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Experimental Study and Numerical Simulation of Epoxy Intumescent Passive Fire Protection Performance

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Epoxy intumescent coatings can be used to protect vessels against fire, delaying the temperature rise and the consequent failure of vessel shell. The behaviour of a commercial epoxy intumescent material exposed to temperatures up to 800ºC was analyzed using thermogravimetric analysis. The results showed two main decomposition regions. Hence, numerical simulations of real scale tanks engulfed by fire were carried out taking into account the actual behaviour of the fireproofing material. The consequences of the thermal exposure of coated and uncoated tanks were compared and the performance of the coating as a passive fire protection was assessed.

1. Introduction

Epoxy intumescent coatings are materials characterized by a swelling behaviour when exposed to high temperatures, due to the generation of gaseous compounds during thermal decomposition of the organic matrix (Jimenez et al., 2006a, 2006b and 2009). The swelling phenomenon contributes in retarding the heat transmission to the protected surface. Thus, these materials may be used as a passive fire protector (PFP), delaying the temperature rise of metal surfaces exposed to fire and preventing the damage of metal structures. The behavior of a commercial epoxy intumescent material exposed to temperatures up to 800ºC was analyzed using Thermogravimetric Analysis (TGA) as well as Differential Scanning Calorimetry (DSC) techniques with aiming to its characterization. The results are shown in section 2. In sections 3 and 4, the numerical simulations of real scale tanks engulfed by fire are described. The simulations were run employing a finite elements model (FEM). The time to failure was evaluated from the simulation results. The performance of the coating as a passive fire protection was assessed also comparing the consequences of the thermal exposure of coated and uncoated tanks.

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2. Apparent kinetics of a commercial epoxy resin

The degradation behavior of a commercial epoxy coating exposed to fire was studied by TGA and DSC. A set of experiments was carried out analyzing the samples up to a final temperature of to 800°C using constant heating rates. Inert gas atmosphere was used for all the experiments. The heating rates used were: 5, 10, 25 and 45°C/min. The results are shown in figure 1. As it can be observed, two thermal decomposition steps are present. These findinga are in agreement with the results of Jimenez et al., 2009.

The first decomposition region, until 270°C, corresponds probably to the boric acid dehydration. This assumption is supported considering the results of a DSC analysis, which showed an endothermic set of reactions occurring during this decomposition step. In the second degradation step, from 270°C to 510°C, the decomposition of the epoxy resin and the ammonium polyphosphate (APP) takes place. A constant amount of residue was found at the end of this thermal degradation step (35% of the initial weight), proving that some inert compounds are contained in the material as fillers.

An apparent kinetic model was developed for the first and second regions, making possible the prediction of the behavior of the material exposed to fire conditions, as well as the identification of the most representative values for the properties to be introduced in the finite elements simulation.

The apparent kinetics of the first degradation region was modeled considering a single-step lumped reaction model, while the second region was divided in two zones, and for each a different kinetic model was developed, again using a lumped reaction model.

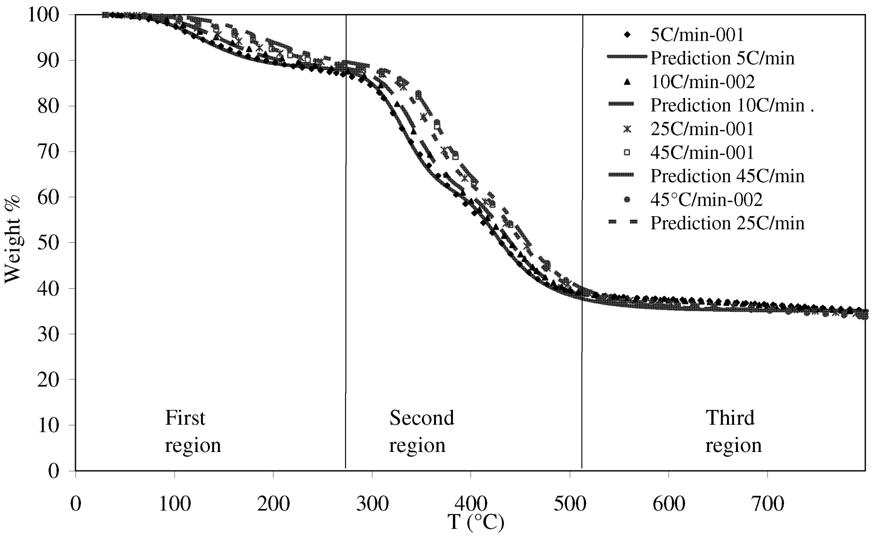

Figure 1: Experimental thermogravimetric curves and predictions at different heating rates of a commercial epoxy coating.

The data were correlated using an Arrhenius rate equation (1):

$$\frac{d\xi}{dt} = Ae^{\frac{-E}{RT}}(1-\xi)^m \tag{1}$$

where ξ is the local conversion for the corresponding phenomena, t is the time, A is the apparent pre-exponential factor, E is the activation energy of the reaction, R the gas constant, T the temperature and m the reaction order.

The best-fit parameters were obtained from the Arrhenius plot for each region. The results are shown in Table 1.

Table 1: Arrhenius rate equation parameters

Region	m	A (s^{-1})	E (J/mol)
1	2	9.78×10^{2}	43001.8
2a	2	5.72×10^{11}	163716.7
2b	4	1.48×10^{19}	287157.9

Table 2: Step function defined for coating performance.

Phase	T_c (°C)	K (W/mK)	*Thickness* (mm)
I	10÷270	0.28	10
II	270÷510	0.066	25
III	>510.	0.22	25

3. Parameters used for Finite Element Modeling

The goal of the kinetic model is to better describe in the numerical modeling the changes of material properties occurring during fire exposure of fireproofed equipment. A preliminary simulation, presented in the current paper, used a simplified model for the behavior of a PFP material exposed to fire. A step function was considered for describing the dynamic behavior the physical properties, considering the aforementioned regions. It has to be pointed out that during the first region the material is mostly unexpanded, while during the second one, it swells. This behavior is simplified considering the properties shown in table 2. The transition temperatures relative to each phase were identified from the weight profile (Figure 1). A reference value for the thermal conductivity was associated to each phase, resorting to literature data set (Liley et al., 1999; Fjellerup et al., 2003).

4. FEM simulation of coated vessels impinged by fires

4.1 FEM set up

A finite elements model (FEM) was set up in order to implement the experimental coating behavior in a real scale simulation of pressurized tanks impinged by fires. The FEM was developed on ANSYS^{TM} software, using the ANSYS^{TM}/Multiphysics module divided in two main frameworks. The first sub-model allowed the detailed calculation of the temperatures on the vessel shell as a function of time and of external thermal loads. In the second sub-model, the simulation of the transient stress field was carried

out, implementing the local temperatures, evaluated in the previous step, as thermal loads, and adding the other loads present on the vessel shell (internal pressure, weight, etc.). The FEM was used to perform detailed simulations of the radiation mode, of the wall temperature and of the stress over the vessel shell under severe fire exposure conditions. The FEM was both applied in case of thermal protection installed on the tanks or in absence of thermal protection. In both cases, a simplified failure criterion was implemented in order to predict the eventual vessel rupture according to ASME codes (ASME, 1989). In particular, comparing the local values of the stress intensity (σ_{eq}), calculated applying the Von Mises criterion, with the local values of the maximum allowable stress (σ_{adm}), which is a function of temperature, the time to failure (ttf) was assumed as the time when the increasing σ_{eq} equals σ_{adm}. Further details on the FEM set up and validation are reported in previous publications (Landucci et al., 2009).
A case-study representative of the European transportation of HazMat was defined to exemplify the methodology application. In particular, a 95m^3 rail tank wagon was simulated with the described FEM tool. The tank, filled with commercial propane (80% filling level), was simulated under the exposure of a full engulfing pool fire, at a constant heat load of 180 kW/m^2 on the outer surface of the tank. The tank was equipped with a pressure relief valve (PRV) set at 2.3MPa. The main parameters implemented in the FEM are reported in Table 3.

Table 3: Input data for the FEM simulation.

Tank wagon properties	Inner fluid properties
Nominal volume: 95m^3	Average liquid temperature: 70°C
Geometry: horizontal cylinder	Average vapour temperature: 170°C
Diameter: 3.1 m	Liquid density: 585 kg/m^3
Length: 15 m	Heat transfer coefficient, liquid side (both protected and non protected): 400 W/m^{2}K
Thickness: 16 mm	Heat transfer coefficient, vapour side; protected case: 6 W/m^{2}K
Material: EN10028-P460NH	Heat transfer coefficient, vapour side; non protected case: 140 W/m^{2}K
Design pressure: 2.5 MPa	Initial temperature: 10°C

An organic intumescent coating, 10 mm thick, was supposed to be installed on the outer surface of the tank. According to the step function defined in Table 2, the three phases of the coating behavior were implemented in the simulation. The coating thickness was supposed to expand up to 2.5 times at the beginning of phase II. In order to evaluate the entity of the degradation effect on the results, the “ideal” coating behavior was also simulated, considering a sudden expansion up the final value with constant thermal conductivity and no degradation (thus, considering only phase II among the whole simulation). Moreover, the non-protected case was simulated.

4.2 FEM results and discussion

An example of FEM results is reported in Figure 2, in which the temperature and stress maps are shown at the end of simulation (100 minutes) in the case of protected tanker, with a coating featuring the behavior summarized in Table 2. As it can be seen in Figure 2a, due to difference in heat transfer coefficient, the highest temperatures are in contact with the vapor phase (more than 350°C), while the wall in contact with the liquid presents extremely lower temperatures (about 92°C). The highest stress region is at the interface between liquid and vapor (see mechanical simulation in Figure 2b). In this zone, the stress is increased by additional secondary stress due to the temperature difference between the upper and lower part of the tank (more than 250°C).

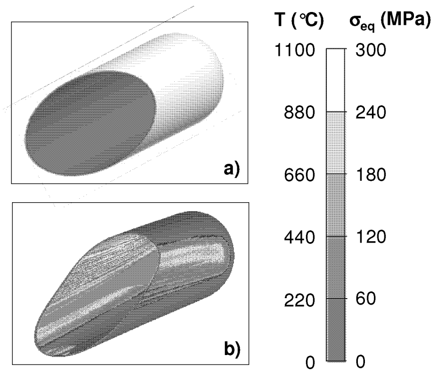

Figure 2: Results of the thermal FEM simulations (a) and mechanical FEM simulations (b) for the protected 95m3 tank. Temperatures in °C and stress in MPa, end of simulation: 100 min.

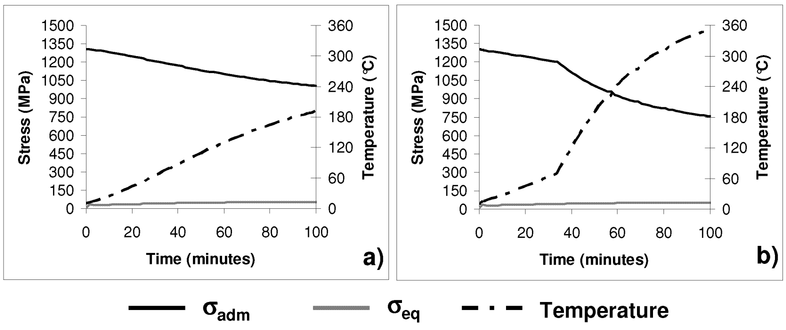

Figure 3: Comparison among the predicted stress intensity, maximum allowable stress, and wall temperature in the more critical point of the structure in case of ideal coating behaviour (a) and with the 3-phase behaviour presented in Table 2 (b). Temperatures in °C and stress in MPa, end of simulation: 100 min.

The simulation of the non protected coating allowed estimating a time to failure of only 13 minutes in the fire scenario considered, with a higher wall temperature of more than 750°C and a quick pressure rise. The implementation of the coating allowed delaying the tank rupture in a drastic manner, since no rupture was predicted among the selected simulation time (100 minutes). This is due to the reduced vessel heat up which allowed preventing the thermal degradation of the construction material, thus allowing a residual vessel strength able to withstand the inner pressure and thermal stresses. In order to quantify the influence of the coating degradation on the resistance of the tank, Figure 3 shows the comparison among the stress intensity (σ_{eq}) with the maximum allowable stress (σ_{adm}) in the more critical point of the structure, together with the correspondent wall temperature. Figure 3a shows the results in case of the mentioned “ideal” coating behavior, while Figure 3b refers to implementation of the 3-phase coating behavior. As it can be seen, a significant temperature increase in the final part of the simulation is shown in the case of coating degradation. This causes a decrease of σ_{adm} which is, nevertheless, still greater than the correspondent σ_{eq}. Thus the tank integrity is not jeopardized for the considered exposure time by the coating degradation.

5. Conclusions

In the present study a methodological approach for the assessment of the behavior of thermal epoxy coatings was developed. The approach integrates experimental and numerical analyses. A commercial epoxy intumescent coating was selected among the more common product for PFP and tested with thermogravimetric analysis, evidencing the critical phases of the thermal behavior and determining an apparent kinetic degradation model. The experimental results were implemented in a FEM, which simulated real scale tankers engulfed by fires, with and without thermal protection installed. The protection resulted critical to enhance the tanker fire resistance, delaying the occurrence of the vessel rupture up to 10 times. The simulations allowed quantifying the influence of the coating degradation of the residual strength of the tank, providing important indication for the passive fire protection system design.

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