



Thermal stability of cellulose and their nanoparticles: Effect of incremental increases in carboxyl and aldehyde groups



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ABSTRACT

Oxidized cellulose containing carboxyl and aldehyde functional groups represent an important class of cellulose derivatives. In this study effect of incrementally increasing COOH and CHO groups at C2, C3, and C6 positions of cellulose and nanocellulose has been investigated, with a view to understanding their effect on thermal treatment of cellulose. The results show that 2,3-dialdehyde cellulose (DAC) is the most thermally stable oxidized product of cellulose while the most unstable derivatives contain carboxyl group at the C6 position (6CC). Carboxymethylcellulose (CMC), with carboxymethyl group on C6 position, is more stable than 6CC. Multi-functionalized celluloses 2,3,6-tricarboxycellulose and 6-carboxy-2,3-dialdehyde, have the same level of thermal stability as 6CC, showing that the presence of carboxyl at the C6 is a key destabilizing factor in the thermal stability of oxidized cellulose products. More the number of reducing end groups on the polymer chain, lower the thermal stability of the cellulose, as proved by comparing the TGA/DTG of monomeric analogs dextrose, cellobiose and glucuronic acid with the oxidized celluloses. The thermal stability trend observed for oxidized celluloses was DAC > DCC > nanoparticles > dextrose > glucuronic acid, caused by extent of reducing ends and COOH groups.

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1. Introduction

Oxidation of cellulose has been one of the earliest reactions studied of cellulose (Witz, 1883) and continues to attract attention even today due the wide-ranging biomedical applications of the reaction products (Marta et al., 2012; Wiseman, Saferstein, & Wolf, 2002). The major products of oxidation of cellulose are: 6-carboxycellulose (6CC), 2,3,6-tricarboxycellulose (TCC), 2,3-dialdehyde cellulose (DAC), 2,3-dicarboxycellulose (DCC) and 6-carboxy-2,3-dialdehyde (6C-2,3-DAC). Such products are widely used in pharmaceuticals, drug delivery, gene delivery, and proteins carrier, food industry, cosmetic products, polymer composites, metal absorbent, chromatography, etc. (Coseri et al., 2013). Further, functional groups like aldehyde, carboxy and their combinations at various positions can serve as platform molecules and

facilitate chemical modifications leading to new molecules, thereby opening up the possibility of myriad applications of cellulose. In recent years, development of nanoparticles of cellulose and their derivatives, including nanoparticles having fibrillar as well as spherical shapes, has opened up exciting new opportunities for researches into newer biomedical applications, nanobiocomposites, hybrid materials, nano-metal complexes, etc. (Kulterer et al., 2012; Nikolajaski, Wotschadlo, Clement, & Heinze, 2012; Sharma & Varma, 2013). We have recently reported our work on the synthesis of quasi-spherical carboxycelluloses and their applications as anti-microbial agents and stabilizers of carbon nanotubes, and their detailed morphological characteristics, thermal properties, and solubility characteristics of 6CC (Sharma & Varma, 2013, 2014). Having noticed the profound effect of carboxyl group at the C6 position of cellulose (6CC), wherein even a 1.7% content of COOH greatly decreased the onset of degradation from 320 °C to 213 °C, we felt it would be most pertinent to compare the 6-carboxycellulose (6CC) with other oxidation reaction products such as 2,3,6-tricarboxycellulose (TCC); 2,3-dialdehyde cellulose (DAC); 2,3-dicarboxycellulose (DCC); 6-carboxy-2,3-dialdehyde cellulose (6C2,3DAC). Therefore this paper compares the thermal stabilities of a series of oxidized cellulose products and their nanoparticles, including their multi-functional derivatives with carboxyl and aldehyde functionalities. Additional comparison has been done

Abbreviations: 6CC, 6-carboxycellulose; TCC, 2,3,6-tricarboxycellulose; DAC, 2,3-dialdehyde cellulose; DCC, 2,3-dicarboxycellulose; CMC, carboxymethyl cellulose; DP, degree of polymerization; NP, nanoparticles; 6C2,3DAC, 6-carboxy-2,3-dialdehyde cellulose; DTG, derivative thermogravimetry; TGA, thermal gravimetry; DS, degree of substitution.

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with their monomeric analogs so as to understand the role of molecular weights and number of reducing end groups. Such a comparative study has not been reported in literature with a wide range of oxidized products and their nanoparticles, although some papers have appeared with the limited scope of addressing single products of oxidation like dialdehyde cellulose (Kim & Kuga, 2001; Vicini et al., 2004), dicarboxycellulose (DCC) (Varma & Chavan, 1995) and 6-carboxycellulose (Fukuzumi, Saito, Okita, & Isogai, 2010; Sharma & Varma, 2014).

2. Experimental

2.1. Material

Cellulose was extracted from sugarcane bagasse using our patented process (Varma, 2013). This cellulose was used to prepare the 6-carboxycellulose, 2,3,6-tricarboxycellulose and 6-carboxy-2,3-dialdehyde cellulose. Dextrose ($\geq 98\%$) was procured from Merck (India), D-glucuronic acid ($\geq 98\%$) was purchased from Sigma Aldrich and Cellobiose (extra pure grade) was purchased from SRL Chemicals (India).

2.1.1. Preparation of 2,3-dialdehyde cellulose (DAC) and 2,3-dicarboxycellulose (DCC)

2,3-Dialdehyde celluloses (DAC) of 5%, 15%, 25% dialdehyde content, were synthesized by using sodium periodate (NaIO_4) oxidant, following previously reported methods (Varma & Chavan, 1994; Varma & Jamdade, 1985). 2,3-Dicarboxycellulose (DCC) was synthesized from 2,3-dialdehyde (15%) using sodium chlorite as oxidant in glacial acetic acid solvent, the quantities being adjusted according to the dialdehyde content of the dialdehyde cellulose (Varma & Chavan, 1994).

2.1.2. Preparation of 6-carboxycelluloses (6CC) and 6-carboxycellulose-nanoparticles (6CC-NP)

The 6-carboxycelluloses (6CC) and their nanoparticles were prepared according to a previously reported method, using the HNO_3 – H_3PO_4 – NaNO_2 oxidation system (Sharma & Varma, 2013). Briefly, this consisted of taking finely powdered sugarcane bagasse cellulose and adding an acid mixture (2:1 ratio, v/v) of 65% HNO_3 and 85% H_3PO_4 over a period of 5 min. The acid mixture was allowed to get absorbed in the cellulose for 10–15 min. This was followed by slowly adding required quantity of NaNO_2 (1.4 w/v %). As soon as the NaNO_2 was added, reddish fumes of NO_2 gas were evolved. The reaction was performed at four different temperatures: 25 °C, 40 °C, 50 °C and 70 °C. The reaction mixture was quenched by diluting with distilled water (five times the volume of acid mixture), allowed to settle down for 30 min, then decanted off. The solid part was washed with water (three times) then with water–methanol mixture (2:1 v/v), then centrifuged at 2000 rpm to remove the solid.

2.1.3. Preparation of 6-carboxy-2,3-dialdehyde cellulose (6C2,3-DAC)

The 6-carboxy-2,3-dialdehyde cellulose (15:9) was synthesized by a two step procedure: first cellulose was oxidized to 6-carboxycellulose (15% carboxyl) using HNO_3 – H_3PO_4 – NaNO_2 oxidation system (Sharma & Varma, 2013). Then, the prepared 6-carboxy cellulose was further oxidized at C2–C3 position, by periodate through the well established method (Varma & Chavan, 1994; Varma & Jamdade, 1985). Periodate oxidation to produce 2,3-dialdehyde cellulose is carried out at 55–60 °C at a pH of approx. 4.2 for 5–6 h in the dark. The product filtered, and the supernatant liquid is titrated for the estimation of residual periodates in order to calculate the aldehyde content of the product.

2.1.4. Preparation of 2,3,6-tricarboxycellulose (TCC)

2,3,6-Tricarboxycelluloses (5:15, 15:15, 25:15; the first number refers to carboxy groups at C2, C3 and the second number refers to carboxy group at C6) were synthesized from 2,3-dialdehyde cellulose (5%, 15%, 25% aldehyde content). 10 g of 2,3-dialdehyde cellulose was taken in 2-neck round bottom flask equipped with a magnetic stirrer and guard tube. To this add the acid mixture (2:1 v/v 65% HNO_3 and 85% H_3PO_4). The ratio of acid to the starting material was 1:14. The reaction mixture was allowed to stir for 10 min, and then 1.96 g of NaNO_2 (1.4 w/v %) was added. The reaction was allowed to proceed at 25 °C for 16 h and the reaction was then quenched by adding distilled water (five times the volume of reaction mixture). The reaction was quenched by adding distilled water (five times the volume of reaction mixture) and allowed to stand for half an hour. The solid residue obtained was the I crop. The decanted portion was centrifuged at 12,000 rpm to obtain a gel like material which was taken as the II crop. The I crop and II crop were continuously washed separately with 2:1 ratio of methanol and distilled water, until the pH of the filtrate was neutral. The final washing was done using dry acetone and the products were dried in a lyophilizer. The II crop obtained was a fine white powder and I crop was in the form of white fibrillar material.

2.1.5. Thermogravimetry (TGA) studies

The thermal stability of partially oxidized cellulose was studied using Perkin Elmer STA-6000 (Simultaneous Thermal Analyzer). All samples were oven-dried at 105 °C for 24 h before thermal analysis. The samples were run at the rate of 10 °C/min under nitrogen atmosphere in the range 30–900 °C.

3. Results and discussion

The thermal stability data of dextrose, cellobiose, glucuronic acid (monomeric analogs of cellulose and 6CC) are compared with various oxidized cellulose derivatives in Table 1. Dextrose, being a monomer unit, shows T_{onset} at 211 °C (sample 1, Table 1), which is much lower than its polymer form cellulose (T_{onset} 320 °C). The dimer of dextrose, i.e. cellobiose, shows T_{onset} of 240 °C (sample 2, Table 1) which is significantly greater than dextrose, since cellobiose has one reducing group for two glucose units, while dextrose has one reducing group per unit. The cellulose used here has a degree of polymerization of ~ 500 , which means an average of one reducing group for 500 monomer units; this explains its much greater T_{onset} of 320 °C. This suggests that as the units in a chain increases the thermal stability of the molecule increases, a fact well accepted in polymer chemistry for all types of polymers.

On breaking some of the C2–C3 bonds of cellulose to convert to C2–C3 dialdehyde groups (DAC), there is only a small decrease in onset of thermal degradation (T_{onset} 303–308 °C) as compared to cellulose (T_{onset} 320 °C). Three different degrees of dialdehyde groups were prepared (5–25%) (samples 5–7, Table 1), and though the stability decreased with extent of reaction, it was not very significant in this range. On converting DAC to their carboxyl derivatives by further oxidation to 2,3-dicarboxycellulose (DCC), we notice a more dramatic decrease in onset of degradation by about 50 °C compared to DAC, and a decrease of ~ 70 °C compared to cellulose (DCC T_{onset} 254 °C). This may be perhaps due to the fact that DAC is present as a hydrated aldehyde molecule (hemialdal structure) and these structures are more stable than free aldehydes. However, when further oxidized to DCC, the carboxyl groups produced can decarboxylate on heating, hence their lower onset of degradation.

Interestingly, for 6CC's having carboxyl functionality at the C6 position, even 1.7% carboxyl content brings down the T_{onset} to 213 °C, going down further to 184 °C for 19.7% carboxyl content.

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