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ACCELERATED THERMOOXIDATIVE AGEING TESTS AND THEIR EXTRAPOLATION TO LOWER TEMPERATURES

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A procedure for the extrapolation of accelerated thermo-oxidative ageing tests to lower temperatures is proposed. The procedure involves a deconvolution of the global process into high- and low-temperature components where the extrapolation to low temperatures is carried out using the low-temperature component. The method was tested on stabilized and unstabilized polyisoprene rubber and was found to produce realistic estimations of the length of the induction period of oxidation so giving a more accurate estimation of the service life. However, to obtain the low-temperature values of the adjustable kinetic parameters, very low heating rates are required (0.04 K min^{-1}, 0.1 K min^{-1}) making the measurement process time consuming. Using this method, more realistic estimates of the durability of a material are obtained.

Keywords: *induction period, service life, thermal oxidation*

Introduction

The combination of oxygen as the reactant and heat as the energy source is a major factor in material degradation. The degradation leads to changes in molecular structure and, consequently, to changes in chemical and physical properties of materials. In most cases, the oxidation processes occurring in the condensed phase exhibit an induction period where seemingly no chemical reaction takes place. The induction period of oxidation is determined as the time of a sudden increase in the rate of oxidation [1]. At the end of induction period, also a sudden change in material characteristics mostly takes place so that the length of induction period is often considered as a relative measure of material stability.

The rate of degradation processes under application conditions is usually too slow. To estimate the stability of materials, a sample is mostly subjected to an accelerated test under standardized conditions where heating is the most common means of accelerating the oxidation. The standard tests for induction period determination are predominantly carried out under isothermal conditions. However, under isothermal conditions, the peak measured using DSC or TG is often flat and its onset, corresponding to the end of induction period, cannot be determined unambiguously. Additionally, a significant period of time is required to achieve the constant elevated temperature. Whilst studying transformation processes at various heating rates [1–3] we realised that, contrary to the problems associated with the measurement of the onset temperature in isothermal measurements, the transformation peak is distinct and the onset temperature can be measured accurately and unambiguously. Hence, a method has been proposed for the determination of the kinetic parameters of induction periods from the onset temperatures of nonisothermal DSC runs using linear heating rates [1].

The principal goal of stability studies is to extrapolate kinetic data, obtained from accelerated stability tests, to the application conditions. The prediction of long-term durability by extrapolation is a very difficult task since many fundamental scientific problems in this field remain unsolved. For example, morphological differences may exist between high- and low temperature experimental conditions which may influence the rate of oxygen diffusion into the specimen resulting in changes in the mechanistic pathways of the oxidation and thus altering the measured rate of the process. A simple extrapolation from high-temperature data to ambient temperature regularly leads to the estimation of unrealistically long durability [3, 4]. In this paper a new method is proposed for the estimation of long-term durability from the accelerated stability tests with linear heating. The method is based on the recently proposed concept of single-step kinetics approximation [5, 6].

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Theoretical part

Rate of the processes in condensed state is generally a function of temperature and conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(T, \alpha) \tag{1}$$

The single-step kinetics approximation employs the assumption that the function Φ in Eq. (1) can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on the temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α. The rate of the complex multi-step condensed-state process can thus be formally described as [5, 6]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T) f(\alpha) \tag{2}$$

Equation (2) is mostly called the general rate equation. Indeed, it resembles a single step kinetics equation, even though it is a representation of the kinetics of a complex, generally multi-step, condensed-phase process. The single-step kinetics approximation thus resides in substituting a generally complex set of kinetic equations by the sole single-step kinetics equation. Hence, Eq. (2) represents a mathematical formulation of the single-step kinetics approximation [5, 6]. The word 'approximation' is the most important in order to make clear and stress that it is not a true kinetic equation. It is just a mathematical tool enabling the description of experimental results without a deeper insight into the mechanism of the process.

In general, Eq. (2) may not be straightforwardly connected with the reaction mechanism [6]. The temperature function in Eq. (2) is mostly considered to be the rate constant and the conversion function is considered to reflect the mechanism of the process. It was discussed in [5] that this interpretation of the both functions may not be correct. Since Eq. (2) is a formulation of the single-step approximation, the functions $k(T)$ and $f(\alpha)$ represent, in general, just the temperature and conversion components of the kinetic hypersurface.

The temperature function $k(T)$ is most frequently expressed by the Arrhenius relationship:

$$k(T) = A_\mathrm{k} \exp\left[-\frac{E}{RT}\right] \tag{3}$$

where A_k is the preexponential factor, E is the activation energy, T is absolute temperature and R stands for the gas constant. Equation (2) can also be used to describe the kinetics of the reactions occurring during the induction period. The existence of these (unspecified) reactions is undetected by the experimental technique used; however, they must take place as a preparatory stage preceding the main oxidation process.

The Arrhenius plot of the oxidation induction time is often observed to be non-linear [4, 7]. For example, in the oxidation of cross-linked low-density polyethylene, a more than four-fold difference in the values of activation energies between high and moderate temperatures has been observed [7]. In some of our unpublished data, we have also observed a decrease in the activation energy of polyisoprene rubber oxidation with decreasing heating rate. This has led us to the conclusion that the temperature function of Eq. (2) could be deconvoluted into two partial functions, the low- (k_L) and high-temperature (k_H) functions:

$$k(T) = k_\mathrm{L}(T) + k_\mathrm{H}(T) \tag{4}$$

A similar function has been suggested for kinetic analysis in references [6, 8]. Combination of Eqs (2) and (4) results in:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)[k_\mathrm{L}(T) + k_\mathrm{H}(T)] \tag{5}$$

From Eqs (3) and (4) the apparent activation energy, E, can be simply determined:

$$E = \frac{k_\mathrm{L} E_\mathrm{L} + k_\mathrm{H} E_\mathrm{H}}{k_\mathrm{L} + k_\mathrm{H}} \tag{6}$$

where E_L and E_H are the activation energies corresponding to the low- and high-temperature functions, respectively. The value of E calculated from Eq. (6) is plotted as a function of temperature for three various pairs of high- and low-temperature parameters in Fig. 1. As can be seen, the apparent activation energy approaches the value of E_H for high temperatures and the value of E_L for low temperatures.

Non-isothermal stability tests are usually carried out at heating rates above 1 K min^{-1}. Under these conditions, the temperature corresponding to the end of induction period decreases with decreasing the heating

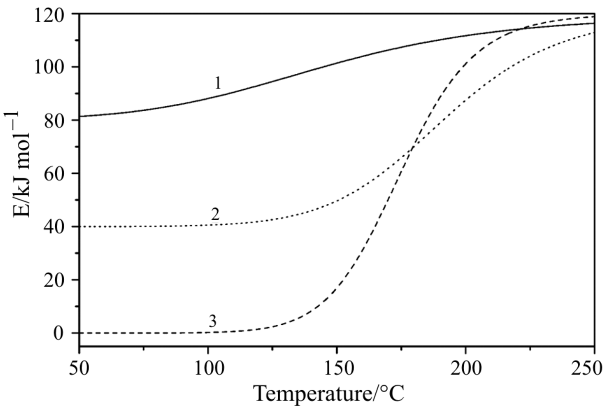

Fig. 1 Apparent activation energy E calculated from Eq. (5) for the values: A_H=1·10^{13} min^{-1}, E_H=120 kJ mol^{-1} and (1) A_L=1·10^{8} min^{-1}, E_L=80 kJ mol^{-1}; (2) A_L=1·10^{4} min^{-1}, E_L=40 kJ mol^{-1}; (3) A_L=0.1 min^{-1}, E_L=0 kJ mol^{-1}

rate [1, 3]; however, a single value of activation energy results from the treatment of the kinetic data obviously approximating the high-temperature value of the activation parameter, E_H. If one desires to deconvolute the low- and high-temperature functions, a considerable part of the process should occur in the low-temperature region. The lower heating rate, the greater part of the process occurs in the low-temperature region. Hence, in the thermooxidation measurements also the heating rates well below 1 K min^{-1} should be included.

Experimental methods

Differential scanning calorimetry

A Perkin Elmer DSC-7 calorimeter was employed to study the thermooxidative stability of the samples. The temperature scale was calibrated using In, Sn and Zn, the enthalpy calibration was determined from the heat of fusion of In. Samples of 2–4 mg were placed in crimped standard aluminium pans, where the lid of each pan was perforated by ten pinholes. The end of the oxidation induction period was determined as the onset temperature of the oxidation peak. Heating rates used were 0.04, 0.1, 0.2, 0.5, 1, 2, 3, 5, 7, 10 and 15 K min^{-1}. The purge gas forming the reaction atmosphere was oxygen.

Materials

Synthetic polyisoprene rubber (PIR) was purchased from Aldrich. The stabilised sample was prepared by solvent casting toluene solutions of PIR and the stabilizer on a glass Petri dish. The solvent was then evaporated in a vacuum oven. The samples of PIR, both stabilized and unstabilized, were stored in a refrigerator until measured. The stabilizer used was *N*-phenyl-*N*′-dimethyl-butyl-*p*-phenylenediamine (6PPD) in the amount of 0.5 phr.

Results and discussion

The experimental data were treated by the procedure described in [1] using the equation:

$$\beta = \int_0^{T_i} \frac{dT}{A\exp[B/T]} \tag{7}$$

where the adjustable kinetic parameters *A* and *B* are given as:

$$A = \frac{F(\alpha_i) - F(0)}{A_k} \tag{8}$$

$$B = E/R \tag{9}$$

where α_i is the conversion of the reactions occurring during the induction period and corresponding to the end of the induction period and *F* is the primitive function of the inverted conversion function $1/f$ [1]. For isothermal measurements, the denominator in Eq. (7) corresponds to the induction period at a given temperature [1]:

$$t_i = A\exp[B/T] \tag{10}$$

The parameters *A* and *B* of Eq. (7) were obtained for unstabilised and stabilised PIR specimens based on the measurement of the onset temperatures, T_i, for

Table 1 Values of the adjustable parameters *A* and *B* obtained from Eq. (5), determined as a function of the range of heating rates

Sample of PIR	Range of β/K min^{-1}	Range of T_i/°C	*A*/min	$10^{-3}B$/K
unstabilized	0.04–1.	97.4–149.6	(3.8±5.7)E–9	9.5±1.3
	0.1–2.	119.5–170.3	(4.3±5.6)E–9	9.5±1.2
	0.2–3.	133.7–172.4	(4.4±6.5)E–10	10.4±1.4
	0.5–5.	142.8–180.7	(3.3±4.0)E–10	10.5±1.2
	1–7	149.6–184.4	(3.2±5.3)E–10	10.5±1.6
	2–10	170.3–192.4	(3.3±4.7)E–10	10.5±1.4
	3–15	172.4–197.8	(2.9±1.7)E–10	10.5±0.6
stabilized	0.04–1.	144.5–214.4	(2.2±1.9)E–7	9.1±0.9
	0.1–2.	172.1–222.3	(3.3±2.4)E–10	12.0±0.8
	0.2–3.	185.1–233.2	(9.0±6.5)E–11	12.6±0.8
	0.5–5.	202.6–240.0	(8.0±6.1)E–12	13.8±0.8
	1–7	214.4–251.3	(4.1±4.4)E–11	13.0±1.2
	2–10	222.3–260.6	(2.3±1.6)E–10	12.2±0.8
	3–15	233.2–264.1	(4.5±5.2)E–11	13.0±1.3

Table 2 High- and low-temperature limits of the parameters *A* and *B* and the estimated lengths of the induction periods for the oxidation of polyisoprene rubber at 298 K calculated using Eq. (8)

Sample of PIR	low/high temp. limit	A/min	$10^{-3}B/K$	induction period/yr
unstabilized	low	4.0E–9	9.5	0.53
	high	3.2E–10	10.5	1.22
stabilized	low	2.2E–7	9.1	7.65
	high	4.3E–11	13.0	722

a sequence of five consecutive heating rates and are listed, based on the range of heating rates used, in Table 1. The experimental and calculated values of the onset temperatures are shown in Fig. 2; it can be seen that the agreement is very good.

As seen from Table 1, the magnitude of the parameter B is a function of the range of heating rates used (or onset temperature T_i). The dependences of B on average T_i resemble those ones shown in Fig. 1. As it has been mentioned above, the lower heating rate, the greater part of the process occurs in the low-temperature region. Provided that the values of the adjustable kinetic parameters for low heating rates represent the low-temperature limit, and for high heating rates the high-temperature limit, the induction periods can be easily determined using Eq. (10) for each temperature limit, respectively; for this calculation a representative application temperature of 298 K was applied (Table 2). The calculated length of the induction period for the oxidation of unstabilized PIR was determined to be 1.22 and 0.53 years for the high- and low-temperature limits, respectively. Both values are quite reasonable for the stability of PIR in oxygen at 298 K. The length of the induction period calculated for the stabilized sample based on the kinetic parameters determined for the high-temperature limit exceeds 700 years. 700 years is obviously not a realistic measure of the stability of stabilized PIR. The estimated length of the induction period using the kinetic parameters determined from the low temperature limit is 7.65 years. This value corresponds much more closely with experience and, therefore, encourages the use of the low-temperature limit as a significantly more accurate method for the estimation of durability.

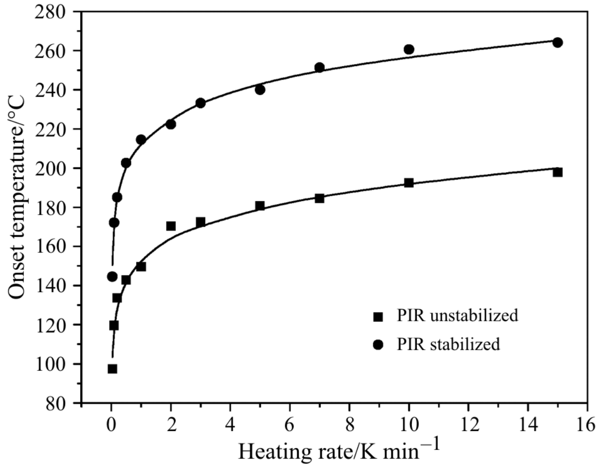

Fig. 2 Experimental (points) and calculated (full lines) values of the onset temperature of oxidation as a function of the heating rate

The procedure for the calculation of the kinetic parameters of the induction periods presented here represents a modification of the non-isothermal isoconversional integral method. The main difference between this method and those used widely in the study of thermoanalytical kinetics [9] is that the processes occurring during the induction period are not registered by the technique used. The end of the induction period is measured indirectly as the onset of the subsequent main oxidation stage. The conversion of the processes occurring during the induction period and corresponding to the end of induction period is unknown; however, as for any isoconversional method, it is assumed that its value is constant and independent of the temperature regime. Since there is no reason to assume that a single reaction occurs during the induction period, Eq. (2) represents the single-step kinetics approximation [5, 6] and, therefore, non-Arrhenius temperature functions may also lead to a satisfactory description of the dependence of the length of induction periods on temperature [5, 9]. The kinetic parameters A and B obtained are apparent so that they should not be used for any mechanistic conclusions. In future, software for the accurate deconvolution of the low- and high-temperature components will be required since the low-temperature limit kinetic parameters obtained may be partly influenced by the high-temperature component (Fig. 1). In future work, it would be advisable to determine which heating rates are needed for the reliable deconvolution of the both components of the temperature function. It can be expected that even lower heating rates than 0.04 K min^{-1} will have to be used for substances more stable than polyisoprene rubber. It would be also advisable to think about the simultaneous treatment of isothermal measurements and the non-isothermal measurements at ultra-low heating rates. The method can be used not only for the determination of oxidative stability, but also for other processes exhibiting the induction period.

Conclusions

A procedure for the extrapolation of accelerated thermo-oxidative ageing tests to lower temperatures, based on the concept of the single-step kinetics approximation, has been proposed. The procedure involves the deconvolution of the global process into high- and low-temperature components where the extrapolation to low temperatures is carried out using the low-temperature component. The method was tested for stabilized and unstabilized polyisoprene rubber. Using the values of low-temperature kinetic parameters, the method provides much more reasonable estimates of the induction period, particularly for the stabilized sample. A drawback of the method is that, for the determination of the low temperature kinetic parameters, very low heating rates (such as 0.04 K min^{-1}) are required. The resulting experiments are, therefore, time consuming, but as the calculated values of the activation parameters produce much more reasonable estimates of the induction period, the application of the method is rewarded with much more realistic estimates of the service life of materials in application.

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References

1 P. Šimon and L'. Kolman, J. Therm. Anal. Cal., 64 (2001) 813.
2 D. W. Bishop, P. S. Thomas, A. S. Ray and P. Šimon, J. Therm. Anal. Cal., 64 (2001) 201.
3 P. Šimon, M. Veverka and J. Okuliar, Int. J. Pharmaceutics, 270 (2004) 21.
4 L. Woo, A. R. Khare, C. L. Sandford, M. T. K. Ling and S. Y. Ding, J. Therm. Anal. Cal., 64 (2001) 539.
5 P. Šimon, J. Therm. Anal. Cal., 79 (2005) 703.
6 P. Šimon, J. Therm. Anal. Cal., in press.
7 S. Y. Ding, M. T .K. Ling, A. R. Khare and L. Woo, Thermochim. Acta, 147 (2000) 357.
8 J. H. Flynn, Thermochim. Acta, 37 (1980) 225.
9 P. Šimon, J. Therm. Anal. Cal., 76 (2004) 123.