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A Laboratory Study of Flame-Retardant Textiles Produced by an Ionizing Radiation Cure¹

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Abstract

Methods for polymerizing triallyl phosphate on a cotton fabric were examined under conditions feasible for application in a commercial radiation textile finishing process. Although triallyl phosphate does not polymerize with irradiation at low dose levels at room temperature in air under the specific conditions described, it was found that copolymerization of triallyl phosphate with acrylic acid derivatives can be used to produce flame-resistant cotton fabric.

A cotton fabric treated with triallyl phosphate and N-methylol acrylamide and exposed to 2 megarads of radiation from high-energy electrons, in air at room temperature produced a flame-resistant fabric durable to 15 accelerated cotton mobile launderings.

Keywords

Fire Retardancy Treatments.
Cotton Fabrics; Phosphorus Compounds, Triallyl Phosphate.
Ionizing Radiation, Grafting; Facilities.
Triallyl Phosphate, Copolymers, Acrylamide, Acrylonitrile; Concentration; Fire Resistance; Laundering; Tear Strength, Elmendorf Tear Strength.
Chemical Analysis.

Introduction

The advantages and recent applications of high-energy radiation to modify the properties of textiles

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have been reviewed by V. Stannett [3]. Equipment for high-energy irradiation of textiles on a commercial scale is now available for use in the textile industry. However, the types of finishes currently available for application by means of irradiation are limited to durable-press and soil-release finishes. The fact that curing with irradiation is possible at room temperature extends the types of compounds having potential as textile finishes to low-boiling monomers

which cannot be used in the conventional finishing processes.

A laboratory-scale study was made to determine the possibility of imparting flame resistance to textiles by curing a phosphorus-containing monomer in a fabric with irradiation under conditions feasible for a commercial radiation finishing process. A low dose level with irradiation at room temperature in air are the most desirable conditions.

Experimental

Radiation Sources

The radiation sources, which have been described earlier [2] were a 24 MeV, 18 kW electron LINAC and a 1.25×10^6 Ci ^{60}Co isotope source. Gamma irradiation was under ambient conditions with a dose rate of $2.84\text{--}3.86 \times 10^4$ rads/min. Electron irradiation consisted of scanning the sample with an electron beam approximately $3\text{--}4/\text{cm}^2$ in area as the sample moved through the beam path on a conveyor. The scan width was 16 in. and the dose rate, while the pulsed beam was on, was 10^7 rads/sec. The repetition rate was 60 pulses/sec and the pulse duration was 5 microsec.

Fabric

The fabric was an 8.2 oz/yd² carded cotton sateen, vat-dyed OG 107, made in accordance with military specification MIL-C-10296. Approximately 1 ft² of samples of the fabric were dipped in the treating solutions and squeezed to a wet pickup range of either 60% or 100%. The samples were placed in 4-mil polyethylene bags. Trials also included fabric samples not enclosed in bags. The samples were held in a vertical position during irradiation. The samples then were rinsed in hot water (40°C) for 2 min and dried at 100°C in an oven.

Test Methods

Nitrogen analysis was by the Kjeldahl procedure. Phosphorus analysis was by conversion to the orthophosphate, precipitation with ammonium molybdate, and titration of the precipitate. Flame resistance was measured by means of the Vertical Bunsen test (Method 5903, Federal Spec. CCC-T-191). Laundering was by Method 5556 of Federal Spec. CCC-T-191, which consists of a series of suds and rinse cycles using a detergent and sour. The highest temperature of the wash was 140°F. Elmendorf tear strength was by Method 5132 of Fed. Spec. CCC-T-191.

Chemicals

The triallyl phosphate was obtained from Hooker Chemical Company and the Borden Company. The methylol acrylamide, a 60% aqueous solution, came from American Cyanamid Company.

Results and Discussion

Triallyl phosphate (bp 93–94°, 1 mm) was chosen as an example of a monomer containing phosphorus and susceptible to a free-radical initiated polymerization. The monomer itself, a liquid, is not a flame retardant. Only the brominated, partially polymerized triallyl phosphate and the fully brominated compound have been reported as flame retardants for textiles [1]. The time and temperature conditions required for polymerizing the monomer with heat and free-radical producing catalysts are not suitable for a finishing process. Geffer [1], lists a typical example of these conditions. A solid polymer was obtained after refluxing triallyl phosphate for 6 hr at 100°C in a nitrogen atmosphere with 1.5% benzoyl peroxide as the catalyst.

Irradiation of Triallyl Phosphate-Treated Cotton

The initial trials, in which the cotton fabric was treated with monomer and irradiated with doses up to 24 megarads, indicated that triallyl phosphate did not polymerize within the required low dose level that would be suitable for a finishing process. The irradiated samples showed no visual evidence of polymerization when subjected to 10 megarads (^{60}Co) and burned both before and after rinsing. With a 24-megarad (^{60}Co) exposure, a polymer formed on the fabric. The rinsed sample showed some evidence of flame resistance. After surface burning, the flame extinguished.

Free-Radical Concentration

Since the initial trials indicated that the monomer itself would not polymerize within low dose levels, inducing conditions were tried and varied to influence the free-radical concentration during irradiation. These were a possible increase in free-radical concentration due to shorter oxygen contact time and a possible increase in free-radical yield due to the presence of water. The extremely high dose rate of the LINAC represents a shorter oxygen contact time for the sample than the same dose level from the ^{60}Co source. The high dose rate of the accelerator

could also result in much greater free-radical recombination, which would mean a larger dose required for polymerization. Fabric samples treated with a solution containing 60% triallyl phosphate, 20% methanol, and 20% water were subjected to 6 megarads (^{60}Co). Samples treated with a solution containing 66% triallyl phosphate, 17% methanol, and 17% water were subjected to 4 megarads (LINAC). However, neither the presence of water nor the shorter exposure time of the LINAC resulted in evidence of polymerization or flame resistance to the samples of triallyl phosphate-treated cotton fabric within the desired low dose level.

Copolymerization

The next inducing condition examined was copolymerization. Geffer [1] points out that the allyl esters of phosphorus acids are not readily polymerized. Their polymerizability is less than that of the

corresponding esters of carboxylic acids. Although both triallyl and diallyl esters can be polymerized, esters of phosphorus acids with one allyl group may form only low molecular-weight polymers or be incapable of polymerizing. However, allyl esters of phosphorus acids may take part in a copolymerization regardless of the number of unsaturated groups present. Since copolymerization is a forcing condition for esters with one allyl group, it is possible that copolymerization could be an inducing condition for the more reactive triallyl esters when subjected to a condition under which they did not polymerize, such as low dose levels of irradiation.

It was found that a cotton fabric treated with triallyl phosphate and a comonomer, when irradiated at low dose levels, produced a flame-resistant fabric. The comonomers were acrylamide, acrylonitrile, and N-methylol acrylamide (Table I).

TABLE I. Copolymerization of Triallyl Phosphate on Cotton Sateen (^{60}Co)

Triallyl phosphate, g	Comonomer, g	TAP/Comonomer, wt	Dose, Me-garads	Flame Resistance				
				Initial		15 washes		
				AF, sec	CL, in.	AF, sec	CJ, in.	
10	Acrylamide	10	1/1	6	0	3.9	burned	
10	Methyl methacrylate	10	1/1	6	burned			
10	Acrylonitrile	7	1/0.7	6	0	7.1	burned	
15	N-methylol acrylamide	9	1/0.6	4	0	3.6	0	3.7
20	Acrylic acid	20	1/1	4	0	4.6		

TAP = Triallylphosphate.

AF = After flame, sec.

CL = Char length, in.

N-methylol acrylamide, which has been introduced as an irradiation-cure, durable-press finish [4], was examined in greater detail. Trials were designed to determine the least solids content on the fabric which would produce flame resistance durable to washing, and also to determine the effect of dose level, comonomer ratio, bath dilution, and wet pickup on the amount of solids formed.

In all trials, the finishing bath was a solution. Triallyl phosphate is miscible in all proportions with a 60% aqueous solution of N-methylol acrylamide. When more dilute aqueous solutions were required, methanol was added to bring the precipitated triallyl phosphate into solution.

Figures 1 and 2 show a typical increase in solids content with dose level. The 8.2-oz cotton sateen was treated with N-methylol acrylamide and triallyl

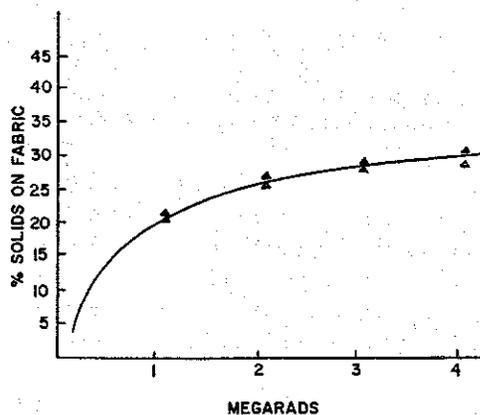


Fig. 1. Increase in solids content with dose for duplicate exposures (LINAC). The cotton sateen was treated with N-methylol acrylamide and triallyl phosphate (1/4.8 wt) with 100% approximate wet pickup.

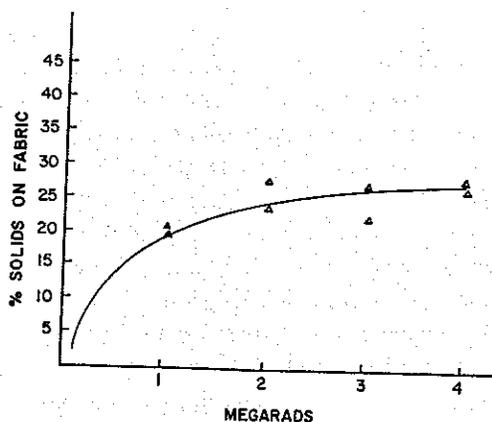


Fig. 2. Increase in solids content with dose for duplicate exposures (^{60}Co). The cotton sateen was treated with N-methylol acrylamide and triallyl phosphate (1/4.8 wt) with 100% approximate wet pickup.

phosphate with approximately 100% wet pickup in a ratio of 1 part by weight of N-methylol acrylamide to 4.8 parts of triallyl phosphate. Figure 1 shows the effect of exposure to electrons from a linear accelerator at doses up to 4 megarads while Figure 2 shows the effect of exposure to the same dose level from ^{60}Co gamma rays. The great difference in dose rates between the two sources had little effect on the percent solids formed.

The flame resistance of the fabric samples (Fig. 1) subjected to 1-4 megarads (LINAC) is shown in Table II.

TABLE II. Flame Resistance of Fabric with N-Methylol Acrylamide and Triallyl Phosphate (1/4.8)

Dose, megarads, (LINAC)		1	2	3	4
Initial flame resistance (rinsed)	AF, sec	0	0	0	0
	CL, in.	5.7	4.8	5.6	4.7
Flame resistance (after 15 launderings)	AF, sec	5	0	0	0
	CL, in.	9.2	5.7	5.2	4.8

In studying the effect of comonomer ratio, it was found that the composition of the finish varied with the composition of the finishing bath. In free-radical copolymerization, a correspondence between the copolymer composition and the monomer ratio is expected. (Most of the copolymers used as textile finishes are condensation copolymers, thus bath monomer ratios have no effect on the finish composition.) The percent of each of the comonomers present in the finish was obtained by elemental analysis, since N-methylol acrylamide was the only nitrogen-containing compound and triallyl phosphate was

the only phosphorus compound present. Figure 3 illustrates the variation in the percent polymerized triallyl phosphate and N-methylol acrylamide in the fabric finish with the variation in the composition of the finishing bath. Elemental analyses are listed in Table III.

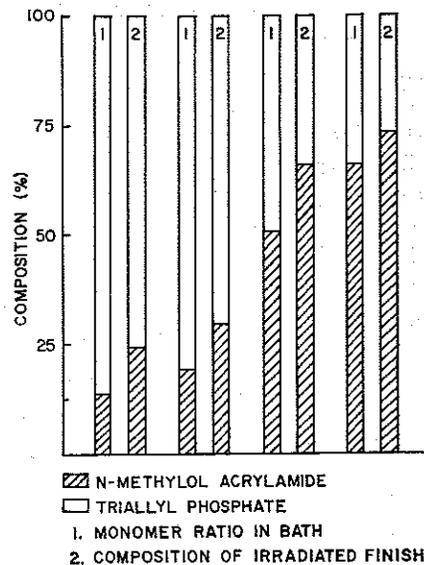


Fig. 3. Variation in composition of the finish with variation in monomer content of the finishing bath.

The monomer ratio also influenced the percent conversion to solids. Figure 4 illustrates the increase in conversion with increasing N-methylol acrylamide content. Although dependent upon the ratio, the percent conversion was independent of the amount of compound present. For the same monomer ratio and dose level, wet pickup of 20-100%

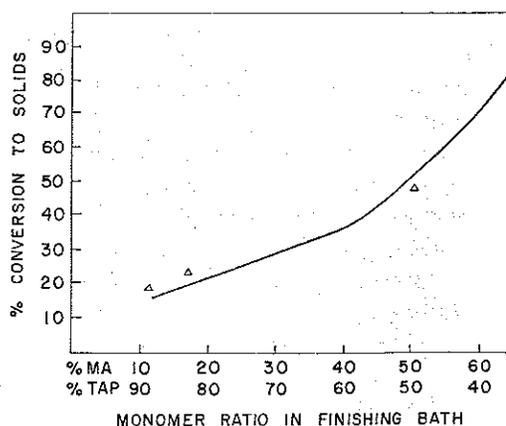


Fig. 4. Variation in % conversion to solids on the finished fabric with variation of monomer ratio in finishing bath.

had the same percent conversion to solids after rinsing. Dilution with water and methanol had little effect on the percent conversion. For example, the percent conversion was the same for a 60% wet pickup as for a 100% wet pickup which contained 60% of the same comonomer ratio.

TABLE III. Effect of Variation in Comonomer Ratio on Finish Composition
(As Shown by Nitrogen and Phosphorus Content)

Bath composition NMA, TAP, wt	Wet, pickup, %	Dose level, megarads (LINAC)	Finished fabric				
			Add-on, wt%	Nitro- gen, %	NMA, % (by anal)	Phos- phorus, %	TAP, % (by anal)
1/8.3	114	2	17 ^a	0.47	3	1.54	11
1/8.3	118	2	16 ^a	0.45	3	1.42	10
1/4.8	110	3	33	1.27	9	1.98	14
1/1	63	3	31	2.86	21	0.67	5
1/1	110	3	22	2.08	15	0.55	4
1/0.5	109	3	19	1.86	13	0.61	4

NMA = N-methylol acrylamide.
TAP = Triallyl phosphate.

^a After 15 launderings.

TABLE IV. Variation of Flame Resistance with Monomer Ratio

NMA/TAP, wt	Dose level, megarads (LINAC)	Add-on, %	Phos- phorus, %	Initial flame resist.		After 15 launderings	
				AF, sec	CL, in.	AF, sec	CL, in.
1/0.5	3	19	0.65	0	5.7	Burned	
1/1	3	31	0.67	0	4.5	Burned	
1/1	3	22	0.55	0	5.1	Burned	
1/3	3	24		0	5.1	0	5.4
1/4.8	3	33	1.98	0	4.7	0	4.8
1/4.8	2	26		0	4.8	0	5.7
1/8.3	2	17	1.54	0	5.6	0	4.0

NMA = N-methylol acrylamide.
TAP = Triallyl phosphate.

Table IV lists the variation in flame resistance of the cotton sateen with variation in the comonomer ratio.

The least amount of add-on that gave flame resistance durable to 15 launderings was 17%, obtained with a dose level of 2 megarads and a comonomer ratio of 1 part of N-methylol acrylamide to 8.3 parts of triallyl phosphate. For the same add-on range of 17-33%, flame resistance not durable to laundering was obtained when the amount of triallyl phosphate equalled or was less than the amount of N-methylol acrylamide present; flame resistance durable to laundering was obtained when the amount of triallyl phosphate was three times the amount of N-methylol acrylamide or greater. The amount of phosphorus present on the fabric for durable flame resistance was

TABLE V. Tear Strength of Cotton Sateen Treated with N-Methylol Acrylamide and Triallyl Phosphate (1/4.8 wt); Dose 3 Megarads (LINAC)

Add-on, %	Initial		After 15 launderings	
	Tear strength (w × f), lb	Add- on, %	Tear strength (w × f), lb	Add- on, %
21	4.4 × 4.6	22	3.1 × 2.1	
26	4.4 × 3.5	25	3.1 × 2.0	
28	4.3 × 3.4	24	3.1 × 2.1	
31	3.6 × 3.1	25	2.8 × 2.1	
30	5.0 × 4.4			
Untreated	12.8 × 13.4			
Untreated (4 megarads)	9.4 × 10.1			

in the range of 1.5%. Examples of the tear strength of the treated fabric are shown in Table V.

Conclusions

Methods of polymerizing triallyl phosphate on a cotton fabric were examined under conditions feasible for application in a commercial, radiation textile finishing process. These conditions were irradiation at low dose levels at room temperature in air.

Triallyl phosphate does not polymerize to produce a flame-resistant fabric under the conditions which included variations designed to maximize the free-radical concentration, such as a high dose rate to decrease oxygen exposure time and the presence of water to increase the free-radical concentration.

It was found that copolymerization is a technique that can be used to polymerize on fabrics unsaturated phosphorus monomers within low dose levels in air at ambient temperature. Comonomers used were acrylic acid, acrylamide, N-methylol acrylamide, and acrylonitrile.

A cotton fabric treated with triallyl phosphate and N-methylol acrylamide and exposed to 2 megarads of radiation from high-energy electrons in air at

room temperature produced a flame-resistant fabric durable to repeated washings.

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