

# Thermal oxidative degradation behaviours of flame-retardant thermotropic liquid crystal copolyester/PET blends

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## Abstract

The flame retardancy and the thermal oxidative degradation behaviors of the blend of poly(ethylene terephthalate) (PET) with a kind of phosphorus-containing thermotropic liquid crystal copolyester (TLCP) with high flame retardancy (limited oxygen index, 70%) have been investigated by oxygen index test (LOI), UL-94 rating and thermogravimetric analysis (TGA) in air. The results show that TLCP can dramatically improve the flame retardancy and the melt dripping behavior of PET. Moreover, the apparent activation energies of thermal oxidative degradation of the blends were evaluated using Kissinger and Flynn–Wall–Ozawa methods. It is found that addition of TLCP improve thermal stability and restrain thermal decomposition of PET in air, especially at the primary degradation stage. Py-GC/MS analysis shows that there are remarkable changes in the pyrolysis products when TLCP are blended into PET. The interaction between TLCP and PET has changed their thermal oxidative degradation mechanism.

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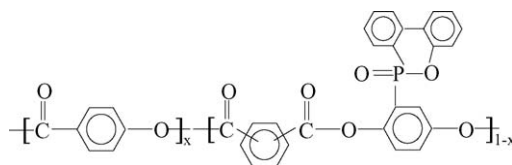
**Keywords:** Flame retardancy; Thermotropic liquid crystal copolyester; PET; Thermal oxidative degradation; Py-MS/GC

## 1. Introduction

Poly(ethylene terephthalate) (PET) is a very important polyester for producing engineering plastics and fibers. In particular, PET fibers account for about 70% of all synthetic fibers, which are employed in a variety of industrial applications, such as tire cords, composites, belts and textiles. However, the flammability and melt dripping limited its applications to a certain extent, thus, the flame retardance of PET is an urgent problem and has received much attention.

Phosphorus-containing compounds are a family of promising flame-retardants as they release less toxic gases and smoke during combustion compared with conventional halogen-based compounds. Some phosphorus-containing flame-retardants and copolyesters have been synthesized in recent years [1–5]. We have also successfully prepared a series of novel phosphorus-containing flame-retardant copolyesters in which phosphorous located in side group or in the main chain [6–12].

Wholly aromatic thermotropic liquid crystal polyesters (TLCPs) have received considerable attention due to their excellent mechanical properties, thermal stability, chemical resistance, flame retardancy and low melting viscosity. The blending of TLCPs with thermoplastics has been studied extensively [13–17]. However, most studies focus on their morphology and mechanical properties, few on their flame retardancy. In fact, TLCP can reach V-0 rating of UL-94 with no addition of any other flame-retardants because it consisted of many aromatic rings and the intumescent carbon will be formed on the surface when burning. In our previous work, a kind of phosphorus-containing flame-retardant thermotropic liquid crystal copolyester with high flame retardancy (limited oxygen index, 70%) has been synthesized [7,8]. The formula of the TLCP is shown as follows:



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The synthetic method, thermal and mechanical properties of TLCP and PET/TLCP blends have been reported in previous articles [7–10]. All these samples show good fire retardancy. The flammability of polymers is related to their thermal oxidative degradation behaviors at high temperature. In an attempt to investigate the effects of TLCP on the flammability of PET, the thermal oxidative degradation behaviors and thermal stability of the PET/TLCP blends were studied and compared with those of PET and Py-GC/MS was used to analyze pyrolysis products of PET, TLCP and PET/TLCP blends in this paper.

## 2. Experimental

### 2.1. Material

PET with an intrinsic viscosity of  $0.64 \text{ dL g}^{-1}$  was provided by Urumuqi Petrochemical Corporation; *p*-acetoxybenzoic acid (*p*-AHB) was supplied by Chenguang Institute of Chemical Engineering (Chengdu, China); terephthalic acid (TPA) was supplied by Guang-Kang Chemical Fibers Company (Guanghan, China) and used as received. The flame-retardant monomer, acetylated 2-(6-oxido-6H-dibenz[*c,e*] [1,2]-oxaphosphorin-6-yl)-dihydroxyphenylene (DOPO-AHQ) was supplied by Weili Flame-Retardant Chemicals Industry Co. Ltd. (Chengdu, China). The thermotropic liquid crystal copolyester was synthesized by the melt-copolycondensation of terephthalic acid, *p*-acetoxybenzoic acid and DOPO-AHQ in the mole ratio 1:3:1 according to the procedure described previously [7,8].

### 2.2. Preparation of PET/TLCP blends for thermogravimetric analysis (TGA) and Py-GC/MS tests

The PET/TLCP blends with different proportions (100/0, 90/10, 80/20) were prepared by the method of solution blending and the solvent and precipitator are phenol/1,1,2,2-tetrachloroethane (60/40, w/w) mixture solution and methanol, respectively. The blends were dried in the vacuum oven at  $80^\circ\text{C}$  for 72 h before use.

### 2.3. Preparation of PET/TLCP blends for flammability tests

PET and TLCP were dried in vacuum at  $100^\circ\text{C}$  for 24 h before use. The blends were prepared by melt blending in the composition of 2, 5, 8, 10, 15 and 20% TLCP in blends by using a twin screw extruder (SLJ-25-05, Longchang, China). During the melt mixing, the temperatures of zones 1–7 and the die zone are 235, 250, 280, 295, 280, 280, 270 and  $260^\circ\text{C}$ , respectively. The strip obtained from the extruder was extended and cooled in air and diced into pellets, which were injected into a mold at about  $250^\circ\text{C}$  and formed into standard test bars for LOI value and UL-94 rating measurement.

### 2.4. Measurement

For all the samples prepared, we analyzed both thermal oxidative degradation behavior and fire behavior. Fire behavior was investigated by means of oxygen index test and UL rating, according to ASTM D-2863 and UL-94, respectively.

TG analysis was conducted in air using a DuPont 2100 thermal system. In each case, a  $6 \pm 0.25 \text{ mg}$  sample was examined under an air flow rate of  $50 \text{ mL min}^{-1}$  at temperature ranging from room temperature to  $700^\circ\text{C}$ , at heating rates of 5, 10, 20 and  $40^\circ\text{C min}^{-1}$ , respectively.

Py-GC/MS analysis was carried out by a system combined with a CDS-2000 Pyrolyzer, a HP AGILENT 6890GC and a Finnigan MAT 95S MS. The pyrolysis temperature is  $900^\circ\text{C}$ , being hold for 20 s. The amount of sample pyrolyzed was about 0.7 mg. A HP DB-5MS capillary column (30 m length, 0.25 mm diameter, 0.25  $\mu\text{m}$  film thickness) was used for separation. The carried gas was helium at flow rate  $0.8 \text{ mL min}^{-1}$ . The injector temperature was  $250^\circ\text{C}$ . The column temperature was programmed from 50 to  $250^\circ\text{C}$  at  $8^\circ\text{C min}^{-1}$  after a hold of 5 min at  $60^\circ\text{C}$ , then to  $280^\circ\text{C}$  at  $6^\circ\text{C min}^{-1}$  after a hold of 5 min at  $250^\circ\text{C}$ . The

Table 1  
LOIs and UL-94 rates of PET/TLCP blends

PET/TLCP	LOI (%)	UL-94
100/0	21.8	–
98/2	26.2	V-2
95/5	27.2	V-2
92/8	29.2	V-0
85/15	32.4	V-0
80/20	35.4	V-0

Finnigan MAT 95S mass spectrometer was operated in electron impact mode at  $70 \text{ eV}$  energy. The mass range was 10–800 amu.

## 3. Result and discussion

### 3.1. Flammability of PET/TLCP blends

The LOI values and UL-94 rating are listed in Table 1. It can be seen that the LOI value of PET is 21.8. However, when 2 wt% of TLCP was blended into PET, the LOI of the blend rapidly increased to 26.2. After that the LOI of blends constantly increase with increasing the amount of TLCP until the LOI value reaches as high as 35.4 when the TLCP content is 20 wt%. These results prove that TLCP can greatly improve the flame retardancy of PET even in a low content. It is also found that the blends have no dripping during burning when TLCP content is more than 8 wt%, showing a UL-94 V-0 rating of flame retardancy.

### 3.2. Kinetics of thermal oxidative degradation of PET/TLCP blends

Figs. 1–3 illustrate the typical TG and DTG curves of PET and PET/TLCP blends (90/10 and 80/20) at varying heating rates in air, respectively. There are two major stages in the thermal oxidative degradation of PET and blends. The first is similar to their thermal degradation in nitrogen, located from about  $320\text{--}520^\circ\text{C}$ . The second is not found in their degradation in nitrogen atmosphere, which is owing to a further oxidative degradation process. Our previous work [10] indicated that the residues are stable in  $\text{N}_2$  even above  $550^\circ\text{C}$ .

Table 2 gives the initial decomposition temperature ( $T_{\text{di}}$ ) that is defined as the temperature at which the weight loss reaches 5 wt%, the maximum decomposition rate temperature ( $T_{\text{max}}$ ) and the residues of samples at 550 and  $650^\circ\text{C}$  corresponding to two decomposition stages.

As can be seen, the  $T_{\text{di}}$  and  $T_{\text{max}}$  of blends are a little higher than those of PET, suggesting that TLCP can improve

Table 2  
Thermogravimetric data for PET and PET/TLCP in air at the heating rate of  $10^\circ\text{C min}^{-1}$

Samples	$T_{\text{di}}$ ( $^\circ\text{C}$ )	$T_{\text{max}}$ (stage 1) ( $^\circ\text{C}$ )	Residue (%)	
			$550^\circ\text{C}$	$650^\circ\text{C}$
PET	362.7	421.0	3.81	0.76
PET/TLCP (90/10)	363.2	422.8	4.38	1.83
PET/TLCP (80/20)	364.5	425.7	10.1	2.67

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