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Evidence of interaction in flame-retardant fibre-intumescent combinations by thermal analytical techniques[1]

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Abstract

Flame retardants when applied to cellulosic fibres, change their decomposition in such a way that significant conversion to carbonaceous char occurs. Intumescents, when dispersed on these flame-retardant (FR) fibres, enhance this property. They not only produce an expanded and thermally protective char barrier, but also interact with FR fibres to form a so-called char-bonded structure which has been shown to possess unusually high resistance to air oxidation at temperatures in excess of 500°C. The effectiveness of the char-bonded structure as a flame and heat barrier is considered to be dependent on the efficiency of the interaction of fibre and intumescent char-forming chemistries. Previous studies have demonstrated the interaction between various flame-retarded viscose fibres and phosphate-based intumescents; current research extends the work to include flame-retardant cottons. In this paper, these interactive properties are studied by using the thermal analytical techniques, TMA, TGA and DSC, which enable the various pyrolysis transitions and associated volatilisation and intumescent char-formations to be studied. In this way a greater understanding of the mechanism of complex char-formation and its subsequent oxidation may be investigated. © 1997 Elsevier Science B.V.

Keywords: Cellulose; Char; DSC; Flame retardant; Intumescent; TGA; TMA

1. Introduction

During the last decade, there has been considerable interest in the field of flame retardancy of textile materials as the demand for improved safety in domestic, public, industrial and transport environment increased. Most successful flame-retardant compounds for cellulosic materials are those which react chemically with the substrate and act in the condensed phase [1]. Examples of such retardants are phosphonium salt-polycondensates (Proban CC, Albright and Wilson, UK) and substituted phosphonamides (Pyrovatex CP, Ciba). On heating, these condensed phase flame retardants change the decomposition path of cellulose in such a way that less volatile combustible products and more carbonaceous char is formed. This char offers heat and flame resistance to some extent, but above 400°C it oxidises and burns.

Use of intumescent systems for polymers is another method of achieving flame retardancy, especially if used in coatings and paints [2]. On igniting such materials, a cohesive foamed char is formed which acts as an insulating barrier between the fire and the substrate. There are two techniques of applying intumescents to polymers:

1. as a coating to the surface of the substrate,
2. as additives during the preparation of the polymer prior to its fabrication into a product.

Intumescent systems usually contain an acid source, a carbonific material and a spumific agent [3]. On

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heating, the acid source decomposes, yielding a dehydrating agent which reacts with the carbonaceous char-forming agent to form an ester. The ester then dehydrates and cross-links to form char. Simultaneously, the blowing agent releases large amounts of gas which helps in expanding the char. The greater char thickness increases the thermal gradient across the polymer surface and char, and thus provides thermal protection for considerable periods of time. But the char is very brittle and slowly oxidises when exposed to temperatures in air >500°C; both factors influence the char-barrier effectiveness.

In order to overcome these deficiencies and to extend the use of intumescents to fibre surface protection in textiles, the authors have initiated a programme of investigation into the combustion behaviour of mixtures of flame-retardant cellulosic fibres and selected intumescent systems which have previously demonstrated unusual char-forming behaviour [4]. It has been noted [4–6] that, on heating such systems, both components char by chemically and physically compatible mechanisms resulting in chemical interaction to form a fibrous char-reinforced intumescent char or 'char-bonded' structure which is unusually resistant to oxidation. In previous works [5,6], we have studied the interaction between flame-retardant viscose fibres and phosphate based intumescents using DSC and TGA. The current study includes flame-retardant cotton fibres and some intumescent systems which, based on the earlier research, should show similar behaviour when studied by thermal analytical techniques.

2. Experimental

2.1. Sample

Experiments were conducted on four samples of commercially bleached light-weight cotton fabrics (127 g m^{-2}), treated with the following selected commercial flame retardants supplied by Albright and Wilson, at different phosphorus levels:

1. FR1 cotton: ammonium polyphosphate (APP) and urea (together as product Amgard TR). This is applied by pad dry method to give a non-durable finish. Three different phosphorus levels (1.9, 2.4 and 3.3%) were used.
2. FR2 cotton: ammonium polyphosphate and urea (as Amgard LR II). This treatment requires a pad dry and heat-cured technique to achieve a semi-durable finish. Only one phosphorus level (1.7%) was used.
3. FR3 cotton: tetrakis(hydroxymethyl)phosphonium chloride (THPC)-urea condensate (as Proban CC). This is cured with ammonia to give a durable finish. Two phosphorus level (2.5 and 4%) were used.
4. FR4 cotton: 2 methyl *N*-methylol phosphonopropionamide (as TFR I). This is again a durable finish applied with a trimethylolated melamine resin to bridge to cellulose molecules. Two phosphorus levels (2.3 and 2.7%) were used.

All these flame-retardant fabrics were prepared and supplied by Albright and Wilson, UK, who applied their flame-retardant finishes by normal commercial practice. These fabrics were pulverised using a Wiley mill with a 0.5 mm screen and mixed with two commercially available intumescent systems, namely Int1 (MPC 1000) and Int2 (MPC 2000), (Albright and Wilson, UK) in 1 : 1 mass ratio.

MPC 1000 contains ammonium polyphosphate (DP ≈ 200, phase 1 structure), melamine, and pentaerythritol in 3 : 1 : 1 mass ratio. MPC 2000 is a development product containing melamine phosphate and dipentaerythritol, believed to be in a ratio between 1 : 1 and 2 : 1.

2.2. Equipment

DSC curves were obtained using a PL-DSC instrument. The tests were carried out under flowing air (10 ml min^{-1}) and at a heating rate of 10 K min^{-1}. About 2.0 mg of the sample was taken in each case and all the curves were then normalised to 1.0 mg for comparison (see Figs. 1 and 2 and Table 1).

A Stanton Redcroft TGA 760 instrument was used for thermogravimetric analyses under static air conditions with a heating rate of 10 K min^{-1}. About 5.0 mg of sample was used in each case. Typical results in static air are presented as % mass in Fig. 3 and although their derivative graphs were also recorded, they are not shown but respective peaks are recorded in Table 2 for all samples. From TGA curves char yields at different temperatures were also

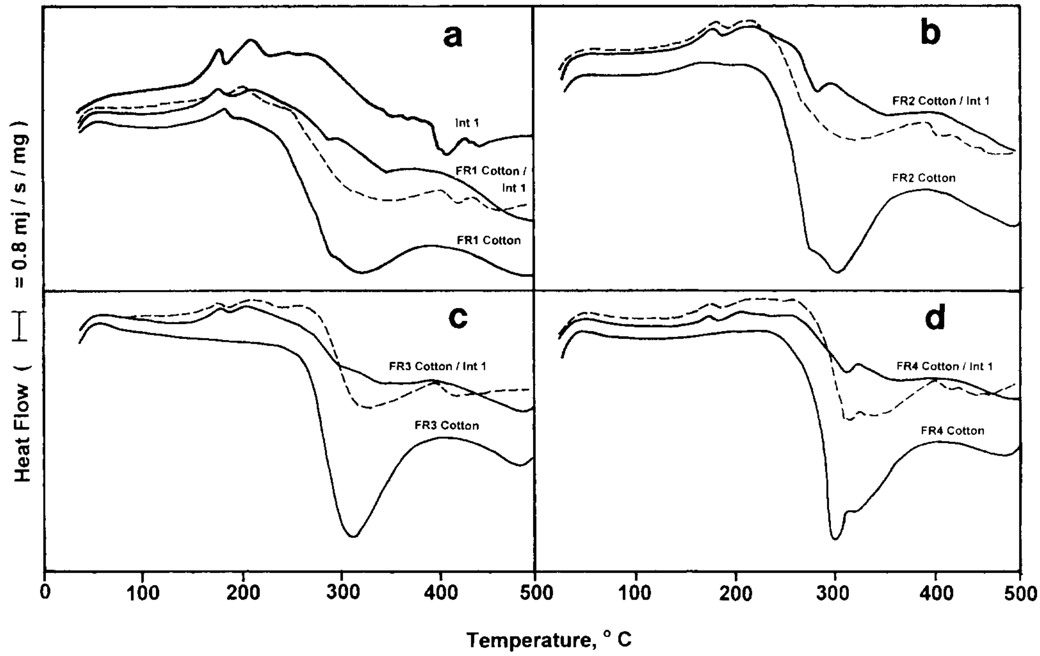

Fig. 1. DSC responses of individual components and mixtures of (a) FR1 cotton (Amgard TR), (b) FR2 cotton (Amgard LR II), (c) FR3 cotton (Proban CC) and (d) FR4 cotton (TFR 1) and Int1 (MPC 1000) and their calculated average responses (-----) under flowing air at 10 ml min^{-1} and 10 K min^{-1}. (Exotherms downwards)

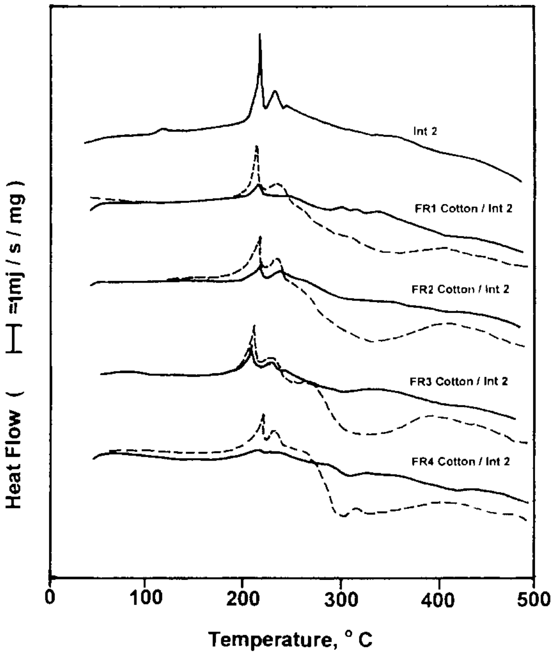

Fig. 2. DSC responses of Int2 (MPC 2000) and its mixtures with FR1 cotton (Amgard TR), FR2 cotton (Amgard LR II), FR3 cotton (Proban CC), and FR4 cotton (TFR 1), and their calculated average responses (-----) under flowing air at 10 ml min^{-1} and 10 K min^{-1}. (Exotherms downwards)

Table 1
Analysis of DSC responses under flowing air (10 ml min^{-1}, 10 K min^{-1}) or FR cotton, intumescents and their mixtures

Samples	Sample			Sample/Int1			Sample/Int2		
	Int. temp./ (°C)	Peak temp./ (°C)	Nature of the DSC peak	Int. temp./ (°C)	Peak temp./ (°C)	Nature of the DSC peak	Int. temp./ (°C)	Peak temp./ (°C)	Nature of the DSC peak
Int1				148	175	Endo			
(MPC 1000)				181	209	Endo			
				230	247, 273	Endo (double peaked)			
				399	408, 438	Exo (double peaked)			
Int2							—	114	Endo (small)
(MPC 2000)							198	215	Endo (sharp)
							219	232	Endo
							239	244	Endo (small)
FR1 cotton	124	182	Endo	138	174	Endo	168	183	Endo (small)
(TR - 2.6%P)	200	317	Exo	185	207	Endo	189	218	Endo (sharp)
	410	487	Exo	—	289	Exo	221	239	Endo
				299	348	Exo	265	294	Exo
							306	332	Exo (small)
							346	404	Exo
FR2 cotton	221	280, 307	Exo (double peaked)	147	178	Endo	198	222	Endo (sharp)
(LR - 1.7%P)	407	492	Exo	184	212	Endo	225	242	Endo
				—	289	Exo	—	303	Exo (small)
				301	362	Exo	311	336	Exo (small)
							350	416	Exo
FR3 cotton	232	310	Exo (large)	151	177	Endo	196	215	Endo (sharp)
(Proban - 2.5%P)	401	484	Exo	184	206	Endo	219	233	Endo
				—	300	Exo	—	304	Exo
				307	350	Exo	329	404	Exo
				392	492	Exo	428	—	Exo
FR4 cotton	252	309, 329	Exo (double peaked)	150	175	Endo	180	218	Endo
(TFRI - 2.7%P)	429	481	Exo	183	209	Endo	222	238	Endo
				265	317	Exo	—	317	Exo
				329	365	Exo	351	423	Exo

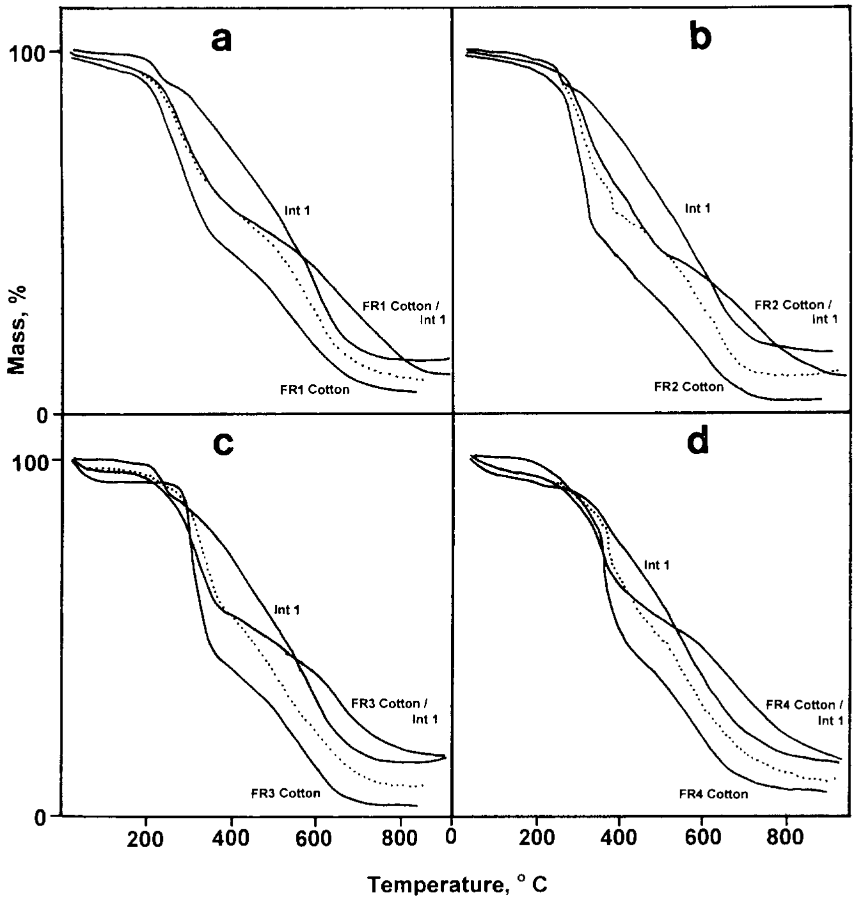

Fig. 3. TGA responses of 5 mg samples under static air at 10 K min^{-1} of individual components and mixtures of (a) FR1 cotton (Amgard TR), (b) FR2 cotton (Amgard LR II), (c) FR3 cotton (Proban CC), and (d) FR4 cotton (TFR 1) and Int1 (MPC 1000), and their calculated average responses (- - - -).

observed and results at 700°C are reported in Table 2. For FR cotton/Int mixtures, the expected char yield values at a particular temperature were calculated as averaged sum of char yields of the respective FR cotton and the intumescent component. The differences in actual and calculated char yields for mixtures at different temperatures are plotted in Fig. 4.

The intumescence or swelling of the sample was measured by a Stanton Redcroft TMA 691 thermal mechanical analyser which recorded linear expansion of heated samples contained in a small crucible and subjected in contact with a probe of 5 mm diameter (compared with crucible diameter 5.84 mm and depth of 2.5 mm) loaded to 1 g. Movement of the loaded probe in the vertical direction was recorded as a millivolt response at each recorded temperature. A heating rate of 10 K min^{-1} was used and samples were surrounded by static air. The results for 2.5 mg of pulverised FR viscose and cotton samples and 5.0 mg of fibre/intumescent mixtures are shown in Figs. 5 and 6, respectively.

3. Results and discussion

DSC, TGA and TMA curves for four pulverised FR treated cotton samples, MPC 1000 and MPC 2000 intumescent systems and their respective mixtures in 1 : 1 ratio are shown in Figs. 1–3 and 5. Although thermal analysis was undertaken for each FR cotton at

Table 2
Weight losses in TG curves and DTG maxima of FR cotton, intumescents and their mixtures

Samples	First stage			Decomposition stage			Char oxidation stage			Char yield at 700°C
	Temp. range/ (°C)	Wt. loss/ (%)	DTG maxima/ (°C)	Temp. range/ (°C)	Wt. loss/ (%)	DTG maxima/ (°C)	Temp. range/ (°C)	Wt. loss/ (%)	DTG maxima/ (°C)	
Int1 (MPC 1000)	—	—	—	200–259	10.5	215	483–856	38.8	571	16.5
				259–368	14.7	335				
				368–483	19.4	429				
Int2 (MPC 2000)	—	—	—	204–300	14.6	248, 263	524–700	29.8	653	10.0
				300–359	10.1	331				
				359–524	34.1	444				
FR1 cotton (TR - 2.6%P)	–200	9.1	175	201–238	8.1	221	388–786	36.8	556	8.2
				238–388	38.6	286				
FR1 cotton/Int1	–200	6.5	180	200–278	13.9	257	433–888	41.2	652	22.0 (12.3) [a]
				278–338	15.1	302				
				338–433	10.7	356				
FR1 cotton/Int2	–200	8.1	180	200–285	13.5	258	478–878	34.4	686	22.9 (9.1) [a]
				285–349	15.9	312				
				349–478	21.4	401				
FR2 cotton (LR-1.7%P)	–200	7.1	173	200–345	47.1	288	345–700	40.6	568	5.2
FR2 cotton/Int1	–200	4.4	183	200–281	11.5	262	467–886	35.6	672	21.5 (10.8) [a]
				281–350	18.4	307				
				350–467	20.3	408				
FR2 cotton/Int2	–200	4.3	178	200–279	10.8	261	484–884	33.7	681	21.1 (7.6) [a]
				279–352	19.8	305				
				352–408	21.2	408				
FR3 cotton (Proban - 2.5%P)	–227	6.7	—	227–386	49.6	317	386–807	38.1	559	6.3
FR3 cotton/Int1	–200	5.3	—	200–239	3.8	220	433–886	39.1	616	23.9 (11.4) [a]
				239–433	36.3	318				
FR3 cotton/Int2	–200	4.2	—	200–293	10.1	255	493–883	35.2	663	21.7 (8.1) [a]
				293–364	21.3	328				
				364–493	19.2	409				
FR4 cotton (TFRI - 2.7%P)	–200	6.8	—	200–245	2.7	220	390–700	37.8	563	9.8
				245–390	42.7	326				
FR4 cotton/Int1	–200	6.4	—	201–229	2.8	209	438–882	39.8	653	27.3 (13.2) [a]
				229–289	9.8	277				
				289–438	24.8	326				
FR4 cotton/Int2	–200	4.5	—	200–298	12.3	265	488–883	35.5	679	24.3 (9.9) [a]
				298–367	18.9	334				
				367–488	18.9	400				

[a] Values in parentheses are calculated average values.

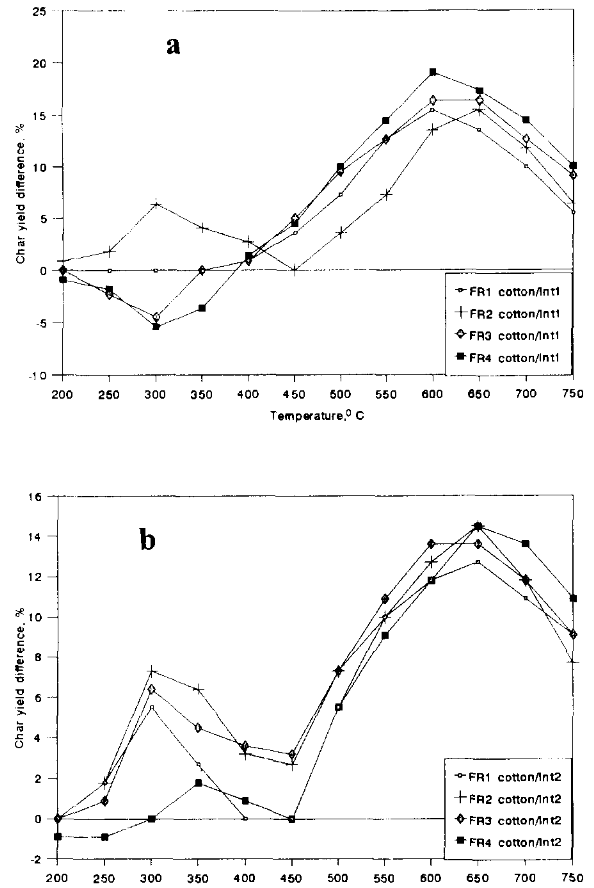

Fig. 4. Difference between actual and calculated residual char yields from TGA curves in static air of mixtures of FR cottons and (a) Int1 and, (b) Int2.

different phosphorus levels, and each level with each of the intumescent systems, it was observed that thermal responses were little influenced by retardant concentration, once phosphorus levels were 2% or greater [7]. Hence, each FR cotton at one phosphorus level which gave optimum results was chosen for discussion. From Figs. 1–3 and 6, it is clear that the results for mixtures of each fibre and intumescent are quite different from the averaged sum of the separate respective fibre and intumescent components as observed previously for FR viscose/intumescent combinations [5,6]. This is also quite clear in the DSC and TGA curves in Figs. 1–3, where their calculated average curves are also shown. Thus, there is some kind of interaction between each FR cotton and intumescent component. Full analyses of DSC curves are presented in Table 1 and TGA and DTG (not shown here) curves in Table 2.

3.1. Differential scanning calorimetry

Thermal analytical studies of the Int1 (MPC 1000) and Int2 (MPC 2000) intumescent systems have been discussed in detail elsewhere [5]. In brief, MPC 1000 shows three endothermic peaks in air (see Fig. 1(a) and Table 1). The first one at 175°C represents fusion of pentaerythritol, and the second at 209°C represents decomposition of ammonium polyphosphate to release phosphoric acid. The third peak is actually a double transition with maxima at 247 and 273°C which may be due to cross-linking of ammonium polyphosphate and formation of polyol-phosphates. The double peaked exotherm at 408° and 438°C may represent aromatization and oxidation of the char, respectively. Also during this same temperature range melamine sublimes and then decomposes, releasing large amounts of ammonia.

The DSC response of Int2 (MPC 2000) shows four endothermic peaks (see Fig. 2(a) and Table 1). The first one at 114°C is most probably due to the loss of sorbed moisture. The intense endothermic peak at 215°C is due to melting of dipentaerythritol (m.p. 214.9°C). At about 280–310°C, melamine phosphate degrades to form melamine pyrophosphate and polyphosphate, which then decompose in the 330–410°C range, releasing melamine, ammonia and water [5,8]. The endothermic peaks at 232° and 244°C may represent these cross-linking and related fusion reactions, respectively.

In order to understand the type of interaction between each flame-retardant cotton–intumescent combination, it is important to discuss in brief the mechanism of degradation of individual components. Our recent publication [9] reviewed the influence of flame-retardant treatments on the mechanism of pyrolysis of cellulose. Thermal degradation of cellulose proceeds essentially through two types of reactions. At lower temperatures, between 200 and 280°C, there is gradual degradation which includes depolymerization, dehydration, etc., leading to the formation of water, carbon monoxide, carbon dioxide and char. At higher temperatures, a rapid volatilisation leads to the formation of laevoglucosan, which further breaks down

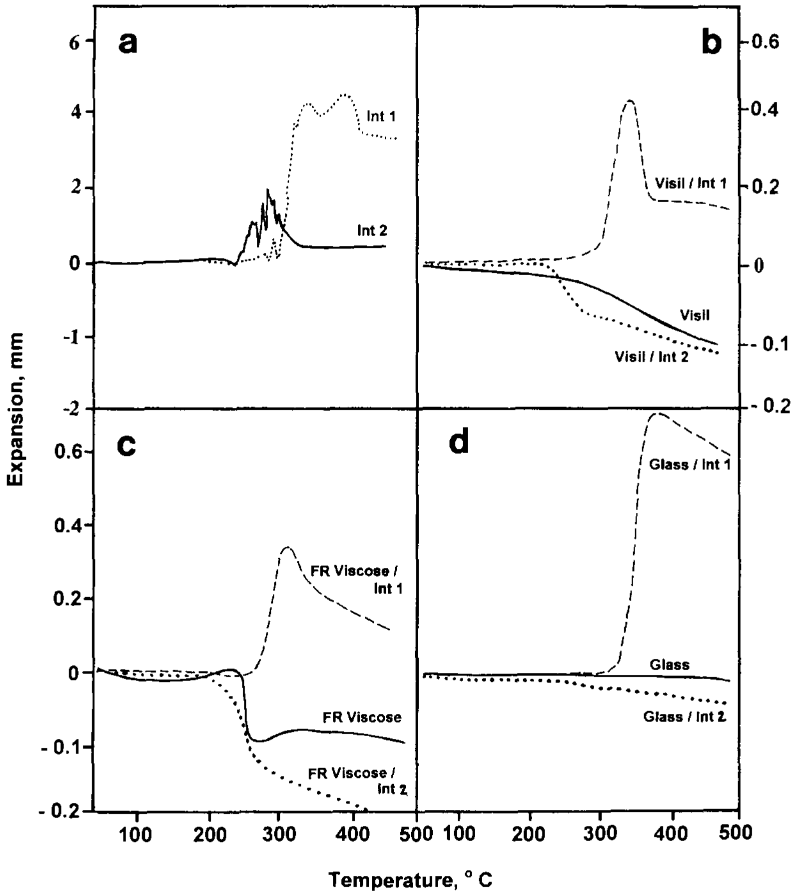

Fig. 5. TMA responses under static air at 10 K min^{-1} of 2.5 mg samples of individual components of (a) Int1 (- - -) and Int2 (———), (b) Visil, (c) FR viscose and (d) glass fibres, and 5 mg samples of their respective mixtures with Int1 (- - -) and Int2 (· · ·).

to give smaller molecular species, namely furans, aldehydes, ketones, aromatic hydrocarbons, etc. Repolymerization of these volatiles may result in char-formation. Condensed phase flame retardants and, especially, those having Lewis acid character favour the former (dehydration) type of reactions, thereby lowering the decomposition temperature of the substrate and increasing the char yield.

The DSC response of the control cotton (cellulose) in air, as discussed elsewhere [10] shows two very sharp exothermic peaks with maxima at 346° and 478°C. The first peak represents decomposition of cellulose to form volatiles and char, and the second one represents oxidation of the char. The DSC of FR1 cotton containing Amgard TR shows an endotherm peaking at 182°C followed by two exotherms with maxima at 317° and 487°C. Amgard TR contains ammonium polyphosphate and there is no chemical bonding between them and the cellulose structure. The endotherm probably represents fusion of the components and release of phosphoric acid. This phosphoric acid can catalyse dehydration reactions of cellulose and can react with cellulose forming cellulose phosphate, which prevents laevoglucosan formation and during decomposition, introduces P–O bonds into the aliphatic char. The mechanism of decomposition of cellulose phosphate has been discussed in detail elsewhere [9]. The exotherms at 317° and 487°C represent the main decomposition reactions of cellulose phosphate and oxidation of char, respectively.

In FR2 cotton containing Amgard LR II, the endotherm is missing and, instead, there is a double

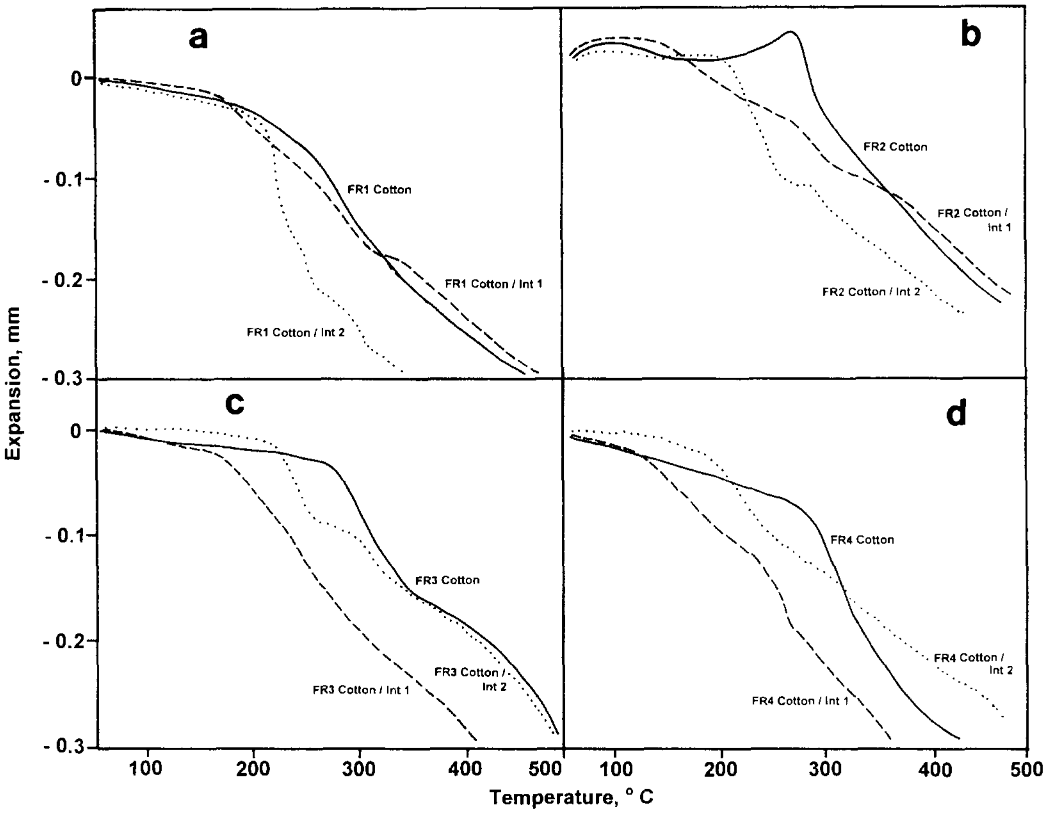

Fig. 6. TMA responses under static air at 10 K min^{-1} of 2.5 mg samples of (a) FR1 cotton (Amgard TR), (b) FR2 cotton (Amgard LR II), (c) FR3 cotton (Proban CC) and (d) FR4 cotton (TFR 1), and 5 mg samples of their respective mixtures with Int1 (- - -) and Int2 (· · ·).

peaked (280°, 307°C) exotherm. The reason is a consequence of the heat-cure treatment which causes the ammonium polyphosphate initially present to phosphorylate cellulose. The double peaked exotherm with maxima at 280° and 307°C then represents acid-catalysed dehydration and the main decomposition reactions. The exotherm peaking at 492°C is due to oxidation of char.

Similarly, in FE3 cotton (Proban-treated) and FR4 cotton (TFR 1-treated) there are two similar exotherms, those at lower temperature representing decomposition reactions and at higher temperatures – char-oxidation. It is evident that in all four samples, however, the decomposition temperature of cellulose has been lowered relative to untreated cellulose (346°C [10]).

In general, the DSC responses of all FR cotton/MPC 1000 are different from their individual components and the calculated mixture, averaged traces (see Fig. 1). In all mixtures, the first endotherms for Int1 (175° and 209°C) are still present but the third double peaked (maxima at 247° and 273°C) endotherm is missing. Instead, there are two exotherms and their maxima are at different temperatures than those of decomposition temperatures of FR cottons (first exotherms). The second exotherm, representing the char-oxidation stage in all the FR cottons, is missing in the mixtures. This suggests that oxidation of char in the mixtures is taking place at much higher temperatures. The same effects are seen with mixtures of FR cottons with Int2 (see Fig. 2). New exotherms have appeared with their maxima at 294° and 404°C in FR1 cotton/Int2, at 336° and 416°C in FR2 cotton/Int2, at 404°C in FR3 cotton/Int2 and at 423°C in FR4 cotton/Int2. This again points towards possible interactions between them, accompanied by an apparent charoxidative resistance under the flowing air conditions used.

3.2. *Thermogravimetry*

The TGA thermograms of all the samples have three stages. Temperature ranges of these stages, weight losses and corresponding DTG maxima (temperatures where maximum weight loss occurs) are shown in Table 2. Any weight loss up to 120°C is due to loss of sorbed moisture. Below 200°C, the weight loss is referred to as the first stage. The second stage, generally speaking, lies in the 200–480°C range and represents the main decomposition reactions, which comprise a two- or three-step process depending on the sample. The third stage, above 480°C, represents oxidation of char. In individual intumescent and FR cotton components, these weight losses correspond to the various reactions discussed in Section 3.1.

As can be seen from Fig. 3, the TGA curves for all FR cottons/Int1 are different from the calculated average responses (shown as broken lines in Fig. 3). In general, the mass loss response is as expected up to 400°C, but above 400°C, residual char masses are greater than expected. The TGA curves for FR cottons/Int2 also showed the same general effect and, hence, are not presented here. Furthermore, it can been seen from Table 2 that DTG maxima for the main decomposition step have shifted to lower temperatures in mixtures as compared with respective FR cottons. The FR1 cotton mixtures are exceptions, as here the DTG maxima have increased from 221°C to 257° and 258°C, respectively, and the FR4 cotton/Int2 mixture where a shift from 220°C to 265°C is observed.

Of particular interest are the observed higher char yields above 500°C in the mixtures compared to yields of either parent FR cotton or intumescent component (see Table 2). Residual char percentage yields and the expected calculated values (in parentheses) at 700°C in air are listed in Table 2. Fig. 4 shows the differences in actual and calculated char yields at different temperatures for each set of FR cotton/intumescent mixture. DTG maxima for char-oxidation stages in all the FR cotton samples are below 600°C, but for their mixtures with intumescents they are above 650°C.

The foregoing indicates that, in the FR cotton/intumescent mixtures, not only have char yields increased, but the chars are more resistant to oxidation as well. These results are in accordance with the conclusions of our previous studies of these intumescent systems with regenerated cellulose (Visil and FR viscose), where there was clear indication that char-bonded structures are formed [4–6].

3.3. *Thermal mechanical analysis*

Before discussing TMA results for FR cottons/intumescents, those for previously studied regenerated cellulose fibres Visil and FR viscose and a neutral glass fibre are presented in order to provide a link with reported findings. Therein, the details of their structure, and the DSC and TGA results of their mixtures with intumescents are given [5,6]. TMA results of Int1, Int2, Visil, FR viscose, glass fibres and their mixtures are shown in Fig. 5.

Int1 (MPC 1000) starts expanding at 280°C (see Fig. 5(a)) after an initial contraction, and reaches maximum volume at 403°C as a consequence of intumescent reactions discussed above. After this maximum, shrinkage can be explained due to oxidation of char. In Fig. 5(a), Int2 (MPC 2000) shows a similar initial contraction up to 245°C, which may be due to fusion of melamine phosphate. This intumescent then starts expanding as it is inflated by subliming melamine. The expansion shown by the TMA response is not very uniform, probably as a consequence of irregular gas evolution or bubbling during intumescence.

Visil (which contains polysilicic acid (30% w/w as silica)), on heating alone, contracts slightly up to 250°C (see Fig. 5(b)) because of dehydration reactions, and from 250–400°C this contraction increases through further decomposition of cellulose structure and full dehydration of polysilcic acid to silica. The Visil/Int1 mixture, however, expands from 280°C onwards, rising to a maximum at 325°C. Similar expansion can be seen in case of FR viscose (which contains an organophosphorus additive (5)) and glass/Int1 mixtures from ca. 300°C. Even at 450°C, there is some expansion remaining when compared to the original structure; expansion is less than that of the pure intumescent, however. As can be seen from Fig. 5(b) and (c), the maxima of expansion in Visil and FR viscose mixtures with Int1 are at the lower temperatures of 325° and 300°C, respectively, than for Int1 alone at 403°C, thus showing evidence of some kind of interaction. Their mixtures with Int2, on the other hand, did not show any expansion. The reason for not expanding can be that, either the char formed – after going through the semi-liquid stage – is not strong enough to withstand the weight on the TMA probe or else an interaction between fibre and intumescent reduces gas formation.

The TMA curves for FR cottons (see Fig. 6) show that they start contracting from about room temperature and their behaviour seems to be similar to respective TGA curves, in terms of loss in property vs. temperature response. Initially, there is smooth and slight contraction up to 200°C, followed by a more rapid stage and then a final more gradual one. The only exception is FR2 cotton, which shows slight expansion up to 270°C (see Fig. 6(b)). Their mixtures with any of the intumescent system do not show any expansion, again indicating that the char-formation stage, which is a semi-liquid stage is not strong enough to withstand the weight of the TMA probe and gas formation is possibly reduced. FR1 and FR2 cotton–Int1 mixtures behave in a similar manner to their parent FR cotton components, except that in FR2 cotton/Int1 there is no initial expansion at 270°C. While their mixtures with Int2 start contracting at lower temperatures than when alone, the overall contractions are greater in the mixtures up to 400°C than compared to respective FR cottons alone (compare Fig. 6(a) and (b)). FR3 and FR4 cotton–intumescent mixtures in Fig. 6(c) and (d) show the converse effect, i.e. their mixtures with Int1 show more contraction starting from lower temperatures than their mixtures with Int2.

Although from these results no new mechanistic information can be gained, the TMA curves for mixtures are different from their individual components and, so, indicate again that some kind of interaction occurs between them which agrees with the conclusions drawn from the DSC and TGA studies. The TMA results do suggest, however, that improved resistance to oxidation noted in small DSC and TGA samples – which mirror results of larger fabric/intumescent combinations compromising flame-retardant viscose fibres and Int1 [4] – does not derive from the thermal insulative effects associated with conventional intumescent, expanded char-formation. Thus, char-bonded structures developed do not expand in the way that pure intumescents do.

3.4. Mechanism of FR cotton/intumescent interaction

Most of the successful flame-retardant cellulosic textiles result in high char yields prior to combustion. The higher the amount of residual char, the less are volatile combustible materials available to sustain the flame and, hence, the higher the degree of flame retardance of the material. A recent publication by Lewin [11] reviews the importance of char structures in flame-retardant polymeric materials. For a material to be used as a barrier fabric, it needs to produce char which has greater mechanical strength, is impermeable to gases and liquids and is resistant to oxidation, otherwise the whole structure will disintegrate. Hence, it is very important to understand the mechanism of char-formation.

The thermal analytical results for two intumescent systems, discussed in the foregoing, correlate with mechanisms of intumescence discussed in the literature [3,12,13]. According to Camino et al. [3] in ammonium polyphosphate/pentaerythritol/melamine intumescent systems, char-formation takes place through following stages:

APP starts to decompose around 210°C, releasing polyphosphoric acid and ammonia. This then forms a liquid medium in which phosphorylation of polyol-hydroxyl groups occurs, forming various products. The character of these products can be determined by the APP : polyol ratio. Between 280° and 330°C, the polyol-phosphate decomposes to char, thereby releasing phosphoric acid, water and ammonia, and swelling of the mass occurs. Polymerization of released phosphoric acid to polyphosphoric acid creates a liquid stage; melamine in the meantime volatilises in the 270–400°C range, adding to the swelling of the liquefied charring matrix. This is shown in a schematically simplified way in Fig. 7(a). In the case of the dipentaerythritol/melamine phosphate (MPC 2000) intumescent system, melamine phosphate acts both as char promoter as well as blowing agent. The degree of char expansion is a balance between the rates of gas/volatile evolution, the viscosity of the liquified pyrolysis products and the transformation of the latter to solid expanded char [14].

Pyrolysis of the condensed phase active-FR cottons used in this work has been studied by various workers [15–18] which has been reviewed in our recent publication [9]. FR cottons, when heated above 200°C or

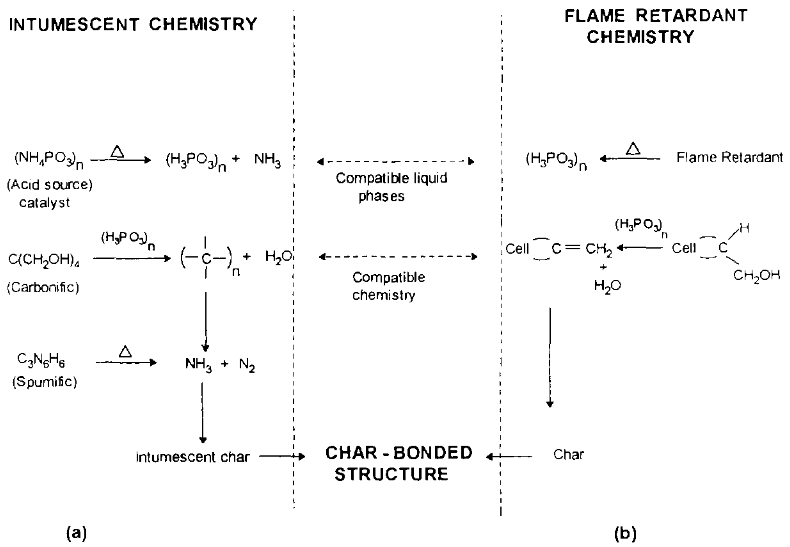

Fig. 7. Simplified mechanism of formation of char-bonded structures.

so, decompose to a variety of products including polyphosphoric acid, which again creates a semi-liquid char-forming stage. There is scanning electron microscopic evidence in support of this mechanism [19,20]. Polyphosphoric acid accelerates dehydroxylation of cellulose and the formation of conjugated double bonds in the glucopyranose rings. This cycle continues until all hydroxyl groups of cellulose structures are removed. On further heating, cross-linking and aromatization of the char takes place, leading to the formation of thermally stable carbonized chains [9]. During this process evolution of flammable gases is retarded and cellulose becomes self-extinguishing [9], as illustrated schematically in Fig. 7(b).

As demonstrated previously for flame-retardant viscose/intumescent mixtures [20], these results for FR cotton–intumescent mixtures also suggest that char-formation of the cellulosic structure and intumescent occurs via respective liquid-phase formation. This will lead to physical mixing and subsequent chemical interaction resulting in the formation of the 'char-bonded' structure. Furthermore, during pyrolysis of the mixtures, the cellulose itself, being a polyhydric compound, can act as an additional carbonific component for intumescent char as suggested by the observed enhanced char yields (see Fig. 4). This intimate interaction being flame retardant, intumescent and cellulose substrates may be considered to be synergistic with regard to char-formation. However, the reason for observed resistance to oxidation from the aforementioned studies is not yet clear, although TMA results suggest that it is not a consequence of char inflation. Further studies are required to interpret this phenomenon and currently the use of mass loss calorimetry is being made to understand this effect.

4. Conclusions

From the DSC, TGA and TMA results, there is a clear indication of FR cotton/intumescent interaction during which enhanced char-formation occurs and a 'char-bonded' structure is formed. Previous studies [20] have indicated that this char-bonded structure has increased mechanical stability, reduced oxygen permeability, and, hence reduced oxygen sensitivity. The expanded char will also entrap most of volatiles and acts as an insulator offering heat resistant properties to underlying substrates.

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