

Review article

Developments in flame retardant textiles – a review

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Received 15 September 2003; accepted 1 October 2003

Available online 26 November 2004

Abstract

The many, and varied flame retardant chemistries researched, and developed during the 1950–1980 period for improving the fire performance of both natural and chemical fibres have not been significantly added to during the last 25 years or so. This is a consequence of increasing commercial demands in terms of cost-effectiveness coupled with increasing concerns for the environmental and general toxicological character of these materials, and treatments. The only real exception to this is the recent inclusion of functionalised nanoclays into polymers which has been found to improve fire performance in terms of reduced peak heat release rates.

This review considers recent developments which have tried to increase the efficiency of known chemistry to enhance char formation by intumescent action on the one hand with the effect of inclusion of nanoclays on the other. Consideration is also given to recent attempts to replace antimony–bromine formulations in textile back-coatings by phosphorus-based species.

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Keywords: Flame retardant; Char; Nanoclay; Nanocomposites; Intumescent; Textile; Fibre

1. Introduction

Most flame retardant treatments, formulations, and additives were derived from chemistry developed in the 1950–1980 period [1], and those having current commercial interest, have been very recently reviewed [2,3]. Since this time, increasing concerns over the toxicological and environmental consequences of using such chemical species on textile substrates which have high specific surface areas, and close contact with the skin, have created a barrier to the development, and applications of new chemistry. Therefore, during the last 20 years or so, reaction to these concerns coupled with the perceived need for enhanced flame retardant performance at an acceptable cost, has caused both research scientists and industry to consider enhancing the efficiency of presently used retardants, replacement

of those where concerns lie with other existing formulations or by using known chemistry in novel ways.

This paper provides an overview of a number of areas of present interest, and recent research, particularly that undertaken in our own laboratories, that attempts to address these. Notable issues include the continuing interest in enhancing char-forming efficiency [4], both by the search for durable intumescent systems which through expanded char formation, increase thermal barrier properties, and invoking nanoparticle presence to assist this same process. In addition, the increasing pressures to replace both antimony–halogen systems in textile back-coatings and formaldehyde-free treatments in durable finishes are discussed.

2. Enhanced char formation

2.1. Substantive intumescent

Considerable work has been undertaken since the early 1990s to investigate the behaviour of intumescent

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in textile structures [4], and our own work, in particular, has demonstrated that certain intumescent-flame retardant fibre combinations produce enhanced chars of improved fire performance [5–12]. However, a major drawback of these systems is that even the most water insoluble intumescent cannot survive textile laundering processes. If, therefore, intumescent are to be successful in fibre and textile applications, they must be either bonded into a hydrophobic resin which assures their wash durability or they are substantive to the textile fibre molecular structure. As a consequence, attempts to develop substantive intumescent treatments for cellulose, flame retarded cellulose, polyamides 6, and 6.6, and wool have been intensively researched since 1999 with varying degrees of success. This work is reviewed below.

Fibre-substantive intumescence requires that:

- (i) the intumescent moiety within the fibre structure is a single molecular species; or
- (ii) the fibre functions as one of the intumescent components.

With regard to (ii), fibrous substrates like cellulose, and to a lesser extent nylon 6.6 are char-formers or cross-linkers, and when heated may form a part of the overall intumescent activity.

Halpern et al. [13] have demonstrated that by reacting spirocyclic pentaerythritol diphosphoryl chloride (SPDPC, structure I in Fig. 1) with melamine, a single intumescent molecule may be synthesised. More recently Ma et al. [14], have incorporated SPDPC as a comonomer in selected polyesters, and demonstrated its char-forming activity in these thermoplastic polymer matrices.

We have extended these ideas to demonstrate that polyol phosphoryl chlorides will substitute active hydrogens in fibre-forming polymers to confer inherent intumescence, and review this work below [15–19].

Active hydrogen sites substituted to date are those in cellulose at primary (C6 position) and secondary hydroxyl (C3 and C4 positions) groups [16,17], some durably flame retarded cellulosic fibres contain functional groups such as secondary amines [17,18] and amine groups in wool and polyamide fibres [19]. For the linear polyamides, nylon 6, and 6.6, for which no effectively durable flame retardant exists when in fibre form, and which are thermoplastic, this is especially relevant.

Based on our initial studies [15], and subsequent work in this project, SPDPC has been shown to transfer its intumescent properties onto cellulosic fibres following their phosphorylation [16]. A feature of SPDPC is the six-membered cyclic phosphate structure which contributes to its high yield during synthesis, and its general stability apart from its tendency to form char when heated. However, its relatively large molecular size may prevent its effective diffusion into fibrous substrate microstructures, and so we have also reported 1,3-propanediol, and its derivative, 2,2-diethyl-1,3-propanediol, as possible alternatives to pentaerythritol as the polyol [17]. Phosphorylation of 1,3-propanediol derivatives should give rise to six-membered ring cyclic propanediol phosphoryl chloride or CPPC (Fig. 1), and its derivatives [16]. Hence, cyclic 1,3-propanediol phosphoryl chloride (CPPC) (or 2-chloro-2-oxo-1,3,2-dioxaphosphorinane), and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) (or 2-chloro-5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinane) have been synthesised (see Fig. 1) [17].

Reactions of SPDPC, CDPPC, CPPC, and cellulosic substrates were carried out in dimethylformamide, DMF in a flask under reflux at various mass ratios, and the preferred reaction temperature of 160 °C [15–17,20]. Table 1 shows that the Proban-treated cotton sample can be more easily phosphorylated than

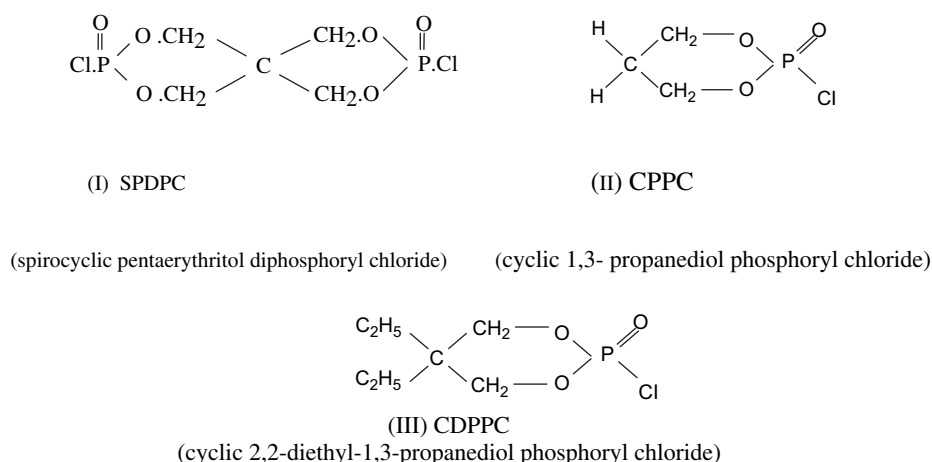


Fig. 1. Full names and structures of SPDPC, CPPC, and CDPPC.

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