

Flame Retardancy of Poly(butylene terephthalate) Blended with Phosphorous Compounds

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ABSTRACT: The thermal degradation and flame retardancy of poly(butylene terephthalate) (PBT) were studied with a focus on the effect of phosphorous compounds. Thermogravimetric analysis, pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS), and elemental analysis were used to analyze the flame retardancy, which were observed by an Underwriters Laboratory UL-94 test and a cone calorimeter. The 50% degradation temperatures of PBT blends with phosphorous compounds were the same as that of neat PBT. Six scission products were assigned by Py/GC/

MS. The burning times of the UL test of several PBT blends were much shorter than that of neat PBT. The relation between flame retardancy and thermal degradation was analyzed with respect to the results of the scission products and the char in burned polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2326–2333, 2004

Key words: degradation; flame retardance; poly(butylene terephthalate) (PBT); phosphorus; thermogravimetric analysis (TGA); cone calorimeter

INTRODUCTION

Environmental problems that have occurred in the past show that polymer blends with halogen compounds are undesirable materials that run the risk of polluting the environment. In particular, the movement to eliminate such pollutants became active in Europe in the 1990s.¹ There have been many efforts to find nonhalogen flame retardants since the 1960s. Inorganic compounds such as aluminum hydroxide,² organic phosphates,³ red phosphorus (red-P),⁴ ammonium polyphosphate,⁵ silicone compounds,⁶ and nanocomposites made with clays⁷ are typical examples of flame retardants.

The thermal decomposition of polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) has been the center of continued attention. One might consider that the thermal decomposition reactions in PET and PBT have already been fully analyzed and described as to the detailed pathways from the polymers to the scission products. However, there are some interesting points that have not yet been elucidated. For example, radical or ionic processes have not yet been determined in the primary thermal decomposition.⁸ Some researchers proposed an ionic process leading to the formation of

oligomers with olefin and carboxylic end groups.^{9,10} Cycling scission products and hydrogen-transfer reactions as well as ionic or radical reactions and other general information have already been discussed in previous studies.^{11–13}

PBT, which is different from PET, is used as an engineering plastic in the fabrication of a wide variety of molded compounds. Because it includes an ester bond, it is easily hydrolyzed under high temperature and moisture.^{14,15} Complex scission products have been recovered from thermal decomposition, although the degradation routes have not yet been fully elucidated.¹⁶

This article reports the study on the flame retardancy of PBT and the degradation processes of PBT by experiments and computer simulations.^{17,18}

EXPERIMENTAL

Polymer and reagents

The PBT used in this study was manufactured by Teijin Co., Ltd. (C7000, density = 1.3, molecular weight = 20,000). The flame retardants used in this experiment are listed in Table I. A small kneader extruder, made by Custom Scientific Instruments (CSI; Max Mixing Extruder CS-194A), was used to blend the flame retardants with the polymers. Specimens were made by standard processes.

Thermal degradation

TGA-50 (Shimadzu, Kyoto, Japan) was used for thermogravimetric analysis. The heating rate was 90°C/

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TABLE I
List of Flame Retardants

Sample no.	Flame-retardant material	Code name	Amount (wt %)	Maker	Grade
1	Polybutylene terephthalate	Neat	—	Teijin Co., Ltd.	C7000
2	Red phosphorus	Red-P	10	Rinkagaku Kogyo Co., Ltd.	Norbaexel 140
3	Bisphenol A bis(cresyl)phosph	BBC	5	Daihachi Chemical Industry Co., Ltd.	CR-741C
4	Triphenylphosphate	TPP	5	Ajinomoto Fine-Techno Co., Inc.	REOFOS
5	Tricresylphosphate	TCP	5	Daihachi Chemical Industry Co., Ltd.	TCP
6	Bisphenol Abis(cresyl)phospha	BBC	4	Daihachi Chemical Industry Co., Ltd.	CR-741C
	Potassium parfluorobutane sulfonate salt	PPFBS	1	MITENI	RM-65
7	Triphenylphosphate	TPP	4	Ajinomoto Fine-Techno Co., Inc.	REOFOS
	Potassium parfluorobutane sulfonate salt	PPFBS	1	MITENI	RM-65
8	Tricresylphosphate	TCP	4	Daihachi Chemical Industry Co., Ltd.	TCP
	Potassium parfluorobutane sulfonate salt	PPFBS	1	MITENI	RM-65
9	Tricresylphosphate	TCP	5	Daihachi Chemical Industry Co., Ltd.	TCP
	Polyhydricphenol	—	0.01	Tohoku Munekata Co., Ltd.	—
10	Tricresylphosphate	TCP	5	Daihachi Chemical Industry Co., Ltd.	TCP
	Polyhydricphenol	—	1	Tohoku Munekata Co., Ltd.	—
11	Ammonium polyphosphate	APP	13	Tisso Co., Ltd.	Teraju S20
	Pentaerythritol	PER	7	Koei Chemistry Ind., Ltd.	Pentarritto
12	Zirconiumpyrophoric acid	ZrP ₂ O ₇	5	Wako Pure Chemical Industries, Ltd.	—
13	Iron phosphate	FePO ₄	5	Wako Pure Chemical Industries, Ltd.	—
14	Aluminum phosphate	AlPO ₄	5	Wako Pure Chemical Industries, Ltd.	—
15	Zincpyrophoric acid	Zn ₂ P ₂ O ₇	5	Wako Pure Chemical Industries, Ltd.	—
16	Titanium pyrophosphate	TiP ₂ O ₇	5	Wako Pure Chemical Industries, Ltd.	—
17	Tin pyrophoric acid	SnP ₂ O ₇	5	Wako Pure Chemical Industries, Ltd.	—
18	Cobalt phosphate	Co ₃ (PO ₄) ₂	5	Wako Pure Chemical Industries, Ltd.	—
19	Copper phosphate (II)	Cu ₃ (PO ₄) ₂	5	Wako Pure Chemical Industries, Ltd.	—

min under an inert atmosphere. The rate was much higher than ordinary thermal degradation experiments because the main purpose of the study was to analyze the degradation during fire, which is a very rapid reaction.

Pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS, GCMS-QP5000, Shimadzu) was applied to analyze the fragmentation by the pyrolysis. The procedures were achieved according to the usual method in the degradation experiments of plastics. The interface temperature between the pyrolyzer and the gas chromatograph was 280°C, a capillary column of 27 m length was used, and the linear velocity of helium as a carrier gas was 26.4 cm/s. The minimum and the maximum mass numbers were set to be 45 and 500, respectively. Elemental analysis was used as an auxiliary method.

Flame retardancy

Ignition and burn times were measured by the Underwriters Laboratory UL-94 method, which has been well established as a burning test for plastics. A cone calorimeter (type-3; Toyo-seiki Co., Japan) was also used to observe flammability. Babrauskas and Huggett developed the cone calorimeter in 1982 by apply-

ing Thornton's principle where the combustion heat of almost all organic materials was about 13.1 kJ/g and the error range was less than 5%.¹⁹⁻²¹ The heat release rate, which is one of the most important data, was not calculated by directly observing the heat emitted, but by measuring the oxygen concentration in the air before and after the combustion chamber is used.

RESULTS AND DISCUSSION

Flammability of PBT and blends

Photographs of the specimen in the UL-94 test are shown in Figure 1. Neat PBT burned with a glittering flame. On the other hand, some of the blended PBT did not ignite immediately and the flames of other blends were smaller than that of neat PBT.

The ignition and the burn time observed in the UL-94 test are summarized in Table II. The ignition time of neat PBT was 5 s, whereas those of some blended PBTs were about 10 s or more. Meanwhile, the burn time of neat PBT was over 200 s and was longer in some of the blended bisphenol-A polycarbonates (PCs) with various phosphorous compounds. The burn times after the second ignition were generally shorter than those after the first ignition, except in

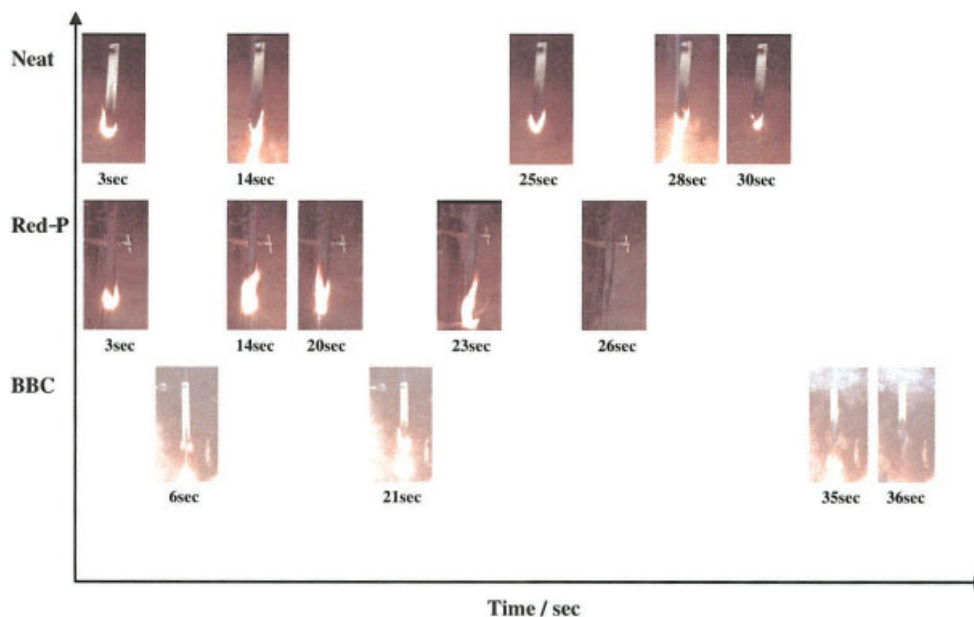


Figure 1 Photos of blended PBT in the UL tests.

some specimens. This suggested that the PBT structure after combustion might change into a different one that is more difficult to burn away.

The typical data are depicted in Figure 2. As the ignition time grows longer and the burn time becomes

shorter, the bar in the figure shifts toward the left. Red-P and organic phosphates showed excellent performance on PBT flame retardancy. Inorganic phosphorous compounds were not effective except for APP/PER (sample 11, Table II).

TABLE II
Data of UL Test

Sample no.	Flame-retardant material		Amount (wt%)	Sample depth (mm)	First ignition (s)			Second ignition (s)		
	Kind	Code			Ignition	Burn	Drip	Ignition	Burn	Drip
1	—	Neat	—	3.2	5.2	115.4	10.6	5.4	3.9	1.7
2	1st FR	Red-P	10	3.2	9.8	5.4	5.4	6.8	1.6	-0.8
3	1st FR	BBC	5	3.2	5.4	8.9	5.8	3.7	1.5	—
4	1st FR	TPP	5	3.2	7.1	13.8	-4.1	4.1	1.3	-1.0
5	1st FR	TCP	5	3.2	7.6	5.8	5.5	5.0	14.1	-1.8
6	1st FR	BBC	4					Burn out		
	2st FR	PPFBS	1	3.2	6.6	80.7	3.5			
7	1st FR	TPP	4							
	2st FR	PPFBS	1	3.2	5.8	10.7	5.4	7.7	4.3	-0.1
8	1st FR	TCP	4							
	2st FR	PPFBS	1	3.2	5.8	45.8	3.6	6.2	76.5	-1.3
9	1st FR	TCP	5							
	2st FR	Polyhydricphenol	0.01	3.2	5.3	36.7	4.8	4.8	15.9	1.4
10	1st FR	TCP	5							
	2st FR	Polyhydricphenol	1	3.2	5.5	42.0	5.1	4.7	40.4	-0.9
11	1st FR	APP	13							
	2st FR	RER	7	6.4	13.9	18.0	17.3	11.9	22.4	—
12	1st FR	ZrP ₂ O ₇	5	3.2						
13	1st FR	FePO ₄	5	3.2						
14	1st FR	AlPO ₄	5	3.2						
15	1st FR	Zn ₂ P ₂ O ₇	5	3.2						
16	1st FR	TiP ₂ O ₇	5	3.2	7.5	77.2	6.0	5.8	78.0	5.3
17	1st FR	SnP ₂ O ₇	5	3.2	4.8	56.8	8.3			
18	1st FR	Co ₃ (PO ₄) ₂	5	3.2	3.1	89.6	5.0			
19	1st FR	Cu ₃ (PO ₄) ₂	5	3.2	4.8	66.4	15.8	2.5	60.2	6.9

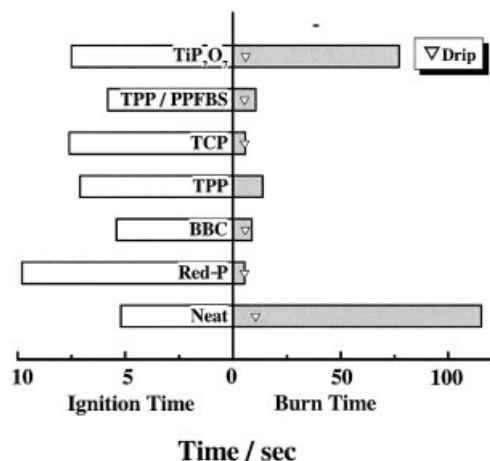


Figure 2 Ignition and burn times of neat and blended PBT.

The peak heat release rate, total heat released, and ignition time measured by a cone calorimeter are listed in Table III. The peak heat release rate of neat PBT was 2134 kW/m², which was the same as that of general flammable plastics. The rates of almost all blended PBTs were smaller. This means that phosphorous compounds, either organic or inorganic, have an effect on the flame retardancy of PBT. In particular, that of blended PC with TiP₂O₇ weakened similarly, whereas the effect was not remarkable in the result of the UL-94 test. Although the UL-94 test is one of the best methods to measure the fire risk, it is not suitable

to observe flammability itself. When the flame is considerably reduced by adding a certain flame retardant, the improvement is not recorded if the small flame continues for a long time. The difference between the results of the UL-94 test and the cone calorimeter is useful in analyzing flammability.

The heat release rates of the ignition times of neat PBT and the blends were from 5 to 10 s. Those of blended PC with red-P in the UL-94 test were the longest, but those in the cone calorimeter test were in the shortest group. The ignition time in the UL-94 test was decided by the researchers' eyesight. On the other hand, that in the cone calorimeter was measured by the consumption of oxygen in the cell. This phenomenon is discussed in the next section after the analysis of PBT thermal degradation.

Five examples among 19 specimens of PBT, as well as neat PC and blended PC with red-P measured by a cone calorimeter, are plotted in Figure 3. PC is a typical resin that forms the char at the combustion and the amount of the char increases by adding red-P. As shown in the figure, the heat release rates were retarded just after the ignition and the levels were about 500 kW/m², which was considered to be attributed to the formation of char on the surface that blocks the spurt of the volatiles. On the other hand, the slope of the heat release rate curve of blended PBT changes to a low gradient several seconds after ignition, which suggested that phosphorous compounds reacted with

TABLE III
Data of the Cone Calorimeter

Sample no.	Flame-retardant material		Amount (wt%)	Peak heat release rate (kW/m ²)	Total heat released (MJ/m ²)	Ignition time (s)
	Kind	Code				
1	—	Neat	—	2133.6	73.5	43
2	1st FR	Red-P	10	1064.4	46.0	36
3	1st FR	BBC	5	1448.3	60.4	48
4	1st FR	TPP	5	1448.2	57.1	47
5	1st FR	TCP	5	1796.4	60.3	47
6	1st FR	BBC	4	1580.2	61.2	35
	2st FR	PPFBS	1			
7	1st FR	TPP	4	1584.9	60.6	36
	2st FR	PPFBS	1			
8	1st FR	TCP	4	1708.4	63.9	29
	2st FR	PPFBS	1			
9	1st FR	TCP	5	1935.4	63.7	44
	2st FR	Polyhydricphenol	0.01			
10	1st FR	TCP	5	1855.8	62.2	48
	2st FR	Polyhydricphenol	1			
12	1st FR	ZrP ₂ O ₇	5	1905.3	63.4	48
13	1st FR	FePO ₄	5	1463.3	65.5	43
14	1st FR	AlPO ₄	5	1534.1	66.9	55
15	1st FR	Zn ₂ P ₂ O ₇	5	1611.7	68.8	47
16	1st FR	TiP ₂ O ₇	5	1445.5	64.0	53
17	1st FR	SnP ₂ O ₇	5	1455.0	66.1	48
18	1st FR	Co ₃ (PO ₄) ₂	5	1475.4	68.2	48
19	1st FR	Cu ₃ (PO ₄) ₂	5	1523.7	67.9	43

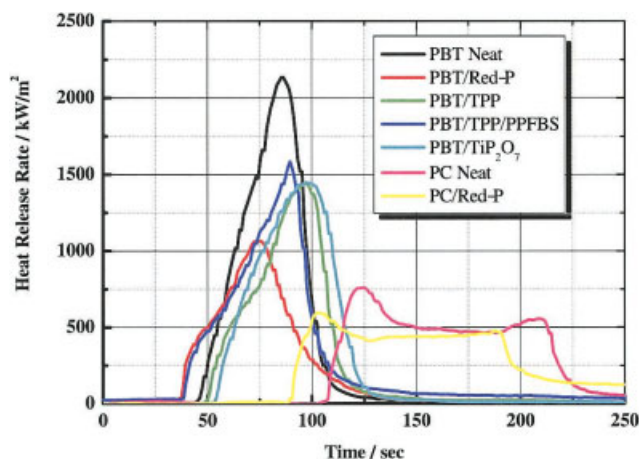


Figure 3 Heat release rate by the cone calorimeter.

the PBT and the surface structure changed into a less-flammable one.

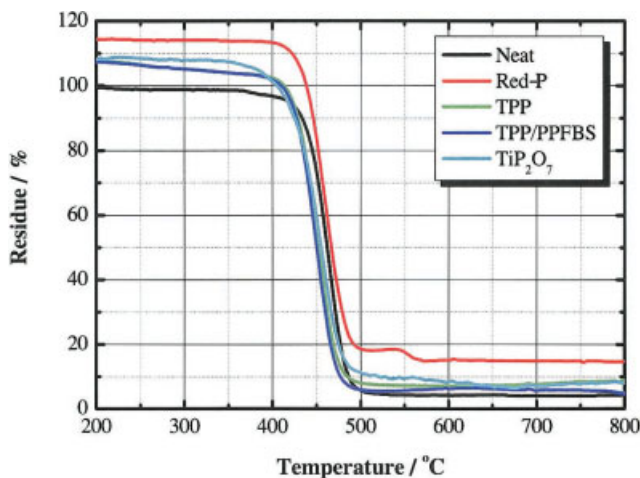


Figure 4 TGA curves of neat and blended PBT.

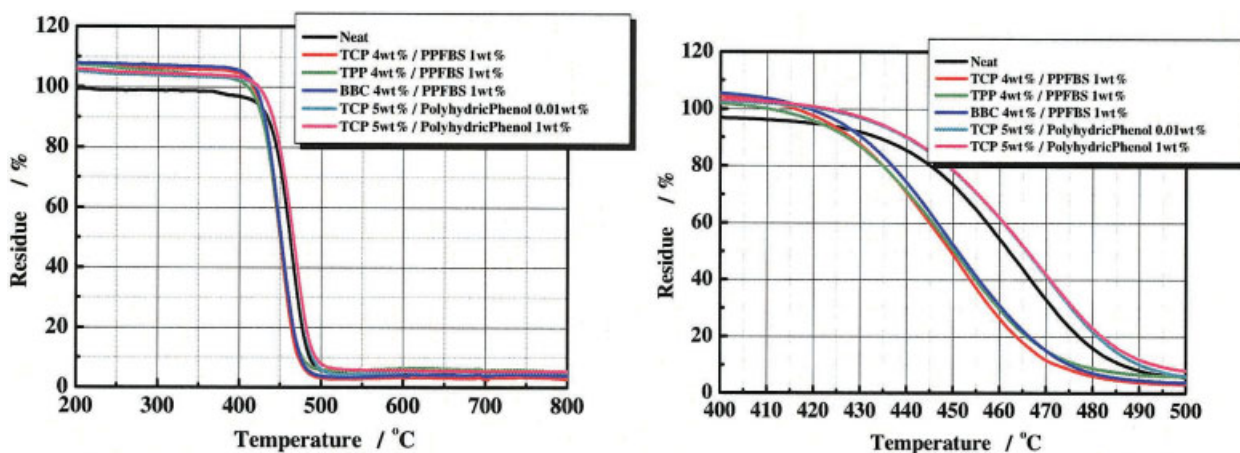


Figure 5 TGA curves of neat and blended PBT.

Thermal decomposition and residue

The thermogravimetric (TGA) profiles of neat and blended PBT are plotted in Figure 4 (left: from 200 to 800°C, right: from 400 to 500°C), and the contents of the flame retardants are listed in Table I. PBT started to thermally decompose at about 420°C and the 50% degradation temperatures were about 460°C under conditions of 90°C/min and in inert atmosphere. (They, as well as the amounts of residue at higher temperature, scarcely changed by blending various phosphorous compounds.)

PPFBS affected the 50% degradation temperature and the shifts of three blended PCs were about 15°C, as shown in Figure 5.

Analysis of scission products

Many studies on PBT thermal degradation have been conducted and a part of the results were reported by Tsuge et al.²² and Montaudo et al.,¹¹ who recovered and assigned the scission products and described them in their reports. Two distinctive features are recognized in the studies. One is that the pyrogram of PBT is relatively simple. This means that the degradation processes are relatively simpler than those of other polymers such as polystyrene, polypropylene, and polyamide. The other is that the peak of terephthalic acid was not observed. This will be discussed later, but many researchers did not recognize the peak.

The assigned scission products are listed in Table IV. The products, except TPA, had already been assigned in the previous studies. The data made the assignment in this study easier. Butadiene (C4), THF (tetrahydrofuran), benzene (B), benzoic acid (A1), benzoic acid ester (B1), biphenyl (DP), and terephthalic acid esters (A2 and B2) were expected to be observed as scission products. The existence of TPA could not

TABLE IV
Assigned Scission Products

Peak	M_w	Structure	Peak	M_w	Structure
C ₄	54	<chem>CH2=CH-CH=CH2</chem>	B1	176	<chem>c1ccc(cc1)C(=O)CH2CH2CH=CH2</chem>
THF	72	<chem>C1CCOC1</chem>	DP	154	<chem>c1ccc(cc1)-c2ccccc2</chem>
B	78	<chem>c1ccccc1</chem>	A2	220	<chem>OC(=O)c1ccc(cc1)C(=O)CH2CH2CH=CH2</chem>
A1	122	<chem>c1ccc(cc1)C(=O)O</chem>	B2	274	<chem>CH2=CHCH2CH2OC(=O)c1ccc(cc1)C(=O)CH2CH2CH=CH2</chem>
TPA	166	<chem>OC(=O)c1ccc(cc1)C(=O)O</chem>			

be confirmed because the peak that was supposed to be assigned to TPA was very broad and could not be distinguished from the baseline.

The recovery ratios of the scission products from neat PBT are plotted in Figure 6. Terephthalic acid monoester was the largest scission product and butadiene, benzoic acid, and terephthalic acid diester were the second largest products.

Neat PBT decomposes to butylterephthalate and subsequently to terephthalic acid. On the other hand, the elimination of carbon dioxide at the initial stage of the decomposition occurs in the case of blended PBT with red-P. It causes the scission products to include butylbenzoate and benzoic acid. The result of elemental analysis listed in Table V is very interesting for the consideration of flame retardancy. For example, the C/H ratio of neat PC at 800°C is 15.42, which is much

higher than that of neat PC before heating. It shows dehydrogenation by dehydration or by simple elimination of hydrogen. The dehydrogenation is accelerated by blending red-P, which can be understood because red-P has been known as a typical flame retardant that withdraws hydrogen from the polymer chain.

On the other hand, the C/H ratios of neat PBT and blended PBT with red-P are 8.64 and 7.06, respectively. The absolute value of neat PBT is not lower than that of neat PC, but that of blended PBT with red-P is much lower.

Generally speaking, aromatic compounds might be generated through thermal treatment, which causes the higher carbon ratio. If a typical structure of the aromatic compounds can be depicted as in Figure 7, the numbers of benzene rings and both carbon and hydrogen atoms are calculated by the following equations:

$$M_n = 1 + \sum_{k=1}^n [8(k-1)] = 4n^2 - 4n + 1 \quad (n \geq 1) \quad (1)$$

$$C_n = 6 + \sum_{k=2}^n [8(2k-1)] = 8n^2 - 2 \quad (n \geq 1) \quad (2)$$

$$H_n = 8n - 2 \quad (n \geq 1) \quad (3)$$

The nearest n in eq. (1) at C/H = 5.0 is 5. Therefore, the aromatic rings of PBT residue at 800°C are considered to be much larger.

The ratio of neat PBT decreases with heating but that of blended PC clearly increases. If the elimination

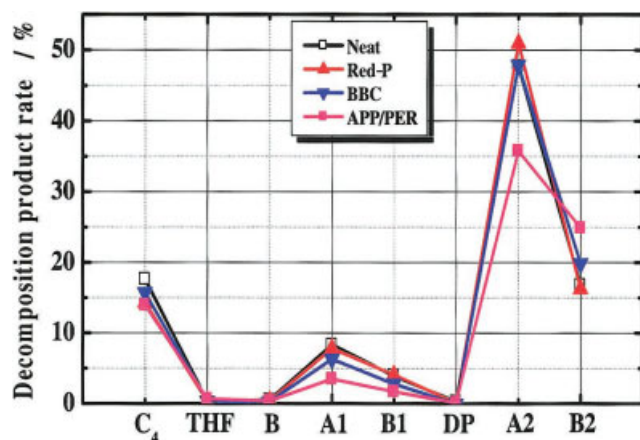


Figure 6 Distribution of scission products of neat and blended PBT.

TABLE V
Elemental Analysis of Neat and Blended PBT

Polymer	Additive	Amount (wt %)	Measured temperature (°C)	C (atm %)	H (atm %)	O (atm %)	C/H	O/H
PBT	—	—	250 ^a	43.22	42.75	14.03	1.01	0.33
	—	—	460	55.15	39.36	5.49	1.40	0.14
	—	—	850	88.38	10.23	1.38	8.64	0.13
	Red-P	10	250 ^a	42.51	43.01	14.48	0.99	0.34
	Red-P	10	460	43.98	39.31	16.71	1.12	0.42
PC	Red-P	10	850	79.14	11.21	9.65	7.06	0.86
	—	—	250 ^a	48.45	42.37	9.18	1.14	0.22
	—	—	500	60.70	34.10	5.21	1.78	0.15
	—	—	800	52.10	40.54	7.36	1.28	0.18
	Red-P	3	250 ^a	47.19	44.64	8.16	1.06	0.18
	Red-P	3	500	47.39	44.39	8.23	1.07	0.19
	Red-P	3	800	92.71	6.01	1.28	15.42	0.21

^a Processing temperature.

of carbon dioxide took priority over the cleavage of the ether bond for blended PBT, oxygen and the O/H ratio were expected to be higher than those of neat PBT. That is, oxygen-poor compounds were richer in the gaseous phase and oxygen-rich structures were in the residues.

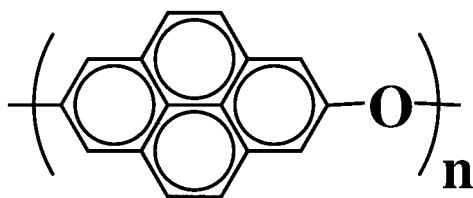


Figure 7 Typical structure of aromatic compounds.

Red phosphorus (red-P) decomposes before the reaction with PBT. The decomposed red-P comes close to the ester bond on the PBT chain. It accelerates the scission and generates compounds by the elimination of carbon dioxide. The phosphorus reacts with the neighboring chain and forms a crosslinking structure. The crosslinking layer covered the polymer surface and restrained the volatile products from gushing out from the polymer phase. The reaction routes can explain the lower heat release rate shown in Figure 8.

CONCLUSIONS

The thermal degradation and flame retardancy of PBT were studied with a focus on the effect of phosphorous compounds. The flame retardancy was much

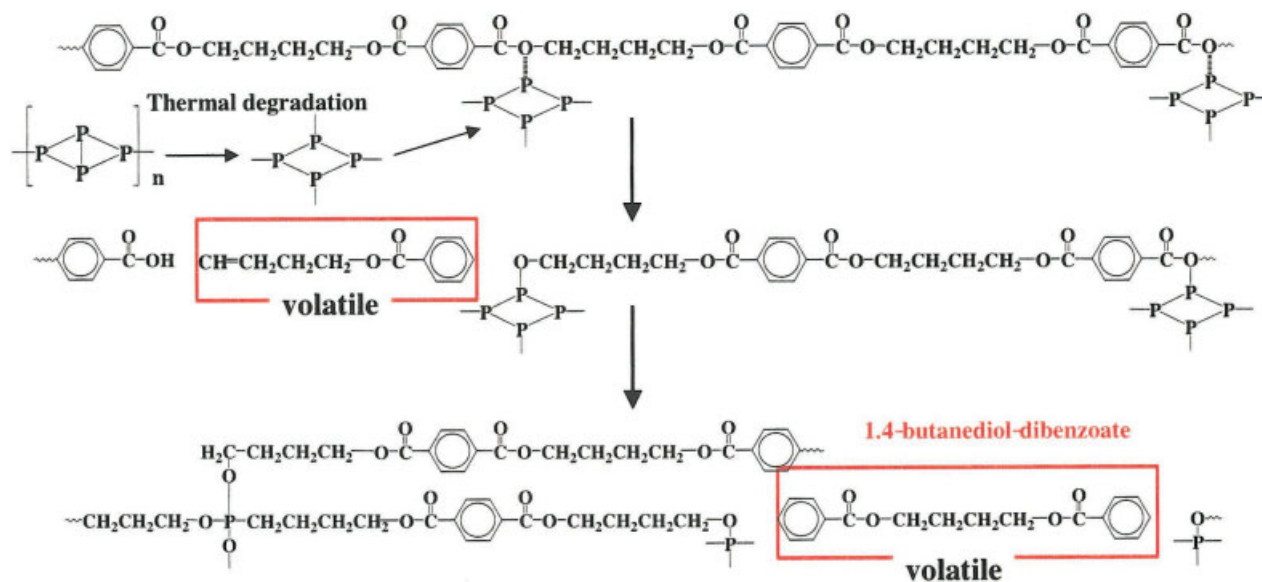


Figure 8 Degradation and crosslinking reactions of PBT and its blends.

improved, as confirmed by UL-94 test and cone calorimeter. Although red-P and organic phosphates such as TPP, TCP, and BBC are known to increase the carbon content, the elemental analysis showed different data. Phosphorous compounds may react with PBT and change it to a less-flammable structure by crosslinking or other reactions.

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