



Contents lists available at ScienceDirect

## Surface &amp; Coatings Technology

journal homepage: [www.elsevier.com/locate/surfcoat](http://www.elsevier.com/locate/surfcoat)

## Thermal decomposition and fire response of non-halogenated polymer-based thermal coatings for concrete structures

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## ARTICLE INFO

## Article history:

Received 31 August 2016

Revised 2 December 2016

Accepted in revised form 4 December 2016

Available online xxxx

## Keywords:

Fire resistance

Polymer coating

Concrete

## ABSTRACT

This work highlights the thermal decomposition and fire-protective behaviour of two polymer-based coatings for concrete. The coatings are entirely free of halogenated compounds. Although the combustion behaviour of the coatings is different from classical intumescence, their action is based on a condensed-phase mechanism, which creates a steep temperature gradient between the coating surface and the coating-concrete interface. When subjected to the ISO 834 heating curve, one of the coatings could prevent the temperature of the interface from rising above 345 °C even after 3 h (corresponding furnace temperature is 1114 °C). Heat transfer simulation corroborates the observed fire-protective behaviour and shows that it may have potential for use on structural members. Analysis of the concentration of several gases produced by the burning of the coatings shows that they do not pose an immediate danger to life and health.

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### 1. Introduction

Though concrete is non-combustible and has a relatively low value of thermal conductivity, use of thermal barriers or flame-retardant coatings on concrete maybe required in some special applications such as tunnel linings. This is because the compressive strength of concrete decreases with an increase in temperature (40% reduction at 500 °C and 96% reduction at 1000 °C for concrete with siliceous aggregates) [1,2]. Flame retardant (FR) coatings have gained attraction in the recent past due to increasingly stringent fire-resistance rating requirements based on hydrocarbon fire curve for structures. Otherwise, the building codes mandate the provision of sufficient concrete cover (and minimum cross-section dimensions) to ensure load-bearing capacity and integrity of concrete members during a fire [3].

In recent years, there is also a trend to use high strength concrete in construction. Exposing high-strength concrete with low permeability to fire permits pressure to build-up within its microstructure, and when the accumulating vapour pressure exceeds tensile strength of concrete, a sudden release of pressure results in explosive spalling [4]. Several methods such as embedding polypropylene fibres or providing supplementary reinforcement have been proposed to mitigate spalling. But for existing structures to meet stringent fire resistance requirement for alteration and addition works, thermal barrier is an effective way to reduce thermal gradient differences, and mitigate pore pressure and thermal stress spalling [5].

Cementitious-based and geopolymer-based thermal barriers are some of the most widely explored passive fire protection solutions, particularly for tunnel linings [6–11]. However, the need for substantial increase in concrete cover (from 20 to 50 mm) will result in a significant increase in the weight of the member, which poses a major obstacle for these passive systems. The increase in thickness reduces tunnel gauge and affects the operational clearance of a tunnel [12]. This is where polymer-based coatings show great potential to replace traditional sprayed coatings. Halogenated compounds are widely regarded as effective FR additives, and 39% of the market is taken up by brominated FRs [13]. Although these systems provide an effective solution to reduce flammability of polymers, there are serious concerns of toxicity related to their application on-site and decomposition products in a fire. Besides, disposal of their residue poses environmental problems [13–15].

Intumescent systems, where materials swell and form a porous mass when exposed to fire or heat, are being increasingly considered for fire protection as an alternative to halogenated systems [16]. For these systems to intumesce and work effectively, three agents – an acid source, a carbonising agent, and a foaming agent, have to decompose systematically and in accordance with the matrix polymer. However, loss of cohesion of char structure and poor adhesion to substrate at high temperatures does not always guarantee the performance of intumescent systems [17]. Even the integrity of the swollen residue is a serious concern.

This manuscript presents the performance of non-halogenated fire-protective coatings (developed in NTU laboratory) for structural applications. Although the coating does not exhibit classical intumescence behaviour, it relies on the condensed-phase mechanism to create a

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huge temperature difference between the surface of coating and the base (interface between coating and substrate), thereby reducing heat transfer to the concrete substrate. Applying these coatings on existing concrete members improves their fire performance without adding excessive weight, and the effects of fire-induced spalling can be alleviated.

## 2. Experimental work

### 2.1. Coatings and their characterisation

It is important to note that the emphasis of this manuscript is to explain the fire and thermo-oxidation performance of the coatings developed from an application viewpoint. Besides, considering the confidentiality of the materials/compositions of coatings (filed as a technology disclosure [18]), detailed information on the chemistry of these coatings will not be discussed here. Therefore, only a brief overview of the coatings is presented in Table 1.

Thermogravimetric analysis (TGA) was used to investigate thermal stability of the coatings in air to simulate thermo-oxidative environment. The samples were analysed using TA Instruments Q500 from ambient temperature to 900 °C at a heating rate of 20 °C/min. Thermo-oxidative atmosphere represents the behaviour of the top most layer of the coating when exposed to an electric furnace in accordance to ISO 834 heating curve. Under direct flame exposure conditions, pyrolysis is expected to dominate within (or under) the exposed zone.

Fourier transform infrared (FTIR) spectra of the coatings (fire exposed and unexposed surfaces) were obtained in attenuated total reflectance (ATR) mode using Perkin-Elmer Frontier Spectrometer (ATR-FTIR). Three specimens for each coating were torched (exposed with a flame temperature calibrated to be 750 ± 50 °C) for a certain duration (10 min, 30 min, and 60 min) before the residues were removed for analysis. All spectra collected were in the range of 600 to 4000 cm<sup>-1</sup> (at 0.5 cm<sup>-1</sup> interval) under a resolution of 4 cm<sup>-1</sup> and 32 scans per condition. Chemical changes on the surface exposed to flame can be studied using ATR-FTIR, which provides an indication of the coatings' decomposition over time.

### 2.2. Toxicity

Toxicity of the gases released during decomposition of coatings is analysed using an air-tight test chamber constructed of an inert non-metallic material (FESTEC NES 713 Toxic Chamber). Gases released will be retained in the chamber throughout the duration of the test, as any leakage will change their concentration and lead to inaccurate results. The burner within the set-up produces a flame height of 100 to 125 mm, and a flame temperature of 1000 ± 50 °C throughout the test. The entire specimen, weighing 0.10 ± 0.01 g, is engulfed in the flame during 1 min of burning. These conditions ensure complete combustion of the whole specimen before the mixing fan stirs the gases in the test chamber for 30 s, dispersing them evenly across the chamber. Gastec sampling pump (Model: GV-100S) connected to Gastec detection tubes are used to extract and analyse the concentration of a particular gas produced by the combustion process. A total of four samples

(two samples each from coatings A2 and B2) were used for the test and the average concentration values are presented in this paper.

### 2.3. Direct flame torching

The coatings were torched with a flame over a sustained period of 2 h to observe the behaviour and to determine their effectiveness as a thermal barrier. The temperature of the flame is calibrated to be 750 ± 50 °C before the test. Coatings with a thickness of ~2 mm were applied on two concrete blocks separately. The torching experiment was conducted in a chamber to ensure a constant atmospheric environment and heating conditions (flame temperature and flame length). Fig. 1 illustrates the experimental set-up and the locations of the thermocouples (represented as black dots). The coating was applied over a type-K thermocouple (thermocouple 1 in Fig. 1) that was embedded into a 50-mm thick concrete block. The thermocouple was flushed with the surface of the concrete and it recorded temperature of the concrete block. An additional type-K thermocouple (Thermocouple 2 in Fig. 1) was used to measure the temperature of the unexposed surface. The burner is placed such that the flame will be heating the area directly above the thermocouple. A laminar flame with minor flicking was produced using the burner, and the same area was heated consistently.

### 2.4. Furnace test using ISO 834 heating curve

A one-directional heat transfer experimental set-up is used to evaluate the fire performance of coatings on a concrete section according to the ISO 834 heating curve (Fig. 2a) [18]. For this purpose, a gypsum board fixture set-up was designed (see Fig. S1 and associated description in Supplementary Information) and placed at the opening of the electrical furnace. Thermal wool was also used to seal off any fine opening around this fixture to prevent heat loss to the surrounding area outside of the furnace, keeping the temperature within the furnace constant. Fig. 2b shows the schematic of a sectional view of the entire set-up.

## 3. Results and discussion

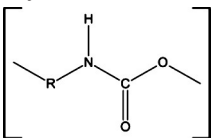
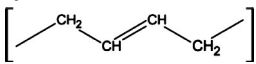
This section describes the efforts to understand the complex thermal behaviour and fire performance of the coatings with the help of different thermo-analytical techniques.

### 3.1. Thermo-oxidative behaviour

From the mass loss curves in Fig. 3, it is evident that the addition of FR additives slightly reduces thermal stability of base matrices. The accurate drop in onset and maximum decomposition temperatures for all samples are listed in Table 2. It is worth noting that, despite the reduction in thermal stability of coatings in the presence of FR additives, they show higher residual weight at 900 °C even in an oxidative environment.

However, before striking off these coatings, it is important to appreciate the differences and the difficulties in correlating TGA data with practical tests like direct flame torching or ISO 834. Some of the

**Table 1**  
Brief overview of the coatings discussed.

Properties	Coating A	Coating A2	Coating B	Coating B2
Base polymer/matrix Typical chemical structure	Polyurethane-based 		Synthetic rubber-based 	
Fire retardant additives	No	Yes	No	Yes

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