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Substantive intumescent flame retardants for functional fibrous polymers

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This paper discusses the potential for developing substantive intumescent, flame retardant fibres. It also reviews very recent work in the authors' laboratories that has demonstrated the successful reaction of char-promoting polyol phosphoryl chlorides with fibres containing active hydrogens such as cellulose flame retarded cellulose, wool and polyamide. Results show that satisfactory char enhancement occurs with evidence that intumescent character exists in some of these and that the chemical treatments are resistant to boiling in water. Using this chemistry, there is the potential, therefore, of creating the first generation of substantive intumescent fibres that will provide a cost-effective range of textiles with significantly enhanced fire resistant properties.

1. Introduction

With regard to the use of the established intumescents based on ammonium polyphosphate, melamine phosphates and pentaerythritol derivatives [1], two major drawbacks are evident within the fibre and textile areas. Firstly, they can only be applied as a fibre surface treatment in a bonding resin which affects desirable textiles properties such as appearance and handle. Secondly, and of perhaps greater importance even for applications whose aesthetics are less important, are their relatively high solubilities in water. Ideally, the intumescent should be integrated within the fibre structure at the molecular level.

This paper presents very recent work based on the premise that char-forming polyol phosphoryl chlorides like spirocyclic pentaerythritol diphosphoryl chloride (or SPDPC) will substitute active hydrogens present in fibre-forming molecules and thereby introduce a substituent which is both a char promoter and char-former which decomposes via a liquid intermediate phase following release of phosphoric acid as the monomeric or polymeric form or both.

Active hydrogen sites in cellulose are primary (C6 position) and secondary hydroxyl (C3, C4 positions) groups and some durably flame retarded cellulosic fibres contain functional groups such as secondary amines. For example, cotton fibres containing the complex polyphosphine oxide (Proban CC, Rhodia, UK) are rich in secondary amine groups and so, successful phosphorylation of cellulose by a polyolphosphoryl chloride should introduce a level of flame retardancy into the polymer. More importantly, phosphorylation of an already durably flame retardant cellulose will introduce intumescent activity and thereby significantly enhance its fire resistance properties.

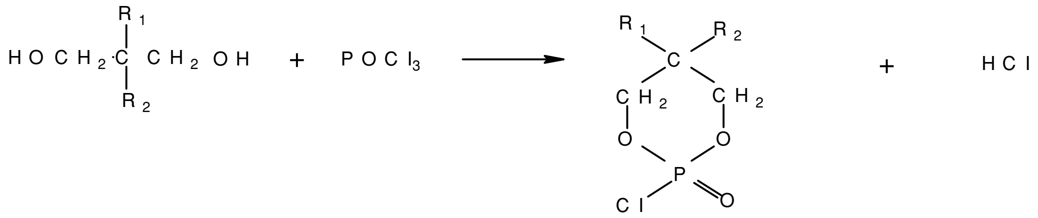
Extending the above argument to other fibrous polymers, suggests that wool and polyamides would offer similar active hydrogens. For the linear polyamides, nylon 6 and 6.6, for which no effectively durable flame retardant exists when in fibre form and which are thermoplastic, this is especially relevant.

2. Synthesis of intumescent flame retardants

Based on our initial studies [2] and subsequent work in this project, SPDPC has been shown to transfer its intumescent properties on to cellulosic fibres following their phosphorylation. Therefore, a major hypothesis underlying this research is that other polyol phosphoryl chlorides would similarly phosphorylate cellulose and its derivatives to yield potentially intumescent flame retardant behaviour. A feature of SPDPC is the 6-membered cyclic phosphate structure that contributes to its high yield during synthesis and its general stability apart from its tendency to form char when heated. However, its relatively large molecular size may prevent its effective diffusion into fibrous substrate microstructures and so we have selected 1,3-propanediol and its derivative, 2,2-diethyl-1,3-propandiol, as possible alternatives to pentaerythritol as the polyol.

Phosphorylation of 1,3-propanediol derivatives should give rise to six-membered ring cyclic propanediol phosphoryl chloride or CPPC and its derivatives if the following reaction holds true [3];

where R_1 and R_2 are hydrogen or aliphatic moieties [4]. If $R_1 = R_2 = C_2H_5$, then in a similar manner,



cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride or CDPPC is formed. It is proposed also that CPPC and its derivatives can also phosphorylate Proban-treated cotton which contains secondary bridge amine groups and possibly unreacted methylol groups [5].

Hence, SPDPC, cyclic 1,3-propanediol phosphoryl chloride (CPPC) (or 2-chloro-2-oxo-1,3,2-dioxaphosphorinane) and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) (or 2-chloro-5,5 diethyl-2-oxo-1,3,2-dioxaphosphorinane) have been synthesised according to the procedure similar to SPDPC described above [3, 6].

3. Reaction of intumescent flame retardants with fibrous polymers

3.1. Cellulose

Reactions of SPDPC, CPPC and CDPPC and cellulose were carried out in dimethylformamide, DMF in a flask under reflux at various mass ratios and the preferred reaction temperature of 160°C [7] for selected SPDPC-cellulose reactions. Extents of phosphorylation were measured as phosphorus levels by the molybdovanadophosphoric acid method [6] and are shown in Table I.

The specific polyol phosphoryl chlorides used, SPDPC and CPPC, are shown to be able to substitute into cellulose (as cotton) in the presence of a suitable solvent (DMF) and base (pyridine and sodium hydroxide) at levels commensurate with phosphorus concentrations up to 2.5% (w/w). This is equivalent to phosphorylation yields of up to 22.7%. The efficiency of phosphorylation is dependent upon reaction temperature and SPDPC: cotton mass ratios. Highest yields occur when reactions are carried out at respective mass ratios of 4:1 (almost equivalent to a molar ratio of an anhydroglucopyranose repeat: $\frac{1}{2}$ SPDPC molecule) at 160°C for 2 h.

TABLE I Phosphorus concentrations in SPDPC/CPPC-phosphorylated cellulose

Ratio (mass) phosphoryl chloride/cellulose	Time, h	Phosphorus, % yield	
		SPDPC-cellulose	CPPC-cellulose
0	0	0	0
2:1	1	0.75	
2:1	2	1.01	
2:1	4	1.03	
2:1	6	1.09	
1:1	2	0.56	
2:1	2	0.98	
3:1	2	1.78	
4:1	2	2.39	2.26
1:1	4	0.63	
3:1	4	1.82	
4:1	4	2.47	

3.2. Proban-treated cotton

Reactions were undertaken according to the same procedure as described above for SPDPC phosphorylation of cellulose [7]. Essentially 200 mg Proban-treated cotton, 50 mg NaOH, 1 ml pyridine and 5 ml DMF reaction mixtures were phosphorylated with SPDPC at SPDPC/Proban-cotton mass ratios of 1:1 to 3:1 at temperatures from 120–160°C for times from 30 min to 6 h. Again 160°C is the preferred temperature and Table II show results for SPDPC and CPPC-reacted samples.

It is seen that the Proban-treated cotton sample can be more easily phosphoralyted than a pure cotton sample at 160°C at all SPDPC:fibre ratios [7] and that yields approaching 80% are possible. The greatest phosphorus value occurs for a Proban-treated cotton:SPDPC ratio of 3:1 at 160°C for 2 h. Similar results for CPPC and CDPPC-phosphorylated samples are shown in Table II. These show similar levels of phosphorylation for the SPDPC and CPPC-reacted samples at the same conditions but lower levels for CDPPC analogues possibly because of steric hindrance caused by the two ethyl substituents present.

3.3. Polyamides; nylons 6 and 6.6

Reactions of CPPC, CDPPC and SPDPC-nylon fabrics were undertaken in DMF solution. Maximum levels of phosphorus addition were less than for the above cellulose-based substrates at 0.7% P.

The results show that the presence of NaOH as well as pyridine promotes the phosphorylation level and that pyridine increases the degree of phosphorylation only when the reaction time is less than 30 min. The swelling agent phenol does not show any significant effect on the phosphorylation level. CDPPC appears to be more difficult to react with nylon 6.6 than CPPC, which may due to the steric hindering effect of the former. If we assume that the amine end group concentration is typically 40 μmoles/g in each polyamide and that phosphorylation only occurs at this group, then calculation shows that maximum phosphorus levels are of the order of 0.6–0.7%. Clearly the results indicate that indeed reaction is occurring only at the amine end group. The ability to increase phosphorus levels may occur only if amine end group concentrations are higher. This could be achieved using deep-dye variants of the fibres or by increasing ends by chain

TABLE II Phosphorus concentrations in SPDPC/CPPC/CDPPC-phosphorylated Proban-treated cotton

Sample	Ratio (phosphoryl chloride/ sample, w/w)	Time, h	Phosphorus, %			
			Control	SPDPC	CPPC	CDPPC
Proban-cotton			3.96^{a}			
	1.5:1	2		6.47		
	1.5:1	6		7.08		
The effect of ratio	1:1	2		4.96^{a}		
	1.5:1	2		6.47^{a}		
	2:1	2		7.53		
	3:1	2		11.15		
The effect of reaction time	1:1	3		5.91^{a}		
	2:1	0.5		4.76^{a}		4.87
	2:1	1		5.47^{a}	5.86	5.03
	2:1	1.5		6.78^{a}		
	2:1	2		7.53^{a}	6.92	6.05
	2:1	3		7.99^{a}		
	4:1	1			5.95	
	4:1	2			6.84	

^{a}Recipe: 200 mg Proban-treated cotton, 5 mL DMF, 1mL pyridine and 50 mg NaOH.

hydrolysis. While this latter is often used by dyers to increase base dye uptake, it is accompanied by strength losses.

3.4. Wool

Results have also been achieved with both SPDPC and CPPC on wool with reaction temperatures being reduced to 120°C and 60 min reaction times yielding 2.06% phosphorus levels; after water boiling, 1.96% P is still present and char enhancement at 700°C is close to 60% [2].

4. Characterisation of reacted samples

4.1. TGA results

The TGA results published elsewhere [7, 8] show that char formation from SPDPC-phosphorylated cellulose and Proban-treated cotton respectively is significantly higher above 500°C than expected from the calculated values. Furthermore, the significant rise in char levels above 400°C for the substituted samples with increasing SPDPC (and also for CPPC or CDPPC [9]): cellulose mass ratio suggests a more quantitative relationship with the degree of substitution as indicated by phosphorus content. Significantly, the enhanced char-forming effect is unaffected by a preboil treatment (30 min, 100°C in detergent water solution) thereby indicating the hydrolysis stability of the —P—O— cellulose bond present.

An alternative way of showing these char enhancements is to plot the function $(C_s - C_c)/C_c$ or $(C_s - C_p)/C_p$ versus phosphorus level where C_s is the char residue from substituted cotton, C_c the value for control cotton sample and C_p is the value of control Proban-treated cotton at any temperature from respective TGA responses [7–9]. The results indicate that enhanced char levels with respect to respective non-phosphorylated substrate values are solely determined by respective phosphorus levels and hence degree of phosphorylation. Increasing $(C_s - C_p)/C_p$ and $(C_s - C_c)/C_c$ values above 500°C suggest that the char formed by SPDPC-treated samples are more oxidation resistant than the char formed by the control samples itself.

4.2. Optical microscopic and SEM analysis of chars

Optical microscopy examination of char samples prepared by heating in the TGA at 20°C/min to 500°C show that for yarn chars from two yarns having almost the same original diameters selected from the untreated and SPDPC-treated Proban-finished cotton fabrics (SPDPC/Proban-treated cotton mass ratio of 2:1 reacted for 2 h) are quite different. The SPDPC-reacted sample char has a larger diameter than both the uncharred and charred untreated Proban-containing cotton, although the reduced integrity of both samples is clear evidence of accompanying oxidation at this higher temperature.

For SEM examination, char samples prepared at various temperatures up to 600°C did not require coating whereas those prepared from reacted cotton and heated in air at 400 and 600°C for 10 min in a furnace were gold sputter-coated. Careful examination showed that the chars from 4:1 SPDPC:cotton mass ratio, 2 h-reacted samples are more defined than respective 2:1 mass ratio samples and this reflects their relative phosphorus contents of 0.56 and 2.39% (see Table I) and measured char enhancements.

SEM images (see Fig. 1) show apparent increases in fibre char diameters following phosphorylation, which are unaffected by preboiling the sample before char formation. Analysis of char diameters suggests that char volume has increased by as much as 70% and hence is intumescent.

4.3. Flammability testing

The additional flame retardancy conferred upon the Proban-treated cotton is demonstrated by limiting oxygen index, LOI measurement and char length measurement according to BS5438:1989 Test 2 (10 s or 20 s

TABLE IV Flammability testing of SPDPC-reacted Proban cotton (mass ratio of 1:1, 2 h at 160°C)

Reaction time, min	0	30	60	120
Phosphorus level, %	3.96	4.34	4.41	5.18
LOI	32.1	32.4	32.8	33.2
Char length, mm	91 (20 s)[a]			78 (20 s)[a]
Damaged length, mm	94 (20 s)[a]			80 (20 s)[a]
	77 (10 s)[a]			75 (10 s)[a]

[a] Ignition time in s.

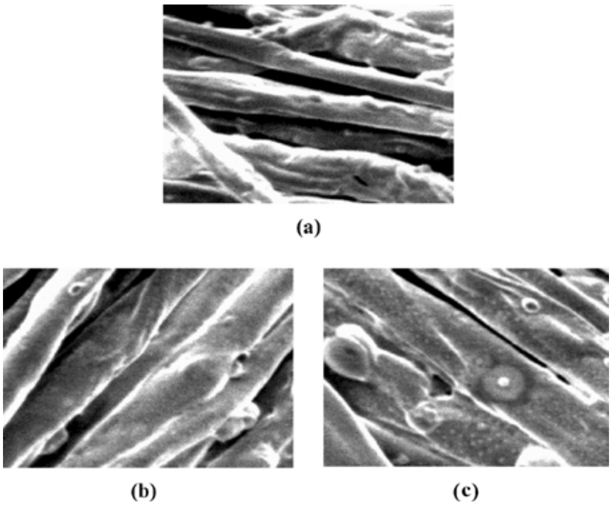

(a)
(b)
(c)

Figure 1 Char structures of (a) Proban cotton control and reacted with SPDPC (b) before and (c) after boiling (SPDPC/Proban-treated cotton mass ratio = 2:1, 160°C, 2 h) heated at 420°C for 10 min, 1170× mag.

ignition times) in Table IV for a separately produced set of larger-sized samples. These were produced by reacting larger Proban-treated cotton samples at 1:1 SPDPC: substrate mass ratio for 2 h at 160°C. (specimen sizes of 14 × 6 cm). The lower ratio was a consequence of the limited quantity of SPDPC available and so phosphorylation was limited. However, the maximum phosphorus level in these samples is similar to that listed in Table II for the 1:1 mass ratio, 2 h reacted sample. Even so, with only an increase in phosphorus level of 1.22% after 2 h reaction, an increase in one LOI unit has been achieved. More importantly, the reduced char and damaged lengths after a 20 s ignition time demonstrates the ability of the SPDPC-phosphorylated Proban cotton to resist igniting sources for longer times because of their increased char-forming capacity.

5. Summary and conclusions

The above results have shown that substantive intumescence may be introduced into conventional fibres and their flame retardant derivatives and that this effect not only creates enhanced fire resistance, but also has durability to boiling in water. Current work is focused upon using more acceptable solvents which might be used with conventional textile processing technologies.

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