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Complex char formation in flame retarded fibre–intumescent combinations: 1. Scanning electron microscopic studies

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A recently disclosed development[1–3] comprising a composite of flame retardant cellulose fibres and an intumescent has shown unusually high flame and heat resistance with a char structure that can withstand air exposure temperatures up to 1200°C. Char structures of selected flame retardant cellulose fibres when alone and blended with inert E-glass and aromatic char-forming novoloid fibres in the presence of an ammonium polyphosphate-based intumescent have been studied using scanning electron microscopy. Evidence suggests that a 'char-bonded' structure is formed in which flame retardant cellulose fibrous chars have interacted with intumescent char during its formation. Similar interactions are not seen with E-glass and novoloid fibre residues. The char-bonded structure is considered to have reduced air permeability and so has considerably enhanced surface oxidative resistance at high temperatures. An outline mechanism is proposed and is based on known pyrolysis mechanisms for the flame retarded cellulose fibre and intumescent components. Copyright © 1996 Elsevier Science Ltd.

(Keywords: flame retardant; intumescent; char)

INTRODUCTION

When organic polymers are heated, their degradation occurs often by competing volatilization and cross-linking reactions, as well as those leading to polymer chain unsaturation. These last two can lead to formation of a so-called carbonaceous char which, depending on the temperature and degrees of cross-linking and unsaturation, will lead to increased aromatization. Van Krevelen[1,2] studied char formation in a number of polymers and showed that the inherent flammability of any polymer reduces as its char-forming tendency increases. This latter is greater for aromatic and heterocyclic ring-containing polymers than aliphatic structures. When polymeric chars are heated above 400°C or so in air, they rapidly oxidize and this is particularly the case of fibre assemblies which have high specific areas and hence oxygen accessibilities.

Therefore textiles comprising flame retardant fibres with enhanced char-forming tendencies (for example by use of flame retardant treatments[3]) or aromatic fibres[2] will not survive elevated temperatures above 500°C in air for periods in excess of 5 min or so. Textiles requiring higher levels of flame and heat resistance usually comprise inorganic fibres which can survive temperatures in excess of 1000°C for considerable periods[4].

It has been demonstrated recently[4,5] that a unique assembly of fibres comprising organic and inorganic components, of which the former is flame retarded, and an intumescent yields composite structures that maintain coherence and thermal barrier properties when exposed in air to temperatures as high as 1200°C for up to 10 min.

These novel and patented[6] structures show superior properties when compared to conventional wholly organic fibre-containing fabrics and fill a performance gap between these and fabrics comprising wholly inorganic and usually ceramic fibres.

A major feature of their high temperature performance is the apparent resistance of the generated char structure to oxidative attack above 500°C. For example, a nonwoven fabric comprising so-called hybrid viscose fibres (e.g. Visil AP, Kemira, Finland), which contain approximately 30% w/w silica as polysilicic acid, and a dispersed intumescent (MPC 1000, Albright and Wilson Ltd, UK), comprising a mixture of ammonium polyphosphate, melamine and pentaerythritol in a 3 : 1 : 1 mass ratio, shows the presence of considerable char content within the fibrous silica residue even after exposure in air to temperatures within the range 1000–2000°C[5,6] for periods up to 10 min.

This paper presents scanning electron microscopic evidence which attempts to explain the observed char-oxidative resistance and discusses the nature of possible interactions between the flame retarded, fibre-forming polymer cellulose and the adjacent intumescent. This interaction has been termed a 'char-bonding' effect in our patent[6] and later report[7]. Subsequent papers will present complementary thermal analytical and related char structural evidence.

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CHAR FORMATION IN FIBRE-FORMING POLYMERS AND FIBRE-INTUMESCENT CHAR INTERACTIONS

It is well-known that many flame retardants for textiles function via condensed phase conversion to carbonaceous char of the organic substrate fibre; in the case of cellulosic fibres this reaction is considered to be one of acid-catalysed dehydration[8]. Preferential formation of char not only reduces the production of flammable volatiles but also maintains a coherent flame and heat barrier between igniting sources and underlying materials. Char-promoting flame retardants for cellulose typically contain phosphorus, either as acidic salts (e.g. ammonium phosphate derivatives) or as organophosphorus (e.g. phosphonium salt and phosphonate derivatives) species, which decompose when heated above 150°C or so to a variety of products including polyphosphoric acid[9]. The formation of such liquid intermediates which catalyse subsequent char formation is supported by electron microscopic evidence[10] which shows fibrous char topographies typical of a previously fluid condition, e.g. presence of craters and

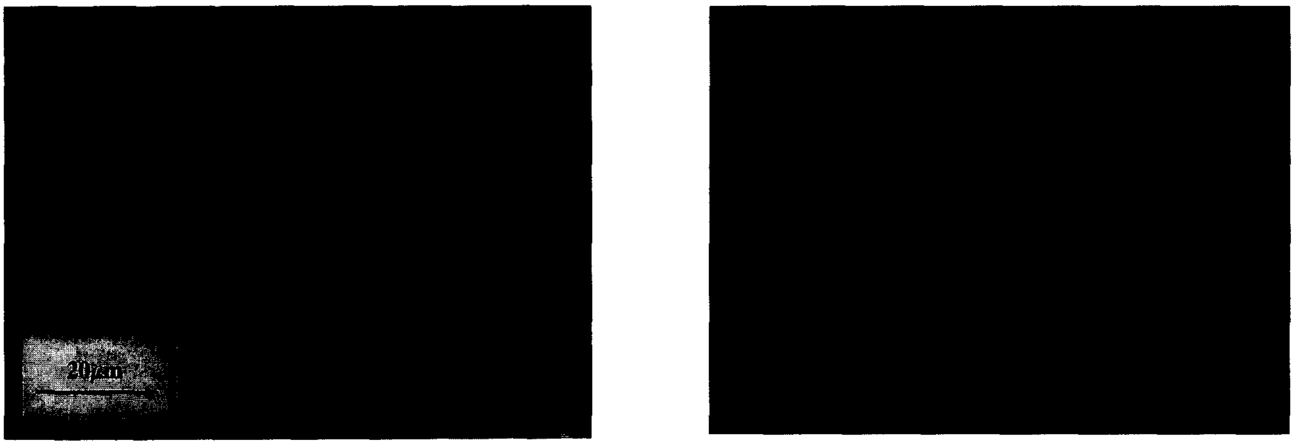
Table 1 Fibres, blends and intumescent selected for study

Fibre components and dimensions
Hybrid viscose (Visil AP, Kemira), 3.5 dtex 40 mm stable length
Hybrid viscose/novoloid (Kynol™, Kynol Europa, 3.3 dtex 50 mm staple length)
Hybrid viscose/E-glass (8 μm diameter)
FR viscose (Lenzing, 3.5 dtex, 51 mm staple length)/hybrid viscose)
FR viscose/novoloid
FR viscoe/E-glass
Intumescent (MPC 1000, Albright and Wilson, Ltd, UK) comprising ammonium polyphosphate, pentaerythritol and melamine in a 3 : 1 : 1 mass ratio present at 50% w/w with respect to the fibre content

Table 2 Fibre blend-intumescent thermal exposure conditions in air

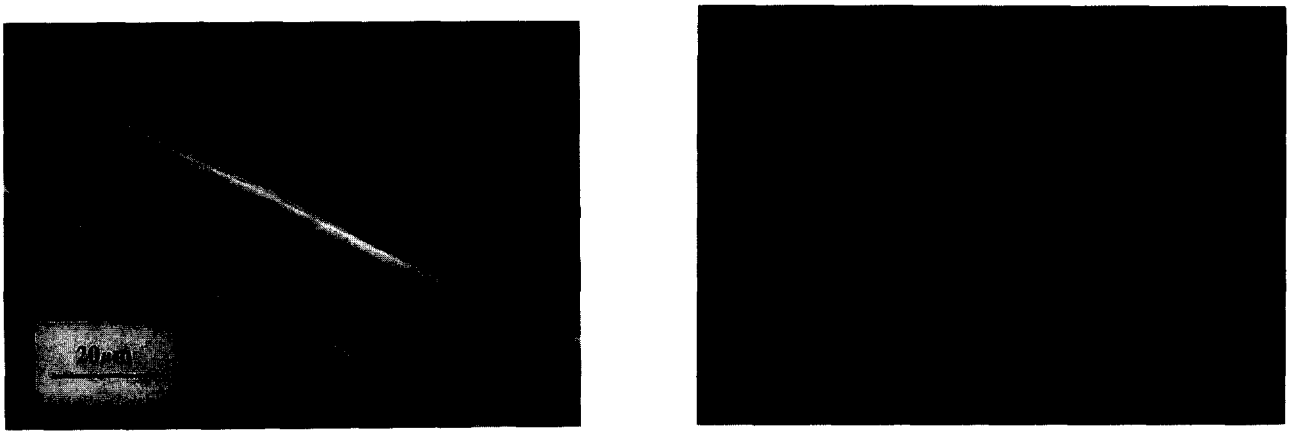
		Exposed fibre and blend conditions:				
Temp. (°C)	Time (min)	Individual fibres	hybrid/ E-glass	hybrid/ novoloid	FR viscose/ E-glass	FR viscose/ novoloid
300	2			x	x	
	5			x	x	
	10			x	x	
400	2		x			x
	5		x			x
	10	x	x			x
500	2		x	x	x	x
	5		x	x	x	x
	10		x	x	x	x

Note: x refers to conditions of exposure chosen for specified samples



(a) before

(a) after



(b) before

(b) after

Figure 1 SEMs of individual fibres exposed at 400°C for 10 min. (a) Hybrid viscose (Visil): before and after exposure at 1200×. (b) FR viscose (Lenzing FR viscose): before and after exposure at 1100×. (c) E-glass: before and after exposure at 1140×. (d) Novoloid (Kynol™, Kynol Europa): before and after exposure at 1100×

nodules formed by concurrent gas evolution and liquid flow. Polysilicic acid, a similar char-catalysing species, has been reported to be released from viscose fibres containing sodium polysilicate when heated above 300°C[11].

Char-promoting intumescent systems function in a similar manner to the above mechanism[12–14]. For example, a typical char promoter like ammonium polyphosphate will generate liquid polyphosphoric acid which will catalyse char formation in any polyol such as pentaerythritol. Simultaneous gasification of so-called spumific material[12] such as melamine (by sublimation and ammonia formation) will cause inflation of the semi-liquid, polyacid-charring polyol suspension.

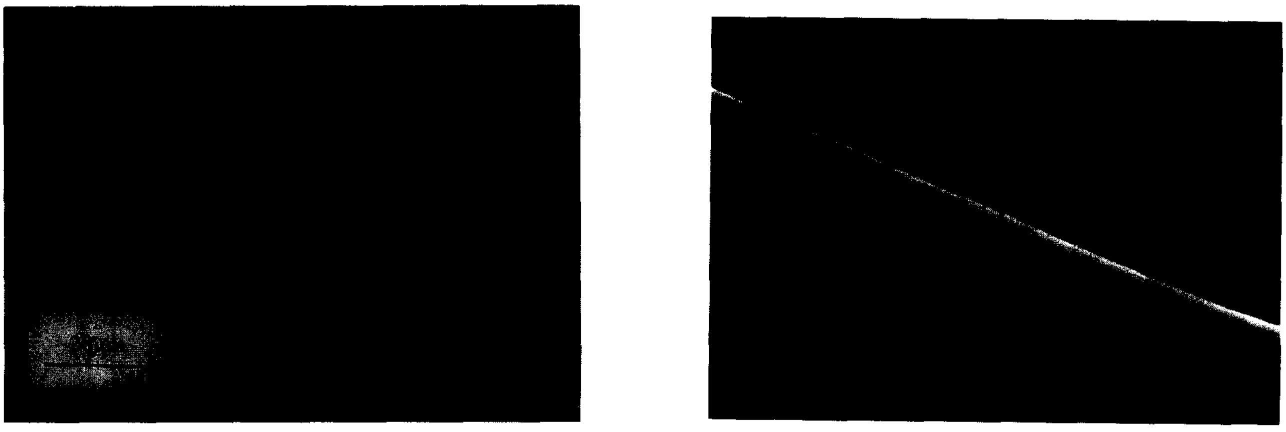
It is likely, therefore, that simultaneous char formation of a flame retardant organic polymer and intumescent via respective liquid stages will lead to physical mixing, chemical interaction and formation of an 'alloyed' or char-bonded structure. If the polymer is fibre-forming and orientated then the structure will comprise an orientated fibrous char embedded within and bonded to an expanded intumescent char; i.e. a fibrous-char-reinforced char will result. Therefore it is probable that any flame retardant, char-forming polymer will interact and hence bond with any intumescent char whose char-forming physics and chemistries are compatible[6,7]. Surprisingly, interactions of this type have not been reported previously and offer the opportunity of modifying charred polymeric structures with improved flame and heat resisting properties.

While the morphology of polymeric chars is not well understood[15], their flame and heat barrier properties arise because of their low permeability to oxygen and hence resistance to oxidation at temperatures above 450°C. However, chars are brittle and if they fall away, reveal underlying material. This is especially the case of textile chars which, because of their fibrous structure, are also highly oxygen-permeable and so offer only limited heat protection. However, if an integrated fibrous-intumescent char structure can be developed then the properties of such a char-bonded structure will be those of increased mechanical stability, reduced oxygen permeability and hence reduced oxygen sensitivity—all these properties have been observed and previously reported[4–6]. These may be further enhanced if an inorganic fibrous component is present which will act as a high temperature-stable support.

EXPERIMENTAL AND RESULTS

A number of fibre–intumescent combinations have been studied to date and are listed in *Table 1*. Each comprises a 50 : 50 blend of two fibre generic types in a nonwoven fibrous array in which the intumescent comprising ammonium polyphosphate, pentaerythritol and melamine in a 3 : 1 : 1 mass ratio (MPC 1000, Albright and Wilson Ltd) is dispersed according to methods previously described[4–6]. The choice of fibres has reflected the need

(c) before (c) after



(d) before (d) after

Figure 1 Continued

to study examples of acid-catalysed, char-forming cellulosic fibres (e.g. flame retarded viscose), a non-acid-catalysed char-former (e.g. novoloid) and their combinations with an otherwise inert inorganic fibre (e.g. E-glass). The flame retardant component of Lenzing flame retardant or FR viscose is Sandoflam 5060 (Sandoz) present at about 10–15% w/w and which is 2,2-oxybis (5,5-dimethyl-1,2,3-dioxaphosphorinane-2,2-disulfide). The Visil (Kemira) flame retardant viscose fibre comprises 30% inorganic content as polysilicic acid, the novoloid fibre is polycondensed phenol and formaldehyde which on heating further cross-links, loses volatiles and generates an aromatized char[16].

Previous studies[4,5] have already shown that full carbonaceous char development has occurred after exposing the composites at 500°C in air for up to 10 min in a refractory furnace. However, polyphosphate intumescent systems start to chemically function at temperatures above 200°C or so[9] and so each of the intumescent–fibre blends in *Table 1* was exposed to temperatures in the range of 300–500°C for times between 2 and 10 min in air as indicated in *Table 2*. From this matrix it is evident that each fibre component experiences each temperature and time condition whilst attempting to minimize the number of total exposures required for the chosen blend and exposure conditions.

Exposed charred samples were investigated by scanning electron microscopy using an ISI 25 instrument with a 25 kV beam without the need for gold sputter coating. Under these conditions, specimens were sufficiently conductive to enable clear, defined images of fibrous and intumescent char formation at the surface of fabric samples to be obtained.

Scanning electron microscopic studies

Individual fibre components. Figures 1a–d respectively show the electron micrographs at similar magnification of Visil viscose, FR viscose, E-glass and novoloid fibres before and after exposure at 400°C in air for 10 min. The two charred cellulosic fibres appear to be narrower but similarly structured replicas of their former striated parents, with the Lenzing FR viscose having undergone considerably more reduction in width as a consequence of its higher cellulose content and hence greater loss in mass during pyrolysis. Both E-glass and novoloid fibres appear rod-like, with the latter having become a carbonized derivative with slightly reduced diameter. These micrographs provide a basis for comparison with those of the charred fibre blend-intumescent mixtures below.

Visil viscose fibre–intumescent. Preliminary SEM studies of this combination have been reported elsewhere[7], where close inspection of the charred fibre–intumescent char structure produced after a 10 min exposure at 500°C shown in *Figure 2a* indicated that an intimate fibre surface–intumescent interaction has occurred. *Figure 2b* shows this in cross-section, where the Visil fibre striated perimeter of the cross-section (see arrows) cannot be distinguished from the encapsulating intumescent char. In addition, that this interaction has occurred through a molten phase is indicated by the surface distortion on the longitudinal micrograph in *Figure 2c* (see arrowed regions). This apparent intermediate fluid presence has been noted by Goynes *et al.*[10] as stated above.

Visil viscose fibre–E-glass fibre–intumescent. The reaction to exposure at 400°C for 5 min in air (see *Figure 3a*) shows the initial stages of intumescent activity following melting and decomposition of the ammonium polyphosphate (150–300°C) and pentaerythritol (m.p. 255–259°C) components[9]. Wetting and encapsulation by these fluid products of both the now indistinct finer E-glass and coarser viscose fibres may be seen. *Figure 3b* shows the more complete wetting of hybrid viscose (foreground) and E-glass (background) fibres with evidence of larger fused nodules of previously molten intumescent

Figure 2 Micrographs of a hybrid viscose fibre–intumescent composite fabric after exposure in air at 500°C for 10 min, (a) 150×, (b) 1630× and (c) 600× magnifications

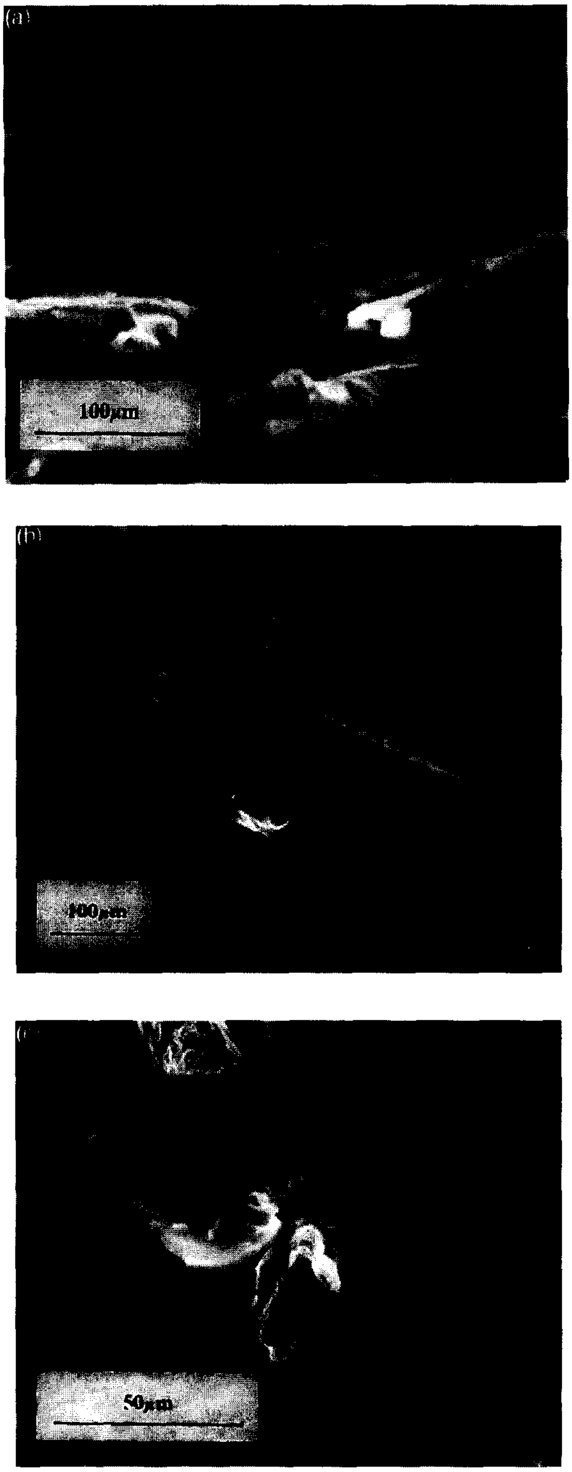


Figure 3 Micrographs of hybrid viscose–E-glass fibre–intumescent mixtures following exposures in air at 400°C for (a) 5 min, 340×; (b) 10 min, 190×; and (c) 10 min, 830× magnification

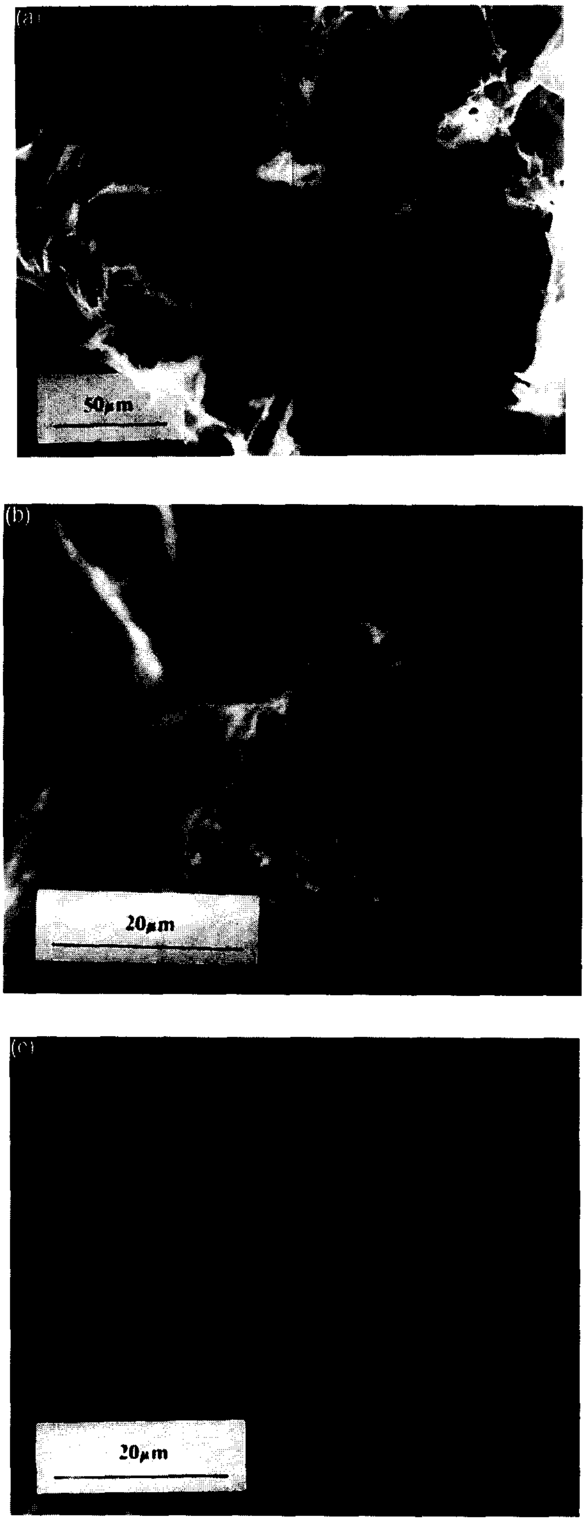


Figure 4 Char formations following heating in air of hybrid viscose–E-glass fibre–intumescent mixtures at 500°C for (a) 10 min, 500×; (b) 5 min, 2090× (note the hybrid, viscose fibre surface); and (c) 2 min; E-glass fibres at only 1900×

(see arrow) after increased (10 min) exposure at 400°C. Raising the temperature to 500°C causes full char formation and the E-glass fibres in *Figures 4a* and *4c* have a distorted, thin char coating where no interaction has occurred between fibre and intumescent other than surface deposition. The cross-section of the Visil fibre in *Figure 4b* is similar to that in *Figure 2b*, where the perimeter of the fibre is also not well-defined, thereby indicating a degree of intumescent–fibre surface interaction. Careful inspection of *Figure 3c* shows that whilst intumescent in contact with glass fibres has been molten after 400°C exposure (see *Figures 3a* and *3b*), that in contact with the Visil fibre surface has charred (see arrowed region). This provides further evidence for the suggested interaction occurring between the flame retardant cellulose and intumescent.

Visil viscose–novoloid–intumescent. *Figure 1d* shows that heated novoloid fibres are circular and of comparable diameter to hybrid viscose charred structures and so are more difficult to distinguish. This is shown in

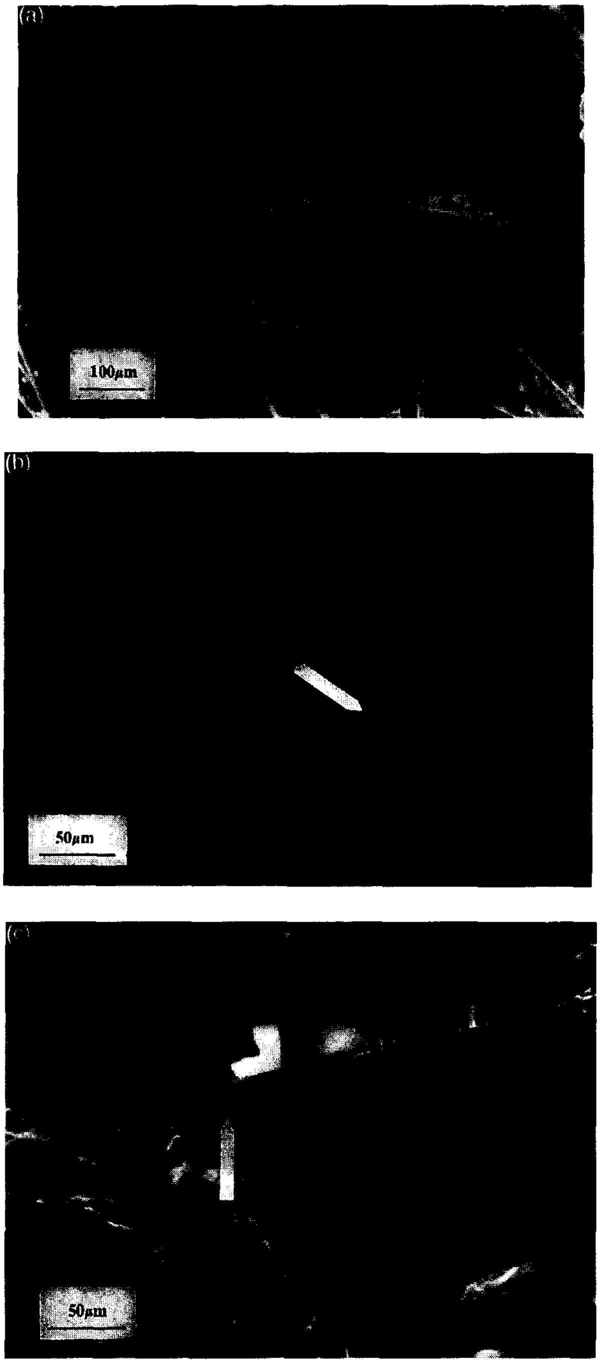


Figure 5 Intumescent structures after heating hybrid viscose–novoloid fibre-intumescent mixtures at (a) 300°C for 5 min 190×; (b) 500°C for 2 min 450×; and (c) 500°C for 5 min, 460× magnification

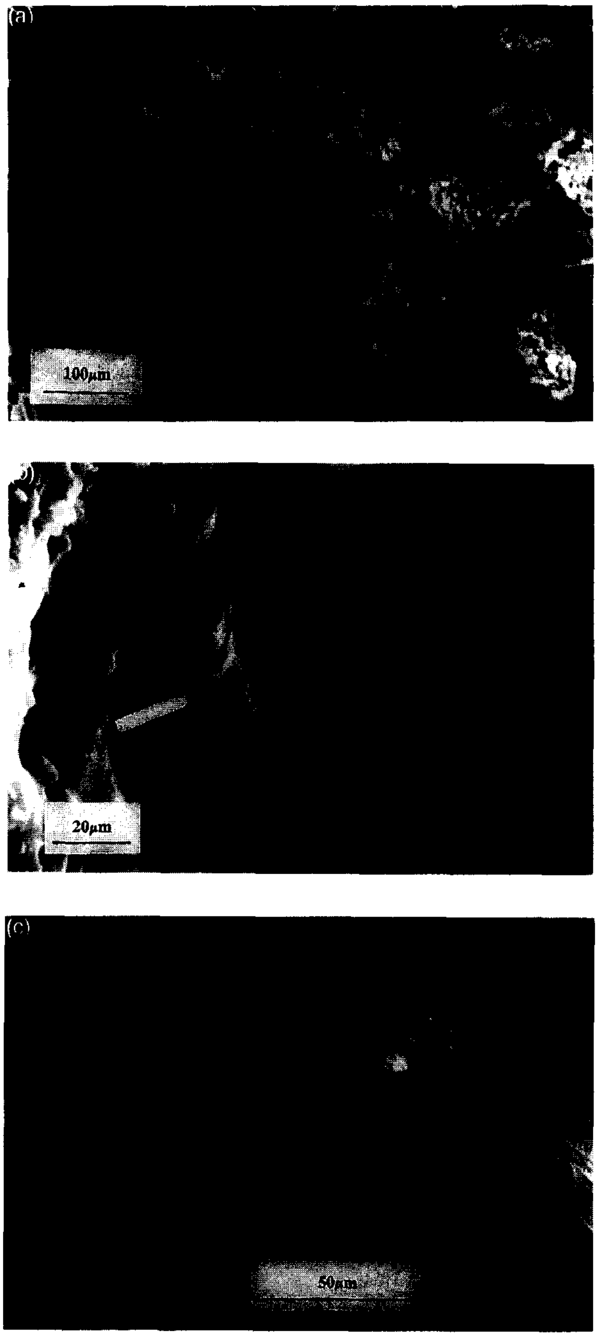


Figure 6 Intumescent melting and wetting of FR viscose and E-glass fibre surfaces after exposure in air at 300°C for (a) 5 min, 250×; (b) 5 min, 1140×; and (c) 10 min, 850× magnification

Figure 5a where both fibre types have been wetted with fused intumescent after heating at 300°C. Once the intumescent char has more fully developed after exposure to 500°C for 2 min, the broader striated viscose fibres (see the diagonal, arrowed fibre in *Figure 5b*) may be distinguished from the more rod-like novoloid fibres. In addition, the former seem to be in contact with more complex intumescent char structures. *Figure 5c* (exposure at 500°C for 5 min) clearly shows that intumescent char formation on the indicated novoloid fibre surfaces is more simple and superficial.

Lenzing FR viscose fibre–E-glass fibre–intumescent. In this composite structure, the striated FR viscose structure is clearly distinguishable from the finer, rod-like E-glass fibres. After 5 min exposure at 300°C, the molten intumescent has surrounded adjacent E-glass (*Figure 6a*) and FR viscose (arrowed in *Figure 6b*) fibres and after 10 min it has wetted the indistinct surfaces of both, as shown in *Figure 6c*.

Exposure to 500°C promotes complete char generation and, as *Figure 7a* shows, an intimate fibrous–char–intumescent–char structure or 'char-bonded' structure has been formed. *Figure 7b* shows the surface intumescent char formation in contact with E-glass fibres which may be distinguished from the more interacted FR-viscose–intumescent chars arrowed in *Figure 7c*, where char structures are more complex and fibre surfaces difficult to discern. There is limited published data regarding the pyrolysis mechanisms occurring in flame retarded cellulose fibres containing the Sandoflam 5060

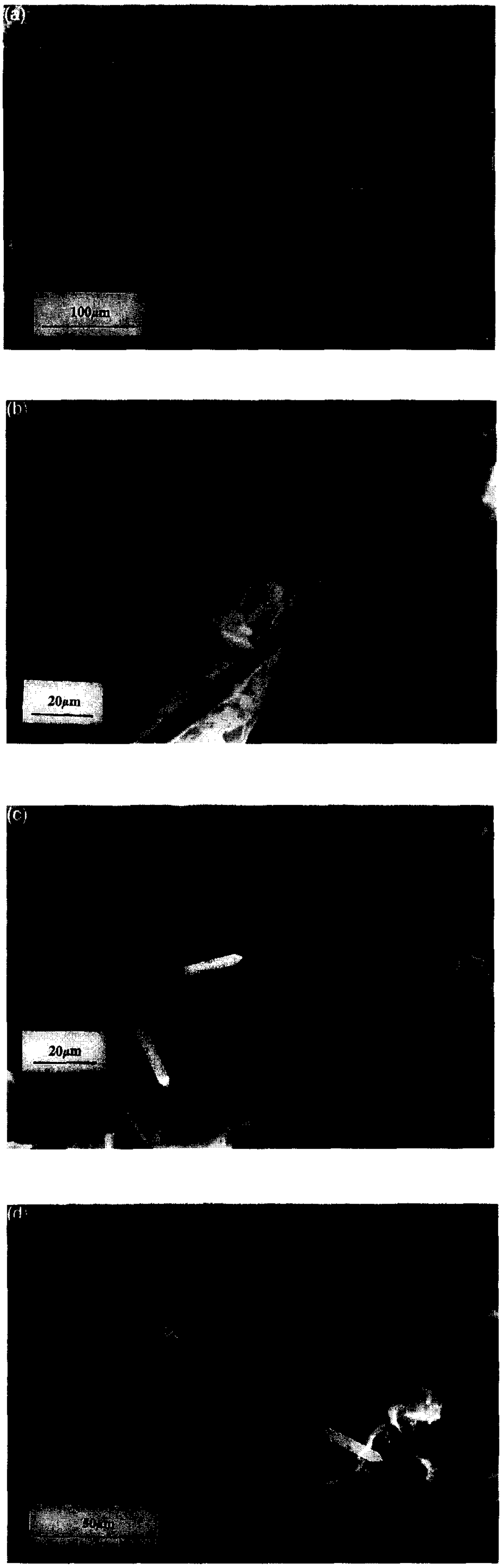


Figure 7 Char structures of FR viscose fibre–E-glass fibre–intumescent compositions after exposure in air at 500°C for (a) 10 min, 330×; (b) 5 min, 1132×; (c) 5 min, 1110×; and (d) 5 min, 870× magnification

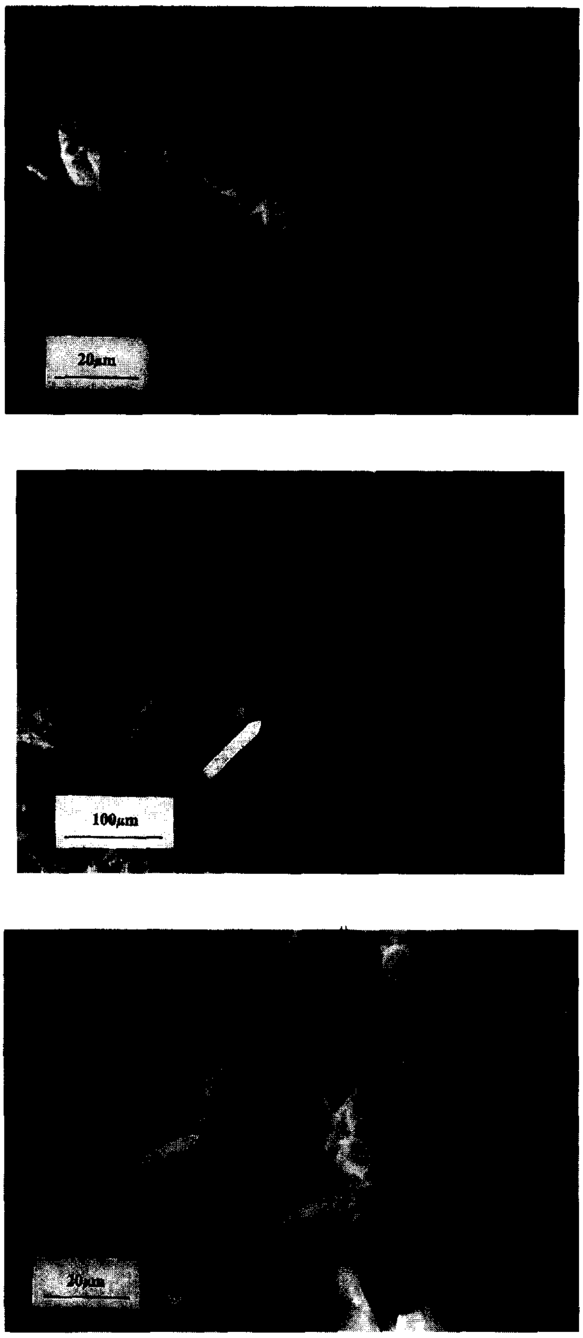
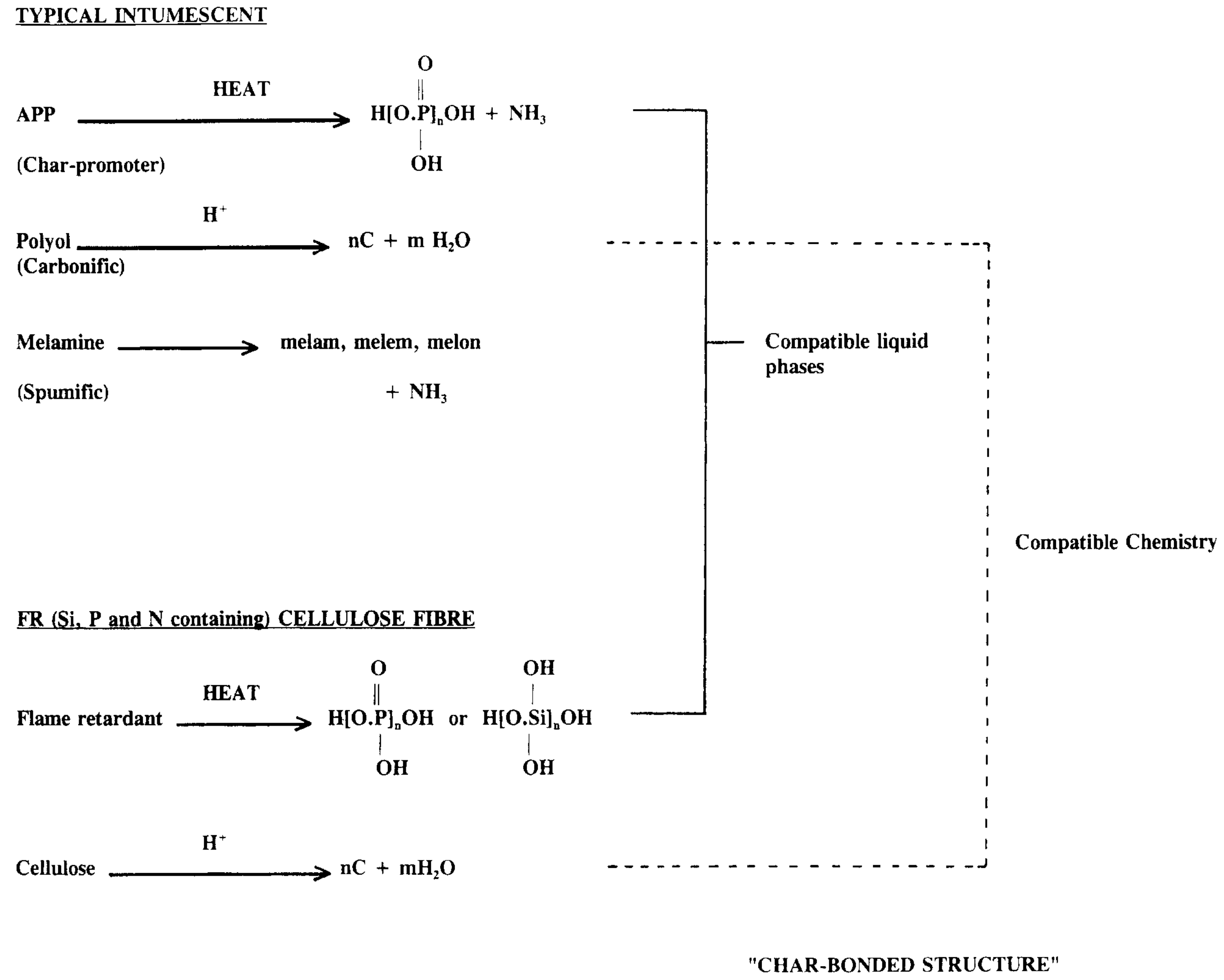


Figure 8 Micrographs of char formation of FR viscose fibre–novoloid fibre–intumescent composite structures after heating in air at (a) 400°C for 10 min, 1280×; (b) 500°C for 5 min, 295×; and (c) 500°C for 2 min, 1280× magnification

organophosphorous and sulfur-containing additive, but studies show that char formation is accompanied by significant production of tars and water[17]. Except for the enhanced tar formation, the action of Sandoflam 5060 is similar to those of other phosphorus-containing organo-compounds such as tetrakis (hydroxy methyl) phosphonium salt condensates [3], although the formation of liquid phosphorus-containing acids has not been observed previously. While the viscose fibre surfaces in *Figure 7c* do not show evidence of significant liquefaction as do hybrid viscose chars (see *Figure 2c*), there does seem to have been a degree of interaction between the fibre surfaces and adjacent intumescent during char formation. This selective interaction is seen more clearly in *Figure 7d* where indicated



Scheme 1 Simple chemistry of cellulosic fibre–intumescent char-forming interactions

intumescent activity is associated with the flame retardant viscose fibres only.

Lenzing FR viscose fibre–novoloid fibre–intumscent. The similarity of diameters of viscose and novoloid fibres makes clear distinction between fibre chars difficult, as already noted for Visil viscose fibre–novoloid fibre chars. However, the distinctive rod-like character of a novoloid fibre after exposure to 400°C for 10 min (see *Figure 1d*) is shown in *Figure 8a* in contact with a superficial presence of intumescent char. Char structures formed after exposures at 500°C indicate that intumescent char interactions and concentrations seem to be greater on the coarser flame retardant viscose char surfaces, as indicated in *Figure 8b* and more clearly in *Figure 8c*. Again, as noted in the FR viscose–E-glass blends, flame retardant cellulose–intumescent interactions do not seem to be as intense for the phosphorus and sulfur-containing viscose system (see *Figures 6, 7* and *8*) as for the polysilicic acid-containing viscose fibres (see *Figures 2b, 2c, 4b* and *5b*).

DISCUSSION AND CONCLUSIONS

The unexpectedly high thermal resistance of composites comprising polysilicic acid-containing viscose fibres and an ammonium polyphosphate-based intumescent is a consequence of the transformation of the former to a silica residue on the one hand and an integrated fibrous-intumescent char on the other. Because char residues remain even after exposures in air at temperatures up to 1200°C it is suggested that char oxidation is significantly reduced compared with the behaviour of textile fibre carbonaceous residues derived from both conventional flame retarded cellulosic and inherently heat and flame resistant polyaramid textile structures. The additional presence of intumescent char is the most probable reason in that air permeability of the composite char is significantly reduced relative to that of a wholly fibrous char. At present, however, we have no air diffusion data to substantiate this conclusion, but measurements will be undertaken in forthcoming studies.

The scanning electron microscope results for Visil viscose fibre-intumescent chars (see *Figures 2b, 2c* and *4b*) indicate that there is an added effect of interaction between the component fibrous and intumescent chars. To a lesser extent this interaction is observed when flame retardant viscose containing an organophosphorus species is present. However, no such interaction is observed when either an inert fibre such as E-glass or a partially aromatic char-forming novoloid fibre is present. In the latter, char promotion probably proceeds via full aromatization and hence carbonization of the structure via solid phase chemical pyrolysis[16].

It is proposed, therefore, that the observed char

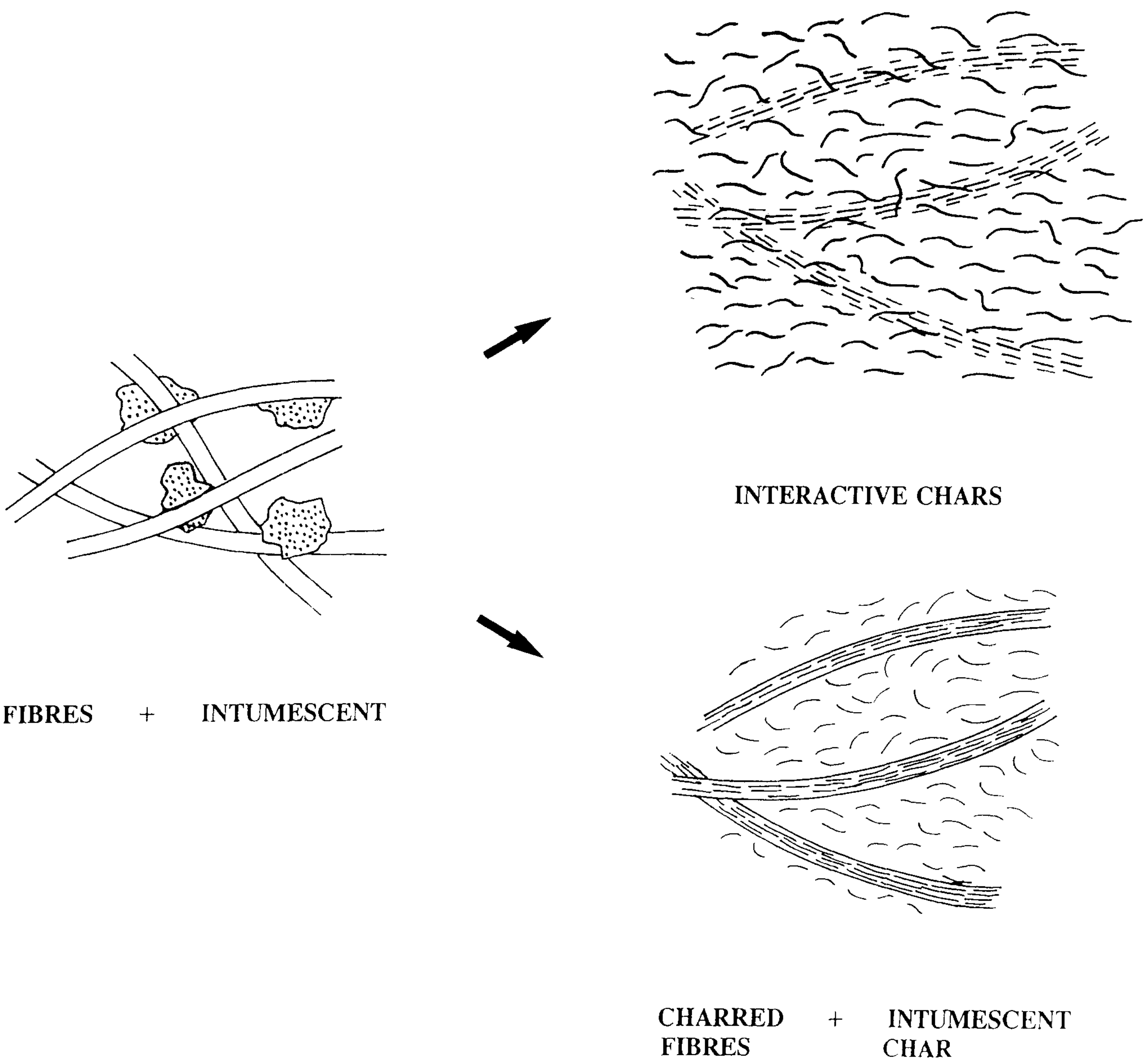


Figure 9 Schematic representation of the formation of non-interactive and interactive or char-bonded structures

interaction or char-bonding effect is a consequence of initial physical interaction of both fibre and intumescent during heating (300–400°C) via partial liquefaction and subsequent mixing of adjacent contact zones. Simultaneously, char formation of the cellulosic fibre matrix and the intumescent char-forming or carbonific[12] component (e.g. pentaerythritol) commences to create a bonded char structure which is fully developed above 400°C.

This reaction may be schematically and simply represented as an interaction of two physically and chemically char-forming reactions[8,9,13–15,18] in *Scheme 1*. The resulting char-bonded structure may be clearly seen in *Figure 4* in ref. 7, and *Figures 5b, 7a* and *8c* above. A simplified view of the physical character of a non-char-bonded structure (e.g. E-glass fibre–intumescent char) and a char-bonded structure is shown in *Figure 9*, where an attempt to represent the low air (hence oxygen) permeability of the char is represented.

In order to more fully understand the nature of this char-bonding effect and the associated physics and chemistry, thermal analytical studies of the above fibre–intumescent composition are currently being undertaken. Initial results[19] corroborate the formation of a char-bonded structure in that d.s.c. and t.g.a. studies indicate the presence of an interaction between charring cellulose fibres and the intumescent. Additionally, research is being extended to include other flame retardant, char-forming fibres and different intumescent formulations.

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