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DIFFERENTIAL THERMAL ANALYSIS OF POLYESTER/COTTON BLENDS TREATED WITH Thpc–UREA–POLY(VINYL BROMIDE)

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ABSTRACT

Differential thermal analyses (DTA) were made on a series of polyester/cotton blend fabrics before and after treatment with Thpc–urea–poly(vinyl bromide). This flame retardant did not affect the polyester melting endotherm, which was proportional to the polyester content and appeared at approximately 250 °C. In nitrogen atmosphere, DTA of the treated blends showed exothermic peaks at 285 °C for the cotton decomposition, and at 415 °C for the polyester decomposition. In air, DTA of the treated blends showed exothermic peaks at 333 °C for cellulose decomposition, at 431 °C for polyester decomposition and at 490 °C for char decomposition. The Thpc–urea component of the flame retardant is effective on the cotton cellulose portion of the blend; the poly(vinyl bromide) appears to decompose and act in the vapor state on the polyester.

INTRODUCTION

Thermal analysis has been used for over ten years to evaluate textile fibers and fiber blends[1–3]. In addition, the effects of flame retardant treatments on cotton fabrics as measured by thermal analyses have been reported by Perkins et al.[4] and by Yeh et al.[5].

This laboratory has investigated the effects of tetrakis(hydroxymethyl)-phosphonium chloride–urea–poly(vinyl bromide) (Thpc–urea–PVBr) on thermal behavior of polyester/cotton blends. In the preceding paper, thermogravimetric (TG) analyses were reported by Neumeyer et al.[6]. This paper reports on the differential thermal analyses (DTA) of the polyester/cotton blend series of fabrics treated with Thpc–urea–PVBr.

EXPERIMENTAL

The blended polyester/cotton textiles used were the 4 oz/yd^2 64 × 64 fabric for the 0, 11, 20, 30, and 50% polyester contents, the 3 oz/yd^2 fabric for the 65% polyester content, and a fine yarn for the 100% polyester content as described by

Neumeyer et al.[6]. These fabrics were treated with two series of Thpc–urea–PVBr formulations: (1) FR-I-a formulation containing 30% Thpc–urea (1:1 molar ratio), 6.4% PVBr, 3% disodium phosphate, 0.1% wetting agent, and 60.5% water, which was applied to all of the blends, and (2) FR-II-a range of formulations containing approximately the same total solids in the padding baths, in which Thpc–urea content decreased from 35 to 26.3% while the PVBr content increased from 1% to 10% as polyester content in the blend rose[6]. Data on these fabrics are shown in Table 1. All of the treated samples passed the Department of Commerce test[7] with acceptable char lengths.

TABLE 1

FLAME RETARDANT-TREATED POLYESTER/COTTON BLEND FABRICS

				Flammability				
Polyester content (%)		*Add-on (%)*		*Oxygen index*			*Char length (in)*	
As labelled	*Clorox method*	*FR-I*	*FR-II*	*Untreated*	*FR-I*	*FR-II*	*FR-I*	*FR-II*
0	0.0	23.9	23.1	0.19	0.37	0.37	2.5	2.0
11	10.4	23.3	21.0	0.19	0.35	0.33	2.2	2.5
20	22.9	22.9	20.6	0.19	0.32	0.31	2.5	3.7
30	35.0	23.1	20.3	0.19	0.32	0.30	6.0	6.0
50	50.1	22.5	20.3	0.19	0.30	0.29	3.0	5.2
65	—	24.0	22.0	0.18	0.29	0.29	6.0	3.7

The DuPont 990 Thermoanalyzer* with the Differential Scanning Calorimeter module was used for the DTA. This system actually measures differential temperature and is, therefore, a differential thermal analyzer (DTA). The DuPont module employs a Boersma[8] type cell which contains small aluminum sample and reference pans mounted on a constantan thermoelectric disk which serves as one half of the sample and reference thermocouples. This arrangement minimizes the common DTA problems caused by changing heat capacities and thermal conductivities and by variabilities in embedding thermocouples in the samples[9]. Quantitative calculation of enthalpy changes follows: $\Delta H = K x A$, where ΔH is enthalpy change, K is the proportionality constant (determined experimentally for the instrument), and A is the peak area for the change involved[10]. A comprehensive discussion of thermal analysis methods and instruments is given by Wendlandt[11].

The procedure and conditions were selected to be similar to those of Neumeyer et al.[6] in order to make valid comparisons. These procedures and conditions were: Sample weight of approximately 10 mg; predrying of the sample to constant weight

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*Mention of companies or commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others mentioned.

at 150°C; atmosphere of 100% nitrogen or 20% oxygen–80% nitrogen at a flow-rate of 50 ml min^{-1}; heating rate of 5°C min^{-1}; and heating range of 150–575°C. The data were plotted on the 990 Thermoanalyzer two-pen recorder. In addition, the data were recorded on paper tape at 3 sec intervals using DuPont 915 computer interface and teletypewriter. The energy rate signal recorded (mcal sec^{-1}) was a composite of three independent effects: (1) Instrument baseline; (2) sensible heat, and, most important; (3) energy due to phase- and/or chemical change.

The instrument baseline was calculated as a function of temperature by means of a fifth-degree polynomial fitted to the blank data by the method of least squares, using data from several runs with empty sample and reference pans. Energy-rate data for each run was algebraically subtracted using a Control Data digital computer CDC-1700.

Continuous changing of both mass and heat capacity of the sample during the run complicated calculation of the sensible heat effect. Heat capacities of fabric measured at temperatures below decomposition and at the end of pyrolysis (char) were very close, and an average value was used. A thermogravimetric (TG) analysis was made for each sample[6]; this and the DTA data were normalized to a dry weight of 1. Weight changes for the TG and DTA runs were matched and the specific heat curve was calculated. This curve was algebraically subtracted from the baseline-corrected curve to eliminate the sensible heat effect.

The net heat effects of the chemical and physical changes occurring between any two arbitrary temperatures were determined by Simpson's Rule—numerically integrating the corrected and normalized DTA data. Instantaneous ΔH (in mcal mg^{-1}) at any temperature was obtained by dividing the DTA value (mcal sec^{-1}) by the TG derivative value (mg/sec). The ΔH's reported in the tables were obtained from computer calculations of the areas under the curves. Corrections were made to account for weight of the particular fiber in the blend that is actually responsible for the thermal effect.

Oxygen Index determinations were made as described by Isaacs[12]. Char length was determined by the Department of Commerce test FF 3-71[7].

RESULTS AND DISCUSSION

Nitrogen atmosphere

Differential thermal analyses. DTA curves obtained in nitrogen for the series of untreated polyester/cotton blends are shown in Fig. 1. Approximate peak temperatures for the three endotherms in the series and their assignments are: 250°C, melting of the polyester; 345°C, pyrolysis of cotton cellulose; and 420°C, pyrolytic degradation of the polyester. Peak temperatures for the pyrolyses of cotton and polyester, respectively, are not significantly affected by changes in polyester/cotton ratio. Peak temperatures, maximum rates of energy change which occur at the peak temperatures, and ΔH's for these endotherms are tabulated in Table 2. Maximum rates of energy change and ΔH's of pyrolysis were proportional to the concentrations

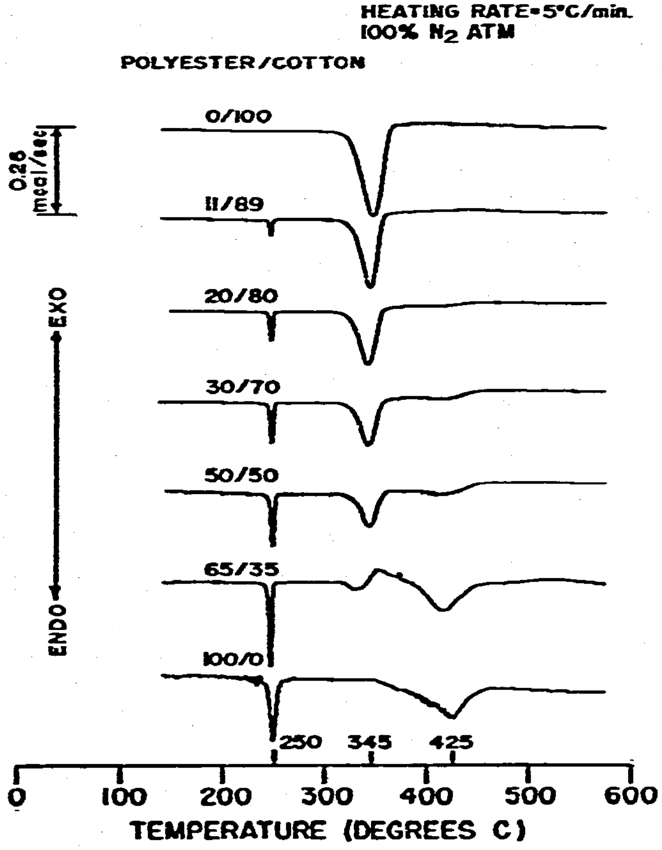

Fig. 1. Differential thermal analysis curves for polyester/cotton blend fabrics in nitrogen.

of components in the blends. A plot of the ΔH from the DTA data (in nitrogen) in Table 2 as a function of the polyester content of the blend is shown for the cotton and the polyester pyrolyses, respectively, in Fig. 2. The linear relationship indicates that the polyester's ΔH is independent of the presence of cotton cellulose. The straight line was drawn to intersect the two most reliable data points, namely, at 0 and 100% polyester contents, respectively. However, a non-linear relationship is apparent between the cellulosic ΔH and the amount of polyester present, suggesting that polyester melt affects cotton pyrolysis.

The DTA results obtained with the flame retardant treated (FR-I) polyester/cotton blend series are shown in Fig. 3. The dotted lines represent the baselines and help to illustrate presence of the polyester endotherm. The treatment had practically no effect on the polyester endotherms (melting at 250°C and pyrolysis in the char at 415°C), but cotton pyrolysis was radically changed. The original endotherm was converted to an exotherm, and the peak temperature was lowered from 345°C to approximately 285°C. Early work by Schuyten et al.[13] described these changes as accompanying the acid catalyzed carbonium ion dehydration and depolymerization of the cellulose. Table 3 shows the normalized rates of energy change and the ΔH's

TABLE 2

DTA FOR UNTREATED POLYESTER/COTTON BLENDS IN NITROGEN[a]

PE (%)				*Polyester*					
	Cotton pyrolysis[b]			*Melting*[b]			*Pyrolysis*[b]		
	Temp.[c] (°C)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[c] (°C)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[c] (°C)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)
0	348	0.260	89.4	—	—	—	—	—	—
11	345	0.205	61.6	248	0.045	2.3	—	—	—
20	343	0.162	53.6	248	0.080	3.8	415	0.006	12.5
30	343	0.131	48.5	249	0.117	6.6	420	0.013	21.5
50	343	0.094	44.5	249	0.147	9.8	417	0.022	31.2
65	332	0.018	—	247	0.239	11.1	419	0.077	—
100	—	—	—	250	0.178	18.7	426	0.092	57.9

[a] Heating rate, 5°C min^{-1}. [b] Endothermic change. [c] Temperature at maximum rate of energy change. [d] Normalized maximum rate of energy change.

TABLE 3

DTA FOR FLAME RETARDANT-TREATED (FR-I) POLYESTER/COTTON BLENDS IN NITROGEN[a]

PE (%)				*Polyester*				
	Cotton pyrolysis[b]			*Melting*[c]			*Pyrolysis*[d]	
	Temp.[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)
0	283	0.174	148	—	—	—	—	—
11	283	0.138	147	248	0.030	2.29	415	0.002
20	281	0.120	152	249	0.056	3.78	415	0.008
30	278	0.081	154	249	0.076	4.92	415	0.008
50	283	0.097	188	250	0.112	9.20	413	0.020

[a] Heating rate, 5°C min^{-1}. [b] Exothermic change. [c] Endothermic change. [d] Endothermic change. Calculations of ΔH's for polyester pyrolyses were not made due to interference of the cellulosic char exotherm. [e] Temperature at maximum rate of energy change. [f] Normalized maximum rate of energy change.

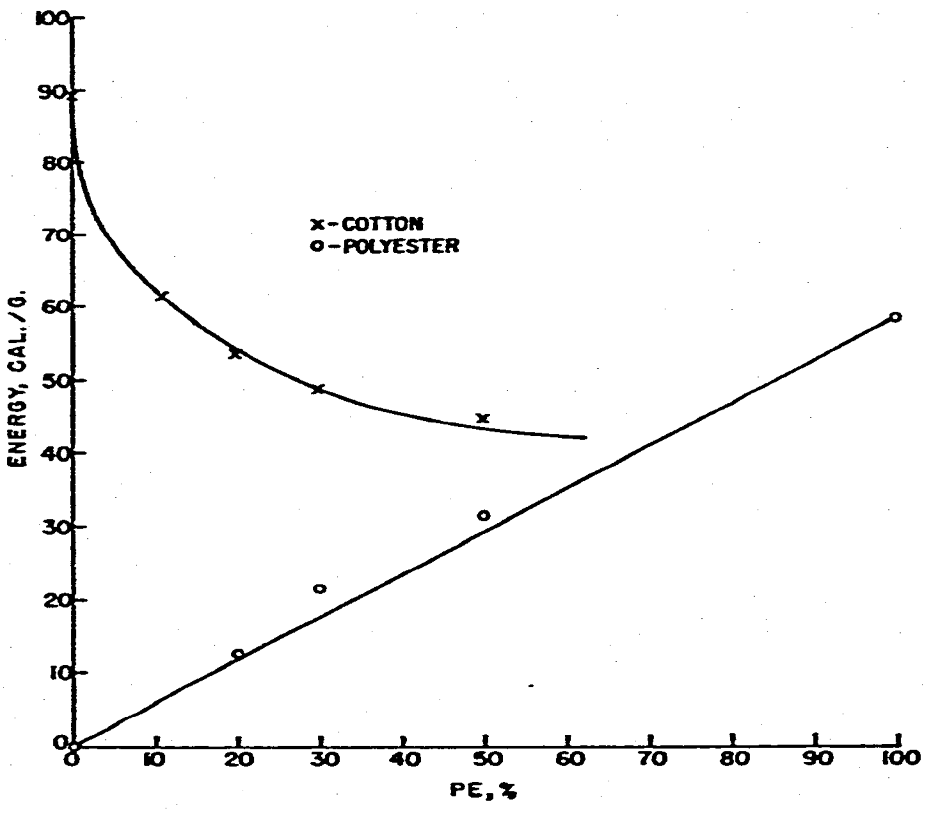

Fig. 2. Endothermic ΔH's for pyrolysis of polyester/cotton blend fabrics in nitrogen. × = cotton; O = polyester.

for the series. Here again, we observed a direct correlation with the amount of cellulose or polyester present. The multiplicity of peaks prevented accurate determination of the areas under the curves, so that ΔH calculations for the polyester pyrolyses could not be made.

Figure 4 shows the DTA curves for the blend fabrics treated with the second series of flame-retardant formulation (FR-II) and run in nitrogen atmosphere. PVBr in these formulations was increased as polyester content of blend increased. These curves are similar to those for the FR-I-treated blends, and the baselines for the polyester pyrolysis endotherms are again shown by dotted lines. However, increasing the PVBr concentration at high polyester levels resulted in a substantial exotherm representing PVBr decomposition which, in the DTA curves, is superimposed on the polyester pyrolysis endotherm. The lower dotted lines represent the latter in the absence of the PVBr exotherm. This observation suggests that PVBr contributed its flame retardant protection to the polyester by providing bromine in the vapor phase in the same temperature range that the polyester decomposed. It has been suggested that bromine acts as a free radical terminator in the presence of combustible vapors in air to provide a non-combustible mixture, thus making the fabric self-extin-

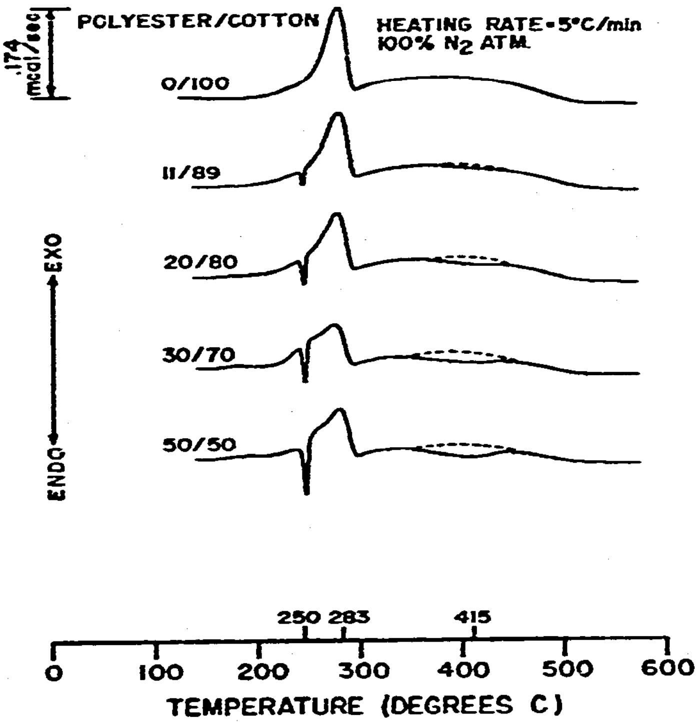

Fig. 3. Differential thermal analysis curves for polyester/cotton blend fabrics treated with Thpc-urea–PVBr (FR-I) in nitrogen.

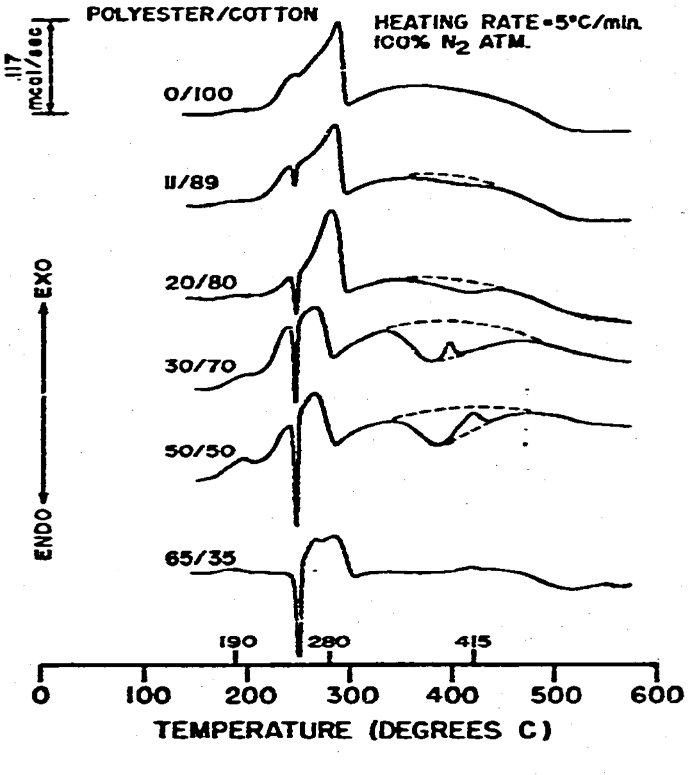

Fig. 4. Differential thermal analysis curves for polyester/cotton blend fabrics treated with Thpc-urea–PVBr (FR-II) in nitrogen.

TABLE 4

DTA FOR FLAME RETARDANT-TREATED (FR-II) POLYESTER/COTTON BLENDS IN NITROGEN[a]

PE (%)	*Cotton pyrolysis*[b]			*Polyester*				
				Melting[c]			*Pyrolysis*[d]	
	Temp.[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[e] (°C)	*Rate*[f] (*mcal sec*$^{-1}$)
0	291	0.117	134	—	—	—	—	—
11	288	0.101	136	248	0.028	1.51	415	0.003
20	283	0.116	125	250	0.054	3.18	420	0.014
30	268	0.076	221	249	0.118	5.76	382	0.052
50	267	0.079	209	249	0.151	9.48	388	0.043
65	285	0.057	158	251	0.126	10.45	—	—

[a] Heating rate, 5°C min^{-1}. [b] Exothermic change. [c] Endothermic change. [d] Endothermic change. Calculations of ΔH's for polyester pyrolyses were not made due to interference of the poly(vinyl bromide) exotherm. [e] Temperature at maximum rate of energy change. [f] Normalized maximum rate of energy change.

guishing[14]. At approximately 190°C, a small exotherm appeared in the DTA curves in nitrogen atmosphere for the FR-I (see above) and FR-II series; this has been attributed to decomposition of flame retardant polymer. It is noteworthy that Hobart and Mack[15] have reported a small weight loss in this temperature range in the TG analysis and an exotherm in DSC analysis in nitrogen for cotton flame retarded with the Thpc-based THPOH–NH_3 finish. Presumably a component derived from Thpc is responsible for the exotherms observed in both these systems; however, further work is required to verify this correlation.

Table 4 shows the maximum rates of energy change and ΔH's for the FR-II series of blends. As with the FR-I series, calculation of ΔH for the polyester pyrolyses was impossible because the multiplicity of peaks prevented accurate determination of the areas under the curves.

The size of the polyester-melting endotherm observed in the DTA curves in nitrogen for the blend series was directly proportional to the polyester content, whether treated or untreated. Figure 5 shows a plot of the endothermic energy absorbed versus the polyester content in the treated and untreated blends. Linear relationship is shown, and the heat of fusion (ΔH_f) obtained from the slope of the line is 18.9 cal g^{-1}.

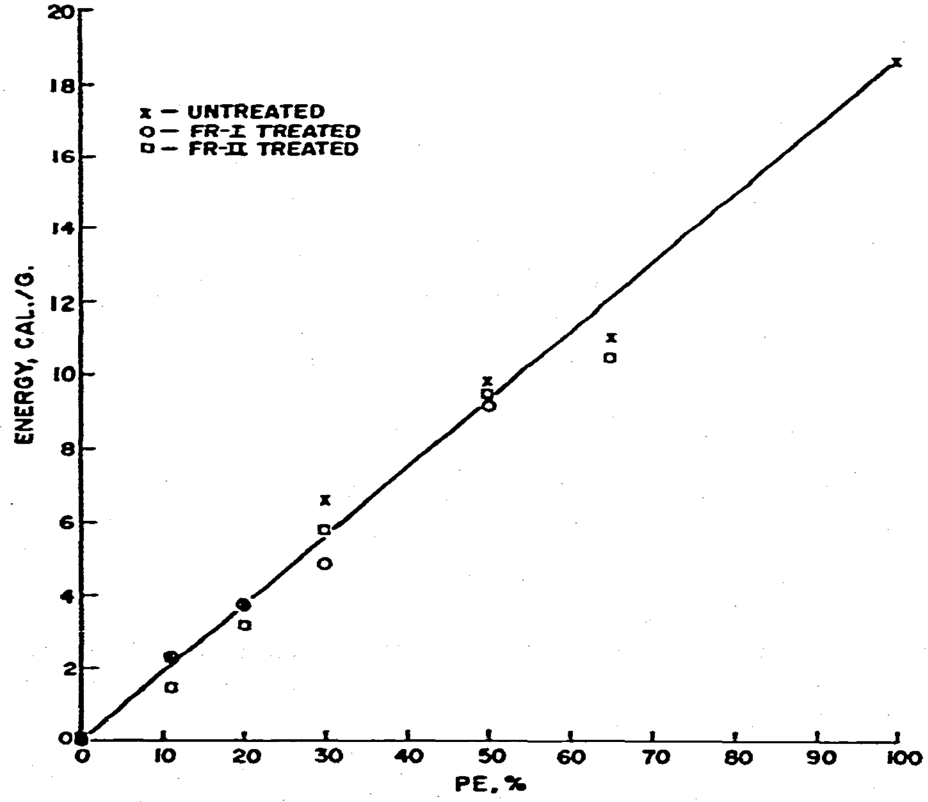

Fig. 5. Endothermic ΔH's for melting polyester in flame retardant and untreated polyester/cotton blend fabrics in nitrogen. × = untreated; ○ = FR-I treated; □ = FR-II treated.

Comparison of DTA and DTG. The DTA and differential thermogravimetric (DTG)[6] curves for untreated polyester/cotton blends are shown in Fig. 6. The polyester melted at approximately 250°C, as shown by the DTA endotherm and the absence of weight loss in the DTG curves for the 50 and 100% polyester. Pyrolysis of cellulose is shown at approximately 345°C by the DTA endotherm and the weight loss in the DTG curves for 0 and 50% polyester. Figure 6 also indicates that the DTA endotherm and DTG weight losses at approximately 420°C are associated with polyester decomposition for the 50 and 100% polyester.

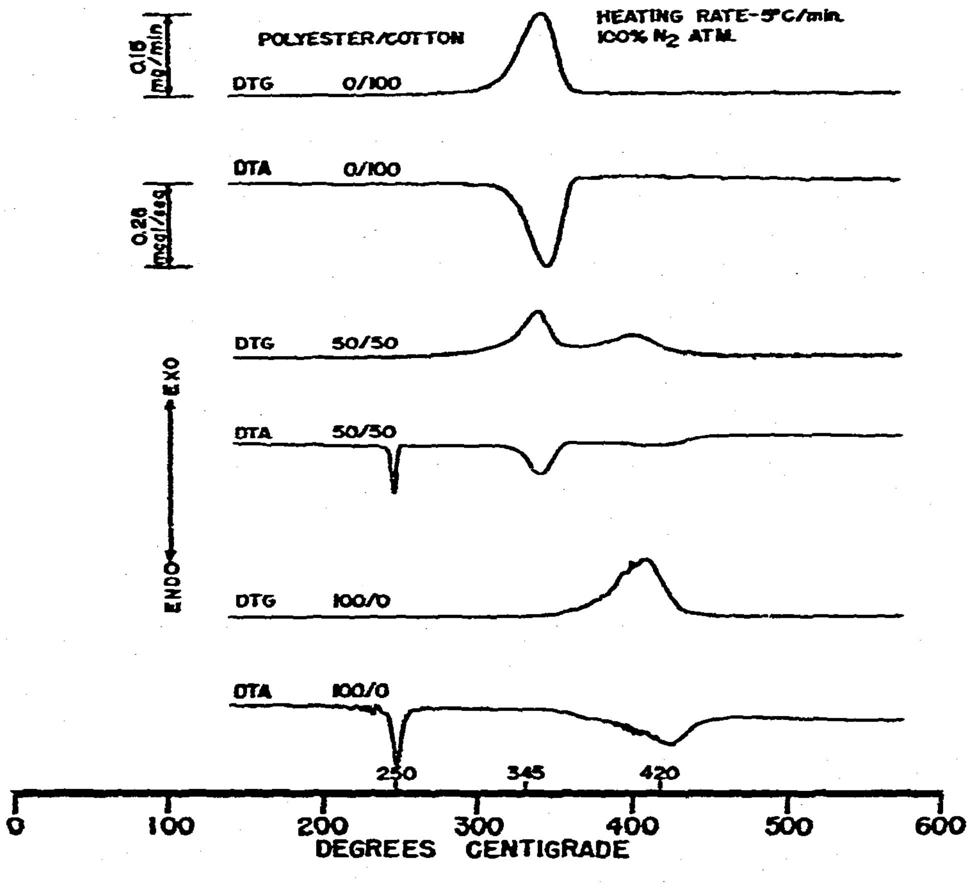

Fig. 6. Comparison of differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for untreated polyester/cotton blend fabrics in nitrogen.

Figure 7 shows DTA and DTG changes in 100% cotton and in a 50% polyester/cotton blend after treatment with a Thpc–urea–PVBr flame retardant formulation (FR-I). Melting of the polyester is shown by the DTA endotherm and absence of DTG weight loss at 250°C in the curves for the 50% polyester blend. At approximately 290°C, the exotherm, which is proportional to the cotton content and the accompanying weight loss, appears in the DTA and DTG curves, respectively; these changes reflect decomposition of the flame-retardant cotton. Changes which are associated with the polyester degradation appear at approximately 415°C in the curves for the 50% polyester blend. A slight inflection at 190°C is also apparent in the curves for the treated fabric. Examination of the curves for the Thpc–urea–PVBr polymer (Fig. 7) reveals significant decomposition, both at 190°C and at approximately 260°C; considering the dilution of the polymer, these peaks are consistent with the curves for treated fabrics.

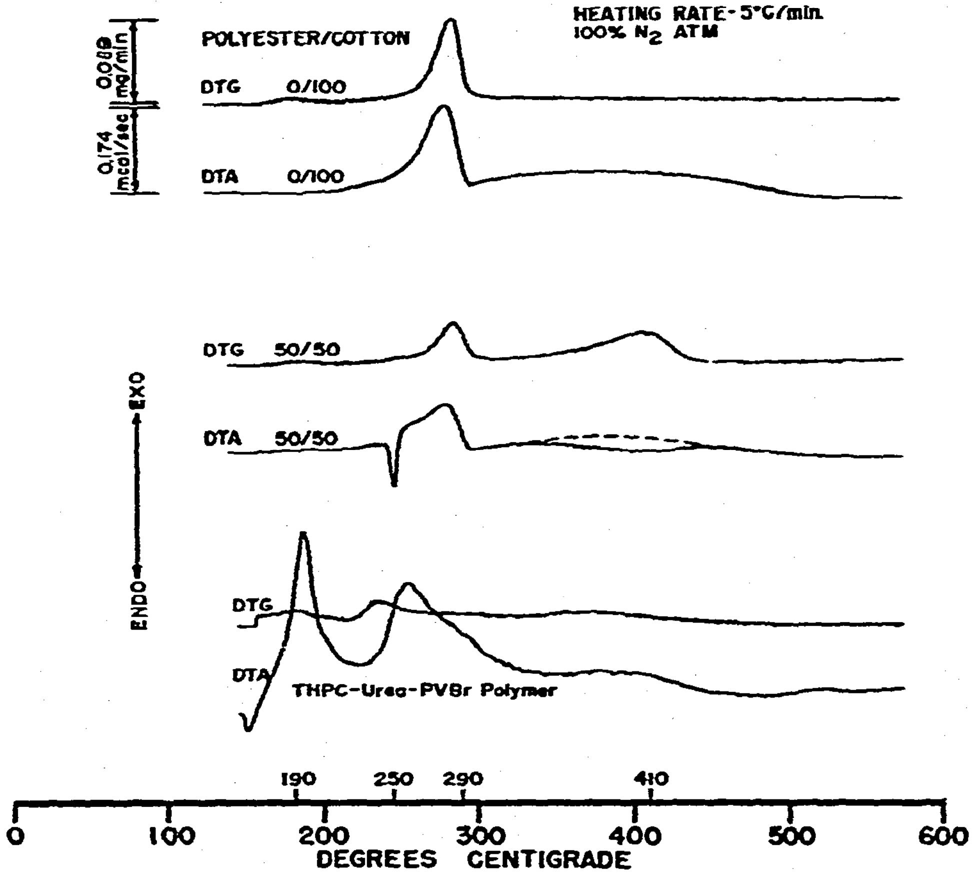

Fig. 7. Comparison of differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for flame retardant-treated (FR-I) polyester/cotton blend fabrics and Thpc–urea–PVBr polymer in nitrogen.

Figure 8 shows the DTA and DTG curves for 0, 30, and 50% polyester blends treated with flame retardants of the FR-II series. In this series of formulations the ratio of PVBr to Thpc–urea was increased in proportion to changes in the ratio of polyester to cotton. As noted in previous figures, the polyester melting endotherm at 250°C, the polyester pyrolysis endotherm and weight loss at approximately 410°C, and the PVBr decomposition exotherm at approximately 410°C are present and all increase with increases in polyester content. When the level of PVBr in the treating formulations was increased, larger amounts of PVBr were deposited on the finished fabrics, reflected by increases in the PVBr exotherms. The cellulose decomposition endotherms and weight losses at approximately 285°C as well as the small exotherms at 190° showing Thpc–urea polymer decomposition are evident in all of the curves.

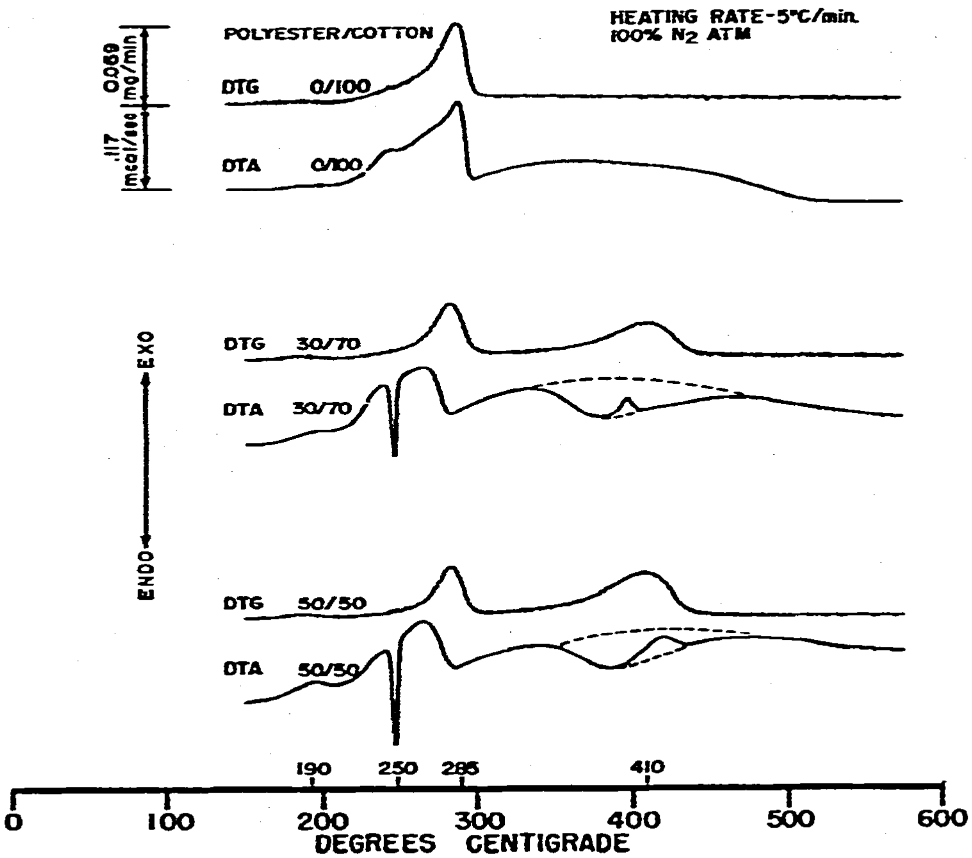

Fig. 8. Comparison of differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for flame retardant-treated (FR-II) polyester/cotton blend fabrics in nitrogen.

The effect of Thpc–urea–PVBr flame retardant on the polyester/cotton blends is shown by a comparison of the results obtained from DTG and DTA in nitrogen. The cotton pyrolysis endotherm is converted to an exotherm at a lower temperature when the fabric is treated with the Thpc–urea–PVBr flame retardant^{4,13}. In contrast, the Thpc–urea–PVBr flame retardant system did not alter the course of polyester decomposition in nitrogen atmosphere. The melting endotherm at 250°C and the decomposition endotherm and weight loss at 425°C are not significantly altered by flame retardants on polyester (Figs. 1, 3, 6–8).

Further confirmation that PVBr has its flame retardancy effect in the vapor phase rather than in alteration of the course of pyrolysis may be inferred from Neumeyer, et al.^{6}, who indicate that residual char of a flame-proofed polyester/cotton blend is composed of the flame-proofed cotton char and the untreated polyester char.

Air atmosphere

DTA. DTA curves obtained in air atmosphere (80% nitrogen–20% oxygen) for the untreated series of polyester/cotton blends appear in Fig. 9. Oxygen becomes a reactant in air, and thermoxidation becomes predominant. Consequently, the pyrolytic endotherms in Fig. 1 are converted to exotherms, as in Fig. 9. The melting endotherm for polyester is again present, although it is not so prominent as in Fig. 1 because of change in the scale by a factor of more than 7. Exotherms that appear at approximately 333, 431, and 490°C are attributed to oxidation of cellulose, polyester, and char, respectively. Numerical data for these oxidative changes are shown in Table 5. The maximum rate of exothermic change and the total ΔH associated with the oxidative degradation of the cellulose increase as the proportion of cotton in the blend increases. The ΔH's for the polyester degradation are 2 to 5 times greater than the corresponding ΔH for the cellulose thermoxidation; conversely, the ΔH in cal g^{-1} of polyester present decreases with increasing polyester content. The maximum rates of change and ΔH's for the char are considerably higher than the pyrolysis values observed in nitrogen atmosphere. The samples containing 11–50% polyester

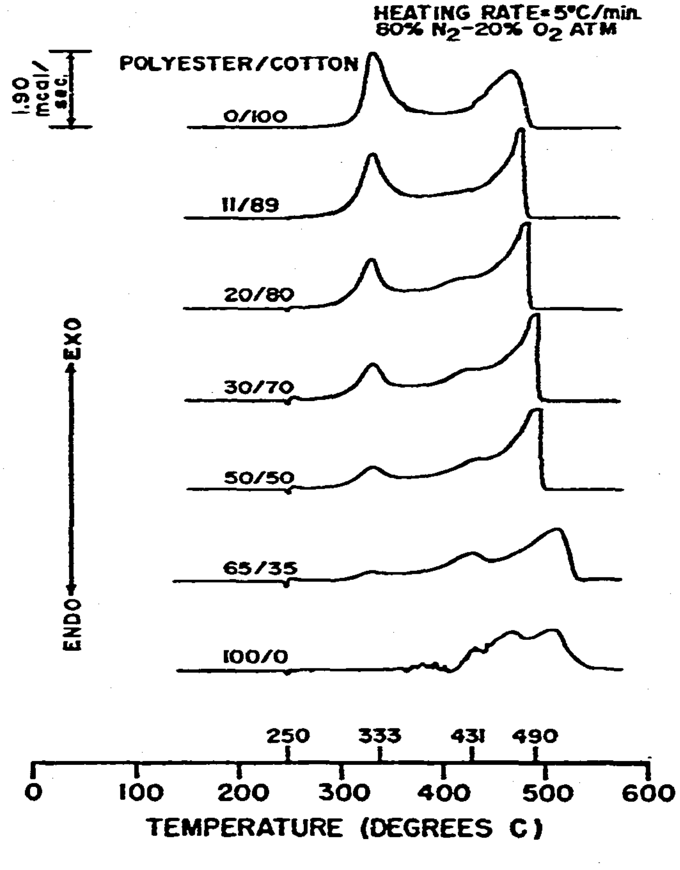

Fig. 9. Differential thermal analysis curves for polyester/cotton blend fabrics in air.

TABLE 5

DTA FOR UNTREATED POLYESTER/COTTON BLENDS IN AIR[a]

PE (%)	*Pyrolytic oxidation*[b]								
	Cotton			*Polyester*			*Char*		
	Temp.[c] (°*C*)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[c] (°*C*)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[c] (°*C*)	*Rate*[d] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)
0	334	1.896	982	—	—	—	469	1.424	6926
11	334	1.670	990	429	0.703	4445	480	2.261	8589
20	332	1.268	744	424	0.777	3996	486	2.185	8454
30	334	0.925	627	431	0.798	2362	495	2.164	8107
50	333	0.622	579	433	0.825	1659	496	2.085	7227
65	331	0.234	276	431	0.701	1105	513	1.326	7578
100	—	—	—	433	0.591	851	469 508	1.013 1.094	5200

[a] Heating at 5 °C min^{-1}. [b] Exothermic change. [c] Temperature at maximum rate of energy change. [d] Normalized maximum rate of energy change.

actually auto-ignited. The polyester or one of its components may catalyze the auto-ignition of the cellulose char. Because polyester decomposition occurs at a lower temperature than that of the char, a residue of inorganic noncombustible impurity from the polyester was suspected as the source of the catalyst. Analysis of the 100% polyester fiber shows 0.28% ash content primarily composed of titanium dioxide. The 100% cotton sample does not auto-ignite, presumably because the catalyst associated with the polyester is not present; because only a small amount of cellulose char is present, 65/35 polyester/cotton does not ignite either.

The series of polyester/cotton blends which were all treated with retardant formulation FR-I was examined by DTA in air. The curves are shown in Fig. 10. As a result of this treatment there is considerable difference in these curves compared with those for the untreated blend. The cellulose decomposition exotherm peak is shifted from 333 to 275°C, and the polyester and char decomposition exotherm peaks are both shifted downward by approximately 10°C; however, the polyester melting endotherm remains at approximately 250°C. Numerical data for the DTA are shown in Table 6. The cellulose was characterized by lower maximum rates of decomposition and higher ΔH's in air with the FR-I series than for the FR-I series in nitrogen or the

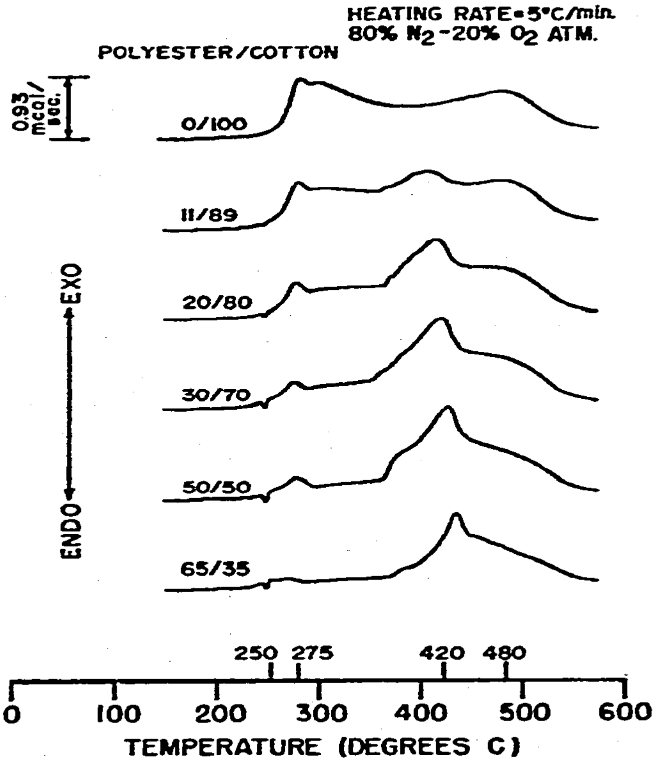

Fig. 10. Differential thermal analysis curves for polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-I), in air.

TABLE 6

DTA FOR FLAME RETARDANT-TREATED (FR-I) POLYESTER/COTTON BLENDS IN AIR[a]

PE (%)	*Pyrolytic oxidation*[b]							
	Cotton			*Polyester*			*Char*[c]	
	Temp.[d] (°C)	*Rate*[e] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[d] (°C)	*Rate*[e] (*mcal sec*$^{-1}$)	ΔH (*mcal mg*$^{-1}$)	*Temp.*[d] (°C)	*Rate*[e] (*mcal sec*$^{-1}$)
0	285 302	0.932 0.877	2458	—	—	—	483	0.743
11	282 307	0.749 0.651	1506	408	0.911	4406	480	0.779
20	280	0.584	1455	417	1.242	4137	475	0.826
30	278	0.429	1326	423	1.429	3725	—	—
50	280	0.355	1067	429	1.449	2580	—	—
65	270	0.173	703	436	1.190	1414	—	—

[a] Heating at 5°C min^{-1}. [b] Exothermic change. [c] Overlapping of the polyester exotherm prevented calculation of the ΔH for the char oxidation. [d] Temperature at maximum rate of energy change. [e] Normalized maximum rate of energy change.

untreated series in air. Lowering of the peak temperatures for cellulose decomposition by the FR-I treatments is attributed to alteration of the course of decomposition by acidic catalysts developed on heating the flame retardant formulation[13,16]. Lowering of maximum decomposition rates can also be attributed to the effect of the flame retardant. Decreased TG weight loss in FR-I-treated samples in air atmosphere[6] is correspondingly accompanied by increased ΔH. Application of FR-I-flame retardant does not cause appreciable changes in decomposition temperature and heats of thermoxidative degradation for polyester. Therefore, we conclude that neither the phosphorus and nitrogen components of the flame retardant nor the poly(vinyl bromide) affect the course of polyester decomposition. These effects reflect changes in the solid phase only, and we believe that the flame retardancy benefit to the polyester from PVBr occurs in the vapor phase by free radical termination[14]. The fire retardant FR-I affects thermoxidation of the char by replacing auto-ignition at about 490 °C with a smoldering exotherm in the same temperature range.

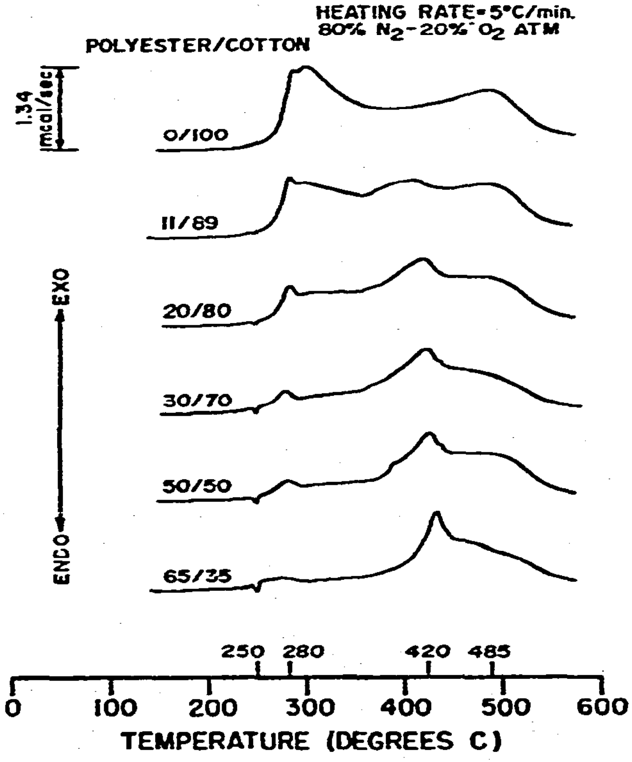

Fig. 11. Differential thermal analysis curves for polyester/cotton blend fabrics treated with Thpc–urea–PVBr (FR-II), in air.

DTA curves in air for blend samples treated with varying Thpc–urea–PVBr formulations (FR-II series) are shown in Fig. 11. These curves are almost identical with those of the FR-I series (Fig. 10).

A summary of the exothermic energy changes for different components of the respective blends and their chars on thermoxidation appears in Fig. 12. The amount of polyester present had little effect on cotton oxidation. The very high (approximately 5000 mcal mg^{-1}) ΔH of polyester oxidation was markedly reduced by decreasing the proportion of cotton, although to a considerably lesser extent at the high polyester contents. Char thermoxidation was even more exothermic that that of the polyester; here, the catalytic effect of polyester is evident because of increase in ΔH at the lowest level of polyester followed by a gradual decline at higher levels.

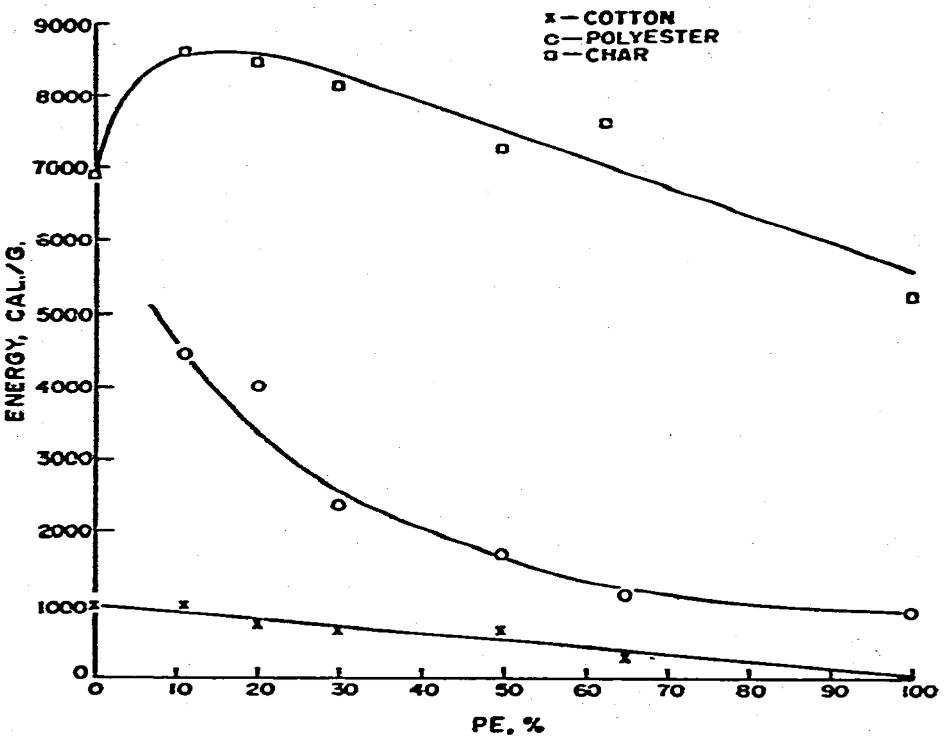

Fig. 12. Exothermic ΔH's for thermoxidation of polyester/cotton blend fabrics in air. × = cotton; ○ = polyester; □ = char.

Effects of treatments FR-I and FR-II on thermoxidation of the blends are shown in Fig. 13. With either flame retardant treatment, the ΔH of the polyester portion declined linearly with increasing polyester content within the same range as for the untreated blends. With either treatment, the ΔH of the cotton portion was less than half as great as the change of the polyester portion, declining rapidly at the start and levelling off as polyester content was increased.

Approximate concurrence of the DTA exotherm at 490 °C with TG weight loss in air atmosphere for the untreated 50/50 blend is shown in Fig. 14. This is associated with oxidation of the char remaining from earlier pyrolysis of the cotton component of the blend. When the cotton content was 50% or more, the char auto-ignited

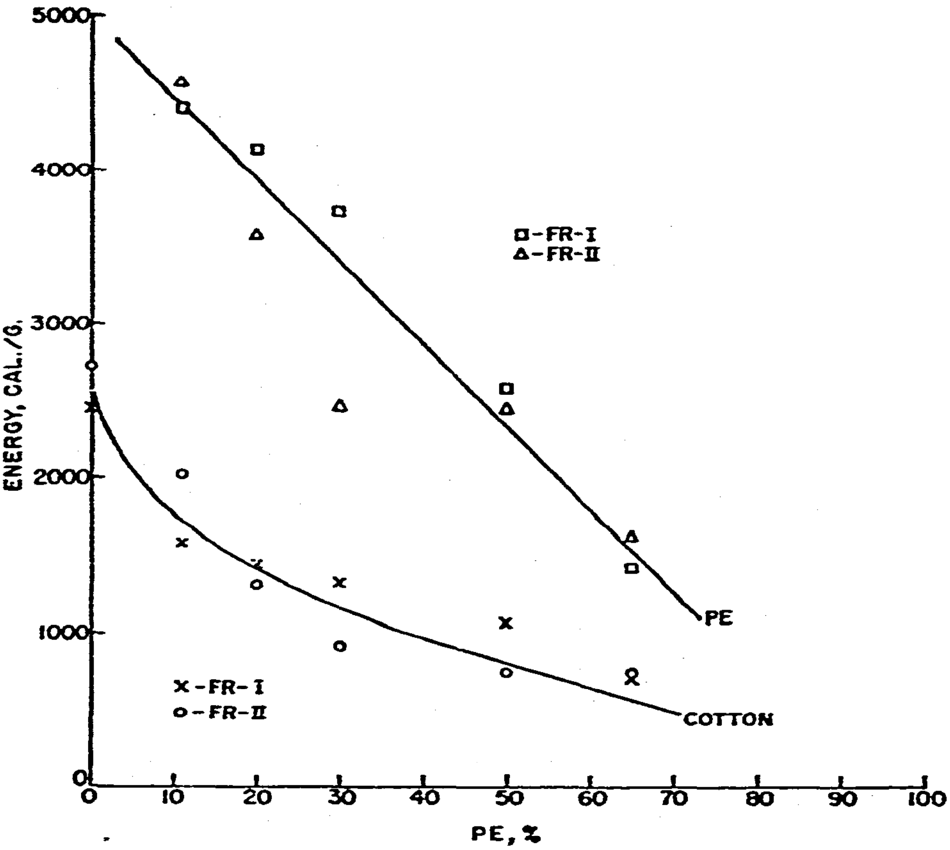

Fig. 13. Exothermic ΔH's for thermoxidation of flame-retardant treated polyester/cotton blend fabrics in air. × = FR-I; O = FR-II; □ = FR-I; Δ = FR-II.

(indicated by the arrow in the figure). The exotherm in the DTA curve for 100% polyester is associated with oxidation of the polyester char. The presence of cotton had almost no effect on this exotherm. A small amount of polyester char, however, appears to catalyze autooxidation of cotton char. As noted above, the polyester ash or char contained a metal oxide which could accelerate this autooxidation.

The DTA and DTG curves in air in Fig. 15 show the results of application of FR-I flame retardant. The curves are for 100% cotton and 50/50 blend fabrics receiving FR-I treatment, as well as for the corresponding Thpc–urea–PVBr polymer. At 190°C there is an exotherm and weight loss for the polymer itself and a small weight loss in the respective curves for the treated samples. The exotherm and weight loss at 280°C associated with the cotton decomposition were observed for both the treated 100% cotton and the 50/50 blend. The exotherm at 410°C for polyester decomposition appeared in the curve for the blend fabric. The FR-I treatment prevented the ignition of the treated blend, as shown in Fig. 14. The curves in air for FR-II-treated fabrics are similar to those in Fig. 15 for FR-I-treated fabrics.

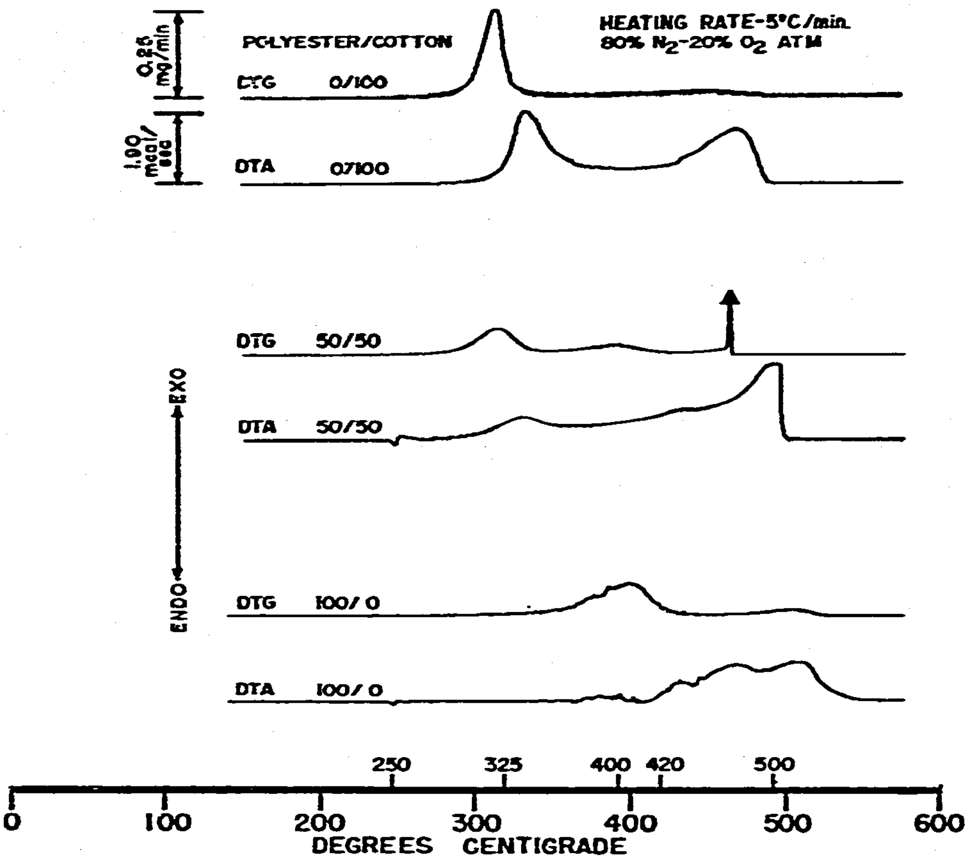

Fig. 14. Comparison of differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for polyester/cotton blend fabrics in air.

Correlation of thermal analyses with flammability measurements. The FR-I series of treated samples showed good correlation of polyester content with maximum rates of decomposition in TG and DTA, as seen in Table 7. The relationship between oxygen index (OI) and polyester content was inverse showing that the FR-I flame retardant was most effective on fabrics with low polyester (high cotton) content.

All of the FR-I and FR-II flame retardant fabrics, as treated, passed the FF 3-71 flammability test. Char lengths ranged from 2.0 in for the most flame resistant to 6.0 in for the least flame resistant. However, the correlation of the thermal analysis data with the DOC FF 3-71 tests was poor, due largely to the use of different techniques.

CONCLUSIONS

(1) Endothermic peaks in DTA curves for polyester/cotton blends run in nitrogen were found and assigned as follows: 250°C, melting of polyester; 345°C, pyrolysis of cotton cellulose; 420°C, pyrolytic degradation of polyester.

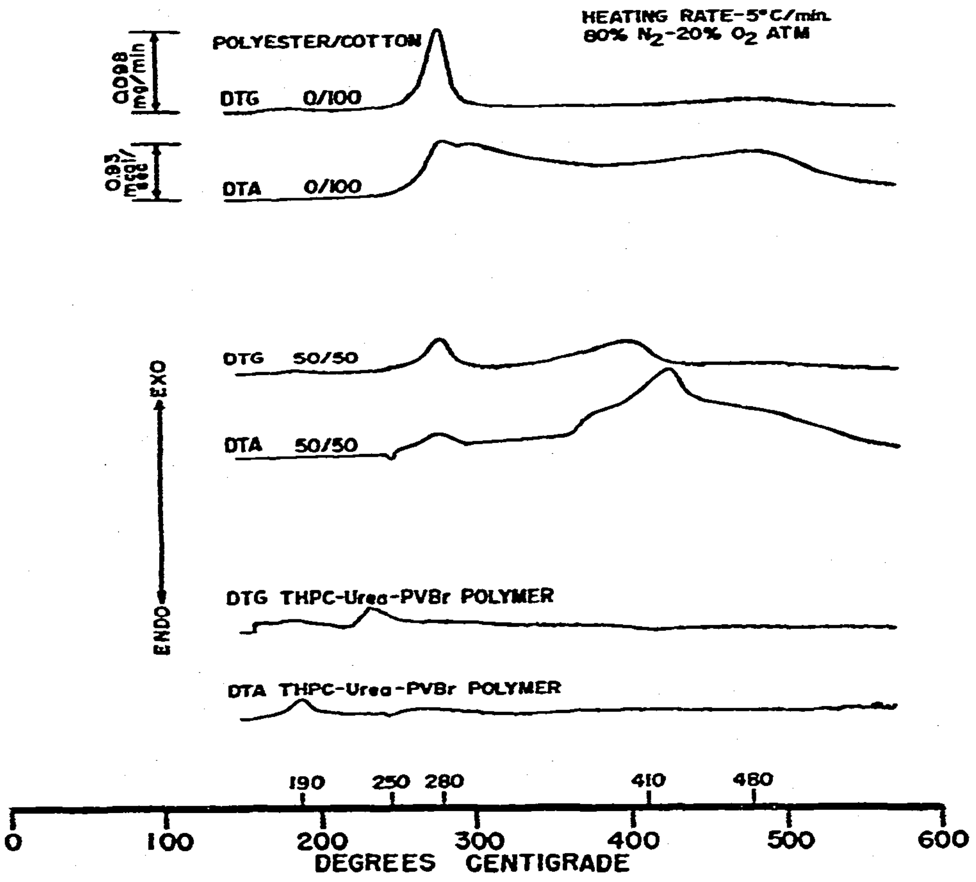

Fig. 15. Comparison of differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves for Thpc–urea–PVBr (FR-I) treated polyester/cotton blend fabrics and Thpc–urea–PVBr polymer in air.

TABLE 7

RELATIONSHIP BETWEEN OI, DTA, AND TG DATA ON FR-I-TREATED FABRICS

PE (%)	*Oxygen index*	*Rate of polyester decomposition*[a]	
		TG *mg min*$^{-1}$ *mg*$^{-1}$	*DTA* (*mcal/sec*$^{-1}$)
0	0.37	—	—
11	0.35	0.013	0.91
20	0.32	0.019	1.24
30	0.32	0.024	1.43
50	0.30	0.037	1.45
65	0.29	0.045	—

[a] Normalized maximum rate in air atmosphere.

(2) The ratio of polyester to cotton in untreated blends does not significantly affect peak locations for DTA run in nitrogen.

(3) The ΔH's of cotton pyrolysis for DTA in nitrogen of untreated polyester/cotton blends increased nonlinearly with increasing proportion of cotton. This is attributed to the catalytic effect of impurities in the molten polyester.

(4) Flame retardancy treatments with Thpc–urea–PVBr formulations had the following effects on the DTA curves in nitrogen of polyester/cotton blends:

a. Polyester melting was unchanged (still was an endotherm at approximately 250°C).

b. Cotton pyrolysis became exothermic (rather than endothermic) and the peak was lowered from 345 to 285°C.

c. Polyester decomposition temperature closely coincided with that for PVBr. The flame retardant effect of PVBr on polyester is consequently explained as resulting from generation of the bromine free radical in the vapor phase.

d. A small exotherm at approximately 190°C is attributed to decomposition of the Thpc–urea polymer.

(5) The polyester melting endotherm of treated and untreated polyester/cotton blends in the DTA in nitrogen was directly proportional to the polyester content. With appropriate standardization a method of quantitative analysis for polyester may be devised.

(6) DTA curves run in air for untreated polyester/cotton blends show the unaltered endothermic peak for polyester melting at approximately 250°C and the following exothermic peaks for which the assignments indicated are made: 333°C, thermoxidation of cellulose; 431°C, thermoxidation of polyester; and 490°C, thermoxidation of char.

(7) The ΔH's for thermoxidation (in air) as determined by DTA are 2 to 5 times greater for polyester than for cellulose for a given blend. However, the polyester ΔH's decrease as polyester in the blend increases.

(8) Auto-ignition of untreated blend samples of 11–50% polyester content in DTA in air suggests that a minor component of the polyester melt, such as titanium dioxide, catalyzes auto-ignition of the cellulose char.

(9) DTA curves in air of Thpc–urea–PVBr-treated polyester/cotton blends showed increased ΔH's of decomposition for cellulose and little change in those for polyester decomposition, compared with those for untreated blends in air or nitrogen. This agrees with previously expressed views that the Thpc–urea component affects only the cellulose in the solid phase, and PVBr produces free radicals and acts on the polyester fragments in the vapor phase.

(10) Earlier TG work on the same blended samples, both treated and untreated, supports the conclusions drawn.

(11) Although there was good direct correlation between polyester content and maximum rates of decomposition, an inverse relationship between oxygen index and polyester content indicated that the Thpc–urea–PVBr flame retardant finish on blends was more effective on cotton than on polyester.

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REFERENCES

1 J. Louglin *et al.*, *Amer. Dyest. Reptr.*, 54 (1965) P74.

2 R. F. Schwenker, Jr. and R. K. Zuccarello, *J. Polym. Sci. C*, 6 (1964) 1.

3 S. T. Tarim and D. M. Cates, in *Thermoanalysis of Fibers and Fiber-Forming Polymers*, Appl. Polym. Symp., 2 (1966) 1.

4 R. M. Perkins, G. L. Drake, Jr. and W. A. Reeves, *J. Appl. Polym. Sci.*, 10 (1966) 1041.

5 K.-K. Yeh, M. M. Birkey and C. Huggett, *J. Appl. Polym. Sci.*, 17 (1973) 255.

6 J. P. Neumeyer, J. I. Wadsworth, N. B. Knoepfler and C. H. Mack, *Thermochim. Acta*, 16 (1976) 133.

7 *Federal Register*, 36, No. 146 (1971).

8 S. L. Boersma, *J. Amer. Ceram. Soc.*, 38 (1955) 281.

9 R. A. Baxter, in R. F. Schwenker, Jr. and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 1, Academic Press, New York 1969, p. 65.

10 R. F. Schwenker, Jr., in *Analytical Methods for a Textile Laboratory*, AATCC Monograph No. 3, American Association of Textile Chemists and Colorists, Research Triangle Park, N. C., 2nd Ed., 1968, p. 386.

11 W. W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, New York, 2nd ed., 1974.

12 J. L. Isaacs, *J. Fire Flammability*, 1 (1970) 36.

13 H. A. Schuyten, J. W. Weaver and J. D. Reid, *Adv. Chem. Ser.*, 9 (1954) 7.

14 J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970, p. 15.

15 S. R. Hobart and C. H. Mack, *Text. Res. J.*, 45 (1975) 667.

16 F. Shafizadeh, *Advan. Carbohyd. Chem.*, 23 (1900) 419 (1968).