

Flame Retardant Polyesters. III. Fibers

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ABSTRACT: Most of the commercial flame retardant (FR) polyester fibers are produced using copolymerization with phosphorous FRs. We investigated the fiber properties, dyeing properties, and flame retardancy according to the phosphorous FR type. The physical properties of both the fibers are similar and suitable for textile application. But the dye adsorption rate is much faster in the case of main chain type. This is resulted from higher chain mobility analyzed by glass transition temperature. The main chain type FR polyester fiber adsorbed the dyestuff at lower temperature and reached exhaustion more quickly. And the resistance to chemicals such as acidic and alkaline solutions at high temperature have similar tendency with

dye absorption. The migration of dyestuffs and chemicals into the polymer chain has good correlation with chain mobility of the polymers. The main chain type polyester fiber shows better flame retardancy than pendant type polyester, which might be brought about from more rapid degradation into polyphosphoric acid. The main chain type polyester fiber shows better flame retardancy than pendant type polyester. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2297–2300, 2008

Key words: flame retardant polyester fiber; flame retardants; main chain type; pendant type; dyeing properties; flame retardancy; chemical treatment

INTRODUCTION

Polyester, mainly poly(ethylene terephthalate), is now widely used for textile fiber, technical fiber, film, and bottles because of its good mechanical properties and thermal stability and its low production cost, and its demand in 2006 is estimated about 35 million tons and will raise annually by 9%.¹ As interest on the danger of fire, the demand for flame retardant (FR) polyesters has been strong and there have been many research and development to improve the flame retardancy of polyester.

The FR polyester fibers have been produced by the incorporation of FRs using blending or copolymerization.^{2,3} However, in the blended fiber, FRs in the fiber are drain away from the fiber and decrease flame retardancy. So, copolymerization with FRs are widely adopted for commercial production of FR polyester.^{4,5}

Among various kinds of FRs, phosphorous FRs and halogenated FRs have been applied to copolymerization. But many kinds of halogenated FRs, especially brominated FRs, are regulated in many nations or area due to formation of dioxin under combustion.⁶ So, almost inherent FR polyesters are now produced using phosphorous FRs.^{7–10}

Two types of FR are widely used for commercial FR polyester production. Main chain type FR^{4,9} and the pendant (side chain) type FR^{5,10} were used. We previously compared the characteristics and esterification behaviors of both FRs.¹¹ Main chain type FR shows faster esterification rate with ethylene glycol (EG) and further etherified to diethylene glycol (DEG) because of the high acidity. Also, we compared the polymerization behaviors and polymer properties of both FRs.¹² Main chain type FR shows faster polymerization rate as esterification reaction, advantage to increase phosphorous content in the polymer. And polyester using main chain type FR was vulnerable to chemicals and easily degraded at lower temperature.

In this article, we produced the FR polyester fiber using the polymers copolymerized with both FRs and compare the dyeing properties, chemically treated behaviors, and flame retardancies.

EXPERIMENTAL

Materials

Two polyesters containing phosphorous FRs 3-(hydroxyphenyl phosphinyl) propanoic acid (HPP) as main chain type FR and 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl-10-phosphophenanthrene-10-oxide (DI) as pendant type FR, reported in previous report¹² were investigated and normal polyester was used for reference. The chemical formula

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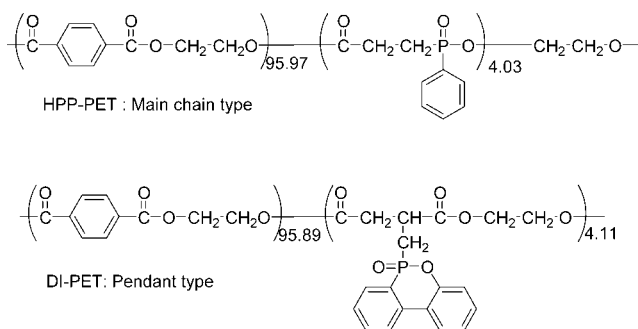


Figure 1 Chemical formula of FR polyesters.

of FR polyesters investigated is shown in Figure 1. For chemical treatment, hydrochloric acid (Daejung Chem.), sodium hydroxide (Junsei Chem.), and *n*-butyl amine (Junsei Chem.) were used without purification.

Fiber formation and characterization

Polymers were dried with a Hosokawa fluid bed dryer. The moisture contents of the polymer were kept under 10 ppm. Then the polymer were extruded at 283°C using Barmag extruder, and winded at 2800 m/min to produce the partially oriented yarn (POY)s. They are draw-texturized using Murata disc type draw texturizer to produce bulky draw textured yarn (DTY)s. The properties of POY and DTY according to FRs are shown Table I. And crystalline structure of the DTYs is analyzed using DMAX III-A type X-ray diffractometer of Rigaku Denki Company and X-ray diffractograms are shown in Figure 2. The crystallinities calculated from the density using density gradient column were 46.0%, 40.0%, and 36.7% for the normal PET, HPP-PET-1, and DI-PET-1, respectively.

Dyeing and fastness

The fibers were knitted to test the dyeing properties and to evaluate the fastnesses. Dye adsorption test were carried out by Korea Institute of Industrial Technology and test conditions are: liquor ratio 1 : 20 (fabric : water by weight), Synthopal SNH of

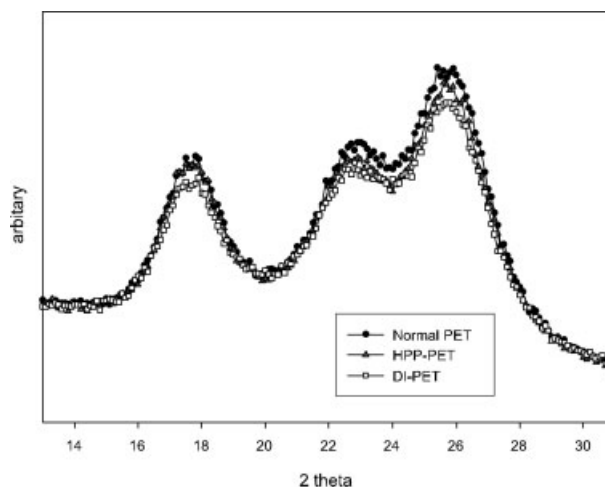


Figure 2 X-ray diffractograms of DTYs.

Dr.th.Boehme Co. 1 g/L as a dispersant auxiliary, acetic acid 0.3 g/L, Synolon Blue KRD of KISCO 2% owf as a dyestuff. The dyeing temperature and dye adsorption with time is shown in Figure 3.

Dyeing fastnesses of the fabrics tested on KSK 0903 are listed in Table II.

Chemical treatment

FR polyester fibers are widely used for upholstery, bedding, apparel, etc. They are finished with various processes such as weight reduction, scouring, and dyeing. They are also used as working clothes under severe conditions. To evaluate the efficiencies under textile processes and the resistance to chemicals, chemical treatments were accomplished as follows.

Chemical treatments were accomplished using hydrogen chloride (HCl) as acid, sodium hydroxide (NaOH), and *n*-butyl amine (BuA) as inorganic and organic alkalis, respectively. Fabrics were treated in the 0.05M water solution at 95°C, and sampled for 1, 2, and 3 h. The weight reduction, IV (intrinsic viscosity) retention, physical properties such as toughness estimated from multiplying tenacity and square root of elongation were evaluated and listed in Figures 4–6, respectively.

TABLE I
Properties of POYs and DTYs

Type	POY			DTY			
	Decitex (dtex)	Tenacity ^a (g/dtex)	Elongation ^a (%)	Decitex (dtex)	Tenacity ^a (g/dtex)	Elongation ^a (%)	BWS ^b (%)
Normal PET	138.7	2.50	126.9	83.4	4.11	17.2	4.0
HPP-PET	134.0	2.30	124.0	80.9	3.97	20.0	4.8
DI-PET	134.9	2.21	136.0	84.7	4.08	17.8	4.6

All fiber consist of 72 filaments.

^a Tenacities and elongations at break.

^b Shrinkage in the boiling water for 30 min.

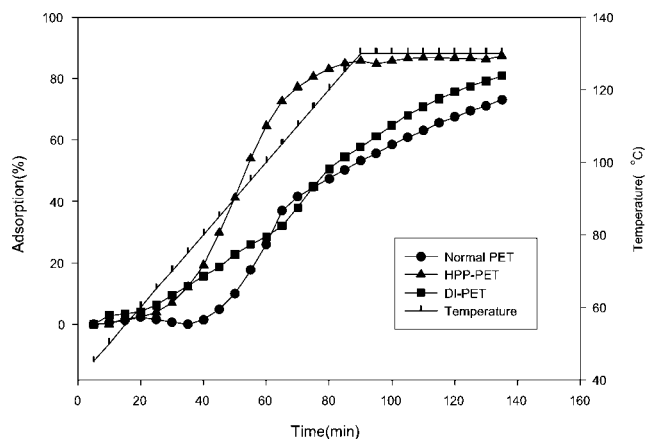


Figure 3 Dye adsorption rates with time.

Flame retardancy

Flame retardancies were evaluated by FITI Testing & Research Institute in Korea by limit oxygen index (LOI, KS M ISO 4589-2 : 2001). Number of flame touches (Korean Fire Services Act, coil method) and carbonized area, after flame time, after glow time (JIS-1091A-1) respectively are listed in Table III.

RESULTS AND DISCUSSION

Fiber properties

The properties of three fibers produced in the same manner shown in Table I are similar. They are suitable for textile application. The tenacities are slightly decreased with the order normal, HPP-PET, DI-PET. This tendency is in accordance with incorporated FR content in the polymers¹² and crystal size analyzed by the wide angle diffractograms shown in Figure 2. FR units incorporated into polymers make it hard to crystal growth under spinning and draw-texturing.¹³

Dyeing behavior

Dye adsorption behaviors shown in Figure 3 have distinct differences. HPP-PET fiber adsorbs dyes at lower temperature than the other fibers. The dye molecules easily migrate into the more flexible polymer chain having lower glass transition temperature by 4°C.¹² The fastnesses of the fibers are shown in

TABLE II
Dyeing Fastnesses of the Fabrics

Fastness	Washing	Rubbing	Sublimation	Light
HPP-PET	4-5	4-5	4-5	3
DI-PET	4-5	4-5	4-5	3
Normal PET	3-4	4-5	4-5	5

Table II. Similar crystal structures shown in Figure 2 lead to similar fastnesses of fibers preventing the dye molecules from draining from the fibers.

Therefore, it is concluded that the dye molecules migrated into the fiber above glass transition temperature and settled in the fiber at below glass transition temperature.

Chemical treatment

The chemically treated fibers showed different phenomena according to the chemicals and FR types.

As shown in Figure 4, the weight retention of the fibers with time is drastically lowered in NaOH solution. It means that easily soluble sodium salt is formed by alkaline hydrolysis of the fibers and dissolved in the water, so the weight reduced. As in the same phenomena of dye adsorption, the small molecules easily migrate into the more flexible polymer chain at 95°C, the weight of HPP-PET fiber decrease more rapidly than the other fibers. But *n*-butyl amine and hydrogen chloride solution do not make soluble organics as sodium hydroxide.

In contrast to weight reduction, IV and toughness are decreased dominantly when treated in amine solution as shown in Figures 5 and 6. This can be explained by chemical stability of ester linkage and formation of water soluble salt.¹⁴ Ester linkage in polyester is more vulnerable to alkali than to acid. So the acid treated fibers show less reduction of weight and IV, which result in stable toughness preservation. Alkaline hydrolysis of polyester with NaOH forms the sodium salt which easily soluble in water. Aminolysis of polyester with *n*-butyl amine forms the terminal amide linkage which is less soluble in water than sodium salt. So when the fibers are treated with NaOH, the hydrolyzed molecules dissolved in water and the remained molecules preserve similar IV. But when the fibers are treated with *n*-butyl amine, the aminolyzed molecules

TABLE III
Flame Retardancies According to Standards

Standard	Item	HPP-PET	DI-PET	Requirement
KS M ISO 4589-3 : 2001	Limited oxygen index (LOI)	38.3	32.7	
Korean Fire Service Act	Number of flame touches	4.0	3.2	Above 3
JIS-1091A-1	Carbonized area (cm ²)	5.1	5.9	Below 30
	Afer flame time (s)	0	0	Below 3.0
	After glow time (s)	0	0	Below 5.0

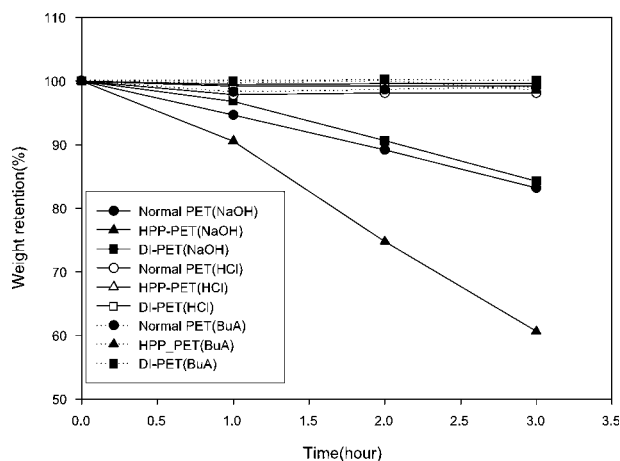


Figure 4 Weight retention with chemically treated time.

remained in the fiber and the weight is kept, but the IV decrease.

Flexible polymer chain of HPP-PET fiber is vulnerable to these chemicals and the changes of weight and IV are large.

Flame retardancy

Flame retardancies of both fibers using main chain type and pendant type are shown in Table III are proper to textile application such as upholstery. But there is a little difference in the flame retardancy. The main chain type polyester fiber shows better flame retardancy than pendant type. Main chain type polyester has a higher susceptibility to thermal degradation at lower temperature and easily degraded into polyphosphoric acid which plays a major role in flame retardancy. It is more appropriate to use main chain type FR for better FR application.

CONCLUSIONS

Two kinds of FR polyester fibers were produced and characterized. The fiber properties are similar and suitable

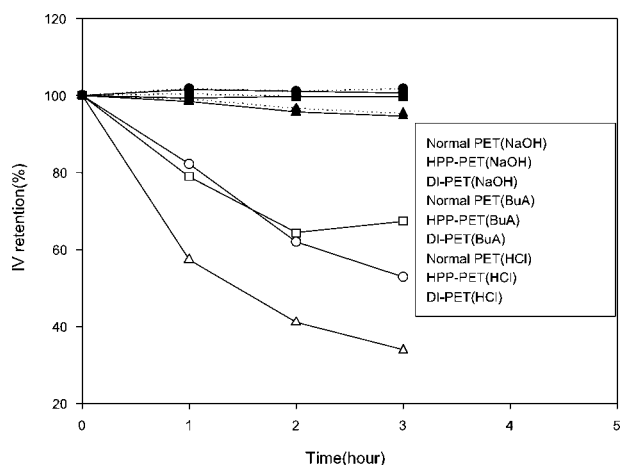


Figure 5 IV variation with chemically treated time.

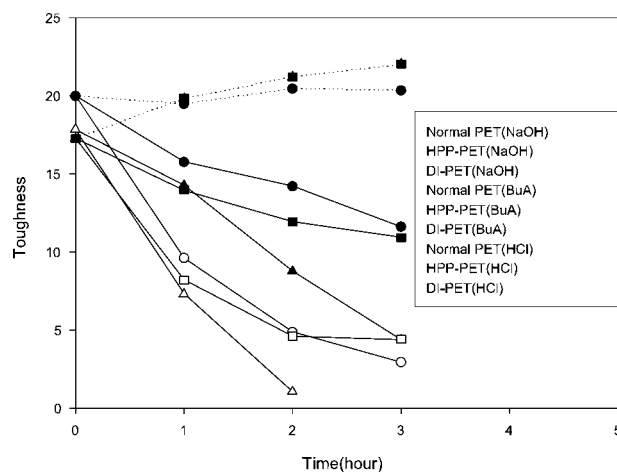


Figure 6 Toughness changes with chemically treated time.

ble for textile application. FRs incorporated into the polymers suppress the crystallization, pendant type polyester fiber has lower crystallinity than main chain type.

The polymer chain of main chain type polyester fiber is more flexible than that of pendant type, it adsorbs the dyestuff at lower temperature and reaches exhaustion more quickly. Also, chemicals migrate easily into the main chain type polyester fiber than pendant type; main chain type polyester fiber shows lower chemical resistance.

As main chain type polyester has higher susceptibility to thermal degradation and low resistance to thermal chain scission, main chain type polyester degraded at lower temperature and more easily degraded into polyphosphoric acid to show better flame retardancy.

References

- Mulliez, L. Polyester and PET Chain Held in December 13–15, 2005. Maack Business Service: Amsterdam. Session 1.
- Levchik, S. V.; Weil, E. D. *Polym Int* 2005, 54, 11.
- Levchik, S. V.; Weil, E. D. *Polym Adv Technol* 2004, 15, 691.
- Hindersinn, R. R.; Wagner, G. M. In *Encyclopedia of Polymer Science and Technology*, Vol. 7; Mark, H. F.; Gaylord, N. G.; Bikales, N. M., Eds.; Wiley: New York, 1967; p 1.
- Babcock, C. I. In *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 9; Mark, H. F.; McKetta, J. J.; Othmer, D. F., Eds.; Wiley: New York, 1966; p 286.
- Troitsch, J. *Plastics and Flame Retardants (Part D); Fire and Environment Protection Service: Wiesbaden, 2001.*
- Endo, S.; Kashihara, T.; Osako, A.; Shizuki, T.; Ikegami, T. *Jpn. Pat. 77-98089* (1980).
- Kleiner, H. J.; Finke, M.; Nollert, U.; Herwig, W. *Ger. Pat. 2,346,787* (1975).
- Jang, D. H.; Lee, I. S.; *Kor. Pat. 236755* (1989).
- Son, Y. K.; Yang, S. C. *Kor. Pat. 308541* (2001).
- Yang, S. C.; Kim, J. P. *J Appl Polym Sci* 2007, 106, 2870.
- Yang, S. C.; Kim, J. P. *J Appl Polym Sci* 2007, 106, 1274.
- Farrow, G. *Polymer* 1960, 1, 518.
- Paszun, D.; Spsychaj, T. *Ind Eng Chem Res* 1997, 36, 1473.