

Thermal Decomposition Studies of Cotton Radiolytically Grafted with Phosphorus- and Bromine-Containing Flame Retardants

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Synopsis

Thermal analysis of cotton samples grafted with triallylphosphate (TAP) and 2,2,2-tribromoethyl acrylate (TBEA) was carried out. Grafting of poly-TAP causes a significant decrease in the decomposition temperature of cotton. The cotton decomposition is acid catalyzed by H_3PO_4 formed during the decomposition of the grafted poly-TAP. The HBr evolved during decomposition was monitored continuously during thermal analysis of cotton grafted with poly-TBEA. No significant flame-retarding effect by HBr was found. Since grafted poly-TBEA causes a decrease in the decomposition temperature of cotton, it is suggested that the flame retardant mechanism for poly-TBEA in cotton occurs mainly in the solid phase before most of the HBr is released.

INTRODUCTION

We have conducted experiments on imparting flame retardancy to cotton fabrics by γ -irradiation grafting of phosphorus- and bromine-bearing monomers. In the present study, thermal analysis was used to follow the route of thermal decomposition of cotton grafted with triallylphosphate (TAP) and 2,2,2-tribromoethyl acrylate (TBEA), in an attempt to obtain a detailed understanding of their flame-retarding mechanism.

The thermal degradation of cellulose has been extensively studied in the last few years.¹ It was suggested that in the thermal decomposition of cellulose the following sequence of reactions takes place¹: (a) endothermic dehydration in the range of 200–280°C where “anhydrocellulose” is formed; (b) depolymerization of the residual cellulose by an endothermic reaction at 270–280°C and formation of levoglucosane tar^{1,2}; and (c) decomposition of the levoglucosane trapped in the char in an exothermic process and formation of flammable volatile fragments; this process competes with the volatilization of undecomposed levoglucosane, which is endothermic.

It is postulated that flame retardation of cellulose by phosphorus compounds involves enhanced dehydration at the expense of organic volatiles. On the other hand, halogens, especially brominated compounds, retard the flame by acting as free-radical scavengers in the gas phase.

Perkins et al.³ investigated the DTA and TGA of cotton fabrics treated with partially brominated poly-TAP. The thermograms given in their work³ show

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that the decomposition temperature of the cotton was lowered by about 120°C as a result of the flame retardant treatment. When the treated cotton was decomposed under oxygen, the added brominated poly-TAP prevented the ignition of the sample. This was interpreted as owing to the early liberation of bromine free radicals which catalyzed the decomposition of cellulose at a temperature below the ignition point of the liberated gases.

Liepins et al.⁴ used radiation for grafting TBEA on poly(ethylene terephthalate) and determined the thermal stability and the flame retardancy efficiency of the grafted poly TBEA.

EXPERIMENTAL

Triallyl phosphate (EGA-Chemie KG, 98% purity) was distilled under reduced pressure in the presence of hydroquinone and only the middle fraction was collected. The 2,2,2-Tribromoethyl acrylate was synthesized from 2,2,2-tribromoethanol and acryloyl chloride (Aldrich) in a way similar to the synthesis of 2,2,2-trichloroethyl acrylate described by Hrabak and Pivcova.⁵

The cotton fabric used was a 4.4 oz/yd² cotton sateen. All samples were pre-washed with a mild detergent and cold water and rinsed several times in distilled water prior to grafting. The dried samples and the monomer were transferred to glass ampuls, degassed by four freeze-thaw cycles, and sealed *in vacuo*. The ampules were then irradiated in a ⁶⁰Co gamma cell at a dose rate of 0.30 Mrad/hr for a period of time that depended on the monomer and the desired amount of grafting. After irradiation, the grafted samples were first washed with water and then extracted continuously for 48 hr with chloroform in a Soxhlet apparatus in order to remove all extractable homopolymer. The samples were dried at room temperature and weighed to a constant value for determination of the apparent graft.

A du Pont 990 thermal analyzer with a DTA module and a du Pont 951 thermogravimetric analyzer were used for thermal analyses. In the DTA experiments glass beads were used as reference material. A heating rate of 10°C/min was used in all experiments, and the flow rate of nitrogen was 50 ml/min.

In experiments where TBEA was present, the gases evolved in the TGA pyrolysis chamber were bubbled through a buffered aqueous solution. Any HBr formed during the thermal decomposition was monitored continuously by a specific bromide electrode and displayed on a recorder. In this way the HBr concentration was obtained as a function of temperature in parallel with the TGA thermogram of the same sample. The specific bromide electrode (Orion model 94-35A), in conjunction with a reference double-junction electrode (Orion model 90-02-00), was connected to a digital pH meter (Orion model 701) with the output connected to one of the pens of a double-pen Yokogawa 3047 recorder. In parallel, on the same recorder, the derivative of the same signal was obtained by introducing an amplifier and an RC differentiation circuit. The details of the continuous HBr monitoring have been described elsewhere.⁶

Oxygen index determinations were made with an apparatus built in our laboratory, as described by Isaacs.⁷

RESULTS AND DISCUSSION

Effect of Radiation on DTA of Cotton

The DTA of a sample of cotton fabric irradiated in nitrogen at a dose of 6.2 Mrad was compared with that of an unirradiated sample (see Fig. 1). The irradiation caused a lowering of the main endotherm peak from 380 to 364°C. Since cellulose is of the degradable polymer type,⁸ this lowering of the decomposition temperature reflects the radiation-induced chain fracture and destruction of crystallinity in the cellulose.

Thermal Decomposition of Poly-TAP

A sample of TAP monomer was irradiated in an evacuated ampule for 20 hr with a total dose of 6.0 Mrad. Under these conditions, only partial conversion of monomer to polymer took place. The TG of the poly-TAP containing a substantial amount of monomer is given in Figure 2. Three distinguishable weight-loss steps were observed. The first, in the range 100–200°C, was a result of monomer evaporation. This weight loss was not observed when the sample was preheated under vacuum at about 80°C for several hours. The second weight loss was at 250°C and proceeds at a very rapid rate. As this temperature was reached, a sudden microexplosion occurred with a large energy release that caused a 50°C temperature rise in the TG and a jump in the DTA of about 200°C (see loops in Fig. 2). Both the TG and DTA samples cooled rapidly, and heating proceeded at the programmed rates. The third weight-loss step started at about 320°C and ended at about 450°C.

The phosphorus content in the residual char was determined at the end of the second and the third decomposition steps and was found to be 13.0 and 19.1%, respectively. Since the amount of phosphorus in undecomposed poly-TAP is 14.2%, it is obvious that some volatile phosphorus compounds were evolved during the reactions taking place at 250°C. However, the residual char when heated to above 450°C had a higher phosphorus content, which means that the reactions taking place in the temperature range of 320–450°C were not accompanied by a major liberation of phosphorus. The portion of poly-TAP which

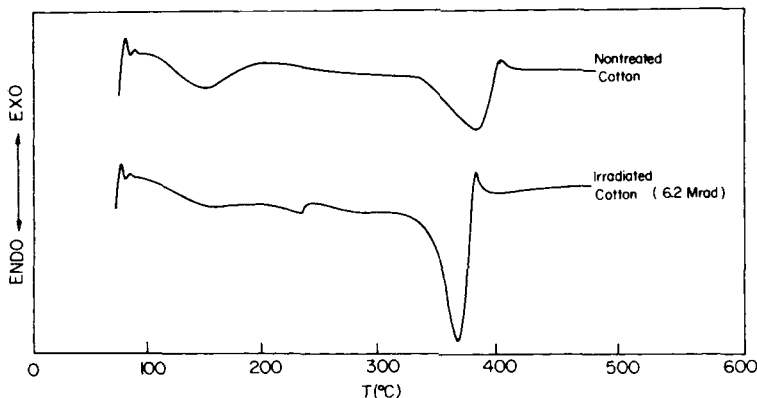


Fig. 1. DTA of cotton fabric and irradiated cotton fabric (6.2 Mrad), under nitrogen atmosphere.

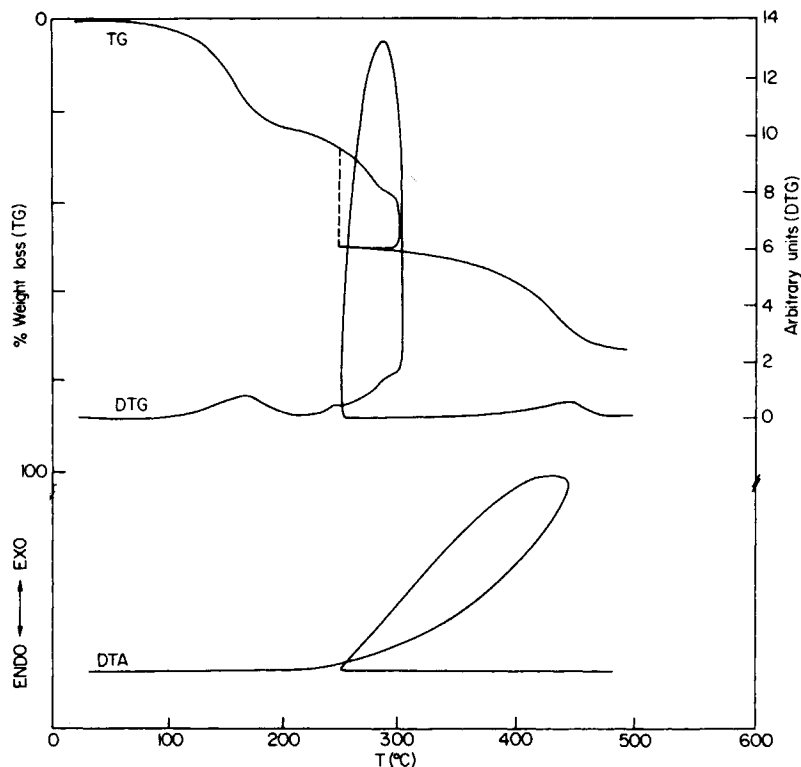


Fig. 2. TG, DTG, and DTA of poly-TAP, under nitrogen atmosphere.

did not produce volatile phosphorus compounds was assumed to decompose to phosphoric acid.

To verify this assumption the residual char obtained at 275°C was transferred to a 0.1N NaOH solution, stirred overnight at room temperature, and the concentration of the acid determined by a back titration with 0.1N HCl. The acidity of the char expressed in equivalents of H^+ /mg char was found to be 10.3×10^{-6} eq/mg. (A blank titration of undecomposed poly-TAP was carried out under the same conditions, and no acidity was found). If we assume that all the phosphorus remaining in the char (13% of the total char weight) exists in the form of H_3PO_4 , the expected acidity would be 12.6×10^{-6} eq/mg. Another char sample obtained at 270°C was rinsed with water and the aqueous extract was analyzed for PO_4^{3-} by the ammonium molybdate test. The amount of extractable PO_4^{3-} found was 10.7×10^{-6} eq/mg, in very good agreement with the titrated acid. By heating the char from 275 to 425°C, the acidity increased by 47% to 15.4×10^{-6} eq/mg. At the same time the phosphorus content increased by 52% from its original value at 275°C to 19.2% of the char weight. It is therefore concluded that most of the weight loss during this decomposition is a result of reactions taking place in the phosphorus-free compounds present in the char.

The extremely exothermic process at 250°C resembles the very fast energy release found in the crosslinking of TAP.⁹ It is possible that in addition to the ester bond fracture, where the phosphoric acid is formed, some crosslinking taking place in the backbone of the polymer is accompanied by a rapid liberation of heat.

Thermal Decomposition of Cotton Grafted with Poly-TAP

Electron-beam irradiation grafting of TAP on cotton has previously been carried out only in air and in the presence of N-methylolacrylamide.^{10,11} In the absence of oxygen, TAP was grafted by us on cotton without the addition of N-methylolacrylamide. The maximum grafting yield obtained by us was 18.2% with a dose of 15 Mrad.

TG and DTG curves obtained in nitrogen for a series of cotton fabrics grafted with TAP are given in Figure 3. It can be seen that the decomposition temperature decreases and char formation increases with increasing TAP content in the cotton. When comparing the DTG curve of cotton grafted with 4.2% poly-TAP with that of the ungrafted cotton sample, one can observe that in addition to the lowering of the decomposition temperature by 42°C a peak is starting to build up at about 275°C. This peak increases and moves toward lower temperatures with increasing poly-TAP concentration and reaches a maximum at 254°C with 18.2% graft. The increase of this peak, which is characterized by its sharpness, is accompanied by a decrease in the main decomposition peak of the cotton. These two distinguishable weight-loss processes are followed by a much slower process which is better observed in the TG representation. The first rapid weight loss seen in curves 3 and 4 of Figure 3 resembles the weight loss obtained in the microexplosion with poly-TAP alone at 250°C. We assume that this step involves the decomposition of the esteric groups in the grafted poly-TAP with the formation of phosphoric acid as found in poly-TAP alone. The phosphorus content in samples 2 and 4 (Fig. 3) after the rapid weight loss was found to be <0.3% and 3.6%, respectively. These values are comparable to those expected (0.5 and 3.2%) if the grafted poly-TAP behaves in the same manner as the homopolymer. Since in poly-TAP alone about 35% of the weight loss takes place in the microexplosion step, in the 18.2% grafted poly-TAP we expect a weight loss of only 6% of the total weight if the same decomposition reactions are as-

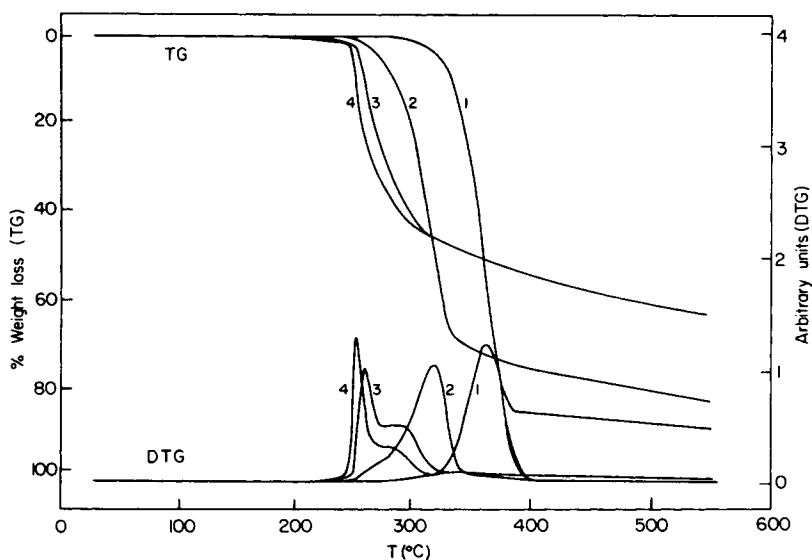


Fig. 3. TG and DTG of cotton fabric grafted with different levels of poly-TAP, under nitrogen atmosphere: (1) irradiated cotton, (2) 4.2% poly-TAP, (3) 14.1% poly-TAP, (4) 18.2% poly-TAP.

sumed. According to the TG curve (curve 4 in Fig. 3), about 20% of the sample weight is lost in the first step. Therefore, we must assume that the major part of weight loss in this step is due to loss of cotton fragments. The phosphoric acid formed in this step most probably catalyzes the decomposition of the cotton into fragments composed mainly of anhydrocellulose, at the expense of some levoglucosane, which is also formed in this stage. The consecutive weight-loss process probably involves the volatilization of these fragments, mainly the levoglucosane, trapped in the char, in competition with a further decomposition of the levoglucosane to more volatile fragments. The third process starting at about 300°C (for the 14.1% and 18.2% grafted poly-TAP samples) involves further decomposition of the char, causing an increase in carbon content.

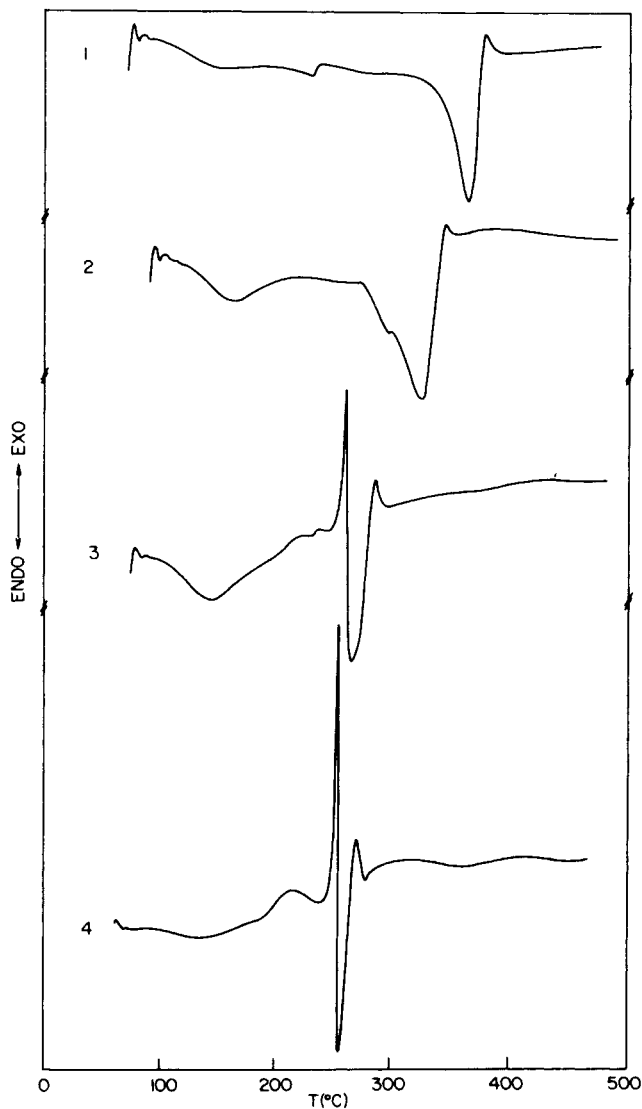


Fig. 4. DTA of cotton fabric grafted with different levels of poly-TAP, under nitrogen atmosphere: (1) irradiated cotton; (2) 4.2% poly-TAP; (3) 14.1% poly-TAP; (4) 18.2% poly-TAP.

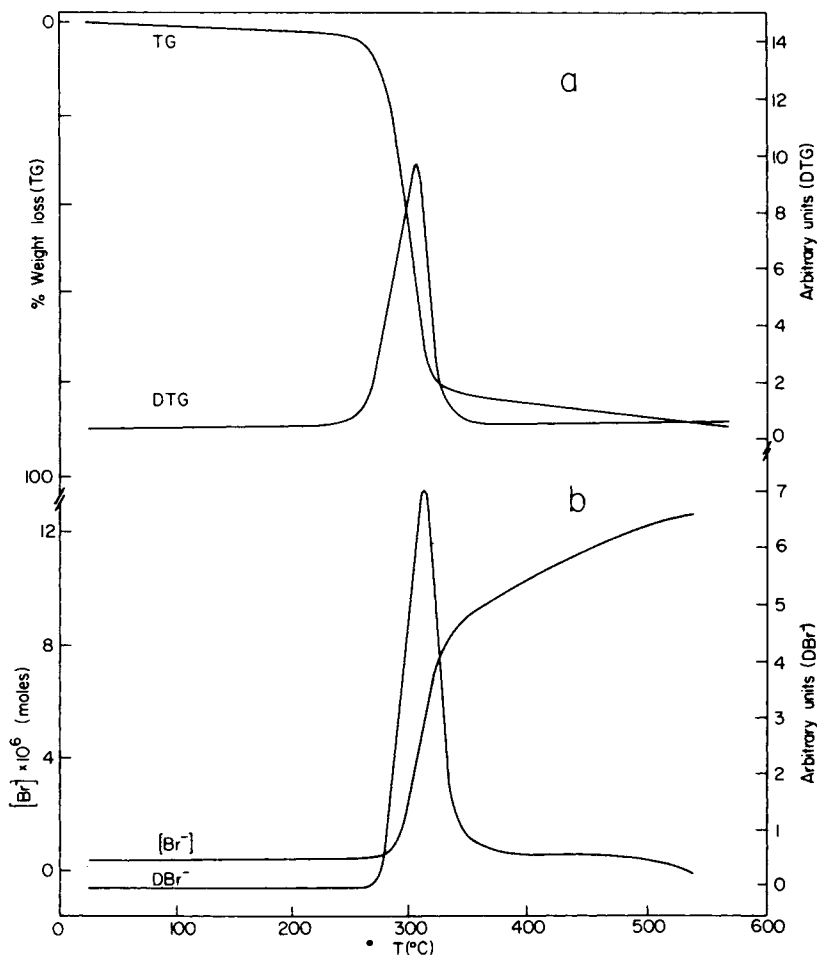


Fig. 5. (a) TG and DTG of poly-TBEA, under nitrogen atmosphere. (b) Br^- concentration accumulated during the thermal decomposition of the sample in (a) and the derivative of the Br^- curve, DBr^- .

The DTA curves in nitrogen for the same treated cotton samples are given in Figure 4. The main endotherm related to volatilization of levoglucosane in untreated cotton¹ becomes much narrower and moves toward lower temperatures with increasing TAP concentration. Meanwhile, a sharp exothermic peak builds up prior to the main endothermic process. We relate the sharp exothermic peak to the reactions taking place in the poly-TAP graft where the phosphoric acid is formed. This exotherm supposedly masks the endotherm related to the formation of the anhydrocellulose. Following this exotherm, the narrow endotherm is related to the formation and volatilization of levoglucosane in competition with its decomposition. The subsequent exotherm is related to the decomposition of trapped levoglucosane into volatile fragments. The temperature of the levoglucosane decomposition assumed here (about 255°C in the 18.2% TAP sample) is significantly lower than the temperature found in the decomposition of pure levoglucosane (about 340°C).¹ This difference in temperatures probably results from the catalytic effect of the phosphoric acid on this decomposition. Limiting

oxygen index measurements of cotton grafted with various amounts of poly-TAP are discussed later.

Thermal Decomposition of Poly-TBEA

TBEA was radiolytically polymerized similarly to the polymerization of TAP. Samples of poly-TBEA were decomposed in the TG apparatus. The gases evolved during the decomposition were bubbled into a beaker containing 40 ml aqueous buffered solution (phosphate pH 6.9) by flushing nitrogen through the TG chamber. This solution was found to contain bromide ions, and it was therefore assumed that HBr had formed during the poly-TBEA decomposition. The concentration of the Br^- dissolved in this solution during the poly-TBEA decomposition was monitored continuously. Figure 5 shows the results obtained with a 5-mg poly-TBEA sample. From the TG curve in Figure 5 it can be seen that the main weight loss starting at about 250°C reaches a maximum rate at 308°C and ends at about 350°C. Above 350°C a slow linear decrease in weight takes place with increasing temperature. The buildup of the bromide concentration in Figure 5 is seen to follow the same pattern as the weight loss of the sample. The peak of the rate of bromide formation expressed in terms of the derivative (DBr^- in Fig. 5) had a delay time of about 10 sec from the appearance of the DTG peak. This delay time depends on the volume of the tubing connecting the pyrolysis chamber with the bromide electrode and on the flow rate of the flushing gas. The amount of HBr evolved during the thermal decomposition of poly-TBEA as calculated from Figure 5 is 45% of the total bromine content of the sample. On the other hand, the residual char at 500°C (which was 13% of the sample weight) had a bromine content of only 3.3%. It is therefore concluded that some volatile bromine-containing fragments other than HBr are formed during the thermal decomposition of poly-TBEA.

The DTA of poly-TBEA is given in Figure 6. The endotherm at 70°C is assigned to melting of poly-TBEA, while the endotherm at 145°C seems to result from evaporation of traces of unpolymerized monomer. In other cases when poly-TBEA was obtained from a different irradiated sample, the 145°C endotherm was absent. In the region 220–280°C, several overlapping thermal processes are observed which could not be distinguished in the thermograms of the TG or Br^- formation. We have no explanation for these transitions.

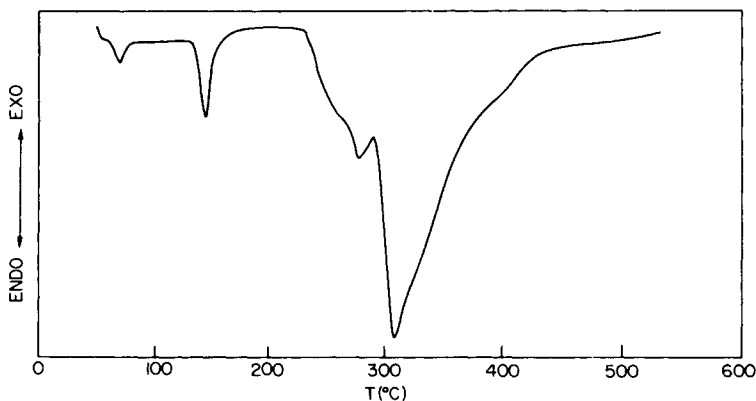


Fig. 6. DTA of poly-TBEA, under nitrogen atmosphere.

Thermal Decomposition of Cotton Grafted with Poly-TBEA

The influence of grafted poly-TBEA on the thermal decomposition of cotton is shown in Figures 7 and 8. Grafting of poly-TBEA causes a decrease in the decomposition temperature of irradiated cotton of about 50°C with 9.4% graft and about 60°C with 23.4 and 46.3% graft. The sample containing 9.4% graft had a single peak in the DTG curve, while those containing 23.4 and 46.3% graft had two distinguishable peaks. It seems that these two peaks result from the decomposition of poly-TBEA and cotton in two separate processes, with some overlapping. Since poly-TBEA alone decomposes at 308°C and irradiated cotton decomposes at 364°C, one might tend to relate the first peak to poly-TBEA and the second one to cotton. In order to clarify this point, we measured continuously the bromide evolved during the thermal decomposition of the grafted samples simultaneously with the DTG measurement. The derivatives of the Br⁻ concentration plots (DBr⁻) are given in Figure 7 together with the DTG curves. As seen, the HBr peaks in the DBr⁻ curves appear at about the same temperature as the second peak in the DTG curves. These findings clearly relate the first peak to the cotton decomposition process and the second peak to the poly-TBEA.

In a previous publication⁶ we described the circuit that differentiated the voltage signal obtained from the bromide electrode. It should be noted here that the voltage obtained from the specific bromide electrode is not linear with the Br⁻ concentration but exponential according to

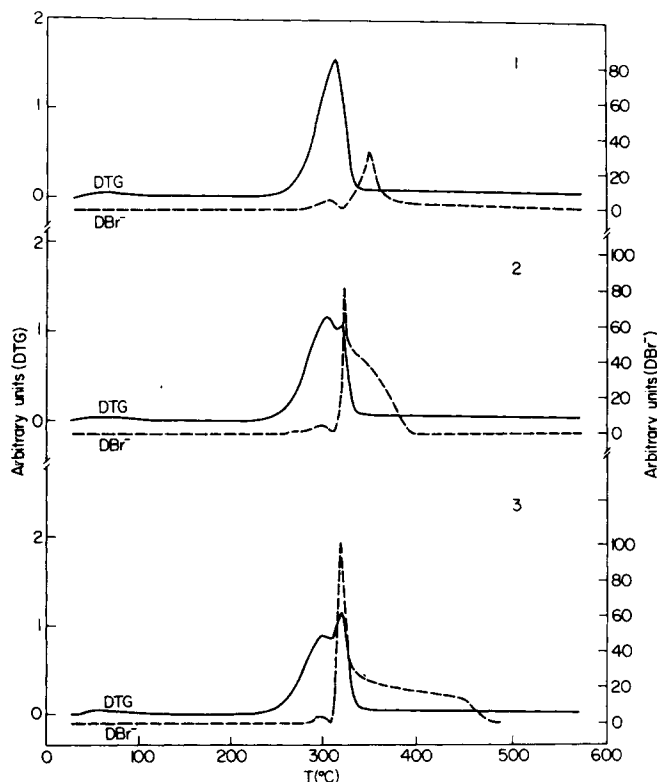


Fig. 7. Simultaneous measurements of DTG and DBr⁻ of cotton fabric grafted with different levels of poly-TBEA, under nitrogen atmosphere: (1) 9.4% poly-TBEA; (2) 23.4% poly-TBEA; (3) 46.3% poly-TBEA.

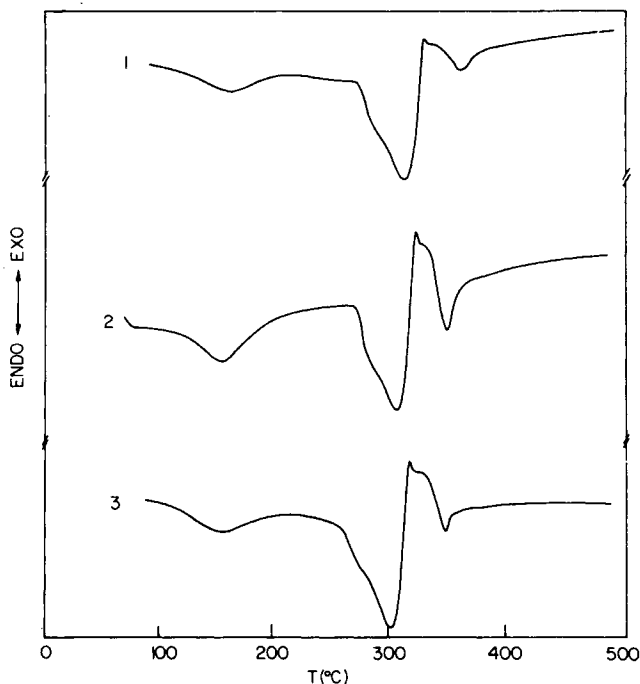


Fig. 8. DTA of cotton fabric grafted with different levels of poly-TBEA, under nitrogen atmosphere. Same samples as in Fig. 7: (1) 9.4% poly-TBEA; (2) 23.4% poly-TBEA; (3) 46.3% poly-TBEA.

$$\log [\text{Br}^-] = -\frac{v}{a} - b \quad (1)$$

where a and b are parameters of the electrode. Therefore, the location of the maximum in the derivative plot of the voltage signal will differ somewhat from the location of the maximum obtained by taking the derivative of the concentration plot. In the present investigation, Br^- concentration plots were calculated from the voltage plots according to eq. (1) and the derivatives were calculated manually. Differences in temperatures of DBr^- maxima found by differentiating concentration plots in comparison to voltage plots were in the range of 1–7°C, depending on the rate of HBr evolution.

As seen in Figure 7, in all cases two peaks were obtained in the DBr^- curves. The first is much smaller than the second and appears together with the main decomposition peak of the cotton.

The DTA curves of the samples measured in Figure 7 are given in Figure 8. The main patterns of the DTA of grafted cotton are similar to those of untreated cotton (see Fig. 1), except for the addition of a new exotherm at about 330°C, which follows the sharp levoglucosane decomposition exotherm and an additional endotherm at about 350°C. These features appear in all samples bearing the grafted poly-TBEA. Because of differences in measured temperatures between the DTA and the TG cells, we ran a single experiment of the 46% graft with a Mettler thermal analyzer where DTA and DTG are simultaneously recorded. It was found that the 302°C peak in the DTG exactly overlaps the main endotherm peak in the DTA, while the 321°C peak in the DTG curve overlaps the exotherm following the main endotherm in the DTA. The decrease in the

temperature of the main cotton decomposition from 364°C to about 300–315°C is probably caused by catalysis of minute amounts of HBr which are formed in the early stages of poly-TBEA decomposition. The subsequent sharp exotherm at about 320°C overlaps a new exotherm peaking at ~330°C which might be assumed to originate from the decomposition of grafted poly-TBEA. This assumption is ruled out, since poly-TBEA alone does not have any exotherms in this temperature region (see Fig. 6). Since at this stage of decomposition (320–330°C) char has already formed and HBr is evolving at the maximum rate, it is reasonable to assume that hydrobromination of unsaturated carbon bonds in the char might take place. Such a reaction will be exothermic, and we believe that the exotherm peaking at ~330°C is a result of such hydrobromination in the char. The subsequent endotherm peaking at about 350°C is believed to be a result of dehydrobromination of the brominated char.

Brominated alkanes normally decompose by a mechanism involving radical chains. However, introduction of olefinic inhibitors reduces the rate of the radical reaction and the unimolecular elimination reaction of HBr predominates. Since char is present above 320°C, it might act to inhibit the chain decomposition reaction, leaving the unimolecular elimination reaction of the brominated char as the main route for decomposition. The elimination reaction of HX from substituted RX compounds in the gas phase ($X = \text{Cl}, \text{Br}, \text{I}$) was found to be endothermic by 12–20 kcal/mole depending on X.¹² A unimolecular dehydrohalogenation reaction has been postulated. The range of temperatures where HBr unimolecular elimination reactions have been investigated falls well within the region of the endotherm peaking at ~350°C, (350–390°C for *n*-PrBr,¹³ 370–420°C for *n*-BuBr,¹³ 325–354°C for *sec*-BuBr,¹⁴ and 360–420°C for *iso*-BuBr¹⁵).

The oxygen indexes of the samples grafted with poly-TBEA and poly-TAP were tested, and the results are given in Figure 9. It can be seen that poly-TBEA is not an efficient flame retardant for cotton. Although relatively high quantities of HBr are evolved during the decomposition of grafted cotton, no substantial flame inhibition was observed. It is possible that the HBr evolved does not retard the flame at all in the gas phase and the only inhibition observed results from a limited interaction in the solid phase. An indication of this is the decrease in the decomposition temperature of grafted cotton from 364 to ~300°C. From

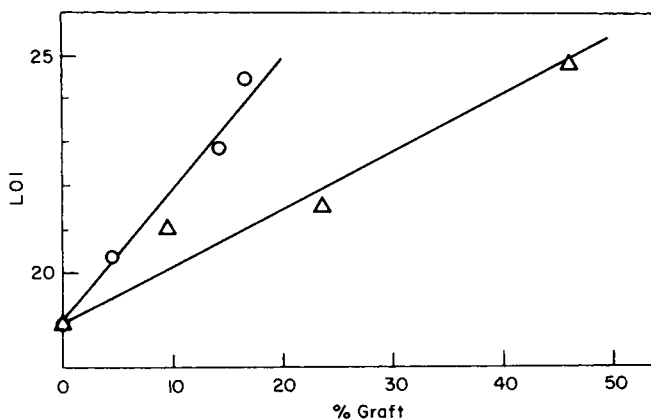


Fig. 9. Limiting oxygen index (LOI) of cotton fabric grafted with poly-TAP (O) and poly-TBEA (Δ), as a function of % graft.

Figure 7 it can be seen that most of the cotton has decomposed before the major amount of HBr is released. This might explain the poor flame retardancy action of poly-TBEA on cotton. A comparison of the limiting oxygen indexes of cotton grafted with poly-TAP to cotton grafted with poly-TBEA shows that the former, which is known to interact in the solid phase like most phosphorus flame retardants, is much more efficient.

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