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Resistance to fire of curable silicone/expandable graphite based coating: Effect of the catalyst

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ABSTRACT

The fire performance of two curable-silicone based coatings containing 25% expandable graphite (EG) are evaluated in hydrocarbon fire scenario (standard UL1709) using a lab-scale furnace test. In this paper, the influence of the catalyst on the fire performance are investigated. Two organometallic titanium based- and tin based catalyst are used to make the curable silicone crosslink. When titanium based catalyst is used, the fire performance are higher and the mechanical properties of the char is better than that when tin is used as catalyst. To explain this surprising different fire behavior, the two residues after the furnace test were analyzed by X-ray photospectroscopy. It has been demonstrated that in the case of titanium based catalyst, the char is composed of graphite embedded by cross-linked silicone structure compare to linear silicone structure in the case of tin based catalyst. The two silicone resins were characterized by Fourier Transform Infrared spectroscopy, ^{29}Si NMR, thermogravimetric analyses, EPMA (electron probe microanalyses). It was highlighted that the tin migrates into the surface during the crosslinking of the matrix leading to a low thermal stability and, thus, low fire performances. Whereas, when titanium based catalyst is used, it participates to the silicone network with the formation of Si–O–Ti bounds increasing the thermal stability of the matrix and so enhancing the fire performance of the silicone/EG based coating.

1. Introduction

The protection of metallic materials against fire has become an important issue in the construction industry. Indeed, steel begins to lose its structural properties above 500 °C and it must be therefore protected against fire [1]. Prevention of the structural collapse of the building is paramount to ensure the safe evacuation of people from the building, and is a prime requirement of building regulations in many countries. One of the most used systems to protect metallic structures is intumescent paint. These coatings have the properties to swell to thick insulative foam when heated above a critical temperature. Intumescent coatings are mostly based on a combination of a char-forming material, a mineral acid catalyst, a blowing agent and a binder resin [2,3]. However, these materials are typically organic-based materials and exhibit some disadvantages. First, organic additives undergo exothermic decomposition which reduces the thermal insulative value of the system. Second, the resulting carbonaceous char in some cases has a low structural integrity and the coating cannot withstand the mechanical stress induced by a fire and/or by other external constraints. And third, the coating releases organic gases (potentially toxic) which are undesirable in a closed fire environment [4].

Currently, some alternative to organic intumescent coating have been studied [5–7]. The use of silicone-based

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protective coating is poorly reported in the literature. We recently evaluated the fire performance of an intumescent silicone based coating [6]. In this study, the fire performance of a phenyl silicone resin containing silica-based modifier was evaluated in pure radiative and convective/radiative heating conditions [6]. We reported the good heat barrier properties of this intumescent silicone based coating in radiative/convective heating whereas fire performance of this coating is rather limited in the case of pure radiative heating. Indeed, in pure radiative heating source, silicone based coatings cracks due to the high vibration of Si–O bond in infrared field and so, it exhibits low fire performances.

Polydimethylsiloxane (PDMS) is widely used in the construction industry and electrical equipments because of its excellent thermal stability and fire properties including low heat of combustion and low rate of heat release compared to conventional organic polymers [8,9]. This polymer is available in different forms from liquid to cross-linked rubber. The rubbers can be found in two main classes [10]: one cross-linked by polyaddition, and another by polycondensation. Silicones prepared via the polycondensation method are used to make sealants that find applications in original equipment manufactories providing a barrier against severe environments such as humidity or dust [11]. These products are ready to use and they require no additional mixing: cross-linking starts when the product is exposed to moisture. Most silicone sealants are formulated from a reactive polymer prepared from an hydroxy-polydimethylsiloxane and a large excess of cross-linker such as tri-acetoxysilane. Organometallic catalysts have to be used to make the resin crosslink. The two most used catalysts are tin and titanium based catalysts. The polycondensation reaction is illustrated in Eq. (1).

$$\mathrm{HO-(Me_2SiO)_{\mathit{x}}-H + exc.\ MeSi(OAc)_3} \\ \times \xrightarrow{-2\mathrm{AcOH}} \mathrm{(AcO)_2MeSiO(Me_2SiO)_{\mathit{x}}OSiMe(OAc)_2} \quad (1)$$

On the other hand, expandable graphite (EG) is a "particular" intumescent additive known to impart fire retardancy to various materials [12]. EG is a graphite intercalation compound in which sulfuric acid and/or nitric acid is inserted between the carbon layers of graphite. Upon heating, exfoliation of the graphite occurs, i.e. expansion along *c*-axis of the crystal structure by about hundred times. The material generates in that way is a puffed-up material of low density with a "worm" like structure. In recent decades, more and more papers reported the use of expandable graphite in intumescent based coatings. This intumescent additive increases the fire performance and anti-oxidant properties of intumescent based coatings [2,13,14]. However, in the above mentioned studies, expandable graphite is only incorporated into complex organic intumescent based formulations. It is noteworthy that in organic based coating, EG decreases considerably the cohesion of the char [14].

We recently reported the used of silicone based coating containing EG for the fire protection of steel [7]. We reported high fire performance of silicone added with 25% of EG in curable silicone resin cross linked with titanium catalyst. The good performances were explained by the formation of an expanded insulative char (3400% expansion) formed with a high expansion velocity (18%/s) and exhibiting a low thermal conductivity (0.35 W/K m at 500 °C). It was shown that the formation of a complex silicone/graphite structures at high temperature is responsible to the extremely high cohesion of the char in fire scenario.

The purpose of this paper is to investigate the heat barrier properties of curable silicone/expandable graphite based coating in hydrocarbon fire scenario (standard UL1709). The effect of two different organometallic catalysts on the mechanical properties of the char will be carefully investigated. To explain the influence of the catalyst on the fire performance, residues obtained after furnace test will be fully characterized. The structure and thermal stability of the silicone resins will be finally studied for the two catalysts.

2. Experimental

2.1. Materials

The first resin, hereafter called S1–Sn, was composed of 83% of an hydroxylated PDMS with a viscosity of 80 cS (viscosity is measured using cone/plate rheometer CP-52), 15.1% of methyltrimethoxysilane (MTM) as crosslinking agent and 1.9% of a tin based catalyst. The tin based catalyst is a di-alkyl alkanoate (alkyl: methyl, butyl, octyl and alkanoate: laurate, decanoate, etc.). The second, hereafter called S1–Ti, was composed of 77% of an hydroxylated PDMS with a viscosity of 80 cS (viscosity is measured using cone/plate rheometer CP-52), 15% of MTM and 8% of a titanium based catalyst. The titanium based catalyst is a tetra alkoxy titanates (alkoxy: n-propoxy, i-propoxy, n-butoxy, t-butoxy).

25% of expandable graphite ES350F5 from Graphitwerk Kropfmuehl (Germany) with an average grain size of 300 μm was added to the silicone matrix. Both formulations were applied on a 10 cm × 10 cm × 3 mm steel plate to obtain 1.0 ± 0.1 mm coating. Steel plates were cleaned before application with ethanol and a primer (Primer 1200 from Dow Corning) was applied to enhance the coating adhesion.

2.2. Fire testing methods

The small scale furnace test was developed in our laboratory to evaluate the fire performance of intumescent coatings in fire scenario. This test was designed to mimic the UL1709 normalized temperature/time curve, related to hydrocarbon fire. The lab-made furnace exhibits an internal volume of 26 dm^3 (Fig. 1). Refractory fibers (stable up to 1300 °C) cover the different sides of the furnace. The furnace was equipped with two gas burners (20 kW propane burners). The gas pressure was fixed at 1.8 bars and the flow was regulated in order to mimic the UL1709 curve. A temperature probe inside the furnace regulates the temperature and a K-type thermocouple allows the furnace temperature profile to be registered. The furnace is equipped with a quartz window allowing to follow the intumescent process taking place during the test.