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Characterization of the carbonization process of expandable graphite/silicone formulations in a simulated fire

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ABSTRACT

The fire performance of curable-silicone based coatings containing expandable graphite (EG) is evaluated in hydrocarbon fire scenario (standard UL1709) using a lab-scale furnace test. From 5% to 25% of expandable graphite is incorporated in the silicone matrix to make the coating swell during the fire experiment. Fire performance of 25%EG/silicone-based coating is better than that of commercial intumescent paint used as reference. This is explained by a high swelling velocity (18%/s), a high expansion (3400%), an impressive cohesion of the char and a low heat conductivity at high temperature (0.35 W/K m at 500 °C). To elucidate this way of charring, the residue after fire testing was analyzed by scanning electron microscopy, transmission electron microscopy, energy dispersive spectrometry, X-ray photoelectron spectroscopy and X-ray diffraction. It is shown that the char is composed of two main parts: the top is composed of quartz and amorphous silica which coat graphite flakes and the heart of the char is composed of graphite flakes embedded in degraded silicone forming a complex structure. It is shown that, the good cohesion of the char is due to: (i) the presence of the undegraded silicone matrix; and (ii) the coating of graphite pellets by silicone.

1. Introduction

Polydimethylsiloxane (PDMS) is widely used in construction and electrical abilities 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 [1,2]. This polymer is available in different forms from liquid to cross-linked rubber. The rubbers can be found in two main classes [3]: 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 for glazing sealing windows and doors for either residential or public buildings. They are also used as a building component providing a barrier against severe environments such as humidity or dust [4]. These products are ready to use and require no mixing: cross-linking starts when the product is exposed to moisture. Most silicone sealants are formulated from a reactive polymer prepared from a hydroxy-polydimethylsiloxane and a large excess of cross-linked agent such as tri-acetoxysilane. The polycondensation reaction is illustrated in Equation (1).

$$HO-(Me_2SiO)_x-H \quad +\text{exc. } MeSi(OAc)_3 \xrightarrow{-2AcOH} (AcO)_2MeSiO(Me_2SiO)_xOSiMe(OAc)_2$$

Equation (1). Polycondensation reaction of hydroxy-PDMS.

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 [5]. 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 [6,7]. However, these materials are typically organic-based materials and exhibit some disadvantages. Firstly, organic additives undergo exothermic decomposition which reduces the thermal insulative value of the system. Secondly,

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the resulting carbonaceous char in some cases has a low structural integrity and the coating cannot withstand the mechanical stress induced by a fire. Thirdly, the coating releases organic gases (potentially toxic) which are undesirable in a closed fire environment [8].

Currently, some alternative to organic intumescent coating has been studied. We recently reported the use of ceramic precursor – polysilazane – based coating as a heat barrier on steel plate. The purpose of this work was to form a ceramic at high temperature which could protect a substrate in fire scenario [9]. The performance of the polysilazane coating can be improved incorporating some fire retardant such as aluminum trihydroxide but it is limited compared to commercial intumescent paint. The use of silicone-based protective coating is very few reported in the literature. We recently evaluated the fire performance of an intumescent silicone-based coating. In this study, fire performance of a phenyl silicone resin added with modifier silica was evaluated in pure radiative and convective/radiative heating source condition [10]. We highlighted the good heat barrier properties of this intumescent based coating in radiative/convective heating source whereas fire performance of this coating is rather limited in the case of pure radiative heating source and therefore in real fire scenario. Indeed, in pure radiative heating source, silicone-based coatings cracks due to the high vibration of Si–O bound in infrared field and so exhibits low fire performances.

Expandable graphite (EG) is a "particular" intumescent additive known to impart fire retardancy to various materials [11]. 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 generated 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 coating. This intumescent additive increases the fire performance and anti-oxidant properties of intumescent based coating [6,12,13]. 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 decreased considerably the cohesion of the char [13].

The use of EG in silicone-based coating to protect material against fire is not reported in the literature. Beigbeder et al. highlight the high adsorption of the PDMS chains onto carbon nanotube mostly triggered by CH–π interactions between the methyl group from PDMS and the π-electron-rich surface of the carbon nanotube [14] and evaluated the fire protective performance of PDMS/Carbone nanotube based coating onto aluminum plate. They showed that in convective/radiative heating test, this coating exhibited improved properties compared to virgin aluminum. However, this silicone-based coating is clearly not intumescent. In this work, passive fire protection of steel using silicone-based coating from polycondensation is investigated using expandable graphite as blowing agent.

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). It is recognized that the governing parameters for intumescent coating to get efficient heat barrier performance are the fast expansion of the coating as a function of temperature and its low thermal conductivity (formation of a dense and porous char) [15]. Those parameters will thus be examined in this paper. The charring process and the expansion of the coating occurring during the fire scenario will be then fully investigated.

2. Experimental

2.1. Materials

The silicone resin called silicone 1 (S1), was composed of a hydroxylated PDMS with a viscosity of 15,000 cS (viscosity is measured using cone/plate rheometer CP-52), methyltrimethoxysilane as a cross-linking agent and a titanium catalyst. All the materials were supplied by Dow Corning, Seneffe (Belgium).

From 5% to 25% of expandable graphite ES350F5 from Graphitwerk Kropfmuehl (Germany) with an average grain size of 300 μm was added to the silicone matrix. Each formulation was 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.

Metallic structures are generally protected with intumescent paint. Epoxy based intumescent paint Fire Tex M93 (M93) from Leigh's Paint, England, was used as reference and for comparison in our study. The same thickness of M93 was coated on the same steel plate as above.

2.2. ^{29}Si solid state NMR resin characterization

^{29}Si NMR spectroscopy is a powerful tool for examining silicon surrounding. This technique can distinguish between several kinds of structures including D [$SiO_2(CH_3)_2$], T [$CH_3Si(O_{1/2})_3$] and Q [$Si(O_{1/2})_4$] structures which characterize silicone network. ^{29}Si NMR spectra were recorded on a Bruker Advance II 400 operating at 9.4T and using a 7 mm probe. NMR spectra were acquired with MAS (magic angle spinning) of 5 kHz. The reference used for ^{29}Si NMR was tetramethylsilane (TMS). A delay of 180 s between the pulses and a $\pi/2$ pulse length were used. 288 scans were accumulated to get an acceptable signal to noise ratio. In order to quantify the amount of D and T structure within the resin, simulation of ^{29}Si NMR spectra was obtained using DMfit99 software [16].

2.3. Fire testing methods

The small scale furnace test was developed in our laboratory to evaluate the fire performance of intumescent coatings in fire scenario (cellulosic and hydrocarbon).

This test was designed to mimic the ISO834 (or ASTME119) and the UL1709 normalized temperature/time curve, respectively related to cellulosic fire and to hydrocarbon fire.

The lab-made furnace exhibits an internal volume of 40 dm^3 (Fig. 1). Refractory fibers (stable up to 1300 °C) cover the different

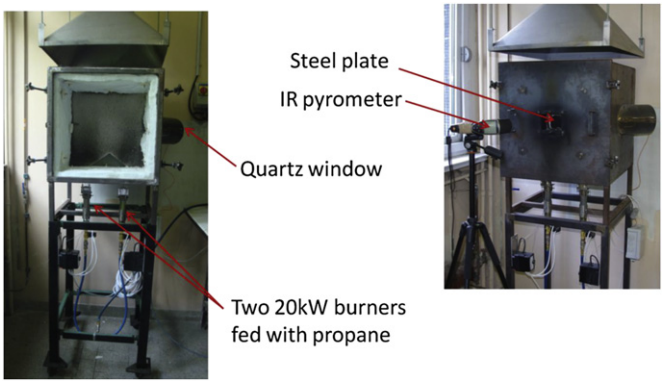

Fig. 1. Furnace set up to mimic hydrocarbon fire scenario.