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INDUCTION PERIODS
Theory and applications

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Methods for kinetic description of induction periods, based on the single-step kinetics approximation and various expressions of the temperature functions, are presented. The formulas for evaluation of both isothermal and non-isothermal lengths of induction periods are derived. Use of the formulas is demonstrated on the thermooxidative degradation of polyolefines. The kinetic parameters obtained from isothermal and non-isothermal experiments are compared and possible reasons of inconsistencies are analyzed. Applications of the determination of induction periods for thermooxidation of various systems are reviewed. The theory outlined in this paper can be applied not only for thermooxidation in condensed phase, but also for other processes exhibiting the induction period, such as the curing of rubber compounds, recrystallization of nickel sulfide and crystallization of silicate and metal glasses.

Keywords: *accelerated ageing, durability, stability, thermooxidation*

Introduction

The combination of oxygen as the reactant and heat as the energy source is a major factor in material degradation. In most cases, 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]. 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 transformation peak is distinct and the onset temperature can be measured accurately and unambiguously. In our previous work, a theory of the kinetic description of IP from non-isothermal measurements has been outlined [1]. The theory was applied for the study of thermooxidation of edible oils and fatty acids methyl esters [1–3], thermooxidation of polyolefines [1, 4], thermooxidative stability of pharmaceuticals [5], antioxidant activity of *p*-phenylene diamines in polyisoprene rubber [6, 7] and determination of residual stability of polyurethane automotive coatings [8].

The theory suggested in [1] and subsequently used in [1–8] has been based on the Arrhenius expression of the temperature function. In the papers analyzing the condensed phase kinetics, we came to the conclusion 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 [9–11]. In this work, methods of description of induction periods, based on the single-step kinetics approximation [10, 11] and various expressions of the temperature functions, are presented. Application of the methods is demonstrated on the thermooxidative degradation of polyolefines, viz. polyethylene (PE) and polypropylene (PP).

Theoretical

Single-step kinetics 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

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their kinetics, methods based on the single-step kinetics approximation are frequently used [10, 11].

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

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

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:

$$\Phi(T,\alpha)=k(T)f(\alpha) \tag{2}$$

Combining Eqs (1) and (2), the rate of the complex multi-step condensed-state process can be formally described as [10, 11]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

Equation (3) 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 kinetics approximation thus resides in substituting the set of kinetic equations by the sole single-step kinetics equation. Equation (3) represents a mathematical formulation of the single-step kinetics approximation [10, 11].

Except very few exceptions, the temperature function in Eq. (3) is exclusively expressed by the Arrhenius equation

$$k(T) = A_k \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where A_k and E are mostly considered the pre-exponential factor and the activation energy, respectively, T is the absolute temperature and R stands for the gas constant. Since there are doubts on the physical meaning of activation parameters in condensed state processes [9–12], Eq. (4) can be rewritten as

$$k(T) = A_k \exp\left(-\frac{B}{T}\right) \tag{5}$$

where A_k and B are adjustable parameters without a clear physical meaning. Two other functions were suggested to be highly suitable to be used as temperature functions [9–11]:

$$k(T)=A_k T^m \tag{6}$$

$$k(T)=A_k e^{DT} \tag{7}$$

where A_k, m and D are adjustable parameters. The same symbol A_k is used to denote the constants in Eqs (5)–(7). Since the functions expressing $k(T)$ are different, it is a matter of course that the numerical values of the constants A_k in Eqs (5)–(7) are different as well.

Isoconversional methods and induction period

Isoconversional methods represent probably the most widely employed category of methods based on Eq. (3). 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. (3) is constant and the reaction rate is a function of temperature only. These methods are often called the model-free methods since the value of conversion function for the fixed value of conversion is implicitly involved in the adjustable parameter A (see below). The isoconversional methods can be crudely divided into two groups, i.e., the isothermal methods and the methods at linear heating. The latter group can be further subdivided into differential, integral and incremental methods [9].

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. There is only one point falling to the IP which is detected by the technique employed, i.e., the end of induction period. The end of IP is determined indirectly as the time/temperature of a sudden increase in the rate of the main oxidation stage [1], 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 [3]. 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 [1].

The separation of Eq. (3) gives after some manipulations

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i} k(T)dt \tag{8}$$

Combinations of Eqs (5) and (8), or Eqs (6) and (8), or Eqs (7) and (8) lead to the results:

$$1 = \int_0^{t_i} \frac{dt}{A\exp(B/T)} \tag{9}$$

$$1 = \int_0^{t_i} \frac{dt}{AT^{-m}} \tag{10}$$

$$1=\int_0^{t_i}\frac{\mathrm{d}t}{A\mathrm{e}^{-DT}} \tag{11}$$

in Eqs (9)–(11), the parameter A is given as:

$$A=\frac{F(\alpha_i)-F(0)}{A_k} \tag{12}$$

Equations (9)–(11) should hold for any temperature regime and enable to calculate the time at which the fixed conversion α_i, corresponding to the end of IP, is reached. They represent three different ways of expressing the length of IP, depending on the functional form employed for expressing $k(T)$. It is a matter of course that the numerical values of the constants A in Eqs (9)–(11) are different.

Induction periods under isothermal conditions

For isothermal conditions, the temperature is constant. Then, the denominator in Eqs (9)–(11) is also a constant and the numerator after integration is equal to t_i. In this case, t_i is the oxidation induction time. Integration and rearrangement of Eqs (9)–(11) gives:

$$t_i=A\exp(B/T) \tag{13}$$

$$t_i=AT^{-m} \tag{14}$$

$$t_i=A\mathrm{e}^{-DT} \tag{15}$$

Equations (13)–(15) represent three different ways of expressing the dependence of the OIT on temperature in the case of isothermal measurements. The functional form of the dependence is determined by the choice of the temperature function. The parameters A and B of Eq. (13), or A and m of Eq. (14), or A and D of Eq. (15) can be obtained from a series of isothermal measurements, even by the direct treatment using Eqs (13)–(15), respectively, or from their linearized logarithmic transformations.

Relationships (13)–(15), or equivalent to them, are being used for years and they are reviewed, for example, in [13]. They have been obtained empirically by fitting the experimental data to an appropriate functional form. The derivation carried out in this paragraph reveals the physical background of Eqs (13)–(15). The expression of the constant A is inverted in comparison to that of the constant A_α used in common isoconversional methods [9–11].

Induction periods at linear heating

As mentioned above, the processes occurring during IP are not registered and, consequently, neither their rate nor the dependence of conversion on time/temperature cannot be observed. The only point falling to the IP which is detected, is the end of the induction period. This is the reason why the differential and incremental isoconversional methods cannot be applied for the kinetic description of induction periods at linear heating, only the integral methods can be used. For the linear heating program, the furnace temperature can be expressed as

$$T=T_0+\beta t \tag{16}$$

where T_0 is the starting temperature of the measurement and β stands for the heating rate. After carrying out the transformation between time and temperature, from Eqs (9) and (16), or from Eqs (10) and (16), or from Eqs (11) and (16) can thus be obtained after integration:

$$\beta=\int_0^{T_i}\frac{\mathrm{d}T}{A\exp(B/T)} \tag{17}$$

$$\beta=\frac{T_i^{m+1}}{A(m+1)} \tag{18}$$

$$\beta=\frac{1}{AD}(\mathrm{e}^{DT_i}-1) \tag{19}$$

where T_i is the temperature at which the fixed conversion α_i is reached, i.e., the oxidation onset temperature. The lower integration limit in Eqs (17)–(19) is set T_0=0 K since it is assumed that no process occurs in the sample at the starting temperature of the experiment.

Equations (17)–(19) express the inverse forms of the dependences of OOT on heating rate in the case of measurements with linear heating. Again, the functional form of the dependence is determined by the choice of the temperature function. The advantage of Eqs (18) and (19) is that the temperature integral can be expressed in a closed form. From Eqs (18) and (19) the original forms of the dependence of OOT on heating rate can be simply obtained:

$$T_i=[A(m+1)\beta]^{1/(m+1)} \tag{20}$$

$$T_i=\frac{1}{D}\ln(AD\beta+1) \tag{21}$$

The integral at the right side of Eq. (17) cannot be expressed in a closed form and has to be solved either numerically or by an expansion into series [14].

Experimental

Polyolefines, polyethylene LDPE Bralen FB2-30, melt flow rate (190°C, 2.16 kg) 2 dg min^{-1}, and polypropylene Tatren TI 902, melt flow rate (230°C, 2.16 kg) 31 dg min^{-1} were obtained from the producer (Slovnaft, Bratislava).

The oxidation of polyolefines was studied by differential scanning calorimeter PerkinElmer DSC-7 with the Pyris software. For the non-isothermal measurements, the temperature calibration was carried out to the melting points of In and Zn, the enthalpy calibration to the melting enthalpy of In. For isothermal measurements, the temperature scale was calibrated using the standards In and Sn where the heating rate was 1 K min^{-1}. Samples of 3–5 mg were placed in open standard aluminium pans. The purge gas, forming the reaction atmosphere, was oxygen; its flow rate was 50 mL min^{-1}.

In isothermal measurements, the sample was heated to the constant temperature in nitrogen atmosphere and kept in the same atmosphere for 5 min. Then the oxygen was switched in; the moment of switching is taken as the start of the thermooxidation stress. The end of induction period was determined as the oxidation induction time. The standard deviation of OIT determination was less than 2 min for all temperatures. For the non-isothermal measurements, the end of IP was determined as the onset temperature of the oxidation peak. The standard deviation of a single measurement of OOT, determined from three measurements, was less than 1.1 K for all scans. The measured values of OIT and OOT are listed in Tables 1 and 2.

Results and discussion

Treatment of experimental data

It has been discussed recently that, when treating the data, it is necessary to keep in mind that the experimental data carry random errors. Any transformation of experimental data leads to the deformation of the distribution of errors, heteroskedasticity and a shift in the position of minima of the sum of squares between experimental and calculated values. Thus, the methods using the objective functions with transformed experimental data have to lead principally to biased estimates of kinetic parameters comparing to the values using directly the source experimental data [9–11]. This is the reason why the dependences of OIT on temperature or OOT on heating rate, listed in Tables 1 and 2, were used without any transformation to obtain the values of kinetic parameters.

Table 1 Oxidation induction times as functions of constant temperature of measurement for polyethylene (PE) and polypropylene (PP)

Temperature/°C	t_i(PE)/min	t_i(PP)/min
167.3	273.8	72.6
172.2	136.7	40.7
177.1	80.2	31.4
182.0	42.1	14.5
186.9	32.5	9.5
191.8	15.4	–
196.7	11.9	–

Table 2 Oxidation onset temperatures as functions of heating rate for polyethylene (PE) and polypropylene (PP)

Heating rate/K min^{-1}	T_i(PE)/°C	T_i(PP)/°C
1	201.2	190.1
2	204.8	193.6
3	210.3	196.3
5	217.0	205.5
7	219.1	208.0
10	224.7	212.3
15	230.0	220.4
20	233.6	220.7

For the isothermal measurements, the kinetic parameters of Eqs (13)–(15) have been obtained by a non-linear fit using the software Origin. For the treatment of non-isothermal measurements using Eq. (17), we wrote the software 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. (17) is carried out by the Simpson method. The standard deviations of A and B were calculated assuming a quadratic surface near the minimum [1–8]. For the treatment of non-isothermal data by Eqs (20) and (21), again the non-linear fit using the software Origin was applied. The values of kinetic parameters, their standard deviations and other statistical parameters are listed in Table 3.

From Table 3 it is seen that the coefficient of variability of the parameters B, m and D is below 10%. On the other hand, except the parameters obtained from non-isothermal data using Eq. (20), the coefficient of variability of the parameter A exceeds 200% and the dependence of a couple of the kinetic parameters is close to one. Regarding the parameters obtained by using Eq. (17), the dependence of the parameters is about 0.76 and the coefficient of variability of the parameter A is below 8%.

The values of parameters A and D in Eqs (19) and (21) are so high that the terms $\exp[DT_\text{i}]$ or $AD\beta$ are by many orders of magnitude higher than one. Equations (19) and (21) thus can be simplified as

$$\beta = \frac{1}{AD} e^{DT_\text{i}} \tag{22}$$

$$T_\text{i} = \frac{1}{D} \ln(AD\beta) \tag{23}$$

Table 3 The kinetic parameters, standard deviation per an experimental point (σ) and dependency between parameters for polyethylene (PE) and polypropylene (PP)

Sample	Eq./measurement	Parameter	Value	σ/dependency
PE	(13)/isothermal	A/min B/K	(5.87±12.8)E-23 (25.0±1.0)E+3	5.36 min/0.9999
	(17)/non-isothermal	A/min B/K	(8.22±15.9)E-18 (19.7±1.0)E+3	1.28 K/1
	(14)/isothermal	A/min m	(3.28±46.8)E150 56.01±2.34	5.75 min/1
	(20)/non-isothermal	A/min m	(2.65±0.12)E114 42.40±2.03	1.32 K/0.7629
	(15)/isothermal	A/min D/K^{-1}	(2.66±6.62)E26 0.1254±0.0056	6.14 min/0.9999
	(21)/non-isothermal	A/min D/K^{-1}	(1.86±4.15)E19 0.0889±0.0044	1.42 K/0.9995
PP	(13)/isothermal	A/min B/K	(1.00±4.00)E-18 (20.1±1.8)E+3	2.99 min/0.9999
	(17)/non-isothermal	A/min B/K	(3.07±8.57)E-18 (19.7±1.4)E+3	1.95 K/1
	(14)/isothermal	A/min m	(9.77±2.36)E120 45.06±3.96	2.98 min/1
	(20)/non-isothermal	A/min m	(8.52±0.60)E110 41.27±2.98	2.00 K/0.7632
	(15)/isothermal	A/min D/K^{-1}	(1.39±5.46)E21 0.1008±0.0089	2.98 min/0.9991
	(21)/non-isothermal	A/min D/K^{-1}	(6.15±19.7)E18 0.08875±0.0065	2.08 K/0.9995

Kinetic parameters and induction periods

From Table 3 it can be seen that the values of kinetic parameters obtained from isothermal and non-isothermal data do not coincide fully. Several reasons can bring about the disagreement. The first one can reside in different temperature regions of the measurements. The highest temperature of isothermal measurements is approximately equal to the lowest value of OOT. Another reason can lie in the way of carrying out the isothermal experiments. Before the OIT measurements, the sample is thermally stressed under inert atmosphere during the heating ramp and then 5 min during establishing the temperature equilibrium. This thermal stress can lead to changes in samples which may shorten the OIT. The start of experiment is taken as the moment of switching the inert atmosphere to the oxygen one. The replacement of inert atmosphere by oxygen takes some time, probably a few minutes. Within this time, there is undefined atmosphere in the apparatus which conveys a systematic elongation of the OIT measured. Another source of systematic errors in isothermal measurements is that the actual temperature is usually by several degrees lower that the preset one. Thus, the kinetic parameters obtained from non-isothermal measurements should be more correct. The lengths of OIT calculated using the kinetic parameters from non-isothermal measurements are hypothetical, corresponding to the case of immediate sample heating to the target temperature.

The last, and probably the most serious reason of the inconsistency in kinetic parameters obtained from isothermal and non-isothermal isoconversional methods might be hidden in the inseparability of the temperature and conversion functions [10, 11]. It has been shown that, in the case when the couple of temperature and conversion functions is not separable, the kinetic parameters depend on conversion [9]. Considering the induction periods, it is impossible to verify whether the kinetic parameters depend on conversion since the processes occurring during IP are not detected. However, the possibility of inseparability should be kept in mind. In that case, the kinetic parameters are averaged over the region <0; α_i>. The way of averaging is different in both cases so that the parameters obtained by the isothermal and integral methods may be different.

The standard deviations per a single experimental point are shown in Table 3. It can be seen that the quality of fit is best for the methods based on Eq. (5) and worst for the methods based on Eq. (7). However, the differences are minute and it can be concluded that any of the methods expressed by Eqs (13)–(15)

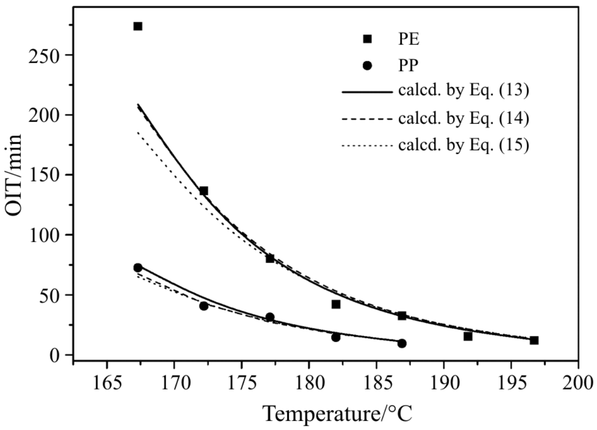

Fig. 1 Comparison of the experimental oxidation induction times (points) and those calculated using the kinetic parameters obtained from non-isothermal measurements (lines) for polyethylene and polypropylene

and (17)–(21) can be used for the treatment of experimental results. In Fig. 1 the experimentally determined OIT values are compared with those calculated using the parameters from non-isothermal measurements. The values of OIT coincide for temperatures above 175°C for both polymers. Below this limit, a considerable difference is seen for PE where the OITs calculated using the parameters from non-isothermal measurements are lower than the experimental points (Fig. 1). This difference can be accounted for by the oxygen diffusion [1]. The good agreement between the OITs resulted from isothermal measurements and those calculated using the kinetic parameters obtained from non-isothermal measurements makes evident that OIT and OOT correspond to the same event, i.e., to the end of IP.

Physical meaning and use of the kinetic parameters

When employing the isoconversional methods, a complex multi-step process is formally treated as a single-step one. The kinetic parameters obtained are thus apparent and do not have any mechanistic significance [10, 11]. Although the parameters do not have any mechanistic interpretation, they enable to calculate the values of induction periods without a deeper insight into the mechanism of the processes occurring during IP. For isothermal conditions, Eqs (13)–(15) can be used to calculate the temperature, at which a given value of OIT is reached or vice-versa. Equations (9)–(11) enable to evaluate the length of IP for any temperature regime. It is possible to calculate the protection factors, antioxidant effectiveness or the residual stability.

From the calculated values of OITs for stabilized and non-stabilized samples, the effect of additives can be assessed. The temperature range of accelerated stability tests differs significantly from the temperature range where the stability of materials should be predicted. The temperature change can lead to the change of the reaction mechanism. Thus, extrapolation of absolute values of OIT can lead to non-realistic estimations. A better estimation of the stabilizing effect can be obtained using the ratio of the lengths of the OITs of stabilized and unstabilized sample since it can be assumed that the stability or instability is brought about by the same structural units both in stabilized and unstabilized sample. This ratio is called the protection factor (*PF*) [3, 4, 6–8]:

$$PF=\frac{t_\mathrm{i}\,(\text{sample}+\text{stabilizer})}{t_\mathrm{i}\,(\text{sample unstabilized})} \tag{24}$$

If the value of *PF* is greater than one, the additive has a stabilizing effect. The greater is the value of *PF*, the higher is the antioxidant effectiveness of the additive. It follows from Eqs (5)–(7) that the value of OIT depends on temperature; hence, the protection factor depends on temperature as well. The antioxidant effectiveness has been introduced lately to recalculate the effect of stabilizer to its concentration unit [4, 6, 7]:

$$AEX=\frac{PF-1}{X} \tag{25}$$

where X is the concentration expressed in phr. In a molar scale, the effectiveness *AEM* can be defined as follows:

$$AEM=\frac{PF-1}{m} \tag{26}$$

where m is the concentration of antioxidant expressed in mol kg^{-1}. Both criteria bring about a normalization of the protection factor so that the values of *PF* for various stabilizer content can be mutually compared. Similarly as *PF*, also both *AEX* and *AEM* depend on temperature. From Eqs (25) and (26) it is obvious that a relationship exists between *AEX* and *AEM*:

$$AEM=10M\cdot AEX \tag{27}$$

where M is the molar mass of the antioxidant expressed in mol kg^{-1}. Since *PF* depends on temperature, also both *AEX* and *AEM* are functions of temperature. *AEX* expresses the antioxidant effectiveness in units better understandable for practitioners whereas *AEM* gives a picture on the antioxidant effect per an antioxidant molecule.

The concept of residual stability has been introduced in paper [1]. For an isothermal process, the residual stability, R, can be defined as [8]

$$R=\frac{t_\mathrm{i}}{t_\mathrm{io}} \tag{28}$$

where t_i is the OIT of the sample after the ageing stress and t_io is the OIT of the unstressed sample. The residual stabilities of the samples indicate the damaging of the samples after various doses of ageing stress [8].

Extrapolation to lower temperatures

The principal goal of stability studies is to extrapolate the kinetic data, obtained from accelerated stability tests, to application conditions. Since the temperature range of accelerated stability tests differs significantly from the temperature range where the stability of the polymer materials should be predicted, the results obtained should be understood as a relative measure of the stability of samples (better/worse). A simple extrapolation from high-temperature data to ambient temperature mostly leads to the estimation of unrealistically long durability [5, 15].

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. In paper [16], a new method has been proposed for the estimation of long-term durability from the accelerated stability tests with linear heating. 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. In order to obtain the low-temperature values of the adjustable kinetic parameters, very low heating rates should be included in the study (0.04, 0.1 K min^{-1}) making the measurements time-consuming. On the other hand, using this method, more realistic estimates of the durability of a material can be obtained.

Induction periods determined by various techniques

For the same sample and the same regime of thermooxidation, the end of induction period may be detected at different times/temperatures when using various techniques for IP determination. For example, OIT by DSC is determined from the sudden change in the heat released. This value of OIT may be different from that determined by TG from a certain level of the mass loss or from measurement of mechanical properties, e.g., the elongation at break. For different techniques, the end of IP can be detected at different values of α_i. The kinetic parameters determined from the treatment of experimental results obtained by different techniques may be different.

To derive a relationship between the OITs obtained by various techniques at the same temperature, one has to express temperature from Eqs (13)–(15). Since the temperature is the same, also the other sides of equations are equal. For two different OITs, from Eqs (13)–(15) one can get the relationship:

$$t_2 = a t_1^{\mathrm{b}} \tag{29}$$

where t_1 and t_2 are OITs determined by two different methods and a and b are constants. In [13], another relationship has been mentioned:

$$t_2=(t_1-a)^{\mathrm{b}} \tag{30}$$

Conclusions

Methods for kinetic description of induction periods, based on the single-step kinetics approximation and various functional forms of the temperature functions, are presented. The formulas for evaluation of both isothermal and non-isothermal lengths of induction periods are derived. Use of the formulas is demonstrated on the thermooxidative degradation of polyolefines where the kinetic parameters have been obtained. Applications of the determination of induction periods for the study of thermooxidation of various systems are reviewed.

The theory outlined in this paper can be applied not only for thermooxidation in condensed phase, but also for other processes exhibiting the induction period, such as the curing of rubber compounds [17], α–β phase recrystallisation in nickel sulfide [18] and crystallization of silicate [19] and metal [20] glasses.

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