Chemical Science Review and Letters ISSN 2278-6783

Research Article

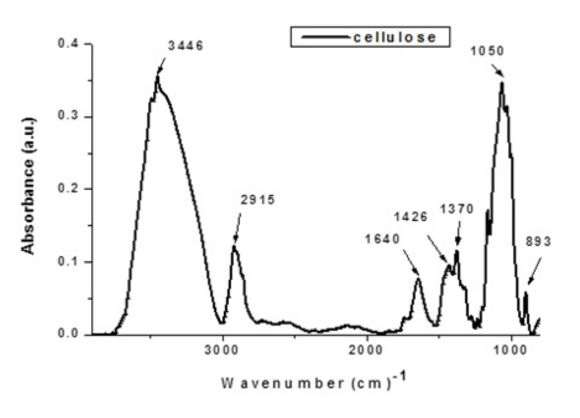
Extraction and Characterization of Cellulose from Agroindustrial Waste of Pineapple (*Ananas comosus* L. Merrill) Crowns

Gloria Ivette Bolio-López[1*], Rubí Esmeralda Ross-Alcudia[1], Lucien Veleva[2], José Antonio Azamar Barrios[2], Genaro Cadenas Madrigal[1], Manuel Mateo Hernández-Villegas[1], Patricia de la Cruz Burelo[1] Samuel Sánchez Córdova[1]

[1]UPCH, Department of Basic Sciences and Engineering, Carr. Cárdenas-Huimanguillo Km.2.0, Cárdenas, Tabasco, México
[2]CINVESTAV-Mérida, Applied Physics Department, Carret. Ant. a Progreso Km.6, Cordemex, 97310 Mérida, Yucatán, México

Abstract

Pineapple crowns are agro-industrial waste generated in high proportions, about 12.0 tons per day in the municipality of Huimanguillo, Tabasco State of Mexico, as a part of the processing process of pineapple fruit pulp. Crown pineapple fibers contain a substantial amount of cellulose that could be extracted and separated from other compounds, which are mainly lignin and hemicellulose. Thus, pineapple agro-industrial waste represents a plant source of biomass with a valuable commercial alternative to obtain cellulose, as reinforcement fibers for biocomposites and paper. The aim of this study was the extraction and characterization of cellulose from the pineapple (*Ananas comosus* L. Merrill) crowns. The process included methods, such as acid hydrolysis, chlorination, alkaline extraction and bleaching. The final product of cellulose had a yield of 11 ± 3%. FTIR interferogramas (Fig.) confirmed an efficiently dissolution of the amorphous regions (lignin and hemicellulose) after the chemical treatments. X-ray analysis revealed 43.05 ± 2% crystallinity of cellulose and a crystal size of 21.6 ± 4 Å.



Keywords: *Cellulose, Extraction, Pineapple crown, Ananas comosus, FTIR, XRD*

***Correspondence**
Gloria Ivette Bolio-López
Email: gloriabolio@hotmail.com; gloriaivette.bolio@upch.edu.mx

Introduction

In the food production process, in addition to the desired final product, by-products waste and non-standard products are generated, each of which can be used for human or animal consumption and industrial application, which would bring economic benefits [1]. These agro-products constitute a serious waste problem in much of the world, due to two main factors: (1) An increase in quantity and, (2) the emergence of stricter environmental laws [2]. For example, published official data which stated that in Mexico in 2006 there were 75.73 million tons of dry matters from 20 crops, of which 60.13 million tons were primary waste [3]. The remaining 15.60 million tons were secondary waste obtained from post-harvest processing. Most of the agricultural industries not have any plans for such waste, due to the high cost of reuse and instead, place them with the trash in landfill [4]. In Tabasco state, in the municipality of Huimanguillo, where pineapple processing industry FREXPORT SA de CV is located, only about 40% of the total mass of this fruit is used for its pulp production, and 60% of the plant are wastes. Discarded crowns generate about 12 tons per day of waste that ends up in landfill and only 5% of them are used by farmers to fertilize plantations [5].

The fibrous plants are composed mainly of cellulose, hemicellulose and lignin [6]. The lignocellulosic materials, especially agro-industrial residues, are important as reinforcement products for building construction material industry, in terms of environmental preferences of the modern society [7]. Biodegradable characteristics of the agro-industrial wastes contribute significantly to mitigate the impacts of consumerism and promote sustainable development model.

Cellulose is the most abundant natural polymer on earth and due to its inherent rigidity has emerged as an important source to obtain useful particles and fibers as reinforcement of thermoplastics [8]. In this sense, it is necessary to study a suitable mechanism for extraction of cellulose fibers from pineapple crowns, followed by adequate characterization of them, for their future proper application. In this way, it could be created a value-added product from a plant source of biomass, presenting a valuable commercial alternative for the agro-industry [9-11].

The cellulose fibers have been widely used as biodegradable loads, because they do not damage the environment and besides, they have also techno-economic advantages. For example, the cellulose fibers are used in the automotive industry, considered an alternative replacement of fiberglass, known as traditional synthetic fibers for reinforcement of thermoplastics, which create many environmental problems.

The incorporation of extracted plant cellulose fibers as components in the formation of a new material has resulted in a large topic of research, which fact is attributed to the high compatibility between these polysaccharides as an effect of reinforcing the polymer matrix [12]. Nowadays, the emphasized increase of the use of natural cellulose fibers show their advantage of being biodegradable, requiring low energy input for production, being less abrasive and having low density, and high specific strength [13].

The aim of this study is the extraction and characterization of cellulose from the agricultural waste pineapple (*Ananas comosus* L. Merrill) crowns, constituting a fibrous fraction plant. This residual source is rich in cellulose, which could be use as reinforcing component in biomaterials.

Experimental

Material and Reagents

Pineapple crowns were collected from trucks waste from FREXPORT S.A. de C.V. industry, located in Huimanguillo, Tabasco. Crowns were dried for subsequent treatments, performed in the laboratory of Polymeric Materials of the Popular University of Chontalpa.

Pretreatment

Pineapple crowns were cut to a length of 20 cm, with four longitudinal cuts, and the solution of 10% NaOH penetrated perfectly into the samples: they were kept in this solution for 20 min when the boiling point was reached. After removing pineapple crowns from the solution, they were allowed to cool and washed with running water, then manually shredded. The fibers were cut into 2 cm long and dried in an oven at a temperature of 60°C for 12 hours.

Cellulose extraction

Cellulose extraction was carried out using the pulping technique of Cazaurang modified method [14], consisting of four steps: (1) mild acid hydrolysis with 0.4% H_2SO_4 for 1 h, and subsequent washing; (2) chlorination with 3.5% NaClO, stirring the solution in a water bath at 30°C to pH 9.2 and then, washing with distilled water until neutral pH; (3) alkaline extraction with 20% NaOH under stirring for 1 h, followed by a washing process; (4) bleaching with a solution of 0.5% NaClO, continuous stirring for 1 hour and a final wash to neutral pH. The obtained material was manually shredded and placed in aluminum pan for one day at room temperature, and after that in an oven for 24 h at 60°C. The final product was weighed to determine the yield.

Fourier Transform Infrared Spectroscopy (FTIR)

The characterization of the functional groups, present in the composition of the dried samples of pineapple crowns and the extracted cellulose from them, was carried out using the Fourier transform infrared spectroscopy (FTIR). FTIR Nicolet Magna 460 Protegé was used in the absorbance mode, with a resolution of 4 cm^{-1} and 100 scans. The tablets were made with 1 mg sample in 100 mg of KBr.

X-ray Diffraction (XRD)

The X-ray diffraction patterns of pineapple crowns samples and extracted cellulose from them were registered with Siemens D 5000 Diffractometer, using CuK radiation (λ = 1.5418 Å) at a 34 kV and a current of 25 mA, in a 2θ angular range, between 10 and 30 degrees, making measurements every 0.04° for 6 s. The percentage of crystallinity of cellulose (Xc %) was calculated, according to Segal equation [15]:

$$X_c \% = (1 - I_1/I_2) X\, 100 \quad (1)$$

where: I_1 is the minimum peak intensity in the XRD patterns and I_2 the crystalline peak intensity, respectively.
The crystal size (t) was calculated with the equation proposed by Scherrer [16]:

$$t = K\lambda/BCos\theta \quad (2)$$

where: λ is the wavelength of the radiation (λCu), B is the width at half height of the diffraction peak of the sample, and K is the dimension less form factor which has a typical value of about 0.9, but varies with the actual shape of the crystallites.

Scanning Electron Microscope (SEM-EDX)

Scanning electron microscope, JEOL JSM 610 LA model, was used to observe the surface morphology of the isolated cellulose fibers from pineapple crowns. EDX analysis revealed the main elements as a part of the cellulose after its extraction of crown pineapple plant.

Results and Discussion

Fiber yield

The extracted cellulose fibers from pineapple crowns showed an average of 11.0 ± 4.0% of yield, as a final dried product.

Fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR spectrum of untreated samples of pineapple crown, presenting a variety of peaks, is shown in **Figure 1**. For example, the peak at 3406 cm^{-1} corresponds to the free O-H stretching vibration of the OH groups in cellulose molecules [17, 18]. The peaks observed at 2916 cm^{-1} and 1622 cm^{-1} are associated with the stretching vibrations of C-H and O-H groups, respectively [19]. The peak at 1622 cm^{-1} is reported also to be corresponding to the OH groups and methyl and methylene [20].

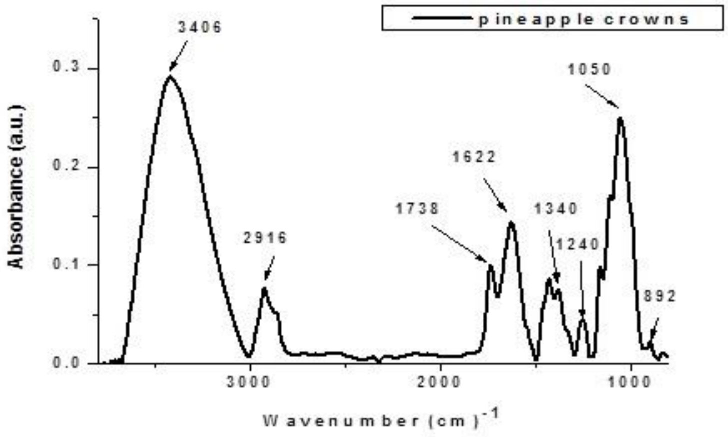


Figure 1 FTIR spectrum of pineapple crowns

The peak at 1738 cm^{-1} was attributed to C=O stretching of the acetyl and uronic ester groups of hemicellulose or of the ester linkage of carboxylic groups of ferulic and p-coumaric acid of lignin [21]. In the spectrum curve could be observed the C-OH peak at 1340 cm^{-1} corresponding to holocellulose [22]. The peak at 1240 cm^{-1} is characteristic for aromatic esters OH (syringyl lignin type), associated with the vibration of the link Caril β-O-O-4 and methoxy groups [20]. The last bands in the FTIR spectra of the untreated plant fibers, considered as most important, those at 1050 cm^{-1} and at 892 cm^{-1}, were are assigned to C-O-C vibration of pyranose ring and to the glycosidic linkages between glucose units in cellulose, respectively [21].

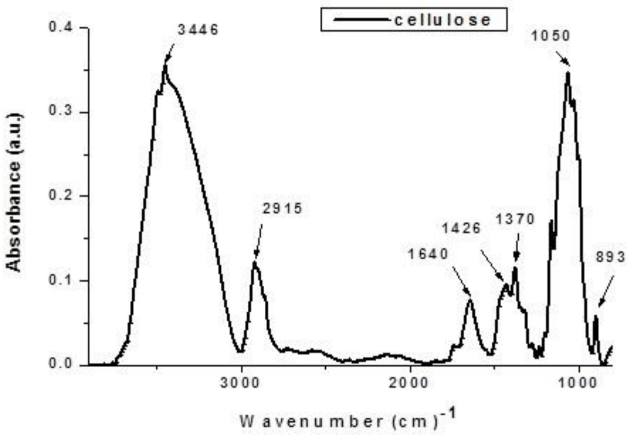


Figure 2 FTIR spectrum of extracted cellulose from pineapple crowns

The FTIR spectrum of extracted cellulose from pineapple crowns is shown in **Figure 2**. The intense and broad band at 3446 cm^{-1} corresponds to the stretching vibration of the OH groups in cellulose molecules [17], while the peak at 2915 cm^{-1} to the stretch of aliphatic alkyl compounds HCH. A peak at 1640 cm^{-1} is attributed to the absorbed water by fibers (fibers-OH) and a skeleton pyranose peak at 1370 cm^{-1} is characteristic of cellulose [6]. The peak of 1060 cm^{-1} was assigned to C-aril-O [20] link, and the peak at 893 cm^{-1} corresponds to aromatic hydrogens [6]. It should be noted than the peak of 1740 cm^{-1} was not observed, probably due to the efficient remove of the hemicellulose with the alkaline extraction. Besides, the peak at 1240 cm^{-1}, corresponding to the type lignin syringyl, was not observed, and probably the lignin was removed by the acid hydrolysis process to which the cellulose fibers were submitted. The observed deformation of the primary alcohol C-O stretching at 1050 cm^{-1} peak corresponds to cellulose [23, 18, and 24]; this peak is also associated with the deformation in the plane C-H type guaiacyl aromatic [20]. It is reported that the cellulose is composed primarily of OH, HCH and COC containing compounds, such as acid-methanol, aliphatic alkyl and aryl-alkyl own cellulose ether [6], compounds that were detected according to the peaks in FTIR spectrum of the extracted cellulose from pineapple crowns (**Figure 2**).

X-ray diffraction (XRD) analysis

The diffraction patterns of untreated samples of pineapple crowns and extracted cellulose from them are shown in **Figure 3** and **Figure 4**, respectively. It can be observed that the pineapple crowns (**Figure 3**) have well pronounced crystalline peaks: one near $2\theta = 21.8^{\circ}$, characteristic of the cellulose, and the peaks at $2\theta = 12.6^{\circ}$ and 34.6°, corresponding to the structure of cellulose I, commonly found in the natural vegetable fibers [25, 26, 27]. These facts are due to the hydrogen bonding and van der Waals interactions, existing between adjacent cellulose molecules, compared to hemicellulose and lignin, which are amorphous in nature.

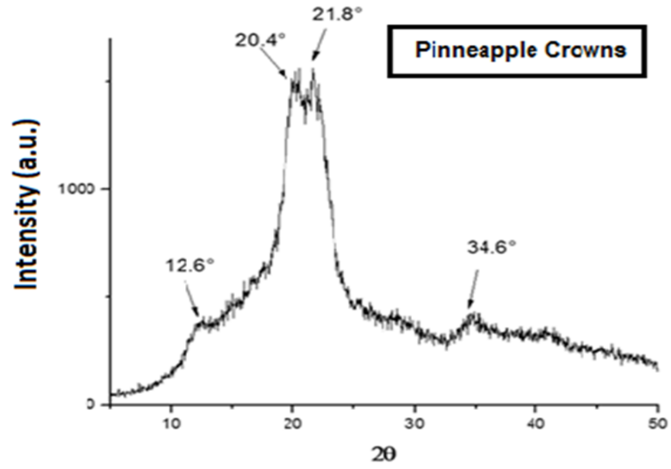


Figure 3 X-ray diffraction patterns of pineapple crowns

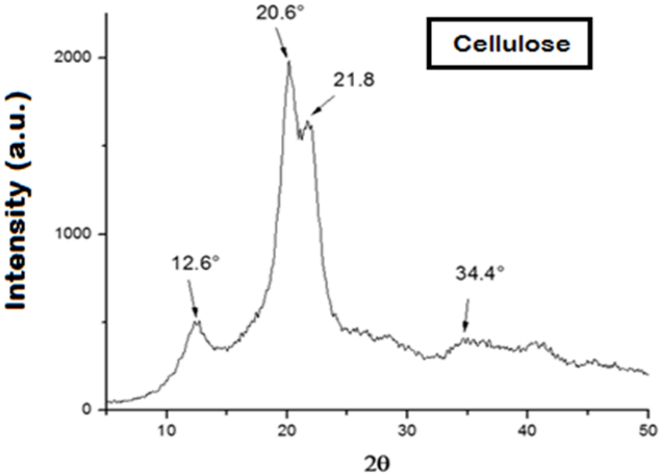


Figure 4 X-ray diffraction patterns of extracted cellulose fibers

The X-ray diffraction patterns of the extracted cellulose fiber from pineapple crowns (**Figure 4**) showed that the relative intensities of the cellulose peaks are higher compared to those in **Figure 3**. This fact indicates that was an efficient removal of noncellulosic polysaccharides and dissolution of amorphous zones after the chemical treatments of the fibers [28]. As a result, the crystallinity index (**Table 1**) of the extracted cellulose fibers increased (43.05%) and their crystal size diminished (2.3 nm), compared to those of untreated pineapple crowns (**Table 1**).

Table 1 Crystallinity index and crystal size of pineapple crowns and extracted cellulose fibers

Samples	**Pineapple crowns**	**Extracted cellulose**
Crystallinity index (%)	39.6	43.05 ±1.5
Crystal size (nm)	5.1	2.3 ±0.48

The increase of the cellulose extracted fibers crystallinity index indicates the removal of amorphous cellulose and other amorphous residues [29], after the acid hydrolysis treatment in our experiments. It has been reported that the crystal size of cellulose may be increased or decreased, depending on the effect of several factors, such as the source of the cellulose, method of its extraction and pumping treatments. The obtained cellulose in this study could be considered having a monoclinic form, corresponding to type I cellulose X-ray patterns, specifically cellulose-1β, commonly found in plant tissues [27].

Scanning electron microscopy (SEM-EDX) analysis

SEM images (**Figure 5**) showed that the cellulose fibers extracted from pineapple crowns have diameter average approximately 1.71 ± 3.90 µc. Elemental analyses SEM-EDX revealed that the extracted cellulose fibers contain as main chemical elements carbon (C) and oxygen (O). Traces of chlorine (Cl), residues of bleaching and chlorination steps, were detected, and calcium (Ca) probably originated from the washing water.

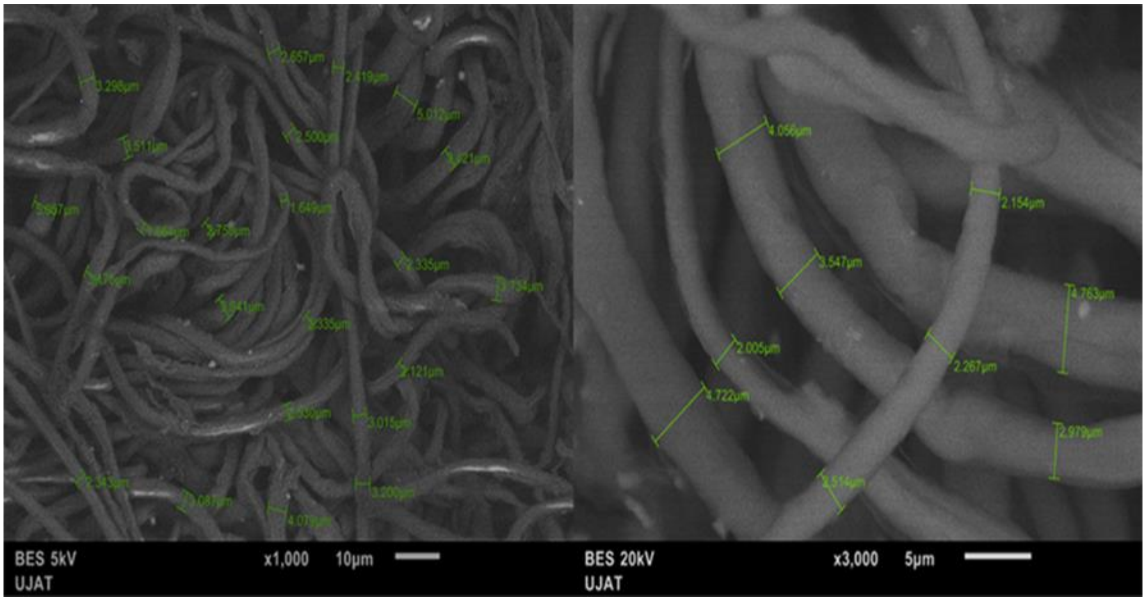


Figure 5 Micrograph (SEM) showing the diameters of the cellulose fibers extracted from pineapple crowns

Conclusions

Cellulose fibers were extracted from pineapple crowns after chemical treatment in several steps, using Cazaurang modified method. The procedures permitted a yield of 11.0 ± 4.0% of cellulose. Patterns of X-ray diffraction showed an increased intensity of the crystallinity peaks of the extracted cellulose, probably due to the efficient dissolution of the amorphous regions after the acid treatments. The infrared analysis (FTIR) confirmed this fact, associated with the disappearance of the typical bands of the removed hemicelluloses and lignin. The calculated crystallinity of the extracted cellulose fibers was 43.05 ±1.50% and their crystal size of 2.30±0.48 Å, approximately. The obtained cellulose could be considered having a monoclinic form, corresponding to type I cellulose X-ray patterns, specifically cellulose-1β stable monoclinic crystals, commonly found in plant tissues. SEM images showed that the cellulose fibers extracted from pineapple crowns have diameter average approximately 1.71 ± 3.90 µc. The results of this study could be considered promising for the use of the extracted cellulose fibers from plant waste as reinforcement in biocomposites, paper production, among other uses.

Acknowledgements

The analysis by X-ray diffraction were performed at the National Laboratory of Nano and Biomaterials (Financed by Fomix-Yucatan and Conacyt), CINVESTAV-IPN. Merida-Unit. We thank PhD. Patricia Quintana for access to LANNBIO and M.S. Daniel Aguilar Treviño for their technical support in obtaining the diffractograms.

References

[1] R. Méndez, Aprovechamiento de subproductos agropecuarios, UNISUR, Colombia, 1995, p 336.
[2] P. Jurado, J. Mutuberría, N. Oliven, R. Charadia, S. Brühl, and M. García M, Jornadas Sam/Conamet/Simposio Materia, 2003, 17, 02, p1118-1121.
[3] I. Valdez, J. Acevedo, and C. Hernandez, Renew. Sust. Energy Rev, 2010, 14, p2147-2153.

[4] S. Milena, L. Montoya, and F. Orozco, Revista de la Facultad Nacional de Agronomía en Medellín, Colombia, 2008, 61, 1, p4422-4432.
[5] E. Rivero, personal interview, November 15, 2012.
[6] J. Morán, V. Alvarez, V. Cyras, and A. Vázquez, Cellulose, 2008, 15, p149-158.
[7] A. Simbaña, and M. Mera, Revista Informativa de Docencia, Investigación y Proyección Social, 2013, p15-16.
[8] K. Arroyo, Biocompósitos de almidón termoplástico con microfibras de Celulosa, Tesis de Maestría, Instituto Politécnico Nacional, México, 2008, p15-22.
[9] S. Saval, BioTecnología, 2012, 16, 2, p14-46.
[10] A. Lopes, B. Cherian, S. Ferreira, S. Thomas, L. Pothan, and M. Kottaisamy, doi: 10.1016/j. Carbpol, 2010, 03,046.
[11] E. Cataño E, Obtención y caracterización de nanofibras de celulosa a partir de desechos agroindustriales, Tesis de Licenciatura, Universidad Nacional de Colombia. Colombia, 2009, p1-17.
[12] S. Kalia, A. Dufresne, B. M. Cherian, B. S. Kaith, L. Avérous, J. Njuguna, and E. Nassiopoulos, J. Polym Sci, 2011, Article ID 837875, 35p.
[13] A. Chaker, P. Mutjé, M.R. Vilar and S. Boufi, Cellulose, 2014, 21, p4247-4259.
[14] M. Cazaurang, S. Peraza, and R. Cruz, Cellulose Chemistry and Technology, 1990, 24, p629-638.
[15] L. Segal, J. Creely, A. Martin, and C. Conrad, Textile Research Journal, 1959, 29, p786-794.
[16] B.D. Cullity, Elements of X–Ray Diffraction, second edition, Addison–Wesley, New York, 1978.
[17] C. J. Chirayil, J. Joy, L. Mathew, M. Mozetic, J. Koetz, and S. Thomas, Industrial Crops and Products, 2014, 59, p27–34.
[18] J. Coates, Interpretation of Infrared Spectra, a Practical Approach in Encyclopedia of Analytical Chemistry, Editorial R.A. Meyers, USA, 2000.
[19] B. Deepa, E. Abraham, N. Cordeiro, M. Mozetic, A.J. Mathew, K. Oksman, M. Faria, S. Thomas and L. Pothan, Cellulose, 2015, 22, p1075-1090.
[20] J. Ramos, F. Dávalo, and F. Navarro, Blanqueo Superficial de Papel con Peróxido de hidrógeno y perborato de sodio, asistido con plasma en frío y luz ultravioleta y visible, Universidad de Guadalajara, Guadalajara, México, 2004.
[21] A. Alemdar, M. Sain, Bioresour Thecnol, 2008, 99, p1664-1671.
[22] O. Faix, and O. J. Beinhoff, Wood Chem Technol, 1988, 8 p505.
[23] Q. Liu., S. Wang, Y. Zheng, Z. Luo and K. Cen, Journal of Analytical and Applied Pyrolisis, 2008, 82, p170-177.
[24] C. Dence, and S. Lin, In Methods in Lignin Chemistry. Lin, S. Y.; Dence, C. W. Eds, Springer-Verlag, New York, 1992.
[25] P. M. Visakh, and S. Thomas, Waste Biomass, Vol. 1, 2010, p121-134.
[26] X. J. Jin, and D. P. Kamdem, Cellulose Chemistry and Technology, 2009, 43,7-8, p229-234.
[27] A. Isogai, U. Makoto, T. Kato, T. Uryu, and R. Atalla, Macromolecules, 1989, 22, p.3168-3172.
[28] H. Chen, and A. Yokochi, Journal of Applied Polymer Science, 2000, 76, p1466 - 1471.
[29] N. Kasyapi, V. Chaudhary, A.K. Bhowmick, Carbohydr. Polym., 2013, 92, p1116-1123.

Publication History

Received	10th Mar 2016
Revised	16th Mar 2016
Accepted	20th Mar 2016
Online	30th Mar 2016