

## THERMOGRAVIMETRIC ANALYSIS OF POLYESTER/COTTON BLENDS TREATED WITH Thpc-UREA-POLY(VINYL BROMIDE)

JULIUS P. NEUMEYER, JAMES I. WADSWORTH, NESTOR B. KNOEPFLER AND CHARLES H. MACK

*Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, La. 70179 (U.S.A.)*

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### ABSTRACT

Polyester/cotton fabric with blend ratios of 0/100, 11/89, 20/80, 30/70, 50/50, and 65/35 were investigated via thermogravimetric analysis in both nitrogen and air atmospheres. The samples were heated from ambient to 750°C at a heating rate of 5°C min<sup>-1</sup>. The same fabrics were analyzed after treatment with tetrakis (hydroxy-methyl) phosphonium chloride-urea-poly(vinyl bromide) (Thpc-urea-PVBr) flame retardant.

Weight losses observed during pyrolysis were assigned to the cotton and polyester portions of the blends. Both cotton and polyester thermally decompose to yield gases and solid char byproducts. In nitrogen the 100% cotton fabric undergoes one major weight loss between 270 and 370°C, with the maximum rate of weight loss, 0.15 mg/min-mg, occurring at 346°C. Thermal decomposition of the 100% polyester occurs over a range of 335-470°C, with the peak rate of weight loss, 0.11 mg/min-mg, measured at 416°C. In an air atmosphere, both volatile gases and solid char byproducts of pyrolysis undergo combustion. The combustion reactions are associated with measured weight losses. The maximum rate of weight loss for the cotton portion increases to 0.25 mg/min-mg and occurs at 317°C. The maximum rate of polyester decomposition remains the same in both air and nitrogen, but the temperature decreases to 405°C.

### INTRODUCTION

Flammability legislation<sup>1</sup> and subsequent issuance of Federal Flammability Standards for consumer products such as children's sleepwear<sup>2</sup>, carpets and rugs<sup>3</sup>, mattresses<sup>4</sup> and upholstered furniture<sup>5</sup> have catapulted the textile industry into flammability research. Polyester/cotton blend fabrics have received considerable attention. These fabrics are important commercially, making up almost 33% of the apparel market. Acceptable flame retardant finishes for all-cotton or all-polyester fabrics are not necessarily effective on polyester/cotton blend fabrics, and promulgation of flammability standards for these products would have considerable impact on the fabric market.

Investigations of flame retardants for polyester/cotton blends have generally called upon knowledge available from previous work on 100% cotton fabrics. In a recent review of fire resistant textiles by Reeves et al.<sup>6</sup>, organophosphorus compounds predominated as the most effective for rendering cellulose durably flame retardant. Tesoro<sup>7</sup> concluded that finishes utilizing tetrakis (hydroxymethyl)phosphonium derivatives may be more effective than phosphonate finishes for polyester/cotton blends.

Halogens, particularly bromine, are effective flame retardants for polyester, the prevalent theory being that halogens can function as chain terminating agents for the free radical combustion reaction<sup>8,9</sup>. Presumably treatment with systems containing both bromine and Thpc might be suitable for flame retarding polyester/cotton blends. In such systems, bromine can be applied as part of the fabric finish or introduced in the polyester fibers during manufacture.

There are many problems to be solved before suitable flame retardants for polyester/cotton blend fabrics are readily available and acceptable. To date, much of the work done has been practical in approach; additional effort is needed on the more fundamental aspects of polyester/cotton flammability. Studies on thermal decomposition and combustion mechanisms of these blends are desirable. The effects of flame retardants on these mechanisms should also be determined.

Thermal methods of analysis have previously been applied for studying thermal decomposition of cellulosic<sup>10-16</sup> and synthetic polymers<sup>17-22</sup>. Tarim and Cates<sup>23</sup> and Godfrey<sup>24</sup> used thermogravimetry to investigate fibers and fiber blends. Perkins et al.<sup>25</sup> utilized both thermogravimetry and differential thermal analysis in a study of flame resistant cotton fabrics.

The objective of this work was to determine if thermogravimetric analysis could be usefully applied to study thermal decomposition of polyester/cotton blend fabrics and, hopefully, develop some fundamental information on the pyrolysis and combustion behavior of these materials.

#### EXPERIMENTAL

A series of polyester/cotton sheeting fabrics with blend ratios of 0/100, 11/89, 20/80, 30/70, and 50/50 were obtained for this study. The fabrics, made of intimate blends of Kodel 421 Polyester and Acala combed cotton, had a weight of 4 oz/yd<sup>2</sup>. A 65/35 blend of the same fibers, but with a fabric weight of 3 oz/yd<sup>2</sup> was also included in the series. The 100% polyester fabric was not available, therefore analyses were made on the yarn only.

Portions of the fabrics were treated with the Thpc-urea-poly(vinyl bromide) flame retardant finish previously described by Donaldson<sup>26</sup>. The Thpc used was an 80% aqueous solution obtained from Hooker Chemical & Plastic Corporation\*. The poly(vinyl bromide) (PVB<sub>r</sub>) used was a 40% nonplasticized emulsion from Ethyl Corporation\*. The treating solution was prepared by dissolving disodium phosphate

\*Use of a company and/or product name by the U.S. Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

in the desired amount of water and then adding Thpc, urea, wetting agent, and PVBr emulsion in the order listed. Fabric samples were padded through the treating emulsion using two dips and two nips, with squeeze pressure adjusted to obtain 90% wet pickup. The padded samples were dried at 85°C for 5 min, cured at 160°C for 1.5 min, rinsed with tap water, and dried again.

Two series of treatments were applied (see Table 1). In the first referred to as FR-I, all fabrics were treated with the same formulation. The Thpc-urea content was approximately 30% solids and the PVBr content was maintained at 6.4% solids. The add-ons obtained were approximately 22–24%. In the second series of treatments, referred to as FR-II, the Thpc-urea content was varied from about 35% solids for the 100% cotton fabric to 26.3% for the 35% cotton fabric. To provide flame retardance for the polyester portion of the blend, the PVBr was increased from 1% for the 100% cotton fabric to about 10% for the 65% polyester fabric. Add-ons obtained were approximately 20–23%.

TABLE I  
TREATING FORMULATIONS

Catalyst, 3% disodium phosphate; wetting agent, 0.1%.

<i>Polyester/ cotton</i>	<i>FR-I Series</i>			<i>FR-II Series</i>		
	<i>Thpc-urea % solids</i>	<i>PVBr % solids</i>	<i>Add-on %</i>	<i>Thpc-urea % solids</i>	<i>PVBr % solids</i>	<i>Add-on %</i>
0/100	30.0	6.4	23.9	34.8	1.0	23.1
11/89	30.0	6.4	23.3	34.8	2.0	21.0
20/80	30.0	6.4	22.9	30.0	3.2	20.6
30/70	30.0	6.4	23.1	26.3	4.8	20.3
50/50	30.0	6.4	22.5	26.3	6.4	19.2
65/35	30.0	6.4	24.0	26.3	10.0	22.0

A DuPont 990 Thermal Analysis System with an attached 951 Thermogravimetric Analyzer was used for this investigation. Samples of approximately 10 mg were heated from ambient to 750°C at a rate of 5°C min<sup>-1</sup>. Analyses were performed both in 100% nitrogen and 80% nitrogen–20% oxygen atmospheres. A flow rate of 50 ml min<sup>-1</sup> was adequate to purge the apparatus of volatile decomposition products. Sample weight and temperature were continuously monitored on the 990 recorder system. A DuPont 915 Computer Interface converted the data to digital form for later processing by a digital computer to perform normalization and derivative calculations.

## RESULTS AND DISCUSSION

In thermogravimetric analysis (TG), the sample weight is continuously monitored as the sample is exposed to heat. Normally the environment is thermally controlled to increase the sample temperature at a constant rate. This mode of

operation is referred to as dynamic thermogravimetric analysis. In dynamic TG the sample weight is usually observed as a function of temperature. If the environment temperature is maintained constant, the operation is referred to as isothermal TG, and the sample weight is observed as a function of time. In either case the resulting "weight vs. temperature" or "weight vs. time" plot provides information such as thermal stability and composition of the original sample, intermediate compounds, and residue remaining after thermal decomposition.

Figure 1 illustrates a "weight vs. temperature" plot obtained via dynamic TG. The sample weight decreases in a stepwise manner as the sample is heated. This weight loss indicates sample decomposition to volatile products. Phase transitions resulting in weight loss (i.e., evaporation, sublimation, vaporization) can also be determined.

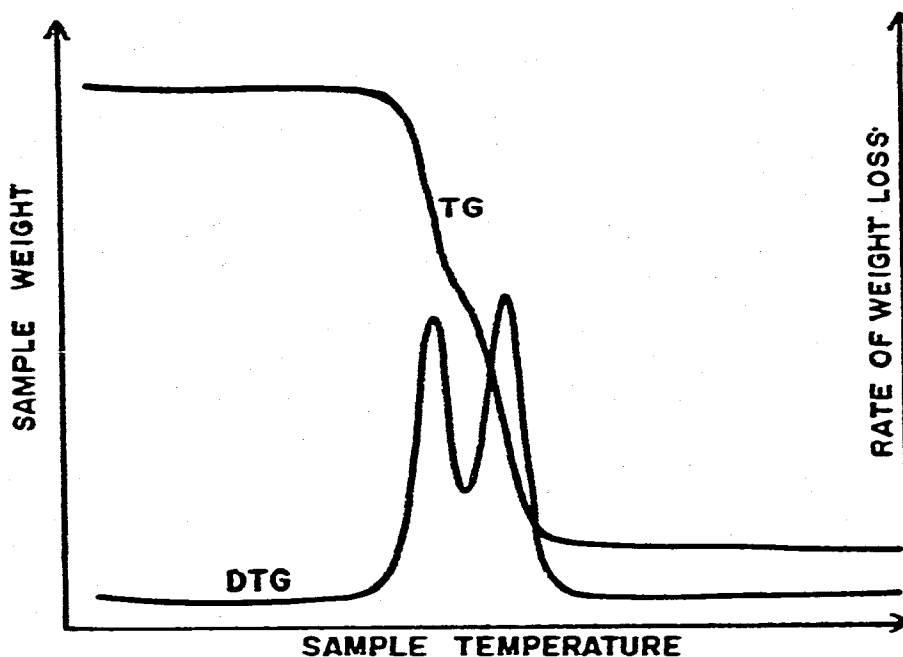


Fig. 1. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves.

Differentiating the dynamic TG curve in time, and plotting the rate of weight loss as a function of temperature results in the differential thermogravimetric curve (DTG) of Fig. 1. In DTG, peaks are observed instead of the step-like curve obtained via dynamic TG. The area under the DTG curves corresponds to the weight loss indicated by the TG curve data. The differential curve is more sensitive to weight changes than the original weight loss curve. Minor weight losses that often are undetected via visual examination of TG data become readily apparent after differentiation.

The differential thermogravimetric data,  $dw/dt$ , are reported in this study. In all cases the data have been normalized by dividing the original data by the sample

“dry” weight corresponding to the temperature of minimum rate of weight loss between 100 and 200°C. Sample “dry” weight could thus be determined during an experiment after allowing for removal of excess moisture.

### *Pyrolysis in nitrogen*

The DTG curves for each of the untreated fabrics and the 100% polyester yarns analyzed in nitrogen are illustrated in Fig. 2. The 100% cotton fabric undergoes one major weight loss between 270 and 370°C. Throughout this temperature range the cellulosic fibers are decomposing to yield both volatile gases and solid char by-products. Maximum rate of weight loss, 0.154 mg/min-mg, was observed at 346°C.

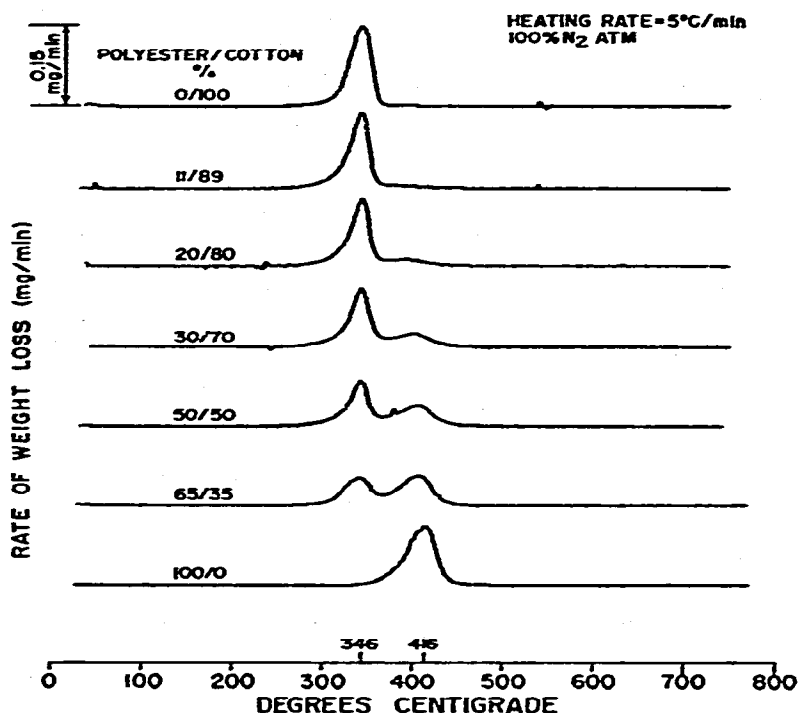


Fig. 2. DTG of untreated polyester/cotton blend fabrics, heating rate = 5°C min<sup>-1</sup>; 100% nitrogen atm.

Thermal decomposition of the 100% polyester yarns was observed over a range of 335–470°C. Polyester, similar to cellulose, also decomposes to volatile gases and solid char byproducts. A maximum rate of weight loss, 0.112 mg/min-mg, was observed at approximately 416°C. It is obvious in Fig. 2 that the maximum rate of weight loss for the cotton portion of the blend decreases as the cotton fraction decreases. This observation is also true of the polyester portion. In each case, the rate of weight loss and the area under the derivative curve are directly proportional to the blend fraction. The weight loss is a direct measure of the volatiles formed during

decomposition, and the rate of weight loss is an indication of the thermal decomposition kinetics.

Although the cotton and polyester decomposition reactions overlap in the range of 335–373°C, there is no evidence, as measured by gravimetric analysis, that either polymer significantly affects thermal stability of the other in a nitrogen atmosphere. This is supported by data in Table 2. In addition to summarizing the maximum rates of weight loss and corresponding temperatures of Fig. 2, Table 2 also lists the maximum rates of component weight loss,  $dw_i/dt$ . Component rate of weight loss is calculated by differentiating the original data after normalization to the component weight  $w_i$  in the blend, i.e.  $w_i = \text{blend fraction } i \times \text{sample dry weight}$ . The blend fraction for these calculations was determined by the clorox<sup>27</sup> procedure.

TABLE 2  
DTG POLYESTER/COTTON BLEND FABRICS  
Heating rate = 5°C min<sup>-1</sup>; 100% N<sub>2</sub> atm.

Polyester content		Cotton pyrolysis			Polyester pyrolysis			Residue at 600°C %
<i>As labeled</i>	<i>Clorox method</i>	Temp. <sup>a</sup>	$dw/dt^b$	$dw_i/dt^c$	Temp. <sup>a</sup>	$dw/dt^b$	$dw_i/dt^c$	
0	0	346	0.154	0.154	—	—	—	8.2
11	10.4	346	0.139	0.155	393	0.005	0.048	10.8
20	22.9	347	0.129	0.167	393	0.014	0.0611	10.4
30	35.0	346	0.108	0.166	401	0.026	0.0742	8.9
50	50.1	345	0.087	0.174	410	0.041	0.0818	10.5
65	—	342	0.054	0.154	408	0.059	0.0907	9.7
100	—	—	—	—	416	0.112	0.112	12.5

<sup>a</sup> Temperature at maximum rate of weight loss. <sup>b</sup> Normalized maximum rate of sample weight loss (mg/min-mg). <sup>c</sup> Normalized maximum rate of component weight loss (mg/min-mg).

The temperature of maximum rate of weight loss (hereafter referred to as peak temperature) does not vary more than a few degrees for the cotton fraction. Its component rate of weight loss  $dw_i/dt$ , is also approximately constant, indicating the same decomposition kinetics regardless of polyester content. Examining the same variables for polyester decomposition indicates that there is some change in peak temperature and considerable decrease in the component decomposition rates as the polyester fraction decreases. This suggests some altering of the polyester decomposition kinetics due to presence of the cotton char and should be investigated further.

Also shown in Table 2 is the quantity of residual solids remaining for each fabric at the conclusion of thermal degradation. The 100% cotton fabric leaves a char residue of 8.2%, and the 100% polyester yields a 12.5% residue. All of the blends analyzed yielded residues of approximately 10%, another indication that their decomposition kinetics were not changed significantly. These residual values, measured at 600°C, indicate that about 90% of the original fabric volatilizes and is therefore available as fuel for flaming combustion reactions.

Figure 3 presents DTG results for the same fabrics treated with Thpc-urea-PVBr (FR-I) flame retardant (approximately 23% add-on) and analyzed in nitrogen. These data are summarized in Table 3. Thermal stability, as measured by the peak temperature, is decreased from 346 to 289°C for the 100% cotton fabric. The maximum rate of decomposition is decreased by more than 40%, from 0.154 to

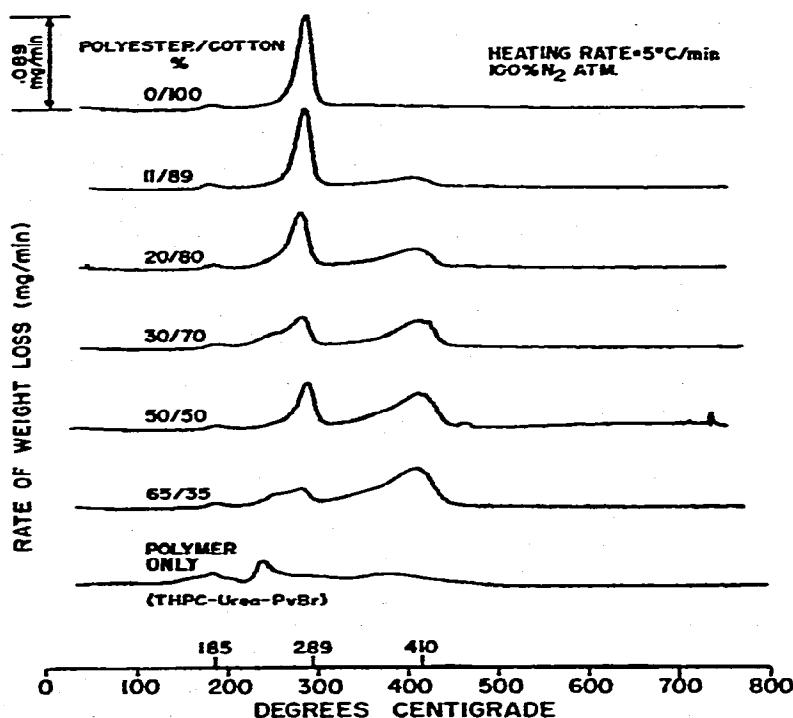


Fig. 3. DTG of polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-I). Heating rate =  $5^{\circ}\text{C min}^{-1}$ ; 100% nitrogen atm.

TABLE 3

DTG COTTON/POLYESTER BLEND FABRICS TREATED WITH Thpc-urea-PVBr (FR-I)

Heating rate =  $5^{\circ}\text{C min}^{-1}$ ; 100%  $\text{N}_2$  atm.

Polyester/ cotton	Polymer degradation		Cotton pyrolysis		Polyester pyrolysis		% Residue at 600°C
	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	
0/100	187	0.0054	289	0.089	—	—	40.7
11/89	182	0.0056	287	0.076	404	0.011	37.9
20/80	185	0.0053	282	0.053	409	0.019	34.6
30/70	188	0.0056	283	0.031	410	0.027	30.9
50/50	187	0.0040	288	0.044	412	0.034	23.8
65/35	184	0.0049	281	0.019	409	0.040	22.5

<sup>a</sup> Temp. at maximum rate of weight loss ( $^{\circ}\text{C}$ ). <sup>b</sup> Normalized maximum rate of weight loss (mg/min-mg).

0.089 mg/min-mg. As much as 40.7% residue remains after decomposition, compared with 8.2% for the untreated sample. Decomposition is altered so that flammable tars and gases are reduced and the amounts of chars are increased. Similar effects are apparent for the cotton portion of all blends studied.

These changes have been observed and attributed by some<sup>11,13,15,25,28-30</sup> to acid catalysis of the dehydration reaction in the cellulose decomposition mechanism. Dehydration of cellulose to dehydrocellulose, with further decomposition to volatile gases and char, is thought to compete with depolymerization of the cellulose to tars, primarily levoglucosan, which undergo further decomposition to volatile gases. The flame retardant thus functions by increasing the quantity of non-flammable vapors (primarily water) *and* by decreasing the amount of flammable gases. One disadvantage, however, is that the greater quantities of char produced provide more fuel for glowing combustion reactions, which are critical in sustaining smoldering combustion<sup>31</sup>.

No significant changes are apparent in the weight loss data for the polyester portion of the treated fabrics. The maximum rate of weight loss and the peak temperatures remain about the same as for the untreated samples of Table 2. The minor variances observed probably result from weight loss activity associated with the polymer alone, shown at the bottom of Fig. 3. The polymer exhibits maximum rates of weight loss at 185, 240, and 380°C.

An interesting observation is presented in Table 4. The measured residue at 600°C is compared with that predicted from the blend fractions, the residue measured for the 100% polyester yarns and the residue measured for the 100% cotton treated

TABLE 4  
PREDICTED RESIDUES IN THE FR-I SERIES (nitrogen atmosphere)

<i>Polyester/cotton content (Clorox method)</i>	<i>Cotton<sup>a</sup> (%)</i>	<i>Polyester<sup>b</sup> (%)</i>	<i>Cotton plus polyester<sup>c</sup> (%)</i>	<i>Measured residue at 600°C (%)</i>
0/100	40.7	—	40.7	40.7
10.4/89.6	36.5	1.3	37.8	37.9
22.9/77.1	31.4	2.9	34.3	34.6
35/65	26.5	4.4	30.9	30.9
50.1/49.9	20.3	6.3	26.6	23.8
65/35	14.2	8.1	22.3	22.5

<sup>a</sup> Calculated from measured residue of 100% cotton treated with FR-I (40.7%). <sup>b</sup> Calculated from measured residue of untreated 100% polyester yarns (12.5%). <sup>c</sup> Sum of <sup>a</sup> and <sup>b</sup>.

fabric. The predicted values were determined assuming the poly(vinyl bromide) does not affect polyester decomposition. Note how closely the predicted residues match the measured values. These data indicate that the PVBr flame retardant does not alter the polyester decomposition to produce less volatiles and more char in a manner similar to acid catalyzed cotton pyrolysis, and thus provide additional support to the prevalent theory that bromine suppresses combustion of the gaseous products.



Table 5 lists the DTG data for the same series of blend fabrics treated with Thpc-urea-PVBr wherein the Thpc-urea and PVBr were mixed in proportions dependent upon the polyester/cotton blend fractions (FR-II series). No significant differences are noted in comparison with observations recorded for the FR-I treated fabrics. Again, only the cotton portion of the blends is affected, as evidenced by decreased thermal stability, decreased rates of thermal decomposition, and increased residues. The rate of weight loss associated with the polymer at about 185°C increases with increasing add-on of PVBr.

TABLE 5

DTG POLYESTER/COTTON BLEND FABRICS TREATED WITH Thpc-urea-PVBr (FR-II)

Heating rate = 5°C min<sup>-1</sup>; 100% N<sub>2</sub> atm.

Polyester/ cotton	Polymer degradation		Cotton pyrolysis		Polyester pyrolysis		% residue at 600°C
	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	
0/100	188	0.0019	289	0.0686	—	—	41.7
11/89	195	0.0025	289	0.0538	407	0.0111	38.9
20/80	185	0.0028	286	0.0578	413	0.0193	35.3
30/70	184	0.0032	286	0.0492	416	0.0308	29.9
50/50	190	0.0040	286	0.0440	414	0.0382	27.0
65/35	186	0.0062	285	0.0273	407	0.0393	22.8

<sup>a</sup> Temp. at maximum rate of weight loss (°C). <sup>b</sup> Normalized maximum rate of weight loss (mg/min-mg).

#### *Pyrolysis in air atmosphere*

In the data presented thus far, thermal degradation was monitored in an inert nitrogen atmosphere. Oxygen in the purge gas introduces additional problems in interpreting the data as it is critical in the decomposition mechanism. However, oxygen is necessary for combustion, and thermal studies on flame retardant systems must consider its presence.

Figure 4 shows DTG data for the untreated fabrics in an 80% nitrogen–20% oxygen atmosphere (hereafter referred to as air atmosphere). It is apparent that the presence of oxygen introduces considerably more weight loss activity during decomposition of all the fabrics analyzed. Where one weight loss peak was observed during decomposition in nitrogen, two peaks are apparent when oxygen is present. The first, attributed to oxidative pyrolysis of the sample with the formation of volatile gases and solid char byproducts, is similar to that which occurs in nitrogen alone, except in the presence of oxygen the gases can undergo further oxidation to produce the observed phenomenon of flaming. The second weight loss results from combustion of the solid char byproducts and cannot occur in the absence of oxygen. If the solid char oxidation reaction occurs rapidly enough, glowing is observed.

Both cotton and polyester undergo oxidative pyrolysis and solid char oxidation reactions. Table 6 summarizes the results shown in Fig. 4. Maximum rate of de-

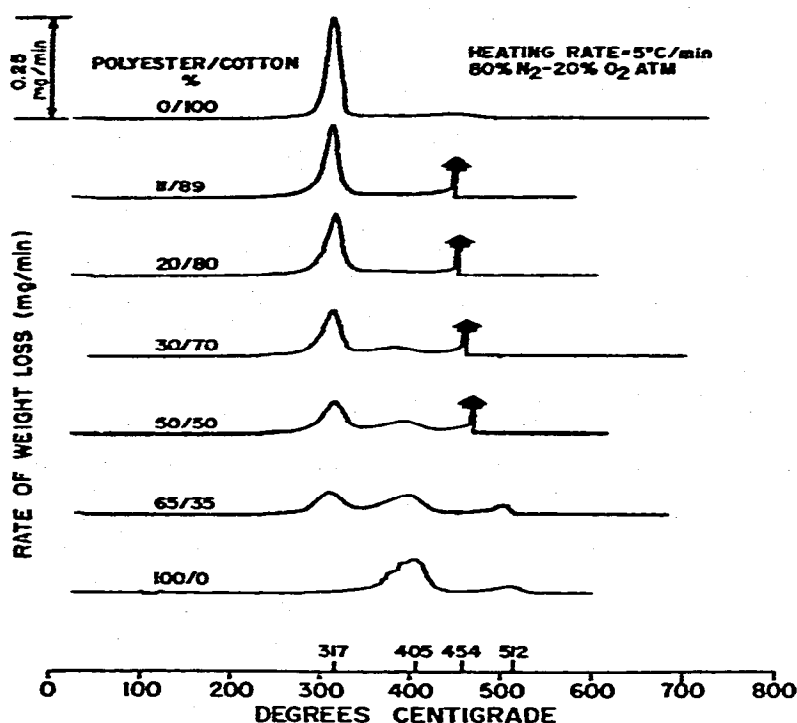


Fig. 4. DTG of untreated polyester/cotton blend fabrics. Heating rate =  $5^{\circ}\text{C min}^{-1}$ ; air atm.

composition is increased from 0.154 to 0.253 mg/min-mg in the 100% cotton fabric, an increase of 64%.

Peak temperature decreased from 347 to  $317^{\circ}\text{C}$ . The char exhibited a maximum combustion rate of 0.011 mg/min-mg at  $454^{\circ}\text{C}$ . Char oxidation continues until all of the carbonaceous residue is consumed, as indicated by zero weight in the TG data. Even though the rate of char oxidation is apparently much slower than the rate of pyrolysis oxidation, differential thermal analysis has shown this reaction to be quite exothermic<sup>31,32</sup>.

The 100% polyester yarns did not show an increase in the rate of weight loss and the peak temperature decreased only by about  $11^{\circ}\text{C}$ . The solid char exhibited a maximum rate of oxidation (0.019 mg/min-mg) at about  $512^{\circ}\text{C}$ , and was completely consumed. Under normal burning conditions, polyester fabric will melt and drip away from the flame without obvious glowing, however, in the configuration of this experiment, the solid char is held within the heated area and the char goes through the entire combustion sequence.

Weight losses associated with oxidative pyrolysis of each blend fraction occurred at the expected temperatures; however, an auto-ignition phenomenon occurred during the char combustion of the 11 to 50% polyester fabrics. The sample thermocouple indicated a large energy release and the samples were completely consumed at a very rapid rate, preventing calculation of meaningful derivative (indicated by arrow in Fig. 4). Temperature of auto-ignition was between the

TABLE 6  
DTG UNTREATED COTTON/POLYESTER BLEND FABRICS  
Heating rate =  $5^{\circ}\text{C min}^{-1}$ ; 80%  $\text{N}_2$ -20%  $\text{O}_2$  atm.

Polyester/ cotton	Oxidative pyrolysis			Char oxidation			% Residue at $600^{\circ}\text{C}$	
	Cotton			Polyester				
	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>		Rate <sup>b</sup>
0/100	317	0.253	—	—	—	454	0.011	0
11/89	314	0.181	383	0.007	453	°	°	0
20/80	319	0.154	379	0.011	455	°	°	0
30/70	315	0.113	385	0.020	464	°	°	0
50/50	318	0.079	396	0.031	473	°	°	0
65/35	313	0.057	399	0.048	506	°	0.019	0
100-0	—	—	405	0.091	512	°	0.019	0

<sup>a</sup> Temp. of maximum rate of weight loss ( $^{\circ}\text{C}$ ). <sup>b</sup> Normalized maximum rate of weight loss (mg/min-mg). ° Auto-ignition.

temperatures of maximum char oxidation for the cotton and polyester blend fractions. One possible explanation for this phenomenon is overheating of the polyester char due to the exothermic cotton char oxidation, resulting in simultaneous oxidation of the polyester char. The additional heat from the polyester char oxidation contributes to the apparent flashing of the remaining residue of both components. Another possibility, suggested by Hobart and Mack<sup>32</sup>, is the presence of an inorganic impurity in the polyester char that catalyzes the overall char combustion. They found an ash content of 0.28% in the 100% polyester fiber, which they speculate might act as the catalyst. They attribute the lack of auto-ignition in the 100% cotton to the absence of the catalyst, and the lack of auto-ignition in the 100% polyester to the absence of cotton. Close analysis of the data points of Fig. 4 indicates that minimal auto-ignition is occurring in the 65/35 blend. This probably results from only minimal amounts of cotton char being present.

Figure 5 and Table 7 show data for the FR-I treated blends analyzed in air. As observed in nitrogen, the flame retardant decreases both the rate and temperature of cotton decomposition. The 100% cotton decomposition rate decreased from 0.253 to 0.098 mg/min-mg, approximately 60%. Peak temperature decreased from 317 to 280°C.

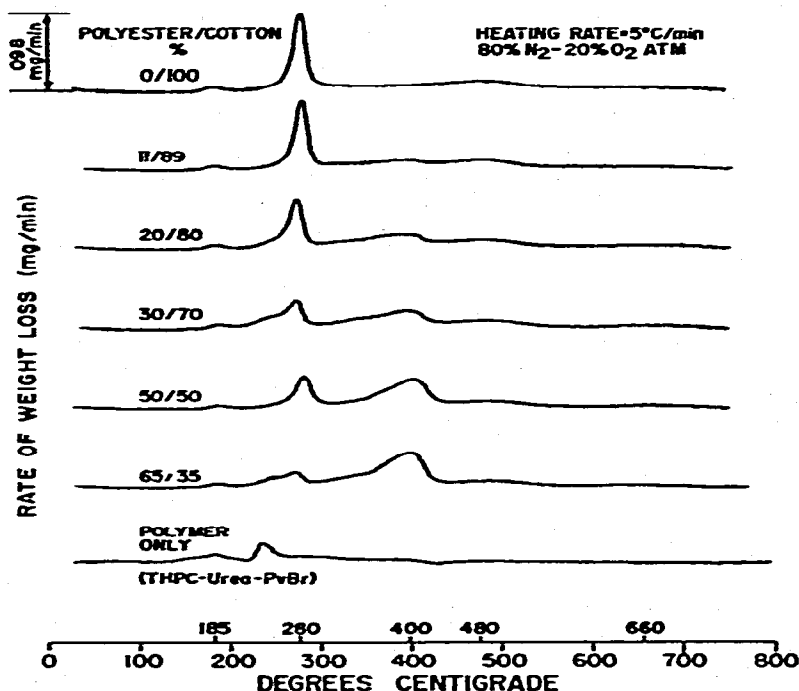


Fig. 5. DTG of polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-I). Heating rate =  $5^{\circ}\text{C min}^{-1}$ ; air atm.

Although the rate of char oxidation was not appreciably changed, its peak temperature increased from 454 to  $470^{\circ}\text{C}$ . Auto-ignition no longer occurred and the

TABLE 7

## DTG POLYESTER/COTTON BLEND FABRICS TREATED WITH Thioc-urea-PVBr (FR-I)

Heating rate = 5°C min<sup>-1</sup>; 80% N<sub>2</sub>-20% O<sub>2</sub> atm.

Polyester/ cotton	Polymer degradation		Oxidative pyrolysis				Char oxidation				% Residue at 600°C	
	Temp. <sup>a</sup>	Rate <sup>b</sup>	Cotton		Polyester		Primary		Secondary			
			Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>		
0/100	185	0.0036	280	0.098	—	—	—	480	0.013	657	0.0047	10.9
11/89	184	0.0059	281	0.088	390	0.013	—	479	0.013	662	0.0044	11.6
20/80	184	0.0055	276	0.064	394	0.019	—	479	0.011	663	0.0048	11.1
30/70	188	0.0061	275	0.037	398	0.024	—	488	0.011	661	0.0047	10.5
50/50	190	0.0044	283	0.040	403	0.037	—	484	0.000	660	0.0041	9.40
65/35	188	0.0055	274	0.020	400	0.045	—	487	0.008	646	0.0036	6.67

<sup>a</sup> Temp. at maximum rate of weight loss (°C). <sup>b</sup> Normalized maximum rate of weight loss (mg/min-mg).

TABLE 8

## DTG POLYESTER/COTTON BLEND FABRICS TREATED WITH Thioc-urea-PVBr (FR-II)

Heating rate = 5°C min<sup>-1</sup>; 80% N<sub>2</sub>-20% O<sub>2</sub> atm.

Polyester/ cotton	Polymer degradation		Oxidative pyrolysis				Char oxidation				% Residue at 600°C	
	Temp. <sup>a</sup>	Rate <sup>b</sup>	Cotton		Polyester		Primary		Secondary			
			Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>	Temp. <sup>a</sup>	Rate <sup>b</sup>		
0/100	191	0.0019	278	0.084	—	—	—	483	0.013	656	0.0047	12.49
11/89	200	0.0025	277	0.071	394	0.013	—	482	0.013	649	0.0048	11.14
20/80	191	0.0029	279	0.071	403	0.019	—	476	0.012	664	0.0045	10.88
30/70	186	0.0036	277	0.058	399	0.027	—	486	0.011	665	0.0045	9.83
50/50	187	0.0047	276	0.042	395	0.035	—	487	0.010	660	0.0043	8.32
65/35	185	0.0068	279	0.026	399	0.043	—	489	0.008	661	0.0033	7.55

<sup>a</sup> Temp. at maximum rate of weight loss (°C). <sup>b</sup> Normalized maximum rate of weight loss (mg/min-mg).

rates of char oxidation were measurable. Oxidation of the cotton and polyester chars appear to coincide over a wide temperature range. A primary char oxidation occurs at about 485°C, and a secondary char oxidation at 660°C. The secondary oxidation is thought to be related to decomposition of a portion of the flame retardant. Residual contents of about 10% are found for each blend.

Table 8 lists DTG data for the FR-II treated blends. Again, the results are similar to those recorded for the FR-I treatment.

## CONCLUSIONS

A series of polyester/cotton blend fabrics was investigated with thermogravimetric techniques. The fabrics were analyzed in both nitrogen and air atmospheres. The same fabrics were also analyzed after treatment with Thpc-urea-PVBr flame retardant. The sample weight vs. temperature data provided information about the thermal stability and decomposition of the fabrics and their blend components, as well as their residues after pyrolysis.

Both cotton and polyester thermally decompose to yield volatile gases and solid char byproducts. The decomposition mechanism of the cotton portion, although not sensitive to presence of the polyester, is greatly affected by the flame retardant. By treating the fabric with flame retardant, its thermal decomposition is radically altered, as evidenced by decreased thermal stability, decreased rate of decomposition, and increased residual chars. For example, the maximum rate of weight loss for the 100%

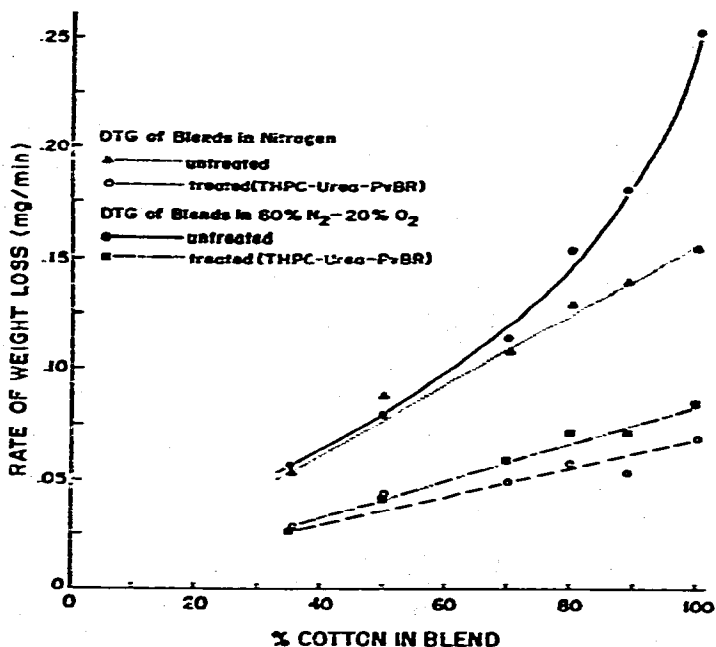


Fig. 6. Maximum rate of cotton degradation vs. blend fraction. ▲ = Untreated in nitrogen atm. ○ = treated in nitrogen atm.; ● = untreated in air atm.; ■ = treated in air atm.

cotton fabric is decreased by more than 40%, from 0.154 to 0.089 mg/min-mg. Peak temperature for the 100% cotton decreases from 346 to 289°C, and the residue remaining after pyrolysis increases from 8 to 40%. Changes in rate of decomposition, apparent in all of the blends studied, are summarized in Fig. 6.

When oxygen is present in the purge atmosphere the weight loss activity is increased considerably. The volatile gases and solid char pyrolysis products both undergo combustion. Rate of decomposition for the 100% cotton fabric increased from 0.154 to 0.253 mg/min-mg and the peak temperature decreased from 346 to 317°C. The char, with a peak decomposition temperature of 454°C, was completely consumed.

The polyester char also undergoes complete combustion in the presence of oxygen. In the blend fabrics the chars exhibited an auto-ignition phenomenon resulting in a large energy release and simultaneous flashing of the entire char. Addition of the flame retardant prevented auto-ignition.

Figure 7 shows data similar to Fig. 6, but for the polyester blend fraction. These data indicate that polyester decomposition is not significantly affected by presence of either cotton, flame retardant or oxygen.

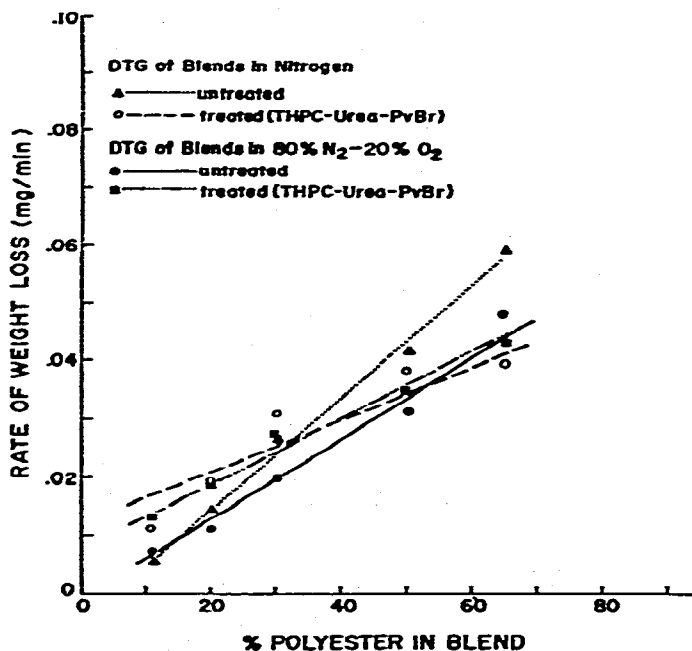


Fig. 7. Maximum rate of polyester degradation vs. blend fraction.  $\blacktriangle$  = Untreated in nitrogen atm.;  $\circ$  = treated in nitrogen atm.;  $\bullet$  = untreated in air atm.;  $\blacksquare$  = treated in air atm.

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