



## Chemical Treatments of Cotton Linter Cellulose Fiber for Composite Application

M. Rahman<sup>1</sup>, G. M. Arifuzzaman Khan<sup>1</sup>, Md. Helal Uddin<sup>1</sup>,  
S. M. Abdur Razzaque<sup>1</sup> and Md. Shamsul Alam<sup>1\*</sup>

<sup>1</sup>Polymer Research Laboratory, Department of Applied Chemistry and Chemical Technology, Islamic University, Kushtia-7003, Bangladesh.

### Authors' contributions

This work was carried out in collaboration between all authors. Authors MR, GMAK and MSA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MHU and SMAR managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

### Article Information

DOI: 10.9734/ACSJ/2016/28730

#### Editor(s):

(1) Marcelo Daniel Preite, Department of Organic Chemistry, Pontifical Catholic University of Chile, Chile.

#### Reviewers:

(1) Hai-Yin YU, Anhui Normal University, China.

(2) Anonymous, Israel.

(3) Matheus Poletto, Universidade de Caxias do Sul, Brazil.

Complete Peer review History: <http://www.sciencedomain.org/review-history/16138>

Original Research Article

Received 2<sup>nd</sup> August 2016  
Accepted 3<sup>rd</sup> September 2016  
Published 10<sup>th</sup> September 2016

### ABSTRACT

In the present research work, cellulose fiber was isolated from cotton linter (CL) collected from local textile mills of Kushtia district, Bangladesh. To remove dirt and impurities, CL was pre-treated with NaOH and NaClO<sub>2</sub>. Fiber was treated with a number of chemicals such as dicumyl peroxide (DCP), acetic anhydride (AA) and acrylamide (AAM). The changes of cellulose molecules during the chemical treatments were detected by FTIR spectra. The crystallinity index of pretreated and treated fibers were measured from the peaks at 14.6 and 22.6 (2θ angles) of WAXD curves. The proportion of crystalline part was increased in case of treated cellulose fiber, which manifests significant conversion of cellulose-I to cellulose-II. A significant variation of thermal properties of pretreated and treated fibers were also observed by TGA.

\*Corresponding author: E-mail: [s.alam@acct.iu.ac.bd](mailto:s.alam@acct.iu.ac.bd)

**Keywords:** Cotton linter; fiber treatments; FTIR; WAXD; TGA.

## 1. INTRODUCTION

Cotton linter (CL) is an unwanted part of finished fabrics that cannot be used in the textile process. At present, it is considered as valuable raw materials for cellulose based industry. It has been used for making absorbent cotton, special papers, cellulose nitrate, and acetate [1]. The quantity of linter produced globally is around 2.5 million metric tons, allowing for the 42 million metric tons of cotton linter produced in 2010 [2]. In Bangladesh, there are about 7000 textile industries which produced a lot of cotton linter every year. Some of them are used directly as tattered clothes and sometimes found its application in pillow or bed mattress making. In a word, it has no value added application in Bangladesh. Therefore, it is crying need to accumulate such huge amount of by product and find out profitable application.

Cotton and lignocelluloses fibers have been beneficially used in composite industries [3-5]. As like cotton and other lignocelluloses fiber, CL fiber might be a potential source of cellulose in the present investigation. This wastage CL has been time honoured curiosity as the raw materials for nano or micro structured cellulose. Cellulose fiber reinforced polymer composites have received much attention because of their low density, nonabrasive, combustible, nontoxic, low cost and biodegradable properties. Plenty of researches have been performed all over the world on the use of cellulose fibers as a reinforcing material for the preparation of various types of composites. Cellulose fibers are being used as potential reinforcing materials because of so many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, interesting specific properties, since these are waste biomass, and exhibit good mechanical properties [6-8]. Yet, lack of good interfacial adhesion, low thermal resistance, and water sensitivity make the use of cellulose-fiber reinforced composites less attractive [8-10]. Pretreatments of the cellulose fibers can modify the fiber surface, such as chemical functionalization stop the moisture absorption process and increase the surface roughness [11-13]. The fiber-matrix interface is the diffusion or reaction zone, in which fiber and matrix phases are chemically and/or mechanically combined. Interfacial adhesion between fiber and matrix plays a predominant part in characterizing the mechanical properties

of the composites. If there is a poor adhesion across the phase boundary, then relatively weak dispersion of force occurs and resulting poor mechanical properties of the composite [14]. For reinforcement of natural fiber in composites, several problems occur along the interface due to the presence of hydrophilic hydroxyl groups on the fiber surface. Chemical treatments can decrease the hydrophilic tendency as well as expose more reactive groups on the fiber surface and thus facilitate efficient coupling with the matrix. Consequently better mechanical and thermal properties of the composites can be achieved [15].

The aim of this work is to proper processing of cotton linter for potential application in composite field. Owing to improve the wettability and interlocking with hydrophilic or hydrophobic matrix fibers were chemically treated with; dicumyl peroxide (DCP), acetic anhydride (AA) and acrylamide (AAm). The treated fibers were characterized by FTIR, WAXD and TGA measurement.

## 2. MATERIALS AND EXPERIMENTAL METHODS

The cotton linter was collected from local Textile Industries at Pabna, Bangladesh. All the chemicals used in the present investigation were analytical reagent grade purchased from Sigma Aldrich.

### 2.1 Fiber Extraction from CL and Pre-treatment

CL fiber was clarified by using several physical methods and then washed to remove small particles like as sand, mud and other dirt. The dry CL fiber was immersed in 17% (w/v) sodium hydroxide solution at room temperature for 3 h with occasional stirring by glass rod where liquor ratio was maintained at 1:50 (w/v). The alkali treated CL fiber was washed several times thoroughly by distilled water and neutralized with very dilute acetic acid. The alkali treated fiber was dried in an electric oven at 105°C for 6 h and stored in air tight bag. The fiber was then treated with 1 wt% sodium chlorite solution for 90 min at 85-95°C. The fiber-liquor ratio was maintained at 1:50 (w/v). pH was controlled at 4 with buffer mixture (acetic acid-sodium acetate) in the proportion of 1 ml of buffer solution for every 10 ml of chlorite solution. After treatment,

bleached CLs were filtered over a sintered funnel and washed thoroughly with distilled water and then treated with 0.2% (w/v) sodium meta-bisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) solution for 20 min with fiber-liquor ratio 1:20 (w/v). The pretreated fiber was filtered and washed thoroughly with distilled water and finally dried in an electric oven.

## 2.2 Chemical Treatments of CL Fiber

In peroxide treatment, fibers were treated with 6% dicumyl peroxide (DCP) in acetone solution for 30 min [16-18]. Saturated solution of the DCP in acetone was used. Fiber was soaked in the solution at 70°C for 30 min. The DCP treated fibers were washed with distilled water and placed in an oven at 80°C for 24 h [19].

Acetylation treatment of CL fiber (1.5 gm) was carried out in a mixture of 7.5  $\text{cm}^3$  of acetic anhydride (AA) and 0.015  $\text{cm}^3$  of sulphuric acid 98 wt % (used as a catalyst) and vigorously stirred. Acetylation was performed at 30°C for 1 h. Sample was separated from suspension by filtration, then washed several times with distilled water and air dried at room temperature [4].

CL fiber was subjected to graft copolymerization in aqueous solution of acrylamide (AAm) by using Ce(IV) sulphate according to the procedure described in the literature [20]. The 8 g CL fiber was added to 200 ml distilled water in a 1-L flask. 0.28 mole AAm solution was prepared with distilled water. Polymerization reaction was carried out in a water bath at 60°C for 90 min in presence of 0.005 mole/L of Ce(IV) sulphate. At the end of the reaction, grafted CL fiber was filtered and transferred into distilled water. After mixing for a while, the washings were decanted. This procedure was repeated 6 times and the solid product transferred into methanol (100 ml) and agitated with a glass rod for 5 min. Then the methanol was decanted off and the graft polymer was dried in oven at 60°C for 3 h. The degree of grafting approximately 16% was calculated by weight gain for fiber.

## 2.3 Fiber Characterization

The FTIR spectra of the fiber samples were recorded by Shimadzu FTIR 8400, Japan in the range of 500–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The samples were ground into powder by a fiber microtome and then blended with KBr followed by pressing the mixture into ultra-thin pellets. The pellets were prepared by mixing approximately 0.5 mg of powder cotton and 100

mg of dry KBr in small agate mortar pestle. For better resolution 5 times scans were taken.

WAXD pattern of fibers were taken with BRUKER D8 ADVANCE wide angle X-ray diffractometer using Cu K $\alpha$  radiation ( $\alpha=0.154$  nm), voltage of 50 KV and current of 40 mA with  $2\theta$  ranges from 5 to 45° increased in step of 2°/min. The data was analyzed by Origin 8 software. Crystallinity Index was calculated by the following equation [21]:

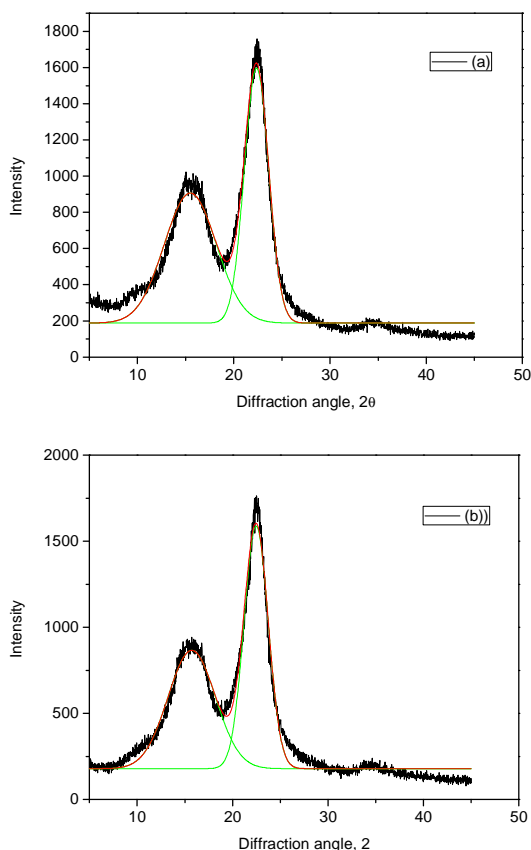
$$\text{Crystallinity Index (CrI\%)} = \left[ \frac{\text{Intensity}_{002} - \text{Intensity}_{\text{AM}}}{\text{Intensity}_{002}} \right] \times 100$$

The Thermal Gravimetric Analyzer (DTA6300) was used to characterize the thermal stability of the cellulose fiber samples. Just about 2 mg of each sample was heated from 30 to 600°C at a heating rate of 10°C/min. All of the measurements were performed under a nitrogen atmosphere with a gas flow of 20 ml/min in order to prevent any thermo oxidative degradation.

## 3. RESULTS AND DISCUSSION

The morphological structures of pretreated and treated (DCP treated, AA treated as well as AAm treated) fibers have been studied by FTIR, WAXD and TGA. The peaks found at FTIR spectra of CL fibers are listed in Table 1. The FTIR spectra of cellulose contain the typical vibration bands of the components mainly corresponding to lignocelluloses fiber. The hydrophilic tendency of the cellulose and different chemically treated cellulose samples is reflected in the broad absorption band in the 3600-3000  $\text{cm}^{-1}$  region, which is related to the –OH groups present in their main components. In the 2000–1180  $\text{cm}^{-1}$  region, it is possible to appreciate in fibers vibrations of chemical components of the lignin at frequencies of 1534  $\text{cm}^{-1}$  for guaiacyl and 1448, 1392 and 1345  $\text{cm}^{-1}$  associated with syringyl. These absorptions are consistent with those of the typical cellulose backbone. Practically the same absorption peaks as shown in the cellulose fibers were also observed in the spectrum of different treated fibers. This shown that the structure of cellulose had not been damaged after the treatments. On DCP treatment, the peroxide-induced grafting onto the cellulose surface and the peroxide initiated free radicals react with the hydroxyl group of the cellulose, the hydroxyl group of cellulose is oxidized to aldehyde (-CHO) or carboxylic acid (-COOH) group thus gives the identical peak at 1760  $\text{cm}^{-1}$ .

Instead of the peak centered at  $1610\text{ cm}^{-1}$ , the FTIR spectrum of pre-treated and treated fibers may be due to the C=O bond of hemicellulose. The intensity of the peak decreases from cellulose to DCP treated, AA treated and AAm treated fiber may be because of block of hydroxyl groups of hemicellulose.



**Fig. 1. WAXD Spectra of a) pretreated and b) DCP treated CL fibers**

The crystallinity index (CrI%) of pretreated and chemically treated CL fibers have been assessed by X-ray diffractometry. From the Fig. 1, it is evident that all kinds cellulose peaks near  $2\theta = 14.6^\circ$ ,  $22.6^\circ$  and  $34.2^\circ$ . Peaks at  $14.6^\circ$ ,  $22.6^\circ$  and  $34.0^\circ$  relate to 001, 002 and 040 lattice planes of cellulose I [22]. Compared with the pretreated fiber, there is no crystalline transformation of the crystalline structure in the treated samples due to invisible changes in the diffraction angle ( $2\theta$ ). From Table 2, it is also found that the CrI% of DCP, AA and AAm treated fibers are increased. It is also seen that the intensity ratio of  $2\theta$  diffraction angle between  $22.6$  and  $14.6^\circ$  was increased for chemical treatment of fiber. The enhancement of crystallinity index by chemical

treatments was also found in the previous study [23].

The TG, DTA and DTG curves of the pretreated and treated fibers (CL) are shown in Fig. 2. In all the cases, initial weight loss at temperature between  $80$  to  $170^\circ\text{C}$  indicates removal of moisture from the fiber. The weight loss below  $350^\circ\text{C}$  is negligible; above that temperature the fibers begin to degrade fast and at  $380^\circ\text{C}$ , only residual char is obtained due to loss of hydroxyl groups and depolymerization of cellulose to anhydroglucose units. The initial stage decomposition of pretreated, DCP treated, AA treated and AAm treated fiber are  $2.5$ ,  $2.1$ ,  $4.3$ , and  $1.3\%$  respectively. It evident that AA treated fiber reduces more moisture than others. The final decomposition of pretreated, DCP treated, AA treated and AAm treated fiber  $4.9$ ,  $6.3$ ,  $15.7$  and  $36.6\%$  respectively and corresponding final decomposition temperature are  $553.5$ ,  $468.0$ ,  $450.1$  and  $510.3^\circ\text{C}$ . It has been observed from above results that AA treated fiber enhanced the thermal stability of CL fiber. The residual char left at  $550^\circ\text{C}$  highest in the case of AAm treated fiber and thereafter AA treated fiber (Table 3). Saha et al. [20], 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 pretreated sample, and this was reflected in the increased amount of residual char. The treatment on CL 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 pretreated CL fiber, the peak I below at  $64.8^\circ\text{C}$  was the result of evaporation of moisture. The peak II at  $300.0^\circ$  and peak III at  $353.7^\circ\text{C}$  were caused by hemicellulose and  $\alpha$ -cellulose degradation, respectively. In this case, 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. 2), facilitating easier evaporation of moisture at a lower temperature. The degradation peak of the  $\alpha$ -cellulose and the hemicelluloses shifted to higher temperatures in all the treated fibers. The disappearance of peaks for hemicellulose degradation observed for DCP treated fiber, AA treated fiber and AAm treated fiber. It may say that the degradation temperature of hemicelluloses affected by DCP, AA and AAm treatment of CL cellulose fiber. An endothermic peak below  $100^\circ\text{C}$  was observed,

resulting from moisture loss. The exothermic peak at 355-385°C were caused by the hemicellulose and α-cellulose decomposition respectively.

**Table 1. Infrared band assignment for pretreated and chemically treated CL fibers**

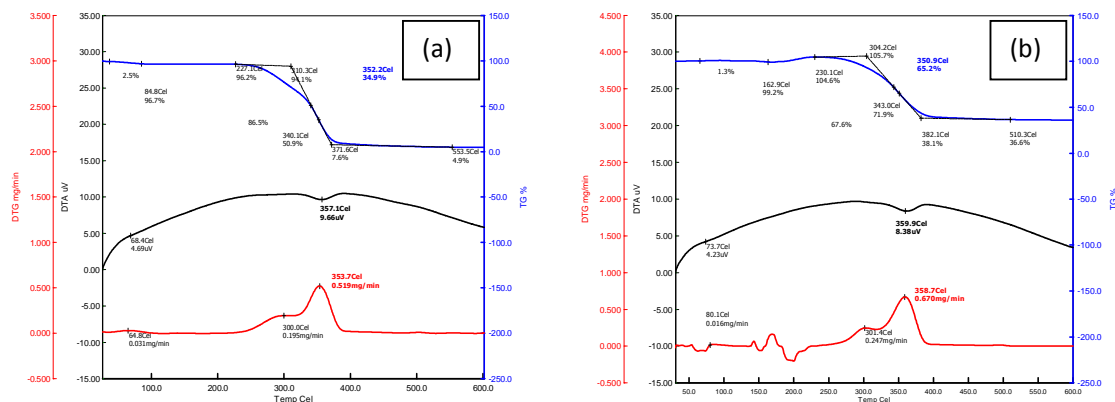
Peaks	Characteristics present
3500	-OH bond stretching in cellulose
3000	C-H bond stretching present in cellulose
1760	C=O group present in fatty acid
1610	C=O bonds of hemicellulose
1597	Aromatic skeletal vibration and C=O bond stretching present in lignin
1503	Aromatic skeletal vibration present in lignin
1465	C-H bond asymmetrical deformation of cellulose
1428	C=C bond aromatic ring of lignin
1372	C-H bond symmetrical deformation of cellulose
1345	C-O bond stretching associated with syringil ring
1244	C-O bond stretching of primary alcohol present in guaiacyl lignin, cellulose and hemicellulose
1157	C-H bond stretching of cellulose
1116	C-H bond stretching of lignin
1059	C-O bond of secondary alcohol
660	β-glycosidic linkages of glucose ring of cellulose

**Table 2. Crystallinity index of pretreated, DCP treated, acetic anhydride treated and AAM treated CL fibers**

Sample name	Full width of half maximum of 2θ=22.6° peak	Peak ratio between the peaks at 22.6 and 14.6°	Crystallinity index (%)
Pretreated fiber	1.98	0.92	62
DCP treated fiber	1.87	1.05	70
AA treated fiber	1.72	1.24	82
AAM treated fiber	1.76	1.14	76

**Table 3. Weight loss of CL fiber and chemically treated CL fiber at various temperature**

Sample name	Wt. loss (%) at 30-210°C	Wt. loss (%) at 211-310°C	Wt. loss (%) at 311-600°C	Residual char content (%)
Pretreated fiber	3.1	19.5	51.9	7.6
DCP treated fiber	2.7	17.7	75.6	9.0
AA treated fiber	1.47	15.6	23	17.4
AAM treated fiber	1.6	24.7	67.0	38.1



**Fig. 2. TGA, DTA and DTG curves of a) pretreated and b) AAM treated fibers**

**Table 4. TGA, DTA and DTG data of pretreated, DCP treated, AA treated and AAm treated fibers**

Sample name	Temperature of 50% wt. loss (°C)	Initial degradation rate (mg/min)	Initial degradation temperature (°C)	Maximum degradation rate (mg/min)	Maximum degradation temperature (°C)
Pretreated fiber	352.2	0.031	64.8	0.519	353.7
DCP treated fiber	361.4	0.027	77.0	0.756	362.5
AA treated fiber	378.8	0.014	70.8	0.228	378.0
AAm treated fiber	350.0	0.016	80.1	0.670	358.7

#### 4. CONCLUSION

The preliminary attempt of introducing cotton linter fiber treatments showed very interesting outcomes. The WAXD and TGA data indicated the treated CL fibers have identical characteristics and quite different to pretreated CL cellulose fiber. Among the treated fibers, acetylated fiber showed greater thermal stability, lower moisture content and higher crystallinity Index. Therefore acetylated fiber might be potential filler of hydrophobic thermoplastic or thermosetting Plastics. Our further work would attempt to fabricate nanocomposite with biodegradable polymer.

#### ACKNOWLEDGEMENT

We hereby acknowledge the assistance of Dr. M.A. Gafur, The Bangladesh Council for Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh during WAXD.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

- Sczostak A. Cotton linters: An alternative cellulosic raw material. *Macromolecular Symposia*. 2009;280:45–53.
- FAOSTAT Agricultural data, Production Crops Food and Agriculture Organization of the United Nations. Available: <http://faostat.fao.org/default.aspx/> (Accessed 02.05, 2012)
- Khan GMA, Shahrear Palash SR, Shamsul Alam M, Chakraborty AK, Gafur MA, Terano M. Isolation and characterization of betel nut leaf fiber: Its potential application in making composites. *Polymer Composites*. 2012;33:764–772.
- Khan GMA, Shaikh H, Alam MS, Gafur MA, Al-Zahrani SM. Effect of chemical treatments on the physical properties of non-woven jute/pla biocomposites. *Bio Resources*. 2015;10(4):7386-7404.
- Kalia S, Kaith BS, Kaur I. Pretreatments of natural fibers and their application as reinforcing material in polymer composites- a review. *Polymer Engineering and Science*. 2009;49(7):1253–1272.
- Hornsby PR, Hinrichsen E, Tarverdi K. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres: Part II analysis of composite microstructure and mechanical properties. *Journal of Materials Science*. 1997;32(4):1009–1015.
- Oksman K, Wallstrom L, Berglund A, Filho RDT. Morphology and mechanical properties of unidirectional sisal-epoxy composites. *Journal of Applied Polymer Science*. 2002;84(13):2358–2365.
- Saheb DN, Jog JP. Natural fiber polymer composites: A review. *Advances in Polymer Technology*. 1999;18(4):351–363.
- Georgopoulos ST, Tarantili PA, Avgerinos E, Andreopoulos AG, Koukios EG. Thermoplastic polymers reinforced with fibrous agricultural residues. *Polymer Degradation and Stability*. 2005;90(2): 303–312.
- Wang B, Panigrahi S, Tabil L, Crerar W. Pretreatment of flax fibres for use in rotationally molded biocomposites. *Reinforced Plastics and Composites*. 2007;26(5):447-463.
- Khan GMA, Alam MS, Razzaque SMA, Saheruzzaman M, Rahman MH, Islam MS. Surface modification of okra bast fiber and its physico-chemical characteristics. *Fibers and Polymers*. 2009;10(1):65-70.
- Khan GMA, Alam MS, Terano M. Thermal characterization of chemically treated coconut husk fibre. *Indian Journal of Fibre and Textile Research*. 2012;37:20-26.

13. Bledzki AK, Reihmane S, Gassan J. Properties and modification methods for vegetable fibers for natural fiber composites. *Journal of Applied Polymer Science*. 1996;59(8):1329–1336.
14. Dash DN, Rana AK, Mishra SC, Mishra HK, Nayak SK, Tripathy SS. Novel low-cost jute-polyester composite. II. SEM observation of the fracture surfaces. *Polymer Plastic Technology and Engineering*. 2000;39(2):333-350.
15. Sreekala MS, Kumaran MG, Joseph S, Jacob M, Thomas S. Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance. *Applied Composite Materials*. 2000;7(5-6):295–329.
16. Paul A, Joseph S, Thomas S. A study of the influence of interfacial damage on stress concentrations in unidirectional composites. *Composites Science and Technology*. 1997;57:67.
17. Sreekala MS, Kumaran MG, Thomas S. Water sorption in oil palm fiber reinforced phenol formaldehyde composites. *Composites Part A*. 2002;33(6):763–777.
18. Wang B, Panigrahi S, Tabil L, Crerar W. Pre-treatment of flax fibers for use in rotationally molded biocomposites. *Journal of Reinforced Plastics and Composites*. 2007;26(5):447–463.
19. Takahashy T, Hori Y, Sato I. Coordinated radical polymerization and redox polymerization of acrylamide by ceric ammonium nitrate. *Journal of Polymer Science*. 1968;6:2091.
20. Saha SC, Ray PK, Pandey N, Goswamy K. IR and X-ray diffraction studies of raw and chemically treated pineapple leaf fiber (PALF). *Journal of Applied Polymer Science*. 1991;42(10):2767.
21. Segal L, Creely JJ, Martin AE, Conrad CM. An empirical method for estimating the degree of crystallinity of native cellulose using the X-Ray diffractometer. *Textile Research Journal*. 1959;29:786.
22. Ford ENJ, Mendon SK, Thames SF, Rawlins JW. X-ray diffraction of cotton treated with neutralized vegetable oil-based macromolecular crosslinkers. *Journal of Engineering Fiber and Fabric*. 2010;5:10–20.
23. Weimer PJ, Hackney JM, French AD. Effects of chemical treatments and heating on the crystallinity of celluloses and their implications for evaluating the effect of crystallinity on cellulose biodegradation. *Biotechnology and Bioengineering*. 1995; 48:169.

© 2016 Rahman et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:*  
<http://sciencedomain.org/review-history/16138>