Evaluating paper degradation progress. Cross-linking between chromatographic, spectroscopic and chemical results

**Tomasz Łojewski · Katarzyna Zięba ·
Arkadiusz Knapik · Jacek Bagniuk · Anna Lubańska ·
Joanna Łojewska**

Abstract The study presents an overview of the chromatographic (SEC), spectroscopic (FTIR, UV/VIS), viscometric (DP) and chemical methods (titration, pH) used for the evaluation of the degradation progress of various kinds of paper under various conditions. The methods were chosen to follow different routes of paper degradation. Model paper samples represented boundary paper types from pure cellulose cotton paper, through softwood to low quality acidic, sized groundwood paper The accelerated ageing conditions were adjusted to achieve maximum effect (climatic chamber RH 59%, 90ºC) and also to mimic the environment inside books (closed vials). The results were settled on the literature data on the degradation mechanisms and compared in terms of the paper types and ageing conditions. The estimators of coupled de-polymerisation and oxidation have been proposed based on the correlation between SEC, UV/VIS and titrative coppper number determination. The overall oxidation index derived from FTIR results was shown to correlate with the summary –CHO and –COOH concentration determined by titrative methods.

1 Introduction

For around 2000 years till now paper has been the main information carrier, however, the addition of alum in a new technology utilizing cheap groundwood introduced around 1850 brought about the dramatic destabilization of cellulose by acidic hydrolysis. The concern of conservators and chemists has been to rescue those collections of historical or archival value, which have not been completely digested by acid catalyzed degradation. As a result, mass deacidification programmes have been launched in libraries in various countries. One of the tasks stated for the researchers of material science and paper conservation is to provide quick and reliable analytical tools for the assessment of the current degradation state of paper. It is important not only for decision making upon a suitable treatment but also in controlling its quality and long-term consequences. The practical requirement for the methods to consider for historical samples is, however, their low invasiveness and destructivity. Since paper is a complex multi-component material, the assessment we talk about is practically impossible without looking into the mechanism responsible for degradation of particular paper type during its storage. For this reason, the consideration of the analytical methods in this work is coupled with the mechanistic approach to paper degradation thus making their selection not purely practical.

Considering degradation mechanism we should take into account spontaneous changes of cellulose (crystallization) and those induced by the environment both internal (additives and degradation products present in paper) and external (atmosphere, temperature). The internal environment may include either aluminium sulphate in acidic papers or magnesium oxides or carbonates in deacidified papers as well as other paper components such as lignin, hemicellulose, fillers and sizing agents. The external environment in general means gaseous atmosphere (oxygen, water vapour, pollutants as NO_2, SO_2, O_3, VOC). This classification is a hint for the choice of the samples and the ageing conditions

T. Łojewski · K. Zięba · A. Knapik · J. Bagniuk · J. Łojewska (✉)
Faculty of Chemistry, Jagiellonian University, Ingardena 3,
30-060 Kraków, Poland
e-mail: lojewska@chemia.uj.edu.pl
Fax: +48-12-6340515

A. Lubańska
Institute of Catalysis and Surface Chemistry, Polish Academy
of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

Table 1 Summary of degradation products of cellulose

Degradation reaction	Catalysing environment	Light sideproducts	Measurable property
Hydrolysis	Acidic	Glucose	DP
	Alkaline	1,6 anhydro β, D glucopyranose	Molecular mass
		Levoglucosan	–CHO end groups
Oxidation	Alkaline	Gluconic acid	DP
		Mannonic acid	Molecular mass
		Arabinonic acid	–CO
	Acidic or alkaline	Aldonic acid	–CHO
		2-methyl 2 carboxy β, D furanosides	–COOH
		Furanosidic acid	Acidity
		Gluconic acid	Gases evolved
End-wise de-polymerisation	Alkaline	Isosaccharinic acid	DP
		Metasaccharinic acid	Molecular mass
		Lactic acid	–CHO end groups
		2-C methylglyceric acid	Gases evolved
Dehydration and condensation	Acidic	Furfural	DP
		5-hydroxymethyl-2-furaldehyde	Molecular mass
		Levulinic acid	C=C
		Acetic acid	Gases evolved
		Formic acid	
		Phenoles	

Fig. 1 Reaction scheme for hydrolysis and oxidation of cellulose
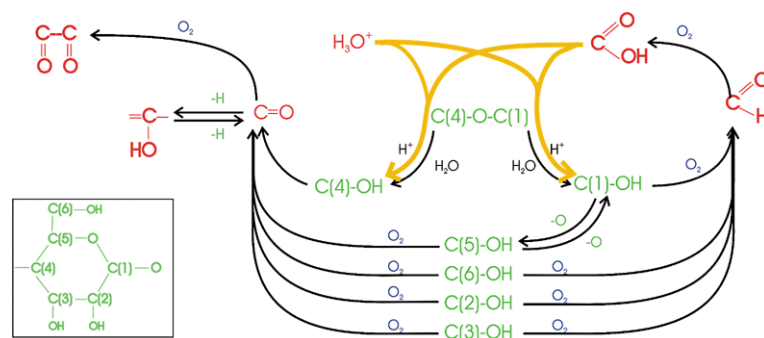
for the study of the paper degradation. The recrystallization which prevents an access of substrates (gases and water) to cellulose chains or, more precisely, to the reaction active centres on cellulose can be treated as a background in which chemical deterioration of the material comes out as shown in the models of degradation proposed by Emsley [1] and Calvini [2].

Independently of paper material complexity, the two principal chemical pathways in degradation are hydrolysis and oxidation [3–5]. The summary of the main reactions for cellulose to occur during natural ageing is presented in Table 1 and Fig. 1 based on our own results [6–10] and the book chapter [11].

For acidic papers at ambient conditions without excess of heat or light, oxidation proceeds slowly, while hydrolysis runs fast due to catalytic effect of hydronium cations. A typical trend for them is that in their initial stage the rates are higher than in the advanced ageing, which can be accounted for the exploitation of the amorphous regions in cellulose. For hydrolysis, the fact is signified by the so-called level off the degree of polymerisation (LODP) [2, 11].

The mechanism of acidic hydrolysis is well settled in the literature [11]. Oxidation running through radical mechanism initiated by active oxygen species (O, $O_2\cdot$)[12] is a much more complex process than hydrolysis (Fig. 1). In fact, the most widespread knowledge concerns cellulose in

water suspensions [11, 13] while the literature data on the oxidation mechanism during natural and accelerated ageing is rather scarce [2, 7, 10, 12, 14, 15]. In acidic and neutral media, oxidation of cellulose can be launched on the hydroxyl groups on C(2), C(3) and C(6) atoms in a glucopyranose unit (Fig. 1). The oxidation initiated through the formation of hydroperoxides [14] propagates through consecutive and parallel paths [7, 9] leading to the formation of various carbonyl groups, starting from ketones on C(2) and C(3), turning into conjugated diketones or starting from aldehydes and to carboxyls on C(6) carbon atoms of glucopyranose. To a lesser extent active oxygen species may also attack directly C(1) atom leading to the oxidative glycosidic bond cleavage. Hydrolysis and oxidation are entangled together exerting a catalytic effect on one another: the formation of carboxylic groups upon oxidation catalyses the hydrolysis and conversely, hydrolysis provides new reducing end groups for oxidation (Fig. 1). Additionally, the appearance of water as oxidation side product provides substrate and the proton carriers for hydrolysis. Taking into account that real paper samples contain already degraded cellulose and lignin, both of which are the source of active oxygen species and radicals necessary to initiate the oxidation, the reaction seems self-sustainable once it has started [12]. The presence of reducing end-groups (–CHO) on cellulose is a prerequisite for the occurrence of β-alkoxy elimination which is favoured by the alkali in paper and the appearance of single ketones, especially on C(2) (Table 1). As a consequence glucopyranose end rings are peeled off the cellulose chain, which is also manifested by the decrease in its degree of polymerisation. The contribution of this kind of de-polymerisation to the overall process caused mainly by hydrolysis is rather small due to a lower abundance of end rings in comparison with the number of glycosidic bonds.

While de-polymerisation of cellulose through either hydrolysis, oxidation or peeling ultimately results in a loss of mechanical strength of paper, oxidation leads also to a paper discoloration through the formation of carbonylic groups. From the structural standpoint, the organic material absorbing visible light contains the chemical ensembles with double bonds (for example functional organic groups as carbonyl –CO, double bonded carbon C=C) which constitute the chromophores. Chromophores in lignin (e.g. conjugated C=C, ortho- and/or para-quinones) emerge upon its oxidation initiated by ultraviolet light. The chemical nature of chromophores in cellulose, relatively resistant to chemical changes, is much more complicated. The conjugated diketones, their tautomers: enols, which are produced in the course of cellulose oxidation, intensely absorb light in the ultraviolet range showing two maxima of absorption, which then diminish slowly in the visible range up to 700 nm [10]. This kind of unspecific absorption most intense in the range

350–500 nm is responsible for the observed effect of yellowing of lignin-free papers. The appearance of the long tail in the visible range of the absorption spectra can be accounted for by the formation of a great many carbonylic groups only slightly differing in the chemical surrounding or by light degradation products (Table 1). Lignin, in fact, takes a double-fold role in cellulose degradation: as a oxidation catalyst (source of radicals) and as an anti-oxidant [16, 17].

The light products of cellulose de-polymerisation [18] (glucopyranose and oligosaccharides) may undergo further dehydration and condensation which is enhanced by acids and temperature (Table 1). In all, acid hydrolysis leads more to the emission of volatile aldehydes, such as formaldehyde or furfural, while oxidation leads more to the volatile organic acids, such as formic and acetic acid [19]. A vast majority of these mobile products together with the products of the degradation of lignin and hemicellulose (which are not listed in Table 1) gradually accumulate in a paper and create a new harmful environment for the remaining cellulose chains through, for example, the catalytic effect exerted by short chain carboxylic acids. Some of them contribute to the familiar odour of old degrading paper. The gaseous products can also be considered as degradation markers as presented in the other paper by us [20].

The overview of the degradation mechanisms indicates that the comprehensive evaluating of the paper degradation state needs several complementary methods, which would be able to grasp various aspects of the paper deterioration from the mechanical to the chemical ones. These are enumerated in Table 1. In this work we focus on the chemical effects of degradation. For the appraisal of cellulose de-polymerisation, viscometry appears as a cheap and relatively easy to use classical analytical method. But since it fails for lignin containing papers, size exclusion chromatography (SEC) seems to be the other method of choice, except determination of reducing end groups (–CHO) or osmometric measurements [21]. The advantage counterbalancing the complexity of the method is small sample amount necessary for the analysis. The oxidation progress can be followed by the instrumental methods, such as in situ FTIR and UV–VIS spectroscopy, what was shown in our previous papers [6, 7, 9, 10], and also by the classical titrative methods, such as modified Schwalbe–Hagglund's method for the determination of the –CHO groups (copper number) [22] or Wilson's method for –COOH groups [23], and finally by simple pH measurements. The titrative methods seem to be extremely useful to follow specific oxidation paths on cellulose. The questions that we try to answer in this work are the following: to what extent and for which paper types the instrumental and classical methods can be used interchangeably and what kind of information of the degradation progress and mechanism can they provide.

Table 2 Description of paper samples

Sample	Type	pH	Lignin	Ash content, wt%
P2	Cotton linters cellulose	7.3	No	0.005
P1	Softwood (bleached sulphite) cellulose 99.5%	6.3	Residual	0.45
P3	Groundwood + softwood (bleached sulphite), sizing, filler	5.9	High (app. 30%)	20 (kaolin, alum)

Table 3 Ageing conditions

Reactor	Type	Conditions	Impact
Dryer	Open	Air $T = 90°C$	Oxygen
Climatic chamber	Open	Air RH 59% $T = 90°C$	+ moisture
Vial	Closed	Air RH = 59% $T = 90°C$	+ gaseous products

2 Experimental details

2.1 Samples

The samples, model papers, were provided by TNO, the Netherlands [24]. The composition and the properties of the samples are described in Table 2.

The samples were chosen in terms of their increasing complexity: from high-quality pure linter cellulose sample of P2, through softwood bleached cellulose P1 (with traces of lignin) and finally to low-quality acidic groundwood lignin containing paper P3.

2.2 Artificial ageing tests

The artificial ageing tests were performed in three types of reactors operating under conditions described in Table 3.

The reactors and the conditions were chosen to spot the influence of moisture (climatic chamber) and gaseous products (closed vials) on the sample during degradation and to be able to follow various degradation paths. Thus, the dryer can be treated as a reference reactor in which in the presence of dry air the dominating reaction should be oxidation. The experiments in the climatic chamber were performed according to the ASTM standard [25]. The procedures concerning experimentation in closed vials are described in detail in [26].

2.3 Analytical techniques and procedures

2.3.1 SEC

Cellulose SEC analyses were done using the derivatives of the original samples—cellulose tricarbanilate (CTC)—

soluble in tetrahydrofuran (THF). The derivatives were prepared according to the procedure described by Stol [27]. Two CTC solutions were prepared for each paper sample and subjected to further analysis.

The average weighted molar mass (M_w) and molar mass distribution were determined using Waters chromatographic system which consists of: isocratic pump, autosampler, column oven, UV–VIS detector (set at the wavelength of 254 nm) and MALLS detector (Dawn Heleos, Wyatt Technology, working at 658 nm). For the separation of the CTC samples, a set of two 25×1 cm mixed–bed polydivinylbenzene columns was used (Jordi). They were thermostated at 35ºC and proceeded by a guard column (Waters). THF (HPLC grade) was used as eluent with a flow rate of 1.0 cm³/min.

The SEC system was calibrated using 11 polystyrene standards of known molecular masses with narrow distributions (Fluka). The extinction coefficient for the UV–VIS detector was determined according to the Lambert–Beer's law with the average value amounts to 7669 cm³/(g cm) (average from 23 measurements for P1 and P2 samples, standard deviation 11.2%).

2.3.2 DP

Viscosity measurements were carried out with a capillary viscometer in a 0.5-M cupri-ethylenediamine (CED) solution according to the standard [28] in the way described in [29]. In brief, samples of P1 and P2 were cut into the little pieces and defibrillated by shaking with pieces of a copper wire in a plastic bottle with 10 cm³ of distilled water, then the paper suspension was dissolved in 10 cm³ of 1-M cupri-ethylenediamine solution (CED) and shaken for additional 0.5 h. For each sample two CED solutions were prepared and each analysis was repeated three times. The concentration of each sample was set as to obtain the viscosity and concentration product [η]·c dropping in the range of 2.6 to 3.4. The DP was calculated from the Mark–Houwink equation:

$$[\eta] = K \cdot DP^{\alpha} \tag{1}$$

with the improved values of the coefficients K and α determined by SEC/MALLS using a method described in our paper [29].

2.3.3 FTIR

Prior to the transmission FTIR in situ measurements the thinned samples of aged paper were prepared in two ways: by mechanical scratching of the paper surface and by preparing thin sheets. To obtain the latter the aged paper samples were defibrillated in $2 cm^2$ of water, spread on the smooth surface of Si plates and removed after drying at 50°C for 0.5 h. No substantial discrepancies in the spectra were noted for the differently prepared thinned samples.

The transmission FTIR in situ measurements were performed in Excalibur 3000 Diglab Spectrometer with DTGS detector. The spectrometer was equipped with a glass cuvette with ZnSe windows, an electrical furnace and a gas supplying/evacuating system. The apparatus scheme is presented in our previous paper [6]. Before a spectrum was collected, the cuvette with the sample inside was evacuated and the temperature was raised to 70°C at which the sample was stored for 10 min to desorb water from paper. The desorption progress was followed by the vanishing of the $1640 cm^{-1}$ band characteristic of bending vibrations of water molecules. Overall, 128 scans were collected per each spectrum. For the sake of comparisons between various samples and conditions, the spectra were normalized using internal standard method (integral of the band between $2800–3000 cm^{-1}$) described in [6, 7] and presented as standardized absorbance (A_{std}). The degradation progress was traced in the range $1500–1850 cm^{-1}$ where the carbonyl groups evolve. Their quantitative analysis was done using the method described in our previous papers [7, 9] to obtain the standardized integral absorbance (in the range $1500–1850 cm^{-1}$ for P1 and P2, $1530–1850 cm^{-1}$ for P3 sample). The standardized integrals are used as a measure of the oxidation progress and the cellulose conversion towards carbonyl groups.
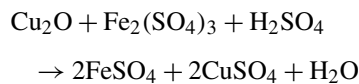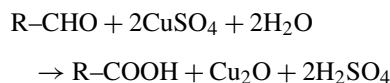
2.3.4 UV–VIS

UV–VIS diffuse reflectance spectra were measured by Nicolet Evolution 600 spectrophotometer equipped with the integrating sphere (Thermo) and red-sensitive photomultiplier-tube detector. The presented spectra resolution was set to 4 nm, while data were collected every 2 nm. All spectra were obtained in reflectance units then recalculated to Kubelka–Munk absorbance (A_{KM}). Each spectrum was measured in the range 190–500 nm with eight scans. For the quantitative measurements the integrated absorbance was obtained in the same range.

2.3.5 pH

The acidity of paper samples was determined using cold extraction method according to TAPPI standard [30]. The pH of each extract was measured with LIQ-GLASS Hamilton electrode using Metrohm Titrino 809 device.

2.3.6 Titrative analyses

Copper number (–CHO concentration) was determined using modified Schwalbe–Hagglund method [22] using oxidation-reduction difference technique:

$$R–CHO + 2CuSO_4 + 2H_2O$$
$$\rightarrow R–COOH + Cu_2O + 2H_2SO_4$$
$$Cu_2O + Fe_2(SO_4)_3 + H_2SO_4$$
$$\rightarrow 2FeSO_4 + 2CuSO_4 + H_2O$$

The excess of $FeSO_4$ was titrated with $KMnO_4$ standard solution. All analyses were carried out with Titrando 809 using redox electrode to determine the equivalence point of titration. The results are expressed in moles of –CHO groups per 1 g of a dry paper sample.

The –COOH concentration was determined using potentiometric acid–base titration according to the Wilson's method described in [23]. The reaction utilized in it is as follows:

$$R–COOH + NaHCO_3 \rightarrow R–COONa + H_2O + CO_2$$
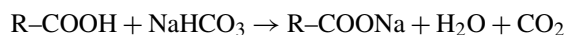
The excess of $NaHCO_3$ from the reaction is titrated using HCl standard solution. The results are expressed as number of –COOH moles per dry mass of the paper sample.

3 Results and discussion

3.1 Trends during ageing

While the results of chemical analyses give direct information on the quantities of the degradation products, the quantification of the chromatographic and spectroscopic results need some more attention. The examples of the chromatograms and spectra obtained for all the samples aged in the climatic chamber with SEC, FTIR in situ and UV–VIS are presented in Figs. 2, 3, 4, respectively.

With regard to the SEC results, the distributions of the molecular masses are presented as the differential (density) function of logarithm from molecular mass, for the clarity of the chromatograms (Figs. 2a, b, c). The common feature of all the samples is that the population of cellulose chains shifts towards lower masses with ageing time. The distribution pattern differs for the P3 sample in that that the most profound changes occur at the initial stage of degradation. Another distinct feature is that the mass distributions for the P1 and P3 are composed of two fractions (Figs. 2b and c) of which the lower maximum mass can be attributed to hemicellulose [31]. In the P1 sample hemicellulose does not undergo significant changes with ageing time unlike the P3 where the small shift towards lower masses can be
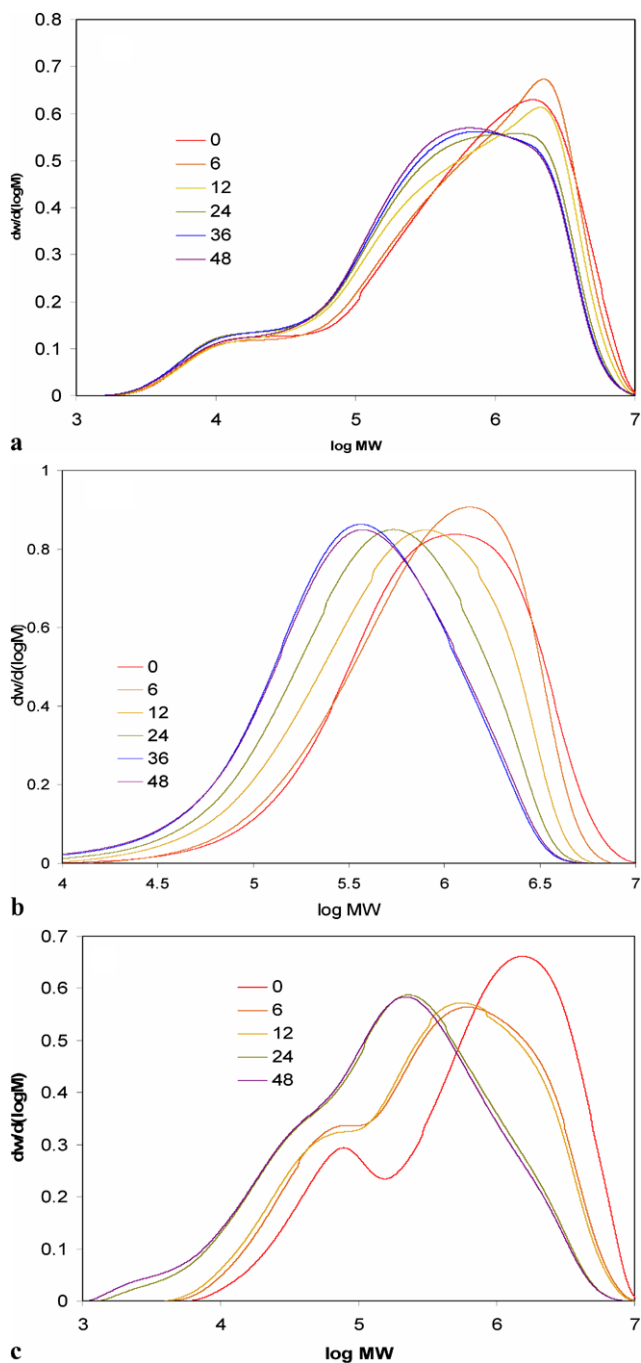
Fig. 2 Degradation progress observed by the changes in molecular mass distribution from SEC: A: P1, B: P2 and C: P3 samples aged in the climatic chamber in air at 59% RH and 90°C
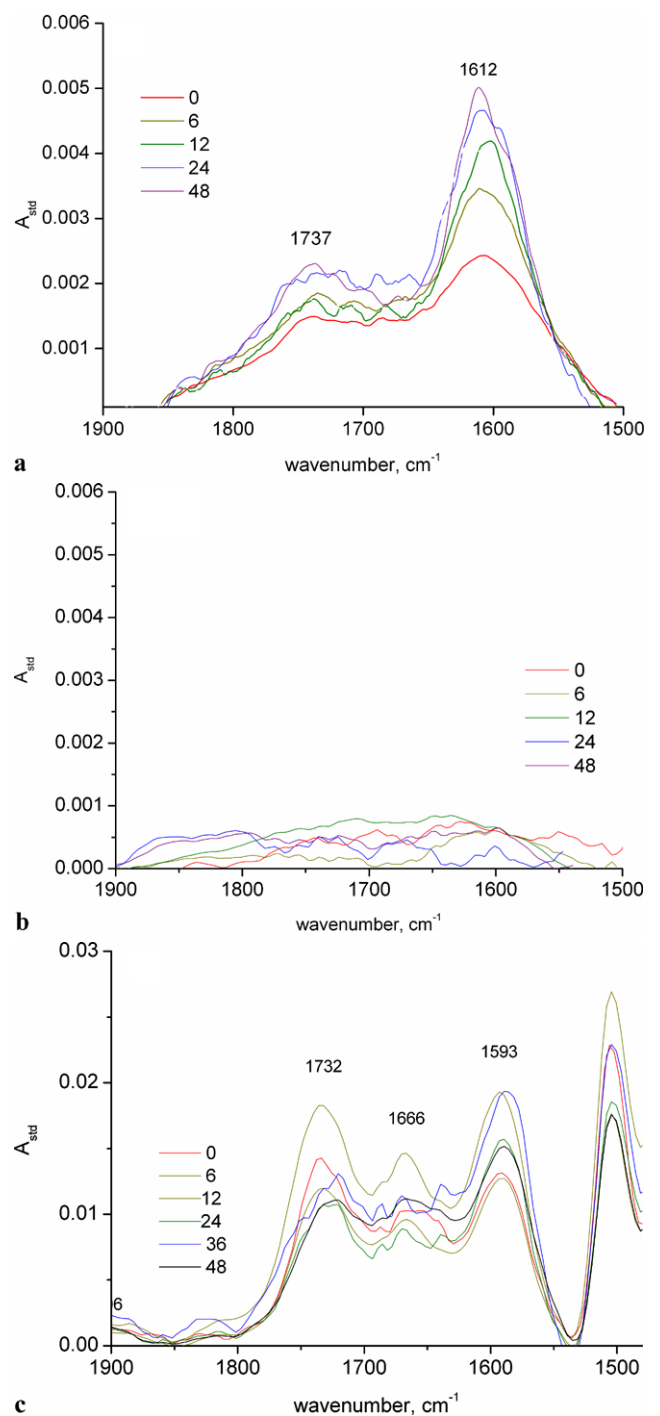

Fig. 3 Degradation progress observed by the changes in FTIR spectra: A: P1, B P2, C: P3 samples aged in the climatic chamber in air 59% RH at 90°C

noted. The presence of the hemicellulose complicates the calculations of the mean molecular mass as a representative gauge (variable) describing the progress of degradation. In the first approach for the further discussion, the weighted mean molecular mass was calculated for both mass populations, knowing that the values for the separate cellulose population should be higher.

The changes in the oxidation state of the samples with propagating degradation are observed in the FTIR spectra in the range 1500–1850 cm^{-1} where the carbonyl groups in various chemical environment appear (Figs. 3a, b, c). Such an observation is possible only when the dry samples are analysed because the bending vibrations of bound wa-
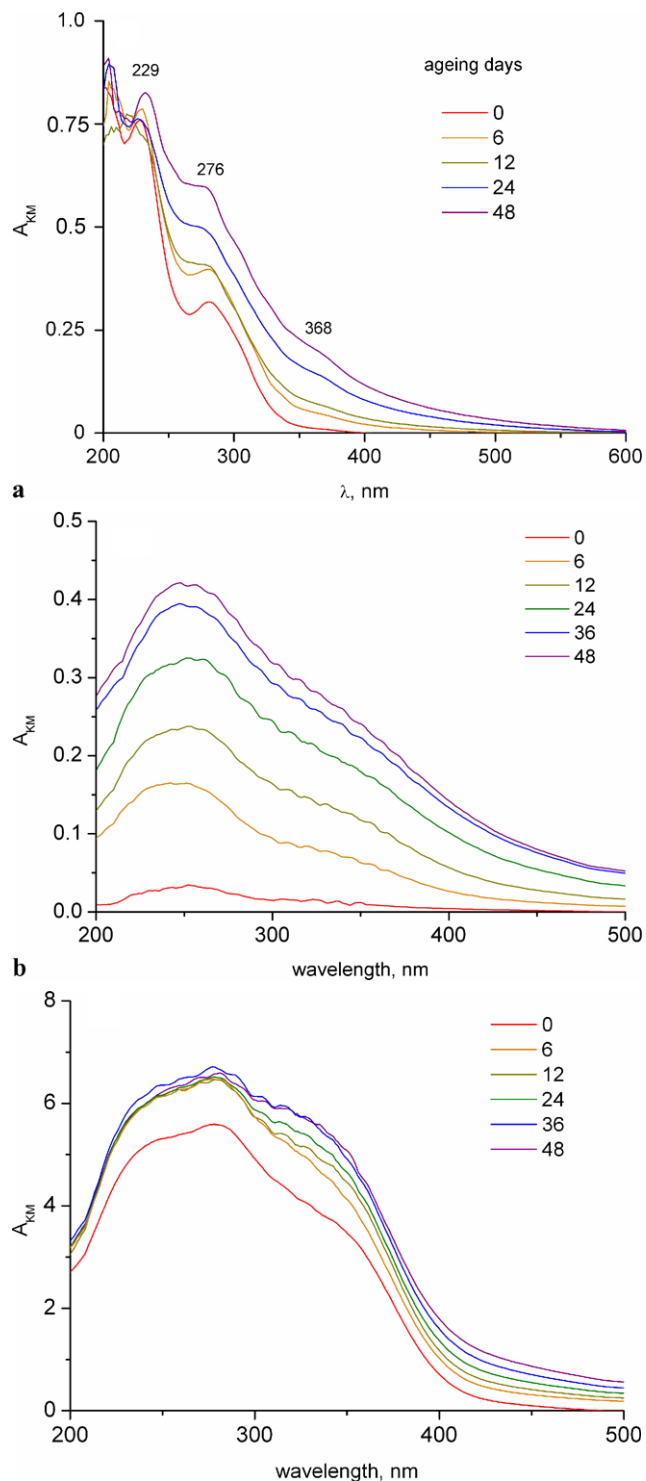
Fig. 4 Degradation progress observed by the changes in UV/VIS spectra: **a**—P1, **b**—P2, **c**—P3 samples aged in the climatic chamber in air 59% RH at 90°C

ter molecules appear at 1640 cm^{-1} masking the products of cellulose oxidation. One of the method to omit the problem used in this work, except the H–D exchange, is to perform the analyses in the vacuum chamber at elevated temperature

in order to desorb water [6, 7]. The trends with ageing time occur only for the P1 sample for which the developing band at around 1612 cm^{-1} has been attributed to the formation of conjugated ketones on the C(2) and C(3) atoms of the cellulose rings (see Fig. 1). These appear also as chromophores in the UV–VIS spectra, which has been discussed in our previous work [10]. For the P2 sample composed of high quality linter paper, oxidation does not proceed intensely to give measurable effect in the spectra. For the groundwood lignin containing P3 sample the most visible bands come from lignin and its oxidized forms: 1732 cm^{-1} single ketones or esters, 1666 cm^{-1} conjugated diketones, 1593 cm^{-1} aromatic skeletal and also carbonyls [32]. The P3 paper does not show any tendency in the overall carbonyl bands pattern; after the initial increase the total area decreases and then increases again with ageing time. This unspecific behaviour can be due to both inhomogeneity of the P3 sample which is a multi-component material and a complicated mechanism of the oxidation of the lignino-cellulosic system in which one carbonyl group transfer into another of different activity in the infrared irradiation.

Contrary to FTIR the trends in the UV–VIS spectra are easy to follow for all the samples (Figs. 3a, b, c). In cellulose the chromophores of high absorbtivity form upon oxidation to the conjugated diketones [10] which appear also in the FTIR spectrum of the P1 sample (Fig. 3a). Unlike the initial P2 sample (Fig. 3b), the P1 sample is already oxidized due to bleaching but the average increase in absorbance is only slightly higher for P1 throughout 48-day ageing period. For the P3 sample because of the aromatic nature of lignin, the increase in absorption is the highest amongst the studied samples especially in first six days of ageing. Also, the characteristic bands of chromophores in softwood lignin appear around 240, 280 and 330–340 nm [32].

3.1.1 Paper composition impact

The oxidation progress can be followed by the concentration of –CHO (copper number), –COOH groups (Wilson's method), chromophores proportional to an integral of absorbance (UV–VIS) and acids expressed as pH (Figs. 5a, b, c, d, respectively). In all, the oxidation extent decreases in the order P3 > P1 > P2 which reflects the ash and lignin content in the samples (Table 2). The huge effect connected with the formation of chromophores in the P3 sample is due to lignin which oxidizes itself apparently suppressing the oxidation of cellulose to more oxidized forms (–COOH) as can be judged from the values in Table 4. By the same token, the difference chromophores amount between the P1 and P2 occurs, however, the concentration of –CHO and –COOH (also pH) is comparable for both samples taking into account the experimental error.

The de-polymerisation progress caused by all hydrolysis, oxidation and peeling can be evaluated by viscometric DP
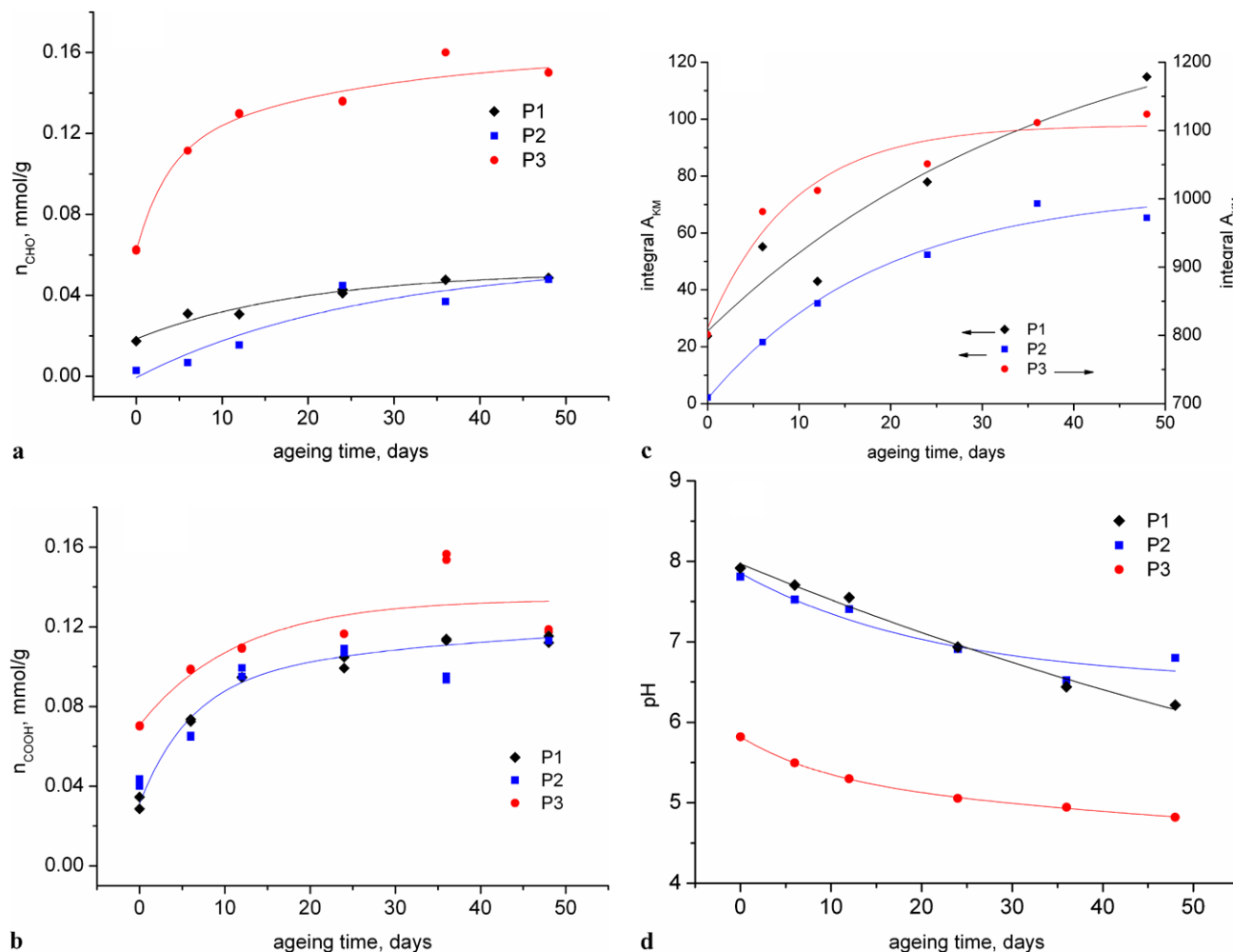
Fig. 5 Comparison of oxidation progress of P1, P2 and P3 samples aged in the climatic chamber in air 59% RH at 90°C as traced by: **a**: concentration of –CHO groups by copper number measurements, **b**: the concentration of –COOH groups by Wilson's method, **c**: chromophores expressed as integrated absorbance in UV–VIS spectra, **d**: pH

Table 4 Comparison of paper oxidation extent towards –CHO, –COOH, chromophores by UV–VIS and acids by pH

Sample	Total changes: (initial-final)			
	–CHO, mmol/g	–COOH, mmol/g	Chromophores, int. A_{KM}	pH
P1	0.032 ± 0.001	0.084 ± 0.007	91	1.29 ± 0.14
P2	0.045 ± 0.001	0.072 ± 0.003	64	1.15 ± 0.22
P3	0.087 ± 0.001	0.047 ± 0.001	322	1.21 ± 0.03

and SEC measurements (Figs. 6a and 6b). The trend in de-polymerisation observed for the samples is P3 > P2 > P1 which is slightly different from that observed for the oxidation. The factor which has not been discussed before and which may influence the observed tendencies is the crystallinity of the samples. The crystallinity index derived from FTIR as the ratio between absorbance of the bands 1372 to

2900 cm^{-1} using the procedure described in [33] is the highest for the P1 sample (8.4) and comparable for the P2 (2.7) and P3 (3.3). The higher crystallinity of the P1 is probably the reason for its higher resistance to de-polymerisation upon ageing than other samples [2]. Apparently, the crystallinity does not affect oxidation to the same extent.

3.1.2 Ageing conditions impact

The highest degradation progress can be noted for the vials as compared to the climatic chamber and the dryer (see exemplary trends of P1 sample in Figs. 7a–d). The gaseous products of degradation apparently accelerate both de-polymerisation causing a significant drop in weighted average molecular mass (Fig. 7a) and pH (Fig. 7c) and oxidation especially towards chromophores (Fig. 7d). For this reason ageing in the vials seems important to draw the accelerated ageing conditions closer to the natural ones. The
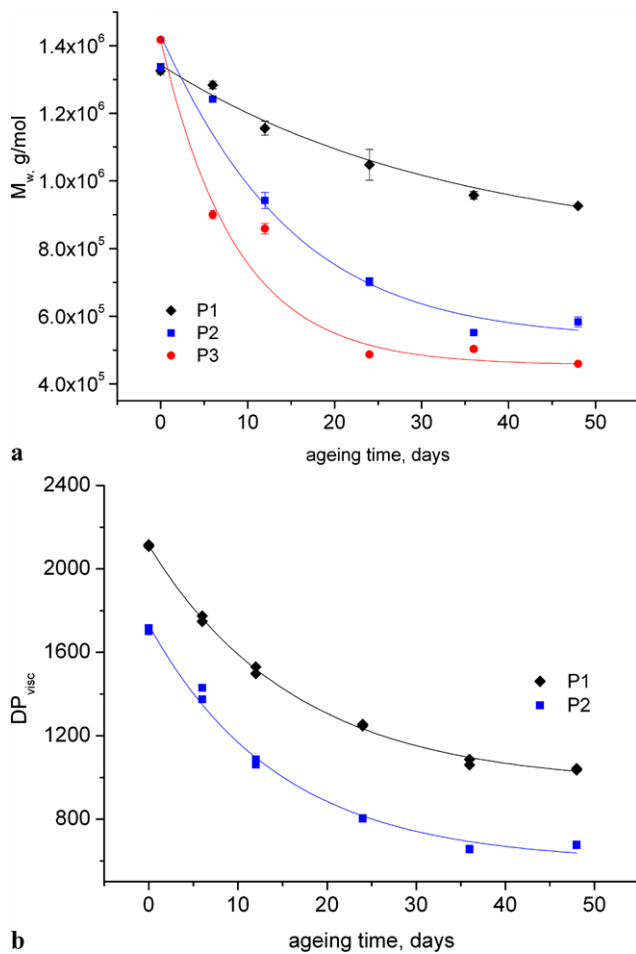
Fig. 6 Comparison of hydrolysis progress of P1, P2 and P3 samples aged in the climatic chamber in air 59% RH at 90°C as traced by changes in: **a**: weighted mean molecular mass M_w obtained from SEC, **b**: viscometric DP for P1, P2 and P3 samples aged in the climatic chamber in air 59% RH at 90°C

second important factor affecting degradation is the moisture content in the gaseous atmosphere. The moisture content in paper at 59% RH is only slightly lower than the initial moisture content in the TAPPI room and amounts to around 6.4 wt% for the P1 sample [26]. High moisture content in paper secures the substrates and catalysts carriers for hydrolysis and also an additional source of radicals for oxidation (OH*). For this reason, in the presence of dry air the degradation progresses to the lesser extent.

3.2 Standardization of degradation extent

The lack of the proper standardization method of the results of the analyses may lead to erroneous conclusions concerning evaluation of the degradation progress. A validation between viscometric and SEC is the first concern we come across. An interesting question to answer is how the results of the viscometric DP and the DP derived from SEC correspond with each other especially because the viscometry

is rather commonly used by the laboratories dealing with paper degradation although it does not apply to the lignin containing papers. The difference in the results can be noticed at a first glance comparing Figs. 8a and 8b and the dynamics of the changes in the DP and M_w values. The correlation curves between viscometric DP and DP calculated from SEC results are presented in Figs. 8a–c for various reactors (reaction conditions). The DP_{SEC} has been calculated from the (2):

$$DP_{SEC} = \frac{M_w}{M_g} \tag{2}$$

where M_w is a weighted average molecular mass of cellulose and M_g is a molar mass of glucopyranose. In all circumstances a good correlation was found for the P2 sample and much worse for the P1. This can be explained by the complexity of molecular mass distribution of P1 paper (Fig. 2a) due to the presence of hemicellulose. In order to improve the correlation, subtraction of the hemicellulose distribution component from SEC chromatograms should be necessary. It is also worth pointing out that the correlation curves do not start at 0,0 point and the small underestimation observed for the P2 samples is a result of the viscometry detection limit for the polymers of low degree of polymerisation. Contrary to the works by Dupont and Strlič et al. [34, 35], in our research even for the most degraded samples the viscometry technique give results being, in general, in an agreement with those obtained by SEC. In our opinion the key factor is the value of the product [η]·c, which in particular for the samples with low DP should be kept within the limits prescribed in the standard [28].

In an attempt to give possibly comprehensive but concise a measure to simultaneously assess both de-polymerisation (hydrolysis) and oxidation extent the results of the SEC and copper number measurements are related in Figs. 9a and 9b. The results were re-calculated to the conversion (scission) of the glycosidic bonds according to the formula:

$$X \approx 1 - \frac{DP_t}{DP_0} \tag{3}$$

where a subscript 0 refers to an initial value for the unaged sample and t to the value measured after a given ageing time. Equation (3) is valid for high DP values. Substituting (2) to (3) we obtain the conversion expressed by the weighted average molecular masses:

$$X_{SEC} \approx 1 - \frac{M_{w,t}}{M_{w,0}} \tag{4}$$

With the assumption that the end reducing –CHO come exclusively from bond scission (not oxidation of primary alcohols) and that the number of moles of cellulose of an average molecular mass M_w is equal to the number of moles
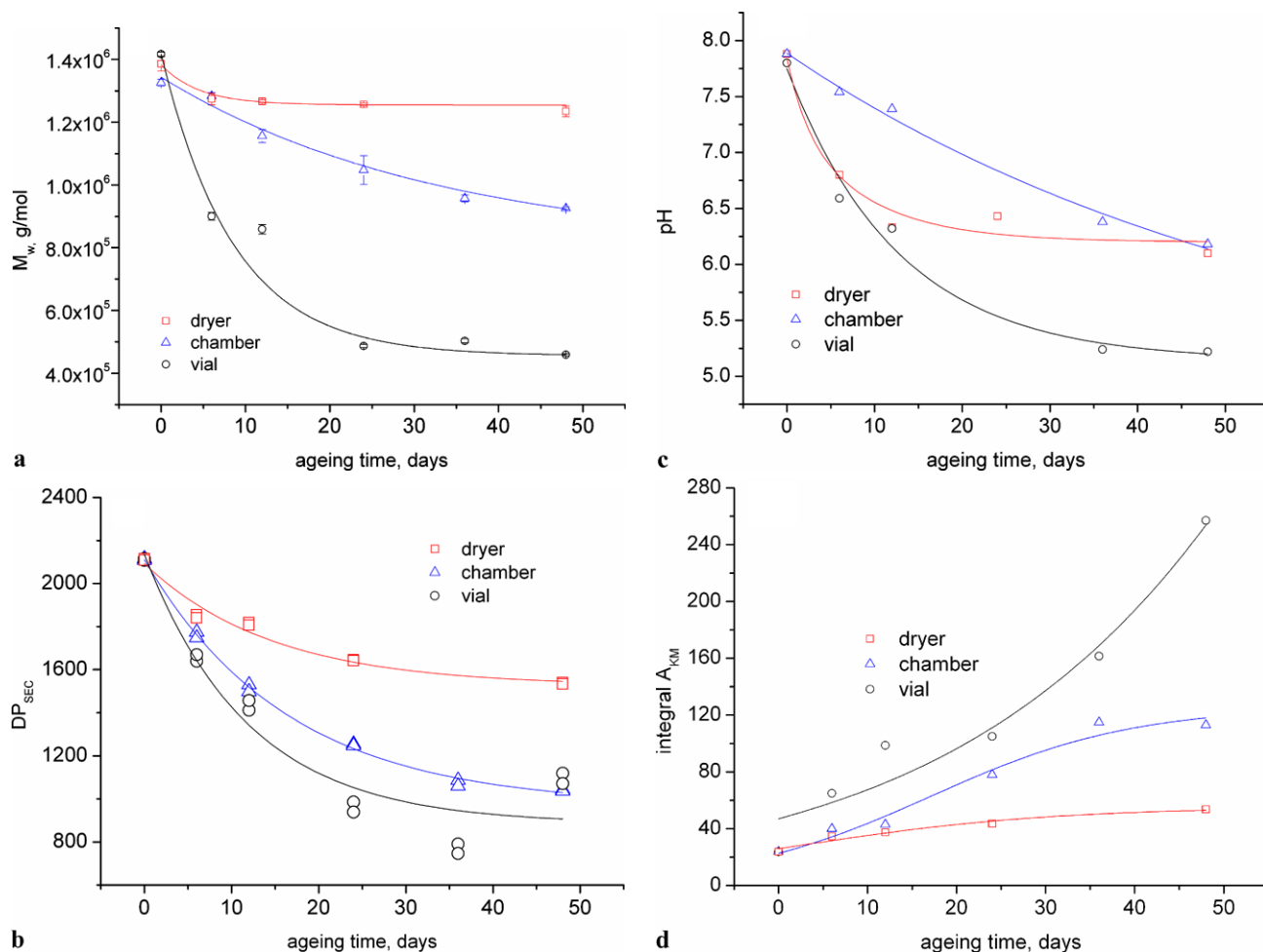
Fig. 7 Comparison of the degradation progress at 90°C various gas mixtures: ○: dry air in the dryer, □: humid air (59% RH) in climatic chamber, △: gaseous products of ageing in humid air (59% RH) in vial; for P1 sample as observed by the changes in: **a**: weighted mean of molecular mass M_w obtained from SEC, **b**: viscometric DP, **c**: pH, **d**: concentration of chromophores expressed as integrated absorbance in UV–VIS spectra

of –CHO groups the conversion can also be expressed using the results obtained by copper number measurements:

$$X_{CHO} \approx 1 - \frac{n_{CHO,0}}{n_{CHO,t}} \qquad (5)$$

In this way the directional coefficient in the correlation curve X_{SEC} versus X_{CHO} can be used as a measure of oxidation contribution. Thus if there is no oxidation in the overall degradation the results of SEC and copper number measurements expressed in such a way should correlate. Conversely, the lower the value of directional coefficient (<1) the higher is the advancement of oxidation (primary alcohols) in comparison with de-polymerisation. Figures 9a and 9b combines the results of SEC and copper number collected in the climatic chamber and in the closed vial and transformed into the conversion units. Almost full correlation is shown by the P3 sample and no correlation by the P2 sample. This can be

accounted for by the effect of lignin which takes up oxidation at the same time protecting cellulose. This effect can also be confirmed by a differently proceeding evolution of the FTIR (Fig. 3) and UV–VIS (Fig. 4) for the P3 paper as compared to the P2 and P1 sample. It has also been indicated in [16, 17]. Although the absolute de-polymerisation is lower for the P1 sample than for the P2 (Fig. 6) the contribution of the oxidation is higher and can be estimated to around 50% from the value of the directional coefficient. It complies with the results of FTIR showing negligible overall oxidation of the P2 sample (compare Figs. 3a and 3b) and of UV–VIS (Figs. 4a and 4b) where the changes were the least.

The last question that arises is whether the –CHO can be used as a universal measure of oxidation. It seems possible that the trends in the oxidation are similar for various oxidation routes (to –CHO, to –COOH and to conjugated ketones) and for the overall oxidation expressed by FTIR results. To check the trends the data have been transformed into rela-
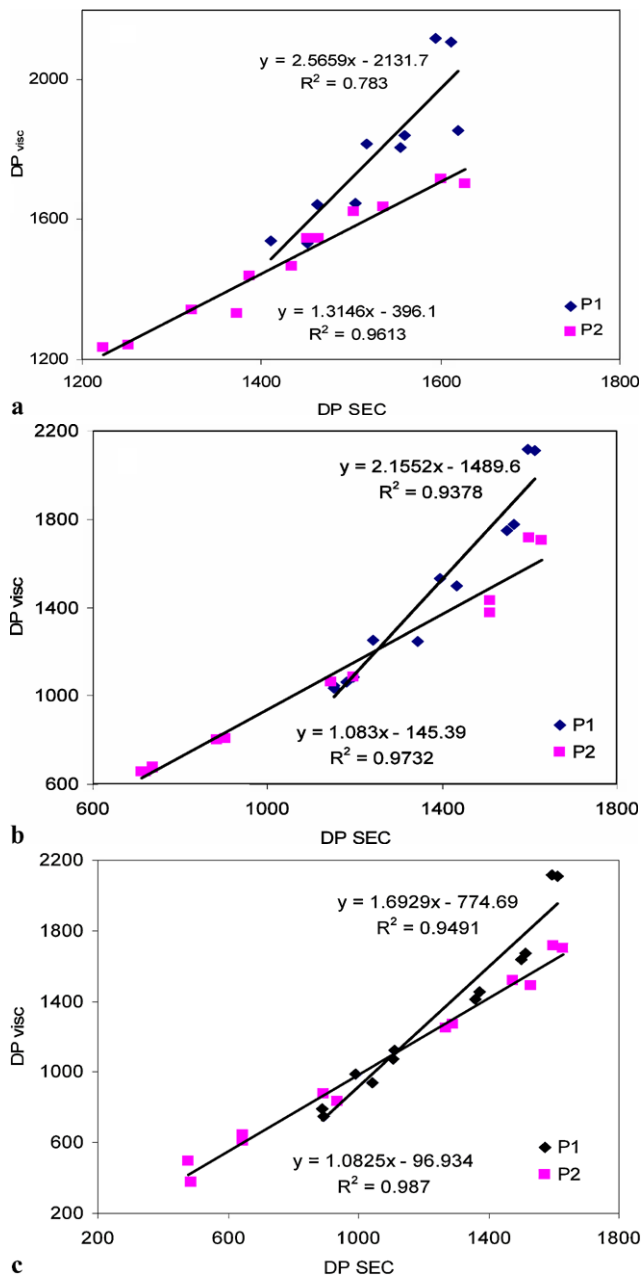
a

b

c

Fig. 8 Correlation between DP obtained from SEC and viscometric measurements for P1 and P2 samples aged in: **a**: dryer, **b**: climatic chamber, **c**: vial. The results are expressed as conversion of glycosidic bonds X

a

b

Fig. 9 Correlation between SEC and copper number results for P1, P2 and P3 samples aged in **a**: climatic chamber, **b**: vial. The values on the axes refer to the normalised conversion of cellulose during hydrolysis

tive conversion towards various products according to the formula:

$$XR = \frac{A_t - A_0}{A_f - A_0} \tag{6}$$

where A is a measured variable (concentration, absorbance), 0 and f subscripts refer to the initial and final observed values, respectively, and t refer to the value measured after a certain period. Thus transformed results show the dynamics of the changes of a given variable. The cross-linking be-
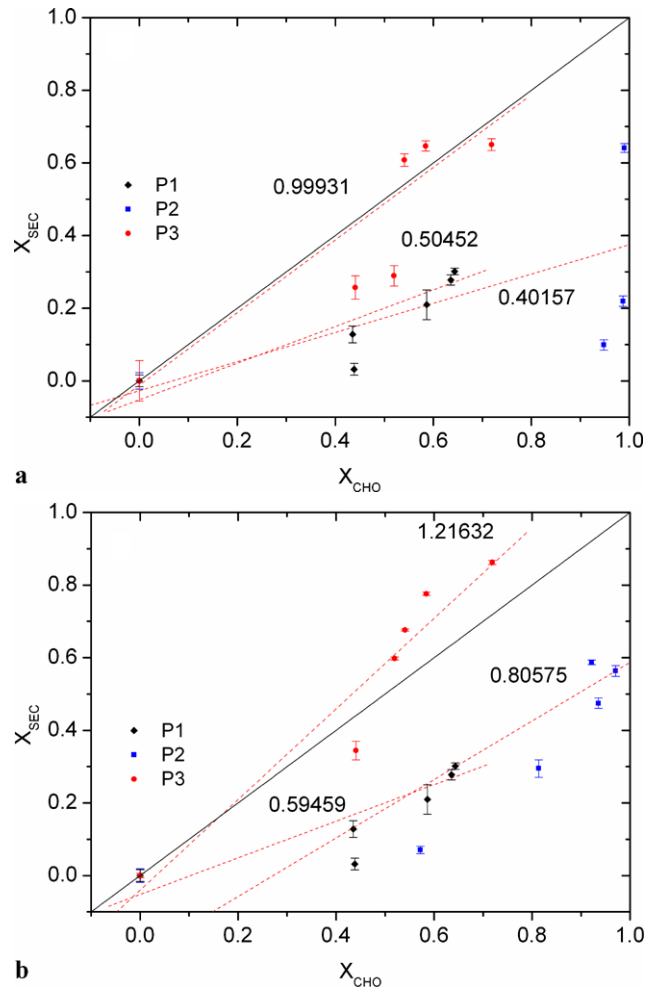
tween various oxidation paths is presented in Figs. 10a and 10b. The projections show the correlation between two chosen variables. The overall trends are similar for all of them, but the XR_{FTIR} effects are higher than those of $XR_{UV/VIS}$ or XR_{CHO} which simply indicates that XR_{FTIR} covers more oxidation products than other variables as already mentioned above. Since $XR_{UV/VIS}$ and XR_{CHO} trends nearly coincide for low lignin containing papers the UV–VIS results could be used alternatively for the de-polymerisation-oxidation evaluation presented in Fig. 9. This is important from the practical point of view as the UV–VIS spectroscopy is a non-invasive method of analysis contrary to the titrative methods.

The alternative gauge for the evaluation of the overall oxidation can be a sum of the –CHO and –COOH concentration expressed again as the relative conversion and correlated with XR_{FTIR} in Fig. 11. This time the trends are almost the same.
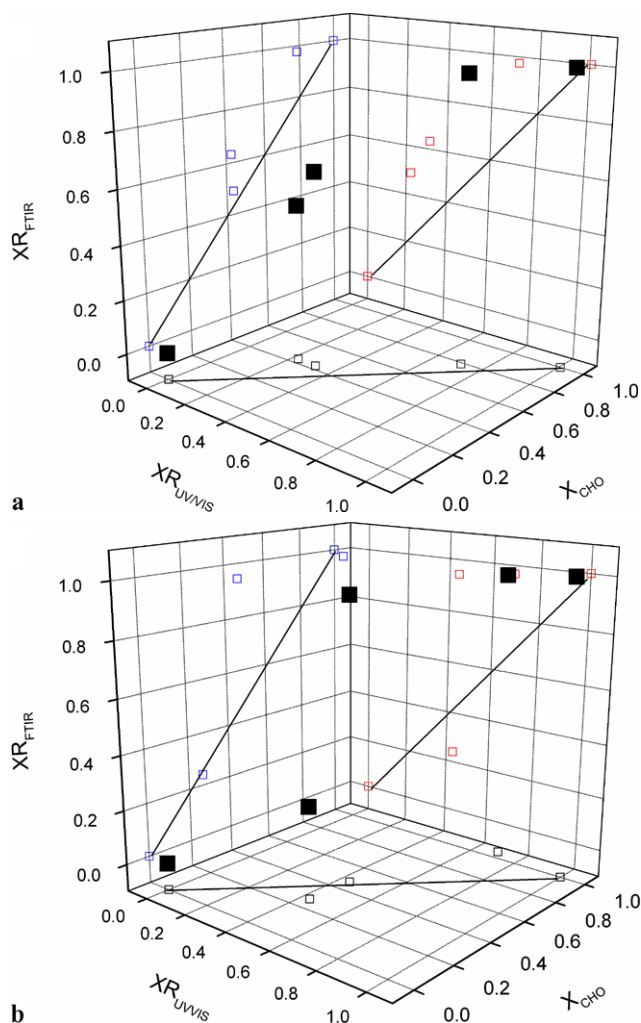
Fig. 10 Correlation between relative conversions of cellulose to –CHO (XR_{CHO}), to chromophores (conjugated ketones, $XR_{UV/VIS}$) and overall oxidation (XR_{FTIR}) obtained for the P1 sample aged in: **a**: climatic chamber, **b**: closed vial

4 Conclusions

As *techne* cannot be split from *episteme* the analytical methods cannot be regarded without the insight into the structure of the studied material and the mechanisms ruling its change. The methods for analyses of degraded paper were considered in terms of their applicability to distinguish between various degradation routes mainly through hydrolysis and oxidation of cellulose chains. The goal was to be able to grasp both the de-polymerisation and oxidation of cellulose. To achieve this chromatographic (SEC), spectroscopic (FTIR, UV–VIS), viscometric (degree of polymerisation) and chemical (titration, pH) techniques were engaged to analyse paper samples at various stages of their degradation at various conditions. In order to place the results in the practical context the model paper samples represented high- (cotton linters) and low-quality (groundwood, acidic,

sized) paper and the ageing conditions in closed vials were designed to mimic the environment in books.

In a view of the results the paper types were classified according to their susceptibility to hydrolysis and oxidation. The oxidation was shown to be the most dependent on the components of paper such as fillers and sizing agents (kaolin, alum) and lignin which acted as catalysts of oxidation. The results showed also that lignin could partly suppress the oxidation of cellulose. Hydrolysis (or more generally de-polymerisation) was affected more by the crystallinity of a paper than oxidation. The autocatalytic effect of the light gaseous products on paper degradation was observed for the samples aged in the vials. The least amount of changes was noted during ageing at dry air atmosphere.

The proper interpretation of the results is also impossible without their validation and standardization. The viscometric DP measurements were validated by SEC measurements of weight average molecular mass of cellulose. The high correlation between the results was observed for the pure cellulose paper using the improved Mark–Houwink coefficients derived from SEC/MALLS experiments for the determination of viscometric DP. The estimators of paper degradation were defined as the conversion of a given property of the paper (number of glycosidic bonds, carbon atoms in cellulose) towards a specific product characteristic of a given degradation path detectable by a specific technique. The correlation coefficients between thus expressed results from SEC and copper number measurements (–CHO groups) allowed the estimation of the contribution of oxidation to depolymerisation. Since the concentration of chromophores in paper (mainly conjugated diketones) correlated well with the –CHO concentration they may be used interchangeably for the estimation of the oxidation contribution. For low lignin containing paper the overall oxidation index (relative conversion of carbon atoms in cellulose) provided by the FTIR measurements was shown to coincide the most with the summary –CHO and –COOH concentration derived from the titrative methods.

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