

Flame retardant challenges for textiles and fibres: new chemistry versus innovatory solutions.

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Abstract

Almost 50 years ago, the 1950-1960 period witnessed the development of the chemistry underlying most of today's successful and durable flame retardant treatments for fibres and textiles. In today's more critical markets in terms of environmental sustainability, chemical toxicological acceptability, performance and cost, many of these are now being questioned. "Are there potential replacements for established, durable formaldehyde-based flame retardants such as those based on tetrakis (hydroxymethyl) phosphonium salt and alkyl-substituted, N-methylol phosphopropionamide chemistries for cellulosic textiles?" is an often-asked question. "Can we produce char-forming polyester flame retardants?" and "Can we really produce effective halogen-free replacements for coatings and back-coated textiles?" are others.

These questions are addressed initially as a historical review of research undertaken in the second half of the twentieth century which is the basis of most currently available, commercialised flame retardant fibres and textiles. Research reported during the first decade of the twenty first century and which primarily addresses the current issues of environmental sustainability and the search for alternative flame retardant solutions, the need to increase char-forming character in synthetic fibres and the current interest in nanotechnology is critically discussed. The possible roles of micro- and nano-surface treatments of fibre surfaces and their development using techniques such as plasma technology are also reviewed.

Keywords: flame retardant, halogen, phosphorus, textile, fibre, environment, nanotechnology, plasma

1. Introduction

Within recent years there has been a number of comprehensive reviews that not only have critically reviewed the research period up to about 1980 during which period most of the presently used commercial flame retardants for fibres and textiles were developed [1], but also have considered developments since that time [2, 3, 4]. During the period up to about the 1970-80 period, the established durable and flame retardant treatments for cotton and wool fibres as well as those additives and comonomers introduced into both regenerated (eg viscose) and synthetic (notably polyester, polypropylene and the modacrylics) fibres during

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manufacture were synthesised and developed into commercially–acceptable products. In fact it is probably true to say that the majority of currently available flame retardants for textiles and fibres reviewed very recently by Weil and Levchik [4] derive from chemical developments prior to 1980.

2. The 1950-1980 “Golden period” of flame retardant research

Why should this period have been so fruitful? There are a number of answers to this question which include the recognition that durable flame retardant treatments, initially developed during the Second World War for service personnel had usefulness in a peace-time environment in which personal safety was becoming more important than hitherto [5]. The commercial development of flame retarded fibres and textiles was and continues to be driven by legislation and regulation. For example, in the both the UK and USA the hazards posed by the flammability of traditional cotton children’s nightwear were not only recognised during the 1950-60 period [6] but legislation to reduce deaths and injury to children was being developed and implemented during the 1960’s exemplified by the UK Nightwear Safety legislation of 1967 (revised in 1985) [7] which required young girl’s nightdresses to have a minimum level of flammability and all nightwear to be labelled as a fire safety hazard. In 1971 in the USA there was a similar drive to introduce such safety legislation [8, 9]. This safety issue produced the first major driver for funding within the USA and in particular for the development of novel flame retardant treatments. However, the first patents for a number of durable organophosphorus-based for cotton stemmed from the 1950 period and are exemplified today by the continuing use of flame retardants based on cross-linked tetrakis(hydroxymethyl) phosphonium salt adducts (often based on so-called THPX chemistry) and N-alkyl substituted phosphonopropionamide derivatives [1, 4].

A second driver was the need by the fast developing synthetic fibre industry to produce flame retardant versions of their otherwise conventional fibres and this was paralleled by the development of inherently fire and heat resistant fibres often based on aromatic-structured polymeric chains. Prime examples of the latter are the meta- and subsequently para-aramids

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and the former meta-aramid Nomex (Du Pont), appeared commercially in the 1960 period as a fibre for use first of all in hot gas filters and then niche products such as racing car driver overalls. This was followed by the para-aramid Kevlar (Du Pont) in the late 1960s as a high tenacity and modulus fibre which also possessed superior heat and fire resistance. The concurrent US efforts to place a man by 1970 on the moon also provided impetus to the development of synthetic fibres having very high fire resistance since the early 1960 space capsules had 100% oxygen atmospheres until the Apollo 1 fire in 1967 after which atmospheres changed to more ambient-like oxygen levels. Nomex® was specified by NASA in 1971 for use in coveralls by aerospace personnel [10]. The poly(benzamidazole) or PBI fibre patented and produced by Celanese during the late 1960s with a limiting oxygen index of about 41 vol% along with many other polyheterocyclic fibre-forming polymers were products of this effort [11]. The more commercially successful aromatic-structured fibres have been comprehensively reviewed elsewhere [12,13].

This same period saw a particularly significant research effort into the development of phosphorus-containing species as possible candidates for commercial flame retardants and this research was partly a consequence of the so-called cold war period and the research into phosphorus-containing nerve gas agents, many of which bear a degree of similarity to flame retardant species. It was during this time that researchers like Ed Weil at Stauffer Chemicals developed and patented the chemistry from which derived a whole portfolio of phosphorus-containing and phosphorus-halogen-containing “Fyrol” commercial products [14, 15, 16]. The “Fyrol” successors of this company, Akzo, then Supresta and now ICL Industrial Products Ltd, are still based on this 1960/70 chemistry and typified by the products Fyrol 6, 51 and 76 each of which was developed for textile applications. Of these Fyrol 6 (diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate) [17] and Fyrol 51 (an oligomeric phosphate-phosphonate: $\text{H}-(\text{O}.\text{CH}_2.\text{CH}_2.\text{O}.\text{P}(\text{O})(\text{OCH}_3))_{2x}.\text{O}.\text{CH}_2.\text{CH}_2.\text{P}(\text{O})(\text{CH}_3)_x.\text{O}.\text{CH}_2.\text{CH}_2.\text{OH}$) were specifically recommended for textile applications. Fyrol 76 comprised a mixture of a vinyl phosphonate oligomer and N-methylol acrylamide as a cellulose cross-linker thereby ensuring reactivity with cellulosic fibres.

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This was truly a “golden age” which many older scientists will say was unfettered by the constraints of subsequent health and safety requirements and now the realisation that many of these species are indeed quite toxic. In fact, research within the USA was brought to quite an abrupt halt in 1977 when the very efficient retardant tris-(2,3 dibromo propyl) phosphate or “tris” was reported to have failed the Ames test and so indicated carcinogenic behaviour [18, 19]. Other flame retardants since deemed to be potentially toxic included Fyrol 76, because of the acrylamide derivative present, and so disappeared from the portfolio of available commercial flame retardants during this time. Students of the scientific literature will find a sudden drop in the numbers of original research articles relating to novel flame retardant synthesis after this date.

Table 1 lists the principal flame retardants researched and developed during this period and which still retain commercial significance for textiles as corroborated by a recent more commercially-focussed review of textile flame retardants [20]. In over forty publications in the commercially-focussed Indian Journal *Colourage*, Nair has published widely regarding the details and variations of most of the commonly available non-durable and durable flame retardants for cellulosic-containing textiles with a more recent emphasis on THPX finishes and their variations [21].

Competing with flame retardant treatments has been the fibre industry’s attempts to develop inherently flame retardant varieties since the 1950 period. While the literature has cited many flame retardant variants of the common man-made fibres (apart from the polyamides which have proved difficult to modify during processing because of their high melt reactivities), those listed in Table 2 have stood the test of time in spite of their imperfections. Of these only flame retardant viscose and modacrylics have char-forming properties and the former may be used in applications very similar to those of flame retardant cotton with the added advantage that it may be blended with other char-forming, inherently flame retardant fibres such as the aramids. While the modacrylics have a history spanning nearly six decades, their use has been in specialised markets where their increased cost relative to normal acrylic fibres is justified. For instance in the flame retardant furnishings market, use

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of back-coatings has largely excluded their use and many formally important acrylic manufacturers such as Du Pont, Monsanto and Courtaulds ceased their manufacture during the 1990 period before they ceased acrylic fibre producing operations altogether. One of the remaining producers is the Kaneka Corporation of Japan and they market the advantages of blending their Kanecaron fibres with cotton and other fibres to yield flame retardant blends having acceptable aesthetic properties. Unfortunately such fibres may contain antimony III oxide as a halogen synergist and this has restricted the use of these fibres in certain markets.

Polyester and polypropylene fibres present particular flame retardancy challenges because neither fibre has an inherent char-forming property and flame retardancy is introduced either by ensuring that molten drips self-extinguish as in the case of Trevira CS or by use of bromine chemistry to introduce gas phase retardancy. The low melt reactivity and process temperatures of polypropylene enable continued use of synergised bromine additives although the recent introduction of hindered amine species has rendered the need for antimony III oxide unnecessary [24]

The aromatic-structured high performance fibres, while also having a history of nearly 50 years, are outside the scope of this paper and details are available elsewhere [11-13].

2. Developments during the 1980- late 1990 period

The next twenty years or so from 1980 to about 2000, witnessed very little new research into novel chemical species and in the main progress, was made in refining earlier chemistry and the addressing the realisation that some flame retardants were demonstrating certain environmental problems associated with possible dioxin formation when flame retarded polymers were incinerated during disposal, coupled with bioaccumulative and bioactive effects. A major driver for flame retardant development during this period were initially the UK furnishing regulations of 1980 amended in 1983 [25] which required cigarette ignition

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resistance of outer cover fabrics. These were superseded in 1988 [26] by the requirement that all UK domestic furnishing fabrics must have both cigarette and simulated match resistance. These regulations promoted the development of flame retardant back-coatings which could be applied to any fabric thereby enabling many rich upholstered fabric designs to be rendered flame retardant in spite of the fibres used [27]. The use of halogen-containing formulations came to the fore here and these innovations were soon the focus of environmental pressures posed by bromine-containing flame retardants in particular, such as decabromodiphenyl ether (decaBDE) [2, 4, 28].

The increasing need for barrier fabrics in the furnishing and other sectors also signalled an increased need for char-promoting flame retardant textiles and the challenges posed by this and the increasing interest in application of intumescent to textiles was reviewed by ourselves in 1996 [22].

3. Developments since 2000

Since 2000, the following areas have been of significance:

- Attempts to develop more cost-effective and environmentally-sustainable alternatives to many of the flame retardants in Table 1.
- Risk assessments of flame retardants for use on textiles with a focus on bromine-containing species
- Attempts to develop char-promoting flame retardants for melt fusible fibres
- Applications of nanotechnology

Reviews that have addressed these and related areas of interest with respect to developments across the whole field of fire and heat resistance of fibres and textiles include that previously cited by Weil and Levchik [4] with a focus of commercial developments, by Bourbigot [3, 29] with an emphasis on new approaches and by Horrocks [30] with respect to the particular challenges of textile coatings.

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Of particular interest is the paper by Lewin in 2005 which reviewed the challenges and questions to be addressed in the general flame retardancy of polymers many of which are relevant to textiles [31]. Of particular relevance to this discussion are his thoughts on alternative treatments to those available for flame retardant cotton including the possible role of simultaneous sulphation and phosphorylation, the continuing failure to achieve an effective flame retardant treatment for polyester-cotton blends, the need for additional gas phase flame retardants to compete with those containing halogens and the possible role of nanocomposites. Most of these issues are included in the list above.

3.1 Attempts to replace established flame retardants with cheaper and environmentally more sustainable alternatives

Interest here has focussed mainly on finding formaldehyde-free flame retardants for cellulosics as well as bromine-free back-coatings for furnishing and barrier fabric fabrics.

Formaldehyde-free flame retardants for cellulosics: The main targets for replacement are the two major and commercially dominant generic types of durable flame retardants for cotton and cotton-rich blends, namely those based on tetrakis(hydroxymethyl) phosphonium salt (THPX) condensates and those based on N-methylol dimethylpropionamide derivatives. The former is typified by the Proban® (Rhodia) product which is based on tetrakis(hydroxymethyl) phosphonium-urea condensate which after padding on to cloth is cross-linked by ammonia gas and followed by peroxide oxidation to stabilise the resulting polymeric matrix which is interdispersed throughout the interfibrillar of the cotton fibres present [1]. Surprisingly, while THPX-ammonia-cured treatments are one of the targets here, there is no published evidence that formaldehyde release is a problem either during the application of the flame retardant or during service life. However, there is commercial evidence that some formaldehyde may be released during use but at levels probably much less than incurred from formaldehyde-based resin finishes used in either crease-resist or flame retardant finishing such as N-methylol dimethylpropionamide derivatives. This is not

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too surprising since following ammonia-curing and subsequent oxidation of the polyphosphine structure to the stable poly(phosphine oxide) with an idealised generic structure $-\text{CO}-\text{NH}-\text{CH}_2-\text{P}(=\text{O})-(\text{CH}_2-\text{NH}-)_2-$, it is difficult to visualise how significant quantities of formaldehyde could be released from this structure during normal use.

However, this is not the case with N-methylol dimethylpropionamide (N-MDMPA) derivatives which are typified by the former Ciba (and now Huntsman) product Pyrovatex CP® and which is available in various modifications such as the dimethylol derivative which is claimed to improve durability and/or reduce formaldehyde release during application and in use [2, 4]. These N-MDMPA derivatives require the presence of a methylolated cross-linking agent in order to bond them on to the cellulose hydroxyl groups to create the required durability. Since the condensation reactions involved are equilibria in which formaldehyde is a product, this will always be present during both application and regenerated during service life. The presence of atmospheric moisture and acidic residues present in N-MDMPA derivative-treated cotton especially favour the reverse reaction and hence generation of formaldehyde during storage and service.

However and notwithstanding the above discussion, both these generic flame retardant types are claimed by respective manufacturers to generate less than 75 ppm free formaldehyde when in contact with skin and 300 ppm formaldehyde from garments and other textile articles not in contact with the skin and so can achieve the internationally recognised Oeko-Tex® 100 certification, for example [32]. In fact a recent New Zealand publication [33] states that there appears to be no problem with clothing being sold in New Zealand giving rise to formaldehyde emissions in contact with the skin no more than 30 ppm, a level considered to be the maximum permissible for wearers having the greatest sensitivity to this chemical. However, this document does not mention specifically flame retarded garments but they may be implied if such garments are in fact being sold there.

With regard to their application and unlike the THPC-based Proban® product which uses a patented ammonia cure process and requires specialised plant, N-MDMPA derivatives, typified by the Pyrovatex® product range [1, 2, 4]] may be applied by a conventional pad-

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dry-cure process. Thus in order to be able to replace either of these generic products and their derivatives, it is appropriate to consider their respective strengths and weaknesses as listed in Table 3. It is instructive to note that many recent research papers assume only the worst properties of these as being reasons for their replacement. Table 3 demonstrates their strengths and explains why both have been the dominant durable flame finishes for cotton and blends for the last 50 years. Although there are possible concerns on where either of these treatments may be used such as in children’s nightwear for the formaldehyde-releasing N-methylol dimethylpropionamide derivatives and certain dyestuff types for the THPX condensates, the two together form a compatible pair in that one or both will address and satisfy most durable 100% cotton flame retarded fabric requirements and, when in blends with synthetic fibres, are usually effective in such cotton-rich blends.

For any new durable flame retardant for cotton to become accepted and therefore compete with these two requires any one of the following properties:

- have equivalent or superior ease of application,
- possess zero formaldehyde-releasing properties,
- have comparable textile service-life properties in terms of durability, effect on handle and tensile properties,
- have an overall comparable cost-effectiveness and preferably be cheaper and
- have equivalent or superior toxicological and environmental impacts.

Because of the formaldehyde issue and in spite of its apparent absence from ammonia-cured-THPX treatments, a considerable literature has appeared in attempts to develop formaldehyde-free flame retardant replacements. While this review is not intended to be a comprehensive review [4], some of the more salient alternatives will be briefly discussed. Abdel-Mohdy et al have published the use of aminomethyl phosphonic acid diamide, and derivatives [34], and triethylamino phosphine oxides [35] as phosphorus, and nitrogen-containing synergistic flame retardants for cotton but unfortunately their respective

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methylolation using formaldehyde is an essential feature for their subsequent reactivity with anhydroglucopyranose -OH groups. Furthermore, their application with methylolated melamine, and similar resins is required in order to achieve desired levels of durability. In a not dissimilar vein, ICL (formerly Akzo Nobel) have re-introduced their former (and previously mentioned) Fyrol 51 product [4, 36] as Fyroltex HP [37] which with a phosphate-phosphonate oligomeric structure has the potential for being a durable flame retardant for cellulosic textiles as initially reported by Wu and Yang in 2003 [38]. Since then these workers have undertaken further research which has shown [39-41] that if it is to achieve acceptable levels of multiple laundering durability, its application requires the presence of methylolated resin species like dimethylol dihydroxyethylene urea (DMDHEU) or methylated formaldehyde-urea. These publications show that up to 12 launderings are feasible if the correct cross-linker is chosen although the problem of formaldehyde release will still remain. Subsequent publications claimed up to 40 wt% retention and 50 laundering durability for a Fyroltex/TMM/DMDHEU combined finish applied to 50%/50% nylon(6 or 6.6)/cotton blends [42].

However, the quest for a truly formaldehyde-free, durable, and effective flame retardant for cellulose in particular remains a challenge sufficient to continue to attract interest. Principal work in this area of late has come from the USA where interest in char-forming polycarboxylated species like butyl tetracarboxylic acid (BTCA) along with other functional species may interact with cellulose in particular to generate levels of flame retardancy acceptable for certain textile applications such as carpets with moderate levels of durability to washing [43]. Unfortunately, because of the ease of hydrolysis of the BTCA-cellulose ester links formed, durability to domestic laundering is limited, and so flame treatments based on this chemistry may only lead to semi-durability. More recent work by Yang and colleagues has combined BTCA as the cellulose bridging species with phosphorylated species such as the hydroxyalkyl organophosphorus oligomer, Fyroltex, discussed above to enhance both flame retardancy, and durability [37, 44]. While the BTCA forms a bridge between the oligomer, and cellulose molecules, and durability is somewhat improved, the

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ease of ion exchange between free carboxylic acid group hydrogen ions with calcium ions during washing in hard water is accompanied by a loss in flame retardancy as a consequence of calcium salt formation [40]. Addition of triethanolamine (TEA) reduces the calcium ion pick-up as a consequence of free carboxylic acid group esterification and using a Fyroltex/BCTA/TEA combination applied to a 35%/65% cotton/Nomex blend, acceptable levels of durability were achieved with vertical strip test (ASTM D6413-99) passes after 30 home launderings [44]. A very recent publication extends this work to show that the mixed Fyroltex/BCTA system may be applied to silk to yield a 15 hand-wash level of durability [45]. Where the use of similar polycarboxylic acid species like BCTA can find application is in the cotton-containing fleece applications where the conventional THPX- and N-MDMPA-based durable finishes cannot be used because of associated stiffness and or processing difficulties and where limited durability is required [46]. Yang’s research team has recently developed this idea further and reported that treatment of cotton fleece with maleic acid and sodium hypophosphite enables Class 1 passes to 16 CFR 1610 (US Federal Standard for the flammability of Clothing Textiles) to be achieved when exposed to the 45° ASTM D1230-94A apparel test after 20 home launderings [47]. These authors propose that the hypophosphite anion interacts with the maleic acid entity to form a cross-link of the type: Cell-O-CO-CH₂-CH(COOH)-P(O).(O⁻)-CH(COOH)-CH₂-CO-O-Cell. Subsequent work has extended this to include succinic, malic and tartaric acids to yield similar flame retardant performance [48].

Their work with maleic acid has been extended to include phosphorus-containing maleic acid oligomers (PMAO) synthesized by aqueous free radical polymerization of maleic acid in the presence of potassium hypophosphite. PMAO is considered to be a mixture of species having the general formulae : H-P(O) (OM).[MA]_x-H, H-[MA]_x - P(O) (OM).[MA]_y-H and HO-P(O) (OM).[MA]_x-H where x and y are between 3 and 5. This mixture is applied to cotton fleece fabrics again in the presence of sodium hypophosphite with no significant changes in fabric properties [49]. Their most recently reported work re-examines the possible role of

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Fyroltex and BCTA in 100% cotton fleece and when TEA is present also achieves Class I after multiple home launderings [50].

Quite different from the above approaches is the recently introduced Firestop product Noflan, a phosphorus-, and nitrogen-containing molecule reported to have the structure in which an alkyl phosphoramidate is stabilized as a salt adduct with ammonium chloride [51]. It is believed to have the structure $[\text{CH}_3\text{-P(O)}\cdot(\text{ONH}_4)\text{-NH}_2] \text{NH}_4\text{Cl}$ [4]. While this is obviously a formaldehyde-free molecule, it may react only with cellulosic substrates via the phosphoramidate - NH_2 group, which is not very reactive. It is most likely that for this to be effective in cellulosic-based textiles, it may be applied either in a resin binder or cross-linked using a methylolated resin. It is claimed to be effective on cotton and cotton-polyester blends with reasonable levels of durability. When applied to wool, it can survive dry cleaning treatments and finds application in technical end-uses such as aerospace interior fabrics. In a not-unrelated paper, work by the Swiss research team [52] has investigated the particular value of organophosphoramidates as flame retardants for cellulose which are claimed to be not only easily synthesised from chlorophosphates but also exert high levels of flame retardancy because of nitrogen-phosphorus synergy which may be varied depending on the level of nitrogen-containing moiety substitution. The research focussed on the behaviour of secondary organophosphoramidates since a previous study by Pandya et al over 25 years ago [53] suggested that they were superior to tertiary analogues. These specially synthesised structures having the general formula $(\text{C}_2\text{H}_5)_2\text{-P(O)-NH-R}$, where $\text{R} = \text{H}$, $-\text{C}_2\text{H}_5$, $-\text{C}_2\text{H}_4\cdot\text{OH}$ and $-\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{CH}_3$ demonstrated high levels of condensed phase activity although no attempt was made to assess or improve their poor durability. The study therefore remains academic although poses the question of whether or not suitable cellulose reactivity can be introduced to confer the necessary levels of durability for commercial exploitation.

An interesting and novel approach has been published by Chang et al., [54] from the USDA Southern Regional Research Centre in New Orleans where much of the pioneering research into durable flame retardant finishes for cotton was undertaken during the 1950-70 period

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[1]. This group has synthesised two new monomers (2-methyl-oxiranylmethyl)-phosphonic acid dimethyl ester and [2-(dimethoxy-phosphorylmethyl)-oxyranylmethyl]-phosphonic acid dimethyl ester which together with dicyandiamide and citric acid impart flame resistance to woven 100% cotton and 80/20 cotton/polyester fleece fabrics. The resulting mono- and bis-(dimethoxy-hydroxymethyl phosphonyl) cyanurate derivatives may be padded on to fabrics and while the former can give rise to LOI values up to 25.5 vol% at about 21 wt % add-on, higher LOI values above 28. vol% were obtained when the latter was applied at add-ons below 20 wt%. Fabrics passed the standard 45° and vertical strip tests ASTM D1230-94 and D6413-99 before laundering. Durability is not, however, very good with only about 5 wash cycles being achievable whilst maintaining acceptable levels of flame retardancy in spite of the claimed cellulose reactivity of cyanurate derivatives. Further research by this group was recently described at the recent conference, FRPM'09 [54].

Finally, one other very recent paper attempts to eliminate the need for a formaldehyde-based cross-linking resin from the N-DMDPA system by converting the latter to the N-1-chloroisopropyl alcohol derivative which may then directly bond to viscose cellulose [56]. This creates the flame retardant, cellulose-reactive species:



The authors claim that after application to viscose by a pad-dry-cure (160°C/3 min) process, the initial LOI of 31 vol% is reduced only to 26 vol% after 50 laundry cycles. While there is no possibility of formaldehyde release from the formerly required cross-linker, whether or not the anticipated reacted product may generate formaldehyde is not clear.

Recent interest has also been shown in the potential for combining phosphorus, nitrogen and silicon on to cellulose substrates to create the potential for carbonaceous and

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siliceous char-forming characteristics. Lecoœur et al [57, 58] have combined monoguanidine diphosphate (MGDP) and 3-aminopropyltriethoxysilane, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, applied in the presence of phosphoric acid which is a required catalyst if water soak durability (20 min in hard water at room temperature) is to be achieved. Treated cottons behave typically of those containing char-promoting flame retardants in that flame retardancy is improved (M1 rating to NF P 92-503), PHRR reduces and residual char increases. The level of durability achieved is a consequence of MGDP phosphorylating cellulose during the 180°C cure and the polymerisation of the silane and its partial reactivity with cellulose. Again, the challenge remains of developing a reactive flame retardant species that effectively bonds to cellulose through the hydroxyl groups, is hydrolysis resistant and withstands normal textile processing conditions.

Non-halogen-containing back-coatings: Within the UK’s furnishing textile back-coatings market, the standard formulations based on antimony III oxide and brominated hydrocarbons, notably decabromodiphenyl ether (decaDBE), and hexabromocyclododecane (HBCD), still dominate the market in spite of environmental concerns (see below). The challenge of replacing these systems by phosphorus-containing species only has been investigated by ourselves [59, 60] and reviewed by Weil and Levchik [4]. The main scientific, and technological hurdles to be overcome in the development of antimony-halogen replacements are primarily the replacement of a diffusive, vapour phase system by an equivalent based on phosphorus/nitrogen in which poor durability, and low volatility/vapour phase activities are key features. We have shown that while replacement by a number of phosphorus-nitrogen formulations including intumescent formulations (eg Flammentin NAH, Thor Chemicals; Antiblaze NH, Albemarle), and cyclic organophosphonate species (Afflammit PE, Thor; Antiblaze CU/CT, Rhodia) is possible, their effectiveness is limited by durability following the 40°C water soak required in the 1988 UK Furniture, and Furnishing (Fire) (Safety) Regulations [7] prior to testing to BS5852:Part 1:1979 for match, and cigarette ignition resistance. Furthermore, for char-forming, phosphorus-based formulations to be effective, we have shown that if the face of the fabric is not to ignite, then the flame retardant

in the back-coating must be released at temperatures well below the ignition temperature, which in the case of cotton, is of the order of 350°C. Ideally, this requires decomposition, and release of active flame retardant species at temperatures below 300°C; these conditions were met only by ammonium polyphosphate-containing formulations, and cyclic organo-phosphonate oligomeric species exemplified by Antiblaze CU (Rhodia). The former, unfortunately, has a water solubility too high, typically 1-4 g/100ml at 25°C, for the durability requirements, although higher degree of polymerization, and/or encapsulated variants may prove otherwise claiming solubilities <1 g/100ml at 25°C². The latter, because it is a high boiling liquid volatilizing at 198°C [60] and above, may generate an unacceptable level of tackiness to the final formulation [59]. However, this volatility, relative to other candidate phosphorus-containing species, will ensure that it is released into the flame under an applied ignition source.

Thus in developing a phosphorus flame retardant strategy for the replacement of decaBDE and similar bromine-based formulations, it is evident that the vapour-phase activity of the latter is a key factor in determining their efficiency apart from their excellent insolubility and general intractability. Notwithstanding these prime issues, the outcomes of our previous research [59, 60] have led to three strategies that may be proposed to achieve these requirements:

- i. the sensitisation of decomposition or flame retarding efficiency of phosphorus-based systems [61];
- ii. the reduction in solubility of successful but soluble systems and
- iii. the introduction of a volatile and possible vapour phase-active, phosphorus-based flame retardant component [62, 63].

With regard to the first, we have demonstrated that the inclusion of small amounts of certain transition metal salts, notably those of zinc II and manganese II can reduce the onset of decomposition of ammonium polyphosphate (APP) from 304°C to as low as 283°C in the case of 2 wt% manganese II sulphate addition [61]. When applied in a back-coating formulation with APP, the presence of metal ions increases LOI values slightly (of the order

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of 1-1.5 LOI vol% for manganese and zinc salts) from 25.1 for APP-only coated cotton to 26.6 vol% in the presence of 2% manganese acetate. However, all coated fabrics still failed the simulated small flame ignition version of BS 5852, which is not perhaps surprising since our earlier research indicated that an LOI value for a coated cotton fabric above 26 and closer to 29 vol% was required for a pass [59]. Furthermore, it was noted that the presence of the transition metal salt reduced the width of the charring area subjected to the flame source when compared with the APP-only sample. It should be pointed out, however, that even if passes had been obtained, the problem of durability to water soaking would still remain.

Recent work by Bourbigot and coworkers [64] has shown that microencapsulation of otherwise soluble flame retardants like ammonium phosphate with polyurethane shells can improve the durability of coatings containing them. However, the preparation of these microencapsulated agents is not an easy process and different techniques are being developed in order to improve yields [65, 66].

The literature does not contain much published research that demonstrates clearly that vapour-phase phosphorus activity in fact can occur. For instance Rohringer et al [67] have proposed that the relatively superior flame retarding efficiency of tetrakis (hydroxymethyl) phosphonium chloride (THPC)-based flame retardants applied to polyester-cotton blends may be associated with the evolution of volatile phosphine oxides, which then act in the vapour phase and retard the burning polyester component. Day et al [68] have also provided evidence that the flame retarding efficiency of now-banned tris (2,3-dibromopropyl) phosphate or “tris”, when applied to polyester, is also a consequence of vapour phase activity of phosphorus species. Hastie and Bonnel [69] used spectroscopic and high pressure sampling mass spectrometry to study possible flame inhibition effects of a number of phosphorus-containing compounds including trimethyl phosphate, phosphoryl chloride and triphenylphosphine oxide. When mixed with methane and propane fuels, flame inhibition was noted in diffusion flames burning in air, although in premixed flames (with air), some P-containing additives could increase flame strength. These same experiments undermined

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previous considerations that the PO· radical was the predominant species in flames and they proposed that the HPO₂· radical was more significant and interacted with H· and OH· radicals in a manner similar to halogen radicals. Very recent work by Babushok et al [70] concerning the inhibition of alkane combustion in premixed flames has suggested that in the vapour phase, phosphorus may be more effective than halogen.

In accordance with these findings, our recent work [62, 63] initially considered four potentially volatile phosphorus flame retardants selected from their reported boiling or decomposition data. These were the monomeric cyclic phosphate Antiblaze CU (mass loss occurs above 197°C [60]), tributyl phosphate (TBP) (m.pt.= -80°C, b.pt. = 289°C with decomposition), triphenyl phosphate (TPP) (m.pt. 48-52°C, b.pt. 244°C at 10mm Hg, 5% weight loss at 208°C) and triphenylphosphine oxide (TPPO) (m.pt. 156-158°C), this last being one studied by Hastie and Bonnel [69]. Because interest lay in generating new back-coatings for both polypropylene and cotton fabrics, thermogravimetric studies suggested that TBP would be most suitable because it begins to lose mass, i.e. produces volatiles, at about 150°C, well below the melting temperature of polypropylene (~165°C) and the ignition temperature of cotton (~350°C), although tackiness was anticipated to be a problem.

Triphenyl phosphate (TPP) was also selected as the next most volatile agent with volatilisation starting at about 200°C. Each was combined with an intumescent char-forming agent, Great Lakes NH 1197(Chemtura) comprising phosphorylated pentaerythritol [60] in formulations that maintained constant overall flame retardant contents, although in varying volatile:non-volatile phosphorus ratios, namely:

- 250 dry mass units NH1197/100 dry mass units resin
- 200 dry units NH1197, 50 dry units TBP or TPP/100 dry mass units resin
- 150 dry units NH1197, 100 dry units TBP or TPP/100 dry mass units resin

Formulating novel flame retardant combinations is often fraught with problems which impede or prevent facile sample preparation. Here the liquid tributyl phosphate produced a very tacky coating at dry unit contents beyond 100 parts while TPP, although a solid thereby

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removing the tackiness problem, tended to agglomerate thus producing a very granular back-coating formulation, which prevented even coating. Nevertheless, formulations were back-coated on to 220 gm⁻² cotton and 260 gm⁻² polypropylene fabrics respectively to achieve nominal dry add-ons in the 40-70 wt% range. Table 4 shows the LOI and small-scale simulation test of BS5852 results after a 30 minute 40°C water-soaking test.

These show that the partial replacement of the char-forming retardant NH 1197 by the volatile TBP and less volatile TPP gave back-coated cotton samples that showed improved performance with the dry mass ratio formulation of 200:50 giving the highest LOI values. It is interesting to note that while the agglomerating effect of TPP at 100 parts presence resulted in a high add-on of 104%, this almost doubled total flame retardant presence with respect to fabric but had minimal effect on the LOI value. This suggests that once the flame retardant presence in the back-coating is sufficient to raise the fabric LOI to just above 26 vol%, this represents an asymptotic maximum value. A similar position may exist for the back-coated polypropylene samples except that this maximum value is just above an LOI value of 22 vol%.

The significance of the simulated match test pass of the NH 1197/TBP-containing coated cotton sample suggested that the presence of the volatile phosphorus-containing component improves flame extinction during front face ignition. This same effect is not obviously seen in the polypropylene fabrics which have relatively low LOI values and excessive thermoplasticity with melting, which is not overcome or supported by the char-promoting elements within the back-coating. In fact the additions of TBP or TPP have little effect on the overall LOI with respect to back-coated PP fabrics containing only NH 1197; however, the 200:50 NH 1197:TPP only just failed the simulated BS 5852 test in spite of an LOI value of only 21.5 vol%.

Further evidence of the volatile phosphorus activity was gained by determining the retention of phosphorus in charred residues from back-coated samples containing the following flame retardants:

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- ammonium polyphosphate (Antiblaze MCM, Albemarle)
- melamine phosphate (Antiblaze NH, Albemarle)
- cyclic phosphonate (Amgard CU, Rhodia)
- oligomeric phosphate-phosphonate (Fyrol 51, Supresta)

where the liquid Amgard CU and Fyrol 51 species were selected as potentially vapour-phase active flame retardants. In order to produce chars having different thermal histories, back-coated samples of known weight were then placed in a furnace at 300, 400, and 500 and 600°C for 5 minutes in an air atmosphere. These experiments were not intended to simulate actual combustion conditions but were designed to create chars having residual phosphorus contents that would be dependent on the volatility of the phosphorus-containing moieties present. Table 5 summarises the results of char phosphorus content analyses expressed as $\Delta P\%$, the respective phosphorus loss from each char, where ΔP equals the theoretical phosphorus content assuming 100% retention in the char minus the experimental value [62, 63].

It is evident that phosphorus loss is lowest for the fabrics containing the char-promoting Antiblaze MCM (APP) and NH (melamine phosphate) retardants and highest for the Amgard CU and Fyrol 51 liquid components. These two also exhibit the highest coated fabric LOI values suggesting that not only is the phosphorus present volatile, but when released into the flame, it reduces flammability.

These results suggested that an ideal back-coating might comprise a non-volatile, char-former like ammonium polyphosphate (APP) in combination with volatile nitrogen- and phosphorus-containing species. Based on the fact that melamine is an insoluble and yet volatile solid which sublimes above 400°C, a final set of experiments was undertaken based on the outcomes of the above including the addition of melamine (Mel). Formulations as listed in Table 6 were prepared comprising 250 parts per hundred total flame retardant with respect to resin binder divided equally in mass proportions determined by the number of components present, coated on to cotton and then tested for LOI and to a simulated BS 5852: Part 1: Source 1 test [59] before a water-soak. In the latter, three flame application

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times, 10s, 20s and 30s were used to demonstrate the superior behaviour of these compositions. The inclusion of melamine appears to be responsible for the raising of LOI values of all samples to exceed 27 vol%. All samples passed the simulated BS 5852: Part 1 test before water-soaking except for the APP/melamine formulation that failed at flame application times above 20s; however, those containing volatile phosphorus-containing agents continue to pass.

Unfortunately, similar high performance was not observed after coated fabrics had been subjected to a water-soak at 40°C as shown in Table 6. The retentions of active flame retardants after water soaking were obtained by weighing before and after and are presented as weight percentages. Although retention of the applied formulations often exceeded 70%, it is clear that the major part of the losses will be the APP component. However, it is notable that the APP/Mel/Fyrol 51 formulation withstood water soaking to yield a pass after a 10s ignition time. This result points the way towards achieving passes after water soaking and after 20s ignition times if the water insolubility of the char-former present can be increased. The presence of a volatile phosphorus component has obviously been a major component within the overall formulation.

3.2 Risk assessments of flame retardants for use on textiles with a focus on bromine-containing species

A major issue facing the flame retardant industry generally for the last 15 years or so, has been the desire to remove from use flame retardant chemicals that have been shown to have an unacceptable level of environmental risk. Because of the often intimate nature of textiles, not surprisingly, this has impacted upon fibres and textiles and especially those used in furnishings where halogen-containing back-coatings are the principle flame resisting method used. This whole issue is too complex for this present discussion but an outline has been presented elsewhere [2]. An extensive risk analysis of 16 commonly used flame retardants was undertaken by the US National Academy of Sciences in 2000 [71] and

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current debate continues as shown by following web-sites belonging to organisations such as the US Consumer Product Safety Commission (CPSC), the European Flame Retardants Association (EFRA) and the Bromine Science and Environmental Forum (BSEF). Other significant and more recent reviews include one by Wakelyn [72]. In summary, all halogen and more specifically, bromine-containing flame retardants have come under scrutiny, and while some like penta- and octabromodiphenyl ether have been banned, others like decabromodiphenyl ether (decaBDE) and tetrabromobisphenol A have been subjected to risk assessments and have been found to be safe [73, 74]. Hexabromocyclododecane (HBCD) has been found to be associated with some degree of risk. The risk assessment [75] concludes that HBCD is persistent, bioaccumulative and toxic and while there is no risk to consumers, either by exposure to products containing HBCD or via the environment, there are possible risks to the workforce during processing. However, in spite of the scientific evidence, the pressures to replace bromine-containing flame retardants remain and work to replace them has been discussed with regard to back-coatings in the previous section.

3.3 Attempts to develop char-promoting flame retardants for melt fusible fibres like polyester and polyamide

Apart from the use of back-coatings which may be applied to any textile comprising any fibre type of blend, most flame retardants applied to fusible fibre-forming polymers act by increasing melt dripping with the added requirement that flaming drips are absent or quickly self-extinguishing. Poly(ethylene terephthalate) (PET) and other aliphatic fibre-forming polyesters tend to volatilise when heated above their melting points and show little cross-linking and hence char-forming characteristics. Polypropylene is in a similar position except that molten drips are difficult to extinguish without the presence of a gas phase flame retardant present. Furthermore and unlike bulk polymers, those used for fibre applications must comprise minimal levels of flame retardant component introduced during fibre production if they are to retain their generally desirable textile properties such as high tensile

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strength, dyeability and aesthetics. This usually means that any flame retardant additive or comonomer must be present at less than 10%wt and so at levels much less than are generally the case for bulk polymer applications. In addition, these fibres suffer from the paradox that if a char-promoting agent is to be introduced during the polymerisation/extrusion stages, then it must be sufficiently stable not to start to react at processing temperatures in the range 250-290°C. Clearly and assuming that a melt-compatible agent has been developed, when the resulting textile is exposed to a flame, it will melt prior to any char-forming reaction being initiated. This may then reduce dripping rates but it will not be sufficient to offset the initial thermoplasticity and loss of fabric dimensions that will then prevent the flame retarded textile acting as a barrier fabric.

In addition, any aftertreatment is handicapped by the similar need to introduce high levels of flame retardant by normal textile wet processing methods and the use of high pressure solution application (3 bar/130°C) or high temperature thermofixation (180-200°C) are exploited usually during polyester processing to achieve the high levels required, although even then flame retardant levels are not high and often marginal. For polypropylene the use of melt additives only is possible and these have been reviewed by ourselves (see Table 2) [24] and are currently based on bromine-containing species.

Ideally, there is a need for flame retardants that reduce melt dripping and encourage char formation thereby allowing pure synthetic fibre-containing fabrics to behave as barriers as do flame retarded cellulosics, wool and high performance, aromatic-structured fibres. However, any agent that reduces melt dripping will increase the polymer and textile flammability unless it has an additional flame retarding character. Wang's recent review [76] discusses this need to reduce melt dripping and the challenges that it poses. He and Bourbigot [3] review recent Chinese research that demonstrates a number of recent novel routes for polyester fibres and fabrics. For instance Chen et al [77] have applied intumescent polymeric units such as poly

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concentrations demanded by fibres in general. However, as shown below, there may be opportunities using nanotechnology to partly address these problems.

3.4 Applications of nanotechnology

Recent applications of nanotechnology as a means of improving the flame retardancy and fire performance of fibres and textiles has been reviewed recently by Bourbigot [3, 29] and Horrocks with regard to potential applications [81]. The literature in this area has been substantial during this millennium and there is no intention of repeating the detailed analyses undertaken by the above review authors. With respect to this discussion and the potential commercial viability of research outcomes, the following salient conclusions may be drawn. In Bourbigot’s reviews [3, 29], he demonstrates the potential of the inclusion of nanoparticles into either fibre-forming polymers or into surface treatments and coatings as a means of either adding improved fire performance directly or adding to an already underlying flame retardant property.

The main issues that influence whether or not nanotechnology can be exploited may be considered to include [81]:

- Compatibility of nanoparticles with polymers during and after processing
- Effects on rheology of adding nanoparticles to polymeric extrusion and coating fluids
- Dispersion of nanoparticles during processing
- Levels of flame retardancy or improved fire performance achieved

These may be briefly discussed below.

Compatibility: To achieve an optimal nanocomposite structure the compatibility of largely organophobic nanoparticulates with surrounding polymeric matrices is essential and this is largely determined by the nature of the functionalising groups present on the former.

Functionalised clays, for example, often comprise hydrophobic, long chain aliphatic substituents within the quaternised functionalising complex. Substituents with variously polar

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side groups such as –OH, –NH– or NH₂ will encourage nanodispersion in polar and hydrogen-bonded polymers (eg polyamides 6 and 6.6 and polyvinyl and polyacrylic coating resins).

However and as noted initially by Gilman and coworkers [82], quaternised ammonium salts with aliphatic side chains tend to decompose at temperatures in the 200-250°C region and so will degrade during the compounding and processing of most conventional melt-processed polymers like polyamide 6 and 6.6, PET. However, whether or not this causes nanodispersion problems may be disputed.

Very recent work by Camino and coworkers [83] has studied the effects of thermal degradation on functionalised clays (Cloisite 30B, Southern Clay, Inc., and Nanofil 784, Nanocor, Inc.) under conditions required for PA6 processing by heating them in the range 200-250°C. These clays contain functionalities based on methyl, tallow, bis-2-hydroxyethyl quaternary ammonium chloride and protonated ω -aminododecanoic acid, respectively, this latter being polyamide-reactive. After heat treatment of clays alone up to 250°C, the reactivity of functionalising groups determines their stability with the latter functionalising group being more reactive than the former tallow based moiety. While both preheated clays produce nanocomposite morphologies when polymerised *in-situ*, those containing Cloisite 30B were still exfoliated and more so than for Nanofil 784-containing composites. In fact, following heating at 350°C both functionalised clays enabled only microcomposite formation. These results suggest, therefore, that while functionalities may be thermally labile above 200°C, such decomposition is insufficient to prevent nanocomposite formation when temperatures as high as 250°C are experienced. Melt compounding both clays at 245°C with PA6 produced exfoliated and intercalated morphologies for 30B and 784 clays respectively. Gilman and his coworkers [82] had previously shown that layered silicate nanoparticles functionalised with higher temperature stable groups such as imidazolium derivatives and crown ethers can increase stability to temperatures in the range 262-343°C under nitrogen compared with a typical alkyl ammonium-based salt such as dimethyl dioctadecyl ammonium bromide which starts to degrade at 225°C. Furthermore, stability depends on the

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anion present with halide ions having a destabilising effect, so it is important to remove all halide residue that may contaminate the intercalated product after the ion exchange.

However, given the greater chemical complexity and cost of these, it is probable that both current and future commercial exploitation will involve the simpler quaternised ammonium derivatives.

Effect on rheology: Generally, the addition of a nanodispersed phase will increase the viscosity of a polymer melt under a given shear stress and temperature and shear stress sensitivity may also be increased as has been noted for nylon 6 thus increasing non-Newtonian behaviour [84]. A similar behaviour has been reported by Sihna Ray and Okamoto [85] for molten polylactide (PLA)/layered silicate nanocomposites at 175°C and these changes have implications on processability efficiencies for high throughput processes such as melt extrusion of filaments. Thus, if nanodispersed particles are present, there may have to be an upper limiting concentration determined by the need to compromise between added property and reduced extrusion efficiency. In addition, any increase in melt viscosity will most likely reduce the ease of melt blending, although the associated increased shear stresses at higher extrusion rates may offset this factor and partly restoring process efficiency [86]. In addition to such physical effects, in both poly(ethyleneterephthalate) [87] and nylon 6 [88] sensitised thermal degradation has been reported in the presence of nanoclays.

Not unrelated to the direct effect of clays on rheology is the possible influence that compatibilising species present to improve nanodispersion might have. For example, the use of grafted-PP, especially with maleic acid functionality, can have adverse rheological effects as well as reductions in the final tensile properties of derived fibres [89].

Rheological effects have also been observed in our own laboratories during the formulation of aqueous copolymeric emulsions for use in textile back-coating formulations [62]. Here the addition of either a nanoclay (5% (w/w) Cloisite 15A (Southern Clay products, Inc.,) with respect to coating solids) or fumed silica (up to a maximum of 17% w/w with respect to coating solids) modifies the paste rheology considerably with the latter especially producing

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significant viscosity changes and hence difficulty in maintaining uniform and reproducible coating applications.

Dispersion: Dispersion and morphology of dispersed clays and other particles at the nanolevel are considered to be essential if fire performance properties are to be optimised [90] and so the challenges of optimising nanodispersion and ensuring that it is unchanged during polymer processing may be considerable. Recently reported work from our own laboratories [89] has shown that compounding nanoclay-polypropylene (PP) and nanoclay-graft PP mixtures more than once prior to screw extrusion into filaments, yields improved dispersion and fibre physical properties. Use of a masterbatch of compatibilised clay-graft PP mixtures and its dilution during melt extrusion also improved dispersion sufficiently to be reflected in resulting improved fibre properties and a reduced peak heat release rate of knitted fabric samples. However, whether or not a clay should be fully exfoliated is not clear if maximum levels of reduced fire performance are to be achieved especially in fibre and textile applications.

Levels of flame retardancy or improved fire performance achieved: Bourbigot has recently reviewed in great detail the recent research with regard to the effectiveness or otherwise of introducing nanoparticles to textiles either directly into fibres or on to fabric surfaces [3, 29]. Horrocks has also reviewed those developments that could give rise to potential commercial application in fibres and textile applications [81].

The major difference between textiles, fibres and bulk polymers, is thickness where individual component fibres are typically 15-30 μm in diameter, yielding yarns of 50-100 μm diameter and fabrics having thicknesses varying from as low as 100 μm to several mm.

While reported fire performance based on cone calorimetric data of bulk polymers [91-93] typically shows that the presence of nanoclays reduces peak heat release rates, they more often than not reduce times to ignition and extend total burning periods while affecting little the total heat release of the polymeric substrate. In addition to slowing down the burning process although encouraging more rapid ignition, they also encourage increased char

formation. In fact, in some cases where polymers are not char-formers, some char development has been reported observed [92, 93] and this is of especial importance to extremely thermoplastic and negligible char-forming fibre-forming polymers such as poly(ethylene terephthalate) and polypropylene.

(i) Nanocomposite fibres

Bourbigot *et al* [94, 95] reported the first fire performance studies of nanocomposite polyamide 6 filaments and these were converted into fabric having an area density of 1020 g/m² and thickness 2.5mm. When exposed to 35 kW/ m² heat flux in a cone calorimeter, peak heat release rate (PHRR) was reduced by 33%, ignition resistance was significantly reduced and total heat release was little, if any, affected. However, thermogravimetric analysis suggested that while presence of nanoclay had little effect up to 400°C, above 450°C there appeared higher char formation. It was clear that the fibres were not flame retardant in the more accepted sense in that ignition resistance was not increased by inclusion of nanoclays alone. A further problem with fibres and fabrics with respect to bulk polymers is their high specific surface areas and their thermally thin character. This is significant since Kashiwagi *et al* [96] suggested that the effectiveness of nanoclays in reducing PHRR values and related fire performance may be a function of sample or composite thickness. Thinner samples appear show lower PHRR reductions because of competition between the formation of a surface carbonaceous-silica shield and the volatilisation to fuel of surrounding polymer. In thicker composites, the competition favours ceramic barrier formation while for thin composites, volatilisation dominates [97]. This can be considered as the difference between so-called thick and thin thermal behaviour [98]. In “thin” textile fabrics it is possible that the “shield-forming” mechanism observed for bulk polymer nanocomposites may be too slow for effective improvement in fire performance. It is likely, however, that the thickness effect observed by Kashiwagi and coworkers will be

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influenced by the heat flux since both competing mechanisms are thermally driven but to different extents.

Thus it may be surmised that nanoclay presence alone in fibres, films and textiles will only be significant at lower heat fluxes. More recent work by Bourbigot et al [99] have extended their polyamide research to include nanoclays into melt-spun poly(lactic acid), PLA filaments where again at loadings of up to 4% w/w, reductions in PHRR values as much as 38% and increased char yields are recorded at a heat flux of 35 kW/ m²; times-to-ignition are still reduced, however.

One means of increasing nanoclay efficiency is the possibility of using char-promoting functionalising groups but since these are present at low concentrations within the particle substrate and the functionalised nanoparticles themselves are introduced only at 2-5% w/w loadings, their effectiveness including possible vapour phase activity might be questioned when present at such low (<<1%) levels in the polymer. However, since the thermal stability of the functionalising species during processing significantly affects the resulting nanoclay behaviour as previously discussed [84, 91], and products of group decomposition have been identified [100], possible char-promoting or vapour phase effects at such low levels should not be ruled out.

However, as observed for bulk polymers, combination of nanoparticles with conventional flame retardants may promote overall additive and even synergistic activity [101]. Work in our own laboratories has shown that this is in fact possible, in polyamide 6 and 6.6 films, used as models for respective fibres [102-104]. Normally, minimal flame retardant additive contents of about 15-20% w/w are required to render these polyamides flame retardant [105], levels which are too high for inclusion in conventional synthetic fibres. We have reported both additive and/or synergistic effects of adding selected flame retardants including ammonium polyphosphate (as Antiblaze MCM, Rhodia), melamine phosphate (as Antiblaze NH, Rhodia), pentaerythritol phosphate (as Chemtura formerly Great Lakes NH 1197), cyclic phosphate (as Antiblaze CU, Rhodia), intumescent mixtures of APP, pentaerythritol and melamine (as Antiblaze MPC, Albemarle, formerly Rhodia) into nylon 6,

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and 6.6 polymer films (~80µm thick) in the presence of a commercial and experimental nanoclays (polyamides supplied by RTP Plastics) [102-104]. Of these, ammonium polyphosphate is not only the most synergistic but also has a decomposition temperature in the range 250-300°C and this overlaps the melting point of nylon 6.6 (~265°C). It is considered that this will encourage flame retardant mechanisms to start alongside polymer fusion. The effectiveness of adding nanoclay is shown by the ability to reduced by 25-33 wt% the concentration of APP to create a defined level of flame retardancy. For example, to achieve LOI values up to 24 in nylon 6.6, the addition of nanoclay at a 2 wt% reduced the normally required level of APP to be reduced from about 28.5 to 20.1 wt%.

There have been other attempts to produce nanoclays in the presence of flame retardants in other fibre-forming polymers, such as polypropylene [106] and polyester [78]. In the case of polypropylene, the addition of nanoclay to a flame retardant formulation based on a hindered amine stabilizer and a char-promoting ammonium polyphosphate at concentrations of the order of only about 5% (w/w) does enhance char formation although insufficiently to increase the LOI above 22 vol% [106]. A similar char-enhancing effect of added functionalized montmorillonite clay was observed by Wang et al [78] in a copolymer of poly(ethylene terephthalate) and a phosphorus-containing monomer in that higher residues above 450°C were recorded.

Both Bourbigot's research group [3, 29, 107] and our own [89] have reported work the effect of nanoclays alone. Bourbigot et al. [107] introduced poly(vinylsilsesquioxane (POSS) nanoparticles at 10 wt% loadings in polypropylene from which multifilament yarns and knitted fabrics were produced. Unlike the same group's results for nylon 6 nanocomposite fabrics [92, 93], no reduction in PHRR values occurred relative to the pure fibre-containing samples. However, the time to ignition under a heat flux of 35 kW/m² increases from 21s for the latter to 76s for the POSS-PP fabrics and TGA results indicate that the presence of POSS stabilizes the PP to the initial stages of thermal oxidative degradation. However, other work described the introduction of multiwalled carbon nanotubes at 1wt% into polypropylene filaments and fabrics [108] described both an increase in the thermal stability arising from

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their presence and a 50% reduction in PHRR values when examined by cone calorimetry at 35 kW/m² heat flux. As seen for the earlier nylon 6 fabrics, so here the presence of nanoparticles reduced the time to ignition considerably from 60s to 30s.

Our work considered the effects of nanoclays alone [89] as well as in the presence of more conventional flame retardants [109]. Table 7 presents tensile and flammability data for polypropylene fibres and fabrics containing Cloisite 20A clay, a maleate-grafted polypropylene (Polybond 3200 (Pb), Crompton Corporation) at various concentrations [89]. All polymer samples were twice compounded to maximise dispersion prior to fibre extrusion and sample 5 differed from sample 4 in its having been produced as a more concentrated masterbatch before being let down during the extrusion stage. While it is clear that the presence of nanoclay alone (sample 2) promotes an expected improvement in fibre tenacity and modulus, there is also a decrease in peak heat release rate determined by cone calorimetry at a heat flux of 35 kW/m². Addition of the compatibilising maleate-grafted PP reduces the tensile properties as expected and, apart from sample 3, suggests that it causes further reduction in PHRR values. This is associated with the improved dispersion as shown by TEM. While there was insufficient sample to enable LOI values to be obtained, values for cast films indicated that all samples had values within the range 19.6-20.0 vol% confirming the absence of any flame retarding property.

Subsequent work [109] investigated the effect of introducing selected phosphorus-containing flame retardants ammonium polyphosphate APP (Amgard MCM, Rhodia Specialities, UK), melamine phosphate, NH (Antiblaze NH, Rhodia Specialities Ltd., UK) and pentaerythritol phosphate (NH1197, Chemtura), the hindered amine stabiliser NOR 116 (Ciba) [24] and the bromine-containing tris (tribromopentyl) phosphate (FR 372, ICL, Israel) and tris(tribromophenyl)cyanurate, FR 245 (ICL, Israel) species. These were compounded with selected clays (Cloisite 20A and 30B, Bentone 107, Elementis: a bentonite clay modified with dimethyl, dehydrogenated tallow quaternary ammonium ion and a montmorillonite modified with vinyltriphenyl phosphonium bromide) and compatibilisers (Polybond) Pb and polypropylene grafted with diethyl-p-vinylbenzyl phosphonate (DEP). Extrusion into

filaments proved to be challenging because of problems with optimising clay and flame retardant dispersion and this was especially the case when APP was present because of its very poor dispersion and relatively large particle size (25-30 μm). As a consequence, extrusion of these formulations often resulted in broken filaments and reduced tenacities and moduli. Because of the limited fibre and hence, derived fabric quantities available, either compounder extrudate or tape samples were used for LOI examination. A selection of the fibre/film compositions and their thermal and LOI properties are shown in Table 8.

It is evident that while the melting temperature of the formulations are unaffected by their contents, melt flow indices generally are seen to increase indicating a general reduction in melt viscosity possibly driven by thermal degradation associated with the extrusion process. Given that clays are introduced at nominal 3% w/w, then char yields at 800°C in air, at which most organic components will have oxidised are close to the nominal inorganic residue expected and vary within a range 1.0-3.3% when clay is present LOI values are also unaffected by either the presence of clays and/or flame retardant but then the low concentrations of flame retardants present (5% w/w except for NOR 116 at 1% w/w) would not be expected to raise the LOI values significantly when present alone [24]. However, the burning behaviours of knitted fabrics having the formulations in Table 8 were recorded as times to burn for successive 60 mm distances, (see Figures 1 (a) and (b)), after which ignited samples have been timed for flame fronts to reach 60, 120 and 180 mm when subjected to the standard vertical strip test BS 5438:1989:Part 3. While 100% polypropylene fabrics burnt their entire length quite rapidly, those containing 3% w/w clay alone, showed slightly longer times to reach the 60 mm mark and hence had slower burning rates during the first 60mm of sample. However, only four fabrics (PP, PP-E, PP-Pb-E and PP-Pb-20A) burnt beyond the 60 mm mark and reached the 120 mm mark; of these only pure PP and PP-Pb-E samples burnt the whole length. Thus it might be concluded that either the Polybond compatibiliser or both clays when present have minimal flame retarding activity; in fact the burning rates of PP compared with PP-Pb-E at 180 mm show that the latter has

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the higher burning rate. The results in Figure 1(a) have been converted to rates for each 60 mm length increment and shown in Figure 1(c).

Nevertheless, samples with flame retardants self-extinguished beyond the 60 mm mark and show longer burning times (see Figure 1(b)) and generally lower burning rates. For the Elementis (E) clay-containing formulations, fabric burning rates are in the decreasing order:

PP > PP-E > PP-Pb-E-APP > PP-Pb-E > PP-NOR-Pb-1197 > PP-NOR-Pb-E-FR372

which demonstrates the obvious effect of small amounts of added flame retardant.

Conversely, the order for Cloisite 20A-containing formulations is:

PP > PP-Pb-20A-APP > PP-Pb-20A

which suggests that the presence of APP has a deleterious effect. However, samples also burned differently, depending upon the flame retardant used. For instance, samples containing APP (PP-Pb-20A-APP and PP-Pb-E-APP) burned up to the 60mm mark quickly and within 4s, although the flames flickered quite significantly, probably due to the poor dispersion of APP. Times to reach the 60 mm point are longer and hence rates of flame spread lower for samples containing NH 1197 and FR372 and they self-extinguished beyond the 60 mm mark after 34 and 45 seconds, respectively.

It must be remembered that normally APP concentrations above 20% would be required to render PP flame retarded [24] and so the observation that in the presence of a nanoclay that only 5% can cause marked effects in PP fabrics is encouraging.

Other recent work in our laboratories [110], has shown that fibre-grade poly(acrylonitrile) copolymer when polymerised in the presence of a functionalised nanoclay, may absorb ammonium polyphosphate during filament extrusion and yield fibres having LOI>40 vol%. In these fibres, a clear synergy between nanoclay and flame retardant is observed and filament

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properties are little changed from those acceptable for normal textile applications. Table 9 summarises some of the results of this work which show that the introduction of clays at the 1% level has no effect on tenacity (although the initial Young's modulus increased) and the tensile values are comparable to commercial values (typically in the range 2.3-3.5 cN/dtex). More importantly, they act synergistically with the APP present to yield improved flame retardancy quantified as values of $\Delta\text{LOI}_{\text{nano}}$. Thus it is seen that the addition of Cloisite Na⁺ in particular is effective in raising the LOI by as much as 5 units above that expected from the APP alone at a similar level. Unfortunately, APP is not durable to water soaking or washing and so introduction of a cross-linkable or insoluble flame retardant would be required to achieve required levels of launderability. Notwithstanding this, the evidence is clear that clays in the presence of a suitable flame retardant benefit the overall fire performance of polyacrylic filaments in a manner similar to that observed in polyamide films [102-104].

(ii) Fibre and textile surface treatments, coatings and back-coatings

Examples of the potential for use of nanoparticulate fillers to enhance the fire performance of polymer coatings have largely been restricted to coatings for textile substrates including back-coatings. Bourbigot et al., [94, 95, 107, 111] have shown that addition of nanoclays and poly(silosesquioxanes) can reduce the peak heat release rates in polyurethane-coated on cotton and knitted polyester fabrics as shown in Figure 2. However, the presence of these nanoparticles alone reduced the time to ignition and prolonged the time of burning – exactly the opposite of what is required for flame retarded coated textiles.

As mentioned above, Horrocks et al., [60, 62, 63] have shown that if a back-coating is to be effective it must have a transferable flame retardant activity from the coating on the reverse face of the textile when ignited from the front face in tests such as BS 5852: Part 1 1979 and 1990 and EN 8191 Parts 1 and 2. The use of purely char-promoting flame retardants within

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the coating does not allow this to occur unless the retardant species becomes mobile and can diffuse through the fabric to the front face. Furthermore, the addition of a nanoclay to a back-coating polymeric film has been shown to have no beneficial effect when alone [60]. Furthermore, when fumed (nanoparticulate) silica was added with ammonium polyphosphate to the back-coating formulation not only was there an adverse effect noted with respect to formulation rheology but also the flame retardant character as determined by LOI was reduced with increasing silica content.

Clearly the potential applications of nanocomposites within the coating area, especially with respect to coated textiles, must be questioned based on the present data available and especially in light of the effectiveness of nanocomposites being inversely related to thickness as also discussed above [96].

4.0 Adding value to currently flame retardant systems: smarter flame retardancy

The above review has outlined the challenges that replacing currently accepted flame retardant treatments for textiles and chemical systems for synthetic fibres is indeed a challenge given that these are well-proven and have been able to demonstrate acceptable general and ecotoxicological properties. In spite of their shortcomings in many cases, replacement at equivalent cost will remain an aspiration in the main. However, there is the good possibility that any given flame retardant substrate may have additional fire resisting value added to it by subsequent aftertreatment using surface modification as a most probable means. If such aftertreatments are to have minimal effects on the underlying textile characteristics then we are probably considering surface modifications and even coatings at the microlevel at worst and nanolevels at best. This also introduces the possibility of so-called smart coatings that may in principle applied to any number of different flame retardant fibre and textile substrates. Horrocks has recently reviewed this possibility and an outline of this will be presented here [112].

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A major issue when considering surface flame retardant treatments for fibres and textiles compared with other treatments such as water or soil repellency is the high concentration required. Hence if the level of flame retardancy to be conferred is high in that the underlying substrate is highly flammable like cotton for instance, then the level of flame retardant formulation applied may be within the region of 20-100 wt% with respect to the underlying fabric and the surface treatment will be quite thick and of tens and possibly hundreds of microns. This problem has been more fully analysed elsewhere [112] suffice it to say that not only must such surface coatings render the underlying fibres flame retardant but also the resin matrix in which they are embedded unless it is inherently flame retardant like poly(vinyl chloride), for example.

Thus any novel or smart means of applying flame retardant coatings must be able to achieve such high levels of application – a severe challenge, unless the underlying fibres have a defined level of flame retardancy and the additional surface treatment is adding to this further. Recent reviews [113-116] highlight the possibilities of conferring films and coatings at nanodimensions on to fibre and textile surfaces in order to achieve high levels of novel effects such as hydrophobicity, soil release, self-cleaning, bioactivity, etc. Methods cited include:

- self-assembly of nanolayer films [114]
- surface grafting of polymer nanofilms [115], and
- synthesis of smart switchable hybrid polymer nanolayers [115, 116]

Even assuming that the conferred nanofilms possessed the required flame retarding functions and efficiencies of conventional coatings, it is likely that none of these will be relevant to the present argument because of the need to achieve high loadings for flame retardancy. The possibility does exist, however, of reducing coating thickness while retaining overall constant levels, if the coating, instead of being applied on textile surfaces is applied only to component fibre surfaces. In the case of the application of fluorocarbons at about 0.6% w/w to a typical polyester fibre of 10dtex (~30 μ m diameter), the surface layer thickness

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is calculated to be above 50nm [113]. At microfibre dimensions ($\sim 10\mu\text{m}$ diameter), the surface layer thickness on the increased fibre surface area reduces to about 10nm and at sub-microfibre dimensions, even thinner films are theoretically possible. However, flame retardant coatings will be required to be present at ten to twenty times these fluorocarbon concentrations yielding much thicker theoretical film thicknesses as well as problems associated with interfibre adhesion and occlusion of fibre interstices unless, of course they are adding only an incremental level of retardancy to an existing level. Thus if such potentially novel fibre surface treatments are to be useful, they must confer an effect disproportionate to their thickness and level of application.

Notwithstanding the above discussion, there are the possibilities of gaining some degree of heat and fire protection using coatings or films applied at the nanolevel if they are not seen to be simple replacements for conventional flame retardant coatings. In normal flame retardant textiles and coated fabrics which may be classed as thermally thin materials [98] unless they are quite thick ($>3\text{-}5\text{mm}$), the ability to form a thick, surface insulating char is limited and the underlying fibres soon reach temperatures approaching that of the igniting source ($>500^\circ\text{C}$) when they degrade and may ignite. Even the most inherently flame resistant fibres such as the poly(meta- and para-aramids), poly(benzimidazole), semicarbons, etc., [12] are only able to offer a thermal barrier during sustained high heat exposures for limited periods.

However, if we are able to convert a thermally thin textile into one showing so-called thermally thick behaviour, its overall fire protective character will increase and many conventional surface treatments and coatings, especially those comprising intumescent additives, attempt to do this. It is highly unlikely that nanocoatings could promote a similar effect unless they could offer a heat shield property of unusual efficiency.

In the area of heat protective textiles [117], use is made of the deposition of reflective metal films on to fabric surfaces to reduce the effects of heat radiation from a fire source and it is in this area that nanofilm and nanocoating deposition may have opportunities.

Plasma technology and its potential: Plasma technology offers a means of achieving the means of developing novel nanocoatings having the desired thermal shielding effects, although the literature is sparse with regard to reported examples. Shi has demonstrated that low pressure, radio frequency discharge plasma treatment of a number of polymer surfaces including poly(ethylene terephthalate) in the presence of gaseous (CF_4/CH_4) leads to flame retardation [118]. Later studies in which ethylene-vinyl acetate copolymers were plasma-exposed for times up to 15 minutes followed by immersion into acrylamide, gave very high yields of surface grafted poly(acrylamide) and LOI values approaching 24 vol% at 47w/w% grafting levels [119]. The more recent studies of low pressure argon plasma graft polymerization by Tsafack et al [120, 121] have reported the successful grafting of phosphorus-containing acrylate monomers (diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl)phosphonate (DEAMP) and dimethyl(acryloyloxymethyl)phosphonate (DMAMP)) to polyacrylonitrile (PAN) fabrics (290–300 g/m²). In the presence of a grafting agent, ethyleneglycoldiacrylate (EGDA), graft yields were optimized (as high as 28% w/w) resulting in limiting oxygen index values as high as 26.5 vol%, although after accelerated laundering this reduced to 21 vol %. This and Shi's techniques would not be expected to provide nanofilms since this type of grafting may be perhaps best considered as a variation of established polymer surface and textile-grafting procedures [122] and the high yields (28% w/w in the case of grafted DMAMP, $\text{CH}_2=\text{CH}.\text{CO}.\text{O}.\text{CH}_2.\text{P}(\text{CH}_3)_2$) would explain both the level of flame retardancy but poor launderability achieved. When extended to cotton (120 and 210 g/m²), low pressure argon plasma graft polymerisation of these same acrylate monomers [123], again yielded grafted fabrics having elevated LOI values as high as 26.0 vol% in the case of DMAMP. However, even higher and more acceptable levels of flame retardancy were achieved only if synergistic nitrogen was also present in grafts which they demonstrated following the grafting of the phosphoramidate monomers, diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) and acryloyloxy-1,3-bis(diethylphosphoramidate)propan (BisDEAEPN). These yielded LOI values of 28.5 and 29.5 vol% respectively at levels of 38.6 (=3.36%P) and 29.7

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(=3.29 %P) w/w %. Launderability was improved when the cross-linking agent, EGDA, was present at high concentration and, in the case of BisDEAEPN, after a simulated laundering, graft level reduced to 26.7 w/w % and LOI reduced to 25.0 vol%. The improved durability achieved here is probably associated with the greater reactivity of the plasma-activated cellulose chains compared with those generated on PAN fibre surfaces. While no grafted film thicknesses have been reported, they are probably within the micron range and not the nanometer range.

The possibility that plasma deposition of silicon-based films might improve the flame retardancy of underlying polymer surfaces has been reported by Jama et al. [124]. Here normal and nanocomposite polyamide 6 films were activated by a low pressure (4.2 mbar) cold nitrogen plasma and then transferred to a reactor containing 1,1,3,3-tetramethyldisiloxane (TMDS) vapour in an oxygen carrier gas for 20 minutes. This remote plasma-assisted polymerization is similar to that used by Tsafack et al. above except that the monomer is in the vapour phase prior to polymeric deposition. Thermogravimetry shows that increasing the oxygen flow rate considerably increases the thermal stability in air of deposited coatings as the increasingly oxygenated polysiloxane coating transforms to a silica-based structure at about 800°C. This gives the opportunity for a thermal barrier effect coupled with a moderate increase in flame retardancy of a coated polyamide 6 film and a surprising increase in the flame resistance of the nanocomposite polyamide 6 films, with LOI values exceeding 45 vol% for the latter. Clearly this rise in LOI is impressive given the low levels of surface polymer present. Char residues mirror respective LOI trends with the former rising from zero with no plasma deposition, through to 53 and 75 residual weight percent (from TGA in air) as the LOI respectively rises from about 23, through to about 47 vol%. Analysis shows that those from the coated nanocomposite films are largely silica-based while those for coated normal polyamide 6 films are essentially polysiloxane-like. The presence of the nanoclay at 2% w/w appears to have synergized the formation of silica from the plasma-generated coating. The thermal barrier efficiency of the coated nanocomposite films is demonstrated by cone calorimetric analysis under an incident heat flux of 35 kW/m².

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Here the peak heat release rates (PHRR) of plasma –coated nanocomposite films are reduced in intensity by 25% compared to the uncoated films. A subsequent paper [125] demonstrates that on scaling up the experiments using a larger low pressure plasma source and reactor, thereby enabling larger and more consistently coated samples to be produced. Of particular interest to the present discussion is that the film thicknesses obtained in the earlier and smaller reactor were about 48µm in thickness whereas those from the larger reactor reduced to only 1.5µm thickness and coated nanocomposite polyamide 6 films continued to yield LOI values as high as 48 vol%. Furthermore if film thickness was increased above 1.5 µm, LOI reduced to a constant value of about 42 vol%. Once again, cone calorimetry showed that PHRR values were advantageously reduced compared with uncoated nanocomposite films (PHRR = 1972 kW/m²) showing an expected reduction of 44% with respect to normal polyamide films (PHRR = 1102 kW/m²) and the additional coating reduced PHRR by a further 59% to a value of 807 kW/m². Analysis of residues after cone calorimetric exposure showed that the coated nanocomposite film transforms to a silica-like structure and it is this that creates the thermal shielding effect.

Very recent work in our own laboratories has led to a patented process [126, 127] in which using atmospheric plasma we have demonstrated that the flash fire resistance of a conventionally flame retarded fabric may be improved by surface treatment in the presence of nanoparticulates and a silicon-containing monomer such as hexamethylene disiloxane (HMDSO). Table 10 shows the changes in cone calorimetric behaviour of a 200 gsm woven meta-aramid fabric subjected to an argon plasma alone and the plasma in the presence of a silicon-containing monomer, a nanoclay alone and a combination of silicon-containing monomer and nanoclay. The fabric alone failed to ignite when exposed at the more typical heat flux of 50 kW/m² but did ignite when exposed at 60 kW/m². Flash fire testing is usually associated with heat fluxes of 80 kW/m² [128] or more and this level was not achievable by our equipment. The results show that even after argon plasma treatment alone, slight increases in both the time-to-ignite (TTI) and time-to-peak heat release (TTP) are observed with a similarly slight reduction in peak heat release rate (PHRR). The loss of mass is

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associated with the effect of surface ablation following plasma treatment. When any of the combinations of silicon-containing monomer and nanoclay are introduced, the fabric becomes non-ignitable under a 60 kW/m² heat flux. The effect of additional components gives rise to either reduced mass loss or an actual increase in sample mass as would be expected if a surface layer were being deposited. Clearly the already high heat flux ignition resistance of the meta-aramid fabric is being significantly improved following plasma treatment. Increasing the incident heat flux to 70 kW/m² causes untreated and treated fabrics to ignite but the presence of the plasma treatment reduces PHRR values both before and after a simulated laundering. Figure 3 shows the heat release curves for simulated laundered samples. PHRR values reduce from 119 to 113 for HMDSO only, 109 for clay-only and 99 kW/m² for HMDSO/clay samples immediately following plasma treatment. After simulated washing, PHRR values show similar reductions from 111 to 107 for HMDSO and clay-only and to 80 kW/m² for HMDSO/clay samples after plasma treatment. Clearly the effects have a level of durability in spite of their surface character.

The advantage of this method is that in principle it may be applied to any textile substrate retrospectively and so offers great opportunity for enhancing the heat and fire resistance of a range of textile substrates.

It should be noted that plasma technological modification of fibre and textile surface has a history spanning about 40 years and although it has gained commercial significance within industrial sectors such as microelectronics and more recently in improving paint/coating adhesion to plastics for automotive and other applications, its adoption by the textile industry has been slow [129]. One of the main reasons for this is that the majority of successful plasma applications occurred using low pressure plasma and it is only recently that atmospheric pressure plasma technologies have been developed which are considered to be more appropriate to continuous processing of textile fabrics [130]. The desire to use atmospheric pressure plasma increases further the challenge of achieving high levels of surface deposition since plasma polymerization can be best controlled in low pressure plasmas which have more well-defined plasma zones [131]. Hegemann [132], also states

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the preference for low pressure plasma systems, at least at the research level, because the greater mean free paths of ions within such plasma enable greater penetration depths within textile materials, hence the potential for more cohesive nanocoatings. Furthermore, plasma metallization sputtering techniques, currently used to confer conductive nanolayers on textile surfaces, but with the potential for thermally reflective coating deposition, favour the use of low pressure plasmas. However and notwithstanding these arguments, it is most likely that any commercial plasma process acceptable for the textile industry will have to be based on atmospheric pressure technologies and so future research efforts should be cognizant of this requirement, especially given that the established non-thermal plasma processes previously feasible at low pressures have been successfully transferred to atmospheric pressure conditions as evidenced by the current (2007) range of Dielectric Barrier Discharge, arc-jet, microwave and hybrid sources available [129, 133].

Conclusions

It is evident that while there is continuing work to develop new flame retardants based on new chemistry taking place, especially within the cellulose cotton and polyester areas, reflecting the respective commercial importance of both these fibres, replacement of established flame retardant systems is still some time away unless legislation or regulations restrict the use of some current examples. The desire to reduce and even eliminate formaldehyde-releasing characteristics from the more commonly used durable, commercial flame retardants for cotton and the efforts in creating char-forming, flame retardant polyester are still goals yet to be realised. Even if success is achieved at the research scale, development and commercialisation of any truly new chemistry will be a significant challenge, not least because of the major toxicological and ecotoxicological regulatory hurdles posed by major political groupings such as the EU and USA where currently the main customer bases for flame retardant fibres and textiles are located. However, this is not to say that new flame retardants based on currently known and understood chemistry will not

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come to the fore within the near future and prime interest will continue to lie in adding value to or modifying currently established flame retardant fibres and textiles. The replacement or reduction in usage of halogen-based retardants offer opportunities in this respect in that other non-halogen-containing species, previously deemed to having been technically and commercially less feasible may now become of interest. In particular, the application of appropriate nanotechnology (eg nanoparticle – flame retardant synergies) not only offers the opportunity of improving current flame retardant systems but also the creates the potential for new flame retardant formulations based on currently known as well as novel chemistries. For example, the beneficial effects of introducing nanoparticles into fibre-forming polymers prior to extrusion to improve resulting fibre fire performance in the presence or absence of other flame retardant moieties is certainly proven in the literature although commercial exploitation has not occurred at the present time.

Finally, there lies real opportunity in enhancing the already present flame retardant properties of currently available fibres and textiles by surface treatment. While surface copolymeric grafting of fibre surfaces has been investigated for over 30 years and not found successful commercial development because of the largely poorly adhered and physically unstructured surface polymers formed, the more recent development of surface modifying techniques such as atmospheric plasma and introduction of nanoparticles into fibre surfaces have been shown to add significant fire resisting properties.

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Table 1: Principal examples of currently available flame retardant treatments for textiles based on 1950-80 chemistry [1,2, 4].

Substrate textile fibre(s)	Generic formula	Comments
Cellulose (cotton, viscose and cotton-rich blends)		
<i>Non-durable</i>	Ammonium phosphates and mixtures with other salts, eg ammonium bromide and sulphamate Ammonium polyphosphates Guanidine phosphates Organophosphorus oxyanion salt Organic nitrogen-containing compounds Organic N- and P-containing compounds Borax Combinations of the above	Available as proprietary formulations; semi-durability may be developed by post-curing to achieve cellulose phosphorylation; addition of resins
<i>Durable</i>	Tetrakis (hydroxymethyl) phosphonium salt (THPX) adduct condensates N-methylol and N,N'-dimethylol dialkyl phosphonoproprionamides and derivatives	Typified by the ammonia-cured Proban® (Rhodia) Exemplified by Pyrovatex® (Ciba/Huntsman) its variations and equivalents. Requires presence of cross-linking resins
Back-coatings (application to most textile substrates)	Halo-organic-antimony III oxide (ATO) formulations (eg decaBDE/HBCD) Intumescent-based systems for back-coatings	Durability is determined by resin choice
Wool: durable to dry cleaning	Zirconium and titanium hexafluoride complexes Tetrabromophthalic anhydride (TBPA)	Typified by Zirpro® Maybe used alone or with Zirpro® to reduce afterflame times
Polyester: durable	Cyclic organophosphonate $(\text{CH}_3\text{O})_{2-n}\text{-P}\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 \end{array}\right)\left[\text{OCH}_2\text{-C}\left(\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{O} \\ \text{CH}_2\text{O} \end{array}\right)\text{P}(\text{O})\text{CH}_3\right]_n$	Based on Antiblaze 19 (Formerly Mobil) and subsequently Antiblaze or Amgard CU (Rhodia) applied by thermofixation
Polyamide: durable	N- and S-containing polycondensates typically based on thiourea derivative-formaldehyde formulations	Find application in technical fabrics
Acrylics and multifibre blends and composites (eg furnishing fabrics)	Back-coatings based on halogen-ATO formulations	The only commercial alternatives to using modacrylic fibres, eg Kanecaron

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Table 2: Inherently flame retardant man-made fibres based on 1950-80 chemistry currently in use [22-24]

Fibre	Additive or comonomer	Comments
Viscose rayon	Cyclodithiophosphoric anhydride additive (2, 2-oxybis (5,5 - dimethyl -1, 2, 3-dioxaphosphorinane - 2,2 – disulphide)	Developed in the 1970s now available as Clariant 5060
Modacrylic	15-65% vinylidene (or vinyl) chloride	Developed in the 1950s and still produced in Japan; eg Kanecaron
Polyester	Difunctional phosphinic acid or ester, HO.P(O)R.X.COOH, where R = CH ₃ and X = CH ₂ .CH ₂	Developed by Hoechst in the 1970s as Trevira CS®: the most established inherently flame retardant polyester
Polypropylene	Halo-organic-synergist (ATO or tin derivatives) formulations	Recent developments of hindered amine chemistry enable single halo-organics to be used (eg tris (tribromoneopentyl) phosphate

Table 3: Comparison of the strengths and weaknesses of tetrakis(hydroxymethyl) phosphonium salt condensate- and N-methylol N, N' dimethylpropionamide derivative-based flame retardants for cotton [1,2]

Flame retardant	Advantages	Disadvantages
THPX condensates	Durable to over 100 75°C (hospital) washes Minimal losses in fabric tensile and tear properties No reported significant emissions of formaldehyde in use	Requires specialist ammonia gas cure unit Can react adversely with some dyes eg sulphur May require softeners to improve fabric handle
N-methylol dimethylpropionamide derivatives	Durable to over 100 75°C (hospital) washes in the absence of bleach only Applied by normal pad-cure methods Compatible with all dyes, hence ideal for prints	Significant losses in tensile (typically up to 20%) and tear (up to 50%) strengths Often forms tarry deposits in curing plant Poor abrasion resistance Formaldehyde release is a problem during application and end-use Autocatalytic hydrolysis during storage releases formaldehyde Cannot be used in sensitive applications such as children's nightwear

Table 4: Flammability testing results of back-coated cotton and polypropylene fabrics after a 40°C water soak treatment [62, 63]

Formulation (dry units FR with 100 dry units resin)	Fabric	Dry add- on, %	Simulated BS 5852	LOI, vol%	Comment
NH-1197 (250)	Cotton	41	-	26.1	
NH-1197 (250)	PP	64	-	22.4	
NH-1197 (200) TBP (50)	Cotton	37	Pass	26.7	
NH-1197 (200) TBP (50)	PP	57	Fail	21.5	Visual observation suggests near to pass
NH-1197 (150) TBP (100)	Cotton	52	Pass	26.3	Char length greater than 200:50 analogue
NH-1197 (150) TBP (100)	PP	66	Fail	22.4	
NH-1197 (200) TPP (50)	Cotton	49	-	26.7	
NH-1197 (200) TPP (50)	PP	53	-	21.5	
NH-1197 (150) TPP (100)	Cotton	104	-	26.4	High add-on is a consequence of agglomeration of solids

Table 5: Back-coated fabric LOI values and loss of phosphorus (ΔP) from chars [62, 63]

Flame retardant/ dry parts by weight	Initial add- on, %	LOI, vol%	ΔP , %			
			300°C	400°C	500°C	600°C
Antiblaze MCM/250	13.9	23.2	0.41	1.35	4.93	3.07
Antiblaze NH/250	11.0	20.8	-0.16	-0.24	0.9	1.87
AmgardCU/250	11.9	26.3	1.91	4.77	10.51	23.95
Fyrol 51/250	16.6	26.1	1.62	2.78	7.64	7.59

Table 6. Durability Results and Flammability Testing (before and after water soak) [63]

	Add-on (%)	LOI (vol%)	Add-on retention after soak (%)	Indicative BS5852 “match” Source 1 test after water soak; Ignition time	
				10s	20s
APP / Mel	52	27.1	75	x	-
APP / Mel / CU	37	27.9	52	x	-
APP / Mel / F51	52	29.6	65	√	x
APP / Mel / TBP	43	28.6	78	x	-

Note: “√” denotes a pass, “x” denotes a fail and “-“ denotes no test undertaken

Table 7. Polypropylene fibre compositions and tensile properties and fabric PHRR values [89]

Sample	Nanoclay, 20A (% w/w)	Graft, Pb (% w/w)	Linear density (tex)	Modulus (N/tex)	Tenacity (cN/tex)	Fabric area density (g/m ²)	PHRR (kW/m ²) at 35 kW/m ² heat flux
1	0	0	4.9 ± 0.3	4.1 ± 1.3	32.6 ± 2.5	430	525 ± 40
2	2.5	0	4.0 ± 0.8	5.6 ± 1.6	36.4 ± 8.0	400	477 ± 105
3	2.5	1	4.3 ± 0.9	3.7 ± 1.1	22.0 ± 6.0	390	531*
4	2.5	3	4.5 ± 0.1	3.4 ± 0.8	16.9 ± 7.0	430	420 ± 90
5**	2.5	3	3.9 ± 0.4	5.2 ± 0.8	26.3 ± 8.2	390	394*

Note: * only one sample tested; ** sample 5 is produced as a concentrated masterbatch before being let down during extrusion to yield the stated additive concentrations

Table 8 Selected combinations of clay, compatibiliser and flame retardant in polypropylene (PP) filaments and tapes [109]

Sample**	DSC melting peak max., °C	Char yield at 800 °C from TGA, %	MFI, g/600s	LOI vol%
PP	164	0.	25.9	19.2
PP-20A	165	2.0	35.4	----
PP-Pb-20A	165	1.7	26.4	20.2
PP- Pb - 20A - APP	166	3.0	31.2	20.6
PP-E	166	1.6	38.4	20.5
PP-Pb-E	167	3.3	39.4	20.3
PP-Pb-E-APP	168	3.2	24.6	20.6
PP-NOR-Pb-E	167	1.0	33.7	17.5*
PP-NOR-Pb-E-APP	168	3.2	24.0	17.8*
PP-NOR-Pb-E-NH	168	2.9	27.0	17.9*
PP-NOR-Pb-E-1197	168	2.2	34.8	17.8*
PP-NOR- Pb-E-FR245	167	2.5	36.0	17.2*
PP-NOR-Pb-E-FR372	166	1.0	38.4	18.7*

Notes : * LOI samples are course filaments form the compounder

**20A, E = Clays, 3% w/w

Pb = Polybond (maleic anhydride grafted PP), 1% w/w

NOR 116 present at 1% w/w

Flame retardants APP, NH, NH1197, FR245 or FR372 present at 5% (w/w).

Table 9. Tensile and limiting oxygen index properties for experimental polyacrylic filaments containing 1% w/w of either Cloisite Na⁺ or 30B clays subjected to ammonium polyphosphate treatment in bath phosphorus, P_L, concentrations 1-6% [110]

	Tenacity, cN/dtex	P _L (nominal), % w/w	P _F , % w/w	Δ P _F , % w/w	LOI, vol%	ΔLOI/P _F	ΔLOI nano, vol%
	2.6						
Dope- blended samples		0	0.0	-	19.0	0.0	-
		1	1.2	-	21.0	1.2	-
		3	3.5	-	26.0	2.0	-
	Control (Courtelle)	6	6.5	-	36.0	2.6	-
Cloisite Na ⁺ , 1%	2.5	0	0.0	0	20.4	0.0	1.4
		1	1.5	0.5	21.8	0.9	0.8
		3	4.4	0.9	31.0	2.4	5.0
		6	6.8	0.3	41.0	3.0	5.0
Cloisite 30B, 1%	2.7	0	0.0	0	19.0	0.0	0.0
		1	1.8	0.6	21.8	1.6	0.8
		3	4.3	0.8	30.0	2.6	4.0
		6	6.5	0	36.6	2.7	0.6

Notes: Notes: P_L = % w/w phosphorus in liquor; P_F = % w/w P on fibre; Δ P_F = (P_F nano – P_F control); ΔLOI_{nano} = (LOI_{nano} – LOI_{FR control})

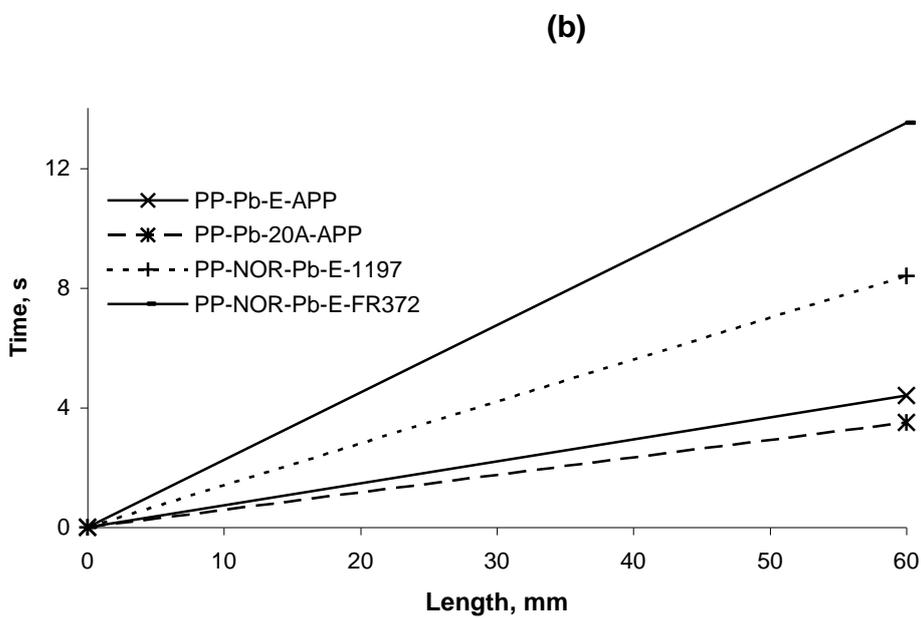
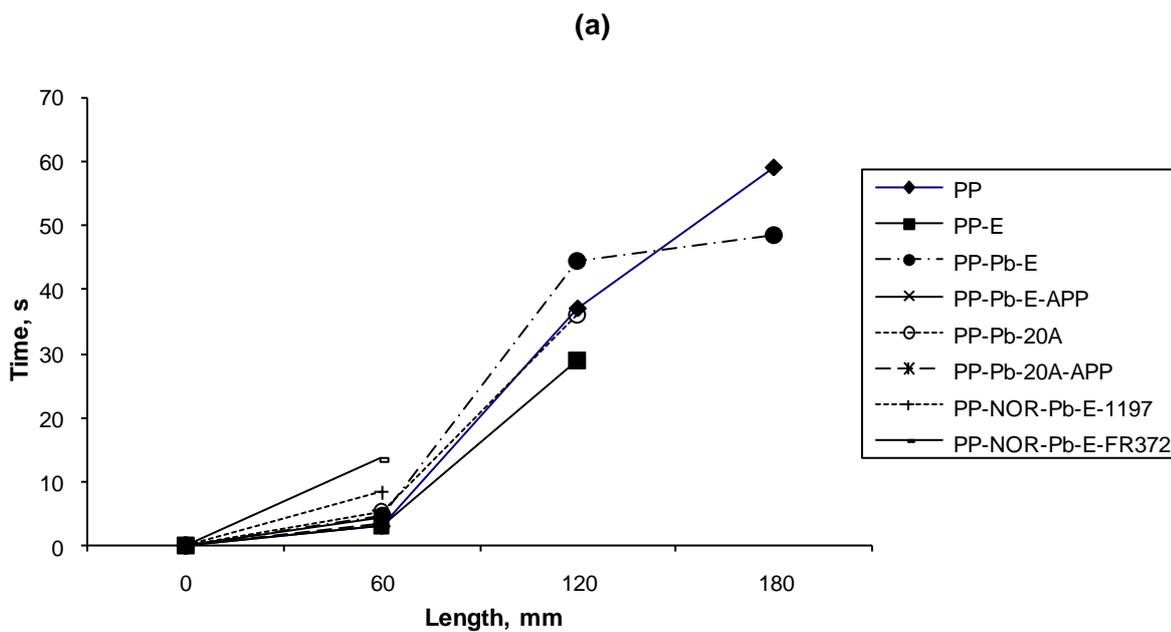
“Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions”, A R Horrocks, Poly Degrad Stab., 96, 377-392 (2011)

“Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions”, A R Horrocks, Poly Degrad Stab., 96, 377-392 (2011)

Table 10: The cone calorimetric behaviour of m-aramid-containing fabrics exposed to 60 kW/m² heat flux after subjecting them to various atmospheric plasma treatments [126, 127]

Sample and treatment	Mass change, %	Time-to-ignition, TTI, s	Time-to-peak heat release, TTP, s	Peak release rate, PHRR, kW/m ²
Meta-aramid alone	-	13	16	83
Argon plasma only	-2.8	16	20	73
Argon plasma with silicon-containing monomer (HMDSO)	-0.6	NI*	-	-
Argon plasma with nanoclay	1.6	NI*	-	-
Argon plasma with silicon-containing monomer and nanoclay	3.5	NI*	-	-

Note: NI indicates that the sample did not ignite.



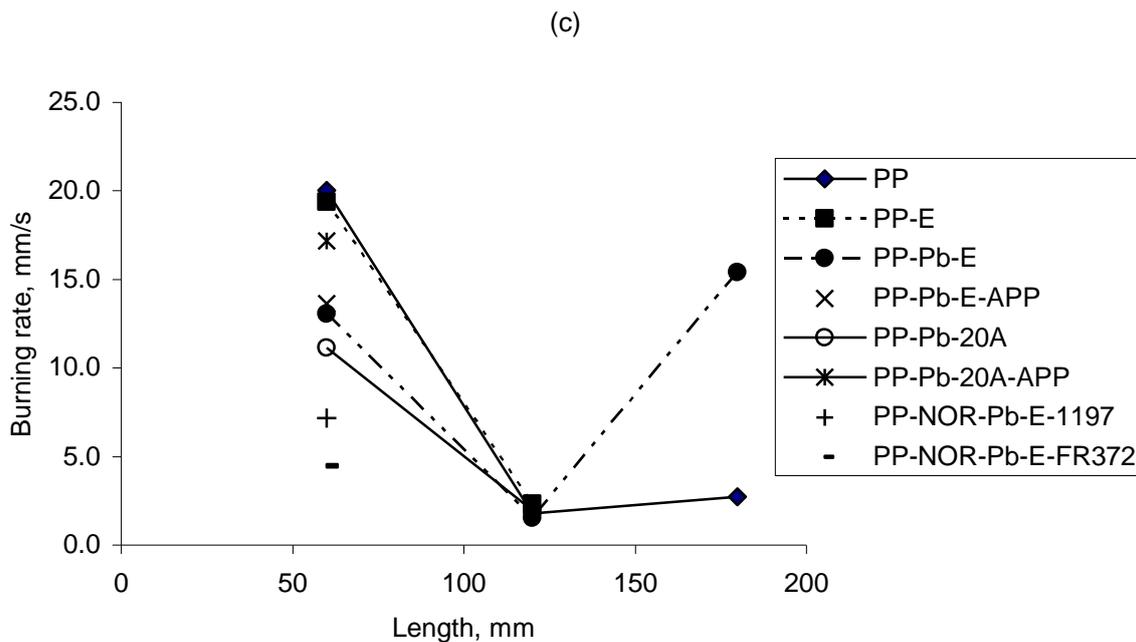


Figure 1: (a) Times to burn (BS5438:1989:part 3), b) times to burn for the first 60 mm only, and (c) burning rates versus fabric distance burned for polypropylene fabric samples comprising clays, compatibiliser and flame retardants listed in Table 8 [109]

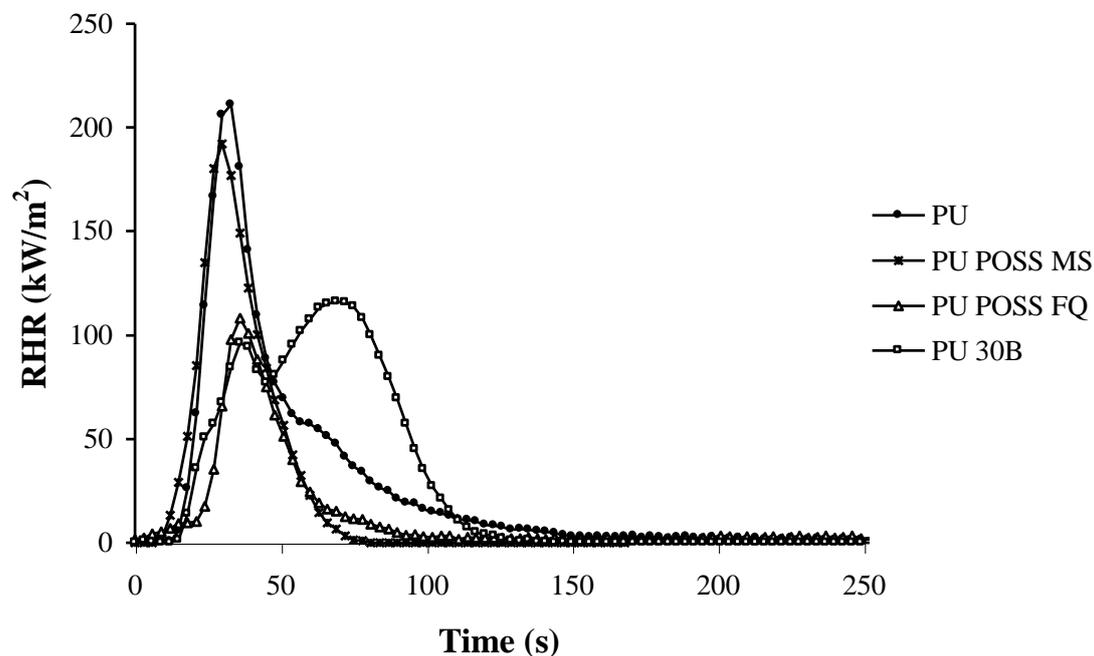


Figure 2: Rate of heat release curves of polyurethane (PU)-nanocomposite coatings on PET knitted fabric samples at 35 kWm⁻² treated with an octamethyl POSS (POSS MS), a poly(vinylsilsesquioxane) (POSS FQ) or a nanoclay (Cloisite 30B) at 10% loadings with respect to PU [94, 111]; (Copyright John Wiley & Sons Limited.)

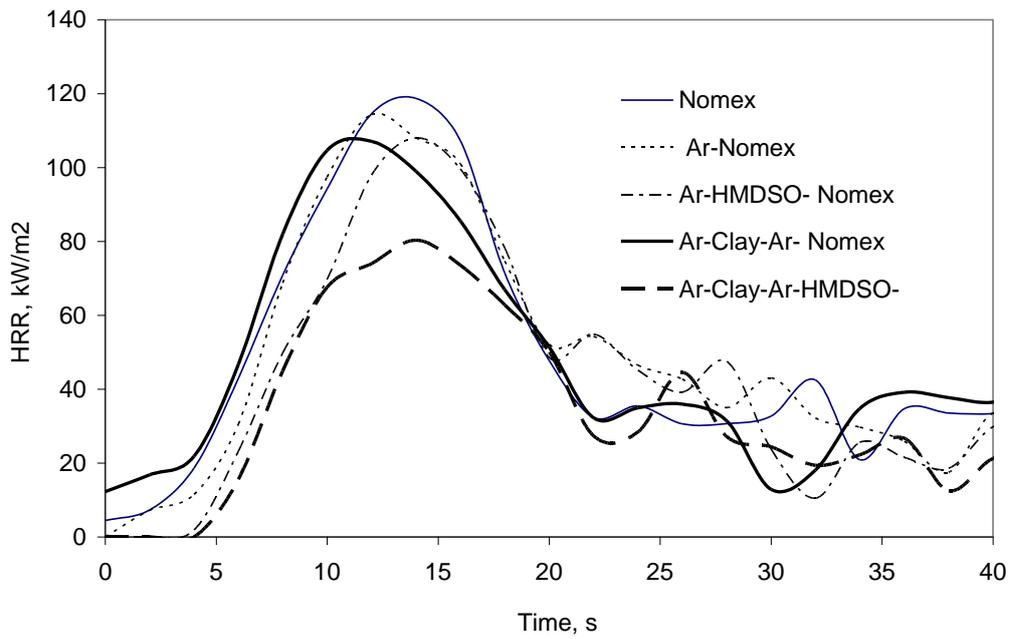


Figure 3: Heat release rate curves for plasma-treated Nomex cotton fabrics after a simulated washing treatment at 70 kW/m² heat flux in cone calorimeter [126].