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Homogeneous esterification of cellulose and characterization of cellulose esters

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Abstract

The present work focus on esterification of cellulose using lithium chloride–*N*,*N*-dimethylacetamide (LiCl–DMAc) solvent system with acetic anhydride and maleic anhydride system using pyridine as catalyst. Reaction temperature varied from 25 to 70 ^{0}C and the time varied from 2 to 24 hours. Small degradation in cellulose chain occurred at a temperature 70 ^{0}C .The esters prepared from cellulose in LiCl/DMAc solvent system were characterized by molecular weight determination and IR studies & viscometrically .Degree of substitution of the ester was found by calculating the amount of anhydride consumed.

Keywords: Cellulose, Pyridine, degree of substitution, IR analysis

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Introduction

Cellulose is biocompatible, derivatizable and offers a broad range of possible applications as it can interact with many other polymers [1, 2].Cellulose esters (CEs) are used in modern coatings, controlled release, optical films, membrane, and biodegradable materials. Different methods are used for the esterification of cellulose using different aceylating agent and medium either in homogenous reaction condition [3-7], using catalyst [8], or in controlled heterogenous modification of cellulose with fatty acids [9]. The system LiCl / DMAc is used as a non-degrading solvent to determine cellulose molecular weight (MW) distribution [10,11].NMR studies also proved that solvent does not form chemical bonds with cellulose[12]. These results have also been confirmed by MW determination [13]. As a non degrading solvent, it has in recent times also been proved usefull in acetylation of cellulose under homogenous solution condition or for the preparation of low DS cellulose derivatives by ring –opening esterification [14,15]. This solvent can be recycled with a high recovery rate, which accounts for its eco-friendliness [16] but reaction rates and final degree of substitution (DS) in heterogeneous reactions are hindered by low accessibility of solid cellulose to the esterification reagents. We have chosen the lithium chloride/N,N-dimethylacetamide (LiCl /DMAc) system to study the esterification of cellulose with acetic anhydride and maleic anhydride in presence of pyridine as a catalysts .Ester of different degree of substitution were prepared at the different temperature and time of reaction. The products were characterized by IR spectroscopy.

Materials and Methods

Experimental

Materials

Cellulose with an average degree of polymerization of 141.1% and 9.435% of filler content was dried to less than 1% moisture before use and then DMAc {CDH} was distilled under diminished pressure and store under nitrogen over riedel type 40A^0 molecular sieves. LiCl was also dried at 200^{0}C under diminished pressure before use. Acetic anhydride & Maleic anhydride obtained from (E-Merck) and pyridine {CDH} were used.

Dissolution of cellulose

A mixture of cellulose (8 g, 8.214% mmol based on glucose units) and DMAc (300 mL) was heated to 150 °C for 26 min in a round bottomed flask equipped with a short path condenser. Then, LiCl (5g, 117.6 mmol) was added and the mixture was heated to 166 °C for 8 min. Finally the reaction mixture was cooled to room temperature and stirred overnight for dissolution [17].

Esterification of cellulose

The cellulose solution prepared above was diluted to 1% by further addition of the solvent. To 50 mL of 1% (3.1 mmol) cellulose solution, 10 ml, 0.124 mol of pyridine was added followed by dropwise addition of 15 ml (0.16 mol) Ac_2O. Reaction times ranged from 2 to 24 hour and temperatures from 28 to 70 °C. The reaction was terminated by pouring the mixture into cold distilled water. The products were filtered in a G-4 crucible, and washed thoroughly with cold distilled water. The filtrates were kept aside for determination of the degree of substitution. Further the products were soxhlet extracted with water and dried under diminished pressure in an oven at 40–45°C and then kept in a desiccator over P_2O_5.

Determination of Ash content

For this two representative samples of the Cellulose (5 g) were weighed into crucibles and then placed in a drying oven until constant weight was achieved and weighed. Then the crucibles were then put into muffle furnace at 575±25^{0}C.After ignition for 4 hour the crucibles were cooled slightly and placed in a desiccator, containing silica gel. When cooled to room temperature, the crucibles were weighed to nearest 0.1mg. The ash content in the sample was calculated using the following equation –

$$\text{Percentage of ash content} = (W_1\text{-}W_2/W_1)*100$$

Where W_1 = weight of the crucible + weight of sample;
W_2 = weight of the crucible + ash content .The ash content was found to be 9.435%.

Determination of average degree of polymerization (DP) and M. Wt. of cellulose

Average degree of polymerization of cellulose was determined by measuring the viscosity of nitrated cellulose, by the method suggested by Tsuji [18]. According to this method, a nitrating mixture was prepared by taking 1000g of 90% HNO_3 in a two liter flask placed in an ice bath. To these 404 grams of P_2O_5 was added slowly. It was kept cool and stirred until complete dissolution of P_2O_5 .Then it was filtered through glass wool and kept in a cool dark place to be used within 2 or 3 days. 80gms of nitrating mixture was weighed into a wide glass stoppered bottle and cooled in constant temperature bath at 20^0C.1 gram of cellulose was then added to it quickly and stirred for 30min.

At the end of the reaction, the nitrated cellulose was filtered and washed repeatedly with cooled distilled water to make it free from acid .The nitrated cellulose was stabilized by steeping in a saturated Na_2CO_3 solution and then in 10% acetic acid and finally washed with distilled water.

A 0.05 %(w/v) solution of the nitrated cellulose was made in absolute acetone and viscosity was determined and by using ubbelohde viscometer. The volume of the liquid which efflux time was recorded as nearly too pure solvent is 39 sec and the solvent 49.6 sec.The following formula was used to calculated the degree of polymerization of cellulose

$$DP=K\,[\eta];\ \textit{Relative}\ \text{viscosity}= \eta_{rel}= t/t_0$$

Where t = efflux time of solution; t_0 = efflux time of solvent

$$[\eta] = \frac{\{\eta sp/C\}}{\{1+k\,\eta_{sp}\}}$$

$$\eta_{sp}= \eta_{rel}-1$$

η_{rel}= (viscosity of solution)/(viscosity of solvent)
= (Efflux time for solution)/ (Efflux time for solvent)
Where, C=concentration of cellulose nitrate (g/100 ml of solvent)
Where η =viscosity of solution; η_{sp}=specific viscosity of the solution
K = 100; k = 0.35

Hence, Molecular weight of cellulose = ***162 x DP.*** The average degree of polymerization (DP) was found to be 141.1 and molecular weight of cellulose is 2300 gm.

Determination of Degree of Substitution (DS)

The filtrates which contained the unreacted anhydride along with liberated AcOH were titrated against 0.1M NaOH. The amount of anhydride consumed in the reaction is equivalent to the amount of AcOH liberated and, from this value the DS was calculated as follows:

$$\text{Anhydride consumed (m mol)} = (k/1000) \times (VSV_1/V_2)$$

Where V is the volume (mL) of NaOH consumed, S is the concentration of NaOH , V_2 is the volume of filtrate taken for titration and V_1 is the total volume of the filtrate.

$$DS=\text{Anhydride consumed}/K$$

Where K is the equivalent amount of anhydride consumed for a degree of substitution. The degree of Substitution (DS) was found to be equal to 1.65 and 2.85 respectively.

Analysis by Infrared spectroscopy (IR)

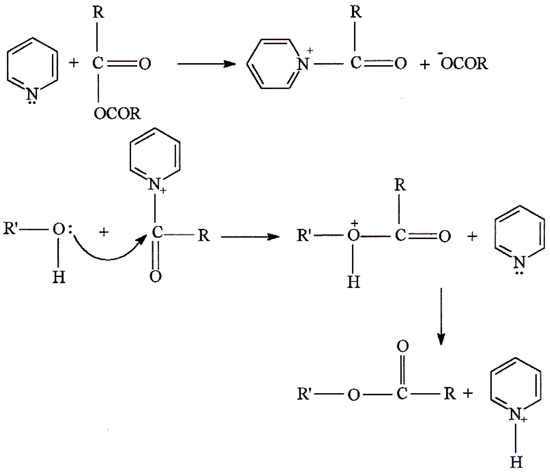
A Nicolet Nexus 870 spectrophotometer with a range of 400 -4000 cm^{-1} was used to examine the formation of ester linkage .The detector is mercury cadmium telluride (MCT-A).The resolution is 4 cm^{-1}.The thickness of the films measured with a digital micrometer at the end of experiment was between 5 and 6 µm. The film was held between the two jaws and 10 spectra of 64 scans each ware taken of the unstretched film . The average position of each peak and the corresponding standard deviation were then determined .One of the jaws was fixed in position and the film was manually stretched in the incresement of 0.05 mm by means of micrometer attached to other jaw. After stretching the film to a new position a 5 mm relaxation period was allowed for purging in order to obtained better signal –to –noise between a spectrum (64 scan) was colleted .Each spectrum was zero- filled twice ,and the peak picking routine in the omnic version 6 software was used to locate the position of each peak . Four sets of experiments were performed at room temperature to ensure reproducibility.

Results and Discussion

Effect of pyridine catalyst

As the reaction is a second order, hence one molecule of anhydride reacts with one hydroxyl group of cellulose monomer unit. The primary hydroxyl groups are more reactive than other two secondary hydroxyl groups, but the secondary groups can be reacted before primary if the latter are rendered non accessible .Dissolution of cellulose in lithium chloride/N, N dimethylacetamide solvent systems leads to the formation of a transition state as given in scheme 1.

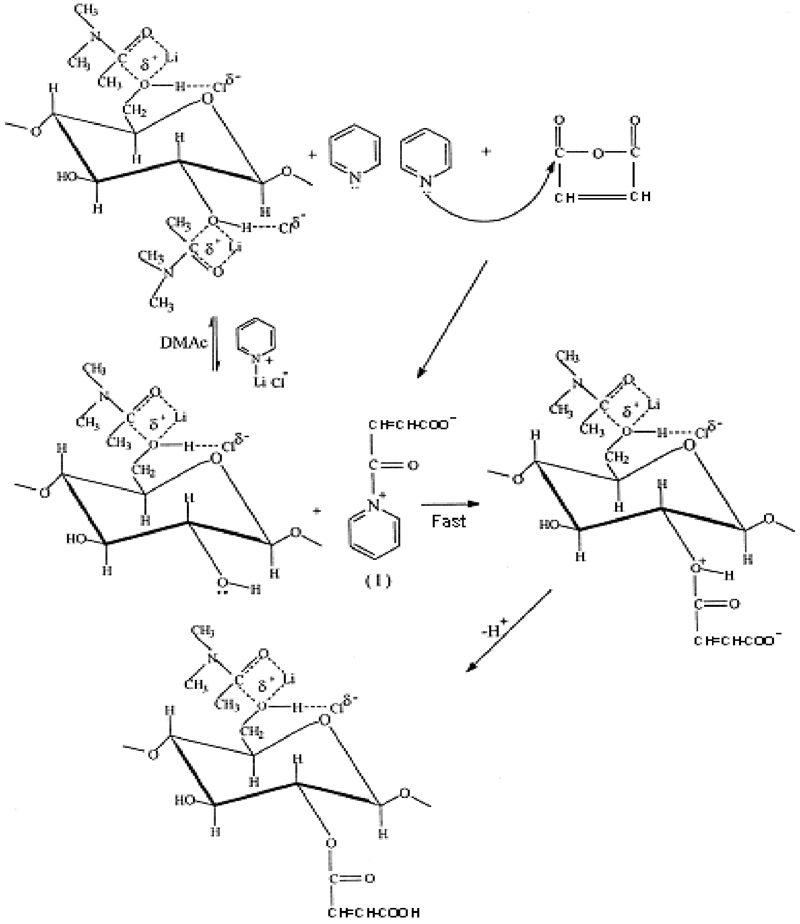
Here, the primary hydroxyl group and to a lesser extent, the secondary hydroxyl groups are solvated. Hence during acetylation , the anhydride attacks to the secondary hydroxyl group first. Again during acetylation, it was found that the molar ratio between hydroxyl group to pydrine was 1:2.by decreasing the amount of the catalyst to half, products with very low DS were formed at 70^{0}C even for as reaction time of 24hrs .the general mechanism for esterification reaction with an alcohol using pyridine as catalyst may be written as given in scheme 1, which indicates that, the molar ratio of alcohol to pyridine is 1:1.



General reaction scheme1 for esterification of alcohol in presence of Pyridine

The role of second molecule of pyridine may be on the cellulose in LiCl/DMAc solvent system. The second molecule of pyridine attacks to the four atomic electropositive center of the transition state detaching the cellulose molecule from the solvent making the hydroxyl group free for acetylation as soon as the hydroxyl group becomes free from the solvent, it reacts with the carbonyl group of the pyridinium derivative of the anhydride to give the product .so the overall mechanism of reaction may be as given below:

The reaction mechanism estererification using pyridine as the catalyst is suggested mechanism of reaction is given in Scheme 2. An *N*-acyl pyridinium ion is assumed to be the esterification reagent. This is reflected by a somewhat higher rate of esterification .The esters obtained were characterized by IR spectral analyses.



Scheme 2 Homogenous Esterification of cellulose with maleic anhydride in presence of pyridine as catalyst

The above reaction scheme shows the reaction between cellulose with the ester and the role of the catalyst in this mechanism the formation of complex and the esterification. It is a fast reaction and a second order reaction.

Effect of molecular weight of cellulose

The degree of substitution of esters increased with decrease in the molecular weight. Kinetic rate constants also increase with the decrease in molecular weight. This is due to the fact that, with the decrease in molecular weight, more numbers of hydroxyl groups become available to undergo esterification reaction giving higher DS values in comparison to high molecular weight cellulose samples.

Determination of Degree of Substitution (DS) - Analysis by Infrared spectroscopy

IR spectra of cellulose esters with acetic anhydride substitution prepared from native cellulose in LiCl / DMAc systems are given in Figure 1and with maleic anhydride given in Fig 2. All the spectra are found to be similar with different substitution. The spectrum of cellulose ester showed peak at 1740 cm^{-1} corresponding to >C=O stretching .Additionally the adsorption in the range of 1380 cm^{-1} was assigned to the C-H deformation and 1240 cm^{-1}(-C-O- stretching of ester group).The esters also showed peaks at 2900cm^{-1} (C-H stretching) and broad peaks between 3550-3300cm^{-1}, which is due to O-H stretching of the unsubstantiated hydroxyl group.

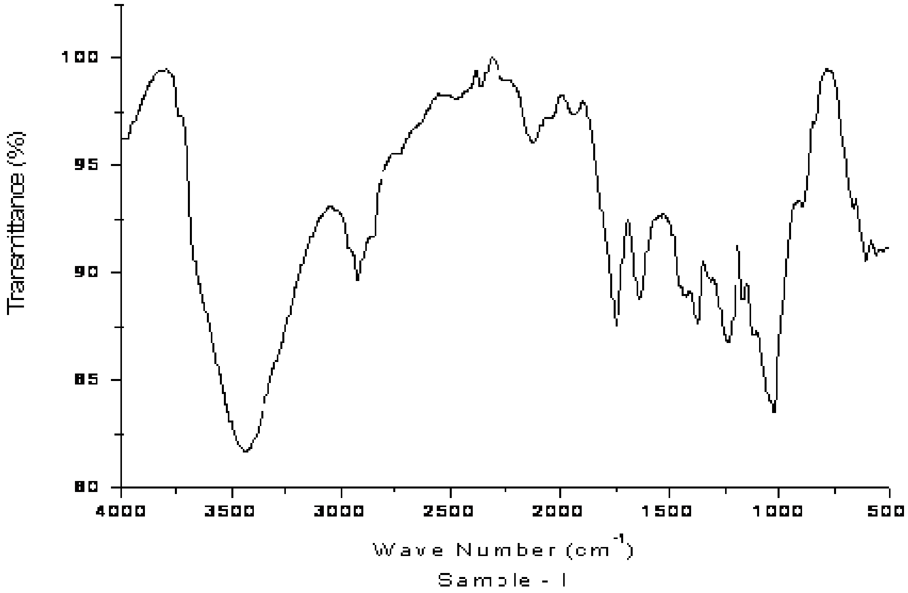


Fig.1 IR studies for cellulose ester with acetic anhydride substitution

The characteristic >C=O stretching vibration of the ester group which is at 1740 cm^{-1} for acetylated product shifted towards lower frequency for other esters and showed 1735cm^{-1}for propionate, 1730cm^{-1} for butyrate, 1715cm^{-1} for crotonate and 1725cm^{-1} for pentanoate. This may be due to the +I effect of the homologous alkyl groups of the substituted ester groups. The absorption decreases due to presence of unsaturation.

In cellulose ester there is a rise of two C=O str. absorption, (around 1800-1900 cm^{-1}, with a separation of about 65 cm^{-1}); coupling occurs between the two carbonyl groups, which are indirectly linked through –O-: the interaction is presumably encouraged because of the slight double-bond character in the carbonyl-oxygen bonds brought about by resonance, since the system is kept co-planar. The high frequency band in this case is the symmetric C=O str. The IR spectra of the cellulose acetates prepared represent the characteristics of esterified products by displaying essential bands of ester compounds at 1740 cm^{-1} (>C=O stretching vibration),1375 cm^{-1} (-C-O-C- st.), 1225cm^{-1} (-CH$_2$- wagging), 1075 and 800 cm^{-1}(rocking vibration of esters).

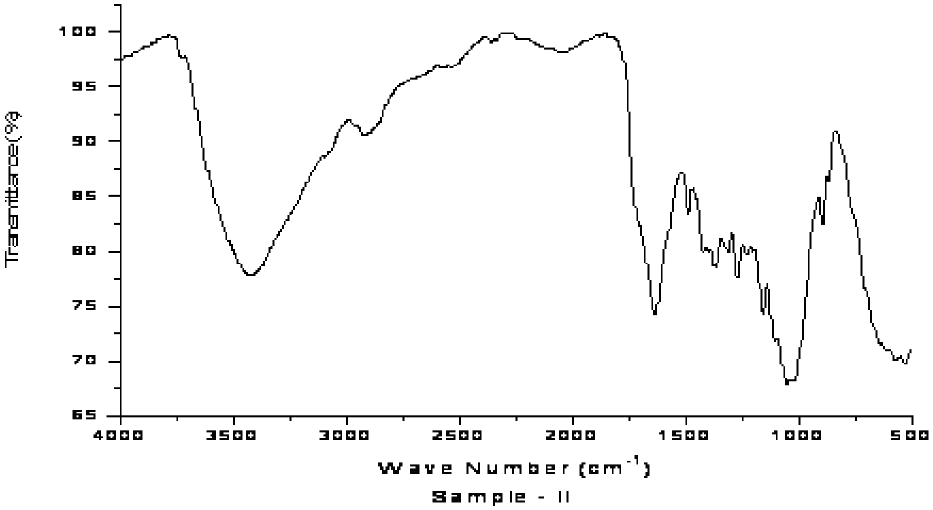


Fig.2 IR studies for cellulose ester with maleic anhydride substitution

Conclusion

Esterified cellulose imparts flexibility to the backbone chain without adversely affecting other properties like hardness. Participation of the hydroxyl groups of starch in the chain transfer reactions resulting in cross-linking is considered to be the cause of the observed behavior. LiCl–DMAc was found to be an excellent solvent system for the acetylation of cellulose with maleic anhydride in the presence of pyridine. The esterification was found to be a second-order reaction. Some degradation of the cellulose chain was observed.

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