

# Flame Retardancy of Polybutylene Terephthalate Blended with Various Oxides

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**ABSTRACT:** The flame retardancy of polybutylene terephthalate (PBT) was studied focusing on the effect of various oxides. Thermo-gravimetric analysis, pyrolysis/gas chromatography/mass spectrometry, and elemental analysis (EA) were used to analyze the flame retardancy, which were observed through the UL-test and a cone calorimeter. Many oxides influenced the flame retardancy and some of them could suppress the flammability of PBT. In particular, the blended-PBTs with ZnO and V<sub>2</sub>O<sub>5</sub> accelerated the degradation and the edges of oxygen con-

sumption were shorter than neat-PBT although the flammability became poorer. The quantitative analysis of the scission products and the results of EA showed that hydrolysis, successive dehydration, and other various reactions changed the scission route to generate less flammable products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 910–917, 2008

**Key words:** thermal degradation; flame retardancy; polybutylene terephthalate; oxides; cone calorimeter

## INTRODUCTION

Polymers blends with halogen compounds are undesirable materials that could pollute the environment. In particular, the environmental campaign became active in Europe in the 1990s.<sup>1</sup> Many efforts have been made since 1960s to find nonhalogen flame retardants. Inorganic compounds, such as aluminum hydroxide,<sup>2</sup> organic phosphates,<sup>3</sup> red phosphorous,<sup>4</sup> ammonium poly-phosphate,<sup>5</sup> silicone compounds,<sup>6</sup> and nano-composite made by clays<sup>7</sup> are typical flame retardants. They are usually added to polymers by 10% or more because the combustion phenomena in fire occur in a few seconds.

The thermal decomposition of polyester such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) has received continuing attention. One might consider that the thermal decomposition reactions in PET and PBT has been fully analyzed and described up to the detailed pathways from the polymers to the scission products. However, there are some interesting points that have not yet been successfully elucidated. For example, radical or ionic processes have not yet been decided in the primary thermal decomposition.<sup>8</sup> Some researchers proposed an ionic process leading to the forma-

tion of oligomers with olefin and carboxylic end groups.<sup>9,10</sup> Cycling scission products and hydrogen transfer reaction as well as ionic or radical reaction and other general information have always been discussed in this studies.<sup>11–13</sup>

PBT, being different from PET, is used as an engineering plastic in the fabrication of a wide variety of molded compounds. As it includes ester bond, it is easy to be hydrolyzed under high temperature and moisture.<sup>14,15</sup> The complicated scission products at high temperatures are recovered and the degradation routes have been not fully elucidated yet.<sup>16</sup>

This article reports the study on flame retardancy of PBT by blending with various oxides through thermal degradation analysis, mass spectrometry, cone calorimeter, and UL-test. The quantitative degradation probability and the mechanism are discussed in the same way of polycarbonate and other polymers.<sup>17–19</sup>

## EXPERIMENTAL

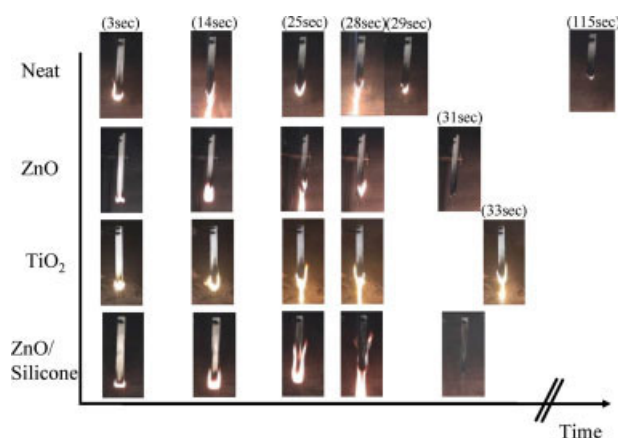
### Polymer and reagents

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

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TABLE I  
Various Oxides Used in this Study

Sample number	Flame retardant material	Code	Amount (wt %)	Maker	Grade	Note
1	Polybutylene terephthalate	Neat	-	Teijin Co., Ltd.	C7000	-
2	Vanadium oxide	V <sub>2</sub> O <sub>5</sub>	5	Wako Pure Chemical Industries, Ltd.	-	-
3	Ditantalum pentoxide	Ta <sub>2</sub> O <sub>5</sub>	5	do.	-	-
4	Copper oxide	CuO	5	do.	-	-
5	Palladium oxide	PdO	1	do.	-	-
6	Molybdenum trioxide	MoO <sub>3</sub>	5	do.	-	-
7	Titanium dioxide	TiO <sub>2</sub>	5	do.	-	Anatase
8	Silicon dioxide	SiO <sub>2</sub>	5	Original	-	Porous silica
9	Dichromium trioxide	Cr <sub>2</sub> O <sub>3</sub>	5	Wako Pure Chemical Industries, Ltd.	-	-
10	Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	10	do.	-	-
11	Aluminum oxide	Al <sub>2</sub> O <sub>3</sub>	5	do.	-	-
12	Zinc oxide	ZnO	10	do.	-	-
13	Dichromium trioxide	Cr <sub>2</sub> O <sub>3</sub>	0.11	do.	-	-
	Silicon dioxide	SiO <sub>2</sub>	4.89	Original	-	Porous silica
14	Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	0.49	Wako Pure Chemical Industries, Ltd.	-	-
	Silicon dioxide	SiO <sub>2</sub>	4.51	Original	-	Porous silica
15	Zinc oxide	ZnO	0.48	Wako Pure Chemical Industries, Ltd.	-	-
	Silicon dioxide	SiO <sub>2</sub>	4.52	Original	-	Porous silica
16	Zinc oxide	ZnO	5	Wako Pure Chemical Industries, Ltd.	-	-
	Silicone oil	Silicone oil	5	Shin-Etsu Chemical Co., Ltd.	KF96-100CS	Dimethyl silicone fluid
17	Zinc oxide	ZnO	5	Wako Pure Chemical Industries, Ltd.	-	-
	Silicone oil	Silicone oil	5	Shin-Etsu Chemical Co., Ltd.	KF50-300CS	Methyl phenyl silicone fluid



**Figure 1** Continuous observation of the UL-test. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Thermal degradation

TGA-50, manufactured by Shimadzu Co., was used for Thermo-gravimetric analysis (TGA). The heating rate was  $90^{\circ}\text{C}/\text{min}$  under 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 was a very rapid reaction.

A Pyrolyzer-gas chromatography and Mass spectrometry made by Shimadzu Co. (GCMS-QP5000) was applied to analyze the fragmentation by the pyrolysis. The procedure was conducted according to the usual way in the degradation experiments of plastics. The interface temperature between the pyrolyzer and the gas chromatography was  $280^{\circ}\text{C}$ , a 27-m-long capillary column was used and the linear velocity of helium as a carrier gas was 26.4 cm/s. The minimum and the maximum mass number were set to be 45 and 500, respectively. Elemental analysis (EA) was used as an auxiliary method.

### Flame retardancy

Ignition and flaming combustion times were measured by the UL (underwriter laboratory)-94 method, which is well known as a burning test for plastics. A cone calorimeter manufactured by Toyoseiki Co. (Cone calorimeter type-3) was also used to observe flammability. Babrauskas and Huggett developed the cone calorimeter in 1982 by applying Thornton's principle where the combustion heat of almost all organic materials was about 13.1 kJ/g and the error range was  $<5\%$ .<sup>20–22</sup> 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 inside the chamber before and after the combustion.

## RESULTS

### Flammability of PBT and blends

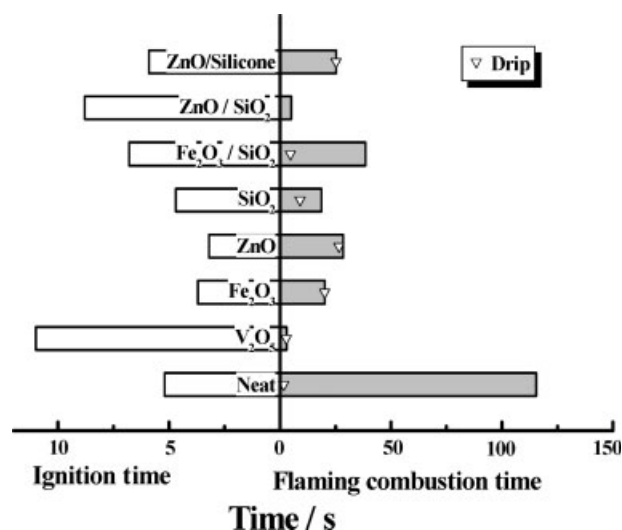
Photographs of the specimen in the UL-94 test are shown in Figure 1. Neat-PBT burnt with a glittering flame. On the other hand, blended-PBT did not immediately ignite and the flames of other blends were smaller than that of neat-PBT.

The ignition and the flaming combustion times of neat-PBT and typical blended-PBT observed in the UL-94 test are summarized in Figure 2. The ignition time of neat-PBT was 5 s while that of blended-PBT was from 3 to 11 s. On the other hand, the flaming combustion time of neat-PBT was over 100 s and that of blended-PBT was much shorter as shown in Figure 2. In particular, the burn times of zinc oxide on porous silica and vanadium oxide were 5.1 and 3.0 s.

The heat release rates measured by a cone calorimeter were plotted in Figure 3. The peak heat release rate of neat-PBT, which was about  $2000\text{ kW}/\text{m}^2$ , was higher than that of blended-PBT with various oxides. The ignition times of neat-PBT and the blends were 45 and 35 s. The tendency was different compared with those by the UL-test. The ignition time in the UL-test was decided by the researchers' eyes. On the other hand, that in the cone calorimeter was plotted by the consumption of oxygen in the cell. This phenomenon will be discussed in the next section after the analysis of PBT thermal degradation.

### Thermal decomposition and residue

The thermal gravitation profiles of neat- and blended-PBT were plotted in Figure 4 where the contents of



**Figure 2** Ignition and flaming combustion times of neat- and blended-PBT (the first ignition).

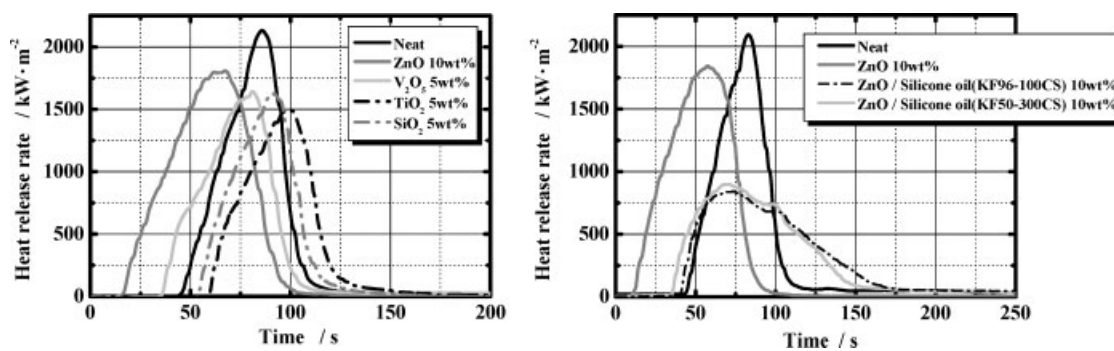


Figure 3 Heat release rate by cone calorimeter neat-PBT and blended-PBT.

the flame retardants are listed in Table II. PBT thermally decomposes at about 460°C and it did not change by blending flame retardants.

Although the profiles of the various blends measured by a cone calorimeter were different from each other, the TGA curves were similar as shown in Figure 4. In particular, the ignition and flaming combustion times of the UL-test and the cone calorimeter profiles of the blends with zinc and vanadium oxides were quite different.

### Scission products

Many studies of PBT thermal degradation have been conducted and a part of the results was reported by Tsuge and coworkers,<sup>23</sup> who recovered and assigned the scission products and described them in their studies. Two distinctive features are recognized in the two charts. One is that the pyrogram of PBT is relatively simple. It means 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 (TPA) was not observed. It will be discussed later, but many researchers did not recognize the peak.

The assigned scission products are listed in Table III. The products except TPA had already been assigned in the previous studies. The data made the assign-

ment in this study easier. Butadiene (C4), 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 be confirmed because the peak that was supposed to be assigned as that of TPA was very broad and could not be distinguished from the baseline.

The recovery ratios of the scission products from neat-PBT are plotted from Table IV.

Four major products were observed in the scission products of neat-PBT. A2 and B2, which were rich in the products at lower temperatures, decreased with elevating temperature. A1 and B1 increased at higher temperatures. A2 and B2 have two carboxyl groups at the 1,4-position of the benzene ring while A1 and B1 have only one carboxyl group. Therefore, the second carboxyl group was considered to have been eliminated at higher temperatures.

In the case of blended-PBT with ZnO, A1 and B1 were rich at lower temperatures like neat-PBT. The amount of B1 and the dependence on temperature of A1 were quite different. Although A1 of neat-PBT decreased with elevating temperature, it did not change at higher temperatures. B1 was not the major product and the peak shifted from 500 to 450°C. It suggests that one of two carboxy groups at the 1,4-position of the benzene ring was difficult to eliminate by

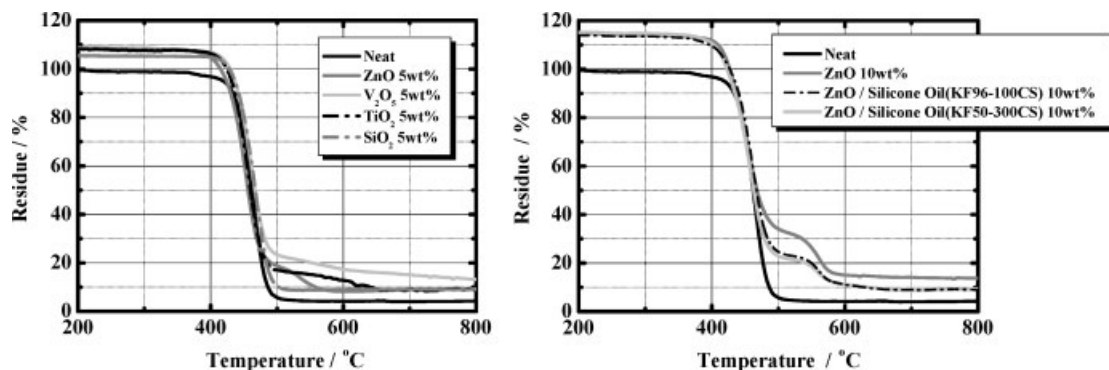


Figure 4 TGA curves of neat-PBT and blended-PBT.

**TABLE II**  
Experimental UL-Test Data of Blended-PBT with Oxides

Sample number	Code	Amount (wt %)	First			Second		
			Ignition (s)	Flaming combustion (s)	Drip (s)	Ignition (s)	Flaming combustion (s)	Drip (s)
1	Neat	–	5.2	115.4	10.6	5.4	3.9	1.7
2	V <sub>2</sub> O <sub>5</sub>	5	11.0	3.0	2.8	10.6	4.9	4.9
3	Ta <sub>2</sub> O <sub>5</sub>	5		Burn out				
4	CuO	5	5.5	119.2	10.9	4.0	51.3	3.1
5	PdO	1		Burn out				
6	MoO <sub>3</sub>	5	5.3	78.8	15.5		Burn out	
7	TiO <sub>2</sub>	5		Burn out				
8	SiO <sub>2</sub>	5	4.7	18.6	9.0	5.1	20.5	–0.7
9	Cr <sub>2</sub> O <sub>3</sub>	5	5.7	164.6	5.4	6.3	47.7	0.0
10	Fe <sub>2</sub> O <sub>3</sub>	10	3.7	20.2	20.2		Burn out	
11	Al <sub>2</sub> O <sub>3</sub>	5	4.8	38.9	5.1		Burn out	
12	ZnO	10	3.2	28.4	26.6	3.9	23.8	10.3
13	Cr <sub>2</sub> O <sub>3</sub>	0.11		Burn out				
	SiO <sub>2</sub>	4.89						
14	Fe <sub>2</sub> O <sub>3</sub>	0.49	6.8	38.5	4.7	6.5	96.0	–2.9
	SiO <sub>2</sub>	4.51						
15	ZnO	0.48	8.8	5.1	–	10.8	6.4	1.2
	SiO <sub>2</sub>	4.52						
16	ZnO	5	10.2	67.7	–	4.7	17.6	17.6
	Silicone oil	5						
17	ZnO	5	5.9	25.3	25.3	4.3	38.7	18.1
	Silicone oil	5						

adding ZnO to neat-PBT. On the other hand, as the butyl group was easier to eliminate, B2 decreased earlier and the peak of A1 was observed at 500°C.

The tendency became more obvious in the case of blended-PBT with TiO<sub>2</sub> as shown in Table IV, where A2 is a major product at lower temperature and the profile of B2 is quite different from those of neat-PBT and blended-PBT with ZnO. The profile led the typical degradation route in which the PBT main chain directly decomposed into A1, and butanic acid and benzoic acid were produced. Actually speaking, the estimated route is too simple to explain the degradation route accurately. The quantitative simulation will be conducted in the next section.

### Elemental analysis

The result of elemental analysis can give us information on the structural change of the PBT polymer chain during decomposition that can be compared with the analysis of the gaseous phase by mass spectrometry. The sum of the two results should be inherently coincident with each other if the experimental data did not include any errors and almost all low volatile products could be trapped. As it is not actually realistic, the elemental analysis is very important to analyze the thermal degradation of polymer.

The elementally analytical data are listed in Table V. The C/H ratios of neat-PBT and blended-PBT with

ZnO were about 1.0 while processing and it changed 1.40 and 1.96 at 460°C, respectively. It suggested that the structure of the blended-PBT deformed earlier than that of neat-PBT by ZnO. However, the C/H and O/H of the blended-PBT were smaller than those while processing. In particular the O/H of the blended-PBT was 0.04 at 850°C. It means about 90% of the oxygen atom on the polymer chain is eliminated with two hydrogen atoms by dehydration. ZnO may play a role as a catalyst.

**TABLE III**  
Assigned Scission Products

Peak	Mw	Structure
C <sub>4</sub>	54	CH <sub>2</sub> CH=CH=CH <sub>2</sub>
THF	72	
B	78	
A1	122	
TPA	166	
B1	176	
DP	154	
A2	220	
B2	274	



TABLE IV  
Ratio of Scission Products of Assigned

Additive	Degradation temperature (°C)	Scission products ratio (%)								
		C <sub>4</sub>	THF	B	A1	B1	DP	A2	B2	etc.
Neat	400	0.3	0.0	0.0	0.6	0.4	0.0	32.7	57.9	8.1
	450	1.9	0.0	0.4	21.1	18.2	0.0	25.3	28.2	4.9
	500	0.0	0.0	0.0	39.0	45.2	0.0	0.0	2.7	13.1
	550	0.0	0.0	1.0	74.2	3.5	1.6	4.6	5.0	10.1
ZnO (10 wt %)	400	1.8	3.6	0.0	1.2	0.5	0.0	42.5	48.4	2.0
	450	1.9	1.1	0.3	28.2	23.0	0.0	37.9	4.2	3.4
	500	2.7	0.1	7.2	43.9	0.6	2.2	36.4	1.6	5.3
	550	0.3	0.0	21.5	7.2	0.0	1.2	19.3	1.3	49.3
TiO <sub>2</sub> (5 wt %)	400	0.0	0.0	0.0	3.9	4.3	0.0	80.9	4.7	6.2
	450	0.0	0.0	0.0	12.8	4.6	0.6	33.3	37.9	10.8
	500	0.0	0.0	0.0	14.0	3.2	0.3	57.3	13.5	11.6
	550	0.0	0.0	0.0	64.2	3.5	2.4	13.5	3.4	13.0

## DISCUSSION

Many scholars have researched the routes of PBT thermal decomposition and the typical routes are depicted in Figure 5. The ester bond is apt to be cut in the first place. There are three points, "a, b, and c" in Figure 5, where the ester bond is subsequently cut. The elimination of carbon dioxide by scission of the bond between a benzene ring and a substituted carbon atom on the benzene ring has been also reported.<sup>24,25</sup> Aliphatic and aromatic hydrocarbons are generated as scission products. Cycling and hydrogen transfer reactions as well as ionic or radical reaction followed and the more complicated compounds including THF and biphenyl were observed.

The details of the small products are not important for the discussion on flame retardancy because the molecules whose molecular weight are less than about 300 have vaporized. On the other hand, a quantitative analysis is much important to analyze flame retardancy. So, the scission processes were simplified to calculate the probabilities of the scission with a lot of the degradation data. The quantitative degradation probabilities were achieved by the simple computer simulation aided by the Molicmouse method.<sup>26,27</sup> The results are illustrated in Figure 6. (top: neat, middle: blend with ZnO, and bottom: blend with TiO<sub>2</sub>, at 400°C).

The entire degradation rate of blended-PBTs at 400°C was about two times when compared with that of neat-PBT. It means that both ZnO and TiO<sub>2</sub>

affected the degradation of the PBT main chain. The blended-PBT consumed oxygen earlier than neat-PBT in the cone calorimeter test as shown in Figure 3. Tables IV and V suggest that it is caused by the acceleration of hydrolysis and hydration.

Generally speaking, the flammability depends on the degradation rate. The larger the rate is, the more easily a polymer burns. Although ZnO accelerates the degradation, it suppresses flammability as shown in Figure 2. It means that not all the degradation reactions generate fuel products but the reaction that produces water and other inflammable compounds can suppress flammability. This is the reason why the blended-PBT with ZnO as a more degradable polymer has excellent flame retardancy.

On the contrary, although the ignition time of blended-PBT with TiO<sub>2</sub> was longer than that of neat-PBT, it burns more easily. It is considered that TiO<sub>2</sub> also accelerates the decomposition of the PBT main chain and the volatiles act as excellent fuels.

The researchers in the field of flame retardancy have considered that the degradation rate of polymer is most important for controlling flammability because the scission products are fuels and the amount is proportional to the degradation rate. However this study showed that the rate does not always decide flammability, but what is important is the kind of chemicals that is generated through the degradation. This is a simple concept and will con-

TABLE V  
Elemental Analysis of Neat-PBT and Blended-PBT with ZnO After Thermal Treatment

Additive (wt %)	Measured temperature (°C)	C (atm %)	H (atm %)	O (atm %)	C/H	O/H
Neat (0 wt %)	As processing	43.22	42.75	14.03	1.01	0.33
	At 460°C	55.15	39.36	5.49	1.40	0.14
	At 850°C	88.38	10.23	1.38	8.64	0.13
ZnO (10 wt %)	As processing	42.87	42.88	14.25	1.00	0.33
	At 460°C	63.60	32.38	4.03	1.96	0.12
	At 850°C	88.43	11.14	0.42	7.93	0.04

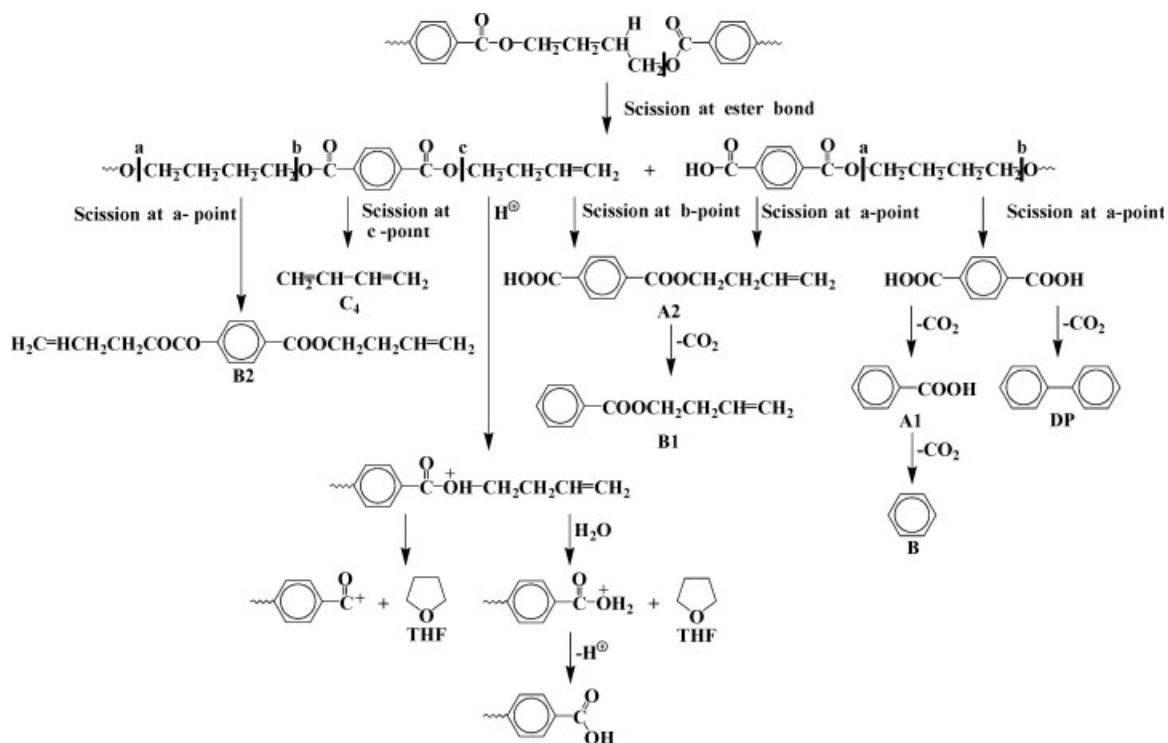


Figure 5 Summarized scission processes of PBT.

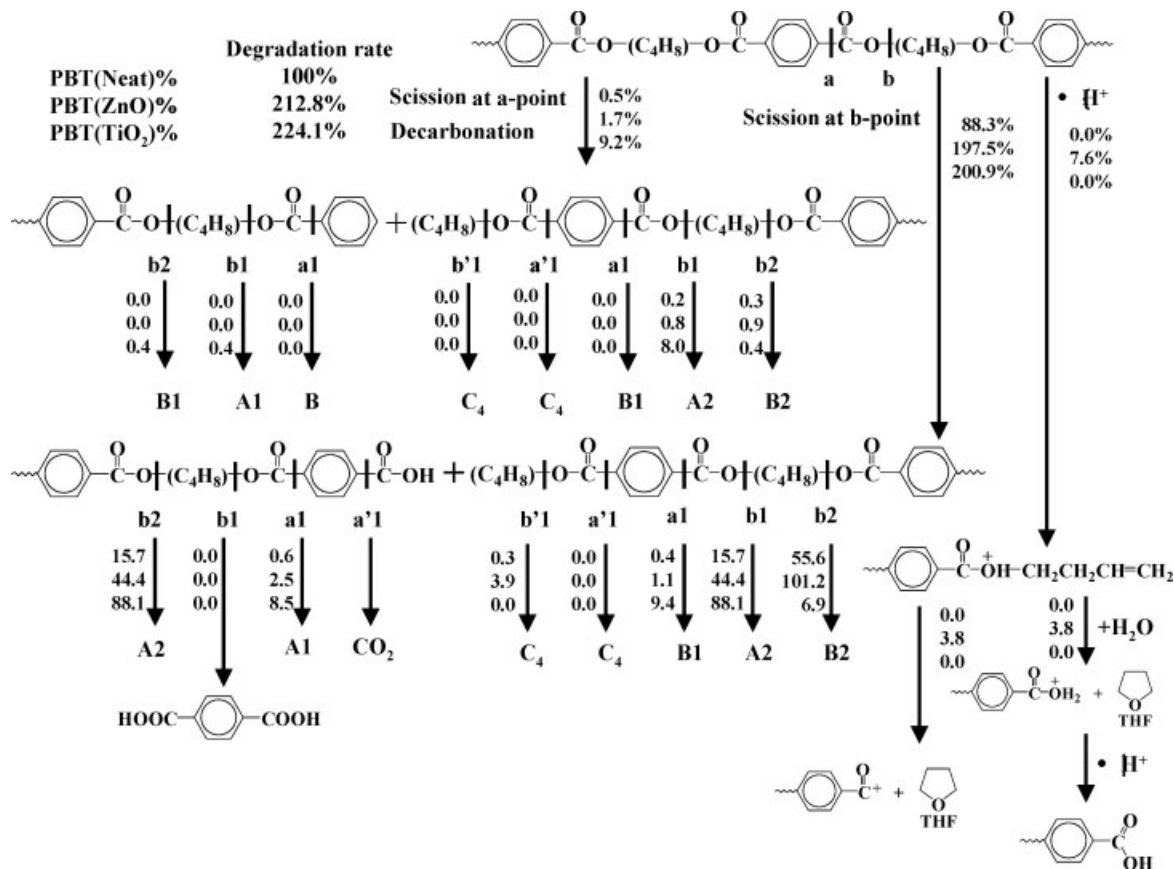


Figure 6 Quantitative estimation of neat- and blended-PBT.

tribute to the development of the study on flame retardancy.

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