

The Flame-Retardant Polyester Fiber: Improvement of Hydrolysis Resistance

MAKI SATO,¹ SEIJI ENDO,² YOSHIO ARAKI,² GO MATSUOKA,¹ SHOICHI GYOBU,¹ HIDEO TAKEUCHI²

¹ Polymer Material Laboratory, Polymer Research Department, Toyobo Research Center Co., Ltd., 2-1-1 Katata, Ohtsu, Shiga 520-0292, Japan

² Toyobo Co., Ltd., 2-2-8 Dodima Hama, Kita-ku, Osaka, 530-8230, Japan

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ABSTRACT: As far as the flame-retardant polyester fibers are concerned, the copolymerization of phosphorus retardants is the most common method. But a serious problem is that the phosphorus-containing polymer is easily hydrolyzed. We investigated the flame retardancy and the hydrolysis properties of two poly(ethylene terephthalate) (PET) fibers, one with a phosphorus compound as a side chain (side-chain type: HEIM® Toyobo Co., Ltd.), and one with a phosphorus compound inserted in the polymer backbone (main-chain type). Both types had almost the same properties of fibers and flame retardancy, but the main-chain type was hydrolyzed about two times faster than the side-chain type, and led to a decrease of toughness immediately. This difference of hydrolysis properties between main-chain type and side-chain type depends on whether a phosphonate ester bond is placed in the polymer backbone or the pendant site. In the case of the main-chain type, the scission of the polymer backbone chain occurs by hydrolysis of phosphonate ester bonds; however, in the case of the side-chain type, this does not occur. These results demonstrate that the flame-retardant polyester fiber with the side-chain type modifier gives sufficient flame retardancy and excellent hydrolysis resistance. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1134–1138, 2000

Key words: polyester fiber; flame retardancy; hydrolysis resistance; phosphorus; side-chain type

INTRODUCTION

The methods being used to make flame-retardant polyester are blending and copolymerizing with flame retardants. However, when a blended fiber is washed, the blended flame retardants migrate to the fiber surface, leading to decreased flame retardancy and increased danger for the customers. Because of these problems, the copolymerizing method is becoming more common.¹

Both halogenated and phosphorus compounds are the most commonly used flame retardants in

polyester fibers. These compounds have different mechanisms for flame retardancy. In the case of halogenated retardants, the mechanism is usually attributed to the gas phase.^{2–4} In this phase, it is generally thought that the inhibiting action of the halogens is attributable to the halogen halides that remove some of the radicals produced in the free radical chain propagation reactions associated with the combustion process.

In the case of phosphorus retardants, the mechanism has not been made clear despite several studies on the subject. But two chemical mechanisms of phosphorus retardants are notable: changing the behavior of pyrolysis in the solid phase,^{5,6} and inhibiting radical reactions in the gas phase.^{7,8} Some researchers concluded that

Correspondence to: M. Sato.

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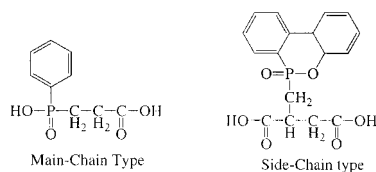


Figure 1 Structures of flame-retardant comonomers.

both mechanisms were effective. The only obvious and significant mechanism that should not be overlooked is the physical one, which is the enhancement of the melt drip phenomenon.⁹ The phosphorus compounds cause the polymer to melt and drip more readily than an untreated material. The burning fabric would be extinguished as the burning molten fabric falls away from the rest of the material.

The use of both halogenated and phosphorus retardants have several disadvantages. Halogenated compounds generally have weak heat resistance and lower light-fastness of dyeing, and emit poisonous gases when exposed to fire.^{10,11} In case of phosphorus compounds, such problems do not occur. For this reason phosphorus retardants have been developed to replace the conventional halogenated retardants in environment protection and public security.¹² But in practical use, the fact that the phosphorus-containing polymer is easily hydrolyzed is becoming a serious problem.

Therefore, we investigated a phosphoric flame-retardant polyester fiber with improved resistance to hydrolysis. The flame retardancy and the hydrolysis properties of two poly(ethylene terephthalate) (PET) fibers—one with a phosphorus compound as a side chain (side-chain type: HEIM® Toyobo Co., Ltd.),¹³ and one with a phosphorus compound inserted in the polymer backbone (main-chain type)¹⁴—were compared. We found that the polyester fiber modified with the side-chain type gave sufficient flame retardancy and excellent hydrolysis resistance.

EXPERIMENTAL

Materials

We prepared two poly(ethylene terephthalate) (PET) copolymers modified with phosphorus compound, main-chain type, and side-chain type. The main-chain type comonomer was purchased from Nihon Chemical Industry Ltd., Japan, the side-

chain type comonomer was purchased from Sanko Ltd., Japan.

Phosphorus-containing copolymers were synthesized by the common method. Terephthalic acid and ethylene glycol and a phosphorus compound and antimony oxide(III) catalyst were added into a stainless reactor equipped with fractional column and stirrer. The reaction mixture was heated to 240°C and maintained at this temperature at a 2.5-kg/cm² pressure until the completion of esterification. The reaction temperature was further raised to 275°C, and the pressure was gradually reduced to 0.1 mmHg and maintained to give the phosphorus-containing copolymer. Both of them contained about 6000 ppm of phosphorus atoms. Structures of comonomers and properties of copolymer are shown in Figure 1 and Table I.

Properties of Fibers

The copolymers were spun to 84 dtex-24 filaments. Table II shows properties of the fibers. Then both types were woven into a knitted fabric.

Flame Retardancy

The knitted samples were tested by the following two methods: JISL-1091A-1 and JISL-1091D (JIS: Japanese Industrial Standard).

Table I Properties of Flame-Retardant Copolymers

		Main-Chain Type	Side-Chain Type
P-content ^a	ppm	5900	6000
Diethylene glycol content ^b	mol %	2.85	2.86
Intrinsic viscosity ^c	dL/g	0.61	0.61
Melting Point ^d	°C	250.0	247.9
Acid value ^e	eq/t	15.5	20.0

^a P-content was analyzed by oxidative degradation–molybdenum blue method.

^b Diethylene glycol (DEG) content was calculated by methanolysis–HPLC method.

^c The intrinsic viscosity was measured at 30°C in phenol/1,1,2,2-tetrachloroethane (60/40 wt/wt).

^d Melting point was determined by DSC.

^e Acid value was calculated by Pohl's method of titration.¹⁵

Table II Properties of Flame-Retardant Fibers

	Actual Dtex	Tenacity ^a (cN/dtex)	Elongation ^b (%)	SHW ^c (%)	SHD ^d (%)
Main-chain type	78	4.5	31.6	9.5	14.3
Side-chain type	79	4.1	31.0	8.5	14.0

^a Tenacity at break.^b Elongation at break.^c Shrinkage in the boiling water for 30 min.^d Shrinkage on the dry condition at 160°C for 30 min.

Hydrolytic Properties

The knitted samples were hydrolyzed by the acetic acid aqueous solution in pH = 4 at 130°C for 1–6 h.

The Ratio of Broken Bonds (%B.B)

The ratio of broken ester bonds to unbroken was estimated from the following equation.¹⁶

$$\%B.B = 0.244\{[IVf]a^{-1.471} - [IVf]b^{-1.471}\}$$

where [IVf]a is the intrinsic viscosity after hydrolysis, and [IVf]b is the intrinsic viscosity before hydrolysis.

Toughness

The knitted samples after hydrolysis were deknitted, then tenacity (*DT*) and elongation (*DE*) were measured by tensile tests. Toughness was estimated from the following equation.

$$\text{Toughness} = DT \cdot (DE)^{1/2}$$

RESULTS AND DISCUSSION

Flame Retardancy

Table III shows the results of standard tests of flame retardancy, JISL-1091A-1 and JISL-

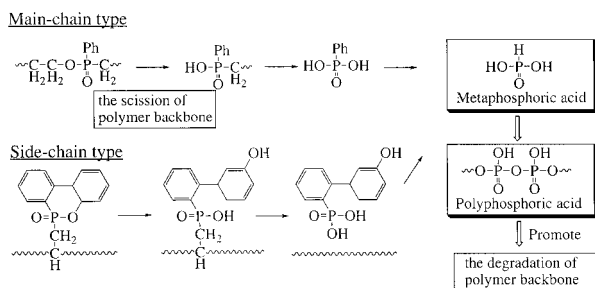
1091D. Both the main-chain type and the side-chain type passed the Japanese Industrial Standards (JIS) flame-retardancy standard.

There are two factors affecting the flame retardancy between both types. One is the difference in the degradation mechanisms, which are derived from the structure of copolyester. The other is the difference in melt viscosities of the copolyesters.

The flame retardancy of phosphorus-containing polymer is mostly achieved by the melt drip phenomenon. The melt drip effect of the polymer is promoted by oxidative degradation, which is accelerated by polyphosphoric acid produced in the process of oxidative degradation in burning. We propose the degradation mechanism of polymer in burning as shown in Scheme 1. When heated, the phosphorus-containing polymer changes into metaphosphoric acid and then into polyphosphoric acid. In the main-chain type, before the phosphorus-containing polymer becomes metaphosphoric acid, the scission of polymer backbone bonds occurs, whereas in the side-chain type, the polymer backbone bonds are not broken yet, when the metaphosphoric acid changes into polyphosphoric acid. It is assumed that the degradation of the side-chain type would be slower than that of the main-chain type. However, we observed that both the main-chain type and the side-chain type have the same flame retardancy. This indicates that the additional steps to degra-

Table III The Results of Flame Retardancy Standard Tests

Flame Retardancy Standard	Item	Requirement	Main-Chain Type	Side-Chain Type
JISL-1091A-1	Carbonized area (cm ²)	30 max.	5.4	5.9
	After-flame time (s)	3.0 max.	0	0
	After glow time (s)	5.0 max.	0	0
	Result		Pass	Pass
JISL-1091D	Number of flame touches	Over 3	4 4 4 4 4	4 5 4 4 4
	Result		Pass	Pass



Scheme 1 Proposed degradation mechanism of polymer in burning.

dation of polymer backbone in the side-chain type do not interfere with the melt drip phenomenon that mostly provides the flame retardancy.

Melt viscosities generally depend upon the intrinsic viscosity. As shown in Table IV, the intrinsic viscosity of the main-chain type is lower than that of the side-chain type. Consequently, the melt viscosity of the main-chain type becomes lower. The low melt viscosity would promote the melt drip phenomenon, which in turn, would increase the flame retardancy of the main-chain type. However, we observed that the side-chain type gave the same flame retardancy as the main-chain type, although the melt viscosity of the side-chain type was higher. If both types had the same melt viscosity, the flame retardancy of the side-chain type would have been superior to that of the main-chain type.

The characteristics of the copolyesters at the same intrinsic viscosity are now investigated.

Hydrolytic Properties

The decrease of intrinsic viscosity by hydrolysis is shown in Table V. The ratio of broken ester bonds

Table IV Melt Viscosity of the Fibers

	IVf (dL/g) ^a	MV (Poise)
Main-chain type	0.56	930
Side-chain type	0.58	1360

^a IVf: The intrinsic viscosity of the fiber.

Table V The Decrease of Intrinsic Viscosity by Hydrolysis

Time		0 h	1 h	3 h	6 h
IVf (dL/g)	Main-chain type	0.554	0.514 (0.067) ^a	0.449 (0.209)	0.374 (0.457)
	Side-chain type	0.600	0.548 (0.030)	0.532 (0.100)	0.490 (0.180)

^a %B.B. is shown inside the parentheses.

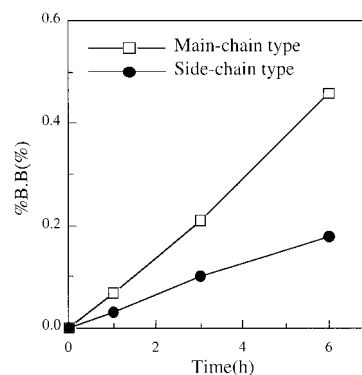
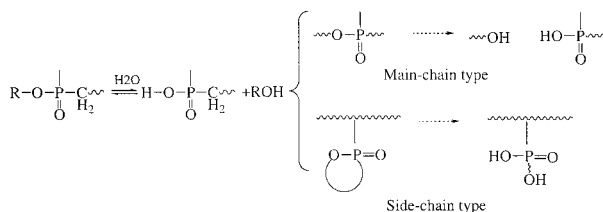


Figure 2 The increase of %B.B. with time of hydrolytic reaction.

to unbroken (%B.B) is shown inside the parentheses. Figure 2 shows a plot of %B.B. vs. the reaction times. It is observed that the main-chain type was hydrolyzed about two times faster than the side-chain type. It is thought that this difference of hydrolysis properties between the main-chain type and side-chain type depends on whether the phosphonate ester bond is placed in the polymer backbone or the pendant site. The equilibrium of phosphonate ester bond in hydrolysis is shown in Scheme 2. This equilibrium thermodynamically moves to the right in the presence of water; a phosphonate ester bond is easier to be broken than other carboxylate ester bonds in a polymer backbone chain. Consequently, in the case of the main-chain type, the scission of the polymer backbone chain occurs by hydrolysis of phosphonate ester bonds, thus leading to rapid decreasing of intrinsic viscosity. On the other hand, in the case of the side-chain type, even though phosphonate ester bonds are hydrolyzed, the polymer backbone chain is not broken.

The decrease of toughness vs. the reaction times is shown in Figure 3. A decrease of toughness was observed as hydrolysis was increased. Obviously, the main-chain type that underwent a more rapid decrease of intrinsic viscosity immediately dropped in toughness as the reaction time increased.



Scheme 2 The equilibrium of the phosphonate ester bond in hydrolysis.

CONCLUSION

Concerning the flame retardancy and hydrolytic properties of polyester fibers modified with phosphorous comonomers, the main-chain type and the side-chain type were compared.

Fire retardancy: Both the side-chain type and the main-chain type gave the same flame retardancy.

Hydrolytic property: the main-chain type was hydrolyzed about two times faster than the side-chain type with the scission of the polymer backbone chain, and led to an immediate decrease of toughness.

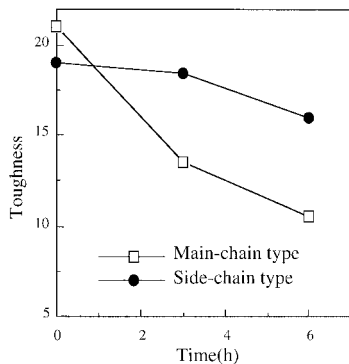


Figure 3 The decrease of toughness with time of hydrolytic reaction.

These results demonstrate that the flame-retardant polyester fiber modified with the side-chain type gives sufficient flame retardancy and excellent hydrolysis resistance.

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