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On the lifetime prediction of old documents

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Abstract The paper deals with the study of thermal degradation of some new and old paper supports. The experimental data allows the prediction of the dependence between the half time and the temperature at which the paper support must to be kept.

Keywords Isoconversional method · Paper supports · Thermal degradation

Introduction

In our previous studies we tried to bring information on the complex mechanisms of aged cellulose degradation, in parallel with approaching the influence of the degradation factors upon the support materials, as well as on materials employed for works of restoration art [1, 2].

Thermal analysis (TG and DSC) made on old paper supported a two consecutive steps thermal degradation mechanism. The conclusion was that special attention should be given to temperature as main activation factor for the degradation processes of the patrimonial documents and their proper conservation.

It is known that the isothermal dependencies of the conversion on time can be predicted with good practical results from data obtained from thermal analysis experiments performed under non-isothermal conditions [3, 4]. Therefore, the aim of the present study was to test the ability of isoconversional methods to produce reliable predictions and mechanisms for the degradation of paper materials with a special interest for the old documents.

Experimental

Samples of new (Japanese) and old (90 and 200 years) manually manufactured paper from vegetable fibres have been subjected to different thermal treatments in nitrogen and air. The paper samples have the following characteristics: new (40 g/m^2, pH = 6.1), 90 years old (81 g/m^2, pH = 5.45) and 200 years old (72 g/m^2, pH = 7.15).

The air supplied by a compressor (4–5 bar) was passed over granular silica gel. The nitrogen was supplied from Linde gas cilinder (150 bar) of 4.6 purity class (99.996%). Thermogravimetric analyses (TG and DTA) were performed under nitrogen or air flow (20cm^3 min^{-1}) at three heating rate 7, 10 and 13 °C/min from 25 to 700 °C with a *Mettler Toledo model TGA/SDTA 851*. The initial mass of the samples was 3–4 mg.

The samples have been jarred, pelleted with KBr and subjected to IR analyses. The measurements, made on a *FT IR Jasco 660 plus* device, have been processed by means of the *Spectra Manager*. Normalization of the spectra was based on an internal standard.

Results and discussion

The experimental results of the analyses performed in nitrogen revealed that the degradation occurred in two stages (see for example Figs. 1, 2, 3).

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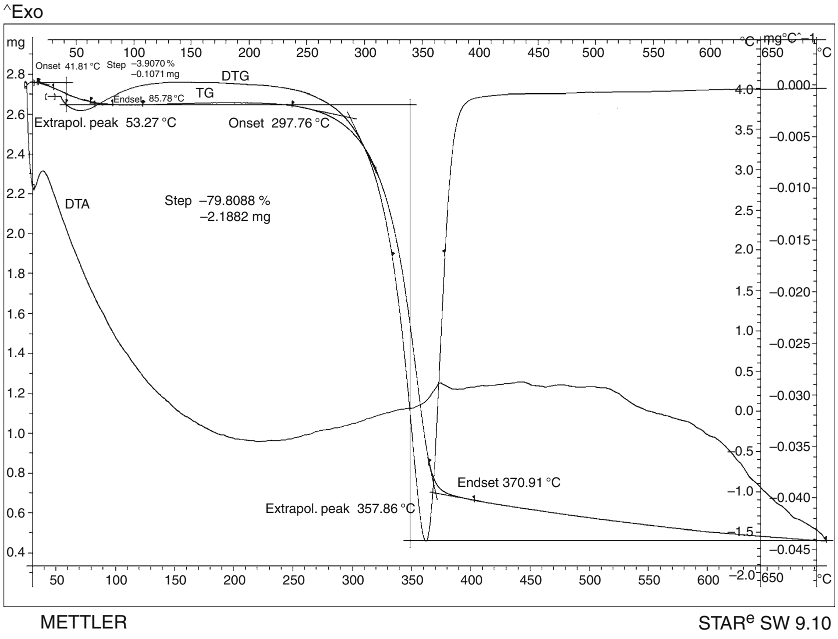

Fig. 1 TG/DTG and DTA curves corresponding to non-isothermal degradation (7 °C/min) of new paper in N_2

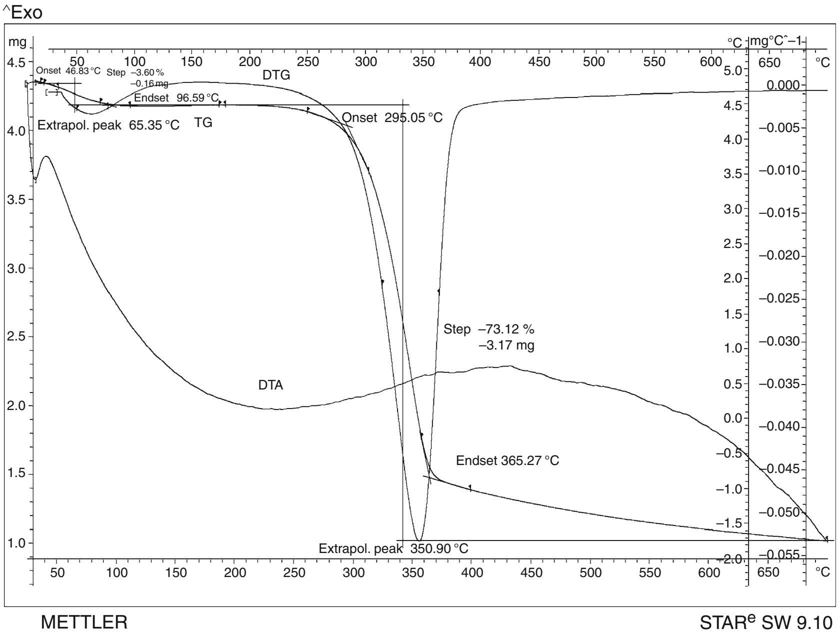

Fig. 2 TG/DTG and DTA curves corresponding to non-isothermal degradation (7 °C/min) of 90 years old paper in N_2

From the data presented in Table 1 one can observe that the first decomposition step concerns the dehydration process while the second one is related to the degradation of the cellulose macromolecular chain. For the dehydration stage, the older the paper the higher the peak temperature, indicating a stronger bond of the water molecules. On the other hand, for the second stage the older the paper the lower the peak temperature. This suggests an already begun degradation process, fact which is in agreement with our previous conclusions.

For each stage the kinetic parameters have been estimated using the TG data. The kinetic calculations were performed by means of the method proposed by Sergey Vyazovkin (Kintool V2.5 software-TAOsoft 1993) [5–7]. The dependence of the apparent activation energy and of the pre-exponential factor on the reacted fraction, were calculated (see for example Figs, 4, 5, 6). The formal models of the decomposition processes giving the best fit with the experimental data were also determined (Table 2).

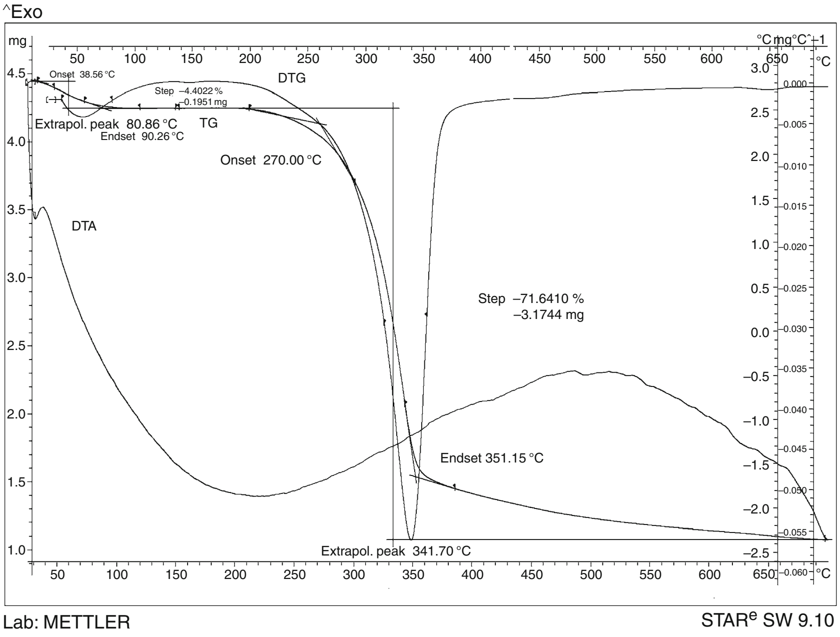

Fig. 3 TG/DTG and DTA curves corresponding to non-isothermal degradation (7 °C/min) of 200 years old paper in N_2

Table 1 Thermogravimetric data concerning the thermal decomposition of the paper samples at three heating rates

Thermogravimetric data	New paper		90 years old paper		200 years old paper	
DTA characteristics	Step 1 exo	Step 2 exo	Step 1 exo	Step 2 exo	Step 1 exo	Step 2 exo
Heating rate 7 °C/min						
T_i/°C	41.8	297.9	46.8	295.1	38.6	270
T_m/°C	**53.3**	**357.9**	**65.4**	**350.9**	**80.9**	**341.7**
T_f/°C	86.8	370.9	96.6	365.3	90.3	351.2
Mass loss/%	3.9	79.8	3.6	73.1	4.4	71.6
Heating rate 10 °C/min						
T_i/°C	39.8	304.1	38.8	301.9	44	286.9
T_m/°C	**55.9**	**357.9**	**62.1**	**360.3**	**62.1**	**314.3**
T_f/°C	96.1	375.5	106	377	99.1	362.4
Mass loss/%	3.6	79.6	4.1	75.4	3.9	73.7
Heating rate 13 °C/min						
T_i/°C	48.4	301.5	51.4	300	51.6	293.4
T_m/°C	**59.9**	**360.8**	**69.4**	**356.9**	**74.8**	**349.3**
T_f/°C	96.3	380.9	103.7	379.5	108.9	366.7
Mass loss/%	3.3	76.4	3.7	73.1	6	94

The method was also used to predict the behaviour in time of the analysed paper samples (Tables 3, 4).

The American chemists R.D. Smith [8] has performed an experiment which evidenced the role played by temperature in promoting chemical reactions of various types, the effect of which is the degradation of patrimonial goods. Experimental investigations have been devoted to the effects of temperature and of pH on the durability of paper. Smith calculated the half time by the method of artificial ageing of various types of paper samples (see Table 4). He considered the half time ($T_{1/2}$) as the period of time over which the material under investigation looses half of its physico-chemical properties.

Therefore, in order to have comparable data with those provided by Smith we calculated the lifetime of the samples as being the time when the mass loss weight reaches 50% at a certain preserving temperature (t_{iso}).

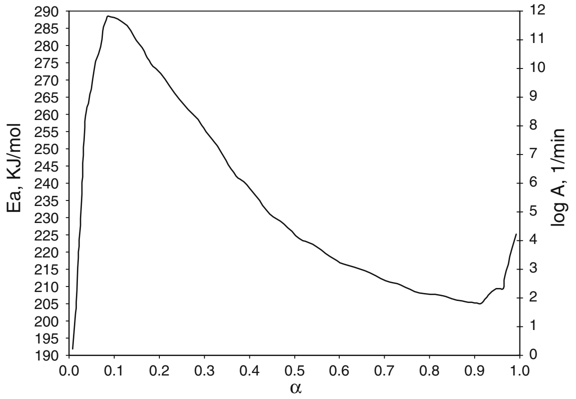

Fig. 4 Variation of the apparent activation energy and of the pre-exponential factor vs. the reacted fraction for the main step (new paper)

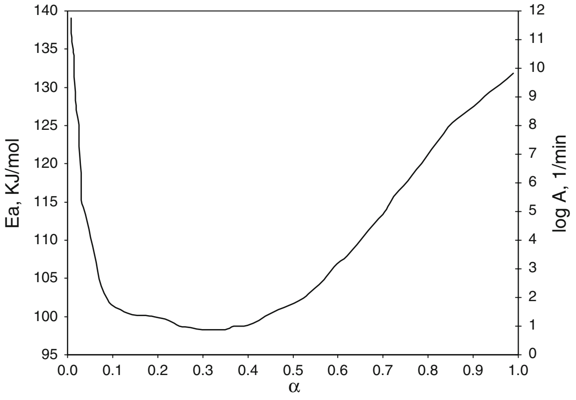

Fig. 5 Variation of the apparent activation energy and of the pre-exponential factor versus the reacted fraction for the main step (90 years old paper)

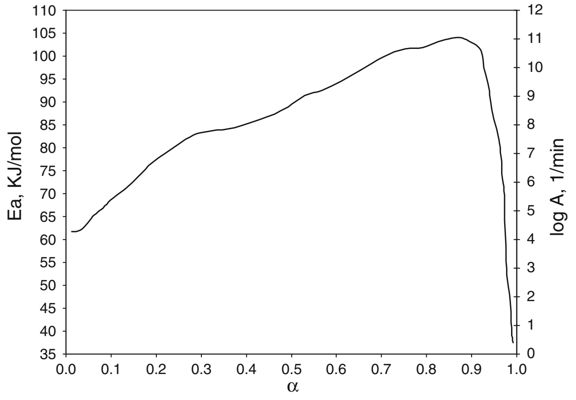

Fig. 6 Variation of the apparent activation energy and of the pre-exponential factor versus the reacted fraction for the main step (200 years old paper)

As it can be observed from Tables 3 and 4 it seems that the dehydration stage has almost nothing in common with the long range stability of the documents. On the other

Table 2 Models of the decomposition processes in nitrogen and the variation of activation energy and pre-exponential factor

Kinetic parameters	New paper		90 years old paper		200 years old paper	
	Step 1	Step 2	Step 1[a]	Step 2	Step 1	Step 2
$f(\alpha)$	$-\ln(1-\alpha)$ first order	$-\ln(1-\alpha)$ first order	$\alpha^{1/2}$ power law	$2[1-(1-\alpha)^{1/2}]$ contracting cylinder	$2[1-(1-\alpha)^{1/2}]$ contracting cylinder	$\alpha^{1/2}$ power law
E_a/kJ/mol	6.15 ÷ 161	189.8 ÷ 285.1	0.1 ÷ 63.91	95.77 ÷ 139.3	11.79 ÷ 62.2	34.33 ÷ 103.7
log A/min^{-1}	0.01–23	15.5 ÷ 24	0.01 ÷ 8	7.5 ÷ 10.5	1 ÷ 8	2 ÷ 8.2

[a] In this case the variation of E_a and log A are for $\alpha < 0.9$

Table 3 Lifetime prediction for the first stage of thermal degradation in nitrogen

Lifetime prediction/hours	New paper	90 years old paper	200 years old paper
t_{iso} (50%) at 10 °C	60	1.9	0.38
t_{iso} (50%) at 20 °C	10	0.87	0.25
t_{iso} (50%) at 30 °C	1.6	0.42	0.18
t_{iso} (50%) at 35 °C	0.7	0.3	0.15

Table 4 Lifetime prediction for the second stage of thermal degradation in nitrogen

Lifetime prediction/ Years	New paper	90 years old paper	200 years old paper	$T_{1/2}$ [8]
t_{iso} (50%) at 10 °C	13×10^{16}	100000	4250	3100
t_{iso} (50%) at 20 °C	5×10^{15}	21000	1150	490
t_{iso} (50%) at 30 °C	2.5×10^{14}	5250	340	88
t_{iso} (50%) at 35°C	6×10^{13}	2800	190	40

Table 5 Thermogravimetric data concerning the thermal decomposition of the paper sample thermally aged in nitrogen

Thermogravimetric data	New paper/1 h at 260 °C in N_2		
DTA characteristics	7 °C/min exo	10 °C/min exo	13 °C/min exo
T_i/°C	305.3	317.1	312.1
T_m/°C	351.7	358.4	359.5
T_f/°C	367.3	374.5	381.5
Mass loss/%	78.5	78.7	73.8

Table 6 Kinetic parameters and lifetime prediction for the samples aged in nitrogen

Kinetic parameters/Lifetime prediction (Years)	New paper/1 h at 260 °C in N_2
$f(\alpha)$	$2[1 - (1 - \alpha)^{1/2}]$ contracting cylinder
E_a/kJ/mol	$111.6 \div 164.1$
log A/min^{-1}	$8.5 \div 13$
t_{iso} (50%) at 10 °C	9×10^{10}
t_{iso} (50%) at 20 °C	8×10^{9}
t_{iso} (50%) at 30 °C	9.5×10^{8}
t_{iso} (50%) at 35 °C	3.3×10^{8}

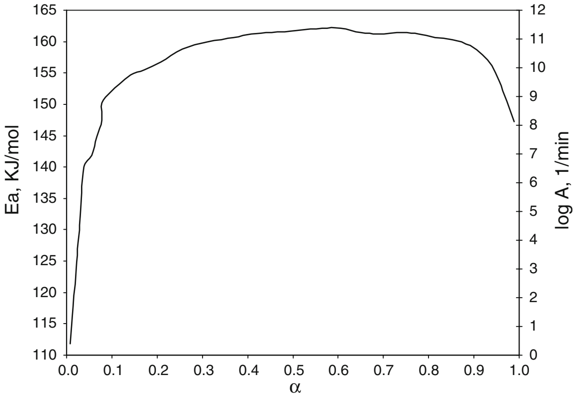

Fig. 8 Variation of the apparent activation energy and of the pre-exponential factor versus the reacted fraction (new paper aged at 260 °C for 1 h in N_2)

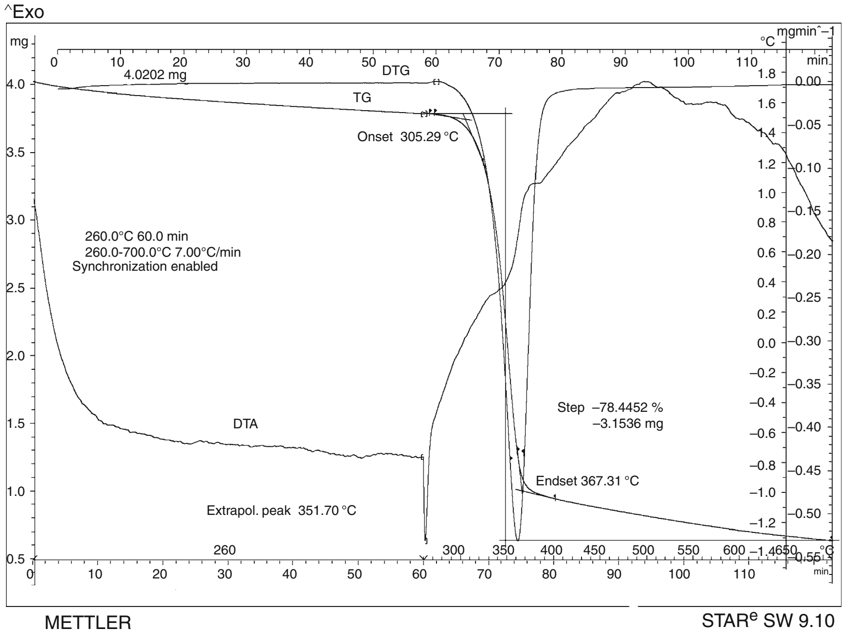

Fig. 7 TG/DTG and DTA curves corresponding to non-isothermal degradation (7 °C/min) of new paper aged at 260 °C for 1 h in N_2

Table 7 Thermogravimetric data concerning the thermal decomposition of the paper samples in air

Thermogravimetric data DTA characteristics	7 °C/min Step 1 exo	 Step 2 exo	 Step 3 exo	10 °C/min Step 1 exo	 Step 2 exo	 Step 3 exo	13 °C/min Step 1 exo	 Step 2 exo	 Step 3 exo
T_i/°C	39	290.7	412	44.5	299.7	413	60	306.6	430
T_m/°C	56.3	330.1	457.4	62.4	345.1	478.6	73.8	339.5	465.2
T_f/°C	83.9	345.9	472.9	94.4	358.6	500.4	102.5	356.8	488.3
Mass loss/%	3.6	67.1	22	3.6	67.5	20.2	4.4	67	23.4

Fig. 9 TG/DTG and DTA curves corresponding to non-isothermal degradation (7 °C/min) of new paper in air

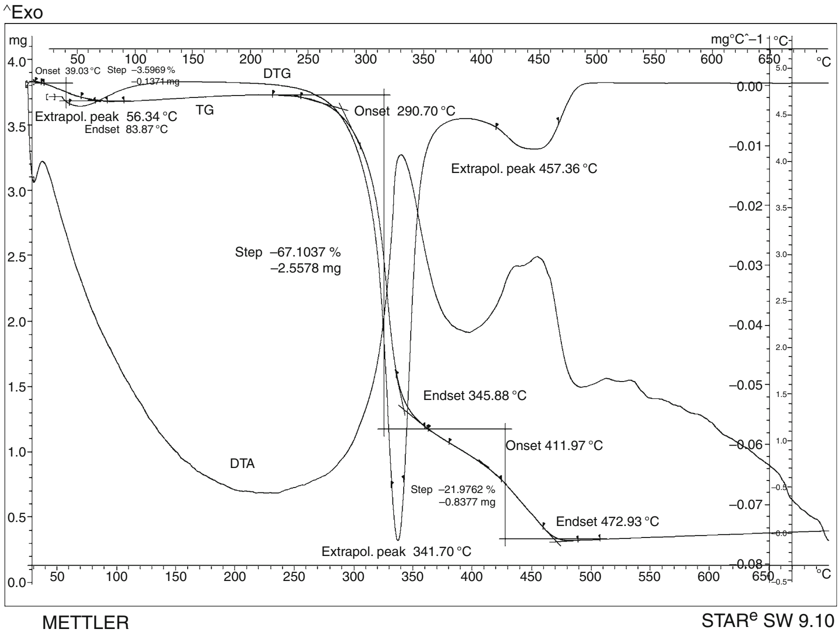

Table 8 Kinetic parameters and lifetime prediction for the samples decomposed in air

Kinetic parameters/Lifetime prediction (Years)	New paper in air Step 2
$f(\alpha)$	$\alpha^{1/2}$ power law
E_a/kJ/mol	85.7 ÷ 119.7
log A/min^{-1}	6.5 ÷ 9.5
t_{iso} (50%) at 10 °C	10500
t_{iso} (50%) at 20 °C	2700
t_{iso} (50%) at 30 °C	750
t_{iso} (50%) at 35 °C	440

hand, the stability in nitrogen of the paper materials is very high; the only sample which comes close to the values provided by R.D. Smith is that of 200 years old.

Further calculations were performed, using the above mentioned software, in order to determine how do affect the thermal ageing the lifetime of the samples. The results indicated, at the limit allowed by the software, that a treatment of 1 h at 260 °C leads to 1% degradation of the new paper. We decided to see how such a thermal treatment in N_2 affects the lifetime prediction of the analysed sample. The thermogravimetric data of the aged sample are listed in Table 5 (Fig. 7), while the kinetic parameters and the lifetime predictions are listed in Table 6 (Fig. 8).

The temperature peak values are similar with those of the 90 years old paper. The activation energy and the pre-exponential factor also vary in a range which is closest to the values of the 90 years old paper. Even the formal model of the decomposition process is the same—contracting cylinder. However, despite the fact that the predicted lifetime strongly decreased when compared with the new paper, is still high if we compare it with that of the 90 years old paper.

These results suggested a degradation mechanism which involves air oxygen. Therefore, we decided to test the thermal degradation in air of the analysed samples (Table 7; Fig. 9).

The degradation occurred in three steps. Obviously, we were interested in the major second step, step similar to that evidenced by the tests performed in nitrogen

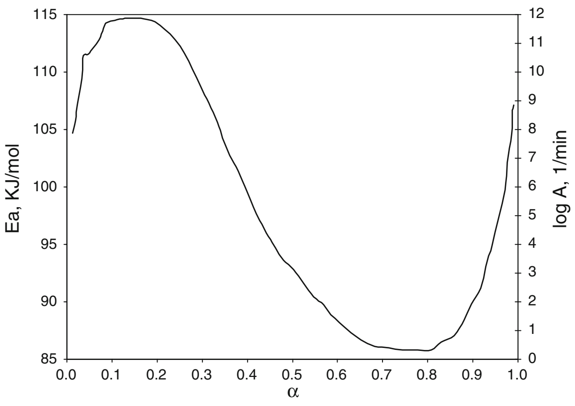

Fig. 10 Variation of the apparent activation energy and of the pre-exponential factor versus the reacted fraction (new paper aged in air—step 2)

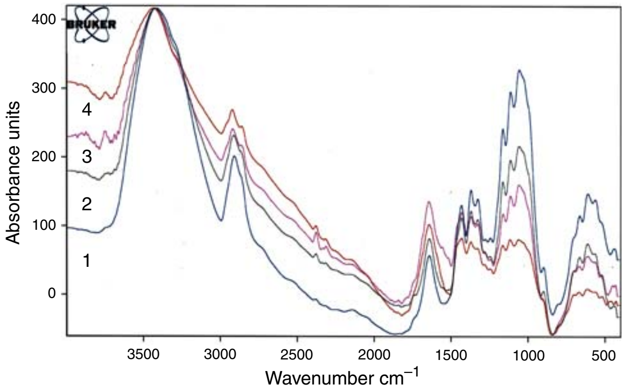

Fig. 11 FTIR spectra of: new paper (1), new paper aged in air at 150 °C for 3 h (2), 90 years old paper (3) and 200 years old paper (4)

atmosphere. However, in this case the characteristic temperatures were at least 20 °C lower than the previous ones.

The kinetic analysis produced values of the activation energy and of the pre-exponential factor in the same range of values as the paper aged in nitrogen and that of 90 years old (Table 8; Fig. 10). When calculated, the predicted lifetimes came much closer to the values proposed by R.D. Smith proving the extremely important role played by the preserving atmosphere for the paper materials.

It is an already know fact that for the degradation reactions affecting graphical records, the source of the activation energy is represented by light and temperature. The Russell effect [9] provides the irrefutable proof that at dark, the paper produces hydrogen peroxides, the sources of which can be exclusively some chemical oxidation processes. Consequently, it seemed that temperature is the source of the most devastating effects on old documents.

However, a large number of chemical processes, mainly of the oxidation type, are provoked by thermal activation. According to some recent findings, cellulose degradation should be regarded in terms of oxidative mechanisms where the reaction paths are autocatalytically accelerated by active oxygen species [10].

In order to verify and compare the results obtained by thermal analysis, we also have obtained the IR spectrum of a new paper sample aged in air at 150 °C for 3 h (Fig. 11). The complex IR spectra of the studied samples presented characteristics bands of the functional groups [11]. The most important ones appear in the following domains:

- 3600–3300 cm^{-1}, valence vibrations corresponding to the OH groups (ν_{OH});
- 3000–2800 cm^{-1}, valence vibrations corresponding to the CH groups from $–CH_3$, $–CH_2–$ and CH ($\nu_{C–H}$);
- 1760–1650 cm^{-1}, valence vibrations corresponding to the carbonylic and carboxylic groups C=O, ($\nu_{C=O}$);
- 1500–1200 cm^{-1}, a series of bands, attributable mainly to the deformation vibrations of the $–CH_2–OH$ primary alcoholic groups, appear along with deformation vibrations of the C–O and CH links;
- 1200–900 cm^{-1}, valence vibrations of the C–O, C–C links, of the piranosic cycles (1050 cm^{-1}), etc.;
- 900–400 cm^{-1}, deformation bands of the $–CH_2–OH$, –CH–OH groups and piranosic cycles.

In our study we tested just the evolution of the absorption IR maxima from 1647 cm^{-1}, corresponding to the C=O groups. As one can see from Fig. 11, the older the paper the higher the C=O maxima in the spectra, indicating the increase in the number of characteristic groups, which is a consequence of the oxidation. Furthermore, when compared with the other samples, the peak's position for the paper aged in air gives evidence on the ageing mechanism.

Therefore, we may say that the IR results support the conclusions brought by the predictions made using Vyazovkin's method.

Conclusions

There are authors claiming that the rate of paper deterioration and other quantitative aspects of the natural ageing of paper, such as durability and permanence, cannot be reliably predicted by means of the present artificial ageing tests [12]. Consequently, the aim of the present study was to test the ability of isoconversional methods to produce reliable predictions and mechanisms for the degradation of paper materials with a special interest for the old documents.

The obtained predictions were close to those proposed by the literature [8]. Even more, we can say that our method gives better predictions. For example, for an average temperature of 23 °C, the half time predicted by Smith is of 350 years, while the half time predicted by

Vyazovkin method is of about 2000 years. The conservation state of some of the scrolls and cellulose based materials found at the Dead See seems to confirm our prediction [13, 14].

Our study also proved that the oxygen from the atmosphere plays the most important role on the degradation process. For example, according to our results a 90 years old paper has the same stability at 35 °C in nitrogen as the new paper at 20 °C in air! This fact suggests, apart of the controlled temperature, the possible use of recipients filled with gaseous nitrogen for the preservation of the valuable old documents. This solution seems also to be a not very expensive one, taking into account the preservation advantages.

However, in order to conclude, we must to say that the amount of research into the predictive value of artificial ageing of paper by means of thermal analysis is not sufficient yet and further efforts have to be made in this direction.

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