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Enhancing polymer char formation by reaction with phosphorylated polyols. 1. Cellulose

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Abstract

The use of polyol phosphonyl chlorides or phosphochloridates as phosphorylating agents for cellulose is considered as means of introducing a char-forming centre in association with an acid-generating moiety into a functional polymer which itself is potentially char-forming. The specific polyol phosphonyl chloride used, spirocyclic pentaerythritol di(phosphonyl chloride) or diphosphochloridate (SPDPC) is 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: 1/2 SPDPC molecule) at 160°C for 2 h.

Thermogravimetric analysis of SPDPC-phosphorylated cellulose shows enhanced char formation over the range 400–740°C with respect to untreated cotton cellulose. Scanning electron microscopy shows chars to be well-defined and quite resistant to oxidation as the temperature rises above 600°C in air.

Keywords: Cellulose; Cotton; Phosphorylation

1. Introduction

Recent research into the application of intumescent fire retardants to fibres and textiles has demonstrated that their introduction on to the surfaces of flame retardant cellulosic fibres significantly increases the fire barrier performance when exposed to temperatures as high as 1200°C for up to 10 min [1,2]. Nonwoven structures based on these fibre-intumescent combinations yield properties similar to those from similar aromatic-structured fibres such as polyaramid and carbonised acrylics [3]. These properties have been shown to result from the formation of a complex charred residue which is more resistant to oxidation above 500°C in air than normal carbonaceous char associated with either the intumescent or flame retardant fibre alone [4–6]. More recently, similar behaviour has been observed for certain wool-intumescent combinations [7].

However, with regard to the use of the established intumescents based on ammonium polyphosphate, melamine phosphates and similar species [8], 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 that 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. While selections of resins and intumescent type can enable a coated textile to survive the 40°C 'water soak' test demanded by current UK furnishing fabric regulations [9] and solvent dry cleaning, durability to laundering procedures is minimal.

Ideally, the intumescent should be substantive to the fibre and like currently available reactive organophosphorus-based and durable finishes for cellulose such as those based on phosphonium salt condensates (Proban, Rhodia) and dimethyl phosphonopropionamide derivatives (e.g. Pyrovatex, Ciba) [10], should integrate with the fibre structure at the molecular level. To date, no polymer or fibre-substantive intumescent flame retardants have been synthesised and successfully applied to fibrous substrates such as textile yarns or fabrics.

Halpern et al. [11] have demonstrated that by reacting spirocyclic pentaerythritol di(phosphonyl chloride) or diphosphochloridate **I** (SPDPC) with melamine, a single

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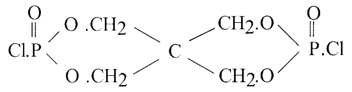
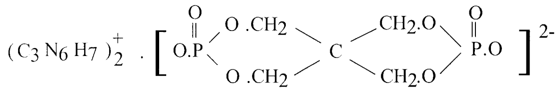
intumescent molecule **II** may be synthesised:

I.

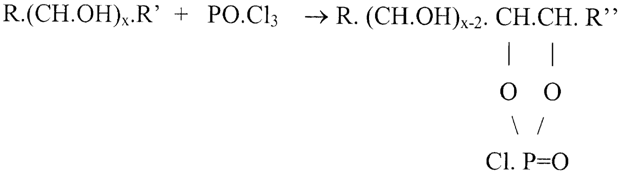


II.



On heating this it is believed that phosphoric acid is released which acid-catalyses the dehydration of the pentaerythritol moeity to a char-forming precursor species. Above 300°C, the released melamine decomposes to release N_2 and NH_3 which inflate the semi-liquid, charring compound. This single molecular intumescent **II** was commercialised by Great Lakes Corporation as Charguard 329 and more recently as NH1511. Subsequently Ma et al. [12], have incorporated SPDPC as a comonomer in selected polyesters and demonstrated its char forming activity in these thermoplastic polymer matrices.

It is proposed, therefore that polyol phosphonyl chlorides like SPDPC will substitute active hydrogens present in fibre-forming molecules and thereby introduce a substituent which is both a char promoter and char-former. In turn, this will decompose via a liquid intermediate phase following release of phosphoric acid as the monomeric or polymeric form or both:



$$R.(CH.OH)_x.R' + PO.Cl_3 \rightarrow R.(CH.OH)_{x-2}.\underset{\underset{Cl.\,P=O}{O\quad O}}{CH.CH}.R'' \qquad (1)$$

$$R'''\cdot(PO)\cdot Cl + PH \rightarrow R'''\cdot(PO)\cdot P + HCl \qquad (2)$$

where R, R′ and R″ are aliphatic moeties, R‴ represents the substituted polyol and PH is a polymer molecule with an active hydrogen. Typical active groups present in common fibre-forming polymers are –OH, $-NH_2$ and –NH–.

Cellulose contains both primary (C(6) position) and secondary hydroxyl (C(3), C(4) positions) groups which are possible phosphorylation sites. Interest in cellulose phosphorylation and a considerable literature developed during the 1940–60 period [13] although little has appeared since then [14]. Research cited in Ref. [13] refers to the phosphorylation of cellulose by pentaerythritol phosphates where temperatures as high as 180°C are required to achieve phosphorus levels of up to 3% (w/w). It is anticipated that use of the more reactive phosphonyl chloride will enable similar yields to be achieved at lower temperatures. This paper reports more fully on our studies [15] of the introduction of SPDPC into pure cellulose and the subsequent effects that this has on the thermal and char-forming characteristics. In order to favour phosphorylation, reactions of SPDPC will be undertaken under basic conditions in the presence of sodium hydroxide and pyridine. The latter has been shown to be effective in assisting cellulose phosphorylation by $POCl_3$

$$\text{Cell–OH} + POCl_3 \rightarrow \text{Cell–O–}POCl_2 + \text{pyridine}\cdot HCl \qquad (3)$$

and by dialkylphosphonyl chorides [16]

$$\text{Cell–OH} + (RO)_2POCl \rightarrow \text{Cell–O–}P(O)(RO)_2 + \text{pyridine}\cdot HCl \qquad (4)$$

2. Experimental

2.1. The preparation of SPDPC

The SPDPC was synthesized according to the following procedure as reported elsewhere [11,16]:

34 g pentaerythritol, (0.25 mole, BDH Chemical, Poole, England), and 82 g of freshly distilled phosphorus oxychloride (0.53 mole, Sigma-Aldrich) were placed in a 50 ml round-bottomed flask under reflux, protected from atmospheric moisture. The mixture was heated for 2 h at 90°C, and held for 20 h at 100°C until evolution of hydrogen chloride had ceased and the mixture changed to a colourless hard cake. The released HCl gas was absorbed by passing into sodium hydroxide solution. The product was crushed and returned to the flask, dispersed by addition of 62.5 g of phosphorus oxychloride and refluxed for 2 h. The vigorous evolution of gas, which initially occurred, had ceased entirely after a 2 h period. Most of the excess phosphorus oxychloride was recovered by decantation and the rest, by heating to 120°C at 10 mm Hg pressure. The crude solid was washed four times with 200 ml portions of ether. Before the last washing, the product was collected on a Buchner funnel, dried in air and crushed to a fine powder. The melting point of the product was 241°C which compares with the reported value of 235–240°C [11].

2.2. Cotton cellulose-SPDPC reaction

SPDPC was weighed and dissolved in dimethylformamide, DMF or dimethylsulphoxide, DMSO in a beaker using a stirring rod. To the solution was added some pyridine and sodium hydroxide and the combined solution transferred into a 50 ml flat bottomed flask. This was heated under reflux on a diethylene glycol bath. Cotton samples, as commercially bleached fabric (ca. 200 mg), were put into the flask after the temperature reached the, respectively, desired temperature of 90, 120 or 160°C. To date both DMF and DMSO have both been found to be acceptable as solvents at temperatures up to 160°C where maximum phosphorylation (as determined by both phosphorus concentration and TGA-derived char yield enhancement at

Table 1
Phosphorus concentrations in SPDPC-phosphorylated cellulose

Sample	Formulation	Mass ratio (SPDPC/sample)	Time (h)	Phosphorus concentration %(w/w)		
				Control	120°C	160°C
Cotton control	200 mg cotton, 5 ml DMF, 1 ml pyridine and 50 mg NaOH		0	0.01		
Effect of reaction time		2:1	1		0.42	
		2:1	2		0.42[a]	
		2:1	6		0.50	
Effect of reaction time		2:1	1			0.75[a]
		2:1	2			1.01[a]
		2:1	4			1.03
		2:1	6			1.09
Effect of ratio		1:1	2			0.56[a]
		2:1	2			0.98[a]
		3:1	2			1.78
		4:1	2			2.39[a]
		0.5:1	4			0.04
		1:1	4			0.63[a]
		3:1	4			1.82[a]
		4:1	4			2.47[a]

[a] Indicates samples for which TGA responses are available and char yields are derived in Fig. 10.

400°C and above, see below) has been achieved after 2 h refluxing. However, there is some indication of reaction occurring between SPDPC and DMSO above 140°C and so DMF is the preferred solvent for these studies. Experimental conditions were selected in order to study SPDPC-fibre interactions at various temperatures, for increasing times, with variable reactant mass ratios at constant pyridine (1 ml) and NaOH (50 mg) concentrations in 5 ml DMF.

2.3. TGA analysis

The TGA curves were obtained for 2.2 mg specimen masses by using a Stanton Redcroft TGA 760 instrument under static air with a heating rate of 20°C/min.

2.4. Scanning electron microscopy

Char samples of SPDPC prepared at various temperatures up to 600°C did not require coating whereas those prepared from SPDPC-reacted cotton and heated in air at 400 and 600°C for 10 min in a furnace were gold sputter-coated prior to SEM examination. Experiments were undertaken at 10 kV beam voltage in a Stereoscan 200, TL2025-OM, (Cambridge Instruments) scanning electron microscope.

2.5. The determination of phosphorus content

Phosphorus analysis of reacted samples (7–12 mg specimen masses) was carried out by the molybdovanadophosphoric acid method [17].

3. Results and discussion

3.1. Extent of reaction: phosphorus analysis

The potential reactivity of SPDPC with cotton was undertaken initially at a number of increasing temperatures (starting at 90°C) and times. Whether or not reaction had occurred was monitored by TGA in the first instance in order to examine whether the char-forming ability of the reacted cellulosic substrate had increased as a consequence of phosphorylation. During preliminary studies, in order to increase the accessibility of the internal fibre structure it was considered that a pre-treatment of cotton samples in 10% sodium hydroxide solution at 20°C for 30 min should be undertaken [13]. Such an aqueous solution pre-treatment enhanced the char residue of SPDPC-reacted cotton samples as shown in the TGA results in the following Section 3.2 (see Fig. 5). Thus, all the cotton samples were pre-treated with 10% NaOH solution in this work. Furthermore, only significant char enhancement occurred at temperatures of reaction of 120°C and above. These samples only were subjected to phosphorus analysis (see Table 1). It is worth noting that during the various experimental series listed, some duplication of SPDPC: cotton mass ratio and time combinations occurred, notably the mass ratio 2:1 at 160°C for 2 h. Phosphorus analyses yielded 1.01 and 0.98% P values showing acceptable reproducibility for the repeated experiment and phosphorus analysis.

The phosphorus content can be used to determine the extent of reaction, if the maximum expected value of phosphorus content is calculated with respect to a defined

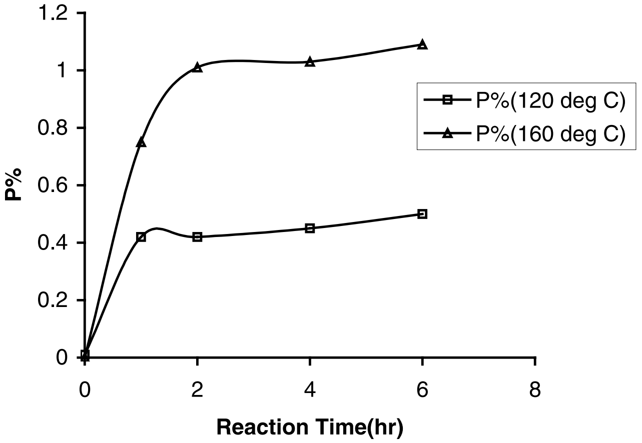


Fig. 1. Percentage phosphorus versus reaction time for cotton reacted with SPDPC at 1:2 mass ratio at 120 and 160°C.

or assumed phosphorylation mechanism. If it is assumed that only the hydrogen atom on the C(6) primary hydroxyl in the glucosan ring may be substituted by 1/2 SPDPC molecule, i.e. by one moiety of >P(O)Cl, then one single SPDPC molecule will phosphorylate two glucosan repeat units (either inter- or intra-molecularly). Furthermore, since at normal laboratory conditions (20°C, 65% RH), 100 g cotton contains about 6 g H_2O (as moisture regain) and 94 g cellulose, then after reaction and assuming an unchanged regain, the total mass of reacted, conditioned cotton should be $(6 + (94 \times 274/162) =)165.0$ g (where the molecular weights of the glucosan and 1/2 SPDPC substituted moieties are 162 and 274, respectively. Thus, the mass of phosphorus present is $(94 \times 31/162 =)18.0$ g, which gives a maximum phosphorus level, P% $(18.0 \times 100/165 =)$ of 10.9% for substitution at the C(6) position. Values in Table 1 may be compared with this value.

3.1.1. Effect of reaction time

Table 1 and Figs. 1 and 2 show that at a constant SPDPC/cotton mass ratio of 2:1, the phosphorus contents of phosphorylated cotton samples rise rapidly with the time of reaction during the first hour at both 120 and 160°C, after which the phosphorus content rises more slowly. The cotton sample phosphorylated at 120°C for 1 h, contains 0.42% phosphorus, while for the sample phosphorylated for 6 h the level has risen only slightly to 0.50% P, suggesting a yield with respect to primary C(6) hydroxide groups of 4.6%. The sensitivity of the SPDPC to moisture and hence hydrolysis during the phosphorylation may be responsible for the levelling off of the degree of substitution at longer times. However, a similar trend occurs at 160°C to give a higher maximum degree of substitution with P = 1.09% and a yield of 10%.

3.1.2. Effect of SPDPC/cotton mass ratio

Since the molecular weights of the glucosan repeat (162) and 1/2SPDPC (148.5) are similar, cotton or cellulose/SPDPC mass ratios will be almost the same as glucosan:1/2SPDPC mole ratios. Thus mass ratios used below and in Table 1 may be considered to be approximate molar ratios. Fig. 2 shows the results of the effect of SPDPC/cotton mass ratio on phosphorus substitution at 160°C for 2 and 4 h. Substitution steadily increases with the increase in SPDPC/cotton mass ratio achieving a maximum phosphorus content of 2.47% and a yield of 22.7% after 4 h.

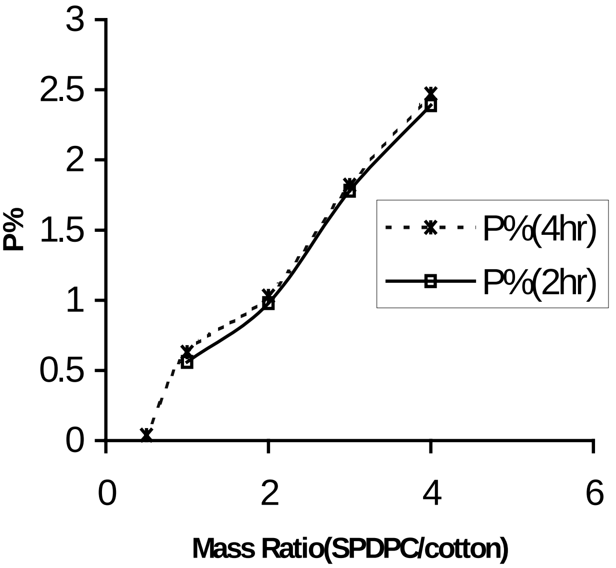


Fig. 2. Percentage phosphorus versus SPDPC/cotton mass ratio at 160°C for 2 and 4 h reaction time.

Therefore, the mass and hence molar ratio of SPDPC/cotton is more sensitive in affecting the substitution than the reaction time.

3.2. TGA results

In order to be able to determine whether any real increases in char formation have occurred additively or synergistically as a consequence of SPDPC-substitution on cellulose, it is necessary to calculate additive TGA responses and compare them with actual experimental responses. Fig. 3 shows individual TGA responses for the cotton used and SPDPC.

3.2.1. SPDPC decomposition

The synthesized SPDPC has a relatively high decomposition temperature at 290°C (see Fig. 3) before producing an intumescent char which, as Fig. 4 shows, is fully formed by 400°C and resists oxidation at temperatures of 600°C and above. The onset temperature and general appearance of the TGA response compares well with that reported by Camino et al. for pentaerythritol diphosphate (PEDP) [18]. These workers, using evolved gas analysis, ascribed the mass loss between 280 and 350°C to be associated with loss of water Subsequent work [19] proposed that this water loss was a consequence of polycondensation of PEDP molecules between the acidic –OH end-groups followed by release of phosphoric acid and acid-catalysed intumescent char formation quite similar to that shown from SPDPC in Fig. 4. While this general degradative mechanism proposed for PEDP may also describe that for SPDPC given their similar TGA responses (compare Fig. 1 in Ref. [18] with Fig. 3 here), the initial stages may differ because of the phosphonyl chloride groups present. If it may be assumed that any initial moisture loss from regain present, for instance, may hydrolyse these >CO·Cl moeities to form the spiro acid PEDP in reaction (5) below by the PEDP formed may then self condense with itself or other SPDPC molecules as in reaction scheme (6) below. These products will catalyze char formation of the C(5) carbon moeity followed by oxidation above 400°C. On heating, therefore, it is proposed that the following reactions occur with SPDPC:

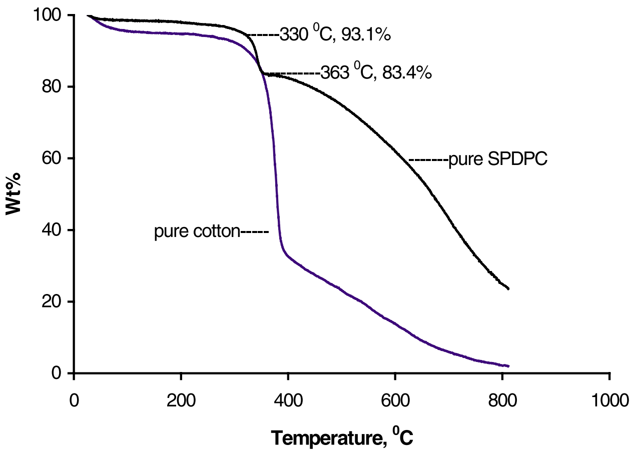
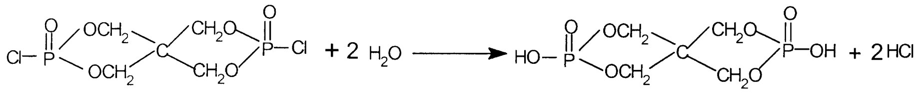


Fig. 3. TGA curves of SPDPC and pure cotton in air.

Hydrolysis

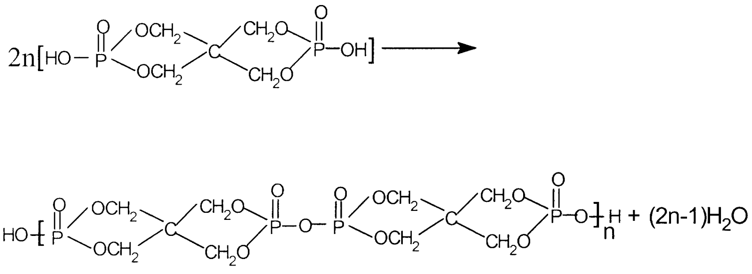


(5)

SDPDC **PEDP**

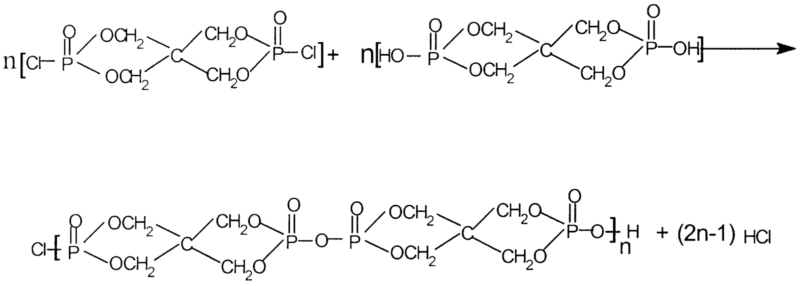
Condensation

(a) Dehydration



(6)

(b) Release of HCl



(7)

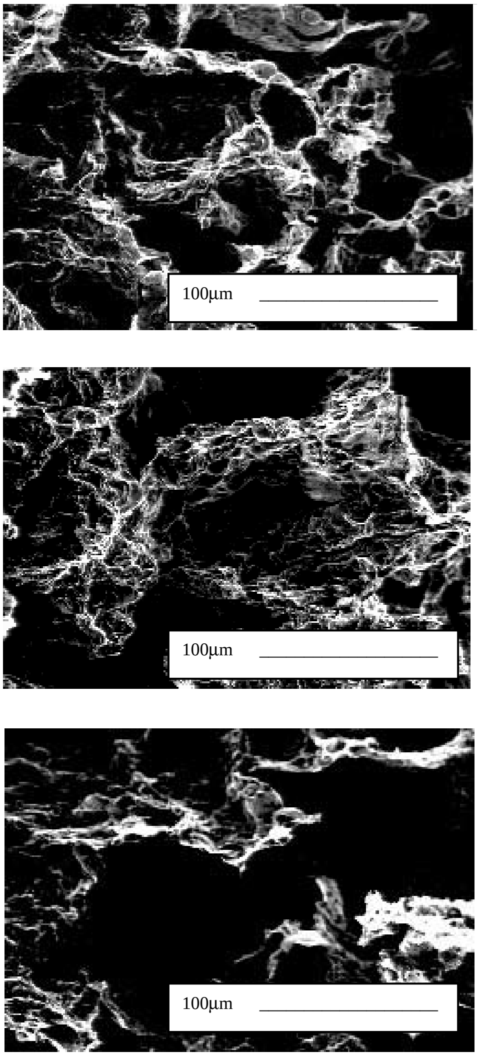


Fig. 4. Scanning electron micrographs of intumescent char residues of SPDPC heated at various temperatures (uncoated samples, 10 kV) (upper: 400°C, middle: 500°C, lower: 600°C).

Once the polycondensed chains are formed then above 363°C (see Fig. 3), subsequent release of phosphoric acid and intumescent char formation will occur by the previously published mechanism [19]. Based on the assumed reaction schemes above, we may calculate the relative contributions of the hydrolysis and condensation reactions from the TG response in Fig. 3. In reaction (5), the two chlorine atoms are initially replaced with hydroxyl groups by hydrolysis to form a spiro diacid, and the mass loss is $(100(71 - 17 \times 2)/297 =)12.5\%$. For the spiro acid condensation reactions (6) and (7), the mass loss is $(100(71 - 16)/297 =)$ 18.5% with respect to the original mass of SPDPC.

Fig. 3 shows that at 330°C, the mass loss from SPDPC is 7%, and it is possible that the main reaction occurring here is the formation of spiro acid. At 363°C, the total mass loss is 16.6%, with condensation reactions probably becoming significant between 330 and 363°C accompanied by the release of hydrogen chloride gas and the production of water. The ratio of the two reactions (5) and (6 and 7) at 363°C can be calculated. If it is supposed that all the SPDPC has reacted via reactions (5)–(7) at 363°C, then if the fraction of condensation is y, the fraction of hydrolysis is (1-y), and the following equation holds:

$$18.5y/100 + 12.5(1 - y)/100 = 16.6\%$$

to give $y = 0.683$. This means the condensation reactions have occurred between 330 and 363°C and a significant fraction of SPDPC has condensed by 363°C. Based on the PEDP mechanism of Camino et al. [18,19], the mass loss occurring above 363°C may be associated with full char formation and subsequent oxidation if air is present.

3.2.2. Calculation of theoretical TGA curves

In order that the experimental curves may be referred to a standard response from which the difference in char-forming character of each cellulose-SPDPC reaction condition might be assessed, it is necessary to calculate the expected response for cellulose-SPDPC reacted samples assuming that they are respectively the weighted averages of individual TGA responses in Fig. 3. The theoretical TGA mass response at any temperature T (°C) of reacted cotton can be calculated from the phosphorus level based on C(6)OH substitution only. For example, the phosphorus concentration of reacted cotton sample at 120°C for 2 h is 0.42%, and so 100 g cotton after reaction contains $(0.42 \times 113/31 =)1.53$ g substituted SPDPC, 6 g H_2O and $(100 - 1.53 - 6 =)92.47$ g partly substituted cellulose. Thus, in order to obtain 100 g reacted cotton sample, $(0.42/(31 \times 2/297) =)2.00$ g SPDPC and $>(92.47(0.42/10.9)(162/161)) + (10.9 - 0.42)/10.9)(100/94) =)98.37$ g cotton are needed. These represent the weighting factors to calculate the expected reacted cotton TGA responses based on individual responses in Fig. 3. Therefore, the theoretical TGA mass response at any temperature T (°C) of reacted cotton can be calculated as follows:

$$\begin{aligned}
&(\text{TGA mass of reacted cotton})_T \\
&\quad = (\text{TGA mass of cotton})_T(98.37/(98.37 + 2.00)) \\
&\qquad + (\text{TGA mass of SPDPC})_T(2.00/(98.37 + 2.00)) \\
&\quad = 0.98(\text{TGA mass of cotton})_T \\
&\qquad + 0.02(\text{TGA mass of SPDPC})_T
\end{aligned}$$

Generally, therefore, for any level of phosphorus concentration, $p\%$, in order to obtain 100 g reacted cotton sample, $p/(31 \times 2/297) = 100p/20.9 = 4.80p$ g SPDPC are required along with $(94 - 3.65p)(p/10.9)(162/161) + ((10.9 - p)/10.9)(100/94) = (100 - 3.88p)$ g cotton, so the TGA mass response at any temperature T (°C) can be calculated

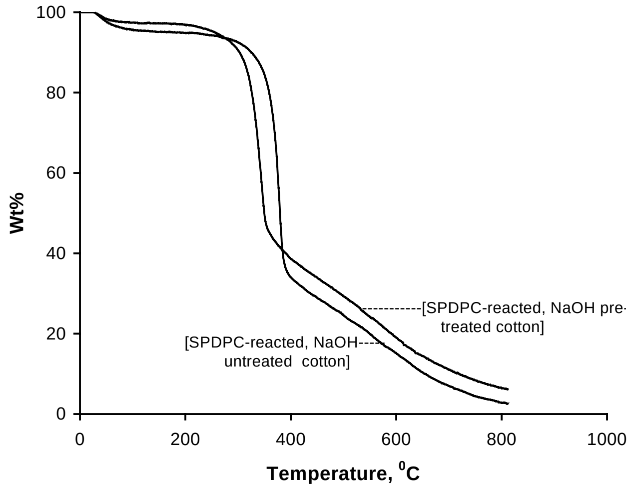


Fig. 5. TGA responses showing the effect of 10%NaOH solution pre-treatment of cotton prior to reaction with SPDPC (120°C, 2 h).

according to the following formula:

$$(\text{TGA mass of reacted cotton})_T = (\text{TGA mass of cotton})_T\,(100 - 3.88p)/(100 + 0.92p) + (\text{TGA mass of SPDPC})_T\,4.80p/(100 + 0.92p) \qquad (8)$$

3.2.3. Enhanced chars of reacted samples

Fig. 5 shows the effect of 10%NaOH pre-treatment on the reactivity of SPDPC with cellulose in terms of the enhanced char produced above 400°C. This corresponds to a phosphorus level of 0.42% (see Table 1). However, preliminary experiments showed that small levels of phosphorylation occurred at reaction temperatures as low as 90°C and Fig. 6 shows the TGA curves of a NaOH-pre-treated cotton sample reacted with SPDPC in a solution of NaOH, pyridine and DMF (NaOH/pyridine/DMF = 50 mg:1 ml:5 ml) at 90°C for 6 and 10 h. Included in this figure is the TGA response for unreacted cotton. Again and as seen in Fig. 5, although the mass loss begins earlier than both the control cotton and calculated curve, more char residue than expected does occur between 400 and 600°C. The shifts to lower temperatures for onset of mass loss and the accompanying higher residual char levels above 400°C confirm that the SPDPC-phosphorylated cellulose is behaving like other phosphorus-substituted cellulose derivatives which often lead to enhanced flame retardancy [14]. For the longer reaction time (10 h) consistently more char is evident above 400°C, which is the consequence of increased reaction between the SPDPC and the hydroxyl groups in cotton.

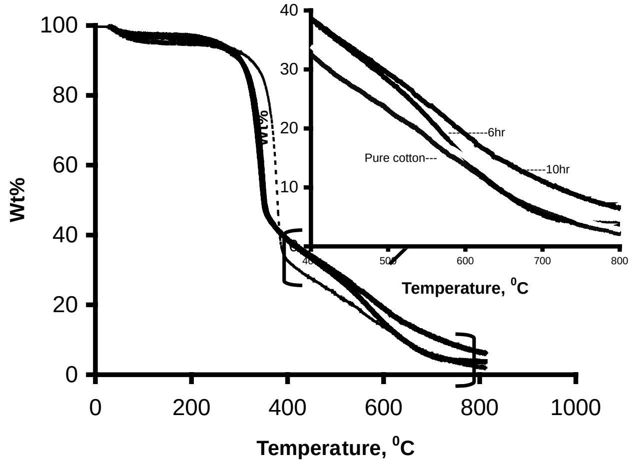


Fig. 6. TGA response of cotton reacted with SPDPC in pyridine and NaOH (mass ratio of cotton/SPDPC/pyridine/NaOH = 200 mg/200 mg/1 ml/50 mg, 90°C, 6 and 10 h).

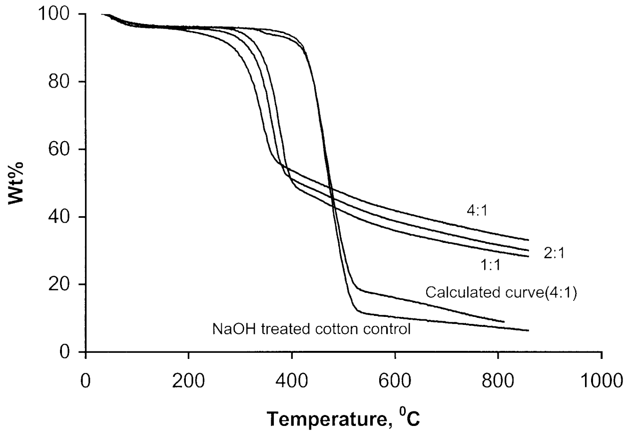


Fig. 7. TGA curves for different SPDPC/cellulose mass ratios (reaction at 160°C for 2 h).

The highest degrees of substitution indicated by phosphorus levels in Table 1 occur at reaction temperatures of about 160°C for times in excess of 1 h for SPDPC/cellulose mass ratios in excess of 1:1 (see Figs. 1 and 2). Fig. 7 shows that magnitudes of TGA response shifts below 300°C and residual char levels above 400°C appear to be proportional to the degree of phosphorylation. Included in this figure are the cotton control and calculated cotton plus SPDPC responses with the latter corresponding to the 4:1 mass ratio phosphorus level of 2.39% (see Table 1). Thus, it

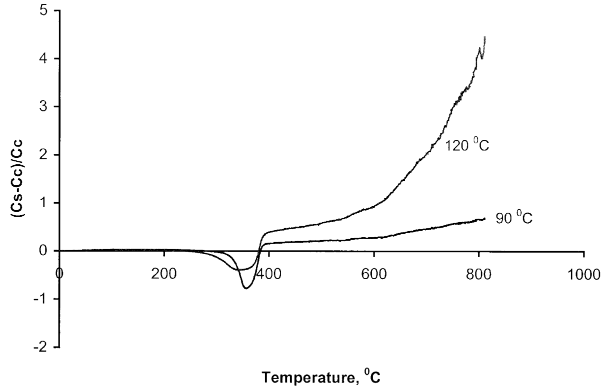


Fig. 8. Plot of $(C_s - C_c)/C_c$ versus temperature for cotton reacted with SPDPC at 120 and 90°C.

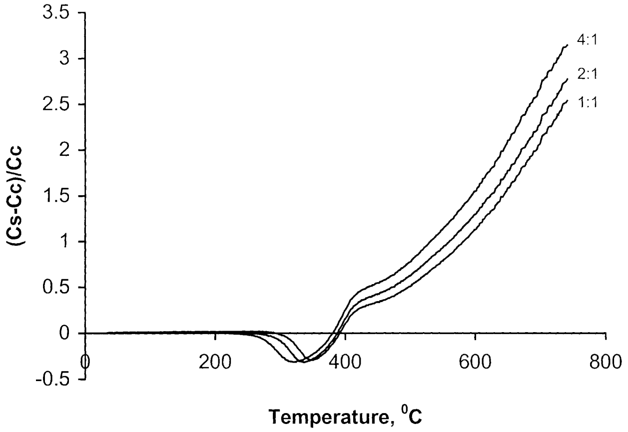


Fig. 9. Plot of $(C_s - C_c)/C_c$ versus temperature for cotton reacted with SPDPC at 160°C for 2 h at different mass ratios.

is seen that char formation from SPDPC-phosphorylated cellulose is significantly higher above 500°C than expected from the calculated, equivalent mixture using Eq. (8). Furthermore, the significant rise in char levels above 400°C for the SPDPC-substituted samples with increasing SPDPC/cellulose mass ratio suggest a more quantitative relationship with the degree of substitution as indicated by phosphorus content.

An alternative way of showing these char enhancements is to plot the function $(C_s - C_c)/C_c$ versus temperature in Fig. 8 for reactions at 90 and 120°C conditions where C_s is the char residue from SPDPC-substituted cotton and C_c the value for pure cotton at any temperature from respective TGA responses. Fig. 9 presents the similar plots for substituted cotton produced at 160°C for a 2 h reaction time. These figures again demonstrate that residual chars above 400°C or so increase with reaction temperature and mass ratio at a given reaction time. These trends may be related to respective phosphorus levels in Table 1 by plotting $(C_s - C_c)/C_c$ values at specific temperatures 500, 600, 700 and 740°C against respective phosphorus levels irrespective of the particular SPDPC-cellulose reaction conditions. Fig. 10 shows these results which indicate that enhanced char levels with respect to pure cotton values are solely determined by respective phosphorus levels and hence degree of phosphorylation. For each curve, the respective cotton char residue or C_c% is included and values reduce from 23.8 to 4.3% between 500 and 740°C.

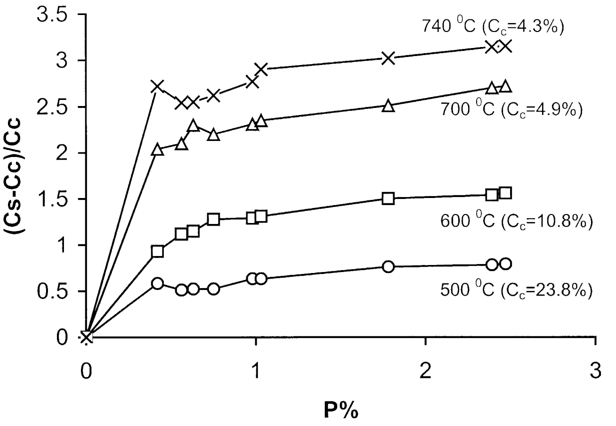


Fig. 10. Plot of $(C_s - C_c)/C_c$ versus P% at different temperatures for selected SPDPC-reacted cotton samples (see Table 1).

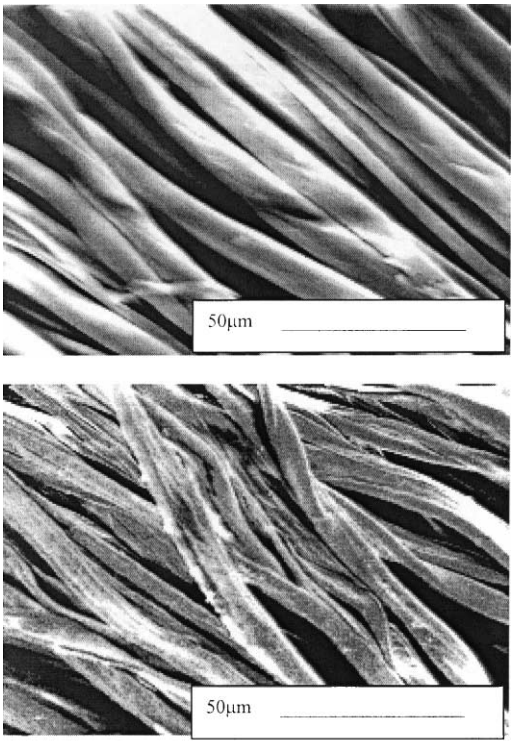


Fig. 11. Scanning electron micrographs of chars of SPDPC-reacted cotton samples after heating in air at 420°C for 10 minutes, 714x, 10kv (upper: 4:1 SPDPC: cotton mass ratio, lower: /: SPDPC: cotton mass ratio).

Furthermore, the reaction conditions do not significantly influence the resulting char-forming abilities. These trends show that at all temperatures residual chars become significant only when phosphorus levels are 0.5% or greater and char enhancements between 0.5 and 2.5% phosphorus levels are approximately linear and almost parallel at each temperature. Because of this last effect, it might be considered that char increases are solely related to the increasing phosphorus concentrations which will probably be present as P_2O_5 at the higher temperatures. That the additional phosphorus in the carbonaceous char is a minor component may be calculated for the 4:1 SPDPC/cotton mass ratio, 4 h-reacted sample which has a phosphorus content of 2.47% (see Table 1). If all the phosphorus remains in the char, then this corresponds to a P_2O_5 content of 5.66% assuming its presence solely as the oxide above 500°C. Fig. 10 shows that the enhanced char $(C_s - C_c)$ for this sample is 18.80% at 500°C and 13.35% at 740°C with respect to the undegraded phosphorylated samples. Both values are well in excess of the maximum possible P_2O_5 content, which in any case may reduce because of its tendency to sublime at these high temperatures. Consequently, the residue enhancements in

Figs. 8–10 are due in the main to increased carbonaceous char formation.

3.3. Scanning electron microscopy results

Micrographs of char structures of SPDPC-reacted cotton fibres produced by heating them in air to 420 and 600°C for 10 min are shown in Figs. 11 and 12, respectively. It may be generally inferred that the presence of substituted SPDPC produces a well-defined char commensurate with those observed in other flame retarded cottons [20]; chars from pure cotton produced under these same conditions are less defined and extremely difficult to handle for preparation for SEM examination. More careful examination shows that in both figures, the chars from 4:1 SPDPC/cotton mass ratio, 2 h-reacted samples are more defined than respective 1:1 mass ratio samples and this reflects their relative phosphorus contents of 0.56 and 2.39% (see Table 1) and measured char enhancements in Fig. 10. Furthermore, the chars obtained at 600°C in Fig. 12 are not well-defined because at this temperature, significant char oxidation is occurring primarily at surfaces.

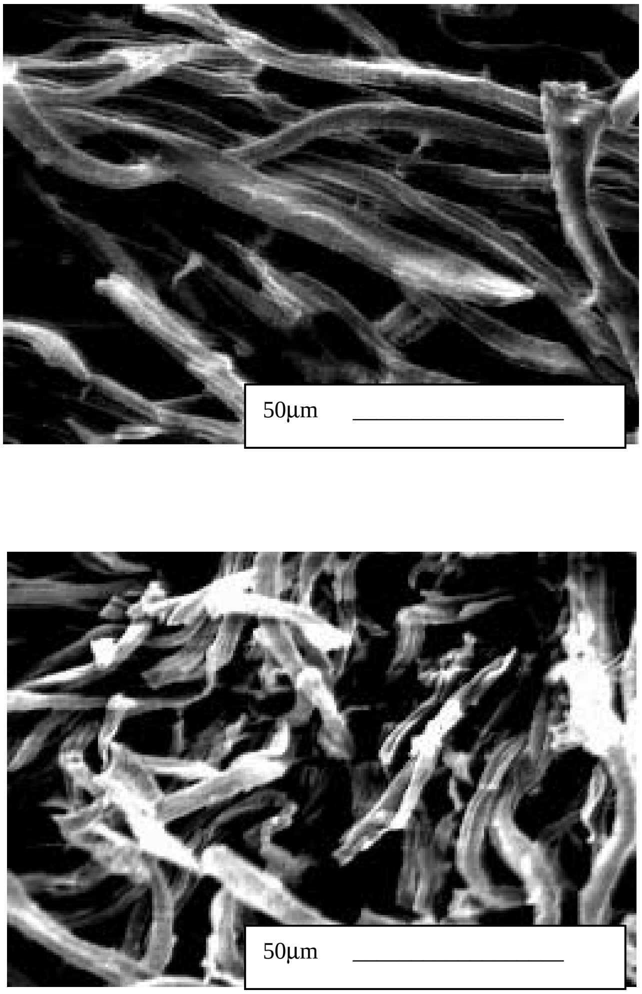


Fig. 12. Scanning electron micrographs of chars of SPDPC-reacted cotton samples after heating in air at 600°C for 10 minutes, 699x, 10kv (upper: 4:1 SPDPC: cotton mass ratio, lower: 1: SPDPC: cotton mass ratio).

4. Conclusions

It is evident that the introduction of phosphorus via a polyol phosphonyl chloride can significantly enhance char promotion in cellulose. Some of this enhanced char will be a consequence of the carbon content from the pentaerythritol component within the SPDPC which is well known to be a source of carbon in flame retardant and intumescent formulations [8]. While SPDPC and its well-characterised derivative PEDP [18,19] show intumescent char formation when heated above 350°C or so by themselves, there is little evidence in the work reported here that the SPDPC-substituted cellulosic chars are similarly intumescent. However, this is not to say that if the char forming reaction occurs via an appropriate liquefied state in the presence of a gas-forming species that intumescent will not occur [4,8]. In our next paper, we shall explore this possibility by substituting SPDPC into an already flame retarded cellulose in an attempt to produce a substantive intumescent fibrous material.

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