

Esterification of Dissolved Sugarcane Bagasse Cellulose with some Acid Anhydrides: Thermal analysis and FTIR studies.

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Abstract: Cellulose was isolated from a well pre-treated mill of sugarcane bagasse using a mixture of NaOH/KOH. The sugarcane bagasse cellulose was dissolved in an aqueous mixture of NaOH/urea precooled to -8 °C in a salt-ice bath. The cellulose solution was reacted with phthalic, maleic and acetic anhydrides in the presence of sodium acetate for 6 h giving the esterification products. The pure cellulose and the modified materials were characterized using FTIR and thermogravimetric analyses. A comparison of the FTIR spectra of the native cellulose and the modified moieties reveal that the appearance of new peaks at 1716, 1719 and 1720 cm⁻¹ in the spectra of the modified materials signified the successful attachment of the anhydrides to the cellulose moiety. The degradation pattern displayed by the materials shows that the modified materials exhibit their first significant weight loss around 180 °C which is earlier than what was observed for the pure cellulose at 245 °C signifying the decomposition of the attached fragments further confirming the successful attachment of the anhydrides. The decreased but similar thermal decomposition pattern observed in the TGA curves of the functionalized materials shows that the unmodified cellulose is more thermally stable than the modified materials.

Keywords: Acid anhydrides, Cellulose, Cellulose dissolution, Modification, Thermal analysis

Date of Submission: 21-07-2017

Date of acceptance: 05-08-2017

I. Introduction

Petroleum, coal, bitumen and rock deposits account for a good percentage of sources of chemical feedstock. With time the non-renewable sources will eventually run out. What then will be the fate of humanity? The answer lie with the wisdom of channeling future approaches to renewable resources. This is indeed the driving force behind the U.S. Department of Energy, through the Technology Road Map to marshalling plans at achieving at least 10 % of its chemical building blocks from plant-derived renewable sources [1]. A typical plant cell material is made up of a very high percentage of cellulose, cotton fiber for instance, a natural pure cellulose contain about 95 – 97 % cellulose [2]. Cellulose is therefore a readily available plant resources. It is a natural polymer with vast application in textiles, pulp, paper, pharmaceuticals, and energy industries. These applications have been investigated and well reported over the years. The traditional sources from which cellulose is derived include, wood [3], cotton [4] and etcetera. Placing cellulose on the larger economic scale has called for a redirection of priorities and hence the current trend is to look away from plant sources of economic value. This trend have shifted attention to non-economic plants such as grass, non-edible fruits with special interest in agricultural/industrial waste such as sugarcane bagasse, rice husk, soya bean husk, seed of fruits and corn straw. These sources are reported to yield good quantities of cellulose and other cellulosic materials [5-9].

With guaranteed sources and relatively easy isolation technique, coupled with its wide applications, it is therefore not surprising why cellulose is thought of as the chemical building block of the future. But this is not to mean achieving this feat with cellulose is not without its challenges. This natural organic polymer, the most abundant of natural polymers is insoluble in water and common organic solvents. This is evidently a drawback in the renewed effort at modification/functionalization of cellulose to achieve increased applications. The earliest attempts at solubilizing cellulose for this purposes made use of the highly toxic carbon disulphide CS₂, to achieve a degree of dissolution of this moiety producing cellulose hydrate fibers [10]. More recently, ionic liquids were solvents of choice in the ease with which they achieve instant dissolution of cellulose and hence provides a suitable route to modification of cellulose materials [11-12]. The high cost of ionic liquids have impeded on their usability to achieve the desired objective. Other environment non-friendly method involving solvents such as pyridine and triethylamine [13] have been used as well as grafting/copolymerization [14]. At the moment an inexpensive and environmentally friendly method involving an aqueous mixture of alkali hydroxide and urea/thiourea have been devised as a safe and easy way of solubilizing cellulose [15-18]. This method achieved dissolution in few minutes thereby providing a leeway for easy functionalization of cellulose.

Esterification of cellulose and cellulosic materials using pyridine and ionic liquid have been reported. The current research investigates the esterification of liquid sugarcane bagasse (SCB) cellulose with phthalic, maleic and acetic anhydrides.

II. Experimental

Reagents and solvent

Potassium hydroxide, sodium hydroxide, hydrochloric acid, sodium metabisulfite, urea, sodium acetate, phthalic, maleic and acetic anhydrides were all analytical reagent grade, sodium hypochlorite was obtained as Jik (3.5 % m/v sodium hypochlorite) by Reckit Benckiser (Nig) Ltd.

Sampling and Pretreatment

Sugarcane (*Saccharum officinarum*) was obtained locally from vendors at Oja-Oba Market, Ilorin, Nigeria. Sample pretreatment and isolation follow methods described in literature [19]. It was crushed to obtain sugarcane bagasse. The sugarcane bagasse was washed thoroughly under running tap water, dried in the oven at 60 °C for 3 days. The bagasse was grinded and sieved using 1.0 mm size screen. Dewaxing was carried out with toluene-ethanol mixture (2:1, v/v %) in a soxhlet apparatus for 6 h in batches. The product was dried in an oven at 50 °C for 3 days.

Isolation of SCB cellulose

The dewaxed sugarcane bagasse was soaked in NaOH-KOH mixture (1:1 v/v 18 %) for 3 hours (the bagasse colour changed to yellow), and then filtered. The fibre was washed with distilled water until it is free of NaOH and KOH. It was then filtered and dried. The treated bagasse was soaked in 30% acetic acid solution for 2 h and later treated at 75 °C for 30 minutes, after which it was filtered off and washed with distilled water. 20% hydrogen peroxide solution was then used to soak the fibre for 2 hours. Afterwards, it was treated with 100 ml of sodium hypochlorite for 2 h to bleach the fibre and was then filtered. After filtration, the residue was washed thoroughly with distilled water and 95% ethanol and dried in an oven for 8 hours at 50 °C.

Preparation of cellulose solution

The SCB cellulose was dissolved using the NaOH/Urea mixture described in literature [15] with slight modification. The solvent for the dissolution was prepared by mixing NaOH : H₂O : Urea at a ratio of 3.5 : 6 : 40.5 by weight. The constituted solvent was cooled to 0 °C and stored at that temperature prior to use. The precooled solvent in a 250 mL reaction flask immersed in an ice-salt cold bath containing a mixture of crushed ice and NaCl further cooling the solution to a subzero temperature -8 °C [20]. The Required weighed quantity of the cellulose was added and the mixture equipped with magnetic stirrer was vigorously stirred for about 5 minutes. A clear transparent cellulose solution obtained was neutralized with 1M HCl.

Esterification of liquid SCB cellulose

Phthalation of SCB cellulose

To the aqueous solution of 1.215 g of cellulose was added 2.220 g of phthalic anhydride and 5 % sodium acetate as catalyst in a 250 mL reaction vessel equipped with magnetic stirrer. The solution mixture was heated under reflux for 4 h. the resultant product was filtered, washed and dried. The preparation involving acetic and maleic anhydride follow similar route.

Characterization of the SCB cellulose and the cellulosic preparations.

The FTIR of solid native SCB cellulose, the liquid cellulose and the three cellulosic preparations were recorded using Shimadzu Scientific FTIR 8400s spectrophotometer. The thermal analysis for the materials were carried out using thermogravimetric and differential thermal analysis recorded on Perkin Elmer, TGA 4000 thermogravimetric analyzer. 20 mg of cellulose sample was heated from 30 °C to 950 °C under nitrogen flow at 10 °C/min. A comparison of the FTIR spectra and thermogram of the starting material and the modified moieties were used to characterize and investigate the esterification processes.

III. Results And Discussion

The SCB cellulose dissolved in the NaOH/urea aqueous mixture solution within few minutes. The resulting cellulose solution is shown in Fig 1. Pre-cooling the aqueous mixture to subzero temperature for cellulose dissolution using the rock salt/crushed ice bath method have not been reported. This method effectively dissolved the cellulose. It is a ready choice in the absence of expensive cooling devices that can achieve the less than zero degree temperature. Characteristic IR bands of the dissolved cellulose is presented in Table 1.

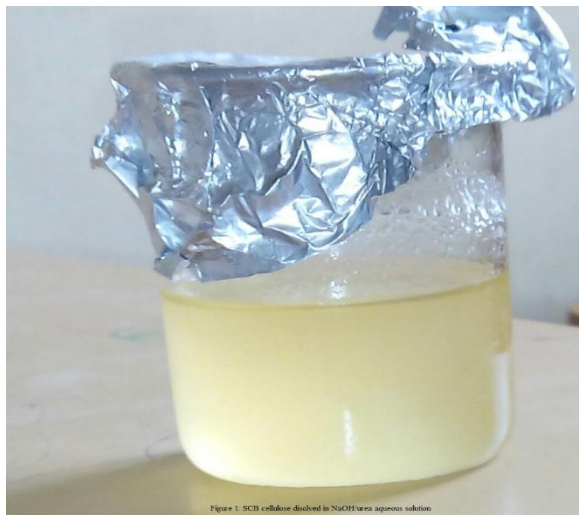
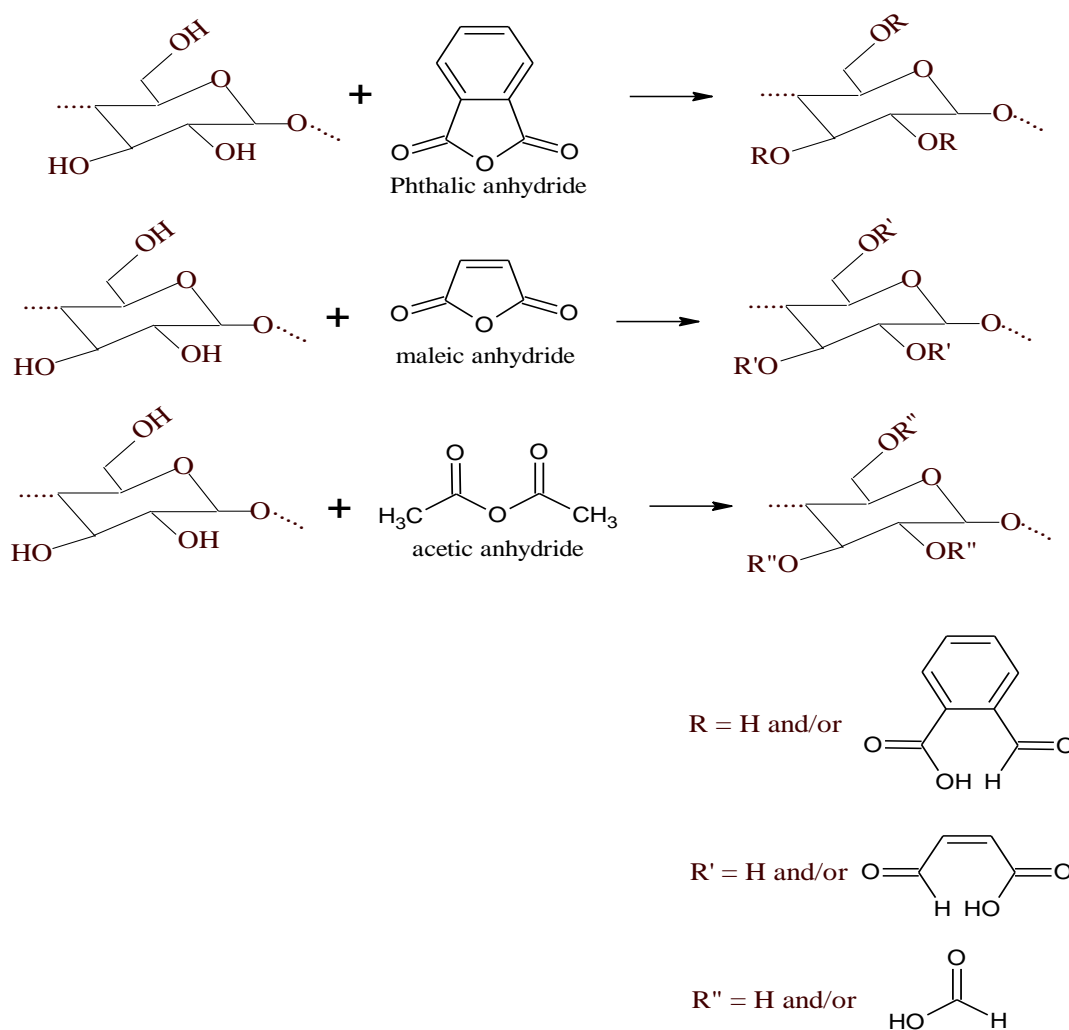


Figure 1: SCB cellulose dissolved in aqueous mixture of NaOH/urea

The white SCB cellulose obtained and the transparent liquid obtained by its dissolution in the aqueous mixture of NaOH/urea and the esterification product of its reaction with phthalic, acetic and maleic anhydrides were analyzed using FTIR and thermal analysis. The esterification route is given in scheme 1.



Scheme 1: Reaction route for the SCB cellulose solution with the phthalic, maleic and acetic anhydrides.

Useful diagnostic bands of the FTIR spectra of the cellulose and the modified materials are presented in Table 1.

Table 1: Characteristic FTIR bands of the compounds

| Compounds | IR bands assignment (cm ⁻¹) | | | | | |
|---------------------|---|-------|--------------------|---------|-------|-------|
| | [O-H] | [C-H] | [CH ₂] | [C-O-C] | [C-O] | [C=O] |
| SCB cellulose | 3437 | 2900 | 1431 | 1161 | 1058 | |
| Dissolved cellulose | 3436 | 2900 | 1433 | 1159 | 1060 | |
| Cellulose phthalate | 3421 | 2902 | 1429 | 1163 | 1040 | 1719 |
| Cellulose maleate | 3436 | 2892 | 1420 | 1156 | 1013 | 1720 |
| Cellulose acetate | 3433 | 2885 | 1416 | 1155 | 1017 | 1716 |

The characteristic band around 3430, 2900, 1636, 1364, 1156 and 1013-1060 cm⁻¹ in the spectra of all the compounds is ascribed to OH stretching vibrations, C-H stretching, bending mode of water molecule, O-H bending, C-O stretching and C-O-C stretching of pyranose skeletal ring vibrations respectively. The peak at 1025 in the spectra of the unmodified cellulose is slightly shifted to 1040, 1017 and 1013 cm⁻¹ in the spectra of the modified moieties. This is due to the degradation of the polymer during dissolution and modification. The appearance of a new peak at around 1733 cm⁻¹ in the spectra of the three modified materials is unambiguously assigned to C=O absorption in carboxyl and esters. The appearance of these peaks is a diagnosis for the successful attachment of the acid anhydrides to the cellulose moiety. A confirmation of this is the absence of peaks around 1850 and 1780 cm⁻¹ in the cellulose derivatives, indicating that the product is free of unreacted anhydrides.

The thermal analysis studies of the compounds were carried out using TGA/DTA. The study investigated the effect of the modification on the thermal behavior of the unmodified cellulose material. The TGA analysis was carried out in the temperature range from 30 °C to 950 °C at 10 °C/min under nitrogen. The thermograms of the SCB cellulose and the modified materials are shown in fig 2.

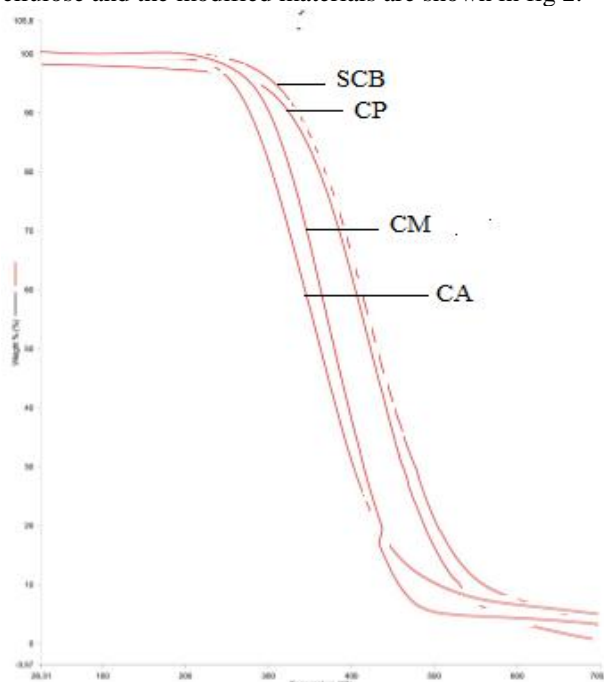


Figure 2: TGA curves of sugarcane bagasse cellulose (SCB), the phthalate (CP), maleate (CM) and acetate (CA)

A comparison of the TGA/DTA curves of the modified cellulosic materials to that of the starting material shows the crude cellulose begins decomposition at 245 °C at 50% weight loss with the decomposition temperature at 338 °C. For the modified materials, the cellulose phthalate, maleate and acetate, the first significant decomposition occur earlier at around 180 °C signifying the temperature at which the attached anhydride fragments decomposes. The decomposition temperatures occurred at 337, 334 and 335 °C respectively reaching a weight loss of 95 % at around 500 °C. The decrease in the decomposition temperature of the modified materials compared to the unmodified sample reveals that the unmodified cellulose is more thermally stable than the modified moieties.

IV. Conclusion

The immense application of cellulose derivatives is now well appreciated and several industries are looking towards that direction. The difficulty fraught with its dissolution is recognised as the major challenge in functionalising this class of material for optimum application. For this reason, the discovery that this polymer is readily soluble in the eco-friendly aqueous NaOH/urea mixture was meted with enthusiasm, however, this enthusiasm was somewhat doused with the challenges yet associated majorly with researchers dwelling in poorly equipped laboratories in developing societies where cooling devices that can achieve the desired subzero temperatures are not readily available. In this report we have been able to solve the problem of pre-cooling the mixture for effective cellulose dissolution using simple method affordable in most laboratories.

Successful functionalization of cellulose with these acid anhydrides vide the cellulose solution has been reported elsewhere for the phthalation process using ionic liquid [19]. The use of solution made from aqueous NaOH/urea for this process and those of maleic and acetic anhydride is not known to us. This method promises to be cheaper, more efficient and environmentally friendly, perhaps even on industrial scale compared to the use of ionic liquids or other hazardous materials.

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Eke U. B. " Esterification of Dissolved Sugarcane Bagasse Cellulose with some Acid Anhydrides: Thermal analysis and FTIR studies." *IOSR Journal of Applied Chemistry (IOSR-JAC)* 10.7 (2017): 75-79.