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DSC STUDY OF OXIDATION INDUCTION PERIODS

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Abstract

A theory of the evaluation of kinetic parameters of induction periods for non-isothermal processes is outlined and a method to obtain the parameters from non-isothermal differential scanning calorimetry measurements, based on the dependence of onset temperature of oxidation peak on heating rate, is presented. The applicability of the method is demonstrated on the study of oxidation induction periods of edible oils and polyolefines. In all cases, the parameters of an Arrhenius-like equation describing the temperature dependence of induction period have been obtained. It is shown that the method gives the parameters not affected by oxygen diffusion which are transferable to be used in modelling the non-isothermal induction periods where the effects of diffusion, heat transfer and evolution of reaction heat are explicitly involved. A method of estimating the residual stability after a thermooxidative stress of the material is suggested.

Keywords: DSC, induction period, non-isothermal process, oxidation, oxygen diffusion

Introduction

Many processes exhibit an induction period (IP), in other words, the stage preceding the main process, where seemingly no chemical reaction takes place. In some cases, an accurate determination of the induction period is of utmost importance for the safety and quality management. A typical example of the processes with the induction period is the oxidation in condensed phase.

The standard tests for IP determination are invariably carried out under isothermal conditions. However, when the material is thermally stressed, isothermal conditions rarely occur in practice. In this paper a theory of the evaluation of induction periods for non-isothermal processes is outlined and a method is presented to obtain the kinetic parameters of induction periods from the onset temperatures of non-isothermal DSC runs with a linear increase of temperature.

In our previous papers the induction periods of rubber compounds vulcanisation [1], oxidation of edible oils [2] and oxidation of polyolefines [3] have been studied under non-isothermal conditions. The oxidations of edible oils and polyolefines are of great practical importance. The oxidative rancidity of edible oils and fats results in the development of unpleasant tastes and odours. A generalized scheme for autooxidation of unsaturated fatty acids can be found in [4]. To estimate the stability of

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oils and fats, the sample is usually subjected to an accelerated oxidation test under standardized conditions where heating is the most common means of accelerating the oxidation. The oxidation is an exothermic process and the evolved heat makes it possible to employ DSC for its study; surprisingly, this technique is not practically used for IP determination. Determination of oxidation induction time for plastics by DSC is published in the standard [5] and the mechanism of oxidation is reviewed in [6–8]. Importance of oxygen diffusion in the determination of the oxidation induction periods of edible oils and polyolefines is also analyzed in this paper.

Theoretical part

For any mechanism, the rate of reaction can be described by the general rate equation [9]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{1}$$

where α is the conversion of the reaction and $f(\alpha)$ is the conversion function. The temperature dependence of the rate constant k is usually expressed by the Arrhenius equation

$$k=A_\mathrm{k}\exp\left[-\frac{E_\mathrm{a}}{RT}\right] \tag{2}$$

where A_k is the pre-exponential factor, E_a is the activation energy, T is absolute temperature and R stands for the gas constant.

Since Eq. (1) is general, we assume that it describes also the kinetics of the reactions occurring during IP. The existence of these reactions is not detected by the experimental technique used; however, they have to take place as a preparatory stage preceding the main process (oxidation, vulcanization). Combination of Eqs (1) and (2), after the separation of variables, gives the result:

$$\int_0^{\alpha_\mathrm{i}}\frac{\mathrm{d}\alpha}{f(\alpha)}k=\int_0^{t_\mathrm{i}}A_\mathrm{k}\exp\left[-\frac{E_\mathrm{a}}{RT}\right]\mathrm{d}t \tag{3}$$

The conversion α_i in Eq. (3) is the conversion of the reactions occurring during IP corresponding to the end of IP, i.e. to the start of the main process detected by the apparatus, and t_i is the length of IP. Further it is assumed that the conversion α_i is the same for any temperature. Then, after integration of the left side of Eq. (3) one can get:

$$F(\alpha_\mathrm{i})-F(0)=\int_0^{t_\mathrm{i}}A_\mathrm{k}\exp\left[-\frac{E_\mathrm{a}}{RT}\right]\mathrm{d}t \tag{4}$$

Since the conversion α_i corresponding to the end of IP is assumed to be independent of temperature, also the value of the integrated function $F(\alpha)$ at the point α_i, $F(\alpha_\mathrm{i})$, is constant. Therefore, Eq. (4) can be rewritten as:

$$1=\int_{0}^{t_i}\frac{\mathrm{d}t}{A\exp(B/T)} \tag{5}$$

where the constants A and B are given as:

$$A=\frac{F(\alpha_i)-F(0)}{A_k}$$
$$B=\frac{E_a}{R} \tag{6}$$

The physical meaning of the denominator in Eq. (5) can be demonstrated very simply for a special case of isothermal processes where the denominator is a constant equal to the induction period at the given temperature. Thus, the temperature dependence of IP can be expressed as

$$t_i=A\exp(B/T) \tag{7}$$

Equation (5) has been intuitively used for the evaluation of non-isothermal IP [1, 2, 10].

For the linear increase of temperature in DSC measurements, the furnace temperature can be expressed as

$$T_f=T_0+\beta t \tag{8}$$

where T_f is the furnace temperature, T_0 is the starting temperature of the measurement and β stands for the coefficient of temperature increase (scan). If one assumes that the temperature of the sample equals that of the furnace, combination of Eqs (5) and (8) gives the result [1, 2]

$$\beta=\int_{T_0}^{T_i}\frac{\mathrm{d}T}{A\exp(B/T)} \tag{9}$$

where T_i is the temperature of the end of induction period, i.e. the onset temperature of the oxidation peak. When deriving Eqs (3) and (4), the assumption is implied that the conversion function $f(\alpha)$ holds during the induction period which means that no change of the reaction mechanism occurs. As Eq. (9) indicates, when increasing the rate of heating, the onset temperature also increases.

Experimental

Refined high-linoleic sunflower and zero-erucic rapeseed oils were taken from industrial semicontinuous deodorizer Lurgi (Palma-Tumys, Bratislava). The main characteristics of the oils are summarised elsewhere [2].

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).

Differential scanning calorimeter Shimadzu DSC-60 was employed to study the edible oils oxidation. The oxidation of polyolefines was studied by differential scanning calorimeter Perkin Elmer DSC-7 with the Pyris software. For non-isothermal measurements, the temperature scale of both calorimeters was calibrated using the standards In and Zn. Samples of 2–3 mg were placed in open standard aluminum pans. The purge gas, forming the reaction atmosphere, was oxygen. The starting temperature of oxidation was determined as the onset temperature of the oxidation peak. The standard deviation of a single measurement of the oxidation onset temperature, determined from three measurements, was less than 1.1 K for all scans. For isothermal measurements, the temperature scale was calibrated using the standards In and Sn where the heating rate was 1 K min^{-1}. The samples of about 5 mg were placed in open standard aluminum pans. The induction period was determined as the oxidation induction time. The standard deviation of IP determination was less than 1 min for all temperatures.

Oxidograph (Mikrolab Aarhus, Denmark) was used to measure the induction periods of edible oils oxidation. In the apparatus, the decrease of oxygen pressure at constant volume under isothermal conditions is followed within the temperature range 100–125°C. The sample size was 5 g. The standard deviation of a single measurement of the induction period, determined from five measurements, was less than 0.15 h.

Results and discussion

For the edible oils, the induction periods have been obtained for non-isothermal DSC measurements and isothermal Oxidograph measurements. Isothermal measurements have been carried out by Oxidograph since this apparatus is widely used for the determination of IP of edible oils. For the polyolefines, both the isothermal and non-iso-

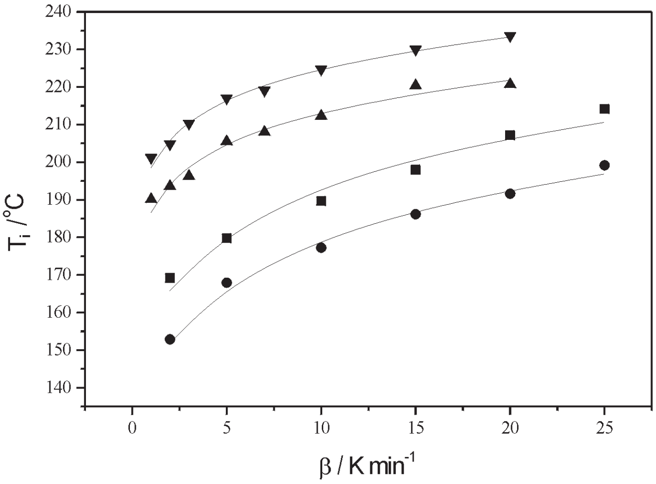

Fig. 1 Experimental and fitted dependences of the onset oxidation temperatures on the scan rates for polyolefines and edible oils; ▼ – polyethylene, ▲ – polypropylene, ■ – rapeseed oil, ● – sunflower oil

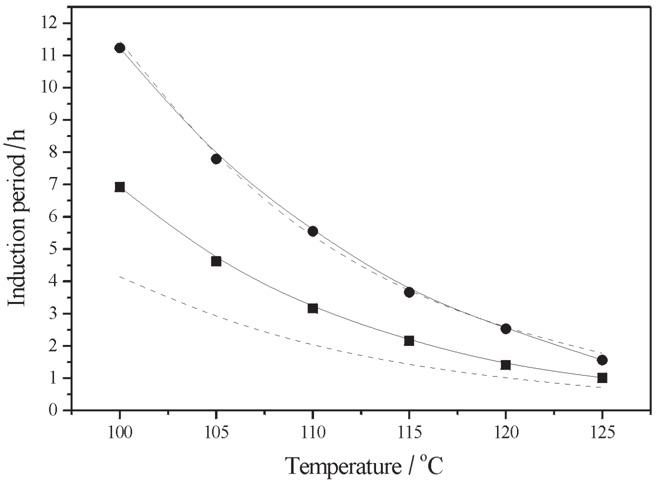

Fig. 2 Comparison of the Oxidograph (solid lines) and DSC (dashed lines) temperature dependences of the induction periods for the rapeseed (●) and sunflower (■) oils

thermal measurements have been carried out by DSC. The parameters *A* and *B* in Eq. (7) have been obtained from non-isothermal measurements by minimizing the sum of squares between experimental and theoretical values of the heating rate by the simplex method [11]. The integration indicated in Eq. (9) has been carried out by the trapezium method. The agreement between experimental and fitted points is demonstrated in Fig. 1. The standard deviations of *A* and *B* were calculated assuming a quadratic surface near the minimum [11]. The kinetic parameters *A* and *B* have been obtained for the isothermal measurements by a direct comparison of experimental and theoretical values of induction periods using the program Origin, where the theoretical values are given by Eq. (7). The values of *A* and *B* and their standard deviations obtained by both procedures are listed in Table 1.

Table 1 Values of the kinetic parameters *A* and *B* and their standard deviations obtained by various methods

Sample	Method	A/min	$10^{-3}\cdot B$/K
Sunflower oil	non-iso-DSC	$(16.6\pm0.7)\cdot10^{-11}$	10.5±0.1
	iso-Oxidograph	$(2.34\pm0.65)\cdot10^{-11}$	11.4±0.1
Rapeseed oil	non-iso-DSC	$(8.73\pm0.36)\cdot10^{-11}$	11.1±0.1
	iso-Oxidograph	$(16.2\pm13.6)\cdot10^{-11}$	10.9±0.3
Polyethylene	non-iso-DSC	$(8.73\pm1.11)\cdot10^{-17}$	19.7±1.0
	iso-DSC	$(5.85\pm12.9)\cdot10^{-23}$	25.0±1.0
Polypropylene	non-iso-DSC	$(4.08\pm0.95)\cdot10^{-17}$	18.5±0.3
	iso-DSC	$(1.00\pm4.00)\cdot10^{-18}$	20.1±1.8

iso – determination of *A* and *B* from isothermal measurements
non-iso – determination of *A* and *B* from non-isothermal measurements

It can be seen from Table 1 that the values of kinetic parameters A and B, describing the IP dependence on temperature, are almost identical for the rapeseed oil, but they differ greatly for the sunflower oil. As it is seen from Fig. 2, the kinetic parameters for the rapeseed oil lead to identical IP values for both techniques used. For the sunflower oil, the parameters obtained by DSC lead to much shorter induction periods than those obtained by Oxidograph. This difference can be ascribed to a better oxygen saturation of the oil in DSC measurements. Oxygen is supplied to the oil by diffusion and it is consumed in the oxidation reactions taking place during the induction period. It has been shown [2] that, when the oxygen diffusion plays an important role, the parameters B can be expressed as

$$B = B_0 + \frac{E_\mathrm{d} - E_\mathrm{a}}{R\left(1 + \dfrac{DS}{kVz}\right)} \tag{10}$$

where B_0 is the kinetic parameter B for the saturated oxygen concentration in the oil, E_d is the activation energy of oxygen diffusion, D is the diffusion coefficient, S is the oil–oxygen interphase area, V is the volume of the oil, z is the thickness of the diffusion film in the oil and k stands for the rate constants of the oxidation reactions occurring during IP. From Eq. (10) it can be seen that the parameters B and B_0 are close for the conditions $D\to\infty$, $(S/V)\to\infty$, $z\to 0$ and $k\to 0$. For DSC, the ratio S/V is approximately 10^4 m^{-1}, for Oxidograph this ratio is about 150. Thus, the ratio S/V is by almost two orders of magnitude higher for DSC so that the kinetic parameter B obtained from DSC is much closer to the value B_0 not affected by diffusion or by the sample size. The sample in Oxidograph is stirred by a magnetic stirrer which accelerates the oxygen diffusion. However, the stirring is obviously not intense enough to make up for the large sample size. From Fig. 2 it can be seen that the rapeseed oil is stabler than the sunflower oil so that the rate constant k is greater for the sunflower oil than for the rapeseed one. Consequently, oxidation of the sunflower oil in Oxidograph experiments is mostly controlled by diffusion since the rate of oxygen uptake is greater than its supply to the sample by diffusion. This is obviously the reason of lower values of induction periods measured by DSC than by Oxidograph for the sunflower oil (Fig. 2) and also of the differences in the kinetic parameters obtained by both methods (Table 1). The rate constant k for the rapeseed oil is obviously so low that the oxygen saturation of the sample is established in Oxidograph measurements. Therefore, for the rapeseed oil the parameters B are practically identical for both the methods and also the induction periods are practically the same (Fig. 2). It can be expected that, for unstable oils, the rate of oxidation in Oxidograph will be governed by the diffusion only and the induction periods will converge to a certain value. For fairly different values of diffusion coefficients of oxygen in the oils, the order of oil stabilities determined by Oxidograph can even be erroneous.

The data in Table 1 for polyolefines show that, within the range of their errors, constants A and B obtained from isothermal and non-isothermal DSC measurements are practically the same for polypropylene. From Fig. 3 it can be seen that also the experi-

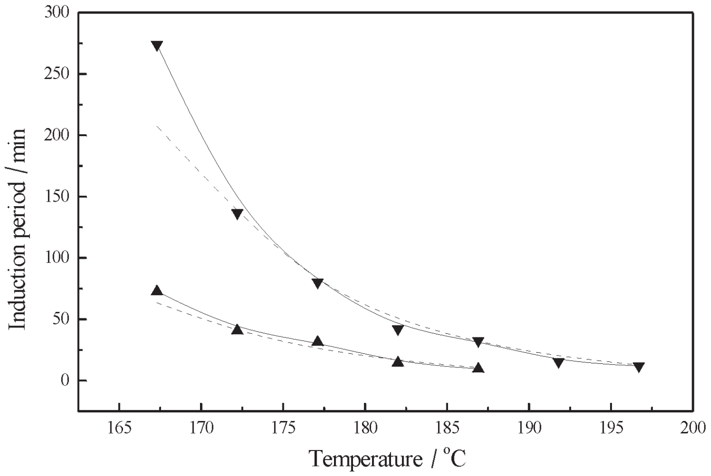

Fig. 3 Comparison of the isothermal DSC (solid lines) and non-isothermal DSC (dashed lines) temperature dependences of the induction periods for polyethylene (▼) and polypropylene (▲)

mentally determined IP values coincide with those calculated using the parameters from non-isothermal measurements. For polyethylene, constant B is much higher for isothermal measurements than for the non-isothermal ones (Table 1). The induction periods coincide for temperatures above 175°C. Below this limit, a considerable difference is seen where the induction periods calculated using the parameters from non-isothermal measurements are lower than the experimental points (Fig. 3). Similarly as in the case of edible oils, this difference can be accounted for by the oxygen diffusion. Equation (10) should also hold for the oxygen diffusion in molten polyolefines. From the difference in constants B obtained from isothermal and non-isothermal measurements it is obvious that the activation energy of oxygen diffusion, E_d, should be much higher than the activation energy of the oxidation reactions occurring during IP, E_a. The oxygen diffusion becomes a limiting step of the oxidation below 175°C. This result points out the utmost importance of oxygen diffusion in testing the polyolefine oxidation stability which is in accordance with [7]. When testing the polyolefine oxidation stability according to the standard [5], the temperature should be above 175°C. Taking into account the strong influence of oxygen diffusion on the length of IP, also the sample mass recommended in [5] seems to be too high.

Modelling of the processes plays an important role in hazard analysis and product quality management. However, it is necessary to bear in mind that the quality of the results of modelling depends on the quality of the kinetic model, i.e. whether the model involves all essential effects, and on the reliability of the input parameters. The kinetic parameters A and B obtained by non-isothermal DSC measurements do not convey the effect of oxygen diffusion within the sample so that they are transferable to be used in modelling the oxidation where the effects of reaction kinetics, oxygen diffusion, heat transfer and evolution of reaction heat are explicitly involved. In practice, the oxidation occurs under non-isothermal conditions, a pure isothermal regime is rare. Equation (5) makes possible to calculate IP for any temperature regime.

The length of IP is understood as a measure of oxidation stability. Equation (7) enables to estimate the residual stability after a thermooxidative stress. If the sample was exposed to the stress under non-isothermal conditions for the time t_s, where $t_s<t_i$, Eq. (5) can be rewritten into the form

$$1=\int_0^{t_s}\frac{dt}{A\exp(B/T)}+\int_{t_s}^{t_i}\frac{dt}{A\exp(B/T)} \tag{11}$$

The first term at the right side of Eq. (11) represents a ratio of the depleted stability and the other term stands for the ratio of residual stability.

We believe that the method of the treatment of non-isothermal DSC runs, based on the analysis of onset temperature of the oxidation on heating rate, can be employed also for the study of many other reactions and processes exhibiting the induction period. The value of the scan rate should not exceed 20–25 K min^{-1} since above this value the temperature T_i steeply increases obviously due to the existence of a temperature gradient in the sample. Then, the temperature of the sample is not equal to the temperature of the furnace which is the condition inevitable for the derivation of Eq. (9). For the treatment of non-isothermal DSC data, the program TIND has been written in Fortran-77. The DOS version of the program is available on request.

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