New Attempt at Flame-Retardation of Polyester/Cotton Fabric Blends

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Synopsis

Two new flame-retardation methods for polyester/cotton blend fabric were attempted with reference to thermal reactions of the blend fabric. One is the combination of phosphorylation of the cotton component and the addition of a phosphorus compound. The phosphorus compound must not interact with cotton component. The other involves the addition of a powerful flame retardant for the cotton component only. The flame retardant must induce only a small amount of carbonous products from the pyrolysis of the cotton component.

INTRODUCTION

This paper describes a new attempt to achieve flame retardation in polyester/cotton blend fabric.

A number of workers[1–7] have investigated the flammability behavior of polyester/cotton blend fabric in order to discover effective flame-retardation methods. Tessor[2] and Miller's[4] conclusions are significant. Phosphates such as tris(2,3-dibromopropyl)phosphate are known to be effective flame retardants for both polyester and cotton fabrics. However, their phosphates are ineffective for polyester/cotton blend fabrics. If we can answer the reason why the phosphate does not operate on the blended fabric, it would be easy to discover a new flame-retardation method for such fabric.

EXPERIMENTAL

Materials

Tris(2,3-dichloropropyl) phosphate, trihexyl phosphate, and trioctyl phosphate were prepeared from the corresponding alcohols and phosphorus oxychloride according to the method of Evans et al.[8] Tris(1,3 dichloropropyl)-2-phosphate was prepared by the method of Yoshino et al.,[9] which involves the reaction of epichlorohydrin with phosphorus oxychloride. Products were identified by IR and NMR spectroscopy. Tris(2,3-dibromopropyl) phosphate was provided by Marubishi Oil Co. Tris(2-ethylhexyl) phosphite and tridecyl phosphite were provided by Johoku Chemical Co. Ltd.

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Fabric and Fabric Treatment

Pure polyester fabric and 65/35 polyester/cotton blend fabric were obtained from Kurary Co. Ltd.: 75 denier, 120 × 90, plain weave, weight 94 g/m^2; 45^s, 142 × 70, plain weave, weight 115 g/m^2, respectively. Polyester/cotton blend fabric (50/50) was provided by Toyobo Co. Ltd.: 20^s, 42 × 40, plain weave, weight 106 g/m^2. We also use 100% cotton fabric (120 g/m^2). The fabrics (10 × 16 cm) were scoured in methanol to remove all residual spinning oils and immersed in benzene solution of phosphorus compounds. The fabrics were then squeezed using a nip roll of a laboratory pad and dried under reduced pressure.

Phosphorylation of Blend Fabric

The fabric (10 × 16 cm) was treated with phosphorous acid in dimethylformamide (DMF) solution of urea according to our previous method.[10]

Flame Retardancy Test

The oxygen index test was used to evaluate the limiting oxygen index of the treated fabrics.

Thermogravimetry

A Shinku-Riko thermogravimetric analyzer DGC-3 was used. All analyses were run in air atmosphere at a programmed rate of 2°C/min.

RESULTS AND DISCUSSION

Flame-Retardant Effect of Phosphates and Phosphites on Polyester/Cotton Blend Fabric

Thermoanalytical investigation has indicated that effective flame retardants for polyester fabric have acidic behaviors near temperatures where the polyester was degraded.[11] The flame retardants operate as an acid catalyzer of aldol condensation of ketones and aldehydes, which are flammable degradation products of the polyester. Acceleration of the condensation depresses the amount of flammable products, diminishing the flammability of the polyester fabric. Our proposed mechanism suggests that even phosphates and phosphites that contain no halogen atoms are effective flame retardants for polyester fabric. Some phosphates and phosphites were used as flame retardants for polyester. The results are shown in Table I. Every phosphate and phosphite used in this experiment was a satisfactory retardant, and their efficiencies were comparable to that of TBPP. Our assumption was supported. The treatment of polyester/cotton blend fabrics with these phosphates and phosphites was examined. With the cotton component blend, the flame retardant effect of these phosphates and phosphites decreased, as did that of TBPP. The decrease is independent of whether the flame retardants contain halogen atoms. Therefore, we assume that the decrease may result from the interaction of phosphorus compounds with the cotton component in the blend fabric. Thermal reactions were investigated.

TABLE I
Flame-Retardant Effect of Phosphates and Phosphites on Polyester/Cotton Fabrics

Phosphate or phosphite	Add-on, wt. %	P, %	Oxygen index, % Polyester	Polyester/cotton Blend Fabric 65/35	50/50	Cotton
None	0	0	22.4	16.7	16.2	17.8
$(CH_2BrCHBr\text{-}CH_2)_3PO$	5	0.24	26.2	19.9	19.0	21.8
	7.5	0.36	28.2	21.9	20.6	23.8
	10	0.48	30.0	23.5	22.1	25.7
$(CH_2ClCHCl\text{-}CH_2)_3PO$	5	0.40	25.2	19.8	18.2	22.7
	7.5	0.61	26.5	21.6	19.7	23.8
	10	0.81	27.8	23.4	23.1	24.8
$\left(\begin{array}{l}CH_2Cl \\ \quad > CH \\ CH_2Cl\end{array}\right)PO$	5	0.40	26.8	19.5	19.0	21.7
	7.5	0.61	29.0	21.0	20.2	23.6
	10	0.81	31.2	22.0	21.3	25.0
$(C_6H_{13}O)_3PO$	0.97	0.1	28.1	18.4	17.5	19.3
	2.9	0.3	28.1	19.3	18.0	20.2
	4.9	0.5	28.9	19.3	19.7	21.1
	7.8	0.8	29.4	20.6	20.2	21.1
$(C_8H_{17}O)_3PO$	1.4	0.1	28.8	18.4	17.1	18.4
	4.2	0.3	29.4	18.4	18.9	20.2
	7.0	0.5	29.8	18.9	19.3	21.1
	11.2	0.8	29.4	20.2	19.7	21.1
$(C_8H_{17}O)_3P$	1.3	0.1	26.8	17.5	17.5	—
	4.0	0.3	26.8	19.3	18.9	20.2
	6.7	0.5	26.8	21.1	19.2	21.1
	10.8	0.8	27.2	21.5	20.2	22.6
$(C_{10}H_{21}O)_3P$	1.6	0.1	27.2	17.5	17.5	19.7
	4.9	0.3	27.2	19.7	18.9	19.7
	8.1	0.5	27.6	20.6	19.7	21.9
	13.0	0.8	28.1	21.1	20.2	23.2

Thermal Degradation of Polyester/Cotton Blend Fabric and Treated Fabric Blends with Phosphate and Phosphite

Thermogravimetric curves for two polyester/cotton blend fabrics are shown in Figure 1. The weight loss for the blend fabrics proceeded in two stages. The first weight loss began near 270°C, and this degradation corresponds to the thermal degradation of cotton. The second occurred near 320°C, corresponding to that of polyester. The dotted lines shown in Figure 1 represent calculated lines of the blend fabric from the thermogravimetric curve for each component. The comparison of the observed curve with the calculated one indicates that blending of polyester and cotton components results in the acceleration of thermal degradation of polyester component in the fabric. The vigorous acceleration appeared at a high blending ratio of cotton component.

The addition of phosphates and phosphites influenced thermogravimetric behaviors of the blend fabrics. Some of the influences are shown in Figures 2

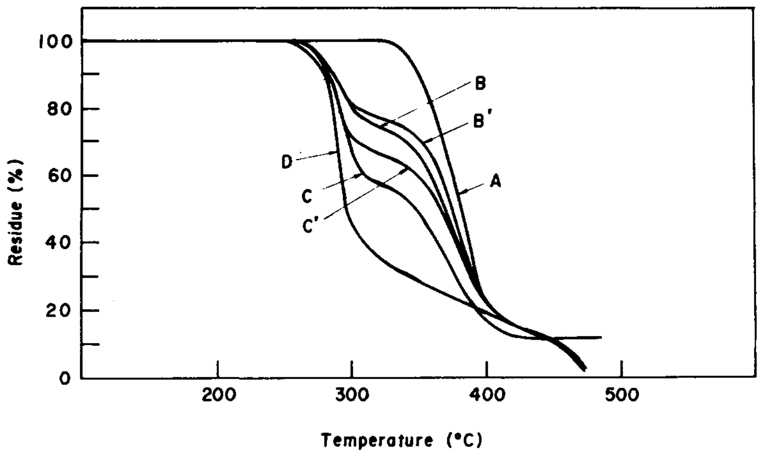

Fig. 1. Thermogravimetric curves for polyester/cotton fabrics: A, polyester; B, polyester/cotton (65/35); B′, calculated; C, polyester/cotton (50/50); C′, calculated; D, cotton.

and 3. The addition of halogen-containing phosphates resulted in shifting the initial temperature for weight loss to low temperatures. However, the addition did not influence the second degradation, that is, the degradation of the polyester component is independent. When other phosphates and phosphites were added, similar changes were observed (Fig. 3). These results indicate that in the presence of phosphates and phosphites, the thermal degradation of the cotton component alone in the blend fabric is accelerated and that the reaction of the polyester component remains unchanged. The selective acceleration is hard to understand from the observation that phosphates and phosphites can accelerate the thermal degradation of polyester fabric. The reason why the acceleration occurs will be considered. If Miller's conclusion that effective flame retardants for the blend fabrics must modify the thermal degradations for both components is true,[4] the selective acceleration contributes largely to the failure to diminish the flammability of the fabrics.

One of the reasons is that the distribution of adsorbed flame retardants in the

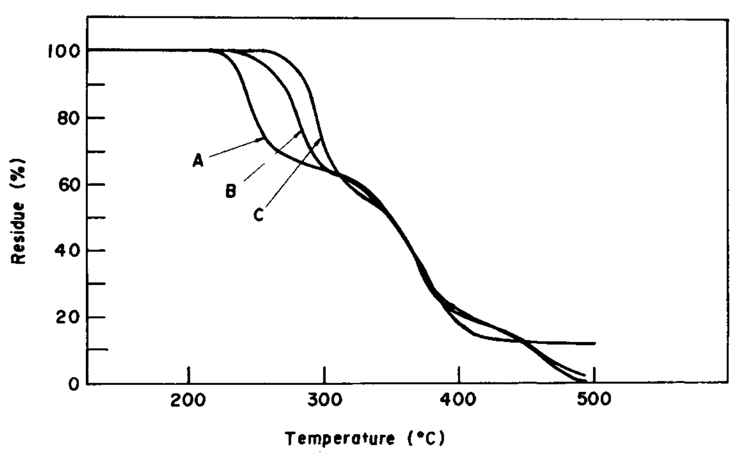

Fig. 2. Thermogravimetric curves for treated fabric blends with phosphorus compounds: A, Tris(2,3-dibromopropyl) phosphate; B, Tris(2,3-dichloropropyl) phosphate; C, untreated.

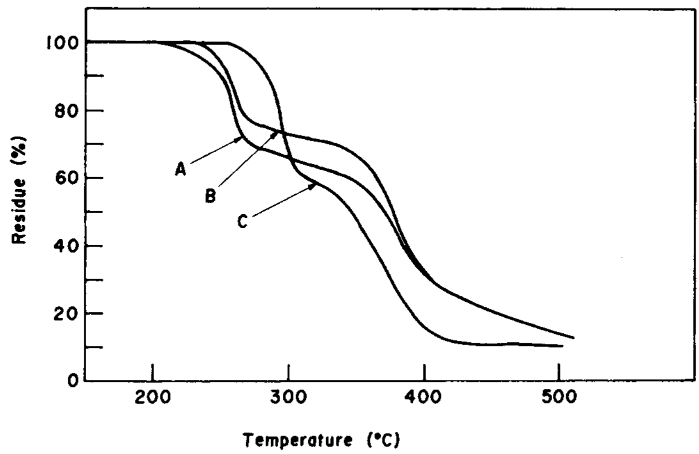

Fig. 3. Thermogravimetric curves for treated fabric blends (50/50) with phosphorus compounds: A, trioctyl phosphate; B, tridecyl phosphite; C, untreated.

blend fabrics is nonuniform. Pensa et al.[12] have already assumed that differences in the adsorption of flame retardants between the cotton and polyester components could contribute to failure of flame retardation of the blend fabrics. In order to equalize the distribution, they used acrylic latex as binder, but their attempt was unsuccessful. We examined whether this nonuniform distribution of flame retardants played an important role in accelerating the thermal degradation of the cotton component in the blend fabrics. TBPP was heterogeneously adsorbed on the polyester/cotton fabric: ground polyester sample (80 mesh) was treated with a benzene solution of TBPP, dried under vacuum, and then mixed with ground cotton sample (80 mesh) using an agate mortar. The thermogravimetric curve for this sample is shown in Figure 4. Despite the heterogenous deposition of TBPP, a similar acceleration of the thermal reaction of the cotton component was observed. It is not unreasonable that a large amount of TBPP deposited preferentially on the polyester component can

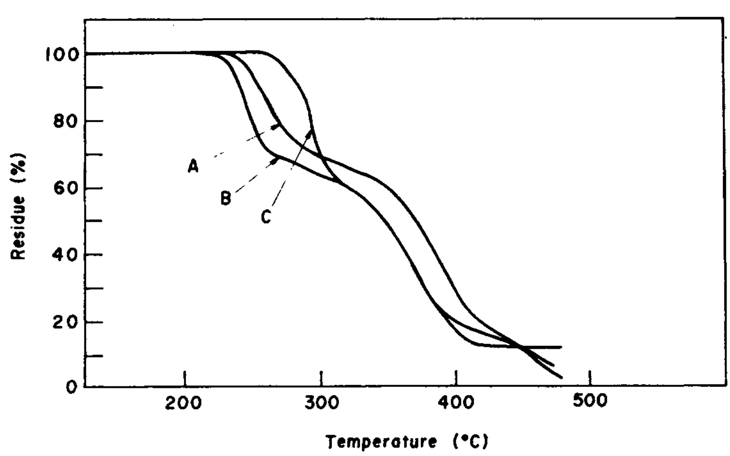

Fig. 4. Effect of the distribution of adsorbed TBPP on the thermogravimetric curve for blend fabrics: A, nonuniform distribution, deposited preferentially on polyester component; B, uniform distribution; C, untreated.

transfer to the cotton component and that the transferred TBPP interacts with the cotton component in the blend fabric. A similar conception, namely, that flame retardants can transfer to the cotton component, has been pointed out independently by Tessoro[2] and Miller.[4]

The acceleration of the thermal reaction of the cotton component was also confirmed by the IR spectroscopy. Figure 5 shows the IR spectrum of residual products from treated fabric blends (50/50) with TBPP. At 250°C the absorption band at 1600 cm^{-1} due to C═C groups appeared. At 350°C the initial changes in the absorption bands due to the polyester component were observed, new absorption bands appearing at 1780, 1200, and 1050 cm^{-1} due to

$$—O—\underset{\underset{O}{\|}}{C}—CH{=}CH_2$$

groups. It is assumed that the C═C groups at 1600 cm^{-1} result from interaction of TBPP with cellulose, that is, phosphorylation and elimination.[13] Therefore, the different reactivity of TBPP towards cellulose and polyester could contribute to the selective acceleration of thermal reactions.

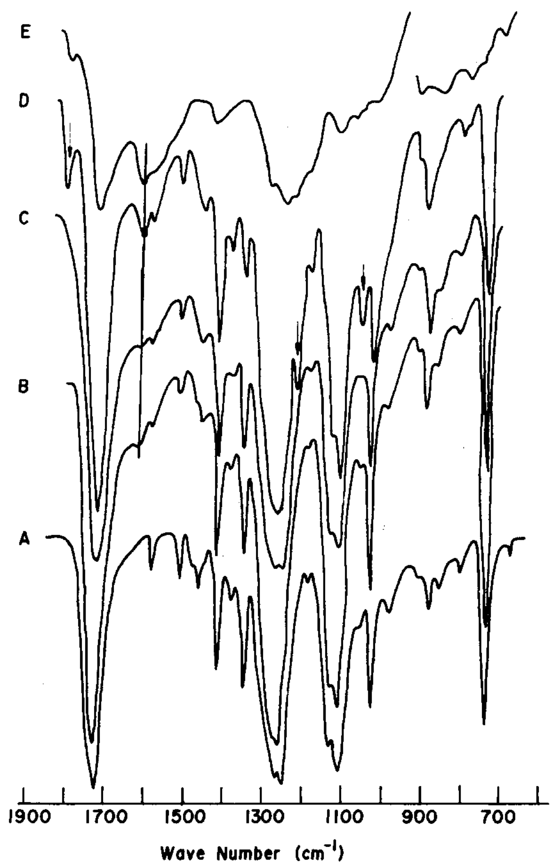

Fig. 5. IR spectra of the residual product from a TBPP-treated blend fabric (50/50): A, unheated; B, 200°C; C, 300°C; D, 350°C; E, 400°C.

New Attempt for Flame Retardation of Polyester/Cotton Fabrics

The results from the previous section indicate the following: phosphates react with the cotton component in polyester/cotton fabrics before the interaction with polyester component, that is, cotton is phosphorylated and the dehydration of cellulose is then accelerated to yield conjugated double bonds in cellulose chains. This behavior of phosphates gives two hints for flame-retardation of the blend fabric.

First hint: Before treatment with phosphates such as TBPP, the cotton component alone is phosphorylated. The effect of the phosphorylation was examined. The cotton component in the polyester/cotton blend (65/35) was phosphorylated using phosphorous acid,[10] and the flame-retardant effect was measured (Tables II and III). As shown in Table II the phosphorylation of the cotton part in the blend improves the flammability of polyester/cotton blends, but the effect is not satisfactory. Table III shows that the combination of phosphorylation and the addition of TBPP greatly improves the flammability, although the combination is not self-extinguishing. If effective phosphorus compounds that interact with the polyester part alone can be found, it is probable that the combination of the phosphorylation and the addition of the phosphorus compounds could be a useful method of flame retardation.

Second hint: The formation of conjugated double bonds by dehydration may induce a scaffolding effect. Flame retardants which result in only slight amounts of carbonous residual products are suitable to inhibit the scaffolding effect. $FeCl_3$ was chosen as one such flame retardant and its flame-retardant effect was examined (Table IV). $FeCl_3$ is effective for cotton fabric but ineffective for polyester fabric. The flame-retardant effect of $FeCl_3$ on the blend fabrics depended on the blending ratio of cotton component. The addition of about 10 wt. % $FeCl_3$ for two blended fabrics (50/50 and 65/35) proved to be self-extinguishing.

TABLE II
Loi Value for Phosphorylated Polyester/Cotton (65/35) Blend Fabric.

Sample	P, %	Loi, %
P-1	1.64 (4.69)[a]	23.7
P-2	1.65 (4.71)	23.7
P-3	1.71 (4.89)	22.4
Original		16.7

[a] Based on the cotton component.

TABLE III
Flame-Retardant Effect of TBPP on Phosphorylated Blend Fabric.

TBPP add-on, %	Loi (%) Polyester/cotton (65/35)	Loi (%) Phosphorylated blend[a]
0	20.6	23.7
5	20.1	25.2
7.5	21.9	25.1
10	23.4	26.6

[a] Sample P-1 from Table II.

TABLE IV
Flame-Retardant Effect of $FeCl_3$ on Polyester/Cotton

$FeCl_3$ add-on, %	Loi, %			
		Blend fabric		
	PET	65/35	50/50	Cotton
0	22.4	16.7	16.2	17.8
2	18.9	21.1	23.7	27.2
6	18.9	22.4	24.6	33.3
10	19.7	26.8	28.9	35.1

These findings suggest two possible flame-retardant finishings for the polyester/cotton fabric:

1. The combination of phosphorylation of the cotton component and the addition of a phosphorus compound. The phosphorus compound must not interact with cotton.
2. The addition of powerful flame retardant for the cotton component. The flame retardant must induce but small amounts of carbonous products resulting from pyrolysis of the cotton component.

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