Thermal Analyses of Flame-Retardant Twills Containing Cotton, Polyester and Wool

BRENDA J. TRASK and JOHN V. BENINATE, *Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

Medium weight twill fabrics constructed from cotton and cotton blended with polyester and/or wool were analyzed under nitrogen by three thermoanalytical techniques. Fabrics were tested both before and after treatment with [tetrakis(hydroxymethyl)phosphonium] sulfate (THPS), urea, and trimethylolmelamine. The presence of all fibers was distinguishable in differential scanning calorimetric analysis (DSC) of untreated fabrics; the relative positions of the endothermic, decomposition peak temperatures were only slightly changed. After flame-retardant (FR) treatment, the blended cotton and wool fibers were altered. Both fibers decomposed as exotherms during DSC analysis. These data supported earlier microscopical, X-ray evidence that wool fibers were actually reacting with the FR treatment. The two DSC peaks for polyester polymer melting and decomposing remained unaffected by either blending with other fibers or the presence of the FR finish on the fabric. There was excellent agreement between DSC peak temperatures and the temperature of maximum rate of weight loss obtained from thermogravimetric analysis (TGA). Blending cotton with either of these fibers increased the residue measured after TGA. The increased residue correlated with increased flame resistance as measured by the 45° angle, edge-ignition burning rate test.

INTRODUCTION

Schwenker and Beck found that cotton cellulose decomposed into many substances when subjected to thermal stress.[1] Some of these products were combustible and contributed to cellulose flammability. These researchers found that approximately the same products were formed whether pyrolysis occurred in oxygen or nitrogen. They concluded that the degradation mechanism was nonoxidative. This finding supported earlier research that claimed cellulose depolymerized under thermal stress by scission of the 1,4-glucosidic linkages followed by rearrangement of the monomer to levoglucosan. They suggested that levoglucosan (1) fragmented further to low molecular weight volatile products leaving tars and (2) polymerized to form chars.

Perkins et al. studied differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of lightweight cotton and modacrylic/cotton blends treated with various flame retardant (FR) formulations including [tetrakis(hydroxymethyl)phosphonium] chloride (THPC).[2] Pensa and co-workers examined lightweight polyester/cotton blends treated with a variety of FR chemicals and examined TGA data in air.[3] Two later papers showed the thermal behavior of lightweight polyester/cotton fabrics treated with THPC–urea–polyvinyl bromide.[4,5] The TG analyses showed no significant changes in polyester decomposition occurred due to the presence of cotton, FR finish, or oxygen atmosphere. Perkins et al. subsequently used TGA and

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differential scanning calorimetric analysis (DSC) to study sheeting and basketweave cotton/polyester fabrics. The specimens were treated with several FR finishes including dibromopropylphosphate (DBPP) for the polyester component.[6] The presence of DBPP had no effect on residues left by TGA because the halogen finish performed its FR function in the vapor phase.

Felix et al. performed DTA studies on a variety of wools under nitrogen atmosphere.[7] They stopped the procedure at approximately 260°C—the point of wool liquefaction. They described three components of wool thermal decomposition: (1) the loss of small molecular species including H_2O, H_2S, CH_3SH, CO_2, and NH_3 from reactive, amino acid side chains; (2) the destruction of crosslinks, —S—S— bonds, H bonds, and salt linkages by a process called denaturation; and (3) the rupture of peptide bonds producing wool liquefaction. Tai and Needles applied a 20% aqueous solution of THPC to cotton and wool fabrics.[8] Under their mild treatment conditions, there was no apparent reaction with the cotton. Wool showed some measurable phosphorus present. The explanation that THPC acted as a reducing agent on the disulfide bonds of wool was supported by reduced fabric strength. Thermoanalysis with DTA showed a small change in wool decomposition endotherms. They measured a sharper peak at a slightly higher temperature.

As part of a program to develop a multipurpose finish for medium weight fabrics to be used in uniforms, Beninate et al. prepared a series of seven twill fabrics blended from cotton, polyester, and wool fibers.[9] The fabrics were treated with five flame-retardant (FR) finishes. The durable press and FR properties were investigated. A collateral study of the burning rates of these same twill fabrics was performed.[10] Both investigations agreed that the best finish was a pad/dry/cure treatment containing bis[tetrakis(hydroxymethyl)-phosphonium] sulfate (THPS), urea, and trimethylolmelamine (TMM).

Subsequently, Goynes and Trask examined three twill fabrics, 100% cotton, 50/50 cotton/polyester, and 60/40 cotton/wool, with the scanning electron microscope before and after treatment with THPS–urea—TMM.[11] Three areas of the fibers were examined. Samples were studied before burning as well as after. Two areas of the fabric chars were investigated and included completely burned fibers and those fibers that were just beginning to respond to the heat. Both polyester and wool fibers visibly melted and flowed before noticeable changes occurred to the cotton fibers. Twills blended with polyester or wool developed more stable chars than those of either fiber alone. The presence of phosphorus was detected by energy dispersive X-ray analyses in both cotton and wool fibers from treated fabrics. This was evidence that the flame-retardant actually reacted with or was deposited on the wool fibers.

The current research was designed to study the thermoanalytical properties of the same twill fabrics that were examined microscopically. A triblend of all three fibers was also included. DSC, TGA, and differential thermogravimetry (DTG) techniques were used to relate the visual effects seen with the scanning electron microscope to measurable thermal effects such as DSC peak decomposition temperatures, and the TGA temperatures at which the maximum rates of weight loss occur. Residue data after TGA analyses were examined as an indicator of flame resistance. We also sought thermoanalytical evidence that wool reacted with the FR finish.

EXPERIMENTAL

Fabric samples used in this research were desized, scoured and bleached, 3/2 twills weighing approximately 8 oz/yd^2. Fabric composition included 100% cotton, and intimate blends of 50/50 cotton/polyester (C/P), 60/40 cotton/wool (C/W), and 60/25/15 cotton/polyester/wool (C/P/W). The four fabrics were previously treated with a 35% solids solution containing bis[tetrakis(hydroxymethyl)phosphonium] sulfate (THPS), urea, and trimethylolmelamine (TMM) (THPS—urea—TMM) and resulted in phosphorus contents ranging from 1.9 to 2.3%.[9] Because no 100% polyester or 100% wool twills were prepared, 100% polyester sliver and a 100% wool fabric were analyzed as controls.

Thermal analyses of samples were performed using the DuPont 1090 Thermal Analyzer.* The DSC 910 and TGA 951 modules were employed and fabric samples were approximately 5 and 10 mg, respectively. The dynamic purge gas was nitrogen flowing at 300 mL/min. The heating rate was 15°C/min. TGA residues were measured at 575°C.

The edge ignition burning rate test was described in detail earlier.[10] Fabric specimens measured 18 in. in the warp and 4 in. in the filling. Samples were held at a 45° angle. The burner flame contacted the lower edge of the test specimen for 5 s. The burning rate was the slope (mm/s) of the least squares line derived from the data of duplicate samples.

RESULTS AND DISCUSSION

In Figure 1 are the thermograms for 100% cotton twill fabric. The DSC curve showed a small endothermic peak that corresponded to water loss and a major endothermic peak at 358°C that represented the decomposition of cellulose. The TGA curve was superimposed over the DSC curve. The cotton began to lose weight rapidly over approximately the same temperature range, and this loss corresponded to cellulose decomposition. The derivative of the weight loss curve (DTG) was plotted at the bottom of the figure and was used to set the integration limits for calculating the temperature at which the maximum rate of weight loss occurred in TG analyses. This temperature will be designated simply as the TGA peak temperature. The vertical axis for each thermogram was identified separately. The DSC units are mW, TGA units are % wt loss, and DTG units are % wt loss/min. For 100% cotton twill, the TGA peak temperature was 369°C. Routinely, the TGA peak temperature was slightly higher than the corresponding DSC peak temperature under our test conditions.

In Figure 2 are shown the thermograms for a sample of 100% polyester. The synthetic polymer showed an endothermic peak for melting that occurred at 252°C. Polymer decomposition occurred as a higher temperature endotherm peaking at 415°C. The TGA curve showed that weight loss was only associ-

*Names of companies or commercial products are given solely for providing scientific information and does not imply endorsement by the Department of Agriculture over others not mentioned.

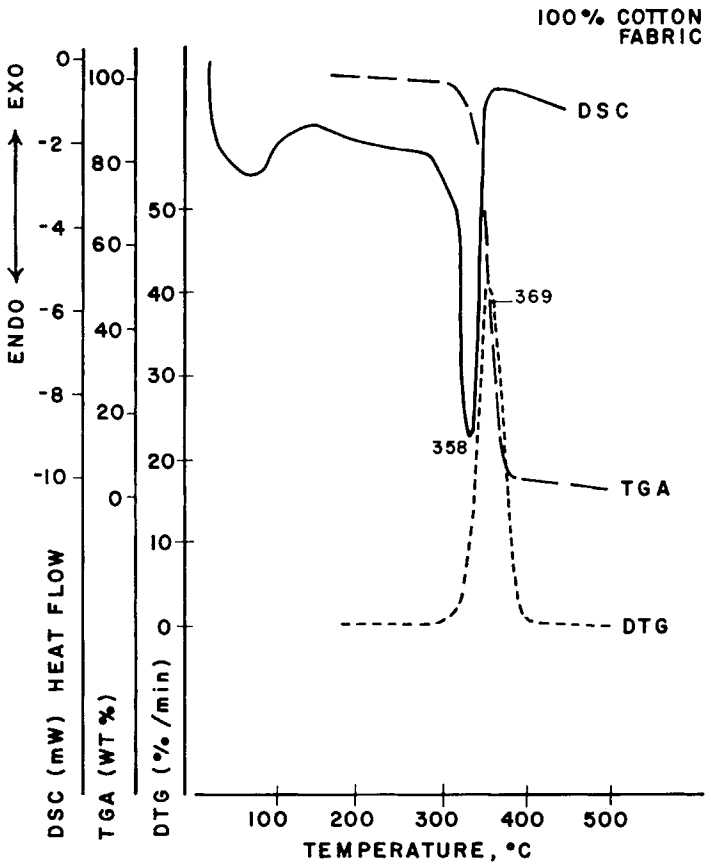

Fig. 1. Differential scanning calorimetric (DSC), thermogravimetric analyses (TGA), and differential thermogravimetric (DTG) thermograms of 100% cotton twill in nitrogen.

ated with decomposition and the rate of loss peaked at 441°C. The derivative curve showed only a single area of weight loss also.

The DSC, TGA, and DTG curves for 100% wool are plotted in the Figure 3. In DSC analysis, wool had a large water-loss endotherm. Between approximately 175 and 400°C, additional endothermic responses were recorded. Three peaks were apparent for this fabric. Our DSC peak temperatures agreed closely with the DTA peak temperatures reported by Felix et al.[7] The final DSC peak occurred at 310°C, and the instrument recorded that peak as jagged, miniendothermic and miniexothermic responses. This portion of the DSC thermogram was recording the process of wool liquefaction. The TGA curve showed that weight loss occurred over a wide temperature range and peaked at 327°C. The derivative curve showed an uneven rate of weight loss with multiple small peaks. The first two DSC peaks appeared mirrored in the earlier portion of the derivative peak. The remainder of the derivative peak reflected the unsteady, liquefaction of the wool. The ballooning and rupturing of the heated fibers viewed in the scanning electron photomicrographs[11] were visual evidence of the liquefaction of wool under thermal stress.

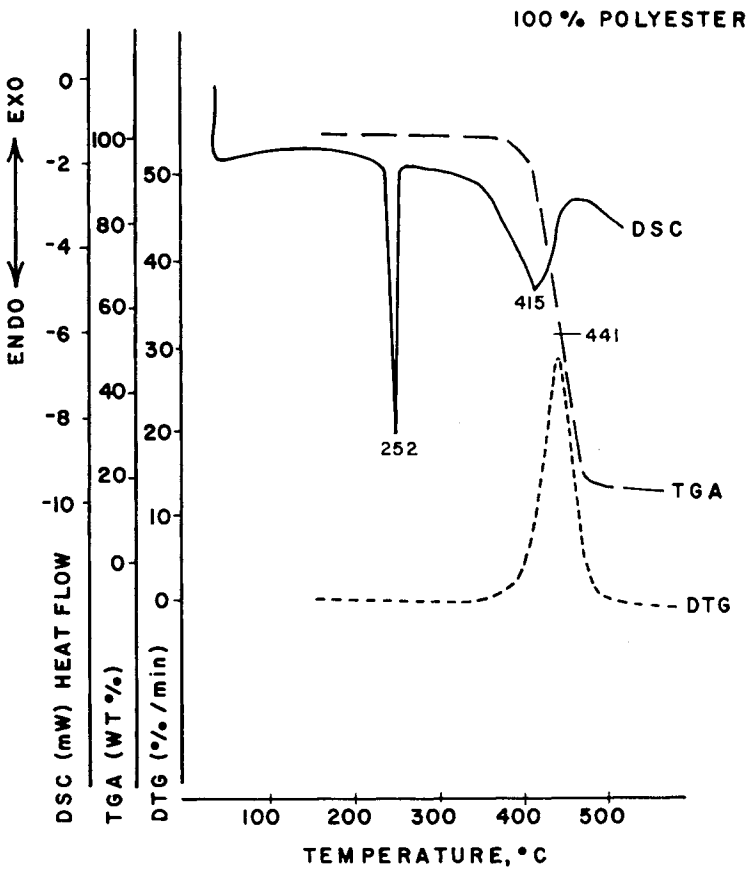

Fig. 2. Differential scanning calorimetric (DSC), thermogravimetric analyses (TGA), and differential thermogravimetric (DTG) thermograms of 100% polyester in nitrogen.

In Figure 4 the DSC curves representing the three fibers used to produce the twill fabrics are replotted for comparison. The melting of polyester occurred prior to cellulose decomposition. The decomposition of polyester began in the same region as cellulose decomposition, but did not peak until after the cellulose endotherm was completed. The decomposition of wool began slightly before polyester melted. The final wool peak maximum preceded the cellulose peak maximum but the decomposition temperature ranges of both cotton and wool fibers overlapped.

The next two figures are composites. The upper portions are the DSC and TGA curves of the untreated twills and the lower portions represent the thermograms of the corresponding FR treated fabric. In Figure 5 are plotted the curves for 100% cotton and 50/50 C/P. The 100% cotton treated with THPS–urea–TMM is shown in Figure 5(b). The DSC endotherm that occurred at 358°C for untreated cotton disappeared, and the main feature of the new curve was an exotherm peaking at 322°C. The appearance of a lower temperature exotherm with cotton treated with phosphorus/nitrogen FR finishes using DSC has been previously reported.[6]

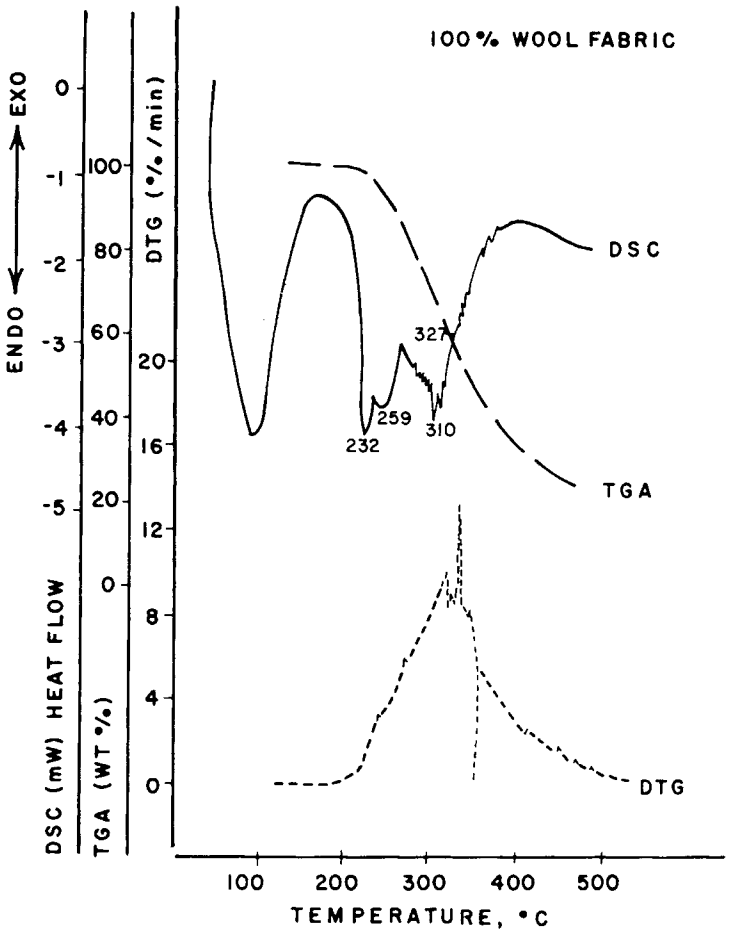

Fig. 3. Differential scanning calorimetric (DSC), thermogravimetric analyses (TGA), and differential thermogravimetric (DTG) thermograms of 100% wool in nitrogen.

The thermograms of the intimate blend of 50/50 C/P twill are shown in Figures 5(c) and 5(d). The DSC curve of the untreated fabric clearly resolved into the three expected peaks—polyester melting at 254°C, cellulose and polyester decomposing at 360° and 436°C, respectively. In the blend, the polyester decomposition peak temperature was slightly elevated. The TGA curve showed a two-step weight loss with peak temperatures corresponding to, but slightly higher than the DSC decomposition peak temperatures.

When the 50/50 blend was treated with THPS–urea–TMM, the DSC curve showed the cotton component again decomposed at a lower temperature and as an exotherm. The polyester decomposition peak dropped from approximately 436 to 412°C. The TGA curve clearly showed a two-step weight loss; cellulose decomposition shifted to a lower temperature, and polyester remained unchanged. The endothermic melting peak of the polyester showed no weight loss. Earlier X-ray analysis[11] found no more phosphorus present on the surface or inside polyester fibers than was present in the background. There

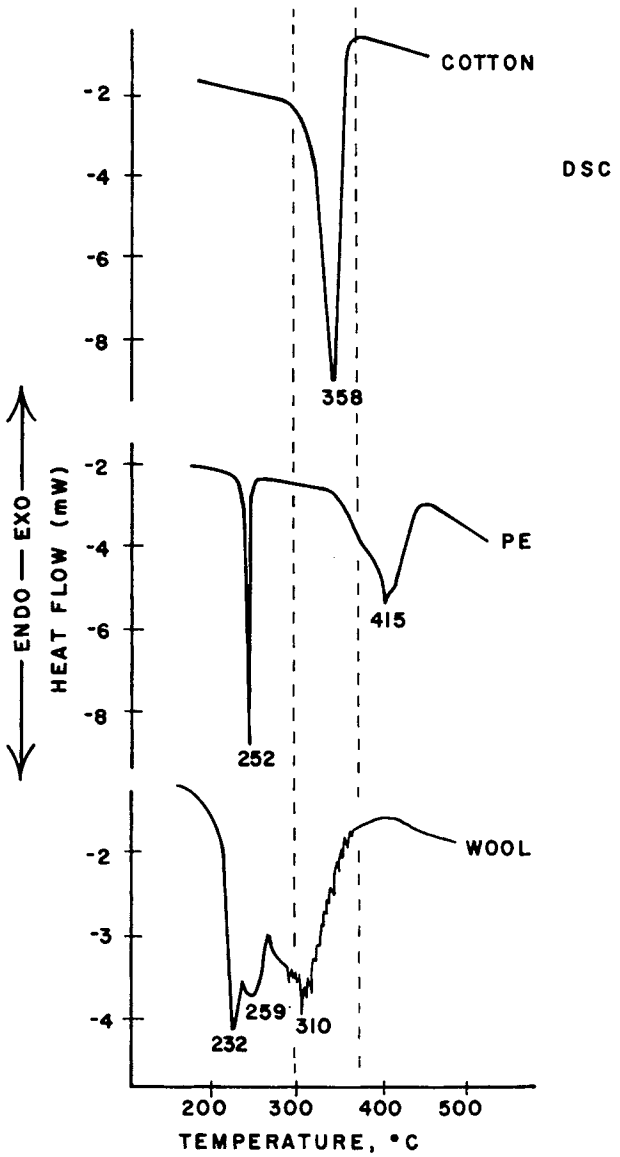

Fig. 4. Comparison of differential scanning calorimetric (DSC) thermograms of 100% cotton, 100% polyester (PE), and 100% wool in nitrogen.

was no thermoanalytical evidence that the presence of the FR affected the polyester.

The DSC curves of both 100% cotton and 50/50 C/P treated fabrics showed a slight exothermic trend following the completion of the major exotherm. This trend was accompanied by continued, slow loss of sample weight. The exothermic portion of the curve was evidence of a small loss of sample heat capacity probably associated with some volatilization of the sample. With 50/50 C/P, the exothermic portion ceased when polyester decomposition began.

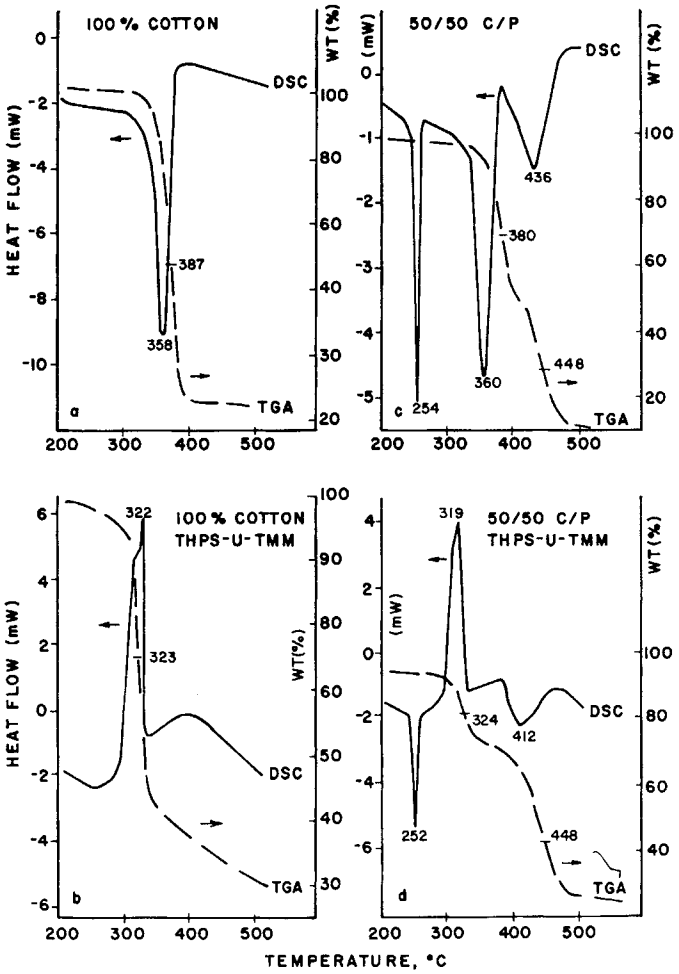

Fig. 5. Comparison of differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) thermograms in nitrogen of twills composed of: (a) 100% cotton, untreated; (b) 100% cotton, treated with [tetrakis(hydroxymethyl)phosphonium] sulfate, urea, and trimethylolmelamine (THPS–U–Tmm); (c) 50/50 cotton/polyester, (C/P) untreated; (d) 50/50 cotton/polyester treated with THPS–U–Tmm.

In Figure 6 are plotted the curves for 60/40 C/W and 60/25/15 C/P/W. The DSC and TGA thermograms of 60/40 C/W twill are contained in Figures 6(a) and 6(b). The curve from the untreated blend showed a broad endothermic area, representing wool decomposition, that peaked at 286°C. The blend showed no multiple peaks as were seen in the 100% wool fabric. The cellulose peak temperature at 377°C was slightly elevated. The TGA curve showed only a single, gradual, sample weight loss. The derivative curve of the TGA (not shown) indicated that a shoulder from approximately 225 to 350°C preceded the sharper rate change that peaked at 379°C. This shoulder probably corresponded to early wool decomposition.

The curves for treated C/W are plotted in Figure 6(b). The DSC curve contained two exothermic peaks: a small peak at 262°C and a large peak at

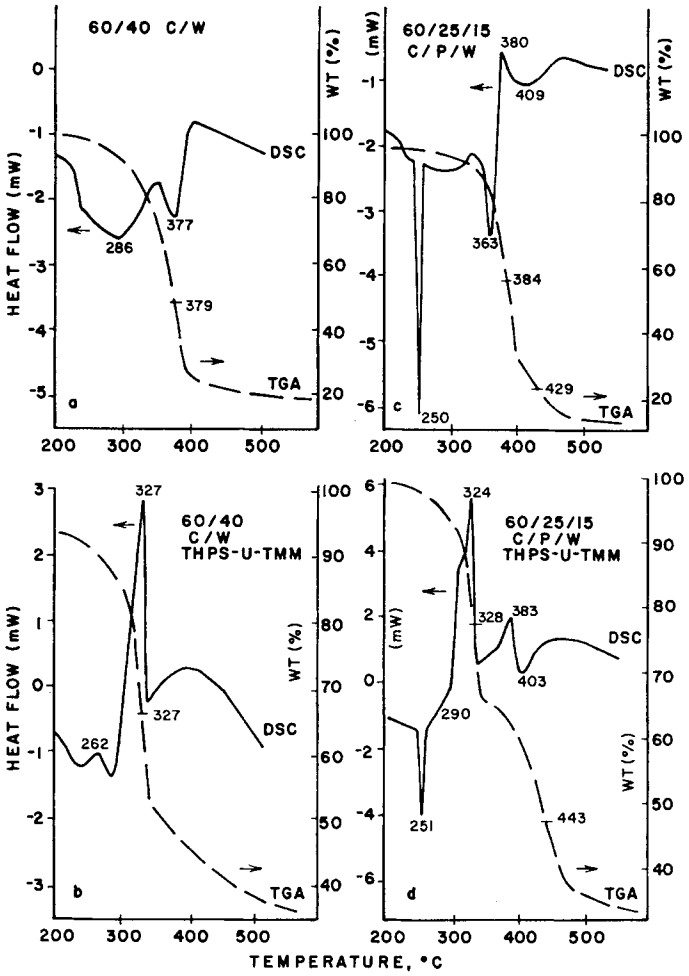

Fig. 6. Comparison of differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) thermograms in nitrogen of twills composed of: (a) 60/40 cotton/wool (C/W), untreated; (b) 60/40 cotton/wool treated with [tetrakis(hydroxymethyl)phosphonium] sulfate, urea, and trimethylolmelamine (THPS–U–Tmm); (c) 60/25/15 cotton/polyester/wool (C/P/W), untreated; (d) 60/25/15 cotton/polyester/wool, treated with THPS–U–Tmm.

327°C. The larger peak corresponded to the treated cellulose fraction observed earlier. The important feature of this thermogram was the lower temperature exotherm that preceded the cotton exotherm. This was strong evidence that wool fibers actually reacted with the phosphorus/nitrogen finish as had the cellulose fibers. Although earlier work with THPC alone did not show this thermoanalytical response,[8] the presence of phosphorus was detected inside the wool fiber in the concurrent microscopical study.[11] In Figure 6(b), the TGA curve showed only one, rapid weight loss region; the derivative curve could not discriminate between treated wool and treated cotton decompositions.

Thermograms of the triblend twill fabric were plotted in Figures 6(c) and 6(d). The triblend contained 60% cotton, 25% polyester, and 15% wool. In the

DSC curve of untreated triblend, the presence of cotton and polyester were recognizable. The small quantity of wool was almost masked. However, from 210 to 330°C there was a broad endotherm out of which the polyester melt peak appeared sharply. This broad endotherm corresponded to the wool fraction. The TGA curve showed two weight loss regions. The decomposition of wool and cotton were combined in the first region; decomposition of polyester occurred in the second weight loss region.

The thermograms of the triblend treated with the FR finish were plotted in Figure 6(d). The DSC curve showed that the endotherm for melting polyester was unchanged. The remaining prominent features included a large exotherm that peaked at 324°C, the appropriate temperature for FR-treated cellulose and the endothermic peak at 403°C for unmodified polyester decomposition. The peak for treated cellulose again contained a shoulder that conceivably represented the treated wool fibers. The TGA curve showed two distinct weight loss regions—wool/cellulose and polyester decompositions. These two weight-loss regions were confirmed by the DTG curve (not shown).

The slight exothermic trend that followed the cellulose major exotherm was clearly present in both treated fabrics of Figure 6. The apparent peak at 383°C is not a real peak but evidence of loss of heat capacity as discussed for Figures 5(b) and 5(d).

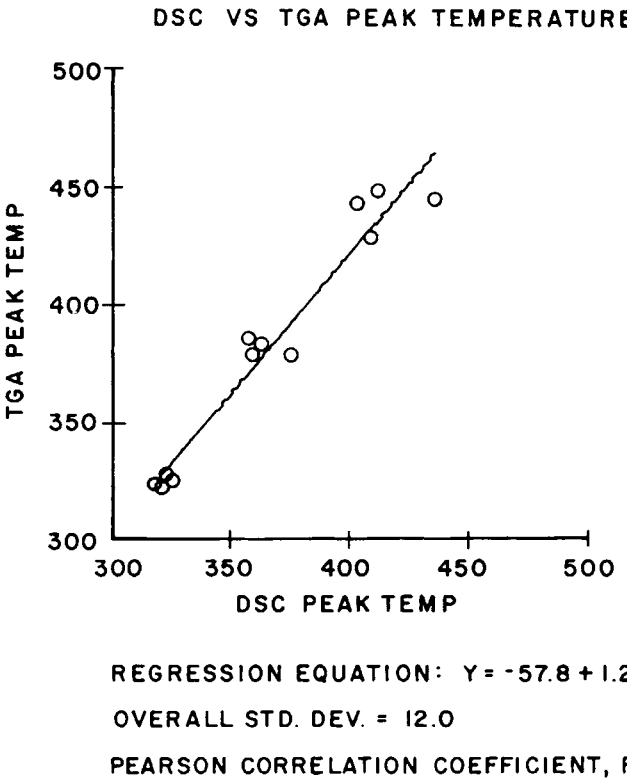

Fig. 7. Differential scanning calorimetric (DSC) peak temperatures vs. thermogravimetric analyses (TGA) temperatures of maximum rate of weight loss.

The DSC peak temperature and the corresponding TGA temperature at which the maximum rate of weight loss occurred are plotted in Figure 7. The linear relationship was excellent with a correlation coefficient of 0.97.

One of the mechanisms used to explain cotton flame resistance involves a change in cellulose decomposition that results in an increase in char formation. The microscopical research[11] indicated that the presence of polyester or wool in cotton blends created physically more stable chars than were found with cotton alone. The chars retained more fabric integrity. The parameter measured in thermoanalysis that most closely relates to that mechanism is the amount of residue remaining after TG analysis. At 575°C untreated 100% cotton retained 3% residue. Blending 50% polyester with 50% cotton raised the residue to 11% and 100% polyester produced 17% residue. The relationship between cotton/polyester fiber content and residue was linear. As polyester content increased, the residue increased. When 40% wool was blended with 60% cotton, the residue increased to 19% and 100% wool retained 21% residue at 575°C. The relationship of cotton/wool to residue was curvilinear—a sharp initial increase with increasing wool content that reached a plateau. The triblend residue was 12% and fell between the two curves, as would be predicted.

When 100% cotton was treated with THPS–urea–TMM, the fabric residue increased from 3% to 39%. When half of the cotton fibers were replaced with

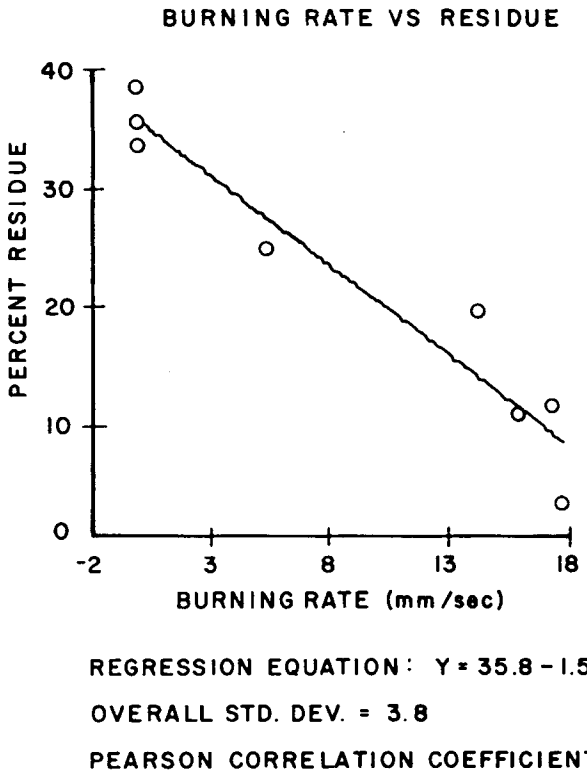

Fig. 8. Burning rate (mm/s) from the 45° angle, edge-ignition burning rate test vs. thermogravimetric analyses (TGA) percent residue measured at 575°C.

unreactive polyester, the residue of the treated sample fell to 25%. If 60% cotton was blended with 40% wool, which has been shown to react with the finish, this treated blend retained 36% residue. When a portion of this wool was replaced with polyester in the treated triblend, the residue dropped to 34%. Based on TGA residue data, the 60/40 C/W blend was the most flame resistant of all the treated blends; it retained only slightly less residue than treated 100% cotton. This finding agrees with two earlier research studies.[9,10] The 60/40 C/W blend was shown to be the best in the DP/FR study; this blend was also found, through statistical analysis, to be the most FR no matter which finish was applied or which FR test was used to evaluate it.

If Figure 8 are plotted the 45° angle, edge ignition burning rate data from the earlier study[10] vs. the percent residue from thermogravimetric analyses. Data for the four twills before and after FR treatment were included. With cotton present, a good straight line relationship was shown and the correlation coefficient was −0.96.

SUMMARY AND CONCLUSIONS

In nitrogen atmosphere cotton twill decomposed during DSC analysis as a single endothermic peak at 358°C. The decomposition was expressed in TG analysis as a single, rapid weight loss region occurring at a slightly higher temperature than the DSC peak. When cotton was intimately blended with 50% polyester, both fibers were identifiable in the DSC thermograms. There was some overlap of decomposition temperatures seen in the individual fiber DSC curves. In the blended fabric, the two decomposition endotherms were separate and the polyester peak temperature was slightly elevated. The low temperature, melting endotherm for polyester remained unchanged in all fabrics whether treated or not.

When cotton was blended with 40% wool, both fibers were distinguishable as adjacent endothermic peaks. The decomposition temperatures of the individual fibers overlapped when analyzed separately. In the triblend, the wool component was more difficult to distinguish. In the TGA thermograms, the wool/cotton decompositions overlapped.

The THPS–urea–TMM FR finish reacted with cotton cellulose and modified the fabric's response to heat. Cellulose decomposition occurred at a lower temperature and as an exotherm. The presence of this exotherm was easily recognizable in all blends with polyester, wool, or both fibers.

In treated twill blends containing polyester, the polyester fraction was relatively unaffected in either DSC or TG analyses. While polyester decomposition peak temperatures varied slightly, there was no significant thermoanalytical evidence that polyester was affected by this FR treatment.

After FR treatment, wool decomposition changed from an endothermic to an exothermic response in DSC analyses. These data, combined with microscopic X-ray data that showed the presence of phosphorus inside wool fibers, were strong evidence that wool fibers react with this THPS, FR finish.

Under nitrogen atmosphere and at a 15°C/min heating rate, DSC peak temperatures and TGA temperatures of maximum rate of weight loss were compared. The relationship was linear and had an excellent correlation coefficient.

Thermoanalysis showed that both polyester (as melting) and wool (as decomposition/liquefaction) are affected by heat at lower temperatures than is cotton. These data corroborate the visual evidence in the concurrent scanning electron microscopy study.[11] Polyester and wool melted and flowed onto unaffected cellulose fibers in the early stages of thermal stress. Photomicrographs of wool blends showed bubbling and burst bubbles as early evidence of thermal stress. The DSC analyses of 100% wool fabric showed a portion of the endothermic decomposition as rapid fluctuations of endothermic and exothermic reactions that apparently correspond to the bubbles visible on the heated wool fibers. In the blends, those fluctuations in the DSC curve were not apparent.

The thermoanalytical research corroborated the microscopical research that indicated the presence of polyester or wool in cotton blends created physically more stable chars than was found with cotton alone. We measured an increase in percent residue of the blends after TGA analyses. In addition, percent residue correlated well with flame resistance as measured by the edge ignition, 45° angle, burning rate test.

The authors wish to acknowledge the suggestion of Dr. T. A. Calamari, Jr., SRRC, that we test a sample of treated, 100% wool as additional support for our conclusion. The DSC curve of a 100% wool fabric treated by Beninate with a related phosphorus/nitrogen FR finish (15% THP hydroxide and an ammonia cure) exhibited an exothermic peak at approximately 307°C.

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