Synthesis of tosylated and trimethylsilylated methyl cellulose as pH-sensitive carrier matrix

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Abstract: Lignocellulosic biomass is one of the most abundant renewable resources that can be processed by chemical reactions for the production of value-added products. In the current study, cellulose and methyl cellulose were synthesized from bleached bagasse pulp and were further modified to cellulose derivatives. Cellulose was first extracted from bagasse by acid–alkali pulping process and was derivatized to prepare methyl cellulose. The products were further chemically modified to tosylated methyl cellulose and trimethylsilylated methyl cellulose. The resulting products were investigated by FT-IR and SEM. Cellulose and all derivatives prepared were evaluated as potential pH-sensitive carrier matrices. The effectiveness as carrier was investigated as function of pH and time in various pH solutions, namely 2.0, 3.5 and 5.0. It was indicated that the type of the modified cellulose plays a role in the obtained results. The present work can be considered as a basic line for drug loading and releasing field.
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1. Introduction

Potential biomass such as agricultural residues consists mainly of three different types of biopolymers i.e. cellulose (35–50%), hemicellulose (25–30%)and lignin (25–30%), which are associated with each other (Ragauskas *et al.,* 2006). Degradation of the polysaccharide constituents i.e. cellulose and hemicelluloses results in the generation of hexose and pentose sugars which could be used as versatile starting materials for further conversion to a range of value-added products. Moreover, cellulose is a naturally occurring organic polymer which forms a major component of all woods, grasses, fibers, and seed hairs. Other sources of cellulose are found in the agricultural residues such as straws, sugar cane, banana plants and the cell wall of some algae and bacteria (Hanley *et al.,* 1997; Yu *et al.,* 2005; Liu and Yu, 2005). One of the agricultural harvesting residues abundantly available in Egypt is bagasse, which is a byproduct results from the sugar manufacture. This lignocellulosic biomass feedstock is a complex mixture of three structural biopolymers, i.e. lignin, cellulose and hemicelluloses (Brodeur *et al.,* 2011).

Cellulose is a promising biopolymer for the formation of many advanced materials for various applications due to the structural uniformity, being a β 1-4 linked polyglucan. Chemical modifications for the cellulose lead to a drastic change of its properties. Thus the conversion of the OH moieties like esterification including carbanilation, etherification, and nucleophilic displacement reaction (Klemm *et al.,* 1998; Heinze *et al.,* 2006) is of increasing interest. Other modifications are ionic and radical grafting, acetalization, deoxyhalogenation, and oxidation (Akira, 2001). Thus, chemical modification of celluloseis performed to produce cellulose derivatives (cellulosics), which can be tailored for specific industrial applications (Akira, 2001), where cellulosics are in general reproducible, recyclable and biocompatible (Conner, 1995).

Most of the cellulose derivatives are safe and non toxic compounds. They are biodegradable and biocompatible with application in industry and pharmacy. Our study aims to synthesize and characterize modified methyl cellulose with trimethylsilylated groups and study of their application as matrix carrier for pH-sensitive study.

2. Material and Methods

2.1. Raw materials:

Bagasse, which kindly was provided by Quena for pulp and paper industry, Quena, Egypt, was used in this study as the lignocellulosic raw material. Characterizations for the raw materials, i.e. moisture content, ash, lignin, holocellulose, alpha cellulose and extracted hemicellulose were carried out before and after pulping and bleaching according to TAPPI standard methods, namely T264 cm-07, T211 om-85, T222 om-88, T257 om-85, T203 cm-99 and T204 cm-07.

2.2. Cellulose isolation

Cellulose was isolated from the agricultural raw material by a pretreatment method in which the raw

material was subjected first to a pulping process followed b bleaching processes as follows:

2.2.1. Pulping

Delignification of the bagasse was carried out firstly with 5.0% sulfuric acid at 160 °C for 2 hours with liquor ratio of 1:10 (raw material: water), where during this step the hemicellulose-lignin bond was broken. After the desired time, the fibers were filtered, washed with water till neutrality and then dried in air at room temperature. After that the fibers was further treated with 10% sodium hydroxide in a second step at liquor ratio of 1:10 and temperature of 170 °C for 2 hours. At the end the pulp was filtered, washed then dried at room temperature and stored for further analysis.

2.2.2. Bleaching

Bleaching was carried out in one stage, where the unbleached bagasse pulp was subjected to sodium hypochlorite solution equivalent to 60% of the chlorine requirement for 1 h at 80 °C. The liquor to fiber ratio was 10:1 and the pH was maintained at 9 during the hypochlorite process. At the end, the bleached bagasse pulp was thoroughly washed with water till neutrality and then left to dry in air and stored for further use.

2.3. Preparation of cellulose derivatives

2.3.1. Methyl cellulose

The isolated cellulose from bleached bagasse pulp was first activated with sodium hydroxide. About 35 g of dimethyl ether was then added to 21 g of the activated cellulose followed up by the addition of 35 g methyl chloride and 28 g 50% aqueous sodium hydroxide under stirring for 30 min at room temperature. Stirring was continued for further 1 h at 55 °C then the temperature was raised to 65 °C and stirring was further continued for another 1h. The reaction was completed at 75 °C for 2h with stirring. At the end of the desired time, the mixture was filtered, washed with acetone and then dried in air (Petzold-Welcke *et al.,* 2010).

2.3.2. Preparation of tosylated methyl cellulose

The prepared methyl cellulose was converted to tosylated methyl cellulose, where 20 g of the methyl cellulose was first stirred in 18% aqueous sodium hydroxide (300 mL) at room temperature for 5 h. The solution was filtered in G3 sintered glass and washed with distilled water for 6 times then finally with dimethylacetamide (DMAc). The resulting cellulosic material was transferred with DMAc solution (800 mL) in a 3 nicked flask and stirred for 2 h at 120 °C under reflux. At the end of the time the temperature was dropped to 100 °C. When the temperature reached 100 °C, 60 g of dried lithium chloride (LiCl) was added and stirring was continued for 24 h at room temperature till complete dissolution.

The solution was cooled to 8 °C and a mixture of 25 mL triethylamine and 25 mL DMAc was added drop wise with stirring. Solution of 17.5 g tosylchloride in DMAc was then added to the reaction mixture and stirring was continued for 24 h. At the end, precipitation was carried out in ice water with vigorously stirring. The precipitate was filtered in G3 funnel crucible and washed for 6 times with distilled water then with ethanol for further 6 times. Finally, the excess ethanol was removed by distillation and the precipitate was dried in a vacuum oven at 40 °C**.**

2.3.3. Preparation of trimethylsilylated methyl cellulose

Silylation of methyl cellulose was carried out firstly by activating the cellulose derivative as mentioned in the preparation of tosyl methyl cellulose. After dissolution of the activated methyl cellulose in DMAc/LiCl, 100 mL of hexamethyldizalane (HMDS) was added drop wise in about 20 to 30 min to the homogenous cellulosic solution with 0.5 mL of chlorotrimethylsilane, as catalyst, with continuous stirring and raising the temperature to 100 °C then left over night. The solution was cooled down to 8 °C and filtered. The product was washed with ethanol twice then with distilled water for 5 times. Finally, the product was dried in vacuum oven at 50 °C.

2.4. Carrier matrix effect

An Anti-acid drug was selected to measuring the effect of the prepared cellulose, methyl cellulose and modified methyl cellulose as pH-sensitive carrier matrix by testing the pH change in different pH solutions at different time intervals. Different pH solutions, namely 2.0, 3.5 and 5.0 were prepared for the test and were selected to be referred to the pH of the stomach during the period of the feeding. 0.5 g of the anti-acid drug was dissolved in 10 mL of ethanol and was placed in the different pH solutions that contain 0.1 g from the modified methyl cellulose as carrier matrix. The pH of each solution was measured at time zero then reported after 2 h. After that, another 10 mL of the pH solutions, namely 2.0, 3.5 and 5.0, respectively, were added to the tested solutions and the pH of each solution was reported after 1 h. This method was repeated once again and the pH of the different solutions was reported.

2.5. Scanning Electron Microscope

Scanning electron microscope (SEM) characterization of bagasse, methyl cellulose and modified methyl cellulose as well as anti-acid loaded compounds was performed using a JEOL JXA-840A electron microprobe analyzer (JOEL USA Inc, Peabody, MA).

2.6. FT-IR analysis

FT-IR spectroscopy was used to confirm fiber results from bagasse, methyl cellulose and modified methyl cellulose. The FT-IR spectra were performed using JASCO FT/IR 6100 Instrument. Samples (~ 2 mg) were mixed and thoroughly ground with ~ 200 mg

KBr to reduce particle size and to obtain uniform dispersion of the sample in the disks. All the spectra were recorded in the absorbance mode from 4000 to 400 cm^{-1} at room temperature.

3. Results and Discussion

3.1. Isolation of cellulose

The selected raw material, i.e. bagasse, was chemically characterized for their constituents of holocellulose, lignin and ash content. From Table 1 (A), one can notice that the holocellulose for the bagasse raw material can reach up to ~ 86% with higher lignin content of 21.13%. Thus treatment strategy that includes breaking the lignocellulosic complex was chosen. In the current work, the alkaline pulping was chosen for breaking down the ligocellulosic structure. The resulting pulp had brown color, where this color change in the pulping is due to degradation of the cell wall components and the incomplete removal of lignin (Ibrahim *et al.,* 2010). A further treatment was applied to bleach the resulting pulp in which a white pulp color was observed due to the removal of the lignin. This can be seen in Table 1 (A) and (B), in which the main effect of the treatment on the composition of the biomass is the decrease in both the lignin and ash contents. The content of the Klason lignin after pulping and bleaching is less than that for the raw material, i.e. ~ 0.1% compared to 21.13% for the raw material. This can be due to the fact that alkaline treatment is basically a delignification process, in which a significant amount of the lignin is dissolved and separated in the resulting black liquor (Ibrahim *et al.,* 2013). After delignification and bleaching of the treated material, an increase in the α-cellulose can noticed where it reached ~ 81%. So the treated baggase is able to be used as source of cellulo**se.**

Figure 1 showed the infrared spectrum of bleached bagasse pulp. It can be seen that the peak at 1735 cm^{-1}, which is assigned mainly to C=O stretching vibration of the carbonyl and acetyl groups in the xylan component of hemicellulose and also typical for structural features of lignin (Ibrahim et al., 2010), has disappeared after bleaching. Also, the absorption bands of lignin at approximately 1595 cm^{-1} (Agblevor *et al.,* 2007) were disappeared in the bleached fibers as well, Fig. 1. Moreover, bands at 3413 cm^{-1}, related to O-H groups, and at 2912 cm^{-1}, related to C-H band, can be seen beside bands between 800 cm^{-1} and 1628 cm^{-1}, where they are specific for cellulose. Generally, typical bands for pure cellulose at 1431, 1372, 1322, 1162, 1033, 896 cm^{-1} can be seen in the FT-IR, where bands at 897 cm^{-1} and 1165 cm^{-1} are assigned as C-O-C starching at the β-(1-4) glucosidic linkage, the linkage which is characteristic for the cellulose, while bands at 1337 cm^{-1} is assigned as the C-O-H bending at C_2 or C_3 and band at 1431 cm^{-1} is assigned to the absorbance of C-O-H bending in plane at C_6.

3.2. Preparation of methyl cellulose

For methyl cellulose preparation, bleached bagasse pulp was first activated with sodium hydroxide to open the polymer chain of the cellulose into relaxed conformation. The washing with water followed by DMAc causes swelling and opening the cellulose structure where the intra- and inter-hydrogen bonds are replaced by hydrogen links with water and DMAc introducing impedes the intra- and inter-hydrogen bonds reforming them. The solvent system used of DMAc/LiCl is very hygroscopic and water is excluded from this solvent system (Yin and Shen, 2007), because the presence of the water accelerates the formation of aggregates of the polymers and this prevents complexation of solvent with cellulose.

The prepared methyl cellulose was analyzed using FT-IR and SEM as illustrated in Fig. 2 (A) and (B). The FT-IR shows the typical absorption of cellulose backbone peaks at about 3427 cm^{-1}, C-O carbonyl stretching at 1640 cm^{-1}, C-H stretching at 2925 cm^{-1} and new bands for the methyl cellulose at 1412 cm^{-1} is assigned to the vibrations of $–OCH_3$ groups. SEM, Fig. 2 (B), shows more bonding between the fibers like matrix for the prepare cellulose derivative fibers.

3.3. Tosylated cellulose derivatives

In the current study, methyl cellulose was modified for the preparation of tosylated cellulose derivatives, in which *p*-toluenesulfonyl (tosylated) group was used as a leaving group during the nucleophilic substitution (SN) reactions making it a practical intermediate for subsequent cellulose modification reactions. The obtained product was investigated by FT-IR and SEM, where FT-IR shows the functions groups of the resulted product. From Fig. 3(A), the FT-IR bands characteristic to cellulose backbone OH group appeared at 3499 cm^{-1} and for C-H stretching appeared at 2917 cm^{-1}. The band for C-O-C appeared at 1048 cm^{-1} and other bands characteristic to tosylated groups appeared at 1118, 1364, 2973 and 1616 cm^{-1} for SO_2, S-O, C-H aromatic and C-C aromatic, respectively. On the other hand, the SEM, Fig 3(B), shows different shape from that characteristic methyl cellulose where tosylated methyl cellulose appears as membrane covered the fibers and tied them together.

3.4. Trimethylsilylated cellulose derivative

The trimethylsilyl (TMS) group is widely used in the protection of hydroxyl functional groups as it easily deprotected in mild conditions (Cooper *et al.,* 1981; Loscher *et al.,* 1998). The FT-IR spectrum, Fig 4(A), shows absorption band for (OH) specific for cellulose at 3437 cm^{-1}, as well as the absorption band at 2912 cm^{-1}, beside absorption bands characteristic to TMS group and both characteristic for (O-Si- CH_3) and Si-

CH_3 at 1246 cm^{-1}, 1015 cm^{-1} and 735 cm^{-1}, respectively. The disappearance of the absorption band at 1437 cm^{-1}, which appeared in cellulose chart, and 1413 cm^{-1}, appeared in MC chart in TMS-and MC charts proofed that TMS group linked to the CH_3 group located at position C_6. Other evidence is the disappearance of the absorption peak at 1265 cm^{-1} in the MC chart which means that TMS group enters into CH_3 group. Moreover, the sharpness and increasing of the absorption bands appeared in TMS-MC compared to those appeared in MC chart indicate that TMS groups are also located in both C_2 and C_3.

On the other hand, the SEM for the trimethylsilyl methyl cellulose, Fig 4(B), shows a membrane like structure with waves which show differs in morphological structure than the resulting cellulose fibers from bleached bagasse pulp.

3.5. Carrier matrix effect

Cellulose and its derivatives has the biocompatible and biodegradable properties and has been investigated extensively for the application in industry and pharmacy (Ohya *et al.,* 1991; Li *et al.,* 2000; Carlmark and Molmstron, 2003; Gupto and Khandekar, 2003; Hntarstoisser *et al.,* 2003; Sturcova *et al.,* 2004; Metroglu *et al.,* 2005; Bontempo *et al.,* 2006; Tong *et al.,* 2007; Meng *et al.,* 2009). Also, cellulose and its derivatives are safe, non-toxic, hydrophilic and come from renewable resources in nature so they have economic advantages over synthetic polymers.

In this work, cellulose and its derivatives were used as a carrier for the active ingredient of the anti-acid drug, in which three different pH solutions, namely pH of 2.0, 3.5 and 5.0, respectively, were prepared and the drug that was carried on pure cellulose was added to the different pH solutions. The pH measured after the addition of the drug loaded cellulose showed neutralize or alkalized pH solution for the prepared acidic solutions due to the effect of releasing of the drug from the cellulose surface to the different pH solutions. The observed results are gathered in Table 2, where we can notice that at zero time all the pHs of the different solutions were raised between 2 to 3 grades, while after 2 h all of them were reached the neutrality, i.e. the pH was 7. Again, looking to the results we can notice that solutions of pHs 3.5 and 5.0 reached the neutrality after 2 h from the addition of the drug loaded cellulose in spite of the addition of acids to the solutions every 1 h (each patch is 10 ml of the acid solution). Moreover, for the sample that has pH = 2.0 it can reach to pH 6.0 after 3 h from the addition of the drug loaded cellulose then decreased to pH 4.0 after 4 h from the addition of the drug. Thus, one can concluded that the cellulose is effective as loading matrix with solutions of pH 3.5 and 5.0 till 4 h after the addition but with solution of pH 2.0, which is the drastic conditions of the stomach, it is good in effect in the first 3 h only.

On a way to try to improve the performance of the cellulosic fiber and its derivatives as loading matrix, the anti-acid drug was further loaded on tosyl methyl cellulose. SEM was instigated as well as measuring of the pHs values with different releasing time. The SEM, Fig. 5a, illustrated that the particles of the anti-acid drug were stuck strongly on the surface of the tosyl methyl cellulose. Following up the pH value cleared that there is an improvement in the rate of releasing the drug, where in solution of pH = 2.0 at zero time after the addition of the drug loaded-tosyl methyl cellulose the pH increased to 4.0 and after 2 h from the addition the pH of the solution reached to neutrality. Comparing this result with that observed with using drug loaded-cellulose, the pH was 5.0 at zero time which means that the cellulose can not hold the drug in its matrix while in case of using tosyl methyl cellulose it can act as holding matrix causing slow release to the drug in the solution. The same observation was noticed for the other pH solutions, namely 3.5 and 5.0, respectively, where the addition of the drug loaded tosyl methyl cellulose results in increasing the pH to 4.0 and 6.0, respectively, at zero time and after that the rate of release was effective and keeps the solutions both at neutrality till 4 h.

Moreover, the anti-acid drug was also loaded on trimethylsilyl methyl cellulose and the SEM was investigated as well as studying the pH values with the time. From SEM, Figure 5b, it was noticed that the sphere particles of the drugs were adsorbed on the surface of the derivatives, where this showed good results in both solutions of pH 3.5 and 5.0 that starts at zero time with an increase of the pH to 5.5 and 6.0, respectively, and continue in both solutions to reach neutrality until 4 h. In case of the pH solution of 2.0, it starts to increase at zero time to pH 3.0 and continued to neutrality till 3 h and after 4 h of the addition of the drug loaded-trimethylsilyl methyl cellulose, it slightly decreased to pH 6.0.

In general, Figure 6 clears the comparison of the release for the three compounds, namely cellulose, tosyl methyl cellulose and trimethylsilyl methyl cellulose in solution with pH = 2.0. The results show that pure cellulose show nearly complete release in zero time and after 2 h but after 3 h the best result was noticed for the trimethylsilyl methyl cellulose and a nice result for the other two compounds. After 4 h the tosyl methyl cellulose was very good that it maintains the pH of the solution to 6.0, while the trimethylsilyl have a solution of pH 5.0 and pure cellulose with pH of 4.0.

Table 1: Characterization of (A) bagasse and (B) bleached bagasse pulps

(A)

Experiment	
Moisture content (%)	8.59
Ash (%)	2.73
Lignin (%)	21.13
Holocellulose (%)	85.95

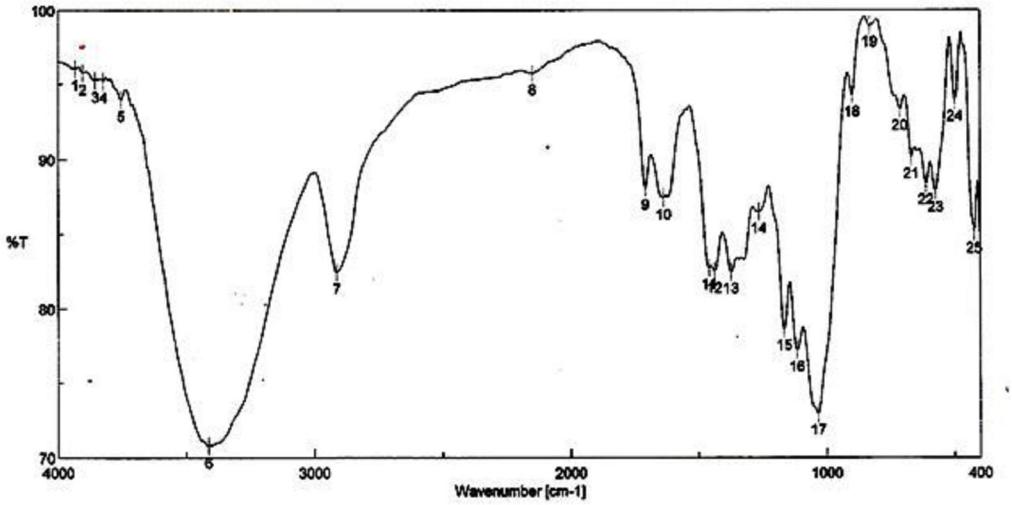
(B)

Moisture content (%)	5.3
Ash (%)	3.7
Lignin (%)	0.08
Alpha cellulose (%)	80.9
Extracted hemicellulose (%)	15.1

Table 2: pH variations of cellulose and modified methyl cellulose for drug release

Matrix	Weight of drug (g)	Time (h)				Time (h)				Time (h)			
		0	2	3	4	0	2	3	4	0	2	3	4
		pH start = 2.0				pH start = 3.5				pH start = 5.0			
Cellulose	0.014	5.0	7.0	6.0	4.0	6.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Tosyl methyl cellulose	0.013	4.0	7.0	6.0	6.0	4.0	7.0	7.0	7.0	6.0	7.0	7.0	7.0
Trimethylsilyl methyl celluloe	0.013	3.0	7.0	7.0	6.0	5.5	7.0	7.0	7.0	6.0	7.0	7.0	7.0

(A)



(B)

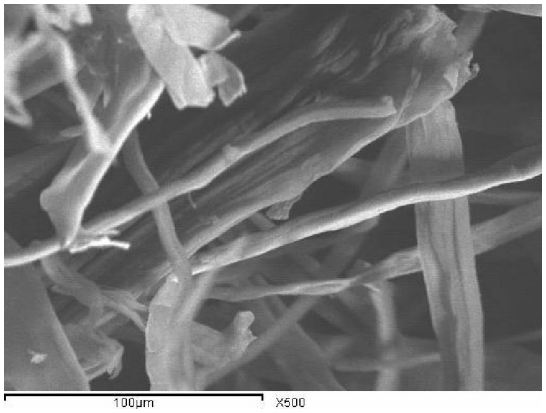
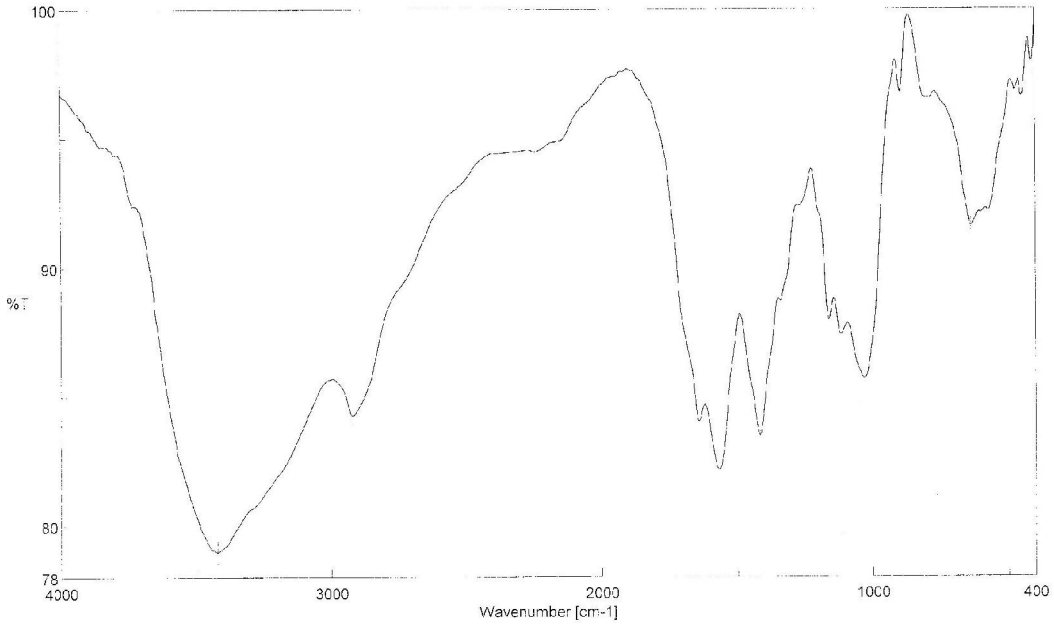


Figure 1: (A) FT-IR for bleached bagasse pulp and (B) SEM for bleached bagasse pulp

(A)



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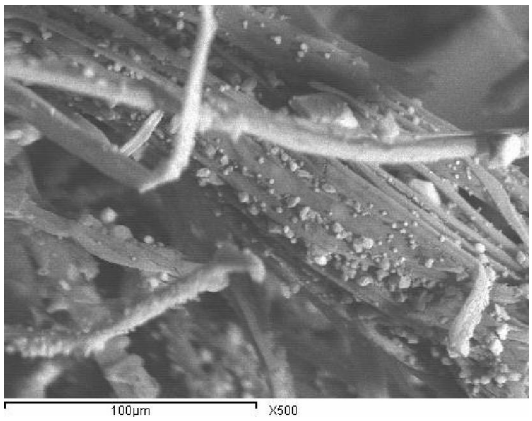
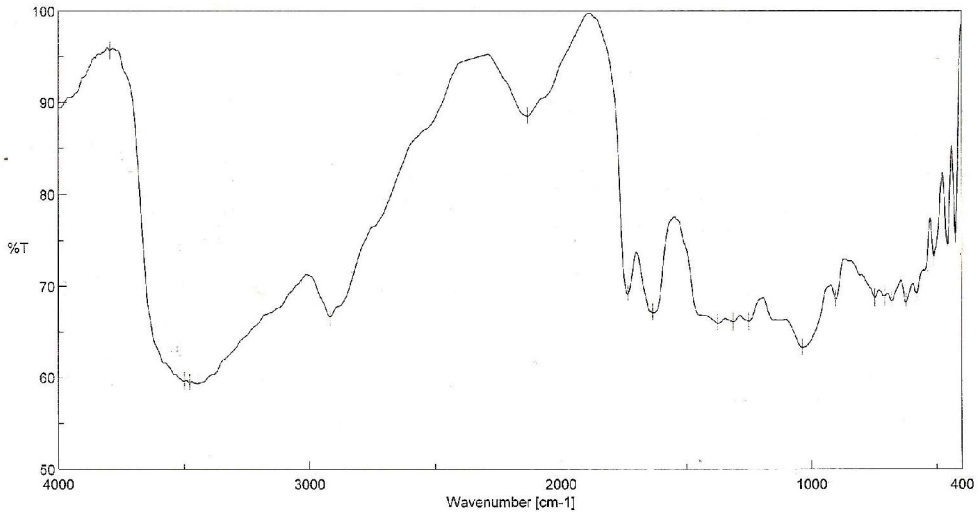


Figure 2: (A) FT-IR for methyl cellulose and (B) SEM for methyl cellulose

(A)



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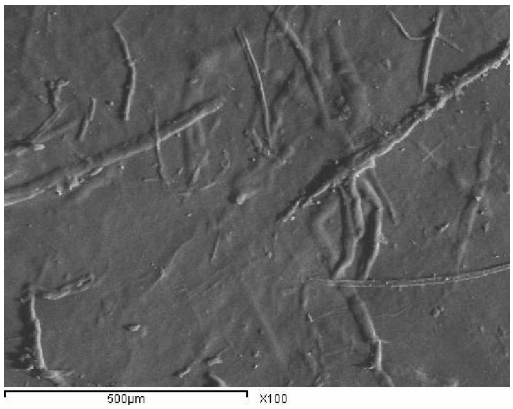
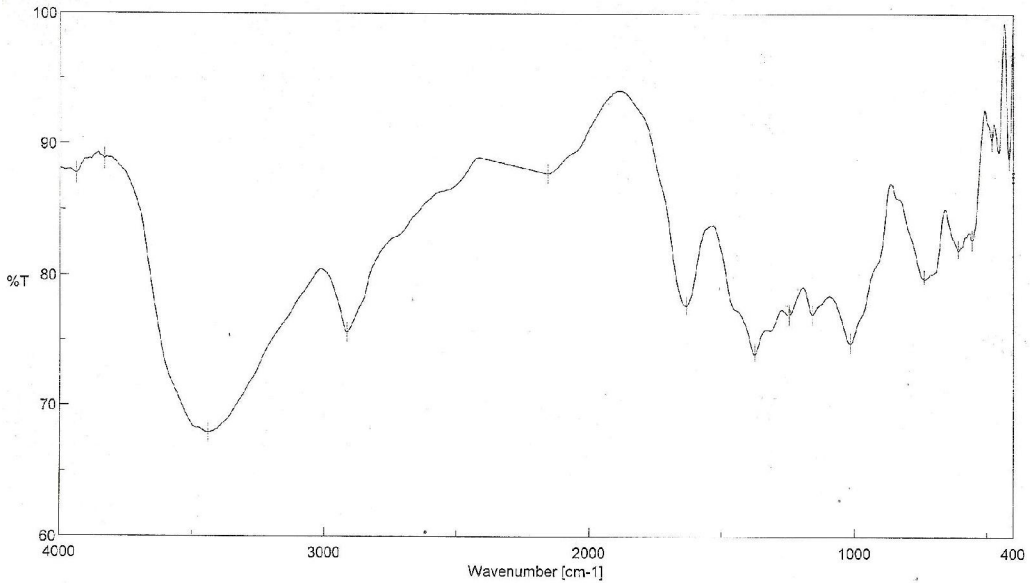
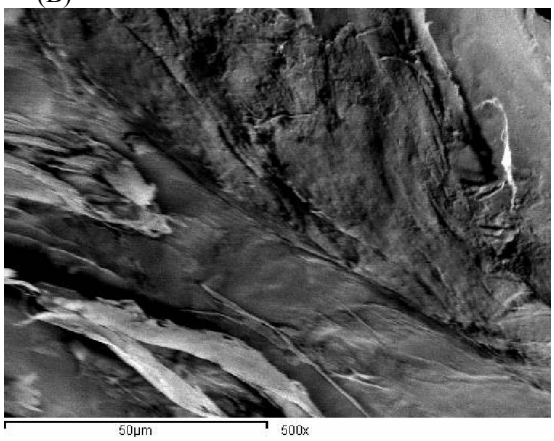


Figure 3: (A) FT-IR for tosyl methyl cellulose and (B) SEM for tosyl methyl cellulose

(A)



(B)



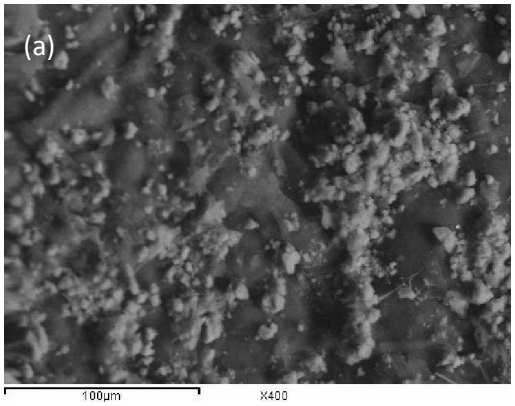


Figure 4: (A) FT-IR for trimethylsilyl methyl cellulose and (B) SEM for trimethylsilyl methyl cellulose

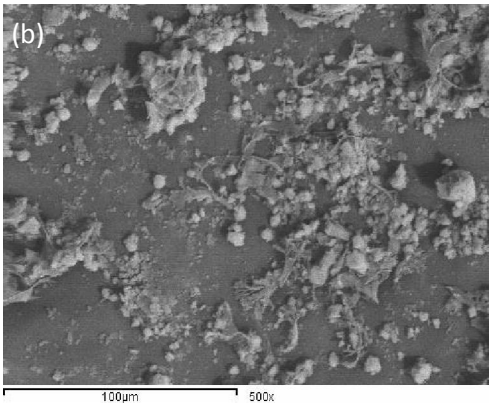


Figure 5: SEM of (a) tosyl methyl cellulose loaded with the anti-acid and (b) trimethylsilyl methyl cellulose loaded with the anti-acid

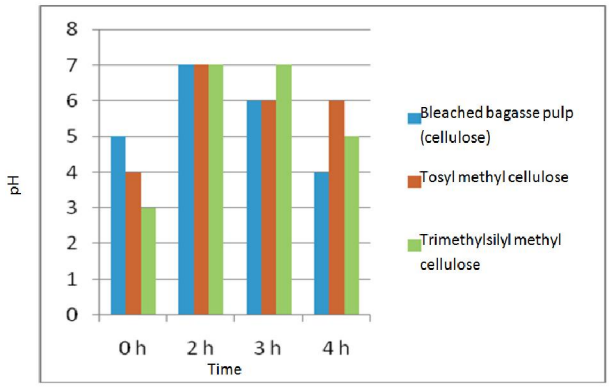


Figure 6: Effect of cellulose, tosyl methyl cellulose and trimethylsilyl methyl cellulose for the release in solution of pH = 2

Conclusion:

Bagasse was used as a source of cellulose fibers, which was derivatized to methyl cellulose and reacted with tosyl and trimethylsilyl groups to prepare tosyl and trimethylsilyl methyl cellulose. Both products were loaded with anti-acid drug and showed a release behavior within the first 2 h in different pH solutions. Moreover, the tosyl methyl cellulose showed constant rate of release after 3 and 4 hours to make the pH constant at 6.0, while the trimethylsilyl methyl cellulose showed better rate of release after 3 hours to make the pH 7.0 but it decreased to 5.0 after 4 hours. This behavior is very good for the rate of release for both of the two derivatives which implies the importance and availability of using cellulose derivatives as carrier matrix and raises the possibility for further investigations in the future.

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References:

1. Agblevor, F.A., Ibrahim, M.M., El-Zawawy, W.K. 2007. Coupled Acid and Enzyme Mediated Production of Microcrystalline Cellulose from Corn Cob and Cotton Gin Waste. Cellulose 14, 247-256.
2. Akira, I. 2001. Chemical modification of cellulose, in: Hon, D.N.-S., Shiraishi, N. (Eds.), Wood and Cellulosic Chemistry. Marcel Dekker, New York, pp. 599–626.
3. Bontempo, D., Masci, G., De Leonardis, P., Mannina, L., Capitani, D., Crescenzi, V. 2006. Versatile grafting of polysaccharide in homogenous mild conditions by using atom transfer radical polymerization. Biomacromolecules 7, 2154-2161.
4. Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K.B., Ramakrishnan, S. 2011. Chemical and Physicochemical Pretreatment of Lignocellulosic Biomass: A Review. Enzyme Research, Volume 2011, Article ID 787532, 17 pages, http://dx.doi.org/10.4061/2011/787532
5. Carlmark, A., Molmstron, E.E. 2003. ATRP grafting from cellulose fibers to create blockcopolymer grafts. Biomacromolecules 4, 1740-1745.
6. Conner, A.H. 1995. Size exclusion chromatography of cellulose and cellulose derivatives, in: Wu, C.-S. (Ed.), Handbook Of Size Exclusion Chromatography And Related Techniques. Marcel Dekker, New York, pp. 331–352.
7. Gupto, K.C., Khandekar, K. 2003. Temperature responsive cellulose by ceric(IV) ioninitiated graft copolymerization of N-isopropylacrylamide. Biomacromolecules 4, 758-765.
8. Hanley, S.J., Revol, J.-F., Godbout, L., Gray, D.G. 1997. Atomic force microscopy and transmission electron microscopy of cellulose from Micrasteriasdenticulata; evidence for achiral helical microfibril twist. Cellulose 4, 209–220.
9. Heinze, T., Liebert, T., Koschella, A. 2006. Esterification of Polysaccharides. Springer laboratory, Berlin Heidelberg.
10. Ibrahim, M.M., El-Zawawy, W.K., Jüttke, Y., Koschella, A., Heinze, T. 2013. Cellulose andmicrocrystalline cellulose from rice straw and banana plant waste: preparation andcharacterization. Cellulose 20, 2403-2416.
11. Ibrahim, M., Agblevor, F.A., El-Zawawy, W.K. 2010. Isolation and characterization of cellulose and lignin from steam-exploded lignocellulosic biomass. BioResources 5, 397-418.
12. Klemm, D., Philipp, B., Heinze, T., Heinze, U., Wagenknecht, W. 1998. Comprehensive Cellulose Chemistry: Fundamentals and

Analytical Methods, Volume 1. Wiley-VCH VerlagGmbH.
13. Li, Y., Mai, Y.-W., Ye, L. 2000. Sisal fiber and its composites: A review of recent developments. Compos. Sci. Technol. 60, 2037-2055.
14. Liu, R., Yu, H., Huang, Y. 2005. Structure and morphology of cellulose in wheat straw. Cellulose 12, 25–34.
15. Löscher, F., Ruckstuhl, T., Jaworek, T., Wegner, G., Seeger, S. 1998. Immobilization of Biomolecules on Langmuir−Blodgett Films of Regenerative Cellulose Derivatives. Langmuir 14, 2786-2789.
16. Meng, T., Gao, X., Zhang, J., Yuan, J., Zhang, Y., He, J. 2009. Graft copolymers preparedby atom transfer radical polymerization (ATRP) from cellulose. Polymer 50, 447-454.
17. Metroglu, M., Garnier, S., Laschewsky, A., Shrabania, K., Storsberg, J. 2005. Stimuliresponsive amphiphilic block copolymers for aqueous media synthesized via reversible addition fragmentation chain transfer polymerization (RAFT). Polymer 46, 7726-7740.
18. Ohya, Y., Huang, T.Z., Ouchi, T., Hasegawa, K., Tamura, J., Kadowaki, K., Matsumoto, T., Suzuki, S., Suzuki, M. 1991. Synthesis and antitumor activity of α-1,4-polygalactosamineand *N*-acetyl-α-1,4-polygalactosamine immobilized 5-fluorouracils through hexamethylenespacer groups via urea, urea bonds. J. Controlled Release 17, 259-266.
19. Petzold-Welcke, K., Kötteritzsch, M., Heinze, T. 2010. 2,3-*O*-Methyl cellulose: studies on synthesis and structure characterization, Cellulose 17, 449-457.
20. Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick Jr., W.J., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., Tschaplinski, T. 2006. The path forward for biofuels and biomaterials. Science 311, 484–489.
21. Sturcova, A., His, I., Apperley, D.C., Sugiyama, J., Jarvis, M. 2004. Structural details of crystalline cellulose from higher plants. Biomacromolecules 5, 1333-1339.
22. Tong, X.D., Gao, L.C., Fan, X.H., Zhou, Q.F. 2007. Controlled grafting of ethyl cellulosewith azobenzene-containing polymethacylates via atom transfer radical polymerization. J. Polym. Sci., Part A: Polym. Chem. 45, 1653-1660.
23. Yin, C., Shen, X. 2007. Syntheses of cellulose carbamate by super critical CO2 asistedimpregenation: strutcure and reheological properties. Eur. Polym. J. 43, 2111-2116.
24. Yu, H., Liu, R., Shen, D., Jiang, Y., Huang, Y. 2005. Study on morphology and orientation ofcellulose in the vascular bundle of wheat straw. Polymer 46, 5689–5694.

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