Preparation of Chlorodeoxycellulose from Shambat Cotton Lint Using Dimethyl Acetamide / Lithium Chloride Solvent System

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ABSTRACT

Cotton cellulose has interesting properties which can be controlled to a large degree by chemical modification. This study was designed to prepare cellulose derivatives with different functional groups using novel homogenous solubilisation media. Raw cotton was modified (mercerized) in (15%) NaOH solution to weaken the aggregation of the bundles of cotton cellulose fibers and; subsequently, to facilitate the dissolution in N,N-dimethylacetamide/lithium chloride (DMA/LiCl) solvent system. Chlorodeoxycellulose was synthesized by treatment of the solubilised cotton cellulose with N-chlorosuccinimide in the presence of triphenylphosphine to convert the hydroxyl groups into the chlorodeoxy derivative of cellulose. The chemical structure of this derivative was investigated using infrared spectroscopy, elemental analysis and thermal analysis (TGA, DSC). Chlorordeoxycellulose proved to be a flame retardant polymer; since thermal analysis showed that it has less thermal stability compared to unmodified cellulose. Thermal analysis also showed different behaviour between modified and unmodified cotton cellulose. Solubility in some organic solvents was tested for the prepared derivative to explore possible new uses and applications. This research has shown the versatility of Shambat cotton cellulose as a raw material for novel and advanced cellulose-based materials; and to widen and simplify the existing synthetic methodologies for cellulose modification, to yield novel derivatives using homogenous reaction media.

INTRODUCTION

Science and technology continue to move towards renewable raw materials and more environmentally friendly and sustainable resources and processes. Cellulose and cellulose derivatives are of growing importance in the development and application of renewable polymeric materials. This has triggered a distinct renaissance of cellulose research and application all over the world. However, a major challenge in cellulose chemistry is dissolving it in agueous or organic media to perform homogenous effective reactions. This difficulty has been overcome by devising novel cellulose solvents [Heinze and Liebert, 2001]. One of these is the N,N-dimethylacetamide/lithium chloride (DMA/LiCl) solvent system [McCormick and Callias, (1987)].

Deoxycellulose is a cellulose derivative with functional groups partially or completely replacing the hydroxyl groups in the glucosyl (anhydroglucose) units (the repeat unit of cellulose polymer chain). Halodeoxycelluloses has recently assumed importance since the halogen groups serve as good living groups to facilitate the preparation of unconventional cellulose derivatives (Nada, 2010). In this study chlorodeoxy derivatives of cellulose are examined in terms of a wide range of their characteristics: synthesis, structure determination methods, and properties. The replacement of some of the hydroxyl groups of cellulose by chloride atoms imparts to it a number of practically important properties; for example, resistance to combustion and acid or enzyme hydrolysis. The reactive chlorodeoxy derivatives of cellulose are used for the synthesis of a wide variety of cellulose derivatives with functional groups, frequently with properties of practical interest. A mild and selective conversion is the chlorination of cellulose dissolved in dimethylacetamide/lithium chloride (DMA/LiCl) with *N*-chlorosuccinimide (NCS) in the presence of triphenylphosphine(Ph_3P). At the early stage, the reaction succeeds only in substituting the 6-hydroxyl group of the glucosyl unit. The maximum degree of substitution (DS) attained by the above method is 1.86. Figure (1) shows the synthesis of chlorodeoxycellulose by the reaction of cellulose with N-chlorosuccinimide/ triphenylphosphine in DMA/LiCl solvent system.

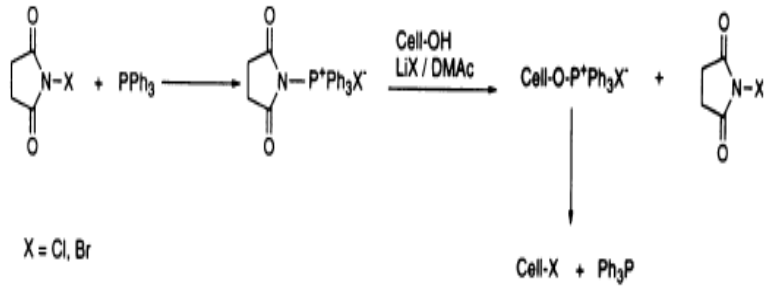

Figure (1): Synthesis of chlorodeoxycellulose by the reaction of cellulose with

N-chlorosuccinimide/triphenylphosphine in DMA/LiCl.

MATERIALS AND METHODS

The cotton lint sample of Shambat variety was obtained from the Cotton Breeding Section, Agricultural Research Corp., Wad Medani, Sudan. It was treated first with the Shirley analyzer machine for removal of trash content, and further treatments of the sample was carried out according to practical requirements.

Cotton mercerization:

Cotton was mercerized by immersion in 15% NaOH solution at 0 ^{0}C for 1.0 h (Buschle-Diller and Zeronian, 1992). The alkali swollen material was washed with distilled water until the pH of the filtrates remained unchanged. The mercerized product was air-dried and kept at 60 ^{0}C under vacuum.

Chlorinaton of cotton cellulose in DMA/LiCl:

0.25 g of dried mercerized cotton was placed in a flask containing 25 ml of DMA, and the mixture was heated for 2 h at 160ºC with stirring. The temperature was lowered to 90ºC and 2.5 g of LiCl were added. The mixture was kept for a further 1 h at this temperature with stirring. The temperature was then lowered to 60ºC and the mixture was kept at this temperature with stirring. A clear solution was obtained within 12 h.

The cellulose solution just mentioned was stirred under cooling with ice-water, and 1.25 g of NCS and Ph_3P (both in 12.5 ml DMA solution) were added in this order. The final volume of DMA was 50 ml. The solution was kept at 70ºC for 2 h with stirring. After the reaction, the solution was poured into 400 ml of acetone and the separated material was washed several times with acetone, dialyzed against tap water, and then distilled water. The sample was dried and weighed.

The Chlorine content of the products was determined by an oxygen flask combustion method (WHO Pharmacopeia, 2011). The DS by chlorine was calculated from the chlorine content. The same above dissolution procedure was repeated for dissolution of a non-mercerized cotton in DMA /LiCl.

Determination of chlorine content:

Using the oxygen flask method described above; a specified quantity of chlorodeoxycellulose was burned. The absorbing liquid consists of 17 ml of hydrogen peroxide (60 g/l) and 3 ml of water. When the process is complete, the stopper and sides of the flask were rinsed with 40 ml of water. 5 drops of bromophenol blue in ethanol were added, then sodium hydroxide (0.1 N) was added dropwise until the colour changed from yellow to blue. Then 1 ml of nitric acid was added followed by 5 drops of diphenylcarbazone in ethanol as an indicator. The mixture was titrated with mercuric nitrate (0.01 M) until the solution turned light violet.

$$Hg^{++} + 2Cl^{-} \rightarrow HgCl_2$$

Each ml of 0.01M mercuric nitrate is equivalent to 0.709 mg of Cl.

FTIR spectroscopy:

To study the chemical structure of cellulose sample and their derivatives, vibration spectroscopy was applied according to Abbott, *et al.* (1988). Fourier transform infrared (FTIR) spectra for cellulose and derivatives were acquired on a Shimadzu FTIR 8400 S.CE instrument using potassium bromide (KBr) discs prepared from the sample mixed with dry KBr in the ratio 1:100. The spectra were performed in the Central Research Laboratories at the University of Khartoum, Sudan.

Thermogravimetric analysis:

Thermogravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA studies were carried out using a powdered form of the samples on a Shimadzu-50 instrument at a heating rate of 10ºC min^{-1} under nitrogen flow (20 ml min^{-1}) over a temperature range from room ºC. The thermogravimetric analyses were carried out in 500temperature up to the laboratories of the Faculty of Science, University of Cairo, Egypt.

Differential scanning calorimetry:

Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q1000 V906 instrument. Samples were analyzed over a temperature range from 30 to 250ºC at ramp: 10ºC/min. all samples were in the powdered form. DSC analysis of samples was carried out in the laboratories of the Faculty of Science, Cairo University,
Egypt.

Solubility:

The solubility of all derivatives was determined at the concentration 0.01 g /ml in various organic solvents (DMA, DMF, DMSO, THF, dioxane, acetone, chloroform and formic acid).

RESULTS AND DISSCUSION

Cotton dissolution:

Strong intermolecular hydrogen bonding is the major cause of the insolubility of cotton cellulose in common solvents; therefore, the breakage of hydrogen bonds is necessary for the dissolution of cellulose. The use of a high concentration of NaOH (15%) for cotton mercerization would weaken the aggregation of the bundles of cotton cellulose fibres and; subsequently, facilitates dissolution in DMA/LiCl. During mercerization, the alkali penetrates the cellulose fibres and causes a rearrangement of the crystal packing of the chains. This change is irreversible and is normally accompanied by a decrease

in crystallinity. It should be stressed that untreated raw cotton cellulose, remains insoluble in DMA/LiCl under the same conditions.

Pretreatment of mercerized cellulose in DMA at 160^0C before the addition of lithium chloride was necessary for smooth dissolution. If pretreatment was omitted, dissolution was slow.

Effects of Reaction Conditions on the Degree of substitution:

In cellulose chemistry, the average degree of substitution (DS) denotes the number of substituted OH groups per anhydroglucose (AGU) unit; Tables (1), (2) and (3) show the effects of reaction time, reaction temperature, reagent ratio; respectively, on the DS of cotton cellulose chlorination in the homogenous solvent system DMA/LiCl. Chlorination proceeds rapidly and levels off in 2 h at 90^0C. The DS increases as the reaction temperature increases and the final DS was 1.5 at 90^0C. A further increase in DS was not observed at 100^0C and a white powdery chlorodeoxycellulose was obtained. A maximum DS of 1.5 is obtained for NCS/Ph_3P:AGU ratio of 5:1. NCS and Ph_3P were used in equimolar amounts for the homogeneous chlorination of cotton cellulose in DMA/LiCl. This reagent system is recommended for the replacement of primary hydroxyl groups in carbohydrates with chlorine. It also replaced secondary hydroxyl groups with Walden inversion under suitable conditions (Hanessian et al., 1972). Reaction conditions affected the extent of chlorination of the products.

Table (1): Effect of reaction time on chlorination of cotton cellulose in homogeneous system (DMA/LiCl) at 90 ºC.

Run	Time (h)	Cl %	DS
1	0.5	18.77	1.15
2	1	23.34	1.43
3	2	24.97	1.53
4	2.5	24.97	1.53

Table (2): Effect of reaction temperature on chlorination of cotton cellulose in homogenous system (DMA/LiCl) for 2 h.

Run	Temperature ^{o}C	Cl%	DS
1	50	2.43	0.14
2	60	4.49	0.30
3	70	11.96	0.73
4	80	14.68	0.90
5	90	24.97	1.53
6	100	24.98	1.54

Table (3): Effect of reagent ratio on chlorination of cotton cellulose in homogeneous system (DMA/LiCl) at 90 ºC for 2 h.

Run	Cotton (g)	NCS /Ph_3P:AGU	Cl%	DS
1	0.25	3:1	4.49	0.30
2	0.25	4:1	14.68	0.90
3	0.25	5:1	24.48	1.50
4	0.25	6:1	24.48	1.50

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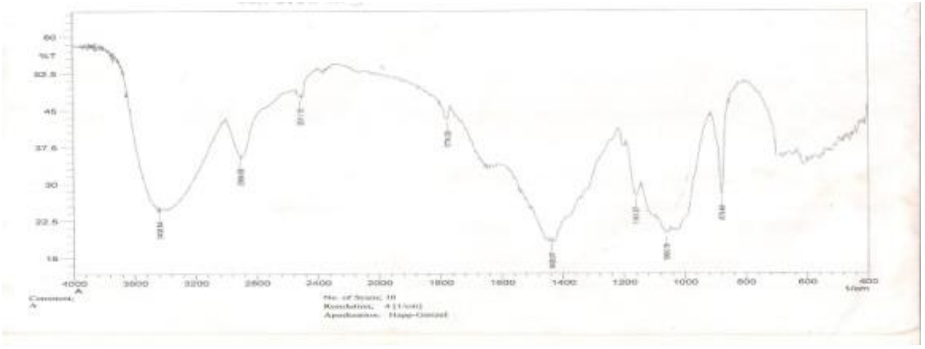
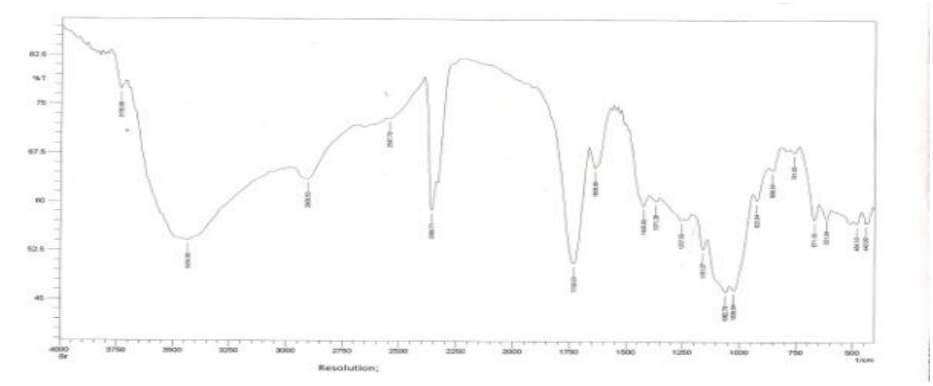
Fourier transform infrared (FTIR) spectroscopy:

The FTIR spectra of the different samples of cellulose derivatives were recorded in the range of 4000–400 cm^{-1}. A slight difference is observed in the re*g*ion of the intermolecular hydrogen bonding (3200–3400 cm^{-1}). Figure (2) shows the FTIR spectrum of unmodified cotton cellulose which has the typical cellulose absorptions centred at 3439 cm^{-1} (O-H stretch), 2904 cm^{-1} (C-H stretch), 1439 cm^{-1} (C-H bend), and 1001 cm^{-1} (C-O stretch). It has two peaks at 1438 cm^{-1} and 879 cm^{-1} that are assigned to the amorphous and crystalline regions, respectively.

FTIR spectrum of chlorodeoxycellulose shows the typical absorptions of the cellulose backbone and shows bands with low intensity at 751 cm^{-1} due to the presence of C-Cl bonds. These FTIR data confirm the presence of C-Cl bonds, as shown in Figure(3).



Figure(2) FTIR spectrum of unmodified cotton cellulose



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Figure(3): FTIR spectrum of chlorodeoxy cotton cellulose

Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) is one of the thermal analysis techniques used to characterize a wide variety of materials. It provides complimentary and supplementary characterization information (Monika and Woolfgang, 2008).

TGA and curves for mercerized cotton lint and the unmercerized one are shown in Figure (4) and (5) respectively. After initial loss of moisture at 100─120^{0}C; a loss of weight in cotton lint cellulose occurred. This loss is attributed to actual pyrolysis by a minor decomposition reaction at 313 and 273 ^{o}C for the untreated and treated cotton linters with sodium hydroxide, respectively. On the other hand, a major decomposition took place at 439 and 389^{0}C for untreated and treated cotton lint with sodium hydroxide, respectively. From Figures (4) and (5) it is clear that the minor and major decomposition temperatures for treated cotton lint with sodium hydroxide is lower than that of untreated one. This can be attributed to an increase in the amorphous or disordered region in the cellulose chains, which is decomposed by thermal treatment faster than the crystalline part**.**

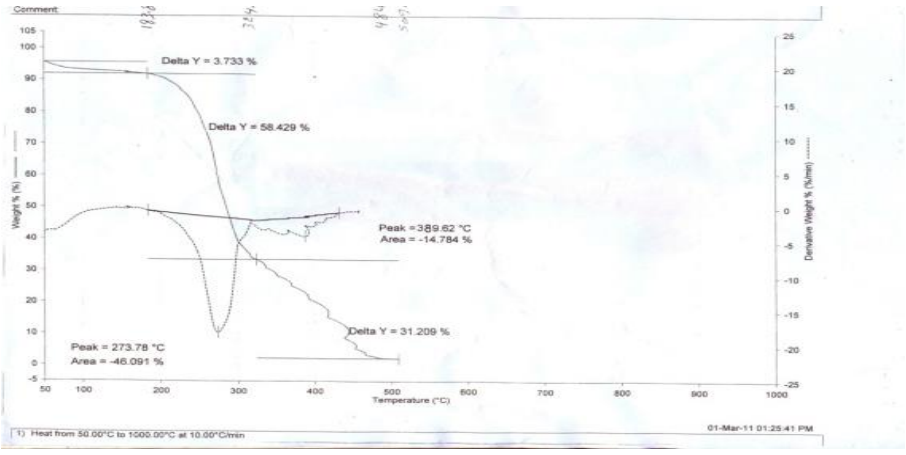

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Figure (4): TGA curve of mercerized cotton cellulose

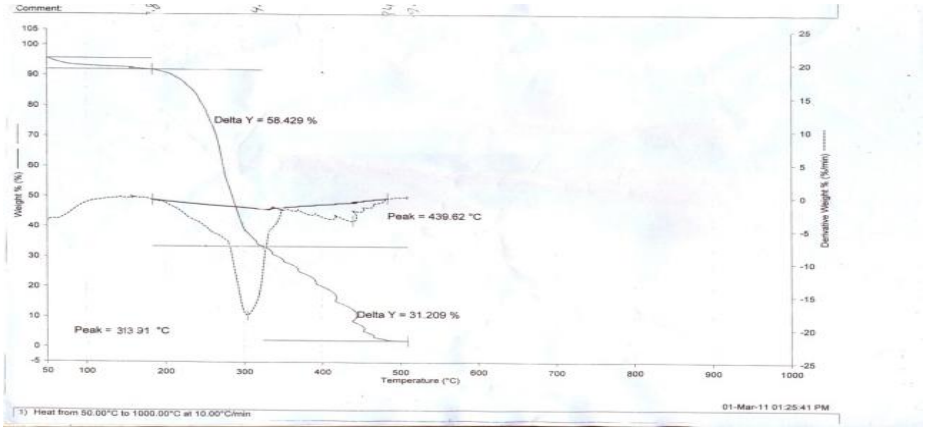

Figure (5): TGA curve of unmerceried cotton cellulose

DSC curves were also used to study the thermal behaviour of treated and untreated cotton with sodium hydroxide celluloses as shown in Figures (6) and (7). DSC curves of mercerized cotton and the unmercerized one present two endothermic peak. The first peak appears due to water desorption (50 – 100 ^{o}C), while the second peak results from glucosidic bond cleavage and formation of levoglucosan (288–300^{o}C) which results in the decomposition of cellulosic chains.

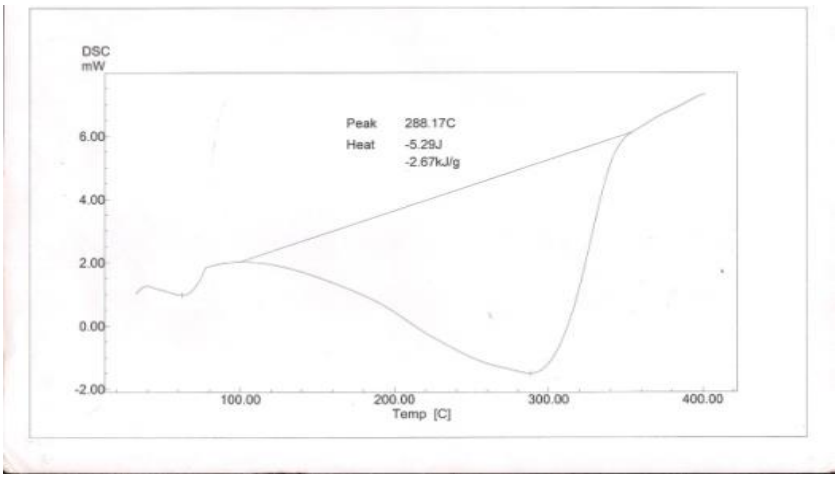

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Figure (6): DSC curve of merceried cottn cellulose

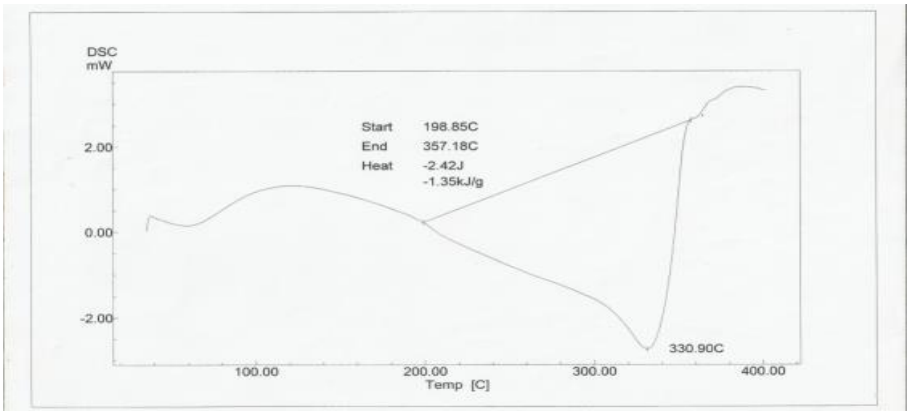

Figure (7): DSC curve of unmerceried cotton cellulose

The TGA curve of chlorodeoxycellulose in Figure (8) shows that chlorodeoxycellulose is thermally less stable than the corresponding unmodified mercerised cotton cellulose(Figure (4)) and begins to decompose at 181 ºC; while unmodified mercerised cellulose is still unchanged and begins to decompose at 250ºC. This can be attributed to the fact that when chlorodeoxycellulose is heated, it generates hydrogen chloride which catalyses a series of heterolytic reactions including transglycosylation, dehydration, inter- and intramolecular etherification, and condensation. The latter products are ultimately carbonized through free-radical reactions producing large amounts of char. So the well-known flame resistance of chlorodeoxycellulose is considered to arise from these thermal reactions and this is in agreement with Shafizadeh (1976).

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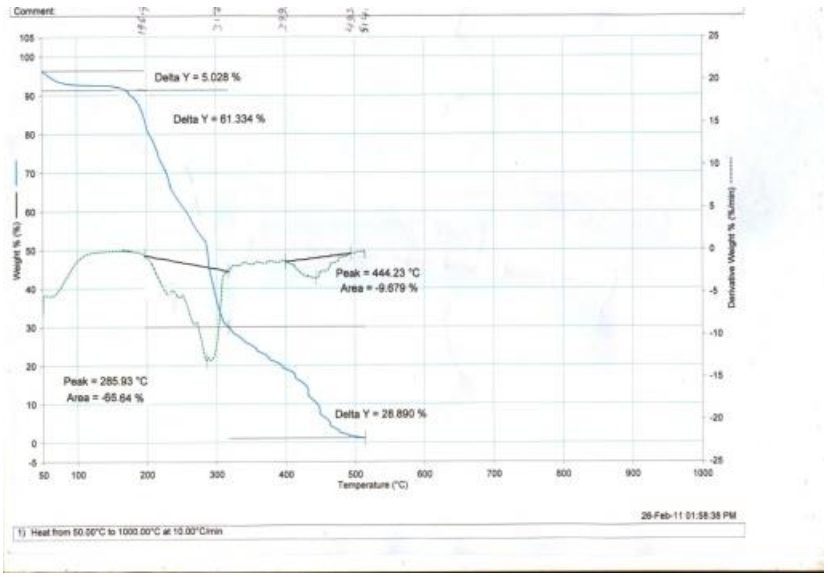

Figure (8): TGA curve of chlorodeoxy cellulose

Solubility of cotton cellulose derivatives*:*

Dissolving a polymer is a process that occurs in two stages. First the solvent molecules slowly diffuse into the polymer to produce a swollen gel. Production of a persistent swollen gel occurs when the polymer intermolecular forces are high because of cross-linking, crystallinity, or strong hydrogen bonding. In the second stage solution takes place if the intermolecular forces are overcome by the introduction of strong polymer-solvent interactions. The gel gradually disintegrates into a true solution. The solution process can be quite slow for materials of high molecular weight (Billmeyer, 1984).

Chlorodeoxycellulose is very soluble in formic acid, and soluble in DMSO and chloroform. It is insoluble in such common organic solvents such as ethanol and acetone; but it swells in the aprotic solvents dimethylforamide (DMF), DMA, and dioxane.

The increased solubility may be reasonably ascribed to the lowered crystallinity (reduction in hydrogen bonding), possible main-chain scission during halogenation, and/or the change in the chemical structure induced by halogenation. The replacement of

hydroxyl groups by halogen will disrupt the hydrogen-bonded structure in which the hydroxyl groups are involved.

CONCLUSIONS

The general approach of this research was to show the versatility of cellulose as a raw material for novel and advanced cellulose-based materials. A more specific aim was to introduce new synthetic methods to widen and simplify the existing synthetic methodologies for cellulose modification and to yield novel derivatives using homogenous reaction media.

ACKNOWLEGDEMENT

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تحضير مركبات كلورودى اوكسى سليلوز من عينة القطن شمبات باستخدام نظام الإذابة ثنائى ميثيل اسيتاميد /كلوريد الليثيوم

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الملخص

يتصف سيليلوز القطن بخواص جذابة يمكن التحكم فيها بواسطة المعالجة الكيميائية. تهدف هذه الدراسة لتحضير مشتقات سليلوز تحمل مجموعات وظيفية مختلفة باستخدام أنظمة إذابة تجانسية جديدة. تم غمر القطن أولاً في محلول هيدروكسيد الصوديوم (15%)وذلك لتضعيف روابط ألياف سليلوز القطن وبالتالي تسهيل الاذابة في محلول N،N ثنائى ميثيل اسيتاميد /كلوريد الليثيوم (DMA/LiCl)، ومن ثم تم إصطناع مركبات كلورو دى أوكسى سليلوز، بتفاعل السليلوز المذاب مع N– كلوروسكسينميد في وجود ثلاثي فينيل فوسفين لتحويل مجموعات الهيدروكسيل في السليلوز إلى مشتقات كلورو. أثبت التحليل بمطياف الاشعة تحت الحمراء (FTIR) وتحليل العناصر وجود روابط C– Cl. وقد أثبتت خاصية مقاومة مركبات كلورو دى اوكسى سليلوز للاشتعال بواسطة التحليل الحراريDSC)، (TGA الذي اثبت امتلاكها ثبات حراري اقل من السليلوز الغير معدل. كما أظهرت التحاليل الحراريةDSC)، (TGA إختلافا في الثبات الحراري لمركبات السليلوز المحضرة من القطن العادى وتلك المعدلة بالغمر فى محلول هيدروكسيد الصوديوم . وكذلك اجري إختبار الذوبانية للمركب المحضر في بعض المذيبات العضوية لمعرفة الإستعمالات الممكنة. أثبت البحث إمكانيات السيليلوز فى القطن شمبات كمادة خام لإصطناع مواد جديدة متقدمة، وكذلك لتنويع وتبسيط طرائق الإصطناع بإستخدام وسائط التفاعل المتجانسة.