

## The Effect of Poly(vinyl Bromide) on the Layering of Cotton Fibers in Flame-Retardant Cotton/Polyester Blends

EILEEN K. BOYLSTON and LINDA L. MULLER, *Southern Regional Research Center, Southern Region, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

### Synopsis

Cotton and cotton/polyester blends treated with phosphorus-nitrogen polymers and poly(vinyl bromide) for flame retardance were examined in the electron microscope. A considerable amount of the poly(vinyl bromide) was retained by the cotton fibers. Expansion studies indicated that the poly(vinyl bromide) acted either as a morphologic adhesive or as a non-polar matrix impervious to penetration by methacrylate before swelling.

### INTRODUCTION

Fabric flammability has become one of the most urgent technical problems confronting the textile industry, particularly since passage of the 1967 Federal Flammable Fabrics Act. Since many of the fabrics produced commercially are blends of cotton and synthetic fibers, flame retardants that are compatible with these blends must be developed. A durable flame-retardant finish developed for 100% cotton sheeting and 50/50 and 89/11 blends of cotton and Kodel polyester sheeting consisted of aqueous emulsions of tetrakis(hydroxymethyl)phosphonium chloride (Thpc), urea, trimethylolmethylglycoluril (TMMGU), and poly(vinyl bromide) (PVBr).<sup>1</sup> PVBr was added to the formulation as a flame retardant for polyester fibers in the blends; however, a considerable amount of the poly(vinyl bromide) was retained by the cotton fibers.

The purpose of this study was to determine the morphologic effect and location of the PVBr in the cotton fiber. In addition, the physical properties of the treated fabrics are reported. Studies were conducted on fabrics both before and after laundering.

### EXPERIMENTAL

Fabric samples of 100% cotton sheeting, 50/50 and 89/11 blends of cotton/Kodel polyester sheeting (all 4 oz/sq yd) were treated with aqueous emulsions of 20.5% Thpc, 6.5% urea, 3.0% TMMGU, and 4%, 8%, or 16% PVBr. A cotton control was treated with an aqueous emulsion containing the same Thpc-urea-TMMGU formulation without PVBr. The samples were padded through squeeze rolls to an average wet pickup of 90%, dried 4 min at 85°C, cured 4 min at 145°C, process washed, air dried, and subsequently treated with a 1% emulsion of mixed polyethylene-polypropylene softener.

Phosphorus contents were analyzed by the phosphomolybdate method, nitrogen by the Kjeldahl method, and bromine by a volumetric procedure using oxygen flask combustion.<sup>2</sup> Stiffness tests were by the Tinus Olsen Stiffness,<sup>3a</sup> and fabric flammability tests were by the Standard Vertical Flame Test,<sup>3b</sup> both of which are described in Federal Test Methods.

Yarns from treated fabrics were defibered, and small bundles of fibers were boiled in a 50% (v/v) aqueous solution of methanol containing 1% Aerosol wetting agent, covered, and left overnight in this solution. Wet fiber bundles were then embedded in partially polymerized butyl methacrylate and heated for 2 hr at 65°C. This thin sheet of poly(butyl methacrylate) containing the embedded fibers was trimmed of excess plastic and reembedded in partially polymerized 3:2 methyl and butyl methacrylate. Ultrathin cross sections of all embedded fiber samples were cut, and the embedding medium was removed with 2-butanone. The sections were platinum shadowed and examined in the Philips transmission electron microscope, Model EM-200.

## RESULTS AND DISCUSSION

All of the fabric samples (100% cotton and both blends) treated with the 4% PVBr were white and had a good hand even before treatment with a softener. Samples treated with either 8% or 16% PVBr were cream colored and felt slightly stiff. However, the hand of these fabrics improved considerably after they were treated with softener (Table I). After five laundry cycles, the all cotton fabric treated with 4% PVBr passed the standard vertical flame test, but both blended fabrics failed. All of the 100% cotton and blended fabrics treated with 8% or 16% PVBr and the cotton control treated with Thpc-urea-TMMGU were dur-

TABLE I  
Stiffness Values (in lb  $\times 10^{-4}$ ) of Flame-Retardant Fabrics and Control Fabrics

% PVBr	100% Cotton		50/50 Blend		89/11 Blend	
	Before	After softener	Before	After softener	Before	After softener
0	5.3	—	—	—	—	—
4	6.0	5.0	12.5	8.1	6.5	5.2
8	25.0	5.1	58.7	14.0	25.3	6.4
16	31.5	9.9	106.0	28.9	93.3	17.0
Untreated control	4.5	—	3.1	—	3.8	—

TABLE II  
Chemical Analysis of Flame-Retardant Fabrics

% PVBr	% P			% N			% Br		
	Cotton	50/50 Blend	89/11 Blend	Cotton	50/50 Blend	89/11 Blend	Cotton	50/50 Blend	89/11 Blend
0	2.3	—	—	3.3	—	—	—	—	—
4	2.1	2.2	2.0	3.0	2.7	2.8	1.8	1.8	1.8
8	2.2	2.2	2.1	3.1	2.8	3.0	3.4	3.6	3.4
16	2.1	2.2	2.1	3.1	2.8	2.9	6.5	6.8	6.7

TABLE III  
Chemical Analysis of Flame-Retardant Fabrics After 70 Laundry Cycles

% PVBr	% P			% N			% Br		
	Cotton	50/50 Blend	89/11 Blend	Cotton	50/50 Blend	89/11 Blend	Cotton	50/50 Blend	89/11 Blend
8	1.7	1.4	1.6	2.7	2.4	2.7	2.6	2.8	2.5
16	1.6	1.3	1.4	2.5	2.3	2.1	5.6	6.0	5.5

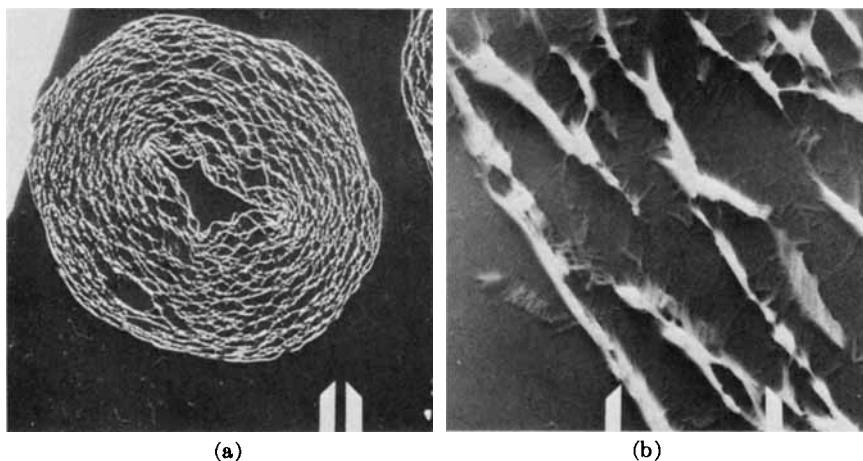


Fig. 1. Electron micrographs of cross sections of untreated control cotton after layer expansion. Distance between markers represents  $1 \mu$  here and in Figs. 2-8.

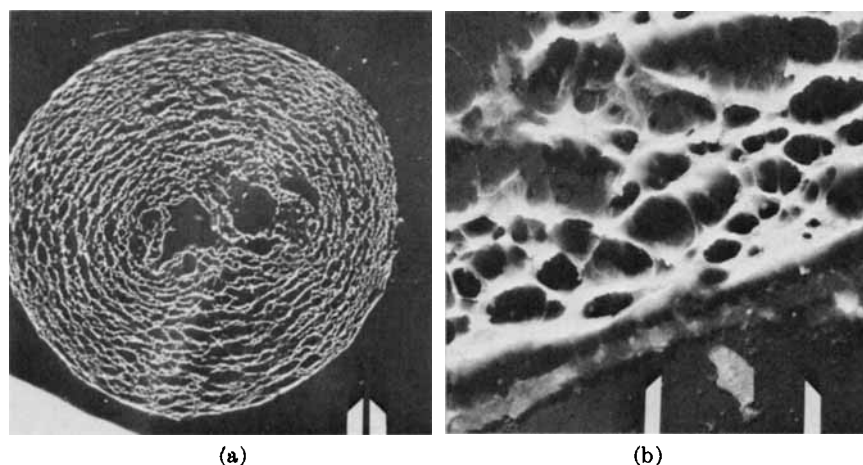


Fig. 2. Electron micrographs of cross sections of cotton from fabric treated with Thpc-urea-TMMGU and subjected to layer expansion.

ably flame retardant. Phosphorus and nitrogen analyses were approximately the same for all treated samples, and bromine contents varied according to the percentage of PVBr in the formulations (Table II). As the number of laundry cycles increased, the phosphorus, nitrogen, and bromine contents of the samples decreased. These contents after 70 laundry cycles are shown in Table III.

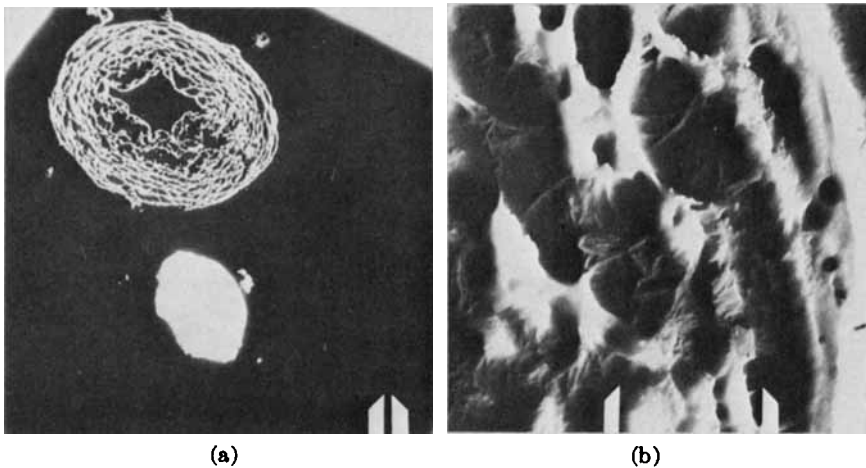


Fig. 3. Electron micrographs of cross sections of cotton from 50/50 blend treated with Thpc-urea-TMMGU and 4% PVBr, and subjected to layer expansion.

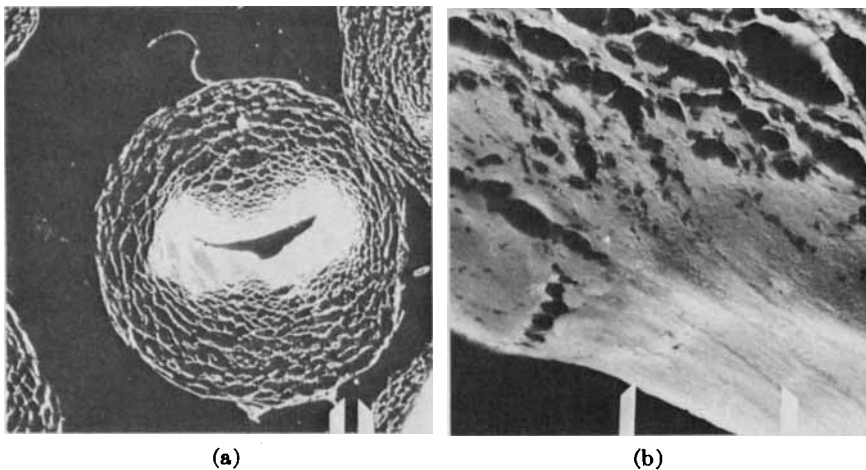


Fig. 4. Electron micrographs of cross sections of cotton from 89/11 blend treated with Thpc-urea-TMMGU and 8% PVBr and subjected to layer expansion.

Rollins and co-workers<sup>4</sup> used the layer expansion technique in electron-microscopic evaluations of mercerized, crosslinked, grafted, and other chemically modified cottons. Untreated wet cotton fibers embedded in methacrylate swell enormously, and the secondary cell wall forms concentric layers (Fig. 1). Dry fibers do not swell and have an almost solid structure. This layering is considered an artifact caused by differential rates of polymerization and concentrations of methacrylate inside and outside the cotton fiber.<sup>5</sup>

The layer expansion technique was utilized in studying the effects of PVBr on cotton fibers in cotton/polyester blends treated for flame retardancy. Representative samples are shown in Figures 2-8. Cotton fibers from fabrics rendered flame resistant with the Thpc-urea-TMMGU formulation but without PVBr fully expanded into concentric layers (Fig. 2). Cotton fibers from 100% cotton fabrics and from both cotton/polyester blends treated with the same formulation

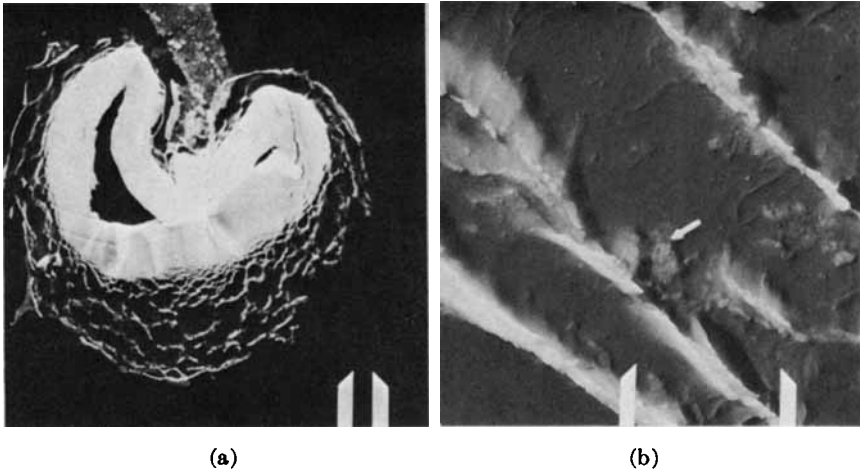


Fig. 5. Electron micrographs of cross sections of cotton from 50/50 blend treated with Thpc-urea-TMMGU and 16% PVBr and subjected to layer expansion. Arrow shows polymer deposited between layers.

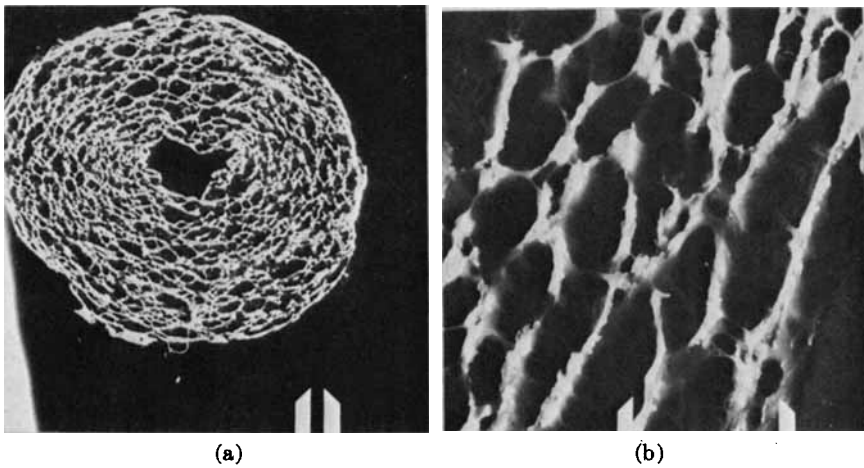


Fig. 6. Electron micrographs of cross sections of cotton from 89/11 blend treated with Thpc-urea-TMMGU and 8% PVBr laundered five times and subjected to layer expansion.

but with 4% PVBr also fully expanded (Fig. 3). However, those fibers from 100% cotton and blends treated with 8% or 16% PVBr expanded from the outer edges only.

Several layers were visible in fibers from fabrics treated with the 8% PVBr (Fig. 4), whereas only a few layers appeared in fibers from fabrics treated with 16% PVBr (Fig. 5). The cores of the fibers were solid. Polymer deposits adhered to the primary wall and occasionally could be detected between the expanded layers of the fibers and within the lumen.

After five laundry cycles, cotton fibers from all samples treated with 8% PVBr had completely expanded (Fig. 6), but those treated with 16% PVBr retained a solid center (Fig. 7). After 70 cycles, complete expansion from primary wall to the lumen was observed in all of the treated samples (Fig. 8).

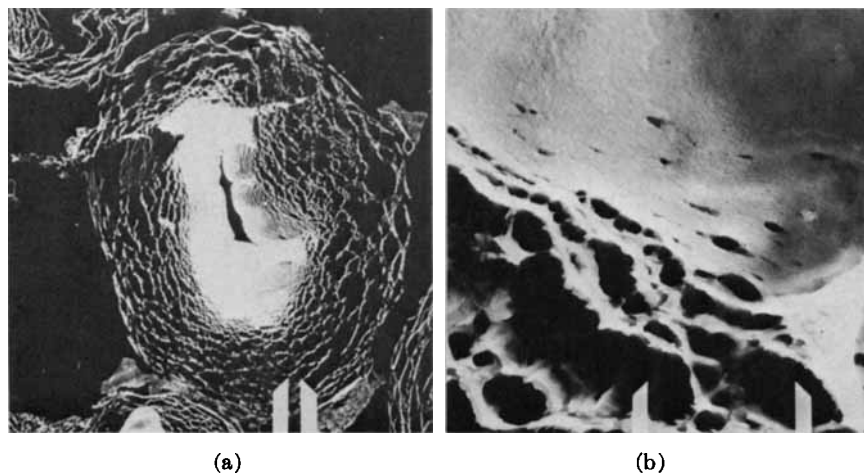


Fig. 7. Electron micrographs of cross sections of cotton from 50/50 blend treated with Thp-urea-TMMGU and 16% PVBr laundered five times and subjected to layer expansion.

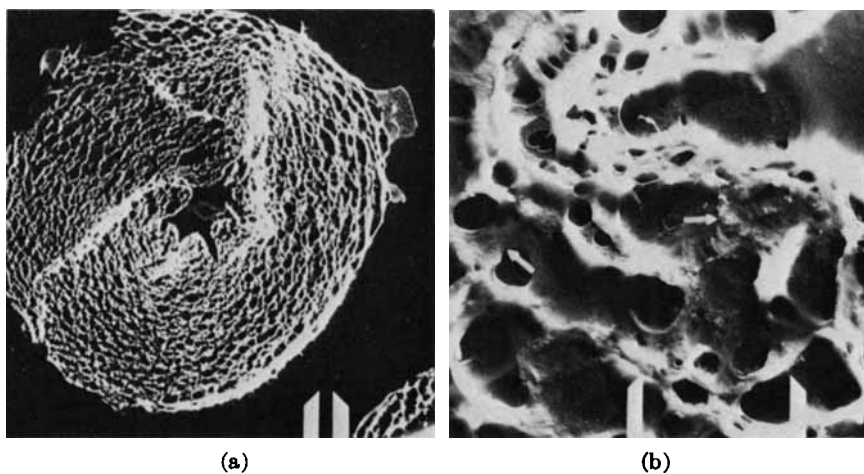


Fig. 8. Electron micrographs of cross sections of cotton from 50/50 blend treated with Thp-urea-TMMGU and 16% PVBr laundered 70 times and subjected to layer expansion.

### SUMMARY AND CONCLUSIONS

Electron-microscopic examination of fibers from flame-resistant fabrics treated with phosphorus-nitrogen and PVBr polymers showed that excess PVBr acted either as a glue preventing the separation of the cellulose layers within the cotton fibers or as a nonpolar matrix that was impervious to penetration by methacrylate before swelling. This excess deposited polymer is gradually removed by the laundering process. The addition of fabric softener aided in improving the hand of the fabrics but did not affect the PVBr deposited in the individual cotton fibers. Both blends treated with 4% PVBr had acceptable physical properties but were not durably flame retardant. The blends treated with 8% PVBr were durably flame retardant but had a slightly objectionable hand and discoloration. Therefore, a PVBr concentration between 4% and 8% could improve the flame

retardancy of cotton/polyester blends of this fabric type and weight without having a detrimental effect upon the cotton fibers in the blend.

The authors wish to thank R. Babin for the photographic reproductions, J. Bogatz for the textile tests, and John Mason for the phosphorus and nitrogen analysis. Throughout this paper, the mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

### References

1. D. J. Donaldson and F. Normand, *J. Fire and Flammability*, in press.
2. F. W. Cheng, *Microchem. J.*, **3**, 537 (1959).
3. Federal Test Method Standard W 191: (Dec. 1968), General Services Administration, Federal Property and Administrative Service Act of 1949, Superintendent of Documents, Washington, D. C., (a) Method 5202; (b) Method 5903.2.
4. M. L. Rollins, A. T. Moore, W. R. Goynes, J. H. Carra, and I. V. deGruy, *Am. Dyestuff Rept.*, **54**, 34 (1965).
5. J. Dlugosz, *Polymer*, **6**, 427 (1965).

Received August 29, 1974

Revised September 24, 1974