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Enhanced Modelling of Exposed PFP Coatings Based on Bench-scale Fire-tests

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Accurate modelling of the behaviour of coatings used as Passive Fire Protections (PFP) is essential for the evaluation of their performance. The changes of the characteristics of PFP materials when exposed to high temperatures can have a significant impact on the safeguard of the protected surface. In this work, laboratory and bench-scale experimental studies of the property changes suffered by a selected PFP coating when exposed to high temperatures were carried out. The results were used in the simulation of a case of study which allowed evaluating the advantages of a detailed model of the coating behaviour. As a conclusion, it was observed that the impact of considering and not considering the property changes of PFP materials when exposed to fire is significant. The results can be used to enhance Finite Element Modelling, leading to a more realistic and better evaluation of the PFP effectiveness.

1. Introduction

Process industries are exposed to the occurrence of major accidents, which can lead to significant material and human losses. The potential hazard of severe events, as fire, has influenced regulations and guided to an improvement of safety measures. Several strategies to avoid fire or at least delay its effects have been developed. Passive Fire Protection (PFP) is one of the tools conceived for these purposes, providing an extra time for mitigation actions. Several materials are used as PFP coatings, to protect tanks or structures that can be exposed to fire and, if damaged, may escalate the severity of the accident. Coating properties may suffer modifications during fire exposure, changing with time and temperature. Accurate modelling of the behaviour of coatings used as PFPs is an important issue for the prevention of major accidents. The evaluation of the protective effect of PFP materials can be based on standard tests or ratings, such as UL 1709 (UL, 2005), ASTM E 119 (ASTM, 2009a), (ASTM, 2006) ASTM E 1529, OTI 95635 (HSE, 1996), ISO 22899-1 (ISO, 2007), among others, but their approach is general and in some cases a more detailed evaluation is required to guarantee the safety of particularly critical facility units. Finite Element Modelling (FEM) is an interesting option which allows the assessment of PFP materials in a practical way. Through FEM modelling, the PFP coating effectiveness can be evaluated quicker, safer, easier and cheaper than in the case of carrying out large scale experiments.
In order to achieve reliable modelling results, the evolution of the coating properties when exposed to fire is a key issue. Properties such as thermal conductivity, density, among others, change substantially

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when the material is exposed to a significant amount of heat. These changes influence on the protection provided by the PFP coatings – diminishing or augmenting it- depending on the type of material. In general, these changes are not considered in the assessment of PFP effectiveness, and conservative constant values are used, which lead to less accurate results.
In this study the variation of the most relevant properties of a selected PFP coating when exposed to fire is analyzed experimentally. The results are used to model the performance of the different properties. Bench scale tests are carried out to verify that the phenomena observed at laboratory scale are representative of bigger scales. Simulations based on the models generated experimentally are used to observe the impact of considering constant properties instead of a more detailed behaviour. The results can be used to enhance Finite Element Modelling, leading to a more realistic and better evaluation of the coating effectiveness as a PFP material. A case of study is developed in order to demonstrate the importance of the inclusion of detailed information about the coating properties behaviour on the PFP performance assessment.

2. Experimental section

In order to analyse the importance of the changes suffered by a PFP material when exposed to fire in the evaluation of PFP performance, an epoxy intumescent coating was selected. This material was chosen since it suffers dramatic changes when exposed to high temperatures: it swells, modifying its characteristics, such as density and thermal conductivity. The transition in key-properties as thermal conductivity is generally disregarded when PFP performance evaluations are carried out, leading to not precise results.
The selected material was a commercial coating supplied by International Protective Coatings (Akzo Nobel). It contains an epoxy resin DGEBA (2,2'-4-butylidenebisphenyleneoxymethylene), Ammonium Polyphosphate (APP), boric acid, an amine and filler materials.
A study of the material degradation as a function of temperature and heating rate was performed using a thermogravimetric analyzer TGA Q500 from TA Instruments. Tests performed at different heating rates (5, 10, 25 and 45 °C/min) until a final temperature of 800 °C allowed obtaining an apparent kinetic model of the degradation phenomena.
The expansion was modeled making use of experimental data obtained from tests carried out on a fixed-bed tubular reactor. A Carbolite HST 12/300 furnace equipped with a W301 controller was used. Coating samples with the thickness actually used on the industry were degraded until 800 °C at 10 °C/min under nitrogen atmosphere.
Real density of non degraded and degraded material was measured by means of a pycnometer. Apparent density was computed based on the apparent kinetic model and the expansion.
Bench scale tests were obtained using a specifically modified ASTM E162 setup (ASTM, 2009b). Sample material boards (460 x 150 mm) were vertically exposed to a 304.8 x 457.2 mm porous gas-operated radiant panel, model RP-1A (Govmark Inc). The sample board was situated parallel to the panel face. The panel initial temperature was among 700 to 725 °C. The temperature-time profile on the cold side of the board was measured using an infrared camera (Thermovision A40M) from FLIR systems, located at 1.3 m perpendicularly to the panel. The material degradation at different exposure times (15, 25 and 50 min) was tested. Thermal conductivity was measured at different temperatures with a transient plane source instrument (TPS2500S, by Hot Disk AB).

3. Medium scale simulation model and property models

Modelling of property changes with temperature for PFP materials is an important issue for a detailed PFP system assessment. The consideration of properties variation can be essential to model accurately the actual protection of these systems to the protected surface. The development of a simple model is possible considering laboratory data. The model can be then employed for FEM simulations.

3.1 Medium scale simulation model

A simplified one-dimension energy balance equation was adopted to model the bench scale experiments (modified ASTM-E162). According to the geometry of the experimental set-up, the heat propagation through the coating takes place mainly orthogonally to the face exposed to the radiant panel. Then, in order to model the experiments, the following simplified one-dimension energy balance equation can be used:

$$\rho \cdot cp \cdot \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[k \cdot \frac{\partial T}{\partial x}\right] + \frac{\dot{q}''_I}{dx} + \left(\sum_j \Delta \hat{H}_{R,j} \cdot \frac{d\xi_j}{dt} \cdot \omega_{0,j} \cdot \rho_0\right) \quad (1)$$

where *T* is the local temperature, *t* is the time dimension, *x* is spatial dimension through the board orthogonal to the exposed face, ρ is the local apparent density, *cp* is the local heat capacity, *k* is the local thermal conductivity, q''_I is the heat flux entering the local interface, $\Delta H_{R,j}$ is the heat effect from reaction j, ξ_j is the mass conversion for reaction j, $\omega_{0,j}$ is the mass fraction of virgin material consumed by reaction j, and ρ_0 is the apparent density of the virgin material.
The heat transport contribution by the released gases was neglected in the model. The property equations and the reaction kinetics used in the simulation are reported in the next section.
Swelling was considered to occur only in the heat flow direction and was represented as a local stretching of the spatial dimension of the material:

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where *dx* is the differential in the spatial dimension used in equation (1), dx_0 is the differential corresponding to the same spatial dimension at the initial condition (virgin unexposed material), and ψ is the local swelling factor (ratio between swollen length and initial length).
The boundary conditions applied to eq. (1) are: i) at t=0 the sample is uniformly at room temperature; and ii) heat flux through the sample interface (q''_I) only occurs at the two faces of the board. Both surfaces are considered to maintain constant temperatures over time. The exposed surface is assumed to exchange radiative heat with the radiant panel. At the back face it is considered that convective heat transfer with surrounding air takes place.
Conventional numerical finite-difference methods were applied to solve equation (1) over space and time. Further information on heat transfer equations and the stability criteria can be found elsewhere (Incropera et al., 2007).

3.2 Property models

Two main decomposition regions were observed during the TGA experiments. A lumped reaction model was developed for describing the apparent kinetics of these phenomena. Details can be found in (Gomez-Mares et al., 2011). From the apparent kinetics, the mass of the coating as a function of conversions can be computed as follows:

$$m = m_0 \cdot (1 - \alpha_1 \cdot \xi_1 - \alpha_2 \cdot \xi_2 - \alpha_3 \cdot \xi_3) \quad (3)$$

Where ξ_j is the conversion of the corresponding degradation region. In each degradation region it is considered that a new pseudocomponent is formed. From the tubular reactor experiments, the expansion was found to be described by the following equation:

$$\psi = \left(\frac{V}{V_0}\right) = \exp(1.321\xi_2 + 0.1693\xi_1) \quad (4)$$

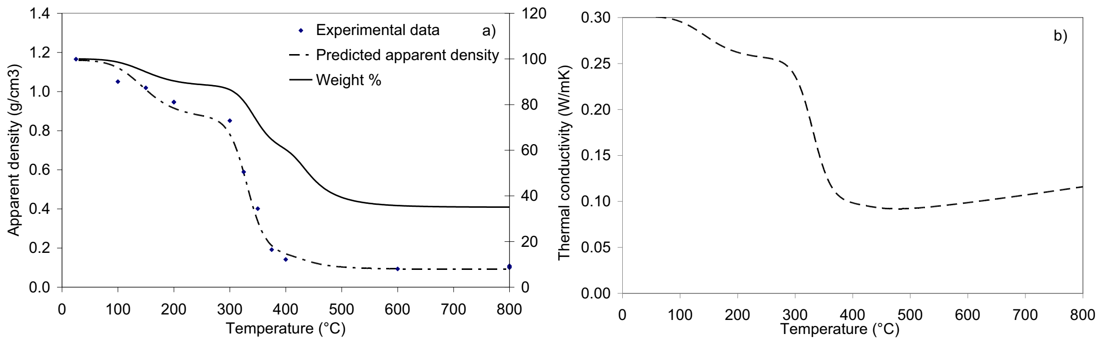

Figure 1: a) Apparent density of the selected epoxy intumescent coating as a function of temperature; b) Thermal conductivity of the selected coating as a function of temperature.

Real density of different pseudocomponents was measured experimentally using a pycnometer. Apparent density was also measured using the Archimede's principle. Pore fraction ϕ can be found from real and apparent density:

$$\phi = 1 - \frac{\rho_{app}}{\rho_{real}} \tag{5}$$

A parallel-layers model was adopted to calculate the bulk thermal conductivity k_{app} of the material. It is a function of the pore fraction ϕ, thermal conductivity of the solid matrix and thermal conductivity of the gas inside the pores:

$$k_{app} = (1-\phi)\cdot\left(\sum_j \omega_j \cdot k_{S,j}\right) + \phi \cdot \left(k_{gas} + \frac{4\sigma d}{\frac{2}{\varepsilon} - 1} T^3 \right) \tag{6}$$

The first term corresponds to the solid thermal conductivity and the second term corresponds to the thermal conductivity inside the pores. In eq.(6), $k_{S,j}$ is the thermal conductivity of the solid, ω_j is the mass fraction of each pseudo-component in the solid, k_{gas} is the thermal conductivity of the gas inside the pores, T is the temperature in K, d is the pore diameter (m), σ is the Boltzman constant, equal to 5.67 x 10 $^{-8}$ W/ (m^2K^4), and ε is the emissivity, assumed equal to 1. Figure 1 shows the results for apparent density and thermal conductivity as a function of temperature.

4. Results

Based on the model and set of equations reported on section 5, a simulation of the bench scaled tests described on section 2 was carried out. Results are plotted on Figure 2a. As shown in the figure, the difference among considering and not considering the variation of key properties is significant, and may lead to a wrong evaluation of the actual protection provided by a PFP system. As an example, curve (1) represents the results obtained considering all the changes of the material properties. If properties are considered to remain constant during the heating process, line (4) is obtained, far from the experimental data.

A preliminary Finite Elements Model (FEM) simulation for LPG real scale vessels was run on ANSYS^{TM} software, using either constant or variable properties of the coating. More details on the FEM set up are reported elsewhere (Landucci et al., 2009). A full engulfment pool fire scenario (total heat load 150 kW/m^2) was simulated for a 110 m^3 LPG rail car, obtaining a detailed transient temperature and stress profile on the vessel. The analysis allowed verifying the effectiveness of the protection, predicting the

eventual occurrence of the vessel rupture. Both considering constant and varying properties, the failure of the vessel was not predicted among a total run time of 100 min, thus demonstrating that even if the coating properties are deteriorated by long fire exposure, the protection is still able to guarantee the resistance of the vessel. In order to quantify the effect of the thermal protection degradation implemented in the FEM, the results were used to calculate specific KPIs (Key Performance Indicators). The KPIs are a quantitative synthetic tool to evaluate the performance of the thermal protection. More details on the KPIs definition are reported elsewhere (Landucci et al. 2009).
The first KPI considered, namely TI – thermal index, is based on the assessment, of vessel shell temperature gradients, and can be defined as the ratio among the maximum and minimum temperature on the whole structure. The second KPI, namely SI – stress index, takes into account the residual

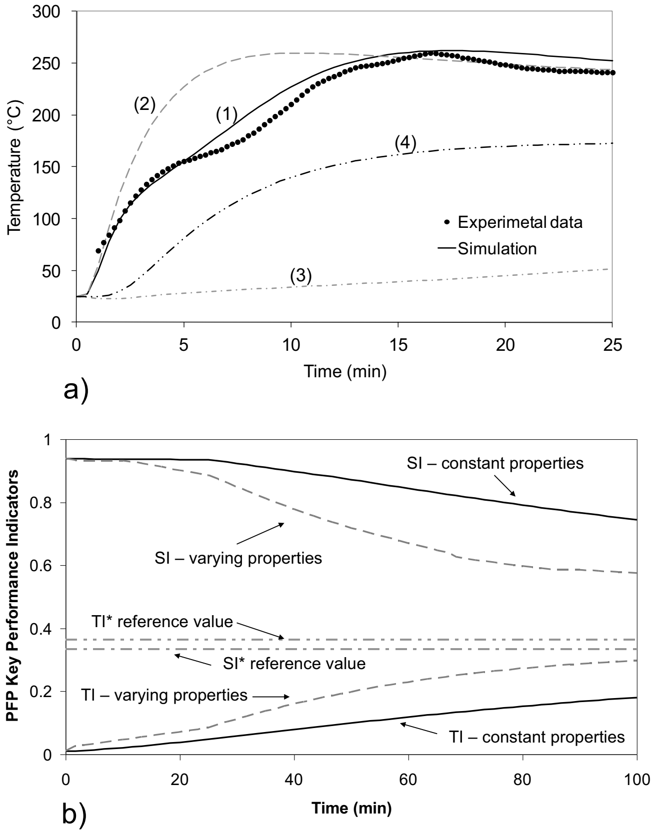

Figure 2: a) Simulations of an epoxy intumescent coating, 25 minutes exposure time (1: simulation considering temperature and conversion dependent properties and thermal effects of reactions; 2: simulation considering property dependence but no thermal effects of reactions; 3: simulation considering constant properties but thermal effects of reactions; 4: simulation considering constant properties and no thermal effects of reactions). b) PFP KPIs calculated for a 110 m^3 LPG vessel in large scale pool fire engulfment scenario.

strength of the vessel compared to the design conditions. The reference values for both TI* and SI* and other details on KPIs for PFP systems are extensively discussed by Landucci et al. (2009)
Figure 2b shows the calculated KPIs aimed at the comparison among the PFP systems considering constant and varying properties. As it can be seen, both TI and SI indexes approaches to the reference threshold limit of effective performance respectively TI* and SI* in the case of varying properties, thus evidencing a critical effect on the thermal protection efficiency due to the coating degradation.

Thus, it is crucial to consider the variation of coating properties with temperature in order to obtain an accurate simulation of the coating performance as a PFP.

5. Conclusions

Small and bench scale experiments were carried out to analyze the changes on the properties occurred when an epoxy intumescent coating is exposed to high temperatures. Models for the properties performance were proposed as well as a model to simulate the bench scale tests. Simulations of the bench scale tests were carried out, and the results suggest that it is essential to consider the variation on the coating properties in order to obtain accurate results of the actual coating performance. A preliminary FEM simulation was performed, confirming the results obtained by the bench scale simulations: the simulated temperature of the protected surface is considerably affected by the fact of considering and not considering the changes on the coating properties, leading, again, to a not precise assessment of the expected performance of the PFP system. If changes in key properties of PFP materials during the exposure to fire are neglected, the results of the simulations may be far from reality, leading to a rough and possibly not conservative assessment of the PFP performance.

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