A rapid method for approximative evaluation of thermooxidative stability of organic materials

Anna Vykydalová1,2 · Zuzana Cibulková1 · Tibor Dubaj1 · Peter Šimon1

Received: 17 November 2021 / Accepted: 16 June 2022 / Published online: 10 July 2022
© Akadémiai Kiadó, Budapest, Hungary 2022

Abstract
In this work, a novel procedure for fast assessment of the material residual stability is proposed. The method resides in integral isoconversional kinetic analysis of the thermal oxidation of unaged material employing the Berthelot–Hood temperature function. Subsequently, the obtained conversion-independent kinetic parameter $D$ is also employed for samples aged in various regimes. The value of conversion-dependent parameter $A$ for aged samples is calculated from the oxidation onset temperature measured at 5 °C min$^{-1}$. The residual stabilities are then calculated as a simple ratio of the parameter $A$ of aged material to that of the unaged one. The method has been applied and verified for the samples of low-density polyethylene aged by thermal, radiation and combined ageing. The method can also be employed for high-throughput screening of the effect of various stabilizers and antioxidants in a given organic matrix.

Keywords Residual stability · Induction period · Thermooxidation · Accelerated ageing

Introduction
In many industrial applications, it is vital to find the most suitable materials in terms of their thermooxidative stability. Moreover, in practice, it is often necessary to examine the effect of different types of ageing on the stability of materials. Accelerated oxidation tests employing methods of thermal analysis, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG), are frequently used to assess the thermooxidative stability of materials [1, 2]. A complete analysis of the thermooxidative stability of a material involves either a series of often time-consuming isothermal measurements at various temperatures or non-isothermal measurements at several heating rates. Subsequently, a kinetic analysis of the data obtained from these measurements can be performed. The main drawback of non-isothermal measurements compared to isothermal ones resides in their non-trivial interpretation and lower discriminating ability, especially for materials with higher oxidation onset temperatures [3]. From the above mentioned, it follows that assessing the thermooxidative stability of materials under different ageing conditions is a time-consuming process, mainly in the initial evaluation of stability with many samples. Moreover, in the case of isothermal measurements, the oxidation peak tends to be flat without well-defined onset [2] and it is often difficult to find out the test temperature which would be appropriate for samples subjected to a wide range of ageing conditions. Thermooxidative degradation of materials in nuclear power plants is a typical example of the application where the materials are exposed simultaneously to radiation and thermal ageing so that many samples should be tested and many experiments should be carried out for the complete kinetic description of the degradation progress. An important task is to test the thermooxidative stability of the samples to assess their lifetime under these specific conditions [4, 5].

The aim of this work is to develop and validate a fast procedure for evaluation of thermooxidative stability of organic materials. The method is based on a complete kinetic analysis of the thermal oxidation of unaged sample. The conversion-independent kinetic parameter obtained from isoconversional kinetic analysis of the unaged sample is then taken over for the other samples aged under different...
conditions or subjected to varying degradation dose. In this manner, only one heating rate is necessary for each sample to assess its residual stability. To verify the correctness and robustness of the procedure, the data were compared with those obtained from complete kinetic analysis based on five heating rates for all samples under study. The procedure was applied for assessing the effects of different types of ageing on the thermooxidative stability of a cable insulation made of low-density polyethylene (LDPE) masterbatch with crosslinking catalyst using non-isothermal DSC measurements. The effect of gamma radiation, elevated temperature, and their combination on the stability of the samples was determined by isoconversional analysis employing a non-Arrhenian temperature function, i.e. the Berthelot–Hood function.

**Results and discussion**

**Non-isothermal DSC measurements**

Figure 1 depicts non-isothermal DSC records of unaged material (PE0) at various heating rates. Two distinct thermal events can be seen upon heating: a phase transition (melting) between 80 and 125 °C followed by a sharp exotherm corresponding to thermal oxidation. Onset of the melting peak remains in the same position; however, the onset of oxidation shifts towards higher temperatures with increasing heating rate thus confirming the kinetic nature of the second thermal event. In the case of aged samples, the overall shape of the DSC traces remained the same with the oxidation peak shifted to lower temperatures.

**Kinetics of processes occurring during induction period**

Generally, thermooxidation of materials involves an induction period (IP), which is a stage preceding the main oxidation process [2]. The end of IP is associated with significant and sudden changes in the properties of the material. Thus, the length of the induction period can be considered proportional to the material thermooxidative stability [6]. Thermooxidative stability of polymers is routinely assessed by standardized tests using differential scanning calorimetry, either in isothermal regime or under linear heating; the resulting stability measure is called oxidation induction time \( t_i \) and oxidation onset temperature \( T_i \), respectively. It has been suggested and also verified [7, 8] that \( t_i \) can be viewed as a special case and

![Fig. 1 DSC records of unaged Visico LE4423/Ambicat LE4476 sample (PE0) at various heating rates (from top to bottom: 1, 3, 5, 7, and 10 °C min⁻¹)](image-url)

---

**Experimental**

**Materials and methods**

The studied material Visico LE4423/Ambicat LE4476 was prepared by Borealis AG (Kongens Lyngby, Denmark). Visico LE4423 is a low-density polyethylene, and Ambicat LE4476 is a masterbatch containing a catalyst: a silane-based crosslinkable natural compound designed for low-voltage power cables up to 6 kV. The unaged cable is denoted as PE0.

The cables were exposed to three types of accelerated ageing at ÚJV Řež facility in Czech Republic. The first type of the accelerated ageing was isothermal stress in an oven at 110 °C in air atmosphere for 744, 1080, 1800, 3168, 5138, and 7344 h; the samples are denoted T1–T6. In the second type of ageing, the samples were irradiated by γ-radiation at room temperature using a ⁶⁰Co γ-ray source, and the average dose rate applied was 500 Gy h⁻¹. The samples were exposed for 163.4, 528.2, and 1098 h (corresponding to total irradiation doses of 81.7, 264.1, and 549 kGy, respectively) and denoted as R1, R2, and R3. The last accelerated ageing was a combination of isothermal stress and γ-irradiation. The samples were stressed isothermally in an oven at 85 °C and by γ-irradiation at 4.5 Gy h⁻¹ for 1462, 3200, 5289, and 9533 h; these samples are denoted as TR1–TR4.

Thermooxidative stability was studied using a differential scanning calorimeter Shimadzu DSC-60 (Tokyo, Japan) under non-isothermal conditions. The sample masses were about 3 mg, and they were placed in standard open aluminium pans. Oxygen at a flow rate of 50 mL min⁻¹ was used as a purge gas. The measurements were carried out at heating rates 1, 3, 5, 7, and 10 °C min⁻¹ in the temperature range of 50–250 °C. The temperature scale of the instrument was calibrated to the melting point of indium, lead, and tin.
isocnversional time and, analogously, \( T_i \) is just a special case of isocnversional temperature. Moreover, since both \( t_i \) and \( T_i \) are evaluated at the onset of the main oxidation process, they should both correspond to the same “event” within the material under study. Therefore, both these stability parameters can be interpreted within the framework of isocnversional kinetic analysis as discussed below.

Thermooxidation of polymers is a typical process occurring in the condensed phase. The methods based on single-step approximation are often used to describe the kinetics of such processes [9–11]. According to this approximation, the rate of the process can be formally described as:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha),
\]

where \( k(T) \) is the temperature function depending only on temperature \( T \) and \( f(\alpha) \) is the conversion function depending only on the conversion of the process, \( \alpha \). The Arrhenius equation is almost exclusively used as a temperature function. The aim of most stability studies is to extrapolate the equation to lower temperatures. It has been reported in several works that the extrapolation based on the Arrhenius temperature function appears as the most reasonable choice for description of induction periods [15]:

\[
k(T) = A_k \exp(DT),
\]

where \( A_k \) and \( D \) are adjustable kinetic parameters. The separation of variables and rearrangements of Eq. (1) under the assumption that the material conversion at the end of the induction period is constant and the reaction rate is solely a function of temperature [9]. This assumption yields

\[
\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i(D)} k(T)dt.
\]

Under isothermal conditions, the combination of Eqs. (2) and (3) after some rearrangements gives the equation which enables to calculate the length of IP [6]:

\[
t_i = A\exp(-DT),
\]

where the parameter \( A \) is given as:

\[
A = \frac{F(\alpha_i) - F(0)}{A_k},
\]

where \( F \) is the primitive function of the inverted conversion function of \( 1/f \), and \( \alpha_i \) is the conversion corresponding to the end of IP. For a non-isothermal measurement with constant heating rate, \( \beta \), from Eq. (3), the following relationship can be obtained:

\[
T_i = \frac{1}{D} \ln (AD\beta + 1),
\]

where \( T_i \) is the temperature at which \( \alpha_i \) is reached, i.e. the oxidation onset temperature.

**Fast method for the thermooxidative stability assessment**

From the non-isothermal DSC records, the oxidation onset temperatures \( T_i \) at various heating rates have been obtained; their values are listed in Table 1. The fast method for the assessment of thermooxidative stability starts with the complete kinetic analysis of the thermal oxidation of unaged sample PE0 based on five heating rates. The stressed samples were measured only at 5 °C min\(^{-1}\); this heating rate was chosen as a reasonable compromise between the duration of experiments and sensitivity of \( T_i \) with respect to the kinetic parameters (considering the logarithm in Eq. (6)). From the onset oxidation temperatures in Table 1, kinetic parameters \( A \) and \( D \) of the unaged sample PE0 were obtained by the non-linear least-squares method (OriginPro 9.1) using Eq. (6). From Eq. (5), it can be seen that the parameter \( A \) is conversion dependent, while the parameter \( D \) should be independent of degradation extent [5]. All the samples under study correspond to the same material with varying degradation extent with respect to oxidation products. Therefore, in the case of stressed samples, the value of the parameter \( D \) obtained from the kinetic analysis of the unaged sample was used. With the known value of \( D \), the value of parameter \( A \) is calculated from rearranged Eq. (6) as \( [\exp(DT_i) - 1]/D\beta \) using \( T_i \) measured at \( \beta = 5 \) °C min\(^{-1}\); the values are summarized in Table 2. The kinetic parameters alone do not carry any clear physical meaning regarding the material stability so that they cannot be applied for assessing the stability. However, the kinetic parameters enable to calculate the values of \( t_i \) which are physical quantities with a clear meaning. From the values of induction periods, the residual stabilities can be calculated. The concept of residual stabilities has been introduced in [1, 16, 17]. Briefly, for an isothermal process, the residual stability \( R \) can be expressed as:

\[
R = \frac{t_i(\text{aged})}{t_i(\text{unaged})},
\]

where \( t_i(\text{unaged}) \) and \( t_i(\text{aged}) \) are the lengths of the induction periods corresponding to the unaged material and material after accelerated ageing, respectively. The residual stability
does not only normalize the material stability within 0 and 100% but also eliminates the temperature dependence present in \( t \) as a result of fitting all data with the same value of \( D \). The values of \( R \) have been calculated for all samples under study and are listed also in Table 1. In [16–18], it is shown that the decrease in residual stability with respect to the degradation dose often follows a first-order exponential decay:

\[
R = \exp(-a \cdot d),
\]  

where \( a \) is the extinction coefficient associated with the corresponding ageing type, and \( d \) is the degradation dose. The obtained values for thermal, \( \gamma \)-irradiation and combined ageing extinction coefficients are \( a_T = (1.41 \pm 0.24) \cdot 10^{-3} \text{ h}^{-1} \); \( a_R = (1.14 \pm 0.05) \cdot 10^{-2} \text{ h}^{-1} \) and \( a_{TR} = (10.8 \pm 0.7) \cdot 10^{-4} \text{ h}^{-1} \), where the subscripts “\( T \)”, “\( R \)” and “\( TR \)” are related to thermal, radiation and combined stress, respectively.

In addition to monitoring the effect of various degradation doses on the stability of materials, the method can also be employed for evaluating the performance of various antioxidants and other stabilizers in organic matrices. Considering

Table 1 Oxidation onset temperatures at different heating rates for unaged sample and for stressed samples at 5 °C min\(^{-1}\); fitted values of \( A \) with standard errors and residual stabilities of the samples under study

| Sample | Oxidation onset temperature, \( T/°C \) | \( \ln A/\text{min} \) (Eq. 6) | \( R \) (Eq. 7) |
|--------|----------------------------------------|---------------------------------|--------------|
|        | 1 | 3 | 5 | 7 | 10 °C min\(^{-1}\) | |
| PE0    | 216.75 | 229.46 | 235.34 | 241.07 | 244.50 | 46.04 ± 1.15 | 1 |
| T1     | 220.43 | 44.67 ± 1.12 | 0.254 |
| T2     | 217.33 | 44.71 ± 1.12 | 0.264 |
| T3     | 215.17 | 44.18 ± 1.10 | 0.155 |
| T4     | 213.98 | 44.38 ± 1.11 | 0.189 |
| T5     | 207.26 | 43.71 ± 1.09 | 0.0973 |
| T6     | 200.35 | 43.07 ± 1.05 | 0.0510 |
| R1     | 213.26 | 43.88 ± 1.10 | 0.115 |
| R2     | 189.21 | 41.93 ± 1.05 | 0.0163 |
| R3     | 181.08 | 41.26 ± 1.03 | 0.00839 |
| TR1    | 216.51 | 38.30 ± 0.66 | 0.228 |
| TR2    | 197.86 | 36.95 ± 0.64 | 0.0588 |
| TR3    | 196.89 | 36.76 ± 0.63 | 0.0488 |
| TR4    | 186.79 | 35.97 ± 0.62 | 0.0221 |

The parameter \( D \) was adjusted as shared among all samples, and its fitted value with standard error is \((0.0762 ± 0.0014) \text{ K}^{-1}\).

Table 2 Onset oxidation temperatures of the stressed samples. Fitted values of \( A \) with standard errors and residual stabilities of the samples under study

| Sample | Oxidation onset temperature, \( T/°C \) | \( \ln A/\text{min} \) (Eq. 6) | \( R \) (Eq. 7) |
|--------|----------------------------------------|---------------------------------|--------------|
|        | 1 | 3 | 5 | 7 | 10 °C min\(^{-1}\) | |
| PE0    | 216.75 | 229.46 | 235.34 | 241.07 | 244.50 | 42.65 ± 1.35 | 1 |
| T1     | 203.82 | 214.37 | 220.43 | 223.88 | 227.39 | 41.36 ± 1.31 | 0.277 |
| T2     | 206.01 | 216.00 | 217.33 | 224.68 | 228.15 | 41.11 ± 1.30 | 0.215 |
| T3     | 196.37 | 209.07 | 215.17 | 218.50 | 223.13 | 40.93 ± 1.30 | 0.180 |
| T4     | 200.88 | 211.39 | 213.98 | 221.53 | 225.47 | 40.84 ± 1.29 | 0.163 |
| T5     | 189.96 | 203.93 | 207.26 | 214.99 | 219.86 | 40.28 ± 1.28 | 0.0941 |
| T6     | 186.78 | 198.70 | 200.35 | 204.84 | 208.96 | 39.72 ± 1.26 | 0.0534 |
| R1     | 190.83 | 208.04 | 213.26 | 214.63 | 218.71 | 40.78 ± 1.29 | 0.154 |
| R2     | 169.94 | 183.71 | 189.21 | 193.98 | 198.69 | 38.80 ± 1.23 | 0.0214 |
| R3     | 162.90 | 176.57 | 181.08 | 185.39 | 192.18 | 38.14 ± 1.20 | 0.0110 |
| TR1    | 196.91 | 210.09 | 216.51 | 220.97 | 225.64 | 41.04 ± 1.34 | 0.201 |
| TR2    | 178.86 | 191.97 | 197.86 | 202.71 | 209.80 | 39.51 ± 1.30 | 0.0435 |
| TR3    | 174.39 | 189.84 | 196.89 | 201.55 | 206.21 | 39.43 ± 1.25 | 0.0402 |
| TR4    | 164.07 | 178.44 | 186.79 | 191.47 | 196.20 | 38.61 ± 1.22 | 0.0176 |

The parameter \( D \) was adjusted as shared for all samples, and its fitted value with standard error is \((0.0820 ± 0.0027) \text{ K}^{-1}\).
the value of parameter $D$ independent of antioxidant presence, Eq. (7) can be rewritten in this case as

$$PF = \frac{t_i\text{(stab.)}}{t_i\text{(unstab.)}} = \frac{A\text{(stab.)}}{A\text{(unstab.)}},$$

(9)

where PF is the protection factor [19, 20], and $t_i\text{(stab.)}$ and $t_i\text{(unstab.)}$ are the length of induction period of stabilized and pristine matrix, respectively. Even though the protection factor tends to be slightly temperature-dependent [21], Eq. (9) allows for fast screening of potential antioxidants or their combinations in a given matrix.

**Method verification**

To verify the results obtained from the rapid method of the assessment of residual stability, measurements of thermal oxidation of the stressed samples were completed at four remaining heating rates, i.e. 1, 3, 7 and 10 °C min$^{-1}$ (Table 2). From the onset oxidation temperatures, the kinetic parameters were obtained by the same procedure as in the case of unaged sample in the previous chapter. The value of the kinetic parameter $D$ was assumed to be the same for all the samples and for all the heating rates. The values of both kinetic parameters with their standard errors are also listed in Table 2. Then, the values of $R$ have been calculated from the kinetic parameters for all samples under study and are given in Table 2. As it can be seen from their comparison with the values obtained from the fast method, a very good agreement has been achieved. The values of extinction coefficients of residual stabilities for individual ageing types, calculated by applying Eq. (8), are summarized in Table 3 and are in a good agreement with those obtained from the rapid method.

Using the complete dataset in Table 2, the fitting procedure can also be done with the $D$ parameter adjusted independently for each degradation dose and thus verifying the assumption of constant $D$ among all samples. Figure 2 demonstrates that no clear trend in $D$ parameter can be observed and the values are randomly scattered for all ageing regimes (TS, TR, and TRS). In general, non-isothermal kinetic models are ill-conditioned and lack robustness due to strong correlation between the kinetic parameters. Thus, locking the value of $D$ provides more robust estimate of the conversion-dependent parameter $A$.

**Arrhenius temperature function**

If the same procedure is repeated with the Arrhenius temperature function, the relationship equivalent to Eq. (6) reads as follows:

$$\beta = \int_0^{T_a} \frac{dT}{A' \exp(E_{app}/R_gT)}$$

(10)

and Eq. (4) then becomes

$$t_i = A' \exp(E_{app}/R_gT),$$

(11)

where $E_{app}$ is the apparent activation energy, $R_g$ is the universal gas constant, and $A'$ is defined in the same manner as in Eq. (5). Compared to Eq. (6), the function (9) is a bit more difficult to work with since the temperature integral does not have a closed form and it has to be calculated numerically. However, as shown in [22], the Arrhenius and Berthelot–Hood temperature functions are practically equivalent in the temperature range of measurement so that both temperature functions should provide practically equivalent results.

Eliminating the temperature dependence of $R$ also brings about an interesting consequence: the values of residual stability, $R$, are almost independent of the choice of the temperature function. For example, the same analysis as described above carried out with the Arrhenius temperature function

| Extinction coefficient | All data | Fast screening method |
|------------------------|---------|----------------------|
| $a_T$ (110 °C), h$^{-1}$ | (1.38 ± 0.26) · 10$^{-3}$ | (1.41 ± 0.24) · 10$^{-3}$ |
| $a_R$ (500 Gy h$^{-1}$), h$^{-1}$ | (1.32 ± 0.05) · 10$^{-2}$ | (1.14 ± 0.05) · 10$^{-2}$ |
| $a_{TR}$(exp), h$^{-1}$ | (9.82 ± 0.69) · 10$^{-4}$ | (10.8 ± 0.70) · 10$^{-4}$ |
(Eqs. (10) and (11)), yields $E_{a_{pp}} = (164.4 \pm 5.2) \text{ kJ mol}^{-1}$ and $\alpha_T = (1.42 \pm 0.23) \cdot 10^{-3} \text{ h}^{-1}$.

**Conclusions**

A fast and simple method to assess the residual thermo-oxidative stability of materials has been introduced. The procedure is able to reliably determine the residual stability of the material without the need to perform standard isoconversional kinetic analysis of data obtained at several heating rates. The main advantage of this method is that it provides results that are in good agreement with the results obtained from a complete kinetic analysis of the data in a substantially shorter time. The procedure was verified on the samples of polyethylene cable insulation stressed by thermal, radiation and combined (thermal and radiation) ageing.

The constancy of the parameter $D$ for all the samples under study implicitly involves the assumption that the processes occurring in the samples are similar. Therefore, the samples should be of the same family, i.e. the constitutive part of the matrix should remain the same. Hence, the method is especially suitable for approximative assessment of the effects of a large number of various ageing factors on the stability of the material, for the effect of antioxidants of the same class on the stability of a polymer matrix, etc.

**Acknowledgements** This article was written thanks to the generous support under the Operational Program Integrated Infrastructure for the project “Strategic research in the field of SMART monitoring, treatment and preventive protection against coronavirus (SARS-CoV-2)”, project no. 313011ASS8, co-financed by the European Regional Development Fund. Financial support from the Slovak Research and Development Agency (APVV-15-0124) is gratefully acknowledged. The financial support from the Scientific Grant Agency of the Slovak Republic (VEGA 1/0498/22) is also acknowledged. The authors are also indebted to Dr. Vít Plaček from ÚJV Řež for providing the samples of coaxial cable for this study.

**Author contributions** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by A.V., Z.C., and T.D. The first draft of the manuscript was written by A.V. and Z.C., and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**References**

1. Šimon P, Kolman L. DSC study of oxidation induction periods. J Therm Anal Calorim. 2001;64:813–20.
2. Šimon P. Induction periods: theory and applications. J Therm Anal Calorim. 2006;84:263–70.
3. Schmid M, Ritter A, Affolter M. Determination of oxidation induction time and temperature by DSC: results of round robin tests. J Therm Anal Calorim. 2006;83:367–71.
4. Plaček V, Bartoniček B. The dose rate effect and the homogeneity of radio-oxidation of plastics. Nucl Instrum Methods Phys Res B. 2001;185:355–9.

5. Vykydalová A, Dubaj T, Cibulková Z, Mizerová G, Zavadil M. A predictive model for polyethylene cable insulation degradation in combined thermal and radiation environments. Polym Degrad Stabil. 2018;158:119–23.
6. Šimon P. Material stability predictions applying a new non-Arrhenian temperature function. J Therm Anal Calorim. 2009;97:391–6.
7. Dubaj T, Šimon P. Validation of the estimation of oxidation induction time from non-isothermal DSC measurements. J Therm Anal Calorim. 2014;118:919–23.
8. Focke WW, Van der Westhuizen J. Oxidation induction time (OIT) and oxidation onset temperature (OOT) of polyethylene in air. Testing Gimzewski’s postulate. J Therm Anal Calorim. 2010;99:285–93.
9. Šimon P. Isoconversional methods: fundamentals, meaning and application. J Therm Anal Calorim. 2004;76:123–32.
10. Šimon P. Considerations on the single-step kinetics approximation. J Therm Anal Calorim. 2005;82:651–7.
11. Šimon P. The single-step approximation: attributes, strong and weak sides. J Therm Anal Calorim. 2007;88:709–15.
12. Šimon P. Single-step kinetics approximation employing non-Arrhenius temperature functions. J Therm Anal Calorim. 2005;79:703–8.
13. Woo L, Khare AR, Sandford CL, Ling MTK, Ding SY. Relevance of high temperature oxidative stability testing to long term polymer durability. J Therm Anal Calorim. 2001;64:539–48.
14. Celina M, Gillen KT, Assink RA. Accelerated ageing and lifetime prediction: review of non-Arrhenius behavior due to two competing processes. Polym Degrad Stabil. 2005;90:395–404.
15. Šimon P, Hynek D, Maliková M, Cibulková Z. Extrapolation of accelerated thermooxidative tests to lower temperatures applying non-Arrhenius temperature functions. J Therm Anal Calorim. 2008;93:817–21.
16. Šimon P, Fratričová M, Schwarzer P, Wilde H-W. Evaluation of the residual stability of polyurethane automotive coatings by DSC: Equivalence of Xenotest and desert weathering tests and the synergism of stabilizers. J Therm Anal Calorim. 2006;84:679–92.
17. Fratričová M, Šimon P, Schwarzer P, Wilde H-W. Residual stability of polyurethane automotive coatings measured by chemiluminescence and equivalence of Xenotest and Solisi ageing tests. Polym Degrad Stabil. 2006;91:94–100.
18. Cibulková Z, Vykydalová A, Plaček V, Šimon P. Influence of gamma radiation and temperature on the ageing of EVA cable insulation studied by DSC. Thermochim Acta. 2005;455:28–32.
19. Cibulková Z, Šimon P, Lehocký P, Balko J. Antioxidant activity of p-phenylenediamines studied by DSC. Polym Degrad Stabil. 2005;87:479–86.
20. Cibulková Z, Šimon P, Lehocký P, Balko J. Antioxidant activity of 6PPD derivatives in polyisoprene matrix studied by non-isothermal DSC measurements. J Therm Anal Calorim. 2005;80:357–61.
21. Atiqullah M, Cibulková Z, Černá A, Šimon P, Hussain I, Al-Harthi MA, Antantaraskul S. Effects of supported metallocene catalyst active center multiplicity on antioxidant-stabilized ethylene homo- and copolymers: evaluation of melt stability by non-isothermal DSC study. J Therm Anal Calorim. 2015;119:581–95.
22. Šimon P, Dubaj T, Cibulková Z. Equivalence of the Arrehnius and non-Arrhenius temperature functions in the temperature range of measurement. J Therm Anal Calorim. 2015;120:231–8.