Possible Phosphorus-Bromine Synergy in Polyester-Cotton Fabrics Treated with Tetrabromobisphenol-A and Diammonium Phosphate

EUI SO LEE

Department of Textile Engineering, Inha University, Inchon 402-751, Korea

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ABSTRACT: Polyester/cotton fabrics were treated with tetrabromobisphenol-A (TBBA)/epichlorohydrin (EPI) aqueous solution, followed by being treated with diammonium phosphate (DAP)/urea solution. The optimum mole ratio of EPI to TBBA was determined. The synergism of TBBA and DAP was found to operate on the treated fabrics. The maximal synergism was obtained when the bath concentration of TBBA was equal to that of DAP. The mechanism of flame-retardancy was analyzed by thermogravimetry and residue number. The flame-retardancy of the polyester/cotton fabrics treated with TBBA/DAP was found operative mainly in the condensed-phase mechanism. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 172–177, 2002; DOI 10.1002/app.10292

Key words: flame retardance; synergism; thermogravimetry; mechanism of flame retardance

INTRODUCTION

Cotton is pyrolyzed to volatiles and carbonaceous char at a lower temperature than polyester. However, polyester melts and drips at temperatures above its melting point of 260°C, and hence, shows self-extinguishing properties. In the case of polyester/cotton-blended fabrics, the molten polymer cannot drip or flow away from the flame sources. It remains dispersed between the charred cotton that brings about the scaffolding effect.[1] Therefore, the flame-retardancy of polyester/cotton-blended fabrics is worse than cotton or polyester alone.[2]A flame-retardant finish of polyester/cotton-blended fabrics can be carried out by treating it with phosphorous compound alone or phosphorous compound plus bromine compound. Durability of finish on treated fabrics is also very important in flame-retardant finishing of polyester/cotton-blended fabrics. In this study, the fabrics were treated with DAP and TBBA in a two-bath process, and flame-retardancy versus treatment condition or add-on of flame-retardant was investigated. The optimum mole ratio of EPI to TBBA was examined. Furthermore, the synergism of TBBA and DAP and the optimum ratio of two chemicals for the maximal synergistic effect were investigated. Finally, the flame-retardancy versus concentration of the flame retardant was analyzed.

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EXPERIMENTAL

Fabrics

Polyester 50%/cotton 50% blended twill fabrics, the yarn count of which was Ne 16 in both warp and weft, were used. The fabric count was 104

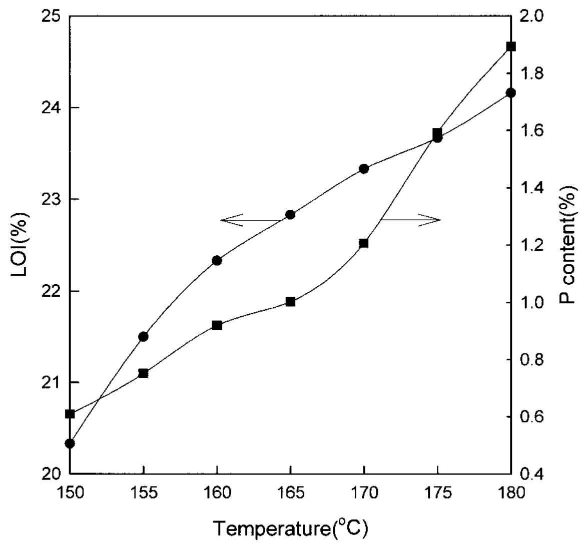


Figure 1 Phosphorus content and limiting oxygen index as a function of curing temperature for 3 min in DAP-treated fabrics. (DAP concentration: 25%; wet pickup: 65%).

ends/in. and 62 picks/in. Its weight was 251g/m^2. Fabrics were obtained as dyed from a mill.

Chemicals

Tetrabromobisphenol-A (TBBA; Great Lakes Co.) and diammonium phosphate (DAP; reagent grade) were used as flame retardants. Epichlorohydrin (EPI), methyl alcohol, urea, sodium hydroxide, and hydrogen peroxide were analytical grade. Sodium carbonate, Invadine LU (penetrating agent for TBBA), and Primazol NF (penetrating agent for DAP) were commercial grade.

Treatment of Fabrics

To determine the optimum mole ratio of EPI to TBBA, the padding solution was prepared as follows: TBBA was dissolved in NaOH solution to be 15%, and EPI was dissolved in methyl alcohol. The two solutions were mixed so that the mole ratios of EPI to TBBA were 0.5, 1.0, 1.25, and 1.5. Invadine LU (0.2%, owf) was added to the mixed solution. The fabrics were padded by 2 dip–2 nip method with wet pickup of 65%, batched in the polyethylene bag for 48 h, and then dried at 85°C for 3 min. Treated fabrics were immersed in 1.5 g/L sodium carbonate solution of liquor ratio 40 : 1 at 70°C for 10 min and then washed thoroughly with cold water. The padding solutions of DAP/urea were prepared as follows: the mole ratio of urea to DAP[3] was 1.0, and aqueous padding solutions with various concentrations of DAP ranging from 5 to 30% plus 0.2% (owf) Primazol NF were prepared. The fabrics were padded by 2 dip–2 nip method with wet pickup of 65%, dried at 85°C for 3 min, and cured at 160°C for 3 min. Treated fabrics were washed in 40°C water for 3 min and then rinsed thoroughly in cold water.

Test and Analysis

Analysis of Elements

The Schöniger flask method[4] for bromine and phosphomolybdate method[5] for phosphorus were used, respectively.

Limiting Oxygen Index (LOI)

ASTM D 2863 (Tester: Suga Co., Japan) standard was used to measure the LOI[6–8].

Thermogravimetric Analysis

A thermogravimetric analyzer (Model SSC-5200, Seiko Co., Japan) was used[9]. N_2 gas flow rate measured 100 ml/min and the temperature rise measured 10°C/min.

Residue Number[10,11]

$$\mathrm{Nr} = \frac{R_f/F}{R_u}$$

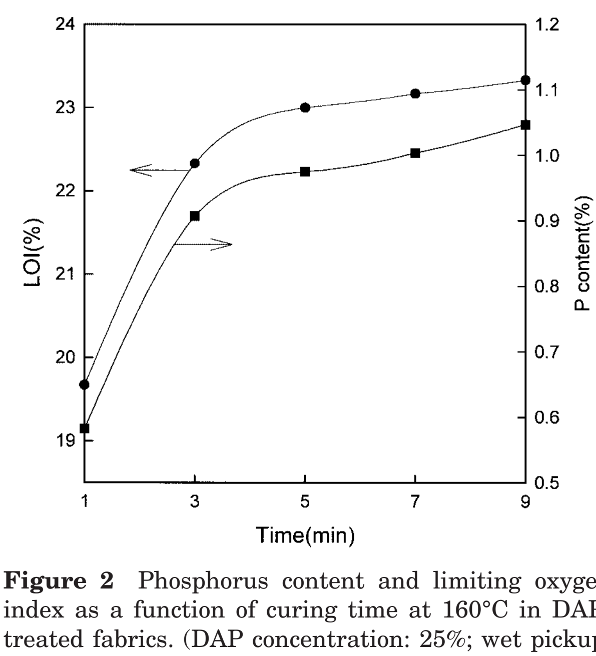


Figure 2 Phosphorus content and limiting oxygen index as a function of curing time at 160°C in DAP-treated fabrics. (DAP concentration: 25%; wet pickup: 65%).

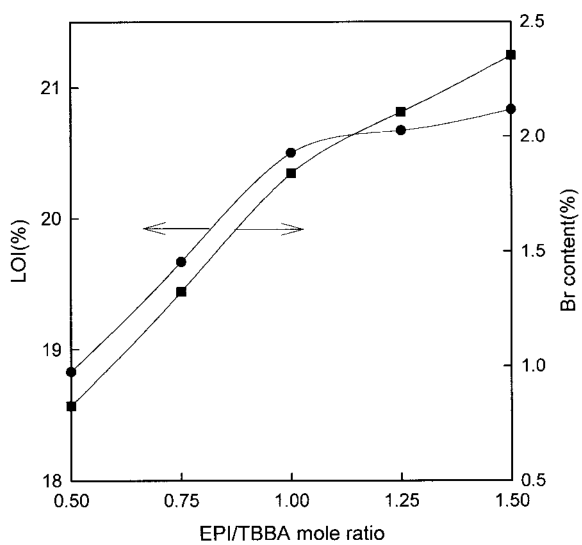


Figure 3 Bromine content and limiting oxygen index as a function of EPE/TBBA mole ratio in TBBA/EPI-treated fabrics. (TBBA concentration: 15%; wet pickup: 65%; batching time: 48 h).

where R_f is the wt % of residual char in the fabrics treated with flame-retardant; F is the weight fraction of fiber in the fabrics treated with flame-retardant; and R_u is the wt % of residual char in untreated fabrics.

Tensile Strength

ASTM D 1682-64 (1-in. raveled strip) was used to measure the tensile strength.

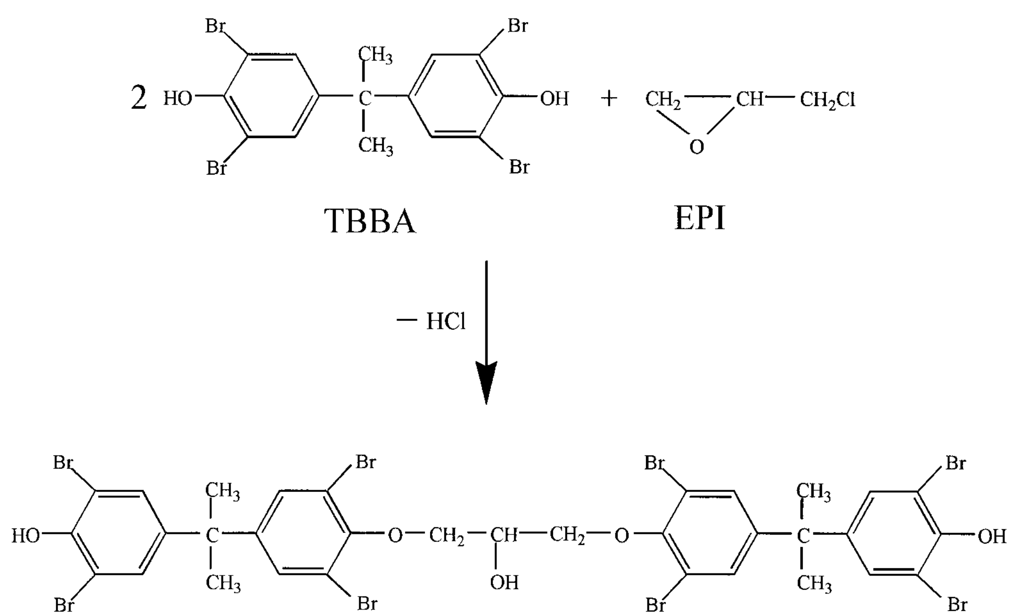
RESULTS AND DISCUSSION

Curing Temperature and Time for DAP Treatment

Figure 1 shows the phosphorus content and LOI as a function of curing temperatures ranging from 150 to 180°C for 3 min. The phosphorus content on treated fabrics increases as curing temperature increases. The LOI also increases almost linearly as curing temperature increases. The shade of treated fabrics shows yellowing above 160°C. The phosphorus content and the LOI of treated fabrics increase as curing time increases, as shown in Figure 2. However, not only their increment becomes small, but also the shade of treated fabrics shows yellowing above 3 min. From the results mentioned above, the curing condition hereafter was set to 160°C, 3 min.

Optimum Mole Ratio of EPI to TBBA

The bromine content and LOI of treated fabrics increase as the mole ratio of EPI to TBBA increases, as shown in Figure 3. This indicates that the add-on of TBBA on treated fabrics increases as the amount of EPI increases. However, when the mole ratio of EPI to TBBA exceeds 1.0, the increment of LOI becomes small and treated fabrics stiffened. Hence, the optimum mole ratio of EPI to TBBA is considered 1.0. It is considered that TBBA reacts with EPI to form insoluble compounds on the fabrics, as shown in Scheme 1.



Scheme 1 Hypotheical structure of TBBA-EPI.

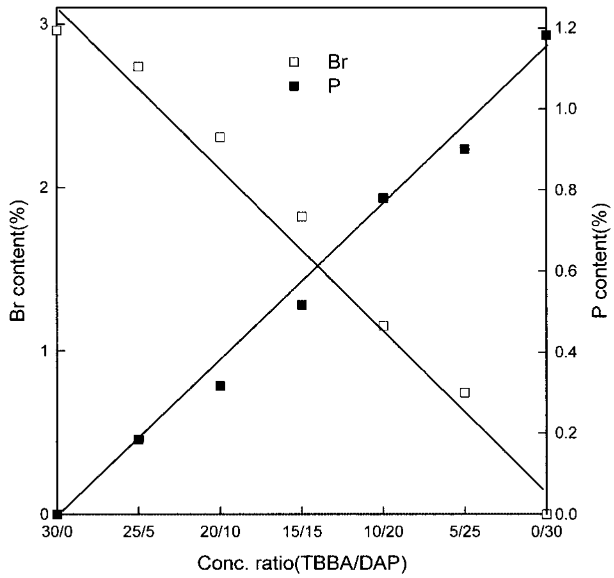


Figure 4 Bromine and phosphorus contents as a function of TBBA/DAP concentration ratio in treated fabrics. (Total concentration of TBBA and DAP: 30%; wet pickup: 65%).

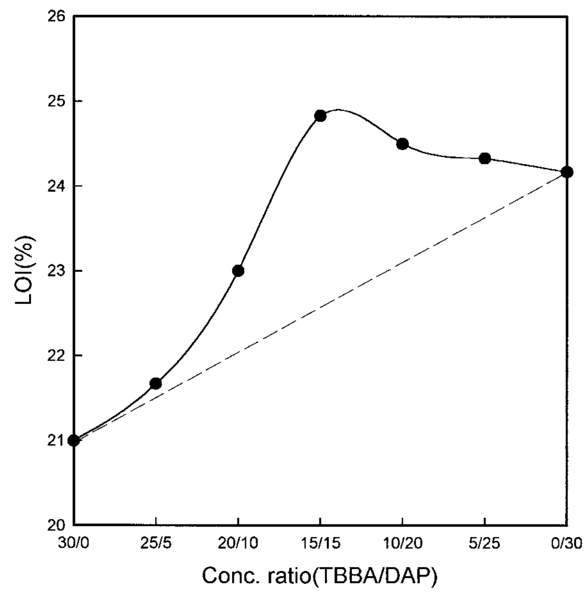


Figure 5 Limiting oxygen index as a function of TBBA/DAP concentration ratio in treated fabrics. (Total concentration of TBBA and DAP: 30%; wet pickup: 65%).

TBBA-DAP Synergism

Figure 4 shows the bromine or phosphorus content on treated fabrics versus concentration ratio of TBBA/DAP when total concentration of TBBA and DAP in the padding solution is 30%. The bromine or phosphorus content on treated fabrics increases linearly as the concentration of TBBA or DAP in the padding solution increases. In Figure 5, the solid curve shows the LOI as a function of the concentration of TBBA/DAP, as mentioned in Figure 4. The broken line indicates the predicted LOI values. We see that the LOI is greater than that predicted on the basis of additivity of the individual flame-retardant component. In other words, it is evident that there exists TBBA-DAP synergism in flame-retardancy.[12] The weight ratio TBBA : DAP of 1 : 1 is found to yield the maximum synergistic effect.

LOI and Strength Retention of Treated Fabrics

When the fabrics are treated with the padding solutions containing TBBA/DAP, the percentage of which is 10/10, 15/15, 20/20, 25/25, and 30/30, their LOI value and tensile strength retention are 23.0, 24.8, 26.2, 27.7, 28.3, and 81, 80, 75, 77, and 74%, respectively. The tensile strength and LOI of untreated fabrics are 79.8 and 18.5 kg, respectively.

Analysis of Mechanism of Flame Retardancy

Thermogravimetric Analysis

Figure 6 shows that cotton fibers begin to be pyrolyzed at much lower temperature than polyester fibers. The temperature where the rate of pyrolysis reaches maximum is very different between two fibers. Furthermore, the residual char after pyrolysis is larger in polyester fiber than in cotton fibers. The curve (Experimental) indicates thermogravimetric curve of the sample consisting of 50% polyester and 50% cotton, whereas the

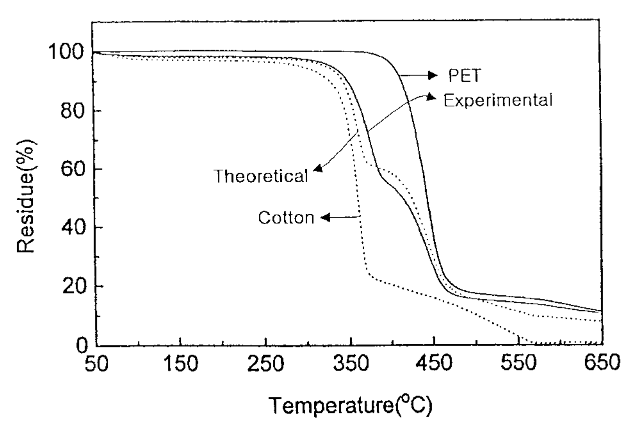


Figure 6 Comparison of thermogravimetric analysis curves for polyester 50%/cotton 50% blended fabrics with theoretical analysis curve.

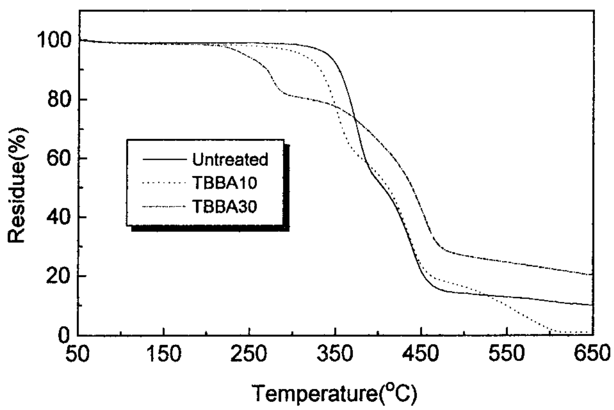


Figure 7 Thermogravimetric analysis curves for TBBA-treated fabrics.

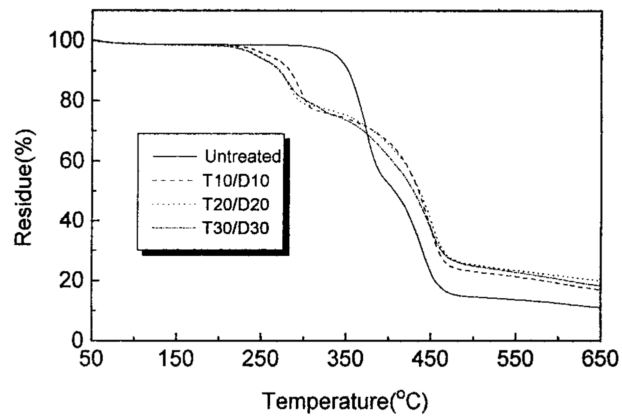


Figure 9 Thermogravimetric analysis curves for TBBA-DAP-treated fabrics.

curve (Theoretical) is the one from combining two curves of PET and cotton in the ratio of 50 : 50%. Two curves show some differences both in the range where the rate of pyrolysis is maximal and in the amount of residual char. This means there exists a certain interaction between two fibers when those are pyrolyzed together. Figures 7 and 8 show thermogravimetric curves of fabrics untreated or treated with TBBA or DAP, respectively. Pyrolysis of the fabrics treated with TBBA or DAP occurs earlier than that of untreated fabrics. Above a certain temperature, the rate of pyrolysis of treated fabrics becomes slower than that of untreated fabrics. The amount of residual char versus the add-on of TBBA does not show any tendency. This means that the gas-phase mechanism is mainly operative in the polyester/cotton fabrics treated with TBBA. However, the amount of residual char increases as the add-on of DAP increases. Therefore, the condensed-phase mechanism is found operative in the polyester/cotton fabrics treated with DAP.[12] As shown in Figure 9, the condensed-phase mechanism mainly operates in the fabrics treated with TBBA/DAP combination, considering the residual char.

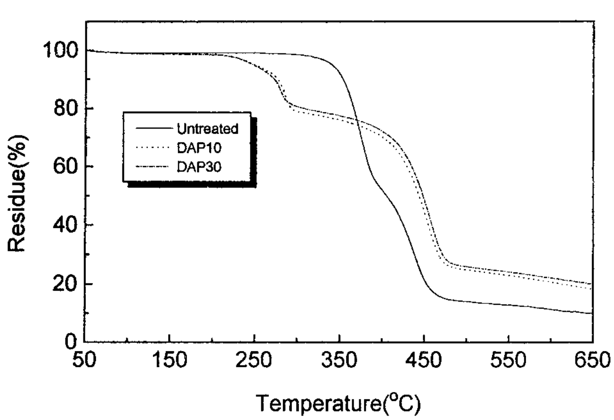


Figure 8 Thermogravimetric analysis curves for DAP-treated fabrics.

Residue Number

Pensa and Sello[11] suggested the concept of residue number to clarify the mechanism of flame-retardancy. In the condensed-phase mechanism, both the LOI and the residue number (Nr) increase as the add-on of the flame retardant on treated fabrics, whereas in the gas-phase mechanism, the LOI increases, but residue number does not increase. The fact that the condensed-phase mechanism mainly operates in the fabrics treated with TBBA/DAP combination is reconfirmed from the data in Table I, because both the LOI and the Nr of the fabrics treated with TBBA/DAP combination increase as the add-on of them increases.

CONCLUSION

Various processing conditions were investigated when polyester 50%/cotton 50% fabrics were pad-

Table I Residue Number and LOI of TBBA-DAP-Treated Fabrics

Sample	R_f (%)	F	Nr	LOI
TBBA 10/DAP 10	16.74	0.87	1.76	23.0
TBBA 20/DAP 20	19.75	0.74	2.45	26.2
TBBA 30/DAP 30	17.98	0.61	2.70	28.3

Weight % of residual char in untreated fabrics (Ru) = 10.91.

ded with TBBA/EPI aqueous solutions, batched, dried, and then treated with DAP/urea aqueous solutions by pad–dry–cure process to give a durable flame-retardancy. The optimum mole ratio of EPI to TBBA is found to be 1 : 1 in a viewpoint of bromine content, LOI value, and handle of treated fabrics. The optimum curing condition for treating DAP/urea is 160°C, 3 min, considering phosphorus content, LOI value, and shade of treated fabrics. The synergistic effect of TBBA and DAP is maximal when the concentrations of each component in each padding solution are equal to each other. The gas-phase mechanism is operative in the polyester/cotton fabrics with TBBA alone, whereas the condensed mechanism is operative when treated with DAP alone. However, the condensed-phase mechanism mainly operates when they are treated with TBBA/DAP combination.

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