

EXTRAPOLATION OF ACCELERATED THERMOOXIDATIVE TESTS TO LOWER TEMPERATURES APPLYING NON-ARRHENIUS TEMPERATURE FUNCTIONS

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Extrapolations of the accelerated thermooxidative tests, based on the Arrhenius and two non-Arrhenius temperature functions, have been tested for 26 data sets. The data cover a wide range of materials from polyolefins and other polymers to biodiesel, edible oils and dried milk. It has been found that the extrapolation from high-temperature data to ambient temperature based on the Arrhenius temperature function leads to the estimations of unrealistically long durability. The best estimations corresponding most with experience are obtained for the extrapolation based on the temperature function $k(T)=A_k\exp(DT)$.

Keywords: accelerated tests, ageing, durability, extrapolation, lifetime, non-Arrhenius temperature function, thermooxidation

Introduction

The oxidation processes occurring in the condensed phase exhibit an induction period (IP) where seemingly no chemical reaction takes place. The induction period is determined as a sudden increase in the rate of oxidation [1, 2]. At the end of IP, also a sudden change in material characteristics mostly takes place so that the length of induction period is often considered a relative measure of material stability.

The rate of degradation processes under application conditions is usually too slow to be measured. 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 IP determination are predominantly carried out under isothermal conditions. However, under isothermal conditions, the peak measured is often flat and its onset, corresponding to the end of induction period, cannot be determined unambiguously. Whilst studying oxidation processes at various heating rates [1, 2] we realised that, contrary to the problems associated with the measurement of the onset time in isothermal measurements, the oxidation peak is distinct and the onset temperature can be measured accurately and unambiguously. In our previous works, a theory of the kinetic description of IP from non-isothermal measurements has been outlined [1, 2]. The theory was applied for the study of thermooxidation of

edible oils and fatty acids methyl esters [1, 3, 4], thermooxidation of polyolefines [1, 2, 5], thermooxidative stability of pharmaceuticals [6], antioxidant activity of *p*-phenylene diamines in polyisoprene rubber [7, 8], determination of residual stability of polyurethane automotive coatings [9, 10], thermooxidative stability of dried milk [11] and stabilization of poly(methyl methacrylate) by TiO₂/SiO₂ and ZrO₂/SiO₂ nanoparticles [12].

The principal goal of stability studies is to extrapolate the 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. The extrapolation is almost exclusively carried out using the Arrhenius temperature function. However, indications are accumulating that the polymer degradation does not obey the Arrhenius kinetics [13–16]. In a recent paper [17] it has been proven that the Arrhenius function is the worst choice of the temperature function in the case of a complex process. Use of the non-Arrhenius temperature functions has been justified in papers [2, 18].

In this work, the extrapolation of the accelerated thermooxidative tests, based on the Arrhenius and two non-Arrhenius temperature functions, are tested. The data published in our papers [2–4, 7, 9–12, 19] are extrapolated.

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Single-step approximation and induction period

Mechanisms of the processes in condensed phase are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, methods based on the single-step approximation are frequently used [17, 18].

It is recognized that the rate of the processes in condensed state is generally a function of temperature and conversion:

$$\frac{d\alpha}{dt} = \Phi(T, \alpha) \quad (1)$$

The single-step 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 thus can be formally described as [17, 18, 20]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

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 condensed-phase process. In general, kinetics of a complex process should be described by a set of rate equations. The single-step approximation thus resides in substituting the set of kinetic equations by the sole single-step kinetics equation [17, 18, 20].

The temperature function in Eq. (2) is mostly expressed by the Arrhenius equation:

$$k(T) = A_k \exp\left(-\frac{B}{T}\right) \quad (3)$$

where A_k and B are adjustable parameters without a clear physical meaning [20]. The parameter B is related to the apparent activation energy, E , via the relationship $B=E/R$, where R stands for the gas constant. In papers [2, 18] we justified that, due to complexity of the processes, the temperature function can hardly be considered the rate constant so that there is no reason to be confined to the Arrhenius temperature function. Two other functions were suggested to be highly suitable to be used as temperature functions:

$$k(T) = A_k T^m \quad (4)$$

$$k(T) = A_k e^{DT} \quad (5)$$

where A_k , m and D are adjustable parameters.

Isoconversional methods represent probably the most widely employed category of methods based on Eq. (2). Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ in Eq. (2) is constant and the reaction rate is a function of temperature only. The isoconversional methods can be crudely divided into two groups, i.e., the isothermal methods and the methods at linear heating [21].

As it has been mentioned above, the induction period is a stage preceding the main oxidation stage. The processes occurring during IP are ‘invisible’ since they are not registered by the experimental technique used. The end of IP is determined indirectly as the time/temperature of a sudden increase in the rate of the main oxidation stage [2], i.e., as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of measurements with linear heating [2]. Denote α_i the conversion of the reactions occurring during IP and corresponding to the end of IP. Since the processes occurring during IP are not registered, the value of α_i is not known. Nonetheless, as for all isoconversional methods, it is assumed that the conversion α_i is always the same irrespective of the temperature regime employed during ageing stress [2].

The separation of Eq. (2) gives after some manipulations:

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i} k(T) dt \quad (6)$$

For isothermal conditions, from Eq. (6) the length of the induction period can be simply obtained for the temperature functions expressed by Eqs (3)–(5) [2]:

$$t_i = A \exp\left(\frac{B}{T}\right) \quad (7)$$

$$t_i = AT^{-m} \quad (8)$$

$$t_i = Ae^{-DT} \quad (9)$$

The parameter A in Eqs (7)–(9) is given as:

$$A = \frac{F(\alpha_i) - F(0)}{A_k} \quad (10)$$

Equations (7)–(9) represent three different ways of expressing the dependence of OIT on temperature in the case of isothermal conditions. The functional form of the dependence is determined by the choice of the temperature function.

For the measurements with constant heating rate, from Eq. (6) it can be obtained for the individual temperature functions (3)–(5) [2]:

$$\beta = \int_0^{T_i} \frac{dT}{A \exp(B/T)} \quad (11)$$

$$T_i = [A(m+1)\beta]^{1/m+1} \quad (12)$$

$$T_i = \frac{1}{D} \ln(AD\beta + 1) \quad (13)$$

T_i is the temperature at which the fixed conversion α_i is reached, i.e., the oxidation onset temperature. For the temperature functions given by Eqs (4) and (5), the temperature integral on the right side of Eq. (6) can be expressed in a closed form and the dependence of OOT on heating rate can be simply obtained as Eqs (12) and (13). The integral at the right side of Eq. (11) cannot be expressed in a closed form and has to be solved either numerically or by an expansion into series [22].

Results and discussion

From the papers [2–4, 7, 9–12, 19], 26 data sets were selected and treated. In all cases, the oxidation onset temperatures were measured as a function of heating rate. The data cover a wide range of materials from polyolefins and other polymers to biodiesel, edible oils and dried milk. The data were obtained using 4 different techniques, i.e. the differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG) and chemiluminescence (CL). The purge gas, forming the oxidation atmosphere, was either oxygen or air. The description of the samples and experimental conditions is given in Table 1.

For the treatment of data using Eq. (11), we wrote the program KINPAR (its DOS version is available on request). In the program, the parameters A and B are obtained by minimising the sum of squares between experimental and theoretical values of oxidation onset temperatures by the simplex method. The integration indicated in Eq. (11) is carried out by the Simpson method. For the treatment of data using Eqs (12) and (13) the non-linear least-squares method of the program ORIGIN was applied. After obtaining the kinetic parameters, the oxidation induction times were calculated for temperatures 150 and 25°C using Eqs (7)–(9). The OITs for 150°C represent an extrapolation of the measured results not far from the temperatures of measurements. The extrapolation to 25°C is far from the range of the measured temperatures and the calculated oxidation induction times represent estimations of durability of

Table 1 Description of the samples evaluated, technique used of measurement and the purge gas used

No.	Sample	Method	Purge gas	Ref.
1	Polyethylene	DSC	oxygen	[2]
2	Polypropylene	DSC	oxygen	[2]
3	PI rubber pure	DSC	oxygen	[19]
4	PI rubber/ SPPD 0.3 phr	DSC	oxygen	[7]
5	PI rubber/ 6PPD 0.3 phr	DSC	oxygen	[7]
6	PI rubber/ DPPD 0.2 phr	DSC	oxygen	[7]
7	PI rubber/ IPPD 0.2 phr	DSC	oxygen	[7]
8	PUR acrylate pure	CL	oxygen	[9]
9	PUR acrylate/UVA	CL	oxygen	[9]
10	PUR polyester pure	CL	oxygen	[9]
11	PUR polyester/ HALS	CL	oxygen	[9]
12	PUR acrylate pure	DSC	oxygen	[10]
13	PUR acrylate/UVA	DSC	oxygen	[10]
14	PUR polyester pure	DSC	oxygen	[10]
15	PUR polyester/ HALS	DSC	oxygen	[10]
16	PUR polyether pure	DSC	oxygen	[10]
17	PUR polyether/ AOX	DSC	oxygen	[10]
18	PMMA pure	TG	air	[12]
19	PMMA/SiO ₂ /TiO ₂	TG	air	[12]
20	PMMA/SiO ₂ /ZrO ₂	TG	air	[12]
21	Biodiesel MERO pure	DTA	oxygen	[4]
22	Biodiesel MERO/BHT	DTA	oxygen	[4]
23	Biodiesel MERO/ pyrogallol	DTA	oxygen	[4]
24	Rapeseed oil	DTA	oxygen	[3]
25	Sunflower oil	DTA	oxygen	[3]
26	Dried whole milk	DTA	air	[11]

the tested material for that temperature. The kinetic parameters obtained and the OITs calculated are summarized in Tables 2–4. The coefficient of variability of the parameter A in Eqs (11)–(13) was mostly between 25–100%, the coefficients of variability of the parameters B , m and D were below 7%.

From Tables 2–4 it can be seen that the kinetic parameters for various material vary within quite a broad range. However, within the framework of the single-step approximation the kinetic parameters have generally no physical meaning [17, 18, 20]. Therefore, no conclusions on the stability of materials

Table 2 Kinetic parameters and the calculated induction periods for the treatment of the results based on the temperature function given by Eq. (3)

No.	A/min	B/K	$t_i(150^\circ\text{C})/\text{h}$	$t_i(25^\circ\text{C})/\text{year}$
1	8.22E-18	19700	22.7	7.76E5
2	3.07E-18	19700	8.47	2.90E5
3	3.14E-10	10500	0.31	1.18
4	8.00E-13	14750	18.34	4653
5	1.22E-10	12310	8.76	197
6	6.10E-13	15080	30.5	1.07E4
7	6.60E-12	13440	6.84	474
8	4.05E-12	13500	4.84	356
9	1.78E-10	11620	2.50	28.5
10	4.82E-13	14290	3.73	600
11	8.97E-21	23620	261	4.34E8
12	7.49E-15	15530	1.08	596
13	3.28E-13	14210	2.10	312
14	1.74E-13	14360	1.59	274
15	3.69E-16	18200	29.4	2.28E5
16	3.83E-21	22100	3.07	1.13E6
17	6.78E-16	17400	8.15	2.86E4
18	6.50E-11	12500	7.31	200
19	1.13E-9	12690	198	6533
20	3.64E-11	14870	1107	3.16E5
21	1.97E-7	7590	0.20	0.043
22	8.26E-9	9060	0.27	0.25
23	1.72E-10	10930	0.47	2.73
24	8.73E-11	11100	036	2.45
25	1.66E-10	10500	0.17	0.62
26	4.66E-13	13070	0.20	9.68

Table 3 Kinetic parameters and the calculated induction periods for the treatment of the results based on the temperature function given by Eq. (4)

No.	A	m	$t_i(150^\circ\text{C})/\text{h}$	$t_i(25^\circ\text{C})/\text{year}$
1	2.65E114	42.40	19.1	6117
2	8.52E110	41.27	5.71	1229
3	1.20E67	25.05	0.32	0.23
4	5.80E81	30.03	13.2	55.6
5	7.50E67	24.86	6.54	4.49
6	1.80E82	30.07	32.3	137
7	1.00E79	29.09	6.45	19.5
8	1.30E78	28.82	4.31	11.9
9	3.80E67	24.92	2.30	1.62
10	1.09E107	39.77	6.56	833
11	4.70E164	60.87	1045	2.15E8
12	3.37E111	41.69	1.75	437
13	4.96E97	36.32	3.40	129
14	6.10E92	34.54	1.92	39.1
15	3.16E86	31.90	8.64	70.0
16	7.91E139	52.37	3.65	3.84E4
17	1.27E97	36.00	5.93	202
18	8.96E67	24.92	5.18	3.64
19	5.68E63	22.87	81.0	27.8
20	2.38E74	26.66	377	4.87
21	6.47E56	21.19	0.24	0.045
22	1.54E78	29.17	0.62	1.94
23	9.02E66	25.00	0.33	0.24
24	1.55E68	25.46	0.35	0.30
25	8.92E64	24.36	0.16	0.09
26	7.06E80	30.36	0.21	1.00

should be drawn just from the values of kinetic parameters (for example, it is not trustworthy to draw conclusions just from the values of activation energies) [17]. The parameters enable to evaluate the induction periods for any temperature regime. For drawing conclusions, the physical properties accessible to measurement, i.e. either OOT or OIT, should be calculated using the parameters.

The oxidation induction times for the constant temperature of 150°C, calculated from the values of kinetic parameters using Eqs (7)–(9), do not differ much. Equation (7) gives mostly the longest values of OIT, however not in all cases. The difference in the values of OIT is in all cases lower than an order of magnitude. A different situation is for the values of OIT evaluated for the temperature 25°C. In all cases but one Eq. (7) gives the longest values of OIT. In many cases the values of OIT exceed 1000 years and in several cases they exceed 10⁵ years. It is a common

experience that the durability of polymers under oxidative atmosphere can be of the order of years or decades of years. The durability of biodiesel, edible oils and dried milk can be several weeks or months at 25°C under air or oxygen. Thus, the extrapolation from high-temperature data to ambient temperature based on the Arrhenius equation leads to the estimation of unrealistically long durability. The estimations based on Eq. (8) are much more reasonable. The best values corresponding most with experience are obtained for the values of OIT evaluated using Eq. (9).

It is necessary to keep in mind that the estimations of durability correspond to the experimental conditions in the accelerated high-temperature tests. In all cases, the samples were in the form of a very thin layer so that the diffusion of oxygen played a negligible role. The estimations are thus valid for the samples with no temperature gradients and no delay

Table 4 Kinetic parameters and the calculated induction periods for the treatment of the results based on the temperature function given by Eq. (5)

No.	A/min	D/K^{-1}	$t_i(150^\circ\text{C})/\text{h}$	$t_i(25^\circ\text{C})/\text{year}$
1	1.86E19	0.08890	14.3	109
2	6.15E18	0.08875	5.02	37.7
3	8.39E11	0.05786	0.33	0.051
4	1.23E14	0.06151	10.2	2.53
5	9.38E11	0.05141	5.50	0.39
6	1.29E14	0.06080	14.4	3.28
7	4.58E13	0.06070	5.34	1.20
8	5.21E13	0.06176	3.88	1.00
9	1.13E12	0.05408	2.18	0.21
10	1.68E18	0.08541	5.63	27.8
11	1.54E27	0.1234	540	3.08E5
12	1.19E19	0.09287	1.70	21.4
13	6.28E16	0.07907	3.08	6.90
14	1.08E16	0.07614	1.82	2.83
15	8.09E14	0.06678	7.20	3.47
16	3.10E23	0.1154	3.18	669
17	4.13E16	0.07689	5.09	8.68
18	6.73E11	0.05127	4.24	0.29
19	1.15E11	0.04171	41.3	0.87
20	4.13E12	0.04728	141	5.93
21	2.77E10	0.05049	0.24	0.015
22	5.74E13	0.06625	0.64	0.29
23	1.07E12	0.05833	0.34	0.057
24	8.72E11	0.05770	0.36	0.056
25	2.73E11	0.05686	0.16	0.023
26	1.52E14	0.07117	0.21	0.18

in the oxygen supply to the reacting species. For polyolefins, the molten polymers undergo oxidation in the accelerated tests so that the estimations of durability are related to the liquid state of the polymers. If the tests were carried out under oxygen, the estimations are related to the atmosphere of pure oxygen.

Conclusions

The extrapolation of the accelerated thermooxidative tests, based on the temperature functions given by Eqs (3)–(5), have been tested for 26 data sets. It has been found that the extrapolation from high-temperature data to ambient temperature based on the

Arrhenius temperature function very often leads to the estimations of unrealistically long durability. The best estimations of durability corresponding most with experience are obtained for the extrapolation based on the temperature function given by Eq. (5).

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