Carbohydrate Polymers 104 (2014) 135–142

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Functionalized celluloses and their nanoparticles: Morphology, thermal properties, and solubility studies

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ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 4 January 2014
Accepted 4 January 2014
Available online 20 January 2014

Keywords:
Cellulose
6-Carboxycellulose
Nanoparticles
DTG
TGA
Morphology

ABSTRACT

Agricultural residues derived cellulose was used to synthesize a new series of carboxy functionalized cellulosic nanoparticles (quasi-spherical shaped, 13.2–21.5% carboxyl content) and macro-sized 6-carboxycelluloses (long-fibril shaped, 1.7–22% carboxyl content). The DP (50–70) and yield (upto 46%) of nanoparticles were manipulated by controlling the reaction temperature and time. TGA/DTG thermographs of the carboxycelluloses gave thermostability data and co-related well with the residual crystalline, amorphous, and anhydroglucuronic acid content. The particle shape and size had no effect on the thermal stability. Some derivatives were fully or partially soluble in aqueous alkali and non-aqueous solvents, which can lead to increased versatility of these polymers.

1. Introduction

In recent years, deforestation concerns have led to the development of non-wood sources of cellulose, especially cellulose extracted from agricultural wastes such as sugarcane bagasse, wheat straw, rice straw, etc. (Nuruddin et al., 2011; Varma, 2013). This source of cellulose is considered environment-friendly, as fewer forest trees have to be cut to produce cellulose. Another major advancement in the field of cellulose chemistry and technology is the development of nanoparticles of cellulose and cellulose derivatives (Eichhorn, 2011; Kulterer et al., 2012; Nikolajaski, Wotschadlo, Clement, & Heinze, 2012). Since most of these cellulose and nanocellulose molecules are biocompatible and biodegradable, their role in several biomedical applications, biosensors, diagnostic molecular probes, drug delivery vehicles, etc. are being vigorously pursued, along with other exciting applications in biocomposites, membranes, electronics, and solar cells (Klemm, Heublin, Fink, & Bohn, 2005; Klemm et al., 2011; Lin, Huang, & Dufresne, 2012; Zhou et al., 2013). As in metal nanoparticles, research on nanocelluloses has expanded to include shape-selective synthesis, such as nanofibres and nanospheres (Isogai, Saito, & Fukuzumi, 2011; Kulterer et al., 2012; Nikolajaski et al., 2012; Sharma & Varma, 2013). Graphene–cellulose paper membranes have been used as electrodes for flexible super capacitors. Celluloses have also been used with carbon nanotubes and combined with conducting polymers for the fabrication of electroconductive composites; further, hybrid inorganic–organic nanocomposites are emerging as a new class of functional nanomaterials (Lin et al., 2012; Shi, Philpis, & Yang, 2013). 6-Carboxycelluloses, prepared by oxidation of cellulose, have been extensively investigated for over seventy years due to their applications in wound dressing gauzes and several other related biomedical applications (Anderson & McIntyre, 1946; Houser, 1946; Kennedy, 1947; Scarff, Stookey, & Garcia, 1949). The earliest report on oxidation of cellulose to produce carboxylated cellulose was reported way back in 1883 (Cross & Bevau, 1883). Since then there have been regular streams of papers and patents on various methods of oxidation of cellulose and their applications (Kumar & Yang, 2002; Nooy, Pagliaro, Bekkum, & Besemer, 1997; Okita, Saito, & Isogai, 2010; Shinoda, Saito, Okita, & Isogai, 2012; Yackel & Kenyon, 1942). In recent years, nanofibres of 6-carboxycelluloses have also been synthesized and their properties have been investigated (Crawford et al., 2012; Nachtkamp et al., 2012; Okita et al., 2010; Shinoda et al., 2012). Indeed, carboxy functionalized nanocelluloses can be expected to vastly expand the range of properties of electroconductive devices and biomedical devices, where currently un-functionalized nanocelluloses are used. This was the motivation for taking up the synthesis and characterization of both macro-sized carboxycelluloses and nano-sized carboxycelluloses, and to compare their thermal properties, morphological changes in the products, and solubility characteristics. These are all key properties for fabricating new devices based on these materials.

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http://dx.doi.org/10.1016/j.carbpol.2014.01.015

Table 1

(A) Percent carboxyl content, yield and DP (degree of polymerization) of 6-carboxycelluloses at different temperatures and time periods (*NP: nanoparticles). (B) Solubility of various carboxyl content 6-carboxycelluloses (6CC) in aqueous alkali solutions. (C) Solubility of various carboxyl content 6-carboxycelluloses (6CC) in organic solvents (the part of the data of (A) showing carboxyl group contents is taken from the Supplementary Data File of our earlier published paper, Sharma & Varma, 2013).

(A)

Time (h)	—COOH content (%)*				Yield (%)/DP			
	25 °C	40 °C	50 °C	70 °C	25 °C	40 °C	50 °C	70 °C
1	1.7	6.17	–	–	84.0/87	83.0/86	–	–
3	3.0	13.2	–	–	73.0/86	72.0	–	–
6	8.6	14.3	–	–	71.0/84	68.0/81	–	–
8	–	–	–	13.9	–	–	–	16.0*/50
12	14.1	14.0	13.2	–	69.0/82	60.0/78	46.0*/70	–
24							–	–
(I crop)	19.7	16.0	–		63.0/79	25.0/77		
(II crop)*		18.0				5.0*/70		
48							–	–
(I crop)	22.0	17.0	–	–	45.0/77	22.0/76		
(II crop)*		21.5				5.0*/70		

(B)

NaOH (%)	22%6CC	14%6CC	8%6CC	3%6CC
10	++	++	++	±
5	++	++	++	– –
2	++	++	++	– –
0.4	++	++	+	– –
0.2	++	+	– –	– –

(C)

Solvents(1% solution)	22%6CC
CH_3CN	– –
DMAc	– –
DMSO	±
Dioxane	– –
Acetone	– –
Methanol	– –
Ethanol	– –
$CHCl_3$	– –
DCM	– –
THF	– –
Toluene	– –
DMF	– –
Pyridine	– –

We recently patented our work based on extraction of cellulose from non-wood sugarcane bagasse (Varma, 2013). This cellulose was oxidized to 6-carboxycellulose, and the synthesis was fine-tuned so as to produce the usual macro-sized fibrils in addition to quasi-spherical shaped nanoparticles of narrow polydispersity, narrow size range (25–35 nm), and low degrees of polymerization (Sharma & Varma, 2013). We studied the solubility characteristics of this new series of 6-carboxycelluloses (1.7–22% carboxyl content) and their nanoparticles, and also made a comparative study of the thermal properties of the materials. These results were used for deciphering gradual changes in the morphology of the cellulosic molecules caused during progressive carboxylation. Several properties of semi-crystalline polymeric molecules are guided by their morphology, thermal properties and solubilities. Hence it is important to have a good knowledge of the thermal properties and morphology as a function of degree of carboxy substitution, molecular weights, molecular sizes, and molecular shapes of the different 6-carboxycelluloses. Our previous work on aldehyde, carboxy, and amine functionalized wood cellulose as reinforcements in epoxy composites had shown interesting advantages as compared to the use of un-functionalized cellulose (Varma & Chavan, 1994). Commercial availability of nano-carboxycellulose will most certainly lead to the development nano-biocomposites of such materials. Therefore we believe our current studies throw useful new light on the utilization of forest-free cellulose for preparing carboxy functionalized celluloses and their nanoparticles for developing their applications.

2. Experimental

2.1. *Synthesis of 6-carboxycellulose in non-nano and quasi-spherical nanoparticle forms*

The methodology to prepare quasi-spherical shaped nanoparticles was recently published (Sharma & Varma, 2013). We could also obtain non-nano sized fibrils by this method. In general, to finely powdered sugarcane bagasse cellulose (10 g) was added 140 ml 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 1.96 g 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 three different temperatures: 25 °C, 40 °C, 50 °C and 70 °C, as shown in Table 1. The reaction mixture was quenched by diluting with distilled water (5 times the volume of acid mixture), allowed to settle down for 30 min, then decanted off. The solid part was washed with water (3 times) then with water–methanol mixture (2:1, v/v), then centrifuged at 2000 rpm to remove the solid.

The reaction products at 25 °C were obtained as single crops, none of which had the form of nanoparticles. In the specific case of the reaction at 40 °C (24 h and 48 h), after centrifugation of the initial solid at 2000 rpm for 15 min, the supernatant liquid was cloudy. This cloudy supernatant liquid was separately centrifuged at 12,000 rpm for 15 min which resulted in the separation of a second crop. The latter on analysis showed it to be