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Surface Chemical Treatments of Jute Fiber for High Value Composite Uses.

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Research Article

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ABSTRACT

In order to confer hydrophobicity, higher mechanical and thermal properties, jute fiber has been chemically modified by means of $NaClO_2$ bleaching, acrylonitrile (AN) grafting and diphenylmethanediisocyanate (DPMIC) treatment. The extent of modification reaction is evaluated by FTIR measurement. Morphologies and crystalline index of jute fibers are investigated using scanning electron microscopy (SEM) and wide angle X-ray diffractometer (WAXD). A significant variation in fibre surface occurred by chemical treatments is clearly observed in SEM images. It has been found that tensile properties (tensile strength, extension at break and Young's modulus) are substantial improved by AN-grafting and DPMIC treatment. Based on findings of hydrophobicity, the DPMIC treated fiber has been showed better properties than other fibers. Chemical treatment also increases the thermal stability. The TG and DTA curves show two-stages of decomposition for all the fibres; first below 100°C indicating the moisture loss and the second between 320°C and 360°C due to major degradation of fibre.

INTRODUCTION

Jute, the golden fiber of Bangladesh gained considerable attention in composite industries as an environmental friendly reinforcement. The fiber has a high aspect ratio, high strength to weight ratio, low energy conversion and has good insulation properties. However, poor compatibility between the hydrophilic jute fiber and the hydrophobic polymer matrix is usually the weakest point in a composite, which makes the performance of the final composite limited by fiber pull-out rather than fiber break. Thus, full strength of the jute fiber as reinforcing material is not utilized, the optimal properties of the composite are not obtained as well as the full commercial potential is not achieved. To improve the compatibility between the fiber and the polymer matrix, the jute fiber should be modified either physically or chemically.

Surface chemical modification with coupling agents is usually applied to optimize the wetting of the natural lignocellulosic fibers by the polymeric matrix and to improve the interaction and adhesion between the non-polar matrix and the polar reinforcement. The chemical surface modification techniques such as alkali treatments [1], bleaching [2], acetylation [3], and graft co-polymerization [4], has also been reported to overcome the incompatible surface polarities between the natural fiber and polymer matrix. Though, surface chemical modification is usually applied to improve the interaction and adhesion between the non-polar matrix and the polar lignocellulosic fibers, the presence of surface impurities such as pectin and waxy substance of the fiber sometime hinder the modification process. Surface pretreatment is necessary before perform chemical modification. $NaClO_2$ bleaching is very efficient pretreatment method to remove wax, pectin and lignin. Therefore, acrylonitrile (AN) grafting and diphenylmethanediisocyanate (DPMIC) treatments were used on bleached jute fiber. The chemical and physical properties of treated fiber was also been studied.

EXPERIMENTAL

Jute fiber was collected from local market of Jhenidha, Bangladesh. Sodium carbonate, acetic acid, sodium acetate, sodium chlorite, sodium metabisulfite, chloroform, toluene, acrylonitrile, and diphenylmethanediisocyanate (DPMIC), were purchased from Merck, Germany. Other chemicals used were analytical reagent grade.

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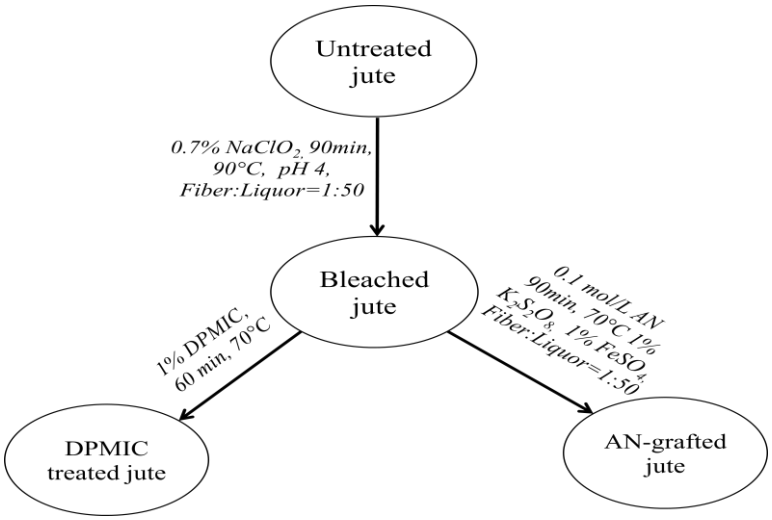
The chemical treatment processes of untreated jute fiber are shown in Scheme 1. About 20 g of untreated jute fiber was bleached in 1 L $NaClO_2$ (7gL^{-1}) solution buffered at pH 4. The reaction was carried out at 90-95°C for 90 min maintaining the fiber to liquor ratio 1:50. After completing the bleaching reaction, the fiber was treated with 0.2 (w/v)% sodium metabisulphite solution for 15 min to reduce chlorite action and then washed thoroughly with distilled water [2]. 1 g bleached jute fiber was taken in 100 ml stopper conical flask. Aqueous solution of acrylonitrile monomer (0.1 mol/L), $K_2S_2O_8$ as initiator (1 wt% of fiber) and $FeSO_4$ as catalyst (1 wt% of fiber) was taken for grafting reaction. Fiber to liquor ratio was maintained 1:50. The reaction was continued at 70°C in a water bath for 90 min. After completing the reaction fiber was washed with methanol and then distilled water to removed adhering homopolymer from jute surface. The grafted fiber was dried in air and finally in oven [2]. Bleached jute fiber was dipped in toluene solution containing DPMIC (1%) for 1 h at 70°C. The fiber was then decanted, washed and dried in an air oven at 70°C for 2 h.



Scheme 1. Chemical treatment processes of jute fiber

The FTIR spectroscopy of jute samples were taken using Perkin Elmer Spectrum One spectrometer. Samples were taken with KBr to make a transparent pellet. For each sample 5 scans were taken at a resolution of 4 cm^{-1}. The surface morphology of jute samples were observed by scanning electron microscope (FEI QUANTA 200 3D) with an accelerating voltage 10 kv. WAXD patterns were obtained with a BRUKER D8 ADVANCE wide angle X-ray diffractometer using Cu Kα radiation (α = 0.154 nm), voltage of 50 kV, and current of 40 mA with 2θ ranges from 5 to 45° increased in steps of 2°/min. The thermogravimetry of fiber was conducted by thermal gravimetric analyzer (TG/DTA 6300, Seiko Instrument Inc., Japan). Tensile tests were conducted according to ASTM D638-01 using a Universal Testing Machine (Hounsfield UTM 10KN).

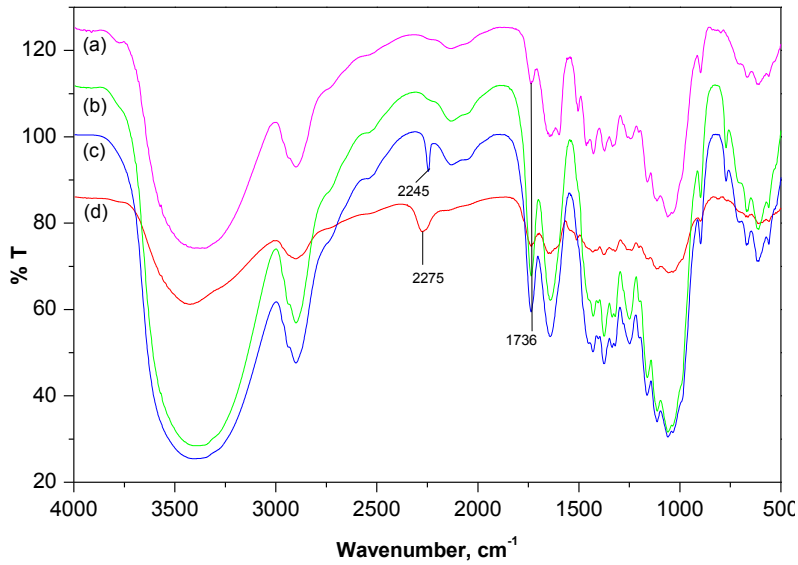


Figure 1: FTIR spectra of (a) untreated, (b) bleached, (c) AN-grafted and (d) DPMIC treated jute fibers

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RESULTS AND DISCUSSION

FTIR spectra of untreated and treated jute fibers are shown in Fig. 1. The FTIR spectra of fibers contain the typical vibration bands of the components mainly corresponding to cellulose, hemicellulose, and lignin. The hydrophilic tendency of jute fibers is reflected in the broad absorption band in the 3700–3100 cm^{-1} region, which is related to the –OH groups present in their main components. In the 1600–900 cm^{-1} region, it is possible to appreciate in fibers vibrations of chemical components of the lignin at frequencies of 1514 cm^{-1} for guaiacyl [5] and 1468, 1433, and 1214 cm^{-1} associated with syringyl [5]. Almost the same absorption peaks as shown in the untreated jute fibers were observed in the spectrum of the treated jute fibers. This indicated that the structure of cellulose had not been damaged after the treatments. The drop in the peak of bleached jute fiber found at the range of 1597, 1503 and around 1374 cm^{-1} indicated the removal of lignin. In the spectrum of bleached jute fibers, the reduction in the peak intensity found at 1372 and 1244 cm^{-1}, indicated the partial removal of hemicellulose. The peak at 1632 cm^{-1} becomes less intense because of the removal of oils and other impurities. In Fig.1(c), the band at 2243 cm^{-1} arising from the stretching vibration of C=N was used for characterization of the AN grafted jute. The peak at 1460 cm^{-1} is due to the CH_2 deformation intensified upon grafting [6]. The FTIR spectrum of the DPMIC treated bleached jute exhibited the characteristic urethane peaks at 2275 cm^{-1} for =N=C=O asymmetric stretching and 1720 cm^{-1} for –C=O stretching (amide -NH=CO-O-) vibrations. The introduction of the cardanol moiety was indicated by the presence of a –C=C peak at 1620 cm^{-1}, –CH aromatic at 3020 cm^{-1} and –C–H aliphatic at 2980 cm^{-1}. The FTIR spectrum of the DPMIC also showed peaks at 1440 and 1590 cm^{-1} due to the C=C aromatic ring stretching.

In order to observe the changes in morphological structure of the jute fibers on chemical treatments were observed by SEM (Fig. 2). The surface of the untreated jute fiber was covered by a number of impurities like hemicellulose, lignin, pectin, waxy substances, and so on. However, the treatment creates a lot of modification on the fiber surface. On comparison of Fig. 2(a) and 2(b), the drastic difference in the surface morphology between the untreated and the bleached fiber can be easily visualized. The multi-cellular nature of a fiber filament is more clearly revealed in Fig. 2(b). Unlike the untreated fiber the surface of bleached fibers seems to be free from surface debris and overgrowths. This is undoubtedly due to the removal of lignin and also a part of hemicellulose during the bleaching from both the surface and the intercellular spaces. On AN grafting, bleached jute fiber became defibrillated (Fig. 2(c)). The deposition of the polymer onto the fiber makes a film and it fills the gap between the fibrils and making it more hydrophobic [6]. Comparison of the micrographs of the bleached and DPMIC treated jute shows that a considerable amount of –ICN groups is grafted onto the jute surface. The intercellular gaps are also reduced due to crosslinking of cellulose.

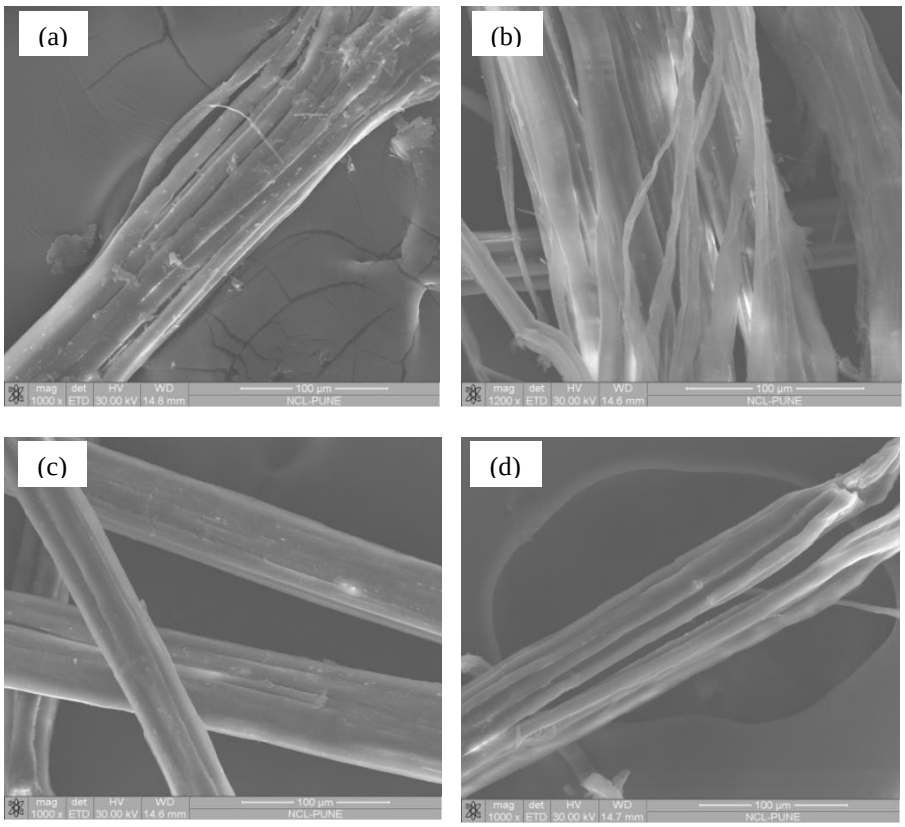

Figure 2: SEM topography of (a) untreated, (b) bleached, (c) AN grafted and (d) DPMIC treated jute fibers

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The wide angle X-ray diffractograms (WAXD) and the crystallinity index of untreated and treated jute fibers are shown in Fig. 3 and Table 1, respectively. The bleached fiber showed highest crystallinity. This may be due to removal of amorphous hemicelluloses and lignin. The reduction of crystallinity index was observed in X-ray diffractogram of AN grafted and DPMIC treated fibers. This result suggests that a degree of crystallinity of cellulose decreased with AN-grafting and DPMIC treatment which is because of deposition of amorphous components on cellulose surface [7].

Table 1. The crystallinity index of the untreated and treated jute fibers

Types of jute	Peaks at 2θ=15.7° angle			Peaks at 2θ=22.6° angle			CrI
	Area	Width	Height	Area	Width	Height	%
Untreated	32481	4.637	5588.8	40442	2.667	12098	70.00
Bleached	37258	4.430	6711.1	45983	2.597	14129	73.07
AN grafted	32718	4.449	5868.2	38880	2.622	11832	68.75
DPMIC treated	39127	4.567	6836.0	44479	2.524	14060	70.99

The effect of chemical treatment of the jute fibers on the physical properties and density values are given in Table 2. The quality of jute fiber largely depends on its physical properties, such as fineness, moisture regain and densities. Splitting of the cemented fibers causes a reduction in the fiber diameter. Further modification through AN-grafting and DPMIC treatment given of jute surface coating hence increase the fiber diameter slightly. The densities of untreated, bleached, AN grafted and DPMIC treated fibers were 1.15, 1.40, 1.32 and 1.25 gcm^{-3}, respectively, showing that the surface treatments have significant affect on density [8]. As seen in Table 2, jute contains 5.01% of moisture, while 60 min is sufficient to dry the fiber. For bleached fibers the moisture content is increased to 6.8%. This may be due the removal of hemicellulose, pectin, waxes and fats, fiber become floppy i.e. contain more pore. Therefore, moisture can easily diffuse in these pore result in moisture regain increase. A significantly decrease in moisture affinity of jute modified by AN-grafting and DPMIC treatments.

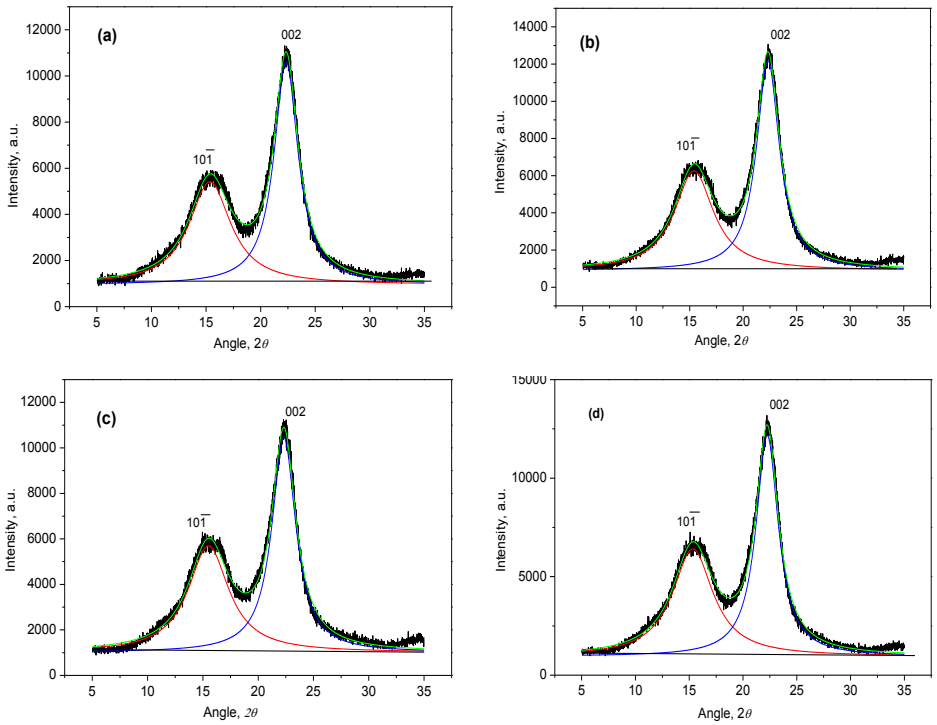

Figure 3: WAXD and fitted data of (a) untreated, (b) bleached, (c) AN grafted and (d) DPMIC treated jute fibers

The tensile properties of untreated and treated jute fibers are shown in Table 2. Bleached fibers show an appreciable decrease in the tensile strength. This decrease may be attributed to substantial delignification and degradation of cellulosic chains during the chemical treatment. The extension at break in these fibers does not change much. AN and DPMIC treated fibers brings about a substantial increase in tensile strength (TS) and tensile modulus (TM). This may be attributed to the fact that AN and DPMIC treatments may create orderly arrangement jute fibrils by surface coating via crosslinking reaction [9]. The TG, DTA and DTG curves of the untreated and treated jute fibers are shown in Figure 4. In all the cases, initial weight loss at temperature between 30 to 150°C indicates removal of moisture from the fiber. The weight loss below 250°C is negligible; above that temperature the fibers begin to degrade fast and at 400°C, only residual char is obtained due to loss of hydroxyl groups and depolymerization of cellulose to anhydroglucose units. The initial stage decomposition of untreated, bleached, AN grafted and DPMIC treated jute are 5.8, 7.7, 3.8, and 3.8% respectively. It evident that bleached fiber reduces more

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moisture than others. The final decomposition of untreated, bleached, acetylated, AN grafted and DPMIC treated jute are 76.1, 66.6, 75.1 and 72.2% respectively and corresponding final decomposition temperature (FDT) are 361.0, 363.7, 380.8 and 372.0°C. It has been observed from above results that AN-grafting and DPMIC treatment enhanced the thermal stability of jute fibers. Maximum thermal stability was presented by AN grafted, fiber followed by DPMIC treated jute fibers.

Table 2: Physical properties of untreated and treated jute fibers

Types of jute	Density ($g.cm^{-3}$)	Diameter (μm)	TS (MPa)	TM (GPa)	Elongation, (%)	Moisture (%)
Untreated	1.15	67.6-75.6	483±11	3.30±1.3	3.85	5.01
Bleached	1.40	30.0-38.4	523±13	4.29±1.1	2.67	6.80
AN grafted	1.32	36.8-45.7	717±15	4.36±1.5	3.20	3.20
DPMIC treated	1.25	31.9-38.7	537±13	4.13±1.6	2.88	3.90

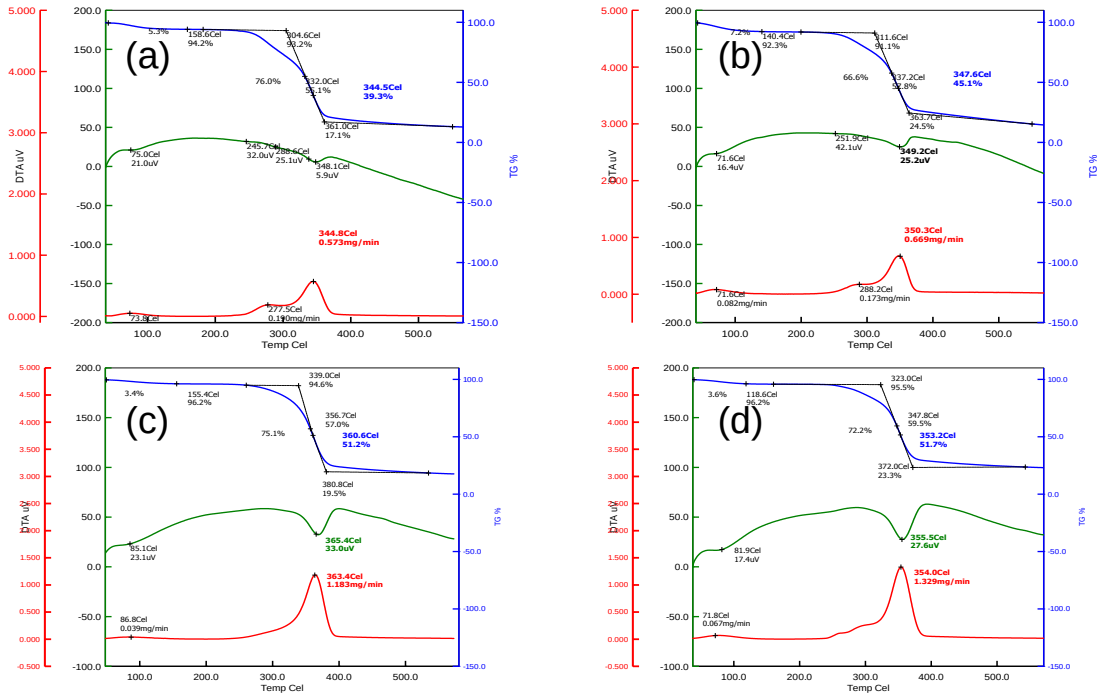

Figure 4: TG, DTA and DTG thermograms of (a) untreated, (b) bleached, (c) AN grafted and (d) DPMIC treated jute fibers

Table 3. TG data of untreated and treated jute fibers

Types of jute	Weight loss % at temperature (°C)			FDT (°C)	Residual Char, (%)
	0-150	150-230	230-400		
Untreated	5.8	1.0	76.1	361.0	17.1
Bleached	7.7	1.2	66.6	363.7	24.5
AN grafted	3.8	1.6	75.1	380.8	19.5
DPMIC treated	3.8	0.7	72.2	372.0	23.3
*FDT- Final decomposition temperature					

The residual char left at 550°C highest in the case of bleached fiber and thereafter DPMIC treated fiber (Table 3). Saha et al. [10], explained that by reduced the hemicellulose to a considerable extent, giving rise to a lignin–cellulose complex, thereby making the product more stable than the untreated sample, and this was reflected in the increased amount of residual char. The treatment on jute fiber decreased the weight loss during pyrolysis, and enhanced the residual char formation with a lowering in the formation of the flammable volatiles, and thus concluded that the thermal stability was decreased in the case of the treated fibers. In the DTG curve of the untreated jute fiber, the peak I below at 73.8°C was the result of evaporation of moisture (Table 4). The peak II at 277.5° and peak III at 344.8°C were caused by hemicellulose and α-cellulose degradation, respectively. In the case of bleached fiber, moisture loss peak shifted to a lower temperature. This tendency toward releasing moisture at a lower temperature might be caused by an increase in the surface area of the split `fibers (Fig. 4), facilitating easier evaporation of moisture at a lower temperature. The degradation peak of the α-cellulose and the

hemicelluloses shifted to higher temperatures in all the treated fibers. The disappearance of peaks for hemicellulose degradation observed for AN grafted and DPMIC treated fiber. It may say that the degradation temperature of hemicelluloses affected by AN-grafting and DPMIC treatment of bleached jute fiber.

Table 4: DTG of untreated and treated jute fibers

Types of jute	Peak I		Peak II		Peak III	
	Temperature (°C)	Rate (mg/min)	Temperature (°C)	Rate (mg/min)	Temperature (°C)	Rate (mg/min)
Untreated	73.8	0.065	277.5	0.190	344.8	0.573
Bleached	71.6	0.082	288.2	0.173	350.3	0.669
AN grafted	86.6	0.039	--	--	363.4	1.183
DPMIC treated	71.8	0.067	--	--	354.0	1.329

Table 5: DTA data of untreated and treated jute fibers

Types of jute	Temperature, °C		
	Peak I (endo)	Peak II (exo)	Peak III (endo)
Untreated	75.0 (endo) (21.0uV)	245.7 (exo) (32.0uV)	348.1 (5.9uV)
Bleached	71.6 (endo) (16.4uV)	251.9(exo) (42.1uV)	349.2(endo) (25.2uV)
AN grafted	85.1 (endo) (23.1uV)	--	365.4 (endo) (33.0uV)
DPMIC treated	81.9 (endo) (17.4uV)	--	355.5(endo) (27.6uV)

An endothermic peak below 100°C was observed, resulting from moisture loss. The exothermic peak at 240-290°C and the endothermic peak at 330-380°C were caused by the hemicellulose and α-cellulose decomposition, respectively. It is apparent that the exothermic peak II was disappeared for AN and DPMIC treated jute may be due to hemicelluloses removal or blocked by those treatments. In the case of AN or DPMIC treatment, where only the hydroxyl groups took part in the chemical reaction, no such inversion was observed.

CONCLUSION

Modification of jute fiber by $NaClO_2$ bleaching, AN-grafting and DPMIC treatment were carried out in this study to obtain better surface properties, while maintaining good inherent mechanical properties. The remarkable morphology changes of treated fiber were observed by FTIR and SEM micrograph. WAXD was used to investigate the crystalline development. The results showed the positive change of degree of crystallinity of treated fiber. The tensile strength, modulus, elongation, hydrophobicity, and the fineness were improved when jute was treated through AN-grafting and DPMIC treatments. On the contrary, the breaking strength and moisture regain decreased for bleached fibers. Thermal stability also improved by AN-grafting and DPMIC treatments. As the treatments significantly improve hydrophobocity, mechanical strength and thermal stability of fiber, it might be compatible with thermoplastic matrix and their composite will be shown high mechanical and thermal values.

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