Different Methods for Calculating Activation Energy in Kinetic Studies as an Assessment Model in Archaeo(Chemo)Metric Applications

F. Marini[1], M. Tomassetti[1], S. Vecchio[2]
[1]Dept. Chemistry, University of Rome "La Sapienza", P.le A. Moro 5, 00185, Rome, Italy.
[2]Dept. S.B.A.I., University of Rome "La Sapienza", via del Castro Laurenziano 7, 00161, Rome, Italy.

Abstract

Thermal oxidative degradation of aged and non aged cellulose samples of commercial paper was studied using thermogravimetry and derivative thermogravimetry under a forced air flow up to 800°C. TG and DTG data were processed according to two non-isothermal-based Model-Fitting methods and one based on the linear least squares E_a trend values, measured as a function of artificially induced sample age, were compared in order to assess their potential for obtaining archaeometric curves. As the trends of first two methods show an inversion in the direction among non aged cellulose samples and artificially aged samples, while the third method does not present this inversion, a deep chemometric study was carried out on the latter method using different iterative procedures of calculation. The results are discussed.

Introduction

The possibility of constructing curves as a function of ageing cellolose of UV irradiated commercial paper in weatherometer was recently investigated. It was endeavoured to detect any links between the breakdown of the cellulose and the physico – chemical parameters that would allow this to be evidenced. Consequently, the thermal oxidative degradation of non aged, or artificially aged cellulose samples of commercial paper (i.e. extra-strong paper) were studied using thermogravimetry (TG) and first-order derivative thermogravimetry (DTG). In this framework the activation energy (E_a) values, which are related to cellulose fibre packing, seem to be more promising for the purpose of constructing archaeometric curves. However there appears to be no recommended literature method for calculating the E_a of the cellulose thermal degradation process. Thus, in a previous study [1], in order to obtain reliable activation energy values and to identify the method yielding the most reliable data, a comparison was made between the results obtained by applying three different methods for calculating the E_a of the oxidative thermal breakdown of the cellulose contained in several different samples of aged and non aged paper; specifically two non isothermal, based Model-Fitting, methods – the Arrhenius differential and Satava's integral methods - were applied and compared using Wyden-Widmann's, based linear least square, method.

Materials & Methods

The TG/DTG measurements were carried out on a Mettler 50 thermobalance, coupled with a Mettler TG 10-TA processor system and a Swiss dot matrix printer.

Paper ageing was achieved by photoirradiation at λ = 310 nm in a weatherometer (Model QUV/spray Q-Panel LAB-Products) for up to 750 hours. The apparatus was equipped with 8 mercury lamps (40 W each) which can simulate sunlight perfectly up to 370 nm.

Samples of extra-strong paper for photocopiers and laser printers (white paper for office photocopiers, Copy blu, Code 13092 - 6IN - Format 21x29.7 cm, A4, basic weight 80 g m^{-2}) were studied either as such or artificially aged in a weatherometer for different ageing periods up to a maximum of 750 h.

Results

A reasonable correlation was found between the trends obtained using Arrhenius' and Satava's methods and partly also using the Wyden-Widmann method, applied to artificially aged paper, while some difficulty was found when comparing E_a values of artificially aged paper with those of non aged paper, the representative point of which was quite anomalous and differed in the trends obtained, so that in the latter case non negligible differences in E_a values were found. In addition it was not clear to what extent this depended on the real differences in the physico-chemical characteristics of the cellulose in the non aged sample versus the aged samples and, conversely, to what extent the kinetic method used to calculate the Ea values actually affects the trend obtained. In the present research we thoroughly tested the Wyden-Widmann method, which is very often applied automatically using computer implemented software coupled to the thermogravimetric apparatus. Repeated tests carried out without the help of commercial software indicated that the E_a value obtained various considerably not only when the amplitude of the temperature range in which the method is applied is extended, but above all by increasing the number of points right and left of the DTG peak with which the method is applied. However, if a sufficiently large number of these experimental points is used (at least > 60), applying the Arrhenius or Satava method.

Conclusions

It was possible to conclude that: (i) the most correct trend E_a trend, as a function of the irradiation time in the veatherometer, seems to be the one obtained using the latter two methods based on model fitting to identify the model function that best fit the experimental trend of the peak DTG value. However, a sufficiently correct trend may be obtained also by applying the Wyden–Widmann method but using only a suitable number of points right and left of the DTG peak and an appropriate temperature range. In other words, simply using the procedures emerging from our investigation; (ii) it therefore seems that the inversion of the trend found on going from the non aged paper sample to the artificially aged samples is real and linked the non aged paper matrix, at least for the E_a values of the commercial paper studied in the present research. Computation of regression parameters in Wyden and Widmann method was also tried using a non-least squares iterative method and results comparable to the MLR solutions were obtained. At present, the effect of using different functions in the Wyden and Widmann method for the estimation of the kinetic parameters is under investigation.

References

1) Luigi Campanella, Cecilia Costanza, Mauro Tomassetti, Stefano Vecchio, Kinetic processing of thermoanalytical curves of cellulose samples and finds, assessment of possible archaeometric applications, *Curr. Anal. Chem.* (in press)

Acknowledgements

Authors are indebted to Dr. C. Costanza and Prof. L. Campanella for making available the paper samples analysed which were artificially aged in a weatherometer.