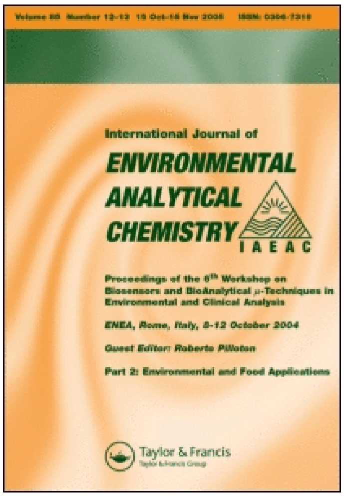

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Studies of volatile compounds emitted during thermo-oxidative degradation of poly(butylene terephthalate)

Małgorzata Dzięcioł[a]
[a] Institute of Organic Chemical Technology, Faculty of Chemical Engineering, West Pomeranian University of Technology, 71-065 Szczecin, Poland

To cite this Article Dzięcioł, Małgorzata(2009) 'Studies of volatile compounds emitted during thermo-oxidative degradation of poly(butylene terephthalate)', International Journal of Environmental Analytical Chemistry, 89: 8, 881 — 889

To link to this Article: DOI: 10.1080/03067310902999124

URL: http://dx.doi.org/10.1080/03067310902999124

Intern. J. Environ. Anal. Chem.
Vol. 89, Nos. 8–12, 15 July–15 October 2009, 881–889

Taylor & Francis
Taylor & Francis Group

Studies of volatile compounds emitted during thermo-oxidative degradation of poly(butylene terephthalate)

Małgorzata Dzięcioł*

Institute of Organic Chemical Technology, Faculty of Chemical Engineering, West Pomeranian University of Technology, Szczecin Al. Piastów 42, 71–065 Szczecin, Poland

(*Received 18 July 2008; final version received 27 April 2009*)

The volatile compounds emitted from poly(butylene terephthalate) (PBT) during thermo-oxidative degradation at different temperatures were studied. The experiments were carried out in a flow tubular furnace at the temperatures of 200, 300, 400, 500, 600 and 700°C in an air atmosphere. The weight losses of PBT at different temperatures were evaluated. The composition and concentrations of emitted volatile compounds were determined using gas chromatography with different detectors (FID, TCD, MSD) and colorimetric method. The studies showed that the main volatile substances evolved from PBT are carbon dioxide, carbon monoxide and 1,3-butadiene. Among the other degradation products, with significantly lower concentrations, tetrahydofuran, 4-vinylcyclohexene, benzene, toluene, ethylbenzene, acrolein, acetaldehyde and formaldehyde were determined. The temperature effect on the composition and the amounts of the emitted compounds was considered.

Keywords: poly(butylene terephthalate); PBT; polyesters; thermo-oxidative degradation; emission of volatiles

1. Introduction

Poly(butylene terephthalate) (PBT) is one of the major thermoplastic polyesters, prepared by polycondensation of 1,4-butanediol with terephthalic acid or dimethyl terephthalate. Because of its very good mechanical, thermal and electrical properties PBT has found application in many fields (e.g. electrical engineering, electronics, construction materials), including use at elevated temperatures. Very easy processing of PBT and the possibility of obtaining different modified grades of this polyester with the special properties caused its intensively rising consumption [1,2].

Under influence of temperature and oxygen polymeric materials undergo degradation and decomposition and emission of degradation products may be observed. Although these processes in relation to polyesters like PET and PBT were subjects of many studies [3–18], there are still some aspects which remain not exactly elucidated (e.g. mechanism of thermal and thermo-oxidative degradation). It was found, that in the thermal degradation process, a β-CH hydrogen transfer is involved, leading to the formation of oligomers with carboxylic and olefin end groups [16]. The degradation routes of PBT in thermo-oxidative conditions are complicated by the participation of oxygene. It was suggested that

---

*Email: dziemal@zut.edu.pl

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902999124
http://www.informaworld.com

thermo-oxidative degradation involves the oxidation at the α-methylene carbon with formation of unstable peroxides, but it was found that, in this process, thermal degradation also plays an important role [13]. More recent studies performed by Carroccio *et al.* [18] using MALDI-TOF MS analysis, provided extended information about thermal- (as well as photo-) oxidation processes occurred in PBT at the temperatures of 250 and 280°C. On the basis of the oxidation products obtained, the authors proposed the exhaustive scheme of PBT thermal-oxidation mechanism. Occurrence of α-hydrogen abstraction was observed, yielding to formation of oligomers terminated with terephthalic acid, 4-hydroxybutanoic acid, phenol and other groups. Moreover, the oxidative coupling of phenyl rings that leads to creation of biphenyl bridges between PBT chains was found.

It can be observed that results obtained by using different techniques may differ significantly. Moreover, in the real conditions during production, processing or combustion of polymeric materials, the composition of the emitted substances may be quite different, because it strongly depends on the temperature, degradation time, participation of oxygen and other factors. The aim of this work was to study the composition and amounts of the volatile compounds emitted from poly(butylene terephthalate) at different temperatures in an air atmosphere. In the literature there is little quantitative data concerning the volatile substances emitted from PBT in different conditions. It was reported that at the temperatures of processing (~300°C) volatile compounds are evolved from PBT: 1,3-butadiene [3,13,16,17], tetrahydrofuran [8,13] and benzene [13]. At higher temperatures the emission of carbon oxides, 1,3-butadiene, tetrahydrofuran, 4-vinylcyclohexene, 1,4-butanediol was dominant [7]. The formation of cyclic and unsaturated linear oligomers of PBT was also observed [5,7,16], as well as the less-volatile compounds such as terephthalic acid, benzoic acid, monobutyl and dibutyl esters of terephthalic acid [5,7,13,17]. Most of the available data are only qualitative and the conditions of studies were more often thermal than thermo-oxidative.

2. Experimental

2.1 *Materials*

The PBT granulate ELDUR pure (Jelchem, Poland) was used for the experiments. The tested material was pure polymer, without additives. All reagents used as the standards were of analytical-grade from various suppliers (Aldrich, Fluka, Supelco). Standard gas mixtures of gaseous analytes in N_2 from Supelco was used for CO_2 and 1,3-butadiene calibration. Active carbon (35–50 mesh) for the adsorption of analytes for the GC–MS analyses was purchased from Merck.

2.2 *Experimental conditions*

The experiments were carried out in a flow tubular furnace under isothermal conditions at the temperatures of 200, 300, 400, 500, 600 and 700°C for 20 min. The air flow through the furnace was kept at $0.025\,m^3\,h^{-1}$ and controlled using a flowmeter. The scheme of used apparatus is shown in Figure 1; it has been described in detail previously [10]. Before the beginning of experiment, the glass container was washed several times with air and evacuated using a vacuum pump. A weighed sample of PBT (0.1 g) in a ceramic boat was placed in a furnace which was heated in advance to the given temperature. The emitted

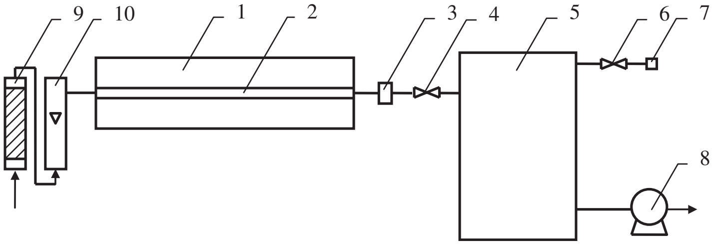

Figure 1. Scheme of apparatus used for the thermo-oxidative degradation studies of polymeric materials: (1) flow tubular furnace; (2) ceramic tube; (3) glass fibre filter; (4) needle valve; (5) 0.0127 m^3–volume vacuum glass container; (6) glass cock; (7) septum; (8) vacuum pump; (9) air-cleaning filter with silicagel and molecular sieves; (10) flowmeter.

volatile substances were collected in a 0.0127 m^3–volume glass container. After the end of the experiment, the ceramic boat with the residue of polymeric material was cooled, stabilised in a desiccator and weighed to evaluate the weight loss of PBT. The volatile degradation products were analysed using mainly gas chromatographic and colorimetric methods.

2.3 *Analytical methods conditions*

Most of the substances were identified and quantitatively analysed using the chromatographic methods. A comparison of the mass spectra and the retention times of the analysed compounds on different chromatographic columns with the analogous data obtained for standards was a basis of the identification. The quantitative analyses were performed using the same apparatus which was used for the degradation experiments. To this purpose, after evacuation of air from the glass container, liquid mixtures of standards were introduced to the apparatus using microsyringe by a heated evaporator. The evaporator was placed before the furnace and the same air flow through the furnace was kept as during degradation of polymeric material. As a result, the gas mixtures of standards were prepared in the glass container and calibration plots for the particular compounds were obtained. The calibration curves were rectilinear over the ranges of 0.005–0.100 $\mu g\,mL^{-1}$ for benzene, 0.003–0.060 $\mu g\,mL^{-1}$ for toluene and tetrahydrofurane, 0.002–0.040 $\mu g\,mL^{-1}$ for ethylbenzene and 4-vinylcyclohexene, 0.003–0.060 $\mu g\,mL^{-1}$ for acrolein, and 0.002–0.040 $\mu g\,mL^{-1}$ for acetaldehyde. The correlation coefficients ranged from 0.995 to 0.999.

The gas samples were taken from the container by gas-tight syringe and analysed on a Chrom 5 (Laboratorni Pristroje Praha, Czech Republic) gas chromatograph with an FID detector and the steel columns packed with: Chromosorb 102, 80–100 mesh (Johns – Manville, USA) (1 m × 3 mm I.D.) and 10% SE 30 + 0.3% Carbowax 20 M (SUPELCO) on a Chromosorb W NAW, 60–80 mesh (Johns – Manville, USA) (2 m × 3 mm I.D.). The injector and detector temperatures were 150°C, and the temperature of columns was 120°C (and additionally 50°C for the second column). As carrier gas nitrogen was used at a flow rate of 40 $mL\,min^{-1}$. A gas chromatograph ELPO N–504 (MERA-ELWRO, Poland) with a TCD detector and steel column (1 m × 4 mm I.D.) packed with silicagel 50–100 mesh (Merck, Germany) was used for carbon dioxide analyses. The analyses were performed at room temperature using hydrogen at a flow rate of 40 $mL\,min^{-1}$ as carrier gas. Formaldehyde was absorbed in 5 mL of redistilled water by aspiration method using a washer connected to the outlet of the container, and analysed on a SPEKOL 11 colorimeter (Carl Zeiss Jena) as a complex with chromotropic acid at 570 nm wavelength [19]. The calibration curve was rectilinear over the range of 0.16–1.60 µg mL^{-1} (correlation coefficient = 0.9989).

The concentration of carbon monoxide was measured using KANE 400 compact combustion analyser (Kane International, UK).

The identification of the evolved compounds was confirmed using an Agilent 6890N gas chromatograph with a 5973N mass selective detector, equipped with a 7683 series injector (Agilent Technologies, USA). In order to prepare samples for the GC–MS analyses, the degradation products were adsorbed on active carbon using aspiration method. Extraction from the active carbon was performed using two different solvents: butyl acetate (for analysis of the very volatile compounds) and acetone (for the less-volatile compounds). A HP–5MS capillary column with 5% phenylmethylpolysiloxane, 30 m × 0.25 mm I.D. and 0.25 µm film thickness (J&W Scientific, USA) was used with the following temperature programme: 50°C (hold 5 min), 10°C min^{-1} to 280°C (hold 2 min). Helium was used as carrier gas at a constant flow rate of 1.2 mL min^{-1}. The injection port temperature was 250°C, 2 µL of extracts was injected via split (1 : 10) injection. The mass selective detector conditions were as follows: electron impact ionisation, full scan mode, MSD transfer line temperature: 280°C, MS quad: 150°C; MS source: 230°C.

3. Results and discussion

Figure 2 illustrates the percentage of the PBT weight loss as a function of the temperature. At lower temperatures (200–300°C) the weight losses of PBT were very small (0.35% and 1.85%, respectively). During experiments at 400°C the weight loss increased intensively

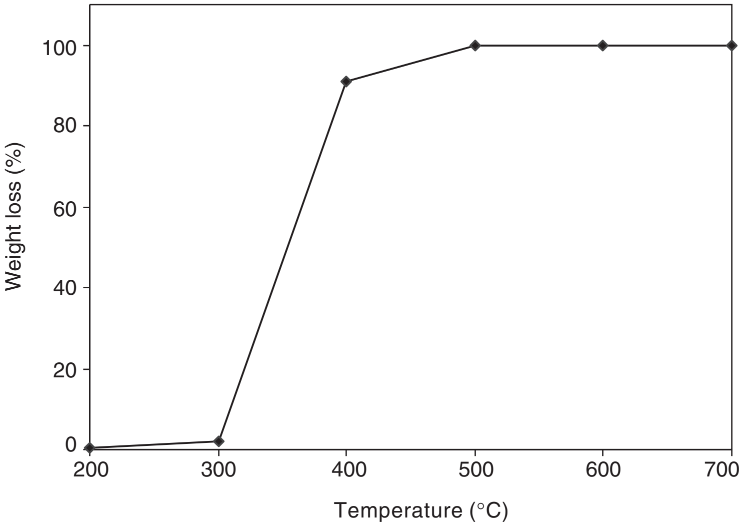

Figure 2. The percentage of the PBT weight loss during thermo-oxidative degradation at different temperatures.

achieving 94%. At higher temperatures (500–700°C) the PBT sample decomposed completely.

Analyses showed that volatile substances emitted during the thermo-oxidative degradation of PBT consist of carbon oxides, unsaturated and aromatic hydrocarbons, heterocyclic compounds and aldehydes. Examples of the GC–MS total ion chromatograms of volatiles emitted during degradation of PBT at 600°C are shown in Figure 3a (using butyl acetate as a solvent) and 3b (using acetone as a solvent). The using of combination of those two solvents allowed to analysing the wide range of analytes, including very volatile ones, which are not separable from acetone. The mass spectra of the determined degradation products compared entirely with the mass spectra of standards available in the NIST02 library.

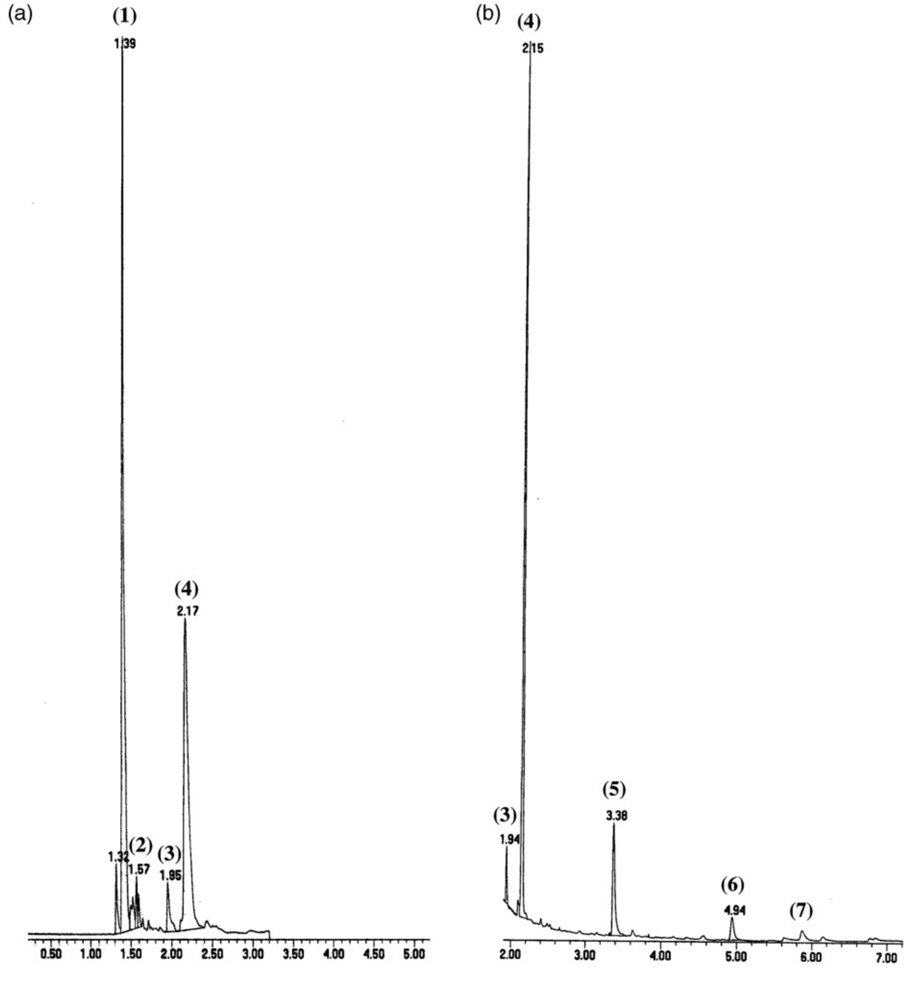

Figure 3. The GC-MS total ion chromatograms of volatiles emitted during thermo-oxidative degradation of PBT at 600°C: (a) using butyl acetate as a solvent; (b) using acetone as a solvent. Identified compounds: (1) 1,3-butadiene, (2) acrolein, (3) tetrahydrofuran, (4) benzene, (5) toluene, (6) 4-vinylcyclohexene, (7) ethylbenzene.

Table 1. Volatile compounds emitted during thermo-oxidative degradation of poly(butylene terephthalate) (ELDUR pure, Jelchem).

	Mass of the substance (mg/1 g PBT) at temperature of					
Substance	200°C	300°C	400°C	500°C	600°C	700°C
Carbon dioxide	35.52	56.77	59.81	118.47	381.69	364.79
Carbon monoxide	<0.20	2.02	21.75	59.40	74.85	64.40
1,3-Butadiene	0.02	0.10	58.40	111.64	131.46	136.44
Benzene	<0.01	<0.01	1.03	1.49	11.04	18.11
Toluene	<0.02	<0.02	0.26	0.64	1.99	8.12
Ethylbenzene	<0.05	<0.05	0.11	0.21	0.48	1.13
Tetrahydrofuran	0.68	1.88	5.67	4.46	2.14	1.16
4-Vinylcyclohexene	<0.05	<0.05	0.35	0.68	1.02	0.46
Formaldehyde	0.08	0.42	1.12	1.53	1.38	1.21
Acetaldehyde	0.16	0.25	1.59	1.73	1.77	1.04
Acrolein	<0.05	1.47	12.18	6.82	3.37	1.41

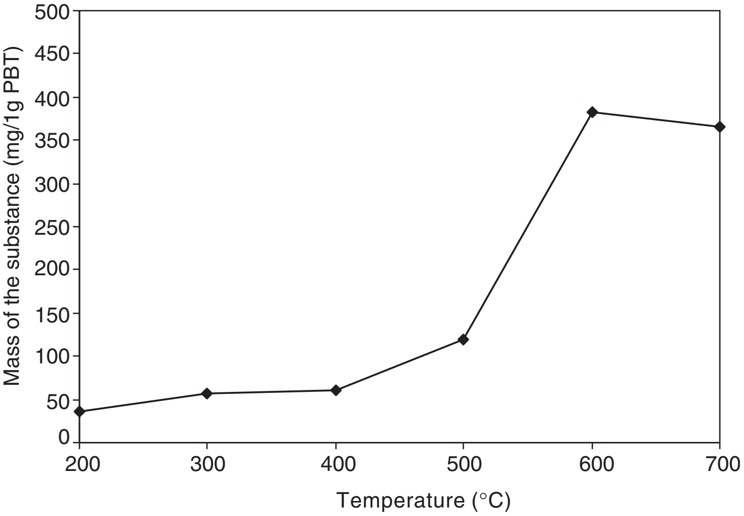

Figure 4. The dependence of the emitted carbon dioxide amount on the degradation temperature.

The concentrations of the particular compounds were evaluated on the basis of calibration plots, expressed in relation to the certain amount of the polymer sample (mg evolved from 1 g of PBT) and summarised in Table 1. The dependences of the amounts of the main evolved substances on the degradation temperature are shown in Figures 4–6.

Within the temperature range of 200–300°C, applied during production and processing of PBT, only small amounts of carbon oxides, tetrahydrofuran and traces of 1,3-butadiene and aldehydes were detected. In these conditions the presence of tetrahydrofuran may be caused by releasing of this compound trapped in the polymer, because it is known that this compound is formed as a by-product during obtaining of PBT in polycondensation reaction. The formation of carbon oxides at these temperatures may be explained by the

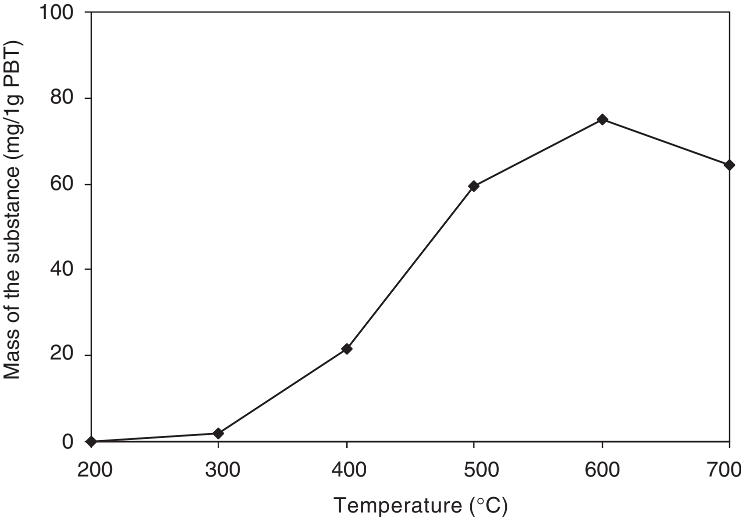

Figure 5. The dependence of the emitted carbon oxide amount on the degradation temperature.

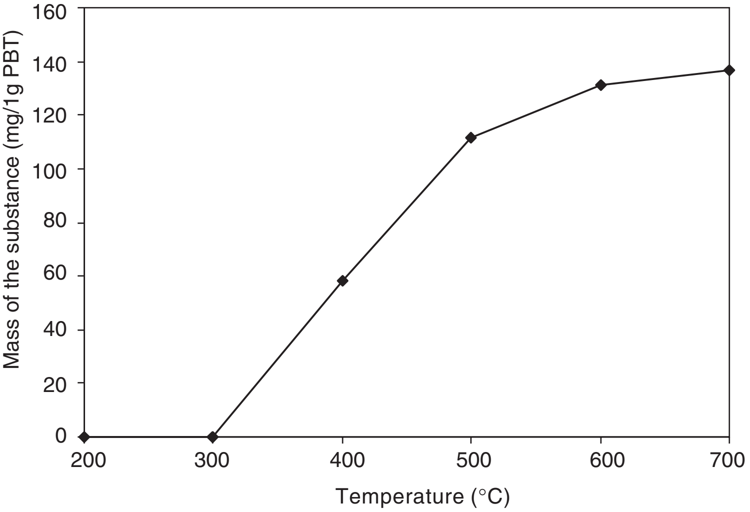

Figure 6. The dependence of the emitted 1,3-butadiene amount on the degradation temperature.

polymer chain homolysis reactions at the alkyl-oxygene or acyl-oxygene link, as was suggested in the literature [7].

At higher temperatures (400–700°C) the emission of volatile decomposition products of PBT was much more intensive and emitted mixtures became more complex. These conditions can be related to destruction of polymeric materials during fires or open-air burning. The maximum yields of carbon oxides were observed at 600–700°C. With the temperature rise the concentrations of the next major volatile product – 1,3-butadiene – increased. The small amounts of 4-vinylcyclohexene, which is a dimmer of 1,3-butadiene, were also detected. Among aromatic hydrocarbons benzene was a dominant product; emission of these compounds increased with the temperature. The maximum amount of tetrahydrofuran and acrolein was obtained at 400°C, and that of acetaldehyde and formaldehyde, at 500°C. The wide variety of emitted volatiles indicates that mechanism of PBT thermo-oxidative destruction at higher temperatures is complex. Probably after a first step of formation of a hydroperoxide at the methylene group [7,13], different secondary reactions including homolytic chain scission occur.

4. Conclusions

The main volatile compounds emitted from poly(butylene terephthalate) during the thermo-oxidative degradation were carbon dioxide, carbon monoxide and 1,3-butadiene. Among the other degradation products, with significantly lower concentrations, tetrahydofuran, 4-vinylcyclohexene, benzene, toluene, ethylbenzene, acrolein, acetaldehyde and formaldehyde were determined. The composition of the emitted mixture strongly depends on the degradation temperature.

Most of the emitted compounds are very toxic, and some of them are possibly carcinogenic to humans (benzene, 1,3-butadiene, 4-vinylcyclohexene). This indicates that non-controlled degradation of PBT at the temperatures above 400°C (e.g. in fire) may be hazardous for human health and for the environment. The problem of PBT combustion is real and important, because this material is widely used in industry, households, automobiles and, moreover, in many electric and electronic applications. To this purpose, accidents of fire with participation of PBT may occur relatively often.

Because of the toxic volatiles emission at the temperatures of 200–300°C (especially tetrahydrofuran, 1,3-butadiene, and aldehydes) it is necessary to provide an adequate ventilation during production and processing of this polyester, e.g. around injection molding or extrusion installations.

References

[1] H.J. Radusch, in *Handbook of Thermoplastic Polyesters*, edited by S. Fakirov (Wiley-VCH, Weinheim, Germany, 2002), Vol. 1.
[2] E.S. Wilks, editor, *Industrial Polymers Handbook – Products, Processes, Applications*, Vol. 1 (Wiley-VCH, Weinheim, Germany, 2001).
[3] V. Passalacqua, F. Pilati, V. Zamboni, B. Fortunato, and P. Manaresi, Polymer **17**, 1044 (1976).
[4] C.T. Vijayakumar and J.K. Fink, Thermochim. Acta **59**, 51 (1982).
[5] H. Ohtani, T. Kimura, and S. Tsuge, Anal. Sci. **2**, 179 (1986).
[6] B. Plage and H.R. Schulten, Macromolecules **23**, 2642 (1990).
[7] I.C. McNeill and M. Bounekhel, Polym. Degrad. Stab. **34**, 187 (1991).
[8] G. Montaundo, C. Puglissi, and F. Samperi, Polym. Degrad. Stab. **42**, 13 (1993).
[9] M. Pellow–Jarman and M. Hetem, Polym. Degrad. Stab. **47**, 413 (1995).
[10] M. Dzięcioł and J. Trzeszczyński, J. Appl. Polym. Sci. **69**, 2377 (1998); **77**, 1894 (2000); **81**, 3064 (2001).
[11] D.N. Bikiaris and G.P. Karayannidis, Polym. Degrad. Stab. **63**, 213 (1999).
[12] N. Manabe and Y. Yokota, Polym. Degrad. Stab. **69**, 183 (2000).
[13] G. Botelho, A. Queirós, S. Liberal, and P. Gijsman, Polym. Degrad. Stab. **74**, 39 (2001).
[14] T. Koshiduka, T. Ohkawa, and K. Takeda, Polym. Degrad. Stab. **79**, 1 (2003).
[15] V.N. Shelgaev, A.K. Mikitaev, S.M. Lomakin, G.E. Zaikov, and E.V. Koverzanova, J. Appl. Polym. Sci. **92**, 2351 (2004).

[16] F. Samperi, C. Puglisi, R. Alicata, and G. Montaundo, Polym. Degrad. Stab. **83**, 11 (2004).
[17] T. Arii and Y. Masuda, J. Anal. Appl. Pyrolysis **71**, 525 (2004).
[18] S. Carroccio, P. Rizzarelli, G. Scaltro, and C. Puglisi, Polymer **49**, 3371 (2008).
[19] J. Trzeszczyński, *Investigations on Air Pollution by Toxic Substances Educed from Plastics* (Szczecin University of Technology, Szczecin, Poland, 1978).