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MATERIAL STABILITY PREDICTIONS APPLYING A NEW NON-ARRHENIAN TEMPERATURE FUNCTION

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A new temperature function, derived from the observed dependence of the isoconversional temperature on heating rate, is suggested. Using the new function, extrapolation of the accelerated thermooxidative tests has been performed for 26 experimental 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 provides estimations corresponding with experience. Coefficients of variability of the adjustable parameters occurring in the new function are low so enabling to make trustworthy stability predictions.

Keywords: *accelerated tests, ageing, extrapolation, lifetime, non-Arrhenian temperature function, stability prediction*

Introduction

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 degradation and thermoanalytical devices are widely used for the measurement of degradation kinetics. 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.

Thermooxidation of organic materials is a very frequent case of material degradation. The oxidation processes occurring in the condensed phase exhibit an induction period (IP) where seemingly no chemical reaction takes place. At the end of IP, also a sudden deterioration in material characteristics mostly takes place so that the length of induction period is often considered a relative measure of material stability. 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 [1, 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]. The standard oxidation tests 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. In the study of oxidation processes at various heating rates [1, 2] the peak is distinct and the onset temperature can be mostly 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 TiO_2/SiO_2 and ZrO_2/SiO_2 nanoparticles [12].

Currently, the extrapolation of the degradation tests to lower temperatures 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-Arrhenian temperature functions has been justified in papers [2, 18]. In paper [19] the extrapolation of accelerated stability tests was carried out for the methods based on the Arrhenius and two

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non-Arrhenian temperature functions for 26 data sets. It has been concluded that the Arrhenius extrapolation often leads to severe overestimation of the material lifetime at ambient temperatures. The most reasonable agreement with the experience was achieved for one of the non-Arrhenian functions. In this paper, we suggest a procedure of obtaining the temperature function from an observed dependence of isoconversional temperature on heating rate. Predictions of the stability based on the new temperature function are carried out.

Single-step approximation and temperature functions

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].

The single-step approximation employs the assumption that the rate of the complex multi-step condensed-state process can be formally described as [17, 18, 20]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \qquad (1)$$

Equation (1) is mostly called the general rate equation. Indeed, it resembles a single-step kinetic 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 kinetic equation [17, 18, 20].

The temperature function in Eq. (1) is mostly expressed by the Arrhenius equation

$$k(T)=A_\mathrm{k}\exp\left[-\frac{B}{T}\right] \qquad (2)$$

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:

$$k(T)=A_\mathrm{k}T^\mathrm{m} \qquad (3)$$

$$k(T)=A_\mathrm{k}\mathrm{e}^{DT} \qquad (4)$$

where A_k, m and D are adjustable parameters.

Isoconversional methods represent probably the most widely employed category of methods based on Eq. (1). 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. (1) 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].

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 variables in Eq. (1) gives after some manipulations

$$\int_0^{\alpha_\mathrm{i}}\frac{\mathrm{d}\alpha}{f(\alpha)}=\int_0^{t_\mathrm{i}}k(T)\mathrm{d}t \qquad (5)$$

After integration and some rearrangements one can get

$$1=\frac{1}{F(\alpha_\mathrm{i})-F(0)}\int_0^{t_\mathrm{i}}k(T)\mathrm{d}t \qquad (6)$$

Equation (6) enables to evaluate the induction period for any temperature regime. Particularly, for a constant heating rate the time *vs*. temperature relationship is given as $\mathrm{d}t=\mathrm{d}T/\beta$ so that Eq. (6) leads to the result

$$\beta=\frac{1}{F(\alpha_\mathrm{i})-F(0)}\int_0^{T_\mathrm{i}}k(T)\mathrm{d}T \qquad (7)$$

where β stands for the heating rate.

The procedure of obtaining the temperature function from an observed dependence of isoconversional temperature on heating rate is reverse to that of deriving Eq. (7). After differentiation of Eq. (7) one can get:

$$\frac{\mathrm{d}\beta}{\mathrm{d}T_\mathrm{i}}=\frac{k(T_\mathrm{i})}{F(\alpha_\mathrm{i})-F(0)} \qquad (8)$$

where $k(T_\mathrm{i})$ is the temperature function at T_i. Isoconversional temperature, T_i, is followed as a function of β. Thus, differentiation of the inverse function is

$$\frac{\mathrm{d}T_\mathrm{i}}{\mathrm{d}\beta}=\frac{F(\alpha_\mathrm{i})-F(0)}{k(T_\mathrm{i})}=t_\mathrm{i}(T_\mathrm{i}) \qquad (9)$$

where $t_\mathrm{i}(T_\mathrm{i})$ is the isoconversional time at temperature T_i [2].

In the degradation tests we very often observed that the dependence $T_i=f(\beta)$ can be plausibly described by the function

$$T_i = T_\infty(1-\exp[-\beta^a]) \tag{10}$$

where T_∞ is the isoconversional temperature at an infinite heating rate and a is an exponent. Applying Eq. (9) one gets:

$$\frac{dT_i}{d\beta} = T_\infty a\beta^{a-1}\exp[-\beta^a] = (T_\infty - T_i)a\beta^{a-1} \tag{11}$$

The heating rate can be expressed from Eq. (10):

$$\beta = \left(\ln\frac{T_\infty}{T_\infty - T_i}\right)^{1/a} \tag{12}$$

Thus, the temperature function corresponding to the observed dependence given by Eq. (10) can be obtained from Eqs (8), (11) and (12) (without writing the index i at T_i):

$$\frac{k(T_i)}{F(\alpha_i)-F(0)} = \frac{\left(\ln\frac{T_\infty}{T_\infty - T}\right)^{\frac{1-a}{a}}}{(T_\infty - T)a} \tag{13}$$

The temperature dependence of the isoconversional time can be obtained from Eq. (9):

$$t_i(T) = \frac{F(\alpha_i)-F(0)}{k(T)} = (T_\infty - T)a\left(\ln\frac{T_\infty}{T_\infty - T}\right)^{\frac{a-1}{a}} \tag{14}$$

The kinetic parameters T_∞ and a are adjustable and they are obtained from the treatment of experimental dependence $T_i=f(\beta)$ using Eq. (10).

Results and discussion

In our recent paper [19], 26 data sets were selected from references [2–4, 7, 9–12, 22], and treated using the methods based on the temperature functions given by Eqs (2)–(4). In all cases, the oxidation onset

Table 1 Description of the samples evaluated, techniques 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	[22]
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]

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 thermoanalytical 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. We treated the same set of data also in this paper using Eq. (10) where the non-linear least-squares method of the program ORIGIN was applied. The stability was estimated as the oxidation induction time calculated using Eq. (14). The description of the samples and experimental conditions is given in Table 1.

The kinetic parameters obtained using the methods based on Eqs (2)–(4) conveyed the coefficients of variability of the parameter A between 25–100 % or even more, the coefficients of variability of the parameters B, m and D were below 7% [19]. In all cases, the dependency between the parameters was close to 1 [19]. Contrary to the methods based on Eqs (2)–(4), the dependency between the parameters of Eq. (10) never exceeded 0.8. As shown in Table 2, the coefficients of variability of the parameter T_∞ is below 2% and the coefficient of variability of a is mostly below 10%, this value is exceeded in only 3 cases. Much lower coefficients of variability of the parameters of Eq. (10) enable to make more trustworthy stability predictions.

After obtaining the kinetic parameters T_∞ and a, the oxidation induction times were calculated for temperatures 150 and 25°C using Eq. (14). The OITs for 150°C represent an extrapolation of the measured results not far from the temperatures of measurements. The oxidation induction times for the constant temperature of 150°C, calculated from the values of kinetic parameters using Eq. (14), do not differ much from those published in [19] for the methods based on Eqs (2)–(4).

The extrapolation to 25°C is far from the range of the measured temperatures and the calculated oxidation induction times represent estimations of

Table 2 Kinetic parameters and the calculated oxidation induction times for treatment of the experimental results applying Eqs (10) and (14)

No.	T_∞/K	a	t_i(150°C)/h	t_i(25°C)/year
1	716.2±1.7	0.0529±0.0022	1.93	2.74
2	737.2±2.6	0.0437±0.0032	7.36	64.2
3	672.6±2.1	0.0703±0.0034	0.33	0.059
4	762.6±1.9	0.0582±0.0025	10.1	4.37
5	756.4±4.9	0.0702±0.0066	5.44	0.58
6	772.4±4.1	0.0581±0.0053	14.3	5.90
7	746.7±5.9	0.0603±0.0079	5.27	1.88
8	737.7±7.5	0.0598±0.0115	3.86	1.56
9	726.6±2.0	0.0694±0.0032	2.16	0.29
10	731.6±4.1	0.0436±0.0062	5.60	50.1
11	775.7±4.3	0.0284±0.0060	561	1.41E6
12	707.7±3.9	0.0414±0.0054	1.69	37.5
13	723.1±3.7	0.0476±0.0050	3.07	11.8
14	713.5±3.6	0.0502±0.0050	1.82	4.46
15	749.0±3.3	0.0545±0.0044	7.15	5.99
16	711.8±2.8	0.0331±0.0038	3.16	1438
17	734.3±2.2	0.0483±0.0029	5.06	15.4
18	748.4±5.4	0.0714±0.0072	4.15	0.41
19	845.1±8.3	0.0777±0.0100	41.2	1.57
20	869.7±2.5	0.0666±0.0029	146	14.0
21	659.9±7.3	0.0820±0.0114	3.0	0.017
22	691.7±3.6	0.0595±0.0052	10.7	0.38
23	674.2±5.6	0.0694±0.0085	0.38	0.068
24	675.5±7.3	0.0703±0.0085	0.36	0.064
25	652.6±4.2	0.0741±0.0051	0.16	0.024
26	667.1±2.6	0.0575±0.0042	0.21	0.22

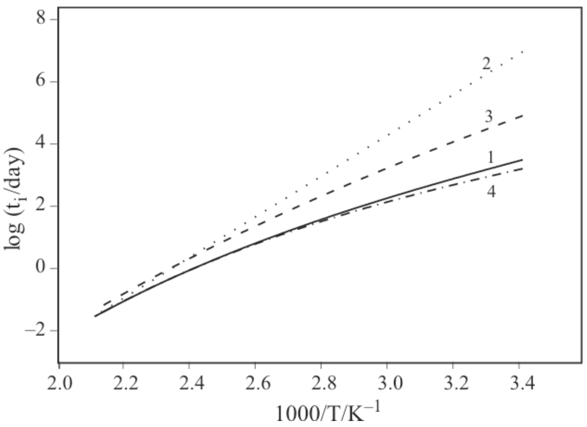

Fig. 1 Dependences of isothermal isoconversional times on temperature for various temperature functions for the sample 6: 1 – method based on Eqs (10) and (14); 2 – method based on Eq. (2); 3 – method based on Eq. (3); 4 – method based on Eq. (4). The data for the calculation of curves 2–4 were taken from [19]

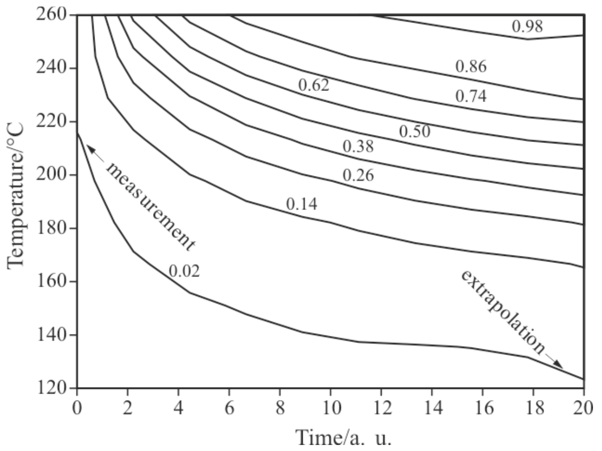

Fig. 2 Contour graph of kinetic hypersurface with the indication of the regions of measurement and extrapolation at the isoconversional contour line α=0.02

durability of the tested material for that temperature. The durability of biodiesel, edible oils and dried milk can be several weeks or months at 25°C under air or oxygen. As seen from Table 2, values of OIT evaluated using Eq. (14) correspond with experience.

Extrapolation of the results of accelerated tests for the sample 6 is shown in Fig. 1 for various methods of prediction. The parameters for the methods based on Eqs (2)–(4) are taken from [19]. It can be seen that, for low temperatures, the Arrhenius-like Eq. (2) gives estimates of stability by several orders of magnitude longer than the methods based on Eqs (3), (4) and (14). The estimates obtained by using the new function are very close to those obtained by using Eq. (4). This can be seen also from the comparison of data in Table 2 and those in Table 4 of [19].

The process of extrapolation of the accelerated tests to lower temperatures can be illustrated in Fig. 2 where a contour graph of the kinetic hypersurface is shown. The concept of kinetic hypersurface has been introduced in [18]; it is a three-dimensional surface representing the dependence of the conversion on time and temperature. The measurements are carried out in the region of high temperatures and low times indicated by an arrow. Using the kinetic parameters obtained from the measurement, the extrapolation is carried out to the other side of the hypersurface to the region of low temperatures and long times indicated by the other arrow in Fig. 2. The single-step approximation represents a mathematical tool to describe the kinetic hypersurface. The methods based on Eqs (2)–(4) and (14) approximate the isoconversional contour line (in Fig. 2 the isoconversional contour line α=0.02 is exemplified). It is a prerequisite for the extrapolation of high-temperature stability tests to lower temperatures that the approximate curve mimics the contour line on the real kinetic hypersurface so closely as possible in a wide range of temperatures and times. It is obvious that not every function describes the contour line well. It is to realize the fact that the Arrhenius function is not suitable to describe the kinetic hypersurface in all its complexity. The most reasonable estimates, corresponding with experience, are obtained for the method based on temperature functions Eq. (4) or by using the new method represented by Eqs (10) and (14).

From Eq. (13) it is seen that the value of new temperature function is zero for T=0 and approaches infinity for $T \to T_\infty$. The kinetic parameter T_∞ can be formally interpreted as the isoconversional temperature at infinite heating rate; the parameter a has no obvious meaning. However, the single-step approximation represents a mathematical tool to describe the kinetic hypersurface and the conversion and temperature functions are just components of the hypersurface [18]. Accordingly, 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 should be drawn just from the values of kinetic parameters [17]. The parameters enable to evaluate the induction periods for any temperature regime using Eq. (6). For drawing conclusions, the physical properties accessible to measurement, i.e. either OOT or OIT, should be calculated using the parameters.

The isoconversional methods are declared to be ‘model-free’ since they do not need to know the conversion function. In fact, as used currently, the isoconversional methods are only ‘semi-model-free’ since the Arrhenius-like temperature function given by Eq. (2) is exclusively applied in the kinetic studies. If one postulates a priori the validity of the Arrhenius function, the experimental data are treated forcely using the theory that may not describe the experimental findings adequately. Application of other temperature equations (Eqs (3) and (4)) gives some versatility to the process of extrapolation; however, the temperature equations are still predetermined and the experimental data are forced to obey the theory. On the other hand, the approach presented here is based on the fact that the observed depence T_i *vs*. β obeys the relationship given by Eq. (10) and for this observed dependence the corresponding temperature function is derived. The experimental data are considered primary and the theory is tailor-made to interpret the experiment. Thus, the approach presented here might lead to a more trustworthy extrapolation. A procedure of deriving the kinetic function analogous to the one presented by Eqs (8)–(14) can be applied for any observed dependence $T_i=f(\beta)$ and may be applied not only for the study of induction periods, but also for any process described by the isoconversional methods.

Conclusions

The extrapolation of accelerated thermooxidative tests, based on Eqs (10) and (14), has been tested for 26 data sets. It has been found that the extrapolation from high-temperature data to ambient temperature corresponds well with experience. Coefficients of variability of the parameters of Eq. (10) are low so enabling to make trustworthy stability predictions.

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