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THERMAL DEGRADATION OF PVC CABLE INSULATION STUDIED BY SIMULTANEOUS TG-FTIR AND TG-EGA METHODS

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Abstract

Thermogravimetry (TG/DTG) coupled with evolved gas analysis (MS detection) of volatiles was used to characterize the thermal behavior of commercial PVC cable insulation material during heating in the range 20–800°C in air and nitrogen, respectively. In addition, simultaneous TG/FTIR was used to elucidate chemical processes that caused the thermal degradation of the sample. A good agreement between results of the methods was found. The thermal degradation of the sample took place in three temperature ranges, namely 200–340, 360–530 and 530–770°C. The degradation of PVC backbone started in the range 200–340°C accompanied by the release of HCl, H_2O, CO_2 and benzene. The non-isothermal kinetics of thermal degradation of the PVC cable insulation in the temperature range 200–340°C was determined from TG results measured at heating rates of 1.5, 5, 10, 15 and 20 K min^{-1} in nitrogen and air, respectively. The activation energy values of the thermal degradation process in the range 200–340°C of the PVC cable insulation sample were determined from TG results by ASTM method.

Keywords: non-isothermal kinetics, PVC, TG-EGA, TG-FTIR, thermal degradation

Introduction

A detailed information about chemical and thermal degradation of polyvinylchloride (PVC) based materials is necessary in the assessment of eco-toxicological risk during accidental burning and/or recycling of building materials, cables and other post-consumer products based on PVC. A number of papers were published in order to determine the thermal stability of polymer materials and mechanism of their thermal degradation. The volatile products of heating were detected in order to assess their risk

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during burning [1–8]. The methods of thermal analysis – DTA, TG and EGA – were the most frequently used in the investigation the thermal degradation processes. The simultaneous techniques represent the possibility to obtain useful information by means of several methods under the same experimental conditions.

The aim of this study was to use simultaneous techniques TG-FTIR and TG-EGA to characterize the thermal stability of PVC cable insulation material and to elucidate processes of its thermal degradation during heating in air or nitrogen.

Moreover, it was of interest to determine the activation energy E_a values of thermal degradation process. The Arrhenius activation energy, E_a was determined from the shift of the effect corresponding to the maximal rate of the mass loss during the materials' degradation, as measured by thermogravimetry at several heating rates [9, 10].

Experimental

Methods and materials

Termogravimetry and evolved gas analysis (Netzsch STA 429 equipment coupled with Balzers quadruple mass spectrometers system QMG 420) were used to characterize PVC cable insulation samples. Sample amounts of 25 mg and corundum crucibles were used for each measurement. The investigations were carried out under dynamic atmospheres at a flow rate of 100 mL min^{-1} in air or nitrogen.

In order to determine the kinetic parameters of the thermal degradation the heating rates used for experimental testing were selected as 1.5, 5, 10, 15 and 20 K min^{-1}.

TG/FTIR apparatus (NETZSCH 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}).

The PVC cable insulation sample from VARIA Prague Co. (supplier) used in this study contained di-octyl phthalate (DOP) as plasticizer.

Results and discussion

Investigation of processes underlying thermal degradation of PVC cable insulation samples on heating in nitrogen and air

The degradation of the PVC based cable insulation sample was characterized during heat treatment in nitrogen and in air, respectively.

Figures 1 and 2 depict results of TG/DTG and Evolved gas analysis (EGA – MS detection) of the of PVC sample measured during heating from 20–800°C at the rate 5 K min^{-1} in nitrogen and air, respectively. From TG results presented in Fig. 3 it follows that the mass loss of 45.6% was observed in the range 200–340 °C on heating in both nitrogen and air. From DTG curves (Figs 1 and 2) it is obvious that the temperature of the maximal rate of this process was 275°C.

From the mass spectrometry results presented in Figs 1 and 2 it followed that the mass loss in this temperature range observed on heating in both nitrogen and air, was ac-

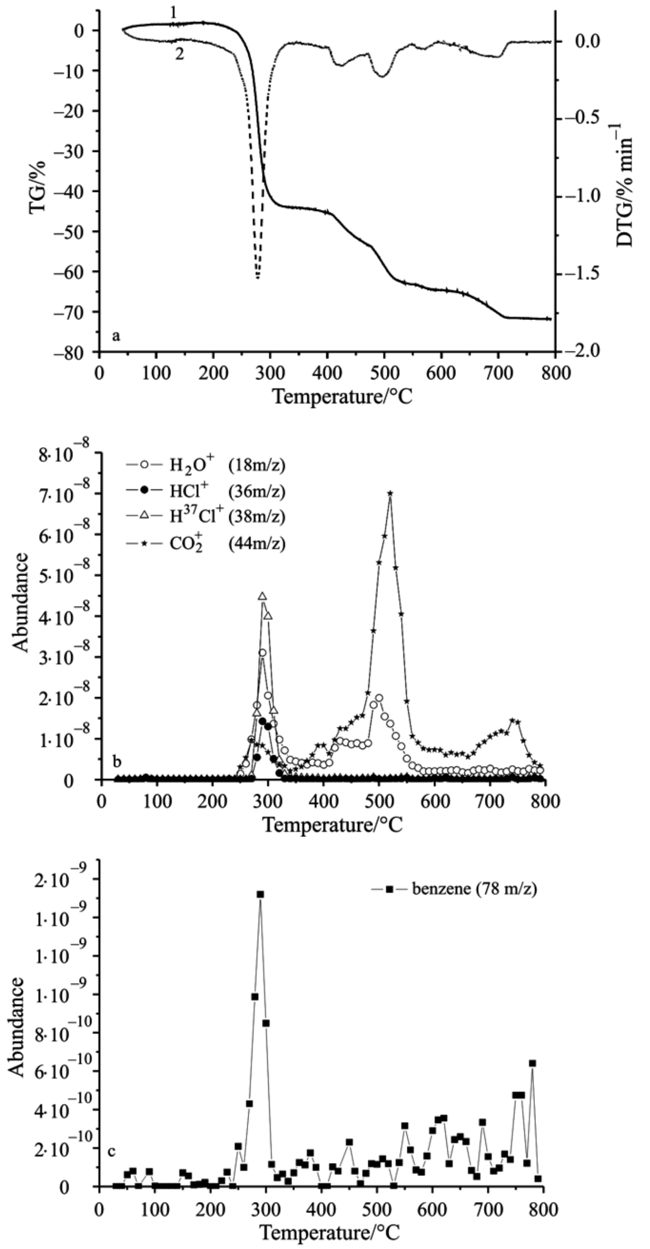

Fig. 1 Results of TG/DTG, and EGA (MS detection) obtained during heating of PVC cable insulation sample in nitrogen; a – thermogravimetry results are represented by curve 1 (TG) and curve 2 (DTG), b – mass spectrometry results of the evolved gases HCl, m/z=38, H_2O m/z=18 and CO_2 m/z=44, c – mass spectrometry results of the evolved benzene m/z=78

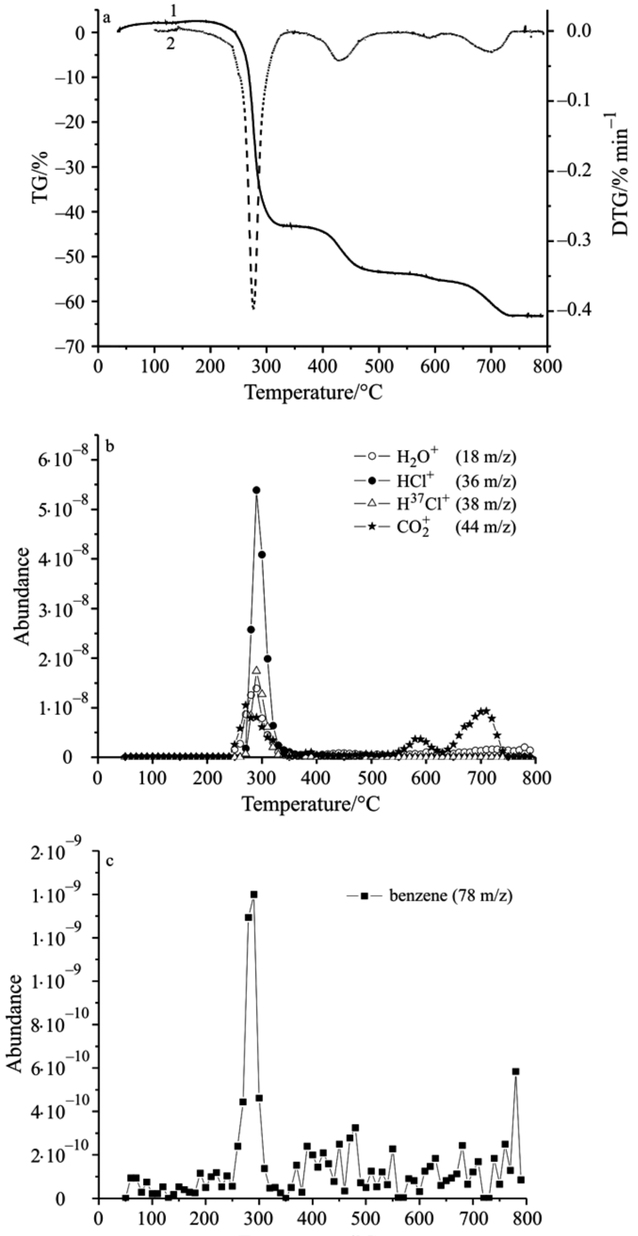

Fig. 2 Results of TG/DTG, and EGA (MS detection) obtained during heating of PVC cable insulation sample in air; a – thermogravimetry results are represented by curve 1 (TG) and curve 2 (DTG), b – mass spectrometry results of the evolved gases HCl, m/z=38, H_2O m/z=18 and CO_2 m/z=44, c – mass spectrometry results of the evolved benzene m/z=78

companied by the evolution of HCl (*m*/*z*=36), which took place due to dehydrochlorination of PVC. Besides HCl, the release of benzene (*m*/*z*=78) and other organic compounds, like di-*n*-octyl phthalate DOP (*m*/*z*=149), used as plasticizer in the PVC sample was detected in the temperature range of 200–340°C. Our results are in agreement with finding published by Matuschek *et al.* [11] 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 besides the dehydrochlorination and evaporation of some additives (e.g. plasticizer) the PVC backbone degradation took partially place in the first degradation step*, i.e.* in the range 200–340°C (maximal rate 275°C) both on heating in nitrogen and air, respectively.

No substantial differences were observed by thermal analysis in the thermal behaviour of the sample in temperature range 200–340°C on heating in nitrogen or air, respectively. From TG results in Fig. 2 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 on heating both in nitrogen and in air, corresponding to the respective mass loss values 11 and 8%. The temperatures of the maximum rate of the mass changes as determined from DTG curves (Figs 1 and 2) were 430 and 710°C, respectively. The mass spectroscopy results (Figs 1 and 2) demonstrated that the volatile products were CO_2 (*m*/*z*=44) and H_2O (*m*/*z*=18). From the differences observed by TG on heating in nitrogen and air (Fig. 3) and the evolution of volatiles in the temperature range from 360 to 530°C it followed that the total burning/degradation of the residual polymer backbone took place in this temperature interval and the char formed by thermal degradation of the PVC sample in the first degradation step was burned out on further heating in air (contrarily to nitrogen). The last step (accompanied by the evolution of CO_2 only) is due to the degradation of the filler material ($CaCO_3$). This also explains the occurrence of water and CO_2 in the first degradation step (200–340°C), which is

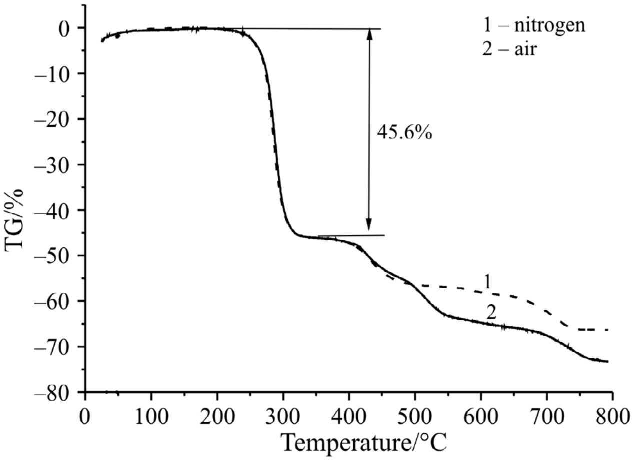

Fig. 3 Comparison of TG results obtained during heating of PVC cable insulation sample in nitrogen and air, respectively

not present in the case of pure PVC. A part of the released HCl reacts with the carbonate forming $CaCl_2$, H_2O and CO_2.

The TG/FTIR results (Fig. 4) are in agreement with the results obtained by means of TG/DTA/mass spectroscopy on heating in air (Fig. 1). The release of HCl was observed in the range 270–330°C and release of CO_2 was observed in the range 450–570°C. Consequently, the use of TG/FTIR enabled us to detect sensitively enough the volatile chemicals released from PVC cable insulation samples and to elucidate chemical processes that caused its thermal degradation. Similar results were published e.g. in [12, 13].

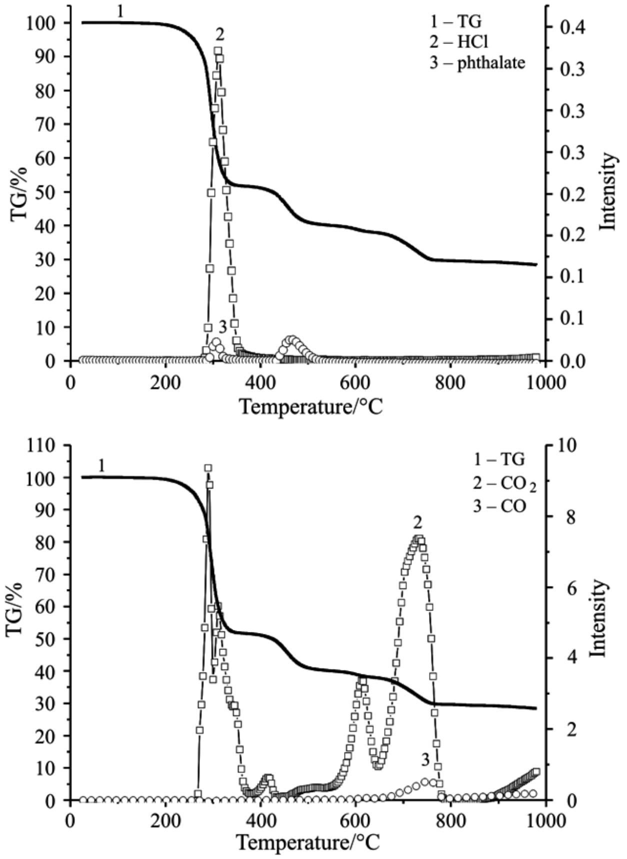

Fig. 4 TG/FTIR results demonstrating the release volatile products (phthalates, CO, CO_2, HCl) during heating of PVC sample in air

Non-isothermal kinetics of thermal degradation

Figures 5a and b depict TG results of the PVC sample measured at the different rates of 1.5, 5, 10, 15 and 20 K min^{-1} on heating in nitrogen (a) and air (b), respectively. The individual degradation steps were observed from TG curves in the same temperature ranges in both nitrogen and air, namely 200–340, 360–530 and 530–770°C.

In order to characterize the non-isothermal kinetics of thermal degradation the PVC sample we have used the first degradation step in the temperature range 200–340°C. The results degradation corresponding TG measurements at different heating rates are presented in Figs 6a (for nitrogen heating) and 6b (for air heating).

The method recommended by ASTM E698 [10] was used for the determination of non-isothermal kinetics and to evaluate the activation energy of the thermal degradation process (in the temperature range 200–340°C). It is to mention that the TG results, corresponding to the second and third degradation steps (Figs 5a and b) were not suitable for the evaluation of the non-isothermal kinetics of the thermal degradation of the sample, most probably due to the fact that several chemical processes overlapped in these temperature ranges and the TG results did not fulfil the requirement necessary for application of above mentioned methods recommended [10, 13, 14].

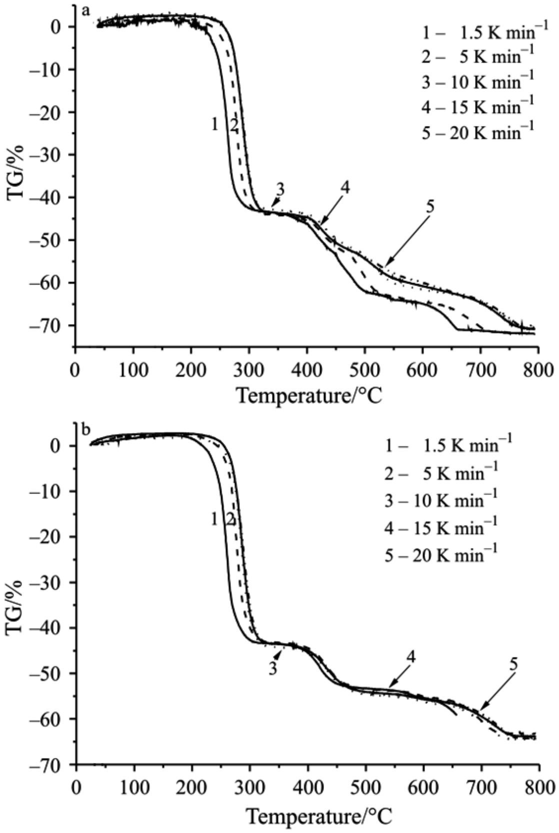

Fig. 5 TG results of PVC cable insulation sample measured at different rates (1.5, 5,10, 15, 20 K min^{-1}) in the temperature range 20–800°C; a – heating in nitrogen, b – heating in air. Curves 1–5 were obtained at the heating rates 1.5, 5, 10, 15 and 20 K min^{-1}, respectively

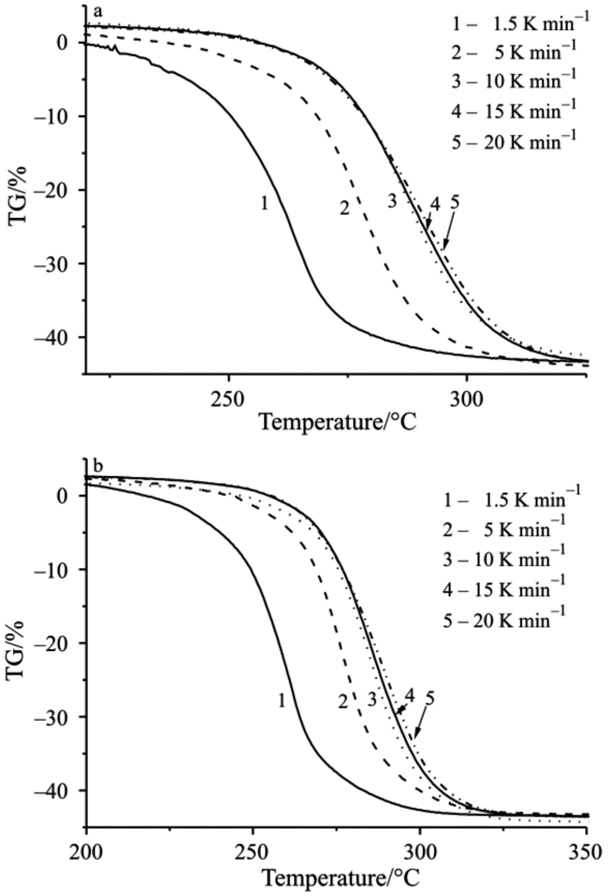

Fig. 6 TG results of PVC cable insulation sample measured at different rates (1.5, 5, 10, 15 and 20 K min^{-1}) in the temperature range 200–340°C that corresponded to the first degradation step of the sample; a – heating in nitrogen, b – in air. Curves 1–5 were obtained at the heating rates 1.5, 5, 10, 15 and 20 K min^{-1}, respectively

In order to evaluate the activation energy E_a, Eq. (1) was used

$$\ln\left(\frac{\beta}{T_{\max}}\right)=-\frac{E_a}{RT_{\max}} \tag{1}$$

where β is heating rate, $T_{\max}$ is the temperature of maximal mass loss rate in the considered temperature range, E_a is activation energy, R is gas molar constant 8.314 J K^{-1} mol^{-1}, T is temperature in K.

The activation energy E_a was calculated from the slope of the straight line plotted according to Eq. (1).

Figures 7a and b present strait lines that were constructed from the experimental TG data by a least square ‘best fit’ line that characterized the non-isothermal kinetics

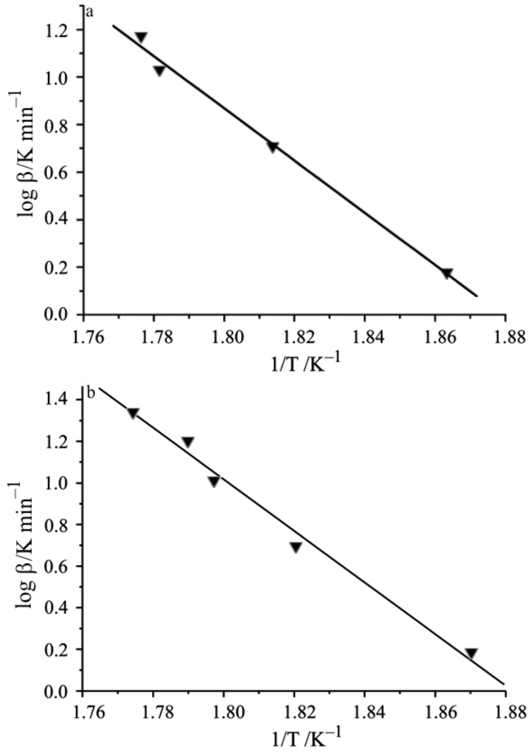

Fig. 7 Dependences of logβ (heating rate in K min^{-1}) *vs.* $1/T$ characterizing the non-isothermal kinetics of the PVC on sample on heating a – in nitrogen and b – in air. The ASTM 698 method was used for the calculation of the activation energy E_a Eq. (1)

of the PVC samples on heating in nitrogen and air, respectively. The respective activation energy values as calculated by ASTM method [10] are 221.6±20.77 and 217.1±24.34 kJ mol^{-1}.

So the activation energy values E_a for the PVC thermal decomposition were found very similar as determined from TG in temperature range 200–340°C in air or in nitrogen, respectively.

Conclusions

Simultaneous methods TG/EGA and TG/FTIR can be recommended for the elucidation of chemical processes taking place on thermal treatment of the PVC cable insulation material. The ASTM method used in this study for the non-isothermal kinetics of the thermal degradation in the temperature range 200–340°C was suitable for the determination of the activation energy E_a of the PVC thermal degradation from the TG results. No substantial differences on heating of PVC in nitrogen or air were observed in this temperature range.

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