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Review

Recent developments in flame retardant polymeric coatings

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ABSTRACT

This paper reviews the recent developments (last decade) in flame retardant polymeric coatings that mostly work by formation of conventional char (condensed phase) and or radical species in gas phase. Advancements in the method of application of such coatings on various substrates, problems of existing flame retardant coatings and new technological developments in terms of flame retardant chemistry are briefly discussed. This review focuses on various approaches in development of flame retardant coatings on various substrates *i.e.* incorporation of reactive and non-reactive organic compounds and organic/inorganic compounds (hybrid systems) based on metal, Si, P, N and halogens in suitable polymeric matrices and evaluation of their flame retardant characteristics using various analytical techniques.

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1. Introduction

With the increasing trend of more stringent fire safety regulations, demands for reduction of the fire hazard posed by highly combustible materials such as wood, plastics, textiles, etc., have gained importance in recent years. A suitable flame retardant (FR) treatment might be able to retard the ignition of these materials and/or decrease flame spread, thereby obviating fire hazards and loss of life and destruction of property [1].

Since a longtime a great deal of effort has been invested in providing different materials with fireproof properties, e.g. wood, plastics, textiles, etc. Three types of approaches have been quite well accepted and commonly used in various domains, such as electrical and electronics, building construction and transportation [2]. The first common approach involves mechanical incorporation of flame retardant additives into the bulk polymeric matrix, which is mostly low cost and fast blending technique. However, the loading of FR needed to be effective is usually too high, which can lead to a significant influence on the strength and elastic modulus of the materials [3,4]. The second way to reduce the flammability of the matrix is to bind units chemically to it by using FR segments that contain functional groups. Through this approach the FR element becomes an integral part of the polymer chain and usually results in higher efficiency and longer durability of FR effect [5]. Such incorporation could change the morphology and physical properties of the bulk polymer, such as melting point, density and glass-transition temperature and presents relatively higher difficulties in industrial manufacturing for certain materials, e.g. fibers, textile and flexible foams, etc. [6,7]. The third approach which mostly involves surface modification is widely exploited in various commercial applications. The use of fireproof coatings has become one of the most convenient, economical and most efficient way to protect the substrates against fire. Some of its advantages are given as follows: FR coatings allow the concentration of fireproof properties at the surface of the substrate along with preserving the bulk properties of the material (e.g. mechanical properties), and can generally be combined with an attractive aesthetic feature [8-10].

In most of the cases a fireproof coating represents the only barrier between the fuel and a possible fire source, thus it must withstand effectively throughout the fire, delaying ignition of the substrate, reducing the heat-and-mass transfer between the gas medium and the condensed phase, and hindering propagation of the flame. Based on the flame retarding mechanism, "flame-safe" coatings are classified as either intumescent or non-intumescent types. Intumescent coating can be described as a mixture that has capability to swell and form a three dimensional char layer on top of the substrate when exposed to fire. Traditional intumescent systems consist of a carbon source that acts as a char former (e.g. pentaerythritol), an acid source that acts as a dehydrating catalyst (e.g. polyphosphate) and a blowing agent that helps form the porous barrier (e.g. melamine, guanidine) [11,12]. This carbonaceous cellular/porous-like residue acts as a barrier to heat, air and pyrolysis products, and finally shields the underlying substrate from fire spread [13]. Bourbigot's group in Lille [14–19] has extensively investigated such kind of systems, while a state of the art

review on this topic has been recently reported by Weil [20]. In contrast to that, there is a lack of comprehensive reviews of non-intumescent flame coating systems published in the last 10 years. Unlike intumescent system such coating exhibits a different mode of action on exposure to heat, where it may release active species acting in gas phase for flame inhibition, catalyze decomposition of the surface of the material to form non-voluminous glassy/char layers, or act as insulative mirror for protection against radiation from heat source.

As stated earlier, conventional non-intumescent coatings contain flame retardant additives and hinder flame spread, however, are in absence of providing a significant voluminous protection to the substrate like intumescent one. Therefore the efficiency of the solely use FR compound in non-intumescent system is insufficient for certain applications and currently experiencing wide revolutions in terms of FR chemistry, which will be shown in a later part.

In this review we summarized the various technological industrial or academic development carried out in the field of non-intumescent coatings over the past 10 years. A brief summary of various application areas and application techniques, a detailed description of development of non-intumescent flame retardant chemistry and their formulations have been presented in this review.

2. Flame retardant application areas and application technologies

2.1. Application areas

Flame retardant coatings have many applications that can be found in different sectors. Popular flame retardant market areas include building construction, electrical applications, electronics and transportation [2,21-24], while textiles represent another large area where flame retardants are used in coatings. In the building and transportation industry, a popular way to impart flame retardancy is by mixing FR additives in the paint/lacquer which are used to coat surfaces. Many formulations have been described that utilize components such as chlorinated paraffin's, antimony trioxide, and titanium dioxide for FR latex and alkyd based paints [24,25], which in case of fire hazard help reduce the flame spread in the gas phase and catalyze decomposition of the surface of the material to form non-voluminous char in the condensed phase. In electrical applications, flame retardant coatings are often used to provide cables and wires with needful properties, as can be seen in a patent by Galletti et al. [26], and can be found in the literature, such as briefly discussed by Coaker and Hirschler [27]. Due to the high flammability of textiles, fabrics are often treated with reactive FR or back coated with a polymer matrix to provide flame retardancy. Such matrix may be composed of polyacrylates, silicones, epoxides, polyurethanes or PVC. Especially PVC based FR coatings are commonly utilized for architectural textiles, as they are able to provide useful weathering properties, as well as adequate flame retardancy over a long time under adverse environmental conditions [28].

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