

Materials engineering for surface-confined flame retardancy



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ABSTRACT

Polymer materials flammability represents a major limitation to their use and hence to the development of most polymer-based advanced technologies. Environmental and safety concerns are leading to progressive phasing out of versatile and effective halogen-based fire retardants which, so far, ensured a satisfactory polymer fire hazard control.

Among the intensive efforts which are being made to develop new, environmentally safe, polymer fire protection approaches, the recognition of the paramount role played by the polymer surface during combustion and the exploitation of the new nanotechnologies developed for polymer surface engineering offer a promising perspective for polymer fire retardance. Indeed, heat transfer to the polymer and diffusion to the gas phase of polymer degradation combustible volatiles, which both fuel the combustion, occur across the polymer surface which characteristics regulate the polymer combustion process.

It is shown that by engineering the polymer material surface by intumescent coatings or layer by layer nano-deposition or by oxidic nanostructures sol-gel synthesis, polymer combustion can be conveniently slowed down to extinguishment, complying fire safety rules of specific applications, through the creation of a surface barrier to heat and mass transfer across the polymer surface.

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Abbreviations: APP, ammonium poly(phosphate); APTES, 3-aminopropyl triethoxysilane; BL, bilayer; bTESB, 1,4-bis(triethoxysilyl)benzene; bTESE, 1,2-bis(triethoxysilyl)ethane; DBTA, dibutyltindiacetate; DEMPhS, diethoxy(methyl)phenylsilane; DNA, deoxyribose nucleic acid; DPTES, diethylphosphatoethyltriethoxysilane; EG, expandable graphite; HRR, heat release rate; LbL, layer by layer; LOI, limiting oxygen index; MF, N,N,N',N',N''-hexakis-methoxymethyl-[1,3,5] triazine-2,4,6-triamine; MMT, montmorillonite; PA 6,6 GF, glass fibres reinforced polyamide 6,6 (PA6,6); PAN, poly(acrylonitrile); PC, polycarbonate; PET, polyester; PHRRp, peak of heat release rate; POSS, polyhedral oligomeric silsesquioxane; PP, polypropylene; PU, polyurethane; SEM, scanning electron microscopy; TBOS, tetrabutylorthosilicate; TEES, triethoxy(ethyl)silane; TEOS, tetraethylorthosilicate; THR, total heat release; TMOSt, etramethylorthosilicate; TSR, total smoke release; TTI, time to ignition; XPS, X-ray photoelectron spectroscopy; ZrP, α -zirconium phosphate.

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1. Introduction

Since industrial production of polymers begun in the sixties, the necessity arose of modifying their properties to produce materials meeting different physical, mechanical, chemical requirements, depending on their application. The simplest technology then available was compounding the polymer with specific additives or fillers, independently of whether bulk properties such as stiffness or surface properties such as hydrophobicity were required.

Now, about fifty years later, new technologies are available for materials surface engineering that allow to bestow on polymers desired surface properties, avoiding bulk addition drawbacks such as high loading owing to low effectiveness due to bulk dilution, detrimental effects on polymer mechanical properties, etc.

Polymer flammability is a typical surface property, in which traditional bulk addition of so-called fire retardant additives, shows a quite poor effectiveness, in some cases requiring up to 60% loading, with impairing effects on polymer properties and giving rise to processing difficulties [1].

On the other hand, the polymer surface is the critical zone in the polymer combustion scenario schematized in Fig. 1 because, being the interface between gas and condensed phase, it controls mass and heat transfers, which are the processes responsible for flame fuelling.

Indeed, heat reaching the polymer surface is transmitted to the polymer bulk, from which volatile products of thermal degradation diffuse towards the surface and the gas phase, feeding the flame. The polymer surface plays thus a key role in polymer ignition and combustion because it is its chemical and physical characteristics that affect the combustible volatiles flux towards the gas phase.

The concern about negative impact on environment and on health by well established, versatile and effective halogenated fire retardants has driven the enforcement of new European regulations, progressively restricting their use and created the need for

environmentally safe alternatives. This event is of great concern for the development of polymer materials because although fire exposure is an accidental event, flammability of polymers still represents a major limitation to their use and to the ensuing beneficial effect on industrial development. Thus, in a number of applications such as in the electrical–electronic, transportation, building and furniture sectors polymer materials can be used only if provided by a satisfactory fire retardant behaviour.

One of the most valuable fire retardant strategy pursued by bulk addition, proved to be the production or accumulation of a thermally stable surface layer able to act as a barrier to mass and/or heat exchange. Such a layer is built during the early stage of combustion as a consequence of polymer surface layer decomposition, in the presence of different kinds of fire retardants, including inorganic nanoparticles. However, the time required for build-up of the surface barrier is straightforwardly connected to the development of the fire in the early stage, consequently adversely affecting the protective barrier action (Fig. 1).

Here it is shown how the combination of advancements in polymer surface engineering and development of nanotechnologies, supplies an innovative environmentally friendly approach to fire retardance, based on providing polymer material products with a surface barrier, which either reradiates heat and/or slows down heat transmission and volatiles diffusion, without affecting the product bulk properties. To this purpose, technologies available include intumescent coatings, layer by layer assembly, sol–gel inorganic nanoparticles synthesis, that will be described below. By building the fire protection onto the original polymer surface, its effectiveness will be larger than in the case of protection created when polymer combustion is already started as it usually happens with bulk addition of traditional fire retardants.

2. Intumescent coatings

Intumescent coatings technology has been widely applied since the 1970s in fire protection of different substrates, mainly on wood boards and steel structures, as an alternative to inorganic protections such as rigid mineral-based boards and fibre blankets.

Despite metals and woods exhibit obviously different reaction and resistance to fire, the coating with an organic intumescent layer aims in both cases to the thermal protection of the substrate, in particular to extend the time to reach its critical temperature, i.e. the thermal decomposition temperature of wood or the temperature corresponding to an elastic modulus drop for steel. Paints and varnishes technology for these substrates is well established and is based on blowing of the coating layer to a thick insulating charred foam when heated above a certain temperature, as a consequence of fire exposure. The thermal resistance for a coating is the parameter quantifying the heat shield from a protective foam and it depends on several factors, including foam thickness, bubble size, defects and intrinsic heat transport characteristics of the foam material. Despite the thermal resistance cannot be measured directly, computational models have been proposed for its calculation [2].

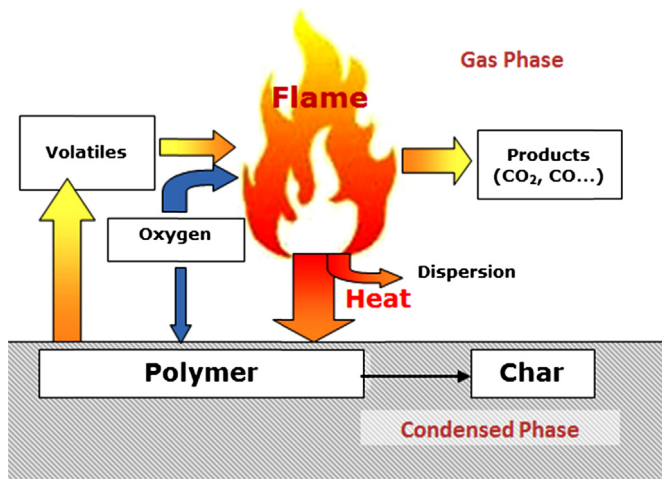


Fig. 1. Polymer combustion cycle.

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