of the grafted fibers decreased after grafting; this was expected because of the disturbance of the crystal lattice of the cellulose. Therefore, we concluded that agave-g-poly(AN) may be a potential reinforcement in -matrix-based composites.

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