THERMOANALYTICAL STUDIES 0); FLAME-KETARDANT YOLYESiER/ COTTON TEXTILE BLENDS: A COMPAKISON OF THPC-urea-PVBr AND THPOH AMMONIA TREATMENTS*

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ABSTRACT

Flame-retardant polyester/cotton fabrics are increasing in importance in the apparel and household fabrics market. Phosphorus-nitrogen flame-retardant systems developed for 100% cotton are not necessarily effective for polyester/cotton blends. **Bromine effectively imparts flame-retardant properties to polyester resins. It has been theorized that systems containing both bromine and phosphorus should be suitable for polyester/cotton blends. A thcrmoanalytical study was undertaken to elucidate the effect of bromine in flame-retardant polyester/cotton blend fabrics. Fabrics** having various ratios of polyester to cotton were treated with THPOH-NH₃, which is particularly effective on 100% cotton, and with THPC-urea-PVBr, which was **designed for 50/50 polycstcr/cotton blends. For comparison, data are also prczsented on a SO/50 polyester blend fabric tt-cated with THPOH-NH, and with THPC-urea flame retardants plus tris(2,3-dibromopropyl) phosphate in a two-step application. TG and DSC data were obtained in atmospheres of either nitrogen or air, using a** DuPont 990 Thermal Analysis System^{***}. The thermal changes are assigned to **decompositions of cotton, polyester, char, and resin finish. A comparison is** made **of the effects caused by the different flame-retardant finishes. 01 values and FF 3-71 data ore reported.**

INTRODUCTION

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The thermogravimetric study by Neumeycr ct al.' and the differential thermal analysis by Hobart et al.² of polyester/cotton fabrics were undertaken to determine **the interaction of the blend components on thermal degradation of the fabric. The**

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THPC-urea-PVBr flame-retardant finish described by Donaldson et af.³ was chosen bccausc it pnovidcs a phosphownitro_een compound and a bromine compound for **treating** both the cotton and polyester blend components, respectively. In this sequel to those eanlier studies, a comparison is made between THPC-urea-PVBr **(FR-I)** and **THPOH-NH**₁, a finish for 100% cotton fabrics that has aroused widespread interest in the textile industry.

Thermal analysis data are also presented for 50/50 polyester/cotton fabrics treated with tris(2,3dibromopropyl) phosphate (DBPP) alone, and in combination with THPC-urea or THPOH-NH₃. DBPP was chosen to gain further information **on interactions of** ihis **particular bromine compound with thermai degradation of po&srrr\$o~ron bknd fabrics- FIame refardazzcy data resulting** *from* **measurements** by Oxygen Index (OI) and FF 3-71 were correlated with observations from thermal analysis.

EXPERIMENTAL

A series of polyutcr[cotton sheeting fabrics with blend ratios of O/100, I I/89, ZOjSO, 30,!70_ and 5Of59 were rrratcd with THPOH-NH, ffamc rttardantGg 5_ These blend fabrics treated with THPC-urez-PVBr flame retardant were described by Donaldson and Knoepfler⁶. The five fabrics were sewn together to form one roll for treatment_ This roll 8% padded through a 35% **THPOH solution, dried at 160°F** for I $\frac{1}{2}$ min, ammoniated for 5 min, and oxidized with H_2O_2 . The phosphorus add-ons ranged from 4.6% for the 100% cotton fabric to 3.9% for the 50/50 blend.

A So/50 poiyesterjcotton basketweave fabric was treated with tris(2,3-dibromopropyl) phosphate via a Thermosol process. Portions of the same treated fabric **~crc treated in a second application with either THPC-urea7 or THPOH-NH,. The** solution concentrations of **THPC-urea** were 25% and of **THPOH**, 20, 25, or 30%.

A DuPont 990 Thermal Analysis System was used for performing thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses. Sample preparation and analysis procedures were the same as those described by Neumeyer **et al. and Hobart CC irl, Flame resistance was measured by the Children's Sleepwear Rammability Standard, FF 3-71"** or **by the vertical flame test'. Nitrogen was determined by the Kjeldahl method; phosphorus by a gavimctric procedure as the phos**phomolybdate following a Kjeldahi digestion; and bromine by a volumetric procedure using oxygen flask combustion. The OI values were determined with a Michigan Chemical oxygen index apparatus according to ASTM procedure¹⁰.

RESULTS AND DISCUSSION

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Diffrrmtial thczmo_gravimetric analysis (DTG) and DSC curves for the treated blend fa'mics ZXQ+Z& in nitrw an= shown in Fig_ 1. Two maximum rates **of** weight loss are apparent in the thermogravimetric data. The first indicates volatilization of

Fig. 1. Normalized DTG and DSC curves for THPOH-NH₃ treated polyester/cotton blend fabrics. Heating rate -- 5°C min-1; 100% nitrogen atm.

Fig. 2. Normalized DTG and DSC curves for untreated polyester/cotton blend fabrics. Heating rate := 5°C min⁻¹; 100% nitrogen atm.

the sample due to decomposition of the cotton portion. The second results from decomposition of the polyester. In each case, the area under the peaks is proportional to the amount of component in the blend.

In comparison to the DTG data for the untreated fabrics reported by Neu-

meyer et al. and reproduced here in Fig. 2, it is apparent that the mechanism of cotton decomposition is altered considerably by the flame retardant. This is evidenced in the 100% cotton sample by a shift in the temperature corresponding to the maximum rate of weight loss (hereafter referred to as peak temperature) from 347 to 278 °C.

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Fig. 3. Normalized DTG and DSC curves for THPOH-NH₃ treated polyester/cotton blend fabrics. Heating rate -5 'C min⁻¹; air atm.

Fig. 4. Normalized DTG and DSC curves for untreated polyester/cotton blend fabrics. Heating rate = 5° C min⁻¹; air atm.

TABLE I

DTO DATA IOR UNTREATED AND HAME-RETARDANT TREATED POLYLSTIN/COTTON SHEETING

Healing rate = 5°C min⁻¹.

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≣ • Temperature nt maximum rate of weight loss (°C). ⁿ Normalized muximum rate of sample weight loss (mg min'
(*°C*), ^a Residue at 600°C (%). * 30% THPC-urea (1:1 molar ratio) and 6% PVBr in padding solution. The DSC data (Fig. 1) show the cotton degradation for treated fabrics to be exothermic, rather than endothermic, as was observed by Hobart et al. for samples which had no treatment (also reproduced in Fig. 2).

Examination of the polyester weight loss and thermal activity during pyrolysis show little differences from those measured in the untreated series. The melting point endotherm of the polyester peaks at 250°C, its peak temperature of decomposition occurs at about 400° C, and its rate of decomposition weight loss is approximately the same as when untreated. Its decomposition remains endothermic, as evidenced by the slight depression of the DSC curve at about 417°C. It is thus concluded that addition of the THPOH-NH, flame retardant does not measurably alter the polyester decomposition.

Figure 3 shows DTG and DSC curves for the same samples analyzed in 80% nitrogen-20% oxygen atmosphere (hereafter referred to as air). The presence of oxygen increases the weight-loss activity in comparison to that obtained in nitrogen. Both cotton and polyester decompositions are exothermic; oxidation of the residual chars remaining after pyrolysis occurs. As in nitrogen, the action of the flame retardant lowers both decomposition temperature and rate of decomposition weight loss for the cotton portion. Auto-ignition of the char is observed in the untreated fabrics.

TABLE 2

DSC DATA FOR UNTREATED AND FLAME-RETARDANT TREATED POLYESTER/COTTON SHEETING

Heating rate -5° C min⁻¹.

* Temperature at maximum rate of energy change ("C). I Normalized maximum rate of energy change (meal sec⁻¹ mg⁻¹). ^e 30% THPC-urea (1:1 molar ratio and 6% PVBr in padding solution.

Auto-ignition is indicated by the large energy release associated with complete and rapid consumption of the residual materials at about 450-500°C, as shown in Fig. 4. **Samples treated with fiame retardants do not auto-ignirc-**

Tables 1 and 2 summarize data presented in Fig. 1 through 4. The peak temperature and decomposition rates of the 100% cotton and the SO/SO polycsster/ cotton samples analyzed in both nitrogen and air atmospheres arc prcscntcd inTable I _ It **is apparent in the cotton decomposition that not only peak tcmprature but also** maximum rate of weight loss is decreased by the presence of the flame retardant. In nitrogen, THPOH-NH₁ reduces the maximum rate of weight loss of the 100% cotton fabric from 0.15 to 0.09 mg min⁻¹ mg⁻¹. A reduction in both peak temperature (from 317 to 278^{\textdegree}C) and decomposition rate (from 0.25 to 0.11 mg min^{-1} mg⁻¹) arc **found by analysis in the air atmosphere. Similar decreases arc measured for the 50/50 polyester/cocron fabric. In comparison with the untreated sample there arc no significant difierenccs in the rate of weight loss ani tcmpcmturc at which polyester decomposition occurs Lhat can be attributed to the addition of THPOH-NH3. 'This is** true **in both nitrogen and air atmospheres.**

The percent char remaining after pyrolysis greatly increases when flame **retardant is added io the fabrics. The char remaining at 600°C after pyrolysis in nitrosen is 48% for the treated Woo/_ cotton fabric. In the air atmosphere, 32%** char remained at 600°C. In comparison, the untreated fabrics yielded about 8% char **in nitroscn and zero char in air atmosphere. The GOO"C residual char of the SO/SO THPOH-NH₃ treated fabric is 31% in nitrogen and 19% in air, compared with 10 and 0% for untreated fabric in the same atmosphere. As the cotton content** decreases in treated fabrics, the char remaining at 600[°]C decreases as expected. These changes in thermal stability and increased char production have been observed **previously and were attributed to acid catalysis of the dehydration reaction in the celIulosic decomposition mechanism'** ' .

Table 2 presents DSC data for samples analyzed in bolh nitrogen and air atmospheres. The peak rempenturc of thermal activity for cotton pyrolysis in nitrogen is lowered by addition of the flame retardant- IIowever, the rate of energy release increases significantly from -0.26 **meal sec⁻¹ mg⁻¹ for the untreated 100% cotton** sample to 0.94 meal sec⁻¹ mg⁻¹ for the sample treated with THPOH-NH₃. Char formation is exothermic², and since the flame retardant increases the amount of char, it is reasonable to expect this change to exothermic activity. In air, the de**composition of the untreated smplc released 1.90 meal** see- '**mg'** I; **the flame** retardant decreased this rate to 0.98 meal sec⁻¹ mg⁻¹. Apparently the flame retardant **controls the heat released during cotton decomposition regardless of the atmosphere.** Similar energy changes are noted for the 50/50 blend fabrics.

There are no measurable effects of the THPOH-NH₃ flame retardant on poly**ester pyrolysis in the nitrogen atmosphere. In air, the large exothermic char oxidation masked the polyester decomposition, thus data in this tempcraturc range were not included in Table 2.**

Comparison of THPOH-NH₃ with THPC-urea-PVBr (FR-1) polyester/cotton sheeting

Pyrolysis data of samples treated with FR-1 are similar to those of the THPOH-**NH,-treated fabrics as can be seen in Fig. 5 and 6. Both** the **cotton and the polyester** decomposition temperatures for the FR-1 samples are close to those measured for the THPOH-NH₁-treated samples. Referring back to Table 1, we note the percent char at 600[°]C in nitrogen is about the same for fabrics treated with either flame retardant. In the air atmosphere, there is more char from THPOH-NH₃ samples **than from FR-J-treated samples. 7he maximum rate of cotton weight loss for the THPOH-NH**, samples appears slightly higher than for the FR-1 samples in either **atmosphere-**

The cotton thermal changes are exothermic in both atmospheres. Referring back to Table 2, we note that there is little activity in the region of the polyester decomposition in nitrogen. In nitrogen atmosphere the rates of energy release during

Fig. 5. Normalized DTG and DSC curves for FR-1 treated polyester/cotton blend fabrics. Heating rate = 5° C min⁻¹; 100% nitrogen atm. and air atm.

THPOH-NH₃ TREATED POLYESTER/COTTON

Fig. 6. Normalizd MG and DSC curws for THPOIJ-NHJ treated polyester,'cotron bknd fabrics. Heating rate -5° C min⁻¹; 100% nitrogen atm. and air atm.

cotton pyrolysis of THPOH-NH₃-treated samples are roughly 5-7 times greater **than for FR-1 samples. An oxidation step after ammoniation is an essential part of the THPOH-NH3 process'*. Perhaps the greater activity is caused by the liberation** of oxygen during pyrolysis of the THPOH-NH₃ fabrics¹³.

In Table 3 are results of elemental analyses and measurements of flame re**tardancy of the treated sheeting fabrics. The 01 values of the FR-I fabrics are higher than those of the THPOH-NH, fabrics. The 100% cotton FR-1 fabric has an 01** of 0.37, and the THPOH-NH₃ of 0.32. As the amount of polyester in the blend fabric **increases, the 01 values decrease down to 0.30 for the FR-** I **and 0.28 for the THPOH-NH3. All of the treated fabrics initially passed FF 3-71. After 50 launderings, ali samples again passed FF 3-71 with the exception of the 50/50 blend fabric treated** with THPOH-NH₃. This sample had lost 15% nitrogen after 25 launderings and **24% after 50 launderings, which is higher than with the FR-1 finish.**

FLAME RETARDANT POLYESTIR/COTTON SHEETING

 \approx 35% THPOH in padding solution. \approx P = passed. \approx BEL \rightarrow burned entire length. \approx 30% THPCurea (1:1 molar ratio) and 6% PVBr in padding solution. • This set not laundered, but would be excepted to pass, based on other data.

Effect of tris(2,3-dibromopropyl) phosphate (DBPP) on 50/50 polyester/cotton **basketweave**

To gain further insight into the relative importance and interactions of phosphorus-nitrogen and bromine systems on the thermal degradation processes of polyester/cotton blends, the effects of DBPP were investigated. Bromine compounds can be introduced into the component fibers during manufacture, or they may be part of the chemical system used for finishing the fabric, in which case the halogen may be applied separately or simultaneously with the other flame-retardant chemicals. In the THPC-urea-PVBr finish the halogen compound and the phosphorus-nitrogen compounds were mixed together and applied in a single pad-dry-cure operation. In treatments containing DBPP the halogen was applied in a separate operation followed by application of the THPOH-NH₃ or THPC-urea finish.

DTG and DSC curves for 50/50 polyester/cotton fabrics treated by the latter method are shown in Figs. 7 and 8 and are summarized in Tables 4 and 5. The effects of DBPP on the thermal degradation of the blend components are most apparent in the nitrogen atmosphere (Fig. 7 and Table 4). The polyester degradation remains essentially the same as in the untreated sample; its decomposition rate was not altered and the process remained endothermic. Thus the bromine introduced with the DBPP does not react in the polyester solid phase; therefore, its effectiveness must be through alteration of the course of oxidation reactions in the gas phase. There is a decrease in both decomposition rate and peak temperature of the cotton portion of the fabric treated with DBPP. The rate after treatment is reduced to 0.04 from 0.08 mg min⁻¹ mg⁻¹ for the untreated, and the temperature goes from 343°C for the

Fig. 7. Normalized DTG and DSC curves for flame retardant polyester/cotton 50/50 blend fabrics. Heating rate = 5° C min⁻¹; 100% nitrogen atm.

Fig. 8. Normalized DTG and DSC curves for flame retardant polyester/cotton 50/50 blend fabrics. Heating rate = 5° C min⁻¹; air atm.

DTO DATA TOR 50/50 POLYESTER/COTTON BASKLTWRAVE, UNTRPATED AND TREATED

Heating rate - 5°C min⁻¹.

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(%). 4 Residue at 600°C (%).

SOME PROPERTIES OF 50/50 POLYESTER/COTTON BASKETWEAVE TREATED WITH THPOH-NH3 AND DBPP

***** Vertical Flame Test; $P =$ passed; BL = borderline (at least one specimen failed); BEL \cdot burned entire length or failed. \triangleright 20% THPOH in padding solution. \cdot 25% THPOH in padding solution. ^d 30% THPOH in padding solution.

untreated to 315°C for the DBPP treated sample. There are also reductions in decomposition rate and peak temperature for the samples treated with THPC-urea or THPOH-NH₃, with an without DBPP. When DBPP was used alone, there was no increase in char formation as with THPOH-NH₃ or THPC-urea, and the cotton degradation remained endothermic, as in the untreated sample. These findings lend additional support to the theory that the exothermic activity associated with thermal degradation of cotton treated with phosphorus-nitrogen flame retardants results from exothermic char forming reactions. Once again we note the higher rate of energy release for the cotton thermal decomposition in nitrogen for the THPOH-NH, samples than for the THPC-urea samples, with and without DBPP.

DTG and DSC curves for these fabrics, pyrolyzed in air, are shown in Fig. 8, and DTG data are recorded in Table 4. There is some lowering of the cotton's decomposition peak temperature (from 317 to 297°C) with the DBPP treatment, but no increase in char formation. With the THPOH-NH₃ or the THPC-urea treatments, there is further lowering of the cotton decomposition temperatures, and a corresponding increase in char formation. Again, the large exothermic char oxidation masked the polyester decomposition.

Because the effect of the bromine occurs primarily in the vapor phase of the thermal decomposition, and thermal analysis examines the reactions in the solid phase, other measurements of the effectiveness of the DBPP on the flame retardancy were made. In Table 5, phosphorus, nitrogen, and bromine contents for three levels of treatment with THPOH-NH₃ are recorded, as well as OI values and results of the vertical flame test. The addition of the halogen increases the OI value at each level of flame retardant application, and at the lowest level (20%) increases the flame resistance so that the samples which failed the vertical flame test were raised to a borderline state, where some specimens passed.

CONCLUSIONS

A thermoanalytical study was undertaken to **determine the influence of selected** flame retardants on polyester/cotton blend fabrics. Treatment with THPOH-NH₃ or with THPC-urea-PVBr lowers the temperature at which the maximum rate of **decomposition occurs and increases the char formation of the cotton component.** Neither retardant significantly affected polyester decomposition. The decomposition of THPOH-NH₃-treated cotton in nitrogen was much more exothermic than was **the THPC-urea-PVBr daaomposition in nitrogen- It is proposed that oxygen Jibcrated** from the oxidized THPOH-NH, polymer by thermal stress contributed to the increased exothermic activity. The two treatments had about the same exothermic activity in the air atmosphere. Auto-ignition did not occur in samples treated with **either cotton flame retardant.**

The 01 values oi the THPC-urea-PVBr treated samples ranged from 0.37 for the 100% cotton to OX *for* **the So;50 blend fabric. 01 values varied front 0.32** for the 100 % cotton to 0.28 for the 50/50 blend for fabrics treated with THPOH-NH₃. **All treated fabrics passed FF 3-71 initially and after 50 launderings, cxccpt the 50/50 blend fabric treated with THPOH-NH,. This sample had the lowest polymer add-on** initially, as **indicated by phosphorus and nitrogen contents, and after 50 laundering. had lost about 25% polymer (based on nitrogen values).**

The addition of bromine increased the flame retardancy of the treated samples, as measured by OI values and the vertical flame test, for the polyester/cotton basketweave fabrics treated first with DBPP then by THPOH-NH₃ or THPC-urea. ThermoanaIytical techniques could not differentiate the effects of the bromine in the presence **of** the **cotton flame rz!tardants_ However, the blend fabric treated with DBPP alone exhibited a lower decomposition temperature of the cotton portion but no noticeable altcrafion of the polyester portion- The DBPP did not decrease the quantity of volatile products of col.ton or polyester de_gadatian, and the amount of char residues** was not increased, as was the case with the phosphorus-nitrogen flame retardants.

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RESULTS FROM THE LLS PROCEDURE FOR TRACE 1

