Multiscale Experimental Approach for Developing High-Performance Intumescent Coatings

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Multiscale Experimental Approach for Developing High-Performance Intumescent Coatings

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The goal of this work is to combine small-scale screening tests permitting, during the laboratory research phase of a development, the optimization of intumescent mastic coatings formulated to protect steel in the case of hydrocarbon fire. This type of coating, applied on steel plates, beams, or columns, is usually evaluated in large industrial furnaces. Such experiments are, however, expensive and time-consuming. The use of such tests, if they are essential since they give a good simulation of a real fire, is a break for the development of new intumescent high-performance intumescent coatings. The original combination of small-scale laboratory tests, such as thermogravimetric analyses and rheological measurements, provides, through a rapid screening of a large number of formulations, a very interesting preliminary tool for the development of new intumescent coatings. A statistical approach involving principal component analysis has been successfully used to correlate the results of the industrial furnace tests with those from the laboratory-scale analyses.

1. Introduction

The use of fire-retardant coatings is one of the easiest, oldest, and most efficient ways to protect a substrate against fire.[1,2] Indeed, it presents several advantages: it does not modify the intrinsic properties of the material (e.g., the mechanical properties), it is easily processed, and it may also be used on several materials including metallic materials,[3] polymers,[4] textiles,[5] and wood.[6]

The protection of metallic materials against fire has become a very important issue in the construction and petrochemical industries, as well as in the marine and military fields. Structural steel loses a significant part of its load-carrying ability when its temperature exceeds 500 °C. Prevention of the structural collapse of a building is paramount to ensure the safe evacuation of people from the building, and it is a prime requirement of building regulations[7] in many countries. Intumescent coatings are designed to perform under severe conditions and to maintain the integrity of the steel for 1−3 h when the temperature of the surroundings is in excess of 1100 °C.[8,9]

The intumescence concept[10−13] allows a balance between the fire properties and the level of additives in the material. Intumescent coatings consist of intumescent additives bound together by a binder. Generally, three intumescent ingredients are used: an acid source (for example, ammonium polyphosphate), a carbon source (it can be the polymer itself or, for example, dipentaerythritol), and a blowing agent (for example, ammonium polyphosphate). The formulation of these coatings has to be adapted in terms of their physical and chemical properties to form an efficient protective char[14] (Figure 1).

The intumescence mechanism is usually described as follows: first the acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbon source to yield the carbon char, and finally the blowing agent decomposes to yield gaseous products. The latter causes the char to swell and hence provide an insulating multicellular protective layer. This shield limits at the same time the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source, resulting in conservation of the underlying material.
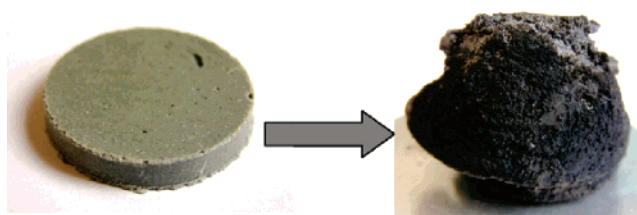

Figure 1. Swelling of an intumescent coating.

It is noteworthy that the random selection of a compound from each of the three classes does not ensure intumescent behavior in their mixture: the three compounds must show a suitably matching thermal behavior.[11] For example, it is obvious that the blowing agent must be available for the expansion action at a temperature above that at which the charring of the mixture begins, but before the solidification of the liquid charring melt occurs. This is why it is essential to study the thermal stability of the different compounds, by thermogravimetric analysis for example. This instrument will also allow determine if there are interactions between the compounds, and so will evaluate the reactivity of the system.

A second point is that the formation of the effective char occurs via a semiliquid phase, which coincides with gas formation and expansion of the surface.[15] Gases released from the degradation of the intumescent material, and in particular of the blowing agent, have to be trapped and to diffuse slowly in the highly viscous melted material in order to create a layer with the morphological properties of interest. That is why it is essential to investigate the dynamic viscoelastic properties of the intumescent shield since control of the melt rheology is necessary to obtain a multicellular and highly expanded structure. Moreover, in the context of hydrocarbon/jet fire coatings, the mechanical integrity of the char is a crucial parameter because it has to resist external stress.

To summarize, the formulation of the coating has to be optimized in terms of physical (char strength, expansion, viscosity, ...) and chemical (thermal stability, reactivity) properties in order to form an effective protective char[16] that will be able to protect the steel for as long as possible on exposure to a fire.

The fire resistance of intumescent coatings in different fire regimes (Figure 2), e.g., cellulosic fires or hydrocarbon fires, is evaluated worldwide by industrial furnace tests. The intu-

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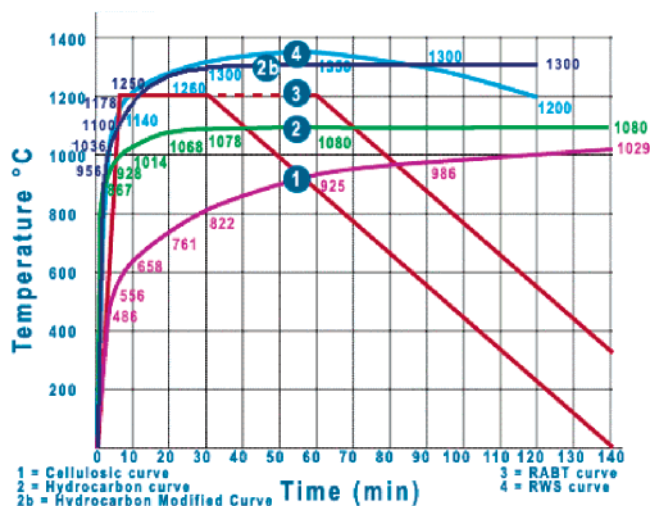
Figure 2. Standard fire time/temperature curves.

Figure 3. Test of mechanical resistance.

mescent formulations used in the current study were designed to provide protection in both hydrocarbon and jet fires (1200 °C reached in less than a few minutes). The industrial hydrocarbon test curve intends to simulate or to be indicative of the rapid temperature rise measured when a hydrocarbon fuel such as oil or natural gas burns: the temperature rises rapidly to 1000 °C within 4 min until reaching a temperature of 1100 or 1200 °C. This hydrocarbon fire test curve, developed by the Mobil Oil Company in the early 1970s and adopted by a number of organizations, is now a well-accepted reference in high-risk environments such as petrochemical complexes and offshore platforms, with a typical rating of 2 h. This hydrocarbon test curve is also used to simulate jet fire scenarios in which leaking high-pressure hydrocarbon gases ignite to produce intense, erosive jet flames that can reach speeds of 150 m/s. The evaluation of coatings in hydrocarbon and jet fire test regimes is both expensive and time-consuming, and the companies involved in the research and development of fire protection coatings are looking for a means to reduce these costs by developing high throughput screening small-scale fire tests.

One of the main objectives of the current study is to examine whether the performance in large-scale industrial fire tests can be correlated with parameters of the intumescent coating measured using laboratory analysis tools. The two parts of this study present the results obtained from large furnace tests and small-scale analyses and examine the potential relevant parameters. The thermogravimetric analysis will evaluate the thermal stability of the several systems, and a parallel-plate rheometer will determine the viscoelastic and mechanical properties of the char. The analysis of possible correlations between the intrinsic parameters of intumescent coatings and their efficiency is carried out using a "principal component analysis" approach.

2. Experimental Apparatus and Methods

2.1. Materials. A commercial intumescent epoxy based formulation is used in this study. The binder is a solvent-free thermoset epoxy resin. It is a mixture of the diglycidyl ether of bisphenol A (DGEBA, Dow Chemical) and of an amine curing agent. The resin is cured at ambient temperature.

The intumescent coatings are formulated using two main fire retardant agents: (i) a mineral acid, boric acid (H_3BO_3) (Aldrich, 99%), and (ii) a commercial ammonium polyphosphate (APP) derivative supplied by Clariant (Germany), containing 20% phosphorus.

The formulations also contain, as usual in intumescent formulations,[17−20] a few percent fibers (e.g., silicate fibers), fillers
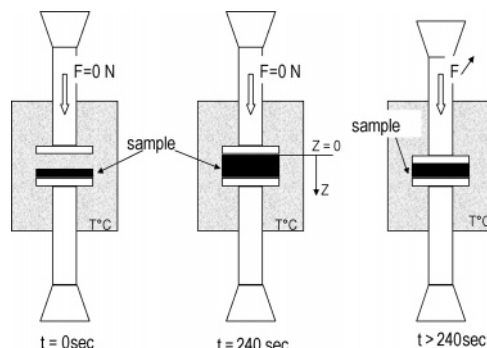
(e.g., calcium carbonate), and pigments (e.g., TiO_2) in order to reinforce the intumescent char strength. The description of all the components of the formulation is not necessary for the understanding of this paper and for the sake of brevity is not given here.

Eleven formulations, labeled from IF1 to IF11, containing various ratios of the previously cited main compounds, have been prepared and compared to the virgin epoxy resin.

The formulations were prepared by mixing the components using an Ultra Turrax mixer (600 rpm). For the large furnace fire tests the coating was applied at 3.5 mm thickness onto grit-blasted steel plates of dimensions 30 × 30 cm² or 15 × 15 cm² and cured for 1 week under ambient conditions. Free films of the coating and pellets of dimensions 25 × 25 × 3 mm³ (for the rheological measurements) were produced by casting the coating between PTFE plates. For the thermogravimetric analysis the cured coating was ground in liquid nitrogen in an ultracentrifuge mill to produce a fine powder.

2.2. Thermogravimetric Analysis. Thermogravimetric analyses were carried out at 10 °C/min in synthetic air (flow rate 50 mL/min, Air Liquide grade), using a Setaram TG 92 microbalance. The samples (approximately 10 mg) in powder form were placed in open vitreous silica pans. The precision of the temperature measurements was 1.5 °C over the whole range of temperature (20−800 °C).

2.3. Rheological Measurements. Rheological measurements were carried out using a Rheometric Scientific ARES-20A thermal scanning rheometer (TSR) in a parallel-plate configuration. Both the viscosity of the coating and its mechanical resistance were measured.

2.3.1. Complex Viscosity Measurements. The TSR was designed for monitoring changes in the rheological properties as a function of temperature and/or time. Samples (25 × 25 × 3 mm³) were positioned between the two plates. A constant normal force was systematically applied to obtain good adhesion between the sample and plates. The heating program used is a "dynamic temperature ramp test": with a heating rate of 10 °C/min in the range 25−500 °C, a strain of 1%, and a constant normal force of 10g (200 Pa).

2.3.2. Mechanical Resistance. Mechanical resistance is evaluated using the protocol described as follows: at $t = 0$ s, the sample (height, $h = 1$ mm) is put into the furnace and heated to 500 °C without applying any strain (the upper plate is not in contact with the sample as shown in Figure 3). This allows the sample to intumesce without any constraint. The upper plate is then brought into contact with the intumesced material, and the gap between the plates is reduced linearly (0.02 mm/s). The compression force is followed as a function of the gap between the two plates (Figure 3). The decreasing gap is calculated, taking into account the initial height of the sample; that is why it is expressed in percentages.
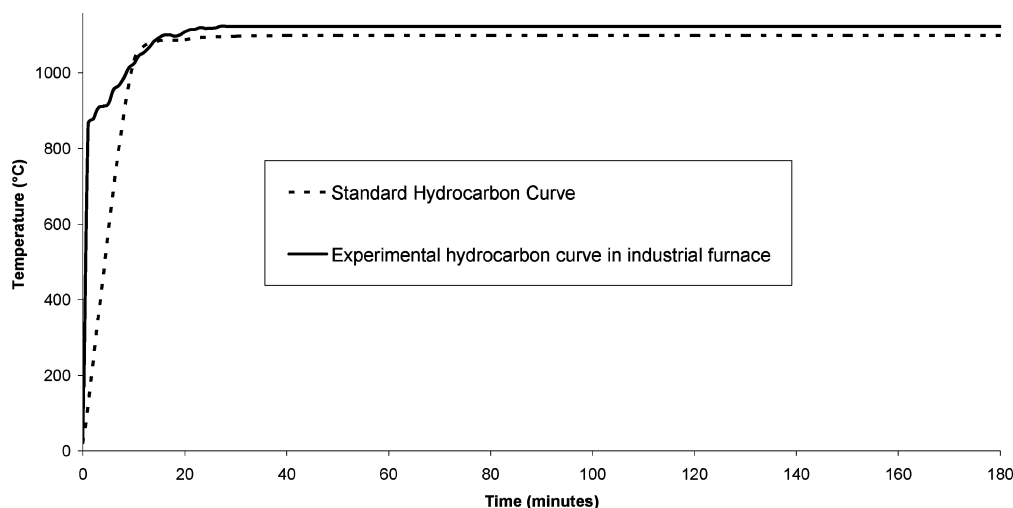
Figure 4. Comparison between standard and experimental hydrocarbon curves.
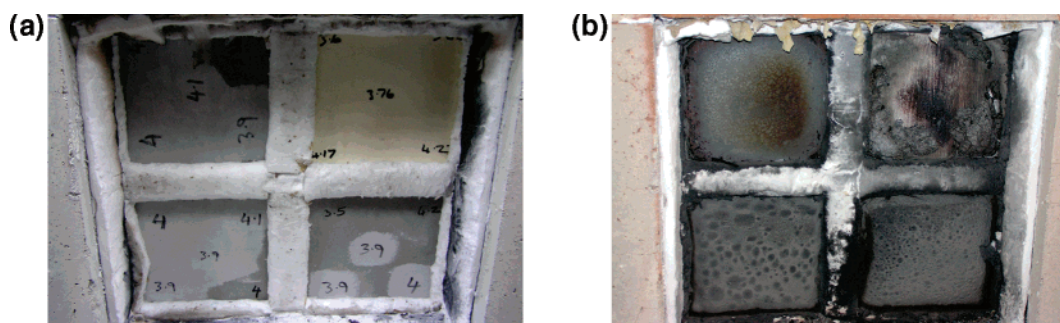

Figure 5. Coated steel plates before (a) and after (b) the burning test.

The upper plate used in this experiment has a diameter of 5 mm in order to increase the pressure on the whole sample and to ensure complete destruction of the char.

2.4. Fire Resistance. Industrial furnace tests have been carried out according to the commonly used standard hydrocarbon fire test UL1709.[21] The specification is to burn steel plates coated with intumescent coatings.

The coatings are applied on a steel plate (thickness 3.5 mm) and cured for 1 week at room temperature. Thermocouples are attached to the back of the coated plates. Five thermocouples are used on each plate, so that an average temperature can be obtained. The burning conditions try to fit as much as possible the ramp of temperature of a hydrocarbon fire (about 200 °C/min up to 1200 °C). Figure 4 shows the difference between the experimental and the standard hydrocarbon curves. The main difference occurs during the first minutes of heating: the increase of temperature is much more rapid during the test compared to the standard. This is acceptable since the aim is to test the coatings under the most severe conditions as possible.

Because four plates are evaluated at the same time, the plates are insulated using glass wool. The plates are mounted vertically in the furnace (Figure 5). The fire protection parameter is the time for which the temperature reaches 400 °C. It is called the time of failure. The longer it is, the higher the protection is achieved.

This test produces time/temperature curves and characterizes the heat protective effect of the different coatings in a hydrocarbon fire.

3. Principal Component Analysis

Thermogravimetric analyses, viscoelastic measurements, and fire tests lead to different results for each of the 11 formulations
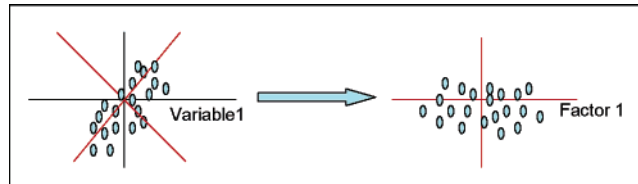

Figure 6. Geometric explanation of PCA.

and the virgin nonpigmented resin. The ultimate goal of this paper is to find potential correlation between the fire industrial test and the laboratory-scale analyses. This will be done using the principal component analysis (PCA) approach.

The PCA method[22−24] involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. The basic idea of a principal component analysis is to reduce the dimensionality of the data set while retaining as much as possible the variation in the data set. Principal components (PCs) are linear transformations of the original set of variables. PCs are uncorrelated and ordered so that the first few PCs contain most of the variations in the original data set.[25,26] PCA helps to produce better visualization because it takes the cloud of data points and rotates it such that the maximum variability is visible. This method allows drawing circles of correlation and so observing the correlations between the different parameters. PCA calculations were done using the software NEMROD (University of Aix en Provence, France).

As shown in Figure 6, after rotating data set of variable 1 (left) to factor 1 (right), the variability is of maximum visibility when the data points are projected onto the axis of factor 1. Thus, factor 1 is the first PCA axis. In fact, the first PCA axis goes through the centroid, but also minimizes the square of the distance of each point to that line. In some sense, the line is as
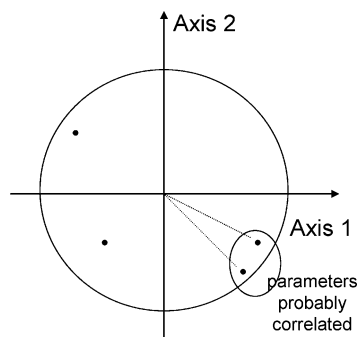
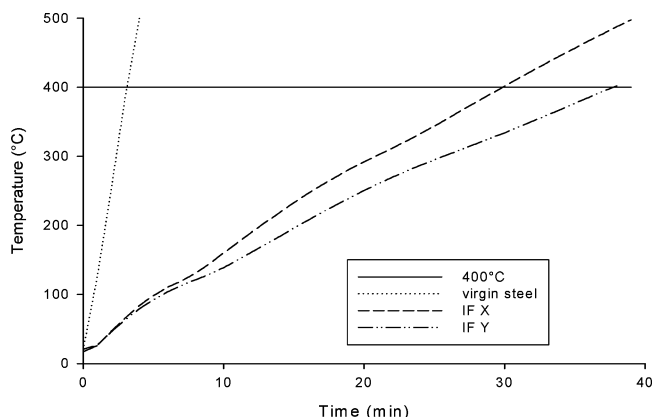**Figure 7.** Example of circle of correlation.

Figure 8. Evolution of temperature as a function of time in a big furnace.

close to all of the data as possible. Equivalently, the line goes through the maximum variation in the data.

All the data are analyzed and the correlation circles are drawn. During the calculation, we define $n - 1$ main axes, where n is the number of parameters studied. The percentages attributed to the axes are characteristic of the repartition of the population of points. The results are said to be considered as possibly correlated and representative when the points are close to the edge of the circle and when they are near each other (Figure 7).

The correlation circles only give a first idea to see if the experimental points have been well chosen and if correlations might be possible. To determine the best correlations, the curves

corresponding to the main possible interactions have then to be drawn. The correlation coefficient R characterizes the interaction: if $0.8 < R < 1$, there is an excellent correlation between the experiments. If $0.63 < R < 0.8$, there is a quite good correlation, but if $R < 0.63$, the parameters may not be considered as correlated.

4. Results and Discussion

4.1. Fire Resistance of the Intumescent Formulation. The 12 formulations have been evaluated under the conditions of a hydrocarbon fire using the furnace test UL1709. Twelve time/ temperature curves are obtained. As a typical example, Figure 8 shows the evolution of temperature as a function of time on the reverse of the steel plates respectively not coated and coated with two random intumescent formulations (IFX and IFY). Steel usually loses its main structural properties around 500 °C. In this kind of test, 400 °C is usually chosen by companies as the failure temperature. The reference (virgin steel plate) very rapidly reaches 400 °C (3 min).

The aim of intumescent coatings is to decrease as much as possible the slope of the time/temperature curve, i.e., reaching 400 °C as late as possible. In Figure 8, the efficiency of the intumescent coatings applied on steel is obvious: the virgin plate reaches 400 °C in 3 min, while this time increases up to 30 min when intumescent coatings are applied.

These times of failure corresponding to the failure temperature (400 °C) of the 12 formulations are summarized in Table 1. "Time of failure" is obviously one of parameters to be optimized: the best result is obtained when the longest time of failure is reached. This means that the coating has the best protective effect. The best results are achieved for IF8 and IF10, which have times to failure of respectively 38.1 and 37.4 min.

The relative expansion is determined by measuring the thickness of the coating before and after each UL1709 test (Figure 9). The expansion in the furnace is considered as a key parameter in the development of fire protective coatings. The major characteristic of an intumescent coating is its ability to swell. This parameter is necessary but not sufficient to ensure the fire protection. Indeed, a high swelling does not necessarily lead to the best performance, because the char formed can be too light and not sufficiently mechanically resistant.[27] The aim

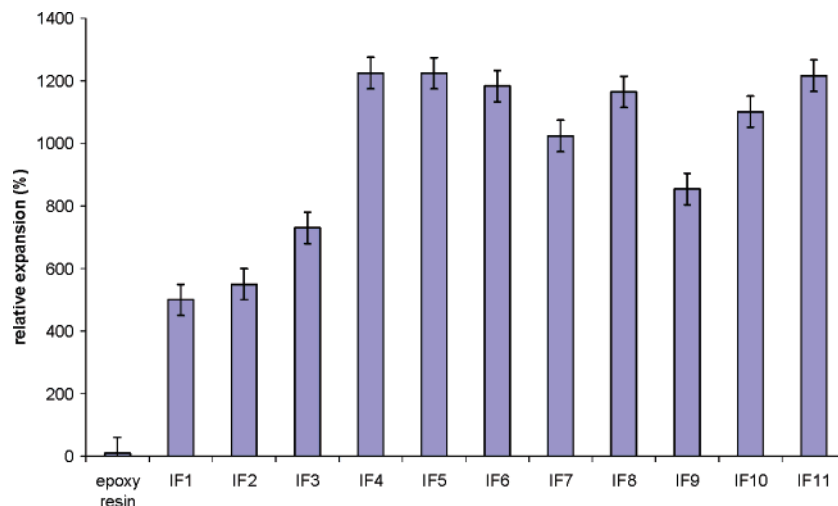**Figure 9.** Relative expansions measured at the end of the furnace test.

Table 1. Time of Failure of the Different Formulations

formulation no.	virgin resin	IF1	IF2	IF3	IF4	IF5	IF6	IF7	IF8	IF9	IF10	IF11
time of failure (min)	3	11.3	18.2	30	31.3	28.1	32.3	31.5	38.1	21.2	37.4	35.5
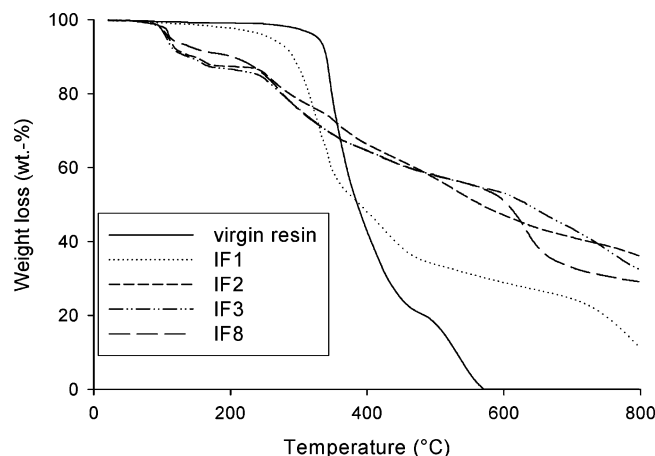
Figure 10. Examples of thermogravimetric analyses.

Figure 11. Development of intumescence (α = conversion degree).

is to obtain a multicellular charred layer in order to minimize the heat transfer to the steel plate and to provide good protection of the substrate.

From Figure 9 and Table 1, it is clearly shown that the coatings having the longest time to failure exhibit high expansion.

The furnace tests suggest the use of two main parameters: the time of failure when the temperature reaches 400 °C and the expansion. The aim of this paper is to find laboratory analysis giving a good simulation of the behavior of these formulations in the furnace test. Since furnace tests are expensive and time-consuming, small-scale laboratory analyses would potentially reduce the cost and time frame for developing new intumescent coatings.

4.2. Small-Scale Analyses. An intumescent coating is working well when there is high char yield and high expansion, when the viscosity during the degradation of polymer is not too high or too low so that the mixture can swell, and when the char created has enough mechanical resistance to resist both the fire and external stress. The idea was to combine different experiments such as thermogravimetric analyses and viscoelastic measurements to try to evaluate all the relevant parameters and finally correlate them with the furnace test results.

In this section, thermogravimetric analyses and viscoelastic measurements are carried out in order to determine the key parameters that will be used afterward to be correlated with the results obtained during industrial tests. Only some of the curves corresponding to the 12 formulations will be presented for each experiment, in order to allow an easier reading and understanding of the curves.

4.2.1. Thermal Degradation. The thermogravimetric analyses (TGAs) carried out under controlled air and temperature conditions give an overview of the degradation process of the coating in thermooxidative conditions and an idea of the reactivity between the components.[27] This study will not take into account these interactions, as the aim is to define the main parameters that could be correlated together. The weight loss is plotted against the temperature, and at the end of the TGA it is possible to have a look at the char to see if effective intumescence occurs. Some TG curves are presented in Figure 10 as typical examples.

The aim is to obtain a high level of homogeneous char at the end of the experiment: the intumescent structure will be more efficient if the residue is large, thick, and homogeneous. This residue will limit the heat transfer to the substrate and will also limit the gases feeding the combustion process. A slow
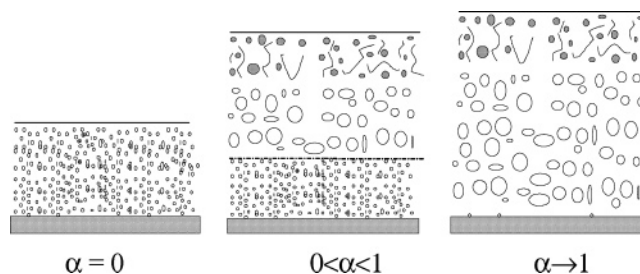
degradation rate is also of benefit, because it will lead to a more homogeneous char.

To summarize, the optimum behavior is a slow degradation rate during the experiment leading to a high residue at 800 °C.

The virgin resin is totally degraded at 600 °C, which means that there is no residue left, so it is obvious that this formulation will not work as an intumescent system in a hydrocarbon fire, in which the temperature reaches 1200 °C. The thermal degradation is improved for the formulation IF1: the degradation rate decreases, there is stabilization at high temperatures, and some residue is left. However, the residue is still small (15%), and there may not be not enough charring to allow a good expansion. The three other formulations degrade more rapidly at the beginning but lead to an increased residue (about 30%) at 800 °C. In these cases there should be some residue left at 1200 °C to still protect the steel.

To conclude this part, the key parameter that is going to be taken into account in this experiment is the "char yield at 800 °C", as it is the closest data to the char yield that can be retrieved at the end of the furnace tests.

4.2.2. Viscoelastic Behavior. During burning of an intumescent system, the formation of the effective char occurs via a semiliquid phase, which coincides with gas formation and expansion of the surface.[28] Gases released from the degradation of the intumescent material, and in particular from the blowing agent, have to be trapped and to diffuse slowly in the highly viscous melt degraded material in order to create a layer with appropriate morphological properties, as shown in Figure 11.

If the degraded matrix has a too low viscosity, easy diffusion of gases takes place and the gases will not be trapped but rather escape to feed the flame. By contrast, if the viscosity is too high, the gases will not be able to diffuse correctly into the char. The viscosity of the degraded matrix in the blowing phase is, as a consequence, a critical factor.[29−31]

Figure 12 presents the relative expansion and the complex viscosity versus time of the virgin resin, IF1, IF2, IF3, and IF8. It is noteworthy that swelling starts about 300 °C, suggesting that the expansion takes place because of the relatively low viscosity of the char combined with the release of volatile degradation products (see TGA experiments, Figure 10). The thermoset resin degrades extensively from 330 °C, leading to a very low viscosity. No expansion is observed since the gases cannot be trapped and easily escape to feed the flame. The intumescent formulations show an increase in the viscosity of the mixture in the same range of temperature, so the gases can be trapped and swelling can develop. The coating IF8 shows the highest viscosity at 330 °C and the highest swelling at the end of the experiment, because the char, which is quite hard, may accommodate the stresses due to the internal pressure created by the evolving gases.

As a conclusion, the key parameters that are going to be taken into account will be the "complex viscosity at 330 °C" and the "expansion measured at the end of the experiment". As the
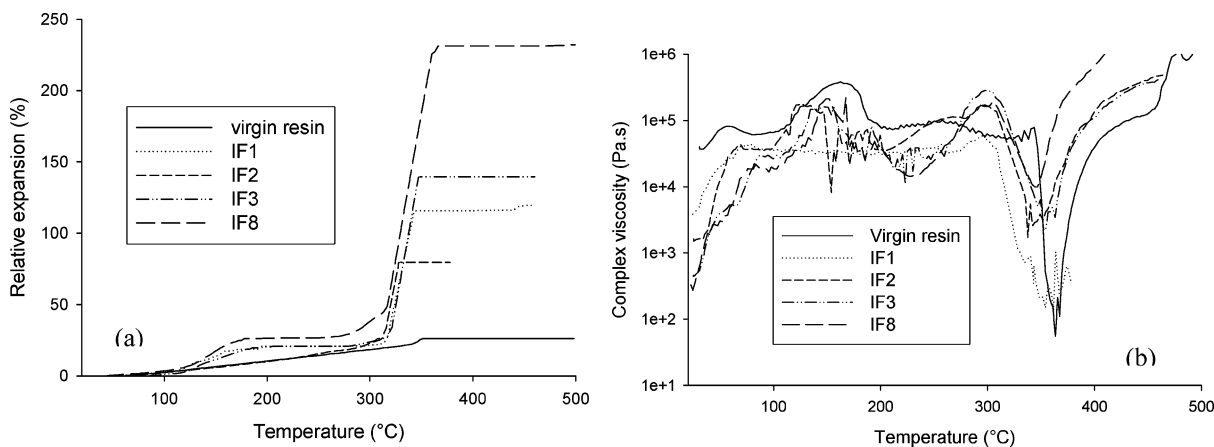
Figure 12. Relative expansion (a) and complex viscosity (b) of different formulations.
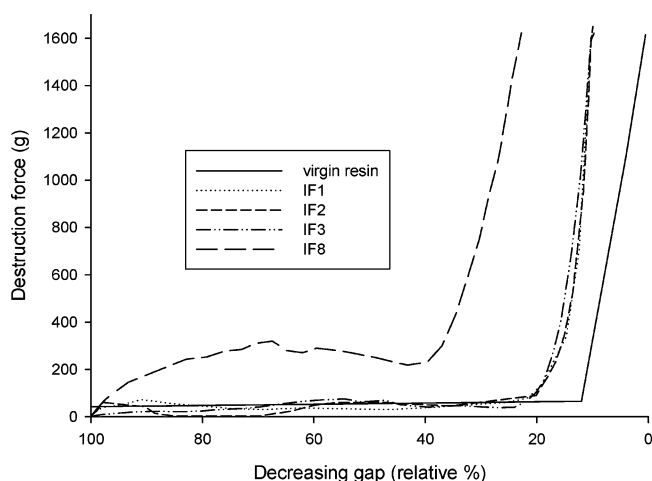

Figure 13. Mechanical resistance of the char of different formulations.

Table 2. Summary of Fire Resistance and of Intrinsic Properties of Intumescent Formulations

	UL1709			rheological measurement		
	failure time (min)	expan- sion (%)	TGA residual weight (%)	complex viscosity (Pa·s)	expan- sion (%)	mechanical resistance (%)
virgin resin	5	10	0	55.59	26	1
IF1	11.3	500	11.84	178.64	99	10
IF2	18.2	550	36	3109.2	116	15
IF3	30	730	32.57	3658	139	17.9
IF4	31.3	1225	29.91	3466	157	16
IF5	28.1	1224	28.69	3135	157	17
IF6	32.3	1183	24.32	4049	123	32
IF7	31.5	1024	31.36	8000	170	40.4
IF8	38.1	1164	28.75	9990	190	42
IF9	21.2	854	29.35	7779	155	24
IF10	37.4	1216	29.20	6287	154	28
IF11	35.5	1101	33.4	9634	170	38

expansion takes place mainly around 330 °C during the degradation of the polymer, it seems relevant to take the value of expansion at 500 °C.

4.2.3. Mechanical Resistance of the Char. Another parameter that we also take into account is the mechanical properties of the char. If the char is destroyed when subjected to external perturbations such as an explosion (e.g., jet fire) or wind turbulence, the coating will not provide effective protection of the steel structure. In the stabilization phase of the intumescent structure, the change in the viscosity of the charred material under stress may explain the loss of the protective character of the intumescent shield. Indeed, if the shield becomes too hard, the creation and propagation of cracks leads to a rapid degradation of the material. If a char has good structural, morphological, and heat insulative properties but is easily destroyed under mechanical action, its efficiency is totally lost in the turbulent regime of combustion.

Figure 13 shows the destruction force of the carbonaceous layer plotted against the decreasing distance between the plates at 500 °C. It is noteworthy that the char created by the burning of the intumescent formulation IF8 is much more resistant than the char of the formulations IF1, IF2, and IF3: the destruction "force" that has to be applied at the beginning ($m > 200g$) is much higher than that applied for all the other samples. This stabilization is due to the use of fibers that maintain the char integrity and provide a higher mechanical resistance.[32,33] Once the char has been compressed, a very high normal force has to be applied to destroy it further. Moreover, in the case of IF8 the force begins to increase earlier (40% relative gap). This

means that the char is very resistant and that the upper shield can resist a pressure applied to it.

The key parameter that will be taken into account from this experiment is the "relative gap (%)" corresponding to the beginning of the maximum increase of the normal force (we consider that this beginning corresponds to $F = 200g$).

4.3. Principal Component Analysis. This section deals with the possible correlations between the identified parameters obtained using the analyses commented above and the industrial furnace tests carried out on the 12 coatings. Six key parameters have been selected from our previous experiments and discussion:

The industrial furnace test gives two parameters: (i) the time of failure; (ii) the expansion of the coating, obtained at the end of the test.

Thermogravimetric analysis (TGA) gives the char yield at 800 °C after a temperature ramp of 10 °C/min.

The experiments using the rheometer give three parameters: (i) The first is the complex viscosity about 330 °C, corresponding to the degradation of the thermoset resin. It is at that time that the swelling occurs, so it is at that time that the viscosity evolution is the most important. (ii) The second parameter is the expansion calculated at 500 °C after a dynamic ramp temperature of 10 °C/min. (iii) The third is the mechanical resistance of the char (i.e., the relative gap (%) corresponding to the beginning of the maximum increase of the normal force).

Table 2 summarizes the data obtained for each of the 12 coatings.

Because six parameters are considered, five axes should be defined (Table 3). The new coordinates of the different parameters on these axes have been calculated.
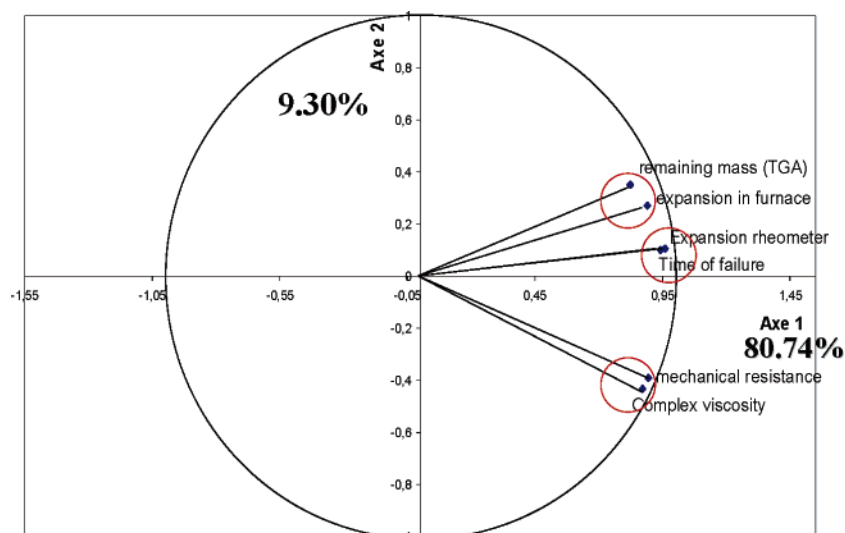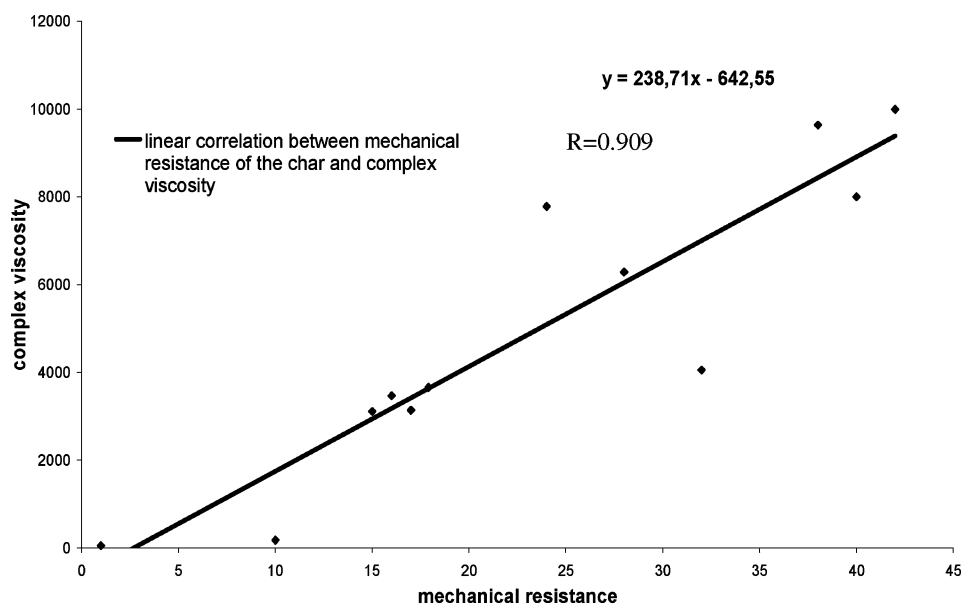
Figure 14. Main correlation circle.

Figure 15. Interaction between the complex viscosity and mechanical resistance of the char.

Table 3. New Coordinates of Parameters on the Five Axes

	axis 1	axis 2	axis 3	axis 4	axis 5
time of failure	0.942	0.101	−0.215	−0.179	−0.145
complex viscosity at 330 °C	0.872	−0.432	0.161	0.085	−0.113
residual weight at 800 °C	0.824	0.351	0.428	−0.107	0.037
expansion in rheometer	0.96	0.106	0.065	0.221	0.008
expansion in furnace	0.891	0.271	−0.334	0.085	0.058
mechanical resistance	0.895	−0.391	−0.062	−0.118	0.163

It is then possible to draw 10 correlation circles, corresponding to combinations between the different axes (axes 1/2, 1/3, ..., 4/5). The percentages attributed after calculation to the axes are very heterogeneous: axis 1 contains 80.74% of the population, axis 2 contains only 9.30%, axis 3 corresponds to 6.25%, axis 4 corresponds to 2.01%, and axis 5 corresponds to only 1.08%. Axis 1 is the major axis: this means that the experimental points have been well chosen, with a good repartition. As axes 1 and 2 contain the major part of points, the most probable correlations will be seen on the circle of correlation that combines these two axes (Figure 14).

Considering the correlation circle presented in Figure 14, it can be assumed that the data of "remaining mass" and "expansion in the furnace" are correlated, just as "expansion in rheometer" and "time of failure", or also "mechanical resistance"

and "complex viscosity". To confirm these possible correlations, the corresponding linear regressions have been calculated. As an example, Figure 15 represents the linear plot exhibiting the interactions between the complex viscosity at 330 °C and the mechanical resistance of the char.

The linear regression between those two parameters gives an excellent regression coefficient ($R = 0.909$). It may be concluded that if the coating has a high complex viscosity at 330 °C then the char should have a high mechanical resistance.

Table 4 presents all the regression coefficients R obtained between the different experiments. The values in italics correspond to the formulations for which $R > 0.8$. Seven excellent correlations can be observed: (i) correlation between the expansion in the furnace and the expansion in the rheometer; (ii) correlation between the expansion in the furnace and the time of failure in the furnace; (iii) correlation between the expansion in the rheometer and the time of failure in the furnace; (iv) correlation between the expansion in the rheometer and the complex viscosity at 330 °C; (v) correlation between the mechanical resistance and the complex viscosity at 330 °C; (vi) correlation between the expansion in rheometer and the residual

Table 4. Summary of Calculated Correlation Coefficients

	time of failure	complex viscosity at 330 °C	residual weight at 800 °C	expansion in rheometer	expansion in furnace	mechanical resistance
time of failure	1					
complex viscosity at 330 °C	0.7397	1				
residual weight at 800 °C	0.7312	0.6256	1			
expansion in rheometer	*0.8667*	*0.8101*	*0.829*	1		
expansion in furnace	*0.9088*	0.6155	0.6834	*0.8693*	1	
mechanical resistance	*0.8167*	*0.9088*	0.5914	0.7932	0.7085	1

weight at 800 °C; (vii) correlation between the mechanical resistance and the time of failure in the furnace.

Considering then all the correlation coefficients obtained from the PCA, it can be concluded that two kinds of correlations, summarized in Figure 16, exist: direct and second-order correlations.
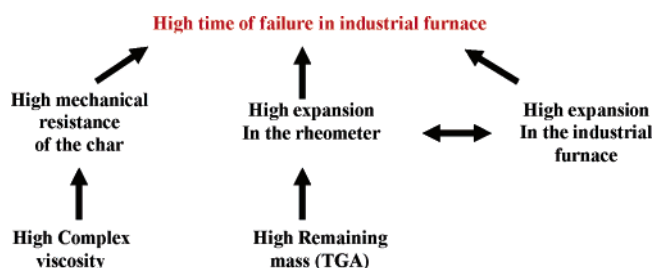
Figure 16. Correlations between the different parameters.

The most important value is to reach a high time of failure in big furnaces. Figure 16 shows three direct correlations with this parameter. The first one concerns the mechanical resistance of the char, which is very well correlated with the time of failure. This means that, in the case of this coating, if a high mechanical strength is measured using the rheometer, a high time of failure should be obtained, which means a highly efficient intumescent coating. This result confirms that the heat insulative properties of the char directly depend on its structural and morphological properties. The expansion of the char both in the rheometer and in the furnace is also directly linked with the time of failure. This means that the insulation will be more efficient if the char swells a lot. This is not surprising, as a significant amount of char will prevent too significant heat transfers. However, in some cases, for example cellulosic coatings, the result can be slightly different: in fact, if the coating sometimes expands too much, the char created can be too light and not stable, whereas a coating that will expand less but which is more resistant to stress will better protect the substrate.[27]

These results are interesting because they suggest that all the experiments made with the rheometer are strongly correlated to those obtained in the industrial furnace. This means that the resistance of the char and its expansion are reliable parameters to evaluate in the first approach of the behavior of intumescent epoxy based coatings in a real fire.

The other correlations presented are "second-order" correlations, which are not directly linked to the furnace test results. For example, the complex viscosity taken at 330 °C and corresponding to the degradation of the polymer matrix is also correlated with the mechanical resistance. This means that if the complex viscosity is high at 330 °C, the mechanical resistance will be high: this confirms that if the viscosity is too low, easy diffusion of gases takes place; the gases will not be trapped but rather escape to feed the flame, leading to a poorly mechanical resistant char. The second correlation concerns the char yield in thermogravimetric analyses linked to the expansion in the rheometer. If there is a high expansion,

the amount of char will be significant, which is essential to have an efficient thermal barrier.

5. Conclusion

This study has compared, using different laboratory analyses, the behavior of different epoxy resin based intumescent formulations. Their fire protective performances were evaluated in industrial furnace tests. The aim of the current study was to determine using small-scale laboratory analyses how these formulations work and if the laboratory and furnace test results can be correlated. Correlations between laboratory analyses and industrial furnace tests results have been proposed using statistical analysis (principal component analysis). Results suggest excellent correlation between the different techniques and in particular with the mechanical resistance and the expansion of the intumescent char.

The aim was to propose to researchers in coatings development a panel of small-scale analyses that could help predict the behavior of the coating in big industrial furnaces. The rheometer has been proven to be a powerful tool, as it allows carrying out two types of experiments (mechanical resistance and expansion), whose results are directly linked to the results of industrial tests. These results are essential to be used as preliminary tests in research, because they permit optimizing the formulations much more rapidly and at very low cost. The selected formulations will be then progressed to full-scale furnace testing, saving both time and money.

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