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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.

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 pharmaceutics, 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; 6C23DAC, 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 (≥98%) was procured from Merck (India), D-glucuronic acid (≥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 baggase 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 fibriller 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.

Table 1
TGA data for multi-functional cellulose derivatives.

S. no.	Oxidation (%)		Sample name	T_{onset} (°C)	$T_{final\ deg}$ (°C)	T_{50} (°C)	Residue (wt.%) at 850 (°C)
	C2,3	C6					
1	0	0	Dextrose	211	339	307	14
2	0	0	Cellobiose	240	331	313	7
3	0	100	D-Glucuronic acid	169	293	266	14
4	0	0	Cellulose	320	377	353	5
5	5	0	DAC	308	357	339	5.6
6	15	0	DAC	306	351	333	7.5
7	25	0	DAC	303	349	333	14.6
8[a]	60	0	DCC	254	369	342	–
9[b]	0	1.7	6CC	213	ND	302	12
10[b]	0	8.6	6CC	204	ND	296	13
11[b]	0	14.1	6CC	188	ND	282	12
12[b]	0	19.7	6CC	184	ND	266	9
13[b]	0	13.2	6CC-NP	172	ND	282	17
14(i)	5	15	TCC	192	ND	288	21.5
14(ii)	5	17	TCC-NP	177	ND	242	20.8
15(i)	15	15	TCC	191	ND	271	21.6
15(ii)	15	18	TCC-NP	190	ND	256	21.2
16(i)	25	15	TCC	192	ND	269	18.1
16(ii)	25	18	TCC-NP	194	ND	265	25.4
17	15	9	6C23DAC	184	ND	294	22.9
18[c]	DS (0.70–0.85)		CMC (two step)	280	–	–	35.2

T_{onset} – onset degradation temperature.
$T_{final\ deg.}$ – final degradation temperature.
T_{50} – temperature at which 50% weight loss occurred.
Residue (wt.%) – weight remaining at 850 °C.
ND – not determined
[a] Varma and Chavan (1995).
[b] Sharma and Varma (2014).
[c] Zohuriaan and Shokrolahi (2004).

For the 2,3,6-tricarboxycellulose (TCC), the T_{onset} was 192 °C, due to the effect of the C6 carboxyl group in conjunction with the destabilizing effects of C2 and C3 carboxyls (Fig. 1A) (samples 14(i), 15(i) and 16(i), Table 1). The thermal stability observed is lowest for carboxycelluloses (6CC and TCC) compared to other types of oxidized derivatives of cellulose such as DAC and DCC. This might be due to disruption in hydrogen bonding of original cellulose on insertion of carboxy group at C6, in addition to the inherently unstable COOH at C6, coupled with low molecular weight of 6CC and TCC which results in increasing number of reducing end groups (free aldehyde groups).

The glucuronic acid shows T_{onset} at 169 °C (sample 3, Table 1) which is lower than 14.1% 6CC and 19.7% 6CC (188 °C and 184 °C, sample nos. 11 and 12, Table 1), since there are less reducing end groups in 19.7% 6CC. The 1.7% 6CC and 8.6% 6CC are slightly more stable due to the higher molecular weight effect, which partially over-rides the number of reducing end groups effect. As was mentioned earlier, higher molecular weight polymers have higher thermal stability as compared to their lower molecular weight analogs. For the 6CC's there is a continual decrease in molecular weight as the degree of oxidation increases.

The substitution of carboxyl at C6 and C2, C3 position (i.e., TCC) via oxidation reactions generates a major change in thermal stability of the oxidized celluloses. This is probably due to decomposition of three carboxyl groups replacing hydroxyl groups. The thermal degradation of 6CC, TCC, DCC, 6C23DAC is thus a result of presence

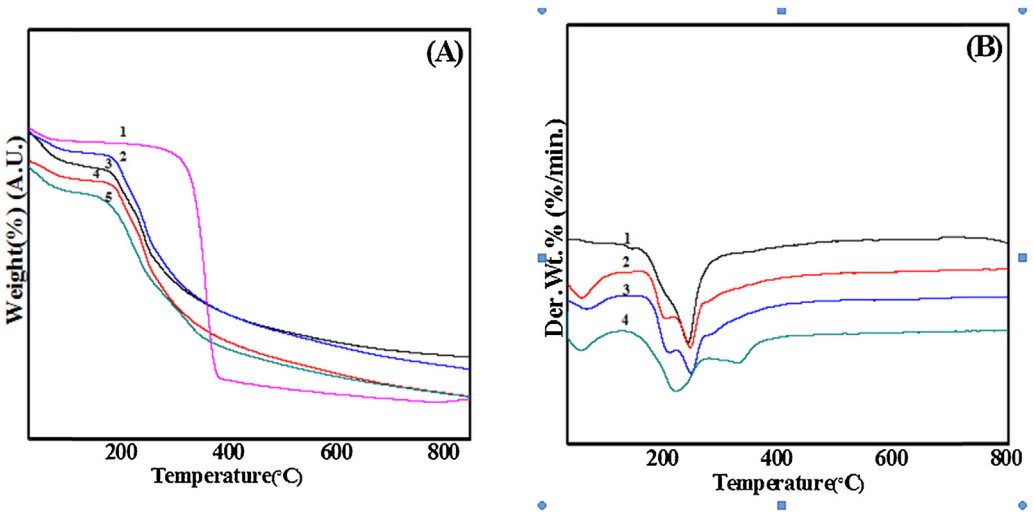

Fig. 1. (A) TGA curves of (1) cellulose, (2) TCC derivatives (25:15), (3) TCC (15:15), (4) TCC (5:15), (5) 6C2,3DAC. (B) DTG of (1) TCC (25:15), (2) TCC (15:15), (3) TCC (5:15), (4) 6C2,3DAC.

Table 2
DTG data of multi-functional celluloses compared with their lower analogs dextrose, cellulobiose and glucuronic acid.

S. no.	Oxidation (%)		Sample name (time/temp.)	T_{max} (°C)	wt. (%) loss	Nature of DTG graph
	C2,3	C6				
1	0	0	Dextrose	227 305		Two peaks, at 227 °C and 305 °C, completely resolved
2	0	0	Cellobiose	254 313		Two peaks, at 254 °C and 313 °C, completely resolved
3	0	100	D-Glucuronic acid	170 220		Two peaks, at 170 °C and 220 °C, completely resolved
4	0	0	Cellulose (Single stage)	363	56	Only one major sharp peak at 363 °C
5	5	0	DAC (Single stage)	339	51	Only one major sharp peak at 339 °C
6	15	0	DAC (Single stage)	334	50	Only one major sharp peak at 334 °C
7	25	0	DAC (One stage)	333	48	Only one major sharp peak at 333 °C
8[a]	0	1.7	6CC (Two stage)	228 302	15 50	Two well resolved sharp peaks, minor at 228 °C, major peak at 302 °C
9[a]	0	8.6	6CC (Two stage)	235 288	23 46	Two peaks, at 235 °C and 288 °C but not completely resolved, tending to merge
10[a]	0	14.1	6CC (Three stage)	211 246 286	20 34 52	Three peaks at 211 °C, 246 °C, 286 °C, tending to merge
11[a]	0	19.7	6CC (Two stage)	198 239	21 40	Major sharp peak at 198 °C and minor at 239 °C, distinctly resolved
12(i)	5	15	TCC (Three stage)	206 244 282	16 33 49	Three distinct peaks at 206 °C,244 °C, 282 °C, tending to merge
12(ii)	5	17	TCC-NP (Two stage)	236 190	45 24	Two distinct peaks at 236 and 190 °C
13(i)	15	15	TCC (Three stage)	202 242 280	22 39 52	Three distinct peaks at 202 °C, 242 °C, 280 °C, tending to merge.
13(ii)	15	18	TCC-NP (Two stage)	240 206	38 20	Two distinct peaks at 240 and 206 °C
14(i)	25	15	TCC (Three stage)	208 247 293	57 39 19	Major sharp peak at 239 °C and minor at 195 °C, distinctly resolved
14(ii)	25	18	TCC-NP (Two stage)	240 209	38 20	Two distinct peaks at 240 and 209 °C
15	15	9	6C23DAC (Two stage)	222 330	43 58	Two separate peaks, major at 222 °C and minor at 331 °C

[a] Sharma and Varma (2014).

of COOH on the C6, and COOH on C2 and C3 of some monomer units of cellulose, the extent depending on the degree of oxidation. Further, as the degree of oxidation increases, the degree of polymerization of cellulose decreases, leading to increasing number of reducing end groups (free aldehyde groups) and consequent thermal instability of the resulting celluloses (Sharma & Varma, 2014).

In order to understand the effect of presence of COOH directly on the glucose monomer unit as opposed to its presence via a methylene spacer group, we also investigated the thermal stability of carboxymethylcellulose (CMC), and compared it to the thermal stability of 6CC. The presence of CH_2COOH on C6 did not cause too much decrease in thermal stability of the cellulose (T_{onset} of CMC 280 °C, sample no. 18, Table 1). Therefore, it is reasonable to conclude that the direct substitution of primary alcohol group at C6 by –COOH caused much more decrease in thermal stability than the substitution of CH_2COOH at C6. Thus not only the presence of carboxyl, but also its location directly on the ring structure of the molecule adversely affects the thermal stability of the molecule. This is most likely due to the mechanism of thermal degradation which is affected more by decarboxylation on the ring carboxyl group than by the decarboxylation at the side chain carboxyl.

In the form of nanoparticles, it was seen that both 6CC (T_{onset} 172 °C) and TCC (T_{onset} 177–190 °C) were slightly more unstable than their macro-sized analogs. This is most likely due to lower molecular weight (Sharma & Varma, 2013), and consequently large number of reducing end groups which are more thermally unstable. The TCCs gave greater quantity of residues at 850 °C. This could be due to increased cross-linking reactions of TCC. 6C2,3DAC (sample 17, Table 1) shows similar thermal stability as 6CC (sample 12, Table 1) since it has a carboxyl group at C6. Thus, in addition to this, the residual solid percent obtained for 6CC-NP's (17%) (sample 13, Table 1) were in the same range of 6CC's macrosized molecule (12%) (samples 9–11, Table 1); likewise the residual solid (~21%) for TCC-NP's were also close to TCC's macro-sized particles (samples 14 and 15(i) and (ii), Table 1). The residual weight % obtained for high carboxyl content TCC-NP (25: 18% carboxyl content) is higher than rest of other analoges (sample 16(ii), Table 1). On the other hand, since 6C23DAC has both aldehyde and carboxyl groups (15% carboxyl:9% aldehyde) and expectedly it shows a low T_{onset} at 184 °C (sample 17, Table 1) which is the same as 19.7% 6CC (sample 12, Table 1).

3.1. DTG studies

DTG peaks show the temperature at which the maximum degradation weight loss occurs. Cellulose shows a single peak with T_{max} of 355 °C. The DTG of monomer dextrose shows two peaks, showing a two-stage degradation having values 227 °C and 305 °C. This result corroborates the TGA data, and confirms the effect of thermal stability on the number of reducing end groups.

On the other hand, DTG for DAC molecule (5%, 15%, 25%) also exhibit the single step degradation while published literature shows DTG for the higher aldehyde content (87%, 98%) exhibited two step degradation (Kim & Kuga, 2001). The DTG observed for the 6-carboxycelluloses (Sharma & Varma, 2014) showed two step degradation processes due to the presence of thermally sensitive carboxyl group at C6. Interestingly, TCC showed a three-step degradation pattern, whereas the lowermost peak at (202–208 °C) appeared seems to be belong to the $-CO_2$ liberation from C6 position while at slightly higher temperature (242–247 °C), the T_{max} observed perhaps belong to $-CO_2$ liberation from C2, C3 positions while the peak at (282–293 °C) belong to the anhydroglucose moiety of cellulose (samples 12(i), 13(i) and 14(i), Table 2). However, the TCC-NP's (samples 12(ii), 13(ii) and 14(ii), Table 2) showed two-step degradation pattern at (190–209 °C) and (236–240 °C), this might be due to low DP (more reducing end groups) and small size of the molecule. The DTG curve for 6C2,3DAC (15% carboxyl:9% carbonyl content), showed a two-step degradation. 6C23DAC (Fig. 1B) (sample 15, Table 2) shows a major peak at 330 °C, which is comparable to the peak in 5% DAC (sample 5, Table 2), and minor peak at 222 °C, which is comparable to one of the minor peaks of 6CC (14.1%), (sample 10, Table 2) at 211 °C (Sharma & Varma, 2014). Therefore the thermal data distinctly discerns the presence of both carboxyl and aldehyde groups in the same oxidized cellulose. On comparing the thermal stability of CMC with DS (0.70–0.85), the DTG of CMC also appeared as a two-step degradation pattern, whereas the T_{max} at 146 °C may be due to evolution of $-CO_2$ from the C6 carboxymethyl group. The T_{max} at 303 °C can be attributed to the anhydroglucose unit (Zohuriaan & Shokrolahi, 2004).

This data can have several applications. It proves that for low molecular weight materials the reducing end groups must be effectively capped to prevent thermal degradation. Much of past research into composites of cellulose with engineering plastics is based on improving the onset of thermal degradation by blocking the reducing end either by reduction, by Schiff's base reaction followed by reduction, reduction followed by further reaction of the primary hydroxyl formed, or by use of a variety of other reactions. The thermal properties of cellulose are an important parameter in composites as well as in applications in the solid and liquid state, including disposable products, low temperature binding materials, additives, superconducting materials, solar cells, thermal sensitive papers etc. (Nadagouda & Varma, 2007). Therefore, the thermal study of various aldehyde and carboxyl functionalized celluloses presented in this paper will help identify applications of these molecules.

4. Conclusions

The study of a series of single and multi-oxidized cellulose and their nanoparticles with varying contents of aldehyde and carboxyl functional groups has given an insight into their thermal stabilities and degradation behavior caused by the presence of functional groups present at specific positions of the cellulose chain, the extent of functionalization, and the molecular weight. The key factor causing destabilization of the molecules is the presence of carboxyl groups at the C6 position. Another major factor affecting thermal stability is the number of reducing end groups present on a polymer chain; the more the reducing end groups, more the thermal instability. DAC is present in the form of hydrated aldehyde, therefore its thermal stability is not much compromised as compared to cellulose. When the DAC is converted to DCC, thermal stability decreases due to the carboxyl groups which can decarboxylate on heating. TCC is also unstable for the same reasons as 6CC and DCC. The nanoparticles are slightly more thermal unstable than their larger analogs due to their lower molecular weight, which results in greater number of reducing end groups which are more unstable. This data enables one to correlate structure with the thermal properties of oxidized celluloses, and will aid in designing new molecules with tailored thermal properties.

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Priyanka Sharma, M.Sc. (Organic Chemistry), is a graduate student working toward her Ph.D. degree. She is building her capabilities in the area of oxidation reactions of cellulose and their nanoparticles.

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