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Temperature influence on volatile compounds emitted during thermo-oxidative degradation of poly(trimethylene terephthalate)

Summary — The emission of volatile compounds formed during thermo-oxidative degradation of poly(trimethylene terephthalate) (PTT) was studied under isothermal conditions. The experiments were performed in a tubular furnace with a 0.025 m³/h air flow, at the temperatures of 200, 300, 400, 500, 600 and 700 °C. The weight loss of PTT and the amount of the solid degradation products were determined by gravimetric analysis. The volatile compounds were identified and quantified using gas chromatography and colorimetry methods. Analyses showed that the emitted volatiles are complex mixtures which consist of carbon oxides, aliphatic and aromatic hydrocarbons, aldehydes (including acrolein) and allyl alcohol. The temperature influence on the emission and composition of the volatile compounds evolved from PTT was discussed.

Keywords: poly(trimethylene terephthalate), PTT, polyesters, thermo-oxidative degradation, decomposition, volatile compounds emission.

WPLYW TEMPERATURY NA SKŁAD I ILOŚĆ LOTNYCH ZWIĄZKÓW EMITOWANYCH PODCZAS ROZKŁADU TERMOOKSYDACYJNEGO POLI(TEREFTALANU TRIMETYLENU)

Streszczenie — Poli(tereftalan trimetyleny) (PTT) poddano termooksydacyjnemu rozkładowi w warunkach izotermicznych, w piecu rurowym (rys. 1) w temperaturze 200, 300, 400, 500, 600 lub 700 °C, przy przepływie powietrza 0,025 m³/h. Za pomocą analizy wagowej określano ubytki masy PTT (rys. 2) oraz ilość emitowanych stałych produktów rozkładu. Lotne związki analizowano jakościowo oraz ilościowo metodami chromatografii gazowej i kolorymetrii. Wykazano, że emitowane lotne produkty rozkładu PTT są złożonymi mieszaninami, składającymi się z tlenków węgla, węglowodorów alifatycznych i aromatycznych, aldehydów (włączając akroleinę) oraz alkoholu allilowego. Omówiono wpływ temperatury procesu na emisję i skład wydzielających się z PTT produktów rozkładu (rys. 3–6).

Słowa kluczowe: poli(tereftalan trimetyleny), PTT, poliestry, rozkład termooksydacyjny, destrukcja, emisja lotnych związków.

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a relatively new polymeric material obtained by polycondensation of 1,3-propanediol and terephthalic acid. PTT was commercialized in 1990s by Shell Chemicals. Its use in fiber, film and engineering thermoplastic applications is growing rapidly [1]. This linear aromatic polyester with the three methylene groups in a glycol unit, shows excellent properties especially in fiber applications, where it competes with poly(ethylene terephthalate) and nylons. The structure and properties of this polyester were studied intensively in recent years [2–9].

Thermal stability and thermal degradation behavior of poly(trimethylene terephthalate) were investigated by several authors using different methods:

TGA, TGA-FTIR, DSC, XRD, ¹H NMR [10–14]. On the basis of the results obtained in non-oxidative conditions, the thermal degradation mechanism of PTT was proposed [14], started by rearrangement of the ester group by formation of a hexatomic ring, which is also characteristic for the other aromatic polyesters: poly(ethylene terephthalate) and poly(butylene terephthalate). In the case of PTT it leads to the formation of chain fragments with carboxyl and allyl ester end groups, which undergo secondary reactions including decarboxylation and deesterification.

Very little was published in the literature relating to the thermo-oxidation of PTT [15, 16]. The mechanism of this process is more complex because of the possible reactions with oxygen and it still needs explanation. In the literature there is no the data related to the amounts of the

volatile compounds emitted during thermo-oxidative degradation of PTT at different temperatures.

The aim of this work was to examine the emission of volatile compounds formed during thermo-oxidative degradation of poly(trimethylene terephthalate) in a wide range of temperatures (200–700 °C). The obtained data allows to establish the temperature effect on the degradation products emission. The results may be useful in assessment of toxicological aspects of real processes in which PTT is subjected to the elevated temperatures (e.g. production, processing, recycling) and during burning in fire conditions [17].

EXPERIMENTAL

Materials

– The PTT in pellet form CORTERRA CP509201 was supplied by Shell Chemicals. According to the producer's information it is clear homopolymer of PTT, suitable for fiber applications.

– All reagents used as analytical standards and solvents were of analytical-grade supplied from various suppliers: Aldrich, Supelco, Fluka. Active carbon (35–50 mesh) used for the adsorption of analytes during preparation samples for the GC-MS analyses was purchased from Merck.

Degradation experiments conditions

Poly(trimethylene terephthalate) was subjected to a thermo-oxidative degradation in the air atmosphere under isothermal conditions. The experiments were carried out in a flow tubular furnace at the temperatures of 200, 300, 400, 500, 600 and 700 °C. The weighed samples of PTT (~0.1 g) in the ceramic boat were placed in the furnace at selected temperature for 20 min, with the air flow kept at 0.025 m³/h. The delivered air was cleaned by passing through the filters with molecular sieves 4A and silica gel. The volatile compounds emitted from PTT were collected in a 0.0127 m³ – volume hermetic glass container,

after previous evacuation of air using a vacuum pump. The gas samples were taken for the analysis after 30 min stabilization at the room temperature. It was checked that the concentrations of the analytes in the glass container remained constant during at least 24 hours. The solid degradation products were trapped on a fiber glass filter placed at the outlet of the tube. Their amount was determined after experiment by weighing, as well as amount of a polymer residue in the ceramic boat. The scheme of the apparatus used for the studies is shown in Figure 1 and described in detail elsewhere [18, 19]. The degradation experiments in all temperatures were repeated twice and the obtained results were averaged.

Methods of testing

The qualitative and quantitative analyses of the volatile compounds emitted during thermo-oxidative degradation of PTT were performed mainly using gas chromatography methods with different detectors (MS, FID, TCD). The identification was based on the comparison of retention times and mass spectra of the particular compounds with the data obtained for standards. In order to prepare the samples for the gas chromatography method with mass selective detector (GC-MS), the analyzed compounds were adsorbed on active carbon and then extracted with two different solvents (acetone or butyl acetate). Using two solvents of different volatility enabled the analysis of both very volatile compounds, which were eluted before butyl acetate and others, eluted after acetone. The GC-MS analyses were performed using an Agilent Technologies 6890N gas chromatograph equipped with the 5973 Network Mass Selective Detector and 7683 Automatic Liquid Sampler. The resolution of analytes was achieved on HP-5MS capillary column (30 m × 0.25 mm I.D. × 0.25 μm film thickness) using programmed temperature from 50 °C (hold for 5 min) to 280 °C (hold for 10 min), with the ramp rate of 10 °C/min.

The quantitative analyses were carried out using a Chrom 5 gas chromatograph with an FID detector and packed columns [A: Chromosorb 102, 80–100 mesh; B: SE 30 (10%) + Carbowax 20M (0.3%) on a Chromosorb W NAW, 60–80 mesh]. In order to perform the quantitative analyses, the liquid mixtures of standards were injected using microsyringe through a heated evaporator to the same apparatus which was applied during the degradation experiments. The evaporator was placed before the furnace and the air flow during introducing the standard mixtures was kept at the same value – 0.025 m³/h. The different volumes of the standard gas mixtures prepared in the glass container were injected to the chromatographic column. The calibration plots obtained for the particular standards were used to determine the concentrations of the compounds emitted from PTT. This procedure, based on using analogue conditions of degradation experiments and preparing standards for calibration, allowed to minimize the effect of analytes adsorption on

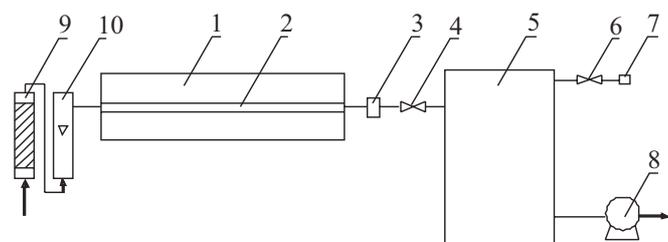


Fig. 1. Apparatus used for the studies of polymeric materials degradation in thermo-oxidative conditions: (1) flow tubular furnace, (2) ceramic tube, (3) glass fiber filter, (4) needle valve, (5) vacuum glass container, (6) glass cock, (7) septum, (8) vacuum pump, (9) air-cleaning filter with silicagel and molecular sieves, (10) flowmeter

the glass walls of the container and other elements of the apparatus.

A gas chromatograph ELPO N-504 with a TCD detector and column packed with silicagel (50–100 mesh) were used for carbon dioxide analyses. The analyses of carbon monoxide were carried out using a KANE 400 Combustion Analyser. Formaldehyde was absorbed in redistilled water and analyzed by colorimetric method as a complex with chromotropic acid.

The gravimetric analyses of a polymer residue and emitted solid products were performed using a Sartorius CP224S-OCE balance, after previous stabilization in a desiccator.

RESULTS AND DISCUSSION

The weight losses of PTT in all studied conditions were calculated and they are presented in Fig. 2 as a function of the degradation temperature. At the temperatures of 200 and 300 °C the weight losses were very low: 0.05 % and 1.57 %, respectively. Increasing the temperature up to 400 °C resulted in significant changes of these values — the sample decomposed in almost 90 %. Decomposition process at 500 °C and above resulted in the weight losses higher than 99.5 %.

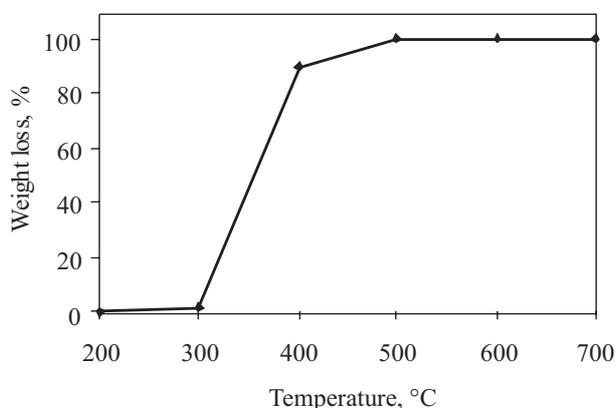


Fig. 2. The percentage of PTT weight loss as a function of the degradation temperature

On the basis of the performed analyses the emission of different volatile compounds (carbon oxides, aliphatic and aromatic hydrocarbons, aldehydes and allyl alcohol) from poly(trimethylene terephthalate) was estimated. The amounts of the volatile degradation products were expressed in relation to the 1 g of the tested PTT and summarized in Table 1. The intensity and complexity of the volatiles emission varied according to the degradation temperature, but generally, carbon dioxide and carbon oxide, formed in several times smaller quantities were the main degradation products. Within the temperature range of 200–300 °C, which corresponds to the conditions during production and processing of PTT, only

traces of acrolein, acetaldehyde, formaldehyde, allyl alcohol and carbon oxides were detected. Degradation process of PTT at 400 °C and higher was accompanied by formation of large amounts of smoke consisted of the solid substances and a complex mixture of volatile compounds. At 400 °C the amount of acrolein increased and it was the major volatile organic product of degradation in these conditions. Significantly smaller amounts of other aldehydes (formaldehyde, acetaldehyde), low-molecular aliphatic hydrocarbons, aromatic hydrocarbons (benzene, toluene, ethylbenzene, styrene) and allyl alcohol were also formed. Raising the temperature to 500 °C resulted in increasing emission of carbon oxides and other volatiles, except acrolein. The small amounts of several new compounds (allylbenzene, 1,2,4-trimethylbenzene and benzaldehyde) also appeared. At 600 °C further increasing emission of the majority of products was observed, especially carbon dioxide, carbon monoxide, aliphatic hydrocarbons C1–C4 and benzene. During destruction process of PTT at 700 °C the amounts of carbon oxides increased not so significantly as aliphatic hydrocarbons C1–C4 and benzene, which was placed among the major degradation products. At this temperature the emission of all aldehydes and allyl alcohol decreased.

Table 1. Volatile compounds emitted during thermo-oxidative degradation of poly(trimethylene terephthalate)

Substance	Mass of the substance (mg/1 g PTT) at temperature (°C) of					
	200	300	400	500	600	700
Carbon dioxide	<5.00	22.34	124.15	243.28	452.67	459.85
Carbon monoxide	<0.20	0.72	23.50	70.84	82.15	87.92
Aliphatic hydrocarbons C1–C4	<0.01	<0.10	5.42	7.82	35.52	75.53
Aliphatic hydrocarbons C6	<0.05	<0.05	1.16	2.60	2.03	0.57
Cyclopentene	<0.03	<0.03	0.05	0.07	0.20	0.31
Benzene	<0.01	<0.01	0.42	1.00	15.98	23.01
Toluene	<0.02	<0.02	0.28	0.45	2.37	3.92
Ethylbenzene	<0.05	<0.05	0.08	0.11	0.75	1.04
Styrene	<0.05	<0.05	0.13	0.37	2.73	5.54
Allylbenzene	<0.05	<0.05	<0.05	0.17	1.38	1.95
1,2,4-Trimethylbenzene	<0.05	<0.05	<0.05	0.13	0.35	0.76
Allyl alcohol	<0.05	0.54	3.90	5.30	6.52	5.07
Formaldehyde	0.05	0.13	2.40	2.43	2.60	1.34
Acetaldehyde	<0.01	0.16	1.68	1.74	1.89	0.72
Acrolein	<0.05	2.93	22.46	17.56	10.15	5.03
Benzaldehyde	<0.01	<0.01	<0.01	0.26	0.79	0.46

The dependences of the main volatile compounds emissions from PTT on the degradation temperature are shown in Figures 3–5. It can be noticed, that with the

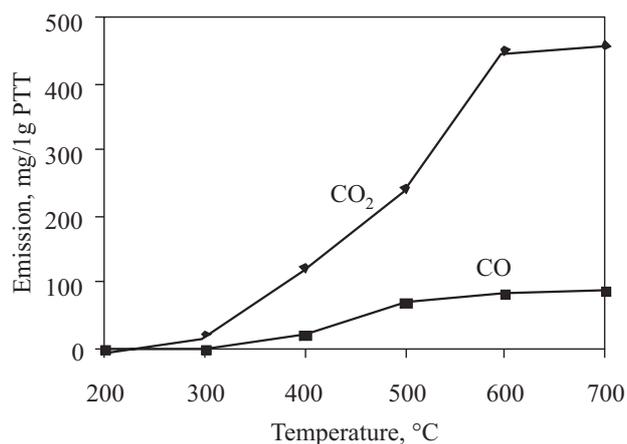


Fig. 3. The dependence of the carbon oxides emissions on the degradation temperature

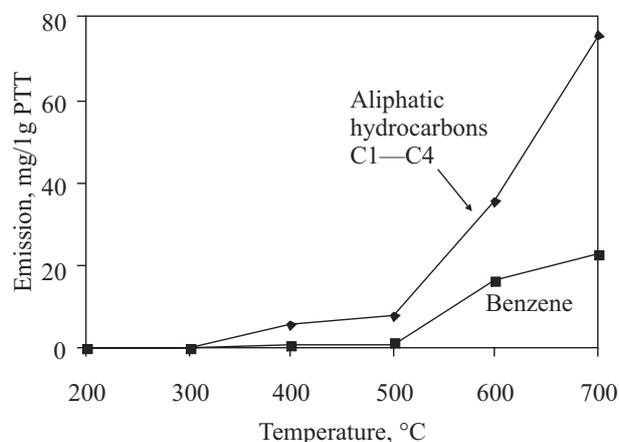


Fig. 4. The dependence of the hydrocarbons emissions on the degradation temperature

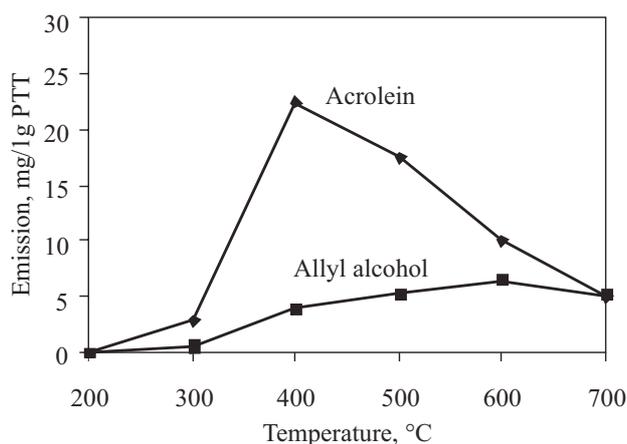


Fig. 5. The dependence of the acrolein and allyl alcohol emissions on the degradation temperature

temperature rise the amounts of carbon oxides increased, especially within the temperature range of 300–600 °C. The similar tendency was observed for aliphatic and aromatic hydrocarbons, but in this case the greatest growth

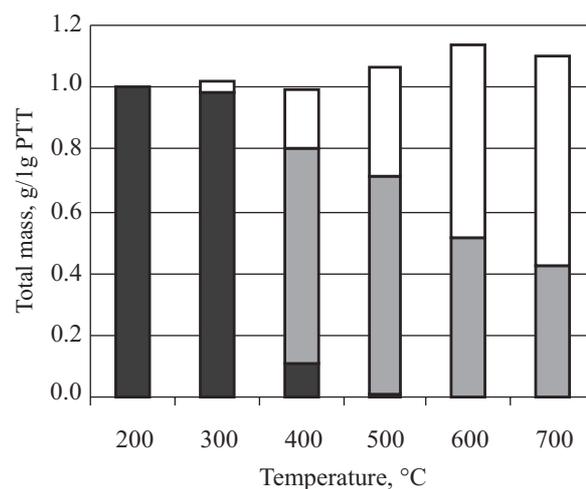


Fig. 6. The distribution of the PTT degradation products at different temperatures

of emission was observed at higher temperatures (above 500 °C). Among the aromatic hydrocarbons benzene was a major product. The maximum emission of acrolein was found at 400 °C; the amounts of other aldehydes formed were significantly smaller. Emission of allyl alcohol reached a maximum at 600 °C.

Figure 6 illustrates the distribution of all fractions of products (polymer residue in ceramic boat, solid products trapped on a filter and summarized amount of volatiles) obtained during degradation experiments of PTT at the studied temperatures. Expressing of the amounts of all products in relation to 1 g of PTT allows noticing that at the temperatures ranging from 500 to 700 °C the obtained total masses exceeded the mass of the degraded polymeric material. This fact suggests that in formation of thermo-oxidative degradation products of poly(trimethylene terephthalate) at higher temperatures atmospheric oxygen is involved.

CONCLUSIONS

The composition and intensity of volatile compounds emission during thermo-oxidative degradation of poly(trimethylene terephthalate) strongly depend on the temperature. The amounts of carbon oxides, aliphatic and aromatic hydrocarbons significantly increased with the temperature rise. The maximum emission of acrolein was observed at 400 °C and that of allyl alcohol, at 600 °C.

At the temperatures applied during production and processing of PTT (200–300 °C) the emission of acrolein is the most important factor, which should be taken into consideration during safety assurance of these processes. This highly poisonous compound may cause severe irritation of eyes and mucous membranes even at very low concentrations in air.

Thermo-oxidative decomposition of PTT within the temperature range of 400–700 °C (e.g. in fire or open-air

burning) is accompanied by the intensive emission of complex mixture of degradation products. Among 16 identified volatile products there are some compounds of very high toxicity (e.g. acrolein, allyl alcohol, carbon oxide, benzene and its homologues). Thus, all the non-controlled thermal processes with the participation of PTT may create health hazard and be dangerous for the environment.

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