Numerical Study of the Decomposition Mechanism of Intumescent Coating

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ABSTRACT

Intumescent coating represents an efficient way to increase the fire resistance of construction materials. During its degradation, intumescent materials expand and form a char layer that acts as an efficient thermal shield between the heat source and the materials.

Encouraging predictions of thermal degradation and expansion of intumescent coatings in experimental conditions representative of fires were reported in the last decade by considering models involving conservation equations for mass and energy for the intumescent material coupled to approximate sub-models for describing the swelling mechanism. These degradation models used generally simplified decomposition mechanisms involving one, two or three reactions. In addition, the dehydration process that occurs in the early stage is usually ignored.

The objective of this article is to assess the relevance of several multi-step reaction mechanisms to describe the mass loss and the mass loss rate of ICWB, an intumescent coating, in TGA at different heating rates in inert atmosphere. The kinetic parameters of the different reactions were optimized using the Shuffled complex evolution (SCE) technique.

Results demonstrate that the drying process, which occurs up to 130°C for ICWB, cannot be neglected since the associated mass loss represents about 5%. In addition, the drying process can be described by a single reaction. The use of a simple mechanism, based on one or two reactions to model the degradation of dry intumescent coating, is insufficient and leads to significant discrepancies on both mass loss and mass loss rate. Considering three reactions improve considerably the predictions but discrepancies are still observed for temperature higher than about 420°C. Model results show that a four-step is required to capture accurately all the details of the degradation of dry intumescent coating under inert atmosphere. Simulations were run under air, showing that an additional reaction for oxidation is required to extend the four-step reaction mechanism for oxidative atmosphere, leading to a five-step reaction mechanism.

KEYWORDS:
Structures in Fires, Intumescent Coatings, Inert Atmosphere, Decomposition, Thermogravimetric Analysis, Multi-Step Reaction Mechanism
INTRODUCTION

Thin films of fire-retardant intumescent coatings have become the main choice as passive fire protection for structural steel and other construction materials in buildings and other facilities. These coatings can expand up to one hundred times their initial thickness when degrade under thermal exposure, forming an insulating char layer over the underlying substrate. This limits the rate of temperature rise of the construction materials and prolongs their loading bearing capability when exposed to fire.

The expansion of intumescent coating when exposed to a heat source is a complex phenomenon that involves a complex mixture of gas, solid and liquid phases. Detailed degradation models based on approximate solutions of mass, momentum, and energy equations at the scale of an individual bubble were developed and found in qualitative agreement with experimental observations [1]. However no quantitative validation of such detailed modelling was reported to date. On the other hand, less sophisticated degradation models, based on the conservation equations of mass and energy for the intumescent material coupled to approximate sub-models for describing the swelling mechanism, have produced encouraging predictions in configurations relevant for fire safety applications [2-6]. These degradation models use generally a simplified decomposition mechanism for the intumescent material. Staggs et al. [5] used a two-step reaction mechanism with one reaction decomposing coating into gas and another reaction decomposing coating into char. Lautenberger and Fernandez-Pello [6] considered also a two-step reaction mechanism where the first reaction converts coating into char and gas and causes intumescence and the second converts char into ash and gases. A natural way to construct the decomposition mechanism is to start from the accepted assumption that intumescent materials are composed of three active components, namely an acid source, a blowing agent, and a charring agent, bound in a binder polymer [7] and to relate the phenomena observed experimentally to the degradation of these three species. The degradation of the acid source, of the blowing agent and of the charring agent are then associated to the melting stage with the formation of a viscoelastic phase, to the swelling stage where a large amount of gaseous products is formed and trapped in the coating to cause the molten matrix to swell and to the charring stage with the formation of the final charred solid residue, respectively. This picture naturally led to the development of a three-step reaction mechanism to model the degradation of the intumescent materials [2-4]:

\[
S_1 \rightarrow G_1 \quad (1)
\]
\[
S_2 \rightarrow G_2 \quad (2)
\]
\[
S_3 \rightarrow v_c S_c + v_G G_3 \quad (3)
\]

where \(S_1, S_2, S_3, \) and \(S_c\) refer to the acid source, the blowing agent, the charring material and the final charred residue, respectively. \(G_1, G_2, \) and \(G_3\) are the volatile species released from the reactions.

The aim of this study is to assess the capability of the simple reaction mechanisms to model the decomposition of intumescent coating and, if necessary, to develop a more complex one. The corresponding kinetic parameters will be determined from TGA data obtained by considering several heating rates under inert and oxidative atmospheres [8]. This kind of approach was already applied to determine kinetic parameters of charring materials undergoing melting and thermal degradation [9, 10].

METHODS

Experiments

TGA experiments were conducted on ICWB, an intumescent coating material devoted to steel protection [8]. More details about ICWB can be found in Ref. [8]. The main components of ICWB are: i) a synthetic binder, Pentaerythritol (C\(_4\)(CH\(_2\)OH)\(_4\)), with a fusion temperature between 250°C and 300°C under both nitrogen and air. It also plays the role of carbon supplier, ii) A fire retardant additive, Ammonium Polyphosphate [NH\(_4\) PO\(_4\)]\(_n\), which also plays the role of acid source. Its decomposition starts around 200°C under both nitrogen and air, and iii) A blowing agent, Melamine (C\(_3\)H\(_6\)N\(_6\)) which also plays the role of nitrogen derivative. Its melting point is around 400°C under both nitrogen and air.

TGA experiments were carried out at different heating rates of 5, 10, 15, 20 and 25°C/min, over a temperature range from 20°C to 600°C [8]. The influence of the atmosphere was investigated by considering either air or
nitrogen (at a flow rate of 50ml/min). Samples were ground to a fine powder using a mechanical grinder prior to the run to make 10mg homogeneous samples in each case. All temperatures are measured by a type K thermocouple.

**Numerical model**

Zero-dimension simulation were performed with Gpyro [11] version 0.8186 to examine thoroughly the thermal degradation of ICWB under multi-step reaction mechanisms. Gpyro solves transient equations of the mass and species evolution of a “lumped” particle having negligible gradients of temperature species as occurs in idealized thermal analysis experiments. For a given reaction, the reaction rate is given by:

\[ \omega_i = A \exp(-\frac{E_a}{RT})m_i^n \]  

(4)

where \( A \) is the pre-exponential factor, \( E_a \) the activation energy, \( n \) the reaction order, and \( m_i \) the mass of the reactant. The Shuffled Complex Evolution (SCE) optimization algorithm [12], is used to optimize these kinetic parameters.

**RESULTS AND DISCUSSIONS**

Figure 1 represents the cumulative mass loss (CML) and the mass loss rate (MLR) evolutions as a function of temperature under inert atmosphere (N₂) for the different heating rates. The experimental evolutions are consistent with previous studies [2-4]. The thermal decomposition is mainly observed between 200 and 500°C and occurs with the different stages enumerated in the introduction: i) Stage 1 (up to 130 °C): drying process; ii) Stage 2 (from 130 °C to 180 °C): melting with no significant expansion and mass loss. Therefore, this stage cannot be considered as a reaction step; iii) Stage 3 (from 180°C to 300 °C): decomposition of the blowing agent with a rapid expansion of coating. The mass loss associated with this stage ranges is about 16%; iv) Stage 4 (from 300°C to 600°C): char formation where maximum rate of mass loss occurs. These results show that all the processes leading to the formation of the char layer occur below 600°C which is selected as upper temperature to calibrate the reaction mechanism. The proposed reaction step should be related to the decomposition mechanism of Ammonium Polyphosphate/ Pentaerythritol mixtures as described in Ref. [13]. This study showed that a relatively large amount of non-flammable volatile products (H₂O, NH₃) is released, the quantity depending on the initial decomposition.

The results reported in Ref. [8] showed that mass loss during the drying process (Stage 1) is about 5 %. As a consequence, this process, occurring up 130°C for ICWB, cannot be ignored as usually done in modeling studies. In the present study, it is introduced via a single reaction:

\[ R1: Wet \text{Char} \rightarrow v_{H2O}H2O + (1 - v_{H2O}) \text{Dry Char} \]  

(5)

The optimized kinetic parameters are provided in Table 1.

| Reagent  | Product  | Kinetic parameters values |  |
|----------|----------|---------------------------|---|
| Wet-Char | Dry-Char | logA (s⁻¹) E_a (kJ mol⁻¹) n [-] v [-] | 6.43 66.2 5 0.945 |

In the following, the focus will be only on reactions that occur after dehydration under different atmosphere conditions (N₂ and air), and R1 and the kinetic parameters reported in Table 1 will be used to model the drying process.

A two-step reaction mechanism was first considered for the degradation process (stage 3 to 4) of dry ICWB (not shown). This mechanism was found to overestimate significantly the mass loss during the swelling process. In addition, although it was able to capture the highest peak of MLR, it was found to miss the first
and third peak. Consequently, a two-step mechanism is not sufficient to describe the degradation process of dry ICWB and a three-step mechanism should be considered (stage 3 to 4):

\[ R2: \text{Dry Char} \rightarrow v_1 \alpha - \text{Char} + (1 - v_1)\text{Gas} \]  
\[ R3: \alpha - \text{Char} \rightarrow v_2 \beta - \text{Char} + (1 - v_2)\text{Gas} \]  
\[ R4: \beta - \text{Char} \rightarrow v_3 \gamma - \text{Char} + (1 - v_3)\text{Gas} \]  

The predicted evolutions of CML and MLR based on the three-step reaction mechanism (Eq. 6-8) are also plotted in Fig. 1 as a function of temperature. The related fitted parameters are given in Table 2. Only the CML for a heating rate of 20°C/min was reported to make the figure readable, the level of agreement between numerical and experimental CML being consistent for the other heating rates. Results in Figs 1a show that CML is well reproduced by the numerical model despite an underestimation for temperatures higher than 420°C. Figure 1b shows that the MLR is well predicted during the blowing (Stage 3) stage. In particular, the first and second peaks are accurately reproduced. However, the model ignores completely the final peak which explains the above-mentioned discrepancies of the CML. As a consequence, the results in Fig. 1 demonstrate that although it provides a quite accurate description of the degradation process, the three-step mechanism is not able to reproduce all the details of the degradation mechanism, especially for temperatures higher than about 400°C.

In order to capture these details, a 4-step reaction mechanism is considered. This mechanism extends the previous one (Eqs. 6-8) by adding another reaction (R5):

\[ R5: \gamma - \text{Char} \rightarrow v_4 \varepsilon - \text{Char} + (1 - v_4)\text{Gas} \]  

All the reaction parameters are summarized in Table 3. It should be pointed out, that all the parameters for reactions R2 to R4 were recalibrated. Figure 2 compares the experimental and predicted CML and MLR.
Results show clearly that the 4-reaction mechanism capture all the details of the degradation process with both CML and MLR being almost perfectly reproduced. These results suggest that a five-step mechanism should be used to model the thermal degradation of intumescent coating with one reaction for the drying process and four reactions for the degradation of the dry material.

![Graphs showing cumulative mass loss and mass loss rate](image)

**Fig. 2:** Evolution of the cumulative mass loss (a) and mass loss rate (b) of four-step mechanism under nitrogen for 4 different heating rates.

| Atmosphere | Reagent   | Product | Kinetic parameters values |
|------------|-----------|---------|---------------------------|
|            |           |         | \( \log A \text{ (s}^{-1}) \) | \( E_a \text{ (kJ mol}^{-1}) \) | \( n(-) \) | \( \nu(-) \) |
| N\(_2\)    | Dry-Char  | \( \alpha\)-Char | 10.7 | 125 | 1.1 | 0.889 |
| N\(_2\)    | \( \alpha\)-Char | \( \beta\)-Char | 10.1 | 139 | 1.6 | 0.698 |
| N\(_2\)    | \( \beta\)-Char | \( \gamma\)-Char | 14.1 | 123 | 4.96 | 0.851 |
| N\(_2\)    | \( \gamma\)-Char | \( \varepsilon\)-Char | 11.1 | 178 | 1.86 | 0.813 |

**CONCLUSIONS**

This study investigates the capability of several multistep reaction mechanisms to describe the thermal degradation of ICWB, an intumescent material, exposed to different heating rates under both inert atmosphere (N\(_2\)). The following conclusions can be drawn:

1) The drying process, usually neglected in numerical modeling of intumescent coatings, cannot be disregarded since it can be related to mass loss of about 5% and is strongly endothermic. Results reported in this study shows that it can be described by a single reaction.

2) A two-step reaction mechanism is unable to predict accurately the degradation of the dry intumescent coating, leading to significant discrepancies on the mass loss and mass loss rate.

3) A three-step reaction mechanism, usually used in literature, improves significantly the two-step reaction mechanism. It reproduces accurately the mass loss and mass loss rate up to about 400°C. However, it is not able to describe accurately the degradation process for higher temperature.

4) Model results show that a four-step reaction mechanism is required to describe capture accurately all the trends of the degradation process of dry intumescent materials.
Only the results and discussions relative to inert atmosphere have been presented in this article. The effects of oxygen have been discussed in Ref. [8], showing that they become significant at temperature higher than 400°C. Simulations were also run under air showing that one additional reaction for oxidation is required to update the four-step reaction mechanism provided by Eqs. 6-9 for oxidative atmosphere, leading to a five-step reaction mechanism.

In the current study, two concentrations of oxygen have been studied (zero and 21% of oxygen). Regrettably, these conditions are not always available in the real case of fire. It is then necessary to complete the present investigation, with an investigation of the thermal degradation under different intermediate concentrations of oxygen [14].

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