Characterisation of cellulose degradation during accelerated ageing by SEC-MALS, SEC-DAD and A4F-MALS methods

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Abstract

During their ageing, paper-based information carriers are subject to degradation, depending on the nature of the paper itself and conditions under which they are stored. Determination of the degree of polymerisation (DP) of the cellulose is most frequently used to evaluate the state of degradation and degradation kinetics. Their alterations affect the loss of mechanical properties of paper. Currently the most frequently used method of determination of the cellulose DP is the size exclusion chromatography (SEC), applied either to derivatized cellulose in form of tricarbanilates (CTC) or non-derivatized cellulose in the solution of lithium chloride in dimethylacetamide (LiCl/DMAc) or to solution of lithium chloride in 1,3-dimethyl-2-imidazolidinone (LiCl/DMI). We have compared three methods of analysis of the cellulose isolated from paper which was subjected to accelerated ageing: size exclusion chromatography in combination with multi-angle light scattering (SEC-MALS) detection, size exclusion chromatography in combination with diode-array detector and calibration using polystyrene standards (SEC-DAD) and asymmetric flow field-flow fractionation in combination with multi-angle light scattering (A4F-MALS). Prior to separation, cellulose samples were derivatized with phenyl isocyanate to CTC and dissolved in tetrahydrofuran. Each of the used methods provides different absolute values of DP however pairwise correlations between them are linear with high correlation coefficients ($r = 0.990$ to 0.992). The highest DP values were obtained by the A4F-MALS method; SEC-MALS and SEC-DAD methods had lower values, especially due to shear degradation of high-molecular cellulose chains.

Keywords:

Cellulose; tricarbanilates (CTC); degree of polymerization (DP); size-exclusion chromatography (SEC); asymmetric flow field-flow fractionation (A4F); paper degradation.

Introduction

Paper as a traditional carrier of information is of high significance for preservation of a large part of our cultural heritage. Mechanical and optical parameters of paper deteriorate during the natural ageing of books, documents and other historical and artistic objects on paper-based carriers which gradually leads to the loss of utility properties. It is important to gain detailed knowledge of the processes accompanying ageing and related to the degradation of paper components through thorough examination in order to apply effective protection, develop methods for stabilisation and prolong the useful life of paper. In case of acidic wood-containing papers (especially from the second half of the 19th and 20th century) which cause serious problems with regard to their permanence and durability, there are several significant, mutually-related factors. The first is the nature of paper-making fibre, which contains in addition to the main component cellulose also hemicelluloses and lignin. Another is acidic environment in which acid hydrolysis of glycoside bond of polysaccharides that form the fibre structure occurs.

Depending on ageing conditions, there are several mechanisms of cellulose degradation (e.g. hydrolysis, oxidation) which take place either in parallel or in combination and which are directly related to the intensity of changes in the polymer structure and subsequently to the loss of utility properties, embrittlement or even decomposition of material. Ageing of paper results in the degradation of macromolecules of cellulose, hemicelluloses and lignin, increase of the share of low-molecular fractions and reduction of the average degree of polymerisation (Bansa 2002; Havermans 2002; Łojewski et al. 2011; Vizárová et al. 2012). These changes are relatively slow and methods of accelerated ageing under increased temperature, humidity, acidity, content of oxygen, emissions, various light conditions etc. are used to investigate them (Area and Cheradame 2011; Strlič et al. 2011; Tétreault et al. 2013).

The main factor that varies in course of the ageing of paper and that affects paper properties is the molecular weight and molecular weights distribution (MWD) of cellulose. One of the methods used to evaluate these changes is viscometry, which is simple and fast, but provides information only about the viscosity average of molecular weights (M_v). Using the size exclusion chromatography, (SEC) it is possible to determine various values of molecular weights: M_w – weight-average molecular weight (MW), M_n – number-average MW, M_z – z-average MW, M_{z+1} – z+1-average MW, M_v – viscosity-average MW, polydispersity ($PD=M_w/M_n$) and MWD, knowledge of which leads to a better understanding of the cellulose structure and degradation mechanisms in the process of cellulose ageing. SEC is currently used for examination of derivatized or non-derivatized cellulose. 8 % LiCl in dimethylacetamide (LiCl/DMAc) or in 1,3-dimethyl-2-imidazolidinone (LiCl/DMI) are used as solvents for non-derivatized cellulose, separation takes place in diluted solutions (0.5 %-1.0 % LiCl) in DMAc at the temperature of 60-80°C (Emsley et al. 2000; Dupont 2003; Yanagisawa et al. 2004; 2005). Free hydroxyl groups of cellulose are during derivatization substituted with phenyl isocyanates and formed cellulose tricarbanilate (CTC) is analysed in tetrahydrofuran at the temperature of 25-35°C (Valtasaari and Saarela 1975; Cao et al. 2012). These methods are generally believed not to degrade the cellulose, but certain changes in structure and loss of some fractions can occur during the process of dissolution or precipitation during derivatization, what in turn leads to incorrect determination of real molecular weights of the examined samples. Deviations from real values occur also at calibration of columns. Absolute values of molecular weights depend to a significant extent on the method of column calibration; especially narrow polystyrene fractions or pullulans are used. Values K and α in the Mark-Houwink equation ($[\eta] = KM^{\alpha}$) can significantly affect results of determination of molecular weights. This problem can be solved by means of the multi-angle light scattering (MALS). However, another source of inaccuracies occurs during the chromatographic separation, where shear degradation can occur, especially in case of high-molecular polymers. Side chains in high-molecular branched polymers can catch on pores of the column filling (so-called anchoring) and their retention time corresponds to much smaller hydrodynamic volume than the real one (Podzimek et al. 2001). The method of asymmetrical flow field-flow fractionation (A4F) can be used for the analysis of such polymers, because this method eliminates anchoring (and also shear degradation) occurring during SEC (Podzimek 2011).

Several authors compared various methods for determination of molecular weights of cellulose, especially for paper degraded in the ageing process (either natural or accelerated) and for papers used as electrical insulation in electric transformers (Jeong et al. 2014; Kes and Christensen 2013). Dupont and Mortha (2004) analysed pure cellulose (Whatman No. 1 filter paper) during accelerated ageing by viscometry in cadoxene, using SEC in LiCl/DMAc with MALS and DRI detection of SEC of cellulose tricarbanilates (CTC) with UV and LALS detection. The highest values of the degree of polymerisation were determined with the method SEC-LiCl/DMAc, lower values with the method SEC-CTC and the lowest using viscometry. Łojewski et al. (2010) found a good correlation between viscometry in cupriethylenediamine (CED) and SEC-CTC with MALS detection for pure cellulose as well as for softwood bleached cellulose. Łojewski et al. (2011) compared various SEC techniques (SEC-UV/VIS, SEC-MALS-UV/VIS) and methods for data evaluation in the analysis of cellulose tricarbanilates of several paper types. They found out that the presence of hemicelluloses negatively affects the determination of correct values of molecular weights and their distribution. Recently, a round robin test of cellulose SEC was performed for direct dissolution of non-derivatized cellulose and cellulose tricarbanilates using RI, MALS, and viscosimetry detectors. The weight-average molar mass obtained showed a variation of 36 % across all methods. The two major influencing parameters were sample preparation, i.e. derivatization and dissolution methods, and the type of molar mass evaluation in GPC, i.e.

through calibration or absolute measurements applying light scattering techniques (Potthast et al. 2015).

Even though many comparative studies and modifications of cellulose samples-preparation procedures and their analyses have been performed, the comparison of SEC and A4F methods on paper samples in the process of its accelerated ageing has not yet been done. Our aim was therefore to compare three methods of analysis of cellulose tricarbanilates isolated from acidic wood-containing paper subjected to accelerated ageing and to determine their suitability for the given type of polymers and their mutual correlations. Samples were analysed with methods of size exclusion chromatography in combination with multi-angle light scattering (SEC-MALS), size exclusion chromatography in combination with diode-array detector and calibration using polystyrene standards (SEC-DAD) and asymmetrical flow field-flow fractionation in combination with multi-angle light scattering (A4F-MALS).

Experimental

Materials and accelerated aging of samples

Newsprint paper (grammage planar density: 45 g/m, liquor pH: 4.5–5.0) containing mechanically bleached groundwood (55 %), bleached sulphite pulp (20 %), catch trash fibres (15 %) and clay (10 %) was aged according to ASTM D 6819-02 method. Samples were conditioned for 24 h at T = 23 ± 1°C, RH = 50 ± 2 % before accelerated ageing. Twenty papers (sheets of paper in A4 size format) were encapsulated inside sheets of PET/Al/PE film by sealing off all four edges completely. The bag of samples was put into the thermostat for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days at the temperature 98 ± 2°C.

Preparation of cellulose tricarbanilates (CTC)

Cellulose tricarbanilates (CTC) were prepared according to modified procedure described by various authors (Evans et al. 1989; Josefsson et al. 2001; Hubbell and Ragauskas 2010). Briefly, the cellulose samples were dried over silica gel for several days. Anhydrous pyridine (8.0 ml), cellulose (50 mg), and phenyl isocyanate (1.0 ml) were sealed in a 50-ml dropping flask and heated in an oil bath at 70°C for 72 h. At the end of the reaction, methanol (2.0 ml) was added to the mixture to eliminate the excess of phenyl isocyanate. The yellow solutions were then added dropwise into a rapidly magnetic stirring 7:3 methanol/water mixture (150 ml). The solids were collected by filtration and washed with 7:3 methanol/water mixtures (1 × 50 ml) followed by water (2 × 50 ml) to neutral reaction. The cellulose tricarbanilate was air dried overnight, then under vacuum at 50°C. For the size exclusion chromatography (SEC), CTCs were dissolved in tetrahydrofuran (THF) and filtered through a Puradisc 25 NYL filter, 0.45 µm (Whatman).

Analyses of samples

SEC-MALS. A set of liquid chromatograph (Waters Alliance 2695) with MALS detector DAWN EOS (Wyatt Technology Corporation) and differential refractometer (RI) (Waters 2414) were used for measurement. Separation was performed in 2 columns PLgel Mixed-C 5 µm 300 × 7,5 mm with THF as a mobile phase at flow rate 1 ml/min and 35°C. Samples were prepared in THF with concentration of 0.25 % w/v and dissolved for at least 24 h. Obtained solutions were filtered through a filter with size of pores 0.45 µm and injected volume was 100 µl. Data were recorded and processed with the program ASTRA 6 (Wyatt Technology). The MALS detector was coupled with online viscometer (VIS) for most analyses. The combination of detectors was in this case as follows: photometer HELEOS, viscometer ViscoStar and RI detector Optilab r-EX (all Wyatt Technology). Columns were the same as in the case of SEC-MALS. The combination SEC-MALS-VIS enables the determination of distribution and averages of internal viscosity and especially the determination of Mark-Houwink plot, which can be used for very sensitive detection and characterization of branching.

SEC-DAD. The second method of analysis was SEC in combination with the detection in the UV area. The system consisted of a quaternary pump, autosampler with thermostat and diode array detector (Agilent 1200 series). The separation was performed at 35 °C with THF at a flow rate of 1ml/min on two columns PLgel Mixed-B 10 µm (300 × 7.5 mm) preceded by PLgel 10 mm (7.5 × 50 mm) GUARD column (Polymer Laboratories). Columns were calibrated with series of polystyrene standards in the range of molecular weights from 162 to 6,035,000 (Agilent, Tosoh). The data from the detector were collected at 240 nm by the ChemStation software (Agilent Technologies) and calculated after data conversion into the Clarity GPC module (DataApex).

A4F. Some samples were analysed also by means of A4F. This method separates molecules according to their size, similarly as SEC. The advantage of A4F is that separation of molecules occurs by flow in empty channel, what eliminates undesirable phenomena related to the interaction of separated molecules with the filling of columns in SEC. Moreover, the separation occurs under pressure several times lower as compared to the SEC, what significantly reduces the possibility of shear degradation. Instrument Eclipse 3+ combined with MALS detector HELEOS and RI detector Optilab r-EX (all Wyatt Technology) were used for measurement. Thickness of channel was 490 μm, THF mobile phase with flow rate through the detector 1 ml/min (1.5 ml/min for sample 0) and gradient of cross flow from 3 to 0.15 ml/min during 15 min.

Results and discussion

Determination of absolute weight of cellulose depends on several factors and results of several works do not lead to unambiguous conclusions. Some authors found good correlation between viscometry and SEC of cellulose tricarbanilates (Valtasaari and Saarela 1975; Danhelka et al. 1976), others found significant difference between these methods (Dupont and Mortha 2004; Pala et al. 2007). Different values were obtained using SEC of non-derivatized cellulose in DMAc/LiCl and tricarbanilates of cellulose in THF (Dupont 2003; Dupont and Mortha 2004). Impact of cellulose derivatization on tricarbanilates as well as of solving of non-derivatized cellulose in DMAc/LiCl on changes of molecular weight are discussed in detail in several works and conclusions are again ambiguous (Danhelka et al. 1976; Wood et al. 1986; Potthast et al. 2002; Sjöholm 2004; Henniges et al. 2014).

We obtained differing results using various techniques of separation and methods for determination of molecular weights of cellulose in samples of paper that was subjected to accelerated ageing (Table 1-3).

TABLE 1

TABLE 2

TABLE 3

The highest values of DP_w were obtained with the method A4F-MALS, lower values with the method SEC-MALS and the lowest with the method SEC-DAD. DP_w values were for original samples prior to accelerated ageing for SEC-MALS by 10 % and for SEC-DAD by 19 % lower as compared to the value obtained with A4F-MALS. Differences between two SEC methods can be explained by used methods for MW determination. MALS provides absolute values and obtained data can be deemed real values of molecular weights obtained by SEC separation. Resulting values of procedures using calibration by means of standards for MW determination depend on the type of standards and coefficients K and α used in the Mark-

Houwink equation. Polystyrenes with narrow polydispersity and various coefficients K and α are most frequently used for calibration in separation of cellulose tricarbanilates in tetrahydrofuran (Kačík et al. 2009; Łojewski et al. 2011). Differences in molecular weights between the separation A4F and SEC can be explained by the fact that in the case of SEC of branched polymers (used samples contained also hemicelluloses) these polymers are anchored and some molecules of the branched polymer are caught on particles of the column filling and exit it upon larger retention volume than would correspond to them according to their molecular weight. This can cause decrease of molecular weights determined with the SEC method (Podzimek 2001; 2014). Another reason can be the shear degradation of high-molecular chains, which occurs during SEC separation, but not during A4F. At shear degradation, the polymer chain can break into smaller pieces. Shear degradation lowers the molar mass of a polymer chain significantly. The molar mass average values such as M_w and M_n will be smaller and the polydispersity index will increase (Hofe et al. 2011).

There are several methods of expression used for the description of changes of the degree of polymerisation of cellulose during the accelerated ageing, e.g. DP = f(t), 1/DP = f(t), DP_0/DP-1 (scissions per chain), 1/DP-1/DP_0 (scissions per monomer), 1-DP/DP_0. Advantages and disadvantages of these relations are discussed in detail by Calvini (2014). Results of all methods show similar trends of DP changes (of molecular weights) – rapid decrease during first days of accelerated ageing, later slowing down of the degradation process, which approaches the limit value, the so-called levelling-off degree of polymerisation (LODP) (Fig. 1). This trend is known from several works and can be explained by the presence of weak glycoside bonds, which are susceptible to hydrolysis. Those are especially bonds in the presence of electrophilic substituents (e.g. carboxyl and carbonyl groups), which due to the induction effect activate the adjacent bond for hydrolytic reactions (Fengel and Wegener 2003). Cellulose polymer is formed by amorphous and crystalline areas together with weak bonds (Calvini et al. 2008). Some authors questioned the concept of weak bonds, but in some sample types (e.g. with high content of hemicelluloses) it can well help to explain the kinetics of degradation at the beginning of the accelerated ageing (Calvini 2014).

FIG. 1

Both SEC methods show faster reduction of DP than the A4F method, what can be explained by anchoring of branched polymers in pores of the column filling, what results in the increase of retention volume of molecules with higher hydrodynamic volume and towards smaller calculated values of DP.

Observation of the number of scissions in the cellulose chain (Fig. 2) shows that the highest values are provided by the method SEC-MALS, lowest by the method SEC-DAD due to used calibration of columns with polystyrenes, what causes different DP values.

FIG. 2

Used methods for determination of the distribution of molecular weights differ in the separation principle (SEC and A4F) as well as detection and calculation of values of molecular weights (MALS and DAD). It is therefore not surprising that every method gives differing absolute values of determined parameters. The nature of analysed samples also affects resulting values. In the case of SEC, linear chains of pure cellulose will behave differently than branched chains of present hemicelluloses, which were isolated from paper. Anchoring of part of branched chains can be expected for such samples, which are eluted from the column with higher retention times and thereby affect determined values of molecular weights. Values determined with the SEC-DAD method depend especially on used coefficients K and α in the Mark-Houwink equation. However, despite all mentioned differences between individual examined methods it can be established on the base of mutual comparison of DP values that they give mutually comparable results (Fig. 3-5) and can be used for the evaluation of kinetics of cellulose degradation in the process of accelerated ageing of paper.

FIG. 3

FIG. 4

FIG. 5

Conclusions

Our aim was to compare three methods of analysis of tricarbanilates of cellulose isolated from acidic wood-containing paper subjected to accelerated ageing and to determine their suitability for the given type of polymers (evaluation of the kinetics of degradation) and their mutual correlations. Samples were analysed with methods of size exclusion chromatography in combination with multi-angle light scattering (SEC-MALS), size exclusion chromatography in combination with diode-array detector and calibration using polystyrene standards (SEC-DAD) and asymmetrical flow field-flow fractionation in combination with multi-angle light scattering (A4F-MALS).

Results confirm that various methods provide different absolute values of the cellulose degree of polymerisation (DP), but mutual correlations between individual methods are linear with high correlation coefficients (r = 0.990 to 0.992). That means that any of tested methods can be used for the determination of DP when monitoring changes of cellulose during various treatments of lignocellulose materials. The highest values are given by the A4F-MALS method; lower values were obtained with SEC-MALS and SEC-DAD methods, mainly due to shear degradation of high-molecular chains of cellulose. These findings are important especially for the study of changes of molecular properties of plant fibrous materials containing in addition to cellulose also hemicelluloses.

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