Modeling heat transfers across a silicone-based intumescent coating

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ABSTRACT

Silicone-based intumescent coatings (SIBC) containing expandable graphite (EG) have been designed and studied in our laboratory and good physical barrier properties have been reported for both cellulosic and hydrocarbon fire scenarios. The aim of this work is to develop a preliminary 2D numerical model of this coating behavior during a fire, which is, to the best of our knowledge, not reported yet in the literature for such coating.

The fire performance of SIBC containing EG was evaluated in pure radiative heating conduction using a cone calorimeter heating element at 50kW/m². The intumescent phenomenon of the SBIC containing EG was considered as a heat transfer problem with a moving boundary. Expansion was assumed to be homogenous and occurring in one dimension and a 2D numerical heat transfer model was developed, taking into account the moving boundary using the Arbitrary Langrangian-Eulerian Method (ALE) implemented in COMSOL Multiphysics V.5.3. A water cooled sample holder with a well-defined temperature condition was used to avoid the assumption of the adiabatic conduction at the backside of the sample. The model was consistent with experimental results and it was able to reasonably predict the temperature profiles. However, it did not capture the temperature increase at times higher than 450s because of cracking in the silicone-based intumescent coating.

KEYWORDS: modeling, heat transfer, intumescence, silicone-based coating

NOMENCLATURE LISTING

\begin{align*}
\rho & \quad \text{density (kg/m}^3) \\
c_p & \quad \text{specific heat capacity (J/kgK)} \\
k & \quad \text{thermal conductivity (W/mk)} \\
T_r & \quad \text{average cone surface temperature (K)} \\
T_a & \quad \text{ambient temperature (K)} \\
h_{ho} & \quad \text{horizontal heat transfer coefficient (W/m}^2\text{k}) \\
h_{ve} & \quad \text{vertical heat transfer coefficient (W/m}^2\text{k}) \\
F & \quad \text{view factor (-)} \\
T & \quad \text{Temperature (K)} \\
\alpha & \quad \text{Conversion rate} \\
c & \quad \text{copper plate} \\
cs & \quad \text{calcium silicate insulation block} \\
\text{intu} & \quad \text{intumescent coating} \\
s & \quad \text{steel plate} \\
\text{pyro} & \quad \text{pyroceram} \\
\text{max} & \quad \text{maximum} \\
\varepsilon & \quad \text{emissivity (-)} \\
\sigma & \quad \text{Stefan Boltzmann constant (Wm}^{-2}\text{K}^{-4}) \\
\lambda & \quad \text{Thermal diffusivity (m}^2\text{/s)} \\
\end{align*}
INTRODUCTION

The strength and stiffness of steel are decreased when this material is exposed to high temperatures, which can lead to a disaster [1]. Intumescent coatings are often used as efficient passive fire protective methods on metallic structures. When exposed to heat, they begin to swell and expand to form an insulative char layer which limits mass and heat transfers between the flame and the substrate [2]. If the efficiency of such a coating can be experimentally measured, the modeling of its behavior is challenging. In the literature, numerical models have been reported to predict the performance of intumescent materials. Complex models [3-5] have been developed for the char layer formation but these models come with limitations. In the approach presented by Di Blasi and Branca [4], the gas-producing step is considered as the most important step in the intumescence phenomenon process, which is only suitable for intumescence resulting from the reaction between an acid source, a carbon source and a blowing agent.

This work aims at modeling the performance of a silicone based intumescent coating (SBIC) containing expandable graphite (EG) developed in our laboratory using a phenomenological approach. SBIC exhibits good physical barrier properties in the case of both cellulosic and hydrocarbon fire scenarios thanks to the fast formation of an expanded structure having low thermal conductivity [6-8]. With EG, the expanded structure is obtained through the decomposition of the intercalation compounds inserted between the carbon layers of graphite which cause graphite exfoliation. Most intumescent paints currently on the market are epoxy or water based paints, the models are consequently exclusively based on these systems [9, 10]. To the best of our knowledge, models for such SBIC are not yet reported in literature and it is noteworthy that the approach considering the gas-producing step is not applicable in our case.

In this study, the fire behavior of SBIC exposed to an external pure radiative heat flux of 50kW/m² is investigated. A 2D numerical heat transfer model taking into account the moving boundary using the Arbitrary Lagrangian-Eulerian Method (ALE) [11, 12] implemented in COMSOL Multiphysics V.5.3. is proposed. The thermal conductivity versus temperature, the expansion versus time and the kinetic parameters have been characterized and used as inputs for the model. The results are then discussed and a comparison between the experimental and predicted data is done.

EXPERIMENTAL

Materials

The silicone-based coating (formulation details found in a previous paper [14]) was applied on 100 x 100 x 3 mm³ steel plates after proper preparation of the surface including degreasing and sand blasting steps. Teflon moulds were used to obtain a repeatable coating thickness of 4mm. The coated plates were left for 24h at room temperature and then cured in an oven at 40°C for 6h as a customized procedure.

Fire Test

A cone calorimeter heating element was used to provide a constant incident radiative heat flux of 50kW/m² on the surface of the sample. The coated steel plate was placed on top of a 100 x 100 x 50 mm³ calcium silicate (calsil) block which was then placed on a 100 x 100 x 10 mm³ copper plate. This multi-layer system (coated steel plate-calsil-copper plate) was mounted on a water-cooled sample holder as shown in Fig 1. The water-cooled sample holder temperature was maintained at 40°C using a cooling system (chiller). Therefore, a constant temperature boundary condition was imposed on the experimental set-up which is implemented in the numerical heat transfer model as a Dirichlet boundary condition.

![Fig. 1. Experimental set-up.](image)
During the experiment, K-type thermocouples were used to record the temperature as a function of time at different locations as shown in Fig. 1. T2 was embedded in the SBIC and T3 was welded at the backside of the steel plate. This set-up allowed evaluating the temperature gradient across the system. The mathematical model described in the next section is based on this set-up.

2D MODEL - MATHEMATICAL FORMULATION

The ‘intumescence’ phenomenon was considered as a heat transfer problem with a moving boundary in our mathematical formulation. To incorporate the expansion of the SBIC, the solver assembles the discretized model on a deformed mesh using the ALE description [11, 12]. The complete mesh comprised of 4900 quadrilateral elements with 900 quadrilateral elements in the intumescent layer and a maximum element size of 0.002m and a minimum element size of 7.5E-6m. Expansion was assumed to be homogeneous and occurring in one dimension. As a first approach, the goal was not to model all the phenomena involved in intumescence but to consider the fundamental parameters affecting its thermal insulation performance i.e. thermal conductivity and its expansion [6-8]. The following 2D numerical model was built up: four distinct layers were selected i.e. (i) the copper plate layer (y ∈ [0, c]), (ii) the calsil layer (y ∈ ]c, cs[), (iii) the steel plate layer (y ∈ ]cs, s[) and (iv) the SIBC layer (y ∈ ]s, l(t)[). Perfect thermal contact was assumed between the layers. Heat is transferred by pure conduction and the boundaries are fixed throughout the test in the first three layers, Eq. 1.

$$\rho c_p \frac{dT}{dt} = \nabla \cdot (k_i \nabla T) \quad \text{where } i = c, cs, s \tag{1}$$

In the fourth layer, i.e. the intumescent layer, the exposed surface moves upwards as the coating expands while the interface steel/coating is fixed (Eq.2), l(t) represents the expansion of the intumescent coating in the y-direction as a function of time.

$$y \in ]s, l(t)[, \rho_{intu} c_{intu} \frac{dT_{intu}}{dt} = \nabla \cdot (k_{intu} \nabla T) - \rho_{intu} h_a A e^{-\frac{k_{intu}}{T_a}}(1 - \alpha)^n \tag{2}$$

In Eq. 1 and Eq. 2, the term on the left hand side (LHS) represents the rate of change of internal energy of the material and the first term on the right hand side (RHS) indicates the heat transfer by conduction. The last term in Eq. 2 accounts for internal heat energy released due to the endothermic decomposition process of the coating which is modelled assuming a n-th order reaction. To solve the governing equations, initial and boundary conditions need to be specified.

Initial and boundary conditions

The surface of the intumescent coating is exposed to radiative heat flux from the cone calorimeter heating element. This is a typical case of surface-to-surface radiation and the view factor has to be considered in boundary condition at the exposed surface. The formula for the view factor used in this study was proposed by Wilson et al. [13] who studied the uniformity of radiant heat fluxes in the cone calorimeter. The effect of expansion on surface radiation heat exchanges is also taken into account. The heat feedback from combustion on the surface is assumed to be negligible as compared to the external radiation [14]. The boundary condition on the exposed surface is shown in Eq. 3. The term on the LHS represents the total heat flux received by the coating. The first term on the RHS represents the surface-to-surface radiation of the material and the cone heating element, the second term and last term are the heat loss by radiation and convection on the surface, respectively.

$$-\vec{n} \cdot (-k_{intu} \nabla T) = \varepsilon \sigma (F T_r^4 + (1 - F) T_a^4) - \varepsilon \sigma T^4 + h_{no}(T_a - T) \tag{3}$$

The boundary condition on the sides of the respective materials is presented in Eq. 4. The first term of the RHS represents heat lost by radiation and the second one is the heat lost by convection.

$$-\vec{n} \cdot (-k \nabla T) = \varepsilon \sigma (T_a^4 - T^4) + h_{ve}(T_a - T) \tag{4}$$

At the backside of the copper plate, a Dirichlet boundary condition is imposed as T=40°C. The heat transfer coefficients are determined using the assumption of natural convection on a hot plate. The initial condition is set at T=40°C i.e. the initial temperature of all the materials. After determining the initial and boundary conditions, the thermophysical properties of SBIC were measured (the properties of the other materials were given by the suppliers) and the governing equations were solved in 2D using the Finite Element Method in COMSOL Multiphysics V.5.3.
THERMOPHYSICAL PROPERTIES

The thermal diffusivity of the coating was measured from 30°C to 150°C using a Laser Flash Apparatus (LFA) from Netzch (LFA 467 Hyperflash). The apparatus uses a non-contact method by heating one side of the sample by a xenon lamp as a flash source and on the other side, an infrared detector records the temperature profile. The temperature profile is analyzed using a mathematical model (penetration model) included in the analysis software and thermal diffusivity is determined.

The specific heat capacity was obtained by a comparative method using measurements from the LFA. The coating and a reference material (pyroceram) with known properties were measured under the same conditions. By comparing the maximum temperatures obtained, the specific heat capacity of the sample can be determined using Eq. 5.

\[ c_{\text{p intu}} = \frac{\tau_{\text{max pyro}}}{\tau_{\text{max intu}}} \left( \frac{\rho_{\text{pyro}}}{\rho_{\text{intu}}} \right) \cdot \rho_{\text{pyro}} \]  

The thermal conductivity was derived from Eq. 6 using the parameters obtained previously.

\[ k_{\text{intu}} = \lambda_{\text{intu}} \cdot c_{\text{p intu}} \cdot \rho_{\text{intu}} \]  

The emissivity of the coating was measured at room temperature using a Vertex 70v vacuum FT-IR spectrometer from Bruker equipped with an integrating sphere.

Kinetics of decomposition: thermogravimetric analysis (TGA) were carried out at different heating rates (1, 5 and 10°C/min) using a SDT Q600 from TA instruments. The Arrhenius parameters were determined using a thermokinetic software package from Netzsch [15].

Expansion measurement

The expansion of the intumescent coating was monitored by an infrared camera (FLIR camera A40) to obtain a good contrast during the experiment. The captured images were analyzed using Image J software (NIH, Bethesda, MD) and the expansion of the coating was determined as a function of time [16, 17]. Using this approach, the expansion was assumed to be homogeneous and occurring in one dimension.

RESULTS AND DISCUSSION

Expansion, thermal conductivity and fire performance

Fig. 2 presents the evolution of expansion (a) and thermal conductivity (b) as a function of time. The temperature versus time curves of the uncoated and coated steel plates are also plotted (Fig 2.c) to demonstrate the coating’s barrier properties. The expansion of the coating when exposed to a pure radiative heat flux of 50kW/m² occurs in four steps (Fig. 2(a)). First, between 0 and 300s, the expansion increases quite steadily with a high expansion rate, it then stabilizes at around 450s up to 560%. The expansion increases again to reach its maximum (725%) after 560s, it then remains steady afterwards until the end of the experiment. The average expansion rate over the whole expansion was 0.05mm/s. The obtained expansion profile was used as an input in the model.

Fig. 2(b) shows that the thermal conductivity obtained by using the comparative method is in the same order
of magnitude as that found for a typical SBIC [7, 8] decreasing from around 0.6 W/m.K at ambient temperature to 0.48 W/m.K at 150°C. It has been reported that for another SBIC (not the same as that used in this work), the thermal conductivity decreases from 1 W/m.K at ambient temperature to 0.35 W/m.K at 300°C and increases up to 0.45 W/m.K at 700°C [8]. In the current study, we assumed that, for temperatures higher than 150°C, the conductivity was constant, which is acceptable considering the values reported by Bourbigot et al. [8]. The temperature (Fig. 2(c)) of the uncoated steel plate rises up to a steady state at approximately 600°C whereas that of the coated steel rises up to a maximum of around 400°C demonstrating the physical barrier properties of the coating. Thanks to the previous measurements, the barrier properties can be attributed to some extent to the expansion rate and low thermal conductivity.

Comparison of experimental and predicted data

Fig. 3 compares the predicted and experimental temperature profiles of the coating at different locations. On the experimental results, the temperature profile T1 starts at around 110s because when the intumescent coating embeds the thermocouple. From this point, the temperature decreases up to around 450°C (after 450s), owing to the barrier effect of the expanding insulative char layer. For temperature profiles T2 and T3, from 0s to 140s (<220°C), conduction governs the heat transfer phenomena during this period and it is controlled by the radiative heat source, thermal diffusivity and expansion of the coating. The onset of thermal degradation is observed from 220°C corresponding to around 140s (TGA analysis not shown here), corresponding to around 140s on Fig. 3. For T1, T2 and T3, from 450s, the temperatures profiles tend to increase rapidly even though we would expect them to reach a steady state because the char layer is near full expansion. This is explained by the formation of some visible cracks at the surface of the coating. It was also claimed by Gardelle et al. [6] that in a pure radiative heating case, SIBC’s cracks were due to the high vibration of the Si-O bond in infrared field. Finally, for the temperature profile T4, heat is transferred by pure conduction inside the calsil block and the temperature tends to increase steadily up to 140°C for the duration of the test which makes sense because of the thermal insulation effect of both the coating and the calsil as well as the cooling effect of the sample holder.

For T4, the numerical results are in excellent agreement with the experimental data for the duration of the test whereas for the other thermocouples, agreement is only observed from 0s to around 450s. The agreement is attributed to the accuracy of the determined thermophysical properties and the appropriate boundary conditions. The assumption of a constant thermal conductivity at temperatures higher than 150°C and a nth order reaction can be validated because for T1, T2 and T3, the temperature profiles are consistent at temperatures higher than 150°C between 0s to 450s. The model fails to capture the temperature increase from 450s because of the phenomenon explained previously which is not included in the model. Work is in progress to include this phenomenon.

Fig. 3. Predicted and experimental temperature profiles of the SBIC at different locations.
CONCLUSION

This work, using a phenomenological approach, aimed at modeling the heat transfers across a silicone based coating containing expandable graphite exposed to an external radiative heat flux of 50kW/m². The first model developed was consistent with experimental results and it was able to reasonably predict the temperature profiles. However, it did not capture the temperature increase at times higher than 450s because of cracking in the silicone-based intumescent coating. Further work on a new model is in progress to include this phenomenon.

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REFERENCES

[1] Quintiere, J.G. and F.A. Williams. (2014) Comments on the National Institute of Standards and Technology Investigation of the 2001 World Trade Center Fires, Journal of Fire Sciences 32:281-291, http://dx.doi.org/10.1177/0734904114528457.
[2] Bourbigot, S., et al. (2004) Recent Advances for Intumescent Polymers, Macromolecular Materials and Engineering 289:499-511, http://dx.doi.org/10.1002/mame.200400007.
[3] Butler, K.M., H.R. Baum, and T. Kashiwagi. "Three dimensional Modeling of Intumescent behavior in Fires," Fire Safety ScienceProceedings of the fifth International Symposium. 1997. Melbourne, Australia.
[4] Di Blasi, C. and C. Branca. (2001) Mathematical Model for the Nonsteady Decomposition of Intumescent Coatings, AIChE J. 47:2359–2370.
[5] Di Blasi, C. (2004) Modeling the effects of high radiative heat fluxes on intumescent material decomposition, Journal of Analytical and Applied Pyrolysis 71:721-737, http://dx.doi.org/10.1016/j.jaap.2003.10.003.
[6] Gardelle, B., et al. (2013) Thermal degradation and fire performance of intumescent silicone-based coatings, Polymers for Advanced Technologies 24:62-69, http://dx.doi.org/10.1002/pat.3050.
[7] Gardelle, B., et al. (2013) Characterization of the carbonization process of expandable graphite/silicone formulations in a simulated fire, Polymer Degradation and Stability 98:1052-1063, http://dx.doi.org/10.1016/j.polymdegradstab.2013.02.001.
[8] Bourbigot, S., B. Gardelle, and S. Duquesne. "Intumescent silicone-based coatings for the fire protection of carbon fiber reinforced composites," Fire Safety Science -- Proceedings of Eleventh International Symposium. 2014. International Association for Fire Safety Science.
[9] Zhang, Y., et al. (2012) Global modelling of fire protection performance of intumescent coating under different cone calorimeter heating conditions, Fire Safety Journal 50:51-62, http://dx.doi.org/10.1016/j Firesaf.2012.02.004.
[10] Bhargava, A. and G.J. Griffin. (1999) A Two Dimensional Model of Heat Transfer Across a Fire Retardant Epoxy Coating Subjected to an Impinging Flame, Journal of Fire Sciences 17:188-208, http://dx.doi.org/10.1177/073490419901700304.
[11] Donea, J., et al., Arbitrary Lagrangian–Eulerian Methods, in Encyclopedia of computational mechanics, fundamentals. 2004, John Wiley & Sons, Ltd: UK.
[12] COMSOL Multiphysics Reference Manual v. 5.3, 2017.
[13] Wilson, M.T., B.Z. Dlugogorski, and K.E. M. (2003) Uniformity of radiant heat fluxes in cone calorimeter, Fire Safety Science -- Proceedings of the Seventh International Symposium:815-827.
[14] Shi, L., et al. (2015) Modeling the Pyrolysis and Combustion Behaviors of Non-Charring and Intumescent-Protected Polymers Using “FiresCone”, Polymers 7:1979-1997, http://dx.doi.org/10.3390/polym201495.
[15] Opfermann, J. (2000) Kinetic Analysis Using Multivariate Non-linear Regression. I. Basic concepts, Journal of Thermal Analysis and Calorimetry 60 641–658.
[16] Bourbigot, S., B. Gardelle, and S. Duquesne. "Intumescent silicone-based coatings for the fire protection of carbon fiber reinforced composites," Fire Safety Science - Proceedings of the Eleventh International Symposium 2014. DOI: 10.3801/afss.fss.11-781.
[17] Bourbigot, S. and S. Duquesne. "Quantitative approach of intumescence by numerical simulation," 243 rd American Chemical Society National meeting. 2012. San Diego.