Preparation and characterization of cellulose hexanoate, octanoate and decanoate from sugarcane bagasse cellulose

Omar E.B. Elnaeim[1] and Yousif Ali Ragab[2]
[1]Department of Chemistry and Biology, Faculty of Education University of Al-Butana, Rufaa, Sudan
[2]Department of Chemical Engineering and Chemical Technology, Faculty of Engineering and Technology, University of Gezira, Medani, Sudan
oelnaeim@yahoo.com

Abstract

In recent years there is a growing urgency to develop renewable biodegradable materials for various applications, and to replace petroleum-based materials. This study aims to extract cellulose as raw material from Sudanese sugarcane bagasse (SCB) to prepare cellulose esters. The (SCB) sample was collected, grounded, dewaxed, delignified, purified and resolved in (DMA/LiCl) solvent system at 160°C. Then, cellulose esters were prepared by long chain acid chlorides namely hexanoyl (C_6), octanoyl (C_8), decanoyl (C_{10}), in the presence of triethylamine for proton capture at optimum reaction condition. The produced cellulose esters were characterized using different instruments and methods. Elemental analysis was carried out to confirm the degree of substitution (DS). Fourier transfer Infra-Red spectroscopy (FT-IR) provide evidence of acylation by the presence of ester carbonyl groups and decrease of the band of the hydroxyl group. Thermo gravimetrical analyzer (TGA) showed that the prepared esters have different thermal stability depending on DS value and chain length at the substitution position. Solubility test shows different solubility of prepared cellulose esters depending, in addition to DS value, on the effect of the substituents on the hydrogen bonds. The study concluded that significant changes occur in the structure, thermal stability, and solubility of cellulose by esterification and the produced esters can be more useful than pure unmodified cellulose.

Keywords: Cellulose, sugarcane, delignification, esterification, eegradable, solubility.

Introduction

The reutilization of natural organic residues to obtain an applicable product is a very useful practice that has many advantages[1]. Utilization of agro-industrial residues as raw materials for useful applications is increase in recent years[2]. Sugarcane (SCB) is the fiber left over after the juice has been squeezed out of sugarcane stalks it is the major by-product of the sugarcane industry[3]. Sugar factory's produces nearly three tons of wet bagasse out of every 10 tons of sugarcane[4]. Sugarcane bagasse (SCB) consists of a bout 40 – 50% glucose polymer cellulose, 25-35% is hemicelluloses and the remainder is mostly lignin (18–24%) in addition to lesser amounts of mineral and wax[5-7]. Cellulose is an unbranched polymer formed by β-1,4 glycosidic bonds between glucose monomers[8]. Cellulose derivatives have been widely used as coatings, optical films, fibers, molded objects, and matrices for controlled release[9]. Esterification of cellulose is one of the most important methods to functionalize it[10]. Cellulose esters are commonly obtained by esterification of cellulose with a carboxylic acid, acid anhydride, or acyl chloride in the presence of a catalyst[11]. The saturated longer-chain fatty acids ester of cellulose has been prepared and their plastic and physical properties were characterized[12,13]. Cellulose esters are commercial products used as films, fibers[14], particle filters and reverse osmosis membranes[15].

Materials and methods

The sample: The sample of this study was sugarcane bagasse (SCB) collected from Guneid Sugar Factory, Gezira state, Sudan. The (SCB) was washed, dried and grounded.

Reagents and solvents: The solvent system used in this study was N, N-Dimethylacetamide (DMA) obtained from Merck KGaA, Darmstadt, Germany; Lithium Chloride (LiCl) obtained from Oxford Lab Chem. Ethanol absolute from CARLO.ERBA Milan, Italy. The reagents used in this study were hydrogen peroxide, triethylamine from Central Dug House (P) Ltd (CDH). Hexanoyl chloride ($C_6H_{11}OCl$), octanoyl chloride ($C_8H_{15}OCl$), decanoyl chloride ($C_{10}H_{19}OCl$), were obtained from Sigma Aldrich, USA.

Elemental Analysis: Elemental analysis (EA) was carried out using LECO CHNS- 932 elemental analyzer in the Petroleum Laboratories Research and Studies (PLRS) Khartoum, Sudan.

Fourier Transfer Infra-Red Spectra (FT-IR): FT-IR spectrometer used was Shimadzu FT-IR 8400 S. CE instrument using potassium bromide (KBr) discs, at the Central Research Laboratory, University of Khartoum, Sudan.

Thermogravimetrical Analysis (TGA): TGA was performed in a TGA Linseys PT 1000 Simultaneous Thermal Analyzer.

Measurements of cellulose hexanoate, cellulose octanoate, cellulose decanoate, were carried out at ramp 2.00^{o}C/min to 600 ^{O}C /min using a platinum pan, the sample gas was oxygen flow was 60m/min^{-1} and the balance gas flow was nitrogen 50 ml/min. All samples were at the powdered form. Measurements were carried out in the laboratory of chemistry, Faculty of Science. Al-Neelain University, Sudan.

Solubility Test: The solubility of cellulose ester samples was determined using some organic solvents and distilled water at concentration of 0.01gm of cellulose ester /1ml of the solvent.

Methods: Dewaxing of sugarcane bagasse (SCB): 20g of the dried powder of sugarcane bagasse (SCB) was dewaxed in Soxhlet apparatus for 6 h using (2:1, V/V) toluene/ethanol[16].

Delignification and Purification: Sugarcane bagasse sample was delignified byalkaline H_2O_2 (pH about11.8) under continued stirring at 48°C overnight. The insoluble part was purified with a mixture of 80% acetic acid and 70% nitric acid (1:1, V/V) at 100°C for 20 min, then it was washed with 95% ethanol, and distilled water until neutralization[17].

Dissolution: 25ml of N,N-Dimethylacetamide (DMA) were added to 0.25g of delignified cellulose in a 250ml conical flask. The mixture of 1% concentration was heated at 160°C with stirring for 2 h using hot plate with magnetic stirrer. Before the mixture was cooled and the temperature was adjusted to 100°C, 2gm of lithium chloride (LiCl) were added under stirring for an hour. Then the mixture was cooled and left with stirring at room temperature for several hours (about 9 hours) until dissolution was completed[18,19].

Preparation of Cellulose Esters: under continued stirring, 2ml of trimethylamine for proton capture were added to (1%) cellulose solution. Then, 2ml of each reagent (hexanoyl chloride, octanoyl chloride and decanoyl chloride) were added to the flask, and it was stored at room temperature for 24h to complete the reaction, then, the product of each cellulose hexanoate, cellulose octanoate and cellulose were precipitated into about 500ml ice water and it was washed with ethanol, acetone and distilled water, and was kept for three days and dried at 50°C for 10 hours. The degree of substitution, amount yield and percentage of esters are shown in Table-1.

Table-1: Degree of substitution, amount yield and yield percentage.

Cellulose Ester	DS- Value	Amount Yield (g)	Yield %
Cellulose Hexanoate	2.35	0.2	28.16
Cellulose Octanoate	2.24	0.4	50.00
Cellulose Decanoate	2.46	0.46	46.93

Results and discussion

The prepared cellulose esters (hexanoate, octanoate, decanoate,) were subjected to elemental analysis, Fourier transfer infra-red (FT-IR) spectroscopy, thermal analysis and solubility tests.

Results of Elemental Analysis: Dry ground samples of esters (cellulose hexanoate, cellulose octanoate, cellulose decanoate) were characterized by the elemental analyzer for the determination of the percentage of carbon in each molecule. The degree of substitution (DS) of cellulose esters were determined depending on carbon atoms percentage measured by elemental analysis and calculated (theoretical) percentage. These results are shown in Table-2. These results show a decrease of DS-value from cellulose hexanoate (2.35) to cellulose octanoate (2.24), and then it shows an increase of DS-value from cellulose decanoate (2.46) as the number of carbon atoms increase. This shows that esterification was efficient sines the maximum DS is (3).

Table-2: Results of (DS) values using elemental analysis.

Cellulose esters	Measured (C%) value	Theoretical (C%) value	DS- value
Cellulose hexanoate	49.42	63.16	2.35
Cellulose octanoate	49.85	66.67	2.24
Cellulose decanoate	56.91	69.23	2.46

Results of FT-IR Spectrum of Cellulose Hexanoate: The FT-IR spectrum of cellulose hexanoate showed the expected characteristic peaks of the ester. The main difference between cellulose hexanoate and unmodified cellulose is the decrease in absorbance intensity of the band at about 3442.70cm^{-1} assigned to hydroxyl group (O-H) stretching, which gives an evidence to relatively uncompleted substitution. The band at 2927.74 cm^{-1} corresponds to (C-H) associated with hexanoyl alkyl chain. The peak at 1741.60 cm^{-1} is evidence of absorption by the carbonyl group of the ester.

Results of FT-IR Spectrum of Cellulose Octanoate: The FT-IR spectrum of cellulose octanoate showed the decrease in the absorbance intensity of the band at about 3380.98 cm-1 assigned to the (O-H) group stretching gives evidence to partial substitution of (OH) groups by acetate group. The peak at 2927.74cm^{-1} corresponds to C-H stretching associated with octanoyl alkyl chain. The band at1637.46 cm^{-1} and 1714.60cm^{-1} are evidence of absorption by the carbonyl group of the ester.

Results of FT-IR Spectrum of Cellulose Decanoate: The FT-IR spectrum of cellulose decanoate indicate more substitution of (OH) groups with decanoate groups. This fact is shown by the decrease of the peak at 3419.56cm^{-1}. The absorption bands from

$2921.96 cm^{-1}$ to $2852.52 cm^{-1}$ are related CH_2- and CH_3- groups associated to the decanoyl group. The characteristic peak around $1714.60 cm^{-1}$ and at $1579.59 cm^{-1}$ gives evidence to presence of ester carbonyl absorption. The peak at $1448.44 cm^{-1}$ is attributed to the presence of CH_2 stretch. The peak at $1161.07 cm^{-1}$ is characteristic of (C-O) stretching. The peak around $1066.56 cm^{-1}$ is due to (C-O-C) stretching within anhydroglucose ring.

TGA for Unmodified Pure cellulose: The first thermogravimetry step of pure cellulose start at 225°C with trace weight loss 1.44mg (7.2%). The rate of weight loss increases with increasing temperature. Decomposition temperature occurs at 355 °C with (13.3mg) 66.5% total weight loss (second step of decomposition). This high weight loss is due to the depolymerization reaction of the cellulose chain at (C-C or C-O-C) bonds. The last step of degradation at 530°C is the volatilization of various decomposition products.

TGA for Cellulose Hexanoate Ester: The thermal decomposition temperature of cellulose hexanoate is known via many steps. The first thermo gravimetry step of water loss and volatiles occurs at 85.00°C with 2.77mg total weight loss which represented (13.85%) of the total weight of the sample. The second step of decomposition occurs at 194.6°C with 5.15mg (25.75%) total weight loss. The third step of decomposition occurs at 301.1°C with 19.18mg (95.9 %) total weight loss. The last step of degradation at 591°C with 20.28mg (100%) total weight loss. the decomposition temperature of cellulose hexanoate is less than that of pure cellulose. The thermal degradation temperature of cellulose hexanoate esters is less than that of pure unmodified cellulose due to the substituents and the ester is less thermo stable than pure unmodified cellulose.

TGA for Cellulose Octanoate Ester: The thermal decomposition temperature of cellulose octanoate known via three steps. The first thermo gravimetric step of water loss and volatiles occurs at 103.7°C with 1.16mg total weight loss represented (5.8%) of the total weight of the sample. The second step of decomposition occurs at 241.2°C with 19.64mg (98.2%) total weight loss.

The last step of degradation at 598°C with 20.63 (100%) total weight loss. The thermal degradation temperature of cellulose esters is influenced by the chain length of the acid chloride substituents. Therefore, the decomposition temperature of cellulose octanoate is less than that of pure unmodified cellulose but it is higher than that of cellulose hexanoate.

TGA for Cellulose Decanoate Ester: The thermal decomposition temperature of cellulose decanoate known via three steps. The first thermogravimetry step of water loss and volatiles occurs at 137.9 °C with 1.00mg total weight loss (5%) of the total weight of the sample. The second step of decomposition occurs at 303.9°C with 15.36mg (76.8%) total weight loss. The last step of degradation at 595°C with 19.35 mg

(96.75 %) total weight loss. The decomposition temperature of cellulose decanoate is less than that of pure cellulose. The thermal degradation temperature of cellulose esters is influenced by the chain length of the ester. This result shows that the thermal stability of cellulose decanoate is lowest than that of pure unmodified cellulose but it is higher than that of lowest chain length esters.

The TGA results of prepared cellulose esters summarized in Table-3. The active temperature of thermal decomposition of cellulose hexanoate was found at 301.1°C and this is higher than that of cellulose octanoate (241.2 °C).

The active temperature of thermal decomposition of cellulose decanoate was found at 303.9 °C, therefore, thermal stability of these esters increases. This fact may be due to the increases of the chain length. Although thermal stability also depends on the degree of substitution (DS) but in current study it is ignored because all of prepared esters have DS value greater than 2.00.

Table-3: Summary of TGA results of prepared cellulose esters.

Ester	Temperature of active decomposition	Weight loss (mg)	Weight loss (%)	DS-value
Pure unmodified Cellulose	377	15.00	75.00	0.00
Cellulose hexanoate	301.1	19.80	99.00	2.35
Cellulose octanoate	241.2	19.64	98.20	2.24
Cellulose decanoate	303.9	15.36	76.80	2.46

Test of Solubility: Test of solubility for prepared cellulose ester was carried out at room temperature and the results are shown in Table-4. Introduction of acyl group into the molecular structural of glucose polymer cellulose break down the highly hydrogen bonds. Cellulose Hexanoate (C_6) is insoluble in tetrahydrofuran (THF), methanol, acetic acid and acetone, but it is moderately soluble in dimethylformamide (DMF) and completely soluble in dimethylsulfoxide (DMSO).Cellulose octanoate (C_8) and cellulose decanoate (C_{10}) solubility is the same, both are moderately soluble in polar aprotic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) so, they are insoluble in acetone or other polar protic solvents such as methanol and acetic acid. Cellulose octanoate (C_8) and cellulose decanoate (C_{10}) are soluble completely in dimethylsulfoxide (DMSO).

The efficiency of organic solvents used for solubility test of cellulose esters can be arranged as follows: DMSO >DMF>THF >Acetic acid >Acetone and Methanol.

Table-4: Solubility results for pure cellulose and cellulose esters at room temperature.

Solvent Sample	H$_2$O	THF	Methanol	Acetic acid	DMSO	DMF	Acetone
Cellulose Hexanoate	-	-	-	-	+ +	+	-
Cellulose Octanoate	-	+	-	-	++	+	-
Cellulose Decanoate	-	+	-	-	++	+	-

Conclusion

Cellulose from SCB was esterified homogeneously in N,N-Dimethylacetamide/ Lithium chloride medium with long chain acid chlorides. Prepared cellulose esters were subjected to several experimental tests to identify the differences from pure unmodified cellulose. The products cellulose esters were characterized. The results show significant changes occurred in the structure, FT-IR spectra, thermal stability, and solubility of cellulose esters.

References

1. David, A. (2013). Technical document on municipal solid waste organics processing. Environment Canada= Environnement Canada.

2. Silva, A. J. P., Lahr, F. A. R., Christoforo, A. L., & Panzera, T. H. (2012). Properties of sugar cane bagasse to use in OSB. *Int J Mater Eng*, 2, 50-56.

3. Andrade Siqueira, T. C., Zanette da Silva, I., Rubio, A. J., Bergamasco, R., Gasparotto, F., Aparecida de Souza Paccola, E., & Ueda Yamaguchi, N. (2020). Sugarcane bagasse as an efficient biosorbent for methylene blue removal: kinetics, isotherms and thermodynamics. *International journal of environmental research and public health*, 17(2), 526.

4. Guilherme, A. A., Dantas, P. V. F., Santos, E. S., Fernandes, F. A., & Macedo, G. R. (2015). Evaluation of composition, characterization and enzymatic hydrolysis of pretreated sugar cane bagasse. *Brazilian Journal of Chemical Engineering*, 32(1), 23-33.

5. Moubarik, A., Grimi, N., & Boussetta, N. (2013). Structural and thermal characterization of Moroccan sugar cane bagasse cellulose fibers and their applications as a reinforcing agent in low density polyethylene. *Composites Part B: Engineering*, 52, 233-238.

6. Sun, J. X., Sun, X. F., Zhao, H., & Sun, R. C. (2004). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer degradation and stability*, 84(2), 331-339.

7. Wirawan, R., Sapuan, S. M., Yunus, R., & Abdan, K. (2012). Density and water absorption of sugarcane bagasse-filled poly (vinyl chloride) composites. *Polymers and Polymer Composites*, 20(7), 659-664.

8. Jacobsen, S. E., & Wyman, C. E. (2002). Xylose monomer and oligomer yields for uncatalyzed hydrolysis of sugarcane bagasse hemicellulose at varying solids concentration. *Industrial & engineering chemistry research*, 41(6), 1454-1461.

9. Zhang, R. (2015). Regioselective synthesis of curdlan derivatives. Doctoral dissertation, Virginia Tech.

10. Wang, Y., Wang, X., Xie, Y., & Zhang, K. (2018). Functional nanomaterials through esterification of cellulose: a review of chemistry and application. *Cellulose*, 25(7), 3703-3731.

11. Hegner, J., Pereira, K. C., DeBoef, B., & Lucht, B. L. (2010). Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis. *Tetrahedron Letters*, 51(17), 2356-2358.

12. Wang, P., & Tao, B. Y. (1995). Synthesis of cellulose-fatty acid esters for use as biodegradable plastics. *Journal of environmental polymer degradation*, 3(2), 115-119.

13. Willberg-Keyriläinen, P., Rokkonen, T., Malm, T., Harlin, A., & Ropponen, J. (2020). Melt spinnability of long chain cellulose esters. *Journal of Applied Polymer Science*, 137(48), 49588.

14. Yuan, H., Nishiyama, Y., & Kuga, S. (2005). Surface esterification of cellulose by vapor-phase treatment with trifluoroacetic anhydride. *Cellulose*, 12(5), 543-549.

15. Lee, K. P., Arnot, T. C., & Mattia, D. (2011). A review of reverse osmosis membrane materials for desalination—development to date and future potential. *Journal of Membrane Science*, 370(1-2), 1-22.

16. Brant, A. J. C., Naime, N., Lugão, A. B., & Ponce, P. (2019). Cellulose Nanoparticles Extracted from Sugarcane Bagasse and Their Use in Biodegradable Recipients for Improving Physical Properties and Water Barrier of the Latter. *Materials Sciences and Applications*, 11(1), 81-133.

17. Sun, R. (2010). Cereal straw as a resource for sustainable biomaterials and biofuels: chemistry, extractives, lignins, hemicelluloses and cellulose. Elsevier.

18. Potthast, A., Rosenau, T., Buchner, R., Röder, T., Ebner, G., Bruglachner, H., ... & Kosma, P. (2002). The cellulose solvent system N, N-dimethylacetamide/lithium chloride revisited: the effect of water on physicochemical properties and chemical stability. *Cellulose*, 9(1), 41-53.

19. Sjöholm, E., Gustafsson, K., Eriksson, B., Brown, W., & Colmsjö, A. (2000). Aggregation of cellulose in lithium chloride/N, N-dimethylacetamide. *Carbohydrate Polymers*, 41(2), 153-161.