3.3. Quantitative evaluation of plastics degradation

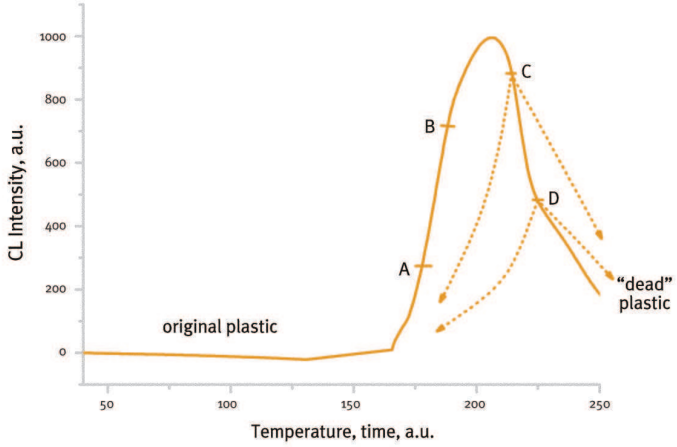

Figure 7. Trajectory of the service life of the plastics determined by chemiluminescence

Evaluation of kinetic parameters from isothermal and non-isothermal runs is rather sophisticated and is based on some a priori assumed models (Rychlý and Matisová-Rychlá 2008).

The philosophy of these mathematics is hidden in the computer's programs developed earlier and adopted to the degradation of plastics in museums as explained below.

3.3.1. Chemiluminescence (CL)

The Figure 7 shows which is the trajectory of the material from original plastic object to the dead plastic, as it may be followed by chemiluminescence. The dead plastic is useless for any other application. At the beginning of the life service the intensity of the light emission is low, then stepwisely increases, passes through the maximum and finally decreases back to a low value. Having unknown material we can be hypothetically at any of the depicted points of the trajectory, as e.g. in point A, B, C, D or in another else. To this also corresponds the shape of the resulting accelerated test of the sample stability. Performing the non isothermal experiment on unknown sample which is aged under certain condition in independent experiment the evolution of the original curve may be observed with the well observed shift to lower temperatures provided that we are in front of the maximum or to higher temperatures if we are behind the maximum. It is of interest that dead plastic performs a relatively low level of the observed light emission simply because of that the sites of further degradation are lacking.

3.3.2. Isothermal measurements

Isothermal CL runs can be fitted by Eq. 1:

Eq. 1:
$$I = \frac{A \exp(-k_1 t)}{[1 + Y \exp(-K_2 t)]^2}$$

Here, *A* is proportionality constant and *Y* is positive for the case of the oxidation following a sigmoidal shape and negative for the case when the oxidation demonstrates a monotonous decay in the curve (Rychlý and Matisová-Rychlá 2008). The main advantage of using this equation which was successfully applied for description of chemiluminescence from polypropylene oxidation is that it is directly related to the oxidation process. k_1 appears to correspond to the rate constant for the unimolecular decomposition of isolated hydroperoxides while k_2 represents the rate constant for the bimolecular decomposition of associated hydroperoxides (See Figure 2).

The induction time is determined not only by the corresponding rate constant but also by the parameter *Y*, which is the ratio of maximum $[POOH]_\infty$ (at an infinitely long process time) and the initial concentration of hydroperoxides $[POOH]_0$ reduced by one (Eq. 2):

Eq. 2:
$$Y = \left\{\frac{[POOH]_\infty}{[POOH]_0}\right\} - 1$$

One should bear in mind that $[POOH]_\infty$ is related to the maximum intensity I_{max} which should be kept constant once reached and not decay as observed in reality.

As the maximum concentration of hydroperoxides is determined by the kinetic parameters and should be constant at a given temperature, the initial concentration of hydroperoxides should be considered as a measurement of the polymer quality, including all structural defects in the polymer due to processing, reactions of residual catalyst, etc. These defects represent the points where degradation starts by the conversion of such irregular structures to hydroperoxides.

3.3.3. Non-isothermal measurements

Non-isothermal chemiluminescence measurements are used for estimation of kinetic parameters which may be linked to the residual service life of plastics. Their advantages consist in the following:

- A one run experiment from which kinetic parameters of polymer degradation may be estimated at different temperatures.
- Method following the gradual reduction of stability of plastics which were aged out of the chemilumnescence instrument under isothermal conditions.

The kinetic model that was developed by Ekenstam (Ekenstam 1936) and Emsley and Stevens (Emsley *et al.* 1994) for the degradation of cellulose is quite simple. Nevertheless, it may quantify the non-isothermal process which is a necessary pre-requisite of any extrapolation or comparison of the effect of various additives. The degree of polymerisation (*DP*) is here understood as the ratio of concentration of monomer units (*N*) and polymer molecules (*i*) according to Eq. 3:

Eq. 3: $$DP = \frac{N}{i}$$

Due to degradation, the concentration of fragmented polymer molecules increases with time. Provided that the process takes place statistically, the kinetics of the concentration of macromolecules increase (for the case of degradation) and may be described by the following equation (Eq. 4):

Eq. 4: $$\frac{di}{dt} = mki^n$$

where n stands for the order of main chain scissions while m=1 for the case of degradation and m=-1 for the crosslinking case. The most frequent reaction orders encountered in the literature are n=0 or n=1.

For the former case of n=0 and m=1 (Eq. 5):

Eq. 5: $$\frac{di}{dt} = k \text{ and } i = i_o + kt$$

where i_o is the initial concentration of macromolecules in the system. Here, the number of fragmented macromolecules increases linearly with the time of degradation. For *DP*, we then have:

Eq. 6: $$DP = \frac{N}{i_o + kt}$$

or $$DP = \frac{DP_o}{1 + \frac{k}{i_o} t} \quad \text{where } DP_o = \frac{N}{i_o}$$

After transformation:

Eq. 7: $$\frac{DP_o}{DP} = 1 + \frac{k}{i_o} t$$

A plot of $1/DP$ vs. time should thus be a straight line with a slope of $\frac{k}{i_o}$ of unit s^{-1}.

Consequently, it enables a direct comparison between samples of different initial *DP*.

To develop an interpretation of non-isothermal CL runs, one needs to go back to the possible reactions leading to the light emission. CL generally expresses the rate of sample oxidation, where the intensity depends on a set of parameters such as the geometry of the sample, temperature, oxygen concentration, concentration of potential emitters, e.g. carbonyl groups in the sample, morphology and water content, etc. In the first approximation, it can be assumed that - similarly to isothermal conditions – that the CL intensity *I* is proportional to the rate of hydroperoxide decomposition. At the same time, it may be assumed that the latter reflects the changes of the polymerisation degree

Eq. 8: $$I = \mu \left[-\frac{d[POOH]}{dt} \right] = \alpha \left[-\frac{dDP}{dt} \right]$$

where μ and α are the proportionality constants.

According to Eq. 7, $-\frac{dDP}{dt} = \frac{k}{i_o DP_o} DP^2$ and for non-isothermal conditions:

Eq. 9: $$-\frac{dDP}{dT}\frac{dT}{dt} = \frac{A \exp(-E/RT)}{i_o DP_o} DP^2$$

Here, *T* is the temperature, *A* and *E* are the pre-exponential factor and the activation energy, respectively, and $\frac{dT}{dt} = \beta$ is the linear heating rate of the sample.

After integration of Eq. 9 and substitution into Eq. 8, we finally obtain Eq. 10:

$$I = \alpha \frac{A \exp(-E/RT)}{i_o} \frac{DP_o}{[1 + \frac{A}{\beta i_0} \int_{T\,room}^{T} \exp(-E/RT) dT]^2}$$

It is noteworthy that while the process of the chain scission is of zero order, the chemiluminescence runs formally correspond to the second order scheme. For complex non-isothermal curves, it is preferable to use the sum of several independent processes, each of which has its proper Arrhenius dependence of the rate constant. In a case, e.g. three processes, the resulting equation suitable for fitting of non-isothermal data is the following (Eq. 11):

Eq. 11:
$$I = \sum_{j=1}^{3} \frac{P_j \exp(-E_j/RT)}{\left[1 + \frac{A_j}{\beta}\int_{T\,room}^{T} \exp(-E_j/RT)dT\right]^2}$$

Here, P_i is the proportionality constant including the corresponding terms from Eq. 8 and A_i and E_i are respectively the pre-exponential factor and the activation energy of component *i* of the initiation reaction. The latter values are used for calculation of the average rate constant of oxidation at a given temperature.

The average rate constant k_{av} for 3 components of initiation (j=3), leading to the light emission, is defined as:

Eq. 12:
$$k_{av} = \frac{P_1}{P_1+P_2+P_3}\,k_1 + \frac{P_2}{P_1+P_2+P_3}\,k_2 + \frac{P_3}{P_1+P_2+P_3}\,k_3$$

where k_1, k_2 and k_3 are rate constants at a given temperature of the respective initiating process. They have the magnitude of the first order reaction (s^{-1}). In practical computation procedures, one determines the corresponding parameters for any of the initiating events by non-linear regression analysis taking into account the experimental runs normalised to one at the maximum temperature of the experiment I_{max}.

3.3.4. TGA

The formation of volatile degradation products as observed by non-isothermal thermogravimetry represents an integral process. The complex non-isothermal thermogravimetry curve that is apparently composed of several independent processes was described by the first-order scheme, i.e. $-\frac{dm}{dt} = km$. In a non-isothermal mode,

Eq. 13:
$$-\frac{dm}{mdT}\,\frac{dT}{dt} = A\exp\left(-\frac{E}{RT}\right)$$

where $\beta = \frac{dT}{dt}$ is a linear heating rate.

After integration, we obtain:

$$m = m_o \exp\left[- \frac{A_i}{\beta} \int_{T_o}^{T} \exp\left(- \frac{E_i}{RT} \right) dT \right]$$

and for the process composed of j temperature dependent components – "waves", we have

Eq. 14: $$m = m_o \sum_{i=1}^{j} \alpha_i \exp\left[- \frac{A_i}{\beta} \int_{T_o}^{T} \exp\left(- \frac{E_i}{RT} \right) dT \right]$$

Provided that mass changes are expressed as a percentage of the original mass, m_o, parameters α_i, A_i, E_i may be found by a nonlinear regression analysis program applied to curves of the experimental mass *m* vs. temperature T, from the initial temperature T_o to a final temperature T of the experiment. The rate constant, k_i, corresponds to a given temperature, and is expressed as:

Eq. 15: $$k_i = A_i \exp(-E_i/RT)$$

Ozawa (Ozawa 1992) proposed to work without any a priori assumed model. The estimation of TG and in some cases also of DSC runs is based on careful measurements at several heating rates and the construction of the plot ln β vs 1/T where β is the slope of the linear increase of the temperature (i.e. the heating rate). This plot follows from the equation 13 which may be rewritten as:

Eq. 16: $$\ln \beta = - \frac{E}{RT} + \ln \left(A \frac{m}{\left[-\frac{dm}{dT} \right]} \right)$$

at a certain mass *m* or its conversion to volatiles products the term involving pre-exponential factor is constant and activation energy may be determined for several heating rates without necessity to consider any model a priori. The model of degradation which is necessary to know for calculation of rate constants is hidden in the term containing the pre-exponential factor.

3.3.5. Non-isothermal DSC

While non-isothermal thermogravimetry covers the decomposition of polymer from the mass loss and extends from evaporation of potentially present low molar mass compounds at low temperatures

into the temperature interval of transformation of eventually formed char residue, DSC covers all exothermic and endothermic processes that may be mutually superimposed. The disadvantage of the use of DSC experiments for the kinetic measurements is the difficulty of determination of the base line over a large temperature interval. This line should be subtracted from the experimental curve. Determination of the so-called induction temperature which was successfully used by Fratričová and Šimon (Fratričová *et al.* 2006) for determination of isothermal parameters from originally non-isothermal runs of the oxidation of polyurethanes appears to be advantageous for stabilised polyolefins and polyurethanes where the increase of the heat release after the inhibitor consumption is much more sharp when compared with pure polymers. However, the method is not suitable for the study of oxidation of PMMA and PS that do not give distinct oxidation exotherm.

The estimation of kinetics based on DSC for PE and PP may take into account the actual intensity of the signal (DSC) which is divided by the remaining area below the curve and for the first order of decomposition reaction it should be proportional to the remaining amount of non-reacted polymer. For the first order rate constant we thus have:

Eq. 17: $$\frac{k}{\beta} = \frac{DSC}{\int_{T_{init}}^{\infty} DSCdT - \int_{T}^{\infty} DSCdT}$$

Here β is the linear rate of heating, DSC is the signal of DSC for the respective temperature and

$$\int_{T_{init}}^{\infty} DSCdT$$

is the total surface below DSC curve from the initial temperature T_{init} to the end of the line while

$$\int_{T}^{\infty} DSCdT$$

are the surfaces from the temperature T to the end of the line. Provided that

Eq. 18: $$\int_{T_{init}}^{\infty} DSCdT \text{ is } << \int_{T}^{\infty} DSCdT \text{ then } \frac{k}{\beta} = \frac{DSC}{\int_{T_{init}}^{\infty} DSCdT}$$

or $$k = \frac{DSC}{\int_{T_{init}}^{\infty} DSCdt}$$ where t is time.

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