European Journal of Science and Theology, September 2009, Vol.5, No.3, 85-91

POLLUTION IMPACT ON THE LIFETIME OF OLD DOCUMENTS

Iulian Rusu[1*], Nicoleta Melniciuc-Puică[2] and Gabriela Lisă[1]

[1] *Technical University, Department of Chemical Engineering, Bd. D. Mangeron 71 OP 10 CP 2014, Iaşi, 700050, Romania*
[2] *University 'Al. I. Cuza', Faculty of Theology, Department of Conservation-Restoration 9 Closca, 700065 Iaşi, Romania*

(Received 24 July 2009)

Abstract

This paper is dealing with the old religious heritage resistance to chemical degradation due to the growth of industrial activities in the contemporary society. Air pollutants have a negative influence upon the physical and chemical properties of organic constitutive materials of old books. Influence of one of the most noxious factors – sulphur dioxide - was studied by means of thermal analysis. The experimental data allowed the prediction of the dependence between the half time and the temperature at which the paper support is kept.

Keywords: religious heritage, chemical degradation, isoconversional method, paper supports, thermal degradation

1. Introduction

The pollution has become one of the main causes of the cultural heritage deterioration, due to the degrading action of the air pollutants generated by the industrial activity. Their presence in outdoor atmosphere, museums, libraries, archives, etc. is a permanent threatening to the cultural heritage items, due to complex chemical processes, mainly oxidation reactions, which irreversibly affect the constituent materials structure [1].

Among the main air pollutants that affect the constituent materials of the heritage objects are the vapours and gases found in the polluted urban atmosphere, such as: oxygen (O_2), water (H_2O), sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3), hydrogen sulphide (H_2S), ammonia (NH_3), etc [2, 3].

The sensitivity of documents to environmental pollutants also depends on the climatic factors, mainly air temperature and relative humidity.

Taking into account our concern regarding the preservation of old books collections from 'D. Stăniloae' Library from the Metropolitanate of Moldavia and Bucovina, in our previous studies we tried bring information on the complex mechanisms of thermally aged cellulose degradation, in parallel with

* e-mail: rusu_iulian@hotmail.com

approaching the influence of the degradation factors upon the paper materials employed for works of restoration art [4]. 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.

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 [5-7].

On the other hand, despite the fact that the old book collections of 'D. Stăniloae' Library are preserved in optimum microclimate conditions the effects of pollution, like red rot (degradation induced by the absorption of airborne SO_2) are present. Therefore, the aim of the present study was to test the effect of sulphur dioxide on the lifetime of old paper documents by means of thermal analysis.

2. Experimental

Samples of new and old (90 and 200 years) manually manufactured paper have been subjected to different thermal treatments in nitrogen and air. In order to be artificially aged, samples of 90 years old were kept in SO_2 atmosphere (concentration of 10 mg/m^3) for different period of time.

Thermogravimetric analyses were performed under nitrogen or air flow (20 cm^{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, pressed as pellets with KBr and subjected to IR analyses. The measurements, made on a *FT IR VERTEX 70* device, have been processed with the *OPUS*. Normalization of the spectra was based on an internal standard.

3. Results and discussion

The experimental results of the analyses performed in nitrogen revealed that the degradation occurred in two stages while the thermal treatments in air revealed a three steps mechanism. The first decomposition step concerns the dehydration process while the second one is related to the degradation of the cellulose macromolecular chain. Therefore, in our study we will deal only with the main step (the second one). In Tables 1-3 are listed the weight losses and the characteristic temperatures. The TG samples are denoted as follows: new paper degraded in air (sample 1), 90 years old paper degraded in nitrogen (sample 2), 90 years old paper aged for 3 hours in SO_2 degraded in nitrogen (sample 3), 200 years old paper degraded in nitrogen (sample 4).

Table 1. Thermogravimetric data at 7 K/min.

TG data	Sample 1	Sample 2	Sample 3	Sample 4
T_i (ºC)	290.7	295.1	305.1	270
T_m (ºC)	330.1	350.9	354.2	341.7
T_f (ºC)	345.9	365.3	366.7	351.2
Mass loss (%)	67.1	73.1	73.8	71.6

Table 2. Thermogravimetric data at 10 K/min.

TG data	Sample 1	Sample 2	Sample 3	Sample 4
T_i (ºC)	299.7	301.9	309.3	286.9
T_m (ºC)	345.1	360.3	357.6	314.3
T_f (ºC)	358.6	377	374.6	362.4
Mass loss (%)	67.5	75.4	74.3	73.7

Table 3. Thermogravimetric data at 13 K/min.

TG data	Sample 1	Sample 2	Sample 3	Sample 4
T_i (ºC)	306.6	300	308.1	293.4
T_m (ºC)	339.5	356.9	360	349.3
T_f (ºC)	356.8	379.5	377.8	366.7
Mass loss (%)	67	73.1	74.1	94

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) [8-10]. The dependence of the apparent activation energy (E_a) on the reacted fraction (α), the models of the decomposition processes for the main step ($f(\alpha)$) and the pre-exponential factor (log A) were thoroughly determined (Table 4).

Table 4. Models of the decomposition processes, the variation of activation energy and of the pre-exponential factor.

Kinetic parameters	Sample 1	Sample 2	Sample 3	Sample 4
$f(\alpha)$	$\alpha^{1/2}$ power law	$2[1-(1-\alpha)^{1/2}]$ contracting cylinder	$\alpha^{1/2}$ power law	$\alpha^{1/2}$ power law
E_a (kJ/mol)	85.7÷119.7	95.77÷139.3	56.2÷203.2	34.33÷103.7
log A (min^{-1})	6.5÷9.5	7.5÷10.5	4÷14.4	2÷8.2

Further on we have used the method in order to predict the lifetime of the analysed paper samples (Table 5).

Table 5. Lifetime prediction as a function of temperature for the analysed samples.

Lifetime prediction (Years)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**
t_{iso} (50%) at 10ºC	10500	100 000	9400	4250
t_{iso} (50%) at 20ºC	2700	21000	2450	1150
t_{iso} (50%) at 30ºC	750	5250	720	340
t_{iso} (50%) at 35ºC	440	2800	385	190

The literature recommends the use as comparative parameter the half time ($T_{1/2}$) as the period of time over which the material under investigation looses half of its physico–chemical properties [11]. Therefore, in order to have comparable data with those provided by literature 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}).

Obviously, in our study we do not take into consideration the effect of the humidity because in the presence of water vapours SO_2 slowly turns to sulphuric acid, a strong acid that causes rapid significant damages to archive materials. Cellulose retains the sulphuric acid and therefore the degradation appears.

As it can be observed from the above table the stability in nitrogen of the 90 years old paper is very high but when treated with SO_2 the lifetime in nitrogen sharply decreases (about one order of magnitude). We also can observe that the method clearly indicate the much lower lifetime of the 200 years old paper comparing with that of 90 years old.

It is somehow striking that a treatment of only three hours into an SO_2 atmosphere ages the paper with almost 100 years (see samples 3 and 4). On the other hand, the role of the surrounding atmosphere is also shown by the behaviour of the new paper in air. Therefore, the new paper kept in air has a calculated lifetime almost equal to that of the 90 years old paper aged with SO_2 but kept in nitrogen afterwards. These results suggested a normal ageing mechanism for paper which normally involves air oxygen.

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 [12] 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. Oxidizing agents break down the cellulose macromolecular chains and damage the paper-made artefacts [1, 13].

In the IR spectra of paper, characteristics bands of these functional groups may be observed [4, 14]. 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 (ν_{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.

Evolution of the absorption maxima for samples 2 and 3 (Figure 1) indicated the depolymerizations of the cellulosic chain occurs, resulting in the formation of –O-CH_2-CH-O- groups, according to a mechanism proposed by J. B. Havermans [15], corresponding to the absorption 1500-1200 cm^{-1}. Therefore, the IR results support the stability conclusions brought by the predictions made using Vyazovkin's method.

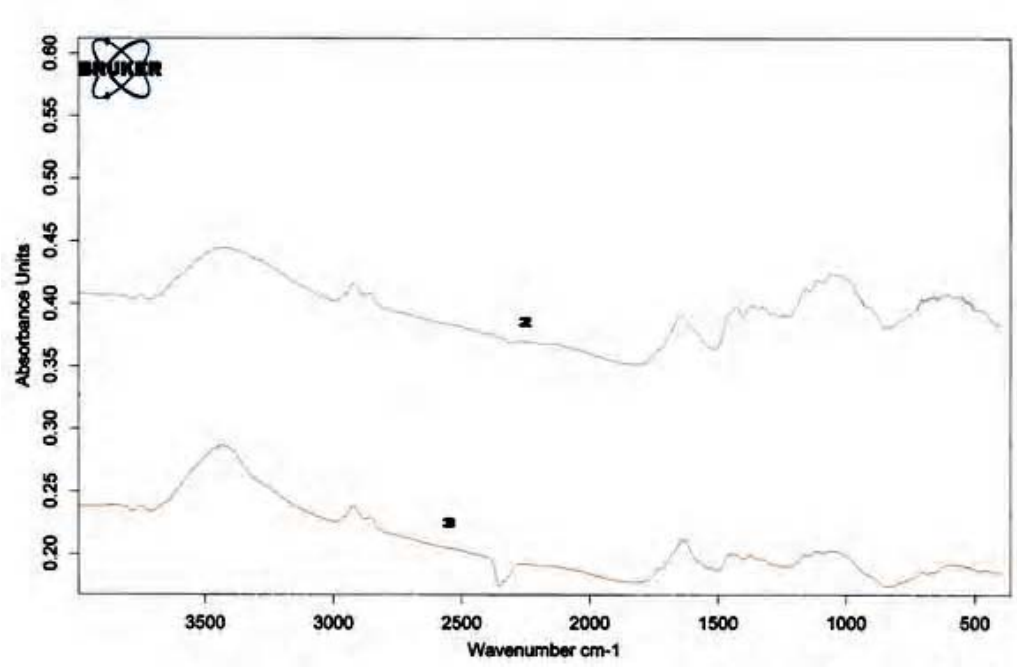

Figure 1. FTIR spectra of samples 2 and 3.

Conclusions

Our study proves that the oxidising agents from the atmosphere (e.g. O_2 and SO_2) strongly reduce the lifetime of the paper documents depending on temperature. The results are in agreement with other predictions one can find in literature data.

Due to the use of fuels with sulphur content, the presence of SO_2 is very difficult to avoid. However, some measures must be taken. For example, air ventilation should be stopped during the maximum pollution periods. Air scrubbing with alkaline solutions is an effective method for the acidity removal, but has a great disadvantage: it increases the air relative humidity and can be used only along with a dehumidification system. Buildings themselves reduce the sulphur dioxide concentration by about one half; which is absorbed by the stone, cement, concrete, woodwork and furnishings. Ozone concentration is reduced in the same way – due to its instability and it gradually turns into oxygen.

These facts suggest, apart of the controlled temperature, the possible use of recipients filled with an inert gas (e.g. 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, we must to say that the amount of research into the predictive value of artificial aging of paper by means of thermal analysis is not sufficient yet and further efforts have to be made in this direction.

References

[1] N. Melniciuc Puica and E. Ardelean, Eur. J. Sci. Theol., **4(2)** (2008) 51.
[2] P.M. Whitmore, G.R. Cass and J.R. Druzik, Journal of the American Institute for Conservation, **26(1)** (1987) 45.
[3] J. Havermans and T. Steemers, *Air pollution and its prevention*, in *Ageing and Stabilisation of Paper,* M. Strlic & J. Kolar, (eds.), National and University Library, Ljubljana, 2006, 165.
[4] N. Melniciuc Puica, A. Pui, D. Cozma and E. Ardelean, Mat. Chem. Phys., **113** (2009) 544.
[5] V. Bulacovschi, A. Stanciu, I. Rusu, A. Cailean and F. Ungureanu, Polym. Degrad. Stabil., **60** (1998) 487.
[6] S. Vyazovkin S. and N. Sbirrazzuoli, Macromol. Rapid Comm., **27(18)** (2006) 1515.
[7] I. Rusu and A. Cailean, Moldavian Journal of Physical Sciences, **6(1)** (2007) 92.
[8] S. Vyazovkin and A. Lesnikovich, Thermochim. Acta, **203** (1992) 1771.
[9] S. Vyazovkin and W. Linert, Anal. Chim. Acta, **295** (1994) 101.
[10] S. Vyazovkin, Int. Rev. Phys. Chem., **19** (2000) 45.
[11] R.D. Smith, in *Deterioration and Preservation of Library Materials*, H.W Winger & R.D. Smith (eds.), University of Chicago Press, Chicago, 1970, 139.
[12] V. Daniels, Studies in Conservation, **29** (1984) 57.

[13] M. Strlic, J. Kolar and D. Kocar, *Thermo-oxidative degradation*, in *Ageing and Stabilisation of Paper*, M. Strlic & J. Kolar, (eds.), National and University Library Ljubljana, 2006, 111.
[14] M. Ursescu, T. Măluțan and S. Ciovică, Eur. J. Sci. Theol., **5(3)** (2009) 71.
[15] J.B. Havermans, *Environmental influences on the deterioration of paper*, Barjesteh, Rotterdam, 1995.