CELLULOSE CHEMISTRY AND TECHNOLOGY

CHANGES IN NEWSPRINT PAPER DURING ACCELERATED AGEING

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Degradation of cellulose is an important factor influencing its physical, mechanical, optical and chemical properties, as well as paper longevity in electrical industry and in stored paper and books. Accelerated ageing of newsprint paper has been performed at 98 °C, for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days. Degradation has been studied by viscometry, gel permeation chromatography (GPC), and determination of tensile strength, brittleness index, folding endurance, surface pH, cold extract pH, colour of paper surface and amount of saccharides. In the first stages of accelerated ageing, cellulose depolymerization takes place homogeneously (as mainly due to hydrolysis), after which other reactions (such as oxidation, crosslinking) occur. The amount of saccharides in paper decreases, the hemicelluloses being degraded faster. Tensile strength and folding endurance decrease. The colour of the surface changes rapidly from light to dark, while lightness decreases and the chromaticity parameters increase. The pH values decrease, while surface pH decreases less than the cold extract pH.

Keywords: paper ageing, cellulose, viscometry, gel permeation chromatography, tricarbanilates, tensile strength, brittleness index, folding endurance

INTRODUCTION

Cellulose, the most abundant natural polymer on Earth, is a very important renewable organic material. It is a linear polymer of β-D-glucose in pyranose form, linked together by 1,4-glycosidic bonds. The study of cellulose-based paper degradation is important especially for archives and museums, where ageing under various conditions reduces the mechanical properties and deteriorates the optical quality of stored papers, books and other artefacts. The low rate of paper degradation requires the application of accelerated ageing tests, involving increasing changes in the paper properties, usually at different values of temperature, humidity, oxygen content and acidity, respectively. The ageing tests are used in studies on the rate and mechanism of degradation. During the degradation process, two main reactions prevail – hydrolysis of glycosidic bonds and oxidation of glucopyranose rings. As a result of some oxidation processes, keto- and aldehyde groups are formed. These groups are highly reactive, being prone to crosslinking, which is the third chemical process of cellulose decay.[1,2]

Many important properties of cellulose depend primarily on their molecular weight and molecular weight distribution (MWD). At present, mainly three GPC methods are used for determining cellulose MWD: GPC of cellulose tricarbanilates (CTC), GPC of the underivatised cellulose dissolved in a solution of lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) or of lithium chloride/1,3-dimethyl-2-imidazolidinone (LiCl/DMI). The excellent properties of tricarbanilates for the structural analysis of cellulose and starch were discussed for the first time by Burchard and Husemann.[3] This method is often used[4-15] on cellulose GPC.

The most widely used method nowadays is the GPC of underivatised cellulose in a LiCl/DMAc solution.[11,16-22] An effective solvent system for the GPC of cellulose is the LiCl/DMI one.[23-28] Different results were obtained when comparing the molecular weights by viscometry and various GPC methods of cellulose tricarbanilates. Some authors describe the good correlation between the results obtained by viscometry and GPC of cellulose tricarbanilates,[5,6] while other papers evidence considerable differences between these methods.[11,16]

For explaining the degradation mechanism, many authors analysed pure cellulose and/or pulps during accelerated ageing of paper, less attention being paid to real paper accelerated ageing. The present investigation provides information on the alteration of newsprint paper during accelerated ageing by viscometry, gel permeation chromatography and carbohydrate analysis, determination of tensile strength, brittleness index, folding endurance, cold extract pH, surface pH and colour of paper surface.

EXPERIMENTAL

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

Tensile strength was determined according to the TAPPI test Method T494 om-88, and folding endurance - according to TAPPI T511 om-88. Besides the standard tensile properties, the brittleness index (BI) was determined from a stress-strain curve.[9] Surface pH was measured according to TAPPI T 529 om-88 (the pH of the paper surface using a flat combined glass electrode) and the cold extract pH was measured according to TAPPI T 509 om-02 (cold extraction, 1 g of sample per 70 mL of water, 1 h).

The precision of pH determinations for cold extract and surface pH – measured on five locations for each specimen – are estimated as < ±0.2, the average value being also calculated. Changes in the colour of paper surfaces due to ageing were measured on an ELREPHO DATACOLOR 2000 model colour measuring system. The color space expressed by the CIE Lab System was specified by the International Commission on Illumination – CIE (Commission Internationale d'Eclairage) – in 1976, where L represents a type of "psychometric brightness" (or lightness). In other words, this parameter is defined by the appropriate function of a psycho-physical value (a colour value) selected in such a way that uniform steps on the scale will reproduce as closely as possible the uniform differences – which are related in terms of lightness – between colours. The values of L range between 0 for black and 100 for white, while a* describes the red-green axis. The negative values are green, the positive ones are red. b* describes the yellow-blue axis. The negative values are blue, the positive ones are yellow. The L, a* and b* parameters were measured on five locations for each specimen, and the average value was calculated.

Viscometry measurements were done in a water bath at 20 °C using an Ubbelohde glass viscometer type UIa with a 0.836 mm diameter and constant A = 0.03129 mm^2.s^{-2}. Five viscosity measurements were carried out for each sample, and the efflux time values were averaged. Cellulose was dissolved in an iron (III) sodium tartarate complex (EWNN, FeTNa) solution, the limiting viscosity number being calculated according to ISO 5351/2-1981. The degree of polymerisation (DP) was calculated with the equation:[29]

$$DP = [\eta]/8.14.10^{-4}$$

Cellulose tricarbanilates were prepared by adding 1 mL of phenylisocyanate (Merck) to 20 mg of dry sample in 6 mL of dry pyridine (Merck), the mixture being heated for 6 h at 110 °C. The resulting clear yellow viscous solution was cooled, and the excess of phenylisocyanate was decomposed by adding 2 mL of methanol and then slowly pouring it into 150 mL of rapidly stirred methanol (Merck). The precipitate was first washed with water containing acetic acid to remove the pyridine, then with water and methanol, and finally dried at 50 °C in a vacuum oven. The white fibrous precipitate was dissolved in dioxane (Merck) and precipitated by pouring the solution in water. The precipitate was first washed with water, then with methanol and finally dried at 50 °C in a vacuum oven. A second precipitation from the dioxane solution into water gives a pure trimester, complete substitution being indicated by a nitrogen content of 8.09%. Carbanilates can be considered[30] as tri-substituted when DS ≥ 2.8, after which the nitrogen content of tricarbanilates of pure cellulose was determined by elemental analysis, using a FLASH EA 1112 equipment (Thermo Finnigan) as 8.08% (DS = 3).

For gel permeation chromatography analyses, the cellulose tricarbanilates (CTC) were dissolved in tetrahydrofuran (THF) (Merck) and filtered through a Puradisc 25 NYL filter (Whatman) with a pore size of 0.45 µm. GPC analysis has been carried out on a system consisting of a manual injector (model 7125, Rheodyne) with a 10 µL loop, L-6200A pump (Hitachi), column thermostate L-5025 (Merck), L-4255 diode array detector (Merck-Hitachi) working at 240 nm. Separation was performed at 35 °C with THF, at a flow rate of 1 mL.min^{-1} on a PLgel 10 µm (7.5 x 300 mm) MIXED B column (Polymer

Laboratories), proceeded by a PLgel 10 µm (7.5 x 50 mm) GUARD column (Polymer Laboratories). The injection volume of CTC was of 5 µL and sample concentration – 2 mg.mL^{-1}. Data acquisition was carried out with a HPLC software manager HSM (Hitachi) and the calculation with a Clarity GPC module (DataApex). The system was calibrated with polystyrene standards with weight-average MW in the 500-6035000 range (Polymer Laboratories, Tosoh). A universal calibration for the determination of molecular weights was used[5] with constants $K = 2.01 \times 10^{-3}$, $\alpha = 0.92$. The values of DP were calculated by dividing molecular weight by the monomer equivalent weight of cellulose tricarbanilate (DP = M/519).

The neutral carbohydrate composition of unaged and aged papers was determined after acid hydrolysis.[31] After derivatisation to aldonitrilacetates, they were analysed by gas chromatography using inositol as an internal standard. Separation was performed on a capillary column DB-5, 30 m x 0.32 mm ID, film thickness of 0.25 µm. The injector and detector temperature was of 250 °C, temperature programme: 175 °C for 4 min, followed by gradient at 4 °C.min^{-1} to 225 °C; helium was used as a carrier gas.

RESULTS AND DISCUSSION

During accelerated ageing of paper, alterations in molecular weight distributions (MWD) of cellulose tricarbanilates take place (Figs. 1, 2). The MWD of the unaged sample shows the presence of two components. One component, at a lower elution volume or high molecular weight, is due to cellulose (DP ≈ 1660), while the shoulder on the curve is due to hemicelluloses (DP ≈ 290), which agrees with the results of Sjöholm *et al.*[17] They found out that the high molecular portions consisted mainly of polysaccharides of glucosic type, while in the low molecular portions, xylose, arabinose, manose and galactose were present, but no glucose. During ageing, the high molecular peak was shifted towards lower values of molar mass.

Figure 3 shows the coefficients of correlation between any pair of individual measurement data, such as time of ageing, DP, molecular weights, parameters of polydispersity and other solution parameters, and depicts their evolution.

A good correlation was observed between the time of accelerated ageing (τ) and M_{z+1}/M_w ($R^2 = 0.88$) and, to a lesser extent, between τ and M_z/M_w (0.86), M_n (0.81). The values for τ are poorly correlated with the (PD), M_p, M_{z+1}, M_z, M_w, DP_w and M_v polydispersity parameters. The correlation between τ and all other characteristics was also evaluated ($R^2 < 0.57$).

As known, some of the kinetic dependencies of the properties are linear, while others are nonlinear. The most similar kinetic curves to DP = f(t), Mn = f(t) are the kinetic functions of:

1. tensile strength: $l_t = 3669 - 55.3.\,\tau$; $R^2 = 0.91$
2. folding endurance: $\omega = 1662.e^{-0.356.\tau}$; $R^2 = 0.99$
3. brittleness index: $Bi = 0.96 - 0.43.e^{-0.09.\,\tau}$; $R^2 = 0.93$
4. CIE Lab optical parameters: $L = 58.4 + 28.9.e^{-0.03.\,\tau}$; $R^2 = 0.99$; $a = 8.8 - 8.9.e^{-0.04.\,\tau}$; $R^2 = 0.95$;
   $b = 23 - 16.1.e^{-0.13.\,\tau}$; $R^2 = 0.90$
5. pH: surface pH = $4.9 + 0.9.e^{-0.32.\tau}$; $R^2 = 0.92$; cold extract pH = $3.6 + 1.8.e^{-0.26.\tau}$; $R^2 = 0.86$.

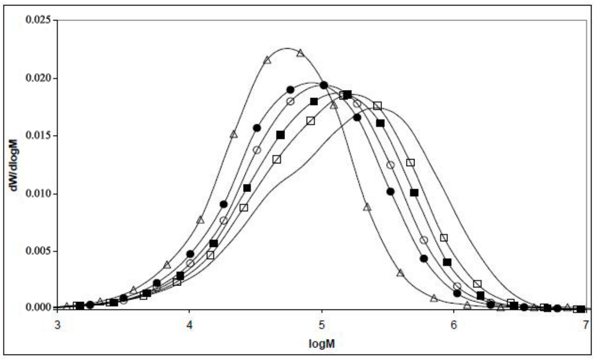

Figure 1: Molecular weight distributions of tricarbanilates of accelerated aged newsprint paper at 0, 2, 5, 10, 20 and 60 da..ys (— 0; □ 2; ■ 5; ○10; ● 20; Δ 60)

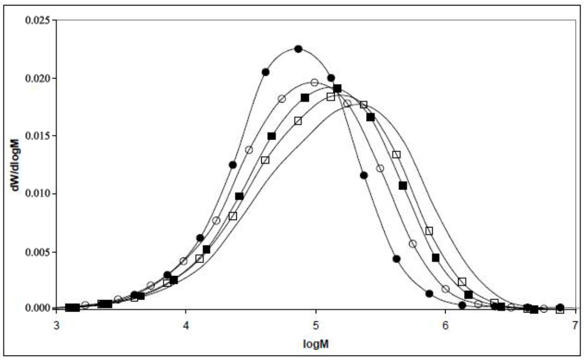

Figure 2: Molecular weight distributions of tricarbanilates of accelerated aged newsprint paper at 1, 3, 7, 15 and 30 days (— 0; □ 2; ■ 5; ○10; ● 20; Δ 60)

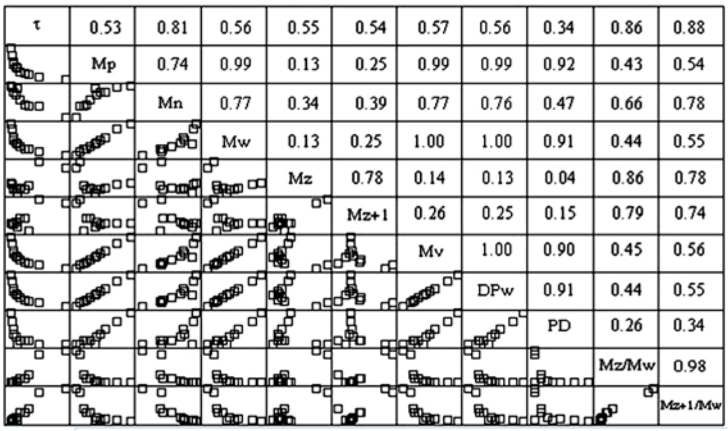

Figure 3: Correlation between each pair of variables. The regression coefficients (R^2) represent the quality of the linear relationship between the variables: τ = time of accelerated ageing

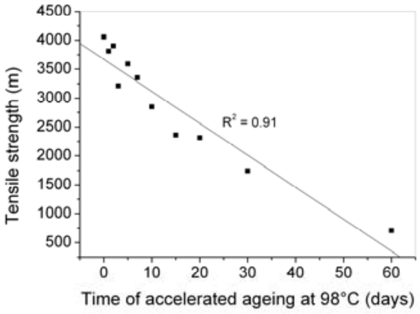

Figure 4: Influence of accelerated ageing on tensile strength at 98 °C

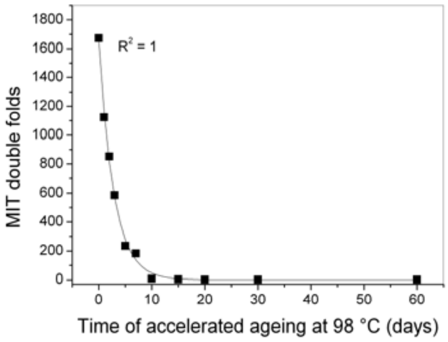

Figure 5: Loss of folding endurance (MIT double folds) under accelerated ageing at 98 °C

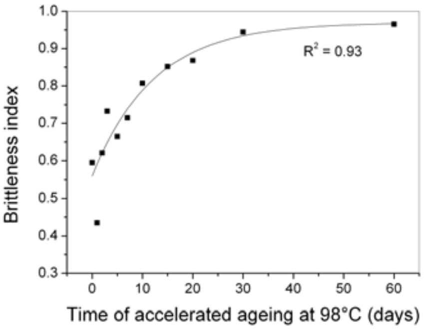

Figure 6: Influence of accelerated ageing on brittleness index at 98 °C

The influence of accelerated ageing on tensile strength is illustrated in Figure 4, showing that tensile strength decreases during accelerated ageing from 4057 m at 0 days to 708 m at 60 days, the corresponding correlation coefficient being $R^2 = 0.91$. The loss of folding endurance (MIT double folds, load – 0.3 kg) under accelerated ageing at 98 °C is shown in Figure 5. The correlation coefficient, R^2, approached 1. The brittleness index was calculated from the stress-strain curves of the aged samples. The effect of accelerated ageing at 98 °C on the brittleness index is illustrated in Figure 6. The influence of accelerated ageing at 98 °C on the CIE Lab parameters is shown in Figures 7(a), (b) and (c), respectively. When exposed to accelerated ageing, the surface colour changes rapidly from light to dark, as indicated by the decreasing value of lightness (L) and by the increased chromaticity parameters a* and b* upon ageing. After 60 days of ageing at 98 °C, the L* value decreases from 87.56 to 58.36, while the chromaticity parameter a* increases from -0.3 to 8.8, and b* from 5.35 to 23.37.

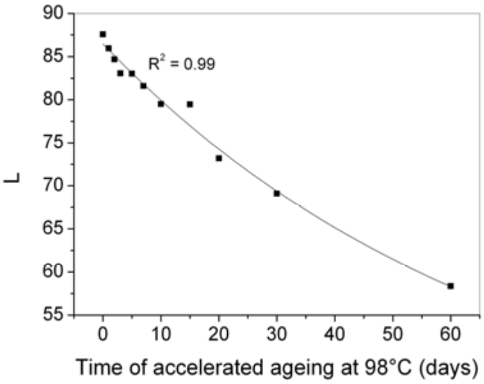

Figure 7a: Influence of accelerated ageing on lightness (L) at 98 °C

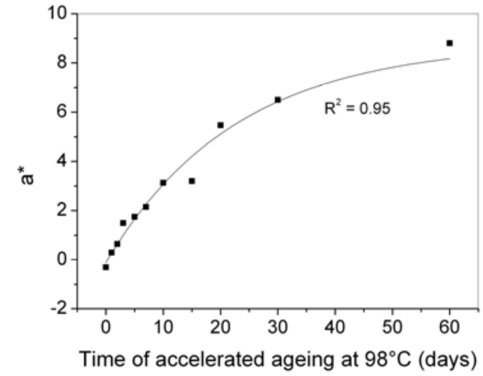

Figure 7b: Influence of accelerated ageing on a* coordinates at 98 °C

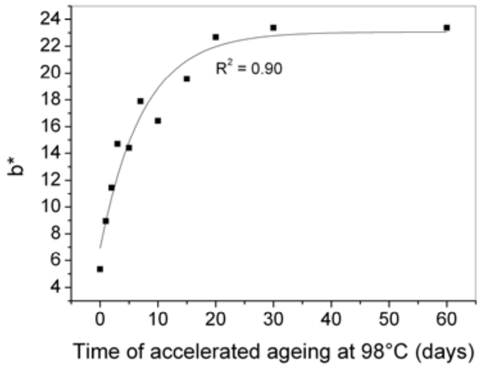

Figure 7c: Influence of accelerated ageing on b* coordinates at 98 °C

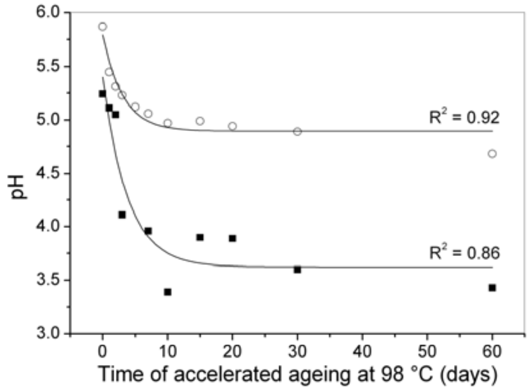

Figure 8: Influence of accelerated ageing on the surface and cold extract pH at 98 °C (○ – Surface pH; ● – Cold extract pH)

Figure 8 shows that the observed surface pH and cold extract pH decrease with the time of ageing. Under accelerated ageing at a temperature of 98 °C, a smaller decrease of surface pH, comparatively with the cold extract pH, was achieved.

Some papers evidenced the correlation between DP and the strength properties of paper, respectively cellulose.[12,13] The determination of the absolute value of molecular weight is questionable and the obtained results differ. Viscometric determination of DP on cellulose after accelerated ageing is, from approximately 1000 for unaged samples, up to a value of 200, the so-called LODP (levelling-off degree of polymerisation). Valtasaari, Saarela,[5] Daňhelka *et al.*[6] found out a good agreement between the DP determined by viscometry and GPC tricarbanilates of cellulose, even if markedly higher values of DP were obtained[11,14,19] by GPS than by viscometry. In this work, a good agreement was found between viscometry and the GPC of tricarbanilates, the GPC values being slightly higher.

Dupont and Mortha[11] found out that the GPC of cellulose in LiCl/DMAc provided the highest M_r averages values, followed by the GPC of CTC, while viscometry yielded the lowest values. The differences between the two GPC methods are explained by several hypotheses, involving cellulose degradation upon derivatisation to CTC and aggregation on cellulose solving in a LiCl/DMAc solution. Dupont and Mortha[12] described cellulose degradation during carbanilation; on the other hand, El Ashmawy *et al.*,[4] Valtasaari, Saarela,[5] Daňhelka *et al.*,[6] Lauriol *et al.*,[7] did not confirm degradation upon derivatisation.

The constant ratio of the average degree of polymerization (DP_z/DP_w) indicates the homogeneity of depolymerisation.[9] In our case, the ratio remains fairly constant up to 15 days of ageing (Table 1). During this period, depolymerisation proceeds randomly, without preferential breakdown of the longest cellulosic chains. In this stage of ageing, the hydrolysis of the glycosidic bonds is dominant, further on the ratio of (DP_z/DP_w) and mainly (DP_z + $1/DP_w$)

increasing (Table 1), which indicates the course of different types of reactions, *e.g.* oxidation and cross-linking. Saccharide yields decrease only slightly in the first days of ageing, their subsequent decrease being probably caused by oxidation reactions. The decrease of the hemicelluloses-to-glucose ratio (Table 2) is due to a more rapid oxidation in hemicelluloses, comparatively with cellulose.

Table 1
GPC results of aged paper

Ageing (days)	M_p	M_n	M_w	M_z	M_{z+1}	M_v	DP_w	PD	M_z/M_w	M_{z+1}/M_w
0	90864	16037	115388	332755	638372	112141	712	7.20	2.88	5.89
1	72309	15743	101581	312469	680272	98679	627	6.45	3.08	6.70
2	57543	14466	82578	267543	683252	80243	510	5.71	3.24	8.27
3	51333	14615	76841	238981	597450	74728	474	5.26	3.11	7.78
5	45793	14023	70432	249726	776572	68407	435	5.02	3.55	11.03
7	43251	15517	67217	192275	429132	65484	415	4.33	2.86	6.38
10	36442	12980	60695	265457	1066449	58838	375	4.68	4.37	17.57
15	32508	11803	55010	236613	1001280	53363	340	4.66	4.30	18.20
20	29000	11451	53118	289521	1237708	51331	328	4.64	5.45	23.30
30	24512	11570	49776	628625	2380852	47444	307	4.30	12.63	47.83
60	19445	9137	39785	544418	2085043	37865	246	4.35	13.68	52.41

M_p = molecular weight (m.w.) at peak maximum; M_n = m.w. number average; M_w = m.w. weight average; M_z = m.w. z average; M_{z+1} = m.w. z+1 average; M_v = m.w. viscosity average; DP = degree of polymerisation; PD (polydispersity) = M_w/M_n

Table 2
Results of monosaccharide determination in accelerated aged paper (%)

Ageing (days)	Rha	Ara	Xyl	Man	Glc	Total	Hemi/Glc
0	0.05	1.06	3.50	7.37	58.05	70.03	0.21
1	0.07	0.83	3.61	7.17	57.74	69.42	0.20
2	0.06	0.69	3.79	7.05	57.53	69.12	0.20
3	0.09	0.69	3.71	7.37	57.32	69.17	0.21
5	0.07	0.66	3.64	6.81	56.97	68.15	0.20
7	0.13	0.63	3.42	6.71	56.40	67.28	0.19
10	0.09	0.59	3.60	6.11	55.72	66.11	0.19
15	0.09	0.50	3.32	6.01	56.43	66.35	0.18
20	0.12	0.49	2.91	5.62	53.87	63.01	0.17
30	0.10	0.34	1.07	2.82	32.26	36.58	0.13
60	0.09	0.31	0.13	0.14	15.13	15.79	0.04

Hemi = Rha + Ara + Xyl + Man

The relatively high value of polydispersity of the unaged sample (PD = 7.20) is due to hemicelluloses, as confirmed by the bimodal form of the MWD curve. Polydispersity decreases in the first days of accelerated ageing, because of the cleavage of the long chains to shorter ones, after which the values are almost constant. The low molecular degradation products, which can increase polydispersity, are degraded on tricarbanilates preparation, having no influence on MWD, which agrees with the idea that low-M_r cellulose may be lost during the precipitation step with methanol or ethanol.[19] The manner of cellulose degradation influences polydispersity alteration. Emsley *et al.*[32] found out that polydispersity slightly increases during cotton linters ageing at 120, 140 and 160 °C. The decrease of polydispersity was observed in chemically irradiated and enzymatically treated celluloses.[33]

CONCLUSIONS

The experimental results obtained during accelerated ageing of newsprint paper permit the following conclusions:

- in the first stages of accelerated ageing, the decrease of DP is rapid, after which it gets slower,
- in the beginning, degradation takes place homogeneously (hydrolysis being the dominant process), later on, other types of reactions (oxidation, crosslinking) occur,
- during accelerated ageing, saccharide yields decrease in paper, hemicelluloses being predominantly degraded,
- a linear relationship and a good correlation are found between the time of accelerated ageing and the M_{z+1}/M_w and M_z/M_w of cellulose,
- tensile strength and folding endurance decrease with the time of ageing,
- lightness decreases, while the chromaticity parameters increase,
- surface pH and cold extract pH values decrease.

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