Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 761–768

LIFETIME SIMULATION AND THERMAL CHARACTERIZATION OF PVC CABLE INSULATION MATERIALS

M. Beneš[1,7]*, V. Plaček*[2]*, G. Matuschek*[3]*, A. A. Kettrup*[4]*, K. Györyová*[5]*, W. D. Emmerich*[6] *and V. Balek*[2,7*]

[1]Faculty of Science, Charles University, Albertov 2030, CZ-128 00 Prague, Czech Republic
[2]Nuclear Research Institute Řež, plc, CZ-25068 Řež, Czech Republic
[3]GSF–National Research Center for Environment and Health, Institute of Ecological Chemistry, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany
[4]Department of Ecological Chemistry and Environmental Analytical Chemistry, Technical University Munich, Weihenstephaner Steig 23, D-85350 Freising, Germany
[5]Faculty of Sciences, University P.J Šafárik, Moyzesova 11, SK-04154 Košice, Slovak Republic
[6]Netzsch-Gerätebau GmbH, Wittelsbacherstr. 42, D-95100 Selb, Germany
[7]Research Center Řež Ltd., CZ-25068 Řež, Czech Republic

Thermal behavior of commercial PVC cable insulation both before and after extraction of plasticizers, fillers and other agents were tested by TG/DTG and DSC during heating in the range 20–800°C in air. The ultrasound enhanced hexane extraction and dissolution in THF with subsequent precipitation of PVC were used to prepare 'extracted' and 'precipitated' samples. The total mass loss measured for the 'non-treated', 'extracted' and 'precipitated' PVC samples was 71.6, 66.6 and 97%, respectively. In the temperature range 200–340°C the release of dioctylphthalate, HCl and CO_2 was observed by simultaneous TG/FTIR. From TG results measured at different heating rates (1.5, 5, 10, 15 K min^{-1}) in the range 200–340°C the non-isothermal kinetics of the PVC samples degradation was determined. Activation energy values of the thermal degradation processes calculated by ASTM E 698 method, for 'non-treated', 'extracted' and 'precipitated' PVC samples were 174.6±17 kJ min^{-1}, 192.8±19 kJ min^{-1}, 217.1±20 kJ min^{-1}, respectively. These kinetic parameters were used for the lifetime simulation of the materials.

Keywords: *extraction, kinetics, lifetime simulation, plasticizers, PVC, TG-FTIR, thermal degradation, thermogravimetry*

Introduction

The lifetime prediction of cables in nuclear power plants (NPP) is based on the isothermal simulation of their ageing at elevated temperatures. To achieve a reliable simulation the main degradation factors that influence the service ageing have to be known. At lower temperatures the degradation of the cable insulation materials is caused mainly by the loss of plasticizers. At the service temperature, i.e. in the range from –20 to 60°C, the plasticizers loss is due to their migration from bulk to surface and due to their evaporation or extraction [1–4]. The cable becomes brittle and the glass transition temperature, T_g, increases. Another consequence of the cable insulation materials degradation due to plasticizer loss is the development of micro voids and microscopic cavities. These cavities can serve as channels for humidity transport into the bulk of the cable and cause short circuits or electrical breakdowns [5]. Therefore, the information about the content and migration of plasticizers in the plastics is of great importance for their lifetime prediction [1, 2].

Plasticizers are organic compounds of low volatility added to polymers to enhance flexibility, impact resistance, melt flow and to depress the brittle point. The function of plasticizers is based on the reduction of T_g point of plastics to a sufficiently low temperature that is below the temperature of the practical application of the cable. By this way a decrease of brittleness of the plastic insulation material at service condition can be achieved. To mention typical plasticizers, we should name di- and tri-esters of aromatic or aliphatic acids and anhydrides. Phthalate esters – namely dioctyl phthalate (DOP), diisooctyl phthalate (DIOP), diisononyl phthalate (DINP) – are the most commonly used (in about 78%) plasticizers. Aliphatic esters, like esters of adipic and tricarboxylic acids (e.g. trimellitates) are also used as plasticizers in PVC. Trimellitates are used for PVC wire insulation, often in conjunction with phthalates. The low volatility of trimellitates increases the service life of the PVC based material subjected to elevated temperatures for long periods of time [2].

---

[*] Author for correspondence: bal@ujv.cz

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The aim of this study is to characterize the thermal behavior of PVC cable insulation materials in the forms as supplied and as chemically treated with organic solvents to remove plasticizers. The thermal behavior of the chemically non-treated and chemically treated PVC cable insulation samples was characterized by TG and by simultaneous TG-FTIR techniques. The TG measurements carried out at several heating rates were used for the determination of the non-isothermal kinetics of the processes that cause the PVC degradation and for the determination of activation energy E_A values of thermal degradation process. The values of activation energy E_A obtained for different PVC samples are used to determine the conditions for simulation of their service ageing.

Experimental

Methods for thermal characterization of samples

For thermogravimetry measurements Netzsch STA 429 equipment was used under following conditions: sample amounts of 25 mg, corundum crucibles, airflow rate of 100 mL min^{-1}. The heat treatment in the range from 20–800°C was carried out to simulate the behavior of the samples under accelerated aging conditions. The heating rates 1.5, 5, 10, 15 K min^{-1} were used for TG measurements in order to determine the kinetic parameters of the thermal degradation. TG/FTIR apparatus (NETZSCH TG 209 system coupled with Brucker Vector FTIR spectrometer) was used under following experimental conditions: sample amount: 25 mg, heating rate: 5 K min^{-1}, airflow rate: 35 mL min^{-1}. DSC experiments were performed by TA Instruments Q100 system. The measurements were carried out in nitrogen in the dynamic mode at the heating rate of 15 K min^{-1} in the temperature range from –50 to +150°C. In order to obliterate the effect of thermal history on the T_g temperature determination, DSC measurements were carried out subsequently during heating, cooling and re-heating runs. The re-heating run was used for determination of glass transition temperature, T_g. Aluminium crucibles were used, sample amount was: 5.0 mg.

Samples and their preparation

Commercial PVC cable insulation sample (supplied by VARIA Prague Co.) contained following additives: di-octyl phthalate (DOP) in the amount of 22% mass/mass as plasticizer, chalk as filler, thermal stabilizer (Pb based compound), lubricants (Pb and Ca stearate) and carbon black.

The chemically extracted samples were prepared from the commercial PVC cable insulation sample by using two methods for the removal of plasticizers, fillers and other agents. Three types of the PVC samples denoted as: ‘not treated’, ‘extracted’ and ‘precipitated’ were investigated. The sample called ‘extracted’ was prepared by ultrasound enhanced hexane extraction whereas and the sample called ‘precipitated’ was prepared by dissolution in THF and the subsequent precipitation of PVC.

Description of processes used for PVC chemical treatment

(*i*) ultrasound enhanced hexane extraction: 1 g of grated PVC sample was shaken with a known volume of hexane followed by ultrasonic treatment (sonication) for 30 min to improve contact between solvent and sample. After filtration the hexane solution of plasticizer was used for GC–MS analysis. It was determined that the efficiency of DOP extraction was 70%. The solid PVC was considered as ‘extracted’ sample.

(*ii*) dissolution by tetrahydrofurane (THF): PVC sample 1 g of grated PVC sample was transferred to glass bottle with a known volume of THF followed by ultrasonic treatment until the solid sample was completely dissolved (approximately 5 min). The turbid solution was filtrated through glass fibber paper (Schleicher & Schnell, Germany), the clear solution was concentrated using rotatory evaporator. The PVC dissolved in THF was precipitated by methanol. Precipitated solid PVC was separated from remaining solution by filtration. The efficiency of this extraction method used for DOP removal from the PVC was 98–99%. The solid PVC was denoted as ‘precipitated’ sample.

The Quadruple mass spectrometry detector (Balzers QMG 420) connected to TG/DTA (Netzsch STA 429) was not sensitive enough to detect the DOP used as a plasticizer. Therefore, we used another approach in order to identify both qualitatively and quantitatively the chemical compound used as a plasticizer in PVC based cable insulation samples investigated in this study. We extracted the compounds used as a plasticizer from the PVC sample and carried out their direct chemical identification and quantification by gas chromatography with mass spectrometry detection (using GC-MS equipment Agilent 6890 Series). The GC–MS results confirmed that DOP compound was used as plasticizer in the PVC cable insulation materials.

The non-isothermal kinetics of the thermal degradation was determined from TG measurements at the heating rates of 1.5, 5, 10 and 15 K min^{-1}, respectively. It is known, e.g. [6] that the activation energy, E_A, of the respective process can be determined from the shift of the effect corresponding to the maximal rate of the mass loss during the materials degradation, as measured at several heating rates in the conditions that simulated the aging of materials.

There are several approaches for the determination of the activation energy, E_A, from the non-isothermal kinetics results, namely the method ASTM E 698 [6], the methods proposed by Ozawa-Flynn-Wall [7, 8] and by Friedman [9]. The ASTM E 698 [6] method was used in this study for the E_A evaluation. This method has been already used for E_A determination to be applied for lifetime assessment of cables used in nuclear power plants [10]. The E_A values calculated in this study for different PVC samples were compared and used for calculation of parameters for simulation of long time service aging.

Results and discussion

Thermal characterization of PVC cable insulation samples before and after chemical treatment

TG/DTG curves characterizing the thermal degradation of the PVC samples on heating in air in the range 20–800°C are presented in Figs 1 A, B, C, namely, the chemically 'non-treated' sample is characterized by the curves in Fig. 1A, the 'extracted' and 'precipitated' PVC samples are characterized by the curves in Figs 1B and 1C, respectively. In order to understand the mechanism of the PVC thermal degradation the TG and FTIR results of the 'non-treated' sample were used (Fig. 2).

Following values of the mass loss were measured by TG during air heating of the PVC 'non-treated' sample (Figs 1A and 2 and Table 1): 45.9 mass% in the range 200–340°C , 17.2 mass% in the range 360–540°C and 8.5 mass% in the range 540–800°C, respectively. From the FTIR spectra (Fig. 2) it followed that in the range 200–340°C the release of HCl, phthalate, and CO_2, occurred. We assumed that the CO_2 release took place as the result of the reaction between HCl and $CaCO_3$ (chalk) that was present as filler in the PVC sample. The release of CO_2 around 400°C was due to the burning of the polymer backbone, while the intense release of CO_2 observed on heating from 500–800°C was due to the thermal degradation of the carbonate fillers.

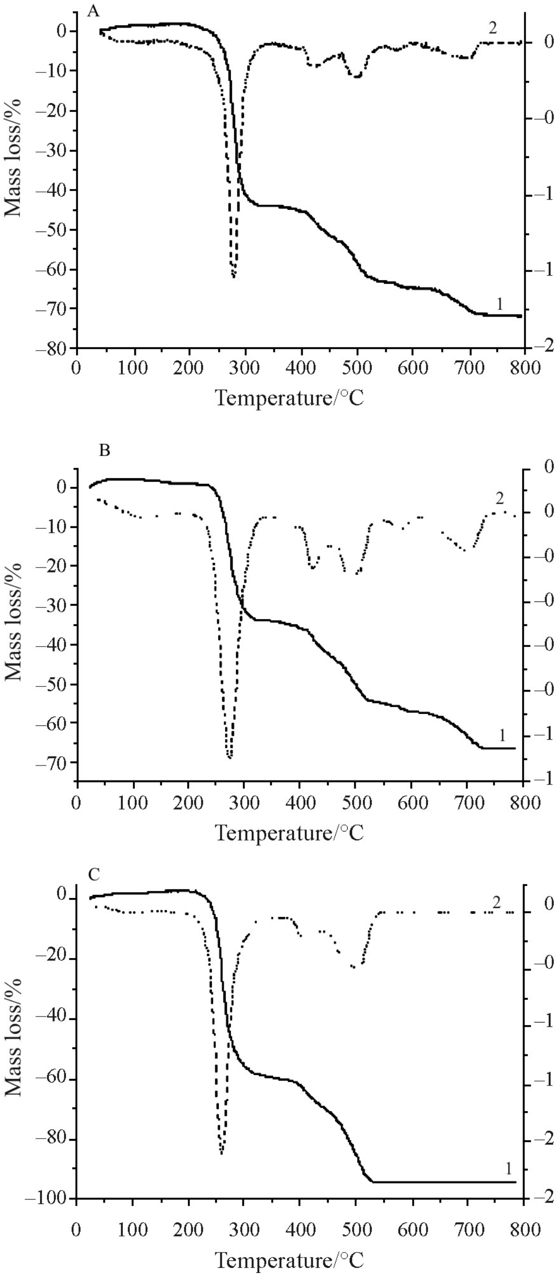

Fig. 1 Results of thermogravimetry: (TG curve -1) and (DTG curve -2) measured during heating of PVC cable insulation samples in air. A – ' non-treated', B – 'extracted' and C – 'precipitated' sample

Table 1 Values of the mass loss (mass/mass%) determined by TG for PVC cable insulation materials on heating in air in the range 20–800°C

PVC Sample	First degradation step	Second degradation step	Third degradation step	Total mass loss	
	200–340°C	Maximum rate	360–530°C	530–800°C	20–800°C
'non-treated'	45.9%	275°C	17.2 %	8.5%	71.6%
'extracted'	35.3%	275°C	19.7%	11.6%	66.6%
'precipitated'	62.3%	260°C	34.7%	–	97%

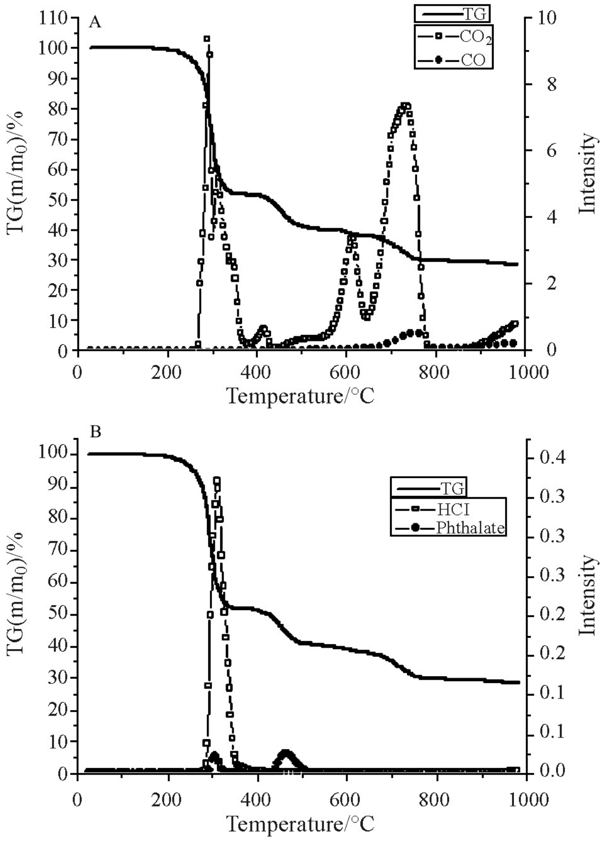

Fig. 2 Release of volatile products – CO, CO_2, A– and HCl, phthalates B – from the 'non-treated' PVC sample as measured by TG/ FTIR

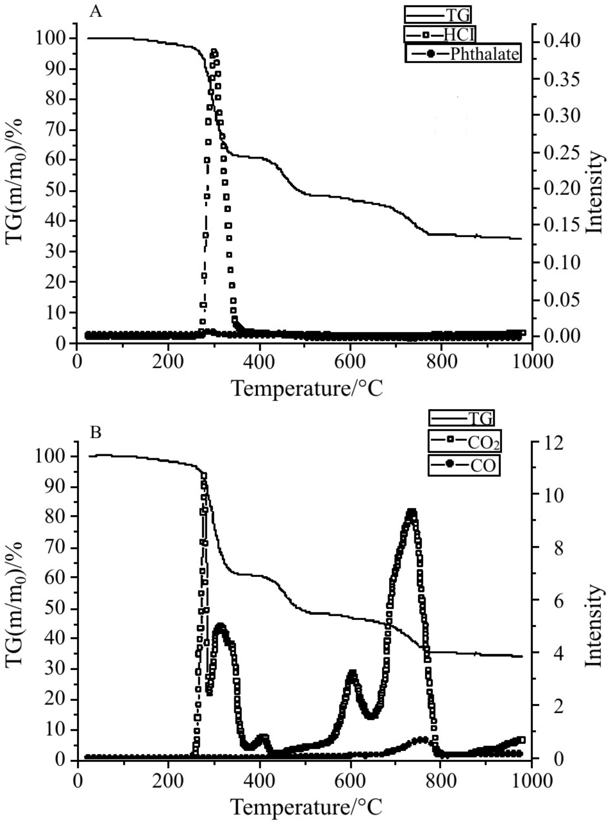

Fig. 3 Release of volatile products – CO, CO_2 A – and HCl, phthalates B – from the 'extracted' PVC sample as measured by TG/ FTIR

It is to mention that the mass spectrometry results presented in our previous study [11] are in good agreement with the findings of this study, namely that the heating of PVC sample in the range 200–340°C was accompanied by the evolution of HCl (m/z=36) due to PVC dehydrochlorination. Moreover, we have demonstrated [11] that besides HCl, the release of benzene (m/z=78) and other organic compounds, like dioctyl phthalate P (m/z=149) was detected in this temperature range. Our results are in agreement with the finding published by Matuschek *et al.* [12] who reported the release of phthalate based plasticizer (m/z=149) along with the release of HCl (m/z=36) from the PVC sample in the range 320–420°C. Therefore, we assumed that along with the dehydrochlorination and evaporation of some additives the PVC backbone degradation took partially place in the first degradation step*, i.e.* in the range 200–340°C (maximal rate 275°C) .

From the TG results of the 'extracted' sample (Figs 1B and 3) it followed that the second and third degradation step of the PVC cable insulation took place in the temperature intervals 360–530°C and 530–770°C, respectively.

Following values of mass loss of the 'extracted' sample were found by TG: 35.3 mass% in the range 200–340°C, 19.7 mass% in the range 360–540°C and 11.6 mass% in the range 540–800°C, respectively. The mass loss values are listed in Table 1.

The peak observed in the FTIR spectrum (Fig. 3) in the range 200–340°C corresponds to release of HCl as the result of the PVC dehydrochlorination. From Fig. 3 it followed that the release of phthalate took place during heating of the 'extracted' sample in a lower amount that in the 'non-treated' sample (Fig. 2). Moreover, in the range 200–340 °C a part of the released HCl reacted with the carbonate forming CO_2 (Fig. 3) similarly to the 'non-treated' sample. From the CO_2 release in Fig. 3 it is obvious that with the 'extracted' sample the degradation of the polymer backbone took place at about 400°C and, again, the decomposition of the carbonate based fillers occurred in the range 540–800°C, similarly to the 'non-treated' sample (Fig. 2).

TG results in Figs 1C and 4 demonstrated that the thermal degradation of the 'precipitated' sample took place in the range 200–340°C (62.3%) and in the range 360–550°C (34.7%). The mass loss values are summarized in Table 1.

The relatively high total mass loss (97%) of the 'precipitated' sample can be explained by the dissolution/precipitation process of the material. Besides the organic additives (plasticizers, etc.) this approach is able to remove the inorganic filler (carbonate) from

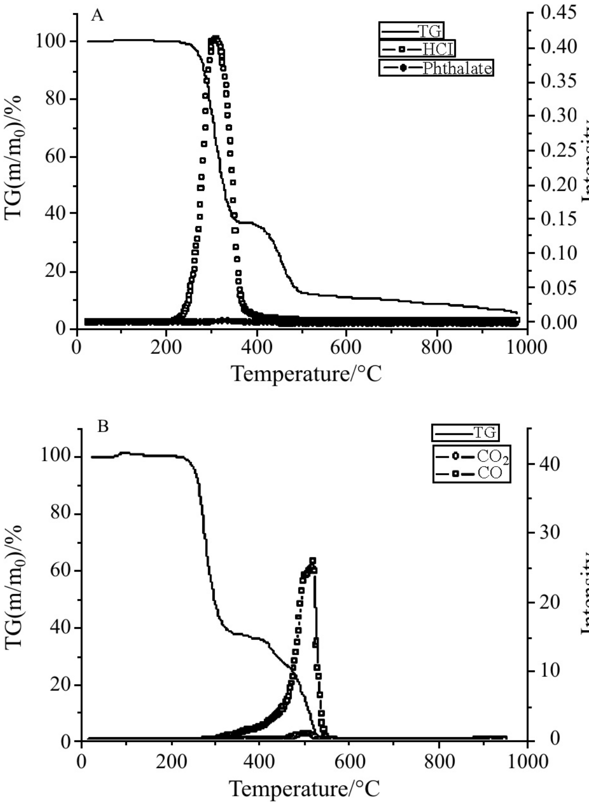

Fig. 4 Release of volatile products – CO, CO$_2$ A – and HCl, phthalates, B – from the 'precipitated' PVC sample as measured by TG/ FTIR

the PVC sample. Consequently, it is not possible to directly compare these values.

With the 'precipitated' sample the release of HCl was observed by FTIR (Fig. 4) in temperature range 200–340°C in agreement with the respective TG results. The maximum rate of the thermal degradation of the 'precipitated' sample was 260°C, hence it was shifted to lower temperature by 15 K in comparison with the 'non-treated' as well as 'extracted' samples, respectively (Fig. 5). The values of the maximum degradation rate determined by TG/DTG for the first degradation step of the investigated samples are summarized in Table 1. The FTIR spectra (Fig. 4) confirmed that no release of phthalate was observed on heating of the 'precipitated' sample and hence that all plasticizer was removed by the PVC dissolution in THF. On heating above 400°C the release of CO$_2$ (Fig. 4) was observed and confirmed the total burning /degradation of the residual polymer backbone. In agreement with our expectations no release of CO$_2$ was observed on heating above 600°C with the 'precipitated' sample that was free of carbonate-based fillers.

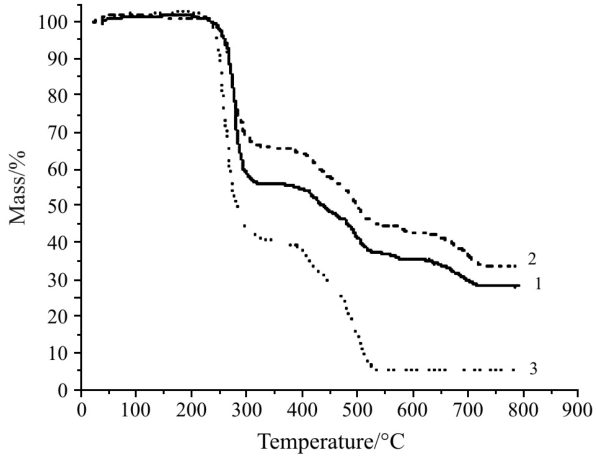

Fig. 5 Results of TG obtained during air heating of PVC cable insulation samples: Curve 1 – 'chemically non-treated', Curve 2 – 'extracted' and Curve 3 – 'precipitated'

It should be mentioned that the TG/FTIR results are in agreement with the results obtained by means of TG/DTA/mass spectroscopy on heating in air [11]. The release of HCl was observed in the range 270–330°C and the release of CO$_2$ was observed in the range 450–570°C (Fig. 2 in [11]).

Our results should complement papers published recently in order to determine the thermal stability of polymer materials and mechanism of their thermal degradation. In the studies presented earlier by other investigators the volatile products of polymer degradation during heating were detected by EGA or FTIR in order to assess their risk during burning [13–17]. The information obtained by means of several thermal analysis methods can be used to characterize the thermal stability of PVC cable insulation material and to elucidate processes of its thermal degradation during heating.

In this study we have demonstrated the effect of plasticizer's extraction on thermal behavior on PVC cable insulation. DSC results of the PVC samples measured before and after extraction of plasticizers are depicted in Fig. 6. For the 'non-treated' PVC cable

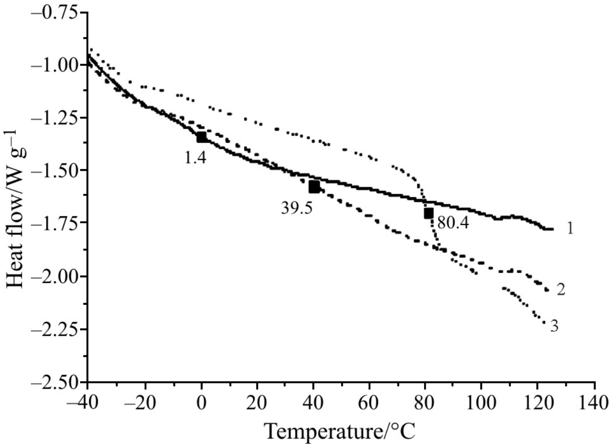

Fig. 6 DSC results characterizing of thermal behaviour of PVC samples: Curve 1 – ' non-treated', Curve 2 – 'extracted' and Curve 3 – 'precipitated' sample. Heating in nitrogen at the rate 15 K min^{-1}

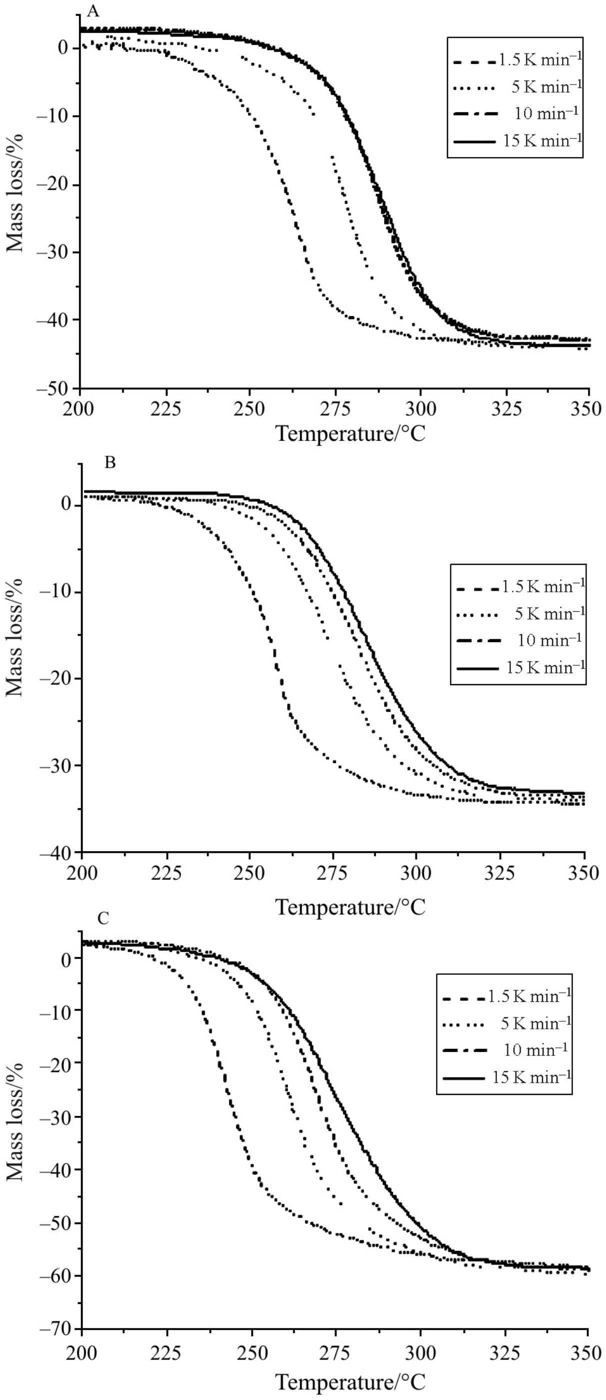

Fig. 7 A, B, C. TG results of PVC cable insulation samples measured at different rates of 1.5, 5,10, 15 K min^{-1} in the temperature range 200-340°C that corresponded to the first degradation step on heating in air. A – 'non-treated', B – 'extracted' and C – 'precipitated' sample

insulation material the value of T_g was observed at the relatively low temperature (T_g=1.4°C) as compared to that for the 'precipitated' PVC sample from where all the amount of plasticizer was removed (T_g=80.4°C). This finding is in agreement with the literature [18].

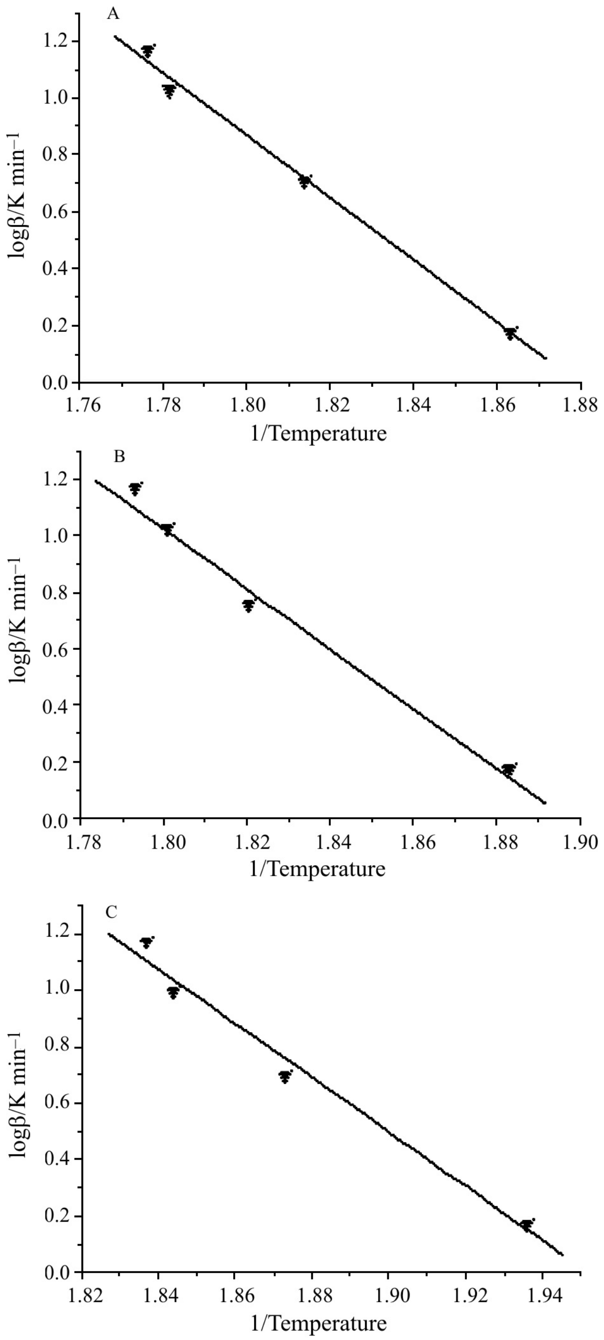

Fig. 8 A,B,C. Dependences of log β (heating rate) *vs.* 1/*T* characterizing the non-isothermal kinetics of the model PVC cable insulation on heating in air. A – 'non-treated', B – 'extracted' and C – 'precipitated' sample

Non-isothermal kinetics of the thermal degradation

Figure 7 depicts TG results of the PVC samples measured on heating in air at the rates of 1.5, 5, 10, 15 K min^{-1}, respectively.

The TG curves of the PVC samples denoted as 'non-treated' (Fig. 7A), 'extracted' (Fig. 7B) and 'precipitated' (Fig. 7C) were measured in the temperature

Table 2 Parameters of lifetime simulation

PVC Sample	Activation energy E_A (kJ mol^{-1})*	Activation energy E_A and calculated time (t_1) to be used for the cable ageing at 80°C**	
		E_A (kJ mol^{-1})	t_1 (days)
'non-treated'	217.1±20	197.1	21.5
'extracted'	192.8±19	173.8	45.0
'precipitated'	174.6±17	157.6	75.1

*E_A was calculated according ASTM E698 method.

**The method is based on the use of activation energy values to determine time suitable for simulation the conditions for aging of PVC cables in the conditions similar to service aging at 50°C. The considered service time of the cables was at least 30 years.

range 200–340°C that corresponded to the first degradation step of the PVC cable insulation material.

The TG results characterizing the mass loss observed on heating of the sample at above mentioned heating rates were used as the feed data for the determination of non-isothermal kinetics.

Figure 8 presents the dependences of log β (heating rate) *vs.* $1/T$ characterizing the non-isothermal kinetics of the PVC cable insulation samples on heating in air for 'non-treated' (Fig. 8A), 'extracted' (Fig. 8B) and 'precipitated' (Fig. 8C) samples, respectively. The ASTM E698 method [6] was used for the calculation of the activation energy E_A. The calculated E_A values of E_A are: 217.1±20 kJ mol^{-1} for 'chemically non-treated', 192.8±19 kJ mol^{-1} for 'extracted' and 174.6±17 kJ mol^{-1} for 'precipitated' sample.

Lifetime simulation of PVC cable insulation

The cables are supposed to be used at NPPs without failure for 30–40 years at the temperatures up to 60°C. To simulate the long-term service ageing under these conditions, the cables have to be in-laboratory aged at elevated temperature and at the end of simulation (ageing) electrical and mechanical properties have to be tested. To calculate the time of aging simulation at selected temperature, following equation can be used:

$$t_1 = t_2 e^{\frac{E_A (T_2 - T_1)}{k_B T_1 T_2}} \quad (1)$$

where t_1 –is time of accelerated ageing, t_2 –is required service life, E_A – activation energy in eV (1 eV=96484.6 J mol^{-1}), T_1 –is the temperature of accelerated ageing (in K), T_2 – is the service temperature (in K), k_B - Boltzmann factor $8.62 \cdot 10^{-5}$ eV K^{-1}. The calculated parameters for the simulation of service aging are presented in Table 2. In the calculation we used the minimum E_A value within the error of calculation given in Table 2. This is the standard way how the uncertainty in the determination of E_A values is taken into account. In this study it was supposed, that the cable will be used at least for 30 years at the temperature up to 50°C. For the accelerated aging, the temperature of 80°C was supposed to be used (at higher temperatures than 80°C, the plasticizer loss is too large to correspond a reliable simulation [3, 4]).

The influence of the E_A value on the simulation time is evident from Table 2. To achieve the aging to the same degradation state as after 30 years of service ageing at 50°C, the PVC cable material characterized by a relatively lower E_A value must be aged for longer time at relatively more severe conditions.

Following simulation times were calculated: the 'non-treated' PVC cable materials should be aged for 21.5 days, the 'extracted' PVC sample should be aged for 45.0 days and the 'precipitated' sample should be aged for 75.1 days, respectively (Table 2).

It is to mention that from different time values of aging simulation it is not possible to assess which sample has better properties. Such a conclusion can be drawn only after the final testing. Nevertheless, we can mention that the quality of the 'extracted' PVC sample after the ageing simulation will not correspond to requirements of the final functional tests. The reason for such a prediction is that during the extraction process not only plasticizers, but also stabilizers and antioxidants were removed from the PVC sample. All of them are important to protect the polymer from the negative environmental influence and to prolong its service time.

Conclusions

Thermal behavior of commercial PVC cable insulation both before and after extraction of plasticizers, fillers and other agents were tested by TG/DTG and DSC during heating in the range 20–800°C in air. The total mass loss measured for the 'non-treated', 'extracted' and 'precipitated' PVC samples was 71.6, 66.6 and 97%, respectively.

The most significant mass loss with all PVC samples was observed in the range 200–340°C. From the FTIR spectra it followed that the release of HCl, phthalate, and CO_2, occurred in the range 200–340°C. We assumed that the CO_2 release took place as the result of the reaction between HCl and $CaCO_3$ (chalk) that was present as filler in the 'non-treated' PVC sample. The release of CO_2 around 400°C was due to the burning of the polymer backbone, while the intense release of CO_2 observed on heating from 500–800°C was due to the thermal degradation of the carbonate fillers.

From TG results measured at different heating rates (1.5, 5, 10, 15 K min^{-1}) in the range 200–340°C the non-isothermal kinetics of the PVC samples degradation was determined. Activation energy values of the thermal degradation processes calculated by ASTM E 698 method, for 'non-treated', 'extracted' and 'precipitated' PVC samples were 174.6±17 kJ mol^{-1}, 192.8±19 kJ mol^{-1}, 217.1±20 kJ mol^{-1}, respectively. These values of the activation energy were used to determine the conditions for the aging simulation of PVC cable insulations.

Moreover, we have demonstrated the effect of plasticizer's extraction on thermal behavior on PVC cable insulation by DSC. For the 'non-treated' PVC cable insulation material the value of the glass transition temperature, T_g, was observed at the relatively low temperature (T_g=1.4°C) as compared to that for the 'precipitated' PVC sample from where all the amount of plasticizer was removed (T_g=80.4°C).

Acknowledgements

This work was supported by the Ministry of Education of Czech Republic (projects LA -040 and MSM 2672244501). The authors (M. B. and V. B.) acknowledge the support received by NATO Science Fellowship Programme and A. von Humboldt Fellowship, respectively.

References

1 Assessment and management of ageing of major nuclear power plant components important to safety: In-containment instrumentation and control cables, IAEA-TECDOC-1188, December 2000.
2 C. A. Harper and E. M. Petrie, Plastics Materials and processes, A Concise Encyclopedia, Wiley-Interscience 2003.
3 Y. R. Shashoua, Polym. Deg. Stab., 81 (2003) 29.
4 T. Kovačic and Ž. Mrklic, Thermochim. Acta, 381 (2002) 49.
5 D. A. Horvath and R. L. Steinman, Microstructure assessments for determining electric cable insulation remaining life, Proceedings of the International Conference on Wire System Ageing, Rockville – Maryland, April 23–25, 2002, pp. 99–105, NUREG/CP0179, November 2002.
6 ASTM E 698, Standard test method for Arrhenius kinetics constants for thermally unstable materials.
7 T. Ozawa, Chem. Soc. Japan, 38 (1965) 1881.
8 J. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 232.
9 H. L. Friedman, J. Polym. Lett., 4 (1966) 323.
10 P. Holzmann and G. Slitter eds.: Nuclear power plant equipment qualification reference manual, EPRI, TR-100516, 1992.
11 M Beneš, N. Milanov, G. Matuschek, A. Kettrup, V. Plaèek and V. Balek, J. Therm. Anal. Cal., 78 (2004) 621.
12 G. Matuschek, N. Milanov and A. Kettrup, Thermochim. Acta, 361 (2000) 77.
13 G. Zulfiqar, K. Masud and Q. Ameer, J. Therm. Anal. Cal., 73 (2003) 877.
14 A. C. de Souza, A. T. N. Pires and V. Soldi, J. Therm. Anal. Cal., 70 (2002) 405.
15 L. Abate, I. Blanco, A. Pollicino and A. Recca, J. Therm. Anal. Cal., 70 (2002) 63.
16 J. J. Suñol and J. Saurina, J. Therm. Anal. Cal., 70 (2002) 57.
17 S. Hirose, T. Hatakeyama, Y. Izuta and H. Hatakeyama, J. Therm. Anal. Cal., 70 (2002) 853.
18 E. A. Turi, (ed.) Thermal characterization of polymeric materials, Vol.2. Academic Press (1997) p. 233.

DOI: 10.1007/s10973-005-6876-4