

Durable Flame-Retardant Treatment of Polyethylene Terephthalate (PET) and PET/Cotton Blend Using Dichlorotribromophenyl Phosphate as New Flame Retardant for Polyester

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Received 12 May 2000; accepted 12 August 2000

ABSTRACT: Dichlorotribromophenyl phosphate (DCTBPP) was synthesized via the reaction of tribromophenol and phosphorous oxychloride and characterized by elemental analysis, IR, ¹H-NMR, thermogravimetric analysis, and differential scanning calorimetry. To impart durable flame retardancy the poly(ethylene terephthalate) (PET) fabric was treated with DCTBPP via pad-dry-thermosol fixation and the PET/cotton (50/50) blend fabric was treated with both DCTBPP and tetrakis(hydroxymethyl) phosphonium chloride (THPC)/urea precondensate via a two-bath sequential treatment. The treated PET fabric's increased limiting oxygen index value was proportional to the increasing DCTBPP application level and showed self-extinguishing properties at 8.1% add-on, even after 50 washes. The blend fabric treated with 15% DCTBPP and 30% THPC/urea precondensate became self-extinguishable and durable to 50 washes, and the treated fabric retained over 85% of its breaking strength without excessive stiffness. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 793–799, 2001

Key words: dichloro-tribromophenyl phosphate; tetrakis(hydroxymethyl) phosphonium chloride/urea; polyethylene fabric; polyethylene/cotton blend fabric; flame-retardant finish

INTRODUCTION

Poly(ethylene terephthalate) (PET) fiber is one of the most widely used synthetic fibers due to its excellent mechanical properties, chemical resistance, good electrical insulation, and so forth; however, it is highly flammable in air. There are

three ways to render flame retardancy to the fiber: copolymerization of a flame-retarding monomer, incorporation of an additive during fiber spinning, and topical treatment with flame retardants.^{1,2} Until 1977 tris (2,3-dibromopropyl) phosphate (TBPP) was extensively used as the most important durable flame retardant for PET fiber. However, the finish with TBPP was withdrawn due to its mutagenic and carcinogenic properties, despite its excellent performance and easy application. Developments of new flame re-

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Journal of Applied Polymer Science, Vol. 81, 793–799 (2001)
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tardants based on halogen and/or phosphorous compounds and the applications of previously known chemicals for PET fibers were extensively investigated,²⁻⁴ for example, condensation polymers of bisphenols and phosphorodichloridates,⁵ polyphosphoroamides,⁶ polyvinylbromide,⁷ meso-1,2,3,4-tetrabromobutane,^{8,9} antimony oxide with brominated polycarbonate or decabromodiphenyl-oxide,^{10,11} and so forth.

In blend fabrics containing both PET and cellulose, it is more difficult to impart durable flame retardancy because of the "scaffolding effect" of the blend, as well as the high level of add-on and wash fastness required for acceptable flame retardancy.^{2,12} There were many studies to produce a durable flame-retardant polyester/cellulose blend fabric; they used various flame retardants, including methyl phosphonic diamide with brominated polyester,¹³ oligomeric vinyl phosphonate,^{14,15} terakis(hydroxymethyl) phosphonium sulfate-urea/trimethylol melamine,¹⁶ and tetrabromobisphenol A and dimethyl *N*-hydroxymethylcarbamoyl ethyl phosphonate or tetrakis(hydroxymethyl) phosphonium chloride (THPC)-urea.¹⁷⁻¹⁹

The flame retardancy of a treated fabric is often explained by two major actions of flame retardants: condensed-phase and/or gas-phase mechanisms.²⁰ Condensed-phase active retardants such as organophosphorous compounds alter the pyrolysis of substrates in such a way that the amount of flammable gases produced is minimized and accordingly the amount of char formed is increased. Gas-phase active retardants such as halogen compounds function as inhibitors that capture flame-propagating species and decrease the heat returned to the substrate surface.

This study was focused on the synthesis of dichlorotribromophenyl phosphate (DCTBPP), a new flame retardant for PET fiber, and its application as a durable flame-retardant finish for PET fabric and PET/cotton blend fabric. The effect of the treatment on the mechanical properties such as the breaking strength and stiffness was investigated, and the flame-retarding mechanism of the treated fabric was also studied by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The fabrics used were 100% scoured PET fabric (225 g/m²) and PET/cotton blend fabric (50:50 blend ratio, 251 g/m²).

2,4,6-Tribromophenol (TBP) and phosphorous oxychloride were obtained from Aldrich and Fluka, respectively. The other chemicals used were all reagent grade. Precondensate of THPC and urea (1:0.5 mole ratio) was obtained from American Cyanamide Co. in 65% aqueous solution. Albegal FFD and Ultratex FMR were used as received from Ciba-Geigy.

Synthesis of DCTBPP

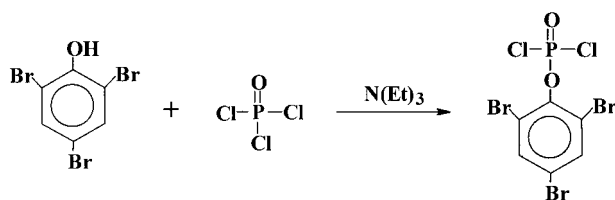
Twenty grams of TBP (0.06 mol) and 6 g of triethylamine (0.06 mol), which were dissolved in 200 mL of acetone under a dry nitrogen atmosphere, were placed in a four-neck flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser. Subsequently, 9.2 g of phosphorous oxychloride (0.06 mol) dissolved in 50 mL of acetone was slowly added into the above solution under stirring at 50°C and the reactants were quenched after 2 h, followed by the evaporation of acetone using a vacuum evaporator. The product was purified by dissolving unreacted TBP and precipitated salt with 3% NaOH aqueous solution, then washing it with distilled water and finally drying it under a vacuum.

Characterization of DCTBPP

The halogen and phosphorous content were determined by potentiometric titration and the phosphomolybdate method using a UV-visible spectrophotometer (model 551S, Perkin-Elmer), respectively.²¹ The IR spectrum of DCTBPP was obtained with a FTIR spectrophotometer (model 1725X, Perkin-Elmer) using a potassium bromide pellet technique, and the ¹H-NMR spectrum was taken by a NMR spectrophotometer (Jeol, JNM-LA-300) using DMSO-*d*₆ as a solvent. The melting point of DCTBPP was measured by a differential scanning calorimeter (DSC-220, Seiko) at a heating rate of 20°C/min under a nitrogen atmosphere, and its thermal decomposition was observed using a TG analyzer (SSC-5200, Seiko) at a heating rate of 50°C/min under air.

Flame-Retardant Treatment of PET Fabric and PET/Cotton (50/50) Blend Fabric

For 100% PET fabric the fabric was impregnated to give an approximately 60% wet pickup via padding through an aqueous formulation bath consisting of various amounts of DCTBPP (3-15%,



Scheme 1 The synthesis of DCTBPP.

w/w), 0.5% (w/w) sodium laurylsulfate as a dispersing agent, and 0.2% (w/w) Albegal FFD as a deforming agent. The padded sample was dried at 100°C for 3 min and subsequently thermofixed at 160°C for 3 min. The treated fabric was washed twice with sodium carbonate aqueous solution and water and finally dried at room temperature.

A sequential treatment was carried out for the PET/cotton blend fabric. We first applied 15% (w/w) DCTBPP to the fabric by the method described above. Then the fabric was padded further with a THPC/urea precondensate formulation to give a 60% wet pickup, dried at 100°C for 3 min, and then cured at 160°C for 3 min. The THPC/urea precondensate bath was prepared as follows: urea was added to various amounts of THPC/urea precondensate solution to make the mole ratio of THPC and urea 1:1, followed by successive additions of 3% (w/w) disodium hydrogen phosphate as a catalyst, 3% (w/w) Ultratex FMR as a softener, and 0.2% (w/w) Triton X-100 as a wetting agent. The formulation was adjusted to pH 6 using 50% NaOH aqueous solution. The cured fabric was oxidized at a liquor ratio of 40:1 by 0.14% (v/v) hydrogen peroxide aqueous solution for 20 min at room temperature and then washed as described above.

Evaluation of Flame-Retardant Fabrics

The flame retardancy of the untreated and treated fabric was assessed by the limiting oxygen index (LOI) method according to ASTM D 2863 using a LOI-type burning tester (model ON-1, Suga Testing Co.). The influence on the stiffness and breaking strength was investigated according to JIS L1079 6.22.5E and ASTM D 1682-64 (raveled strip), respectively, using a Handle-O-Meter (HOM-2, Daiei Kagaku Mfg. Co.) and a tensile strength tester (Scott Tester). The durability of the treatment to washing was tested according to the accelerated laundering method proposed by McSherry et al.: the samples were boiled for 4 h in a solution of 0.5% Na₃PO₄·12H₂O and 0.1% Triton X-100 at an approximate liquor ratio

of 40:1.²² The thermal decomposition behavior of the flame-retarded fabric was observed at the temperature range of 50–550°C at a heating rate of 50°C/min using the TG analyzer.

RESULTS AND DISCUSSION

Synthesis and Characterization of DCTBPP

The DCTBPP was prepared via the reaction of TBP and POCl₃ in the presence of triethylamine as an acid scavenger as shown in Scheme 1. Table I shows the general features of the synthesized DCTBPP. The DCTBPP was characterized by IR spectroscopy and is compared with TBP in Figure 1. The O—H stretching of TBP at around 3500 cm⁻¹ disappeared in DCTBPP and new absorption bands appeared near 1300 cm⁻¹ and at two peaks of 1200 and 950 cm⁻¹, which corresponded to P=O and P—O—C (aromatic) stretching of DCTBPP, respectively.⁵ The ¹H-NMR spectra of TBP and DCTBPP are shown in Figure 2. In the spectrum of DCTBPP, the proton of the phenolic O—H in TBP at 10.3 δ disappeared and the aromatic protons resonated downfield to 7.9 from 7.7 δ. TGA thermograms of TBP, DCTBPP, and PET fabric are shown in Figure 3. DCTBPP starts to decompose near 260°C and stops at 470°C with 8% of residual char whereas TBP decomposes initially at 140°C and yields no residue after 250°C, indicating the excellent thermal stability of DCTBPP. It is generally desirable that pyrolysis of flame retardants for PET should occur synchronously with or slightly lower than that of PET.¹ It may be expected that DCTBPP could impart efficient flame retardancy to the PET fabric because of the similar thermal decomposition behavior.

Treatment of PET Fabric with DCTBPP

Flame retardancy may be rendered to synthetic fibers by one of the following ways: copolymeriza-

Table I General Features of DCTBPP

P (wt %)	Calculated	6.9
	Found	6.7
Br (wt %)	Calculated	46.8
	Found	45.9
Cl (wt %)	Calculated	15.8
	Found	15.8

The yield was 54.8%, the melting point was 148.6°C, and the color/shape was a white powder.

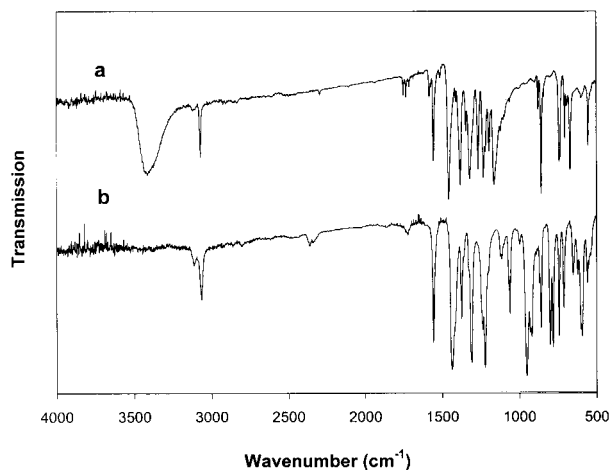


Figure 1 IR spectra of (a) TBP and (b) DCTBPP.

tion of fire-retarding monomers or incorporation of a flame-retardant additive during fiber extrusion to produce flame-resistant fibers or the application of a topical finish. In this study the pad-dry-thermosol fixation method, which is a topical finish, was employed to impart flame retardancy to PET fabric with an aqueous DCTBPP dispersion. DCTBPP may diffuse into the amorphous region within PET fiber and form intermolecular bonds with it by physical forces such as van der Waals interaction and hydrophobic bonding.

Figure 4 shows that the LOI values of treated PET fabric increased proportionally with increasing DCTBPP application level. The treated PET fabric is considered to be flame retardant above 12% (w/w) because those materials with a LOI value greater than 27 are generally known to be self-extinguishing.¹ The thermal behavior of the treated PET fabric was compared with untreated fabric and the results are given in Figure 5 and Table II. The residue number (N_r) of the treated fabric was calculated from the following equation:

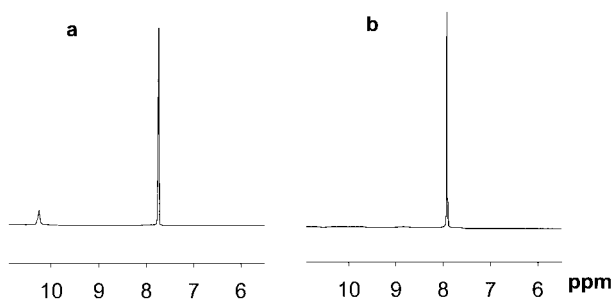


Figure 2 $^1\text{H-NMR}$ spectra of (a) TBP and (b) DCTBPP.

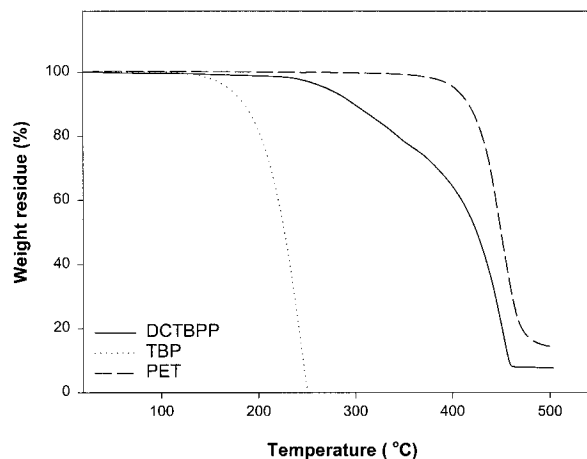


Figure 3 TGA thermograms of untreated PET fabric, TBP, and DCTBPP.

$$N_r = (R_f/F)/R_u$$

where R_f and R_u represent the weight percentages of the residual carbonaceous char of the finished PET fabric and the untreated determined after pyrolytic decomposition, respectively; and F is the weight fraction of the fiber in the treated fabric.

Although the DCTBPP-treated PET became less flammable with higher application concentrations, the N_r of the treated fabric remained rela-

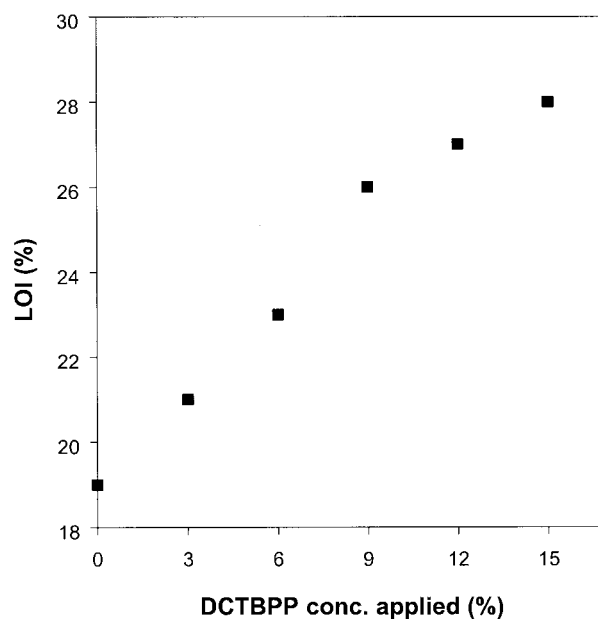


Figure 4 The effect of the DCTBPP application level on the LOI values of treated PET fabrics.

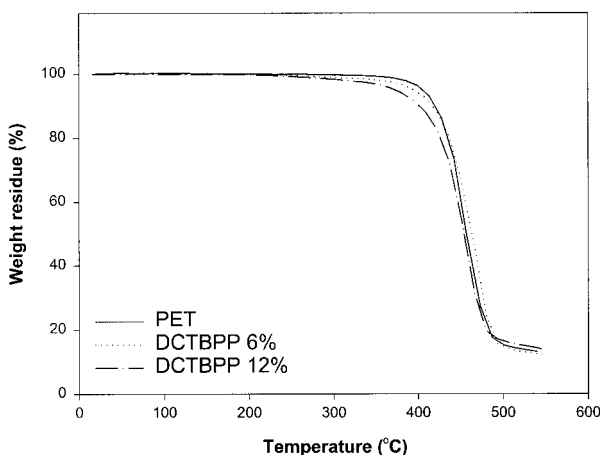


Figure 5 TGA thermograms of untreated and treated PET fabric with DCTBPP.

tively constant, even with higher LOI values. Although the phosphorus in DCTBPP could reduce the flammability of the PET fabric, the principal factor in decreasing the flammability of the treated PET fabric was attributed to the presence of the halogen components in DCTBPP because of the abundance of halogens compared to phosphorus. The DCTBPP in PET may liberate hydrogen halides during pyrolysis, particularly HBr, and inhibit the propagation of fuel combustion by affecting the branching oxidation of $H \cdot$ and $HO \cdot$ radicals in the gas phase, resulting in decreasing the amount of fuel consumed in the flame and, as such, the amount of heat generated. The treatment adversely affected the stiffness of the treated fabric, which increased with increasing application levels.

Treatment of PET/Cotton (50/50) Blend Fabric with DCTBPP and THPC/Urea Precondensate

The difficulty in rendering effective flame retardancy to PET/cotton blends is mainly due to the

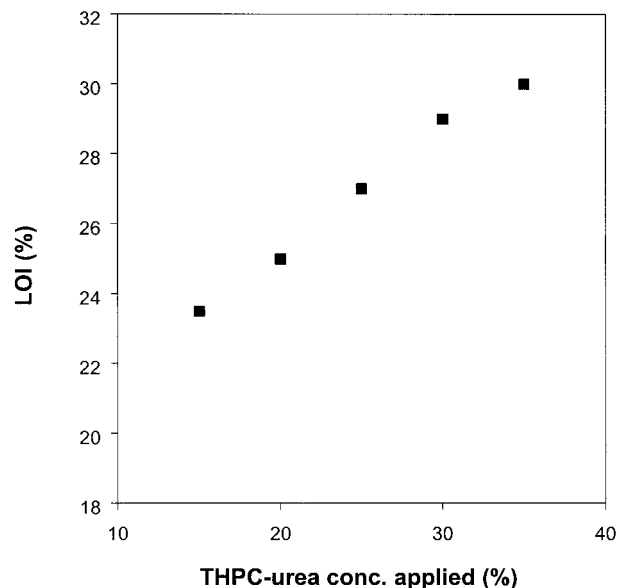


Figure 6 The LOI variation of PET/cotton blend fabrics treated with a formulation of different THPC/urea precondensate concentrations and 15% (w/w) DCTBPP.

scaffolding effect between the cotton and PET during burning, where the molten PET component wicks onto the char of the cotton and avoids its melt dripping.¹⁵

The blend fabric was treated with a DCTBPP dispersion at a constant concentration of 15% (w/w) and then various THPC/urea concentrations of 15–35% (w/w) were applied to the DCTBPP-treated blend fabric via the pad-dry-cure method. Figure 6 shows the dependence of the LOI values on the THPC/urea application at a fixed DCTBPP concentration. It was found that 25% (w/w) of the precondensate was sufficient to impart self-extinguishability to the blend fabric. The TGA thermograms of the treated PET/cotton blend are compared with that of the untreated fabric in Figure 7, and other characteristic prop-

Table II Characteristic Values of PET Fabrics Treated with DCTBPP

DCTBPP Concentration (% w/w)	Add-on (%)	LOI (%)	R_f (%)	F	N_r	Stiffness (gf)
Untreated	0	19	0	0	0	233
3	1.7	21	13.4	0.984	1.04	236
6	2.7	23	12.8	0.973	1.04	320
9	4.9	26	13.2	0.953	1.06	344
12	6.7	27	13.6	0.938	1.11	508
15	8.1	28	13.8	0.928	1.13	619

$$R_u = 13.1\%$$

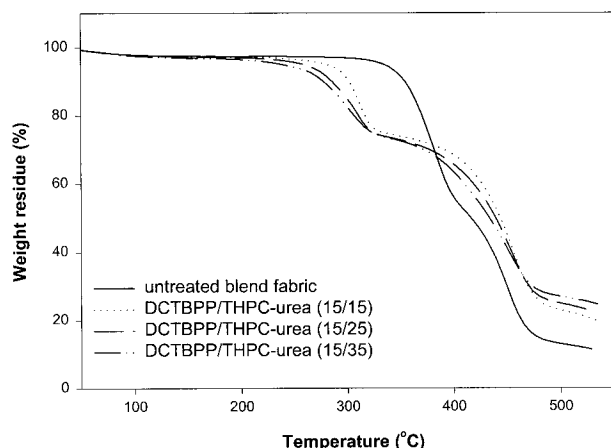


Figure 7 TGA thermograms of the blend fabrics sequentially treated with DCTBPP and THPC/urea precondensate.

erties of the blend are represented in Table III. With increasing precondensate concentration the initial pyrolytic decomposition shifted to significantly lower temperatures and the amount of char formation increased compared with the untreated blend, as also shown by the higher N_r , suggesting that the reduced flammability was due to condensed-phase retardation through P—N synergism of the precondensate. It is known that phosphorous compounds reduce cellulose flammability, primarily by dehydration, phosphorylation, and phosphate-ester decomposition mechanisms, which are enhanced by nitrogenous compounds, and by formation of a crosslinked network within the cellulose that inhibits release of volatile combustible fragments and encourages char formation.¹⁴ Therefore, the self-extinguishing property of the treated PET/cotton blend may result from the condensed-phase retardation of cotton by THPC/urea, as well as the gas-phase retardation

of PET by DCTBPP. The breaking strength and stiffness of the treated blend fabric were compared with those of the untreated as shown in Table III. The treatment brought about a decrease in breaking strength of less than 15% and some deterioration in stiffness at high application levels, which would be applicable in areas such as curtains, protective working uniforms, and so forth.

Durability of Treated PET Fabric and PET/Cotton Blend

The 4-h boiling procedure of flame-retardant fabric with tribasic sodium phosphate solution is known to correlate very closely with domestic 50-wash cycles, which is an important criterion for the durability of the finish.²² The LOI values were measured before and after boiling, and the results are shown in Figure 8. While the flame-retardant PET fabric with an add-on of 8.1% DCTBPP still retained the LOI value of 27 after the accelerated laundering, the self-extinguishable blend fabric was durable even after 50 washes when the fabric was treated with 15% (w/w) DCTBPP and 30% (w/w) precondensate. The carcinogenic and mutagenic properties of DCTBPP have not been investigated yet and further research is necessary to determine the toxicity of the compound.

CONCLUSION

The DCTBPP was synthesized via the reaction of tribromophenol and phosphorous oxychloride and was characterized with IR, NMR, and elemental analysis. Durable flame retardancy was rendered to PET fabric and PET/cotton (50/50) blend fabric by pad-dry-thermosol fixation of DCTBPP and

Table III Characteristic Values of PET/Cotton Blended Fabrics Sequentially Treated with DCTBPP and THPC/Urea

DCTBPP/ THPC Urea	Add-on (%)	LOI (%)	R_f (%)	F	N_r	BS (%)	Stiffness (gf)
Untreated	0	19	0	0	0	100	432
15/15	8.1	23.5	19.8	0.927	1.94	88	704
15/20	9.9	25	20.6	0.908	2.06	87	748
15/25	14.1	27	22.2	0.876	2.30	87	776
15/30	18.2	29	23.2	0.846	2.49	86	788
15/35	22.6	30	24.6	0.819	2.73	85	796

R_u = 11.0%; BS, breaking strength retention.

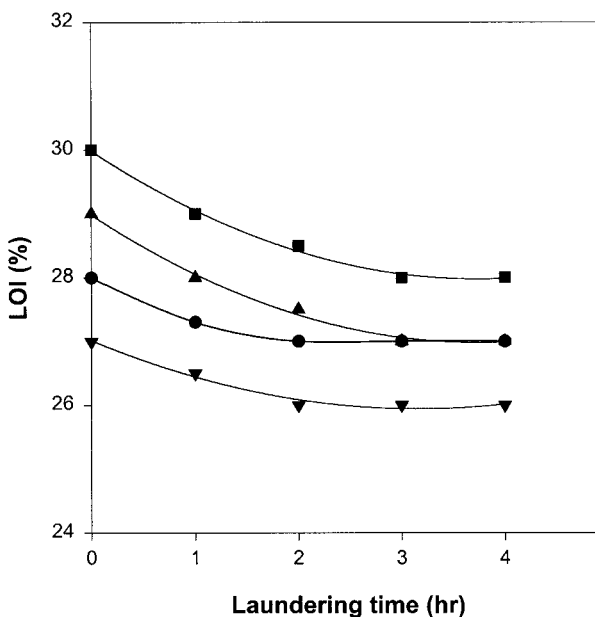


Figure 8 The LOI variation of flame-retardant PET fabric and PET/cotton blend fabrics according to the laundering time. (●) PET fabric treated with 15% (w/w) DCTBPP, (▼) blend fabric treated with 15% (w/w) DCTBPP and 25% (w/w) THPC/urea, (▲) blend fabric treated with 15% (w/w) DCTBPP and 30% (w/w) THPC/urea, and (■) blend fabric treated with 15% (w/w) DCTBPP and 35% (w/w) THPC/urea.

by a sequential treatment of DCTBPP and THPC/urea precondensate, respectively. The durable flame retardation of the blend fabric was not accompanied by severe tensile strength loss and stiffness.

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