

Studies of Temperature Influence on Volatile Thermal Degradation Products of Poly(ethylene terephthalate)

MAŁGORZATA DZIĘCIOŁ, JERZY TRZESZCZYŃSKI

Institute of Fundamental Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland

Received 2 September 1997; accepted 17 February 1998

ABSTRACT: The temperature influence on the thermal degradation products evolved from poly(ethylene terephthalate) (PET) was investigated. The experiments were carried out within the temperature range of 200–700°C in air. The main volatile toxic products and weight losses during thermal degradation of PET were determined. The results are presented on plots as a function of the degradation temperature. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2377–2381, 1998

Key words: poly(ethylene terephthalate) thermal degradation; volatile products evolved from poly(ethylene terephthalate); plastics thermal degradation

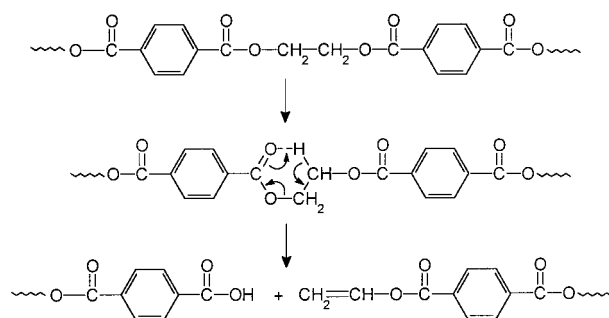
INTRODUCTION

Knowledge about the thermal degradation of poly(ethylene terephthalate) (PET) involving the emission of toxic substances is very important on account of many commercial applications of this polymer. The use of PET is growing very rapidly, especially for carbonated beverage bottles.

Although the thermal stability of PET is relatively high, the volatile toxic substances are emitted within the temperature range 200–300°C applied to the production, processing, and material recycling. Studies^{1–4} have shown that acetaldehyde and formaldehyde are the main degradation products at these temperatures. At higher temperatures (400–700°C), the decomposition products of PET form mixtures, the complexity of which depends on the temperature, atmosphere, or time.^{5–9}

The mechanism of PET degradation has been studied by several authors.^{1,2,5–9,11,12} Most of them agree that the thermal degradation is initiated by random scission of the chain at the ester linkage, leading to carboxyl and vinyl ester end groups.

This reaction is believed to occur through a six-membered transition state:



The primary degradation products undergo secondary processes (decarboxylation, hydrogen transfer, transesterification) to give a wide variety of substances, such as carbon oxides, aldehydes, hydrocarbons, and aromatic acids and their esters.

The reactions of thermooxidative degradation are additionally complicated by the participation of oxygen. It has been suggested that the process starts by formation of a hydroperoxide at the methylene group, followed by homolytic chain scission.^{1,2} The mechanism of the thermooxidative degradation of PET is rather complex and still needs a reasonable explanation. It is known that

Correspondence to: M. Dzięcioł

Journal of Applied Polymer Science, Vol. 69, 2377–2381 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/122377-05

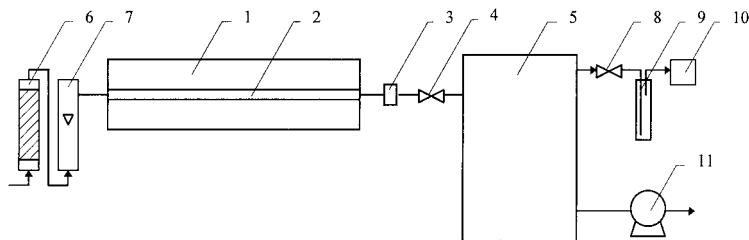


Figure 1 Scheme of apparatus used for the thermal degradation studies of materials: (1) flow tubular furnace; (2) ceramic tube; (3) glass fiber filter; (4) needle valve; (5) vacuum container; (6) air-cleaning filter; (7) flowmeter; (8) glass cocks; (9) absorption bubbling washer; (10) aspirator; (11) vacuum pump.

the thermooxidative stability of PET depends on the nature of the transesterification catalysts used and the nature of the polymer chain, especially on the content of the diethylene glycol linkage, which increases the rate of degradation.

Although many authors have studied the products of PET thermal degradation, there are only scarce data in the literature concerning the concentrations of emitted toxic substances. The very often used techniques, like pyrolysis–gas chromatography or direct pyrolysis mass spectrometry, appear to be convenient for studying the primary products and the primary thermal degradation mechanism of plastics. However, during thermal degradation under real conditions, as processing or fire, the residence time of plastic in a hot zone is much longer and secondary products of further degradation can be observed. Moreover, if the degradation takes place in an air atmosphere, the substances emitted may differ from those obtained by pyrolysis. The aim of this article was to study the temperature influence on the composition and amounts of the volatile toxic substances emitted during the thermal degradation of PET in air.

EXPERIMENTAL

The PET granulate for bottle processing Polyclear-T 86 of Hoechst was used for the experiment. According to the producer's information, the PET granulate does not contain any additives (halogens, sulfur, or others). The experiments were carried out using the test apparatus shown schematically in Figure 1. The samples of PET (0.1 g) in the ceramic boat were placed in the ceramic tube heated to the given temperature. The experiments were carried out under isothermal conditions at the temperatures of 200, 300,

400, 500, 600, and 700°C for 20 min. The rate of air flow through the tubular furnace was kept at 0.025 m³/h and controlled using a flowmeter. The delivered air was cleaned using filters with silica gel and 4 Å molecular sieves. At the outlet of the tube, a fiber glass filter was placed to trap nonvolatile thermal degradation products. The volatile products were collected in a 0.0127-m³-volume glass container. Before beginning the experiment, air was evacuated from the glass container using a vacuum pump. During the thermal degradation, the container was filled with the reaction gases.

To determine the composition and concentrations of the volatile thermal degradation products, gas chromatographic and colorimetric methods were used. A Chrom 5 gas chromatograph with

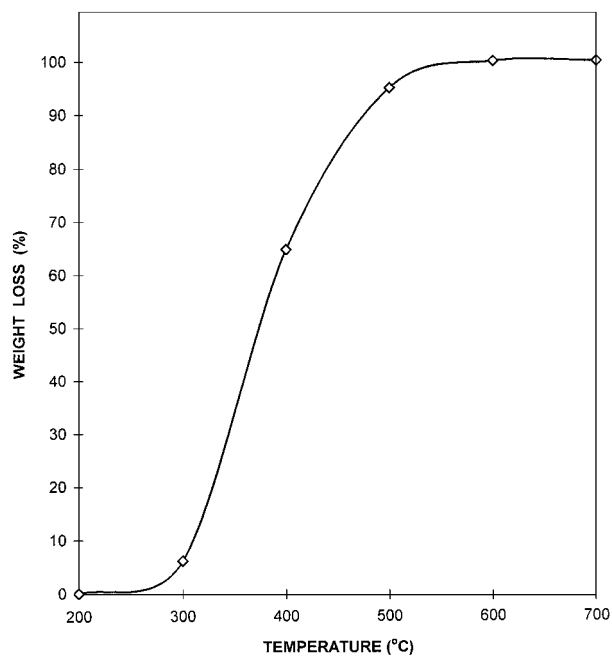


Figure 2 Weight loss changes of PET (Polyclear-T 86) as a function of degradation temperature.

Table I Test Results of Volatile Thermal Degradation Products of PET (Polyclear-T 86) in Air

Substance	Temperature (°C)					
	200	300	400	500	600	700
Acetaldehyde	< 0.2	1.3	302.5	235.8	84.5	73.0
Formaldehyde	0.3	0.8	31.0	44.0	13.4	12.8
Benzaldehyde	< 0.8	< 0.8	1.1	3.2	4.6	10.7
Benzene	< 0.1	0.1	2.0	12.0	47.5	95.0
Toluene	< 0.2	< 0.2	0.7	1.2	6.8	17.4
Ethylbenzene	< 0.2	< 0.2	0.3	1.0	2.3	10.4
Styrene	< 0.5	< 0.5	0.8	2.4	6.5	26.0
C ₁ -C ₄ aliphatic hydrocarbons	< 0.1	< 0.1	2.0	15.0	43.0	51.0
Dioxane	< 0.8	< 0.8	5.0	10.8	4.2	2.0
Methyl acetate	< 0.8	< 0.8	1.5	3.0	14.8	20.5
Methyl alcohol	< 0.5	< 0.5	1.8	4.5	1.8	1.0
Carbon monoxide	< 5	62	1240	2480	3400	3540

an FID detector and the following packed columns were used: SE 30 (10%) + Carbowax 20M (0.3%) on a Chromosorb W NAW, 60–80 mesh, and XE 60 (8%) + Carbowax 20M (0.3%) on a Chromosorb W NAW, 60–80 mesh.

Formaldehyde was absorbed in water and analyzed colorimetrically as a complex with chromotropic acid.¹³ Carbon monoxide was analyzed using Dräger tubes.

RESULTS

The percentage of the PET weight loss as a function of the degradation temperature is shown in Figure 2. The greatest changes of the sample weights were observed at 300–500°C. At higher temperatures (above 500°C), the sample decomposed almost completely.

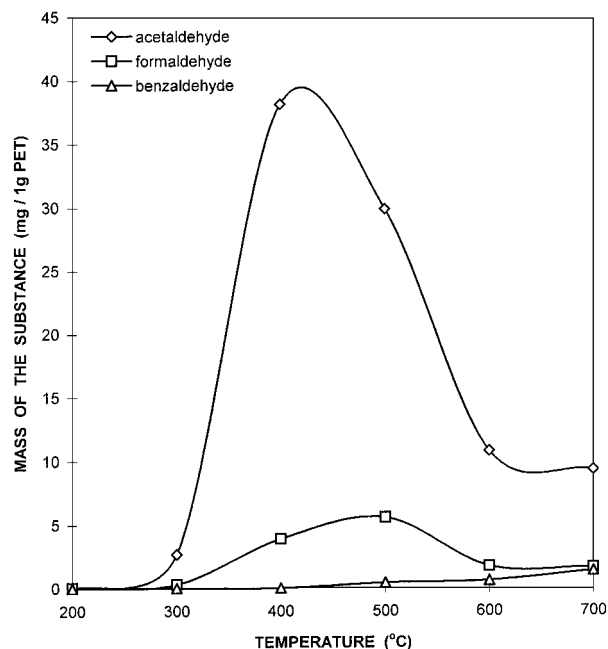


Figure 3 Mass changes of aldehydes evolved from PET (Polyclear-T 86) as a function of degradation temperature.

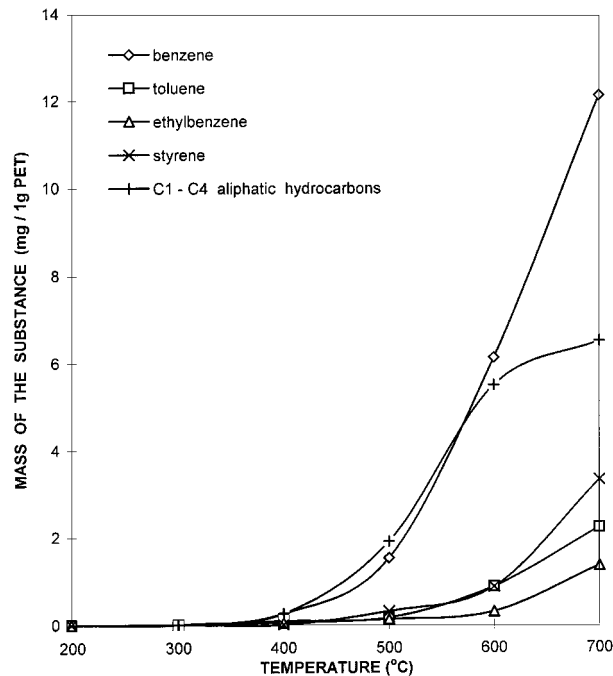


Figure 4 Mass changes of hydrocarbons evolved from PET (Polyclear-T 86) as a function of degradation temperature.

Analysis showed that the toxic volatile thermal degradation products consist of carbon monoxide, aldehydes (acetaldehyde, formaldehyde, benzaldehyde), C₁–C₄ aliphatic hydrocarbons, aromatic hydrocarbons (benzene, toluene, ethylbenzene, styrene), methyl alcohol, methyl acetate, and dioxane (1,4-diethylene dioxide). The concentrations of the determined substances in the thermal degradation products of the PET granulate are given in Table I. For each of the compounds, the mass evolved from 1 g of PET was calculated using the following formula:

$$m = \frac{cv}{m_0}$$

where c is the concentration of the substance in the container after the thermal degradation (mg/m³); v , the volume of the container (0.0127 m³); and m_0 , the mass of the PET sample (g). The dependence of the volatile substance masses evolved from PET on the degradation temperature is shown in Figures 3–6. The maximum amount of acetaldehyde was obtained at 400°C, and that of formaldehyde, methyl alcohol or, dioxane, at 500°C. The amounts of carbon monoxide, C₁–C₄ aliphatic hydrocarbons, aromatic hydro-

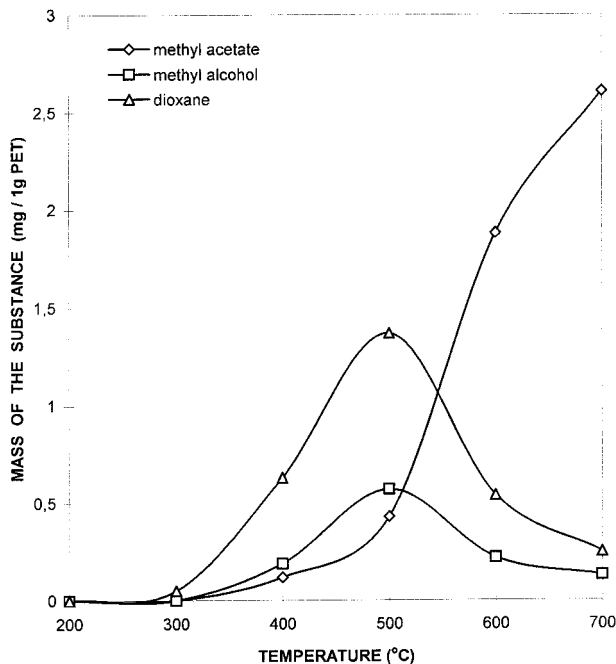


Figure 5 Mass changes of methyl acetate, methyl alcohol, and dioxane evolved from PET (Polyclear-T 86) as a function of degradation temperature.

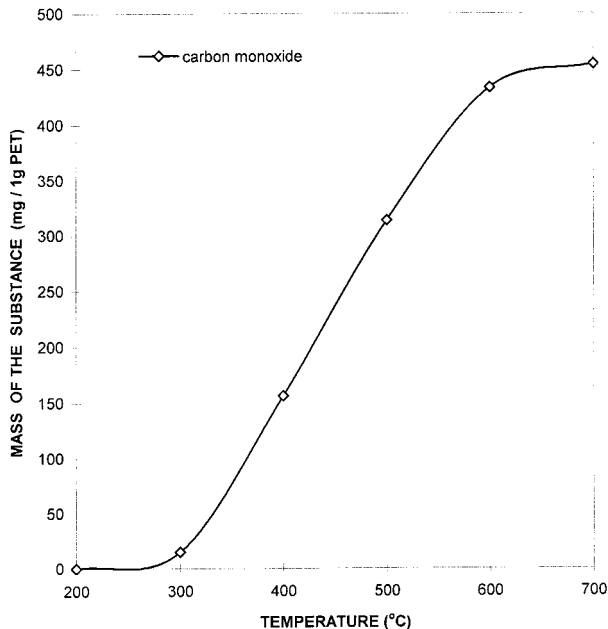


Figure 6 Mass changes of carbon monoxide evolved from PET (Polyclear-T 86) as a function of degradation temperature.

carbons, benzaldehyde, and methyl acetate were increased with temperature.

CONCLUSIONS

The studies on the thermal degradation of PET in a tubular furnace with an air flow have shown that the main evolved compounds were carbon monoxide, acetaldehyde, formaldehyde, benzene, styrene, and aliphatic C₁–C₄ hydrocarbons. The composition of the volatile products depends strongly on the degradation temperature. At lower temperatures, acetaldehyde, formaldehyde, and carbon monoxide are the main degradation products. The concentrations of carbon monoxide, aromatic and aliphatic hydrocarbons, and methyl acetate were increased with temperature. The maximum yields of formaldehyde, methyl alcohol, and dioxane were observed at 500°C, and that of acetaldehyde, at 400°C.

REFERENCES

1. B. M. Kovarskaya, I. I. Levantovskaya, A. B. Blumenfeld, and G. V. Draluk, *Plast. Massy*, **5**, 42 (1968).

2. H. Zimmermann, in *Developments in Polymer Degradation*, Vol. 5, N. Grassie, Ed., Applied Science, London, 1984, p. 79.
3. F. Villain, J. Coudane, and M. Vert, *Polym. Degrad. Stab.*, **43**, 431 (1994).
4. F. Villain, J. Coudane, and M. Vert, *Polym. Degrad. Stab.*, **49**, 393 (1995).
5. Y. Sugimura and S. Tsuge, *J. Chromatogr. Sci.*, **17**, 269 (1979).
6. M. E. Bednas, M. Day, K. Ho, R. Sander, and D. M. Wiles, *J. Appl. Polym. Sci.*, **26**, 277 (1981).
7. C. T. Vijayakumar and J. K. Fink, *Thermochim. Acta*, **59**, 51 (1982).
8. H. Ohtani, T. Kimura, and S. Tsuge, *Anal. Sci.*, **2**, 179 (1986).
9. I. C. McNeill and M. Bounekhel, *Polym. Degrad. Stab.*, **34**, 187 (1991).
10. R. Kinoshita, Y. Teramoto, T. Nakano, and H. Yoshida, *J. Thermal Anal.*, **38**, 1891 (1992).
11. G. Montaudo, C. Puglisi, and F. Samperi, *Polym. Degrad. Stab.*, **42**, 13 (1993).
12. H. Ohtani and S. Tsuge, in *Applied Pyrolysis Handbook*, T. P. Wampler, Ed., Marcel Dekker, New York, 1995, p. 97.
13. J. Trzeszczyński, *Investigations on Air Pollution by Toxic Substances Educued from Plastics*, Technical University of Szczecin Press, Szczecin, 1978.