

Temperature and Atmosphere Influences on Smoke Composition During Thermal Degradation of Poly(ethylene terephthalate)

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ABSTRACT: The less-volatile compounds forming a smoke emitted during the thermal degradation of poly(ethylene terephthalate) (PET) in different conditions were studied. Thermal degradation of PET was carried out within the temperature range of 200–700°C in both a nitrogen and an air atmosphere. The less-volatile thermal degradation products were trapped on a glass-fiber filter and analyzed by capillary gas chromatography with mass selective detector (GC-MS) and high performance liquid chromatography (HPLC). The results are collected in tables and presented on plots as a function of the degradation temperature. The temperature and atmosphere effects on the emission and composition of the smoke during PET thermal degradation were considered. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3064–3068, 2001

Key words: poly(ethylene terephthalate); PET thermal degradation; smoke emission from PET; plastics thermal degradation

INTRODUCTION

The thermal degradation of plastics may be a source of useful materials (e.g., fuels, monomers). On the other hand, however, the substances emitted during plastics thermal degradation in non-controlled conditions may create a serious hazard for the environment.^{1–4}

In recent years thermal degradation of poly(ethylene terephthalate) (PET) was the subject of interest to a large number of investigators, who focused mainly on the degradation mechanism,^{5–14} kinetics,^{15,16} emission of the volatile substances,^{5,6,8,17} and influence of stabilizers and flame retardants on PET thermal stability.^{18–24} In our earlier studies,^{25,26} we examined the temperature influ-

ence on the volatile substances emitted during the thermal degradation of PET. During the degradation of PET at higher temperatures, the emission of a pale yellow smoke was observed. This study reports the results of our investigations on the emission and composition of the smoke during the thermal degradation of PET in different temperatures (200–700°C) and atmospheres (nitrogen, air). The effects of temperature and atmosphere on the composition and amounts of the emitted less-volatile compounds were considered.

EXPERIMENTAL

The experiments were carried out in a flow tubular furnace at the temperatures of 200, 300, 400, 500, 600, and 700°C for 20 min. The PET samples (0.1 g) in the ceramic boat were placed in the furnace at constant temperature and nitrogen or

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Table I Total Masses of the Smokes Emitted During Thermal Degradation of PET (Polyclear-T 86)

Temperature (°C)	Total Mass of the Smoke (mg/l g PET)	
	Nitrogen Atmosphere	Air Atmosphere
200	<0.50	<0.50
300	<0.50	<0.50
400	441.19	442.46
500	571.87	555.33
600	569.52	251.00
700	485.01	414.24

air flow (0.025 m³/h). The apparatus used for the experiments was described in detail previously.^{25,26} The less-volatile compounds emitted during the thermal degradation of the tested PET (granulate for bottle processing Polyclear-T 86; Hoechst, Frankfurt/Main, Germany) were trapped on a glass-fiber filter (Staplex, Brooklyn, NY). After the thermal degradation, the total mass of the collected substances was estimated by weighing.

The compounds trapped on the filter were extracted with methanol and analyzed.

To determine the composition and amounts of the less-volatile thermal degradation products, GC-MS and HPLC methods were employed. A Hewlett-Packard 6890 gas chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a mass selective detector MSD 5973 (70 eV) and capillary column HP-5 ms (30 m × 0.25 mm I.D.) was used for the qualitative analyses. The instrument control and data handling were performed using HP ChemStation software. LC-5B liquid chromatographs with UV-VIS detectors and glass columns (150 × 3.3 mm I.D.) filled with SEPARON SGX C-18 stationary phases were used for the qualitative and quantitative analyses. Methanol-water (8 : 2) and methanol-water-acetic acid (50 : 49 : 1) mobile phases were used. The monitoring wavelength was 254 nm.

RESULTS AND DISCUSSION

During the degradation of PET at lower temperatures (200–300°C), the emission of the smoke was not observed, which was confirmed by the

Table II Less-Volatile Compounds Evolved from PET (Polyclear-T 86) During Thermal Degradation in Nitrogen Atmosphere

Substance	Mass of the Substance (mg/l g PET) at Temperature (°C) of					
	200	300	400	500	600	700
Terephthalic acid	<0.05	<0.05	143.08	139.96	132.61	132.41
Benzoic acid	<0.15	<0.15	45.96	86.27	96.26	135.95
4-Acetylbenzoic acid	<0.01	<0.01	<0.01	7.33	37.86	86.98
4-Methylbenzoic acid	<0.05	<0.05	3.04	5.47	7.10	11.83
4-Vinylbenzoic acid	<0.05	<0.05	6.72	8.59	8.95	11.48
4-Ethylbenzoic acid	<0.05	<0.05	4.40	6.51	6.99	8.25
4-Phenylbenzoic acid	<0.30	<0.30	5.24	10.60	15.05	25.02
4-Hydroxybenzoic acid	<0.01	<0.01	0.57	0.74	0.75	0.76
2-Naphthoic acid	<0.50	<0.50	2.42	5.52	7.66	13.40
Monovinyl terephthalate	<0.05	<0.05	146.34	167.10	141.21	<0.05
Divinyl terephthalate	<0.05	<0.05	9.87	18.16	20.87	<0.05
Monoethyl terephthalate	<0.05	<0.05	11.74	11.83	1.16	<0.05
2-Benzoiloxyethylvinyl terephthalate	<0.10	<0.10	15.70	29.99	12.07	<0.10
Cyclic dimer of PET	<0.10	<0.10	7.84	5.35	<0.10	<0.10
1,4-Diacetylbenzene	<0.01	<0.01	<0.01	<0.01	3.53	9.45
4-Acetylbiphenyl	<0.01	<0.01	<0.01	3.21	4.76	5.40
Dibutyl phthalate	<0.05	<0.05	1.61	1.98	1.46	1.67
Biphenyl	<0.01	<0.01	0.03	0.39	0.52	0.63
Phenantrene	<0.01	<0.01	<0.01	<0.01	0.16	0.27
<i>p</i> -Terphenyl	<0.01	<0.01	<0.01	0.24	0.45	0.66

Table III Less-Volatile Compounds Evolved from PET (Polyclear-T 86) During Thermal Degradation in Air Atmosphere

Substance	Mass of the Substance (mg/l g PET) at Temperature (°C) of					
	200	300	400	500	600	700
Terephthalic acid	<0.05	<0.05	198.09	180.82	86.74	124.01
Benzoic acid	<0.15	<0.15	39.26	76.69	41.38	113.14
4-Acetylbenzoic acid	<0.01	<0.01	<0.01	6.38	23.81	69.92
4-Methylbenzoic acid	<0.05	<0.05	4.09	6.82	6.01	11.25
4-Vinylbenzoic acid	<0.05	<0.05	6.01	7.66	5.15	8.65
4-Ethylbenzoic acid	<0.05	<0.05	3.61	4.68	4.19	7.32
4-Phenylbenzoic acid	<0.30	<0.30	3.22	11.96	9.54	16.20
4-Hydroxybenzoic acid	<0.01	<0.01	1.87	4.45	5.43	4.09
2-Naphthoic acid	<0.50	<0.50	2.20	8.02	5.82	8.56
Monovinyl terephthalate	<0.05	<0.05	123.47	143.19	26.74	<0.05
Divinyl terephthalate	<0.05	<0.05	9.99	18.11	3.26	<0.05
Monoethyl terephthalate	<0.05	<0.05	17.39	13.99	<0.05	<0.05
2-Benzoiloxymethylvinyl terephthalate	<0.10	<0.10	7.44	22.86	2.36	<0.10
Cyclic dimer of PET	<0.10	<0.10	7.64	3.04	<0.10	<0.10
1,4-Diacetylbenzene	<0.01	<0.01	<0.01	<0.01	0.72	4.33
4-Acetylbiphenyl	<0.01	<0.01	<0.01	1.31	2.51	3.70
Dibutyl phthalate	<0.05	<0.05	2.02	1.67	0.92	2.25
Biphenyl	<0.01	<0.01	<0.01	0.01	0.14	0.88
Phenantrene	<0.01	<0.01	<0.01	<0.01	0.14	0.39
<i>p</i> -Terphenyl	<0.01	<0.01	<0.01	0.15	0.29	0.47

chromatographic analyses. Within the temperature range of 400–700°C the thermal degradation of the tested polymer was accompanied by the emission of a pale yellow smoke. The amounts of the less-volatile compounds evolved at the temperatures 400–500°C were similar in both nitrogen and air atmospheres. At higher temperatures the smoke emission was lower in air than that in nitrogen atmosphere. The greater differences were observed at 600°C, because at this temperature the PET samples decomposed explosively during experiments in air atmosphere. The total amounts of the trapped less-volatile compounds (estimated by weighing and related to 1 g of PET) during the degradation at different temperatures and atmospheres are given in Table I.

The identification of the particular compounds in the emitted smoke was performed by the comparison of their mass spectra and the retention times with those obtained from the analyses of standards described elsewhere.^{27,28} The analyses showed that the less-volatile thermal degradation products of PET form complex mixtures, which consist of terephthalic acid and its esters, benzoic acid, *p*-substituted benzoic acid, low oligomers of PET, 1,4-diacetylbenzene, 4-acetylbiphenyl, polycyclic aromatic hydrocarbons, and others. The

quantitative analyses were carried out on the basis of the calibration plots, prepared using chromatographic standards. The masses of the determined substances were related to the polymer sample (mg/1 g PET) and collected in Tables II and III. For the main products (terephthalic acid and monovinyl terephthalate) the comparisons of the evolved amounts during PET thermal degradation in nitrogen and air atmospheres are presented in Figures 1 and 2.

CONCLUSIONS

The studies have shown that the composition of the smoke emitted during PET degradation depends strongly on the degradation temperature. At lower temperatures (200–300°C), the emission of the smoke was not observed. During PET destruction at the temperature range of 400–700°C, the large amounts of the less-volatile compounds were emitted, forming a pale yellow smoke. The analyses have shown that the emitted smoke is a complex mixture of aromatic compounds: terephthalic acid and its esters, benzoic acid, *p*-substituted benzoic acid, low oligomers of PET, and acetylated and polycyclic aromatic hydrocarbons.

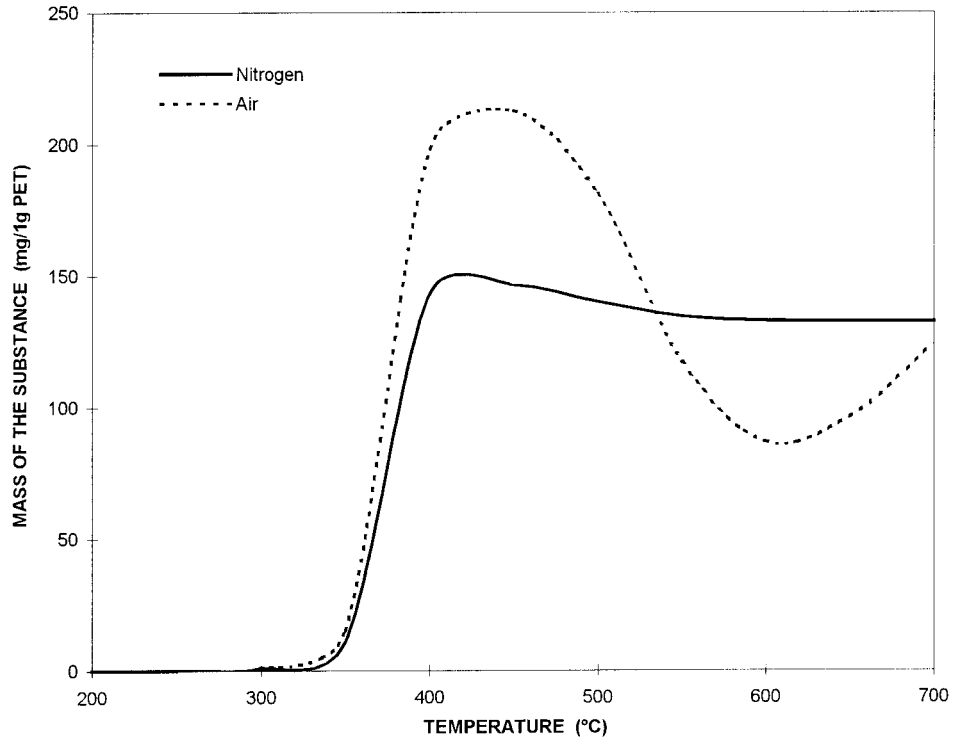


Figure 1 Mass changes of terephthalic acid evolved from PET as a function of degradation temperature in nitrogen and air atmospheres.

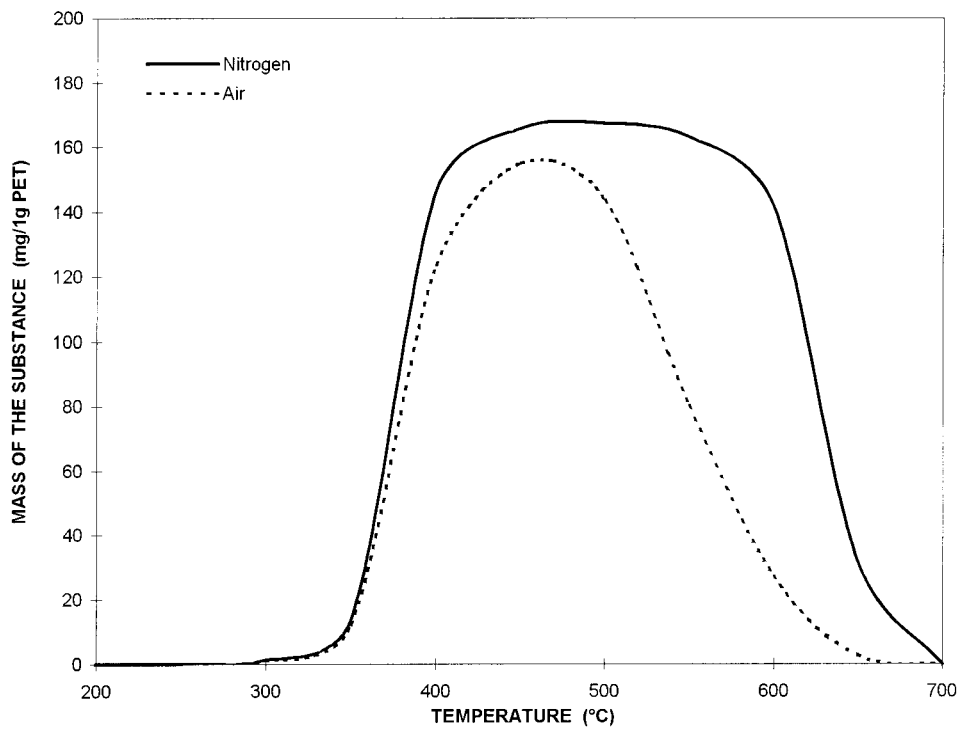


Figure 2 Mass changes of monovinyl terephthalate evolved from PET as a function of degradation temperature in nitrogen and air atmospheres.

At the temperature range 400–600°C, in both nitrogen and air atmospheres, the main products were terephthalic acid, monovinyl terephthalate, and benzoic acid. At 700°C the main degradation products were terephthalic acid, benzoic acid, and 4-acetylbenzoic acid. At this temperature the esters of terephthalic acid and oligomers were already not detected. On the contrary, the increase of the temperature caused the formation of acetylated hydrocarbons (1,4-diacetylbenzene and 4-acetylbi-phenyl) as well as polycyclic aromatic hydrocarbons (biphenyl, phenantrene, *p*-terphenyl), although their amounts were relatively small.

The composition of the atmosphere also influences the process of PET thermal degradation and the evolved compounds. In the air atmosphere the smoke emission at higher temperatures was lower than that in nitrogen, especially at 600°C, whereas the PET samples decomposed explosively in the presence of oxygen. At this temperature the total mass of the less-volatile compounds during the experiments in the air atmosphere was twofold smaller than that in nitrogen and the greater differences in the amounts of the particular compounds were observed. The masses of all less-volatile products in those conditions were considerably smaller, except for that of 4-hydroxybenzoic acid, the amount of which was about sevenfold greater. During the experiments at the other temperatures, the effect of the atmosphere composition on the thermal degradation products was not so significant. Nevertheless, at temperatures ranging from 400 to 500°C the amounts of benzoic acid and monovinyl terephthalate were greater in the nitrogen atmosphere and terephthalic acid greater in the air atmosphere. During PET destruction at 700°C, the emissions of all carboxylic acids (except 4-hydroxybenzoic acid), as well as acetylated aromatic hydrocarbons, were observed to be higher in nitrogen than in air atmosphere. The amounts of polycyclic aromatic hydrocarbons were similar.

The significant participation of terephthalic acid and its derivatives in the less-volatile thermal degradation products of PET indicates the possibility of the recovery of those compounds during controlled degradation of these polymer wastes. The maximum yield of terephthalic acid was achieved during the thermal degradation of PET at 400°C in the air atmosphere. In those conditions from 1 g of PET about 200 mg of terephthalic acid is evolved, which corresponds to 46% of the less-volatile products.

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