A hint on the correlation between cellulose fibers polymerization degree and their thermal and thermo-oxidative degradation

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Abstract The degree of polymerization is one of the main parameters reflecting cellulose ageing. Viscometry is a method frequently used for determination of cellulose fibers polymerization degree, however, sample preparation and viscosity measurement are demanding, time consuming and do not provide reproducible results. In this study, the relationship between polymerization degree of cellulose fibers obtained by viscosity measurement and their degradation parameters obtained by thermal analysis were investigated. Differential scanning calorimetry provided values of effective combustion heat and thermogravimetry (TG) was used for the determination of temperatures and associated mass losses during the cellulose degradation. Effective combustion heat did not show any correlation with degree of polymerization of investigated cotton fabrics. In contrast, results from TG suggested several promising nonlinear correlations which could be used as a hint to develop a method useful for quick determination of cotton fabrics polymerization degree. The most promising correlations with cellulose polymerization degree were found for both rates of thermal and thermo-oxidative degradations.

Keywords Cellulose fibers · Degree of polymerization · Viscometry · Thermogravimetry · Differential scanning calorimetry

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Introduction

Degree of polymerization (DP) is the main factor playing role in the ageing of cellulose fibers. Processes of ageing are associated with the degradation of cellulose macromolecules, increasing the proportion of low molecular weight fraction and decreasing DP. The adverse consequence of cellulose fibers ageing is the deterioration of mechanical and optical properties. In order to clarify the mechanism of ageing, chromatography and spectral methods are frequently used [1, 2].

One of the most attractive applications of thermal analysis is the prediction of material stability under specified conditions [3]. In principle, methods of thermal analysis provide indirect information, however, sometimes it is crucial to understand the mechanism of processes occurring at elevated temperatures. In the case of textile materials this information is of particular importance since several processing in textile industry are carried out at relatively high temperatures. This is also the case of cotton fibers [4]. Many studies showed that thermal degradation of cellulose molecules occurs between 250 and 360 °C. The minor decomposition reaction takes place around 250 °C and the major decomposition around 320 °C [5, 6].

Physical and chemical properties of cellulose depend on the chain length and therefore on the polymerization degree

(DP). The DP can be used as a measure of cellulose degradation, caused mainly by physical or chemical influences or by irradiation [7, 8]. In turn, the DP has a dramatic influence on the mechanical properties of cellulose and correlates with higher melting temperature. As chain length increases, mechanical properties such as ductility, tensile strength, and hardness rise sharply and eventually level off [9, 10].

This study was aimed to investigate the degree of polymerization of cotton fabrics by both "traditional" and "nontraditional" techniques and to find the potential correlations between those two approaches. Viscometry is traditionally used for determination of DP by measuring viscosity of cellulose solutions. However, this way is relatively time consuming and demanding on the sample preparation since cotton fabric for viscometry has to be cut in very small pieces and dissolved in solution. Therefore, the search for more effective, precise, reproducible, and faster method is of a great importance. The first aim of the study was the determination of the degree of polymerization of cotton fabrics and testing if and how the dying and number of washing influence the DP. Next part was focused on the determination of the thermal and thermo-oxidative degradation records of cotton fabrics and a raw cotton sample using thermogravimetry (TG) and differential scanning calorimetry (DSC), respectively. In the last part, obtained data from DSC and TG were correlated with values of polymerization degree obtained by viscometry and showed several promising correlations.

Materials and methods

Cotton samples

Raw cotton wool (*genus Gossypium*) and ten samples of cotton fabrics, which underwent different chemical treatments, were provided by Textile Testing Institute in Brno (Czech Republic). Table 1 summarizes their properties.

Prior to analysis, textile samples were cut into small pieces (average 2–3 mm). For viscometry measurements, samples were dissolved in an ammonium solution of cupric sulfate. Solution was prepared according to the Czech standard CSN 68 4061. In brief, 160 g of $CuSO_4 \cdot 5H_2O$ were dissolved in 800 mL H_2O and then 200 g of NH_4OH were added. Obtained solution was diluted to gain 2,000 mL of stock solution. Then the viscosity of samples was measured and degree of polymerization was determined as described below.

Thermal analysis

TG measurement

TG of small textile pieces (2–3 mm) was carried out using TA Instruments TGA Q5000IR under dynamic air or nitrogen atmosphere. The furnace was calibrated using Curie temperatures of nickel and alumel. Each fabric sample was loaded into an open platinum crucible. The sample mass was typically between 1.5 and 3 mg. The air (thermo-oxidative degradation) and nitrogen (thermal degradation) flow rates were set at 25 mL min^{-1}, heating rate was in all cases 10 °C min^{-1}; experiments started at the room temperature and finished at 650 °C. The records were evaluated by means of TA Universal analysis 2000 software.

DSC measurement

Calorimetric measurements of textile samples were performed by Shimadzu DSC-60. The DSC furnace was calibrated using fusion temperatures of indium, tin, lead, and zinc. Each cotton sample was measured in the open

Table 1 Degree of polymerization and combustion heat of cotton samples

Description of sample for measurement	Color	Properties	Degree of polymerization/n	Combustion heat/kJ g^{-1}
1	Beige	Cotton wool	2,450	4.51
2	Red		563	3.20
3	Beige		1,026	2.54
4	Beige		710	2.30
5	Red		353	2.86
6	Beige	0× washed	1,583	4.16
7	Beige	50× washed	1,421	4.60
8	Beige	0× washed	1,561	2.01
9	Beige	10× washed	1,536	1.72
10	Beige	30× washed	1,382	4.44
11	Beige	50× washed	1,301	3.38

aluminum pan and an empty pan was used as a reference. The sample mass was typically between 1 and 2 mg. The air flow rate was 25 mL min^{-1}. Samples were heated 10 °C min^{-1} from room temperature to 600 °C. Obtained results were evaluated by means of TA-60WS software.

Both DSC and TG experiments were conducted in three replicates in order to check the reproducibility of measurements. Standard deviation curves are reported in respective figures.

Viscometry

Viscosity measurements were carried out using Ubbelohde viscometer (U2, diameter of capillary 0.65 mm). Viscosity was measured at 25 °C (±0.05 °C) for three times. Solution was placed into capillary using compressed nitrogen. Flow times were determined repeatedly by means of a split-second electric stop clock. A solvent blank (ammonium solution without cellulose) was measured repeatedly as well. Obtained results were evaluated by means of MS Excel®.

Degree of polymerization was calculated according to the Staudinger's formula [11]:

$$[\eta] = K' \cdot \mathrm{DP} \qquad (1)$$

where $[\eta]$ is intrinsic viscosity, $K' = 6.1 \times 10^{-3}$ (temperature 25 ± 0.05 °C). Intrinsic viscosity was calculated by the formula:

$$[\eta] = \frac{\frac{\eta_{sp}}{c}}{1 + K \cdot \eta_{sp}} \qquad (2)$$

where K is 0.28 (constant of Mark–Houwink's equation), c is the concentration of cellulose (g/100 mL) [7].

$$\eta_{sp} = \frac{t - t_0}{t_0} \qquad (3)$$

t_0 is the time of solvent flow, t is the time of cellulose sample solution flow.

Results and discussion

Viscometry

Table 1 summarizes properties of cellulose materials which varied in the number of washing and in their colors. The reason of this selection was to cover a wide range of fiber materials with respect to their treatment and resistance to degradation of cellulose fibers during washing.

Degree of polymerization obtained for 11 cotton samples varied in the range from 353 to 2,450. Standard deviation of the measurement was not greater than 1% of the measured value. As expected, cotton wool, which was

modified neither physically nor chemically, showed the highest degree of polymerization (2,450). As it can be seen, the fiber dying is an important factor causing a decrease in DP. The comparison of the same fiber dyed by red and beige color showed a significant reduction of DP in the case of red color. This difference can be attributed to the mechanisms of processes which were used for dying of investigated cellulose materials. This confirms that dying has a great influence on the DP [12, 13]. Data listed in Table 1 summarize also the effect of number of washing on the DP. As expected the degree of polymerization decreased with increasing number of washing [12, 13].

DSC measurements

In this part, the influence of variable DP and physical properties of cotton material on apparent combustion heat was tested. The representative DSC record (Fig. 1) shows the enthalpy change in the course of the thermo-oxidative degradation of cotton material. The exothermic peaks represent the total heat evolved during degradation, and therefore, it is likely that they include several overlapping processes. This fact, together with the notion that DSC due to experimental arrangement cannot provide the combustion enthalpy as defined by physical chemistry textbooks, is the reason that enthalpy values obtained in this study are called "effective combustion enthalpy". All DSC records of processed samples showed similar patterns. In principal, the exothermic peaks reflect the mechanism of degradation of tested samples and imply that the degradation proceeded in two main steps. In all cases, first exothermic peak maximum (including cotton wool) was observed in the temperature interval 300–330 °C. Second peak appeared around 500 °C for all modified samples and around 450 °C for cotton wool.

DSC record of cotton wool showed higher number of degradation steps in comparison with DSC of processed fibers. Further, the onsets of exothermic was at lower temperature and the kinetics of degradation of cotton wool was faster. Therefore, modified cotton samples were more resistant against thermo-oxidative treatment. The peaks area integration provided the values of effective combustion heat (reported in Table 1). Their values varied in the range from 1.72 to 4.60 kJ g^{-1}.

Thermo-oxidative degradation determined by TG

The main goal of this part was the evaluation of the thermo-oxidative stability, and determination of degradation profiles of cotton samples from TG records (Fig. 2).

The TG records showed two-stage process of mass loss, reflecting the thermo-oxidative decomposition of modified cotton. Figure 2 shows the decrease in the mass of the
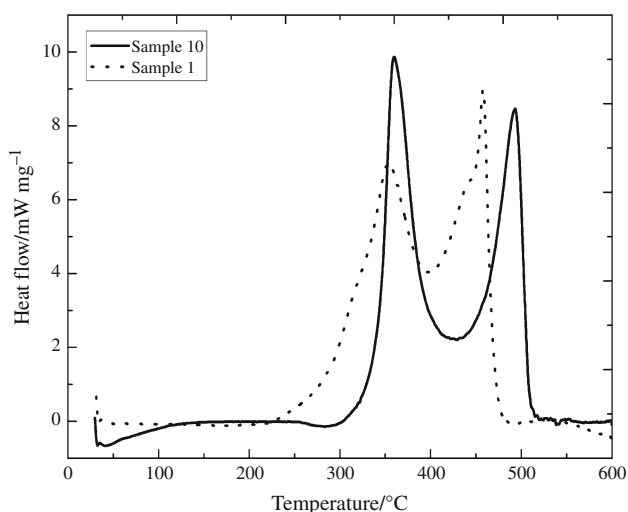
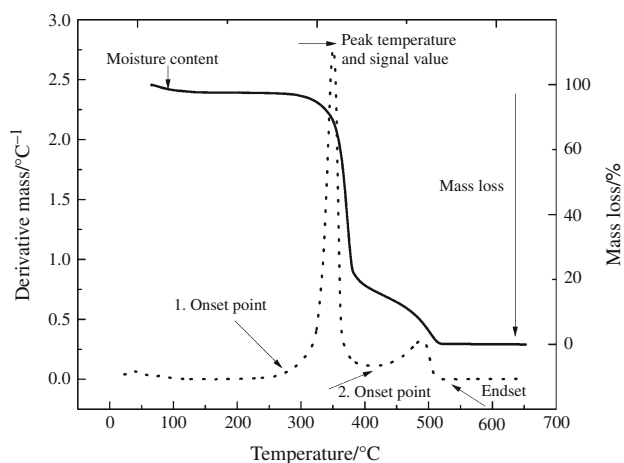**Fig. 1** Representative DSC curves of cotton material (samples 10 and 1)

Fig. 2 Degradation profile of cotton sample and determination of characteristic properties from TG and DTG records

sample from 2.6 to 3.8% up to 120 °C. This process corresponds to the moisture evaporation. Further temperature increase caused additional mass loss. The first one can be observed between 304 and 314 °C for modified cotton, around 285 °C for dyed cotton (onset point), followed by the second one in the range between 429 and 470 °C. The maximum peak values of derivative curves for the first step of degradation are in the temperature range between 335 and 352 °C. For the second step, peak maxima were observed in the temperature range between 488 and 504 °C. These two steps are connected with change of the initial mass of cotton of 51.5–59.4% (colored cotton around 64%) and 23.6–33.9%, respectively. At the end of the analyses, i.e., 503–521 °C for unmodified samples, 495–497 °C for colored cotton, cotton samples have 0% of their initial mass and degradation is clearly finished. The two-step thermal decomposition of cotton samples above

220 °C confirms earlier observation of Szcześniak et al. [5]. Similar records were obtained also for the rest of modified cotton samples.

TG/DTG records obtained for cotton wool were slightly different in comparison with other samples. Similarly as in case of DSC the DTG curve indicated degradation in three steps which is in contrast to the literature data, describing degradation of cellulose as a two-step decomposition process. This result can be attributed to the contamination of raw cotton samples by other molecules such as for example proteins [5].

Comparison of data obtained by TG measurement reveals the most important differences between cotton wool and modified samples. Temperature of onset points and first peak temperature of cotton wool occurred at lower temperature, cotton wool contained higher moisture content, rate of the degradation for the first step is lower but second step is higher. First mass loss and also rate of degradation was higher for colored samples in comparison with cotton wool.

Thermal degradation determined by TG

Thermal degradation profile and stability of cotton samples were obtained using TG in the nitrogen atmosphere. Unlike the degradation in oxidative atmosphere only two stages of mass loss were observed which can be attributed to the moisture evaporation (up to 120 °C) followed by one-step decomposition at higher temperature. Apparently the mechanism of thermal degradation differs from the combustion in air atmosphere.

Decomposition temperatures of colored samples started between 289 and 296 °C similarly to temperatures for the first degradation steps of thermo-oxidative degradation. Onset temperature of cotton wool was recorded at 279 °C. The maxima value of derivative curves degradation were determined between 336 and 366 °C, in this temperature range were highest both the degradation rate and mass loss. This step was connected with mass change between 64.9 and 69.4% of modified cotton (for colored cotton around 72%) and 58.5% for cotton wool. The end of the pyrolysis was between 390 and 395 °C for modified samples and 376 °C for cotton wool; the char of modified cotton samples was between 6 and 12% of their initial mass, cotton wool had 17.6% and its degradation was not terminated yet. Similar records were obtained also for the rest of cotton samples.

As in case of TG in the air, cotton wool, and colored samples showed differences from washed samples. Degradation began at lower temperature in cotton wool, followed by degradation of colored samples and washed cotton at higher temperatures. Cotton wool showed the slowest degradation kinetics and the highest amount of char. In contrast, the colored cotton was subjected to fastest degradation and only 6% of initial mass remained at 650 °C.

Fig. 3 Relationship between degree of polymerization and **a** effective heat combustion, **b** nitrogen TG mass loss, **c** thermo-oxidative TG mass loss, **d** rate of thermal degradation, **e** moisture content, and **f** rate of thermo-oxidative degradation
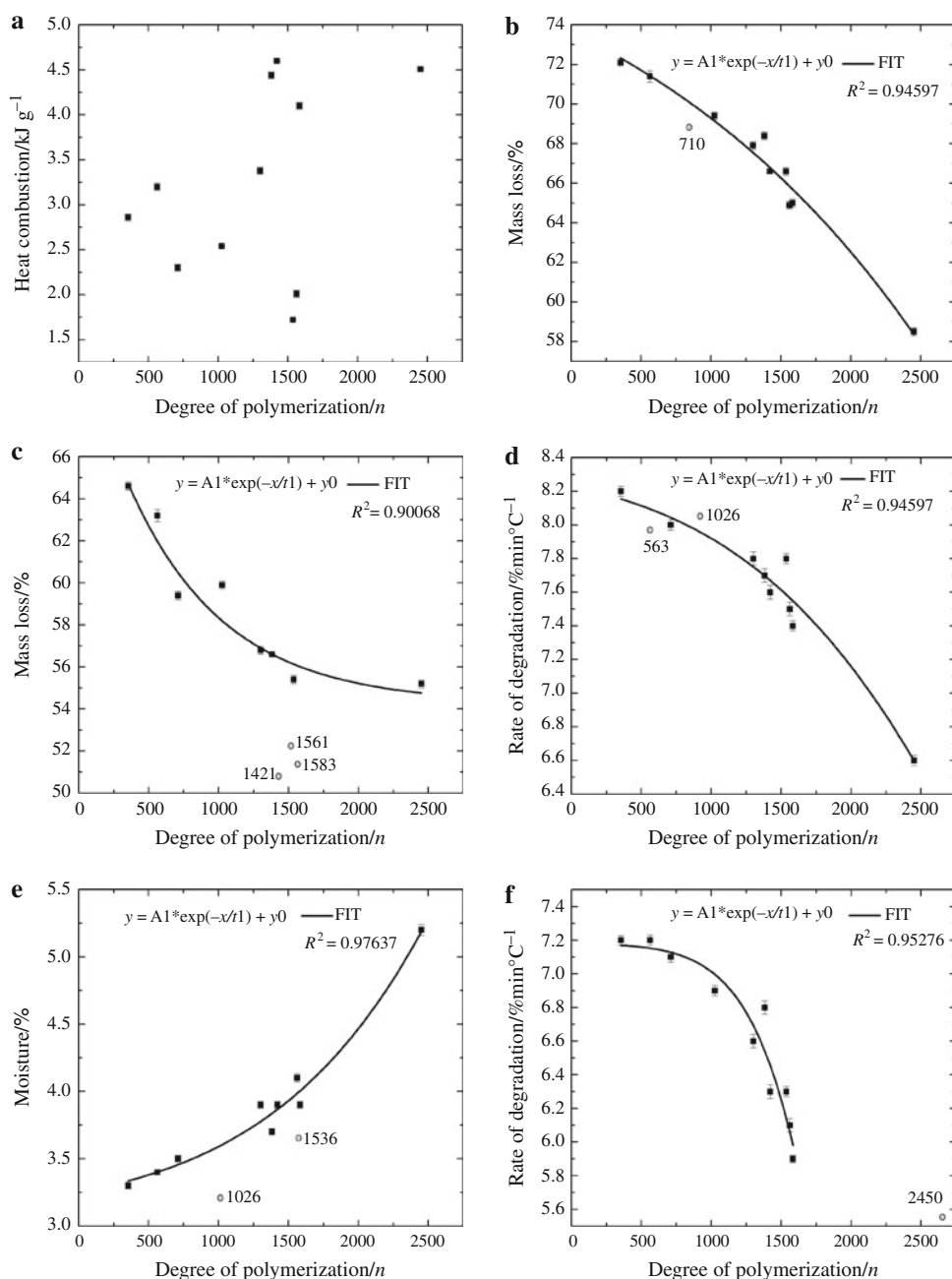
Correlation between DSC, TG results, and viscometry data

The results from TG thermal and thermo-oxidative degradations of cotton samples were used for correlation with their polymerization degree. Figure 3 shows examples of those correlations. Points which are not included into correlations are marked by their DP values. Correlation is fitted by the most suitable function and the equation is reported in the graph including the R^2 correlation coefficient.

Figure 3a shows no correlation between DSC effective combustion heat and DP. One of the reasons of this

observation can be the fact that DSC combustion enthalpies are always by 20–30% lower than the corresponding values obtained by isothermal calorimeters [14]. In contrast, as it can be seen in Fig. 3c, a correlation exists between DP and total mass loss in thermo-oxidative degradation experiments. Data points reported in Fig. 3c indicate at least three possible fitting curves while the one with highest correlation coefficient is reported. Other two options, ignoring the DP 2,450, are linear correlation coefficient $R^2 = 0.85$ and exponential decay resembling the dependency in Fig. 3b with correlation coefficient $R^2 = 0.77$. Comparison with results reported in Fig. 3b where the results from pyrolysis

experiments are reported indicates the difference in degradation mechanisms. In both cases, the higher DP is associated with mass loss but in a different way (i.e., different curve shape). Other examples of possible correlations between TG parameters and DP are reported in Fig. 3f, d. Here, the correlation between the DP and rate of thermo-oxidative and thermal degradation, respectively, are depicted. In this case, despite the mechanisms of degradation being different, the dependences on polymerization degree are similar.

Finally, very close correlation between moisture content and degree of polymerization is reported in Fig. 3e. As could be expected, the higher moisture content is associated with higher polymerization degree. In this case only DP = 1,026 is out of the range of the correlation.

Figures indicate weaker or stronger correlations between results from TG under different conditions and degree of polymerization and no connection with DSC results. It is noteworthy that dyed cotton samples fit well into the correlations and can be included into the possible prediction of DP. Further, also the sample of raw cotton material is in most cases part of correlation despite it is rather different properties. Nevertheless, it must be taken into account that reported equations can be considered only as a hint to push forward further effort to predict the degree of polymerization if specific results from TG measurements are known.

Conclusions

In this study, the degree of polymerization of cellulose was assessed by means of viscometry of 11 different cotton samples. Results were compared with results obtained by techniques of thermal analysis—DSC (thermo-oxidative degradation) and TG measurements (both thermal and thermo-oxidative degradations). This approach revealed relationship between degree of polymerization and some parameters of thermoanalytical-degradation which implies that thermal analysis can be used for the quick prediction of polymerization degree and potentially replace time consuming and demanding viscometry.

The results revealed some relatively close correlations between measured parameters, partially justifying the idea about relationship between results from thermal analysis and degree of polymerization. It is the task for the next study to collect higher number of cotton samples, confirm and extend conclusions given in this study.

The conclusions and observations are summarized in next paragraph.

- Washing and dying of cotton fibers have an important influence on decreasing of the polymerization degree.
- Effective combustion enthalpy showed no relationship with the degree of polymerization.

- Modified samples showed similar thermal and thermo-oxidative degradation mechanisms.
- Cotton wool showed completely different behavior in thermal properties and also different degradation profile (3 degradation steps instead of two) but despite this observation it fitted well in most of correlations.
- Colored cotton fibers showed different thermal properties in comparison with washed white samples but also in this case they fitted well into determined correlations.
- Some relationship, basically nonlinear, between degree of polymerization and results obtained from TG measurement were found.

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